ISSN : 0974 - 7524 Volume 11 Issue 1

Physical CHEMISTRY
An Indian Journal

Full Paper

PCAIJ, 11(1), 2016 [035-044]

IR and NMR spectral hammett correlations in (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones

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ABSTRACT

A series of some novel (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones have been synthesized by aqueous phase fly-ash catalyzed [4+2] Diels-Alder reaction of 2-naphthyl chalcones and cyclopentadiene according to literature. The yields of the methanones are more than 60%. These methanones were characterized by their physical constants and spectral data. The assigned characteristic infrared and NMR spectral data are correlated using Hammett equation with Hammett substituent constants, F and R Swain-Lupton's parameters by single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the spectral data has been discussed with correlation co-efficient value in all correlations.

INTRODUCTION

Methanone and its derivatives are important biological substrates[1]. Due to the presence of keto, unsaturation moieties and polar substituents are origin for the biological potentials. Presence of substituents enhances the structural activity relationships(SAR) of organic compounds[2]. Spectroscopic data of organic compounds including methanone derivatives are useful for prediction of ground state equilibrations[3]. From infrared spectra the *s-cis* and *s-trans* conformers of unsaturated ketones, *anti*- and *syn*- form of ω-bromo esters have been predicted[4]. Shielding light on plant biology was reported thorough the study of FT IR spectroscopy of pollen[5]. NMR spectroscopy was applied to confirm E or Z isomers of all types of ketones, unsaturated ketones, spatial arrangements of protons in pyrazoline and its derivatives, oxazine derivatives[6, 7]. Now-a-days physical organic chemist paid much more interest for spectral and biological activity correlations such as QSAR, QPR, QSR and SAR using Hammett equation with its constants and Swain-Lupton's[3,4, 8,9] constants by single and multi-linear regression analysis. Recently, Thirunarayanan et al have studied the effect of substituents on spectral data of pyrazolecarbothioamides[8]. Arulkumaran et al have studied the spectral correlation study and predict the substituent effects on the spectral frequencies on pyrimidine carboxamides[10]. Thirunarayanan and Sekar[11-14] have studied the spectral linearity of some oxazine thione derivatives, pyrimidine diazenyl benzoic acids, hydrazides and N-acetyl pyrazolines. Mayavel et. al.,[15] have studied the effect of substituents on some *E*-Schiff's bases through spectral data using Hammett equation. Kalyanasundaram et al[16] have studied the spectral linearity of some phenoxyphenyl chalcones. Within

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the above view there is no report available for the spectral correlation study of novel (2-naphthyl)-3-(substituted phenyl) bicyclo[2.2.1]hept-5-ene-2-yl)methanones in literature in the past. Therefore the author has taken efforts to prepare the above mentioned methanones and recorded infrared and NMR spectra for studying the spectral correlation analysis.

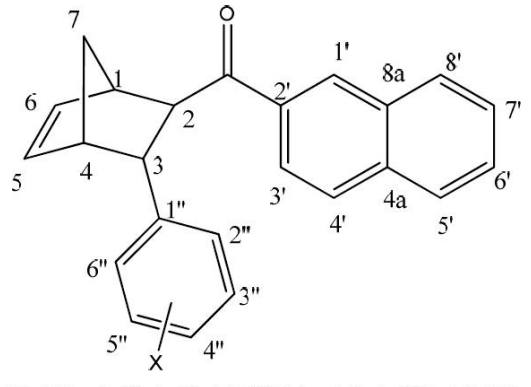
EXPERIMENTAL

General

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

Synthesis of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl) methanones[2].

The (2-naphthyl)-3-(substituted phenyl) bicyclo [2.2.1] hept-5-ene-2-yl) methanones were synthesized and the purities of the compounds were examined by literature method[1, 29-31]. Appropriate equimolar quantities of 2-naphthyl chalcones (2 mmol) in 15 mL of ethanol, cyclopentadiene (2 mmol) and 4 g of fly-ash in 20 mL of water were stirred for 6 h at 0–4 °C overnight. Progress of the reaction was monitored by thin-layer chromatography. Dichloromethane (10 mL) was added and the extract was separated by filtration. The filtrate was washed with water, brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated to give a solid product. The crude product was further purified by recrystallization with ethanol. The general structure of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl) methanones is shown in Figure 1. The physical constants and analytical data of these methanones are presented in TABLE 1. The infrared characteristicstretches (ν, cm^{-1}) and NMR chemical shifts (δ, ppm) of methanones are presented in TABLE 2.



