



ECO-FRIENDLY SYNTHESIS AND SPECTRAL CORRELATIONS IN SOME 1-PHENYL-3-(5-BROMOTHIOPHEN-2-YL)-5-(SUBSTITUTED PHENYL)-2-PYRAZOLINES

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A series containing eight 1-phenyl-3(5-bromothiophen-2-yl)-5-(substituted phenyl)-2-pyrazoline derivatives have been synthesized by microwave assisted, solid acidic green catalyst $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyzed cyclization of 5-bromo-2-thienyl chalcones and phenyl hydrazine hydrochloride under solvent free conditions. The yields of the pyrazolines were more than 85%. The purities of these pyrazolines were checked by their physical constant, micro analysis, Infrared, Nuclear magnetic resonance and Mass spectroscopic data published earlier in literature. From the spectral frequencies, infrared $\nu(\text{cm}^{-1})$ of C=N, C-S, C-Br, ^1H and ^{13}C NMR chemical shifts (δ , ppm) of pyrazoline ring proton, carbon and C=N carbons were assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analysis the effects of substituent on the spectral frequencies have been discussed.

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INTRODUCTION

The ^1H pyrazolines are well-known important di-nitrogen containing five membered heterocyclic stereo-bioorganic molecules. Hydrazine hydrate or phenylhydrazine hydrate or phenylhydrazine hydrochloride were used for synthesis of pyrazoles derivatives by cyclization of enones. The pyrazoline ring protons were bonded with carbon atoms spatially different environment. The α,β -unsaturated ketones can play the role of versatile precursors in the synthesis of the corresponding pyrazolines.¹⁻⁶ Numerous solvent assisted and solvent-free methods have been reported for the preparation of pyrazoline derivatives. Cyclization of chalcones with phenyl hydrazine hydrochloride using ultrasonic sound assisted synthesis of pyrazolines was reported by, Li *et al.*,⁷ The K_2CO_3 -mediated microwave irradiation has been shown to be an efficient method for the synthesis of pyrazolines.⁸ The regioselective formation of pyrazolines have been synthesized by the reaction of substituted hydrazine with α,β -unsaturated ketones.^{9,10} Many solvent free catalysts and methods such as solution phase MWI,¹¹ K_2CO_3 /Basic alumina,¹² Surfactant THAC,¹³ $\text{KF}/\text{Al}_2\text{O}_3$,¹⁴ HSBM,¹⁵ fly-ash: H_2SO_4 ,¹⁶ Thermal solvent-free¹⁷ heating were available for synthesis of pyrazoline derivatives. These pyrazolines used widely in the current decades due to various biological and pharmacological activities such as analgesic,¹⁸ anti-inflammatory,^{19, 20} anti-microbial,²¹ anti-amoebic,^{22, 23} anti-tubercular,^{24,25} hypoglycemic,²⁶ anti-coagulant,²⁷ anti-depressant,²⁸⁻³⁰ pesticides,³¹ fungicides,³² anti-bacterial³³ and anti-con-vulsant activities.³⁴ Recent report shows some new pyrazoline substituted thiazolone based compounds exhibit anti-cancer activity.³⁵ Apart from biological

activities, pyrazolines are also extensively used as synthons in organic synthesis,³⁶⁻³⁸ optical brightening agent for textiles, paper, fabrics, and as a hole-conveying medium in photoconductive materials.³⁹⁻⁴³

Spectroscopic data is useful for predicting the ground state equilibrium of organic compounds.⁴⁴⁻⁴⁷ The ultraviolet spectroscopic data of absorption maxima (λ_{max} , nm) is also applied for prediction of effects of substituent.⁴⁸ In pyrazoline molecules (^1H pyrazoles), the infrared spectra is used for predicting the effects of substituents on the vibrations of C=N, C-H, N-H. From NMR spectroscopy, the spatial arrangements of the protons Ha, Hb and Hc or Ha, Hb, Hc and Hd of the types shown in Fig. 1 were predictable by their frequencies with multiplicities viz., doublet or triplet or doublet of doublets. Based on the geometry, the chemical shift of the protons of respective pyrazoles has been predicted and the effects of substituents will be studied. The effects of substituents on the pyrazoline ring protons were studied first by Sakthinathan *et. al.*⁴⁴ In their study, they synthesized some 2-naphthyl based pyrazolines and characterized by infrared and NMR spectroscopic data.

