**8Recent studies on substituent effects on**

**1H and13C NMR chemical shifts**

**Purpose and scope of the present investigation**

In the present study, the substituted-5-benzylidenebarbituric acids were prepared with the following objectives.

1. To study the correlations between the Hammett substituent constants and 13C NMR substituent induced chemical shifts (SCS) of substituted-5-benzylidenebarbituric acids.
2. To study the use of SCS to monitor the transmission of electronic effects in molecular structures and to understand the mode of transmission of long-range effects in extended π-systems.

**EXPERIMENTAL**

**Preparation of Compounds**

5-benzylidenebarbituric acid and its substituted compounds were prepared by the modified procedure1.

To the calculated amount of the pure benzaldehyde (2 g, 0.015 mol) and barbituric acid (1.55g, 0.015 mol) in warm ethyl alcohol was added a 10% solution of sodium hydroxide (catalytic amount) and the reaction mixture stirred for 2 hours. After completion of the reaction as indicated by TLC, the reaction mixture was left overnight (scheme I). Solid product was separated by filtration and washed several times with cold methanol.



(Scheme I)

**CHARACTERIZATION**

All the compounds were characterized as 5-benzylidenebaarbituric acid and its derivatives by 1H and 13C NMR spectral techniques. 1H and 13C spectra were obtained on a BRUKER AMX 400 MHz spectrometer. Chemical shift of 1H were measured with the peak of DMSO at δ 2.51 as the internal reference, while those of 13C were recorded with the central peak of DMSO at δ 39.90 as the internal reference.



Fig ( 8 )

**Assignment of 1H NMR Signals**

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**1H NMR** Spectra of 5-benzylidenebarbityric acids are given below.

1. 5-(4’-methoxybenzylidene)barbituric acid

δ 3.877 (s,3H), 7.065 (d,2H), 8.252(s,1H), 8.369 (d,2H), 11.175 (s,1H), 11.302 (s,1H).

2. 5-(4’-hydroxybenzylidene)barbituric acid

δ 6.878 (d,2H), 8.213 (s,1H), 8.320 (d,2H), 10.851 (s,1H), 11.117(s,1H), 11.249 (s,1H).

3. 5-(4’-methylbenzylidene)barbituric acid

δ 2.385 (s,3H), 7.304 (d,2H), 8.094 (d,2H), 8.255 (s,1H), 11.218 (s,1H), 11.365 (s,1H).

4. 5-benzylidenebarbituric acid

δ 7.485 (m,3H), 8.073 (d,2H), 8.285 (s,1H), 11.238 (s,1H), 11.397 (s,1H).

5. 5-(4’-chlorobenzylidene)barbituric acid

δ 7.518 (d,2H), 8.069 (d,2H), 8.243 (s,1H), 11.275 (s,1H), 11.425 (s,1H).

6. 5-(4’-bromobenzylidene)barbituric acid

δ 7.670 (d,2H), 7.979 (d,2H), 8.223 (s,1H), 11.272 (s,1H), 11.421 (s,1H).

7. 5-(4’-nitrobenzylidene)barbituric acid

δ 8.017 (d,2H), 8.245 (d,2H), 8.324 (s,1H), 11.329 (s,1H), 1.504 (s,1H).

