

Snakes and Ladders. The Sigmatropic Shiftamer Concept

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Received March 23, 2006

ABSTRACT

Sigmatropic shiftamers are organic molecules (conceived originally as polymers) in which bonds migrate back and forth along their frameworks. In this Account, we describe the origins of the sigmatropic shiftamer concept, theoretical predictions of molecular architectures that may support shiftamer behavior, and possible future directions for research on this class of molecules.

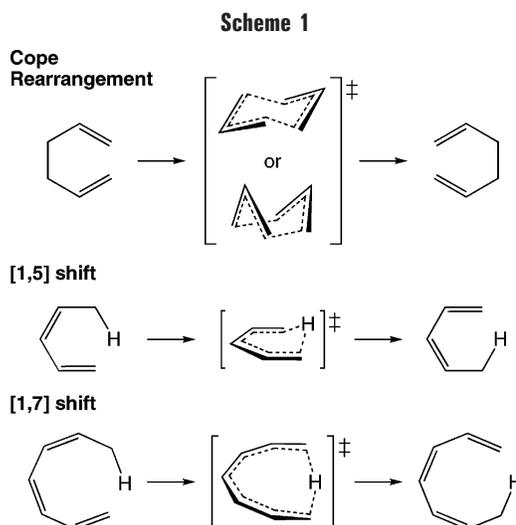
Introduction

The idea of sigmatropic shiftamers arose from a juxtaposition of a family of orbital-symmetry-allowed concerted molecular processes with ways of thinking of the transport of charge and electrons in polymeric organic conductors. The discrete molecular processes are sigmatropic reactions, typically with a reasonably low activation energy. Examples are the Cope rearrangement¹ (a [3,3] sigmatropic reaction), a suprafacial [1,5] hydrogen shift, and an antarafacial [1,7] hydrogen shift,² all shown in Scheme 1.

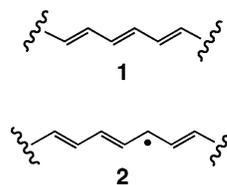
The polymeric system, fashionable 20 years ago, quiescent now, is polyacetylene, **1**. Aside from the question of bond alternation (yes, it takes place), polyacetylene has engendered an industry of solitons, polarons, bipolarons, and other defect structures,³ exemplified by **2**. Some of these may be real and responsible for the fascinating charge transport properties and conductivity of hole or electron-doped polyacetylene. Could one create molecular analogues of the menagerie of quasiparticle states of

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Roald Hoffmann was born in 1937 in Złoczwów, Poland. Having survived the war, he came to the U.S. in 1949 and studied chemistry at Columbia and Harvard Universities (Ph.D. in 1962). Since 1965, he has been at Cornell University, now as the Frank H. T. Rhodes Professor of Humane Letters. He has received many of the honors of his profession, including the 1981 Nobel Prize in Chemistry (shared with Kenichi Fukui). "Applied theoretical chemistry" is the way Professor Hoffmann likes to characterize the particular blend of computations stimulated by experiment and the construction of generalized models, of frameworks for understanding, that is his contribution to chemistry. He is also a writer of essays, nonfiction, poems, and plays.



doped polyacetylene, analogues in which a single or double bond, an H atom, or a set of these, could move with alacrity (and electricity) down a polymer chain?



The Ladders: [3,3] Shiftamers

Sigmatropic shiftamers were originally conceived as hydrocarbon polymers in which localized bonds could be transported back and forth along the polymer chains via sequential [3,3]-sigmatropic shifts.⁴ Two polymer systems were considered: ladderanes⁵ and parallel polyacetylenes^{3,6} (Scheme 2). In the former, a pair of parallel π bonds (derived, in a thought experiment, from a retro [2 + 2] reaction of one of the cyclobutane rings of the polymer) was envisioned as the bonding unit that would move via Cope rearrangement. In the latter, a single single bond connecting the two polyacetylene chains (derived, again hypothetically, from the combination of a soliton from each chain) constituted the proposed migrating unit. Both of these systems were explored using quantum chemical calculations,^{4,7} but only one of them turned out to behave as a shiftamer.

Ladderane Shiftamers. Let us first consider the ladderane case. Our approach here, used also in studying the other systems described below, was to start from small model systems and build up to larger and larger systems until the rearrangement barriers reached a consistent level. Systems ranging from divinyl cyclobutane to the structures shown in Scheme 3 (a “broken” [7]-ladderane; relative energies in kcal/mol below each structure) were

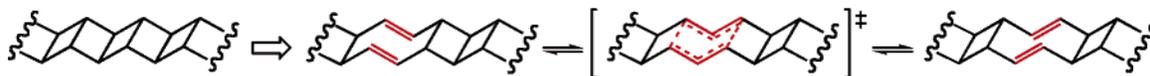
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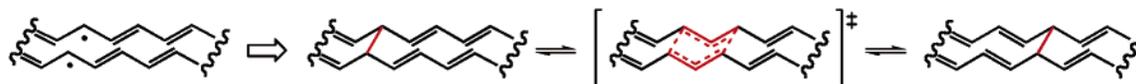
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Scheme 2

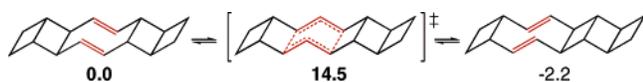
a pair of double bonds migrating down the polymer



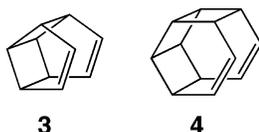
a single bond migrating down the polymer



