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Synthesis, characterization, and photophysical properties of a new pentacyclic helicene

Sondes Raouafi, Faouzi Aloui*, Nesrine Hafedh

University of Monastir, Laboratory of Asymmetric Organic Synthesis and Homogenous Catalysis (UR11ES56), Faculty of Sciences, avenue de l'Environnement, Monastir 5019, Tunisia

ARTICLE INFO

Article history:

Received 6 July 2017

Accepted 19 October 2017

Available online xxxx

Keywords:

Photolysis

Cyclization

Photooxidation

UV–vis spectroscopy

Cyclic voltammetry

ABSTRACT

A new helically chiral pentacyclic compound bearing suitable functional groups has been prepared, in a good overall yield, through a four-step sequence involving mild experimental conditions. The target polyfunctional [5]-helicene showed a good solubility in common solvents and interesting optoelectronic properties. Its photophysical properties have been evaluated using UV–vis absorption and photoluminescence spectroscopies and an emission in the visible region was observed. Highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the chiral organic material have been estimated by cyclic voltammetry, and the electrochemical band gap was found to be 2.7 eV.

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1. Introduction

Helicenes are polycyclic aromatic hydrocarbons made of *ortho*-fused aromatic rings, forming an inherent regular helical shape, which arises from the steric hindrance between aromatic rings. The surprising combination of exhibiting full delocalization of π electrons with a chiral nonplanar structure has fascinated chemists from the early years of helicene research. Their specific backbone and their structural characteristics make them very stable toward acids, bases, and relatively high temperatures [1].

For many years, a synthetic chemistry research program to develop a new method or to design novel molecules for important photophysics measurements has been reported. Because of their inherent chirality, high optical stability, and their rigid helical framework, they have always brought a large interest from transversal disciplines such as liquid crystals [2], sensors [3], chiral catalysts [4] and ligands [5] for asymmetric synthesis and polymer synthesis [6,7] and molecular motors [8] as they have been used in biology [9].

Hence, the synthesis of new helical molecules remains a tough challenge and exciting field. Helical molecules bearing one or more cyano groups are of considerable interest because of their photophysical properties. The first example is 1,4-dicyano-13-methyl[5]helicene **1** (Fig. 1), which has been reported by Stammel et al. [10]. It has been synthesized in 33% overall yield through a multistep procedure. Sahasithiwat and co-workers [1,11] reported the synthesis of 7,8-dicyano-3,12-dimethoxy[5]helicene **2** and 3,12-dimethoxy-5,6,9,10-tetrahydro-7,8-dicyano[5]helicene **3** in three steps through the Diels–Alder reaction and used them for organic light-emitting diodes. Recently, Ito et al. [12] reported the synthesis of 5,10-dicyano[5]helicene **4** in 67% overall yield, through a double photocyclization reaction of 1,4-bis(2-cyano-2-phenylethenyl)benzene.

Photochemical reaction appears as a convenient method for the synthesis of large helicenes under mild reaction conditions. By using this method, the preparation of a target helicene from 2-(*p*-bromophenyl)-3-(*m*-methoxyphenyl)acrylonitrile should be feasible. In addition, the photochemical approach may sometimes fail with pentahelicenes even under the most drastic conditions. Indeed, attempts at the photochemical synthesis of

* Corresponding author.

E-mail address: aloui.faouzi@laposte.net (F. Aloui).

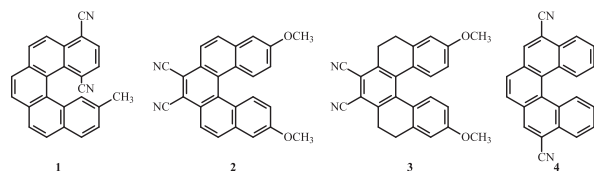


Fig. 1. Representative examples of cyanopentahelicenes.

pentahelicenes have led to benzo[ghi]perylene as a result of overannulation [10,12].

In this study, a short and efficient synthetic strategy was developed for the synthesis of new pentahelicene. Using Knoevenagel condensation, palladium-catalyzed Heck coupling, and classical oxidative photocyclization reactions, we have successfully synthesized a new target polyfunctional pentahelicene. The method is efficient for the formation of helicenes because of the easy preparation of stilbene-type starting materials via Knoevenagel condensation.

The solubility of helicenes could be increased by adding selected functional groups containing polar unsaturated bonds such as cyano group, which improve the photo-physical properties.

