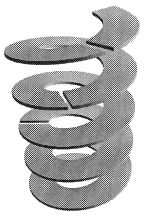
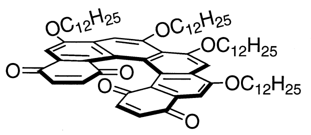
Syntheses of Functionalized and Aggregating Helical Conjugated Molecules**

Thomas J. Katz*

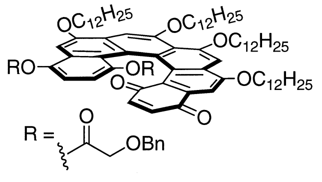
Although almost 100 years have passed since Meisenheimer and Witte prepared the first helicenes—helical molecules comprised of *ortho*-fused aromatic rings—it wasn't until Newman pointed out their chirality and in 1955, with Lednicer synthesized the first in nonracemic form that they attracted general interest. Many helicenes were prepared after Martin showed that all that was required was to expose diarylethylenes to light and oxidants.[1] Nevertheless, although their helical structures could be imagined to endow unusual and useful physical and chemical properties, in the half-century after Newman's synthesis, almost no application was found for helicenes. The reason was probably that the photochemical procedures gave neither appreciable amounts nor materials with significant functional groups.



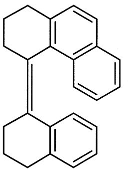
1



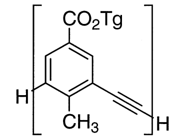
2



3

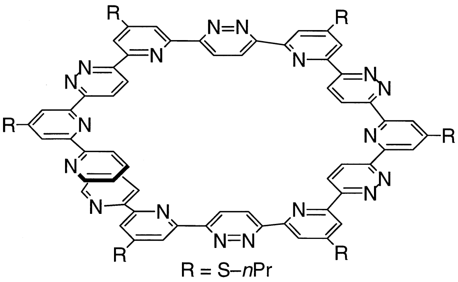


4



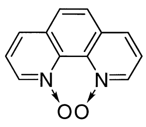
Tg = $(CH_2CH_2O)_3CH_3$

5



R = S–*n*Pr

6



7

However, during the past few years the combination of bis enol ethers of diacetyl aromatic species with *p*-benzoquinone,[2] supplemented by an efficient procedure for effecting the required resolutions,[3] has provided large quantities of helicenes with five to eight fused carbocyclic and heterocylic rings. Their availability in turn has led to two kinds of discoveries that promise to make helicenes useful. One relates to the idea that, like planar aromatic compounds surrounded by alkyl chains, appropriate helicenes also might stack into long columns in the liquid phase, in solution, or as solids (see structure **1**). However, unlike the columnar discotic liquid-crystal phases formed by planar aromatic species, those of nonracemic helicenes should twist into large corkscrew configurations. The first examples were structures **2** and **3**.[3a, 4] In the case of **2**, the twisted columnar configuration makes the pure material exhibit a unique, long fibrous morphology, very large circular dichroisms and specific rotation. Because of the mobile electrons and noncentrosymmetry of **2**, a large second-order nonlinear optical response is observed.[5] In the case of **3**, the organization into columns has made it the first helically twisted columnar discotic liquid crystal.[4] The other application for which helicenes have shown promise is in asymmetric catalysis. Although only two helicene-based catalysts are now known,[6] the availability of functionalized helicenes in large amounts might be

---

[*] Prof. T. J. Katz
Department of Chemistry
Columbia University
New York, NY 10027 (USA)
Fax: (+1) 212-932-1289
E-mail: tjk1@columbia.edu

[**] I thank the US National Science Foundation for support (CHE98-02316).

expected to stimulate the design, synthesis, and application of others.

