Hydrogen Migration Over Organic Tapes: [1,5] Sigmatropic Shiftamers

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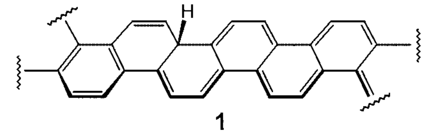
Keywords: Sigmatropic rearrangement / Polycyclic aromatic hydrocarbons / Hydrogen migrations

We explore the possibility of suprafacial hydrogen atom migration over several organic tapes—infinite chains of polycyclic conjugated hydrocarbons. It's not easy.

Introduction

Facile hydrogen migration over metal surfaces is commonplace,[1] but is an analogous process feasible in a fully organic system? Herein we describe several polycyclic conjugated organic tapes over which hydrogen atoms may migrate (**1**−**4**).[2] Barriers for these hydrogen migrations are estimated using computations[3−8] on molecular model systems of various sizes.



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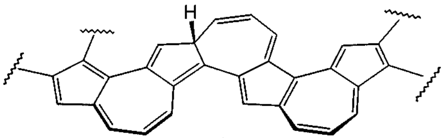

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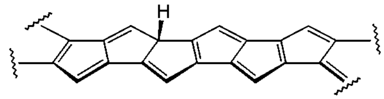

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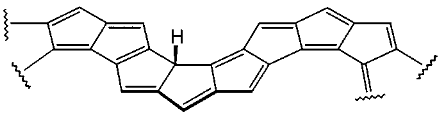

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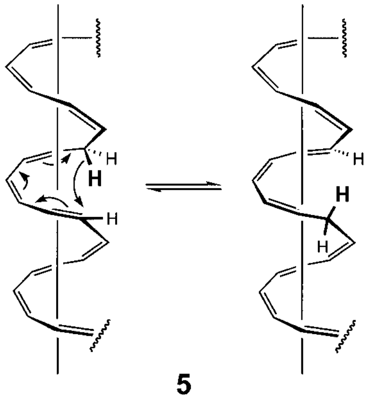
The design of these systems arose out of our recent studies on helicoid sigmatropic shiftamers (for example, **5**).[9a] Sigmatropic shiftamers are organic polymers with localized substructures that can propagate along the polymer chain by sigmatropic shifts.[9] Shiftamer **5** features antarafacial [1,7] hydrogen shifts with low barriers (approximately 15 kcal/mol);[9a] it was logical then to inquire whether related systems involving [1,5] shifts are also possible. The helical geometry of the transition structure (**6**, selected distances in Å)[3−8] for the parent [1,7] hydrogen shift (resulting from the orbital symmetry-based preference for antarafacial migration) led naturally to extension into infinite systems such as **5**.[9a] However, the C_s geometry of the transition structure **7** for the parent symmetry-allowed suprafacial [1,5] hydrogen shift,[3−8] does not lend itself towards one-dimensional extension as easily. Consequently, we focused our attention on systems in which the termini of the [1,5] transition structure are linked together into a ring. Use of five-, six-, and seven-membered rings led us to monohydropolyphenacenes **1**, polyazulenes **2**, and polypentalenes **3** and **4**.[2] The underlying "π-tapes" are quite hypothetical as polymers (so far), but, as we will see near the end of the paper, not as outlandish as one might think.



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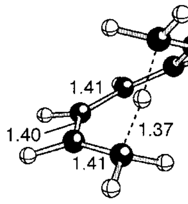
DOI: 10.1002/ejoc.200300583



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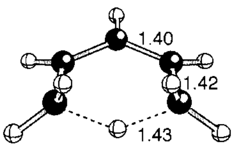

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Polyphenacenes

Structure **1** is an infinite polyphenacene to which a hydrogen atom has been added. Several [1,5] shifts are possible in this system, the relationships between which are not necessarily obvious due to the variety of resonance structures (benzenoid and quinoid) possible for polyphenacenes and to the symmetry relationships one must consider for infinite systems.

Consider, for example, structure **A** in Figure 1. The hydrogen atom at its single site of saturation has four sites that are ("ringwise") each five carbon atoms away from it (labeled a, 5, 5′, and 5″). There is an interesting ambiguity in these systems in that a [1,5] shift around the ring in one direction is a [1,3] shift the other way around. The suprafacial [1,3] shift is of course symmetry-forbidden, while the suprafacial [1,5] shift is symmetry-allowed. We will look for π-bond arrangements (resonance structures), therefore, that allow us to "push arrows" for [1,5] shifts. There is no uncharged resonance structure of the infinite tape that arranges the π-bonds in **1** appropriately for a [1,5] hydrogen shift to carbon atom a (although there are many that are set up for a [1,3] shift). We therefore consider a sigmatropic shift to site a to be very unlikely. There are, however, resonance structures (**A** and **B** in Figure 1) that position the π-bonds in the vicinity of the H atom so as to allow for [1,5] shifts to sites 5, 5′, and 5″.