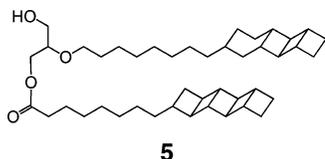
Scheme 3



examined for the ladderane system. When at least one intact cyclobutane ring separated the pair of π bonds from the ends of these oligomers, rearrangement barriers of approximately 15 kcal/mol were computed. We take this to be a reasonable estimate of the rearrangement barrier in the infinite system, indicating that such systems are likely to be fluxional at relatively low temperatures. The barrier for Cope rearrangement in these systems is so low (the barrier for the boatlike [3,3] shift of divinyl cyclobutane itself is computed to be 31 kcal/mol⁸) because the fusion of cyclobutanes onto the ends of an octadiene unit preorganizes it into a conformation that is quite similar to the structure of the transition state for Cope rearrangement; compare, for example, the structures in Figure 1. Cases involving *syn*-fused cyclobutanes are also possible, with some of the simplest of these being ring-opened prismanes such as **3** and **4**.⁴

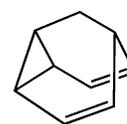


Interest in ladderanes is on the rise, sparked in part by their recent discovery as membrane constituents in certain bacteria (**5** is an example of a naturally occurring ladderane lipid), and several clever strategies for ladderane synthesis have been described (a recent example⁹ is shown in Scheme 4).⁵ Hopefully, systems suitable for testing our theoretical predictions will soon become available.



σ -Polyacenes. The second type of [3,3] shiftamer proposed involves the migration of a σ bond along a pair of polyene chains (see the bottom of Scheme 2).⁴ In the simplest such system (that shown in Scheme 2), the only direct connection between the two polyene chains is the migrating σ bond. In hopes of encouraging [3,3] sigmatropic shifts to occur, we attempted to remove the flexibility

of the polyene arms by tethering them together.¹⁰ Our first design of this type was based on the framework of the classic organic molecule barbaralane, which is known to undergo a degenerate [3,3] sigmatropic shift with a very low barrier (~ 6 kcal/mol).¹¹ Our shiftamer design is shown in Scheme 5.



barbaralane

Models of varying length were examined computationally; in all cases, shiftamer behavior was *not* observed.

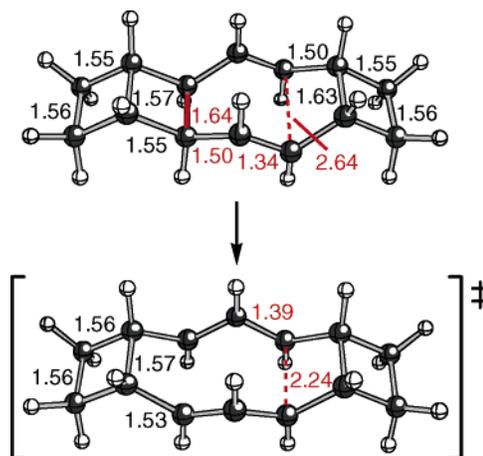
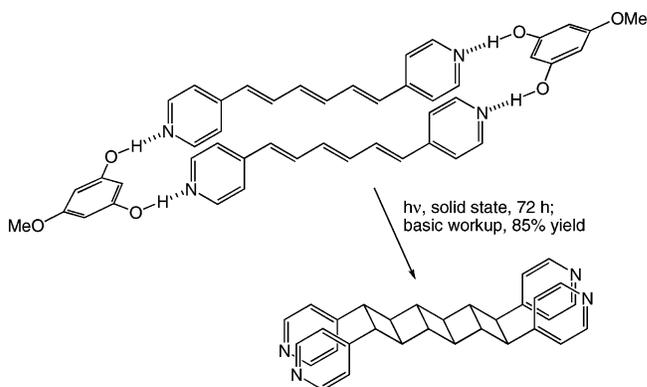
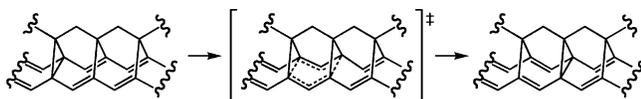


FIGURE 1. Reactant and transition-state structures for the [3,3] sigmatropic shift in a broken [6]-ladderane [B3LYP/6-31G(d)]. Selected distances are shown in angstroms.⁴

Scheme 4



Scheme 5



Instead of a localized σ bond next to polyene chains, the preferred geometries of these systems involved the delocalization, through space, of two polyenyl chains. As shown in the example at the top of Figure 2, the 1, 3, 5, ...

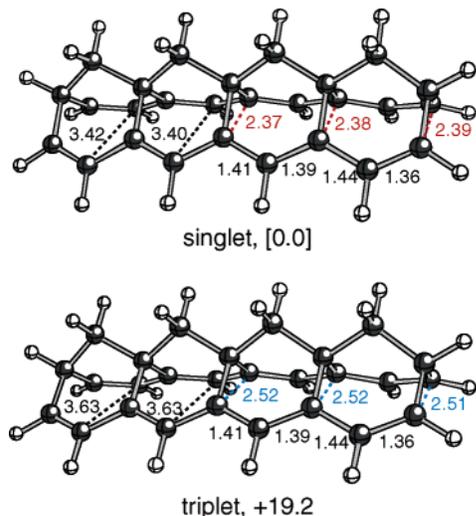


FIGURE 2. Geometries (selected distances shown in angstroms) and relative energies (kcal/mol) of fully optimized singlet and triplet models of the proposed shiftamer shown in Scheme 5 [B3LYP/6-31G(d)].¹⁰

carbons of each polyenyl chain approach those of the other at distances <2.4 Å. For comparison, in the corresponding triplet structures (e.g., see the bottom of Figure 2), in which favorable interpolyenyl interactions are not possible, these distances are >2.5 Å. The delocalized molecular orbitals involved in the interpolyenyl interactions of a representative singlet structure are shown in Figure 3.

