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Application of Hammett equation to intramolecular hydrogen bond strength in para-substituted phenyl ring of trifluorobenzoylacetone and 1-aryl-1,3-diketone malonates

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RESEARCH ARTICLE

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ABSTRACT

The stability of two stable *cis*-enol forms in two categories of β-diketones, including para-substituted of trifluorobenzoylacetone (X-TFBA) and 1-aryl-1,3-diketone malonates (X-ADM, X: H, NO_2, OCH_3, CH_3, OH, CF_3, F, Cl, and NH_2) has been obtained by different theoretical methods. According to our results, the energy difference between the mentioned stable chelated enol forms for the titled compounds is negligible. The theoretical equilibrium constants between the two stable *cis*-enol of the mentioned molecules are in excellent agreement with the reported experimental equilibrium constant. In addition, the effect of different substitutions on the intramolecular hydrogen bond strength has been evaluated. The correlation between Hammett para-substituent constants, σ_p. with the theoretical and experimental parameters related to the strength of hydrogen bond in p-X-TFBA and p-X-ADM molecules also investigated by means of density functional theory calculations. The electronic effects of para-substitutions on the intramolecular hydrogen bond strength were determined by NMR and IR data related to intramolecular hydrogen bond strength, geometry, natural bond orbital results, and topological parameters. These parameters were correlated with the Hammett para-substituent constants, σ_p. Good linear correlations between σ_p and the several parameters related to the hydrogen bond strength, in this study were obtained.

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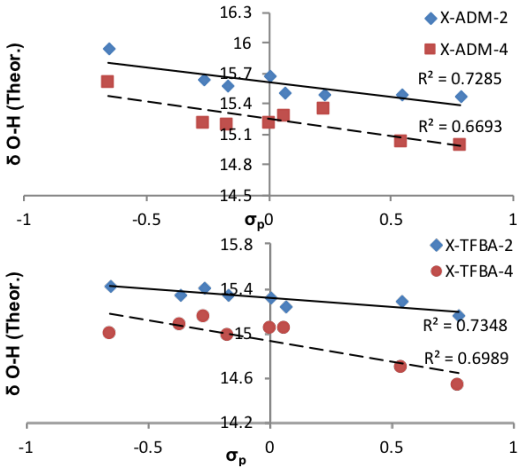
Supplementary materials



http://dx.doi.org/10.5155/eurjchem.9.3.213-221.1713

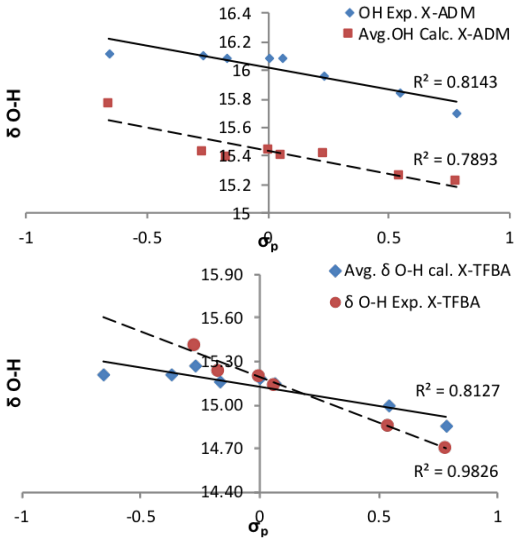


Figure S1. The linear correlations between the theoretical and experimental δ_{OH} with σ_p.