A subtle question is whether the [1,5] hydrogen shifts to sites 5 and 5′ are distinct or equivalent. The answer to this question becomes clear when the corresponding transition structures for these two rearrangements are compared; these are shown schematically in the center of Figure 1. If the top transition structure (that for hydrogen migration to site 5) is translated a short distance to the right, it becomes clear that it is merely the mirror image of the transition structure for hydrogen migration to site 5′. Thus, these two transition structures are equivalent to each other—they are related by a glide plane—and have identical activation barriers. The products of these two rearrangements are also each equivalent to **A** by glide plane operations, and are equivalent to each other by simple translations.

The [1,5] hydrogen shift to site 5″ is distinct. One can most easily push arrows for this rearrangement from resonance structure **B** (Figure 1). Hydrogen migration in this case produces a structure, **C**, in which the site of saturation has moved from an interior carbon atom of **1** to a carbon atom on the perimeter.

The barriers and reaction energies for the two distinct types of [1,5] shifts that are likely to be available for **1**—those in which an interior hydrogen atom migrates to an-

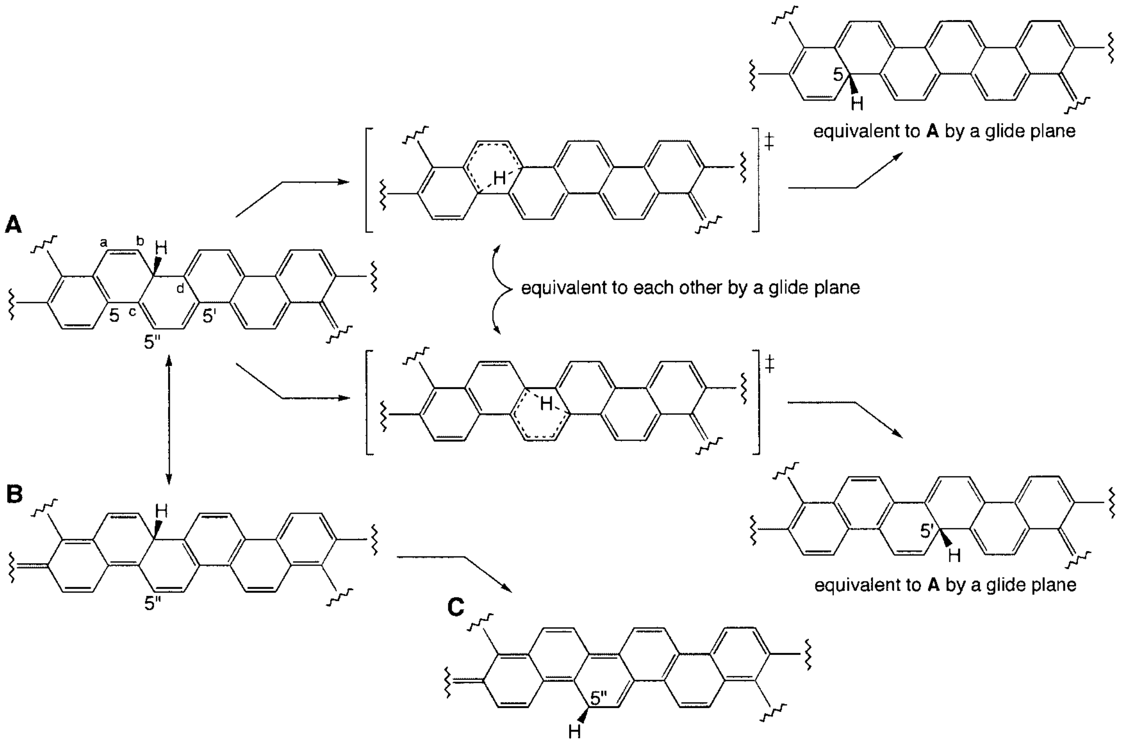


Figure 1. Symmetry considerations for [1,5] hydrogen shifts possible for **1**

other interior position or to a perimeter position—were estimated using hybrid Hartree−Fock/density functional theory calculations[3−8] on various molecular model systems. Models were used since we did not have available to us a reliable theory for calculating nonperiodic infinite systems. The results of these calculations are summarized in Figures 2−6.[10] Our best models for shifts in which an interior hydrogen atom migrates to another interior position are shown in Figure 5, and those for shifts in which an interior hydrogen atom migrates to a perimeter position are shown in Figure 6.

