Available online at www.ilcpa.pl

International Letters of Chemistry, Physics and Astronomy

4 (2014) 109-116 ISSN 2299-3843

IR and NMR spectral studies of some 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines: Assessment of substituent effects

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ABSTRACT

A series containing thirteen title compounds were synthesized and recorded IR and NMR spectra. The infrared νNH, C=N(cm^{-1})stretches, ^{1}H NMR δNH, ^{13}C NMR δC=N(ppm) chemical shifts of synthesized oxazine amines were assigned and correlated with Hammett substituent constants, F and R parameters. From the results of statistical analyses, the effect of substituents on the above spectral frequencies can be discussed.

***Keywords*:** Oxazine-2-amines; IR spectra; NMR spectra; Hammett correlation; Substituent constants

1. INTRODUCTION

Spectroscopic data are useful for ground state equilibration of organic compounds [1]. From the infrared spectral frequencies *E s-cis* and *s-trans* conformers of styrenes [2], polyenes [3], chalcones [4], unsaturated aldehydes [5], acid chlorides [6], unsaturated esters [7], *gauche* and *anti*- form acyl halides and its esters [8]. Nuclear magnetic resonance spectral chemical shifts was used for prediction of the spatial arrangement of protons such as *cis* and *trans* of organic stereo chemical compounds [9]. Now-a-days chemists and spectroscopic researchers [10-15] have paid much more interest for correlation of spectral data with Hammett substituent constants. Thirunarayanan and Ravi [15] have synthesized and studied the effect of substituents of some pyrazoline-1-ethanones. Substituent effects on the spectral group frequencies of 9*H*-fluorenayl bromides were investigated by Thirunarayanan [16]. Sakthinathan et al., have studied the effect of substituents on naphthyl based pyrazoline derivatives [17]. Sasikala et al., [18] have investigated the effect of substituents and antimicrobial activities of some 5-bromo-2-thienyl based pyrazolines. The spectral correlation of infrared and nuclear magnetic resonance spectra of *E*-imines have been studied by Sakthinathan et. al. and Suresh et al., [19,20]. Thirunarayanan and Sekar have studied the substituent effects on the IR and NMR spectral frequencies of some 3-(3,4-dichlorophenyl)-pyrazoline carbothiomides [21]. Spectral correlation study was first studied on the Trogers

bases by Thirunarayanan [22]. Recently, Janaki et al, Vanangamudi et al, Subramanian et al. and Thirunarayanan et al., [23-26,29-32] have been studied the effects of substituents on the spectral data of various chalcones. Within the above view, there is no report available for the study of spectral correlation analysis on 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}H-1,3-oxazine-2-amines. Therefore the author have taken effort to synthesis and recorded the IR and NMR spectra for studying spectral correlation of above title compounds.

2. EXPERIMENTAL

2. 1. General

All chemicals and solvents used in this present study were procured from Sigma-Aldrich and Merck companies. The infrared spectra of all oxazine imines have been recorded in SHIMADUZ Fourier Transform IR spectrophotometer using KBr disc. The NMR spectra of all compounds were recorded in BRUKER AV 400 type spectrometer, Using $CDCl_3$ as a solvent, 400 MHz frequency was applied for recording ^{1}H, 100 MHz for ^{13}C NMR spectra, taking TMS as standard.

2. 2. Synthesis of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}H-1,3-oxazine-2-amines [27]

The title oxazine-2-amines were synthesized and their purities were checked by literature method.

3. RESULTS AND DISCUSSION

In the present study, the author have investigated the effect of substituents on the infrared νNH, C=N (cm^{-1}) stretches, ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}H-1,3-oxazine-2-amines by Hammett correlation (Table 1).

Table 1. the infrared νNH, C=N (cm^{-1}) stretches, ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}H-1,3-oxazine-2-amines.

