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Mono/double 3-methoxypropan-1-amine substituted pyridone azo dyes having isomeric *ortho/para*-aminobenzoic acids and corresponding methyl esters components

Yuan-Yuan Wang[a], Xiao-Lei Zhao[b], Hui-Fen Qian[a,*], Wei Huang[b,**]

[a] College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, Jiangsu Province, 210009, PR China
[b] State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, PR China

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ABSTRACT

Ortho/para-aminobenzoic acids and corresponding methyl esters were selected as the diazo components to couple with two mono functional group transformation (FGT) precursors with different pyridine *N*-substituted groups [1-ethyl-6-((3-methoxypropyl)amino)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile and 1-(3-isopropoxypropyl)-6-((3-methoxypropyl)amino)-4-methyl-2-oxo- 1,2-dihydropyridine-3-carbonitrile] and one double FGT precursor [2,6-bis((3-methoxypropyl)amino)-4-methylnicotinonitrile], so as to produce a series of isomeric pairs of heterocyclic azo dyes. In comparison with conventional 2,6-pyridone based hydrazone dyes bearing the same *ortho/para*-aminobenzoic acids and corresponding methyl esters azo components, the pH stability of synthesized mono and double FGT azo dyes has been improved to different extents because of the removal of the active hydrazone proton via 3-methoxypropylamine substitution. Among them, double FGT azo dyes with methyl ester units show extremely high pH stability, but the ones with benzoic acid groups exhibit low pH stability due to the presence of carboxylic acid proton. In contrast, methyl ester involved mono FGT products display less pH stability (pH ~ 10) owing to intra-ring azo-keto⇌azo-enol tautomerism under strong alkaline condition. It is noted that two distinguishable deprotonated processes could be observed for mono FGT products with benzoic acid groups, and two-step deprotonation mechanism is proposed by forming monovalent and bivalent anions under weak and strong alkaline conditions involving intra-ring azo-keto⇌azo-enol tautomerism.

1. Introduction

Studies on the heterocyclic dyes have attracted great attention in the past decades because of their advantages of high sublimation fastness, bright color, and good dyeing performance [1–3]. Among them, 2,6-pyridone based compounds are one type of important heterocyclic dyes and become a hot research object [4–8]. It has been clear that they generally exist in the hydrazone form under the neutral and acidic conditions and they can be transformed to the deprontonated azo form under the basic condition, which can be verified by UV–Vis and NMR spectra, X-ray single-crystal structures and quantum chemical calculations [9–14]. In our previous work, the azo⇌hydrazone tautomerism driven by solvent polarity, acid-base titration and metal-ion complexation has been extensively studied [15–18].

However, it should be noted that the color of 2,6-pyridone dyes is unstable under the basic condition in the process of dyeing owing to the presence of acidic hydroxyl groups in their molecular structures [19,20]. In order to overcome this shortcoming, the introduction of certain alkali-stable groups to replace the acidic hydroxyl groups of 2,6-pyridone moiety is proved to be an effective approach to improve the corresponding pH stability. Our previous investigations have demonstrated that the functional group transformation (FGT) synthetic strategy by using one or two secondary amines (-$NHCH_2CH_2CH_2OCH_3$) to replace the acidic hydroxy groups can significantly enhance the pH stability of resultant dyes to different extents, in which the original hydrazone dyes have been converted into corresponding azo dyes after either mono or double FGT and the active proton migration is greatly hampered especially for double FGT products [21–23].

Based upon our studies related to several pairs of isomeric 4- and 2-aminobenzoic acid based 2,6-pyridone hydrazone dyes [24,25], herein we extend the FGT strategy to prepare a family of mono or double 3-methoxypropylamino substituted heterocyclic azo dyes involving

* Corresponding author.
** Corresponding author.
E-mail addresses: qhf@njtech.edu.cn (H.-F. Qian), whuang@nju.edu.cn (W. Huang).

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isomeric *ortho/para*-aminobenzoic acid components (**1**, **2**, **3**, **7**, **8**). Since the carboxylic acid group is an acidic radical with low solubility also leading to the alkaline instability of resultant dyes, corresponding methyl esters heterocyclic dyes (**4**, **5**, **6**, **9**, **10**, **11**) have been synthesized for further comparisons on their electronic spectra and pH stability. As a result, the pH stability of the obtained mono and double FGT azo dyes **1–11** has been improved to different extents in comparison with conventional 2,6-pyridone based hydrazone dyes bearing the same *ortho/para*-aminobenzoic acid and corresponding methyl ester azo components. Furthermore, the *ortho*-isomers (**7** and **9**) have better pH stability compared with corresponding *para*-ones (**1** and **4**) in all mono FGT products. In contrast, the double FGT azo dyes **6** and **11** with methyl ester units show extremely high pH stability because of the absence of acidic hydroxyl and carboxylic acid groups.