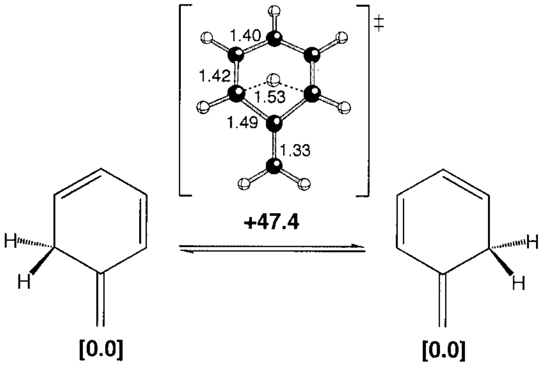


Figure 2. Relative energies (kcal/mol, in bold) for species involved in the [1,5] hydrogen shift in 1-methylene-2,4-hexadiene, a model for **1**; selected distances for the transition structure are shown in Å

Large barriers are found for all of the model systems examined (the ur-system, 1,3-pentadiene, has a barrier of 33 kcal/mol, computed from its productive *cisoid* conformer).[7] The absolute magnitudes of the rearrangement barriers, as well as the relative energies of reactants and products for each rearrangement, vary somewhat due to the subtle interplay of ring strain, steric clashes between the hydrogen atoms on the perimeter of each molecule, and the possibilities for forming various benzenoid, quinoid, and polyene substructures in each.[7h,11] The transition structures for all of these rearrangements bear considerable strain due to the formation of a four-membered C,C,C,H ring system (adorned with an exocyclic alkene), and consequently none are predicted to rearrange with barriers low enough that rapid, fluxional hydrogen migration would be observed at low temperatures.

The barriers for [1,5] hydrogen shifts in cyclohexadiene, dihydronaphthalene and dihydrophenanthrene were also recently computed.[7h] These systems are similar to the structures in our Figures 2−4, but with exocyclic alkenes replaced by methylene groups. The barriers computed for

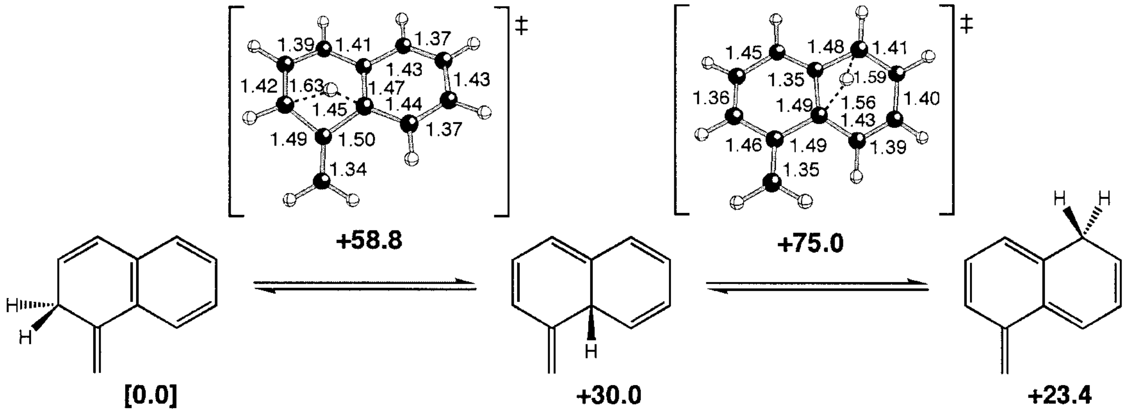


Figure 3. Relative energies (kcal/mol, in bold) for species involved in hydrogen shifts in bicyclic models for **1**; selected distances for the transition structures are shown in Å

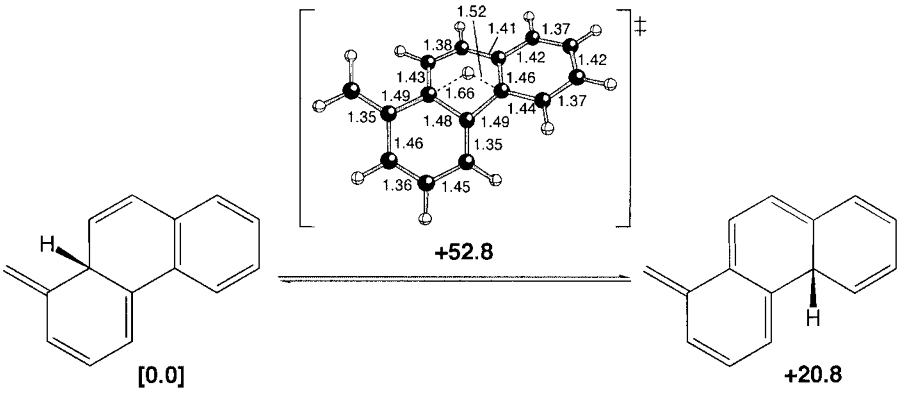


Figure 4. Relative energies (kcal/mol, in bold) for species involved in the [1,5] hydrogen shift in a tricyclic model for **1**; selected distances for the transition structure are shown in Å

