



Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: <http://www.elsevier.com/locate/molstruc>

Synthesis of new azo schiff bases of pyrazole derivatives and their spectroscopic and theoretical investigations

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ARTICLE INFO

Article history:

Received 11 January 2018

Received in revised form

11 May 2018

Accepted 18 June 2018

Available online xxx

Keywords:

Pyrazole

Schiff bases

Azo

Pyrazole schiff bases

Azo-imine

DFT

ABSTRACT

New pyrazole Schiff bases containing azo groups, 4-((*E*)-phenyldiazenyl)-3-(4-nitrobenzylidene)-1-phenyl-pyrazole-5-amine and its series, were synthesized using the condensation reaction between *p*-nitrobenzaldehyde and (*E*)-1-phenyl-4-(phenyldiazenyl)-1H-pyrazole-3,5-diamine in the molar ratio of 1:1. The compounds were characterized using IR, UV–Vis, ¹H-NMR and ¹³C-NMR spectroscopies. The UV–Vis spectral data were obtained in ethanol, chloroform, N,N-dimethylformamide (DMF), DMF (pH = 2) and DMF (pH = 12), which have different polarity and pH values. Meanwhile, the experimental spectral analyses were supported by the theoretical calculations based on the density functional theory (DFT) using the B3LYP/cc-pvtz level. Structural analyses, vibrational frequencies, UV, and NMR calculations were performed at the same level of the theory. In addition, via using HOMO-LUMO energies, the electrochemical quantities such as chemical hardness and electronegativity were calculated and analyzed.

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1. Introduction

Pyrazole is one of the most interesting five-membered hetero-aromatic compounds, and its structural core is found in a variety of natural products such as 3-n-nonylpyrazole which is extracted from the plant of the ‘piperaceae’ from tropical Asia and levo-β-(1-pyrazoyl)alanine which is extracted from watermelon seeds (*Citrullus Vulgaris*) [1,2]. Pyrazole derivatives are potential bioactive molecules in pharmaceutical industry [3]. Due to their structures, pyrazole derivatives possess a wide range of biological activities, such as antimicrobial [4–7], anticancer [5], anti-inflammatory [4], anti-depressant [5], anticonvulsant [5], anti-hypertensive [6], anti-epileptic [6], anti-tumor [8–10], and analgesic [5] ones. Besides, the pyrazole ring which consists of a doubly unsaturated bond and two nitrogen atoms can act as a hard donor site and has attracted considerable attention as a coordination ligand for complex formation [6,11]. Due to the presence of basic and acidic NH groups, a large number of hydrogen bonds can be formed, leading to supra-molecular architectures [5,11,12]. The versatility of pyrazole

derivatives allows the synthesis of new organic intermediates and plays a vital role in medicinal, pesticide and coordination chemistry [5,9].

Schiff bases, which are carrying the azomethine functional group (CH=N) have attracted much attention because they not only present antimicrobial, antituberculosis, anticancer, anti-inflammatory, antifungal, and antibacterial activities but have been used as catalyst carriers, dyes and pigments, metal complexation agents, thermo-stable materials and corrosion inhibitors as well [13,14]. Such Schiff bases can be obtained easily via the condensation reaction between primary amines and carbonyl compounds, while cheap starting materials can be used. In addition, Schiff bases which have strong coordinating abilities toward metal ions are greatly used in coordination chemistry and intensively studied as ligands [14]. Although many studies focusing on pyrazoles and Schiff bases have been reported [15–19], DFT studies of the pyrazole Schiff bases having azo groups are not seen in the literature. In this study, we synthesized new pyrazole Schiff bases containing azo groups and characterized their structures using ¹H-nuclear magnetic resonance (NMR), ¹³C NMR, Infrared (IR), and Ultraviolet-Visible (UV–Vis) spectroscopies. The experimental results were complemented by the DFT studies.

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2. Experimental section

All reagents and solvents were analytical grade and purchased from commercial suppliers (Merck, Germany and Aldrich, US). The chemicals were used without further purification. Melting points were obtained using a melting point apparatus (Stuart Melting Point 30). 3,5-Diamino-4-aryazo-1-phenylpyrazole was synthesized and purified according to the literature [20] Pyrazole Schiff bases were obtained by the condensation reaction between *p*-nitrobenzaldehyde and (*E*)-1-phenyl-4-(phenyldiazenyl)-pyrazole-3,5-diamine, (*E*)-4-((4-nitrophenyl) diazenyl)-1-phenyl-pyrazole-3,5-diamine, (*E*)-4-((4-methoxyphenyl) diazenyl)-1-phenyl-pyrazole-3,5-diamine, (*E*)-4-((4-chlorophenyl) diazenyl)-1-phenyl-pyrazole-3,5-diamine, or (*E*)-1-phenyl-4-(*p*-tolyl diazenyl)-pyrazole-3,5-diamine, respectively, all in molar ratios of 1:1 and at pH = 4–5. The crude products were purified by recrystallization from ethanol–water mixture. The synthetic route of Schiff bases containing the pyrazole core is given in Fig. 1.