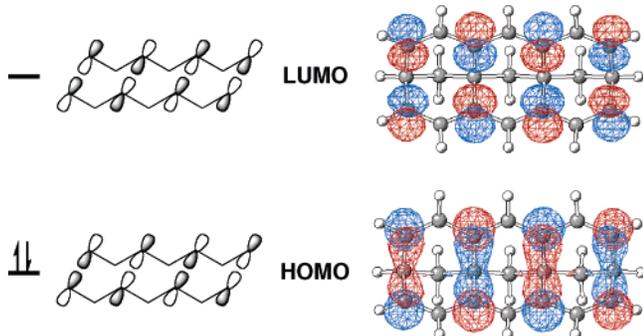


FIGURE 3. Delocalized molecular orbitals [B3LYP/6-31G(d)] for a singlet σ -polyene.¹⁰

Thus, such systems are not sigmatropic shiftamers. Instead, in analogy to polyacenes,¹² we call these molecules σ -polyacenes (Chart 1). While normal polyacenes consist of two polyene chains interacting with each other in a π sense, σ -polyacenes consist of two polyene chains interacting with each other in a σ way. A variety of

Chart 1

polyacenes

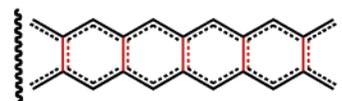
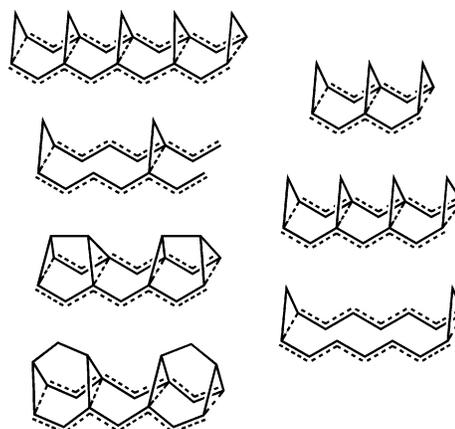
 σ -polyacenes

Chart 2



σ -polyacenes have thus far been examined theoretically (e.g., Chart 2) but none longer than the barbaralane analogue of tetracene.¹⁰

Recent theoretical studies have predicted that the ground states of polyacenes larger than hexacene should be singlet diradicals; thus, these molecules can be thought of as possessing two delocalized but essentially noninteracting polyenyl chains.^{12a} It will be interesting to see if longer σ -polyacenes behave similarly.

The Snakes: [1,*n*] Shiftamers

7-League Boots: [1,7] Shiftamers. Shiftamers can also be constructed on the basis of other sorts of sigmatropic rearrangements. Take, for example, the parent [1,7] shift (Scheme 1). The transition structure for this rearrangement,^{2b,13} shown in Figure 4, is helical because of the orbital-symmetry-dictated preference for antarafacial migration of the hydrogen with respect to the heptatrienyl substructure.¹⁴ Extending the ends of this system by appending all *Z* polyenes leads to the helicoid shiftamer structure shown in Scheme 6. In this shiftamer, the net

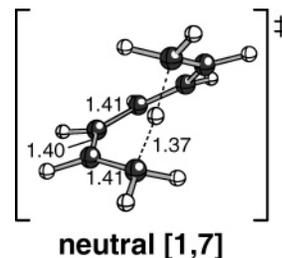
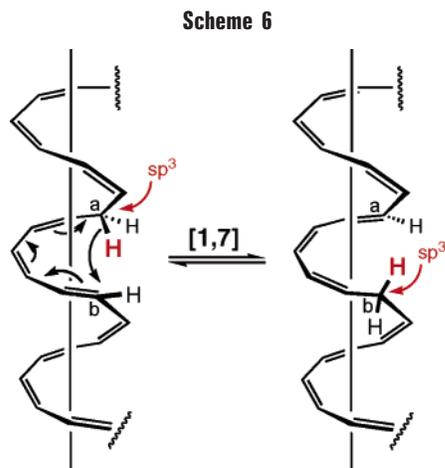


FIGURE 4. Transition structure for the [1,7] sigmatropic shift of heptatriene [B3LYP/6-31G(d); distances shown in angstroms].^{2b,13}



transport of a hydrogen atom along a polyene chain is achieved by a series of [1,7] shifts (e.g., from C_a to C_b). Note, however, that a different hydrogen atom transfers in each [1,7] shift. This shiftamer can also be viewed as a means for transporting a single site of saturation along an otherwise unsaturated hydrocarbon chain.

This [1,7] shiftamer was again modeled using oligomers of various lengths. The transition structure for one of these is shown in Figure 5.^{7,13} As for the [3,3] shiftamer described above, barriers of approximately 15 kcal/mol are predicted for the infinitely extended case.¹³ Interestingly, the polyene minima have relatively straight backbones, but as the transition state for a given [1,7] shift is reached, a kink in the backbone develops (Figure 6), making for an inchworm-like motion of the backbone as sequential rearrangements occur. Thus, this [1,7] shiftamer propagates hydrogen atoms, sp^3 centers, and kinks along polyene chains.