2. Experimental section

2.1. Materials and apparatus

Two mono 2,6-pyridone FGT precursors with different *N*-substituted groups ($-CH_2CH_3$, $-(CH_2)_3OCH(CH_3)_2$) and one double 2,6-pyridone FGT precursor 2,6-bis((3-methoxypropyl)amino)-4-methylnicotinonitrile were synthesized by previously reported methods [21,22]. *Ortho/para*-aminobenzoic acids and corresponding methyl esters were purchased from Shanghai Ascender Chemical Co., Ltd (China). The other reagents and solvents with analytic grade were purchased from Beijing Sinopharm Chemical Reagent Co., Ltd (China) and used without any further purification. Infrared spectra in the region of 4000–500 cm^{-1} were obtained using a Nicolet FT–IR 170X spectrophotometer on KBr disks. ^1H NMR spectral measurements were performed on a Bruker DMX400 MHz spectrometer in DMSO-d6 with tetramethylsilane (TMS) as the internal standard at room temperature (25 °C). 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). Electrospray ionization mass spectra (ESI–MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 50–500 amu. Elemental analyses (EA) for C, H, and N were performed on a Perkin-Elmer 1400C analyzer.

2.1.1. Preparation of compound *1* (4-((5-cyano-1-ethyl-2-((3-methoxypropyl)amino)- 4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl) benzoic acid)

4-Aminobenzoic acid (0.68 g, 5.00 mmol) was dissolved in a mixture of concentrated hydrochloric acid (3 mL) and water (2 mL) at −5 °C in an ice-salt bath. Sodium nitrite (0.38 g, 5.50 mmol) was dissolved in water (3 mL) and added dropwise to the reaction mixture for 30 min under vigorous mechanical stirring. The diazonium salt was obtained and used for the following reaction. 1-Ethyl-6-((3-methoxypropyl)amino)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1.25 g, 5.00 mmol) was dissolved in a methanol-water mixture (30 mL, v:v = 1:1) immersed in an ice bath, and freshly prepared diazonium salt solution was added dropwise for 15 min under vigorous mechanical stirring (0–5 °C). After additional stirring for 3 h, the mixture was neutralized with aqueous solution of sodium hydroxide to pH 6–7 and the precipitate was filtered and dried after thorough washing with distilled water. The crude product was recrystallized from $CHCl_3$/MeOH in a yield of 1.23 g (62%). ^1H NMR (400 MHz, DMSO-d6, ppm, TMS): δ = 13.01 (s, 1H), 8.08–8.01 (m, 2H), 7.75 (d, J = 8.6 Hz, 2H), 4.13 (d, J = 7.0 Hz, 2H), 3.85–3.78 (m, 2H), 3.46 (t, J = 6.0 Hz, 2H), 3.33 (s, 3H), 2.62 (s, 3H), 2.01 (t, J = 6.3 Hz, 2H), 1.30 (t, J = 7.0 Hz, 3H). Main FT–IR absorptions (KBr pellets, ν, cm^{-1}): 2922 (m), 2221 (s), 1673 (vs), 1574 (vs), 1385 (s), 1295 (s), 873 (m), 775 (m). Negative ESI–MS in methanol: (m/z) = 397.18 (100%), $[M-H]^-$. *Anal. Calcd.* for $C_{20}H_{23}N_5O_4$: C, 60.44; H, 5.83; N, 17.62%. Found: C, 60.32; H, 5.75; N, 17.69%. UV–Vis in ethanol, $\lambda_{max}/\varepsilon$ (dm^3 mol^{-1} cm^{-1}) = 436 nm/5.06×10^4.

2.1.2. Preparation of compound *2* (4-((5-cyano-1-(3-isopropoxypropyl)-2-((3- methoxypropyl)amino)-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl) benzoic acid)

The synthesis of dye **2** was similar to that described for dye **1** except that 1-(3-isopropoxypropyl)-6-((3-methoxypropyl)amino)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (1.61 g, 5.00 mmol) was used to replace 1-ethyl-6-((3-methoxypropyl)amino)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile. Yield: 1.52 g (65%). ^1H NMR (400 MHz, DMSO-d6, ppm, TMS): δ = 13.07 (s, 1H), 8.05 (d, J = 8.7 Hz, 2H), 7.78–7.73 (m, 2H), 4.21 (t, J = 7.0 Hz, 2H), 3.81 (dd, J = 11.3, 6.5 Hz, 2H), 3.50–3.42 (m, 3H), 3.38 (t, J = 5.6 Hz, 2H), 3.22 (s, 3H), 2.63 (s, 3H), 2.00 (p, J = 6.3 Hz, 2H), 1.93–1.84 (m, 2H), 1.03 (d, J = 6.1 Hz, 6H). Main FT–IR absorptions (KBr pellets, ν, cm^{-1}): 3309 (w), 2976 (m), 2213 (s), 1673 (vs), 1574 (vs), 1368 (vs), 1259 (vs), 1152 (vs), 1107 (vs), 873 (w). Negative ESI–MS in methanol: (m/z) = 469.23 (100%), $[M-H]^-$. *Anal. Calcd.* for $C_{24}H_{31}N_5O_5$: C, 61.39; H, 6.65; N, 14.92%. Found: C, 61.41; H, 6.59; N, 14.97%. UV–Vis in ethanol, $\lambda_{max}/\varepsilon$ (dm^3 mol^{-1} cm^{-1}) = 436 nm/5.07×10^4.

