**The Nature and Mechanism of Transmission of Electronic Effects**

In order to assess the influence of substituents on the chemical shift of organic molecules a clear understanding of the nature and transmission of the different types of substituent effects is necessary.

**The Inductive Effect**

The basis of this electronic perturbation is originating in part from differences in electro-negativity which cause polarization of both σ- and π- bonds

and also from electrostatic effects experienced at the reaction center due to charges and dipoles resident on the substituent. A polarization of both σ- and π- bond by the substituent group is known as inductive effect Fig. (2), becoming progressively attenuated. The other, known as a field effect Fig. (3) is propagated through space and depends more for its intensity on proximity than on the number of bonds separating source and receptor. The electronic dipole field of the polar substituent-substrate bone can influence the reaction center across the space and this is called field effect51'55

δ+ δ+ δδ+

X - CH2 – CH2 – CH2-

Fig(2)



Fig (3)

The substituent effects in various aromatic systems act through polarization of π-electrons whether the polar nature of a substituent or substituent-carbon bond can polarize a π-system without charge transfer. This has been generally referred to as a π- inductive effect56 , which can arise in two ways, i) induction of charge differences on the underlying σ- framework may lead to compensating changes in the π- electronic distribution and is designated as πσ effect51,57,58. The partial charges on CH2-X, which in turn cause a redistribution of charge by an alternately polarization of π- electrons as in Fig. (4). ii) the π-system may also be polarized by a through-space electrostatic interaction with a remote dipole and this effect is termed as πF effect.

Fig (4)

The π- system may also be perturbed by repulsive interactions with neighbouring filled orbital on the substituent. This orbital repulsion effect is designated as πorbital Fig. (5).



Fig (5)

The π-electron system may also be polarized as in Fig. (6) by charge or   
dipoles located on the substituent. This effect called **π**-polarization, is basically  
different form π-inductive effect in the magnitude of charge density reorganization  
at *ortho*- and *meta-* positions.



Fig. (6)

**The Resonance Effect:**

The interaction of substituent orbitals of suitable systems with the π-orbitals of the ring can lead to charge transfer either to or from the substituent and this is called resonance effect (R). In order to exercise a resonance effect, a substituent must possess a p- or π- orbital which is available to conjugate with the π-MOs of the aromatic system.

(i) X- is a donor group and typically possesses an unshared electron pair or  
**π-**electrons on atom directly attached to the ring.  
 -NR2, -OR, -SR2, -Cl, -CH= CH2  
 (ii) substituents Z have a π*-* acceptor centre adjacent to the ring.



This effect, important in systems such as C6H5-X, is transmitted to a remote

probe site (Fig. 7) through the π-systems in appropriate molecules such as biphenyls etc.,



Fig. (7)

In systems like C6H5-CH2-Y, hyperconjugation59 (Fig. 8) involving σ-π  
bond interaction accounts for the resonance properties. A final possible effect is  
any perturbation of σ-electron populations arising from a change occurring in the  
π-system and this has been designated as σ- πeffect (σπ).



Fig. (8)

Of the various modes of transmission of electronic effects, the Iσ, F, πσ, and

πF effects depend on substituent polarity, while R and σπ, effects depends on charge

transfer ability.

**Recent Studies on the Substituent Effects on 13C Chemical Shifts**

Aleksandar D.Marinkovic et al.34 studied on ,13C SCS with N-l-p-substituted phenyl-5-methyl-4-carboxy uracils. They presented calculation relative to the polar and resonance effects accounts satisfactorily for substituent effects at uracil carbon atoms. Negative ρ values were found for several correlations shows reverse substituent effects.

Natasa V. Valentic *et* al.35reported that linear free energy relationships  
(LFER) were applied to the 1H and 13C NMR chemical shifts in the unsaturated  
backbone of cross-conjugated trienes 3-methylene-2-substituted-l,4-pentadienes.

Pal Perjesi and Co-workers36 reported that the SSP and DSP analyses were applied to study the transmission of substituent effects on selected 13C NMR chemical shifts of the cyclic chalcone analogues, E-2-(4'-X-benzylidene)-l tetralones and E-2-(4'-X-benzylidene)-l-benzosuberones

.M. Misic-Vukovic et al.37 studied correlation analysis of IR, 1H NMR and

UV spectral data of alkyl and aryl 4,6-disubstituted-3-cyano-2-pyridones using SSP and DSP as well as the more sophisticated multiparameter regression approaches. B.Z.Jovanovic et al.39 studied 13C NMR spectra of two series of pyridine chalcone analogs and discussed the transmission of electronic effects.

A D Marinkovic *et al.*61studied the l3C chemical shifts of the azomethine  
carbon atom for N- (substituted phenyl methylene)-3- and -4- amino benzoic acids  
having a wide range of substituent effects. The demand for electrons by the  
azomethine carbon atom in both investigated series has been compared, discussing  
the mode of transmission of substituent effects, both inductive and resonance, in  
relation to the geometry of investigated imines.

Pal Perjesi *et* al.61 studied SSP and DSP analysis was applied to study the  
transmission of substituent effects on IR carbonyl stretching frequencies E-2-(X  
benzylidene)- l -indanones, -tetralones and -benzosuberones. Similar analyses  
were performed for selected 13C NMR chemical shifts of some E-2-(X  
benzylidene)-l-indanones.

I. Wawer *et al.*62studied on the substituent effects and the molecular  
planarity by 1H and 13C NMR and AMI calculations of some azobenzenes and N  
benzylidene anilines.

S.Z. Dramanic *et al.*63studied the effect, of substituents on the 13C NMR  
chemical shifts of *para-* substituted α-phenyl-β-pyridylacrylic acids, using linear  
free energy relationships and multiple regression analysis as applied to 13C NMR  
chemical shifts of the C α and C β of the ethylenic bond and the carboxylic group  
carbon.

V A. Lopyrev *et al.*64reported the transmission of the substituent effects in  
2-substituted-1-methylbenzimidazoles by 13C NMR, the electronic effects of the  
substituents are transmitted to C-4 and C-7 mainly by the resonance mechanism, and to C-5, C-6 and N-CH3, by approximately equal contributions of the resonance  
and inductive components.

Hiroko Suezawa et al65 studied the substituent effects on the 1H, 13C and 15N

NMR spectra of a series of substituted benzanilide, XC6H4NHC6H4Y, measured in four solvents of different polarity were correlated with the electronic effects substituents by the use of the Hammett equation.

Mona jaiswal *et al*66studied the QSAR calculation of 13C NMR chemical shifts on carbinol carbon atoms have been attempted using a largest of distance based topological indices.  
 C.A.Van Walree *et a1*67reported some 29Si and 13C NMR studies were performed on series of 4-substituted phenyl trimethyl silanes and 4-substituted and 4,4’ -disubstituted diphenyl dimethyl silanes, within each series linear relationships  
are found between the chemical shifts and the Hammett substituent constant σp*.*

Kyu ok jeon *et al*68 prepared a series of m and p-substituted benzyl  
derivatives of pyrrole and tetra methyl 1-benzyl-3a,7a-dihydro indole and their 13C  
chemical shifts were correlated with SSP and DSP.