X= H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2

Figure 1 : General structure of(2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl) methanones

RESULTS AND DISCUSSION

Infrared spectral study

In the present investigation, the author have studied the effects of substituents on the characteristic infrared frequencies νCO, -CH=CH-$_{op}$ and >C=C<$_{op}$(cm^{-1})of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones by single and multi-linear regression analysis[3, 4, 6, 7, 10-20] using Hammett equation with Hammett substituent constants and Swain-Lupton's constants[8] F and R parameters. The assigned νCO, -CH=CH-$_{op}$ and >C=C<$_{op}$of of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones are presented in TABLE 2. In infrared spectral correlations, the Hammett equation was employed as,

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

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

The results of statistical analysis are presented in TABLE 3. TABLE 3 reveals that the single parameter correlation of νCO (cm^{-1}) with Hammett σ, σ^+, σ_R constants and R parameters gave satisfactory correlations(σ: r=0.909; σ^+:r=0.905; σ_R: r=928 and R: r=0.907). Remaining Hammett σ_I constant and F parameter were fail in correlations.The single of -CH=CH-$_{op}$ (cm^{-1}) frequencies with Hammett σ, σ^+, σ_R constants and R parameters gave satisfactory correlations (σ: r=0.907; σ^+: r=0.906; σ_R: r=0.908and R: r=0.907). Hammett σ_I constant and F parameter

TABLE 1 : The physical constants, analytical and mass fragments of the of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones

Entry	X	M.F.	M.W.	Mp(°C)a	Mass (*m/z*)
1	H	$C_{20}H_{18}O$	324	116–117	324 [M^+], 197, 155, 121, 93, 77, 68, 52, 42, 29, 27
2	3-Br	$C_{20}H_{19}BrO$	403	127-128	403 [M^+], 405 [M^{2+}], 323, 247, 231, 203, 196, 120, 111, 79,77, 35, 29
3	3-Cl	$C_{20}H_{19}ClO$	358	142–143	358 [M^+], 360 [M^{2+}], 323, 247, 231, 203, 155, 127, 111, 77, 35, 29
4	4-Cl	$C_{20}H_{19}ClO$	358	142–143	358 [M^+], 360 [M^{2+}], 323, 247, 231, 203, 155, 127, 111, 77, 35, 29
5	4-$N(CH_3)_2$	$C_{26}H_{25}NO$	367	128–129	367 [M^+], 352, 337, 323, 247, 240, 212, 155, 127, 120, 93, 77, 15
6	4-F	$C_{20}H_{19}FO$	342	130–132	342 [M^+], 344 [M^{2+}], 323, 247, 187, 155, 127, 95, 93, 77, 29, 19
7	4-OH	$C_{20}H_{20}O_2$	340	152–153	340 [M^+], 323, 247, 213, 185, 169, 155, 127, 93, 77, 29, 17
8	4-OCH_3	$C_{25}H_{22}O_2$	354	120–121	354 [M^+], 339, 323, 247, 199, 155, 107, 93, 91, 77, 31, 15
9	4-NO_2	$C_{24}H_{19}NO_3$	369	132–134	369 [M^+], 323, 247, 242, 214, 155, 127, 122, 93, 88, 77, 46, 27, 15

a=Ref. 2

TABLE 2 : Infrared and NMR spectroscopic data of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1]hept-5-ene-2-yl)methanones

Entry	X	IR, ν(cm^{-1})			^{1}H NMR δ(ppm)							
		CO	CH=CH_{op}	C=C_{op}	H_1(*dd*)	H_2 (*t*)	H_3(*t*)	H_4 (*dd*)	H_5(*d*)	H_6 (*d*)	H_7(*dd*)	H_{7a}(*dd*)
1	H	1662	1062	675	2.66	3.19	3.62	2.02	5.50	5.93	2.15	1.58
2	3-Br	1648	1046	608	2.88	3.22	3.65	2.72	5.49	5.96	2.14	1.54
3	3-Cl	1659	1055	673	2.85	3.76	3.58	2.86	5.40	5.98	2.20	1.63
4	4-Cl	1653	1063	614	2.49	3.88	3.5	2.55	5.01	5.10	2.13	1.48
5	4-$N(CH_3)_2$	1644	1046	613	2.78	2.61	3.48	2.73	5.49	5.96	2.67	1.40
6	4-F	1628	1050	667	2.84	3.76	3.68	2.83	5.57	5.68	2.56	1.63
7	4-OH	1637	1019	671	2.85	3.66	3.99	2.72	5.47	5.77	2.72	1.75
8	4-OCH_3	1655	1035	633	2.81	2.82	3.18	2.71	5.58	5.62	2.55	1.56
9	4-NO_2	1685	1087	682	3.03	3.75	3.58	2.75	5.96	5.39	2.20	1.44