Variations on this [1,7] shiftamer were also explored. Consider the system shown in Scheme 7.^{13b} Here, we have replaced the polyene arms of the system in Scheme 6 with alkane chains. [1,7] Sigmatropic shifts are still possible in

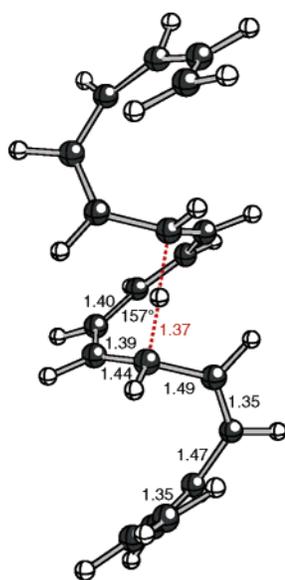


FIGURE 5. Transition structure [B3LYP/6-31G(d)] for a model of the [1,7] shiftamer shown in Scheme 6 (distances shown in angstroms).¹³

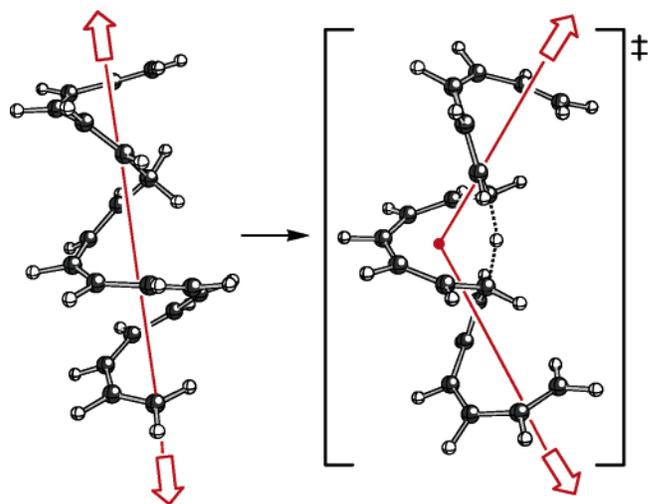
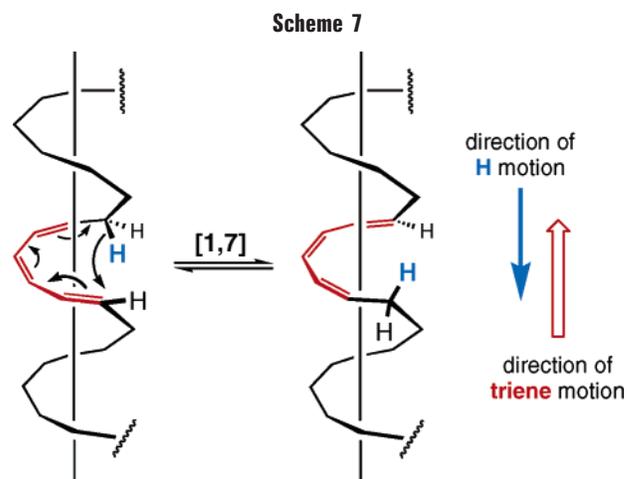


FIGURE 6. Different view of the transition structure shown in Figure 5 and its precursor. The reorientation of the hydrocarbon chain as the reaction proceeds is emphasized by the red lines and arrows.



this system, but a different localized substructure, a “ π clump”, is propagated along the polymer backbone. As a given hydrogen moves (e.g., “down”, as in Scheme 7), the hexatriene substructure moves in the opposite direction. If another hydrogen, one carbon away from the original migrating hydrogen, does a [1,7] shift in the same direction as the first, then the hexatriene unit moves one carbon further in the opposite direction. Thus, one hydrogen at a time moves out of the way of the migrating triene (like the go in stop-and-go traffic).

Many twists on these architectures are possible. One is shown in Scheme 8. Here, a helical polyethylene polymer is “seeded” with two hexatriene “defects” separated by some number of saturated carbons.^{13b} Various [1,7] hydrogen shifts involving these intervening methylene groups can eventually allow for coalescence of the two hexatrienes into a single dodecahexaene. In principle, any number of short polyethylene and polyacetylene blocks could be reorganized into long polyethylene and polyacetylene blocks through [1,7] shifts. The favored lengths for the blocks will depend upon the balance between geometric effects and the benefits of increasing conjugation through coalescence.

Scheme 8

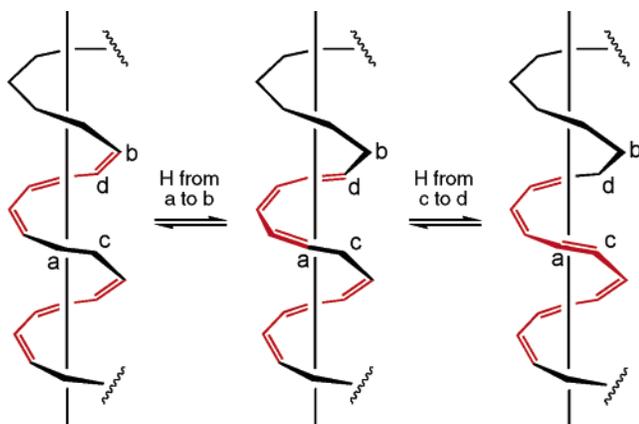
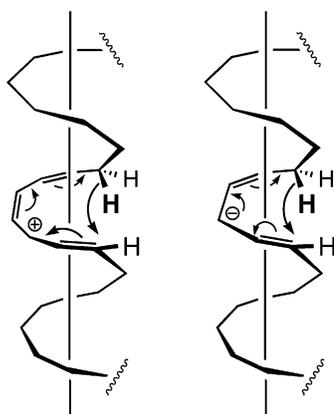


Chart 3



Adding Charges: [1,6] and [1,8] Shiftamers. Ionic versions of helicoid shiftamers are also possible.^{13b} Examples based on cationic [1,8] and anionic [1,6] shifts, which each involve the same number of rearranging electrons as neutral [1,7] shifts, are shown in Chart 3. In these systems, the movement of charges accompanies the transport of hydrogen atoms. Transition structures for simple [1,8] and [1,6] shifts are shown in Figure 7.^{13b} The barriers for these two rearrangements are computed to be 6 and 14 kcal/mol, respectively. In systems with differently charged localized π clumps (e.g., Scheme 9), coalescence can lead to charge annihilation.

