Spectroscopic and theoretical studies of some 4'-substituted-phenyl 2-(ethanesulfonyl)acetates. Structure of 4'-nitrophenyl 2-(ethanesulfonyl) acetate

Resumo
An analysis of carbonyl bands in the infrared spectra of some 2-ethylsulfonyl 4'-substituted phenylacetates bearing substituents NO2 (1), H (2) and OMe (3), supported by B3LYP/6-31G(d,p) and SM5.42R at PM3 level calculations, along with natural bond orbital analysis (NBO) and X-ray diffraction (for 1) was performed. Theoretical data indicated the existence of two stable gauche conformations (g(1) and g(2)). The g(1) conformer is the most stable, least polar and has the lowest $\nu$(CO) frequency. The more intense, lower frequency carbonyl doublet component found in CCl4 solution is assigned to the g(1) conformer. As the solvent dielectric constant increases (going from CCl4 to MeCN) the higher frequency $\nu$(CO) doublet increases in intensity. This behaviour is reproduced by the solvation free energy calculations, supporting the conformer assignments. NBO calculations indicate that the most important orbital interaction is LPO9 $\rightarrow$ pi* C7 = O8 for both conformers, which corresponds to $[\text{C} = \text{O} \leftrightarrow \text{C}^{+}\text{O}^{-}]$ conjugation. This stabilises the g(1) conformer to a greater extent and is responsible for the lower $\nu$(CO) frequency. The sum of the selected NBO delocalisation energies for 1-3 indicates that the g(1) conformer is more stable. It is concluded that the calculated greater stability of the g(1) conformer is due to a balance of attractive electrostatic and orbital interactions along with relevant hydrogen bonds. The X-ray crystal structure analysis of 1 shows the presence of two crystallographic independent but almost superimposable molecules each which adopt a cis geometry. The molecules are consolidated into the three-dimensional crystal packing by C-H...O interactions as well as by nitro-N-O...pi(phenyl) contacts.