Fe(II) form to a purple species. The model chemistry supports the notion that the purple lipoxygenase species is a Fe(III)-linoleyl peroxide complex; however, whether the alkyl peroxide is coordinated in an η^2 fashion remains to be established by corresponding Raman studies on the enzyme complex. Metastable **2** represents the first spectroscopically characterized alkylperoxo complex of iron in a non-heme environment.[24] **2** may also be relevant to the chemistry of "activated bleomycin"[25] and that of alkane functionalization systems utilizing a combination of alkyl hydroperoxide and iron complexes.[26] The reactivity of this novel species toward a number of potential substrates is currently being investigated.

Acknowledgment. This work was supported by the National Institutes of Health (GM-33126). We thank Ms. Elizabeth C. Wilkinson for experimental assistance.

Supplementary Material Available: Tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles for [Fe(TLA)(OBz)](BPh$_4$) (20 pages). Ordering information is given on any current masthead page.

(24) Nishida and Akamatsu recently reported the generation of a metastable species in the reaction of Fe(NTB)Cl$_3$ with TBHP in DMSO but did not characterize this species in detail (Nishida, Y.; Akamatsu, T. *Chem. Lett.* **1991**, 2013-2016). On the other hand, alkylperoxo complexes of iron porphyrins have been characterized; see, for example: Arasasingham, R. D.; Balch, A. L.; Cornman, C. R.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357-4363.

(25) (a) Hecht, S. M. *Acc. Chem. Res.* **1986**, *19*, 383-391. (b) Stubbe, J.; Kozarich, J. W. *Chem. Rev.* **1987**, *87*, 1107-1136.

(26) (a) Leising, R. A.; Norman, R. E.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 2553-2555. (b) Leising, R. A.; Zang, Y.; Que, L., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 8555-8557. (c) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898-6900. (d) Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 5473-5476.

A Hydrogen-Bonded, Double-Helical Macrocycle

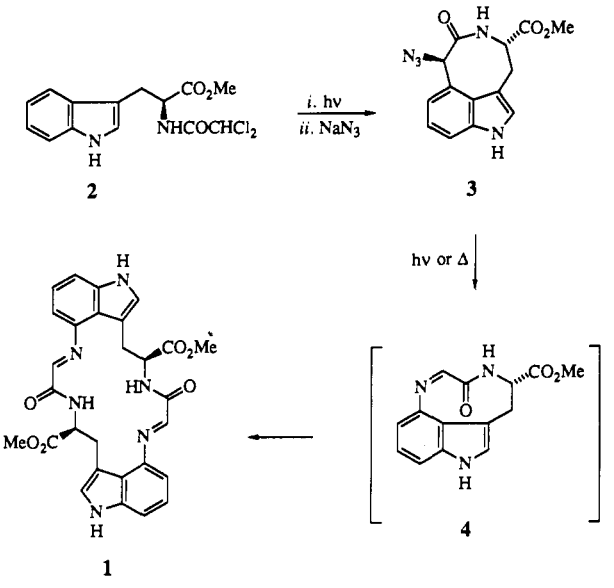
Mark Mascal,*[†] Christopher J. Moody,[‡] Andrew I. Morrell,[‡] Alexandra M. Z. Slawin,[§] and David J. Williams[§]

Department of Chemistry, University of Nottingham Nottingham NG7 2RD, U.K.
Department of Chemistry Loughborough University of Technology Loughborough LE11 3TU, U.K.
Department of Chemistry Imperial College of Science, Technology and Medicine, London SW7 2AZ, U.K.

Received October 2, 1992

Helical structures are common in nature, both on the macroscopic and microscopic level. Honeysuckle (*Lonicera sempervirens*) and field bindweed (*Convolvulus arvensis*) are examples of vines which wind helically about a vertical support, the former in a left-handed and the latter in a right-handed sense. On the molecular scale, the double-helical structure of nucleic acids and the α-helix of proteins are such important and familiar architectural principles that no further discussion is warranted. Synthetic macromolecules may also adopt a helical geometry, such as is the case for both iso- and syndiotactic polypropylenes, and a host of chiral propeller molecules, helicenes, and twistanes have also been described.[1] Of particular current interest is the helical assembly around metal ions recently reported by Lehn,[2] Constable,[3] and Williams.[4] Yet to our knowledge, in no case has hydrogen bonding been analogously exploited to fix double-helical secondary structure in a nonnatural product.

Scheme I. Synthesis of Helical Azamacrocycle **1**[a]



[a] A discussion of the stereochemical course of photocyclization reactions analogous to that which gives **3** is found in ref 5.

