

Crystal structures, phosphorescent and magnetic properties of novel 1,2-dihydroisoquinoline radicals

Liusong Ni, Guoping Yong*

Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China

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ABSTRACT

We unprecedentedly synthesized two novel 1,2-dihydroisoquinoline radicals through cascade ion-type, radical-type and pericyclic reaction mechanisms. This work indicates that from a radical precursor and triethylamine that also was used as a solvent, the 1,2-dihydroisoquinoline framework can be constructed through cascade reactions under high temperature and high pressure condition. Interestingly, 1,2-dihydroisoquinolines not only reveal the phosphorescence, but also the interesting magnetic properties due to their radical nature. The present work provides a promising approach for synthesizing 1,2-dihydroisoquinoline radical materials and a new access to develop cascade reaction for constructing complicated organic compounds by facile high temperature and high pressure synthetic approach.

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1. Introduction

Nitrogen-containing heterocycles are an important class of compounds which attract much attention as biologically active agents and play an important role in material science or medicine. Among of them, the isoquinoline and 1,2-dihydroisoquinoline possess especial structures encountered in many natural products, and are promising bioactivity molecules [1–5]. Accordingly, a variety of synthetic methods have been developed towards their synthesis. The 1,2-dihydroisoquinoline structure can be synthesized through different approaches, such as functionalization of the parent isoquinoline or denovo synthesis [6–15]. According to their industrial value and application in pharmaceuticals and materials, the development of new strategies for the synthesis of 1,2-dihydroisoquinoline derivatives is still highly desired.

Under the high temperature and high pressure condition, hydro(solvo)thermal *in situ* ligand reaction has become a powerful approach in organic chemistry, crystal engineering and preparing unexpected organic compounds [16–18]. As a facile and high-efficiency synthetic approach, the *in situ* ligand preparation strategy is becoming increasingly popular for its advantage of discovery of new organic reactions that are inaccessible or not easily

obtainable by conventional means. So far, the typical compound/ligand generated *in situ* reactions are the decarboxylation, dehydrogenation, hydroxylation of carboxyl group or aromatic ring, carbon–carbon coupling, cycloaddition of organic nitriles with azide, acylation of multicarboxylic acids with N_2H_4 , [2 + 2] or [3 + 3] cycloaddition, *N*-alkylation of heterocyclic compounds with alcohols, and so on [19–34]. Among these cases, various organic molecules and important coordination polymers with interesting structures or significant functions were obtained. However, the hydro(solvo)thermal synthesis of the radical molecules and *in situ* generated radical ligands is still very scarce [35–37].

3-Formyl-2,3'-biimidazo[1,2-*a*]pyridin-2'-one radical can be easily transferred into two radical derivatives (Fig. 1A and B) by the aldol condensation [38]. Such radical derivatives possess extended π -conjugated system and exhibit the stacking-induced near infrared absorption [38], and proton triggered chemical structure and property transformation [39]. In this study, another radical derivative (Fig. 1C) was synthesized through similar procedure to that previously reported [38]. Interestingly, when triethylamine was used as solvent, compounds **B** and **C** were unexpectedly transformed to two novel organic crystals **1** and **2** (1,2-dihydroisoquinoline derivatives) by employing high temperature and high pressure under solvothermal conditions (Scheme 1). Therefore, this work reports novel synthetic strategy for the 1,2-dihydroisoquinolines by using environmental friendly one-pot

* Corresponding author.

E-mail address: gpyong@ustc.edu.cn (G. Yong).

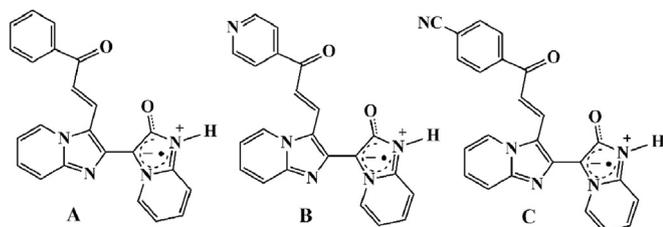
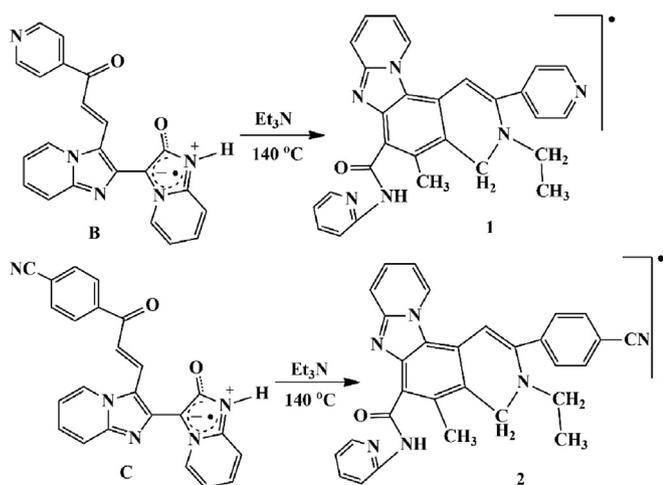


Fig. 1. Radical derivatives.