Entry	X	^{13}C NMR δ(ppm)										
		CO	C1	C_2	C_3	C_4	C_5	C_6	C_7	$C_{1'}$	$C_{1''}$	C_{ipos}
1	H	190.53	40.33	54.47	46.03	50.29	135.47	45.86	130.02	127.29	127.24	190.53
2	3-Br	190.53	40.34	54.81	46.22	50.37	135.64	45.41	129.85	136.96	148.48	190.53
3	3-Cl	189.57	39.37	54.98	38.42	48.44	135.83	45.87	131.15	142.96	127.49	189.57
4	4-Cl	190.15	41.16	54.08	46.07	51.29	135.17	46.83	130.12	144.85	132.48	190.15
5	4-$N(CH_3)_2$	190.55	41.20	54.81	45.19	50.37	135.27	46.22	130.25	136.26	148.80	190.55
6	4-F	191.37	42.81	54.03	46.27	50.90	135.37	47.17	131.05	142.34	161.40	191.37
7	4-OH	189.21	42.72	54.22	46.21	51.32	135.62	46.74	131.19	129.30	158.29	189.21
8	4-OCH_3	190.05	42.72	54.77	46.17	51.32	135.58	45.86	131.97	139.49	158.82	190.05
9	4-NO_2	189.39	43.72	52.48	44.54	50.36	135.72	46.57	132.01	153.29	146.82	189.39

were fail in correlations. The single of >C=C<$_{op}$ (cm^{-1}) frequencies with Hammett σ and σ$^+$gave satisfactory correlations(σ: r=0.963 and σ$^+$: r=0.903). The Hammett σ$^+$, σ_I constants, F and R parameters gave poor correlations.. All correlations gave positive ρ values. This implies that the normal substituent ef-

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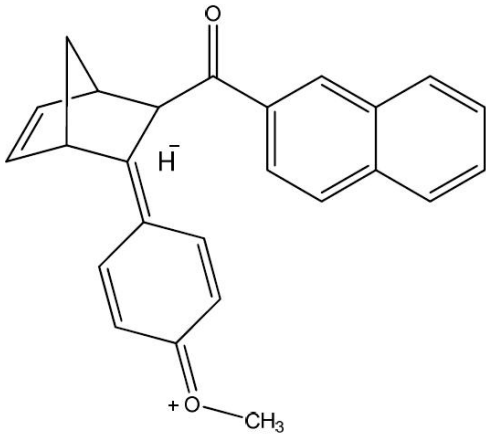

Figure 2 : The resonance-conjugative structure

fect operates in all systems. The fail in correlation was due to the inability of prediction of effect of substituents on the frequencies along with the resonance-conjugative structure as shown in Figure 2

In single parameter correlations of characteristic infrared frequencies νCO, -CH=CH-$_{op}$ and >C=C<$_{op}$ (cm^{-1})of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl)methanones with Hammett substituents and F and R parameters, some of them produced poor correlation coefficients. While seeking in multi-parameter correlations of these frequencies with Swain-Lupton's constants[8] gave satisfactory correlation coefficients. The generated multi-linear regression analysis equations are shown in (2-7).

$$\nu CO(cm^{-1}) = 1669.49(\pm 8.809) + 6.222(\pm 1.760)\sigma_I + 59.842(\pm 15.760)\sigma_R \quad (2)$$
(R= 0.984, n = 9, P > 95%)

$$\nu CO(cm^{-1}) = 1670.10(\pm 9.741) + 12.051(\pm 1.854)F + 35.588(\pm 11.737)R \quad (3)$$
(R = 0.977, n = 9, P > 95%)

$$\nu\text{-CH=CH-}_{op}(cm^{-1}) = 1061.10(\pm 11.700) + 14.987(\pm 2.259)\sigma_I + 58.701(\pm 20.868)\sigma_R \quad (4)$$
(R= 0.979, n = 9, P > 95%)

$$\nu\text{-CH=CH-}_{op}(cm^{-1}) = 1060.40(\pm 11.756) + 13.047(\pm 2.232)F + 37.955(\pm 14.161)R \quad (5)$$
(R = 0.976, n = 9, P > 95%)

$$\nu\text{-CH=CH-}_{op}(cm^{-1}) = 656.85(\pm 29.455) + 6.353(\pm 2.566)\sigma_I + 42.628(\pm 12.516)\sigma_R \quad (6)$$
(R= 0.934, n = 9, P > 90%)

$$N\text{>C=C<}_{op}(cm^{-1}) = 651.79(\pm 27.139) + 18.432(\pm 51.646)F + 28.316(\pm 32.689)R \quad (7)$$
(R = 0.937, n = 9, P > 90%)

