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Helicoid Shiftamers

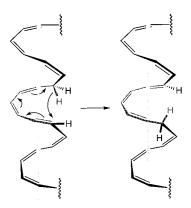
Dean J. Tantillo and Roald Hoffmann*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301

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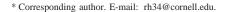
Sigmatropic shiftamers are organic polymers (so far, hypothetical) containing isolated bond substructures that propagate along the extended structure via sigmatropic shifts. Our first shiftamer designs involved localized π - and σ -bonds that migrate via [3,3]-shifts. We now describe an interrupted polyacetylene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

Scheme 1



Orbital symmetry control³ 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 $^{4-10}$ for 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 atomwhen 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) level⁴ 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 the [1,7]-hydrogen shift transition structure in (3*Z*,5*Z*)-1,3,5-heptatriene (1, Figure 1)⁹ is in excellent agreement with that computed at the RMP2(fu)/6-31G(d)¹⁰ and B3LYP/6-311+G(d,p)^{4,10} levels. C···H distances are consistently predicted to be 1.35–1.37 Å and C–C distances in the heptatrienyl substructure are consistently computed



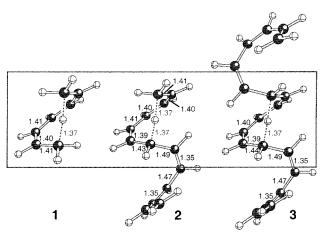


Figure 1. Transition structures for [1,7]-hydrogen shifts. Selected distances are shown in Å. The unlabeled carbon—carbon bonds at the ends of the polyene chains in **2** and **3** are 1.46 and 1.34 Å long, respectively—the same in each structure.

to be extremely delocalized, varying only slightly between 1.40 and 1.41 Å. The activation barrier computed at the B3LYP/6-31G-(d) level for this [1,7]-shift⁹—24 kcal/mol from the most stable *s-trans*, *s-trans* conformer of (3*Z*,5*Z*)-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—20 kcal/mol at RMP2(fu)/6-31G(d)¹⁰ and 25 kcal/mol at B3LYP/6-311+G(d,p)^{4,10}—and to the experimental E_a of 21 kcal/mol measured at 400 K.^{10–12} 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. ¹³ 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==C 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. ¹⁴

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.

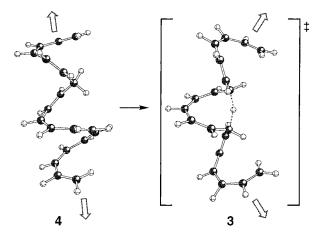


Figure 2. Another view of transition structure 3, preceded by the coiled reactant conformer from which it arose. The arrows show the direction of the helical axis on either side of the central heptatrienyl substructure.

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.