Elemental (C, H, and N) analyses were carried out on a Leco-CHNS-932 (US) elemental analyzer. UV–Vis spectra were obtained using Thermo Scientific Genesys 10S UV–Vis (UK) in the range of 600–190 nm and were taken in chloroform (apolar aprotic), ethanol (polar protic), *N,N*-dimethylformamide (DMF, polar aprotic), acidic (in DMF) and basic (in DMF) media. Infrared spectra were obtained on a Thermo Scientific Class 1 Laser product FTIR (US) using ATR in the range of 4000–400 cm^{-1} . $^1\text{H-NMR}$ 400 MHz/ $^{13}\text{C-NMR}$ 100 MHz spectra were recorded by a Bruker (Germany) AC 400 (400 MHz) spectrophotometer in deuterated dimethylsulphoxide (DMSO- d_6) solvent.

2.1. Synthesis of 4-((*E*)-phenyldiazenyl)-3-(4-nitrobenzylidene)-1-phenyl-pyrazole-5-amine

Schiff bases were prepared by reacting *p*-nitrobenzaldehyde with (*E*)-1-phenyl-4-(phenyldiazenyl) pyrazole-3,5-diamine in molar ratio of 1:1 in dry tetrahydrofuran (THF). (*E*)-1-phenyl-4-(phenyldiazenyl)-1H-pyrazole-3,5-diamine (1g, 4.95 mmol) was dissolved in THF (35 mL) and then 4-nitrobenzaldehyde (0.745 g, 4.95 mmol) was added to this solution. Glacial acetic acid was added dropwise to the ultimate solution until pH = 4–5. Subsequently, the mixture was refluxed for 24 h. The byproduct water was removed by distillation in order to increase the yield. The remaining solution was refluxed for another 3 h. The product was precipitated by cooling the solution to the room temperature, and the precipitate was then filtered and dried. The orange product was purified from ethanol/water mixture. Yield: 70.6%, mp 215–216 °C. IR ν (cm^{-1}) = 3415, 3257 ($-\text{NH}_2$), 3066 ($\text{C-H}_{\text{arom.}}$), 2918, 2849 ($\text{C-H}_{\text{aliph.}}$), 1604 ($-\text{CH}=\text{N}-$), 1538 ($-\text{C}=\text{C}-$), 1509, 1338 ($-\text{N}=\text{N}-$), 1492, 1377 ($-\text{NO}_2$). $^1\text{H-NMR}$ (d_6 -DMSO, ppm): δ = 7.36 (s, H1), 7.36 (s, H4), 7.50 (t, J = 7.4 Hz, H2, H5, H6), 7.83 (s, H7), 7.73 (s, H8), 8.36 (s, H9), 9.36 (s, $-\text{NH}_2$); $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO, ppm) δ = 167.09 ($-\text{CH}=\text{N}$), 147.99, 147.31, 145.58, 139.30, 134.35, 129.84, 129.34, 127.15, 125.71, 124.74, 122.10, 118.79, 115.54 ($\text{C}_{\text{arom.}}$) Elemental Analysis calc. (%) for $\text{C}_{22}\text{H}_{17}\text{N}_7\text{O}_2$: C 64.23, H 4.16, N 23.83; found: C 63.52, H 4.69, N 22.97.

$\text{H}_{\text{aliph.}}$), 1604 ($-\text{CH}=\text{N}-$), 1538 ($-\text{C}=\text{C}-$), 1509, 1338 ($-\text{N}=\text{N}-$), 1492, 1377 ($-\text{NO}_2$). $^1\text{H-NMR}$ (d_6 -DMSO, ppm): δ = 7.36 (s, H1), 7.36 (s, H4), 7.50 (t, J = 7.4 Hz, H2, H5, H6), 7.83 (s, H7), 7.73 (s, H8), 8.36 (s, H9), 9.36 (s, $-\text{NH}_2$); $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO, ppm) δ = 167.09 ($-\text{CH}=\text{N}$), 147.99, 147.31, 145.58, 139.30, 134.35, 129.84, 129.34, 127.15, 125.71, 124.74, 122.10, 118.79, 115.54 ($\text{C}_{\text{arom.}}$) Elemental Analysis calc. (%) for $\text{C}_{22}\text{H}_{17}\text{N}_7\text{O}_2$: C 64.23, H 4.16, N 23.83; found: C 63.52, H 4.69, N 22.97.

