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Edith M. Sevick and David R. M. Williams

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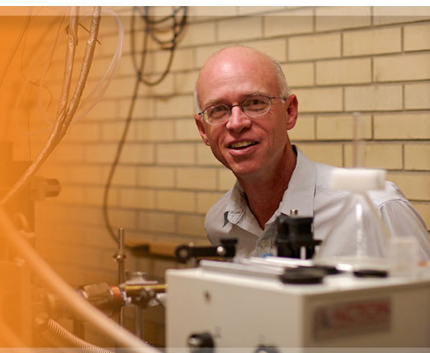
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Conformational isomers of linear rotaxanes

Edith M. Sevick^{1,a)} and David R. M. Williams^{2,b)}

¹Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia

²Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia

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We examine a simple model of rotaxane structure, with 3 asymmetric rings interacting via repulsive power-law forces. This interlocked molecule exhibits conformational isomerisation which is different from that of molecules whose connectedness is through covalent bonds. The rings are free to translate along and rotate around the axle, and hence weak interaction forces between the rings can lead to distinct rotamer states. We use energy minimisation to determine these states exactly, and show that there can be transitions from asymmetric to symmetric states by varying the bond lengths. We also use classical statistical mechanics to show the effect of thermal noise. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4895556>]

I. INTRODUCTION

Rotaxanes are molecules that are composed of two or more covalently bonded structures that are interlocked topologically into a single molecular structure.¹⁻³ The simplest picture of a rotaxane is that of rings threaded through a molecular axle that is capped with bulky steric groups to keep the rings from falling off of the axle. These rings are not covalently bonded to the other parts of the rotaxane and can move, much like a bead on an abacus. They thus can provide a basic building block for the design of a molecular machine.⁴⁻¹²

Mobility in the rings of a rotaxane leads to interesting possibilities: with ring mobility there is the possibility of designing molecular machines that dissipate energy as well as store energy. To date rotaxane synthesis has focussed predominantly upon creating “switches,” where rings are localised at specific “stations” on the axle; however, recently, a method for pumping rings onto an axle has been demonstrated which is capable of producing rings that are not localised, and highly mobile along the axle.¹³ An illustrative, theory-based example of such a molecule is a “piston-rotaxane,” where the mobile rings are threaded on a rigid axle and translate along the axle, behaving as a 1-D gas.^{4,8,9} These rings have significant entropy which give rise to a non-equilibrium response that is similar to an automobile shock absorber and spring combination. In addition, translationally mobile rings threaded on a long flexible axle, or a polymer, are predicted to impart a single-chain yield force, which can have implications in materials design.

Although much of the focus up until now has been either on synthesis or on molecular switches, there is another fundamental area of interest: molecular structure arising from the mobility of asymmetric rings. In traditional chemistry, a molecule can convert into different structural isomers exclusively by rotations about single bonds.¹⁴ That is, one can con-

vert from one structural isomer or conformer to another without breaking and reforming bonds. These conformers are distinct when there is an appreciable, but surmountable, energy barrier to rotation. For example, butane’s trans and gauche isomers are separated by barriers of 3.5 and 5 kcal/mol (or 6 and 8 $k_B T$ at room temperature). Here we show rotaxanes can also exhibit conformational isomerisation, although these result through rotation of interlocked rings about the axle, and not rotation about a single bond. However, because the rings are not bound by bonds or strong interactions to the axle, the “rotamerisation” can also involve ring translation. Under circumstances described here, this relationship between rotation and translation of the ring along the axle leads to a molecular screw.

II. THE MODEL

In this paper, we present a simple model of conformational isomerisation that predicts a non-trivial and rich, behaviour for the conformational structure of rotaxanes. We consider a rotaxane where the asymmetric rings are individually free to translate along the axle, but are rotationally hindered by repulsive ring-ring interactions, whose strength depends upon the pair’s relative orientation. An example of such a repulsive ring-ring interaction would be a Coulombic interaction associated with electrically charged rings, where the force centre on each ring is fixed at one point on the ring. To represent this asymmetric interaction, we append a stem to each ring as shown in Fig. 1, where the force-centre is fixed at the end of the stem. The stems are in reality not needed. All that is necessary is a rotational asymmetry in the ring-ring interaction.

