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Macrocyclic Compounds |*Hot Paper*|

Spacer Length-Independent Shuttling of the Pillar[5]arene Ring in Neutral [2]Rotaxanes

Tomoki Ogoshi,*[a, b] Daisuke Kotera,[a] Shungo Nishida,[a] Takahiro Kakuta,[a] Tada-aki Yamagishi,[a] and Albert M. Brouwer*[c]

Abstract: For a series of neutral [2]rotaxanes consisting of a pillar[5]arene ring and axles possessing two stations separated by flexible spacers of different lengths, the free energies of activation for the ring shuttling between the stations were found to be independent of the spacer length. The constitution of the spacer affects the activation energies: replacement of CH_2 groups by repulsive oxygen atoms in the axle increases the barrier. The explanation for the observed length-independence lies in the presence of a barrier for re-forming the stable co-conformation, which makes the ring travel back and forth along the thread in an intermediate state.

[2]Rotaxanes with two identical binding sites (stations), exhibit shuttling of the ring component between the two stations.[1] This constitutes one of the simplest types of movement in a prototypical molecular machine, and has been studied ever since the birth of the research field.[2]

The constitution and length of the spacer that connects the two stations is expected to influence the ring movement,[3] and understanding these effects can contribute to the design of optimized molecular machines. In many cases, introduction of polar functionalities, such as amide or urethane groups, or ionic units, such as ammonium groups, is required to create effective binding stations in [2]rotaxanes, because most macrocyclic rings form stable host–guest complexes with polar units. However, these polar groups in [2]rotaxanes cause limited solubility of [2]rotaxanes, and electrostatic interactions between ring and stations may affect the ring shuttling, and make it difficult to understand the intrinsic effects of spacer constitution and length on the ring shuttling.

There are few examples that reveal the effect of spacer lengths on the ring shuttling motion. If the diffusive motion of the ring along the thread is not rate limiting, it enters into the rate as the probability of a successful random walk, in which the ring reaches the end of the axle. Rowan and Nolte and co-workers studied threading rates in a series of pseudo-rotaxanes with threads of different lengths. The expected inverse dependence of the rate on chain length was observed for long chains,[3a] but with a different macrocycle, the diffusion along the thread was rate limiting for very long chains.[3b] Panman et al. proposed a biased random walk model to explain the rather steeply decreasing rate of ring translational motion in a series of hydrogen-bond-based [2]rotaxanes with increasing length of the alkyl chain between the stations.[3a] Hirose and co-workers investigated shuttling of crown ether rings in a series of [2]rotaxanes consisting of axles with two equivalent cationic ammonium stations connected by linear rigid rod-like oligo-paraphenylene linkers and found that the shuttling rate did not depend on the length of the spacer.[3c] Loeb and co-workers also investigated shuttling of crown ether rings by varying the number of phenyl rings in the spacer—both charged and neutral systems.[3d] However, to the best of our knowledge, clear spacer effects have not been reported in [2]rotaxane systems with simple flexible alkyl and oligo(ethylene oxide) chain spacers connecting the two stations. We considered that neutral [2]rotaxane systems should be ideal to clarify the effect of constitution and length of the spacer on the ring shuttling motion, avoiding complicating effects of electrostatic interactions. Recently, we developed an easy synthetic procedure of neutral pillar[5]arene-based [2]rotaxanes containing two identical stations by a stepwise copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reaction approach.[4] Pillar[5]arenes, which were first reported by our group, are able to form stable host–guest complexes even with neutral compounds.[5] In the [2]rotaxane structure, a neutral butylene (C4) chain sandwiched by two triazole moieties is an excellent station ($K > 10^4\ M^{-1}$),[6] because this fits to the height of pillar[5]arenes. In the [2]rotaxane, there are two C4 stations, thus shuttling of pillar[5]arene ring takes place between the two C4 stations in the [2]rotaxane.

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Herein, we systematically synthesized a series of neutral pillar[5]arene-based [2]rotaxanes with two equivalent stations connected by various lengths of linear alkyl and oligo(ethylene oxide) spacers. We investigated how the constitution and length of the spacer affect the ring shuttling. Surprisingly, the length of the spacer does not affect the rate of the shuttling of the pillar[5]arene ring. The constitution of spacer on the other hand, does affect the free-energy barrier.

