

The Aromaticity of P-Substituted O-(N-Dialkyl)Aminomethylphenols

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Abstract : Aromaticity, one of the most important concepts in organic chemistry, has attracted considerable interest from both experimentalists and theoreticians. The geometry optimization of p-substituted o-(N-dialkyl)aminomethylphenols, o-DEAMPH $\text{XC}_6\text{H}_4\text{CH}_2\text{Y}$ (X=p-OCH₃, CH₃, H, F, Cl, Br, COCH₃, COOCH₃, CHO, CN and NO₂, Y=o-N(C₂H₅)₂, o-DEAMPHs have been performed in the gas phase using the B3LYP/6-311+G(d,p) level. Aromaticities of the considered molecules were investigated using different indices included geometrical (HOMA and Bird), electronic (FLU, PDI and SA) magnetic (NICS(0), NICS(1) and NICS(1)zz indices. The linear dependencies were obtained between some aromaticity indices. The best correlation is observed between the Bird and PDI indices ($R^2 = 0.9240$). However, not all types of indices or even different indices within the same type correlate well among each other. Surprisingly, for studied molecules in which geometrical and electronic cannot correctly give the aromaticity of ring, the magnetism based index successfully predicts the aromaticity of systems. ¹H NMR spectra of compounds were obtained at B3LYP/6-311+G(d,p) level using the GIAO method. Excellent linear correlation ($R^2 = 0.9996$) between values the chemical shift of hydrogen atom obtained experimentally of ¹H NMR and calculated using B3LYP/6-311+G(d,p) demonstrates a good assignment of the experimental values chemical shift to the calculated structures of o-DEAMPH. It is found that the best linear correlation with the Hammett substituent constants is observed for the NICS(1)zz index in comparison with the other indices: $\text{NICS}(1)\text{zz} = -21.5552 + 1,1070 \sigma_p$ ($R^2 = 0.9394$). The presence intramolecular hydrogen bond in the studied molecules also revealed changes the aromatic character of substituted o-DEAMPHs. The HOMA index predicted for R=NO₂ the reduction in the π -electron delocalization of 3.4% was about double that observed for p-nitrophenol. The influence intramolecular H-bonding on aromaticity of benzene ring in the ground state (S₀) are described by equations between NICS(1)zz and H-bond energies: experimental, E_{exp} , predicted IR spectroscopical, E_{ν} and topological, EQTAIM with correlation coefficients $R^2 = 0.9666$, $R^2 = 0.9028$ and $R^2 = 0.8864$, respectively. The NICS(1)zz index also correlates with usual descriptors of the hydrogen bond, while the other indices do not give any meaningful results. The influence of the intramolecular H-bonding formation on the aromaticity of some substituted o-DEAMPHs is criteria to consider the multidimensional character of aromaticity. The linear relationships as well as revealed between NICS(1)zz and both pyramidal nitrogen atom, $\Sigma\text{N}(\text{C}_2\text{H}_5)_2$ and dihedral angle, $\varphi \text{C}_{\text{Ar}} - \text{C}_{\text{Ar}} - \text{CCH}_2 - \text{N}$, to characterizing out-of-plane properties. These results demonstrated the nonplanar structure of o-DEAMPHs. Finally, when considering dependencies of NICS(1)zz, were excluded data for R=H, because the NICS(1) and NICS(1)zz values are the most negative for unsubstituted DEAMPH, indicating its highest aromaticity; that was not the case for NICS(0) index.

Keywords : aminomethylphenols, DFT, aromaticity, correlations

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