^{1}H NMR spectral study

TABLE 3 : Resultsofstatisticalanalysis of IR spectral data of (2-naphthyl)-3-(substituted phenyl)bicyclo [2.2.1] hept-5-ene-2-yl)methanones with Hammett σ, σ$^+$, σ$_I$, σ$_R$constants, F and rparameters

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
νCO(cm^{-1})	σ	0.906	1651.10	22.063	13.82	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 4-OH, 4-OCH$_3$, 4-NO$_2$
	σ$^+$	0.905	1654.49	11.012	14.76		
	σ$_I$	0.812	1647.26	14.348	17.10		
	σ$_R$	0.928	1666.38	58.018	9.35		
	F	0.803	1653.41	2.820	17.42		
	R	0.907	1664.94	34.298	11.33		
νCH=CH$_{op}$(cm^{-1})	σ	0.907	1049.73	30684	14.03	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 4-OH, 4-OCH$_3$, 4-NO$_2$
	σ$^+$	0.906	1054.62	16.239	15.10		
	σ$_I$	0.881	1039.30	34.666	18.71		
	σ$_R$	0.901	1067.16	62.860	12.69		
	F	0.823	1042.60	23.056	19.58		
	R	0.907	1065.91	39.333	13.50		
νC=C$_{op}$(cm^{-1})	σ	0.963	647.27	20.946	31.37	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 4-OH, 4-OCH$_3$, 4-NO$_2$
	σ$^+$	0.903	651.06	13.379	30.97		
	σ$_I$	0.814	641.02	21.006	32.50		
	σ$_R$	0.834	659.56	44.491	31.67		
	F	0.819	638.51	25.900	32.34		
	R	0.835	659.57	30.264	30.18		

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

TABLE 4 : Resultsofstatisticalanalysis of^{1}H MNR spectral data of (2-naphthyl)-3-(substituted phenyl)bicyclo [2.2.1] hept-5-ene-2-yl)methanones with Hammett σ, σ$^+$, σ$_I$, σ$_R$constants, F and Rparameters

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
δH_1(ppm)	σ	0.829	2.793	0.098	0.15	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.818	2.805	0.035	0.15		
	σ$_I$	0.804	2.699	0.280	0.14		
	σ$_R$	0.801	2.816	0.071	0.16		
	F	0.845	2.683	0.301	0.13		
	R	0.821	2.803	0.012	0.14		
δH_2(ppm)	σ	0.906	3.368	0.664	0.37	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.916	3.482	0.391	0.36		
	σ$_I$	0.907	2.879	0.491	0.35		
	σ$_R$	0.837	3.589	0.736	0.45		
	F	0.906	2.905	1.304	0.37		
	R	0.848	3.632	0.617	0.43		
δH_3(ppm)	σ	0.806	3.582	0.028	0.22	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.803	3.589	0.225	0.22		
	σ$_I$	0.811	3.554	0.085	0.22		
	σ$_R$	0.802	3.589	0.018	0.22		
	F	0.815	3.528	0.145	0.22		
	R	0.801	3.580	0.100	0.22		
δH_4(ppm)	σ	0.804	2.651	0.045	0.26	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.800	2.651	0.145	0.27		
	σ$_I$	0.906	2.404	0.706	0.21		
	σ$_R$	0.803	2.547	0.425	0.24		
	F	0.906	2.367	0.748	0.19		
	R	0.817	2.556	0.265	0.25		
δH_5(ppm)	σ	0.824	5.489	0.133	0.25	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.815	5.506	0.047	0.25		
	σ$_I$	0.819	5.419	0.219	0.25		
	σ$_R$	0.806	5.563	0.788	0.25		
	F	0.800	5.385	0.291	0.25		
	R	0.815	5.534	0.100	0.25		
δH_6(ppm)	σ	0.803	5.722	0.221	0.30	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.802	5.689	0.131	0.31		
	σ$_I$	0.841	5.945	0.667	0.28		
	σ$_R$	0.823	5.634	0.302	0.31		
	F	0.841	5.920	0.548	0.29		
	R	0.821	5.621	0.240	0.31		
δH_7(ppm)	σ	0.907	2.939	0.438	0.16	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.908	2.317	2.631	0.14		
	σ$_I$	0.832	2.497	2.361	0.25		
	σ$_R$	0.908	2.143	0.900	0.13		
	F	0.806	2.395	0.064	0.26		
	R	0.913	02.139	0.621	0.11		
δH_{7a}(ppm)	σ	0.811	1.558	0.028	0.11	9	H, 3-Br, 3-Cl, 4-Cl, 4-N(CH_3)$_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ$^+$	0.800	1.556	0.005	0.11		
	σ$_I$	0.801	1.558	0.048	0.11		
	σ$_R$	0.811	1.528	0.111	0.11		
	F	0.805	1.546	0.628	0.11		
	R	0.812	1.543	0.036	0.11		

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

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In NMR spectral correlations, the Hammett equations was taken as,

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

whereδ_0 is the chemical shift of the corresponding parent compound.

