



Synthesis and study of the structural properties of oxa[5]helicene derivatives



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ABSTRACT

The preparation of the (–)-menthyl carbonate of 2-hydroxy-7-oxa[5]helicene and its structural characterization is reported. Single crystal X-ray diffraction analysis established the relatively flat structure of oxa[5]helicene unit thus indicating the absence of stable helical isomers. The unit cell of the crystal includes one molecule in the *P*-conformation and another in the *M*-isomer. However, its nitro derivative, 1-nitro-2-hydroxy-7-oxa[5]helicene, provides sufficient steric crowding to observe two helical isomers at low temperature, as confirmed by ¹H NMR at –20 °C.

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1. Introduction

The chemistry of screw shaped helical molecules has grown into an important field of research due to the fascinating optical and electronic properties of the π -conjugated *ortho*-annulated aromatic molecules. Such molecules have been widely studied in recent years due to the unique properties associated with their structure. The steric hindrance of the terminal rings and the repulsion between the substituents present force the molecule to adopt a helical conformation.¹ These structures are known as helicenes, which present noteworthy left- or right-handed chiral helical structures. Primarily, there are two types of helical molecules: carbahelicenes and heterohelicenes, with the former class being more studied initially. There are other molecules with a helical shape such as peptides, DNA and helical polymers.² However, recently due to more interesting properties and thus wider possible applications, heterohelicene (i.e., oxa-, aza-, and thiahelicene) has become the subject of intense research. The introduction of heteroatoms in the helical framework have proven to be especially beneficial to the electronic, optical, and photorefractive properties of heterohelicene-based materials.³ Also heterocyclic compounds have been known to facilitate interactions with the biological receptors and hence have opened up applications in pharmaceutical sciences. Considerable attention has been devoted to thiahelicenes **2**,⁴ and aza-helicenes **1**⁵ but less on oxa-helicenes **3** (Fig. 1). Dinaphtho[2,1-*b*:1',2'-*d*]furan **3** can be classified as an oxygen-containing heteroaromatic system with a unique structure.

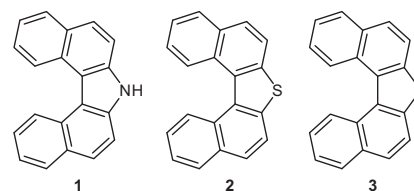


Figure 1. Examples of hetero[5]helicenes.

Despite its helical structure, the molecule does not exhibit optical activity due to rapid racemization at ambient temperature. The molecule has received much attention recently due to its potential as a precursor for the synthesis of axially chiral binaphthyl derivatives, which are effective chiral building blocks in asymmetric reactions, in particular fused furans, are expected to provide relatively high HOMO levels⁶ and are known to show interesting utility in electronic devices such as organic light-emitting diodes⁷ or organic field-effect transistors.⁸ The synthesis and study of oligonaphthofurans has also recently been reported,⁹ where the systematic correlation of the number of naphthofuran units and the physical properties were evaluated. Compounds belonging to the general class of oxahelicenes have been synthesized, and their various properties have been studied.¹⁰

In addition to our work on the synthesis and study of helicene-like compounds,¹¹ and aza[*n*]helicenes,¹² recently we presented the synthesis and study of large oxygen-containing trioxa[11]helicene from axial chiral molecules.¹³ Herein we present our

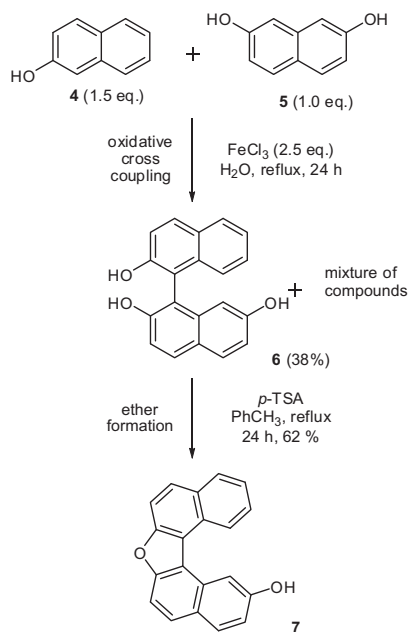
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attempts to resolve and the single crystal X-ray analysis of novel 7-oxa[5]helicene derivative (Fig. 1).

2. Results and discussion

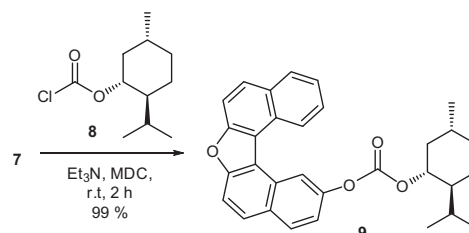
In order to synthesize 2-hydroxy-7-oxa[5]helicene **7**, we have employed the cross-coupling of 2-naphthol **4** with 2,7-dihydroxynaphthalene **5** in the presence of FeCl_3 (Scheme 1). The reaction afforded 1,1'-binaphthalenyl-2,2',7'-triol **6** as the desired product of the cross-coupling reaction, which upon acid-catalyzed ether formation procedure yielded desired product **7**. The reaction involving the dehydration of the triol is a difficult conversion of a nearly perpendicular structure of binaphthyl framework to a more planar oxa[5]helicene unit. The calculated dihedral angle of dinaphthofuran system, similar to triol, was expected to be close to 85° changes, but merely change to approximately 15° when the cyclization occurred.



