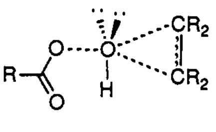
The Bartlett mechanism has been widely used to rationalize the results of olefin epoxidations by peroxides, and this determination of the disposition of the atoms in the transition structure can be reasonably extended to related oxygen-transfer reactions.



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Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

Supplementary Material Available: Experimental details and spectral data for compounds **1**, **2**, **7**, and **8** and experimental procedures for double-label crossover experments and control studies to rule out label scrambling (6 pages). Ordering information is given on any current masthead page.

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(9) We note that our work does not distinguish between spiro and planar arrangements of the olefin, a topic discussed in detail by Rebek. See: Rebek, J., Jr.; Marshall, L.; McManis, J.; Wolak, R. *J. Org. Chem.* **1986**, *51*, 1649.

Expanded Heterohelicenes: Molecular Coils That Form Chiral Complexes

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Helical structures are ubiquitous in nature and are essential to life itself (e.g., polypeptides and nucleic acids). In recent years chemists have discovered several metal–ligand combinations that lead to spontaneous assembly of multicomponent helical and double-helical structures.[1] In this communication, we report the first examples of a new class of preorganized, monohelical polypyridine ligands. These "molecular coils" composed of fused six-membered rings wrap around guest ions, forming helical 1:1 complexes. Helicenes[2] such as [6]helicene (**2**) consist only of angularly fused rings; their ideal, planar analogue is coronene (**1**). Combination of angular with linear fusion of benzene rings leads to planar cycloarenes[3] (e.g., kekulene, **3**) and conceptually to unknown, "expanded" carbocyclic helicenes, such as **4**. Replacement of internal C–H groups in cycloarenes with heteroatoms gives torands,[4] such as **5**,[4b-e,5] which tightly bind alkali metals.[4c]

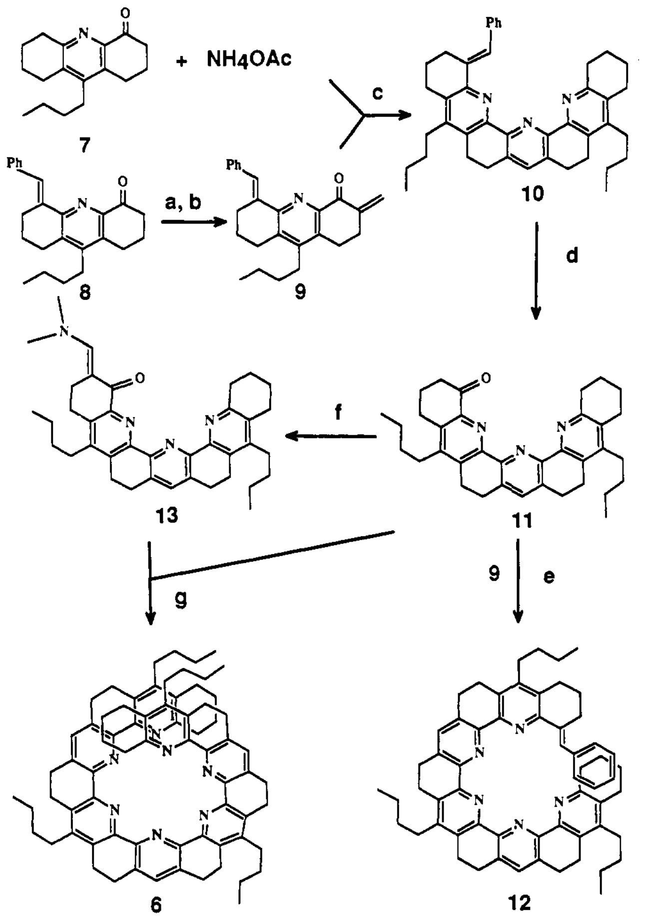

Figure 1. Syntheses of expanded heterohelicenes: (a) Me_2NCH_2Cl, CH_3CN (95%); (b) NaOH, H_2O, $CH_2Cl_2/CH_3I/Et_3N$, CH_2Cl_2 (78%); (c) DMSO (55%); (d) O_3, CH_2Cl_2, CH_3OH/Me_2S (92%); (e) NH_4OAc, DMSO, 95 °C (22%); (f) t-$BuOCH(NMe_2)_2$, 80 °C (82%); (g) NH_4BF_4, DMF, 150 °C.

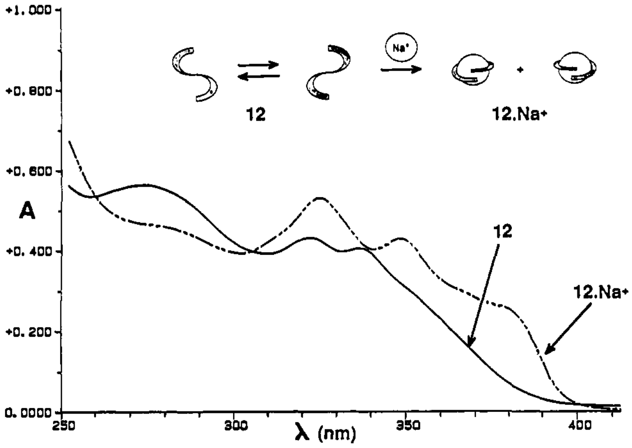

Figure 2. UV-visible absorption spectra of **12** and **12**·Na^+.

