**Effect of substituents on the 13C - NMR chemical shifts of substituted 5-benzylidenebarbituric acids**

**P. Mohandass1, K. Radhakrishnan\*1, S.Manimekalai2, V.Suriyanarayanan3 and**

**S. Radhakrishnan4**

1Research Department of Chemistry, Saraswathi Narayanan College, Perungudi, Madurai –

625022, Tamil Nadu, India.

2Department of Chemistry,E.M.G. Yadava Women’s College,Madurai, Tamil Nadu, India.

3Electro-organic chemistry division, CSIR-CECRI, Karaikudi-630003, Tamil Nadu, India

4Central Instrumentation facilities, CSIR-CECRI, Karaikudi-630003, Tamil Nadu, India.

\*Corresponding author: Email: prskradha61@gmail.com; Contact:9443686474

**ABSTRACT**

Substituted 5-benzylidenebarbituric acids have been prepared and characterized by 1H and 13C NMR spectral analysis. Investigation of substituents effect and mode of transmission of electronic effects have been carried out by 13C NMR chemical shifts measurement, correlated it with LFER parameters in substituted 5-benzylidenebarbituric acids.

**Key words:** 1H, 13C NMR,substituted 5-benzylidenebarbituric acids, substituent effects.

**INTRODUCTION**

Correlation of the chemical shift with substituent constant has been widely used to investigate the nature of the effect of the substituent on the physical properties of compounds. Electron density around the nucleus of interst (H,C) is mostly affected by the electro-donating and electron-withdrawing ability of the substituent.

Therefore, a correlation between the observed chemical shift and any parameter representing such ability seems to be well-founded, and there are numerous reports on the subject1.

The single substituent parameter(SSP) approach which os represented by equation (1) has been used to correlate the chemical shift of *m*- and *p*- substituted aompound to unsubstituted compound using the Hammett *σm*and *σp* values. Values of 13C were reported for the system of *m-*and *p-*substituted cinnamic acids2. The dual substituent parameter (DSP) approach, on the other hand, divides the effect of substituent effect into inductive (*σI*) and resonance (*σp*) parameters as represented in Eq. (2).

*δ = ρσ + δo* (1)

*δ = ρIσI + ρRσR +δo* (2)

Yukawa and Tsuno proposed Eq (3) for dealing with enhanced resonance effects

*δ = ρσ +*r (*σ*+ - *σ*- ) *δo* (3)

The magnitude as well as the sign of *ρ* should have a profound meaning on the mechanism of the transmission of the substituent effect. For example, correlations of the chemical shift of carbonyl carbonyl carbon with the Hammett *σ* for the system of benzanilides, X-C6H4-CO-NH-C6H4-Y show normal correlation when Y is varied, but reverse correlation is observed when X is varied. Π Polarisation has been attributed for such observation.3,4 The magnitude of *ρx* (-2.838 ppm, r=0.940) is larger than that of *ρy* 90.853 ppm, r= 0.975) in DMSO -d6. The carbonyl carbon is directly bonded to the phenyl ring of X-C6H4, but it is separated by the nitrogen atom from C6H4-Y and therefore, the *ρx* should be larger than *ρy*. The estimation of sign and magnitude of the substituent chemical shift, however , seems to be complicated by many factors which affect the chemical shift.

Recently we reported the effect of substituents on the antimicrobial activities of substituted 2-benzylidene-1,3-indandiones1 and substituted

5-benzylidenebarbituric acids2.These above reports prompted us to undertake a detailed 13C NMR spectral and correlation study of substituted

5-benzylidenebarbituric acids.

**EXPERIMENTAL**

**Materials**

All chemicals used were purchased from Sigma Aldrich. Purity of the compounds was checked by TLC on silica gel G plate.Substituted 5-benzylidenebarbituric acids (Figure-I) were prepared by reaction of the corresponding substituted benzaldehyde with barbituric acid as reported earlier2.



