



Figure 2. Another view of transition structure **3**, preceded by the coiled reactant conformer from which it arose. The arrows show the direction of the helical axis on either side of the central heptatrienyl substructure.

The rearrangement barrier is also not significantly affected when the hexatriene arms are appended to the heptatrienyl core. The computed (B3LYP/6-31G(d)) barriers for [1,7]-hydrogen shifts through transition structures **1**, **2**, and **3**—now starting from the helical conformation of the reactant in each case—are very similar:¹³ 15.6, 13.0, and 15.5 kcal/mol, respectively. This gives us confidence that the barrier for [1,7]-hydrogen shift in the infinite helix will also be in this range (13–16 kcal/mol), making the rearrangement accessible in the absence of elevated temperatures, and leading to a fluxional system.¹⁵

The main impediment to 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* (3*Z*,5*Z*)-1,3,5-heptatriene is approximately 9 kcal/mol higher in energy than the fully extended *s-trans*, *s-trans* conformer.^{4,9} The situation will only get worse as the polyene chains get longer and more low-energy, nonproductive (from the shiftamer perspective) reactant conformations become possible. While helical *cis*-polyacetylene stretches have been implicated in some experimental systems, such conformations rarely, if ever, predominate.^{16–19} Recent density functional theory calculations¹⁴ also indicate that the helical *cis*-gauche form is considerably less stable than the *cis*-transoid, *trans*-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 shiftamers analogues of helical proteins that transport protons across biological membranes;^{22,23} in the shiftamer 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.

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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>.

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