We now report the preparation of a tryptophan-derived azamacrocycle (**1**) which through strong transannular hydrogen-bonding interactions is tightly wound into the form of a left-handed double helix. A completely novel approach was taken to the synthesis of **1** as described in Scheme I. Thus, (dichloroacetyl)tryptophan methyl ester (**2**) was cyclized with UV light[5] and worked up in the presence of sodium azide to give the 7-azidopyrrolobenzazocine **3** (49%), presumably via the 7-chloro intermediate. Azide **3** could be decomposed either thermally or photochemically to provide the tetraazacyclooctadecane **1** as a result of dimerization and metathesis of strained imine **4**.[6] Well-defined, bright yellow crystals of compound **1** were grown from acetonitrile, and solution of the crystal structure[7] confirmed that the macrocycle exists in the form of a double helix (Figure 1). Models show that **1** is locked in a single conformation and cannot change screw sense without introducing serious steric interactions between the ester groups and the indole ring; thus, the tryptophan asymmetric centers direct the *M* helicity. This chirality is sacrificed on reduction of the carbon-nitrogen double bonds since the resulting diamine cannot, according to models, participate in transannular hydrogen bonding (compare $[\alpha]_D$ 1303° (*c* 0.132) in MeOH for **1** vs $[\alpha]_D$ 39° (*c* 0.125) in MeOH after reduction).

[†] University of Nottingham.
[‡] Loughborough University of Technology.
[§] Imperial College of Science, Technology and Medicine.

(1) For a comprehensive review of helical phenomena in chemistry, see: Meurer, K. P.; Vögtle, F. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1985; Vol. 127, pp 1-76.

(2) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565. Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304 and references therein.

(3) Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1675.

(4) Williams, A. F.; Piguet, C.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1490. Rüttimann, S.; Piguet, C.; Bernardinelli, G.; Boquet, B.; Williams, A. F. *J. Am. Chem. Soc.* **1992**, *114*, 4230.

(5) Beck, A. L.; Mascal, M.; Moody, C. J.; Slawin, A. M. Z.; Williams, D. J.; Coates, W. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 797. Beck, A. L.; Mascal, M.; Moody, C. J.; Coates, W. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 813.

(6) Although compound **1** is the only product ever isolated (37%), the reaction also produces a quantity of intractable, dark yellow polymer. Correct elemental analyses were obtained for compounds **2** and **3** in addition to spectroscopic data (NMR, IR, MS, UV-vis) consistent with their structures. Compound **1** also gave a satisfactory high-resolution M$^+$.

(7) Single crystals of **1**, mp 330 ± 5 °C (rapid heating), were grown from acetonitrile and belong to the space group $C222_1$ with a = 10.696(2), b = 15.986(3), c = 17.347(3) Å, U = 2966 Å^3, D_c = 1.29 g cm^{-3}, and Z = 4 (disposed about a 2-fold axis). The structure was solved by direct methods and refined to R = 0.053, R_w = 0.054 for 1037 independent reflections.

0002-7863/93/1515-813$04.00/0

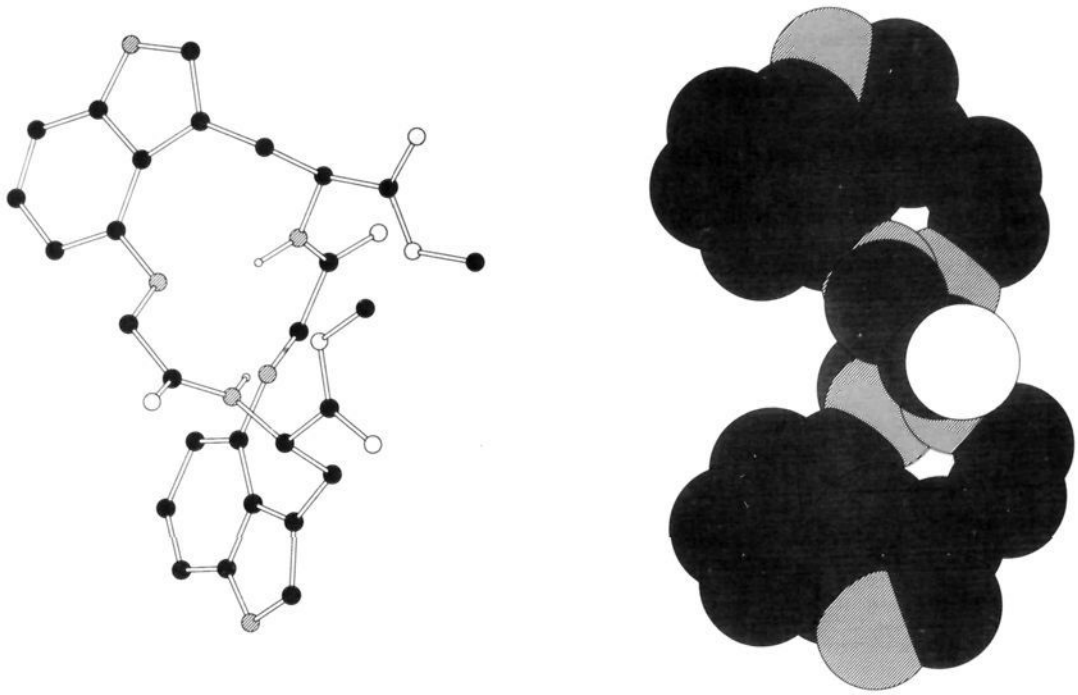


Figure 1. Plot of the X-ray crystal structure of **1** (solvent molecule omitted) (left); space-filling diagram concentrating on the helical macrocyclic region (right).