Scheme 1. Synthesis of 2-hydroxy-7-oxa[5]helicene.

The identification of compound **7** was carried out by analyzing its spectroscopic data; mass spectrometry showed the formal loss of the water molecule from compound **6**, only one hydroxyl proton signal was seen in the ^1H NMR spectra of **7**. The HPLC analysis of 2-hydroxy 7-oxa[5]helicene **7** on the chiral stationary phase showed only a single peak at room temperature. The possible enantiomers of **7** could not be separated from the rapidly interconverting, unresolvable helical structures due to an ineffective overlap of the terminal rings, due to small dihedral angle of the helical framework of oxa[5]helicene. In order to change the dihedral angle and possibly increase the barrier of the isomerization, we envisioned to prepare its carbonate derivative with optically active (–)-menthyl chloroformate **8**. This derivative may provide an opportunity to resolve the isomers of this helical molecule. Accordingly, compound **7** was treated with (1*R*,2*S*,5*R*)-(–)-menthyl chloroformate **8** in the presence of triethylamine at room temperature to afford diastereomeric carbonate **9** in good yield (Scheme 2).

The diastereomers of carbonate **9** could not be isolated by careful column chromatography and several crystallizations. This was further confirmed when a racemic sample of **7** was obtained after removal of the carbonate auxiliary using standard conditions (aqueous KOH/MeOH, rt).



Scheme 2. Preparation of (–)-menthyl carbonate of 2-hydroxy-7-oxa[5]helicene.

Compound **9** was characterized by ^1H NMR spectroscopy; for further structural information see supporting information. In this spectrum, the terminal aromatic protons (C11H and C12H) were observed as multiplet signals at δ 7.78 and 7.62 ppm, respectively, and the signal of C1H gave a doublet at δ 9.04 with a *meta*-coupling with C3H proton ($J = 2.4$ Hz). A comparison of the C1H proton for compounds **7** (δ 8.51) and **9** (δ 9.04), indicated an upfield shift in **9**. The hydrogen of C3H appeared as a doublet of doublet in **7** (δ 7.20), which shifted downfield in **9** (δ 7.44). This splitting is due to its coupling with the *ortho*-C4H proton and *meta*-C1H ($J = 8.8$ and 2.4 Hz). The inside C13H proton showed a doublet in the downfield region δ 9.12 for **7** and δ 9.15 for **9**, thus indicating its position in the ring of the other aromatic ring, rather than below the ring, as typically seen in helical molecules.

In order to analyze the helical structure of **9**, a suitable single crystal of **9** was developed by the slow evaporation of hexane. Compound **9** crystallizes in the monoclinic chiral space group $P2_1$ with the asymmetric unit composed of two heterochiral helical molecules *P*-**9** and *M*-**9** in crystal packing in the solid state.¹⁴ Select bond lengths, distances of non-bonded atoms, and torsion angles are presented in Table 1. Some of the bonds of the outer side C–C bonds were of the order of 1.315–1.371 Å, much shorter compared to the average bond of benzene (1.39 Å). For the helicene structure, the inside bond lengths were found to be elongated in the range of 1.394–1.470 Å (Fig. 2). The internuclear distance between the C1 and C13 carbon atoms for (*P*) helical is 3.312 Å, and for (*M*) is 3.341 Å, which is adequate to accommodate the two aryl C–H bonds [for (*P*) 0.929 Å, for (*M*) 0.931 Å] in the same plane, as seen in the space-filling model (see Supporting information). This distance confirms that there is limited steric repulsion between the hydrogen atoms attached to the C1 and C13 carbon atoms, which results in the low racemization barrier. Molecule **9** exists in a

Table 1
Structural parameters of 7-oxa[5]helicene **9**

<i>P</i> -Helix		<i>M</i> -Helix	
C–C bonds at inner helix (Å)	C–C bonds at outer helix (Å)	C–C bonds at inner helix (Å)	C–C bonds at outer helix (Å)
C5–C11 (1.394)	C43–C27 (1.365)	C6–C15 (1.414)	C13–C24 (1.371)
C11–C23 (1.432)	C29–C40 (1.348)	C15–C8 (1.441)	C25–C37 (1.372)
C23–C16 (1.470)		C8–C14 (1.464)	
C16–C26 (1.428)	C45–C63 (1.358)	C14–C34 (1.427)	C44–C55 (1.315)
C26–C28 (1.424)	C60–C65 (1.334)	C34–C31 (1.399)	C64–C54 (1.353)
Average 1.429	1.351	1.429	1.353
Torsion angle ($^\circ$) (<i>P</i>)		Torsion angle ($^\circ$) (<i>M</i>)	
C5–C11–C23–C16 (φ_1)	9.27	C6–C15–C8–C14 (φ_1)	6.97
C11–C23–C16–C26 (φ_2)	12.02	C15–C8–C14–C34 (φ_2)	9.00
C23–C16–C26–C28 (φ_3)	7.39	C8–C14–C34–C31 (φ_3)	10.84
$\varphi_1 + \varphi_2 + \varphi_3$	28.68	$\varphi_1 + \varphi_2 + \varphi_3$	26.81

The numbering in the table refers to the ones given in ORTEP diagram.

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