C. R. Chimie xxx (2018) 1–7

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Helically chiral functionalized [6]helicene: Synthesis, optical resolution, and photophysical properties

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ARTICLE INFO

Article history:
Received 24 February 2018
Accepted 3 April 2018
Available online xxxx

Keywords:
Helicenes
Photooxidation
Photolysis
Enantiomeric resolution
Photophysical properties

ABSTRACT

A short and efficient synthetic pathway leading to a new chiral π-conjugated system is reported. The X-ray structure of the target compound was determined and showed a helical conformation. Its resolution was successfully accomplished, leading to two enantiomers in high optical purity, and their chiroptical properties were examined experimentally. The photophysical properties of the organic material were also evaluated, showing an emission in the visible region, and HOMO and LUMO levels have been estimated experimentally, demonstrating an electrochemical band gap of 2.37 eV.

1. Introduction

Helicenes have attracted great attention due to their distinct helical backbone [1–9], which incorporates nonplanar π-electrons and makes them highly stable in harsh experimental conditions [10–13]. These helically shaped molecules have shown exceptional chiroptical properties [14–21] and have been applied as suitable components for chiral discotic crystal materials [22,23], conjugated polymers [24–26], and as rotors [27,28]. They have also been used as organic materials for light emitting diodes [29–32], photovoltaic cells [33,34], and circularly polarized luminescence [35–43], thanks to their suitable HOMO and LUMO levels and their thermal and chemical high stability. Their high configurational stability allows appropriately functionalized heterohelicenes to be exploited as optically active or pure ligands and catalysts for enantioselective transformations [44–53].

In this article, we report the synthesis and structural characterization of a new *S*-containing helically chiral architecture substituted with nitrile groups at defined positions. Our synthetic approach highlights the use of 10-bromobenzo[*b*]naphtho[2,1-*d*]thiophene-7-carbonitrile as a new key teracyclic building block to achieve the target helically shaped compound. The nitrile function in this chiral helicene tends to enhance its solubility in organic solvents and may improve its photophysical properties. To the best of our knowledge, no positional isomers of cyano-5-thia[6]helicene have been reported before for making a comparison.

2. Results and discussion

The synthetic pathway to the helical compound began with the condensation of commercially available *p*-bromophenylacetonitrile (**1**) with benzo[*b*]thiophene-2-carboxaldehyde (**2**) in the presence of sodium methoxide in dry MeOH (Scheme 1). The reaction mixture was stirred

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https://doi.org/10.1016/j.crci.2018.04.001
1631-0748/

for 6 h at room temperature to provide (*Z*)-3-(benzo[*b*]thiophen-2-yl)-2-(*p*-bromophenyl)acrylonitrile (**3**) in 90% yield. The resulting α,β-unsaturated nitrile was irradiated with a 500 W high-pressure mercury immersion lamp, on an 800 mg scale per 1.2 L of toluene, in the presence of stoichiometric amounts of iodine and a large excess propylene oxide [54], to produce the expected 10-bromobenzo[*b*]naphtho[2,1-*d*]thiophene-7-carbonitrile (**4**) in 95% yield, and overall 85% yield.

After getting the desired new [4]helicene **4**, we have planned to complete the synthesis of the helical chiral compound **5**. Thus, **4** has been coupled with 4-cyanostyrene (1.5 equiv) using 0.5 mol % of Hermann's catalyst and sodium acetate in *N*,*N*-dimethylacetamide (DMA) according to Scheme 2. After heating at 140 °C, for about 12 h, the coupling product **6** was obtained in 74% yield. Different fractions of the latter compound were subjected to photolysis in dilute solutions using a 500 W high-pressure mercury immersion lamp. The photolysis was carried out on a 200 mg of compound **6** per fraction in a reactor filled with 1.2 L of toluene in the presence of iodine and propylene oxide, leading to 7,14-dicyano-5-thiahexahelicene (**5**) in 60% yield, and overall 38% yield, after 2.5 h of irradiation.

The photocyclization reaction did not lead to other regioisomers of helicene **5** indicating that ring-closure of alkene **6** had occurred in the periposition of the [4]helicene skeleton. In particular, the S-shaped compound **7** was not formed along this step, as these derivatives would be supposed to exhibit characteristic signals for protons H-1 and H-8 at low field in the proton nuclear magnetic resonance (^{1}H NMR) spectrum [55–57].