2.2. Synthesis of 3-((*E*)-4-nitrobenzylidene)-4-((*E*)-(4-nitrophenyl) diazenyl)-1-phenyl-pyrazole-5-amine

This compound was prepared using the similar method as described in Section 1.2 by reacting *p*-nitrobenzaldehyde with ((*E*)-4-((4-nitrophenyl) diazenyl)-1-phenyl pyrazole-3,5-diamine. The yellow product was obtained. Yield: 65.3%, mp 249–250 °C. IR ν (cm^{-1}) = 3457, 3278 ($-\text{NH}_2$), 3055 ($\text{C-H}_{\text{arom.}}$), 2917, 2849 ($\text{C-H}_{\text{aliph.}}$), 1617 ($-\text{CH}=\text{N}-$), 1596 ($-\text{C}=\text{C}-$), 1500, 1375 ($-\text{NO}_2$), 1447, 1339 ($-\text{N}=\text{N}-$). $^1\text{H-NMR}$ (d_6 -DMSO, ppm): δ = 7.36 (d, J = 8.9 Hz, H1), 8.32 (dd, J = 13.6, 8.8 Hz, H2, H8), 7.68 (d, J = 7.9 Hz, H4), 8.40 (d, J = 8.6 Hz, H7), 7.62 (t, J = 7.7 Hz, H5), 7.50 (t, J = 7.3 Hz, H6), 8.01 (s, H9), 9.40 (s, $-\text{NH}_2$). $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO, ppm) δ = 164.16 ($-\text{CH}=\text{N}$), 157.58, 155.16, 149.77, 146.32, 141.78, 137.60, 131.16, 130.55, 130.14, 128.41, 125.43, 124.61, 124.53, 122.10, 119.12 ($\text{C}_{\text{arom.}}$) Elemental Analysis calc. (%) for $\text{C}_{22}\text{H}_{16}\text{N}_8\text{O}_4$: C 57.89, H 3.53, N 24.55; found: C 57.69, H 4.36, N 23.24.

2.3. Synthesis of 3-((*E*)-4-nitrobenzylidene)-4-((*E*)-(4-methoxyphenyl) diazenyl)-1-phenyl-pyrazole-5-amine

This compound was synthesized using the similar method as described in Section 1.2 via the reaction between *p*-nitrobenzaldehyde and ((*E*)-4-((4-methoxyphenyl) diazenyl)-1-phenyl pyrazole-3,5-diamine. The yellow product was obtained. Yield: 72.8%, mp 199–200 °C. IR ν (cm^{-1}) = 3427, 3272 ($-\text{NH}_2$), 3107 ($\text{C-H}_{\text{arom.}}$), 2918, 2848 ($\text{C-H}_{\text{aliph.}}$), 1622 ($-\text{CH}=\text{N}-$), 1595 ($-\text{C}=\text{C}-$), 1544, 1381 ($-\text{NO}_2$), 1516, 1340 ($-\text{N}=\text{N}-$). $^1\text{H-NMR}$ (d_6 -DMSO, ppm): δ = 7.07 (d, J = 8.8 Hz, H1), 6.54 (s, H2), 3.83 (s, H3), 7.51 (m, H4), 8.39 (d, J = 8.1 Hz, H7), 7.78 (m, H5, H8), 7.33 (s, H6), 8.19 (s, H9), 9.41 (s, $-\text{NH}_2$). $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO, ppm) δ = 160.20 ($-\text{CH}=\text{N}$), 152.50, 149.52, 148.21, 145.11, 141.96, 139.14, 130.94, 129.59, 128.39, 124.76, 124.41, 123.38, 122.20, 118.03, 114.99 ($\text{C}_{\text{arom.}}$), 55.97 ($-\text{OCH}_3$). Elemental Analysis calc. (%) for $\text{C}_{23}\text{H}_{19}\text{N}_7\text{O}_3$: C 62.58, H 4.34, N 22.21; found: C 62.56, H 4.34, N 21.93.

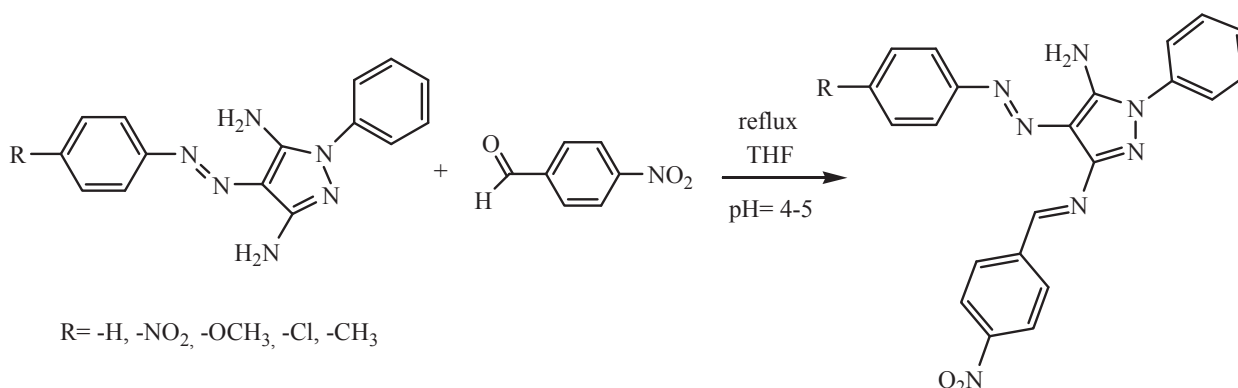


Fig. 1. Synthetic route of Schiff bases containing the pyrazole cores.

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