

Diffusion of Vinyl Bromide through the Crystals of *p*-Bu^t-calix[4]arene

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The mechanism for the diffusion of vinyl bromide (VB) through the nonporous van der Waals organic solid of *p*-*tert*-butylcalix[4]arene (tBC) is examined by molecular mechanics calculations. In a “squeeze” mechanism, a VB molecule passes through the interstitial space in the rim regions of tBC bowls, after the partial filling of nearby inclusion sites, and couples with the both the rotation of butyl groups and the translational sliding of the bilayers, until it encounters and falls into a empty site. In a “relay” mechanism, translational sliding shifts the skew angle between two tBC bowls and makes it possible to pass a VB from one bowl to another and throughout the solid. The barrier for the “relay” mechanism is 4 kcal/mol lower than the “squeeze” mechanism, although the “squeeze” mechanism is favored by entropy. The “squeeze” mechanism should be more sensitive to the size of the diffusion molecule and should leave residue VB molecules in the interstitial regions. In contrast, the VB molecule hops from one site to another in the “relay” mechanism, and the kinetically limiting step is the translational sliding of the bilayer. Such contrasts should help resolve the relative importance of the two mechanisms in future kinetic studies.

Introduction

p-*tert*-Butylcalix[4]arene (tBC) is a bowl-shaped ring molecule that is a well-known building block in supramolecular chemistry.^{1,2} In the solid state, it can adopt different crystal forms depending on the temperature and growth conditions.^{3–5} As tBC molecules are immobilized by van der Waals interactions, their bowl shapes produce considerable voids in the solid. As shown in Figure 1 for two such structures, the bottoms of these bowls are first stacked together to form a bilayer, and these bilayers are further stacked to form a solid. Between two bilayers, a pair of tBC molecules facing each other could form a skewed capsule which can be filled by all kinds of guest molecules. The crystal structures for these inclusion compounds vary considerably, depending on the guest molecule, which has been studied extensively for insights into the assembly of supramolecular lattices.^{6,7}

Inclusion of guest molecules into organic host frameworks is typically achieved either in solution via solvation-based molecular recognition or in solid via diffusion through porous channels. It was a big surprise when Atwood and co-workers discovered that vinyl bromide (VB) molecules could find their ways into the tBC capsules by immersing a pure tBC crystal in VB.^{8,9} The inclusion induced translational shift in the bilayer stacking from ABCD shown as **1A** in Figure 1 to the ABAB stacking in **1C**. It cannot be due to solvation since the tBC crystal was intact. Furthermore, no porous diffusion channels were found after careful examinations on the crystallographic structural data. The presence of such mysterious diffusion channels in a nonporous organic van der Waals solid has aroused renewed interests in tBC and functionalized calixarene crystals as potential materials for gas storage and separation, and indeed,

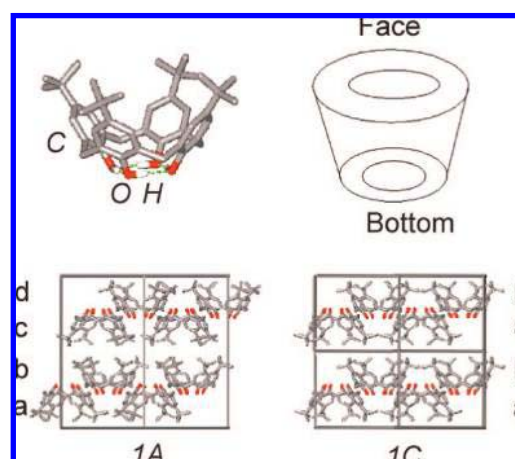


Figure 1. Top: schematics for the structure of a bowl-shaped *p*-Bu^t-calix[4]arene (tBC) molecule. Bottom: stacking of tBC bilayers into solids with ABCD (**1A**) and ABAB (**1C**) stacking.

the list of molecules that can be taken up by such crystals now includes CF₃ Br, CF₄, C₂H₂, CH₄, N₂, O₂, CO, CO₂, H₂O, NO₂, NO, SO₂, and Xe.^{10–18}

