Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 679–685

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

New non-protienogenic fluorescent amino acids: Benzoxazol-5-yl-alanine derivatives containing acetylene unit. Synthesis, spectral and photophysical properties

Irena Bylińska*, Katarzyna Guzow, Justyna Wójcik, Wiesław Wiczk

University of Gdańsk, Faculty of Chemistry, 80-308, Gdańsk, Wita Stwosza 63, Poland

ARTICLE INFO

Keywords:
Non-proteinogenic amino acids
Benzoxazoles
Acetylene derivatives
Absorbance
Fluorescence
Fluorophore

ABSTRACT

New derivatives of non-proteinogenic amino acids benzoxazol-5-yl-alanine containing substituted acetylene derivative were synthesized according to Sonogashira coupling reaction. All of the obtained compounds are fluorescent. They are characterized by high or moderate molar absorption coefficients, large Stokes shifts, high fluorescence quantum yields and very high brightness. All of these parameters as well as the positions of absorption and emission bands depend on the type and size of substituent and the solvent polarity. Their high brightness enables working with low concentrations, simple and easy detection of spectral absorption and fluorescence analyzes. Moreover, amino acid part of studied compounds allow to use them as covalently attached to a peptide or protein fluorescent probes in biological system studies.

1. Introduction

The subject of the presented studies are 2-phenylbenzoxazol-5-ylo-alanine derivatives with triple bond in position 4 of phenyl ring and 2-pyridinbenzoxazol-5-ylo-alanine derivative with triple bond in position 5 of benzoxazole ring. The presence of a triple bond results in an increased electron coupling which facilitates the charge transfer without causing steric hindrance. It makes such derivatives to be an interesting subject of research from their spectroscopic properties point of view. In the past decades benzoxazoles are the unfailing subject of research as they are an important class of heterocyclic compounds with huge potential application in many areas such as chemistry, medicine, technology and industry. They are known as photostable, highly efficient UV dyes, laser dyes [1], organic brightening agents [2], organic plastic scintillators [3], photonic devices [4], light emitting diodes [5,6] and chemosensors [7–10]. Moreover, benzoxazole skeleton occurs in a number of biologically active compounds [11–13] and natural products [14,15]. Their antifungal [16], antibacterial [17], anti-inflammatory [18], antitumour [19], anti-HIV [20] activities have been reported. A benzoxazole derivatives are also used as a fluorescent probe for intracellular imaging in living cells [21–24].

On the other hand introduction of the triple bond to the system results in electron relocation (blurring) due to the coupling extension. An acetylene unit is also used between a donor and an acceptor as a linker (D-π-A) in so-called push-pull compounds which show a large nonlinear optical response (NLO) [25]. Hydrocarbon aromatic derivatives of acetylene exhibit bathochromic shift of the absorption and emission spectra, large Stokes shifts, high molar absorption coefficients and high quantum fluorescence yields [26]. Asymmetrically substituted acetylene derivatives containing aromatic or heteroaromatic substituents are fluorescent compounds. They can be applied as polarity-sensitive probes [27], sensors of metal or pH [28], fluorescence switches [29,30], for labelling biological molecules [31] or as oligonucleotide analogues [32].

Benzoxazole derivatives containing substituents with unsaturated carbon bond, such as styrylbenzoxazoles, especially their Pt(II) complexes, have shown biological activity (cytotoxicity) [33,34]. They are also applied as sensitizers for photographic halide emulsion [35]. 2-(4-Dimethylaminostyryl)benzoxazole can be used in electroluminescence devices [36].

All the information mentioned above indicates that the benzoxazole derivatives containing acetylene unit seems to be an interesting combination with potential new application of obtained derivatives. Hence, we have synthesized and measured spectral and photophysical properties of six new derivatives of 2-phenylbenzoxazol-5-ylo-alanine (BoxPh) and one derivative of 2-pyridynylbenzoxazol-5-ylo-alanine (Fig. 1). We also included into the study BoxPhBr, which was the substrate for most of the obtained derivatives and at the same time is a good reference for investigating the effect of acetylene on the studied properties. It is worth emphasizing that derivatives under study as non-

* Corresponding author.
E-mail address: irena.bylinska@ug.edu.pl (I. Bylińska).

https://doi.org/10.1016/j.jphotochem.2018.07.012
Received 25 April 2018; Received in revised form 3 July 2018; Accepted 6 July 2018
Available online 07 July 2018
1010-6030/