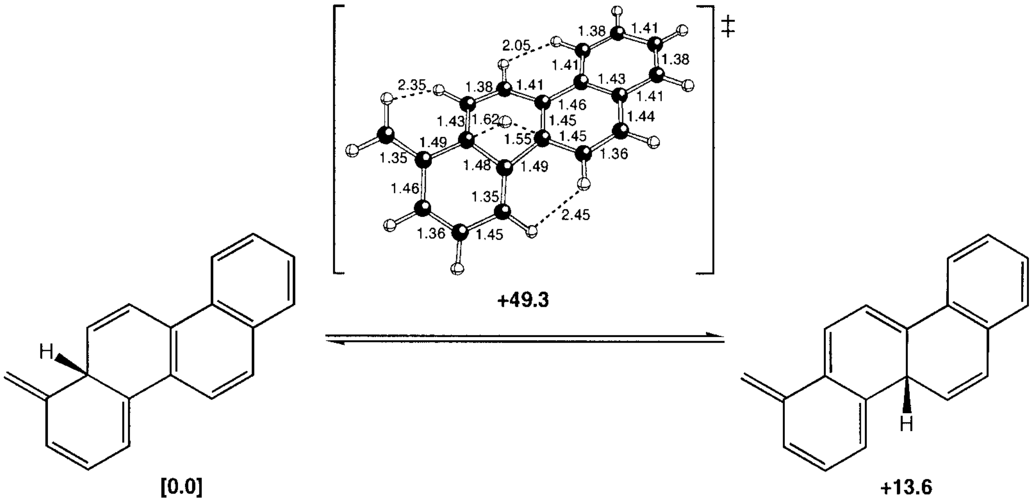


Figure 5. Relative energies (kcal/mol, in bold) for species involved in the [1,5] hydrogen shift in a tetracyclic model for **1**; selected distances for the transition structure are shown in Å

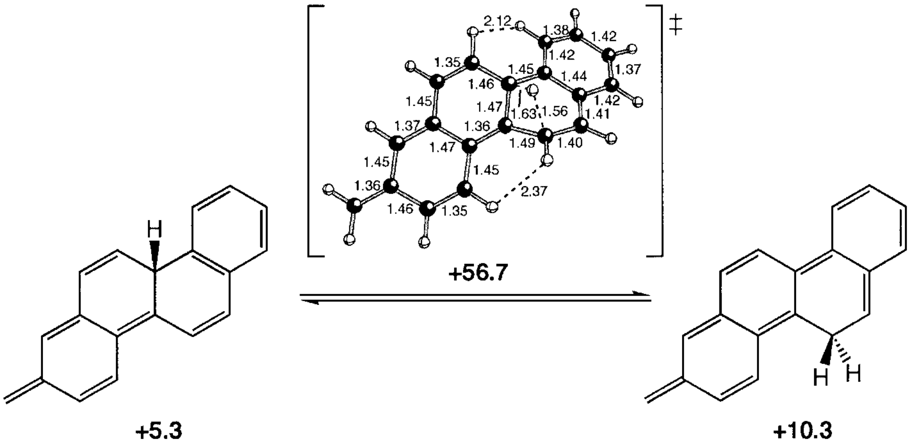


Figure 6. Relative energies (kcal/mol, in bold, on same scale as those in Figure 5) for species involved in hydrogen shifts in tetracyclic models for **1**; selected distances for the transition structure are shown in Å

both types of models were quite comparable, although migration over an exocyclic alkene seems to be slightly more difficult than migration over a methylene group in a six-membered ring.[12]

Polyazulenes

Systems with five- and seven-membered, rather than six-membered, rings were also examined. Our initial efforts focused on the monohydropolyazulene **2**. Six distinct types of [1,5] hydrogen shifts are possible in this system (Figure 7). Each of these alters the distribution of azulene and polyene substructures in **2**. These six types of shifts can be divided into two groups: those that involve migration over the face of a seven-membered ring (type 1, Figure 7), and those that involve migration over the face of a five-membered ring (types 2−6, Figure 7). Correspondingly, five distinct isomers are accessible via these six types of [1,5] shifts (**A**−**E**, Figure 7).

