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ScienceDirect
Karbala International Journal of Modern Science 2 (2016) 56–62
http://www.journals.elsevier.com/karbala-international-journal-of-modern-science/

Synthesis, assessment of substituent effect and antimicrobial activities of (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one compounds

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Received 19 December 2015; revised 19 January 2016; accepted 19 January 2016
Available online 19 February 2016

Abstract

A series of substituted (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one compounds has been synthesized from 4-aminoantipyrine and substituted benzaldehydes. Their structures have been confirmed by their physical constants, UV, IR and NMR spectral data. The observed UV absorption maximum λ_{max}(nm), IR frequencies νC═N(cm^{-1}), NMR δ(ppm) of C−H & C═N chemical shift values have been correlated with Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analyses. From the results of statistical analysis, the effect of substituents on the spectral data has been studied. The antimicrobial activities of all the Schiff bases synthesized have been studied using Bauer−Kirby method.

Keywords: Synthesis; UV, IR and NMR spectra; Correlation analysis; Antimicrobial activities

1. Introduction

Schiff's base compounds have been derived using condensation reaction of aldehydes or ketones with primary amino compounds. They contain −N═CHR group. Many Schiff's bases have been synthesized from heterocyclic compounds [1]. Schiff's bases and their metal complexes have been reported to exhibit vast applications in biological systems [2,3].

Though Schiff's bases contain a heterocyclic nucleus have efficient biological activities, the study of spectral correlation of these compounds has not been done well so for [4–6]. Antipyrine is used in the field of medicine [7] very much and it is believed that its amino derivative would equally be of important in drug industries possibly as intermediates in antipyretic and analgesic drugs [8].

In recent years, correlation analysis has been applied by chemists [9–12] for assessing the effect of substituents of Schiff's bases through spectral data.

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Peer review under responsibility of University of Kerbala.

http://dx.doi.org/10.1016/j.kijoms.2016.01.004

Literature survey shows that there is a little information available regarding the study of UV, IR and NMR spectral correlation and antimicrobial activities of substituted (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one compounds. Hence the authors have taken efforts for synthesizing (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one compounds and studying the effect of substituents through the spectral data as well as their antimicrobial activities.

2. Experimental

2.1. General

In the present investigation, all the chemicals used for synthesis have been procured from Sigma–Aldrich and E-Merck chemical companies. Mettler-FP51 melting point apparatus has been used for the observation of melting points of all (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one compounds in open glass capillaries and are uncorrected. The SHIMADZU-1650 SPECTROMETER instrument has been utilized for recording UV spectra of all synthesized compounds using spectral grade methanol solvent. For recording infrared spectra (KBr, 4000–400 cm^{-1}) of these compounds AVATAR-300 Fourier transform spectrophotometer has been used. The NMR spectra of all the synthesized compounds have been recorded using BRUKER 400 spectrometer operating at 500 MHz for ^{1}H NMR spectra and 125.46 MHz for ^{13}C NMR spectra in $CDCl_3$ solvent using TMS as internal standard.

2.2. Synthesis of substituted (4E)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-ones

Equimolar quantities of 4-amino-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (0.01 mol) and substituted benzaldehydes (0.01 mol) were stirred well with 0.5 ml of acetic acid and the mixture refluxed [13] for 10–12 h at 70–80 °C. The completion of the reaction was monitored by TLC continuously. Then the reaction mixture was cooled to room temperature and poured into crushed ice with constant stirring. Nearly yellow–orange precipitate settled down which was filtered and washed several times with cold water and recrystallized from ethanol to collect glittering pale yellow solid. The general reaction is as shown in Scheme 1.

3. Results and discussion

3.1. Correlation analysis of substituted (4E)-4-(benzylidene amino)-1,2-dihydro-2,3-dimethyl-1-phenyl pyrazol-5-one compounds

3.1.1. Uv–visible spectral correlations

The assigned UV absorption maximum λ_{max} (nm) values of all the substituted (4*E*)-4-(benzylidene amino)-1,2-dihydro-2,3-dimethyl-1-phenyl pyrazol-5-one compounds are presented in Table 1. These UV spectral values are correlated with Hammett substituent constants and *F* and *R* parameters using single and multilinear regression analyses [9–12,14]. Hammett equation employed for the correlation analysis, involving the UV absorption maximum is shown in equation (1).

$$\lambda = \rho \cdot \sigma + \lambda_0 \quad (1)$$

where λ_0 is the absorption maximum of the parent member of this series.

The results of statistical analysis [9–12,14] are shown in Table 2. From the Table it is evident that the UV absorption maximum λ_{max} (nm) values of all the substituted (4*E*)-4-(benzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-ones except those with 3-Br and 3-Cl substituents have shown satisfactory correlations with Hammett constant σ (r = 0.900), σ^+ (r = 0.900) and σ_R (r = 0.904) and *R* (0.904) parameter. The remaining Hammett constants have shown poor correlations. This is due to the inability of substituents for predicting the reactivity on the absorption and it is associated with resonance-conjugative structure as shown in Fig. 1. However the multi-correlation analysis produce satisfactory correlations as shown in equations (2) and (3).

$$\lambda_{max}(\mathrm{nm}) = 255.050\,(\pm 22.89) + 30.539\,(\pm 9.88)\,\sigma_I - 74.801\,(\pm 16.84)\,\sigma R \quad (2)$$

$(R = 0.948,\ n = 10,\ P > 95\%)$

$$\lambda_{max}(nm) = 259.702\,(\pm 22.94) + 17.667\,(\pm 6.463) \times F - 54.679\,(\pm 10.37)\,R \quad (3)$$

$(R = 0.948,\ n = 10,\ P > 95\%)$

3.1.2. IR spectral correlation

The assigned infrared stretching frequency ν C=N (cm^{-1}) values of all the substituted (4E)-4-(benzyli-