

## Helicoid Shiftamers for the Transport of $\pi$ -Clumps and Charges

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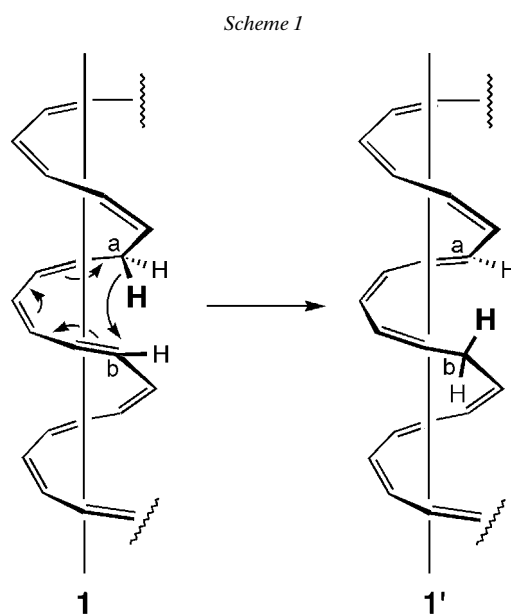
Dedicated to an inspired and inspirational chemist, *Duilio Arigoni*

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Hypothetical helical organic polymers with localized electrons, charges, and/or atoms are described, in which these localized substructures can move along the backbones of the polymers *via* sigmatropic H shifts.

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**Introduction.** – Sigmatropic shiftamers are (so far hypothetical) organic polymers in which localized electrons and/or atoms can be transported along the polymer chains by sequential sigmatropic shifts [1]. Recently, we described a shiftamer for the net transport of H-atoms along a polyacetylene chain *via* [1,7] shifts (*Scheme 1*) [1b]. We now show variants of this system that allow for the net transport of localized polyenes and polyenyl ions.



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Our original helicoid shiftamer design ( $1 \rightarrow 1'$ ; *Scheme 1*) was based on the helical geometry required for facile orbital-symmetry-allowed antarafacial H transfer for the parent [1,7]-H shift in (all-*Z*)-hepta-1,3,5-triene (the transition structure for this rearrangement, **2**, is shown in *Fig. 1*). Extending this helical structure out towards infinity by appending polyacetylene chains to its ends resulted in a locally saturated polymer **1** in which H-atoms could move along its helical polyene backbone in seven C leaps<sup>2)</sup> (*i.e.*, a H-atom is transferred from site a to site b in **1**, but then it is the other H-atom at site b that is transferred in the next jump)<sup>3)</sup>. B3LYP/6-31G(d) Computations<sup>4)</sup> [2–4] on models in which the polyacetylene arms were treated as hexatriene groups [1b] suggested that the barrier for one such jump in the infinite system is *ca.* 15 kcal/mol, essentially unchanged from the barrier of 15.6 kcal/mol computed for [1,7] shift through transition structure **2**. A simplified model with two vinyl rather than hexatriene groups (see transition structure **3** in *Fig. 1*) has a computed barrier of 18.5 kcal/mol. In short, attachment of unsaturated arms has only a small effect on the rearrangement barrier (and core geometry) of the parent system.

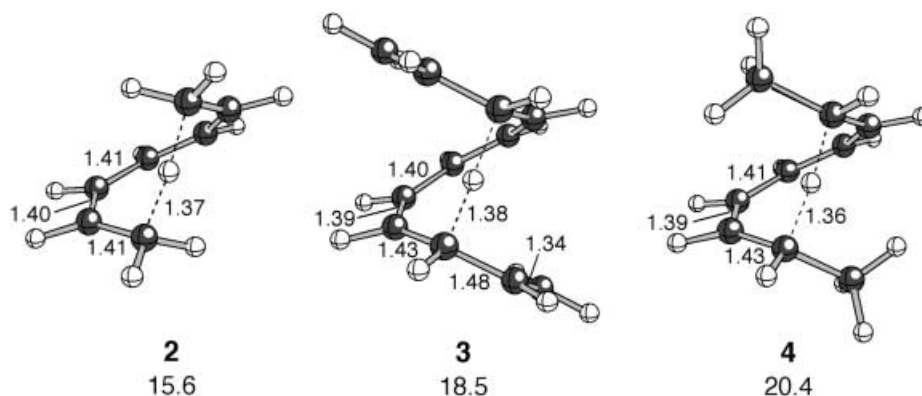


Fig. 1. Computed<sup>4)</sup> (B3LYP/6-31G(d)) transition structures **2–4** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

