Solvent-free synthesis and spectral linearity of some (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamides

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ABSTRACT

Some (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives have been synthesized by $SiO_2:H_3PO_4$ catalyzed solvent-free condensation of 2-amino-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta [*b*]thiophene-3-carboxamide and various substituted benzaldehydes in microwave irradiation. The yield of the imine-carboximido derivatives has been found to be more than 85 %. The purity of all imine-carboximido derivatives has been checked using their physical constants and spectral data. The spectral data of the imine-carboximido derivatives such as infrared ν (cm⁻¹) of CO, NH, C-N, C-Cl, C-F, C=N, and the NMR chemical shifts (δ, ppm) of NH, CH, CO and C=N have been correlated with Hammett substituent constants, F and R parameters. From the results of statistical analysis, the effects of substituent on the above spectral group absorptions have been discussed.

Keywords: Solvent-free condensation; $SiO_2:H_3PO_4$; Imine-carboximido derivatives; IR and NMR
              spectra; Hammett correlations.

1. INTRODUCTION

Imines are generally known as Schiff bases, to honor Hugo Schiff, who had synthesized such compounds earlier. Schiff bases are bimolecular condensation products of primary amines with carbonyl compounds. Schiff bases are characterized by the –N=CH– (imine) group which finds importance in elucidating the mechanism of transamination and racemization reactions in biological systems [1, 2]. Schiff bases of aliphatic aldehydes are relatively unstable which readily undergo polymerization while those of aromatic aldehydes having an effective conjugation system are found to be more stable.

Schiff bases have been reported to play very important role in many biological and chemical reactions, due to the presence of the imine linkage. Schiff bases are generally bi- or tri- dentate ligands capable of forming very stable complexes with transition metals [3, 4]. Schiff bases, derived from aromatic amines and aromatic aldehydes are reported to be involved in the study of asymmetric catalysis [5] ,magnetic properties [6], photochromism [7], binding with DNA [8], construction of supra molecular structures [9], the study of activity against Ehrlichascites carcinoma (EAC) [10], the field of dyes and pigments [11], the development of corrosion inhibitors [12], anti-HIV [13] and in the evaluation of physical properties in the crystalline state [14].

Optically active imine derivatives possess multipronged biological activities such as antimicrobial [15], anticancer [16, 17], antiplasmodic-antihypoxic [18], antitubularcular [19, 20], nematicidal-insecticidal [21], anti-inflammatory, and lipoxygenase [22]. The imine moieties are important intermediates and versatile starting materials for the synthesis of chiral amines [23, 24], pyrimidine derivatives [25], phenylhydrazones [26, 27], Mannich bases [28], indoles [29], quinoxalines [30], imidazoles [31], amino triphenylmethanes [32], Michael adducts [33], allyl products [34], optically active α-alkyl aldehydes [35, 36] by hydrogenation [37], nucleophilic addition with organometallics [38] and cycloaddition reaction [39]. Many reagents have been used for the synthesis of optically active imines such as solid super acids, K-10 montmorillonite [40, 41], Tandam catalysts [42], MnO_2 [43], CaO [44], $ZnCl_2$ [23,24], $MgSO_4$-PPTS [26, 27], alumina [45], $Ti(OR)_4$ [46], CuCl [47], MCM-41-SO_3 nanocatalyst [48], P_2O_5-SiO_2 [49] promoted by microwave irradiation [43], Cinchona alkaloid-thiourea [50], Infrared [51, 52] and ultrasound radiation [53].

These catalysts have been applied for the synthesis of chiral amines by oxidative coupling of amines [54, 55], with carbonyl compounds [19, 21, 41, 42] alcohols [34] and acid chlorides [38, 56]. The microwave assisted synthesis has become popular in academic and pharmaceutical areas since this involves a new enabling technology for developing new drugs. Chemists and scientists [19, 21, 41, 57, 58] preferred solvent free microwave synthetic methods for synthesizing organic compounds, since they involve shorter duration, operational simplicity, easy workup procedure, less hazardousness to humans and environment, and better yields. Spectroscopic data is applied for studying the ground state equilibrium of organic molecules through linear free energy relationships [58].