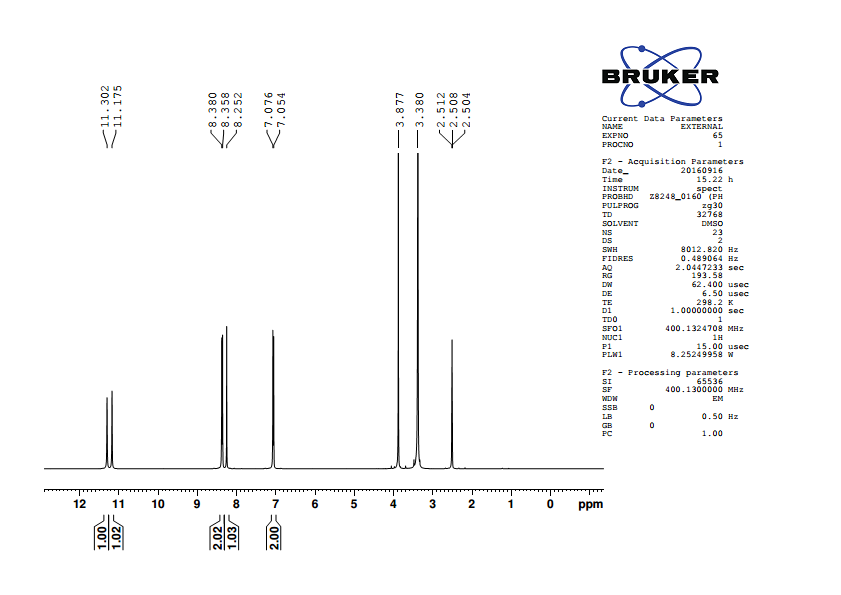


Fig.9. 1H NMR spectrum of 5-(4’-methoxybenzylidene)barbituric acid

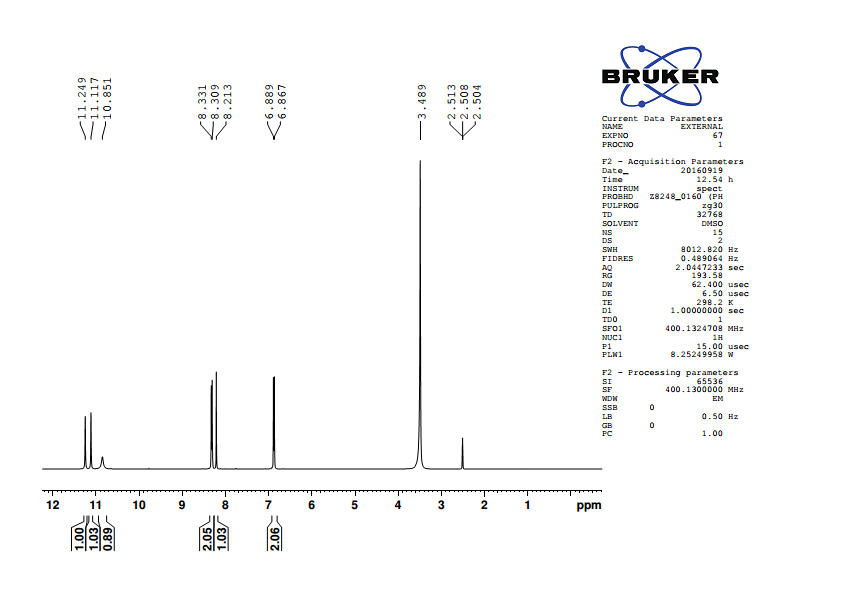


Fig.10. 1H NMR spectrum of 5-(4’-hydroxybenzylidene)barbituric acid

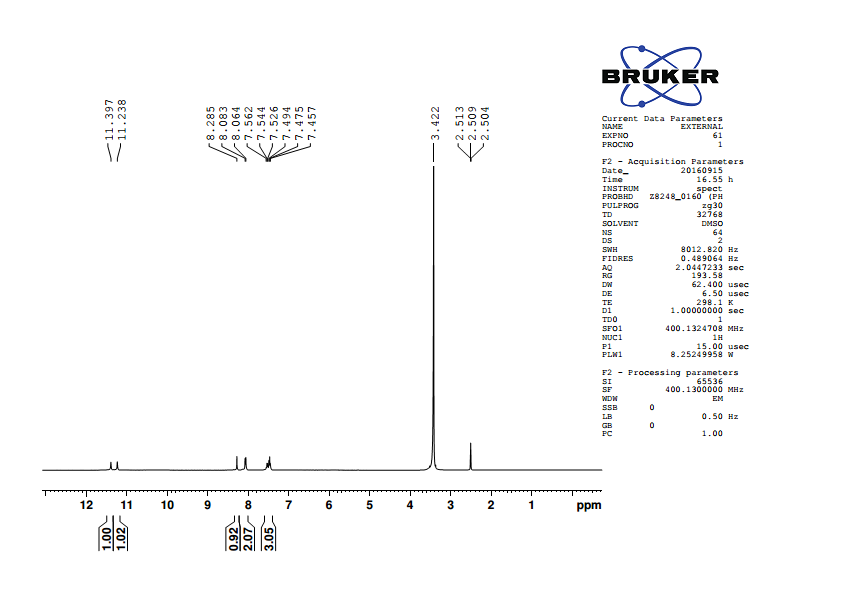


Fig.11. 1H NMR spectrum of 5-(4’-methylbenzylidene)barbituric acid

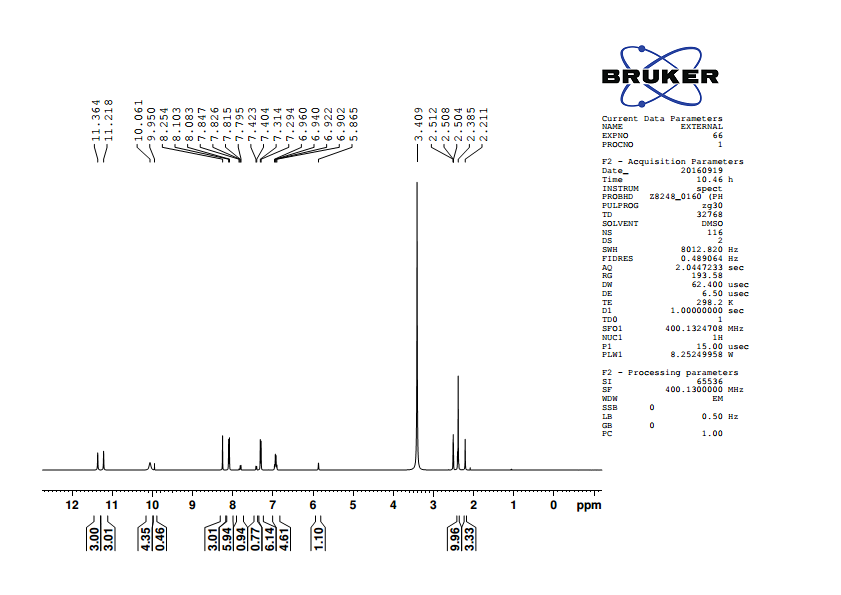
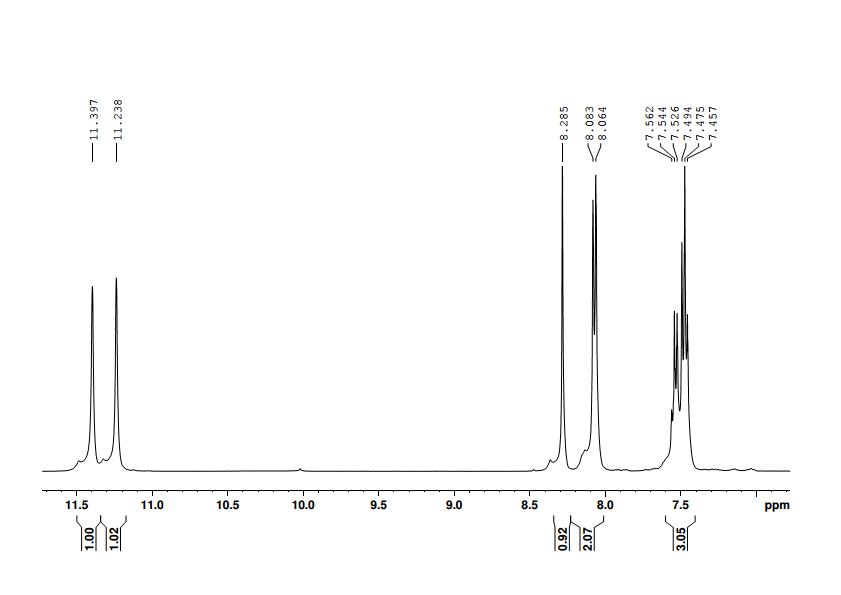


Fig.12. 1H NMR spectrum of 5-benzylidenebarbituric acid



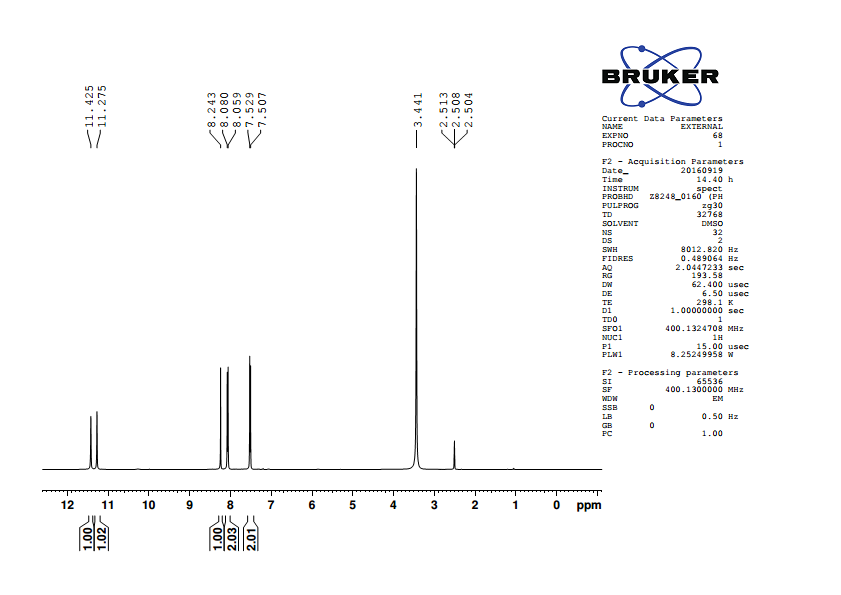


Fig.13. 1H NMR spectrum of 5-(4’-chlorobenzylidene)barbituric acid

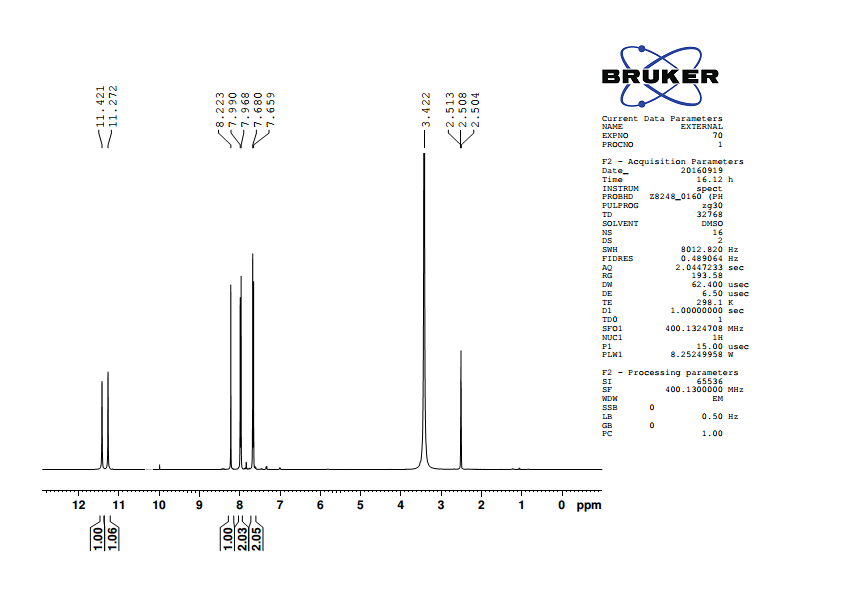


Fig.14. 1H NMR spectrum of 5-(4’-bromobenzylidene)barbituric acid

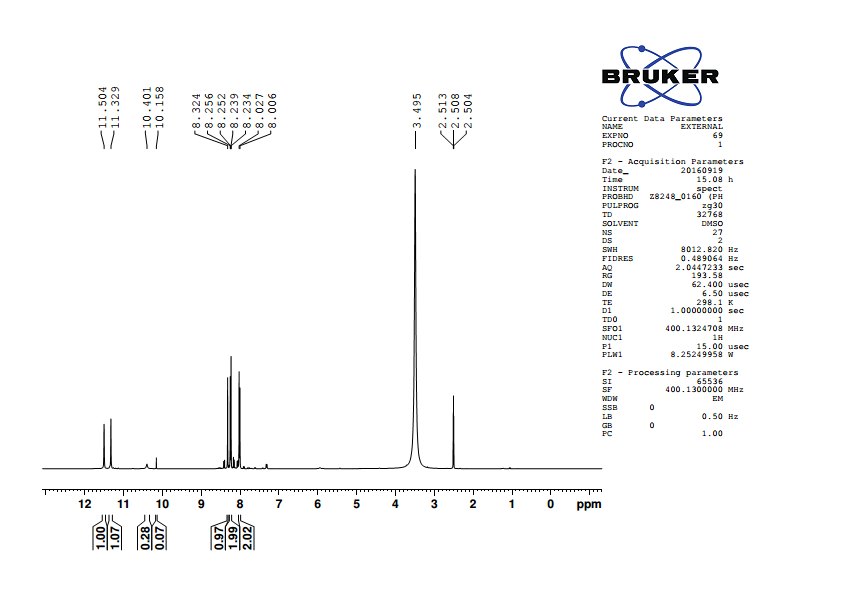


Fig.15. 1H NMR spectrum of 5-(4’-nitroobenzylidene)barbituric acid

**Table (1): 1H NMR chemical shifts of** **substituted 5-benzylidenebarbituric**

**acids**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |
| S.No. | Substituent X |  | H22’ | H33’ | H5 | H8 | H10 |
|  |  |  |  |  |  |  |  |
| 1. | -OCH3 |  | 7.065 | 8.369 | 8.252 | 11.175 | 11.302 |
|  |  |  |  |  |  |  |  |
| 2. | -OH |  | 6.878 | 8.32 | 8.213 | 11.117 | 11.249 |
|  |  |  |  |  |  |  |  |
| 3. | -CH3 |  | 7.304 | 8.094 | 8.255 | 11.218 | 11.365 |
|  |  |  |  |  |  |  |  |
| 4. | -H |  | 7.485 | 8.073 | 8.285 | 11.238 | 11.397 |
|  |  |  |  |  |  |  |  |
| 5. | -Cl |  | 7.518 | 8.069 | 8.243 | 11.275 | 11.425 |
|  |  |  |  |  |  |  |  |
| 6. | -Br |  | 7.670 | 7.979 | 8.223 | 11.272 | 11.421 |
|  |  |  |  |  |  |  |  |
| 7. | -NO2 |  | 8.245 | 8.017 | 8.324 | 11.329 | 11.504 |

**H5 – Hydrogen atom**

The chemical shift of H5 hydrogen appeared over a relatively very narrow range of 0.111 ppm. The SSP analysis of H5 hydrogen atom gave poor correlation with *σp****,*** *σp+/ σp-, σp+/ σp/ σp-* (Table . 2). The best fit of SSP analysis is given in equation (15 ).