2.1.3. Preparation of compound *3* (4-((5-cyano-2,6-bis((3-methoxypropyl) amino)-4- methylpyridin-3-yl)diazenyl)benzoic acid)

The synthesis of dye **3** was similar to that described for dye **1** except that 2,6-bis((3-methoxypropyl)amino)-4-methylnicotinonitrile (1.46 g, 5.00 mmol) was used to replace 1-ethyl-6-((3-methoxypropyl)amino)-4-methyl-2-oxo- 1,2-dihydropyridine-3-carbonitril. Yield: 1.65 g (75%). ^1H NMR (400 MHz, DMSO-d6, ppm, TMS): δ = 12.98 (s, 1H), 10.90 (t, J = 5.4 Hz, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.73 (t, J = 5.6 Hz, 1H), 3.63 (dd, J = 12.6, 6.6 Hz, 2H), 3.50 (dd, J = 12.9, 6.5 Hz, 2H), 3.40 (dd, J = 12.3, 6.1 Hz, 4H), 3.25 (d, J = 1.2 Hz, 6H), 2.65 (s, 3H), 1.85 (dt, J = 13.7, 6.6 Hz, 4H). Main FT–IR absorptions (KBr pellets, ν, cm^{-1}): 3354 (s), 2932 (w), 2203 (s), 1700 (vs), 1574 (vs), 1368 (vs), 1268 (vs), 1152 (vs), 864 (w), 775 (s). Negative ESI–MS in methanol: m/z = 440.22 (100%), $[M-H]^-$. *Anal. Calcd.* for $C_{22}H_{28}N_6O_4$: C, 59.99; H, 6.41; N, 19.08%. Found: C, 59.96; H, 6.45; N, 19.12%. UV–Vis in ethanol, $\lambda_{max}/\varepsilon$ (dm^3 mol^{-1} cm^{-1}) = 446 nm/3.36×10^4.

2.1.4. Preparation of compound *4* (methyl 4-((5-cyano-1-ethyl-2-((3-methoxypropyl)amino)-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl) benzoate)

The synthesis of dye **4** was similar to that described for dye **1** except that methyl 4-aminobenzoate (0.76 g, 5.00 mmol) was used as the starting material to replace 4-aminobenzoic acid. Yield: 1.29 g (63%).^1H NMR (400 MHz, DMSO-d6, ppm, TMS): δ = 13.03 (s, 1H), 8.07 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 4.13 (q, J = 6.9 Hz, 2H), 3.87 (s, 3H), 3.82 (dd, J = 11.2, 6.5 Hz, 2H), 3.46 (t, J = 6.0 Hz, 2H), 3.22 (s, 3H), 2.63 (s, 3H), 2.05–1.97 (m, 2H), 1.30 (t, J = 7.0 Hz, 3H). Main FT–IR absorptions (KBr pellets, ν, cm^{-1}): 3309 (m), 2958 (m), 2221 (s), 1709 (vs), 1673 (vs), 1565 (vs), 1377 (vs), 1287 (vs), 1107 (s), 765 (m). Negative ESI–MS in methanol: (m/z) = 411.19 (100%), $[M-H]^-$. *Anal. Calcd.* for $C_{21}H_{25}N_5O_4$: C, 61.30; H, 6.12; N, 17.02%. Found: C, 61.26; H, 6.15; N, 17.08%. UV–Vis in ethanol, $\lambda_{max}/\varepsilon$ (dm^3 mol^{-1} cm^{-1}) = 439 nm/4.81×10^4.

2.1.5. Preparation of dye *5* (methyl 4-((5-cyano-1-(3-isopropoxypropyl)-2-((3- methoxypropyl)amino)-4-methyl-6-oxo-1,6-dihydropyridin-3-yl) diazenyl)benzoate)

The synthesis of dye **5** was similar to that described for dye **2** except that methyl 4-aminobenzoate (0.76 g, 5.00 mmol) was used as the starting material to replace 4-aminobenzoic acid. Yield: 1.57 g (65%).^1H NMR (400 MHz, DMSO-d6, ppm, TMS): δ = 13.08 (s, 1H), 8.07 (d, J = 8.7 Hz, 2H), 7.80–7.75 (m, 2H), 4.21 (t, J = 7.0 Hz, 2H), 3.87 (s, 3H), 3.81 (dd, J = 11.3, 6.5 Hz, 2H), 3.48–3.42 (m, 3H), 3.38 (t, J = 5.6 Hz, 2H), 3.22 (s, 3H), 2.63 (d, J = 2.8 Hz, 3H), 2.03–1.97 (m, 2H), 1.93–1.83 (m, 2H), 1.03 (d, J = 6.1 Hz, 6H). Main FT–IR absorptions (KBr pellets, ν, cm^{-1}): 2958 (m), 2239 (s), 1736 (vs), 1547