



5-Phenyl-1,2,3,4-tetrahydronaphthalene derivatives: Synthesis, spectroscopic and electrochemical investigation

Marek Pietrzak*, Agnieszka Bajorek

University of Technology and Life Sciences, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

ARTICLE INFO

Article history:

Received 21 May 2012

Received in revised form

12 July 2012

Accepted 13 July 2012

Available online 20 July 2012

Keywords:

Biphenyls

Synthesis

Spectroscopic and electrochemical properties

Red-edge effect

Fluorescence probes

ABSTRACT

A series of novel dyes, whose structures are based on 5-phenyl-1,2,3,4-tetrahydronaphthalene skeleton have been fully synthesized and characterized. The dyes were prepared in two-stage synthesis reaction. The 2-cyano-3-[4-aminophenyl]-2-propenamide derivatives, and the final dyes were characterized by ^1H and ^{13}C NMR spectroscopy and their purity was checked by thin-layer chromatography and finally HPLC. The spectroscopic properties of the prepared dyes were studied in four different solvents.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years dyes have been widely used as fluorescence probes. They are spectroscopic tools used in chemistry, biology and physics for monitoring specific properties of the medium in which they are incorporated. It is possible because their fluorescence is sensitive to changes in temperature, polarity, viscosity, pH or rigidity of the environment [1–4]. Readers can find many articles which focus on studies based on the concept of the changing of fluorescence depolarization, fluorescence yield, the position of fluorescence maxima [5,6] and others for the monitoring of the properties of environment [7,8]. In recent years, spectroscopic probes have been extensively used in the detection of nucleic acids and the determination of their structure [9,10]. The fluorimetric probes which show significant red-edge effect are found to be one of important type of probes [11–13]. Described in our earlier papers derivatives of ethyl 5-(4-aminophenyl)-3-amino-2,4-dicyanobenzoate are examples of such probes [14,15]. Studying the solvent polarity effect on the spectroscopic properties of the compounds, it was found that conformations with coplanar donor and acceptor groups absorb and emit at longer wavelengths than those observed for donor–acceptor groups oriented orthogonally. Equilibrium between these two forms is controlled by solvent properties and, due to the low energy of the

barrier separating these forms, can be, in part, controlled by viscosity and the temperature of environment.

In the present paper we report on the synthesis of new organic molecules and the characterization of their photophysical and electrochemical properties. The tested compounds possess strong electron acceptors substituents in the first phenyl ring and a strong electron donor group in the *para* or *meta* position in the second ring. Compounds of similar structure have previously been synthesized by several different methods [16–20]. In this study, the synthesis of the dyes was implemented using a modification of the method described earlier by Elgemeie and co-workers [20] giving the possibility of obtaining compounds with different amino groups.

2. Experimental

2.1. Measurements

All starting reagents and solvents (reagent grade) were purchased from Aldrich Chemical Co. and Lancaster Chemical Co. and were used without further purification.

Melting points (uncorrected) were determined on the Boëthius apparatus.

2.1.1. Spectral measurements

The ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded with the use of a Varian spectrometer Gemini 200. Dimethylsulfoxide

* Corresponding author. Tel.: +48 52 374 9034; fax: +48 52 374 9009.

E-mail address: marek@utp.edu.pl (M. Pietrzak).

(DMSO- d_6) was used as the solvent and tetramethylsilane as the internal standard.

The IR spectra of the synthesized compounds were recorded using a Bruker spectrophotometer Vector 22, in the range 400–4500 cm^{-1} , by KBr pellet technique.

The UV–vis absorption spectra were recorded using a Shimadzu UV–vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. The fluorescence quantum yields for the dyes in the tested solvents were determined as follows. The fluorescence spectrum of a dilute ($A = 0.1$) dye solution was recorded by excitation at the absorption band maximum of the reference. A dilute Coumarin I in ethanol solution ($\Phi = 0.64$ [21]) was used as a reference. The fluorescence spectrum of Coumarin I was obtained by excitation at its absorption peak at 366 nm. The fluorescence quantum yield of the tested dyes (Φ_{dye}) was calculated using equation:

$$\Phi_{\text{dye}} = \Phi_{\text{ref}} \frac{I_{\text{dye}} A_{\text{ref}}}{I_{\text{ref}} A_{\text{dye}}} \cdot \frac{n_{\text{dye}}^2}{n_{\text{ref}}^2}$$

where Φ_{ref} is the fluorescence quantum yield of the reference (Coumarin I) sample in ethanol, A_{dye} and A_{ref} are the absorbances of the dye and reference samples at the excitation wavelengths (366 nm), I_{dye} and I_{ref} are the areas (in arbitrary units) under the corrected fluorescence spectra for the dyes and reference samples, n_{dye} and n_{ref} are the refractive indices of the solvents used for the dyes and the reference, respectively.