The characteristic proton chemical shifts(δ, ppm) H_1, H_2, H_3, H_4, H_5, H_6, H_7 and H_{7a} of (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl)methanones were assigned and tabulated in TABLE 2. The H_1, H_4, H_7 and H_{7a} protons gave double doublets (dd). The H_2 and H_3 protons gave triplets(t). The H_5 and H_6 protons gave doublets(d). These chemical shifts (δ, ppm) were correlated with Hammett substituent constants, F and R parameters. The results of statistical analyses are presented in TABLE 4. TABLE 4 reveals that the chemical shifts(δ, ppm) of H_1, H_3, H_5, H_6 and H_{7a} protons were fail and produce poor correlation with Hammett substituent constants, F and R parameters in single regression analysis. The chemical shift(δ, ppm) of H_2 proton with Hammett σ, σ^+, $\sigma_I$constants and F parameters gave satisfactory correlations (σ: r=0.906; σ^+: r=0.916; σ_I: r=907 and F: r=0.906) in single regression analysis. The Hammett $\sigma_R$constant and R parameter were fail in correlations. The fail in correlation is due to the complete absence of resonance effects of substituents and inability of prediction of substituent effects on the δH_2 protons along with the conjugative structure as shown in Figure 2. The correlation of δH_4 with Hammett σ_I constant and F parameter were satisfactory (σ_I: r=906 and F: r=0.906). The remaining Hammett σ, σ^+, $\sigma_R$constants and R parameters gave poor correlations. The inductive and field effects of the substituents predict the reactivity on this proton. A satisfactory correlations were obtained for H_7 proton chemical shifts (δ, ppm) with Hammett σ, σ^+, $\sigma_R$constants and R parameters (σ: r=0.907; σ^+: r=0.908; σ_R: r=908 and R: r=0.913) in single regression analysis. The Hammett $\sigma_I$constants and F parameters gave poor correlations. All correlations gave positive ρ values. This positive ρ values implies that the normal correlations operates in all system. The reason for fail and poor correlation was already stated and along with the resonanace-conjugtive structure ash shown in Figure 2.

Some of the single parameters correlation of chemical shifts(δ, ppm) of H_1, H_3, H_5, H_6 and H_{7a} protons were fail and produce poor correlation coefficients with Hammett substituent constants, F and R parameters[8]. While seeking in multi-regression analysis, these protons gave satisfactory correlations with σ_I and σ_R constants and Swain-Lupton's parameters. The multi-regression analysis equations are given in (9-24).

$$\delta H_1(ppm) = 2.695(\pm0.140) + 0.284(\pm0.024)\sigma_I + 0.011(\pm0.004)\sigma_R \quad (9)$$
$$(R = 0.940, n = 9, P > 90\%)$$

$$\delta H_1(ppm) = 2.673(\pm0.127) + 0.306(\pm0.024)F + 0.019(\pm0.001)R \quad (10)$$
$$(R = 0.945, n = 9, P > 90\%)$$

$$\delta H_2(ppm) = 3.002(\pm0.325) + 1.375(\pm0.628)\sigma_I + 0.333(\pm0.058)\sigma_R \quad (11)$$
$$(R = 0.972, n = 9, P > 95\%)$$

$$\delta H_2(ppm) = 3.313(\pm0.292) + 1.173(\pm0.557)F + 0.493(\pm0.035)R \quad (12)$$
$$(R = 0.974, n = 9, P > 95\%)$$

$$\delta H_3(ppm) = 3.551(\pm0.215) + 0.087(\pm0.021)\sigma_I + 0.064(\pm0.004)\sigma_R \quad (13)$$
$$(R = 0.908, n = 9, P > 90\%)$$

$$\delta H_3(ppm) = 3.516(\pm0.199) + 0.152(\pm0.034)F + 0.026(\pm0.002)R \quad (14)$$
$$(R = 0.916, n = 9, P > 90\%)$$

$$\delta H_4(ppm) = 2.143(\pm0.124) + 0.948(\pm0.241)\sigma_I + 0.704(\pm0.222)\sigma_R \quad (15)$$
$$(R = 0.987, n = 9, P > 95\%)$$

$$\delta H_4(ppm) = 2.201(\pm0.130) + 0.844(\pm0.248)F + 0.354(\pm0.157)R \quad (16)$$
$$(R = 0.984, n = 9, P > 95\%)$$