Let the rigid axle have length L with n threaded rings, each having an appended stem of length p in the plane of the ring and perpendicular to the axle. We adopt a generalised pairwise interaction energy $U = \alpha d^{-m}$ where $\alpha > 0$ for the repulsive interaction, $m > 0$, and d is the distance between the force centres. That distance between stem ends i and j , for

^{a)}Electronic mail: Edie.Sevick@anu.edu.au

^{b)}Electronic mail: D.Williams@anu.edu.au

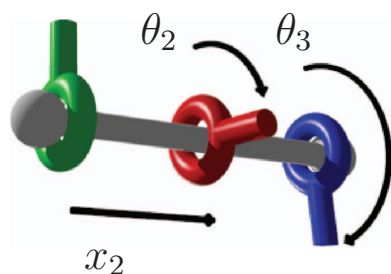


FIG. 1. A 3 ring rotaxane whose asymmetrically charged rings are represented by rings with stems of length p . These rings are labeled 1 (green), 2 (red), and 3 (blue). The location of each ring along the axle of length L is given by x_n and the angle relative to the first ring is θ_n .

rings located at x_i and x_j along the axle at angles θ_i and θ_j is

$$d_{ij} = L\sqrt{2\lambda^2(1 - \cos[\theta_i - \theta_j]) + (\xi_i - \xi_j)^2}, \quad (1)$$

where we have introduced dimensionless coordinates $\xi_i \equiv x_i/L$ and a ratio of the rod length to the axle length $\lambda \equiv p/L$. The “conformational” potential energy of this rotaxane with n ring-rods is then

$$U = \alpha L^{-m} \sum_{i=1}^{n-1} \sum_{j=i+1}^n [2\lambda^2(1 - \cos[\theta_i - \theta_j]) + (\xi_i - \xi_j)^2]^{-m/2}. \quad (2)$$

This defines a potential energy hypersurface in a $2n - 1$ dimensional space with coordinates $\xi_1, \dots, \xi_n, \theta_1, \dots, \theta_n$, where the angles are measured relative to the first ring.

In the absence of thermal fluctuations, there will be an equilibrium rotamer state that we can determine from minimisation of the potential energy over the ξ and θ coordinates. The ratio of stem to axle length, λ , is the only relevant control parameter. As we consider only repulsive interactions, the first and last ring will be positioned at the opposite ends of the axle, $\xi_1 = 0$ and $\xi_n = 1$, and we need only minimise over the remaining $2n - 3$ coordinates. The constant αL^{-m} has no effect on the minimum, and so we will minimise the dimensionless energy, $u \equiv UL^m \alpha^{-1}$ to determine the minimum energy rotamer state as a function of $\lambda = p/L$.

III. EQUILIBRIUM STATES FOR 3 RINGS

The case of a rotaxane with $n = 2$ rings is trivial and needs no calculations: the minimum energy rotamer is one where the force centres are furthest apart, i.e., the rings are located at the ends of the axle ($\xi_1 = 0, \xi_2 = 1$) with their stems oriented opposite to one another ($\theta_1 = 0, \theta_2 = \pi$). However, as the number of rings increases, so does the complexity, with some interesting transitions.