[1,5] Shiftamers: Tapes. Suprafacial hydrogen shifts can also be incorporated into sigmatropic shiftamer architectures.¹⁵ The transition structure for the parent [1,5]

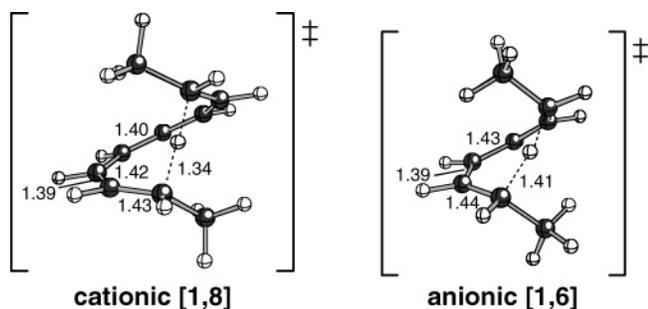
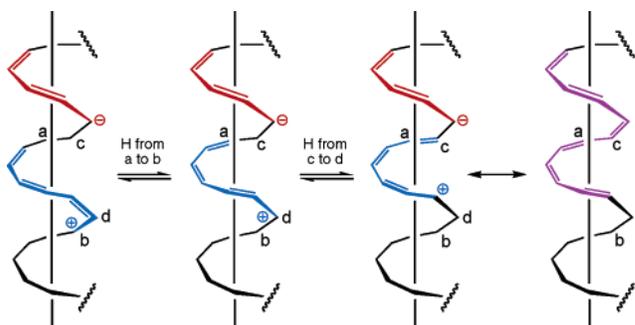


FIGURE 7. Transition structures for dimethyl-substituted cationic [1,8] and anionic [1,6] rearrangements (selected distances are shown in angstroms).^{13b}

Scheme 9



H shift is shown in Figure 8. Because of the orbital symmetry requirement¹⁴ that a [1,5] H shift be suprafacial, shiftamers based on open-chain polyenes are not geo-

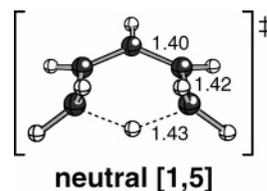
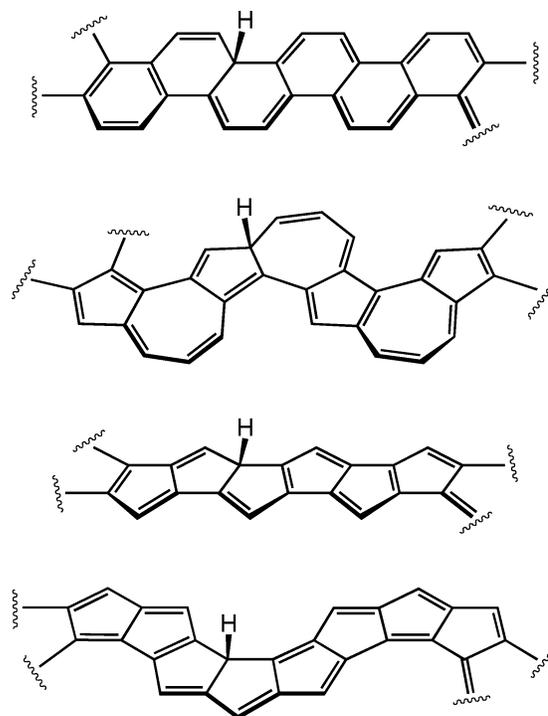


FIGURE 8. Transition structure for the neutral [1,5] shift of 1,3-pentadiene (selected distances are shown in angstroms).^{2b}

metrically feasible. Shiftamers constructed from polycyclic conjugated π systems¹⁶ were therefore explored.¹⁵ In these systems, hydrogen atoms migrate over the faces of organic “tapes” (Chart 4). Unfortunately, the barriers computed

Chart 4



on the basis of model systems tend to be quite high. A representative example is shown in Figure 9.

Cyclic versions of tapes—belts—can also accommodate suprafacial hydrogen shifts. One example described thus far is based on **6**,¹⁷ a cyclic version of a polyphenanthrene