The infrared red and NMR spectroscopic data determines the structure of unsaturated systems, such as E- or Z, *s-cis* and *s-trans* conformers of styrenes, enones, unsaturated acid chlorides, acyl chlorides, and their esters [59, 60]. Recently Suresh et al., [61] have synthesized some aryl *E*-imines and studied the UV, IR and NMR spectral liner free energy relationships through Hammett equation. In their investigations they observed satisfactory and good correlations for the above spectroscopic data with Hammett substituent constants and Swain Lupton's[62]. There is no report has been found in the literature regarding the synthesis and spectral correlations of (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*] thiophene-3-carboxamide derivatives by SiO_2:H_3PO_4 catalyzed solvent-free condensation of 2-amino-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide and various substituted benzaldehydes in microwave irradiation.

Therefore the authors have taken efforts to synthesis the above said chiral imine-carboximido derivatives by solvent free condensations of respective amine with substituted benzaldehydes and studied the effects of substituents on the spectral group frequencies through Hammett correlation using single and multi-regression analysis.

2. EXPERIMENTAL

2. 1. Materials and Methods

All the chemicals involved in the present investigation, have been procured from Sigma-Aldrich and E-Merck chemical company. Melting points of all imines have been determined in open glass capillaries on SUNTEX melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm^{-1}) have been recorded on AVATAR-300 Fourier transform spectrophotometer. Instrum AV300 NMR spectrometer was used for recording NMR spectra operating 500 MHz for recording ^{1}H NMR and 125 MHz for ^{13}C spectra in CDCl$_3$ solvent using TMS as internal standard. Electron impact (EI) (70 eV) and chemical ionization mode FAB$^+$ mass spectra have been recorded on as XHIMADZU MS2010 spectrometer.

2. 3. Synthesis of imines

The starting compound 2-amino-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide[63] and the SiO$_2$-H$_3$PO$_4$ catalyst [64] were prepared by the procedure published in literature.

An appropriate equi-molar quantities of 2-amino-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide (2 mmol), substituted benzaldehydes (2 mmol) and SiO$_2$-H$_3$PO$_4$ (0.5 g) have been taken in borosil beaker and closed with lid. The mixture has been subjected to microwave irradiation for 6-8 minutes in a microwave oven (Scheme 1) at 600W(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 with benzene-hexane mixture gives 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. The analytical, yield, physical constants and mass fragments of the synthesized imido-imine derivatives were presented in Table 1.

(1-10)
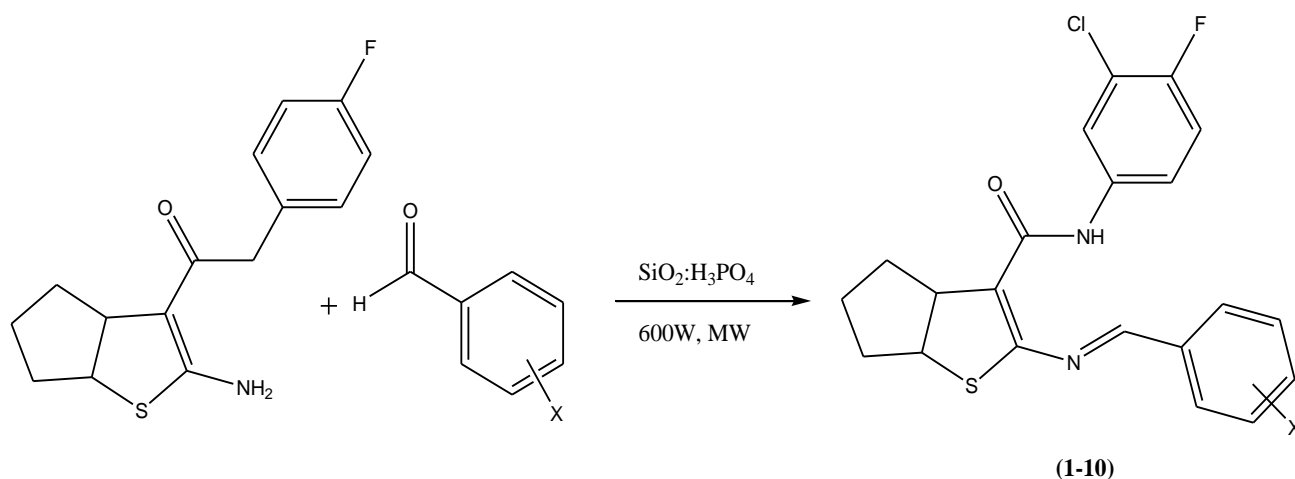
Entry	1	2	3	4	5	6	7	8	9	10
X	H	2-Cl	4-Cl	4-N(CH$_3$)$_2$	2-OH	4-OH	4-OCH$_3$	4-CH$_3$	2-NO$_2$	4-NO$_2$