The pillar[5]arene-based [2]rotaxanes containing the two C4 stations connected by C4, C8, C12, and C16 alkyl chains (Cn[2]rotaxane, $n=4$, 8, 12, and 16) and mono-, di-, and tri(ethylene oxide) (EOn[2]rotaxane, $n=1$, 2, and 3) spacers were synthesized by the stepwise CuAAC reaction by using linear alkanes and oligo(ethylene oxide) with two alkyne reactive groups at both ends as a starting compound. First, CuAAC reactions between diynes and excess 1,4-diazidobutane afforded axles containing various lengths of alkyl and oligo(ethylene oxide) chains bearing two azido moieties at both ends (Figure 1 a). Secondly, CuAAC reactions between the diazides and a stopper bearing one alkyne moiety in the presence of the pillar[5]arene ring afforded [2]rotaxanes, in which the ring is located on one of the two C4 stations on the axle. In the second CuAAC reaction, an intermediate containing one C4 station was produced in situ by reaction between one alkyne moiety in the diynes and the azido moiety in the stopper. The C4 station in the intermediate is a stable station for a pillar[5]arene, so the pseudo[2]rotaxane structure forms (Figure 1 b). The next CuAAC reaction between the alkyne at the end in the pseudo[2]rotaxane and azido moiety in the stopper then afforded [2]rotaxanes (Figure 1 c). This second CuAAC reaction also generates the second C4 station.

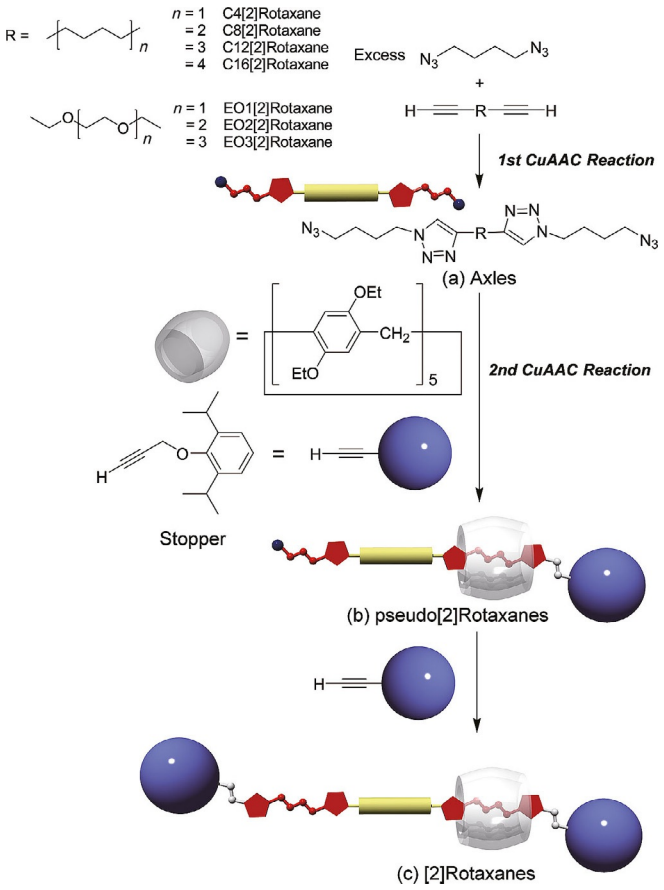

Figure 1. Synthesis of [2]rotaxanes containing the two C4 stations, which are connected by various lengths of alkyl and oligo(ethylene oxide) chains.

The pillar[5]arene ring shuttling rates in the [2]rotaxanes were evaluated by variable temperature ^{1}H NMR measurements. Figure 2 a shows a series of ^{1}H NMR spectra of C4[2]rotaxane in [D$_6$]DMSO. Due to slow shuttling of the ring between the two stations on the NMR time scale at 25 °C, proton signals