The case of 3 rings is the simplest of the interesting cases. If the stems had zero length ($p = 0$), meaning the rings are symmetric, then the rotaxane reduces to a simple axle with 3 translatable repulsive centres – here it is clear that we would find the rings to be evenly spaced along the axle or $\{\xi_1, \xi_2, \xi_3\} = (0, 1/2, 1)$. As the stem length is increased we might expect that this symmetric arrangement of rings on the axle is

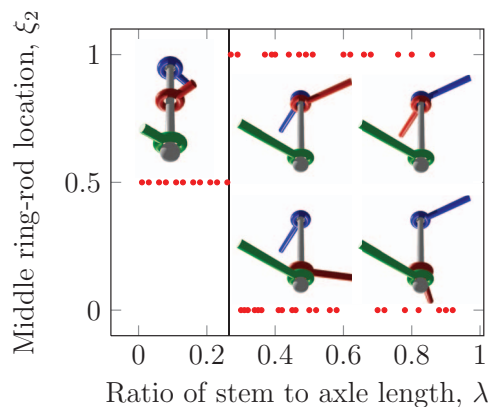


FIG. 2. Fractional position of the middle ring, $\xi_2 \equiv x_2/L$, versus ratio of stem to axle lengths, $\lambda = p/L$, for a 3-ring rotamer at minimum conformational energy with $m = 1$. For $\lambda < \lambda_c \approx 0.266$, the minimum energy rotamer has symmetric placement of the rings along the axle. However, at λ_c , the middle ring location changes discontinuously and significantly from $\xi = 1/2$ to $\xi = 1$ or 0, or to an asymmetric placement of rings on the axle. Pictured are minimum energy conformers below and above λ_c . For $\lambda < \lambda_c$, the minimum energy conformer is unique. For $\lambda > \lambda_c$, the minimum energy state has a degeneracy of 4, i.e., there are 4 distinct rotamer conformations with minimum energy at any λ greater than λ_c .

no longer the global energy minimum and that, for example, the middle ring may nudge closer to the first ring, but compensate for its decrease in axle separation through variation in its relative stem angle. The actual situation is more subtle. As the first and last rings are separated as far apart as possible or $\xi_1 = 0$ and $\xi_3 = 1$, there remains only 3 coordinates over which to minimise energy, i.e., the angle and coordinates of the middle ring (ξ_2, θ_2), and the angle of the last ring, θ_3 . When we numerically determine the coordinates of the rings that minimise the energy for various λ , we find that there is a critical value of λ , $\lambda_c(m)$, which separates two distinct rotamer states. For $\lambda < \lambda_c(m)$ (or stems short relative to axle length) the global minimum conformation is always symmetric in position and angle $\{\xi_1, \xi_2, \xi_3\} = (0, 1/2, 1)$ and $\{\theta_1, \theta_2, \theta_3\} = (0, \pi, 0)$. However, when the stem length becomes sufficiently large or $\lambda > \lambda_c(m)$, the rotamer state becomes asymmetric with the middle ring adopting a position near the ends of the rod. This transition from symmetric to asymmetric rotamer states is shown in Fig. 2 as the middle ring location varies from $\xi = 1/2$ below λ_c to $\xi = 0$ or $\xi = 1$ above λ_c .

The critical value of λ , $\lambda_c(m)$ at which this rotamer transition occurs depends explicitly on the power law for the force, through m . For particular values of m the critical λ 's are found numerically,

$$[m, \lambda_c(m)] \equiv [1, 0.2655], [2, 0.3199], [3, 0.3534], \\ [4, 0.3753], [5, 0.3905], \\ [6, 0.4016] \dots$$

Moreover, the asymmetric rotamer state is 4-fold degenerate. Rings 1 and 2 can be co-located at one end with coordinates $(\xi_1, \xi_2, \xi_3, \theta_1, \theta_2, \theta_3) = (0, 0, 1, 0, \theta_2, \frac{1}{2}\theta_2)$ or $(0, 0, 1, 0, \theta_2, \pi + \frac{1}{2}\theta_2)$ or rings 2 and 3 can be co-located at the other end with $(\xi_1, \xi_2, \xi_3, \theta_1, \theta_2, \theta_3) = (0, 1, 1, 0, \theta_2, 2\pi - \theta_2)$ with a choice of $\theta_2 < \theta_3$ or $\theta_2 > \theta_3$. Here θ_2

depends on λ . These states might seem complicated, but they are very simple. Ring 2 either pairs with ring 1 at one end, or with ring 3 at the opposite end. The ring which is separate from the other two then has a stem which bisects the reflex angle made by the paired ring stems. At any given $\lambda > \lambda_c$, the rotamer states are geometrically identical with the same energy, but they are distinct when the rings are labelled.

