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# Synthesis and characterization of phenanthrene derivatives for optoelectronic applications

Sondes Raouafi <sup>a</sup>, Faouzi Aloui <sup>a,\*</sup>, Amal Raouafi <sup>b</sup>, Béchir Ben Hassine <sup>a</sup><sup>a</sup> University of Monastir, Laboratory of Asymmetric Organic Synthesis and Homogenous Catalysis (UR11ES56), Faculty of Sciences, Avenue of Environment, 5019 Monastir, Tunisia<sup>b</sup> University of Tunis El-Manar, Laboratory of Analytical Chemistry and Electrochemistry (LR99ES15), Faculty of Sciences, 2092 Tunis El-Manar, Tunisia

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## ABSTRACT

New phenanthrene derivatives, bearing cyano group at selected positions, have been prepared in good yields through Knoevenagel condensation and classical oxidative photocyclization. The optical properties of the cyanophenanthrenes have been investigated by UV–vis absorption. A cyclic voltammetry analysis showed a relatively high electronic affinity, indicating that they may be good candidates for electron-injection hole blocking layers in organic light-emitting diodes.

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## 1. Introduction

Phenanthrenes belong to an important skeleton of organic compounds owing to their core structure in natural products [1–5]. A great number of these alkaloids exhibit interesting biological activities such as anti-inflammatory [1,6,7], anticancer [4,8,9], antimicrobial [10–12], or antiviral [13–15]. *N*-(2,3-Methylenedioxy-6-methoxyphenyl)-9-ylmethyl-4'-cyanopiperidine, **1** (Fig. 1), is well known for its inhibition of the growth of cancer cells [16]. Moreover, phenanthrene is of great interest to organic chemists because of its important properties either in materials science based on their photoconducting, photochemical, and electroluminescent properties [17–24].

During the past few years, conjugated polymers and oligomers based on various aromatic building blocks have received considerable attention, owing to their intriguing photoluminescent and electroluminescent properties as

well as their promising applications in the field of organic light emitting diodes (OLEDs) [25–30]. Phenanthrene and its derivatives, as their physical properties, including UV–vis, photoluminescence, thermal, and electrochemistry, have been extensively studied and have demonstrated that these compounds could serve as emitters for OLEDs [31–39].

Among the reported work, Nayak [40] reported the synthesis of novel class of blue-green fluorescent phenanthromidazoles like 2-(1-phenyl-1*H*-phenanthro[9,10,*d*]imidazol-2-yl)aniline **2** and reported on its optical, electrochemical, and thermal properties.

For the last several decades, much attention has been focused on the development of synthetic methods for the synthesis of phenanthrene derivatives. The most practical and widely used route to the synthesis of these compounds is the photocyclization of stilbenes [41–44], as it is well suited to the laboratory scale. Our research group has previously reported the synthesis of 3,6-dibromophenanthrene **3**, using a photochemical procedure, and described its use in the synthesis of a helical optically active phosphine [41].

\* Corresponding author.

E-mail address: [alouifaouzi0@gmail.com](mailto:alouifaouzi0@gmail.com) (F. Aloui).

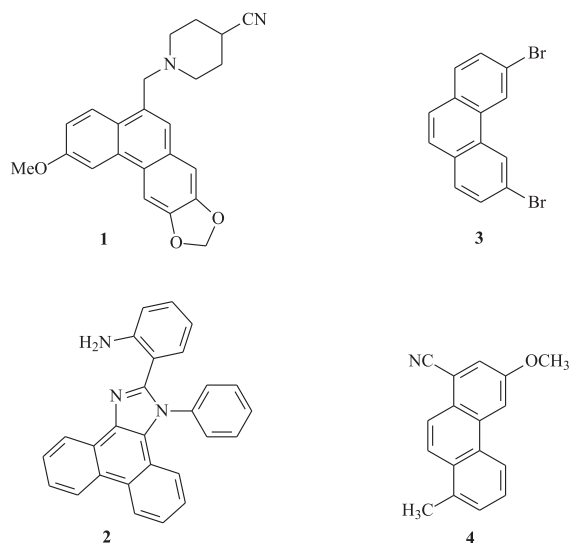


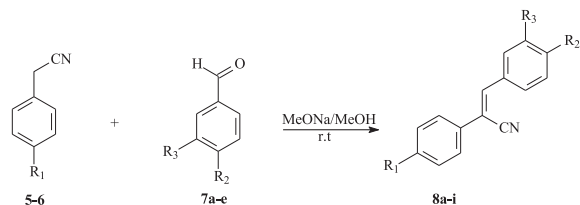
Fig. 1. Representative examples of phenanthrene derivatives.