References

- (1) Tantillo, D. J.; Hoffmann, R. Angew. Chem., Int. Ed. 2002, 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 98.5 Geometries were optimized at the B3LYP/6-31G(d) level,⁶ 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/6-311+G(d,p) level were performed. As described in the 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.
- (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (6) (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (b) Becke, A. D. J. Chem. Phys. 1993, 98, 1372-1377. (c) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem. 1994, 98, 11623-11627.
- 1 193. Rev. B 1366, 37, 763-769. (a) Stephens, F. J.; Devinh, F. J.;
 Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem. 1994, 98, 11623-11627.
 Reviews: (a) Wiest, O.; Montiel, D. C.; Houk, K. N. J. Phys. Chem. A 1997, 101, 8378-8388. (b) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. J. Mol. Struct. (THEOCHEM) 1997, 398-399, 169-179.
- (8) Scott, A. P.; Radom, L. J. Phys. Chem. 1996, 100, 16502-16513
- (9) Energetics and stationary point geometries computed at the B3LYP/6-31G(d) level for the [1,7]-hydrogen shift in (3Z,5Z)-1,3,5-heptatriene were reported previously: Hess, B. A., Jr. J. Org. Chem. 2001, 66, 5897–5900. References to earlier SCF calculations on this system can be found in this paper and in ref 10a.
- (10) (a) Jiao, H.; Schleyer, P. v. R. Angew. Chem., Int. Ed. Engl. 1993, 32, 1763–1765. (b) Jiao, H.; Schleyer, P. v. R. J. Phys. Org. Chem. 1998, 11, 655–662.
- (11) Gurskii, M. E.; Gridnev, I. D.; Il'ichev, Y. V.; Ignatenko, A. V.; Bubnov, Y. N. Angew. Chem., Int. Ed. Engl. 1992, 31, 781–783.
- (12) The computed values listed include zero-point energy, but not thermal corrections.
- (13) Adding methyl substituents also has only a very small effect on the rearrangement barrier and transition state geometry.⁹
- (14) (a) Hirata, S.; Torii, H.; Tasumi, M. Bull. Chem. Soc. Jpn. 1996, 69, 3089—3106. (b) Hirata, S.; Torii, H.; Tasumi, M. Phys. Rev. B 1998, 57, 11994—12000 and references therein.
- (15) This barrier is essentially the same as that predicted for the fluxional [3,3]-shiftamer described in ref 1.
- (16) It has been suggested, based on X-ray experiments and computations,¹⁷ that helical cis-polyacetylene stretches may exist in some preparations of polyacetylene and in certain diblock copolymers, but several subsequent studies argue convincingly against a predominance of cis-gauche helices in these systems,^{14,18}
- (17) (a) Bates, F. S.; Baker, G. L. Macromolecules 1983, 16, 1013–1015. (b) Elert, M. L.; White, C. T. Phys. Rev. B 1983, 28, 7387–7389. (c) Elert, M. L.; White, C. T.; Mintmire, J. W. Mol. Cryst. Liq. Cryst. 1985, 125, 329–335. (d) Rao, B. K.; Darsey, J. A.; Kestner, N. R. Phys. Rev. B 1985, 31, 1187–1190. (e) Springborg, M. Phys. Rev. B 1988, 37, 1218–1227. (f) Chien, J. C. W. Polyacetylene; Academic Press: Orlando, FL, 1984.
- (18) Bozovic, I.; Rakovic, D.; Gribov, L. A. Phys. Rev. B 1985, 32, 4286-4288.
- (19) Acetylene polymerization in chiral nematic liquid crystals has been shown to produce films of helical fibrils composed of helical polyacetylene chains, although the amount of actual cis-gauche helices in these films is predicted to be low: Akagi, A.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. Science 1998, 282, 1683–1686.
- (20) For a recent review on helical organic polymers, including polyacetylenes, see: Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038.
- (21) This concept has been widely applied in organic synthesis: (a) A recent review: Gauthier, D. R., Jr.; Zandi, K. S.; Shea, K. J. Tetrahedron 1998, 54, 2289–2338. (b) Additional leading references: Sprott, K. T.; McReynolds, M. D.; Hanson, P. R. Org. Lett. 2001, 3, 3939–3942. (c) A particularly interesting example: Matsushima, T.; Horita, K.; Nakajima, N.; Yonemitsu, O. Tetrahedron Lett. 1996, 37, 385–388.
- (22) For a recent study and leading references on factors influencing the folding and stability of transmembrane peptide helices, see: Yano, Y.; Takemoto, T.; Kobayashi, S.; Yasui, H.; Sakurai, H.; Ohashi, W.; Niwa, M.; Futaki, S.; Sugiura, Y.; Matsuzaki, K. Biochemistry 2002, 41, 3073–3080.
- (23) For leading references on proton transfer across membrane helices, see:
 (a) Oliver, A. E.; Deamer, D. W. Biophys. J. 1994, 66, 1364–1379.
 (b) Åkerfeldt, K. S.; Kim, R. M.; Camac, D.; Groves, J. T.; Lear, J. D.; DeGrado, W. F. J. Am. Chem. Soc. 1992, 114, 9656–9657.
 (c) Ichinose, S.; Minato, T. J. Phys.: Condens. Matter 1993, 5, 861–866.

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