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 the compounds. Electron density around the nucleus of interest (C, H) is mostly affected by electron-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 is represented by Eq. (1) has been used to correlate the chemical shift of *m-* and *p-*substituted compound to unsubstituted compound using the Hammett σ*m*and σ*p* values. Values of 13σ were reported for the system of *m*- and *p*-substituted cinnamic acids in order to have a better correlation of 13C chemical shift2. The dual substituent parameter (DSP) approach, on the other hand, divides the effect of substituent effect into inductive (σ*I*) and resonance (σR) parameters as represented in Eq. (2).

*δ =* *ρσ* + *δo* (1)

*δ* = *ρIσI* + *ρRσR*  + *δo* (2)

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 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 polarization has been attributed for such observation3,4. The magnitude of *ρ*x (-2.838 ppm, r=0.940) is larger than that of *ρ*y (0.853 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 *ρ*x should be larger than *ρ*y. The estimation of sign and magnitude of the substituent chemical shift, however, seems to be complicated by many factors which affect the chemical shift.