

Novel Correlations for P-Substituted Phenols in NMR Spectroscopy

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Abstract : Substituted phenols are widely used for the synthesis of advanced polycondensation polymers. In terms of the structure regularity and practical value of obtained polymers are of special interest the p-substituted phenols. The lanthanide induced shifts (LIS) of the aromatic ring and the OH protons by addition Eu(fod)₃ to various p-substituted phenols in CDCl₃ solvent were measured Nuclear Magnetic Resonance spectroscopy. A linear relationship has been observed between the LIS of protons ($\Delta\delta_{\text{complex}} - \delta_{\text{substrate}}$) and Eu(fod)₃/substrate molar ratios. The LIS protons of the investigated phenols decreases in the following order: OH > ortho > meta. The LIS of these protons also depends on both steric and electronic effects of p-substituents. The effect on the LIS of protons steric hindrance of substituents by way of example p-substituted alkyl phenols was studied. Alkyl phenols exhibit pronounced europium- induced shifts, their sensitivity increasing in the order: CH₃ > C₂H₅ > sym-C₅H₁₁ > tert-C₅H₁₁ > tert-C₄H₉, i.e. in parallel with decreasing steric hindrance. The influence steric hindrance p-substituents of phenols on the LIS of protons in sequence following decreases: OH > meta > ortho. Contrary to the expectations, it is found that the LIS of the ortho protons an excellent linear correlation with meta-substituent constants, σ_m for 14 p-substituted phenols: ΔH_2 , $\delta = 8.165 - 9.896 \sigma_m$ ($r^2 = 0.999$). Moreover, a linear correlation between the LIS of the ortho protons and ionization constants, PKa of p-substituted phenols has been revealed. Similarly, the linear relationships for the LIS of the meta and the OH protons were obtained. Use the LIS of the phenolic hydroxyl groups for linear relationships is necessary with care, because of the signal broadening of the OH protons. New constants may be determinate with unusual case by this approach.

Keywords : novel correlations, NMR spectroscopy, phenols, shift reagent

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