



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis of novel boron chelate complexes and proposed mechanism of new rearrangement

Rui-Zhe Zhang¹, Xiao Feng¹, Ying Liu, Sheng-Qing Wang, Jin-Ting Liu*, Bao-Xiang Zhao*

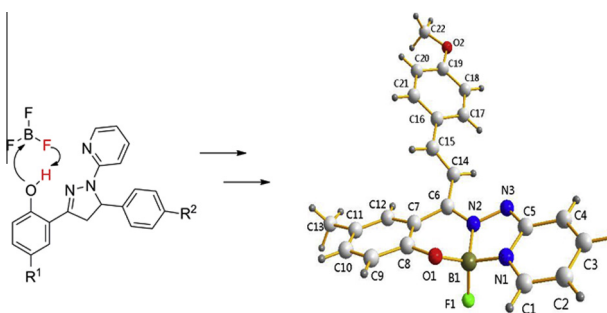
Institute of Organic Chemistry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- A series of novel boron azo chelate complexes were synthesized.
- A new rearrangement mechanism was proposed.
- The structure was characterized by single crystal X-ray analysis.

GRAPHICAL ABSTRACT

A series of boron chelate complexes were synthesized and a mechanism of the rearrangement was proposed.



ARTICLE INFO

Article history:

Received 1 August 2014

Received in revised form 22 November 2014

Accepted 25 November 2014

Available online 24 December 2014

Keywords:

Pyrazoline

Boron chelate complexes

Rearrangement

Single crystal

ABSTRACT

We synthesized novel boron chelate complexes by the reaction of pyrazoline derivatives and boron trifluoride diethyl etherate followed by a new rearrangement. The structures of the compounds were characterized by IR, NMR and HRMS, especially, a typical compound **3c** was confirmed by X-ray single crystal analysis. We proposed a mechanism of the rearrangement. Moreover, the absorption and fluorescence spectroscopy of these compounds were measured.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Multidisciplinary research on novel organic luminescent dyes is stimulated by potential applications in optical electronics and biomedical sciences. These new functional fluorescent dyes should possess over standard chemical and photochemical stability, high absorption coefficient and quantum yields, as well as a tunability

of both absorption and emission bands, which allow them to fit the application requirements. The construction of sophisticated fluorescent dyes based on tetrahedral boron is a particular strategy. Much attention have focused on novel boron complex, such as aniline-imines [1], triazaborolopyridinium [2], 2-(2'-pyridyl)imidazole [3], 2-(2'-hydroxy phenyl)benzoxazole [4,5], boranil fluorophore (I) [6], naphthyridine [7,8], 1,8-naphthyridine [9], hydrazone [10], azo compound [11], iminocoumarin [12], *N*-alkylated 2-(2'-hydroxyphenyl) benzimidazole or *N*-arylated 9,10-phenanthroimidazole [13], phenanthro[9,10-d]imidazole-quinoline [14], indigo-*N,N'*-diarylimine (II) [15], β -diketone-boron

* Corresponding authors. Tel.: +86 531 88366425; fax: +86 531 88564464.

E-mail addresses: jintliu@sdu.edu.cn (J.-T. Liu), bxzhao@sdu.edu.cn (B.-X. Zhao).¹ Equal contribution.

difluoride dyes [16,17], phenylpyrriin [18], curcumin [19], azadiquinomethene [20], dipyrriins (III) [21], β -diketimines (IV) [22,23], formazanate [24,25]. The structures of complexes (I–IV) were shown in Fig. 1. Recently, boron-containing materials displayed morphology-dependent solid-state NIR emission was reported [26].

Pyrazoline derivatives have attracted much attention because of their excellent blue fluorescence property and high fluorescence quantum yield [27,28]. We have previously developed some fluorescent probe based on pyrazoline derivatives for the detection of metal ions and biothiols [27–38]. However, they suffer from some drawbacks, such as excitation and emission wavelength at ultraviolet region [36,39–41], poor solubility in water [28,37]. Considering boron complex could display unusual spectroscopic behavior, we attempted to construct the complex of substituted pyrazoline with boron to improve fluorescence excitation wavelength and emission or discover novel solid fluorescent dyes (Scheme 1). We obtained rearrangement products (3), to our surprise, which were characterized by IR, NMR and HRMS, especially, a typical compound 3c was confirmed by X-ray single crystal analysis, but expected compounds (2). Here, we would like to report the characterization of products 3, the proposed mechanism of the novel rearrangement, and the absorption and fluorescence spectroscopy properties of these new compounds.