Scheme 1. Synthesis of (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives under solvent-free conditions.

Table 1. Physical constants and mass spectral data of (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives.

Entry	X	M. F.	M. W.	Yield (%)		m.p. (°C)	Mass (m/z)
				Without catalyst	With (SiO$_2$-H$_3$PO$_4$) Catalyst		
1	H	C$_{21}$H$_{16}$N$_2$OSClF	398	67	90	177-178 178 [65]	398[M$^+$], 400[M^{2+}], 402[M4$^+$]
2	2-Cl	C$_{21}$H$_{15}$N$_2$OSCl$_2$F	432	74	92	190-191 192 [65]	432[M$^+$], 435[M^{2+}], 437[M^{4+}], 439[M^{6+}]
3	4-Cl	C$_{21}$H$_{15}$N$_2$OSCl$_2$F	432	71	89	195-196 195 [65]	432[M$^+$], 435[M^{2+}], 437[M^{4+}], 439[M^{6+}]
4	4-N(CH$_3$)$_2$	C$_{23}$H$_{21}$N$_3$OSClF	441	73	88	216-217 219 [65]	441[M$^+$], 413[M^{2+}], 415[M^{4+}]
5	2-OH	C$_{21}$H$_{16}$N$_2$O$_2$SClF	414	63	87	240-242 245 [65]	414[M$^+$], 416[M^{2+}], 485[M^{4+}]
6	4-OH	C$_{21}$H$_{16}$N$_2$O$_2$SClF	414	66	86	212-123 214 [65]	414[M$^+$], 416[M^{2+}], 485[M^{4+}]
7	4-OCH$_3$	C$_{21}$H$_{18}$N$_2$O$_2$SClF	428	72	92	176-177 178 [65]	428[M$^+$], 430[M^{2+}], 432[M^{4+}]
8	4-CH$_3$	C$_{21}$H$_{18}$N$_2$OSClF	412	65	90	196-197 195 [65]	412[M$^+$], 414[M^{2+}], 416[M^{4+}]
9	2-NO$_2$	C$_{21}$H$_{15}$N$_3$O$_3$SClF	431	59	89	181-182 180 [65]	431[M$^+$], 433[M^{2+}], 435[M^{4+}]
10	3-NO$_2$	C$_{21}$H$_{15}$N$_3$O$_3$SClF	431	67	89	185-186 186 [65]	431[M$^+$], 433[M^{2+}], 435[M^{4+}]

3. RESULTS AND DISCUSSION

3. 1. IR Spectral study

The synthesis of imine derivatives are shown in Scheme 1. In the present study, the authors have chosen a series of imine derivatives for studying the effects of substituent on the spectral group frequencies. The νCO, NH, C-N, C-Cl, C-F, C=N stretching frequencies (cm^{-1}) of these imines have been recorded and are presented in Table 2. These data are correlated with Hammett substituent constants [59-61, 64, 66-72] and Swain-Lupton's [62] parameters. In this correlation the structure parameter Hammett equation employed is as shown in equation (1).

$$\nu = \rho\sigma + \nu_o \qquad \qquad ...(1)$$

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

The observed νCO, NH, C-N, C-Cl, C-F, C=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 parameters[62] . The results of statistical analysis of single parameter correlation are shown in Table 3. The correlation of νCO (cm^{-1}) frequencies of imines with Hammett substituent constants gave satisfactory correlations. The correlation of F and R parameter was fail with these carbonyl frequencies. This is due to the inability of effect of substituents on the carbonyl frequencies and associated with resonance-conjugative structure shown in Fig. 1.