More recently, Mallory et al. [43] prepared 3-methoxy-8-methylphenanthrene-1-carbonitrile **4** using the same approach. Several nonphotochemical approaches have been investigated, among them are Diels–Alder reaction [45], Friedel–Crafts reaction [46,47], the photochemical procedure radical cyclizations [48], ring-closing metathesis [49–52]. In addition, complicated precursors, expensive and sensitive metallic catalysts, or harsh reaction conditions were needed for the synthesis of aromatic compounds [53–55]. Phenanthrene synthesis via photocyclodehydrogenation of stilbene derivatives still represents a simple and efficient synthetic method.

In this article, we describe the synthesis and characterization of new phenanthrene derivatives with cyano groups at selected positions on the aromatic rings. Our synthetic approach relies on the easy preparation of cyano-diarylethylenes via Knoevenagel reaction, which are then converted into phenanthrenes through the classical photocyclodehydrogenation.

## 2. Results and discussion

In the first part of our work, we have used the Knoevenagel condensation for the synthesis of several functionalized 1,2-diarylethylenes containing the powerful electron-withdrawing cyano group, using a simple and efficient route shown in Scheme 1. First, we have carried the reaction between arylacetonitriles **5–6** and the



Scheme 1. Synthetic pathway for the synthesis of 1,2-diarylethylenes **8a–i**.

aromatic aldehydes **7a–e** in dry methanol, in the presence of sodium methoxide as a base at room temperature, to obtain the resulting 1,2-diarylethylenes **8a–i** in 51–85% yield (Scheme 1, Table 1).

To prepare a novel and highly valuable polysubstituted phenanthrenes, we have envisaged to subject the resulting diarylethylenes for photocyclization. Thus, 500 mg of each olefin **8** have been dissolved in 1.2 L of toluene, and then irradiated using a 500 W high-pressure mercury immersion lamp, in the presence of a stoichiometric amount of iodine as the oxidizing agent and an excess of propylene oxide as a hydrogen iodide scavenger to produce the corresponding phenanthrene. This allowed us to obtain phenanthrenes **P1–P9** in 51–83% yield (Scheme 2, Table 2).

To extend the scope of these reactions, a new derivative of cyclopenta[*a*]naphthalene has been prepared according to the same synthetic approach. Our procedure uses 2-(*p*-tolyl)acetonitrile **9** and thiophene-2-carbaldehyde **10** as key building blocks for the synthesis olefin **8j**, which is then converted to 5-methylnaphtho[2,1-*b*]thiophene-8-carbonitrile **P10** by photolysis (Scheme 3). The <sup>1</sup>H NMR data of compound **P10** showed that proton H<sub>9</sub> is manifested in the form of a deshielded singlet at 8.24 ppm, a doublet at 7.98 ppm is ascribed to H<sub>3</sub>, and H<sub>4</sub> takes the form of a singlet at 8.14 ppm, which is observed in the most deshielded aromatic area.

The optical properties of the target cyanophenanthrenes have been investigated using UV–vis absorption spectroscopy in dilute chloroform solutions ( $7 \times 10^{-5}$  M) as depicted in Fig. 2. The UV–vis spectrum of these compounds exhibited a strong absorption in the region of 250–450 nm. These absorption bands are associated with  $\pi-\pi^*$  and  $n-\pi^*$  electronic transitions. The gap energy ( $E_g$ ) values of the phenanthrenes determined from the absorption edge of the solution spectra are given in Table 3.

To investigate the redox behavior of phenanthrenes and to estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) was applied to the materials. Knowledge of the HOMO and LUMO energy levels is of crucial importance for the selection of the cathode and anode materials for OLED devices. The use of CV analysis is of good reliability as the electrochemical processes probed therein are similar to those involved in charge injection and transport processes in OLED devices.

The cyanophenanthrenes **P1–P10** have been scanned both positively and negatively, in solutions of tetra-*n*-

Table 1  
Chemical yields of 1,2-diarylethylenes **8a–i**.

1,2-Diarylethylene	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Yield (%) <sup>a</sup>
<b>8a</b>	H	Br	H	85
<b>8b</b>	H	OCH <sub>3</sub>	H	76
<b>8c</b>	H	CN	H	82
<b>8d</b>	H	OCH <sub>3</sub>	OCH <sub>3</sub>	75
<b>8e</b>	H	H	OCH <sub>3</sub>	73
<b>8f</b>	CH <sub>3</sub>	Br	H	71
<b>8g</b>	CH <sub>3</sub>	OCH <sub>3</sub>	H	75
<b>8h</b>	CH <sub>3</sub>	CN	H	78
<b>8i</b>	CH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	74

<sup>a</sup> Isolated yields.

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