Sigmatropic shiftamers are organic polymers (so far, hypothetical) containing isolated bond substructures that propagate along the extended structure via sigmatropic shifts. Our first shiftamer designs involved localized π- and σ-bonds that migrate via [3,3]-shifts. We now describe an interrupted polyacetylene in which hydrogen atoms are transmitted along the polyene chain via [1,7]-shifts (Scheme 1).

Scheme 1

Orbital symmetry control provides the construction principle on which our [1,7]-shiftamer design is based. Transition structures for [1,7]-hydrogen shifts involve migrating hydrogen atoms that are antarafacial with respect to the heptatrienyl systems they are traversing. This geometric requirement for allowedness—and this is the key—forces the polyene backbone to adopt a helical conformation. This is apparent in the computed geometry of the transition structure for [1,7]-shift in (3Z,5Z)-1,3,5-heptatriene (1, Figure 1). Appending additional cis-gauche (or cis-cisoid) alkenes to the termini of the heptatrienyl unit leads to an extended polyacetylene helix with a single saturated site that can migrate along the helix in 7-carbon jumps (Scheme 1). While this process results in the net transfer of a hydrogen atom along the chain, each jump in the same direction involves a different hydrogen atom—when one hydrogen atom migrates, the next migration in the same direction involves the other hydrogen of the methylene unit.

[1,7]-Hydrogen shifts for several oligomeric systems—chains ranging in size from 7 to 19 carbon atoms—were computed at the B3LYP/6-31G(d) level in an effort to approximate the geometric and energetic parameters for the infinite [1,7]-shiftamer. The geometry computed at the B3LYP/6-31G(d) level for this [1,7]-shift is 24 kcal/mol from the most stable s-trans, s-trans conformer of (3Z,5Z)-1,3,5-heptatriene (the barrier is only 15.6 kcal/mol from the helical reactant conformer)—is also comparable to that computed at other levels of theory. The B3LYP/6-31G(d) method was therefore used for our calculations on larger systems.

Appending polyene arms to the parent transition structure has little effect on the geometry of the heptatrienyl core. Consider, for example, transition structures 2 and 3 (B3LYP/6-31G(d)) shown in Figure 1. Since the hexatriene arms in 2 and 3 are rotated out of conjugation with the electrons of the delocalized heptatrienyl unit (C=CH dihedral angles for 2 and 3 are −66 and −69°, respectively), this core geometry is essentially unperturbed (box, Figure 1), and the C=C bond distances in the arms alternate between 1.34–1.35 and 1.46–1.47 Å, resembling those in short polyenes.

Along with the net transport of hydrogen atoms by consecutive [1,7]-shifts along the helical chain, another geometrical distortion will also be propagated. In the transition state, the heptatrienyl substructure becomes somewhat compressed, its ends pinching-in toward the migrating hydrogen. As shown in Figure 2 for the largest system we studied, this leads to a crimp in the helix at the transition structure (3) that is not present in the reactant (4). This crimp should accompany the migrating hydrogen atom down the chain—a geometric distortion of the polymer backbone not unlike a superposition of the motion of an inch-worm with that of a wave running down a string.

Figure 1. Transition structures for [1,7]-hydrogen shifts. Selected distances are shown in Å. The unlabeled carbon–carbon bonds at the ends of the polyene chains in 2 and 3 are 1.46 and 1.34 Å long, respectively—the same in each structure.
The helical conformation of the reactant in each case is very similar.13,16,18 The situation will only get worse as the polyene chains get longer and more low-energy, nonproductive (from the shifter's perspective) reactant conformations become possible. While helical cis-polyacetylene stretches have been implicated in some experimental systems, such conformations rarely, if ever, predominate.16–18 Recent density functional theory calculations14 also indicate that the helical cis-gauche form is considerably less stable than the cis-transoid, cis-cisoid, and trans-transoid forms of various polyene oligomers and of infinite polyacetylene.

Several strategies could be employed, however, to promote helix formation. For example, the synthesis of oligomers could incorporate pendant groups20 or tethers21 that lock-in desired conformations. Alternatively, supramolecular interactions could be used to preorganize helicity.19,20 One can also imagine in these shifters analogues of helical proteins that transport protons across biological membranes;22,23 in the shifter case, however, hydrogen atoms rather than protons would be transported.

In conclusion, we have proposed a helical molecular architecture that allows for facile transport of hydrogen atoms over large distances by sequential [1,7]-sigmatropic shifts.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (CHE 99-70089) and the National Computational Science Alliance.

Supporting Information Available: Coordinates and energies for structures 2–4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References
(1) Tantillo, D. J.; Hoffmann, R. Angew. Chem., Int. Ed. 2002, 41, 1033–1036. (2) Studies on systems involving [1,5]-hydrogen shifts are also in progress. (3) Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry; Verlag Chemie: Weinheim, Germany, 1970. See also: Hoffmann, R.; Woodward, R. B. Acc. Chem. Res. 1968, 1, 17–22. (4) All calculations were performed with GAUSSIAN 98.2 Geometries were optimized at the B3LYP/6-31G(d) level,5 which has been shown to be quite reliable for describing structures and energetics for pericyclic reactions.7 All structures were characterized by frequency calculations at the B3LYP/6-31G(d) level, and zero-point-energy corrections (scaled by 0.9806)8 from these calculations are included in the reported energies. For selected structures, additional optimizations and frequency calculations at the B3LYP/311+G(d,p) level were performed. As described in this text, the geometries and activation barriers obtained at this level of theory did not differ significantly from those computed at the B3LYP/6-31G(d) level.


(9) Energetics and stationary point geometries computed at the B3LYP/6-31G(d) level for the [1,7]-hydrogen shift in (Z)-polyacetylene stretches may exist in some preparations of infinite polyacetylene. Although the amount of actual fluxionality in this [1,7]-shiftamer will likely be the difficulty in achieving a coiled reactant conformation. In the parent system, for example, helical s-cis, s-cis (3Z,5Z)-1,3,5-heptatriene is approximately 9 kcal/mol higher in energy than the fully extended s-trans, s-trans conformation.13 The situation will only get worse as the polyene chains get longer and more low-energy, nonproductive (from the shifter’s perspective) reactant conformations become possible. While helical cis-polyacetylene stretches have been implicated in some experimental systems, such conformations rarely, if ever, predominate.16–18 Recent density functional theory calculations14 also indicate that the helical cis-gauche form is considerably less stable than the cis-transoid, cis-cisoid, and trans-transoid forms of various polyene oligomers and of infinite polyacetylene.

Several strategies could be employed, however, to promote helix formation. For example, the synthesis of oligomers could incorporate pendant groups20 or tethers21 that lock-in desired conformations. Alternatively, supramolecular interactions could be used to preorganize helicity.19,20 One can also imagine in these shifters analogues of helical proteins that transport protons across biological membranes;22,23 in the shifter case, however, hydrogen atoms rather than protons would be transported.

In conclusion, we have proposed a helical molecular architecture that allows for facile transport of hydrogen atoms over large distances by sequential [1,7]-sigmatropic shifts.