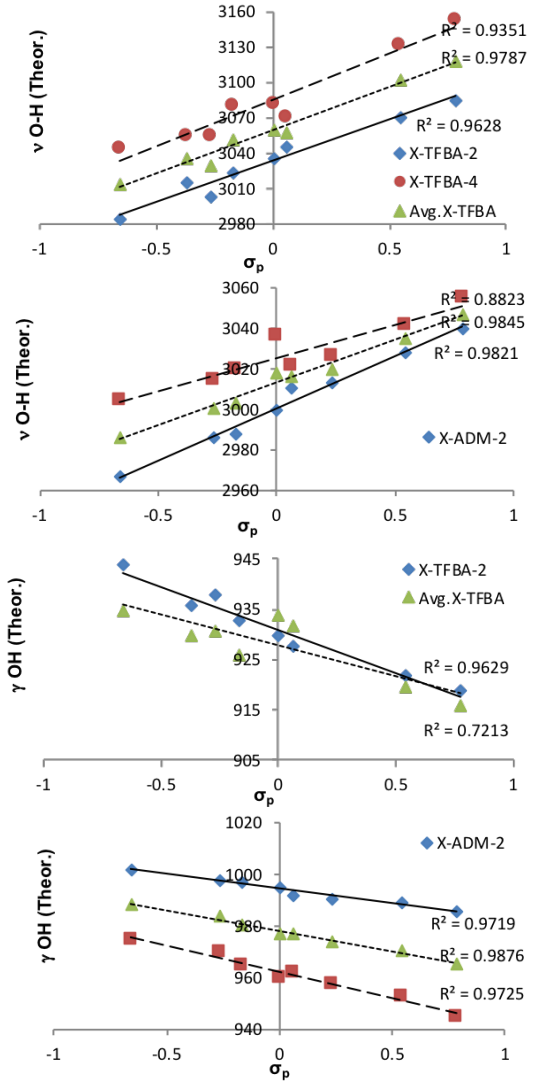


Figure S2. The linear correlations between the theoretical ν_{OH} and γ_{OH} frequencies of enol-2, enol-4 and their average values and σ_p.

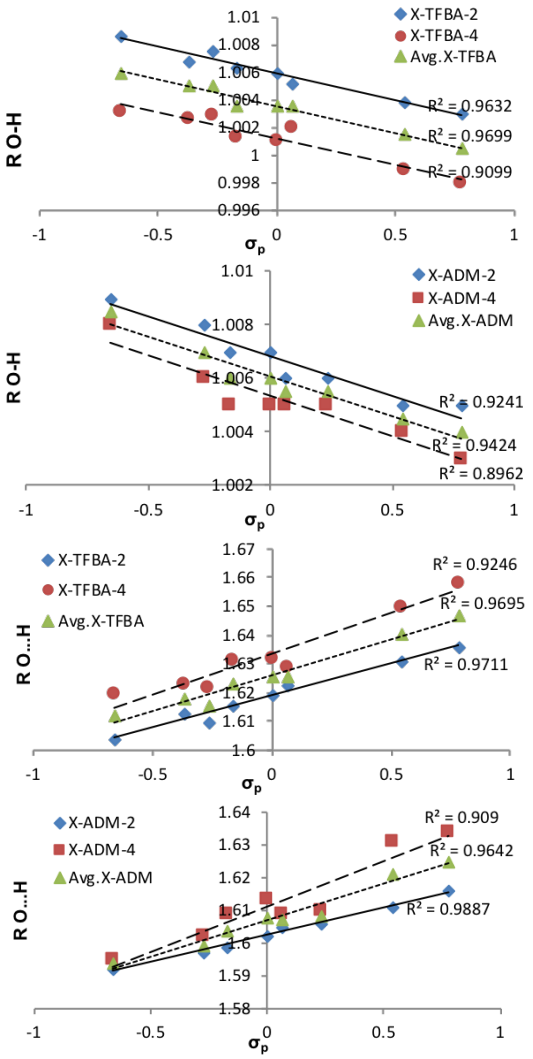
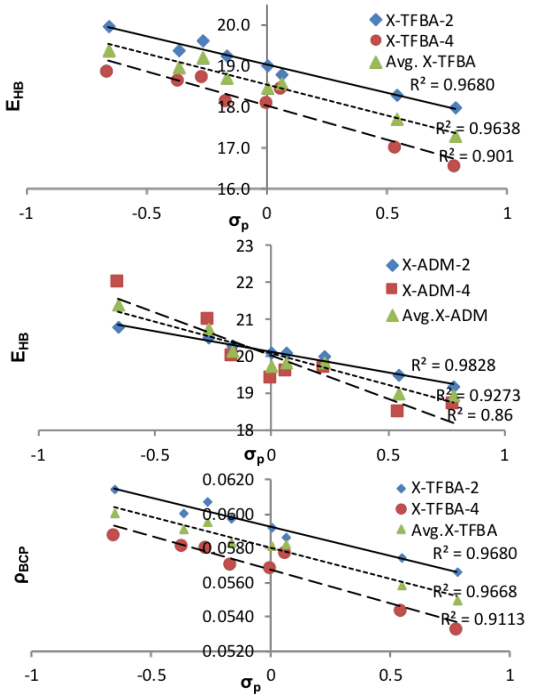