Experimental

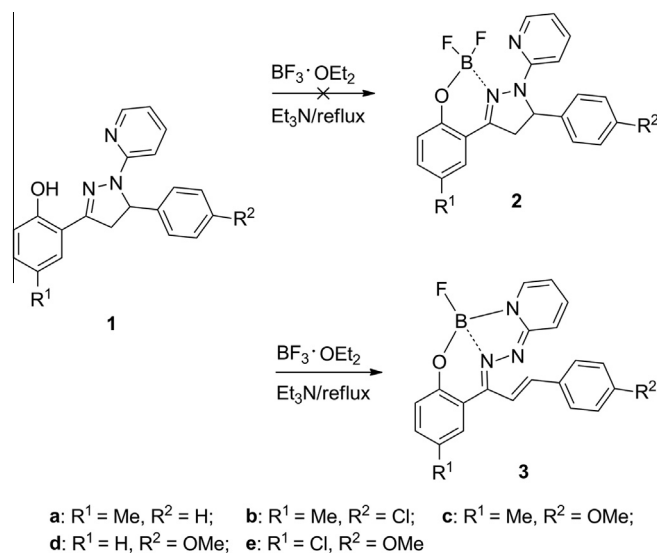
Materials and methods

General information and materials

Thin-layer chromatography (TLC) involved silica gel 60F₂₅₄ plates (Merck KGaA) and column chromatography involved silica gel (mesh 200–300). ¹H (300 MHz) and ¹³C NMR (75 MHz) spectra were acquired on a Bruker Avance 300 spectrometer, with CDCl₃ or DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. ¹¹B NMR (96.3 MHz, DMSO) and ¹⁹F NMR (282.4 MHz, DMSO) were also acquired on a Bruker Avance 300 spectrometer. Melting points were determined with an XD-4 digital micro-melting-point apparatus. IR spectra were recorded with the infra-red (IR) spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were obtained on a Q-TOF6510 spectrograph (Agilent). UV-vis spectra were measured by use of a Hitachi U-4100 spectrophotometer. Fluorescent measurements were performed on a Perkin-Elmer LS-55 luminescence spectrophotometer. Quartz cuvettes with a 1-cm path length and 3-mL volume were used for all measurements. Unless otherwise stated, all reagents were purchased from Aladdin, J&K or Sinopharm Chemical Reagent Co. and used without further purification. Twice-distilled water was used throughout all experiments.

Fluorescence quantum yield

Quantum yield (Φ_F) was determined by the relative comparison procedure, with quinine sulfate dehydrate ($\geq 99.0\%$) in 0.1 N H₂SO₄



Scheme 1. Synthesis of compounds 3.

as the main standard. The corrected emission spectra were measured for the quinine sulfate dehydrate standard (A (Absorption) < 0.01 ; $\Phi_F = 0.560$) [36]. The general equation used in the determination of relative quantum yields from earlier research is Eq. (1) [42].

$$\Phi_F = (\Phi_{Fs})(F_{Au})(A_s)(\eta_u^2)/(F_{As})(A_u)(\eta_s^2) \quad (1)$$

where Φ_F and F_A are fluorescence quantum yield and integrated area under the corrected emission spectrum, respectively; A is absorbance at the excitation wavelength; η is the refractive index of the solution; and subscripts u and s refer to the unknown and the standard, respectively.

General procedure for the preparation of compounds 3

The starting materials 1 were easily synthesized according to our previous report [29]. Compounds 1 (0.5 mmol) and triethylamine (50 mL) were added to a 100 mL flask, and the mixture was heated under reflux for 40 min to dissolve the reactant. BF₃·Et₂O (10 mL) was slowly added by a dropping funnel, and then kept refluxing for 24 h. After the reaction was completed by TLC monitoring, the mixture was cooled to room temperature and the deep red oil liquid layer solidified. After triethylamine was removed under reduced pressure, anhydrous ethanol (20 mL) was added to dissolve the solid. The mixture was heated under reflux for 20 min to make ethanol react with the redundant BF₃·Et₂O. After remove the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with dichloromethane as eluent to obtain products 3.

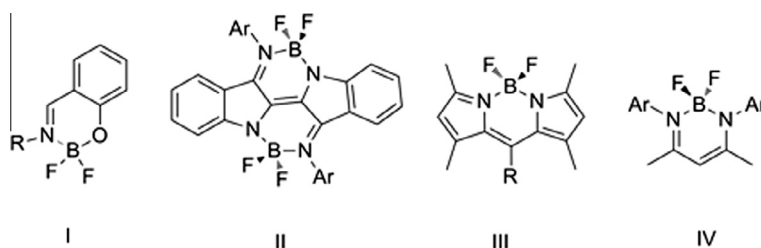


Fig. 1. Structures of typical boron complexes (I–IV).

Download English Version:

<https://daneshyari.com/en/article/1232694>

Download Persian Version:

<https://daneshyari.com/article/1232694>

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