	X	IR (ν, cm^{-1})		^{1}H (δ, ppm)	^{13}C (δ, ppm)
		NH	C=N	NH	C=N
1	H	3553	1592	2.234	165.67
2	3-NH_2	3545	1592	2.114	165.46
3	4-NH_2	3532	1598	2.123	165.25
4	3-Br	3543	1606	2.223	164.15
5	3-Cl	3540	1592	2.121	165.35
6	4-Cl	3545	1618	2.124	164.89
7	4-$N(CH_3)_2$	3540	1602	2.034	164.89
8	4-OH	3553	1589	2.223	165.87
9	4-OCH_3	3538	1634	2.242	164.48
10	4-CH_3	3544	1623	2.219	164.98
11	2-NO_2	3559	1622	2.334	165.62
12	3-NO_2	3555	1615	2.324	165.40
13	4-NO_2	3555	1634	2.190	165.35

3. 1. Infrared spectral study

In infrared spectral study, the νNH, C=N (cm^{-1}) stretches of synthesized amines were correlated by the Hammett equation as shown in equation (1).

$$\nu = \rho\sigma + \nu_o \quad \ldots(1)$$

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

The assigned νNH, C=N (cm^{-1}) stretches, ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were presented in Table1. These data were correlated with Hammett substituent constants, F and R parameters linear regression analysis. The result of statistical analysis was presented in Table 2.

The correlation of infrared νNH (cm^{-1}) stretches of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were satisfactorily with Hammett substituent constants, F and R parameters excluding H, 3-NH_2, 4-$N(CH_3)_2$, 4-OH and 4-CH_3 substituents. When these substituents were included in the correlation, the correlation was reduced considerably. All correlations gave positive ρ values. This implies that the normal substituent effects operates in all systems.

The correlation of infrared νCN (cm^{-1}) stretches of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were satisfactorily with Hammett substituent constants, F and R parameters excluding H, 3-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3 and 4-CH_3 substituents. When these substituents were included in the correlation, the correlation was reduced considerably. All correlations gave positive ρ values. This implies that the normal substituent effects operates in all systems.

Table 2. Results of statistical analysis of infrared νNH, C=N, ^{1}H NMR δNH, ^{13}C NMR of δC=N (ppm) of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines derivatives with Hammett substituent constants σ, σ^+, σ_I, σ_R, F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
νNH	σ	0.953	3545.02	9.278	7.07	10	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.946	3546.63	5.080	7.42	10	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.948	3541.40	15.390	7.33	11	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-NO_2 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 2-NO_2, 3-NO_2,
	σ_R	0.972	3550.73	22.304	5.73	11	H, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.953	3540.65	17.596	7.10	11	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.965	3550.64	13.325	6.34	13	H, 3-NH_2,4-NH_2,3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3,2-NO_2, 3-NO_2, 4-NO_2
νC=N	σ	0.934	1607.31	12.971	15.90	10	H, 3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-OH, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.962	1609.37	5.821	16.39	10	H, 3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-OH, 2-NO_2, 3-NO_2, 4-NO_2

	σ_I	0.941	1600.54	26.540	15.41	10	H, 3-NH_2, 4-NH_2, 3-Br, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.945	1614.54	27.913	15.17	11	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.945	1599.27	30.247	15.16	9	H, 3-NH_2, 4-NH_2, 3-Br, 4-Cl, 4-$N(CH_3)_2$, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.944	1614.90	18.690	15.26	11	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δNH	σ	0.953	2.178	0.099	0.07	12	H, 3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.951	2.196	0.060	0.07	12	H, 3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.944	2.148	0.152	0.08	13	H, 3-NH_2,4-NH_2,3-Br, 3–Cl, 4-Cl,4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.968	3.248	0.222	0.06	10	H, 3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.947	2.130	0.168	0.07	11	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.966	2.240	0.151	0.06	13	H,3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
δCN	σ	0.915	165.15	0.162	0.50	11	H, 3-NH_2, 4-NH_2, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ^+	0.915	165.18	0.100	0.50	11	H, 3-NH_2, 4-NH_2, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_I	0.810	165.17	0.030	0.50	13	H,3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	σ_R	0.916	165.25	0.364	0.49	10	H, 4-NH_2, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	F	0.801	165.16	0.037	0.50	13	H,3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl,4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2, 4-NO_2
	R	0.901	165.24	0.189	0.50	9	3-NH_2, 4-NH_2, 3-Br, 3–Cl, 4-Cl, 4-$N(CH_3)_2$, 4-OH, 4-OCH_3, 4-CH_3