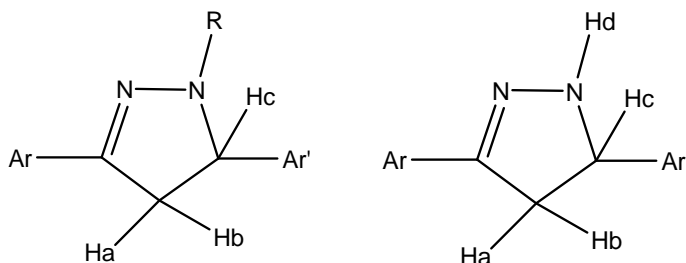


Figure 1. General structure of pyrazoles

From infrared spectra, the C=N stretches(cm^{-1}) have been assigned and these vibrations were correlated with Hammett substituent constants. In this correlations they observed satisfactory r values. From ^1H NMR chemical

shifts of these pyrazolines the H_a , H_b and H_c values were assigned and studied the effects of substituents by correlation with these frequencies and Hammett substituent constants, F and R values. Similarly the ^{13}C chemical shifts (δ , ppm) of these pyrazolines also correlated. In this present study the authors have taken efforts to synthesis some 1-aryl-3(5-substituted aryl-2-yl)-5-(substituted phenyl)-2-pyrazolines from various chalcones and phenyl hydrazine hydrochloride in presence of $\text{SiO}_2\text{-H}_3\text{PO}_4$. The purities of these pyrazolines were checked by their physical constants and spectral data published earlier in literature. The infrared and nuclear magnetic resonance spectral group frequencies of 5-bromo-2-thienyl based pyrazolines have been assigned and correlated with Hammett substituent constants, F and R parameters.

EXPERIMENTAL

Materials and methods

All chemicals used were procured from Sigma-Aldrich and E-Merck companies. Melting points of all pyrazolones have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr , $4000\text{-}400\text{ cm}^{-1}$) have been recorded on BRUKER (Thermo Nicolet) Fourier transform spectrophotometer. The NMR spectra of all pyrazolines have been recorded on Bruker AV400 spectrometer operating at 400 MHz for recording ^1H and 100 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard. Mass spectra have been recorded on SHIMADZU spectrometer using chemical ionization technique.

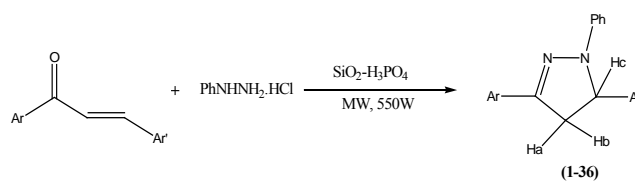
Preparation of solid $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyst

In a 50mL Borosil beaker, 2g of silica (10-20 μ) 2mL of ortho phosphoric acid were taken and mixed thoroughly with glass rod. This mixture was heated on a hot air oven at 85°C for 1h, cooled to room temperature, stored in a borosil bottle and tightly capped. This was characterized by infrared spectra and SEM analysis.⁴⁹

Infrared spectral data of $\text{SiO}_2\text{-H}_3\text{PO}_4$ were $\nu(\text{cm}^{-1})$: 3437(P-OH); 2932, 2849 (P-O-H); 1747, (O=P-OH); 1091(P=O), 800(P-O).

Synthesis of pyrazoline derivatives

An appropriate equi-molar quantities of chalcones (2 mmol), phenyl hydrazine hydrochloride (2 mmol) and $\text{SiO}_2\text{-H}_3\text{PO}_4$ (0.5 g) have been taken in borosil tube and tightly capped. The mixture has been subjected to microwave irradiation for 6-8 minutes in a microwave oven at 550 watts, 2540 MHz frequency (Scheme 1) (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100-750W (IEC-705), and then cooled to room temperature. After separating the organic layer with dichloromethane the solid product has been obtained on evaporation. The solid, on recrystallization from benzene-hexane mixture afforded glittering product. The insoluble catalyst has been recycled by washing with ethyl acetate (8 mL) followed by drying in an oven at 100°C for 1h and reused for further reactions.



Scheme 1. Synthesis of pyrazolines

RESULTS AND DISCUSSION

In our organic chemistry research laboratory, we attempts to synthesize pyrazoline derivatives by cyclization of electron withdrawing as well as electron donating group substituted chalcones and phenylhydrazine hydrochloride in the presence of acidic catalyst $\text{SiO}_2\text{-H}_3\text{PO}_4$ in microwave irradiation. Hence the authors have synthesized the pyrazoline derivatives by the cyclization of 2 mmole of chalcone, 2 mmole of phenylhydrazine hydrochloride in microwave irradiation with 0.5g of $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyst at 550W, 6-8 minutes (Samsung Grill, GW73BD Microwave oven, 230V A/c, 50Hz, 2450Hz, 100-750W (IEC-705), (Scheme 1). During the course of this reaction $\text{SiO}_2\text{-H}_3\text{PO}_4$ catalyzes cyclization between aryl enones and phenylhydrazine hydrochloride to elimination of water followed by proton transfer gave the pyrazoline derivatives. The yields of the pyrazolines in this reaction are more than 85%. The proposed general mechanism of this reaction is given in Scheme 2. Further we have investigated this cyclization reaction with equimolar quantities of the styryl-5-bromo-2-thienyl ketones (entry 21) and phenylhydrazine hydrochloride.