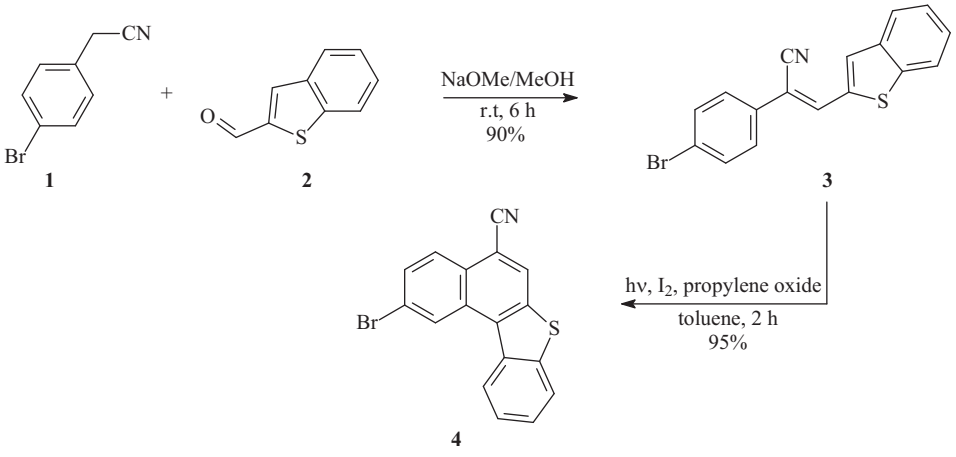
Single crystals of **5** were collected as yellow plates by slow evaporation of a dichloromethane solution at room temperature. The product appears to be highly stable in air and to light. The X-ray analysis was carried out on a single crystal obtained from the racemic form of **5** as shown in Fig. 1. The torsion angles, at the inner helical rim, represented by $C_{19}–C_{20}–C_{21}–C_{22}$ and $C_{22}–C_{23}–C_{24}–C_{25}$ are unequal and were found to be shorter than $C_{20}–C_{21}–C_{22}–C_{23}$ and $C_{21}–C_{22}–C_{23}–C_{24}$ (Table 1).

The separation of the racemic helicene **5** into its enantiomers was accomplished on a preparative scale by HPLC using a Chiralpak IG column (250 × 10 mm) and *n*-hexane/2-propanol/dichloromethane (70:20:10) as the mobile phase. The sample was dissolved, then injected on the chiral column, and detected with a UV detector at 280 nm. Thus, a total of 48 mg of pure product was separated, starting from 50 mg of *rac*-**5**, equivalent to a yield of 96% (Scheme 3). The earlier eluting fractions contained the dextrorotatory enantiomer in 48% yield with 100% ee. Later eluting fractions gave the levorotatory enantiomer in 48% yield and 100% ee. The enantiomeric purity of both enantiomers was checked by chiral HPLC using the same stationary phase.

Optical rotations were measured in dichloromethane using a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578, 546, and 436 nm), in a 10-cm cell, thermostated at 25 °C with a Peltier controlled cell holder. The specific rotations obtained for both enantiomers of helicene **5** are mirror image and are summarized in Table 2.

The chiroptical properties of 7,14-dicyano-5-thihexahelicene (**5**) in the form of the circular dichroism (CD) spectrum were also measured in dichloromethane (Fig. 2), indicating that complete optical resolution had occurred, which makes assignment of the absolute configurations possible. The dextrorotatory enantiomer (+)-**5** recorded a distinct positive maximum at 324 and two distinct negatives maximum at 230 and 352 nm, as depicted in Fig. 1. According to the case of (+)-*P*-helicene derivatives reported [58,59], the absolute configuration of (−)- and (+)-helicenes **5** could be attributed to *M* (*left*-handed helix) and *P* (*right*-handed helix), respectively.

The optical properties of helicene **5** have been evaluated in solutions, on the basis of UV–vis absorption and photoluminescence (PL) spectroscopies, at room temperature and the results are gathered in Table 3. The UV–vis absorption spectrum, recorded from a dilute chloroform solution (ca. 1 × 10^{-6} M) is characterized by several bands between 287 and 450 nm. Three typical strong absorption bands can be found around 314, 354, and 374 nm,



Scheme 1. Synthetic approach for the benzo[*c*]phenanthrene-like system (**4**).

Please cite this article in press as: N. Hafedh, et al., Helically chiral functionalized [6]helicene: Synthesis, optical resolution, and photophysical properties, Comptes Rendus Chimie (2018), https://doi.org/10.1016/j.crci.2018.04.001