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

Similarly the multi-functional regression analysis of these stretches shows satisfactory correlation with σ_I and σ_R or F and R Swain-Lupton [28] parameters. The generated multi-regression analysis equations are given in (2-5)

$$\nu NH(cm^{-1}) = 3549.99(\pm4.373) + 1.699(\pm0.873)\sigma_I + 21.282(\pm8.533)\sigma_R \quad ...(2)$$
(R = 0.973, n = 13, P > 95 %)

$$\nu NH(cm^{-1}) = 3547.38(\pm4.788) + 7.430(\pm0.948)F + 10.961(\pm6.007)R \quad ...(3)$$
(R = 0.967, n = 13, P > 95 %)

$$\nu CN(cm^{-1}) = 1608.41(\pm 11.357) + 13.998(\pm 2.268)\sigma_I + 19.509(\pm 2.192)\sigma_R \quad ...(4)$$
(R = 0.948, n = 13, P > 90 %)

$$\nu CN(cm^{-1}) = 1606.25(\pm 11.443) + 19.713(\pm 2.262)F + 11359(\pm 1.435)R \quad ...(5)$$
(R = 0.950, n = 13, P > 95 %)

3. 2. NMR spectral study

^{1}H NMR spectral study

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 (6).

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \quad ... (6)$$

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

The assigned ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were presented in Table1. These data were correlated with Hammett substituent constants, F and R parameters linear regression analysis. The result of statistical analysis was presented in Table 2. From Table 2, the δNH (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were satisfactorily correlated with Hammett substituent constants, F and R parameters excluding H, 4-OH, 4-OCH_3, 4-CH_3, 2-NO_2, 3-NO_2 and 4-NO_2 substituents. If these substituents were accomplished with regression, they reduced the regression coefficient considerably. All correlations gave positive ρ values. This means that then normal substituent effects operates in all systems.

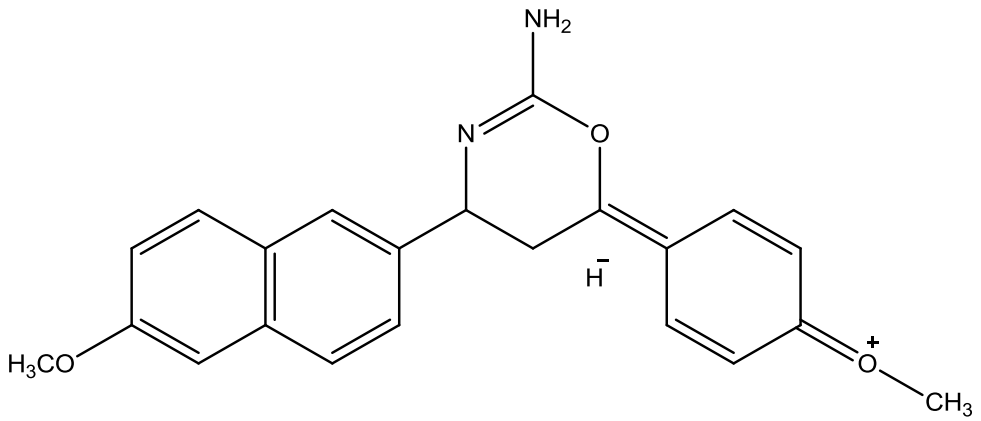

Fig. 1. The resonance-conjugative structure.

From Table 2, the ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines were satisfactorily correlated with Hammett σ, σ^+, σ_R substituent constants and R parameters excluding H, 3-NH_2, 3-Br, 4-OH, 2-NO_2, 3-NO_2 and 4-NO_2 substituents. If these substituents were accomplished with regression, they reduced the regression coefficient considerably. The Hammett σ_I constant

and F parameter were fail in correlation. This is due to the inability of substituent constants for prediction of reactivity on the chemical shifts of oxazine amines and associated with resonance conjugative structure shown in Fig. 1. All correlations gave positive ρ values. This means that then normal substituent effects operates in all systems.