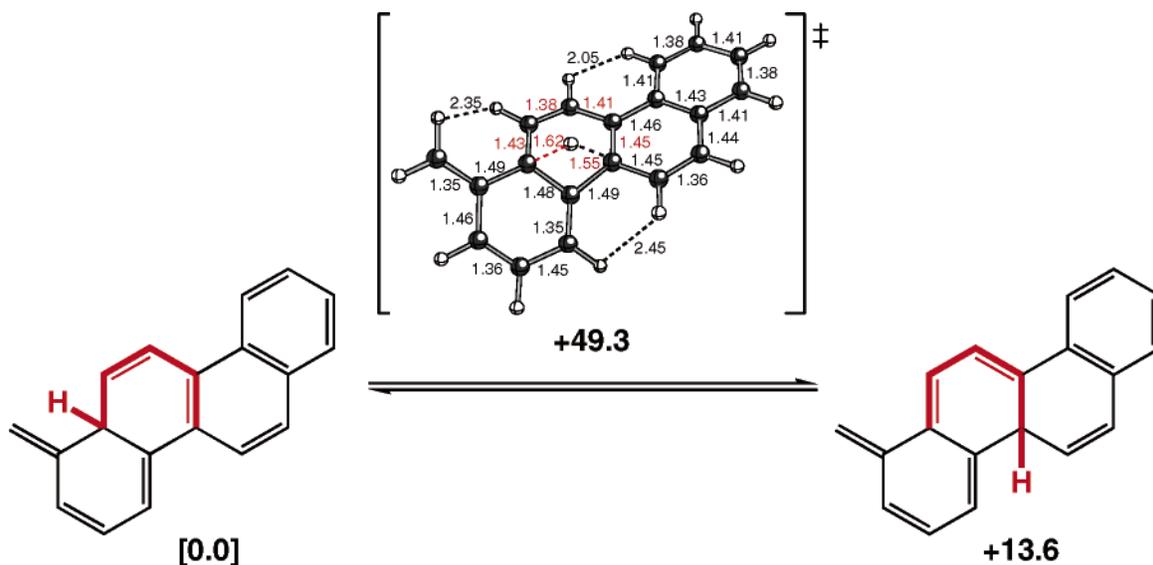


FIGURE 9. [1,5] Shift (highlighted in red) in a model of the top system shown in Chart 4, studied at the B3LYP/6-31G(d) level (selected distances are shown in angstroms, and relative energies are shown in kcal/mol).¹⁵

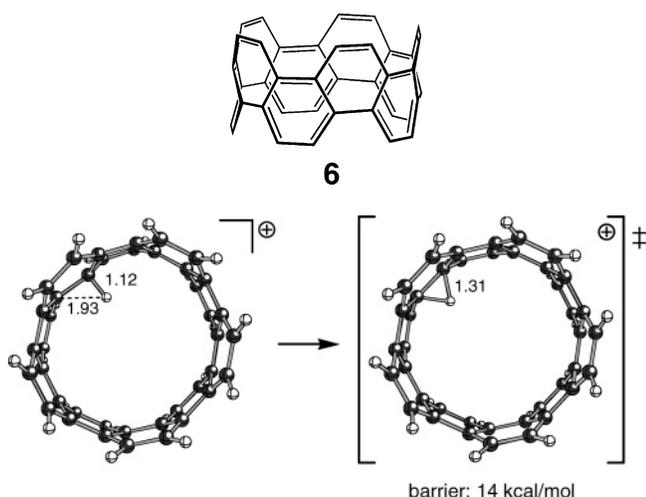


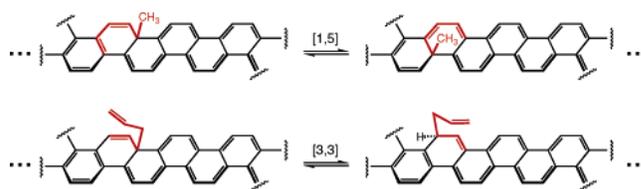
FIGURE 10. "In-protonated" **6** and the transition structure for its [1,2] hydrogen shift (selected distances are shown in angstroms).¹⁵

tape. Protonation on one of the central carbons of the inner surface of this hoop-shaped hydrocarbon leads to a structure (at the left of Figure 10) whose "in"¹⁸ hydrogen can migrate via a transition structure (at the right of Figure 10) for a suprafacial [1,2] shift. No transition structures for [1,5] shifts were found for this system; our attempts at locating such structures led instead to [1,2] transition structures.¹⁵

Future Directions

Other polymeric/oligomeric architectures for supporting sigmatropic shifts are possible. The most obvious include manipulations of charge and the lengths and shapes of the π systems in the systems described above (e.g., varying the linkers and including *Z*-alkenes for [3,3] shiftamers based on polyacetylene chains, endless mixing up of different sized rings and charged versions of [1,5] shiftamer tapes, and systems based on other [*m,n*] sigmatropic shifts). The migration of groups other than hydrogen is

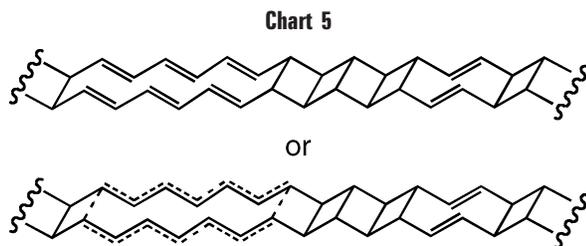
Scheme 10



also possible. In principle, any group that can shift suprafacially can replace the hydrogens in shiftamer tapes such as those shown in Chart 4; two such possibilities are shown in Scheme 10. Several other types of possible shiftamers are described below.

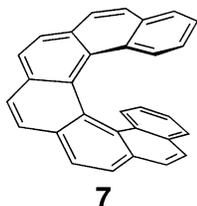
Metals and Heteroatoms. Migrating groups are not restricted to organic moieties. Various metals are well-known to migrate over π systems via so-called haptotropic shifts.¹⁹ This could occur on organic tapes as well, leading to what we refer to as "haptotropic shiftamers", in which metals (or ML_n fragments) migrate over extended hydrocarbon surfaces. If the hydrocarbon surface is a belt such as **6**, several interesting issues arise.^{19d} First, how do the barriers (rates) for migration of the ML_n fragment differ when the fragment is on the inner (concave) or outer (convex) faces of the hoop? If there are ML_n fragments on both the inner and outer surfaces at the same time, is there a preference for migration in the same versus opposite directions? Can the two fragments pass each other (either moving in opposite directions or in the same direction at different rates)?