These results were obtained from a numerical search for minima over the three free variables ξ_2 , θ_2 , and θ_3 . However knowing the two kinds of states allows us to state analytically the minimum energy. For the symmetric state there are no free variables in ξ and θ ; so that the minimum energy depends upon λ only. Thus the symmetric state energy is simply Eq. (2) with $\{\xi_1, \xi_2, \xi_3\} = (0, 1/2, 1)$ and $\{\theta_1, \theta_2, \theta_3\} = (0, \pi, 0)$,

$$u_{\text{symm}} = 1 + 2 \left(4\lambda^2 + \frac{1}{4} \right)^{-m/2}. \quad (3)$$

In contrast, the energy of the asymmetric rotamer state depends upon λ as well as θ_2 . All of the degenerate asymmetric states have the same energy, so let us choose the one with $\theta_3 = \pi + \frac{1}{2}\theta_2$ and $\xi_2 = \xi_1 = 0$. Eliminating θ_3 and defining $c \equiv \cos(\theta_2/2)$ with the identity $\cos(\theta_2) \equiv 2\cos^2(\theta_2/2) - 1$, Eq. (2) becomes

$$u = (4\lambda^2(1 - c^2))^{-m/2} + 2(2\lambda^2(1 + c) + 1)^{-m/2}. \quad (4)$$

θ_2 of the asymmetric state is determined from the value of c for which $du/dc = 0$ or c_{min} . Unfortunately, there is no analytic solution for c_{min} . However, if we are interested in the crossover between the symmetric and asymmetric states we can make progress by noting that this crossover occurs for $\theta_2 \approx \pi$ or $c \approx 0$. Expanding Eq. (4) about $c = 0$, assuming $\lambda \ll 1$ and minimizing, gives

$$c_{\text{min}} = 2^{1+m}\lambda^{m+2} - (m+2)2^{m+1}\lambda^{m+4} + \dots \quad (5)$$

with the energy of the asymmetric state being

$$u_{\text{asymm}} \approx 2 + 2^{-m}\lambda^{-m} - 2m\lambda^2. \quad (6)$$

By equating u_{symm} to u_{asymm} we can get an approximate value of $\lambda_c(m)$ for $m < 4$ the transition between symmetric and asymmetric rotamer states

$$\lambda_c(m) = 0.184 + 0.0895m - 0.0107m^2. \quad (7)$$

A more brute force approach is just to do the job numerically, as done above.

Fig. 3 shows the analytical form of u_{min} , Eqs. (3) and (6), together with the numerically obtained minimised value of u_{min} . The energy of the system is $U = \alpha L^{-m} u_{\text{min}}$, hence the energy increases with $\lambda \equiv p/L$ as shown in the inset. The stem length p is a physically fixed quantity however, the available axle length L , can be varied by controlling the first ring's position and re-positioning it to $\xi_1 > 0$. An example of such ring manipulation on an axle was achieved experimentally by AFM, and control of ring's axle position is central to the design of molecular machines, such as piston rotaxane. The equilibrium force needed to reduce the axle length through re-positioning of the first ring is $f = -\partial U/\partial L$; and is discontinuous through the symmetric/asymmetric transition. Moreover, in this minimum energy model, the decrease in

