



Extremely high pH stability for a class of heterocyclic azo dyes having the common N^2, N^6 -bis(3-methoxypropyl)pyridine-2,6-diamine coupling component



Xiao-Lei Zhao^a, Teng Jun^a, Ya-Nan Feng^b, Hui-Fen Qian^b, Wei Huang^{a,*}

^a State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province, 210093, PR China

^b College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, Jiangsu Province, 210009, PR China

ARTICLE INFO

Article history:

Received 30 April 2017

Received in revised form

10 June 2017

Accepted 13 June 2017

Available online 15 June 2017

Keywords:

Pyridone dye

Functional group transformation

UV–Vis spectrum

Push-pull substituent

pH stability

ABSTRACT

A series of N^2, N^6 -bis(3-methoxypropyl)pyridine-2,6-diamine azo dyes, prepared by coupling 2,6-bis((3-methoxypropyl)amino)-4-methylnicotinonitrile and diazotized substituted anilines with distinguishable electron push-pull abilities, have been described in this paper. The new dyes undergoing double functional group transformation (FGT) show extremely high pH stability compared to corresponding mono FGT dyes, which could be ascribed to the introduction of the second 3-methoxypropylamino group forming the new pyridine-2,6-diamine backbone. It is noted that the unusual transformation from D- π -A to A- π -D system has been verified for our multi-substituted phenyl-azo-pyridine FGT products. The adjustment of electron-donating and electron-withdrawing phenyl and pyridine substituted groups narrows the discrepancy of electron push-pull capabilities for diazo and coupling components, which makes possible the transformation for roles of donor and acceptor. It is believed that the achievement of extremely high pH stability for pyridine-2,6-diamine based heterocyclic azo dyes is regarded as a useful exploration for designing new FGT modified pyridone dyes.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Since their discovery in the 20th century, heterocyclic disperse dyes have spurred tremendous interest among researchers because of their applications not only in the dyestuff industry [1,2] as high level-dyeing agents but also in the electronic industry including nonlinear optical devices [3], colorimetric sensors [4,5] and dye-sensitized solar cells [6]. Among them, pyridine-2,6-dione based intermediates are considered as useful coupling components in the syntheses of heterocyclic disperse dyes with a variety of diazo components [7–12], and the resultant dyes have exhibited bright hues and excellent performance on versatile fastness [13–16]. For instance, Jang et al. have investigated the various color range and dyeing properties for several pyridine-2,6-dione based arylazo dyes on polytrimethylene terephthalate (PTT) fabric, where the wash and light fastness were improved in comparison with C.I. Disperse

Yellow 241 [17].

Regrettably, the color of these pyridine-2,6-dione based dyes fades quickly under the basic condition in the dyeing process [18,19], so the fine control of pH values should be taken into account. The possible reason is suggested to be the following: Pyridine-2,6-dione based heterocyclic dyes generally exist in the hydrazone tautomeric form under the neutral and acidic conditions, but they turn to the deprotonated azo form under the basic condition resulting in the alteration of the π -conjugated system and the color instability of the whole molecules simultaneously. The proton transfer is originated from the azo-hydrazone tautomerism in pyridine-2,6-dione based dyes, and our previous studies have demonstrated that azo-hydrazone tautomerism can be driven by the solvent polarity, pH titration and metal-ion coordination [20–24].

To avoid the color variation problem for pyridine-2,6-dione based dyes, we have previously proposed a functional group transformation (FGT) strategy, where the acidic hydroxyl (–OH) has been transformed into a basic secondary amine (–NHCH₂CH₂CH₂OCH₃) accomplished by the configuration transformation from the hydrazone form to azo one [25]. As a result, the

* Corresponding author.

E-mail addresses: zhaoxiaolei2016@163.com (X.-L. Zhao), 18648450506@163.com (T. Jun), 1179759806@qq.com (Y.-N. Feng), qhfn@njtech.edu.cn (H.-F. Qian), whuang@nju.edu.cn (W. Huang).

above-mentioned proton transfer and azo-hydrazone tautomerism have been successfully obstructed which can be verified by their increased pH stability. Actually, FGT strategy has been widely used in the antimicrobial surface modification [26], membrane modifications [27], polymer grafting and cross linking [28,29], and the introduction of reactive centers for further reactions [30]. However, there appear to be no references using FGT strategy to modify pyridine-2,6-dione precursors before us.

In this work, we have selected a special pyridine-2,6-dione precursor, i.e. 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile, to fulfill the double FGT for both acidic hydroxyl groups. As a result, six N^2,N^6 -bis(3-methoxypropyl)pyridine-2,6-diamine based azo dyes (Scheme 1) have been produced via a 2,6-dichloropyridine intermediate, where two basic secondary amine units ($-\text{NHCH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$) are successfully introduced. From the viewpoint of molecular design, the targeting azo dyes with N^2,N^6 -bis(3-methoxypropyl)pyridine-2,6-diamine backbone are no longer pyridone derivatives, so they exhibit extremely high pH stability (1–13) evidenced by the acid-base titration. More interesting, in the studies on structure-performance relationship for this family of double 3-methoxypropan-1-amine substituted heterocyclic azo dyes, the uncommon transformation for roles of donor and acceptor ($D-\pi-A$ and $A-\pi-D$) has been observed because of very close electron donating/withdrawing capabilities of substituted phenyl rings, which can be deduced from related electronic absorption spectral comparisons. As far as we are aware, this is the first report on N^2,N^6 -bis(3-methoxypropyl)pyridine-2,6-diamine heterocyclic azo dyes prepared from 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile via the FGT strategy.