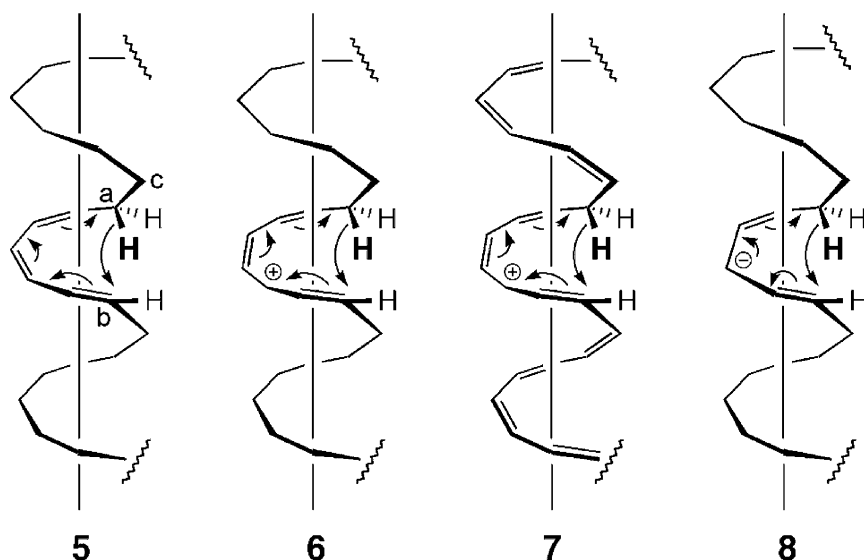
**Polyenes Creeping Along, Pretty Quickly.** – Instead of attaching polyacetylene chains to the ends of (all-*Z*)-hepta-1,3,5-triene, we could alternatively append saturated

<sup>2)</sup> Made perhaps in ‘seven league boots’, which appear in legends of various cultures.

<sup>3)</sup> This assumes a series of shifts in the same direction along the helix. However, in structures like **1**, shifts in both directions are degenerate. Dynamic effects could play a role in determining the actual probabilities of ‘forward’ and ‘backward’ shifts, especially in systems where the shifting barriers are low. Tunneling is also a possibility (see *Footnote 5*).

<sup>4)</sup> All calculations were performed with GAUSSIAN 98 [2]. Geometry optimizations and frequency calculations were performed at the B3LYP/6-31G(d) level [3]. Zero-point-energy corrections are included in all reported energies and were scaled by 0.9806, as recommended in [4]. All reported barriers are calculated by using the productive helical conformers of the reactants. Issues associated with achieving such conformations were discussed in [1b]. For leading references on previous calculations on [1,7] shifts, see [1b][5][6]. Ball-and-stick drawings were produced with Ball & Stick (Norbert Müller and Alexander Falk, Ball & Stick V.3.7.6, molecular graphics application for MacOS computers, Johannes Kepler University Linz, 2000).

(i.e., polyethylene) chains. This construction leads to the locally unsaturated polyethylene polymer **5**, in which a hexatriene substructure could be transported *via* antarafacial [1,7]-H shifts along its helical alkyl chain. Note that this would be accomplished in rather small steps – a steady vermiform burrowing of the triene substructure along the chain (by the movement of a H-atom from site a out of its way, followed then by the movement of a H-atom from site c out of its way, and so on) rather than the hopping from place to place characteristic of the localized substructure in **1**. A simple model of **5** is (all-*Z*)-nona-2,4,6-triene – the parent heptatriene system with Me groups attached to its ends. The barrier for [1,7]-H shift in this system, through transition structure **4** (Fig. 1), is computed to be 20.4 kcal/mol<sup>5</sup>) [5][6] and slightly higher than the barrier for the parent system and the models of **1** discussed above<sup>6</sup>) [7].