A number of recent efforts have been directed at finding other ways to obtain helical, conjugated molecules but only a few can be mentioned here. One interesting and previously unexplored way uses the trimerization of acetylene to prepare helicenes.[7] Another dispenses with helicenes and instead ingeniously twists a polyacene around its long axis.[8] Other methods eliminate parts of the helicene framework. Derivatives of **4** are examples, some of which have been shown to exhibit remarkable properties as switches and unidirectional molecular rotors.[9] Still others use cyclophane scaffolds to bind and twist stacks of substituted benzenes.[10] Finally, some ways eliminate completely the need for a rigid structure to construct unsaturated molecules designed to adopt a helical conformation.[11, 12] Of these last methods, that of J.-M. Lehn[11c] and his coworkers, is discussed in greater detail below. This work is related to that of Moore et al., who, in a superb series of papers, showed that solutions of oligo-(*m*-phenylene ethynylene) **5** (and related structures) in an appropriate solvent (acetonitrile) adopt helical conformations and that the direction of the helical winding can be determined by chiral centers in the molecules.[11a,b]

The idea that Lehn et al. have pursued in a number of recent publications is based on the principle that 2,2′-bipyridine adopts an s-*trans* conformation. Lehn attributes this preference to three effects: attraction between the nitrogen lone pairs and adjacent C–H atoms, repulsion between nitrogen-centered dipoles, and repulsion between the 6,6′-C–H atoms. The consequence, as illustrated in structure **6**, is that if the carbon atoms adjacent to the nitrogen atom of pyridines are united with the carbon atoms adjacent to the nitrogen atoms of various diazenes, the resulting structures are oligomeric derivatives of 2,2′-bipyridine. Because the bonds to the pyridines are in a *meta* relationship (as in **5**), the oligomers are bent; because the nitrogen atoms of the 2,2′-bipyridine substructures prefer to be *trans* orientated, the conformation adopted should be helical.[13] That the structure of **6** is helical is evidenced by the positions of the NMR signals corresponding to the outermost protons of the end pyridine rings. These signals are at higher fields than in simple pyridines, which can be explained if the protons are subject to the ring currents of cofacially disposed benzene rings.

Similar, although smaller, structures with similar properties have been reported before.[11c] New in the most recent paper is that the helical oligomers aggregate, supposedly into the kinds of columnar stacks (structure **1**) that are formed by the more rigid helicenes **2** and **3**. Moreover, pairs or triplets of columns are thought to twist about one another. Evidence that the molecules aggregate in solution is good: Solutions in CH_2Cl_2 and in pyridine are viscous and gel, the molecular weights (according to vapor pressure osmometric analyses) of the molecules as 2–18 mM $CHCl_3$ solutions[14] are 2.5 times that of monomeric **6**, electron micrographs of freeze-fractured gels show fibrous structures, and the chemical shifts of the aromatic protons in solutions of $CHCl_3$ change with concentration. Evidence that the aggregates are columnar and that the columns twist about one another is less strong. For the columnar structure, this evidence is that the direction of these NMR shifts are all upfield, which is the same direction that aromatic proton resonances of planar discotic molecules shift upon aggregation.[15] For the columnar twist, the evidence is features in the electron micrographs of the freeze-fractured gels but these are not clearly related to the proposed structural model. Evidence for the twisted aggregate structures from other methods, such as electron- or X-ray diffraction, absorption or emission spectroscopy, polarized-light microscopy, or scanning-probe microscopy is, as yet, not available. However, the most interesting results to be anticipated would be from studies that could be carried out when the flexible structures are obtained in a nonracemic form: How circular dichroisms, specific rotations, transport properties, and other properties depend on concentration. Lehn draws particular attention to the transport properties because the diameter of the central cavity in **6** is large (8 Å). The channels formed by stacks of derivatives of **6** could therefore be similarly large. Moreover, their pitch should be more flexible than in aggregates of helicenes such as **2** or **3**.

A completely different approach to functionalized helical conjugated structures is suggested by the recent syntheses of 1,10-phenanthroline-*N*,*N*′-dioxides (**7**).[16] Even though the structures are simple, it was only during the past three years that they were synthesized. Although it should be possible to prepare them by oxidizing 1,10-phenanthrolines, an effective oxidizing agent remained unknown until Rozen recently showed that $HOF \cdot CH_3CN$ was effective. This novel oxidant is formed when fluorine is passed into aqueous acetonitrile. Previously, the only way to obtain the structure was a clever method by Antkowiak and Antkowiak that, following the precedents for preparing 4,5-disubstituted phenanthrenes, constructed the fully aromatic structure only after the nitrogen atoms of a dihydro- (and therefore nonplanar) derivative of phenanthroline had been oxidized.[17] The 1,10-phenanthroline-*N*,*N*′-dioxides have within their helical structures possibly useful functional groups that are polar and that should ligate to metals. It remains, however, for these dioxides to be obtained, as 4,5-dimethylphenanthrene has been,[18] in nonracemic form and for the direct oxidation to be applied to higher helicenes, such as 1,16-diaza[6]helicene.[19]

---

[1] W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63.