Previous theoretical studies have been focused on the structural aspects of calixarene conformations and guest–host interactions.^{19–23} Three recent molecular dynamics studies are more focused on the adsorption of gaseous molecules in tBC crystals, as related to the diffusion processes. Alavi et al. have tested the force field parameters by comparing optimized lattice parameters with X-ray crystal structural data and calculated the binding energy for guests such as Xe, N₂, H₂, CH₄, and SO₂, which can vary considerably.^{24,25} Their dynamic simulations on guest motions inside the tBC cages indicated that the periods of motions were around 1 ps at 300 K for Xe and N₂. These results lent support to the proposition that the diffusion occurred by site hopping.²⁴ Also using molecular dynamics method,

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Daschbach et al. studied the interaction of CO₂/H₂ with a single tBC molecule and with a pair of facing tBC molecules. In agreement with experiment, they found that the adsorption for CO₂ was more favorable.²⁶

The most intriguing question, that how could a molecule as big as VB penetrate a nonporous solid without damaging the crystal, remains unanswered. Its answer is not only important for understanding the fundamental dynamics in such van der Waals organic solids but also essential for the rational design of such crystals for gas storage and separation. However, two mechanisms have been proposed.

The first was suggested by the experimentalists that the diffusion involves some kind of “extensive cooperation between one another, much like the components of a machine.”⁸ More specifically, the gas molecules were supposed to move along the upper rims of the tBC bowls, where they should come into contact with the bulky Bu^t groups. The rotation of these Bu^t groups would produce “turnstile” effects to make the diffusion of molecules possible.¹⁵

The other mechanism was suggested by our own group, which was based on the facile translation of the tBC bilayers in the solid. Translational sliding of bilayers could bring two bowls facing each other to form a capsule, similar to the transition of **1A** to **1C** shown in Figure 1, within which a VB molecule could move from one tBC bowl to another and throughout the crystal. However, the study was based on a density functional theory method which was not well suited for the description of van der Waals interactions. It also exacted too high a computational cost for a supercell containing more than two bilayers, which made it impossible to model the local effects of bilayer translation.²⁷

In this report, we present a molecular mechanics study on these two mechanisms for the diffusion of VB molecule inside a tBC crystal. By constrained optimization, the diffusion paths for both mechanisms are mapped out and the related energy barriers are estimated. Our results provide a look into the molecular details as a VB molecule passes through the nonporous tBC solid and identifies distinct kinetic features which should be measurable in future experiments.

Computational Method

The Tinker package²⁸ is employed in our calculations, with the molecular interactions described by the MM3 force fields.²⁹ Structure optimization is straightforward with the conjugate gradient method. The initial geometry is produced by using the experimental crystal structure. To map out the path for VB diffusion and for the translational shift of the bilayer, a constrained minimization is implemented using the augmented Lagrangian method.³⁰

In such a method, the total energy is augmented by geometrical constraints on the guest and host molecules, to produce a Lagrangian in the form of

$$L = E(X) + \frac{\sigma}{2} C^2(X) - \lambda C(X)$$

where E is the total energy of the system, σ the penalty parameter, λ the Lagrangian multiplier, and $C(X)$ the geometrical constraints. The minimization for such a Lagrangian is performed by the conjugated gradient method. The gradients are calculated by

$$F_L(X) = F(X) + F_c$$

$$F_c = \sigma C(X) - \lambda$$

where $F(X)$ are the forces produced by the force fields and F_c are the constraint forces that keep the system on a particular point along the diffusion or translation path. In our calculations, such a constraint is typically to keep certain distances at a constant value, and $C(X)$ takes the form

$$C(X) = d_{ab}^* - d_{ab}$$

$$d_{ab}^* = \frac{1}{N_a} \sum_{i=0}^{N_a} x_i^a - \frac{1}{N_b} \sum_{j=0}^{N_b} x_j^b$$

where x is one of the three spacial dimensionalities; a and b label the mass center of the atoms selected to be constrained; d_{ab} is the target distance between a and b to represent the diffusion or translation coordinate, while d_{ab}^* is the current value. For the diffusion of VB in tBC solid, the mass center of the eight oxygen atoms on the bottoms of two tBC molecules is chosen as a , and the Br atom on VB is b . For the translation of bilayers, a and b are the mass centers of the oxygen atoms on two specific tBC bowls.

Starting from an optimized initial configuration, the system is moved stepwise toward a predetermined final configuration. At each step, the system is forced to move a small step along the translational or diffusion path by constraining the relevant distance to a constant value, while all other coordinates are left free in the minimization of the total energy. The collection of the energy data set provides the minimum-energy translation or diffusion path.