2.1.2. Electrochemical measurements

The oxidation potentials of the dyes were measured by cyclic voltammetry using an Electroanalytical Cypress System Model CS-1090. The typical three-electrode setup was employed for electrochemical measurements. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile, which was purged with argon prior to a measurement. Platinum 1 mm electrode was applied as working electrode and platinum and Ag/AgCl were used as auxiliary and reference electrodes, respectively.

2.1.3. High performance liquid chromatography

A Waters 1525 Binary HPLC Pump coupled to a Waters 2489 UV/visible detector and a Symmetry C18 column (3.5 μm , 4.6 \times 75 mm) was used.

DFT calculations were carried out using B3LYP/6-311G(2d,p) method to estimate the ground state dipole moments of the dye molecules under investigation. All calculations were carried out with Gaussian 03 program [22].

2.2. Synthesis

2.2.1. Aldehydes

4-(Dimethylamino)benzaldehyde (**1b**) and 4-(diethylamino)benzaldehyde (**1c**) were purchased from Aldrich. The synthesis of

4-(dimethylamino)-2,3-dimethylbenzaldehyde (**1g**) and 4-(dimethylamino)-2,5-dimethylbenzaldehyde (**1h**) are described elsewhere [23], other aldehydes were synthesized according to the procedures found in literature [24,25].

A general method for the synthesis of the 2-cyano-3-[4-aminophenyl]-2-propenamide derivatives (**2a–n**) is presented in Scheme 1 (general procedure (A)). These compounds were obtained using *p*-aminobenzaldehydes and cyanoacetamide, adopting the method described in literature [26].

2.2.2. General procedure (A)

To a solution of appropriate *p*-aminobenzaldehyde **1a–n** (20 mmol) and cyanoacetamide (20 mmol) in ethanol (20 ml) a few drops of potassium hydroxide solution (10% in water) at 50 °C was added. The solution was set aside for seven hours at room temperature. The precipitate was filtered off and recrystallized from ethanol.

Characteristics of the synthesized propenamides are presented in Table 1.

The procedure described by Elgemeie and co-workers, was adapted to the synthesis of tested dyes, 3,4'-diamino-2,4-dicyanobiphenyl derivatives [20]. The dyes were prepared according to the method presented in Scheme 2 (general procedure (B)).

2.2.3. General procedure (B)

To a magnetically stirred solution of appropriate amide **2a–n** (10 mmol) and cyclohexylidenepropanedinitrile (10 mmol) in anhydrous ethanol (50 ml), piperidine (1 ml) was added. The mixture was then heated under reflux for 6 h. The solution was cooled and filtered. The residue was recrystallized from ethanol.

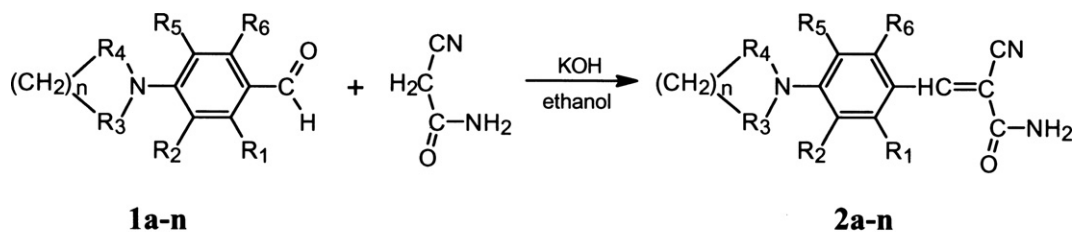
2.2.4. Compound **3o**

Compound **3o** was obtained by reducing the corresponding nitro compound, as shown in Scheme 3. Reagents: (i) cyanoacetamide, ethanol, KOH_{aq} , 50 °C to room temperature (according to general procedure (A)); (ii) cyclohexylidenepropanedinitrile, anhydrous ethanol, piperidine, reflux (according to general procedure (B)); (iii) tin powder, hydrochloric acid, ethanol.

3. Results and discussion

3.1. Synthesis of dyes

Thirteen dyes have been synthesized in a two-stage reaction. In the first stage, the appropriate 2-cyano-3-[4-aminophenyl]-2-propenamides were obtained from *p*-aminobenzaldehyde and cyanoacetamide, (Scheme 1, compounds **2a–n**). The structural analysis of the compounds is presented in Table 1 and Supplementary data. In the second stage, the 2-cyano-3-[4-aminophenyl]-2-propenamides reacted with cyclohexylidenepropanedinitrile (Scheme 2, compounds **3a–n**) yielding corresponding dyes. The reaction was carried out in anhydrous ethanol using piperidine as a catalyst. The



where: R_1, R_6 : H, CH_3 , R_2, R_5 : H, CH_3 , $-\text{CH}_2-$ R_3, R_4 : H, CH_3 , C_2H_5 , $-\text{CH}_2-$ n : 2, 3

Scheme 1. A general route for the synthesis of 2-cyano-3-[4-aminophenyl]-2-propenamide derivatives.

Download English Version:

<https://daneshyari.com/en/article/176875>

Download Persian Version:

<https://daneshyari.com/article/176875>

[Daneshyari.com](https://daneshyari.com)