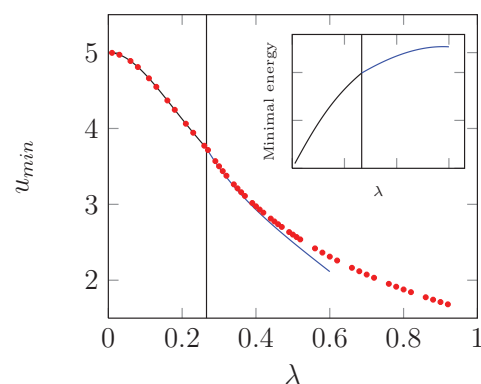


FIG. 3. u_{min} versus λ for $m = 1$ where $\lambda_c \approx 0.266$, for (1) the exact analytical form of u_{min} for $\lambda < \lambda_c$ (black line, Eq. (3)); (2) the approximate form for $\lambda < \lambda_c$ (blue line, Eq. (6), together with (3) the numerically obtained minimised value of u_{min} (dots). The inset shows the total energy of the system, $\alpha L^{-m} u_{\text{min}}$ versus λ with fixed p for the analytic forms of u_{min} .

axle length brings about a discontinuous change not only in the middle ring position, but also rotation of the other rings. Fig. 4 shows the discontinuous jumps in rotation angles, θ_2 and θ_3 , as the molecule passes from the symmetric to asymmetric states. In this way, control of the position of one ring brings about a rotational response in the other rings, much like the action of a screw.

IV. THE EFFECT OF FINITE TEMPERATURE

So far, we have eliminated thermal effects, so these results are exact only in the $T \rightarrow 0$ limit. At finite temperature, the ring coordinates will no longer be associated strictly with the minimum energy states defined above. The parameter $\mu \equiv \frac{\alpha}{k_B T} L^{-m}$ characterises the typical system energy relative to the thermal energy. If μ is large, $\mu \gg 1$, the minimum energy conformer states will dominate; if μ is small, $\mu \ll 1$, entropy will dominate and the ring coordinates will be random. An example is a spare electron on the end of each stem where Coulomb forces in vacuo give $\alpha \equiv \frac{1}{4\pi\epsilon_0} e^2$; at room

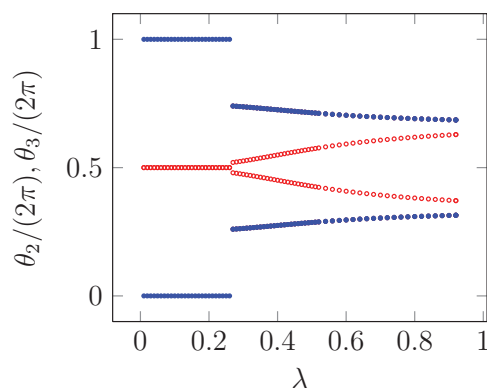


FIG. 4. Ring angles θ_2 (red open circles) and θ_3 (blue dots) versus λ for minimum energy rotamers, determined from numerical minimisation. Below λ_c where the rotamer is symmetric, θ_2 and θ_3 are unique and do not vary with λ . At λ_c , there is a discontinuous rotation of the third ring, θ_3 , with an attendant translation of the second ring (Fig. 2). This simultaneous translation and rotation of different rings can be achieved by variation of the length of the axle, or the axle distance between first and last rings.

temperature and an axle length $L = 50 \text{ \AA}$, the characteristic energy would be $\mu \approx 11$. This value of μ would increase with more substantially charged groups, but would be reduced by the presence of a solvent or by screening. It is thus important to consider the effect of thermal noise, via classical statistical mechanics.

To include thermal fluctuations, we evaluate the conformational partition function

$$Z = \int d\theta_2 d\theta_3 d\xi_1 d\xi_2 d\xi_3 \exp(-\beta U), \quad (8)$$

where $\beta \equiv 1/(k_B T)$ and the integral is over the full range of the angles that the rings make relative to the first ring rod, $0 \leq \theta_2, \theta_3 \leq 2\pi$, but the ξ_i 's are restricted to $0 \leq \xi_1 < \xi_2 < \xi_3 \leq 1$. As we allow fluctuations, both ξ_1 and ξ_3 are no longer restricted to the axle ends. Although analytical calculation of Z and the related probability distributions is difficult, this system has only 5 degrees of freedom, so an exact numerical solution is possible. Here we focus on the behaviour of the middle ring and calculate the probability distribution for the angle, θ_2 , and position, ξ_2 , or $P(\theta_2)$ and $P(\xi_2)$.