Results and Discussion

1. Structures. The tBC solid, without any guest molecules, is optimized using two separate initial geometries, as shown in Figure 1. The first one, **1A**, corresponds to the ABCD structure identified in experiment and the second one, **1C**, to the ABAB structure, produced experimentally after the inclusion of VB molecules.⁸ In both cases, the optimization leads to a stable structure, and as shown in Table 1, the total energy is -14.32 kcal/mol for **1A** and -11.57 kcal/mol for **1C**. It indicates that **1A** is more stable than **1C**, in agreement with the experimental observation of **1A** before guest inclusion.

When VB molecules are enclosed in the tBC solid, the energy ordering for these two structures is reversed, with a value of -70.24 kcal/mol for **1A-VB** and -78.60 kcal/mol for **1C-VB**.

TABLE 1: Calculated Lattice Parameters and Energy

	empty cell without VB	
	1A	1C
$a*b*c$ (Å)	12.49*12.31*26.20	12.59*12.59*26.43
$\alpha*\beta*\gamma$ (deg)	90.00*90.00*90.00	90.00*90.00*90.00
E_{total} (kcal/mol)	-14.32	-11.57
	cell with VB enclosed	
	1A-VB	1C-VB
$a*b*c$ (Å)	12.46*12.43*26.73	12.63*12.63*25.74
$\alpha*\beta*\gamma$ (deg)	90.00*89.24*90.00	90.00*90.00*90.00
E_{total} (kcal/mol)	-70.24	-78.60
E_1 (VB removed)	-5.82	-10.62
E_2 (tBC removed)	-0.61	0.25
$E_{\text{total}} - E_1 - E_2$	-63.81	-68.23

Obviously, **1C-VB** is now more stable, again in agreement with the experimental observation. The total energy can be roughly broken down into several components, including the tBC–tBC, tBC–VB, and VB–VB interactions. By freezing the geometry at the **1A-VB** or **1C-VB** values and removing either all the tBC or the VB molecules from the unit cell, the energies of the remaining structures provide a measure of the tBC–tBC (E_1 in Table 1) and VB–VB interactions (E_2 in Table 1). The VB–tBC interaction can be obtained by subtracting the above two interaction energies from the total energy. Along similar line of reasoning, in the case of **1A** and **1C** the total energy is an indication on the strength of tBC–tBC interaction. As shown in Table 1, the interaction between VB molecules (E_2) is fairly small. Before the inclusion of VB, the interactions between tBCs are more favorable in **1A** (−14.32 kcal/mol) than in **1C** (−11.57 kcal/mol), which makes **1A** slightly more stable. After the inclusion of VB, this value changed slightly for **1C-VB**, which is now −10.62 kcal/mol, but the change is more appreciable in the case of **1A-VB**, which is now only −5.82 kcal/mol. It indicates that the inclusion of VB does induce small but appreciable changes in the host structure. But the most significant difference between **1A-VB** and **1C-VB** is in the tBC–VB van der Waals interaction energy. Its value is −63.81 kcal/mol for **1A-VB** and −68.23 kcal/mol for **1C-VB**. All these changes are due to the subtle variations in the layer stacking and inclusion sites that affect the van der Waals interactions.

With four VB molecules in the lattice, this amounts to a guest–host interaction energy around 17.1 kcal/mol for each VB molecule in the experimentally observed **1C-VB** and 16.0 kcal/mol per VB molecule in **1A-VB**. Such values should be compared with the interaction energy of 10.8 kcal/mol for Xe and 6.6 kcal/mol for CH₄, calculated by the same scheme. Our value for CH₄ inclusion is in excellent agreement with the previously value of 6.7 kcal/mol reported by Alavi and Ripmeester,²⁵ but their value for Xe at 24 kcal/mol is significantly larger than our value and also much larger than the value of only 3 kcal/mol reported before also by Alavi and co-workers.²⁴

The larger value for VB can be understood as due to the larger size of VB molecule, compared with Xe or CH₄. Our value for Xe is also more reasonable since the van der Waals radii for both Xe and CH₃ are just above 2 Å. It is unlikely that their inclusion energy could differ by almost 17 kcal/mol.