Simple models for the possible rearrangements in **2** are shown in Figure 8.[10] Calculations on these models show that migrations over five-membered rings (top row of Figure 8) proceed with reasonably low barriers (approximately 20 kcal/mol). This is consistent with the experimentally observed barrier of 24 kcal/mol for the [1,5] shift in cyclopentadiene.[13] A [1,5] hydrogen migration over the face of the seven-membered ring (center of Figure 8), however, involves a much higher barrier—greater than 40 kcal/mol—that is several kcal/mol higher even than the barriers reported previously for analogous [1,5] hydrogen shifts in simple cycloheptatrienes.[7c,7e,7f] This is probably due to the strain imposed on the seven-membered ring during the hydrogen migration, which is accentuated by its fusion to two five-membered rings. We calculate similar barriers for [1,5] hydrogen

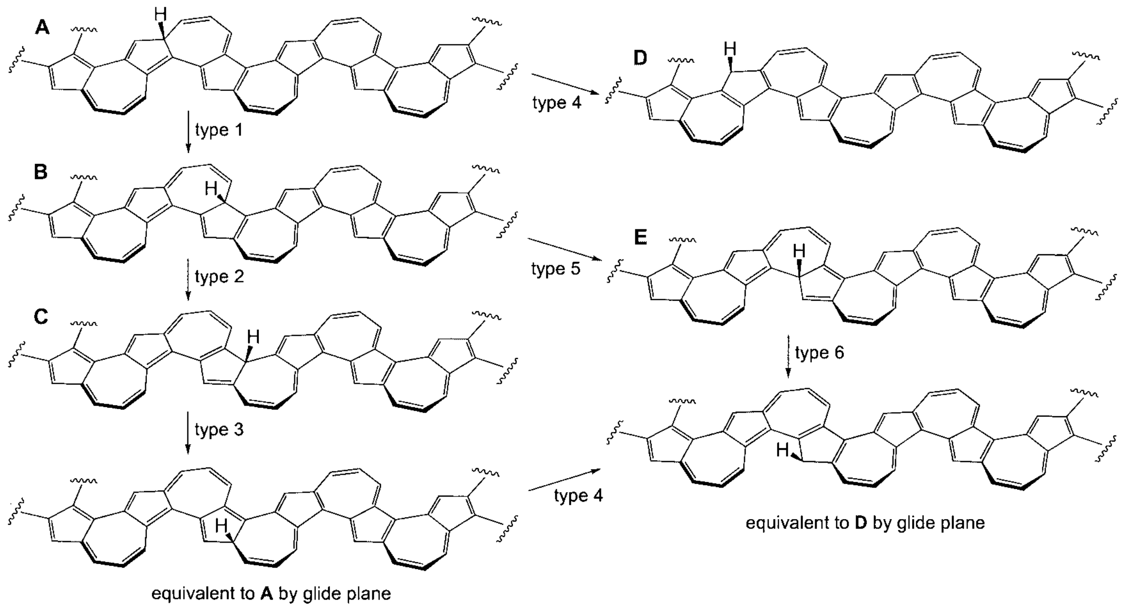


Figure 7. The six types of [1,5] hydrogen shifts possible for monohydrogenated polyazulene tape **2**

migration to the methine groups of the seven-membered rings (Figure 9, for example).

The possibility of a [1,13] shift that allows for direct migration of a hydrogen atom from one five-membered ring to the other was also explored (left of Figure 8). In a simple cycloheptatriene this would correspond to a [1,7] shift, which is symmetry-forbidden for the suprafacial geometry enforced by the ring junctures, and for which barriers of 65−70 kcal/mol have been computed previously.[7e][7f] However, by extending the π-system over the two five-membered rings, a $4n+2$ array is produced. The barrier for this rearrangement is only 29 kcal/mol, much lower than that expected for a [1,7] shift, considerably lower than that for a [1,5] shift across the face of the seven-membered ring, but still higher than those for [1,5] shifts over a single five-membered ring. Nonetheless, the [1,13] shift provides a potential