Antarafacial migration of non-hydrogen groups in helical systems is also theoretically possible, provided that suitable modifications are made. For example, replacing all of the hydrogen atoms in the helicoid shiftamers discussed above with fluorines could allow for the net transport of fluorine atoms along helical chains. In fact, perfluorination may help favor helical conformations for such systems, given the preference for gauche conformations in fluorocarbons.²⁰



Hybrid Ladders. Many possible architectures that combine two or more different types of shiftamers are possible. Several examples are described here. First, the two types of [3,3] shiftamers described initially above, both being related to ladderane polymers, are easily combined as shown in Chart 5. In these systems, coalescence of the ladderane and polyene substructures could occur by the movement of the single pair of π bonds toward the longer polyenes (regardless of whether they are delocalized as σ -polyacenes or not). Alternatively, the longer polyenes could be cut up into isolated π -bond pairs via different [3,3] shifts. The energetics of such processes have not yet been explored.

Sliding Down a Spiral Staircase. Combinations of [1, n] shiftamer “snakes” and [1, m] shiftamer “tapes” are also possible. How might we achieve such a combination? A good source of inspiration in this area is the helicenes²¹, helical polycyclic aromatic hydrocarbons (e.g., **7**, [7]-helicene). Protonation of such helicenes, for example, leads to structures that can, in principle, undergo a variety of tape-like and snake-like shifts. An example of the latter based on protonated [7]helicene is shown in Figure 11.



Our preliminary calculations [B3LYP/6-31G(d)] on this system indicate that such shifts can proceed with low barriers. Several features of these systems are noteworthy. First, the rearrangement shown in Figure 11 involves a methine group. To accomplish long-range hydrogen transport in long helicenes, however, methylene groups must be involved. Thus, shifting of hydrogens from the “inner” helix of the helicene to its “outer” hydrogen-coated perimeter would be necessary.

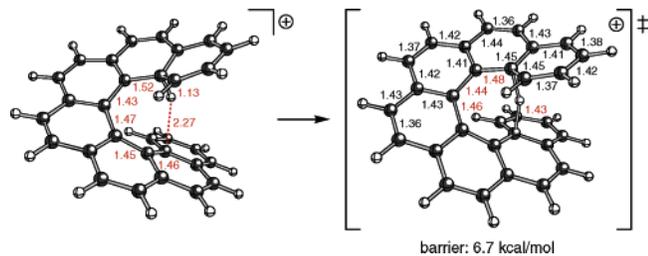


FIGURE 11. Protonated **7** and the transition structure for its antarafacial [1,6] hydrogen shift (selected distances are shown in angstroms).

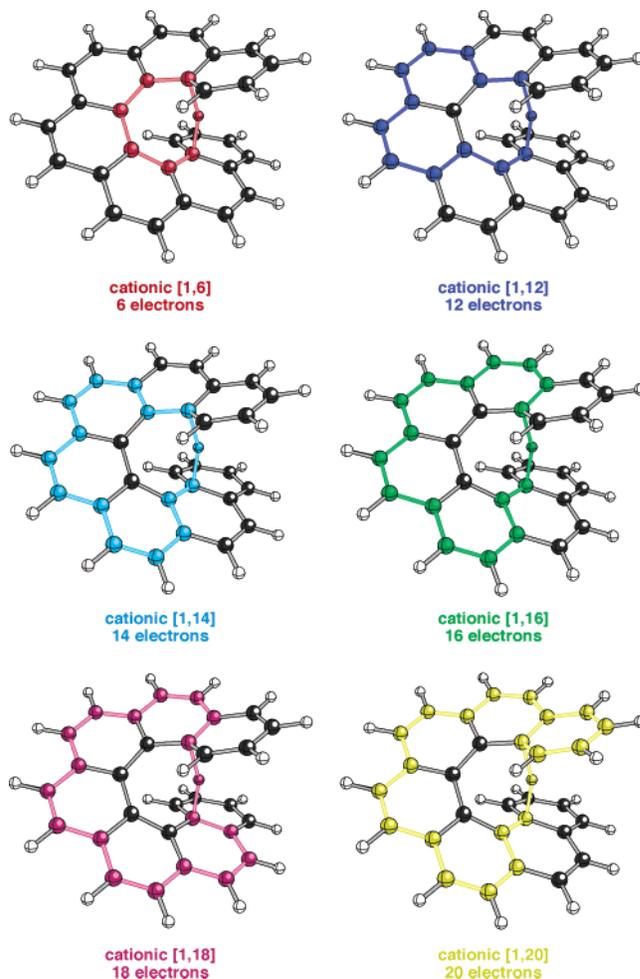


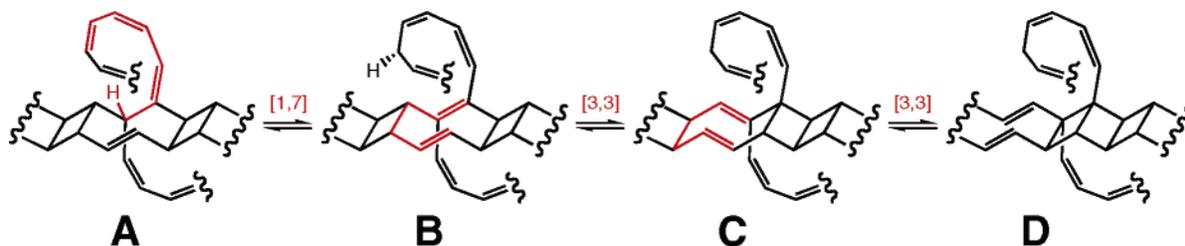
FIGURE 12. Various π circuits present in the transition structure shown in Figure 11.