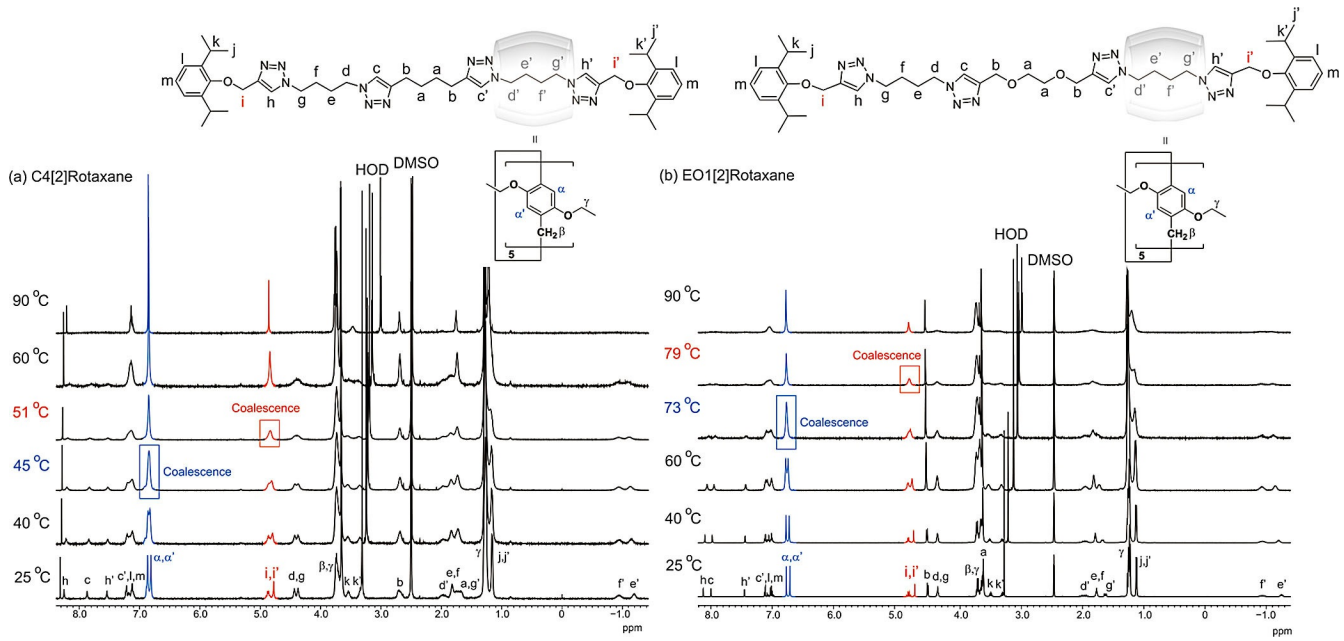

Figure 2. Variable-temperature ^{1}H NMR spectra of (a) C4[2]rotaxane and (b) EO1[2]rotaxane in [D$_6$]DMSO.

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from the axle moieties complexed and un-complexed with the pillar[5]arene ring were observed individually. Proton signals from the axle section surrounded by the pillar[5]arene ring were shielded and observed at lower frequencies. Two sets of the signals at approximately 5.4 and 5.3 ppm were assigned to the non-equivalent methylene protons (i and i′), respectively.[7] Coalescence of these signals occurs at 51 °C (^{1}H NMR spectra around the coalescence temperatures are shown in the Supporting Information). From the coalescence temperature, the rate constant of the ring shuttling in C4[2]rotaxane at 25 °C (k) was determined to be 11.0 s^{-1}. The free energy of activation ($\Delta G^{\ddagger}$) for ring shuttling calculated by using the Eyring equation was 16.1 kcal mol^{-1}. Two sets of signals from the benzene moiety of the pillar[5]arene ring (α and α') were also clearly observed in all spectra at 25 °C under slow exchange. These signals can be also used to evaluate the rate constant k and free energy of activation $\Delta G^{\ddagger}$. From the coalescence temperature $T_C = 45$ °C, we find the rate constant $k = 10.6$ s^{-1} and $\Delta G^{\ddagger} = 16.1$ kcal mol^{-1}, respectively, almost the same as the values calculated by using the proton signals from the methylene groups (i and i′).

Figure 2b shows variable temperature ^{1}H NMR spectra of EO1[2]rotaxane. Similar to C4[2]rotaxane, the two sets of proton signals from the methylene of the axle (i and i′) and phenyl of the pillar[5]arene ring (α and α') were also clearly observed individually at 25 °C. The coalescence temperatures in EO1[2]rotaxane were higher than those in C4[2]rotaxane: coalescence of these signals occurs at 79 and 73 °C in the proton signals from the methylene and phenyl moieties, respectively, indicating that the free energy of activation $\Delta G^{\ddagger}$ in EO1[2]rotaxane was higher than that in C4[2]rotaxane. We measured variable temperature ^{1}H NMR in all [2]rotaxanes, and determined the rate constants k and the free energies of activation $\Delta G^{\ddagger}$ by the same method (Table 1). Surprisingly, the free energies of activation $\Delta G^{\ddagger}$ were independent of the spacer lengths (15.9 ± 0.2 kcal mol^{-1}) in C4-, C8-, and C12- and C16[2]rotaxanes. In the cases of oligo(ethylene oxide) spacers, the free energies of activation $\Delta G^{\ddagger}$ were larger than those of Cn[2]rotaxanes but also independent of the spacer lengths (17.5 ± 0.2 kcal mol^{-1}). The higher $\Delta G^{\ddagger}$ for the polyethers is probably due to repulsive interaction between the oxygen atoms and the electron-rich cavity.[9]