In view of the inability of prediction of effect of substituents by single regression analysis with Hammett substituent constants, F and R parameters, they are worthwhile when seeking in multi-regression analysis for ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines. The generated multi-regression[28] analysis equations are given in (7-10)

$$\delta NH(ppm) = 2.231(\pm0.054) + 0.013(\pm0.001)\sigma_I + 0.216(\pm0.090)\sigma_R \quad ...(7)$$
(R = 0.968, n = 13, P > 95 %)

$$\delta NH(ppm) = 2.221(\pm0.051) + 0.042(\pm0.012)F + 0.135(\pm0.061)R \quad ...(8)$$
(R = 0.967, n = 13, P > 95 %)

$$\delta CN(ppm) = 165.39(\pm0.377) - 0.332(\pm0.075)\sigma_I + 0.563(\pm0.072)\sigma_R \quad ...(9)$$
(R = 0.923, n = 13, P > 90 %)

$$\delta CN(ppm) = 165.33(\pm0.390) - 0.211(\pm0.077)F + 0.267(\pm0.049)R \quad ...(10)$$
(R = 0.917, n = 13, P > 90 %)

4. CONCLUSIONS

Totally thirteen 4-(6-methoxy-2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amine compounds were synthesized and recorded IR and NMR spectra. The infrared νNH, C=N (cm^{-1}) stretches, ^{1}H NMR δNH, ^{13}C NMR δC=N (ppm) chemical shifts of synthesized oxazine amines were assigned and correlated with Hammett substituent constants, F and R parameters. From the single parameter correlation analyses, the infrared νNH, C=N (cm^{-1}) stretches and ^{1}H NMR δNH (ppm) chemical shifts correlated satisfactorily with Hammett substituent constants, F and R parameters. The ^{13}C NMR δC=N (ppm) chemical shifts of synthesized amines All the above spectral frequencies were satisfactorily correlated with σ_I and σ_R or F and R Swain-Lupton parameters in multi-regression analysis.

ACKNOWLEDGEMENT

The author thank DST- NMR Facility, Department of Chemistry, Annamalai University, Annamalainagar-608002 for recording NMR spectra of compounds.

References

[1] G. Thirunarayanan, M. Gopalakrishnan G. Vanangamudi, *Spectrochim. Acata* 67A (2007) 1106-1612.

[2] A. Perjessy, M. Laucova, *Coll. Czech. Chem. Commun*. 36 (1971) 2944-22950.

[3] W. F. Winecoff and D. W. Boykin Jr., *J. Org. Chem*. 37 (4) (1972) 676.

[4] G. Thirunarayanan, P. Ananthakrishna Nadar, *Asian J. Chem*. 14(3-4) (2002) 1518-1522.

[5] D. Seebach, R. Gilmour, U. Grosˇelj, G. Deniau, C. Sparr, M. O. Ebert, A. K. Beck, *Helvi. Chem. Acta.* 93 (2010) 603-634.

[6] T. A. Foglia, P. A. Barr, M. J. Idacavage, *J. Org. Chem.* 41 (1976) 3452-3455.

[7] V. Všetečka, J. Pecka, M. Procházka, *Collect. Czech. Chem. Commun.* 47 (1982) 277-285

[8] G. Thirunarayanan, G. Vanangamudi, V. Sathiyendiran, K. Ravi, *Indian J. Chem*. 50B(4) (2011) 593-604.

[9] G. Thirunarayanan, P. Mayavel, K. Thirumurthy, S. Dineshkumar, R. Sasikala, P. Nisha, A. Nithyaranjani, *European Chem. Bull*. 2(9) (2013) 598-605.

[10] K. Rajasekharan, C. Gnansekaran, *J. Chem. Soc*, Perkin Trans II (1987) 263-266.