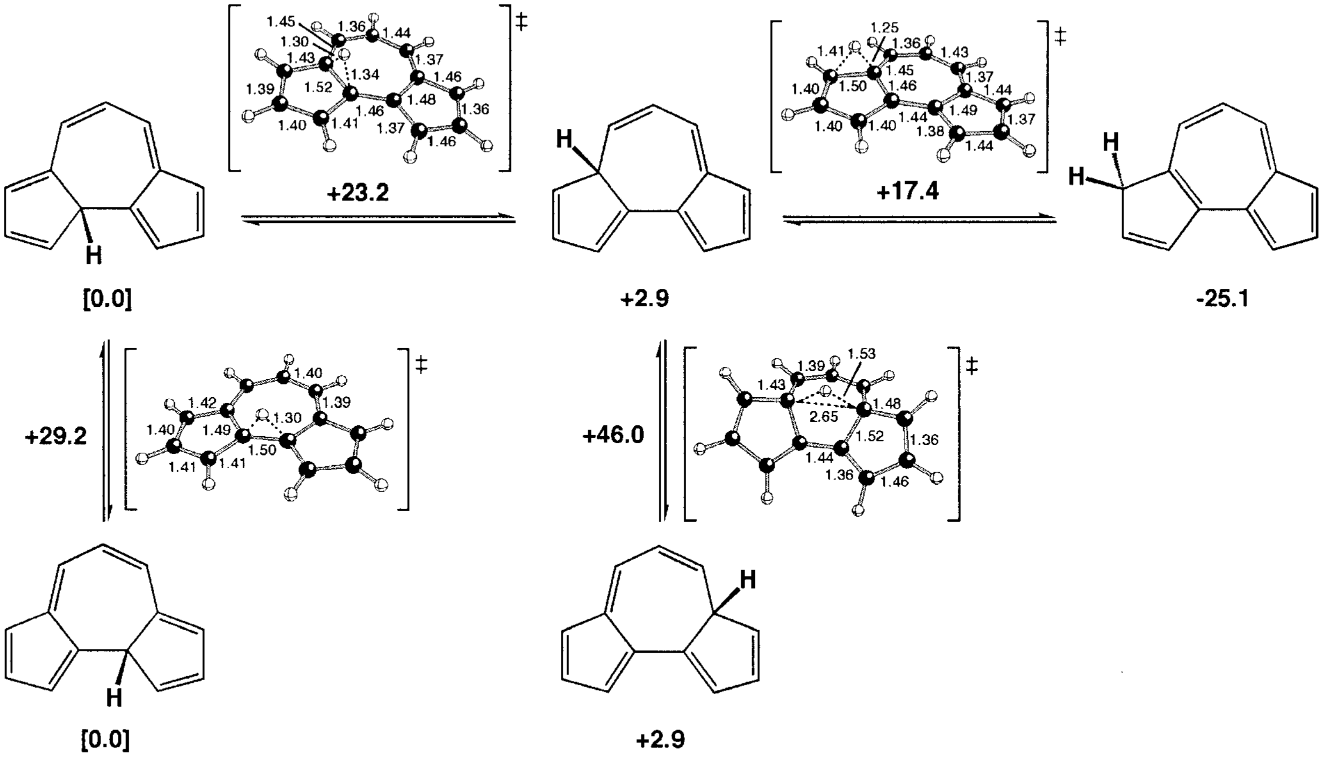


Figure 8. Relative energies (kcal/mol, in bold) of small models for **2**; selected distances are shown in Å

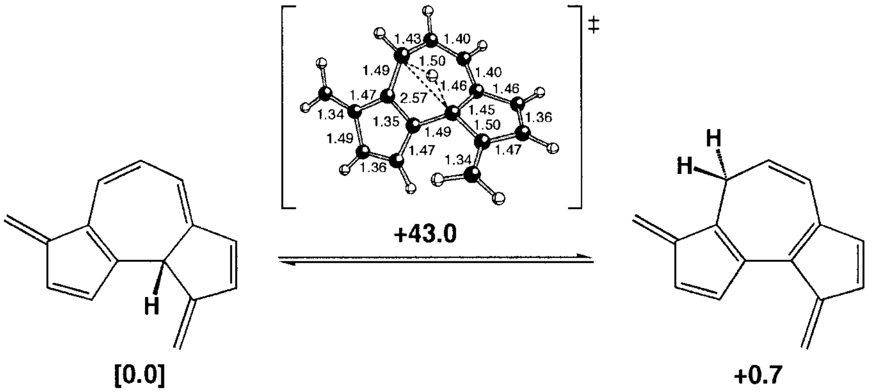


Figure 9. Relative energies (kcal/mol) of models for **2**; selected distances are shown in Å

avenue for hydrogen migration between five-membered rings that avoids the high barrier associated with bridging across the interior of a seven-membered ring.

It should also be noted that minima in which azulene substructures are possible are found to be considerably more stable than those that lack this type of substructure. For example, the rightmost structure in Figure 8 is 25−30 kcal/mol more stable than all of the other isomers shown. This also seems to be true for larger models of **2**, such those shown in Figure 10. Of these systems, the structure with two distinct azulene subunits is most stable, that with two fused azulene subunits is slightly higher in energy, and that with no isolated azulene subunits is much less stable. A similar situation exists for the polyphenacene models shown in Figures 3−6, where species with benzenoid substructures are preferred. This is related to the "isolated benzene rule" sometimes invoked in explaining the relative stabilities of polycyclic aromatic hydrocarbons.[2a][7h,14] How important this effect would be in the infinite system is difficult to estimate, however.