$$\delta H_5(ppm) = 5.503(\pm0.237) + 0.141(\pm0.045)\sigma_I + 0.226(\pm0.042)\sigma_R \quad (17)$$
$$(R = 0.928, n = 9, P > 90\%)$$

$$\delta H_5(ppm) = 5.419(\pm0.221) + 0.271(\pm0.042)F + 0.037(\pm0.002)R \quad (18)$$
$$(R = 0.928, n = 9, P > 90\%)$$

$$\delta H_6(ppm) = 5.901(\pm0.268) + 0.621(\pm0.051)\sigma_I + 0.114(\pm0.047)\sigma_R \quad (19)$$
$$(R = 0.949, n = 9, P > 90\%)$$

$$\delta H_6(ppm) = 5.832(\pm0.754) + 0.498(\pm0.048)F + 0.187(\pm0.030)R \quad (20)$$
$$(R = 0.946, n = 9, P > 90\%)$$

$$\delta H_7(ppm) = 2.169(\pm0.130) + 0.610(\pm0.251)\sigma_I + 0.882(\pm0.232)\sigma_R \quad (21)$$

TABLE 5 : Resultsofstatisticalanalysis of[13]C MNR spectral data of (2-naphthyl)-3-(substituted phenyl)biyclo [2.2.1] hept-5-ene-2-yl)methanones with Hammett σ, σ^+, σ_I, $\sigma_R$constants, F and Rparameters

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
δCO(ppm)	σ	0.820	190.16	0.309	0.71	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.811	190.13	0.100	0.72		
	σ_I	0.811	190.31	0.469	0.72		
	σ_R	0.830	189.91	0.925	0.69		
	F	0.804	190.97	0.136	0.73		
	R	0.824	199.98	0.461	0.70		
δC_1(ppm)	σ	0.802	41.60	0.651	1.55	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.811	41.55	0.219	1.54		
	σ_I	0.813	40.85	2.089	1.47		
	σ_R	0.812	41.40	0.769	1.54		
	F	0.846	40.46	2.941	1.38		
	R	0.816	41.35	2.666	1.53		
δC_2(ppm)	σ	0.905	54.34	0.926	0.68	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.881	54.96	0.429	0.73		
	σ_I	0.905	54.21	1.588	0.68		
	σ_R	0.905	53.87	1.683	0.69		
	F	0.905	53.98	1.803	0.68		
	R	0.814	53.94	0.954	0.72		
δC_3(ppm)	σ	0.831	45.11	1.794	2.57	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.829	44.82	1.966	2.59		
	σ_I	0.821	45.89	2.507	2.65		
	σ_R	0.820	44.47	2.150	2.66		
	F	0.808	45.38	0.963	2.70		
	R	0.822	44.41	0.616	2.64		
δC_4(ppm)	σ	0.836	50.55	0.721	0.89	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.836	50.43	0.417	0.89		
	σ_I	0.809	50.64	0.362	0.95		
	σ_R	0.832	50.20	1.245	0.90		
	F	0.802	5048	0.096	0.96		
	R	0.832	50.22	0.799	0.91		
$\delta C_{5,6}$(ppm)	σ	0.845	135.50	0.218	0.20	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.843	135.54	0.118	0.20		
	σ_I	0.831	135.40	0.305	0.21		
	σ_R	0.838	135.60	0.348	0.21		
	F	0.813	135.42	0.174	0.21		
	R	0.837	135.60	0.224	0.21		
δC_7(ppm)	σ	0.804	46.78	0.088	0.61	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ^+	0.807	46.27	0.056	0.61		
	σ_I	0.328	45.91	0.854	0.58		
	σ_R	0.824	46.13	0.896	0.89		
	F	0.905	45.79	1.277	0.53		
	R	0.821	46.15	0.340	0.60		

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Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
$\delta C_{1'}$(ppm)	σ	0.815	130.82	0.288	0.86		
	σ^+	0.806	130.88	0.073	0.87		
	σ_I	0.839	130.32	1.458	0.80	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ_R	0.800	130.84	0.011	0.88		
	F	0.842	130.26	1.541	0.79		
	R	0.801	130.88	1.330	0.88		
$\delta C_{1''}$(ppm)	σ	0.911	138.71	10.367	7.32		
	σ^+	0.903	141.16	6.341	7.00		
	σ_I	0.817	134.71	0.376	11.64	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ_R	0.800	139.74	0.015	13.68		
	F	0.811	140.71	0.617	11.68		
	R	0.843	141.76	0.117	10.11		
δC_{ipso}(ppm)	σ	0.906	134.55	11.46	6.49		
	σ^+	0.905	130.22	5.231	7.28		
	σ_I	0.918	128.77	26.635	4.93	9	H, 3-Br, 3-Cl, 4-Cl, 4-$N(CH_3)_2$, 4-F, 4-OH, 4-OCH_3, 4-NO_2
	σ_R	0.833	132.04	11.291	8.02		
	F	0.907	129.27	25.871	5.76		
	R	0.835	132.10	7.962	7.91		

