



Synthesis and spectroscopic characterization of azoic dyes based on pyrazolone derivatives catalyzed by an acidic ionic liquid supported on silica-coated magnetite nanoparticle



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ABSTRACT

Novel family of azoic dyes pyrazolone based were prepared by an efficient and rapid methodology through diazotization reaction of different pyrazolone amine derivatives, in the presence of acidic ionic liquid supported on silica-coated magnetite nanoparticles as acidic catalyst at room temperature and under solvent-free conditions.

The attractive advantages of the present process include short reaction times, milder and cleaner conditions, higher purity and yields, easy isolation of products, easier work-up procedure and lower generation of waste or pollution. This catalyst was easily separated by an external magnet and the recovered catalyst was reused several times without any significant loss of activity. Therefore, this method provides improved protocol over the existing methods.

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1. Introduction

In the last few years, the azoic compounds were widely used in biological–pharmacological activities [1–4], and in different research activities as dyeing textile fibers [5–13] and optical materials with excellent chemosensing properties [14–20]. The synthetic pathways of azoic dyes generate toxic and dangerous reagents, which have proved to be valuable reactive intermediates in the preparation of different compounds of interest [21].

The aliphatic and aromatic amines diazotization reaction is a common method to prepare azoic dyes by using a different of nitrosating agents under strong acids such as silica sulfuric acid [22], sulfanilic acid [23], p-toluene sulfonic acid [24], potassium hydrogen sulfate [25], nano sized iron-promoted [26], and ammonium salts [27]. The azo coupling is carried out at low temperature (0–5 °C) in the presence of nucleophilic coupling compounds. This method is used in the synthesis of azoic compounds; the diazonium

salts preparation from the anilines and also in azides synthesis from the corresponding hydrazines [28–30]. However, the most of these techniques present limitations such as long reaction time, the modest yields obtained, the toxicity of the used materials, the instability of the diazonium salts at room temperature, the use of acids, alkalis and toxic solvents under low temperature, and tedious work-up. The high versatility of these reagents combined with their dangerous handling make them perfect candidates for the development of novel methodologies for their safer use in the synthesis of organic compounds.

In order to overcome the limitations of the diazotization reaction under the standard conditions, various approaches were developed such as a solid acid based on immobilization of acidic ionic liquid in inorganic or polymeric supports, which produces a new class of acidic catalyst systems [31–35]. Recently, the nano-support materials were used for different applications [36–39], in particular as the heterogeneous catalysis. In this context, we are recently developed an acidic ionic liquid supported on silica-coated magnetite nanoparticles as a green catalyst for one-pot diazotization–halogenation of the aromatic amines [40]. These magnetic nanoparticles (Fe₃O₄@SiLnP) present excellent catalytic activities and it can be considered environmentally benign as the filtration steps are omitted in the reaction. For instance, the catalyst can be

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recovered with an external magnetic field.

Encouraged by our previous results [40] and our interest to develop efficient, sustainable and greener pathways for azoic dye synthesis compared to the existing methods [8,9,12], we report herein a simple synthesis of azoic dyes through a one-pot diazotization reaction of the pyrazolone amines in the presence of the acidic $\text{Fe}_3\text{O}_4@\text{SiLnP}$ as new proton source to afford their diazonium salts which are stable and react rapidly with the other pyrazolone moiety to produce azoic compounds in excellent yield. The Brønsted acidity of the $\text{Fe}_3\text{O}_4@\text{SiLnP}$ and the generation of protons required for the formation of diazonium salts starting from the corresponding amines is probably due to the $[\text{HSO}_4]^-$ anion that can be introduced by ion exchange [41–46].

The $\text{Fe}_3\text{O}_4@\text{SiLnP}$ was prepared by grafting an acid ionic liquid with catalytic activity based on N-propyl-2-pyrrolidonium hydrogen sulfate ($[\text{H-NMP}][\text{HSO}_4]$) moiety in the surface of the nano-sized silica-coated magnetite. The co-precipitation method was used to produce the Fe_3O_4 nanoparticles and they were subsequently coated with tetraethoxysilane (TEOS) via asilanization process.