The calculated lattice parameters are also listed in Table 1, and the overall agreement with experiment is quite reasonable, with relative error in lattice length within 2.5%. Our results are also comparable with the results obtained by Alavi et al.,²⁴ in which the unit cell volume and the density of the solids have been used as the measure for the quality of the potential parameters for a number of calixarene inclusions compound. Our calculated volumes are 4028.3 Å³ and 4106.0 Å³, as compared to the experimental value of 4105.4 Å³ for **1A** and 4212.3 Å³ for **1C-VB**.⁸

2. Bilayer Sliding. Calixarene solids are known to exist in several phases.⁶ The bilayers in these solids are bound by van der Waals interactions, similar to graphite, and sliding along these bilayers should be quite facile. Experimentally, the inclusion of VB induced a single-crystal to single-crystal transformation from **1A** to **1C**, which in itself also involves a sliding process.⁸

Shown in Figure 2 is a path for the sliding of one bilayer within a unit cell containing a total of six bilayers and no VB molecules. The initial configuration is similar to **1A**, with an ABCD stacking of the bilayers, and labeled as **SA** in Figure 3.

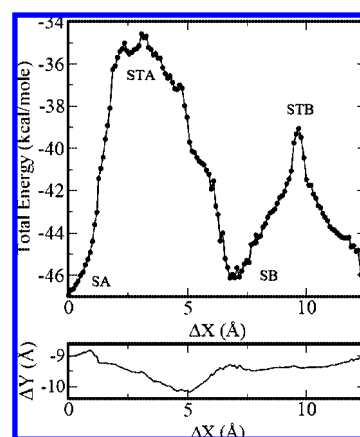


Figure 2. Total energy plotted against ΔX , the coordinate for translation sliding of a bilayer. The lower panel shows the concurrent movement along the y direction. **SA**, **STA**, **SB**, and **STB** correspond to structures shown in Figure 3.

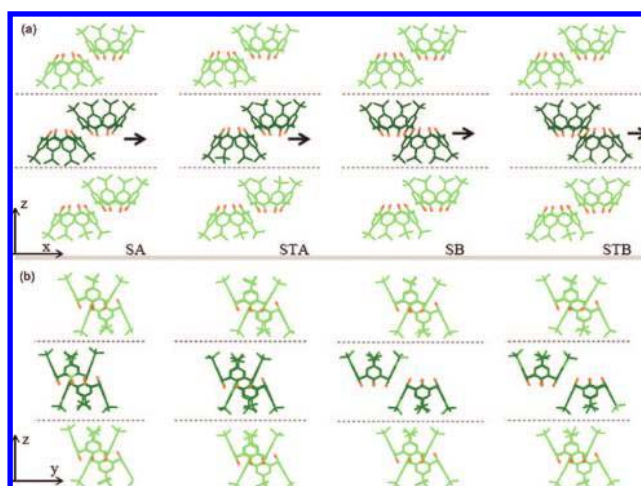


Figure 3. Structures along the sliding path shown in Figure 2, from (a) the x direction and (b) the y direction.

As the highlighted bilayer is moved to the right, the total energy is raised by 13 kcal/mol at the structure **STA**, which can be considered as a transition barrier and is similar to the ABAB stacking in **1C**. Passing **STA**, the total energy is gradually lowered, to reach another minimum at **SB**, which is only slightly higher in energy than **SA**. Moving further to the right, there is another barrier 8 kcal/mol, beyond which the **SA** is fully recovered as the unit cell has been moved by one period along the x direction, over 12.46 Å. During such a translation, there is also sliding along the y direction, as shown in the lower panel of Figure 2, although its extent is within only 1.5 Å.

Along the z direction, there is no translation, as the shift is restricted to the xy plane. However, there is expansion in the lattice c parameter, as the bilayer moves. The magnitude can be gauged from the difference in the c value between **1A** and **1C**, which is around 0.5 Å.⁸ It is natural to ask how much is the translation barrier when the c parameter is not allowed to relax. Shown in Figure 4 are the energy curves for translation movement, with 2, 4, 6, and 8 bilayers respectively in the unit cell, with the c parameter fixed in all calculations. It is obvious that the energy barrier drops with the number of bilayers, as there are more spaces around the moving bilayer to adjust for its translation movement. It indicates that along the z direction, the translation could be localized within a few bilayers, without affecting the overall crystal lattice. It is also due to the