log δ H5 **=** 0.002 *σp+/ σp-* + 0.92 ( 15 )

(±0.001) (±0.001)

r = 0.746; s = 0.002; F = 6.29; n = 7

The result of DSP analysis is given in table (3) and the best fit of DSP analysis is given in equation (16).

log δ H5 **=** 0.001 *σI* + 0.006 *σRo* **+**0.92 ( 16)

(±0.001) (±0.001) (±0.0006)

R = 0.923; SE = 0.001; F = 2.05; n = 6

**H8 – Hydrogen atom**

The chemical shift of H8  hydrogen appeared over a narrow range of 0.159 ppm. The SSP analysis of H8 hydrogen atom gave good correlations with σp, σpo, σp+, σp+/ σp- (Table .2). The best fit of SSP analysis is given in equation ().The plot of log δ H8  vs *σp+* is shown in Fig. (17 ).

log δ H8 **=** 0.004 *σp+* + 1.05 (17 )

(±0.0005)

r = 0.975; s = 0.001; F = 27.35; n =6

**Table (2): Results of statistical treatment of 1H – Chemical shift with σp,σpo,**

**σp+, σp+/ σp, σp+/ σp-, σp+/ σp/ σp- substituent constants using single**

**parameter equation**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No** | **Protons** | **Scale** | **ρ** | **r** | **s** | **F** | **log δo** | **n** |
| 1 | H5 | *σP* | 0.003±0.002 | 0.658 | 0.002 | 3.81 | 0.92±0.006 | 7 |
|  | *σPO* | 0.003±0.002 | 0.550 | 0.002 | 1.74 | 0.92±0.008 | 6 |
|  | *σP+* | 0.002±0.001 | 0.679 | 0.002 | 4.27 | 0.92±0.001 | 7 |
|  | *σP+/ σP* | 0.002±0.001 | 0.535 | 0.002 | 2.01 | 0.92±0.001 | 7 |
|  | *σP+/ σP-* | 0.002±0.001 | 0.746 | 0.001 | 6.29 | 0.92±0.001 | 7 |
|  | *σP+/ σP/ σP-* | 0.002±0.001 | 0.650 | 0.002 | 3.66 | 0.92±0.001 | 7 |
|  |  |  |  |  |  |  |  |  |
| 2 | H8 | *σP* | 0.0007±0.001 | 0.940 | 0.001 | 38.04 | 1.05±0.0004 | 7 |
|  | *σPO* | 0.005±0.001 | 0.934 | 0.001 | 27.35 | 1.05±0.0004 | 6 |
|  | *σP+* | 0.004±0.0005 | 0.975 | 0.001 | 99.39 | 1.05±0.0002 | 7 |
|  | *σP+/ σP* | 0.005±0.001 | 0.877 | 0.001 | 16.67 | 1.05±0.005 | 7 |
|  | *σP+/ σP-* | 0.003±0.001 | 0.942 | 0.001 | 39.58 | 1.05±0.0003 | 7 |
|  | *σP+/ σP/ σP-* | 0.004±0.001 | 0.856 | 0.001 | 13.72 | 1.05±0.001 | 7 |
|  |  |  |  |  |  |  |  |  |
| 3 | H10 | *σP* | 0.008±0.001 | 0.948 | 0.001 | 44.25 | 1.06±0.0004 | 7 |
|  | *σPO* | 0.006±0.001 | 0.917 | 0.001 | 21.26 | 1.06±0.0005 | 6 |
|  | *σP+* | 0.005±0.0003 | 0.999 | 0.0005 | 245.58 | 1.06±0.0002 | 7 |
|  | *σP+/ σP* | 0.006±0.001 | 0.903 | 0.002 | 22.20 | 1.06±0.0006 | 7 |
|  | *σP+/ σP-* | 0.004±0.0005 | 0.962 | 0.001 | 62.96 | 1.06±0.0004 | 7 |
|  | *σP+/ σP/ σP-* | 0.004±0.001 | 0.887 | 0.002 | 18.44 | 1.06±0.0006 | 7 |
|  |  |  |  |  |  |  |  |  |
| 4 | H22’ | *σO* | 0.06±0.02 | 0.838 | 0.02 | 11.81 | 0.81±0.006 | 7 |
|  | *σO\** | 0.05±0.007 | 0.966 | 0.007 | 56.20 | 0.86±0.003 | 6 |
|  | *Es* | -0.04±0.012 | 0.831 | 0.016 | 11.16 | 0.87±0.006 | 7 |

**Table (3 ): DSP analysis of 1H-chemical shift data with dual parameter equations ( ) and ( ).**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No** | **Protons** | **Scale** | ***ρI*** | ***ρR*** | **R** | **SE** | **F** | **log δo** | **n** | **λ=ρR/ρI** |
|
| 1 | H5 | *σI ,σR* | 0.001±0.003 | 0.005±0.003 | 0.711 | 0.002 | 2.05 | 0.92±0.001 | 7 | 5.0 |
|  |  | *σI ,σRo* | 0.001±0.001 | 0.006±0.001 | 0.923 | 0.001 | 8.50 | 0.92±0.0006 | 6 | 6.0 |
|  |  | *σI ,σR+* | -0.001±0.004 | 0.002±0.002 | 0.384 | 0.002 | 0.35 | 0.92±0.002 | 7 | 2.0 |
|  |  | *σI ,σR-* | -0.0003±0.002 | 0.05±0.001 | 0.905 | 0.001 | 6.85 | 0.92±0.001 | 6 | 50.0 |
|  |  | *F,R* | 0.0006±0.03 | 0.005±0.0002 | 0.783 | 0.002 | 3.17 | 0.92±0.001 | 7 | 8.33 |
|  |  |  |  |  |  |  |  |  |  |  |
| 2 | H8 | *σI ,σR* | 0.005±0.003 | 0.008±0.003 | 0.880 | 0.002 | 6.88 | 1.05±0.001 | 7 | 1.6 |
|  |  | *σI ,σRo* | 0.005±0.002 | 0.003±0.002 | 0.838 | 0.001 | 3.54 | 1.05±0.001 | 6 | 0.6 |
|  |  | *σI ,σR+* | 0.003±0.005 | 0.002±0.002 | 0.609 | 0.003 | 1.18 | 1.05±0.003 | 7 | 0.66 |
|  |  | *σI ,σR-* | 0.004±0.002 | 0.003±0.002 | 0.883 | 0.001 | 5.31 | 1.05±0.008 | 6 | 0.75 |
|  |  | *F,R* | 0.004±0.002 | 0.008±0.001 | 0.966 | 0.001 | 27.96 | 1.05±0.001 | 7 | 2.0 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3 | H10 | *σI ,σR* | 0.005±0.003 | 0.01±0.003 | 0.912 | 0.002 | 9.89 | 1.06±0.001 | 7 | 2.0 |
|  |  | *σI ,σRo* | 0.006±0.003 | 0.005±0.003 | 0.829 | 0.002 | 3.29 | 1.06±0.001 | 6 | 0.83 |
|  |  | *σI ,σR+* | 0.003±0.006 | 0.003±0.003 | 0.622 | 0.003 | 1.27 | 1.06±0.003 | 7 | 1.0 |
|  |  | *σI ,σR-* | 0.005±0.002 | 0.005±0.002 | 0.886 | 0.001 | 5.47 | 1.06±0.001 | 6 | 1.0 |
|  |  | *F,R* | 0.005±0.001 | 0.01±0.001 | 0.984 | 0.001 | 63.96 | 1.06±0.001 | 7 | 2.0 |
|  |  |  |  |  |  |  |  |  |  |  |
| 4 | H22’ | *σI ,σR* | 0.05±0.02 | 0.08±0.02 | 0.950 | 0.01 | 18.69 | 0.87±0.01 | 7 | 1.6 |
|  |  | *σI ,σRo* | 0.06±0.02 | 0.04±0.02 | 0.851 | 0.02 | 3.93 | 0.87±0.01 | 6 | 0.66 |
|  |  | *σI ,σR+* | 0.03±0.04 | 0.02±0.02 | 0.684 | 0.02 | 1.76 | 0.87±0.02 | 7 | 0.66 |
|  |  | *σI ,σR-* | 0.04±0.01 | 0.05±0.01 | 0.951 | 0.01 | 14.96 | 0.87±0.006 | 6 | 1.25 |
|  |  | *F,R* | 0.05±0.006 | 0.07±0.005 | 0.992 | 0.04 | 132.74 | 0.87±0.003 | 7 | 1.4 |

The DSP analysis is given in table (3 ) and the best fit of DSP analysis is given in equation (17).

log δ H8  = 0.004 *F* + 0.008 *R* + 1.05 ( 17 )

(±0.002) (±0.001) (0.001)

R = 0.966; SE = 0.001; F = 27.96; n = 7



Fig. 16. The plot of log δ H8  vs *σp+*

**H10 – Hydrogen atom**

The chemical shift of H10 hydrogen atom shows a range of about 0.255 ppm.The result of SSP analysis shown in table (2), afford an excellent correlation by *σp+* constant given in equation (18 ), and the plot of log δ H10 vs *σp+* is shown in Fig.(17).

log δ H10  = 0.005 *σp+* + 1.06 (18)

(±0.0003) (±0.0002)