Figure - I

**Spectra**

1H and 13C spectra of substituted 5-benzylidenebarbituric acids were obtained on a BRUKER AMX 400 MHz spectrometer. Chemical shifts 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.The 1H and 13C chemical shifts of the substituted 5-benzylidenebarbituric acids are presented in Tables 1 and 2 respectively.

**Assignment of 1H and 13C chemical shifts**

Assignments of 1H chemical shifts were made using considerations of splitting patterns, spin decoupling and additivity of chemical shifts. The 13C chemical shifts were assigned by intensity and SCS considerations.

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

**Acids.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |
| S.No. | Substituent-X | H2,2’ | H3,3’ | 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 |

**Table (2): 13C NMR chemical shifts of substituted 5-benzylidenebarbituric**

**acids**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | **X** | **C1** | **C2,2’** | **C3,3’** | **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 compounds7-10 . However, in many published studies summarized by Craik11 it has been apparent that the SCS values of X and Y at positions 4’ and 1’ in disubstituted benzenes Fig. (2) are non-additive. Lynch12 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



Figure -2

SCSX (Y) = a + b [ SCSX (H)] (4)

carbon *para-*to X in the series of 1’,4’-disubstituted benzenes (Fig. 2, X, Y ≠ H), SCSX(H) is the corresponding substituent chemical shift of the carbon *para* to X in monosubstituted benzenes (Fig. 2, 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. (2) with the value of ‘b’ ranging from 0.6 to 1.513. 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. (4) is less than one, then the fixed substituent at C-1’ Fig (2) 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 good 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 (3) and the plots of Lynch correlations shown in fig. (3).

**Table ( 3 ) : Results of Lynch correlationsa of 13C chemical shifts of compound**

**fig (1) 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. (3).** Lynch plot of SCS of C4 vs Sp

**Hammett and dual-substituent parameter correlations**

The 13C chemical shifts of the carbon atoms of the 5-benzylidene barbituric acid series afford several reasonable correlations using Hammett substituent parameters Eqn (1) and the data are given in Table (4).

The results of the correlations of 13C SCS values of 5-benzylidene barbituric acid series with *σI* and *σR* constants according to equation (2) are presented in Table (5)

**Table ( 4): 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(2)**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (5 ): DSP analysis of chemical shift data with dual parameter equation (3 ) .**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (6):Results of multiple regression analysis of 13C chemical shifts with σp,( σp+- σp)  and σpo,**

**(σp+- σpo) constants using Yukava – Tsuno equation (3).**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 |

**Substituent effects on the 13C NMR chemical shifts of the substituted 5-benzylidenebarbituric acids**

The use of 13C NMR SCS is to monitor the transmission of electroniceffectsin molecular frame works 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-benzylideneanilines14, N-benzylidenebensylamines15,chalcones16, benzophenones17, phenylacetylenes18,β-nitrostyrenes19,20, cinnamic acids21,22 and cinnamates23.

The 13C chemical shift data of several carbon atoms of 5-benzylidenebarbituric acid has been correlated with SSP equation (Eq. 1), DSP equations (Eq.2 ) and Yukawa-Tsuno equation (Eq.3)

**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 (4), an excellent correlation afford by σp+ / σp- constant given in equation (5), and the plot of log δ C4 vs

σp+ / σp-  as shown in Fig (4).

log δ C4 = 0.024 σp+ / σp- + 2.12 (5)

(±0.002) (±0.001)

r = 0.989; s = 0.003; n = 7

The result of DSP analysis in table (5), afford an excellent correlation are shown in equations (6 ) and (7).

log δ C4 = 0.02 σI + 0.005 σR + 2.12 (6)

(±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 (7)

(±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 (2), electron-withdrawing substituent causes downfield



log

**Fig. 4. 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 (3) is given in table (6).

The result of best fit eq. (3) is given in equation (8)

log δ C4 = 0.028 σp + 0.032 ( σp+- σp) + 2.12 (8)