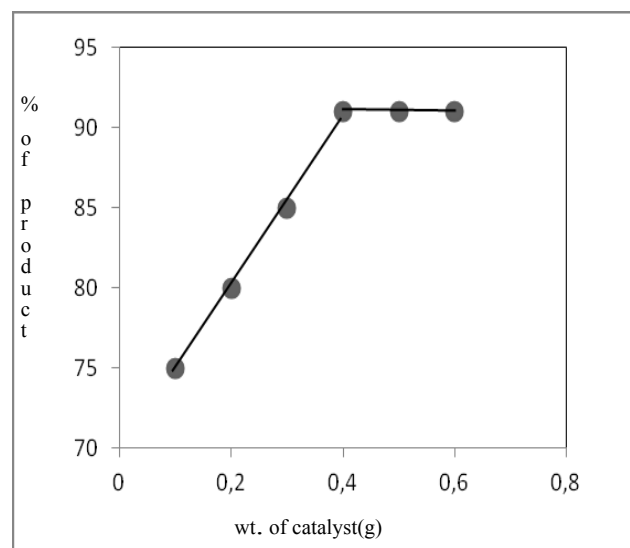
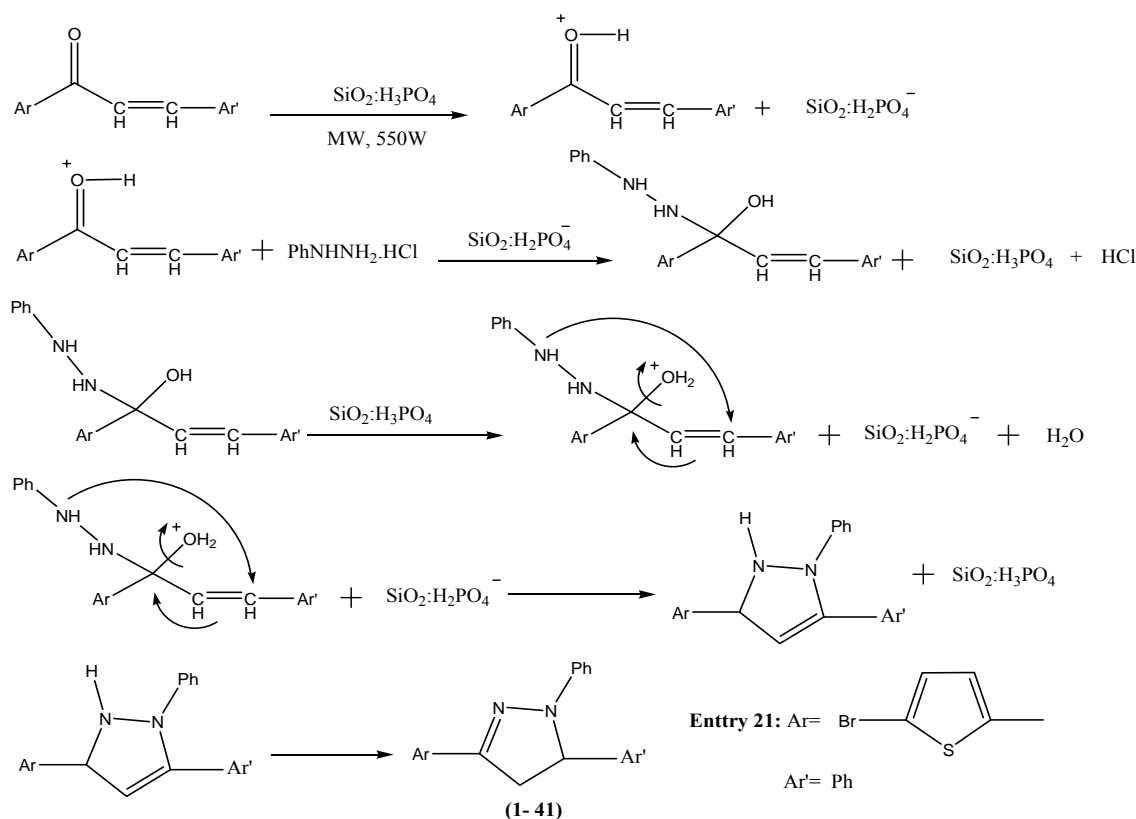


Figure 2. Effect of catalyst loading

In this reaction the obtained yield was 91%. The effect of catalyst on this reaction was studied by varying the catalyst quantity from 0.1 to 1g. As the catalyst quantity is increased from 0.1 to 1g, the percentage of yield of product is increased from 75 to 91%. Further increase the catalyst amount, there is no significant increasing of the percentage of product.



Scheme 2. Proposed mechanism for synthesis of pyrazolines by cyclization of chalcones and phenylhydrazine hydrochloride in presence of $\text{SiO}_2:\text{H}_3\text{PO}_4$ under microwave irradiation

This catalytic effect is shown in (Fig. 2). The optimum quantity of catalyst loading was found to be 0.4g. We have carried out this reaction with various aryl chalcones and phenyl hydrazine hydrochloride. There is no significant effect of substituents on the cyclization reaction. The results, analytical and mass spectral data are summarized in Table 1. The reusability of this catalyst was studied the cyclization of 5-bromo-2-thienyl chalcone and phenyl hydrazine hydrochloride (entry 21) and is presented in Table 2.