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

(*R*= 0.985, n = 9, P > 95%)

$$\delta H_7(ppm) = 2.098(\pm0.091) + 0.097(\pm0.018)F + 0.633(\pm0.120)R \quad (22)$$

(*R* = 0.990, n = 9, P > 95%)

$$\delta H_{7a}(ppm) = 1.513(\pm0.106) + 0.036(\pm0.021)\sigma_I + 0.112(\pm0.018)\sigma_R \quad (23)$$

(*R*= 0.925, n = 9, P > 90%)

$$\delta H_{7a}(ppm) = 1.527(\pm0.101) + 0.036(\pm0.019)F + 0.040(\pm0.012)R \quad (24)$$

(*R* = 0.914, n = 9, P > 90%)

^{13}C NMR spectral study

The ^{13}C NMR chemical shifts(δ, ppm) of CO, norbornyl ring, $C_{1'}$, $C_{1''}$ and ipso carbons of (2-naphthyl)-3-(substituted phenyl)bicyclo [2.2.1] hept-5-ene-2-yl)methanones have been assigned and tabulated in TABLE 2. These chemical shifts were correlated with Hammett substituent constants, F and R parameters. The results of statistical analyses are shown in TABLE 5. TABLE 5 reveals that the correlations of CO, C_1, C_3, C_4-C_6 and$C_{1'}$ chemical shifts (δ, ppm) with Hammett substituent constants, F and R parameters were fail. A satisfactory correlation obtained for C_2 chemical shifts (δ, ppm) with Hammett σ, σ_I, σ_R constants and F parameters(σ: r=0.902; σ_I: r=0.905; σ_R: r=0.905 and F: r=0.905). The Hammett σ^+ constant and R parameters were fail in correlation. The C_7 chemical shifts (δ, ppm) gave satisfactory correlation with F parameter(r=0.905). Remaining Hammett σ, σ^+, σ_I, σ_R constants and R parameters gave poor correlations. The correlation of $C_{1''}$ chemical shifts (δ, ppm) with Hammett σ and σ^+constants were satisfactory(σ: r= 0.911 and σ^+:0.903). A poor correlation were obtained for $C_{1''}$ chemical shifts (δ, ppm) with Hammett σ_I, $\sigma_R$constants, F and R parameters. Hammett σ, σ^+, σ_I constants and F parameters produce satisfactory correlation (σ: r=0.900; σ^+: r=0.905; σ_I: r=0.918 and F: r=0.907)with C_{ipso} carbon chemical shifts (δ, ppm). The resonance component of the substituents was fail in correlations. All correlations gave positive ρ values and it is the evident for the normal substituent effects operates in all system. The reason for failure in correlation was stated earlier and it associated with the resonance-conjugated structure as shown in Figure 2.

In ^{13}C NMR spectral correlation of the methanones many single regressions gave poor correlations. When seeking the multi-regressions of these ^{13}C NMR chemical shifts (δ, ppm) with σ_I, σ_R constants or Swain-Lupton's parameters[8] produced

satisfactory correlations. The multi-linear regression analysis equations are presented in (25-44).

$\delta CO(ppm) = 189.99(\pm0.658) + 0.168(\pm0.012)\sigma_I + 0.876(\pm0.117)\sigma_R$ (25)
(R= 0.932, n = 9, P > 90%)

$\delta CO(ppm) = 189.86(\pm0.621) + 0.265(\pm0.112)F + 0.489(\pm0.075)R$ (26)
(R = 0.925, n = 9, P > 90%)

$\delta C_1(ppm) = 40.28(\pm1.364) + 2.615(\pm0.235)\sigma_I + 1.530(\pm0.243)\sigma_R$ (27)
(R= 0.939, n = 9, P > 90%)

$\delta C_1(ppm) = 39.99(\pm1.181) + 3.207(\pm2.244)F + 1.005(\pm0.142)R$ (28)
(R = 0.952, n = 9, P > 95%)

$\delta C_2(ppm) = 54.49(\pm0.583) + 1.452(\pm0.113)\sigma_I + 1.255(\pm0.104)\sigma_R$ (29)
(R= 0.965, n = 9, P > 95%)

