Bridge effect of the C=N bond and long distance electronic effects of electron-donor (D) substituents on N-(4-D-benzylidene)-4-nitroanilines and N-(4-nitrobenzylidene)-4-D-aniline

Leiva, Manuel A.

Vargas, Victor

Morales, Raúl G. E.

By means of 13C-NMR spectroscopy and ab initio molecular orbital theory calculations we have analyzed the bridge effect of the C=N bond and the long distance electronic effect of the electron-donor substituents (D: -NO2, -Cl, -H, -CH3, -OCH3, and -N(CH3)2) on N-(4-D-benzylidene)-4-nitroanilines (DCNA) and N-(4-nitrobenzylidene)-4-D-ani-line (DNCA), in the ground electronic state. From the 13C-NMR spectral assignment signals and our molecular orbital calculations on a Gaussian HF/6-31G* basis set, we have found a linear functional dependence of the chemical shifts on the electronic charge of the C1, C4, C1?, and C4? centers. Furthermore, we have determined the effect of the nitrogen centres on the molecular bridge by means of the chemical shifts of the carbon centres, the theoretical charge densities and the dipolar moments. From an electronic point of view, our results permit determine in a quantitative way the local charge accumulation capacity on the C=N bond induced by the electron-