From the Table 2, first two runs gave 91% product. The third, fourth and fifth runs of reactions gave the yields 90.5%, 90.5% and 90% of pyrazolines. There was no appreciable loss in its effect of catalytic activity were observed up to fifth run. The effect of solvents on the yield also studied with methanol, ethanol, dichloromethane and tetrahydrofuran from each component of the catalyst (entry 21). Similarly the effect of microwave irradiation was studied on the each component of the catalysts. The effect of solvents on the yields of pyrazolines were presented in Table 3. From the table highest yield of the pyrazolines obtained from the condensation of chalcone and phenylhydrazine hydrochloride with catalyst $\text{SiO}_2:\text{H}_3\text{PO}_4$ in microwave irradiation.

IR SPECTRAL STUDY

The synthesis of pyrazoline derivative is shown in Scheme 1. In the present study, the authors have chosen a series of pyrazoline derivatives namely 1-phenyl-3(5-bromothiophen-2-yl)-5-(substituted phenyl)-2-pyrazolines (entries 21-27) for studying the effects of substituent on the spectral group frequencies.

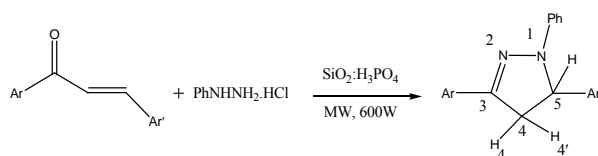
The infrared $\nu\text{C}=\text{N}$ stretching frequencies (cm^{-1}) of these pyrazolines have been recorded and are presented in Table 4. These data are correlated with Hammett substituent constants⁴⁴⁻⁴⁹ and Swain-Lupton's⁵¹ parameters. In this correlation the structure parameter Hammett equation employed is as shown in equation (1).

$$\nu = \rho\sigma + \nu_0 \quad (1)$$

where ν_0 is the frequency for the parent member of the series.

The observed $\nu\text{C}=\text{N}$ stretching frequencies (cm^{-1}) are correlated with various Hammett substituent constants and F and R parameters through single and multi-regression analyses including Swain-Lupton's⁵¹ parameters. The results of statistical analysis of single parameter correlation are shown in Table 5.

The correlation of $\nu\text{C}=\text{N}$ (cm^{-1}) frequencies of pyrazolines with R parameter was satisfactorily ($r=0.907$). The remaining Hammett substituent constants and F parameter were found to be poor in correlation. A satisfactory correlation was obtained for $\nu\text{C}-\text{S}$ (cm^{-1}) frequencies of pyrazolines with Hammett substituents and F parameter. The R parameter was fail in correlation. All correlations produce positive ρ values. This implies that there is a normal substituent effect operates in all systems. The correlation of $\nu\text{C}-\text{Br}$ (cm^{-1}) frequencies of pyrazolines with Hammett substituent constants, F and R parameters were gave poor correlation. This failure in correlation was due to the absence of inductive and polar effects of the substituent and is associated with the conjugated structure shown in Fig.3.

Table 1. Analytical and mass spectral data of pyrazolines synthesized by solvent-free cyclization of chalcones and phenylhydrazine hydrochloride reaction of the type