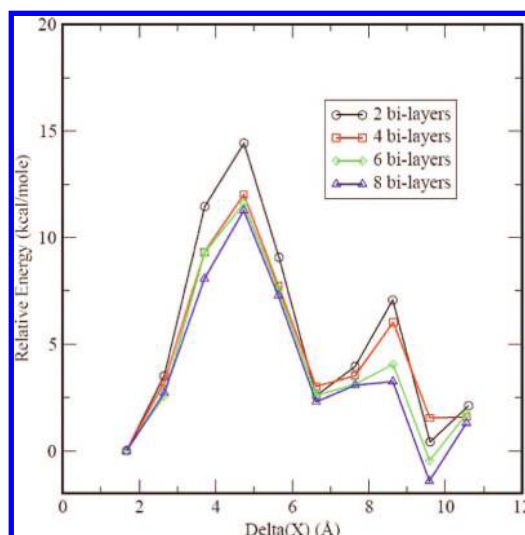


Figure 4. Energy change along the sliding path calculated with a unit cell containing 2–8 bilayers. The c parameter is not relaxed. The energy changes little when the number of bilayers reaches 6, indicating that sliding could take place locally within a few bilayers.

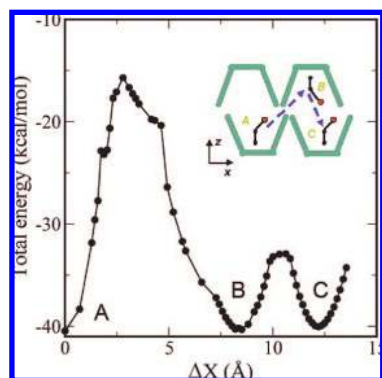


Figure 5. Energy profile for a single VB molecule to migrate from one inclusion site to the next empty site. The energy barrier is 24.6 kcal/mol because it costs energy to push the VB molecule from its inclusion site.

observation of very small differences between the calculated energies for 6 and 8 bilayers that we choose a unit cell with 6 bilayers as our model for the detailed calculations along the diffusion and translation paths, in which the c parameter is fixed.

3. “Squeeze” Mechanism. Within each tBC bowl, there is no open channel for a VB molecule to force its way through the circular wall or the bottom. However, in a solid, there are interstitial spaces around the bowl rims, where tBC molecules are stacked together. In principle, it is possible for a VB molecule to squeeze through bowl rims and diffuse from one bowl to the next, as shown in Figure 5, which has been suggested before.¹⁵ Such a path would produce local distortions in the solid as the diffusing VB disrupts the packing of tBCs and bumps into the bulky Bu' groups, which results in barriers. However, as the interactions between tBC bowls are van der Waals in nature, the spaces between bowl rims are more flexible than either the bowl wall or bottom.

Two types of situations are considered for such a “squeeze” mechanism. In the first case, a supercell similar to **1A** (ABCD stacking) with eight tBC bowls and one single VB molecule is considered, with the z direction fixed, and the VB molecule migrating from one inclusion site to the next empty bowl as shown in Figure 5. It corresponds to the initial diffusion, when

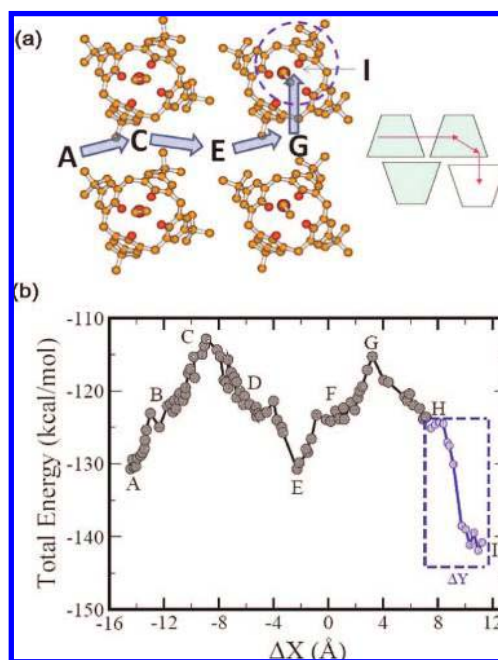


Figure 6. (a) The “squeeze” mechanism: a VB molecule passes through the rim region of the occupied sites, until it falls into an empty site (circled). Starting from point A, it goes through a number of points and squeezes between Bu' groups, as indicated by the arrow. The inset in the right shows the same process from a different angle. (b) The corresponding energy profile, which indicates a barrier around 17 kcal/mol (from A to C). ΔX is the diffusion coordinate. At each point the structure is fully relaxed under a geometrical constraint forcing VB along the diffusion path.

a tBC crystal is immersed in VB and most of the inclusion sites are empty. The barrier obtained is 24.6 kcal/mol.

