Helicoid Shiftamers for the Transport of π -Clumps and Charges

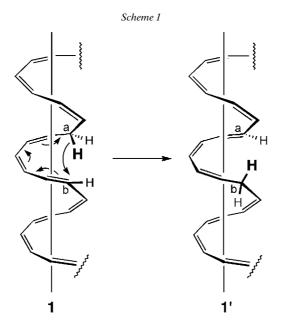
by Dean J. Tantillo1) and Roald Hoffmann*

Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, NY 14853-1301, USA

Dedicated to an inspired and inspirational chemist, Duilio Arigoni

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.

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.



Present address: Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA 95616.

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 leaps²) (*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)³). B3LYP/6-31G(d) Computations⁴) [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.

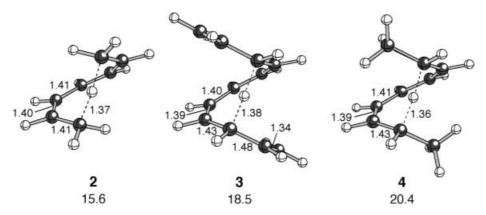


Fig. 1. Computed⁴) (B3LYP/6-31G(d)) transition structures **2-4** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

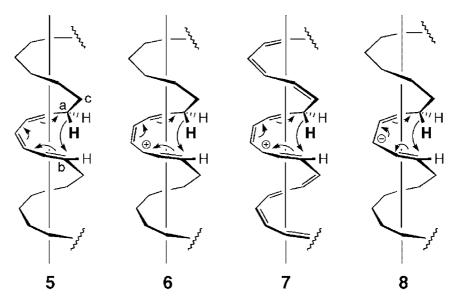
Polyenes Creeping Along, Pretty Quickly. – Instead of attaching polyacetylene chains to the ends of (all-Z)-hepta-1,3,5-triene, we could alternatively append saturated

²⁾ Made perhaps in 'seven league boots', which appear in legends of various cultures.

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*).

⁴⁾ 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/mol⁵) [5][6] and slightly higher than the barrier for the parent system and the models of **1** discussed above⁶) [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⁺ 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] shift⁷). A similar

⁵⁾ 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]).

⁶⁾ 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]).

⁷⁾ 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 $\mathbf{10}$ (Fig. 2) is by ca. 15 kcal/mol lower than for the analogous [1,7] shift through transition structure $\mathbf{4}$ (Fig. 1)⁷). 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 ($\mathbf{11}$; Fig. 2) is much higher in energy than $\mathbf{9}$ (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] shifts⁷)⁸). [1,8] Shifts in systems such as $\mathbf{6}$ thus appear to provide a viable mechanism for charge transport along alkane helices.

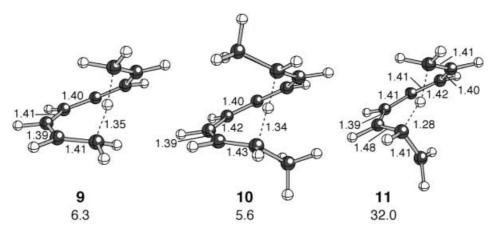


Fig. 2. Computed⁴) (B3LYP/6-31G(d)) transition structures **9–11** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

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))⁷). 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 CH₂ 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

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.

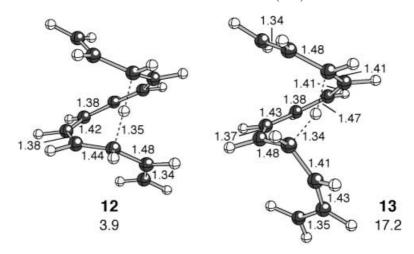


Fig. 3. Computed⁴) (B3LYP/6-31G(d)) transition structures **12** and **13** and corresponding rearrangement barriers [kcal/mol] for antarafacial H shifts discussed in the text

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 CH₂ group). [1,8] Shifts involving this CH₂ 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.