Entry	Ar	Ar'	M.W.	Yield (%)	M.p. (°C)	Mass (m/z)
1	C ₆ H ₅	C ₆ H ₅	298	90	134-135; (134-135)[7]	298[M ⁺]
2	C ₆ H ₅	3-BrC ₆ H ₄	376	89	142-143; (141-143)[7]	376[M ⁺], 378[M ⁺²]
3	C ₆ H ₅	2-ClC ₆ H ₄	333	87	135-136; (134-135)[7]	333[M ⁺], 335[M ⁺²]
4	C ₆ H ₅	3-ClC ₆ H ₄	333	87	133-134; (134-136)[7]	333[M ⁺], 335[M ⁺²]
5	C ₆ H ₅	4-ClC ₆ H ₄	333	87	134-135; (135-136)[7]	333[M ⁺], 335[M ⁺²]
6	C ₆ H ₅	4-N(CH ₃) ₂ C ₆ H ₄	341	85	219-220; (220)[11]	341[M ⁺]
7	C ₆ H ₅	2-OHC ₆ H ₄	314	87	192-193; (192)[11]	314[M ⁺]
8	C ₆ H ₅	4-OCH ₃ C ₆ H ₄	328	87	112-113; (110-112)[7]	328[M ⁺]
9	C ₆ H ₅	4-NO ₂ C ₆ H ₄	343	66	157-158 (trace)[7] (225)[11]	343[M ⁺]
10	4-ClC ₆ H ₄	C ₆ H ₅	333	87	144-145; (143-145)[11]	333[M ⁺]
11	4-OHC ₆ H ₄	C ₆ H ₅	314	88	279-280; (281) [11]	314[M ⁺]
12	4-OHC ₆ H ₄	4-ClC ₆ H ₄	348	86	234-235; (234) [11]	348[M ⁺], 350[M ⁺²]
13	4-OHC ₆ H ₄	4-N(CH ₃) ₂ C ₆ H ₄	357	87	265-266; (265) [11]	357[M ⁺]
14	4-OHC ₆ H ₄	2-OHC ₆ H ₄	330	86	195-196; (194) [11]	330[M ⁺]
15	4-OHC ₆ H ₄	4-NO ₂ C ₆ H ₄	359	89	196-197; (198) [11]	359[M ⁺]
16	3-NO ₂ C ₆ H ₄	C ₆ H ₅	343	90	132-133(trace) [7]	343[M ⁺]
17	C ₄ H ₃ S	C ₆ H ₅	349	92	164-165; (161-165) [6d]	349[M ⁺]
18	C ₄ H ₃ S	4-BrC ₆ H ₄	382	91	249-250; (241-252) [6d]	382[M ⁺], 384[M ⁺²]
19	C ₄ H ₃ S	4-N(CH ₃) ₂ C ₆ H ₄	347	89	212-213; (212-215) [6d]	347[M ⁺]
20	C ₄ H ₃ S	2,4,5-(OCH ₃) ₃ C ₆ H ₂	394	88	170-171; (170-174) [6d]	394[M ⁺]
21	C ₄ H ₂ BrS	C ₆ H ₅	383	91	152-153; (152-153)[16]	383[M ⁺]
22	C ₄ H ₂ BrS	4-BrC ₆ H ₄	462	92	148-149; (148-149)[16]	462[M ⁺], 466[M ⁺²], 468[M ⁺³]
23	C ₄ H ₂ BrS	2-ClC ₆ H ₄	417	90	142-144; (142-144)[16]	417[M ⁺], 419[M ⁺²], 421[M ⁺³]
24	C ₄ H ₂ BrS	4-ClC ₆ H ₄	417	93	147-149; (147-149)[16]	417[M ⁺], 419[M ⁺²], 421[M ⁺³]
25	C ₄ H ₂ BrS	4-IC ₆ H ₄	509	91	146-148; (146-148)[16]	509[M ⁺], 511[M ⁺²], 513[M ⁺³]
26	C ₄ H ₂ BrS	4-OCH ₃ C ₆ H ₄	413	90	128-130; (128-130)[16]	413[M ⁺], 415[M ⁺²]
27	C ₄ H ₂ BrS	4-CH ₃ C ₆ H ₄	397	93	148-149; (148-149)[16]	397[M ⁺], 379[M ⁺²]
28	C ₄ H ₂ BrS	3,4-(OCH ₃) ₂ C ₆ H ₃	443	92	140-142; (140-142)[16]	443[M ⁺], 445[M ⁺²]
29	C ₁₀ H ₇	C ₆ H ₅	348	92	116-117; (116-117)[44]	348[M ⁺]
30	C ₁₀ H ₇	3-BrC ₆ H ₄	426	89	64-65; (64-65)[44]	426[M ⁺], 428[M ⁺²]
31	C ₁₀ H ₇	4-ClC ₆ H ₄	383	91	62-68; (62-68)[44]	383[M ⁺], 385[M ⁺²]
32	C ₁₀ H ₇	2-OCH ₃ C ₆ H ₄	378	87	104-105; (104-105)[44]	378[M ⁺]
33	3-CH ₃ C ₆ H ₄	C ₆ H ₅	326	93	110-111; (110-111)[50]	326[M ⁺]
34	3-CH ₃ C ₆ H ₄	3-BrC ₆ H ₄	391	92	60-61; (60-61)[50]	391[M ⁺], 393[M ⁺²]
35	3-CH ₃ C ₆ H ₄	3-ClC ₆ H ₄	346	90	54-55; (54-55)[50]	346[M ⁺], 348[M ⁺²]
36	3-CH ₃ C ₆ H ₄	4-NO ₂ C ₆ H ₄	326	91	58-59; (58-59)[50]	326[M ⁺], 328[M ⁺²]

Table 2. Reusability of catalyst on cyclization of styryl 5-bromo-2-thienyl ketone (2 mmol) and phenylhydrazine hydrochloride (2 mmol) under microwave irradiation (**entry 21**).

Run	1	2	3	4	5
Yield, %	91	91	90.5	90.5	90

Table 3. The effect of solvents in conventional heating and without solvent in microwave irradiation on yield of pyrazoline (**entry 21**)

Solvents											Microwave irradiation			
MeOH			EtOH			DCM			THF					
SiO ₂	PA	SiO ₂ :PA	SiO ₂	PA	SiO ₂ :PA	SiO ₂	PA	SiO ₂ :PA	SiO ₂	PA	SiO ₂ :PA	SiO ₂	PA	SiO ₂ :PA
73	77	78	74	75	80	73	80	80	75	81	81	82	80	91

MeOH=Methanol; EtOH=Ethanol; DCM= Dichloromethane; THF=Tetrahydrofuran; PA=Phosphoric acid

Table 4. The infrared $\nu(\text{cm}^{-1})$ of C=N, C-S, C-Br, ^1H and ^{13}C NMR chemical shifts (δ , ppm) of pyrazoline ring proton, carbons of 1-phenyl-3(5-bromothiophen-2-yl)-5-(substituted phenyl)-2-pyrazolines(entries 21-28)