The correlation of νNH (cm^{-1}) these imine derivatives fail with Hammett substituent constants and F and R parameters. All correlations ρ values. This implies that there is a normal substituent effect operates in all system. The failure in correlation was the reason stated earlier and the conjugative structure in Fig. 1.

The νC-N stretches (cm^{-1}) of these imines were correlated satisfactory with Hammett σ, σ^+ and R parameter. The remaining Hammett substituent constants and R parameter were fail in correlation. All correlations produce positive ρ values. This implies that there is a normal substituent effect operates in all systems. The failure in correlation is due the reason stated earlier and associated with resonance-conjugative structure shown in Fig. 1.

The correlation of νC-Cl (cm^{-1}) frequencies of imines with Hammett σ and σ^+ substituent constants gave satisfactory correlations. The remaining Hammett substituent constants, F and R parameter were failing in correlation. All correlations produce positive ρ values. This implies that there is a normal substituent effect operates in all systems. The failure in correlation is due the reason stated earlier and associated with resonance-conjugative structure shown in Fig. 1.

The νC-F stretches (cm^{-1}) of these imines were correlated satisfactory with Hammett σ, σ^+ and R parameter. The remaining Hammett substituent constants and R parameter were fail in correlation. All correlations produce positive ρ values. This implies that there is a normal substituent effect operates in all systems. The failure in correlation is due the reason stated earlier including inductive effects of the substituents and associated with resonance-conjugative structure shown in Fig. 1.

The νC=N stretches (cm^{-1}) of these imines were correlated satisfactory with Hammett σ and σ^+ substituent constants. The remaining Hammett substituent constants, F and R parameter were fail in correlation. All correlations produce positive ρ values. This implies that there is a normal substituent effect operates in all systems. The failure in correlation is due the reason stated earlier including inductive, field effects of the substituents and associated with resonance-conjugative structure shown in Fig. 1.

Table 2. The IR absorptions (v, cm^{-1}) and NMR chemical shifts (δ, ppm) of (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-*2H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives

Entry	X	IR							^{1}H			^{13}C		
		CO	NH	C-N	C-Cl	C-F	C=N	X	NH (s, 1H)	CH (s, 1H)	X	CO	C=N	X
1	H	1683.14	3257.71	845.36	683.09	1241.39	1654.76	---	11.032	8.427	---	166.79	161.54	---
2	2-Cl	1680.33	3298.47	825.94	694.71	1235.22	1619.00	---	11.273	8.623	---	165.81	160.07	---
3	4-Cl	1674.89	3342.11	822.24	689.27	1241.26	1651.06	---	10.415	8.523	---	164.72	159.25	---
4	4-N(CH$_3$)$_2$	1683.68	3354.36	872.09	719.66	1210.32	1623.23	---	11.261	8.762	---	167.14	161.32	26.73 N(CH$_3$)$_2$
5	2-OH	1680.19	3281.59	824.23	684.32	1212.24	1653.23	3456.80 (OH)	10.941	8.791	---	167.73	161.18	---
6	4-OH	1678.26	3101.37	825.34	660.91	1216.21	1656.50	3451.41 (OH)	10.541	8.846	---	168.81	163.25	---
7	4-OCH$_3$	1678.19	3236.42	825.26	676.68	1215.19	1651.08	1256.29 (C-O-C)	10.934	8.401	3.614 (s, 3H, OCH$_3$)	168.71	164.43	58.74 (OCH$_3$)
8	4-CH$_3$	1677.04	3241.43	818.85	683.72	1220.28	1649.00	---	11.209	8.371	2.18 (s, 3H, CH$_3$)	167.27	163.38	27.24 (CH$_3$)
9	2-NO$_2$	1680.98	3289.84	813.18	681.74	1215.88	1645.46	---	11.741	8.931	---	168.71	164.80	---
10	3-NO$_2$	1681.84	3288.85	815.12	685.46	1220.81	1651.41	---	11.841	8.972	---	168.83	165.68	---