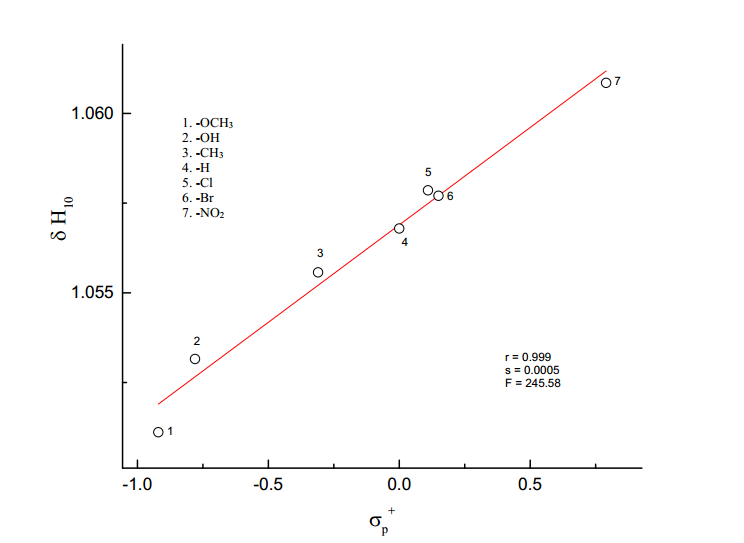
r = 0.999; s = 0.0005; F = 245.58; n = 7

The DSP analysis on table (3), afford an excellent correlation is shown in equation (19).

log δ H10  = 0.005 *F* + 0.01 *R* + 1.06 (19 )

(±0.001) (±0.001) (0.001)

R = 0.984; SE = 0.001; F = 63.96; n = 7



log

**Fig. 17 . The plot of log δ H10 vs *σp+***

**H22’ – Hydrogen atom**

The chemical shift of H22’ hydrogen atom shows a range of about 1.367 ppm. The result of SSP analysis shown in table (2), afford a satisfactory correlation with σo\* constant given in equation (20).

log δ H22’  = 0.05 *σo\** + 0.86 (20)

(±0.007) (±0.003)

r = 0.966; s = 0.007; F = 56.20; n = 6

The result of DSP analysis is given in Table () and the best fit of DSP analysis is given in equation (21).

log δ H22’  = 0.05 *F* + 0.07 *R* + 0.87 (21)

(±0.006) (±0.005) (±0.003)

R = 0.992; SE = 0.04; F = 132.74; n = 7

The result of TSP is given in table (4) and the best fit of TSP analysis and the results are given in equation (22).

log δ H22’  = -0.6172 *σI* + 0.5140 *σR*+ + 0.780 ν (22)

(±0.019) (±0.038) (±0.061)

R = 0.998; s = 0.039; n = 6

A better description of the composition of electrical effect is given by the equation (23).

PR = (23)

PR  is the percentage of delocalized effect. The value of PR is found to be 45.44. The magnitude of steric factor is given by the equation (24),

PS = (24)

The magnitude of the steric effect is given by the quantity PS. The value of PS is found to be 40.81, which shows that steric effect is also operating to some extent.

**Table (4): TSP analysis of SCS data of H22’ hydrogen atom of** **substituted**

**5-benzylidenebarbituric acids employing equations (19).**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |
| S.No. | Scale | α | β | φ | r | s | n |
|  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
| 1. | *σI ,σRo,ν* | 0.6499  (±0.871) | 0.5754  (±0.567) | 0.2806  (±0.554) | 0.876 | 0.304 | 6 |
|  |  |  |  |  |  |  |  |
| 2. | *σI, σR+, ν* | -0.6172  (±0.119) | 0.5140  (±0.038) | 0.780  (±0.061) | 0.998 | 0.039 | 6 |
|  |  |  |  |  |  |  |  |
| 3. | *F, R, ν* | 0.711  (±0.207) | 1.187  (±0.114) | 0.128  (±0.120) | 0.994 | 0.065 | 7 |
|  |  |  |  |  |  |  |  |

**Assignment of 13C NMR signals**

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**13C NMR Spectra of 5-benzylidenebarbituric acids**

1*.* 5-(4’-methoxybenzylidene)barbituric acid

δ 56.22, 114.41, 116.00, 125.62, 137.96, 150.67, 155.46, 162.64, 163.92, 164.39.

2. 5-(4’-hydroxybenzylidene)barbituric acid

δ 114.61, 115.97, 124.24, 138.77, 150.70, 156.05, 162.75,163.48, 164.59.

3. 5-(4’-methylbenzylidene)barbituric acid

δ 118.30, 129.33, 130.31, 134.43, 143.96, 150.68, 155.46, 162.26, 164.08.

4. 5-benzylidenebarbituric acid

δ 119.55, 128.52, 132.69, 133.11, 133.54, 150.69, 155.20, 162.03, 163.87.

5. 5-(4’-chlorobenzylidene)barbituric acid

δ 120.09, 128.55, 132.01, 135.15, 137.21, 150.65, 153.52, 162.04, 163.67.

6. 5-(4’-bromobenzylidene)barbituric acid

δ 120.24, 126.29, 131.51, 132.40, 135.15, 150.65, 153.56, 162.04, 163.67.

7. 5-(4’-nitrobenzylidene)barbituric acid

δ 123.15, 123.37, 132.69, 140.48, 148.49, 150.68, 151.63, 161.62, 163.13.

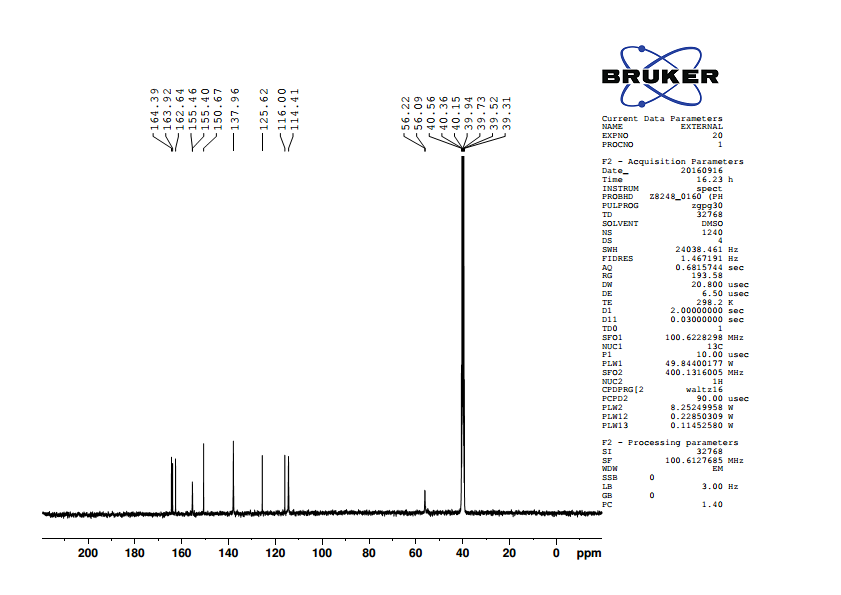
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Fig.18. 13C NMR spectrum of 5-(4’-methoxybenzylidene)barbituric acid

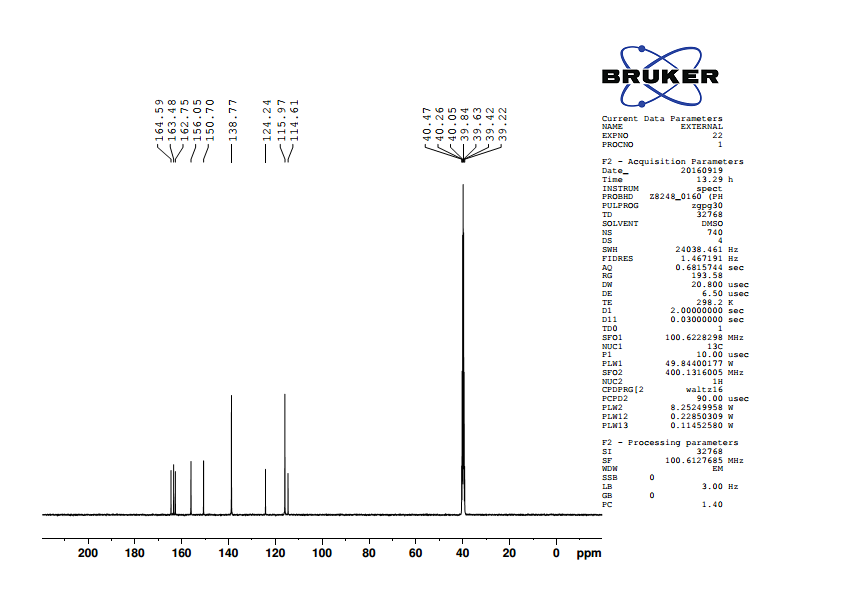
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Fig.19. 13C NMR spectrum of 5-(4’-hydroxybenzylidene)barbituric acid