(±0.006) (±0.009) (±0.002)

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

**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 (4). It gave negative correlation (Eq.9) and negative slope indicates that a reverse substituent effect operates on the carbonyl carbon. The Hammett plot of log δ C5 vs *σpo* gives,

log δ C5 = -0.01 *σpo*  + 2.19 (9)

(±0.001) (±0.0003)

r = 0.988; s = 0.001; n = 6

Examination of chemical shift data (table 2) of C5 carbon, electron releasing group cause downfield shift by increasing the shielding and electron withdrawing group cause upfield 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 (10) and (11)

log δ C5 = -0.01*σI* - 0.007 *σR* + 2.19 (10)

(±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 (11)

(±0.001) (±0.01) (±0.01)

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

From DSP analysis……………………

The results of Yukawa-Tsuno equation (12), also indicate that the magnitude of ‘r’ is very low(< 1).

log δ C5 = -0.015 *σp* + 0.004 (*σp+- σp*) + 2.19 (12 )

(±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 (4), excellent correlation afford by σp+ constant given in equation (13).

log δ C6 = 0.018 *σp+* + 2.08 (13)

(±0.001) (±0.00004)

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

The results of DSP analysis in table (5), afford an excellent correlation are shown in equations (14) and (15).

log δ C6 = 0.016 *σ I*+ 0.026 *σR* +2.08 (14)

(±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 (15)

(±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 (2), electron withdrawing substituent causes downfield shift and electron releasing substituent causes upfield. The magnitude of *ρR* greater than*ρI*indicates that the predominance of resonance effect over inductive effect in the chemical shift of C6 carbon atom.

The results of Yukawa-Tsuno equation (16), also indicate that the magnitude of ‘r’ is very low (<1).

log δ C6 = 0.016 *σp*+ 0.061 (*σp+*- *σp*) + 2.08 (16)

(±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 (4), fairly well correlation afford by *σp+/σp* constant is given in equation (17), and the plot of log δC7 vs σp+/σp is shown in Fig.(31).The result is shown in equation (17).

log δC7 = -0.004 *σp+/σp* + 2.21 (17 )

(±0.007) (±0.003)

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

The examination of chemical shift data (table 2) of C7 carbon electron-releasing group causes downfield shift by increasing the shielding and electron withdrawing group cause upfield shift by decreasing the shielding. The DSP analysis of C7 carbon with various *σR* scale is shown in table (5), the best fit is given in Eq.(18)

log δC7 = -0.001*σI* - 0.008 *σR* + 2.21 (18)

(±0.002) (±0.002) (±0.0018)

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

The result of Yukawa-Tsuno equation (3), is given in table (6). The result of best fit of Eq. (3) is given in Eq.(19)

log δC7 = -0.001*σpo* - 0.005( *σp+*/ *σpo*) + 2.21 (19)

(±0.001) (±0.001) (±0.0007)

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

**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 (4). It gave negative correlation (Eq. 20) and negative slope indicates that a reverse substituent effect operates on the C11 carbon.

log δ C11 = -0.002 *σp+* + 2.21 (20)

(±0.0001) (±0.0004)

Examination of chemical shift data in table (2) shows that the electro-releasing substituent causes downfield shift while electron-withdrawing substituent causes upfield shift .The DSP analysis of C11 carbon with various *σR* scale is given in table (8), the best fit is given in equations (21) and (22).

log δ C11 = -0.002 *σI*  - 0.003 *σR* + 2.21 (21)

(±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 (22)

(±0.0003) (±0.0002) (±0.0001)

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

The result of Yukawa-Tsuno equation (3), is given in table (6) also indicate that the magnitude of ‘r’ is very low (<1).

log δ C11 = -0.003 *σp*  - 0.002 (*σp+ -σp*) + 2.21 (23)