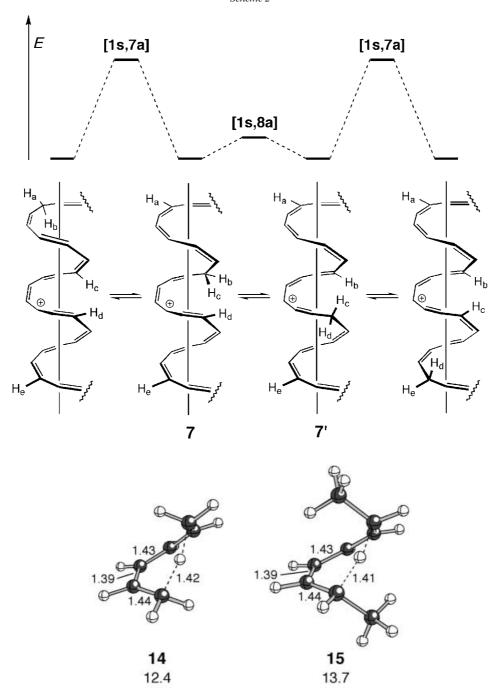
Anionic analogs of 6 and 7 are also possible. While fully unsaturated systems should show the same sort of unusual behavior predicted for 7, saturated structures such as 8 should display typical shiftamer behavior. Transition structures for the parent anionic antarafacial [1,6]-H shift (14) and that 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) 9) 10) [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

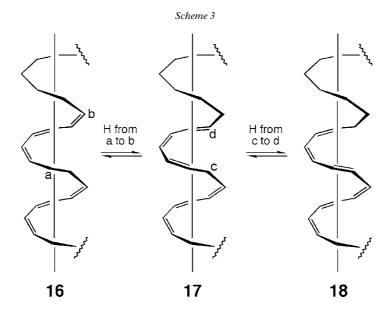
An experimental activation energy of 18 kcal/mol has been reported for the anionic [1,6]-H shift in (1,1-dimethylpentadienyl)lithium. This barrier is somewhat higher than the barriers we have predicted for anionic [1,6] shifts, but our barriers have been computed from the productive (all-Z)-conformers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

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



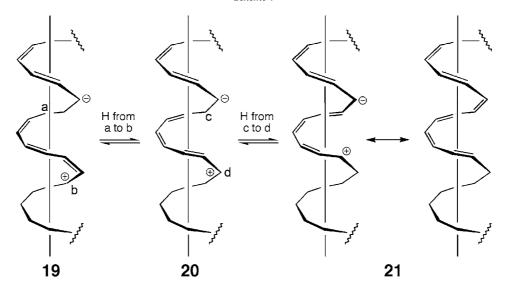
separated by saturated CH₂ groups – two in the case illustrated. If a [1,7]-H shift from site a to site b in **16** occurs, structure **17** would be obtained. A subsequent [1,7]-H shift from site c to site d in **17** would produce structure **18**. In **18**, however, the distinction between the two 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 π -clumps into larger ones. In this case, oppositely charged π -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?). 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 π -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*.

REFERENCES

- a) D. J. Tantillo, R. Hoffmann, Angew. Chem., Int. Ed. 2002, 41, 1033; b) D. J. Tantillo, R. Hoffmann, J. Am. Chem. Soc. 2002, 124, 6836.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. R. Komaromi, R. Gomperts, L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. P. Challacombe, M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh PA, 1998.
- [3] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; b) A. D. Becke, J. Chem. Phys. 1993, 98, 1372; c) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B: Condens. Matter 1988, 37, 785; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623.
- [4] A. P. Scott, L. Radom, J. Phys. Chem. 1996, 100, 16502.
- [5] B. A. Hess Jr., J. Org. Chem. 2001, 66, 5897.
- [6] O. Dmitrenko, R. D. Bach, R. R. Sicinski, W. Reischl, Theor. Chem. Acc. 2003, 109, 170.
- [7] R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, D. E. Potter, J. Am. Chem. Soc. 1970, 92, 6345.
- [8] J. C. W. Chien, 'Polyacetylene', Academic Press, Orlando, FL, 1984.

Received August 5, 2003