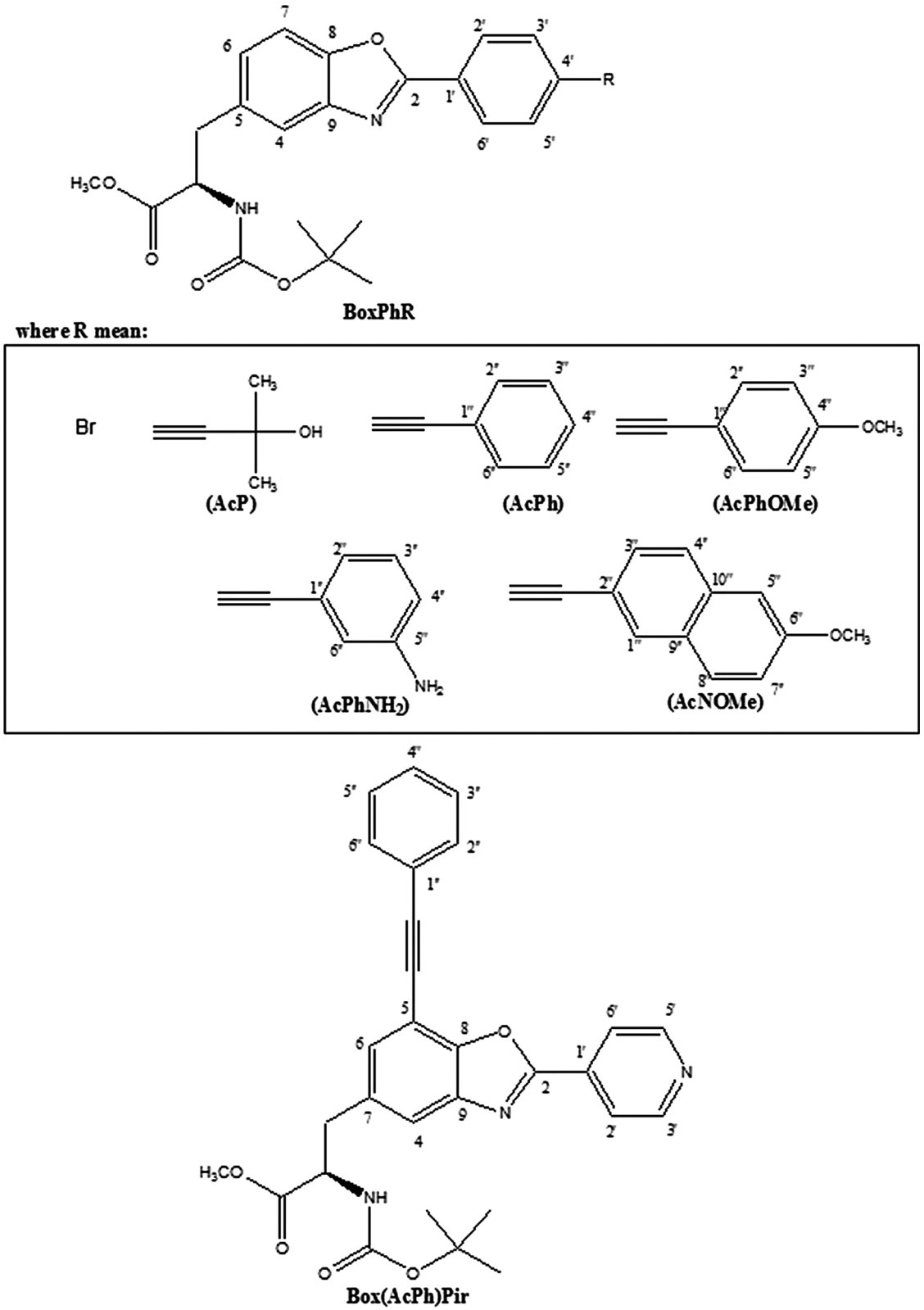
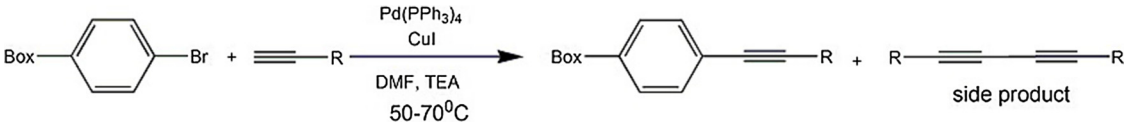


Fig. 1. Structures of synthesized acetylene derivatives of 3-(2-benzoxazol-5-yl)alanine.



Scheme 1. Scheme of synthesis of acetylene derivatives of 3-(2-benzoxazol-5-yl)alanine.