In our synthetic approach, a suitable phenanthrene moiety has been used as a key building block for the preparation of appropriately substituted α,β -unsaturated nitrile, then UV-light-promoted photocyclodehydrogenation remains the most widely used route to obtain our helically chiral pentacyclic system.

2. Results and discussion

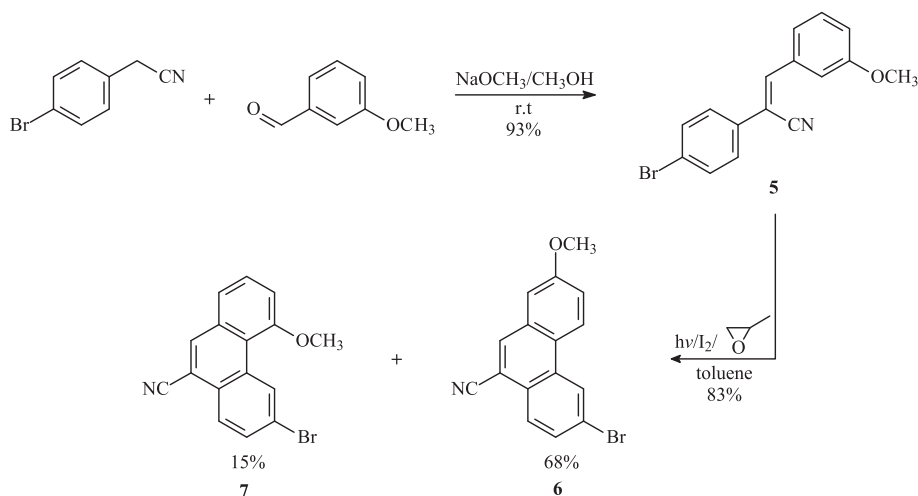
The synthesis of the phenanthrene-like system **6** began with the Knoevenagel reaction of commercially available (*p*-bromophenyl)acetonitrile with 3-methoxybenzaldehyde using sodium methoxide as a base in dry methanol (Scheme 1). The reaction mixture was stirred for 4 h at room temperature to give the desired cyanostilbene **5** in 93% yield. The latter compound was irradiated in toluene in the

presence of a stoichiometric amount of iodine as oxidizing agent and excess propylene oxide as hydrogen iodide scavenger, to provide the expected 6-bromo-2-methoxyphenanthrene-9-carbonitrile (**6**) in 68% yield. The ring closure of olefin **5** was not completely regioselective because 6-bromo-4-methoxyphenanthrene-9-carbonitrile (**7**) was isolated in 15% yield and identified as a byproduct in the reaction mixture (Scheme 1). Compounds **6** and **7** have different polarity and have been successfully separated by column chromatography on silica gel using cyclohexane/AcOEt (95:5) as the eluent.

To obtain the helically chiral pentahelicene **9**, we envisaged the coupling of the phenanthrene moiety **6** with 4-bromostyrene (1.5 equiv) using 0.5 mol % of Hermann's palladacycle {*trans*-di(μ -acetato)-bis[*o*-(*di*-*o*-tolylphosphino)benzyl]dipalladium} as the catalyst, sodium acetate as a base, and *N,N*-dimethylacetamide as a solvent. The desired coupled product **8**, possessing (*E*)-stereochemistry at the double bond, is obtained in 81% yield after 48 h heating at 140 °C according to Scheme 2. To complete the synthesis of the target helicene, precursor **8** was exposed to photocyclization in the presence of a stoichiometric amount of iodine and excess of propylene oxide. Thus, photolysis of **8** was performed in 1.2 L of toluene, on a 150 mg scale per run for about 3 h to afford the expected 13-bromo-3-methoxypentahelicene-6-carbonitrile **9**, as a yellow solid in 60% yield and 31% overall yield after purification by column chromatography (Scheme 2).

After the photocyclization of precursor **8**, only the desired 13-bromo-3-methoxypentahelicene-6-carbonitrile (**9**) was observed as a cyclization product and no other regioisomer, such as **10** (Fig. 2), was isolated from the reaction mixture. The latter would be expected to show characteristic signals for both protons H-7 and H-14 at low field in the ^1H NMR spectrum [13].

The obtained helicene was fully characterized by NMR spectroscopy and was found to show good solubility in common organic solvents such as dichloromethane, chloroform, toluene, and ethyl acetate.



Scheme 1. Synthetic pathway for the synthesis of phenanthrenes **6** and **7**.

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