We first examine the limiting case, of $T \rightarrow \infty$ or no interactions between the rings, so that $\mu = 0$. In this case $P(\theta_2) = \frac{1}{2\pi}$ and $P(\xi_2) \propto \int_0^{\xi_2} d\xi_1 \int_{\xi_2}^1 d\xi_3$, so that $P(\xi_2) = \xi_2(1 - \xi_2)(\int_0^1 d\xi_2 (\xi_2 - \xi_2^2))^{-1} = 6(\xi_2 - \xi_2^2)$. The distribution $P(\xi_2)$ is broad for an interaction-less rotaxane, with most probable $\xi_2 = 1/2$. That is, irrespective of the value of λ the second ring lies near the middle of the axle in the limit $T \rightarrow \infty$.

Next we reintroduce the potential so that μ is finite, and numerically evaluate the partition function

$$P(\xi_2) \propto \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_3 \int_0^{\xi_2} d\xi_1 \int_{\xi_2}^1 d\xi_3 \exp[-\beta U]. \quad (9)$$

We consider cases where the potential energy dominates over entropy, so $\mu = 10$ is chosen (see Fig. 5). We keep the axle length set at $L = 1$ and we vary the stem length p on each ring, which varies $\lambda = p/L$. For the smallest value of λ that we present, $\lambda = 0.1$, the stem is short compared with the axle

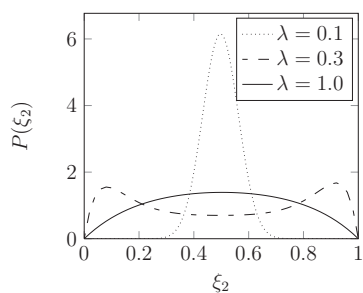


FIG. 5. Probability distribution of the middle ring position, $P(\xi_2)$ with $\mu = 10$, for different values of $\lambda \equiv p/L$, where p is the stem length and $L = 1$ is axle length. At small λ , $\lambda = 0.1$, the symmetric state is the minimum energy state so we have a single peak in the centre. At intermediate λ , $\lambda = 0.3$, the minimum energy corresponds to the middle ring being close to either end of the axle, so we get two peaks with some thermal broadening. At larger λ , $\lambda = 1$, the stem lengths have become so long that the force centres no longer interact strongly, and thermal broadening gives us a single broad peak.

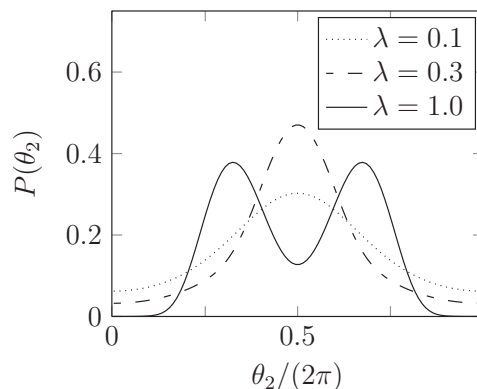


FIG. 6. Probability distribution of the middle ring angle, $P(\theta_2)$, with $\mu = 10$ for different values of $\lambda \equiv p/L$, where p is the stem length and $L = 1$ is the axle length.

length and we find a sharp peak in $P(\xi_2)$ at the minimum energy location $\xi_2 = \frac{1}{2}$. This corresponds to the symmetric state with thermal fluctuations imposed on it. For $\lambda = 0.3$, $P(\xi_2)$ has changed so that the peak has split into two, and the most probable locations of the middle ring are at either end of the axle. The axle centre is the least likely location. However, further increase in λ to $\lambda = 1$ where the rod length is comparable to the axle length, again re-introduces a broad distribution in the middle ring location, with the most probable location being $\xi_2 = \frac{1}{2}$. At first sight this is unexpected, since at $\lambda = 1$ the asymmetric rotamers should dominate. However, as the stems get longer, the interaction potentials are smaller and the minimum conformational energy is small compared with thermal energy. Thus at large λ , $P(\xi_2)$ always approaches the result for zero potential irrespective of the value of finite μ . This would also be true for the case of fixed finite stem lengths, p , and for very long axles, corresponding to $\lambda \rightarrow 0$.