[2] S. D. Dreher, D. Weix, T. J. Katz, *J. Org. Chem.* **1999**, *64*, 3671, and references therein.

[3] a) C. Nuckolls, T. J. Katz, G. Katz, P. J. Collings, L. Castellanos, *J. Am. Chem. Soc.* **1999**, *121*, 79, and references therein; b) T. Thongpanchang, K. Paruch, T. J. Katz, A. L. Rheingold, K.-C. Lam, L. Liable-Sands, *J. Org. Chem.* **2000**, *65*, 1850, and references therein.

[4] C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 9541.

[5] Moreover, since this response arises in essence entirely from the material's chirality, a structure comprised of alternating layers of the *unpoled* enantiomers, in which each layer is one coherence length thick, gives rise to second harmonics that are quasi-phase matched (B. Busson, M. Kauranen, C. Nuckolls, T. J. Katz, A. Persoons, *Phys. Rev. Lett.* **2000**, *84*, 79, and references therein).

[6] a) M. T. Reetz, E. W. Beuttenmüller, R. Goddard, *Tetrahedron Lett.* **1997**, *38*, 3211; b) A. Terfort, H. Görls, H. Brunner, *Synthesis* **1997**, 79; c) S. D. Dreher, T. J. Katz, K.-C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000**, *65*, 815.

[7] I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, Š. Vyskočil, D. Šaman, *Tetrahedron Lett.* **1999**, *40*, 1993, and references therein.

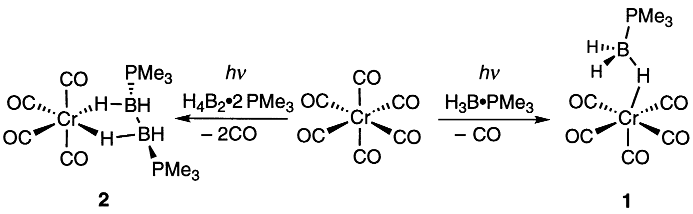
[8] X. Qiao, D. M. Ho, R. A. Pascal, Jr., *Angew. Chem.* **1997**, *109*, 1588; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1531.
[9] B. L. Feringa, N. P. M. Huck, A. M. Schoevaars, *Adv. Mater.* **1996**, *8*, 681.
[10] a) S. Misumi in *Cyclophanes*, *Vol. II* (Eds.: P. M. Keehn, S. M. Rosenfeld), Academic, New York, **1983**, p. 573, and references therein; b) J. Harren, A. Sobanski, M. Nieger, C. Yamamoto, Y. Okamoto, F. Vögtle, *Tetrahedron: Asymmetry* **1998**, *9*, 1369, and references therein; c) S. Grimme, J. Harren, A. Sobanski, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1491.
[11] a) M. S. Gin, T. Yokozawa, R. B. Prince, J. S. Moore, *J. Am. Chem. Soc.* **1999**, *121*, 2643, and references therein; b) M. S. Gin, J. S. Moore, *Org. Lett.* **2000**, *2*, 135; c) L. A. Cuccia, J.-M. Lehn, J.-C. Homo, M. Schmutz, *Angew. Chem.* **2000**, *112*, 239; *Angew. Chem. Int. Ed.* **2000**, *39*, 233, and references therein.
[12] A short review: A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65; *Angew. Chem. Int. Ed.* **1998**, *37*, 63.
[13] Lehn, using a vitalistic vocabulary, attributes the helical conformation of **6** to a "helicity codon" rather than to a directing effect.
[14] The precise meaning of these figures is unclear.
[15] A. S. Shetty, J. Zhang, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 1019.
[16] S. Rozen, S. Dayan, *Angew. Chem.* **1999**, *111*, 3682; *Angew. Chem. Int. Ed.* **1999**, *38*, 3471.
[17] R. Antkowiak, W. Z. Antkowiak, *Tetrahedron Lett.* **1997**, *38*, 1857; R. Antkowiak, W. Z. Antkowiak, *Heterocycles* **1998**, *47*, 893.
[18] R. N. Armstrong, H. L. Ammon, J. N. Darnow, *J. Am. Chem. Soc.* **1987**, *109*, 2077.
[19] H. A. Staab, M. Diehm, C. Krieger, *Tetrahedron Lett.* **1994**, *35*, 8357.