(±0.0002) (±0.0003) (±0.0001)

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

**Table (10): TSP analysis of SCS data of C22’ carbon atom of** **substituted**

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

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |  |  |
| S.No. | Scale | α | β | φ | R | s | F | PR | PS |
|  |  |  |  |  |  |  |  |  |  |
| 1. | *σI ,σR,ν* | 0.019  (±0.045) | 0.084  (±0.03) | -0.007  (±0.029) | 0.895 | 0.016 | 2.68 | 76.4 | 6.4 |
|  |  |  |  |  |  |  |  |  |  |
| 2. | *σI ,σRo,ν* | -0.0077  (±0.09) | 0.0187  (±0.06) | 0.0215  (±0.06) | 0.492 | 0.03 | 6.0 | 39.0 | 43.8 |
|  |  |  |  |  |  |  |  |  |  |
| 3. | *σI ,σR+,ν* | -0.09  (±0.07) | 0.035  (±0.02) | 0.057  (±0.03) | 0.760 | 0.155 | 1.37 | 19.2 | 31.3 |
|  |  |  |  |  |  |  |  |  |  |
| 4. | *σI ,σR-,ν* | 0.006  (±0.08) | 0.039  (±0.05) | 0.01  (±0.06) | 0.595 | 0.03 | 0.36 | 84.7 | 2.17 |
|  |  |  |  |  |  |  |  |  |  |
| 5. | *F, R, ν* | -0.0009  (±0.05) | 0.078  (±0.027) | 0.005  (±0.03) | 0.904 | 0.016 | 7.0 | 92.0 | 5.95 |
|  |  |  |  |  |  |  |  |  |  |

**C22’-Carbon atoms**

The chemical shift of C22’carbon atom appearedover a relativelynarrow range of about 2.116 ppm. The SSP analysis of C22’ *σo,*and *σo*\* gave poor correlation coefficients (r) 0.632 and 0.691 respectively The results of SSP analysis are given in Eqs. (45) and (46).

log δ C22’ = 0.044 *σo* + 2.09 (45)

(±0.02) (±0.008)

r = 0.632; s =0.02; n =7

log δ C22’ = 0.038 *σo*\* + 2.09 (46)

(±0.02) (±0.01)

r = 0.691; s =0.02; n =6

But the same parameter for *Es* gave satisfactory correlations, given in Eq.(47)

log δ C22’ = -0.044 *Es* + 2.13 (47)

(±0.01) (±0.006)

r = 0.825; s = 0.016; n =7

The best fit of DSP analysis is given in Eqs. (48) and (49).

log δ C22’ = 0.01 *σI*  + 0.08 *σR* + 2.11 (48)

(±0.02) (±0.02) (±0.01)

R = 0.891; SE = 0.01; n = 6

log δ C22’ = 0.006 F + 0.08 R + 2.12 (49)

(±0.02) (±0.02) (±0.01)

R = 0.903; SE = 0.01; n = 7

The sign of slopes *ρI* and *ρR* are positive reveals that the normal substituent effects operate on C22’ carbon atom. The magnitude of *ρR*is higher than the *ρI* indicate that the resonance effect is predominant over resonance effect on C22’ carbon atom.

The TSP analysis Charton steric parameter (ν) gave poor correlations that are given in table (10). The best fit of TSP analysis is taken from high correlation coefficient (R) and least standard error (SE) of the regression equation and the results are given in Eqs. (50) and (51).

log δ C22’ = 0.019 *σI*  + 0.084 *σR* - 0.007 ν + 2.11 (50)

(±0.045) (±0.03) (±0.029) (±0.015)

R = 0.895; SE = 0.016; n = 6

log δ C22’ = -0.0009 F + 0.078 R - 0.05 ν + 2.11 (51)

(±0.05) (±0.027) (±0.03) (±0.01)

R = 0.904, s =0.016, n = 7

A better description of the composition of the electrical effect24 is given by the equation,

PR =

PR is the percentage of delocalized effect. The result of TSP analysis is given in table (10) shows that the delocalized effect is predominant over the localized effect. The magnitude (%) of the steric factor97 is given by the equation,

PS =

The results of table (10) shows that steric effect is also operating to some extent.