Thermal effects are also marked if we look at the angular distribution of the middle ring via (Fig. 6)

$$P(\theta_2) \propto \int_0^{2\pi} d\theta_3 \int_0^1 d\xi_1 \int_{\xi_1}^1 d\xi_2 \int_{\xi_2}^1 d\xi_3 \exp[-\beta U]. \quad (10)$$

At $\lambda = 0.1$, we see a single thermally broadened peak at $\theta_2 = \pi$ corresponding to the symmetric state. However, at $\lambda = 0.3$ and $\lambda = 1$, the minimum energy states are asymmetric, with θ_2 taking on two different values that straddle π as shown in Fig. 4. However, unlike the discontinuous change in ξ_2 , (from $1/2$ to either 0 or 1), θ_2 varies smoothly with λ , i.e., $\theta_2 = \pi \pm \delta$ where δ varies smoothly from λ_c . At $\lambda = 0.30$, the energy barrier between the $\theta_2 + \delta$ and $\pi + \delta$ is not appreciable compared to thermal energy, so that thermal fluctuations make these asymmetric states indistinguishable. However, at $\lambda = 1.0$, the θ_2 -difference between the asymmetric states is greatest and the barrier is significant compared with thermal energy; consequently, the distribution $P(\theta_2)$ demonstrates two distinct asymmetric states through θ_2 . This however does not mean that the different rotamer states cannot be identified close to λ_c because the distributions for ξ_2 clearly show the transition from symmetric to asymmetric, as would distribution $P(\theta_3)$.

V. CONCLUSIONS

In summary, we have produced a study of the structure of a simple rotaxane system, where there are repulsive interactions between the rings. Of course many such systems are possible, and given the richness of structure found in our system, more complicated rotaxanes will have significantly more states. Some approximations have been made. We have assumed that the stems remain perpendicular to the axle so the rings are a reasonably tight fit to the axle. This could be relaxed, but at the cost of significant mathematical complexity. We have also assumed that the rings effectively have zero excluded volume and can lie on top of each other in the asymmetric states. We could also relax this constraint, but it would not add anything significantly different or interesting to the behaviour. Thermal broadening in our system clearly has some effect, but at least in some cases it does not destroy the identity of the rotamer states. There are obvious extensions here to more than 3 rings particularly to the case of very large numbers of rings.

At present there are few examples of experimental determination of rotaxane structure. Indeed many rotaxane systems focus on rings which are bound to the axle, thus removing the interesting freedom associated with translation, if not rotation. It is often assumed that rotation is possible, and in one study,¹⁵ this is in fact noted as important. Systems where the rings can translate between fixed stations are the basis for molecular switches.⁴ In order to experimentally verify our predictions one would need a rotaxane for which both translation and rotation were possible and, for example, one in which there were charges placed on the rings. Our motivation here is however not to examine any specific system, but to point out that mechanically interlocked molecules can have rotational isomers, just like their chemically bonded counterparts, and that these isomeric states should be easily accessible, and should be present even in cases where thermal motion downgrades their signature.

This kind of study represents a new kind of structural chemistry. It differs from ordinary bonded chemistry, because the interactions are weak, but it also differs from the usual soft matter systems because the topological constraints on the rings prevent the system just falling apart, and allow the structure of real molecules to be controlled by rather weak forces. As an aside, this kind of molecular structure has a long history

albeit a rather inexact one, as both Democritus and Descartes both considered bonding between atoms as a series of hooks into rings.¹⁶

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