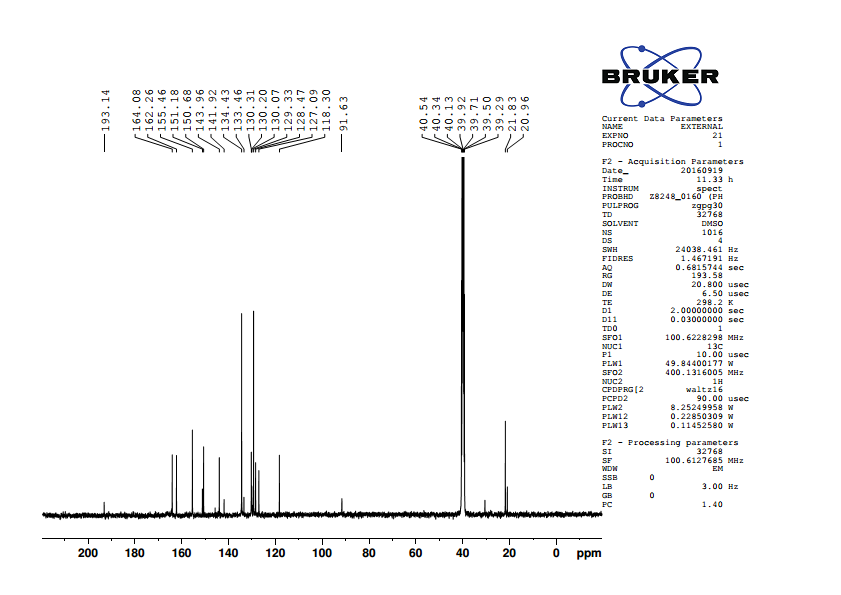
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Fig. 20. 13C NMR spectrum of 5-(4’-methylbenzylidene)barbituric acid

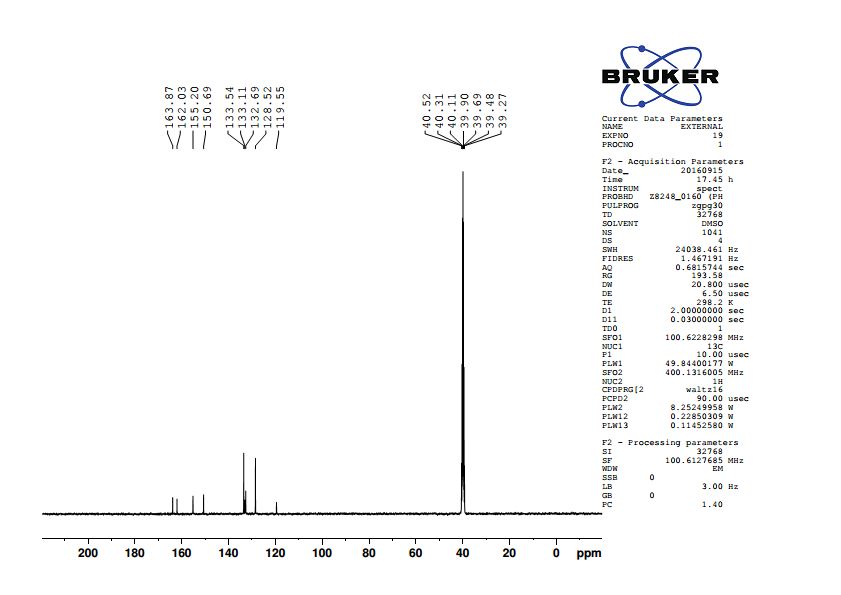
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Fig.21. 13C NMR spectrum of 5-benzylidenebarbituric acid

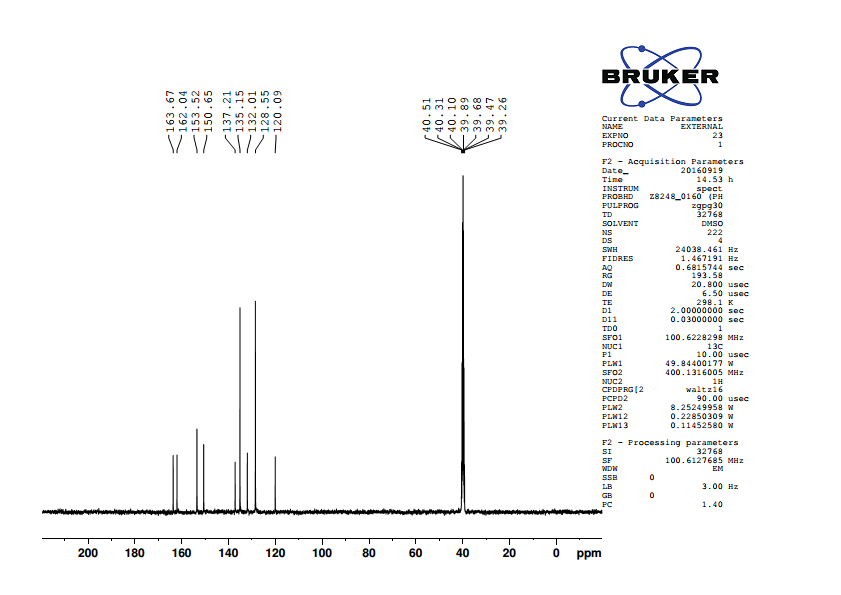
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Fig. 22. 13C NMR spectrum of 5-(4’-chlorobenzylidene)barbituric acid

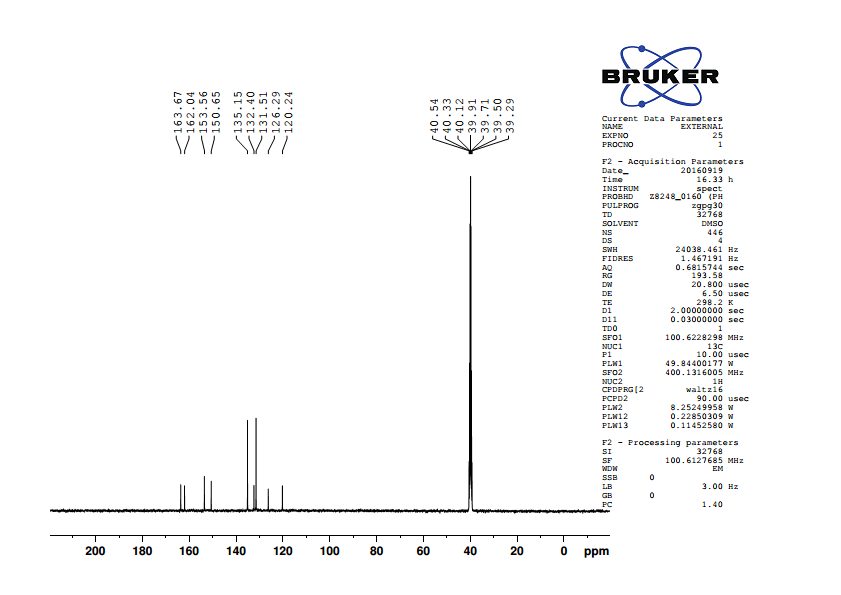
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Fig. 23. 13C NMR spectrum of 5-(4’-bromobenzylidene)barbituric acid

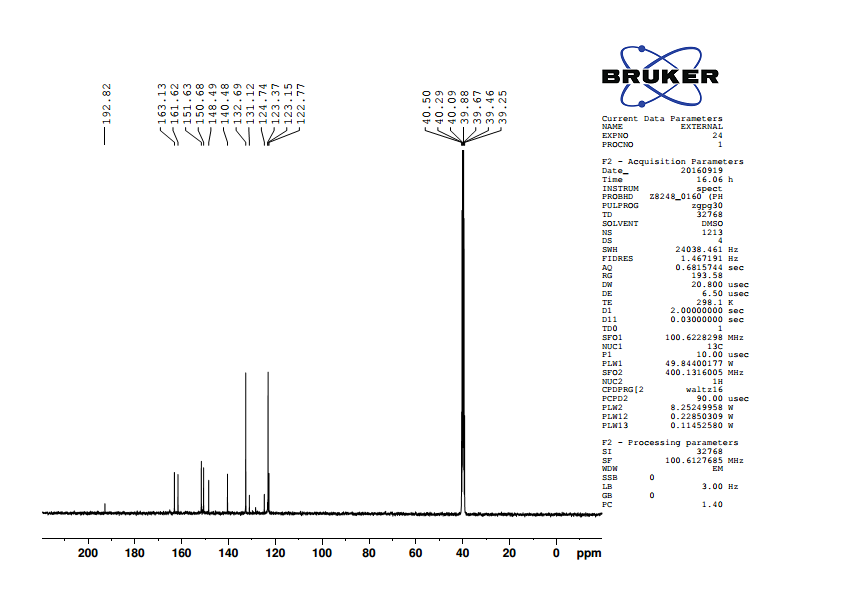
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Fig.24. 13C NMR spectrum of 5-(4’-nitrobenzylidene)barbituric acid

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**;**

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**;**

**Table (5): 13C NMR chemical shifts of substituted 5-benzylidenebarbituric acids**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | **GROUP** | **C1** | **C22’** | **C33’** | **C4** | **C5** | **C6** | **C7** | **C9** | **C11** |
|  |  |  |  |  |  |  |  |  |  |  |
| 1 | -OCH3 | 162.64 | 114.41 | 137.96 | 125.62 | 155.46 | 116 | 163.92 | 150.67 | 164.39 |
|  |  |  |  |  |  |  |  |  |  |  |
| 2 | -OH | 163.48 | 115.97 | 138.77 | 124.24 | 156.05 | 114.61 | 162.75 | 150.7 | 164.59 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3 | -CH3 | 143.96 | 129.33 | 134.43 | 130.31 | 155.46 | 118.3 | 162.26 | 150.68 | 164.08 |
|  |  |  |  |  |  |  |  |  |  |  |
| 4 | -H | 133.11 | 128.52 | 133.54 | 132.69 | 155.2 | 119.55 | 162.03 | 150.69 | 163.87 |
|  |  |  |  |  |  |  |  |  |  |  |
| 5 | -Cl | 137.21 | 128.55 | 135.15 | 132.01 | 153.52 | 120.09 | 162.04 | 150.65 | 163.67 |
|  |  |  |  |  |  |  |  |  |  |  |
| 6 | -Br | 126.29 | 131.51 | 135.15 | 132.4 | 153.56 | 120.24 | 162.04 | 150.65 | 163.67 |
|  |  |  |  |  |  |  |  |  |  |  |
| 7 | -NO2 | 148.49 | 132.69 | 123.37 | 140.48 | 151.63 | 123.15 | 161.62 | 150.68 | 163.13 |