$\delta C_2(ppm) = 54.61(\pm0.558) + 1.595(\pm0.104)F + 0.788(\pm0.066)R$ (30)
(R = 0.965, n = 9, P > 95%)

$\delta C_3(ppm) = 45.31(\pm0.215) + 1.966(\pm0.481)\sigma_I + 1.157(\pm0.445)\sigma_R$ (31)
(R= 0.925, n = 9, P > 90%)

$\delta C_3(ppm) = 44.65(\pm2.351) + 0.553(\pm0.014)F + 1.557(\pm0.283)R$ (32)
(R = 0.923, n = 9, P > 90%)

$\delta C_4(ppm) = 50.187(\pm0.864) + 0.631(\pm0.166)\sigma_I + 1.259(\pm0.015)\sigma_R$ (33)
(R= 0.932, n = 9, P > 95%)

$\delta C_4(ppm) = 50.08(\pm0.807) + 0.316(\pm0.015)F + 0.833(\pm0.097)R$ (34)
(R = 0.933, n = 9, P > 95%)

$\delta C_{5,6}(ppm) = 135.51(\pm20.761) + 1.331(\pm0.117)\sigma_I + 8.734(\pm0.817)\sigma_R$ (35)
(R= 0.915, n = 9, P > 90%)

$\delta C_{5,6}(ppm) = 135.601(\pm12.361) + 4.017(\pm0.817)F + 12.361(\pm0.417)R$ (36)
(R = 0.938, n = 9, P > 90%)

$\delta C_7(ppm) = 45.628(\pm0.512) + 1.179(\pm0.099)\sigma_I + 0.942(\pm0.091)\sigma_R$ (37)
(R= 0.948, n = 9, P > 95%)

$\delta C_7(ppm) = 45.564(\pm0.445) + 1.339(\pm0.084)F + 0.488(\pm0.053)R$ (38)
(R = 0.990, n = 9, P > 95%)

$\delta C_{1'}(ppm) = 130.15(\pm0.763) + 1.636(\pm0.147)\sigma_I + 0.467(\pm0.013)\sigma_R$ (39)
(R= 0.941, n = 9, P > 90%)

$\delta C_{1'}(ppm) = 130.20(\pm0.708) + 1.547(\pm0.135)F + 0.124(\pm0.085)R$ (40)
(R = 0.942, n = 9, P > 90%)

$\delta C_{1''}(ppm) = 144.76(\pm65.31) + 13.760(\pm1.441)\sigma_I + 8.361(\pm0.018)\sigma_R$ (41)
(R= 0.957, n = 9, P > 95%)

$\delta C_{1''}(ppm) = 146.68(\pm31.245) + 8.211(\pm0.171)F + 5.643(\pm1.311)R$ (42)
(R = 0.958, n = 9, P > 95%)

$\delta C_{ipso}(ppm) = 129.798(\pm4.655) + 28.365(\pm8.988)\sigma_I + 2.897(\pm0.830)\sigma_R$ (43)
(R= 0.989, n = 9, P > 95%)

$\delta C_{ipso}(ppm) = 129.01(\pm5.121) + 12.141(\pm3.214)F + 1.331(\pm0.877)R$ (44)
(R = 0.980, n = 9, P > 95%)

CONCLUSIONS

A series containing nine novel (2-naphthyl)-3-(substituted phenyl)bicyclo[2.2.1] hept-5-ene-2-yl)methanones have been synthesized by aqueous phase fly-ash catalyzed [4+2] Diels-Alder reaction of 2-naphthyl chalcones and cyclopentadiene according to literature. The assigned characteristic infrared and NMR spectral data are correlated using Hammett equation with Hammett substituent constants, F and R Swain-Lupton's parameters by single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the spectral data has been discussed. Many of the single and multi-parameter correlations gave satisfactory correlation co-efficient.

Novelty and Highlights

Aqueous phase fly-ash catalyzed [4+2] Diels-Alder reaction was performed to synthesis of some novel (2-naphthyl)-3-(substituted phenyl) bicyclo [2.2.1] hept-5-ene-2-yl)methanones.

The synthesized methanones were characterized by their physical constants and spectral data.

The assigned characteristic infrared and NMR spectroscopic data are correlated with Hammett equation using single and multi-linear regression analysis.

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The IR and NMR spectroscopic data of novel (2-naphthyl)-3-(substituted phenyl) bicyclo [2.2.1] hept-5-ene-2-yl) methanones have been correlated using Hammett equation with Hammett substituent constants, F and R Swain-Lupton's parameters by single and multi-linear regression analysis. From the results of statistical analysis, theeffect of substituents on the spectral data has been discussed with correlation co-efficient value in all correlations.

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