In the second case, a similar **1A** supercell is employed, but the number of host sites is doubled by increasing one period in the x direction. The crystal is partially filled, with only one empty site. A VB is introduced between the occupied sites in the rim region as shown in Figure 6. It then moves along the xy plane and squeezes through the inter-rim region until it finds and settles into an empty enclosure site. Physically, it corresponds to the situation when a tBC crystal has been immersed in VB for a while, and many inclusion sites have already been occupied, especially near the surface area. To penetrate the inner sites, VB molecules must squeeze through between the occupied sites.

It turns out that the diffusion barrier of 17.0 kcal/mol in such a partially filled crystal is lower than the barrier of 24.6 kcal/mol for a VB molecule to migrate from one inclusion site to another. This can be understood by the fact that for a VB in an inclusion site its adsorption energy is already ~ 16 kcal/mol. For it to migrate to another site, it must be first forced out of this adsorption potential well. In contrast, when a VB is squeezed into the rim region between occupied sites, it is already in a high-energy state.

The energy profile for this process is also shown in Figure 6. The VB molecule moves through the points A–G, in which the VB molecule stays between bowl rims in close contact with the Bu' arms which are forced to rotate and bend, as shown in Figure 7. The structure on the left is at point C, in which the VB molecule is squeezed among three Bu' groups, labeled as t1, t2, and t3, and the total energy is raised to a maximum. As the VB molecule moves a few steps to the right, both the t1 and t2 groups become more relaxed, while the Bu' group labeled

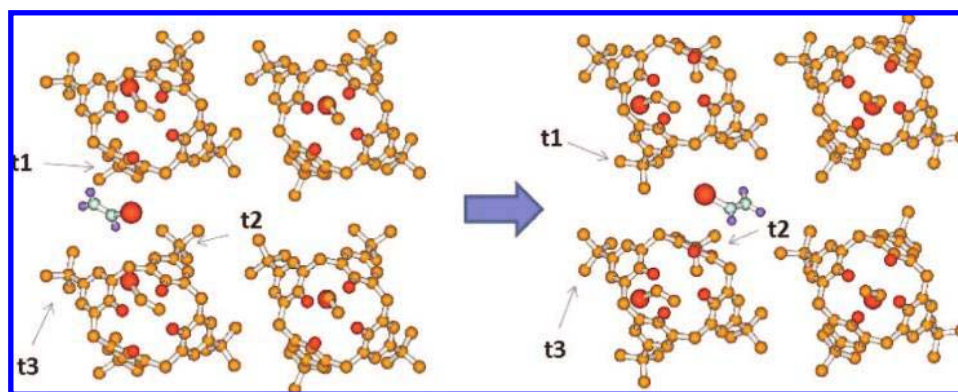


Figure 7. Left: the structure at point C, where the VB molecule is trapped among three Bu' groups, t1, t2, and t3. Right: the structure a few steps after point C. H atoms are not shown on the tBC molecules.

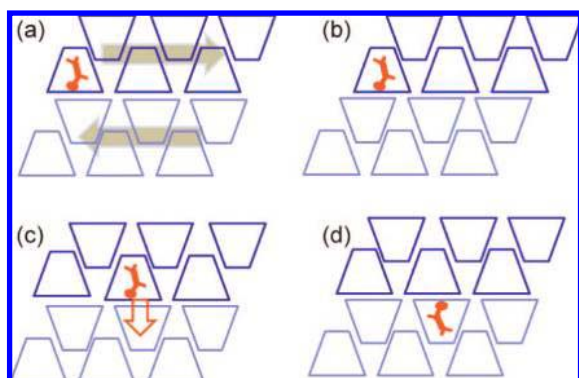


Figure 8. The steps in a "relay" mechanism. The sliding of bilayers from (a, b, c) realigns the tBC bowls to form a new capsule. The VB molecule is then flipped and passed to another tBC bowl (d). The energy profile is similar to that shown in Figures 2 and 3, with (a) being SA and (c) being SB.

as t2 is further bent. Such "squeezes" between the VB molecule and Bu' groups induce not only rotations in the affected Bu' groups but also the orientation flipping of the VB molecule.