B–H Bond Activations in the Alkane Analogues $H_3B\cdot PR_3$

Warren E. Piers*

The selective, catalytic functionalization of normally inert C–H bonds has been called one of the "Holy Grails" of chemistry.[1] Consequently, much effort has been expended towards understanding the mechanism of C–H bond activation by homogeneous transition metal compounds. In contrast, comparatively little has been done on the activation of bonds in compounds which are isoelectronic to alkanes. The relationship between BH_4^- and CH_4 has been noted, but analogies between complexes formed through ligation of BH_4^- and the more elusive σ complexes of CH_4 are tenuous, based on the obvious difference in charge for these two species. For instance, with the exception of a few examples, BH_4^- tends to bind metals in an η^2 fashion, while CH_4 has been computationally predicted to assume an η^1, end-on bonding posture.[2] Thus, while the borohydride complexes $[(CO)_4M(\eta^2\text{-}BH_4)]^-$ (M = Cr, W) are known,[3] they serve as poor structural models for the methane complexes $[(CO)_5M\cdot CH_4]$ observed when $[M(CO)_6]$ is photolyzed in a methane matrix.[4]

To eliminate this difference and provide a more useful chemical analogy, Shimoi et al. have recently examined the photolysis of $[M(CO)_6]$ in the presence of $H_3B\cdot L$ (L = PMe_3, PPh_3, NMe_3),[5] methane analogues which are both isoelectronic and neutral. The products isolated, in excellent yield, are remarkable η^1-borane complexes of the $M(CO)_5$ fragment that contain an unsupported M-H-B interaction (exemplified by **1**; Scheme 1). The increased stability of these alkane-analogue σ complexes allowed for complete characterization, including four examples crystallographically.



Scheme 1.

All the structural and spectroscopic data for $[(CO)_5M(\eta^1\text{-}BH_3\cdot L)]$ support a bonding picture in which σ donation from a B–H bond into the a_1 orbital of $M(CO)_5$ is the dominant feature of the interaction. Molecular orbital calculations show that π back donation from $M(CO)_5$ to $H_3B\cdot L$ is negligible, a combination of the poor π donating ability of the former and the high energy of the B–H σ* orbitals. These complexes are more stable than the alkane complexes due to the greater degree of polarization and electron richness inherent in the B–H bond in $H_3B\cdot L$ as opposed to the C–H bonds in CH_4. Interestingly, η^2 complexes are not observed upon further photolysis, although the same authors have shown that related species, for example **2**, are formed when $[M(CO)_6]$ is photolyzed in the presence of diborane $B_2H_4\cdot 2PMe_3$ (Scheme 1).[6] Taken together, the experimental and computational data on the η^1 complexes provide convincing support for a valid and valuable analogy between complex **1** and the methane adducts $[(CO)_5M\cdot CH_4]$.[2,4] The nature of these adducts also has implications for the reaction pathway for B–H bond activation, which was investigated in a subsequent paper by these same authors.[7]

Photolysis of a metal carbonyl that contains a somewhat more electron rich metal center, and also a sacrificial alkyl ligand, in the presence of the borane–phosphane alkane analogues leads to formation of Lewis base stablized boryl compounds. Photolytic loss of CO from $[Cp^*M(CO)_3CH_3]$ (M = Mo, W; Cp* = C_5Me_5) generates "$[Cp^*M(CO)_2CH_3]$", a highly reactive molecular fragment capable of interacting with X–H σ bonds. When those bonds are the B–H bonds of

---

[*] Prof. W. E. Piers
Department of Chemistry, University of Calgary
2500 University Drive N. W., Calgary, AB T2N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: wpiers@ucalgary.ca

0570-0833/00/3911-1923 $ 17.50+.50/0