Entry	Substituent	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{S}$	$\nu\text{C}-\text{Br}$	δH_4	$\delta\text{H}_{4'}$	δH_5	δC_3	δC_4	C_5	$\delta\text{C}=\text{N}$
21	H	1593	679	562	3.06	3.77	5.25	155.60	43.66	64.68	154.56
22	4-Br	1596	685	562	3.07	3.82	5.26	155.56	43.53	64.10	155.56
23	2-Cl	1595	690	566	3.01	3.93	5.66	157.50	42.08	61.50	157.50
24	4-Cl	1594	688	531	3.10	3.80	5.28	155.82	43.70	64.75	155.82
25	4-I	1595	680	531	3.04	3.78	5.21	156.11	43.52	64.21	156.11
26	4-OCH ₃	1596	670	553	3.07	3.77	5.24	155.81	43.75	64.29	159.13
27	4-CH ₃	1594	680	546	3.07	3.77	5.24	156.10	43.72	64.47	156.10

The single parameter correlations of $\nu\text{C}=\text{N}$, C-S and C-Br (cm^{-1}) frequencies with Hammett substituent constants of resonance and inductive effects fail. So, the authors think that it is worthwhile to seek the multi regression analysis and which produce a satisfactory correlation with Resonance, Field and Swain-Lupton's⁵¹ constants. The corresponding equations are given in (2-7).

$$\nu_{\text{CN}}(\text{cm}^{-1}) = 1593.76(\pm 0.553) + 3.805\sigma_{\text{I}}(\pm 1.627) + 2.584\sigma_{\text{R}}(\pm 1.611) \quad (2)$$

($R=0.978$, $P > 95\%$, $n=7$)

$$\nu_{\text{CN}}(\text{cm}^{-1}) = 1593.06(\pm 0.512) + 2.388\text{F}(\pm 1.429) - 4.173\text{R}(\pm 1.714) \quad (3)$$

($R=0.998$, $P > 95\%$, $n=7$)

$$\nu_{\text{CS}}(\text{cm}^{-1}) = 677.98(\pm 1.947) + 7.680\sigma_{\text{I}}(\pm 1.535) + 24.399\sigma_{\text{R}}(\pm 5.668) \quad (4)$$

($R=0.931$, $P > 90\%$, $n=7$)

$$\nu_{\text{CS}}(\text{cm}^{-1}) = 682.05(\pm 3.402) + 24.577\text{F}(\pm 9.496) + 31.947\text{R}(\pm 11.386) \quad (5)$$

($R=0.985$, $P > 95\%$, $n=7$)

$$\nu_{\text{CBr}}(\text{cm}^{-1}) = 552.39(\pm 11.595) - 6.515\sigma_{\text{I}}(\pm 3.407) + 5.965\sigma_{\text{R}}(\pm 3.337) \quad (6)$$

($R=0.915$, $P > 90\%$, $n=7$)

$$\nu_{\text{CBr}}(\text{cm}^{-1}) = 554.19(\pm 13.979) + 13.627\text{F}(\pm 3.972) + 0.576\text{R}(\pm 0.041) \quad (7)$$

($R=0.918$, $P > 95\%$, $n=7$)

^1H NMR SPECTRAL STUDY

The ^1H NMR spectra of seven pyrazoline derivatives under investigation have been recorded in deuteriochloroform solution employing tetramethylsilane (TMS) as internal standard. The signals of the pyrazoline ring protons have been assigned. They have been calculated as AB or AA' systems respectively. The chemical shifts (δ , ppm) of H_4 are at higher fields than those of $\text{H}_{4'}$ and H_5 in this series of pyrazolines. This is due to the deshielding of $\text{H}_{4'}$ and H_5 which are in different chemical as well as magnetic environment. These H_4 protons gave an AB pattern and the $\text{H}_{4'}$ proton doublet of doublet in most cases was well separated from the signals H_5 and the aromatic protons. The assigned chemical shifts (δ , ppm) of the pyrazoline ring H_4 , $\text{H}_{4'}$ and H_5 protons are presented in Table 4.

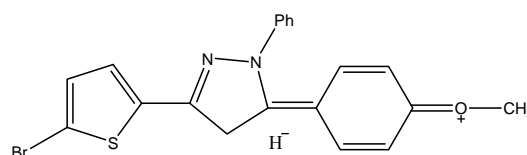
In nuclear magnetic resonance spectra, the ^1H or the ^{13}C chemical shifts (δ , ppm) depend on the electronic environment of the nuclei concerned. These chemical shifts have been correlated with reactivity parameters. Thus the Hammett equation may be used in the form as shown in (8).

$$\log \delta = \log \delta_0 + \rho \sigma \quad (8)$$

where δ_0 is the chemical shift of the corresponding parent compound.

The assigned H_{44} , $\text{H}_{4'}$ and H_5 proton chemical shifts (ppm) of pyrazoline ring have been correlated with various Hammett sigma constants.⁴⁴⁻⁴⁹ The results of statistical analysis are presented in Table 5.

The H_4 proton chemical shifts (ppm) with Hammett σ^+ and R parameters gave satisfactory correlation. The remaining substituent constants and F parameters were fail in correlation. The failure in correlation is associated with the conjugative structure shown in Fig. 3.