**Charges Can Move, Too.** – The systems discussed so far do not bear any net charge. Modifying **5** by inserting into its triene core a CH<sup>+</sup> unit leads to **6**. This structure allows for the movement of a heptatrienyl cation substructure, rather than a hexatriene unit, along the otherwise saturated hydrocarbon helix. Rearrangement in this system involves an antarafacial [1,8]-H, rather than [1,7]-H shift. The parent [1,8]-H shift in (all-*Z*)-octatrienyl cation occurs through transition structure **9** (Fig. 2), whose structure is quite similar to that of transition structure **2** (Fig. 1). The barrier for the [1,8]-H shift is considerably lower, however, than that for the analogous [1,7] shift<sup>7</sup>). A similar

<sup>5</sup>) The [1,7]-H shift in a system with two Me groups at the C-atom from which the H-atom is transferred ((all-*Z*)-7-methylocta-1,3,5-triene) has been studied previously, also at the B3LYP/6-31G(d) level. The computed barrier for this H-shift from the productive helical conformer of the reactant is 14.8 kcal/mol (see [5]; for leading references on additional calculations on [1,7]-H shifts, see also [6]).

<sup>6</sup>) The increase in the rearrangement barrier upon alkyl substitution may be due to steric crowding involving the alkyl groups in the transition structure (see also [7]).

<sup>7</sup>) Additional studies on the spectacularly low barriers for cationic [1,8]-H shifts (and their potential eradication) will be reported separately.

situation is observed when the Me-substituted systems are compared; the barrier for [1,8] shift through transition structure **10** (Fig. 2) is by *ca.* 15 kcal/mol lower than for the analogous [1,7] shift through transition structure **4** (Fig. 1)<sup>7</sup>. A [1,7]-H shift could potentially compete with the [1,8] shift in the (all-*Z*)-octatrienyl cation, but the transition structure for this rearrangement (**11**; Fig. 2) is much higher in energy than **9** (and typical [1,7] shifts). This is likely due to a combination of *i*) the fact that such a [1,7] shift would generate a localized primary cation, and *ii*) the fact that, as described above, the barriers for cationic [1,8] shifts are inherently lower than those for neutral [1,7] shifts<sup>7,8</sup>). [1,8] Shifts in systems such as **6** thus appear to provide a viable mechanism for charge transport along alkane helices.

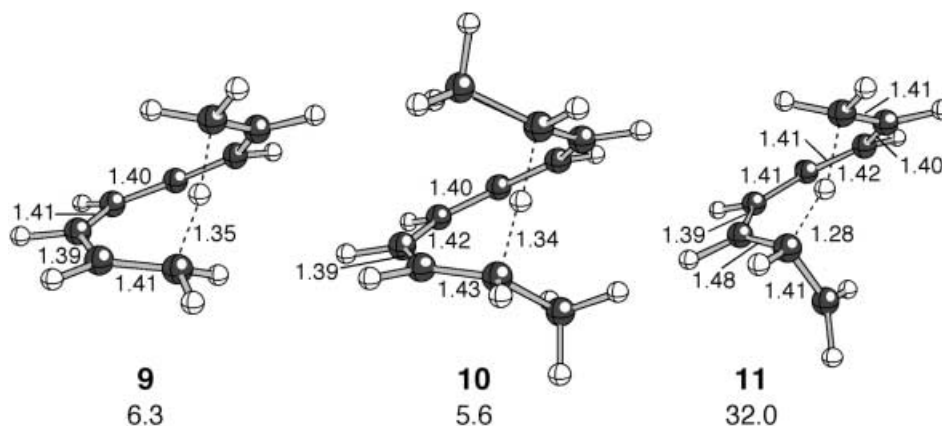


Fig. 2. Computed<sup>a</sup>) (B3LYP/6-31G(d)) transition structures **9–11** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

A cationic analog of shiftamer **1** (structure **7**) can also be formulated. Cationic [1,8]-H shifts in this type of system again involve lower barriers than those computed for analogous neutral [1,7] shifts (compare, *e.g.*, rearrangement through transition structures **3** and **12** in which the polyacetylene arms are modeled by vinyl groups (Fig. 1 and 3, respectively))<sup>7</sup>. Direct competition from [1,7] shifts in this system (through transition structure **13**, which is isomeric to **12**; Fig. 3) is more likely than in structures like **6** because the incipient cation can be stabilized directly by conjugation. But the barrier for [1,7] shift is still higher (by *ca.* 13 kcal/mol) than that for [1,8] shift.