Table 3. Results of statistical analysis of IR νCO, NH, C-N, C-Cl, C-F, C=N, NMR δ^1H (ppm) of NH, CH=N and δ^{13}C (ppm) of CO, C=N of (*E*)-2- (substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives with Hammett substituent constants σ, σ^+, σ_I, σ_R, F and R parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated Derivatives
νCO	σ	0.901	1679.85	7.078	2.09	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ^+	0.900	1680.11	8.693	2.09	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_I	0.900	1680.06	9.205	2.10	7	2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ_R	0.903	1680.00	4.593	2.01	7	2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-CH$_3$, 4-NO$_2$
	F	0.800	1679.80	4.144	5.00	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.791	1669.15	3.172	5.23	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
νNH	σ	0.813	3268.46	32.506	7.27	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ^+	0.791	3272.60	16.431	7.57	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_I	0.817	3254.02	50.111	8.00	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_R	0.711	3276.34	31.406	8.34	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.714	3254.74	44.523	8.14	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.801	3277.43	25.055	8.00	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
ν C-N	σ	0.906	829.32	24.492	1.39	8	2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ^+	0.900	825.50	15.801	1.38	8	2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_I	0.850	841.17	40.981	2.37	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_R	0.844	822.39	28.051	2.39	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.851	842.81	43.251	2.39	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.905	820.13	26.296	1.25	8	2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
ν C-Cl	σ	0.901	686.09	6.025	1.54	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ^+	0.900	685.01	4.540	1.55	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ_I	0.710	688.60	8.753	3.55	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ_R	0.715	684.04	8.437	3.67	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$

	F	0.810	689.06	9.561	3.55	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.823	683.00	9.000	3.52	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
ν C-F	**σ**	0.903	122.704	7.635	1.19	8	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 4-NO$_2$
	σ$^+$	0.904	1224.36	7.165	1.10	8	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 4-NO$_2$
	σ$_I$	0.704	1222.19	2.258	1.37	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.814	1226.68	17.591	1.35	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.811	1224.86	6.105	1.24	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.905	1228.86	6.716	1.20	7	4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
ν C=N	**σ**	0.901	1645.38	3.841	1.38	8	H, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$^+$	0.900	1645.93	2.221	1.39	8	H, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_I$	0.903	1646.08	2.011	1.28	8	H, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.813	1647.54	9.113	1.47	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.801	1645.75	0.851	1.50	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.823	1648.09	8.800	1.49	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
δ NH	**σ**	0.905	11.106	0.538	0.39	8	H, 2-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$^+$	0.904	11.713	0.263	0.40	8	H, 2-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_I$	0.817	10.916	0.667	0.44	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.856	11.329	0.982	0.43	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.835	10.866	0.777	0.44	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.847	11.303	0.562	0.42	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
δ CH=N	**σ**	0.903	8.660	0.179	0.22	7	H, 2-Cl, 4-Cl, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$^+$	0.901	8.676	0.555	0.23	7	H, 2-Cl, 4-Cl, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_I$	0.761	8.497	0.552	0.31	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.800	8.682	0.077	0.30	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.719	8.432	0.713	0.31	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.800	8.664	0.701	0.30	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH,

						4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
δ CO	**σ**	0.907	167.44	0.211	1.48	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ$^+$	0.908	167.42	0.153	1.48	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ$_I$	0.801	167.21	0.786	1.57	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.795	167.53	0.275	1.60	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.725	166.94	1.570	1.62	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.805	167.38	0.203	1.49	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
δ C=N	**σ**	0.903	162.45	1.540	2.12	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ$^+$	0.903	162.58	0.471	2.00	7	H, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$
	σ$_I$	0.812	161.82	2.212	2.48	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ$_R$	0.841	163.21	3.202	2.51	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	F	0.793	161.50	3.031	2.61	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	R	0.829	163.02	1.629	2.50	10	H, 2-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$

r = correlation co-efficient; ρ = slope; I = intercept; s = standard deviation;
n = number of substituents.