**RESULTS AND DISCUSSION**

**Correlations with Lynch-Equation**

The SCS of monosubstituted benzenes have been very useful in signal assignment of polysubstituted compounds70-73 . However, in many published studies summarized by Craik74 it has been apparent that the SCS values of X and Y at positions 4’ and 1’ in disubstituted benzenes Fig. (25) are non-additive. Lynch75 has proposed that the non-additivity of the chemical shifts of C-1’ and C-4’ is reflected in the relationship Eq. (25) where SCSX(Y) is the substituent chemical shift of the carbon



Fig. (25)

SCSX (Y) = a + b [ SCSX (H)] ( 25)

*para-* to X in the series of 1’,4’-disubstituted benzenes (Fig. 25, X, Y ≠ H), SCSX(H) is the corresponding substituent chemical shift of the carbon *para* to X in monosubstituted benzenes (Fig. 25, Y=H), ‘b’ is the slope parameter and ‘a’ is the shift calculated for the parent spices with X=Y. A wide range of successful correlations (using Lynch equation) have been established for the SCS of carbons bearing Y in Fig. () with the value of ‘b’ ranging from 0.6 to 1.542. When the slope is close to unity, experimental results could be reproduced by additivity relationship and when b ≠ 1, the Lynch equation can be used to predict the SCS values through proportionality relationships. The slope b of the Lynch equation Eq. (25) is less than one, then the fixed substituent at C-1’ Fig (25) diminishes the substituent effect. When slope b is larger than one, showing that the fixed substituent undergoes an amplification of the substituent effect.

In case of C1 there is satisfactory correlation with (r=0.988) appropriate SCS (Si) values, slope b is 0.97, which reveals that the fixed substituent Y=-CH-C-C3H2N2O3, has little effect on the additivity of this shifts42.

A satisfactory correlation exists between SCS of C22’ and So with correlation coefficient (r=0.828) and the slope value (b=0.84), indicating that the fixed substituent Y, significantly diminishes the substituent effect42.

A poor correlation exists between SCS of C33’ and Sm with correlation coefficient (r=0.113) and the slope value (b=0.71) which reveals that the fixed substituent Y diminishes the substituent effect42.

The C4 carbon afford a good correlation with Sp with correlation coefficient r=0.993 and the slope value b=0.94 demonstrates that the fixed substituent Y has little effect on the additivity of these shifts42. The results of Lynch correlations are given in table (6) and the plots of Lynch correlations shown in fig. (26) and ((27)

**Table ( 6 ) : Results of Lynch correlationsa of 13C chemical shifts of compound fig ( ) with SCS values for mono substituted benzenes.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| S.No. | Carbons | Benzene  SCS  (Sb) | Slope  (b) | Intercept  (a) | rc | nd | Se |
| 1. | C1 | Si | 0.97 | 132.23 | 0.988 | 6 | 2.17 |
|  |  |  |  |  |  |  |  |
| 2. | C22’ | SO | 0.84 | 129.73 | 0.828 | 6 | 4.14 |
|  |  |  |  |  |  |  |  |
| 3. | C33’ | Sm | 0.71 | 132.69 | 0.113 | 6 | 5.63 |
|  |  |  |  |  |  |  |  |
| 4. | C4 | Sp | 0.94 | -126.43 | 0.993 | 6 | 0.61 |

1. SCSX (Y) = a + b SCSX (H)
2. SCS values in Appendix (I)
3. Correlation coefficient
4. Number of data points
5. Standard deviations



**Fig. (26 ).** Lynch plot of SCS of C1 vs Si



**Fig. (27 ).** Lynch plot of SCS of C4 vs Sp

**Substituent effects on the 13C NMR chemical shifts of the substituted**

The use of 13C NMR SCS is to monitor the transmission of electroniceffectsin molecular frameworks in general and to understand the mode of transmission of long-range substituent effects in extended π-electron systems in particular are topics of current interest. Thus long-range 13C SCS have been reported for N-benzylideneanilines76, N-benzylidenebensylamines77, chalcones78, benzophenones79, phenylacetylenes80,β-n-trostyrenes81,82, cinnamicacids83,84 and cinnamates85.

In this chapter, the 13C chemical shift data of several carbon atoms of 5-benzylidenebarbituric acid has been correlated with SSP equation (Eq. 15.), DSP equations (Eq.17. ) and Yukawa-Tsuno equation (Eq.19.)

**C4 - Carbon atom**

The Chemical shift of C4 carbon appeared over a relatively narrow range of 16.24 ppm. The result of SSP analysis shown in table (7), an excellent correlation afford by σp+ / σp- constant given in equation (26), and the plot of log δ C4 vs σp+ / σp-  as shown in Fig ( 28).

log δ C4 = 0.024 σp+ / σp- + 2.12 ( 26)

(±0.002) (±0.001)

r = 0.989; s = 0.003; n = 7

The result of DSP analysis in table (8 ), afford an excellent correlation are shown in equations (27 ) and (28 ).

log δ C4 = 0.02 σI + 0.005 σR + 2.12 (27 )

(±0.003) (±0.003) (±0.001)

R = 0.995; SE = 0.002; n = 6: F = 154.44

log δ C4 = 0.025 F + 0.05 R + 2.12 (28 )

(±0.003) (±0.002) (±0.001)

R = 0.996; SE = 0.002; n = 7; F = 279.61

The sign of *ρ*I and *ρ*R are positive, reveals that the normal substituent effect operates on C4 carbon atom, i.e., an electron withdrawing substituent decrease the C4 carbon atom shielding and an electron releasing substituent increase it. Examination of chemical shift of data in table (), electro-withdrawing substituent causes downfield



log

**Fig. 28. The plot of log δ C4 vs σp+ / σp-**

shift and electron releasing substituent causes up field. The magnitude of *ρ*R is greater than *ρ*I indicate that the predominance of resonance effect over inductive effect in the chemical shift of C4 carbon atom.

This result is also shown from Yukawa-Tsuno equation (18 ) is given in table (9 ). The result of best fit eq. (18) is given in equation (29)

log δ C4 = 0.028 σp + 0.032 ( σp+- σp) + 2.12 (29 )

(±0.006) (±0.009) (±0.002)