To investigate the effect of solvent polarity, we measured variable-temperature ^{1}H NMR spectra of the [2]rotaxanes in [D_8]toluene (except for the insufficiently soluble C16[2]rotaxane). Similar to [D_6]DMSO, protons of the axle segment gave two sets of signals (i and i′) due to slow shuttling on the NMR time scale at 25 °C. Coalescence of the signals was observed at 78 °C for C4[2]rotaxane, which is 27 °C higher than in [D_6]DMSO. The rate constant k at 25 °C in [D_8]toluene is 0.5 s^{-1}, which is approximately 20 times slower than in [D_6]DMSO. The same trends were observed in all [2]rotaxanes. The free energies of activation $\Delta G^{\ddagger}$ in [D_8]toluene are larger than in [D_6]DMSO, because solvation of the stations competes more effectively with the noncovalent interaction between pillar[5]arene and the stations in polar solvent ([D_6]DMSO) compared with nonpolar solvent ([D_8]toluene). The solvent effect on the shuttling in C4[2]rotaxane was recently investigated by calculation.[8] In [D_8]toluene, the free energies of activation $\Delta G^{\ddagger}$ for both series were also independent of the spacer lengths.

We propose an explanation for the spacer length-independent shuttling rates in terms of an energy profile as sketched in Figure 3.

When the macrocycle is located on the thread ($M_2 \rightleftarrows M_{2'}$), its energy is so much higher than in the absolute minima ($M_1/M_{1'}$) that its steady-state population is not detectable by for example, NMR spectroscopy. Movement along the thread has only a small barrier ($TS_{22'}$), allowing the ring to go back and forth several times before either re-binding to the original station

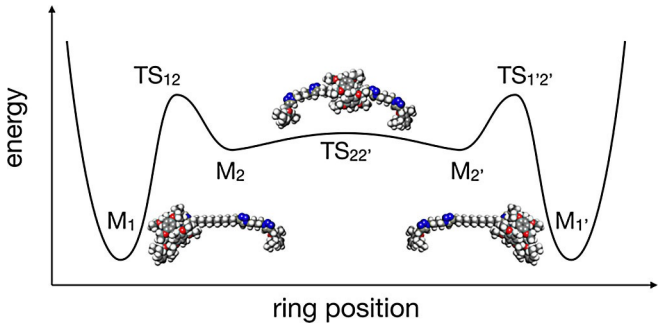

Figure 3. Schematic representation of the energy profile for the shuttling in a degenerate two-station rotaxane that accounts for spacer-length-independent shuttling rates observed in the present work.

Table 1. Kinetic data for pillar[5]arene ring shuttling in [D_6]DMSO and [D_8]toluene for variety of [2]rotaxanes from dynamic NMR studies.

	From proton signals i and i" in [D_6]DMSO			From proton signals α, α' in [D_6]DMSO			From proton signals i, i" in [D_8]toluene		
[2]Rotaxanes	T_c [°C]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	k (25 °C) [s^{-1}]	T_c [°C]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	k (25 °C) [s^{-1}]	T_c [°C]	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	k (25 °C) [s^{-1}]
C4[2]rotaxane	51	16.1	11.0	45	16.1	10.6	78	17.9	0.5
C8[2]rotaxane	46	16.0	12.4	42	16.1	11.5	77	17.9	0.6
C12[2]rotaxane	41	16.1	10.3	39	15.9	14.3	76	17.8	0.6
C16[2]rotaxane	39	16.0	12.1	37	15.7	20.6	_[a]	_[a]	_[a]
EO1[2]rotaxane	79	17.5	1.0	73	17.6	0.9	99	19.0	0.1
EO2[2]rotaxane	77	17.5	1.1	71	17.5	1.0	100	19.0	0.1
EO3[2]rotaxane	77	17.5	1.0	68	17.4	1.3	98	18.9	0.1

[a] Due to the poor solubility of C16[2]rotaxane in [D_8]toluene, we could not determine the coalescence temperature.

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(crossing TS_{12}), or reaching the other station (crossing $TS_{1'2'}$). The time scale for this motion is short compared to that of the macroscopically observed reaction. This is illustrated by molecular-dynamics simulations of C12[2]rotaxane (Figure 4).