Scheme 1. The high temperature and high pressure syntheses of the 1,2-dihydroisoquinolines **1** and **2**.

approach under high temperature and high pressure condition. Moreover, the crystal structures, luminescent and magnetic properties of 1,2-dihydroisoquinoline derivatives (**1** and **2**) are also investigated.

2. Experimental

2.1. Materials and methods

All of chemicals were AR reagents obtained from commercial sources and used without further purification. The precursors **B** and **C** were synthesized according to the previous procedure [38]. ¹H NMR spectra were collected on Bruker Avance 400 MHz NMR spectrometer using dms-*d*₆ as solvent. Microanalytical data (C, H, N) were collected on Vario ELIII elemental analyzer. FT-IR spectra were recorded using a Bruker EQUINOX55 FT-IR spectrophotometer. Mass spectrometry was carried out with Thermo Scientific Velos Pro mass spectrometer. The solid-state photoluminescence (PL) spectra and the decay lifetime were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The solid-state quantum yield was measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a BaSO₄-coated integrating sphere. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X'pert PRO SUPER diffractometer operating with nickel-filtered Cu-K α radiation ($\lambda = 1.540598 \text{ \AA}$) at 40 kV and 200 mA. Temperature dependence of magnetic susceptibilities was measured for microcrystalline samples with a magnetic field of 1000 Oe using a SQUID magnetosusceptometer (Quantum Design MPMS) from 350 K to 4 K.

2.2. High temperature and high pressure syntheses of 1,2-dihydroisoquinolines **1** and **2**

A mixture of radical precursor **B** or **C**, Zn(NO₃)₂ and triethylamine (Et₃N, 4 mL) was sealed in a Teflon-lined autoclave, and heated at 140 °C for one day (Scheme 1). After the autoclave was cooled to room temperature, yellow single crystals of 1,2-dihydroisoquinoline derivative **1** and red single crystals of 1,2-dihydroisoquinoline derivative **2** were obtained which were filtered, washed with EtOH, and dried in air (yield ~20% and ~28% based on precursor **B** and **C**, respectively). Anal. Calcd for C₂₈H₂₄N₆O (**1**): C, 73.03; H, 5.25; N, 18.25. Found: C, 72.45; H, 5.52; N, 18.06. Anal. Calcd for C₃₀H₂₄N₆O (**2**): C, 74.36; H, 4.99; N, 17.34. Found: C, 73.87; H, 5.08; N, 17.12. IR (KBr, cm⁻¹) for **1**: 2973(w), 2935(w), 1659(m), 1637(s), 1582(s), 1541(s), 1503(s), 1424(s), 1385(m), 1356(m), 1305(m), 1283(s), 1227(m), 1199(m), 1135(m), 1058(w), 839(w), 778(m), 722(m), 598(w). IR (KBr, cm⁻¹) for **2**: 2974(w), 2934(w), 2232(s), 1654(s), 1632(s), 1575(s), 1536(s), 1497(s), 1435(s), 1379(m), 1288(s), 1235(m), 1188(m), 1137(s), 1047(w), 851(m), 772(m), 722(m), 609(w), 548(s).

2.3. X-ray crystallography

The X-ray diffraction measurements were performed at 293(2) K on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) using graphite monochromated Cu-K α ($\lambda = 1.54184 \text{ \AA}$) or Mo-K α ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct method (SHELXL) and completed by difference Fourier method (SHELXL). Refinements were performed against F^2 by weighted full-matrix least-squares (SHELXL), and empirical absorption correction (SCALE3 ABSPACK) was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically and refined by the riding mode. Weighted R factor (R_w) and all goodness of fit S are based on F^2 , conventional R factor (R) is based on F .

3. Results and discussion

3.1. Syntheses and mechanism study

Under the high temperature and high pressure condition, the reaction of radical precursor **B** or **C** (Fig. 1) with triethylamine (Et₃N) that also was used as a solvent unprecedentedly generated two novel 1,2-dihydroisoquinoline crystals **1** or **2** (Scheme 1). This cascade reaction mechanism under the high temperature and high pressure condition is shown in Scheme 2. The Et₃N undergoes nucleophilic attack precursor **C** to afford a zwitterionic intermediate **a**, which then performs Hofmann elimination reaction of the quaternary ammonium to give compound **b** and ethylene. The radical addition reaction between **b** and ethylene gives rise to intermediate **c**, which undergoes H transfer reaction to afford intermediate **d**. **d** performs intramolecular radical addition reaction to construct six-membered ring intermediate **e** which carries out hydrogen migrate to give stable allyl-type radical **f**. The dehydration from **f** results in formation of intermediate **g** which then undergoes ring-opening reaction to give triradical intermediate **h**. The dehydrogenation from **h** gives rise to radical **i** that performs 6 π electrocyclic to construct another six-membered ring radical **j**. The final product (i.e. 1,2-dihydroisoquinoline radical crystal **2**) can be obtained by dehydrogenation from **j** (Scheme 2). Accordingly, through a facile and high-efficiency synthetic approach, two novel 1,2-dihydroisoquinoline derivatives were synthesized by cascade reactions under the high temperature and high pressure condition which concern ion-type, radical-type and pericyclic reaction mechanisms. The structure of two 1,2-dihydroisoquinoline

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