R = 0.986; SE = 0.003; n = 7; F = 72.76

**Table ( 7): Results of statistical treatment of 13C – Chemical shift with σp, σpo ,σp+, σp+/ σp, σp+/ σp-,σp+/ σp/ σp-substituent constants using single parameter equation**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | **Carbons** | **Scale** | **ρ** | **r** | **s** | **F** | **log δo** | **n** |
|  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
| 1 | C4 | *σp* | 0.04±0.006 | 0.949 | 0.006 | 43.33 | 2.11±0.002 | 7 |
|  | *σpO* | 0.038±0.01 | 0.882 | 0.008 | 13.99 | 2.11±0.004 | 6 |
|  | *σp+* | 0.0320.002 | 0.986 | 0.003 | 179.37 | 2.12±0.001 | 7 |
|  | *σp+/ σp* | 0.03±0.006 | 0.924 | 0.007 | 29.11 | 2.12±0.003 | 7 |
|  | *σp+/ σp-* | 0.024±0.002 | 0.989 | 0.003 | 226.34 | 2.12±0.001 | 7 |
|  | *σp+/ σp/ σp-* | 0.026±0.004 | 0.938 | 0.006 | 37.12 | 2.12±0.002 | 7 |
|  |  |  |  |  |  |  |  |  |
| 2 | C5 | *σp* | -0.01±0.001 | 0.984 | 0.001 | 152.18 | 2.19±0.0003 | 7 |
|  | *σpO* | -0.01±0.001 | 0.988 | 0.001 | 163.39 | 2.19±0.0003 | 6 |
|  | *σp+* | -0.007±0.001 | 0.916 | 0.002 | 25.94 | 2.19±0.001 | 7 |
|  | *σp+/ σp* | -0.008±0.002 | 0.887 | 0.002 | 18.40 | 2.19±0.001 | 7 |
|  | *σp+/ σp-* | -0.006±0.001 | 0.938 | 0.002 | 36.47 | 2.18±0.001 | 7 |
|  | *σp+/ σp/ σp-* | -0.006±0.001 | 0.917 | 0.002 | 26.68 | 2.19±0.001 | 7 |
|  |  |  |  |  |  |  |  |  |
| 3 | C6 | *σp* | 0.03±0.004 | 0.950 | 0.004 | 45.95 | 2.07±0.001 | 7 |
|  | *σpO* | 0.02±0.005 | 0.900 | 0.004 | 17.16 | 2.07±0.002 | 6 |
|  | *σp+* | 0.018±0.001 | 0.995 | 0.001 | 508.52 | 2.08±0.0004 | 7 |
|  | *σp+/ σp* | 0.02±0.004 | 0.917 | 0.005 | 26.46 | 2.07±0.002 | 7 |
|  | *σp+/ σp-* | 0.014±0.002 | 0.970 | 0.003 | 80.18 | 2.07±0.001 | 7 |
|  | *σp+/ σp/ σp-* | 0.015±0.003 | 0.902 | 0.005 | 21.75 | 2.07±0.002 | 7 |
|  |  |  |  |  |  |  |  |  |
| 4 | C7 | *σp* | -0.004±0.002 | 0.722 | 0.001 | 5.43 | 2.21±0.001 | 7 |
|  | *σpO* | -0.004±0.002 | 0.620 | 0.002 | 2.51 | 2.21±0.001 | 6 |
|  | *σp+* | -0.003±0.0008 | 0.820 | 0.001 | 10.24 | 2.21±0.0004 | 7 |
|  | *σp+/ σp* | -0.004±0.0007 | 0.917 | 0.001 | 26.41 | 2.21±0.003 | 7 |
|  | *σp+/ σp-* | -0.002±0.001 | 0.775 | 0.001 | 7.51 | 2.21±0.0005 | 7 |
|  | *σp+/ σp/ σp-* | -0.003±0.001 | 0.836 | 0.001 | 11.63 | 2.21±0.0005 | 7 |
|  |  |  |  |  |  |  |  |  |
| 5 | C11 | *σp* | -0.003±0.0003 | 0.979 | 0.0003 | 116.72 | 2.21±0.0001 | 7 |
|  | *σpO* | -0.003±0.0005 | 0.945 | 0.0004 | 33.30 | 2.21±0.0002 | 6 |
|  | *σp+* | -0.002±0.0001 | 0.996 | 0.0001 | 640.41 | 2.21±0.0004 | 7 |
|  | *σp+/ σp* | -0.002±0.0004 | 0.935 | 0.0005 | 34.80 | 2.21±0.002 | 7 |
|  | *σp+/ σp-* | -0.002±0.0001 | 0.983 | 0.0003 | 145.26 | 2.21±.0001 | 7 |
|  | *σp+/ σp/ σp-* | -0.002±0.0003 | 0.930 | 0.0005 | 32.23 | 2.21±0.0002 | 7 |
|  |  |  |  |  |  |  |  |  |
| 6 | C22’ | *σo* | 0.044±0.02 | 0.632 | 0.02 | 3.33 | 2.09±0.008 | 7 |
|  | *σo\** | 0.038±0.02 | 0.691 | 0.02 | 3.66 | 2.09±0.01 | 6 |
|  | *Es* | -0.04±0.013 | 0.825 | 0.016 | 10.69 | 2.13±0.006 | 7 |

**Table (8 ): DSP analysis of chemical shift data with dual parameter equations (16 ) and (17 ).**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No** | **Carbons** | **Scale** | ***ρI*** | ***ρR*** | **R** | **SE** | **F** | **log δo** | **n** | **λ=*ρR*/*ρI*** |
|
| 1 | C4 | *σI ,σR* | 0.02±0.003 | 0.005±0.003 | 0.995 | 0.002 | 154.44 | 2.12±0.001 | 6 | 0.25 |
|  |  | *σI ,σRo* | 0.03±0.017 | 0.04±0.016 | 0.849 | 0.01 | 3.89 | 2.12±0.007 | 6 | 1.33 |
|  |  | *σI ,σR+* | 0.01±0.03 | 0.018±0.016 | 0.640 | 0.016 | 1.39 | 2.12±0.015 | 7 | 1.8 |
|  |  | *σI ,σR-* | 0.02±0.01 | 0.04±0.009 | 0.943 | 0.007 | 12.10 | 2.12±0.005 | 6 | 2.0 |
|  |  | *F,R* | 0.025±0.003 | 0.05±0.002 | 0.996 | 0.002 | 279.61 | 2.12±0.001 | 7 | 2.0 |
|  |  |  |  |  |  |  |  |  |  |  |
| 2 | C5 | *σI ,σR* | -0.01±0.001 | -0.007±0.001 | 0.998 | 0.0003 | 349.25 | 2.19±0.003 | 6 | 0.7 |
|  |  | *σI ,σRo* | -0.014±0.003 | -0.005±0.002 | 0.956 | 0.002 | 16.09 | 2.19±0.001 | 6 | 0.36 |
|  |  | *σI ,σR+* | -0.01±0.006 | -0.002±0.003 | 0.838 | 0.003 | 4.74 | 2.19±0.003 | 7 | 0.2 |
|  |  | *σI ,σR-* | -0.012±0.002 | -0.005±0.001 | 0.980 | 0.001 | 36.20 | 2.19±0.001 | 6 | 0.42 |
|  |  | *F,R* | -0.014±0.001 | -0.01±0.001 | 0.993 | 0.001 | 146.55 | 2.19±0.005 | 7 | 0.71 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3 | C6 | *σI ,σR* | 0.016±0.002 | 0.026±0.002 | 0.996 | 0.001 | 176.46 | 2.08±0.001 | 6 | 1.63 |
|  |  | *σI ,σRo* | 0.02±0.01 | 0.016±0.01 | 0.810 | 0.006 | 2.86 | 2.07±0.004 | 6 | 0.8 |
|  |  | *σI ,σR+* | 0.008±0.019 | 0.01±0.01 | 0.636 | 0.01 | 1.36 | 2.07±0.009 | 7 | 1.25 |
|  |  | *σI ,σR-* | 0.014±0.008 | 0.017±0.007 | 0.885 | 0.005 | 5.43 | 2.07±0.003 | 6 | 1.21 |
|  |  | *F,R* | 0.015±0.003 | 0.032±0.002 | 0.990 | 0.002 | 105.40 | 2.08±0.001 | 7 | 2.13 |
|  |  |  |  |  |  |  |  |  |  |  |
| 4 | C7 | *σI ,σR* | -0.001±0.002 | -0.008±0.002 | 0.928 | 0.001 | 9.34 | 2.21±0.0018 | 6 | 2.0 |
|  |  | *σI ,σRo* | -0.002±0.004 | -0.004±0.004 | 0.550 | 0.002 | 0.649 | 2.21±0.002 | 6 | 2.0 |
|  |  | *σI ,σR+* | 0.0014±0.002 | -0.003±0.002 | 0.669 | 0.002 | 1.618 | 2.21±0.002 | 7 | 0.21 |
|  |  | *σI ,σR-* | -0.001±0.003 | -0.004±0.003 | 0.648 | 0.002 | 1.087 | 2.21±0.01 | 6 | 4.0 |
|  |  | *F,R* | -0.001±0.003 | -0.005±0.002 | 0.806 | 0.001 | 3.719 | 2.21±0.001 | 7 | 5.0 |
|  |  |  |  |  |  |  |  |  |  |  |
| 5 | C11 | *σI ,σR* | -0.002±0.0002 | -0.003±0.0002 | 0.998 | 0.0001 | 341.86 | 2.21±0.0001 | 6 | 1.5 |
|  |  | *σI ,σRo* | -0.003±0.001 | -0.002±0.001 | 0.859 | 0.0007 | 4.22 | 2.21±0.0005 | 6 | 0.66 |
|  |  | *σI ,σR+* | -0.001±0.002 | -0.0012±0.001 | 0.699 | 0.001 | 1.91 | 2.21±0.001 | 7 | 1.2 |
|  |  | *σI ,σR-* | -0.0023±0.001 | -0.002±0.001 | 0.915 | 0.001 | 7.70 | 2.21±0.0004 | 6 | 0.87 |
|  |  | *F,R* | -0.002±0.0003 | -0.004±0.0002 | 0.993 | 0.002 | 152.18 | 2.21±0.001 | 7 | 2.0 |
|  |  |  |  |  |  |  |  |  |  |  |
| 6 | C22’ | *σI ,σR* | 0.01±0.02 | 0.08±0.02 | 0.891 | 0.01 | 5.81 | 2.11±0.01 | 6 | 8.0 |
|  |  | *σI ,σRo* | 0.02±0.01 | 0.03±0.04 | 0.438 | 0.03 | 0.35 | 2.10±0.02 | 6 | 1.5 |
|  |  | *σI ,σR+* | -0.01±0.05 | 0.02±0.02 | 0.475 | 0.03 | 0.58 | 2.11±0.03 | 7 | 2.0 |
|  |  | *σI ,σR-* | 0.008±0.04 | 0.04±0.03 | 0.595 | 0.02 | 0.82 | 2.10±0.02 | 6 | 5.0 |
|  |  | *F,R* | 0.006±0.02 | 0.008±0.02 | 0.903 | 0.01 | 8.85 | 2.12±0.01 | 7 | 1.33 |

