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[123]Tetramantane: Parent of a New Family of σ-Helicenes[¶]

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Helical chirality is ubiquitous in nature and has also been generated synthetically, including in pure hydrocarbon structures. While chiral π-helicenes, with benzo[*c*]phenanthrene (**1**) as the first member (although it has a very low barrier for enantiomerization),[1] have been known for many years,[2] the first enantiopure σ-helicenes, with [4]triangulane (**2**) as the parent, were only introduced in 1999;[3] other examples of spiro-helicenes followed soon thereafter.[4] Here we present a new (nonspiro) class of enantiopure σ-helicenes based on nanometer-scale diamondoids (nanodiamonds), for which [123]tetramantane (**3**) is the simplest representative. These types of structures aid in our understanding of chirality, especially when chromophores are absent, as in the case of σ-helicenes.[5] Notably, alkanes with four different substituents are crypto-optically active[3] (sometimes also known as crypto-chiral[6]) because they typically show no or very small values for optical rotation at the standard Na D-line.[7]

Diamondoids are nanometer-sized, hydrogen-terminated diamond-like molecules consisting of fused adamantane cages; their chemical names imply this close relationship: adamantane, diamantane, triamantane, and so forth.[8,9] The higher diamondoids begin with tetramantane and show isomerism: [121]tetramantane has C_{2h} symmetry and is rod-shaped, while C_2-symmetric [123]tetramantane (**3**) is helical (Figure 1). A third isomer, [1(2)3]tetramantane, is disk-like and has C_{3v} symmetry.[10] Some of the smaller diamondoids are available by synthesis (up to [121]tetramantane),[11] albeit in low yield. Fortunately, diamondoids are available from crude oil, and several congeners are now available in sizable quantities.[8] Diamondoids share some of the outstanding properties of macroscopic diamond, such as negative electron affinity;[12] many functional derivatives are accessible through straightforward chemical synthesis.[13] Chiral derivatives are likely to find applications as well-defined building blocks for catalysts[14] or as materials for nonlinear optics.

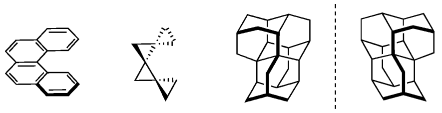
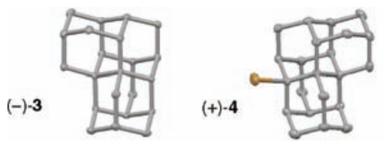

(*M*)-**1** (*P*)-**2** (*M*)-**3** (*P*)-**3**

Figure 1. Parent structures of π- and σ-helicenes.

Samples of (±)-**3** were isolated from petroleum by multiple HPLC separations.[8] The (+) and (−) enantiomers of **3** were resolved using methylated γ-cyclodextrin HPLC columns in reversed-phase mode. One of the enantiomers eluted at 20.2 min and the other at 21.0 min. This procedure was quite elaborate, and all of the preparative experiments as well as the measurements were carried out with less than 20 mg. The racemic crystals of (±)-**3** were highly disordered and glassy between 90 and 298 K; they only diffracted to a resolution of 1.54 Å in a cubic *F* lattice. However, the enantiomerically pure crystals yielded good crystal structures (Scheme 1).

Scheme 1. X-ray Structures of (−)-**3** and (+)-**4** (Hydrogens Have Been Omitted for Clarity)



Our first strategy for determining the absolute configurations was the preparation of an enantiopure monobromo derivative, whose X-ray crystal structure was solved under conditions of anomalous dispersion.[15] Bromination of (+)-**3** in CH_2Cl_2 gave a separable mixture of monobromo derivatives, with a marked preference for the $C^7{-}H$ position. This is in line with our earlier computations that predicted the highest stability of the 7-cation relative to other tertiary [123]tetramantanyl carbocations.[16] Two recrystallizations from *n*-hexane gave (+)-7-bromo[123]tetramantane [(+)-**4**] in 37% yield (Scheme 1).

Indeed, the X-ray structure could be resolved [for details, see the Supporting Information (SI)] and the absolute configuration then assigned as (*P*)-(+)-**4**. As the structure of the hydrocarbon moiety does not change upon bromination, we deduced that the structure of the enantiopure hydrocarbon starting material is (*P*)-(+)-**3**.