Some of the single parameter correlations of νCO, NH, C-N, C-Cl, C-F, C=N stretching frequencies (cm^{-1}) with Hammett substituent constants, F and R 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's [62] constants. The corresponding equations are given in (2-13).

$$νCO \ (cm^{-1}) = 1680.96(\pm2.201) - 1.617(\pm0.456) \ σ_I + 1.556 \ (\pm0.412) \ σ_R \qquad …(2)$$
$$(R = 0.916, \ n = 10, \ P > 90 \ \%)$$

$$νCO \ (cm^{-1}) = 1679.79(\pm2.358) - 0.4277(\pm0.049) \ F - 0.598 \ (\pm0.297)R \qquad …(3)$$
$$(R = 0.903, \ n = 10, \ P > 90 \ \%)$$

$$νNH(cm^{-1}) = 3259.65(\pm55.871) + 43.194(\pm11.546) \ σ_I + 14.411 \ (\pm9.104) \ σ_R \qquad …(4)$$
$$(R = 0.918, \ n = 10, \ P > 90 \ \%)$$

$$νNH(cm^{-1}) = 3264.16(\pm59.142) + 33.881(\pm12.386) \ F + 17.867(\pm7.301)R \qquad …(5)$$
$$(R = 0.917, \ n = 10, \ P > 90 \ \%)$$

$$νC\text{-}N(cm^{-1}) = 835.69(\pm11.108) + 33.917(\pm12.955) \ σ_I + 14.711 \ (\pm2.743) \ σ_R \qquad …(6)$$
$$(R = 0.962, \ n = 10, \ P > 95 \ \%)$$

$\nu\text{C-N}(\text{cm}^{-1}) = 832.483(\pm10.860) +31.248(\pm2.267) \text{ F} + 19.602(\pm7.314)\text{R}$ ...(7)
       ($R = 0.968$, n = 10, $P > 95$ %)

$\nu\text{CCl}(\text{cm}^{-1}) = 686.31(\pm11.765) - 5.794(\pm2.413) \, \sigma_I + 6.157(\pm2.200) \, \sigma_R$ ...(8)
       ($R = 0.918$, n = 10, $P > 90$ %)

$\nu\text{CCl}(\text{cm}^{-1}) = 684.84(\pm12.241) - 4.655(\pm2.556) \text{ F} + 8.011(\pm1.511)\text{R}$ ...(9)
       ($R = 0.924$, n = 10, $P > 90$ %)

$\nu\text{CF}(\text{cm}^{-1}) = 1229.87(\pm8.631) - 7.646(\pm1.783) \, \sigma_I + 20.599(\pm6.173) \, \sigma_R$ ...(10)
       ($R = 0.943$, n = 10, $P > 90$ %)

$\nu\text{CF}(\text{cm}^{-1}) = 1225.52(\pm7.923) - 18.491(\pm6.545) \text{ F} + 20.225(\pm9.781)\text{R}$ ...(11)
       ($R = 0.962$, n = 10, $P > 95$ %)

$\nu\text{C=N}(\text{cm}^{-1}) = 1650.64(\pm10.394) - 7.892(\pm2.147) \, \sigma_I + 12.232(\pm1.972) \, \sigma_R$ ...(12)
       ($R = 0.923$, n = 10, $P > 90$ %)

$\nu\text{C=N} (\text{cm}^{-1}) = 1650.71(\pm10.908) - 6.623(\pm0.227) \text{ F} + 9.421(\pm3.146)\text{R}$ ...(13)
       ($R = 0.925$, n = 10, $P > 90$ %)

3. 2. ^{1}H NMR Spectral study

The ^{1}H NMR spectra of these synthesized imido-imine derivatives under investigation have been recorded in deuteriochloroform solution employing tetramethylsilane (TMS) as internal standard. The chemical shifts of (δ, ppm) NH and CH of these imine protons have been assigned and tabulated in Table 2.

In nuclear magnetic resonance spectra, the ^{1}H 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 (14).

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \qquad ... (14)$$

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

The assigned NH and CH of these imido and imine proton chemical shifts (ppm) of these imido-imine derivatives have been correlated with Hammett sigma constants, F and R parameters [59-61, 64, 66-72]. The results of statistical analysis are presented in Table 3. The NH and CH proton chemical shifts (ppm) with Hammett σ and σ[+] constants gave satisfactory correlation. The remaining Hammett substituent constants F and R parameters were fail in correlation. The failure in correlation is due to inability of the effects of substituents including inductive, field, resonance and associated with the conjugative structure shown in Fig. 1.

In view of the inability of the Hammett sigma constants to produce individually satisfactory correlation, the authors think that it is worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's [62] F and R parameters.