Polypentalenes

A simple model for polypentalenes **3** and **4** was also examined (Figure 11). The barrier for [1,5] hydrogen shift in structure **A** (top right in Figure 11) leading to structure **B** is approximately 30 kcal/mol. Interestingly, structure **B** displays considerable bond length alternation, apparently so that a delocalized antiaromatic pentalene substructure is avoided.[15] A much more delocalized structure (**C**) was found to be a transition structure (presumably for the interconversion of localized pentalene substructures).[15] The **A**-to-**B** [1,5] hydrogen shift can also be thought of as a [1,11] shift, if one considers the entire π-system of **A**, although the bond lengths in the transition state for this rearrangement indicate that the entire π-system is not involved. This makes sense in that a suprafacial [1,11] shift is formally forbidden. Another [1,11] shift is possible for **A** (top left of Figure 11), and this involves a much higher barrier, consistent with its more delocalized nature. Note that no closed-shell, non-zwitterionic resonance structure can be drawn for **A** that puts two double bonds into the central five-membered ring and thus allows for a localized [1,5] shift.

Cyclic Systems

While all of the examples discussed so far involve models of organic tapes whose ends do not approach each other, cyclic alternatives in which the ends of such tapes become fused are also possible. We explored hydrogen shifts in one such system, inspired by the recent report of the synthesis of a derivative of [10]cyclophenacene (**8**).[16] We added a single hydrogen atom to the interior of **8** (in this case as a proton, to arrive at a cationic, but closed-shell, system; Figure 12, left), and looked for transition structures for [1,5] shifts across the interior surface of the hoop.[17] Our attempts to locate transition structures for [1,5] hydrogen shifts led instead to a species (Figure 12, right) which appears to be a transition structure for a [1,2] hydrogen shift with a low rearrangement barrier of 14 kcal/mol.[18] This transition structure boasts an unusual "protonated ethylene" substructure with four-coordinate "umbrella" carbon atoms, locally like **9**.[19]

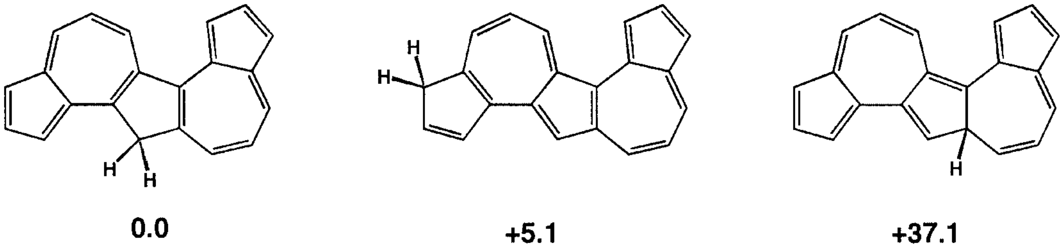


Figure 10. Relative energies (kcal/mol) of large models for monohydrogenated polyazulene **2**