2. Experimental section

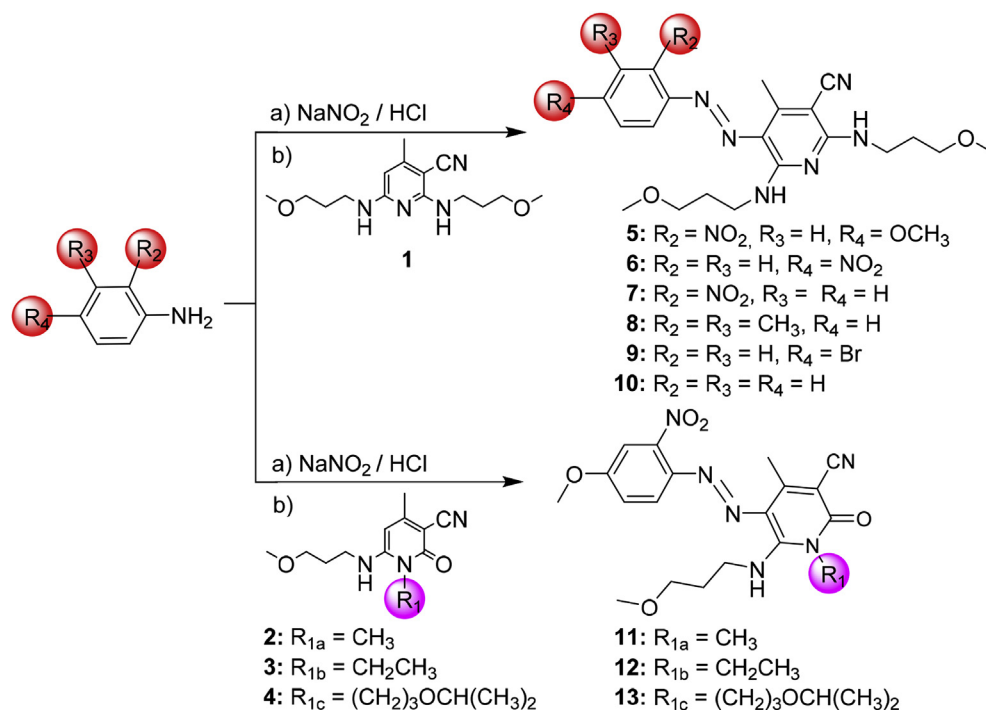
2.1. Materials and physical measurements

Analytical grade reagents were purchased from commercial suppliers and used without any further purification unless

otherwise stated. Intermediates **3** and **4** were prepared according to our previously reported procedure [25]. Column chromatography was carried out on silica gel (200–300 mesh). All melting points were measured without corrections. Ultraviolet-Visible (UV-Vis) spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm at room temperature (25 °C). ^1H NMR spectral measurements were performed on a Bruker DMX300 MHz NMR or a Bruker DMX400 MHz spectrometer, using chloroform- d (CDCl_3) as a solvent with tetramethylsilane (TMS) as the internal standard at room temperature (25 °C). Infrared spectra in the region of 4000–500 cm^{-1} were obtained using a Nicolet FT-IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT S50 710 mass spectrometer in a scan range of 50–500 or 50–1000 amu. Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 1400C analyzer.

2.1.1. Preparation of compound **1** (2,6-bis((3-methoxypropyl)amino)-4-methylnicotinonitrile)

2,6-Dichloro-4-methylnicotinonitrile (1.86 g, 10.0 mmol) was added to 3-methoxypropan-1-amine (3.98 g, 44.0 mmol) under stirring, and the mixture was refluxed for 3 h. After being cooled to room temperature, 30 mL of water and 30 mL of ethyl acetate were added into the reaction solution. The aqueous layer was separated, and the ethyl acetate layer was washed twice by brine and dried with anhydrous MgSO_4 . The solvent was removed by a rotary evaporator after removing MgSO_4 , and the crude solid was recrystallized by ethyl acetate and hexane (v:v = 4:1) to give compound **1** in a yield of 2.19 g (75%). Mp: 41–43 °C. Main FT-IR absorptions (KBr pellets, ν cm^{-1}): 3376 (s), 2923 (m), 2871 (w), 2188 (vs), 1598 (vs), 1526 (s), 1356 (m) and 1119 (s). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 5.55 (s, 1H), 5.40 (t, J = 4.8 Hz, 1H), 4.98 (t, J = 5.0 Hz, 1H), 3.51 (m, 6H), 3.41 (m, 2H), 3.37 (s, 3H), 3.35 (s, 3H), 2.24 (s, 3H) and 1.86 (m, 4H). Anal. Calcd. For $\text{C}_{15}\text{H}_{24}\text{N}_4\text{O}_2$: C, 61.12; H, 8.27; N, 19.16%. Found: C, 60.92; H, 8.48; N, 19.02%. Positive



Scheme 1. Synthetic route of heterocyclic azo dyes 5–13.

Download English Version:

<https://daneshyari.com/en/article/4765787>

Download Persian Version:

<https://daneshyari.com/article/4765787>

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