The reported catalytic system presents the advantages of heterogeneous catalysis and a large surface area that is conferred by the nanoparticles. Therefore, we intend to use this convenient and green procedure based on magnetic solid acid catalyst $\text{Fe}_3\text{O}_4@\text{SiLnP}$ to synthesis a large class of azoic dyes pyrazolone based.

2. Experimental methods and characterization

2.1. Materials

Chemical compounds (Aldrich Chemical Co.) were used as purchased without further purification. TLC analysis was performed using Fluka aluminium foils coated with 25 mm particle size silica gel matrix F254, and they are development involved either UV (254 and 366 nm) or visible light inspection, followed by either treatment with an acid solution of *p*-anisaldehyde or a basic solution of KMnO_4 and heating. Flash column chromatography was performed on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh ASTM) Uv–vis spectra were recorded on a Cary - 4000 Varian spectrophotometer, using either 0.1 or 1 cm quartz cuvettes. Infrared spectra were recorded in KBr disk on a Perkin Elmer-Spectrum BX FTIR system. Absorptions are quoted in wave numbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded at 200 MHz ^1H (50.0 MHz ^{13}C) on a Varian Gemini spectrometer. Spin resonances are reported as chemical shifts (δ) in parts per million (ppm) and referenced to the residual peak as an internal standard of the solvent employed, as follow: CDCl_3 7.27 ppm (1H NMR), 77 ppm (^{13}C NMR, central band), DMSO-d_6 2.50 ppm (1H NMR, central band), 39.5 ppm (^{13}C NMR, central band). Spin multiplicity is showed by s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants *J* are reported in Hertz. Mass spectra were recorded on a Thermo Scientific LCQ-Fleet mass spectrometer under electrospray ionization (ESI, +c or -c technique). Nanostructures were characterized using a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK, radiation, $\lambda = 0.154056$ nm), at a scanning speed of $2^\circ/\text{min}$ from 10° to 100° (2θ). High Resolution Mass Spectra (HRMS) were recorded on an LTP Orbitrap mass spectrometer from Thermo Electron Corporation under ESI (+c) technique. Mass spectrometric analysis is quoted in the *m/z* form. Elemental analyses were recorded on a Perkin Elmer 240C Elemental Analyzer. The $\text{Fe}_3\text{O}_4@\text{SiLnP}$ catalyst and compounds **1a-c**; **2a-f**, **5a-c** and **4a-f** were prepared following our previous work [9,10,40].

2.2. Standard procedure for the diazotization and azo coupling reactions

To a solution of the pyrazolone amine (1 mmol) and $\text{Fe}_3\text{O}_4@\text{SiLnP}$ (200 mg) in a few drops of water to obtain a homogeneous mixture, NaNO_2 (3 mmol), was added at 0°C and the resulting mixture was stirred at room temperature for few minutes. Then, an aqueous solution of the pyrazolone derivatives (1 mmol) with AcONa (1 mmol) a few drops of water was added immediately and the resulting mixture was stirred for a few minute at room temperature. After the reaction, the crude product was extracted with DCM (3×10 ml) and the catalyst was magnetically separated and washed several times with water and methanol to ensure unreacted reactive does not remain on the surface of magnetic nanoparticles. The crude products were purified by recrystallization from ethanol. The recovered catalyst was dried and reused for subsequent runs.

2.3. Synthesis of compounds

2.3.1. 4 - (2 - (5 - hydroxyl - 3 - methyl - 1 - phenyl - 1H - pyrazol - 4 - yl) hydrazono) - 1 - phenyl pyrazolidine - 3,5 - dione (**3a**)

^1H NMR (200 MHz, CDCl_3): $\delta = 12.63$ (s, 1H, OH), 11.14 (s, 1H, NH), 7.71–7.54 (m, 6H, Ar-H), 7.46–7.02 (m, 4H, Ar-H), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, CDCl_3): $\delta = 169.5, 165.8, 147.9, 143.5, 137.4, 137.1, 136.6, 128.9, 126.4, 125.8, 123.4, 122.7, 120.8, 11.5$ ppm. MS (ESI): *m/z* = 377,35 [*M* + 1] $^+$. C₁₉H₁₆N₆O₃ (376,13): calcd C, 60.63; H, 4.28; N, 22.33; found: C, 60.75; H, 4.39; N, 22.41.