At first glance, it appears that system **7** achieves the net transport of both a H-atom and a positive charge (in a sense, a proton that has been decoupled) along the polyene chain. However, this system actually would not demonstrate typical shiftamer behavior. Although an antarafacial [1,8] shift in **7** would be extremely facile, such a rearrangement would switch the side of the polymer backbone (relative to the CH<sub>2</sub> group) that bears the positive charge. Consequently, after the first [1,8] shift, the only [1,8] shift available to the product would be the reverse shift to regenerate the original structure (Scheme 2). The H-shifts could continue in the initial direction, but these would

<sup>8</sup>) The transition structure for a competing cationic suprafacial [1,6]-H shift is also much higher in energy (by 15.8 kcal/mol) than transition structure **9**.

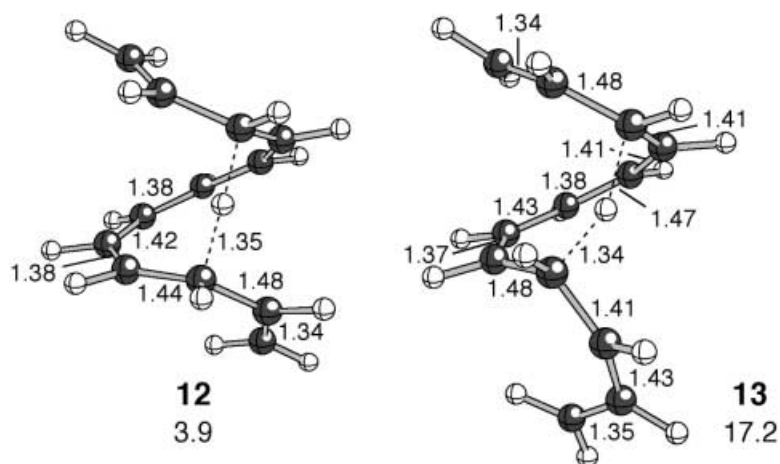


Fig. 3. Computed<sup>a)</sup> (B3LYP/6-31G(d)) transition structures **12** and **13** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

necessarily involve [1,7] shifts (of the type modeled by **13**). Still, this system would demonstrate interesting behavior: at low temperatures (when [1,7] shifts become very slow), it should behave as two long wires – one a normal polyacetylene and the other a cation-doped polyacetylene – separated by a piece of insulation (the CH<sub>2</sub> group). [1,8] Shifts involving this CH<sub>2</sub> group would switch the wire bearing the positive charge; in other words, the piece of insulation would really be part of a gate, which controls the passage of the positive charge. At high temperatures, sequential [1,7] and [1,8] shifts would be possible, thereby allowing for the net transport of a H-atom along with the positive charge.

Anionic analogs of **6** and **7** are also possible. While fully unsaturated systems should show the same sort of unusual behavior predicted for **7**, saturated structures such as **8** should display typical shiftamer behavior. Transition structures for the parent anionic antarafacial [1,6]-H shift (**14**) and that of a dimethyl-substituted analog (**15**) are shown in Fig. 4. The barriers for these rearrangements are slightly lower than those in their uncharged relatives (**2** and **4**; Fig. 1)<sup>9)</sup> [7].

**Coalescence and Annihilation.** – Many other interesting shiftamer architectures are conceivable. For example, while the backbone of **1** is fully unsaturated, and that of **5** is fully saturated, intermediate structures with varying degrees of unsaturation can also be imagined. Consider structure **16** (Scheme 3), which contains two hexadiene units

<sup>9)</sup> An experimental activation energy of 18 kcal/mol has been reported for the anionic [1,6]-H shift in (1,1-dimethylpentadienyl)lithium. This barrier is somewhat higher than the barriers we have predicted for anionic [1,6] shifts, but our barriers have been computed from the productive (all-*Z*)-conformers of the reactants and also do not include lithium counterions (see [7]).

<sup>10)</sup> Test calculations with a larger basis set with added diffuse and polarization functions (B3LYP/6-311+G(2d,p)) yielded similar reactant and transition-state geometries and a slightly higher but similar (15.1 vs. 12.4 kcal/mol) barrier for the parent anionic [1,6] rearrangement.

