



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, spectroscopic and DFT studies of novel fluorescent dyes: 3-Aminoimidazo[1,2-a]pyridines possessing 4-pyrone moieties



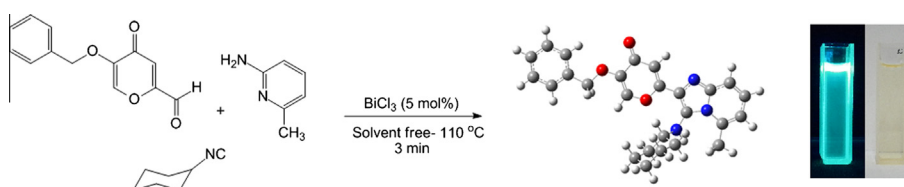
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HIGHLIGHTS

- New bis-heterocyclic compounds were synthesized using GBB multicomponent reaction.
- UV–Vis absorption and fluorescence emission spectra, TGA and CV of compounds were studied.
- Two of these novel compounds showed high fluorescence emissions.
- Optimized molecular geometries and orbital distributions were calculated using DFT.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 April 2013

Received in revised form 4 August 2013

Accepted 7 September 2013

Available online 19 September 2013

Keywords:

Multicomponent reactions

4-Pyrone derivatives

UV–Vis spectra

Fluorescence

Density functional theory (DFT)

ABSTRACT

A series of novel imidazo[1,2-a]pyridines possessing 4-pyrone ring were synthesized by three-component condensation of 4-pyrone carbaldehydes, 2-aminopyridines and isocyanides. Bismuth (III) chloride was used as a catalyst in these reactions and desired products were synthesized in good yields at a very short period of time under solvent free conditions. UV–Vis absorption and fluorescence emission spectra of these compounds were investigated. It shown that two of these compounds (**10f** and **10g**) exhibit intense fluorescence in dichloromethane. Optimized ground-state molecular geometries and orbital distributions of these two fluorescent dyes were obtained using density functional theory (DFT). Thermo-gravimetric analysis and electrochemical properties of these compounds were also studied.

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Introduction

Design and synthesis of novel organic fluorescent compounds is one of interesting and active areas in the organic chemistry. Fluorescent dyes have wide applications in the biological labels, photovoltaic cells, light emitting diodes (LEDs), optical sensors, materials for collecting solar energy, fluorescent films for greenhouses, fluorescent colorants and etc [1–15]. In the last decade synthesis of various organic compounds via multicomponent reactions (MCRs) have attracted a great interest, because most of these reactions are simple, one-pot, fast and high yielding [16–21]. Therefore synthesis of fluorescent compounds via MCRs is so favor-

able and there are some reports on the use of MCRs for the synthesis of fluorescent dyes [22,23].

One of isocyanide based multicomponent reaction (IMCR) is Groebke–Blackburn–Bienaymé multicomponent reaction (GBB MCR) [24–26] in which three-component condensation of aldehyde, isocyanide and 2-aminoazine enables synthesis of imidazo[1,2-a]azines. Compounds containing imidazo[1,2-a]azine ring system have been shown to possess a broad range of useful pharmacological and biological properties [27–29]. Moreover in the recent years fluorescence properties of these compounds have also been investigated [30].

On the other hand, pyran-containing fluorescent dyes are an important class of organic light emitting diodes (OLEDs) and also have been used in dye lasers, sensors, dye-sensitized solar cells (DSSCs), fluorescent probes, logic gates and optical chemosensors

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[31–39]. Most of these compounds are dicyanomethylene pyran derivatives and the fluorescence properties of 4*H*-pyran-4-ones are rarely investigated.

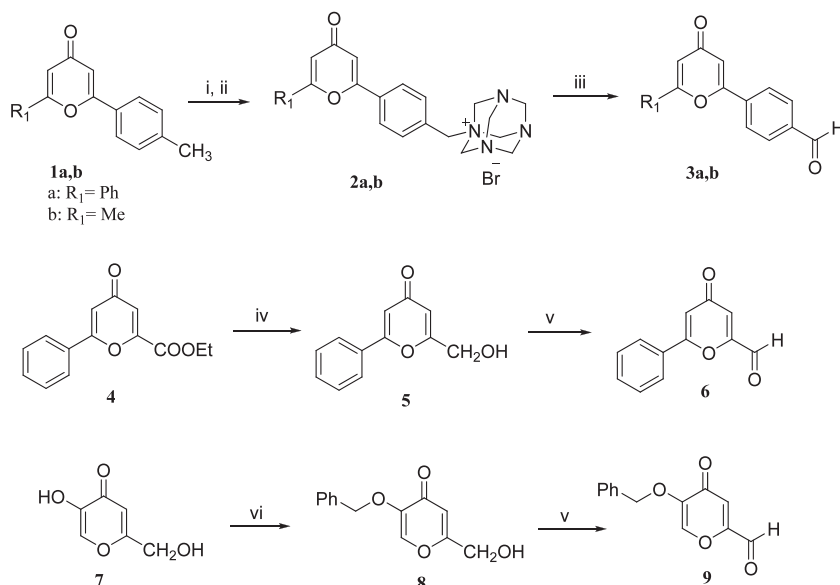
Because of the wide applicability of these types of compounds, the synthesis and studies of their chemical and photophysical properties is an interesting research field. Therefore, as a part of our ongoing interest in the multicomponent reactions and synthesis of novel derivatives of 4-pyrones [40–43], in this investigation we used GBB MCR for the synthesis of novel 3-aminoimidazo[1,2-*a*]pyridines possessing 4-pyrones by three-component reaction of aldehydes, isocyanides and 2-aminopyridines catalyzed by BiCl₃ under solvent free conditions and then UV–Vis absorption spectra, fluorescence emission spectra, DFT structure optimization, thermogravimetric analysis and electrochemical properties of these compounds were also studied.