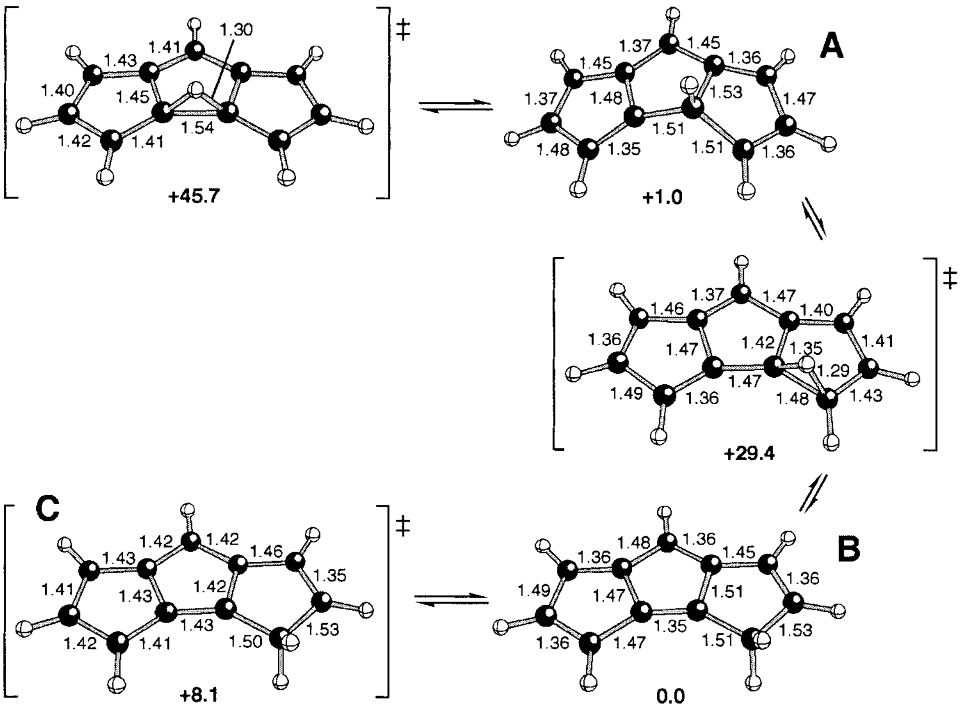


Figure 11. Relative energies (kcal/mol, in bold) of tricyclic models for monohydropentalenes **3** and **4**; selected distances are shown in Å

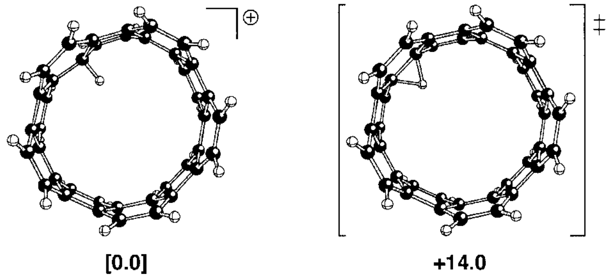
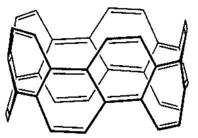


Figure 12. Relative energies (kcal/mol) of **8**-H^+ and the transition structure for [1,2] shift



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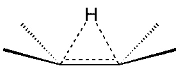

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Conclusions

At first sight, one might have thought that the orbital-symmetry-enforced suprafacial geometry for [1,5] hydrogen shifts would allow hydrogen atoms to scoot over a tape with facility. This is clearly not so. Model systems indicate that the activation energies for such processes, whether in benzene-, azulene-, or pentalene-based polymers, are substantially high (and interestingly, higher than the antarafacial transition state geometries we have explored elsewhere).[9] Too bad, because there are some fascinating selectivities in such shifts, illustrated by the parent system **1** in Figure 1. Still, we calculate reasonably low activation energies for sequential suprafacial shifts in tapes such as **2** and the hoop-shaped molecule shown in Figure 12.

Supporting Information Available: Coordinates and energies for all structures shown in Figures 2−6, 8−9, and 11−12 (see also the footnote on the first page of this article).

Acknowledgments

We gratefully acknowledge support from the National Science Foundation (CHE02-04841) and the National Computational Science Alliance.

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[2] [2a] For a thorough review on benzenoid and nonbenzenoid polycyclic conjugated hydrocarbons, see: M. Randic, *Chem. Rev.*, in press. See also: [2b]Z. Zhou, R. G. Parr, *J. Am. Chem. Soc.* **1989**, *111*, 7371−7379. [2c] B. A. Hess Jr., L. J. Schaad, *J. Org. Chem.* **1971**, *36*, 3418−3423.

[3] All calculations were performed with GAUSSIAN 98.[4] Geometry optimizations and frequency calculations were performed at the B3LYP/6-31G(d) level.[5−7] Zero point energy corrections are included in all reported energies, unless otherwise noted, and were scaled by 0.9806.[8] Ball-and-stick drawings were produced using *Ball & Stick* (Norbert Müller, Alexander Falk, *Ball & Stick V.3.7.6*, molecular graphics application for MacOS computers, Johannes Kepler University of Linz, **2000**).

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[10] In each case the reactant and product geometries are consistent with the simple classical structures drawn in the Figures. See the Supporting Information for more details.

[11] The barrier for hydrogen migration over a graphite surface—via formal [1,2] shifts—has been estimated to be approximately 30 kcal/mol. See: Y. Ferro, F. Marinelli, A. Allouche, *Chem. Phys. Lett.* **2003**, *368*, 609−615 and references cited therein.

[12] In some cases, we also located transition structures for apparent [1,2] migrations of hydrogen atoms (i.e. transition structures with triangular C···H···C substructures), with barriers similar to those for the highest energy [1,5] shifts. Intrinsic reaction coordinate calculations[4] indicated, however, that these transition structures likely connect species related by formal suprafacial [1,3] hydrogen shifts. This is not entirely surprising in that [1,2] shifts should produce zwitterionic or diradical species—extended analogues of trimethelene methane or the trimethylene diradical. It is likely, however, that the potential energy surfaces for such migrations are complex and will require multiconfigurational methods to treat adequately.

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Received September 16, 2003
Early View Article
Published Online November 26, 2003