Scheme 2

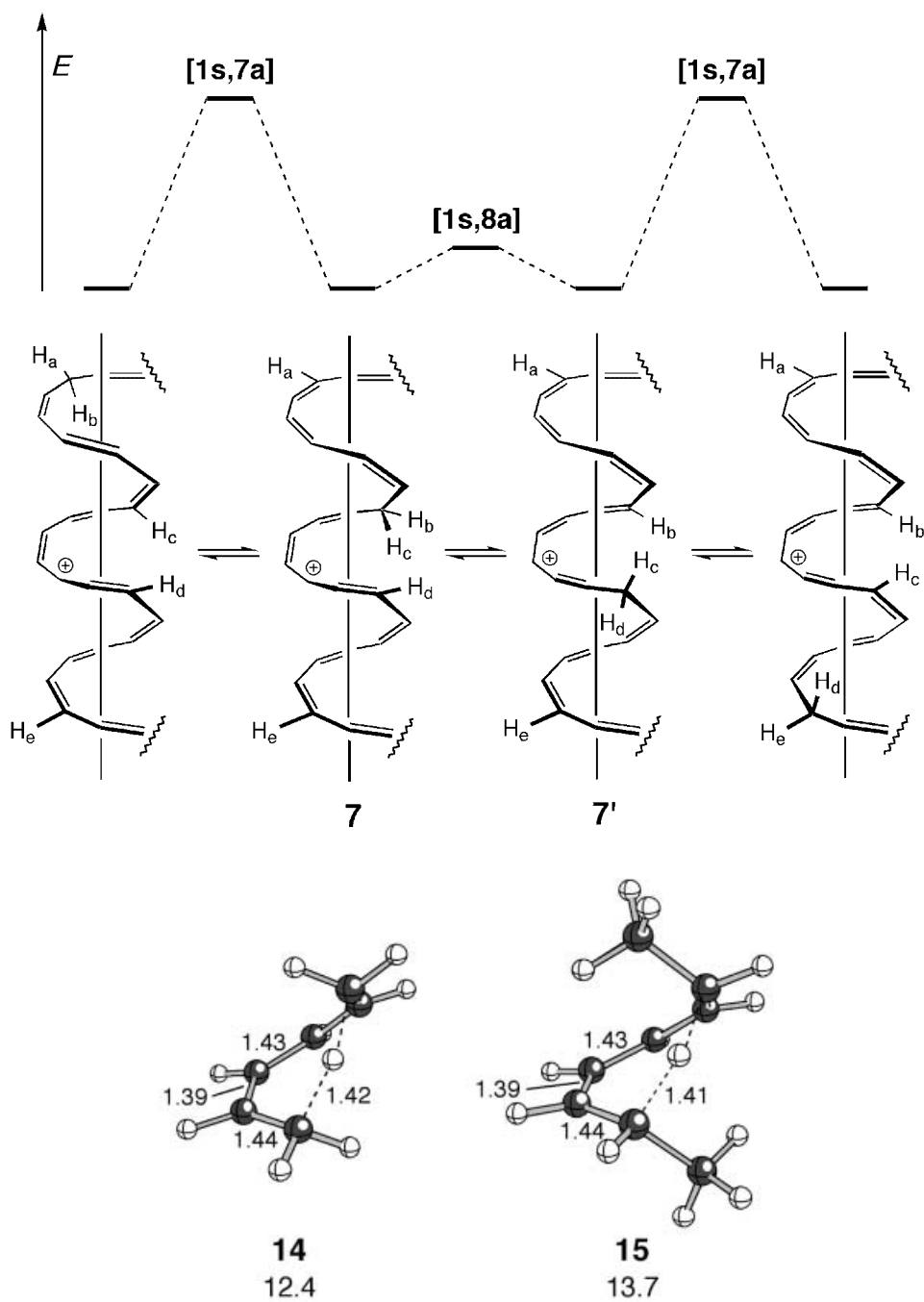
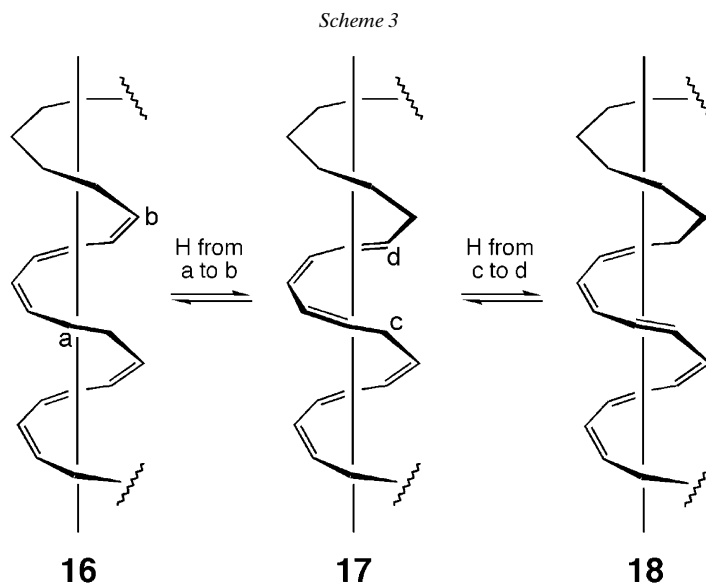