[11] K. Rajasekharan, C. Gnansekaran, *Indian J. Chem.* 25A (1986) 64-66.

[12] V. Mala, K. Sathiyamoorthy, S. P. Sakthinathan, D. Kamalakkannan, R. Suresh, G. Vanangamudi and G. Thirunaryanan, *Q-Science Connect*, 2013:7; DOI http://dx.doi.org/10.5339,2013.7

[13] G. Vanangamudi, M. Subramanian, P. Jayanthi, R. Arulkumaran, D. Kamalakkannan and G. Thirunarayanan, *Arabian J. of Chemistry*, (2011). doi:10.1016/j.arabjc.2011.07.019

[14] R. Arulkumaran, S. Vijayakumar, R. Sundararajan, S. P. Sakthinathan, D. Kamalakkannan, R. Suresh, K. Ranganathan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 17-38.

[15] G. Thirunaryanan, K. Ravi, *International Letters of Chemistry, Physics and Astronomy* 14 (2013) 44-57.

[16] G. Thirunarayanan, *International Letters of Chemistry*, *Physics and Astronomy* 9(2) (2013) 152-161.

[17] S. P. Sakthinathan, G. Vanangamudi, G. Thirunarayanan, *Spectrochim. Acta* 95A (2012) 693-700.

[18] S Sasikala, K Thirumurthy, P. Mayavel, G. Thirunarayanan, *Org. Med. Chem. Lett*. (2012) doi:10.1186/2191-2858-2-20

[19] S. P. Sakthinathan, R. Suresh, V. Mala, K. Sathiyamoorthy, D. Kamalakkannan, K.Ranganathan, S. John Joseph, G. Vanangamudi, G. Thirunarayanan, *Int. J. Sci. Res. Know.* 1(11) (2013) 472-483.

[20] R. Suresh, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, R. Sundararajan, S.P. Sakthinathan, S. Vijayakumar, K. Sathiyamoorthy, V. Mala, G. Vanangamudi, K. Thirumurthy, P. Mayavel, G. Thirunarayanan, *Spectrochim. Acta.* 101A (2013) 239-248.

[21] G. Thirunarayanan, K. Sekar, *Organic Chem: An Indian J.* 9(12) (2013) 483-492.

[22] G. Thirunarayanan, M. Suresh, *International Letters of Chemistry, Physics and Astronomy* 1 (2014) 67-73.

[23] P. Janaki, K. G. Sekar, G. Thirunarayanan, *Journal of Saudi Chem. Soc*. (2012) Doi.10.1016/j.jscs.2012.11.013

[24] G. Vanangamudi, M. Subramanian, G. Thirunarayanan, *Arabian J. Chem*. (2013) DOI: 10.1016/j.arabjc.2013.03.006,

[25] M. Subramanian, G. Vanangamudi, G. Thirunarayanan, *Spectrochim. Acta* 110A (2013) 116-123.

[26] G. Thirunarayanan, G. Vanangamudi, M. Subramanian, *Organic Chemistry: An Indian J* 9(1) (2012)1-16.

[27] G. Thirunarayanan, *Int. J. Sci. Res. Know*. 1(12) (2013) 480-596.

[28] Swain C. G., Lupton E. C. Jr., *J. Am. Chem. Soc*. 90 (1968) 4328-4337.

[29] G. Thirunarayanan, K. G. Sekar, *International Letters of Chemistry, Physics and Astronomy* 10(1) (2013) 18-34.

[30] K. G. Sekar, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 8(3) (2013) 249-258

[31] S. Vijayakumar, R. Arulkumaran, R. Sundararajan, S. P. Sakthinathan, R. Suresh, D. Kamalakkannan, K. Ranganathan, K. Sathiyamoorthy, V. Mala, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 9(1) (2013) 68-86.

[32] S. P. Sakthinathan, R. Suresh, V. Mala, K.Sathiyamoorthi, D. Kamalakkannan, K. Ranganathan, R. Arulkumaran, S. Vijayakumar, R. Sundararajan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 6 (2013) 77-90.

(Received 26 November 2013; accepted 30 November 2013)