

Note

Crystal structures of amarine and isoamarine and copper(I) coordination chemistry with their allylation products

Xue-Feng Huang¹, Yu-Mei Song¹, Xi-Sen Wang¹, Jie Pang, Jing-Lin Zuo, Ren-Gen Xiong^{*}

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, Hankou Road, Nanjing, Jiangsu 210093, PR China

Received 24 August 2005; received in revised form 13 October 2005; accepted 18 October 2005
Available online 5 December 2005

Abstract

The crystal structures of amarine (**1**) and isoamarine (**2**), important intermediates in the preparation of 1,2-diphenyl-diaminoethane, were successfully determined. Their allylation products, 1,3-diallyl amarine (**1**)(CH₂—CH=CH₂)₂Br (**3**) and isoamarine bromide (**2**)(CH₂—CH=CH₂)₂Br (**4**) [the crystal structures of (**1**)(CH₂—CH=CH₂)₂PF₆ (**3**-Br + PF₆) and (**2**)(CH₂—CH=CH₂)₂PF₆ (**4**-Br + PF₆) are also successfully determined to confirm allylation products], react with CuBr to afford (**1**)₂(CH₂—CH=CH₂)₄(Cu₂Br₄) (**5**) and (**2**)(CH₂—CH=CH₂)₂(Cu₂Br₃) (**6**), respectively. Crystal structures of **5** and **6** reveal that **5** is an anion discrete complex without olefin moiety coordination, and **6** has a 1D infinite chain with olefin moiety coordination as a bridging spacer. The fluorescent emission spectra of **5** (λ_{emax} = 570 nm) and **6** (λ_{emax} = 642 nm) were measured, and display a significant difference that can be used for solid state fluorescent sensing them.

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Keywords: Amarine; Isoamarine; Allylation; Copper(I) olefin complex; Crystal structures; Fluorescent emission

1. Introduction

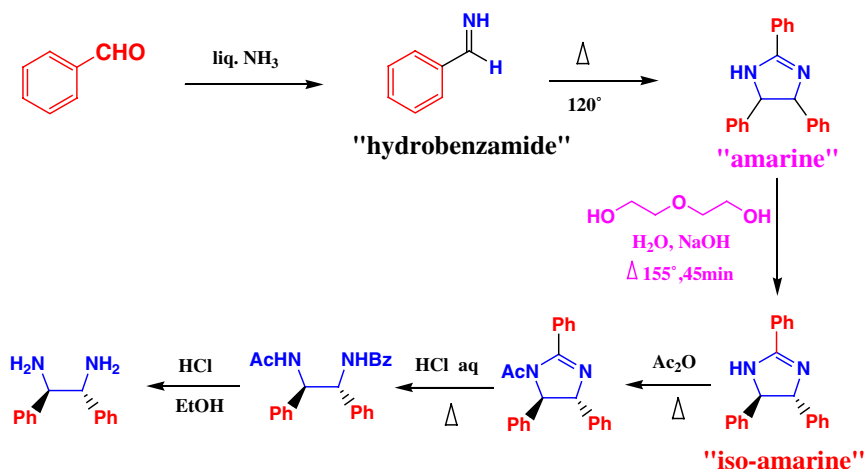
Chiral 1,2-diphenyl-diaminoethane (stilbenediamine, stein) have been widely used in enantioselective catalysis as a very useful chelating ligands [1], such as the enantioselective titanium-mediated addition of diethylzinc to aldehydes [2a], the V complexes with tetradentate Schiff base ligands containing optically active stein [2b], and optically active β-ketoiminato cobalt complexes with optically active stein as effective Lewis acid catalysts for enantioselective hetero Diels–Alder reactions [2c]. On the other hand, the olefin-copper(I) complex with chiral bidentate ligand (1S,2S)-N,N'-bis-(mesitylmethyl)-1,2-diphenyl-1,2-ethane-diamine has been used to resolve racemic 1-buten-3-ol [3]. Consequently, the preparation of racemic stein demonstrates the great importance. Corey and coworkers [4]

reported a simplified synthesis of racemic stein from benzaldehyde and liquid ammonia, and determined the crystal structures of hydrobenzamide and protonated amarine by HCl (meso-2,4,5-triphenyl-2-imidazoline hydrochloride ethanol solvate). This work revised the structures of the well known intermediates “hydrobenzamide” and “amarine” (Scheme 1). However, as shown in Scheme 1, the crystal structure of one of the important intermediates, “isoamarine (racemic-trans-2,4,5-triphenyl-2-imidazoline)” still remains unknown. In addition, there have been no reports of the chemistry of two intermediates, amarine and isoamarine, which serve a potential building block through N atom of imidazoline or its derivatives through 1,3-N atoms allylation. As a part of our studies of the olefin-copper(I) coordination polymers [5], we have determined the crystal structures of amarine (**1**) and isoamarine (**2**) and carried out the crystal structure determinations of the products of their 1,3-N atom allylation reactions and the copper(I) coordination chemistry of the allylation products with bromide anion. Herein, we report