Experiments

General

Melting points were determined with a MEL-TEMP model 1202D and are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks. The ¹H NMR spectra were recorded with a Bruker Spectrospin Avance 400 spectrometer with CDCl₃ as solvent and TMS as internal standard. ¹³C NMR spectra were determined on the same instrument at 100 MHz. All chemical shifts were reported as δ (ppm) and coupling constants (*J*) are given in Hz. UV–Vis spectra were recorded on analytikjena SPECORD 250 spectrometer. Fluorescence spectra were obtained on a Jasco FP-750 spectrofluorometer. The fluorescence quantum yields (Φ_f) were determined in CH₂Cl₂ dilute solutions by using quinine sulfate ($\Phi_s = 0.546$ in 0.05 M H₂SO₄) as standard. Calculations are done by Eq. (1), where Φ_f is the fluorescence quantum yield of the sample, Φ_s the fluorescence quantum yield of the standard, *F* and *F_s* are the areas under the fluorescence emission curves of the samples and the standard, respectively. *A* and *A_s* are the relative absorbance of the samples and standard at the excitation wavelength, respectively. η and η_s are the refractive indices of solvents for the sample and standard, respectively [44]:

$$\Phi_f = \Phi_s(F/F_s)(A_s/A)(\eta/\eta_s)^2 \quad (1)$$



Scheme 1. Synthesis of 4-pyrone carbaldehydes. Reagents and conditions: (i) NBS, BPO, CCl₄, reflux, 48 h; (ii) HMTA, CHCl₃, reflux, 30 min; (iii) EtOH/H₂O (3:2), reflux, 24 h; (iv) NaBH₄ (4eq), MeOH, reflux, 3 h; (v) Active MnO₂ (8eq), CH₂Cl₂, rt., 3 days; and (vi) PhCH₂Br (1eq), NaOH (1eq), MeOH/H₂O: 10/1, 60 °C, 4 h.

Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10 °C min⁻¹ with a TGA/SDTA851 (Mettler Toledo) from 50 °C to 600 °C under 20 ml min⁻¹ of argon flow. Electrochemical experiments were performed using Autolab PGSTAT 30 electrochemical analyzer system and GPES 4.9 software package (Eco Chemie, The Netherlands). The utilized three-electrode cell was composed of a glassy carbon electrode with 2 mm diameter as the working electrode, a platinum wire as auxiliary electrode, and SCE (saturated calomel electrode) as reference electrode (0.01 M AgNO₃) in CH₂Cl₂ solution (10⁻³ mol L⁻¹) in the presence of TBAPF₆ (tetrabutylammonium hexafluorophosphate) (0.10 mol L⁻¹) as supporting electrolyte. Mass spectra (MS) were measured by a Shimadzu (70 eV) spectrometer and elementary analyses (C, H, N) were performed on a Vario EL III analyzer. Thin-layer chromatography was done with prepared glass-backed plates (20 × 20 cm², 500 μ) using silica gel (Merk Kieselgel 60 HF₂₅₄, Art. 7739). The chemical reagents used in synthesis were purchased from Merck and Sigma–Aldrich CO. Synthetic details and characterizations of compounds **3a**, **6** and **9** are given in [Supplementary material](#).

General procedure for the synthesis of 3-aminoimidazo[1,2-*a*]pyridines **10a–g**

To a mixture of 4-pyrone carbaldehyde (0.5 mmol), 2-amino-pyridine or 2-amino-6-methyl pyridine (0.5 mmol) and isocyanide (0.5 mmol) was added BiCl₃ (5 mol%) and the reaction mixture was stirred on a preheated oil bath at 110 °C. After completion of the reaction (monitored by TLC), the crude residue was either treated with ethyl acetate/n-hexane (1:3) to afford the product as a precipitate, or was subjected to silica gel preparative layer chromatography (ethyl acetate: n-hexane; 1:3).

2-[4-(3-(Cyclohexylamino)imidazo[1,2-*a*]pyridin-2-yl)phenyl]-6-phenyl-4*H*-pyran-4-one (**10a**)

Yellow solid. Yield: 97%. M.p: 180–182 °C. FT-IR (KBr): 3249 (N–H), 3072 (aromatic C–H), 2924 (aliphatic C–H), 1646 (pyrone C=O). ¹H NMR (400 MHz, CDCl₃): δ 1.19–1.90 (m, 10H); 3.04 (m, 1H); 3.17 (bs, 1H); 6.82–6.87 (m, 2H); 6.90 (d, *J* = 2 Hz, 1H); 7.18–7.22 (m, 1H); 7.55–7.59 (m, 4H); 7.88–7.94 (m, 2H); 7.97 (d, *J* = 8.4 Hz, 2H); 8.13 (d, *J* = 6.8, 1H); 8.31 (d, *J* = 8.4 Hz, 2H). ¹³C

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