Fig. 4. Computed<sup>4)</sup> (B3LYP/6-31G(d)) transition structures **14** and **15** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

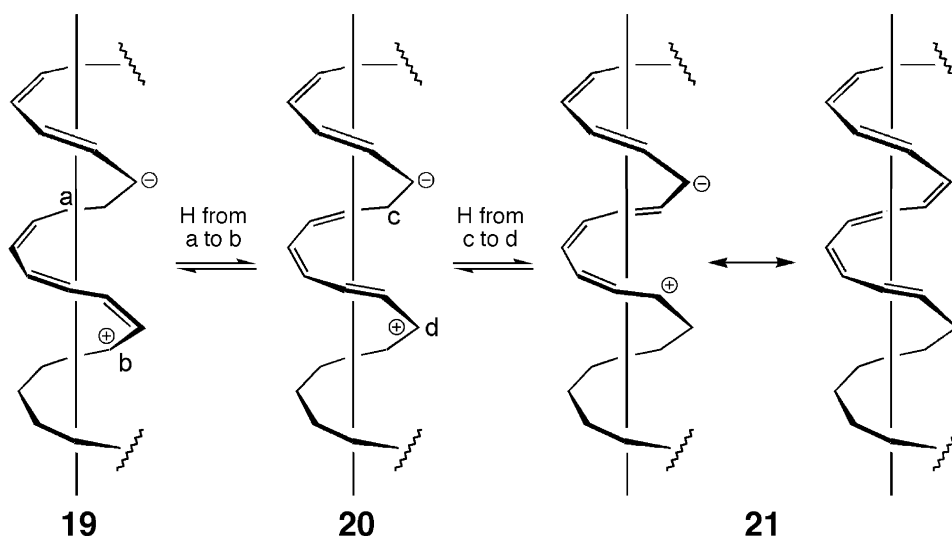
separated by saturated  $\text{CH}_2$  groups – two in the case illustrated. If a [1,7]-H shift from site a to site b in **16** occurs, structure **17** would be obtained. A subsequent [1,7]-H shift from site c to site d in **17** would produce structure **18**. In **18**, however, the distinction between the two hexadiene units is lost – they have condensed into a single larger polyene, like merging drops of water combining into a single large drop.



A related scenario is exemplified by structure **19** (*Scheme 4*), a relative of **16** whose different sites of unsaturation are differently charged – in this case, one is set up for cationic [1,8] shifts and the other for anionic [1,6] shifts. Here, sequential H-shifts such as those that convert **19** to **20**, and **20** to **21**, again lead to a condensation of small  $\pi$ -clumps into larger ones. In this case, oppositely charged  $\pi$ -clumps attract each other, their charges ultimately annihilating each other when they meet. There is a relation here to the properties of bipolarons in polyacetylene [8].

Thus, we have described a variety of new helical sigmatropic shiftamer architectures that vary in charge and extent of unsaturation. We predict that sigmatropic shiftamers **1**, **5**, **6**, and **8** will have relatively low barriers for the shuttling of their localized substructures along their polymer chains – roughly 5–20 kcal/mol – with rearrangement in cationic shiftamer **6** likely to be considerably faster than in the neutral and anionic systems<sup>7)</sup>. For each of these systems, the localized substructure that can be transported is different: for **1**, a H-atom; for **5**, a clump of three conjugated  $\pi$ -bonds; for **6**, a heptatrienyl cation, and for **8**, a pentadienyl anion. Structure **7** should behave as a ‘compound’ shiftamer, in which sequential neutral [1,7] and cationic [1,8] shifts could occur. We look forward to the synthesis of architectures of these types and the development of strategies for exploiting their transport properties.

Scheme 4



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

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Received August 5, 2003