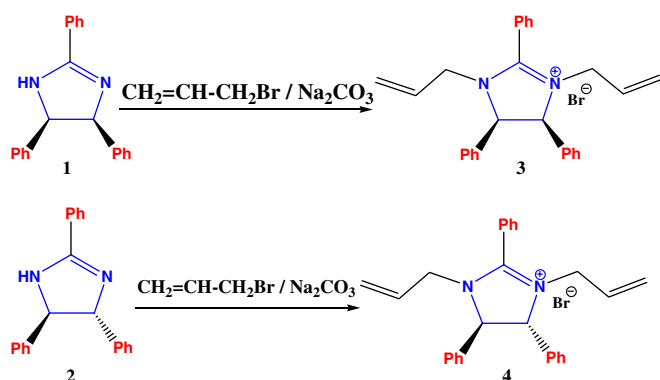
^{*} Corresponding author. Fax: +86 25 83317761/83314502.

E-mail address: xiongrg@netra.nju.edu.cn (R.-G. Xiong).

¹ These authors contributed equally to this work.



Scheme 1.



Scheme 2.

the synthesis and crystal structures of amarine (**1**) and isoamarine (**2**), and their 1,3-N atom allylation products as well as the fluorescent properties and crystal structures of the copper(I) complexes with their allylation bromide products as shown in Scheme 2.

2. Results and discussion

Amarine (**1**) and isoamarine (**2**) were prepared according to the literature reported by Corey et al. Their single crystals were obtained through the evaporation of solvent in air at room temperature. Crystal structure determination of **1** (Fig. 1(a)) shows that two amarine molecules and one water co-crystallize together through H-bonds and two phenyl rings are in *cis*-configuration, as the meso isomer. Compared to the crystal structure of the protonated **1**, the 1-N atom of imidazoline in **1** is un-protonated. As expected, the C–C and C–N bond distances (Table 1) in amarine are comparable to those found in protonated amarine [4].

The crystal structure of **2** (Fig. 2(a)), different from that found in **1**, reveals that two phenyl rings are *trans* and **2** is a racemic mixture. Similar to **1**, there is no protonated N atoms in **2**. The C–C and C–N bond lengths (Table 2)

are unexceptional and comparable to those in **1** and protonated **1** [4].

The reactions of **1** and **2** with allyl bromide afford 1,3-diallyl **1** [(**1**)(CH₂–CH=CH₂)₂Br] (**3**) and 1,3-diallyl **2** [(**2**)(CH₂–CH=CH₂)₂Br] (**4**), respectively, in the presence of Na₂CO₃ as shown in Scheme 2. Due to the difficulty of the formation of single crystals of **3** and **4**, we use PF₆[–] anion to replace the Br[–] anion in **3** and **4** successfully to determine their crystal structures of **3**–Br + PF₆[–] and **4**–Br + PF₆[–] as shown in Scheme 3.

Figs. 1(c) and 2(c) clearly confirms the above-mentioned diallylation reactions. Meanwhile, the *cis*- and *trans*-configurations of two phenyl rings in **3** and **4** still remain unchanged. As expected, the C–C and C–N bond lengths of **3**–Br + PF₆[–] and **4**–Br + PF₆[–] (Tables 3 and 4) are unexceptional and comparable to the corresponding **1** and **2**. Furthermore, the solvothermal reactions of **3** and **4** with CuBr give (**1**)₂(CH₂–CH=CH₂)₄(Cu₂Br₄) (**5**) and (**2**)(CH₂–CH=CH₂)₂(Cu₂Br₃) (**6**), respectively (Scheme 4). The crystal structure of **5** (Fig. 3) discloses that the olefin moiety of the allyl group does not take part in the coordination to Cu(I) probably due to the steric hindrance in which two phenyl groups and two olefin moieties in **3** are on the opposite plane of imidazole, and (**1**)(CH₂–CH=CH₂)₂ only acts as cation to balance the charge of dimeric Cu₂Br₄ anion in which the local coordination environment around Cu atom can be best described as three-coordinated planar trigonal. Interestingly, the crystal structure determination of **6** (Figs. 4 and 5) shows that the olefin moiety of the allyl group in (**2**)(CH₂–CH=CH₂)₂(Cu₂Br₃) participates in the coordination to Cu(I) to result in the formation of 1D infinite chain with two different local coordination geometry Cu atoms probably due to one of two phenyl rings being in the same plane of imidazole as one of two olefin moieties which is quite different from that found in **3** [6]. In one coordination geometry, Cu(I) is in a slightly distorted tetrahedron defined by two μ₂-bridging Br atoms, one terminal Br atom and the olefin moiety (Fig. 4). In the second coordination geometry, the

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