Both of the new "expanded" heterohelicenes (**6** and **12**) were synthesized from 9-*n*-butyl-2,3,5,6,7,8-hexahydro-4(1*H*)-acridinone (**7**) and 5-benzylidene-9-*n*-butyl-2,3,5,6,7,8-hexa-

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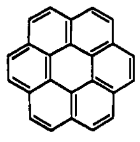

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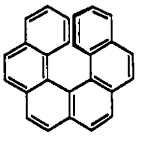

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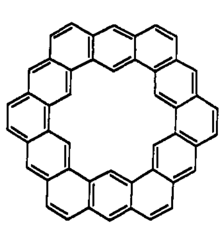

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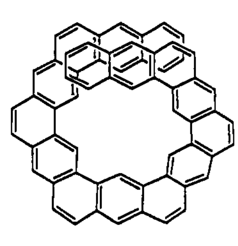

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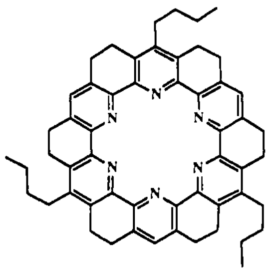

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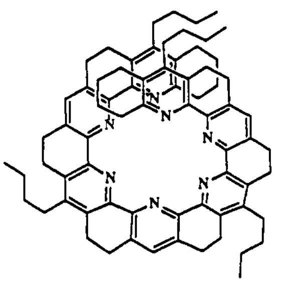

6

hydro-4(1*H*)-acridinone (**8**) by variations of previously reported methods[4b,d,e] (Figure 1). These intermediates were synthesized in several steps from cyclohexanone and valeraldehyde by published methods.[4b,d,e,6] Ketone **8** was converted to enone **9** by a new coupling procedure[7] using dimethylmethyleneammonium chloride.[8] Reaction of ketone **7** with enone **9** gave unsymmetrical heptacyclic terpyridyl **10**.[9] Ozonolytic cleavage of the benzylidene group in **10** gave heptacyclic ketone **11**,[9] the key intermediate for synthesis of expanded heterohelicenes. Homologation of **11** by reaction with ammonium acetate and **9** and chromatography of the crude product on basic alumina gave free ligand **12** (22%)[9] and a later fraction, which proved to be a sodium complex (**12**·Na^+).[10] Reaction of **11** with Bredereck's reagent[11] gave β-dimethylamino enone **13**, which was coupled with **11** by the method of Firestone.[12] Chromatography on basic alumina again gave two fractions, apparently containing free ligand **6** and **6**·Na^+.[13]

Geminal protons of **6** and **12** become diastereotopic when their enantiomeric helical conformations interconvert slowly. In free host **12** various methylene groups are observed as distinct two-proton multiplets in the 600-MHz ^1H NMR spectrum, indicating that helix inversion is rapid on the NMR time scale. The ^1H NMR spectrum of **12**·$NaCF_3SO_3$, prepared by treatment of **12** with sodium triflate in methanol, shows broadened CH_2 peaks due to slow helix inversion; the benzylidene peak remains sharp but is shifted upfield by 2.0 ppm. These results show not only that helix inversion is slow in **12**·Na^+ but also that complexation alters the helix conformation. Figure 2 shows that a large bathochromic shift of the longest wavelength UV absorption also occurs upon binding sodium.

We conclude that expanded helix **12** consists of rapidly interconverting enantiomers in solution; complexation of sodium increases the barrier to helix inversion. This potentially useful conformational change and the resulting optical response are more extreme than those observed in expanded systems comprising less than one full turn of a helix.[4a] Complexation and conformational properties of **6** are currently under investigation.[14]

Acknowledgment. We thank Richard Ludwig for recording 600-MHz ^1H NMR spectra and for assistance with preparing figures. This project was supported by the National Institutes of Health (GM 32937). The Bruker AMX-600 NMR instrument was obtained with grants from the NIH (RR05547A) and the NSF (CHE 8911350) and with support from the Center for Biotechnology and SUNY, Stony Brook.

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(10) The ^1H NMR spectrum of this material was identical with that of **12**·$NaCF_3SO_3$. Continuous extraction of its solution in $CHCl_3$ with pure water gave free **12**.

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(13) As observed for **12** and **12**·Na^+, the ^1H NMR spectrum of the first-eluted fraction was less broad than that of the later fraction. The principal high-mass peak in the FAB-MS spectra of both fractions was *m/z* 1052 (M + 23).

(14) During the course of this research we learned of efforts by G. Balavoine et al. (Université de Paris-Sud, Orsay) to prepare compounds of related structure.

Traveling Fronts of Methacrylic Acid Polymerization

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We report here the preliminary investigation of traveling fronts in methacrylic acid polymerization in unstirred solutions of the monomer and benzoyl peroxide, with and without a promoter.

An autocatalytic reaction in an unstirred vessel can support a constant-velocity wave front resulting from the coupling of diffusion to the chemical reaction. Numerous reactions in solution have been described in which a front of chemical reactivity propagates through the medium from the site of an initial concentration perturbation.[1-11] Traveling wave fronts in populations of short self-replicating RNA variants have been created in thin capillary tubes,[12] but fronts have not been studied in synthetic polymerization reactions. We have set out to do so in an attempt to observe ultimately the sorts of nonlinear propagation phenomena seen in solid-fuel, gasless combustion such as pulsating and spinning fronts.[13-15]

Coupling the exothermic addition polymerization of methacrylic

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