The correlation equations for NH and CH protons chemical shifts (δ, ppm) are given in (15-18).

$$\delta NH(ppm) = 11.222(\pm0.298) + 0.272(\pm0.061)\ \sigma_I + 0.821(\pm0.055)\ \sigma_R \qquad \ldots(15)$$
$$(R = 0.958,\ n = 10,\ P > 95\ \%)$$

$$\delta NH(ppm) = 11.106(\pm0.329) + 0.498(\pm0.068)\ F + 0.455(\pm0.404)R \qquad \ldots(16)$$
$$(R = 0.953,\ n = 10,\ P > 95\ \%)$$

$$\delta CH(ppm) = 8.432(\pm0.139) + 0.635(\pm0.288)\ \sigma_I + 0.172(\pm0.026)\ \sigma_R \qquad \ldots(17)$$
$$(R = 0.964,\ n = 10,\ P > 95\ \%)$$

$$\delta CH(ppm) = 8.340(\pm0.122) + 0.820(\pm0.255)\ F - 0.174(\pm0.015)R \qquad \ldots(18)$$
$$(R = 0.977,\ n = 10,\ P > 95\%)$$

3. 3. ^{13}C NMR spectra

Physical organic, spectroscopic chemists and organic chemistry researchers [59-61, 64, 66-72] have made extensive study of ^{13}C NMR spectra for a large number of different ketones, styrenes and keto-epoxides and imines. They have studied linear correlation of the chemical shifts (ppm) of C_α, C_β, CO, C=N and carbons with Hammett σ constants in alkenes, alkynes, acid chlorides styrenes and imines. In the present study, the chemical shifts (δ, ppm) of CO and C=N carbons of the synthesized imido-imine derivatives have been assigned and are presented in Table 2. 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 (ppm) observed for the δ CO and C=N have been correlated with Hammett constants and the results of statistical analysis are presented in Table 3. The δCO and C=N chemical shifts (ppm) gave satisfactory correlations with Hammett σ, σ^+ constants. The remaining Hammett substituent constants, F and R parameters were fail in correlations. All correlations gave positive ρ values. This means that the normal substituent effect operqtes in all systems. The failure in correlation is due to the reason stated earlier and it is associated with the resonance - conjugative structure shown in Fig. 1.

In view of inability of some of the σ constants, F and R parameters to produce individually satisfactory correlation, the authors think that it is worthwhile to seek multiple correlation involving all σ_I, σ_R, F and R parameters [62] . The correlation equations are given in (19-22).

$$\delta CO(ppm) = 167.19(\pm1.122) + 0.806(\pm0.235)\ \sigma_I - 0.941(\pm0.020)\ \sigma_R \qquad \ldots(19)$$
$$(R = 0.914,\ n = 10,\ P > 90\ \%)$$

$$\delta CO(ppm) = 166.61(\pm1.141) + 1.952(\pm0.238)\ F - 0.621(\pm0.140)R \qquad \ldots(20)$$
$$(R = 0.930,\ n = 10,\ P > 90\ \%)$$

$$\delta C=N(ppm) = 162.89(\pm1.561) + 0.828(\pm0.322)\ \sigma_I + 2.877\ (\pm0.029)\ \sigma_R \qquad \ldots(21)$$
$$(R = 0.942,\ n = 10,\ P > 90\ \%)$$

$$\delta C=N(ppm) = 162.09(\pm1.688) + 2.339(\pm0.352)\ F + 1.128(\pm0.028)\ R \qquad \ldots(22)$$
$$(R = 0.937,\ n = 10,\ P > 90\ \%)$$

4. CONCLUSION

Some aryl imido-imines, (*E*)-2-(substituted benzylideneamino)-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta[*b*]thiophene-3-carboxamide derivatives have been synthesized by coupling of 2-amino-N-(3-chloro-4-fluorophenyl)-hexahydro-2*H*-cyclopenta [*b*]thiophene-3-carboxamide and various substituted benzaldehydes using microwave irradiation in the presence of SiO_2-H_3PO_4 catalyst under solvent free conditions. This reaction protocol offers a simple, eco-friendly, non-hazardous, easier work-up procedure and better yields. These imido-imine derivatives are characterized by their physical constants and spectral data. The effects of substituents on the group frequencies have been studied.

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