Second, the antarafacial shift shown in Figure 11 is most simply formulated as a [1,6] shift, but, on the basis of orbital symmetry considerations, cationic [1,6] shifts should be suprafacial with respect to the π system involved. Of course, more than the six carbons highlighted in the top left panel of Figure 12 can be involved in the rearrangement. Examples of alternative π circuits are highlighted in the other panels of Figure 12. Note that both Hückel and Möbius circuits are possible, but in some cases, the use of such circuits would isolate odd polyenes that would be accompanied by additional charges or unpaired electrons. A more in-depth exploration of the orbitals involved is necessary, however, to characterize the nature of this rearrangement. Again, ML_n fragments might also stand in for hydrogens, leading to helical haptotropic shiftamers.

In general, the investigation of these shiftamers uncovers an interesting neither-here-nor-there land of potentially concerted reactions, in which a given reaction is allowed along one π -electron circuit but forbidden along another. This electronic ambivalence bears investigation.

Rococo Shiftamers. Given that both [3,3] and [1,7] shifts involve alkenes, it should be possible to create architectures, part snake and part ladder, in which [3,3] and [1,7] shiftamer structures intersect. One such pos-

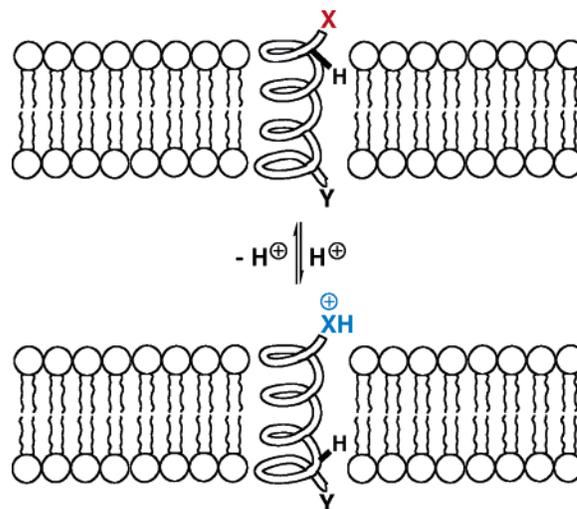
Scheme 11



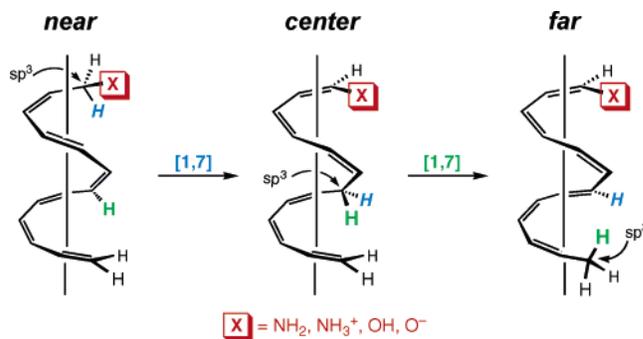
sibility is shown in Scheme 11. The second, third, and fourth structures in this scheme (B, C, and D) can support both types of shifts. Note, however, that in C and D, the [1,7] shifts are restricted to one side of the ladderane chain (here, the top); i.e., the two snakes are insulated from each other. The second structure, B, is therefore special; when the π pair moving along the ladderane chain arrives at its position in this structure, previously impossible [1,7] hydrogen shifts can now occur that allow for the site of saturation on the polyacetylene chain to move from one side of the ladderane to the other. A is special in a different way; when the site of saturation in the polyacetylene chain is also a carbon in the ladderane chain (or if it moves further “below” the ladderane), [3,3] shifts along the ladder can no longer occur. Thus, traveling of the snake’s site of saturation past the ladder requires the ladder to stop rearranging, and movement of the ladder’s π pair past the snake requires the site of saturation to restrict itself to only one-half of the snake. This is one of many rather complicated “gates” that can be contrived using shiftamer components. Here is stop-and-go with a vengeance.

Preorganization and Directional Transport. Let us return now to simpler shiftamers. The main problem with realizing [1,7] shiftamers experimentally is their helical nature. Although helical polyacetylenes and polyethylenes^{6,22} have been described, it is likely that the helical conformations that are essential for [1,7] shiftamer behavior will not predominate in simple systems without some sort of preorganization. How might preorganization be achieved? One strategy is to append groups to the backbone of the polymer that either sterically enforce helical conformations or electronically favor them (e.g., difluoroethylene substructures as described above or a series of oppositely charged groups that interact most favorably in helical conformers²³). Another strategy is shown in Scheme 12. Here, a simple polyacetylene oligomer with one saturated site is adorned with polar endgroups (X and Y). This structure could then be mixed with amphiphiles that tend to form bilayers. If the height of the bilayer matches the length of the polyacetylene oligomer when it is coiled into a helix, then perhaps the system will be driven toward helix formation. In addition, if one or both of the polar endgroups can be readily protonated and deprotonated and this change in the protonation state biases the preferred location of the saturated site, then switchable directional transport of the saturated site (reminiscent of biological “proton pumps”)²⁴ is possible. This is, of course, only speculation at this point, although computations on systems such as those shown in Scheme 13 have begun.²⁵

Scheme 12



Scheme 13



Conclusions

Our trek through the land of sigmatropic shiftamers has thus far been one of speculation and simulation; nonetheless, this chemistry is rich with experimental implications. As Rolf Huisgen once stated, “playfulness is an incentive for the scientist and a motor of progress”.²⁶ We invite you to join in our snakes and ladders game.

We gratefully acknowledge the University of California—Davis, the donors of the American Chemical Society Petroleum Research Fund, the National Science Foundation (through research grants CHE 99-70089 and CHE 04-49845), and the National Science Foundation’s Partnership for Advanced Computational Infrastructure for support.

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AR0680926