After the VB reaches point G, it can fall into a nearby empty inclusion site and reaches point I with an energy drop of almost 30 kcal/mol. Configurations at point A or E can be thought as an adsorption site in the rim region, and its energy is around 10 kcal/mol higher than the energy of point I, an inclusion site. It indicates that in the "squeeze" state at a rim region adsorption site such as point A or E the adsorption energy for a VB molecule is 10 kcal/mol less than the value at an inclusion site, at a value around only 6 kcal/mol.

It is also important to note that while a VB molecule passes through the bowl rims, which is modeled by constraining the x coordinate, there is significant bilayer sliding along the y axis. Since the sliding of the bilayer is facile, it is understandable that when the VB is compressed against the blocking Bu' arms along its diffusion path, sliding along the unconstrained y direction is easily induced. The shift in y is about 4 Å.

4. "Relay" Mechanism. The facile sliding of bilayers makes it possible for a "relay" mechanism, illustrated in Figure 8.²⁷ It involves two steps. First the sliding of the bilayers brings a tBC bowl, in which a VB molecule is enclosed, to form a new capsule with another empty tBC bowl. Then the VB molecule into the other bowl. In such a way, a guest molecule is passed from one bowl to another and diffuses through the molecular crystal.

The sliding process is actually the same one discussed previously and shown in Figures 2 and 3, with an energy barrier

of 13 kcal/mol. In the second step, the VB is flipped inside a capsule made of two tBC bowls, and the barrier is only ~8 kcal/mol. It indicates that such a flipping is easily achieved at room temperature, and a VB molecule should eventually finds the energetically most favorable orientation.

5. Conclusions. Energetically, both mechanisms are accessible around room temperature. The calculated barrier for the "relay" mechanism is 4 kcal/mol lower than the "squeeze" mechanism. Without explicit consideration of the entropy factor and extensive dynamic sampling on all the possible diffusion paths, it is difficult to assert the relative importance of these two mechanisms.

Translational sliding of the bilayers is an important consideration in both mechanisms. For the "relay" mechanism, sliding is the prerequisite, although such a sliding is less favorable, as far as entropy is concerned, since it requires the collective movement for all the atoms on a bilayer. For the "squeeze" mechanism, sliding could also be induced, since the repulsion between a diffusing VB and the Bu' groups in the bowl rim region is a localized interaction depending on the specific structure at a particular point along the diffusion path. An individual interaction as such cannot be isotropic. However, if there are a large number of VB molecules diffusing through the crystal, their total effects on the translational sliding may cancel each other out. In other words, translation is not a prerequisite for the "squeeze" mechanism.

On the basis of our results, we predict different kinetic behaviors which should help resolve the relative importance of these two mechanisms by future experiments. In the "relay" mechanism, the diffusing molecule hops from one site to another, made possible by bilayer sliding. For molecules with sizes smaller than VB, their diffusions through the "relay" mechanism should be almost the same kinetically, with bilayer sliding as the rate-determining step. For molecules larger than VB, there is the possibility that the guest molecule could protrude out of a tBC bowl, which may make the translation difficult.

In contrast, a guest molecule can not jump from one site to another in the "squeeze" mechanism. The inclusion sites are filled sequentially. Guest molecules squeeze through the bowl rims only after the sites immediately around them are already filled and they also fill any empty site encountered along the diffusion paths. The diffusion channel in this mechanism is fairly jammed, due to the presence of the Bu' groups in the rim region, and the diffusion barrier must be quite sensitive to the molecular size. The diffusion rate is expected to change significantly as the molecular size changes. In light of the many types of

molecules already studied in experiments, comparisons in the diffusion kinetics should provide valuable insights.

Another difference in the two mechanisms is that for the "squeeze" mechanism there should be guest molecules which have entered the crystal through the diffusion channels but cannot find empty sites to fill. They could leave these rim sites at raised temperature but must overcome many a barrier of 17 kcal/mol before existing the crystal. By lowering the temperature, it is possible to trap them in the rim region. The presence or absence of such guest molecules can provide another important indication on the preference of the two mechanisms.

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