**Table (9):Results of multiple regression analysis of 13C chemical shifts with σp,( σp+- σp)  and σpo,**

**(σp+- σpo) constants using Yukava – Tsuno equation (18 ).**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | **Carbon** | **scale** | **ρ** | **r** | **R** | **SE** | **F** | **n** |
| 1 | C4 | *σp,( σp+- σp)* | 0.028±0.006 | 0.032±0.009 | 0.986 | 0.003 | 72.76 | 7 |
|  |  | *σpo,( σp+- σpo)* | 0.027±0.009 | 0.02±0.009 | 0.954 | 0.006 | 15.15 | 6 |
|  |  |  |  |  |  |  |  |  |
| 2 | C5 | *σp,( σp+- σp)* | -0.013±0.001 | 0.004±0.02 | 0.994 | 0.001 | 167.30 | 7 |
|  |  | *σpo,( σp+- σpo)* | -0.01±0.001 | -0.0001±0.001 | 0.988 | 0.001 | 61.27 | 6 |
|  |  |  |  |  |  |  |  |  |
| 3 | C6 | *σp,( σp+- σp)* | 0.016±0.002 | 0.02±0.003 | 0.996 | 0.001 | 274.61 | 7 |
|  |  | *σpo,( σp+- σpo)* | 0.01±0.003 | 0.012±0.003 | 0.989 | 0.002 | 65.94 | 6 |
|  |  |  |  |  |  |  |  |  |
| 4 | C7 | *σp,( σp+- σp)* | -0.007±0.002 | -0.006±0.003 | 0.866 | 0.001 | 6.01 | 7 |
|  |  | *σpo,( σp+- σpo)* | -0.001±0.001 | -0.005±0.001 | 0.937 | 0.001 | 10.76 | 6 |
|  |  |  |  |  |  |  |  |  |
| 5 | C11 | *σp,( σp+- σp)* | -0.003±0.0002 | -0.002±0.0003 | 0.998 | 0.0001 | 518.04 | 7 |
|  |  | *σpo,( σp+- σpo)* | -0.002±0.0002 | -0.001±0.0002 | 0.994 | 0.0001 | 133.10 | 6 |

**C5 - Carbon atom**

The chemical shift of C5 carbon appeared over a relatively narrow range of 4.42 ppm. The SSP analysis with various σ parameters, σpo gave satisfactory correlation, results shown in table (7). It gave negative correlation (Eq.30) and negative slope indicates that a reverse substituent effect operates on the carbonyl carbon. The Hammett plot of log δ C5 vs *σpo* is shown in figure (29).

log δ C5 = -0.01 *σpo*  + 2.19 (30)

(±0.001) (±0.0003)

r = 0.988; s = 0.001; n = 6

Examination of chemical shift data (table 5 ) of C5 carbon, electron releasing group cause upfield shift by increasing the shielding and electron withdrawing group cause downfield shift by decreasing the shielding.

;

The DSP analysis of C5 carbon with various σR scale is given in table (8),the best fit is given in equations (31) and (32)

log δ C5 = -0.01*σI* - 0.007 *σR* + 2.19 (31)

(±0.001) (±0.0003) (0.003)

R = 0.998; SE = 0.0003; n = 6; F = 349.25

log δ C5 = -0.014 *F*  - 0.01 *R*  + 2.08 (32 )

(±0.001) (±0.01) (±0.01)

R = 0.993; SE = 0.001; n = 7; F= 146.55



log

**Fig. 29. The plot of log δ C5 vs *σpo***

From DSP analysis……………………

The results of Yukawa-Tsuno equation (33), also indicate that the magnitude of ‘r’ is very low(< 1).

log δ C5 = -0.015 *σp* + 0.004 (*σp+- σp*) + 2.19 (33 )

(±0.001) (±0.002) (±0.0004)

R = 0.994; SE = 0.001; n = 7; F = 167.30

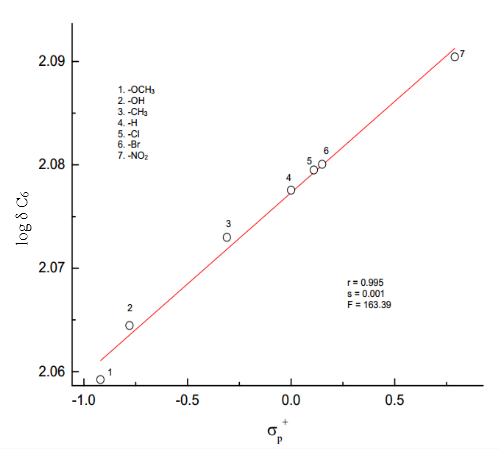
**C6 – Carbon atom**

The chemical shift of C6 carbon atom appeared over a relatively narrow range of 7.15 ppm. The results of SSP analysis shown in table (7), excellent correlation afford by σp+ constant given in equation (34), and the plot of log δ C6 vs σp+ is shown in Fig. (30).

log δ C6 = 0.018 *σp+* + 2.08 (34)

(±0.001) (±0.00004)

r = 0.995; s = 0.001; n = 7; F = 508.52



**Fig. 30. The plot of log δ C6 vs *σp****+*

The results of DSP analysis in table (8), afford an excellent correlation are shown in equations (35) and (36).

log δ C6 = 0.016 *σ I*+ 0.026 *σR* +2.08 (35)

(±0.002) (±0.002) (0.001)

R = 0.996; SE = 0.001; F = 176.46; n =6

log δ C6 = 0.01 *F*+ 0.032 *R* +2.08 (36)

(±0.003) (±0.002) (0.001)

R = 0.990; SE = 0.002; F = 105.40; n =7

The sign of *ρI and ρR*  are positive, reveals that the normal substituent effect operates on C6 carbon atom, i.e., an electron withdrawing substituent decrease the C7 carbon atom shielding and an electron releasing substituent increase it. Examination of chemical shift data in table (5), electron withdrawing substituent causes downfield shift and electron releasing substituent causes upfield. The magnitude of *ρR* greater than*ρI*indicate that the predominance of resonance effect over inductive effect in the chemical shift of C6 carbon atom.

The results of Yukawa-Tsuno equation (37), also indicate that the magnitude of ‘r’ is very low (<1).

log δ C6 = 0.016 *σp*+ 0.061 (*σp+*- *σp*) + 2.08 (37)

(±0.002) (±0.003) (±0.0008)

R = 0.996; SE = 0.001; F = 274.61; n =7

**C7 – Carbon atom**

The chemical shift of C7 carbon atom appeared over a range of about 2.3 ppm. The result of SSP analysis shown in table (7 ), fairly well correlation afford by *σp+/σp* constant is given in equation (38 ), and the plot of log δC7 vs σp+/σp is shown in Fig.(31).The result is shown in equation (38).

log δC7 = -0.004 *σp+/σp* + 2.21 (38 )

(±0.007) (±0.003)

r = 0.917; s = 0.001; F = 26.41; n = 7

The examination of chemical shift data (table 5 ) of C7 carbon electron-releasing group causes upfield shift by increasing the shielding and electron withdrawing group cause downfield shift by decreasing the shielding. The DSP analysis of C7 carbon with various *σR* scale is shown in table (8), the best fit is given in Eq.(39)

log δC7 = -0.001*σI* - 0.008 *σR* + 2.21 (39)

(±0.002) (±0.002) (±0.0018)

R = 0.928; SE = 0.001; F = 9.34; n = 6

The result of Yukawa-Tsuno equation (18 ), is given in table (9 ). The result of best fit of Eq. (18 ) is given in Eq.(40)

log δC7 = -0.001*σpo* - 0.005( *σp+*/ *σpo*) + 2.21 (40)

(±0.001) (±0.001) (±0.0007)

R = 0.937; SE = 0.001; F = 10.76; n = 6



log

**Fig. 31. The plot of log δC7 vs *σp+/σp***

**C11 – Carbon atom**

The chemical shift of C1 carbon appeared over a relatively narrow range of 1.46 ppm. The SSP analysis with various σ parameters, *σp+* gave excellent correlation, results shown in table (7). It gave negative correlation (Eq. 41) and negative slope indicates that a reverse substituent effect operates on the C11 carbon. The Hammett plot of log δ C11 vs *σp+* is shown in figure (32).

log δ C11 = -0.002 *σp+* + 2.21 (41 )

(±0.0001) (±0.0004)

Examination of chemical shift………

The DSP analysis of C11 carbon with various *σR* scale is given in table (8), the best fit is given in equations (42) and (43).

log δ C11 = -0.002 *σI*  - 0.003 *σR* + 2.21 (42)

(±0.0002) (±0.0002) (±0.0001)

R = 0.998; SE = 0.0001; F = 341.86; n =6

log δ C11 = -0.002 *F*  - 0.004 *R* + 2.21 (43)

(±0.0003) (±0.0002) (±0.0001)

R = 0.993; SE = 0.002; F = 152.18; n = 7

The result of Yukawa-Tsuno equation (18), is given in table (9) also indicate that the magnitude of ‘r’ is very low (<1).

log δ C11 = -0.003 *σp*  - 0.002 (*σp+ -σp*) + 2.21 (44)

(±0.0002) (±0.0003) (±0.0001)

R = 0.993; SE = 0.002; F = 152.18; n = 7



log

**Fig. 32 . The plot of log δ C11 vs *σp+***

**C22’-Carbon atoms**

The chemical shift of C22’**-**carbon atom appearedover a relativelynarrowrange of 18.28 ppm. The substituent effects on C22’ – Carbon atomswere investigated. The result of SSP analysis, is given in equation (7), a satisfactory correlation affords by Es constant and the plot of log δ C22’vs *Es*is shown in Fig. ().

log δ C22’ **=** -0.004 *Es* **+** 2.13 (45)

(±0.013) (±0.006)

r = 0.825; s = 0.016; F = 8.85; n = 7

The result of DSP analysis is given in table (8). Satisfactory correlation was obtained and the result is shown in equation (46).

log δ C22’ **=** 0.006 *F* **+** 0.008 *R* + 2.12 (46)

(±0.002) (±0.002)

R = 0.903; SE = 0.01; F = 8.85; n = 7