REFERENCES

1. Craik, D.J.; Brownlee,R.T.C.*Prog.Phys.Org.Chem.*1983,14,1.

2. Slater,C.D.;Robinson,C.N.;Bies,R.; ryan,D.W.;Chang,K.;Hill,A.W.;Moore,

W.H.,Jr.;Otey T.G.; Popperireiter, M.L.; Reisser, J.R.; Stablein, G.E.; Waddy,

V.P. III; Willkinson, W.O.; Wray, W.A. *J.Org.Chem*. 1985, 50, 4125.

3. Suezawa, H.; Yuzuri, T.; Hirota, M.; Ito, Y.; Hanada, Y.

*Bull.Chem.Soc.Jpn*.1990,63,328.

4. Yuzuri, T.; Suezawa, H.; Hirota, M.; *Bull.Chem.Soc.Jpn*.1994,67,1664.

5. Radhakrishnan, K.; Mohandass, P.; Sankaralingam, S. and Chandramohan, S.

*Der Chemica Sinica,*2016,7(4), 1-7.

6. Radhakrishnan, K.; Mohandass, P.; Sankaralingam, S. and Chandramohan, S.

*International Journal of Chem.Tech. and Research (in press)*

7. Gronowitz, S.; Johnson, A.; Maholanyinova, S.; Tomo and Sokaniova,

*Org.Magn.Reson.,*1975,7,732.

8. Dana, G.; Convert, J.P.; Girault and Mathoz, E. *Can.J.Chem.,*1976,54,1827.

9. Ray, G.J.;Kurland, R.J. and Colter, A.K, *Tetrahedron,* 1971,27,735.

10. Hinton, J.F.; Layton,B.; *Org.Magn.Reson.,*1972,4,353.

11. Craik. D.J.; in Annual Reports on NMR spectroscopy, ED., Webb, G.A.;

*Academic Press*, London, Vol. 15, P.1. 1983.

12. Lunch. B.M.; *Can. J.Chem.*, 1977,541,55.

13. Suppu Perumal, Rama Suppu, Chandrasekeran and Veerappan Vijayabaskar

and David,A. Wilson, *Magn.Reson.chem.,* 1995,33,779.

14. Inamoto,N.; Kushida,K.;Masuda,H.Ohta,; Satoh,S.; Tamwa.Y,;

Tokomara,K.Tori and Yoshida,M. *Tetrahedran Lett.,* 1974,3617.

15. Arrowsmith,J.E.,; Cook,M.J. and Hardstone,D.J. *Org.Magn.Reson.,*

1978,11,160.

16. Solcaniova,E.; Toma and Gronowitz, *Org.Magn.Reson.,* 1976,8,439.

17. Shapiro,M.J.; *Tetrahedran*,1977,33,1091.

18. Dawson,D.A. and Reynolds,W.F. *Can.J.Chem.* 1975,53,373.

19. Happer,D.A.R. *Aust.J.Chem.*, 1976,53,373.

20. Happer,D.A.R.; McKerrow, S.M. and Wilkinson, A.L *Aust.J.Chem.*,

1977,2,1479.

21. Gunthor, H.; Prestein,J. and Watan, P.J., *Org.Mafn.Reson.,* 1975,7,339.

22. Modro,T.A., Renolds,W.F. and Kovupowa,E.S. *J.Chem.Soc., Perkin Trans.,*

1977,2,1479.

23. Happer,D.A.R*.* and Steenson, B.E.,*J.Chem.Soc., Perkin Trans.,*1983,2,843.

24. Charton, M. *J.Org.Chem.,*1975,40,407.