To confirm these assignments, we employed a combination of experiment and theory to determine the absolute configuration independently. Following a recent suggestion,[17] we decided to use both optical rotatory dispersion (ORD) and vibrational circular dichroism (VCD) spectroscopy; these spectra can now be computed with very high confidence for rigid molecules.[5,18]

The ORD curves measured at four different wavelengths (Figure 2) are slightly different for the first and second eluted enantiomers, indicating a very small impurity in the vial of the first eluted enantiomer; indeed, an IR spectrum hints at an ester (most likely a softener), probably introduced during the purification or storage

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[¶] Functionalized Nanodiamonds, part 19. For part 18, see: Schwertfeger, H.; Würtele, C.; Hausmann, H.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2009**, *351*, 1041.
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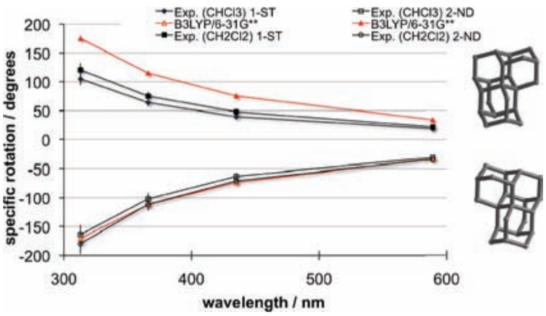

Figure 2. (red) Computed and (black) experimental (in CH_2Cl_2 and $CHCl_3$) ORD curves for the first and second eluted enantiomers and assignment of the absolute configurations of **3**. Conditions: $c_{\text{first}} = 3.3 \times 10^{-3}$ g/mL; $c_{\text{second}} = 4.3 \times 10^{-3}$ g/mL; $d = 0.5$ dm. For all of the tabulated values, see the SI.

process. However, this is inconsequential, as the agreement between the computed [at the density functional theory (DFT) B3LYP/6-31G(d,p) level of theory] and measured ORD curves for the second eluted enantiomer is excellent; the absolute deviation is less than 5% and well within experimental error.

Again, we assigned a negative sign (−) to (*M*)-**3**, the second eluted enantiomer. As expected, $[\alpha]_D$ for (*M*)-(−)-**3** was small (34°) but increased with decreasing wavelength.[19] Indeed, our time-dependent DFT computations indicate that the first significant UV absorption should occur at 170 nm, which is far enough away from the ORD wavelengths to allow the observed very good agreement between experiment and theory.

The agreement between the computed and measured ORD data for (*P*)-(+)-**4** is equally good (see the SI); remarkably, the values of the optical rotations for the bromo derivative are much smaller (by a factor of 4−6), even when corrected for molar mass (see the SI).

As a second independent method, we utilized VCD spectroscopy. We analyzed the IR spectrum of the pure second eluted enantiomer of **3** to identify the absorptions that may be useful for subsequent VCD spectral assignments and also to check the reliability of the employed computational level. The C−H absorption region was poorly resolved (for the full spectrum, see the SI), and we concentrated on the 1000−1600 cm^{-1} region, which shows several well-separated bands (Figure 3). The agreement with the computed spectrum again is excellent; although the computed absorptions are shifted to higher wavenumbers, we did not apply scaling because the agreement is quite obvious. The same was found for the first eluted enantiomer, which shows a perfectly mirrored VCD spectrum (see the SI). A comparison of the experimental VCD data with the computed results confirmed the assignment as (*M*)-(−)-**3**.

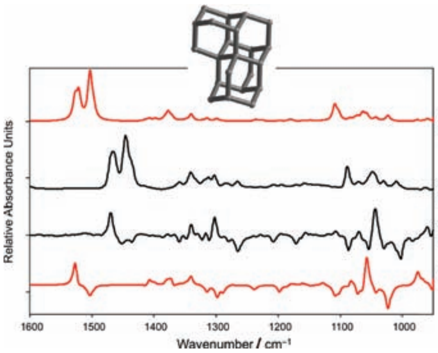

Figure 3. (red) Computed and (black) experimental IR and VCD spectra of the second eluted enantiomer and the optimized structure of matching (*M*)-**3**. Conditions: $c = 26$ mg/mL, $d = 0.2$ mm ($CDCl_3$/subtracted, BaF_2).

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Supporting Information Available: Experimental and computational details, X-ray crystallographic data for (−)-**3** and (+)-**4**, and complete ref 12b. This information is available free of charge via the Internet at http://pubs.acs.org.

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