**Figure 3.** Resonance-conjugative structure

The results of statistical analysis of $\text{H}_{4'}$ proton chemical shifts (δ , ppm) with Hammett substituents are shown in Table 5. The $\text{H}_{4'}$ proton chemical shifts (δ , ppm) with Hammett substituent constants and F parameters gave satisfactory correlation excluding 2-Cl and 3-OCH₃ substituents. The R parameter was fail in correlation. This is due to the absence of resonance effect of substituents on the $\text{H}_{4'}$ proton chemical shifts and it is associated with the conjugative structure shown in Fig. 3.

The results of statistical analysis of H_5 proton chemical shifts (ppm) with Hammett substituents are presented in Table 5. The H_5 proton chemical shifts with Hammett σ , σ^+ , σ_{I} constants and F parameters gave satisfactory correlation excluding 2-Cl substituent. All correlations produce positive ρ values. This means that the normal substituent effect operates in all systems. This failure in correlation is associated with conjugative structure shown in Fig. 3.

Table 5. Results of statistical analysis of $\nu(\text{cm}^{-1})$ of C=N, C-S, C-Br bands, ^1H and ^{13}C NMR chemical shifts (δ , ppm) of pyrazoline ring protons, carbons of 1-Ph-3(5-bromothiophen-2-yl)-5-(aryl)-2-pyrazolines, Hammett σ , σ^+ , σ_{I} , σ_{R} constants and F and R parameters (entries 21-28).

Functionality	Constants	r	I	ρ	s	n	Correlated derivatives
vC=N	σ	0.806	1594.71	0.032	1.21	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.805	1594.71	0.153	1.21	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.806	1593.84	3.000	0.97	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.802	1594.80	1.432	1.16	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.866	1593.65	3.703	0.91	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.907	1593.49	5.255	0.75	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-I, 4-OCH ₃
vC-S	σ	0.908	680.24	27.109	3.95	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.981	681.82	13.765	3.47	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.905	677.30	15.206	3.32	5	2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.989	680.07	26.720	3.01	5	2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.904	697.57	14.510	3.06	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.705	686.53	20.815	6.28	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
vC-Br	σ	0.701	550.52	-7.121	15.98	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.701	550.13	5623	15.84	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.782	552.56	-8.355	15.93	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.821	550.63	7.931	15.94	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.789	554.10	-13.810	15.78	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.707	551.70	6.752	16.02	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
δH_4	σ	0.802	3.061	-0.026	0.03	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.903	3.068	-0.025	0.02	5	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-I
	σ_{I}	0.781	3.065	-0.020	0.03	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.812	3.062	0.033	0.02	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.715	3.066	-0.021	0.03	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.902	3.058	-0.005	0.02	5	4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I
$\delta\text{H}_4'$	σ	0.905	3.797	0.147	0.05	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.906	3.805	0.087	0.04	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-I, 4-OCH ₃
	σ_{I}	0.906	3.763	0.147	0.05	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.904	3.797	0.178	0.05	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I
	F	0.901	3.763	0.145	0.05	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I
	R	0.803	3.808	0.171	0.06	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
δH_5	σ	0.903	5.297	1.257	0.16	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.904	5.308	1.025	0.15	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-I, 4-OCH ₃
	σ_{I}	0.903	5.228	1.266	0.15	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.801	5.289	1.271	0.15	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.903	5.236	0.246	0.16	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.803	5.312	0.036	0.17	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
δCN	σ	0.822	156.03	0.722	0.712	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.823	156.07	0.511	0.681	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.729	155.82	0.861	0.697	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.703	156.00	1.166	0.674	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.825	155.82	0.858	0.704	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.805	156.02	0.245	0.728	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
δC_4	σ	0.841	43.48	-1.181	0.59	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.751	43.42	-0.783	0.54	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.742	43.75	-1.129	0.59	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.900	43.49	1.761	0.58	6	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I
	F	0.903	43.73	1.095	0.61	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.900	43.35	0.145	0.65	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
δC_5	σ	0.735	64.09	1.671	1.17	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ^+	0.704	64.00	1.121	1.09	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{I}	0.904	64.61	2.137	1.11	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	σ_{R}	0.803	64.10	1.974	1.16	7	H, 4-CH ₃ , 2-Cl, 4-Cl, 4-Br, 4-I, 4-OCH ₃
	F	0.937	64.61	2.145	1.14	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃
	R	0.904	64.15	0.685	1.22	6	H, 4-CH ₃ , 4-Cl, 4-Br, 4-I, 4-OCH ₃

r = correlation coefficient; ρ = slope; I = intercept; s = standard deviation; n = number of substituents

In view of the inability of the Hammett σ constants to produce individually satisfactory correlation, the authors think that it is worthwhile to seek multiple correlations involving either σ_1 and σ_R constants or Swain-Lupton's⁵¹ F and R parameters. The correlation equations for H₄-H₅ protons are given in (9-14).

$$\delta_{H_4}(\text{ppm}) = 3.065 (\pm 0.021) - 0.119 (\pm 0.006)\sigma_1 + 0.290 (\pm 0.005)\sigma_R \quad (9)$$