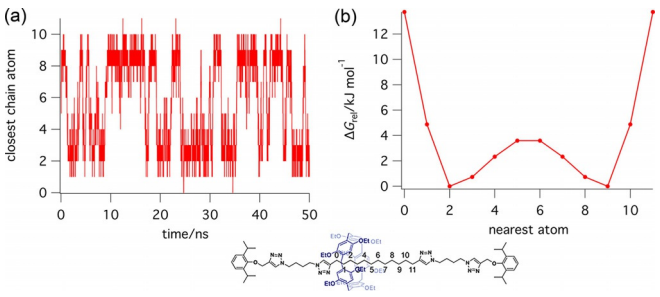

Figure 4. Molecular dynamics simulations of C12[2]rotaxane; (a) position of pillar[5]arene ring on thread as a function of time in a 50 ns run, (b) average free energy versus position over three 50 ns runs.

The results show that when the ring is on the C12 axle, it prefers to sit near the ends of the chain by weakly binding to the triazole moiety in the axle ($M_2/M_{2'}$), and the wheel moves back and forth up to 10 times in 50 ns at 350 K. The small barrier at $TS_{22'}$ arises from the loss of the weak interaction of the pillar[5]arene with a triazole group in the energy minima M_2 and $M_{2'}$. The barrier for re-binding to one of the favorable stations does not overcome in the simulation on this timescale. The calculated average energy is approximately 10 kcal mol^{-1} lower when the wheel is on the binding site with the C4 station ($M_1/M_{1'}$). This agrees with the observation that population of the ring on the central thread is negligible. The reaction rate is limited by the highest barriers, corresponding to approximately 16 kcal mol^{-1}. The barrier for re-binding would then be approximately 6 kcal mol^{-1}. Crossing this barrier requires slipping of the ring over the triazole, which gives rise to electrostatic repulsion between the triazole and the electron-rich inside of the cavity.

From the simulations, we extracted the position of the center of the macrocycle with respect to the chain atoms. From the probability distribution of the positions, we then calculated the relative free energies according to the Boltzmann equation. The energy profiles thus obtained are shown in Figure 4b.

Additional results of MD simulations of EO3[2]rotaxane are given in the Supporting Information. The wheel in this case moves back and forth along the thread a bit more frequently than in C12[2]rotaxane. The cavity of pillar[5]arene has negative electrostatic potential, thus the frequent shuttling of the pillar[5]arene ring is probably due to electrostatic repulsion between the pillar[5]arene wheel and negative oxygen atoms of the tri(ethylene oxide) chain.

In conclusion, we synthesized pillar[5]arene-based [2]rotaxanes with two equivalent stations connected by different lengths of alkyl and oligo(ethylene oxide) chains. Although the constitution of the spacer and solvent polarity did affect the shuttling motion, we clearly showed that the spacer length has no influence on the rate of ring shuttling. This is explained by a combination of factors, as schematically depicted in Figure 3. The rate-limiting step is the crossing of the barrier for detachment of the wheel from the initial binding station, placing the wheel on the linker ($TS_{12}/TS_{1'2'}$). The energy level of the wheel on the linker ($M_2/M_{2'}$) is lower than in the transition states $TS_{12}/TS_{1'2'}$. Diffusive motion along the linker is fast compared to the timescale of the barrier crossing ($TS_{12}/TS_{1'2'}$) for re-binding to either station.

Although we find spacer-length-independent shuttling rates in the present work, it should be expected that depending on molecular structural details, for a certain length of the linker the diffusion itself will become rate limiting.[3b] We hope that the insights obtained in the present work will contribute to the further development of fast molecular shuttles and molecular machinery.

Experimental Section

Dynamic NMR studies

The free energy of activation for the exchange $\Delta G^{\neq}$ was estimated by using the approximate expression [Equation (1)]:

$$\Delta G^{\neq} = 8.314\,T_c\,[22.96+\log(T_c/\delta\nu)] \quad (1)$$

in which $\delta\nu$ is the chemical-shift difference between the proton signals from complexed and un-complexed species.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: macrocyclic compounds · molecular dynamics · NMR spectroscopy · pillar[5]arenes · rotaxanes

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[9] Recently, we showed that the interaction between polyTHF and pillar[5]arene in $CDCl_3$ was too weak to confirm complex formation (T. Ogoshi, T. Aoki, S. Ueda, Y. Tamura, T. Yamagishi, *Chem. Commun.* **2014**, *50*, 6607 – 6609). In contrast, in the case of linear alkane guests, formation of the host – guest complexation was confirmed by ^{1}H NMR measurements, indicating that linear alkanes are better guests than polyTHF. These results suggest that the pillar[5]arene wheel does not bind well to oxygen-containing threads. Qualitatively, the less favorable binding to the oxygen-containing thread can be expected to slightly increase the barrier to escape of the macrocycle from the stable station, consistent with the experimental observation.

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