2.3.2. 4 - (2 - (5 - hydroxyl - 3 - methyl - 1 - (4 - nitrophenyl) - 1H - pyrazol - 4 - yl) hydrazono) - 1 - phenylpyrazolidine - 3,5 - dione (**3b**)

^1H NMR (200 MHz, CDCl_3): $\delta = 12.71$ (s, 1H, OH), 11.13 (s, 1H, NH), 8.33–8.17 (m, 4H, Ar-H), 7.55–7.31 (m, 2H, Ar-H), 7.05 (m, 1H, Ar-H), 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, CDCl_3): $\delta = 168.7, 165.4, 147.4, 145.8, 144.2, 143.1, 137.6, 136.4, 129.4, 126.9, 124.9, 122.8, 122.1, 119.6, 11.1$ ppm. MS (ESI): *m/z* = 422,29 [*M* + 1] $^+$. C₁₉H₁₅N₇O₅ (421,11): calcd C, 54.16; H, 3.59; N, 23.27; found: C, 54.27; H, 3.66; N, 23.35.

2.3.3. 4 - (2 - (5 - hydroxyl - 1 - (4 - methoxyphenyl) - 3 - methyl - 1H - pyrazol - 4 - yl) hydrazono) - 1 - phenyl pyrazolidine - 3,5 - dione (**3c**)

^1H NMR (200 MHz, CDCl_3): $\delta = 12.64$ (s, 1H, OH), 11.32 (s, 1H, NH), 7.74–7.28 (m, 6H, Ar-H), 7.03 (m, 3H, Ar-H), 2.31 (s, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, CDCl_3): $\delta = 168.2, 164.3, 154.2, 144.9, 143.5, 137.4, 135.8, 129.6, 128.8, 126.3, 122.1, 120.2, 115.4, 112.6, 55.5, 11.3$ ppm. MS (ESI): *m/z* = 407,28 [*M* + 1] $^+$. C₂₀H₁₈N₆O₄ (406,14): calcd C, 59.11; H, 4.46; N, 20.68; found: C, 59.25; H, 4.59; N, 20.77.

2.3.4. Ethyl 4-(2-(3,5-dioxo-1-phenylpyrazolidin-4-ylidene)hydrazinyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**3d**)

^1H NMR (200 MHz, CDCl_3): $\delta = 12.66$ (s, 1H, OH), 11.17 (s, 1H, NH), 7.73–7.52 (m, 6H, Ar-H), 7.35–7.04 (m, 4H Ar-H), 4.29 (q, 2H, CH_2), 1.34 (t, 3H, CH_3) ppm. ^{13}C NMR (50 MHz, CDCl_3): $\delta = 168.6, 163.9, 160.2, 141.3, 139.5, 137.5, 137.1, 136.4, 129.8, 128.7, 126.6, 122.8, 122.2, 119.6, 61.8, 15.4$ ppm. MS (ESI): *m/z* = 435,34 [*M* + 1] $^+$. C₂₁H₁₈N₆O₅ (434,13): calcd C, 58.06; H, 4.18; N, 19.35, 20.68; found: C, 58.21; H, 4.25; N, 19.48.

2.3.5. Ethyl 4 - (2-(3,5-dioxo-1-phenylpyrazolidin - 4 - ylidene) hydrazinyl)-5-hydroxy-1-(4-nitrophenyl)-1H-pyrazole-3-carboxylate (**3e**)

^1H NMR (200 MHz, CDCl_3): $\delta = 12.63$ (s, 1H, OH), 11.12 (s, 1H,

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