(R=0.927, P> 90%, n=7)

$$\delta_{H_4}(\text{ppm}) = 3.063 (\pm 0.260) - 0.247 (\pm 0.007)F + 0.158 (\pm 0.002)R \quad (10)$$

(R=0.917, P > 90%, n=7)

$$\delta_{H_4}(\text{ppm}) = 3.765 (\pm 0.341) - 0.119 (\pm 0.007)\sigma_1 + 0.929 (\pm 0.004)\sigma_R \quad (11)$$

(R=0.966, P> 95%, n=7)

$$\delta_{H_4}(\text{ppm}) = 3.777 (\pm 0.046) + 0.173 (\pm 0.001)F + 0.960 (\pm 0.015)R \quad (12)$$

(R=0.955, P > 95%, n=7)

$$\delta_{H_5}(\text{ppm}) = 5.234 (\pm 0.111) + 0.202 (\pm 0.0326)\sigma_1 - 0.207 (\pm 0.002)\sigma_R \quad (13)$$

(R=0.947, P> 90%, n=7)

$$\delta_{H_5}(\text{ppm}) = 5.297 (\pm 0.143) + 0.292 (\pm 0.004)F + 0.162 (\pm 0.002)R \quad (14)$$

(R=0.934, P > 90%, n=7)

¹³C NMR SPECTRA

Spectroscopic chemists and organic chemistry researchers⁴⁴⁻⁴⁹ have made extensive study of ¹³C NMR spectra for a large number of different ketones, styrenes and keto-epoxides. They have studied linear correlation of the chemical shifts (δ , ppm) of C_α, C_β and CO carbons with Hammett σ constants in alkenes, alkynes, acid chlorides and styrenes. In the present study, the chemical shifts (δ , ppm) of pyrazoline ring C₃ (C=N), C₄, and C₅ carbon, have been assigned and are presented in Table 4. Attempts have been made to correlate the above said carbon chemical shifts (δ , ppm) with Hammett substituent constants, field and resonance parameters, with the help of single and multi-regression analyses to study the reactivity through the effect of substituents.

The chemical shifts (δ , ppm) observed for the δ_{C_3} (C=N), C₄, and C₅ have been correlated with Hammett substituent constants and the results of statistical analysis are presented in Table 5. The $\delta_{C=N}$ chemical shifts (δ , ppm) gave poor correlation with Hammett substituent constants and F and R parameters. Here the polar, inductive and resonance effects were incapable for predicting their effects on the C=N carbon chemical shifts (δ , ppm). The chemical shifts (δ , ppm) observed for the δ_{C_4} carbon have been correlated satisfactorily with Hammett σ_R constant, F and R parameters. Here the polar and inductive effects were incapable for predicting their effects on the C₄ carbon chemical shifts (δ , ppm). The chemical shifts (δ , ppm) observed for the δ_{C_5} carbon have been correlated satisfactorily with Hammett σ_1 constant, F and R parameters. Here the polar and resonance effects were incapable for predicting their

effects on the C₅ carbon chemical shifts (δ , ppm). This is due to the reason stated earlier and it is associated with the resonance - conjugative structure shown in Fig. 3.

In view of inability of some of the σ constants to produce individually satisfactory correlation, the authors think that it is worthwhile to seek multiple correlation involving all σ_1 , σ_R , F and R parameters. The correlation equations are given in (15 and 20).

$$\delta_{C_N}(\text{ppm}) = 155.848 (\pm 0.480) + 0.560 (\pm 1.411)\sigma_1 - 0.991 (\pm 0.137)\sigma_R \quad (15)$$

(R=0.943, P> 90%, n=7)

$$\delta_{C_N}(\text{ppm}) = 155.852 (\pm 0.623) + 9.235 (\pm 0.173)F + 0.198 (\pm 0.002)R \quad (16)$$

(R=0.926, P> 90%, n=7)

$$\delta_{C_4}(\text{ppm}) = 43.724 (\pm 0.480) - 0.845 (\pm 0.111)F + 0.920 (\pm 0.010)R \quad (17)$$

(R=0.953, P> 95%, n=7)

$$\delta_{C_4}(\text{ppm}) = 43.281 (\pm 1.024) + 0.525 (\pm 1.424)\sigma_1 - 0.981 (\pm 0.125)\sigma_R \quad (18)$$

(R=0.916, P> 90%, n=7)

CONCLUSION

A series of some aryl pyrazolines including 1-phenyl-3-(5-bromothiophen-2-yl)-5-(substituted phenyl)-2-pyrazoline derivatives have been synthesized by microwave assisted, solid acidic green catalyst SiO₂-H₃PO₄ catalyzed cyclization of 5-bromo-2-thienyl chalcones and phenyl hydrazine hydrochloride under solvent free conditions. The yields of the pyrazolines were more than 85%. The spectral frequencies, infrared $\nu(\text{cm}^{-1})$ of C=N, C-S, C-Br, ¹H and ¹³C NMR chemical shifts (δ , ppm) of pyrazoline ring proton, carbon and C=N carbons were assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analysis the effects of substituents on the spectral frequencies have been discussed.

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