The proton NMR spectrum of **1** in chloroform shows a single set of sharp peaks with the amide NH signal at 10.2 ppm, about 4 ppm downfield of its normal range due to hydrogen bonding.[8] A strong NOE enhancement between the proton at the indole 5-position and the CH of the imine is also observed, consistent with the structure in Figure 1. The kinetics of unwinding the helix is beyond the range of dynamic NMR techniques, with no significant changes being seen in the spectrum between −55 and 65 °C in $CDCl_3$ and between 25 and 125 °C in DMSO-d_6. The ester groups at the asymmetric centers extend outward from the same face of the molecule and describe a deep groove in its surface; attempts to determine whether optical activity is conserved in the absence of these groups have proved unsuccessful due to difficulties associated with the radical decarboxylation of **1**. The indole rings reside in fixed planes inclined 21.7° to each other, and when viewed down the crystallographic *c* axis they define elliptical channels in which rows of disordered acetonitrile molecules are located.

Molecular modeling also reveals that the 18-membered macrocycle should include metals to form pseudotetrahedral helicates. Indeed there is evidence for the formation of a neutral copper(II) complex of **1** on standing with excess cupric acetate in dimethylformamide at room temperature. Chromatography on silica gives an olive green solid, which runs slightly behind the parent macrocycle and shows a strong M + 1 peak in the FAB mass spectrum at m/z 604, corresponding to **1** −2H + Cu. Work continues on the complexation properties of **1**.

The stereocontrolled generation of a novel hydrogen-bonded helix is of particular interest from a number of perspectives. There are analogies to the restriction of conformational equilibria of biologically active cyclic peptides by transannular hydrogen bonding,[9] and repetition of the same H-bonding motif would make possible the characterization of extended, helically wound, conformationally rigid macromolecules of controlled chirality. The helical backbone self-assembles through molecular events which involve recognition, as do metallohelicates,[2-4] and elaboration to analogous, extended systems would also make possible the spontaneous organization of substituents in the helical periphery.

Acknowledgment. This work benefited from support by the SERC and Fisons Pharmaceuticals.

Supplementary Material Available: Full details of the determination of the crystal structure, tables of atom coordinates, bond lengths, bond angles, torsion angles, anisotropic temperature factors, and the numbering scheme and a view down the crystallographic *c* axis of a 4 × 10 unit cell region of the crystal of compound **1** (9 pages); table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

(8) We observe amide NH signals in a range of precursor and related compounds between 6.4 and 6.6 ppm in $CDCl_3$.

(9) For a recent example, see: Rizo, J.; Koerber, S. C.; Bienstock, R. J.; Rivier, J.; Hagler, A. T.; Gierasch, L. M. *J. Am. Chem. Soc.* **1992**, *114*, 2852. Rizo, J.; Koerber, S. C.; Bienstock, R. J.; Rivier, J.; Gierasch, L. M.; Hagler, A. T. *J. Am. Chem. Soc.* **1992**, *114*, 2860.

Photochemical Functionalization of Polymer Surfaces and the Production of Biomolecule-Carrying Micrometer-Scale Structures by Deep-UV Lithography Using 4-Substituted Perfluorophenyl Azides

Mingdi Yan,† Sui Xiong Cai,† M. N. Wybourne,‡ and John F. W. Keana*,†

Departments of Chemistry and Physics
University of Oregon, Eugene, Oregon 97403

Received October 8, 1992

Polymer,[1] silica,[2] and graphite[3] surface modification by the introduction of functional groups has been the subject of intensive research toward the development of resist materials,[4] biosensors,[5] and biomaterials.[6] Recently, surface modification has been combined with photolithography to spatially direct the synthesis of peptides or oligonucleotides[7] and the immobilization of biopolymers.[8] Most of the surface modification processes involve sequential treatment of surfaces with chemical reagents.[8] Few studies have employed azides as surface modification reagents.[9] We now report the surface modification of polymers with *N*-

† Department of Chemistry.
‡ Department of Physics.

(1) Braybrook, J. H.; Hall, L. D. *Prog. Polym. Sci.* **1990**, *15*, 715-734.
(2) Bhatia, S. K.; Hickman, J. J.; Ligler, F. S. *J. Am. Chem. Soc.* **1992**, *114*, 4432-4433.

0002-7863/93/1515-814$04.00/0