On the transmission of substituent effect through bicyclo[2.2.2]octane and triptycene . A ^{19}F and ^{13}C substituent chemical shift investigation.

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Abstract

The substituent effect on the ^{19}F substituent chemical shift of four series namely: 1-X-4-p-fluorophenylbicyclo[2.2.2]octane (I), 1-X-4-m- fluorophenylbicyclo [2.2.2] octane(II), 1-X-4-o-fluorophenylbicyclo [2.2.2] octane (III), 1-X-4-(1,1-difluoroethynyl) bicyclo [2.2.2]octane (IV) and (V) has been investigated by the statistical technique "Factor Analysis ". Results have indicated the involvement of two types of substituent effects. Target Factor Testing has indicated a significant role for the Unity parameter U, σ_q, σ_m, $\sigma^{13}{}_p$, and Reynolds' σ_R and σ_F . Model designing has been utilized to quantify the substituent effect in terms of the above substituent parameters giving the following general models form: $\delta^{19}F$ SCS=$\rho_1\ \sigma_1 + \rho_2\ \sigma_2$. The ρ generally is a weighing factor. The ρ^{13} value for each series was compared giving the following order III < II < IV < I < V, slightly different order for Reynolds' ρ_F was observed according to this order, a previously proposed π-polarization structure of π-system was confirmed. Different order of ρ_R was observed than that of ρ_F. The order being IV< II < I < III < V. This indicates the insensitivity of substituent resonance parameter. A mechanism like the hyperconjugation might be possible route for the transmission of resonance effect. ^{13}C substituent chemical shift (SCS) of carbon (10) in 9-substituted-triptycene were successfully modeled by Taft's dual substituent parameters namely σ_I and σ_R giving the following model:

$$^{13}C\text{-}10\ SCS = -0.81\sigma_I + 1.25\ \sigma^-_R\ ;$$

multiple regression coefficient(R) = 0.98, F-Fisher= 47.4, n=6.

The negative ρ_I indicates reverse field effect, however, ρ_R being normal, which indicates a through three bonds (TB-3), in which electron deloclaization interaction which takes place between C-X and C-H of the C-10 through the intervening C-C double bond i.e. double hyperconjugation.

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