Figure S3. The linear correlations between σ_p and some geometrical parameters related to IHB strength.



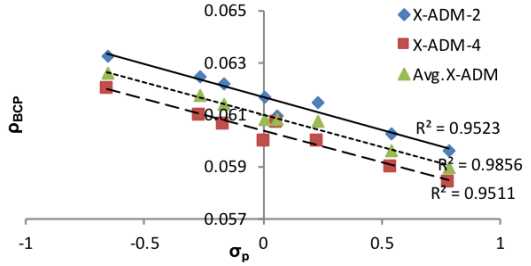


Figure S4. The linear correlations between σ_p and the topological parameters related to IHB strength.

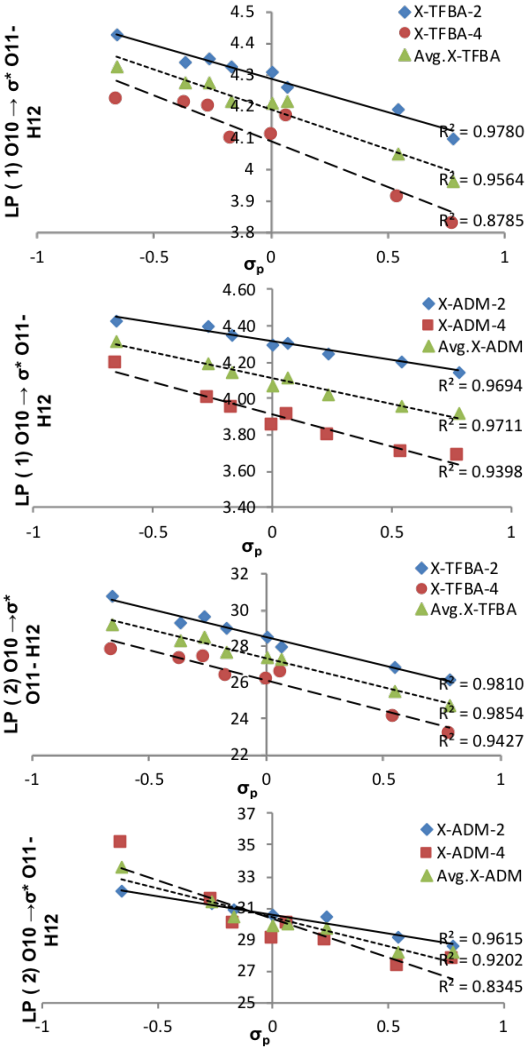
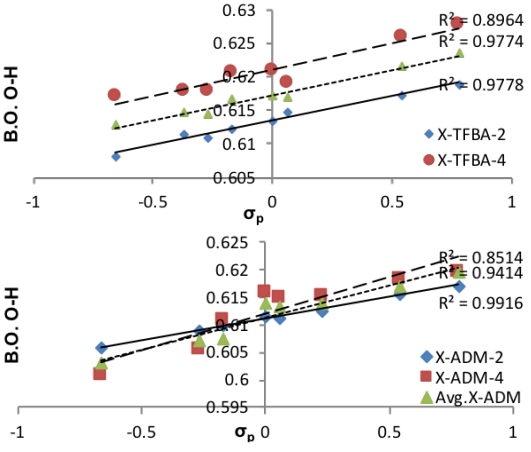


Figure S5. The linear correlations between second order perturbation energy (E^2) as lp(O)→σ*(O–H) with σ_p.



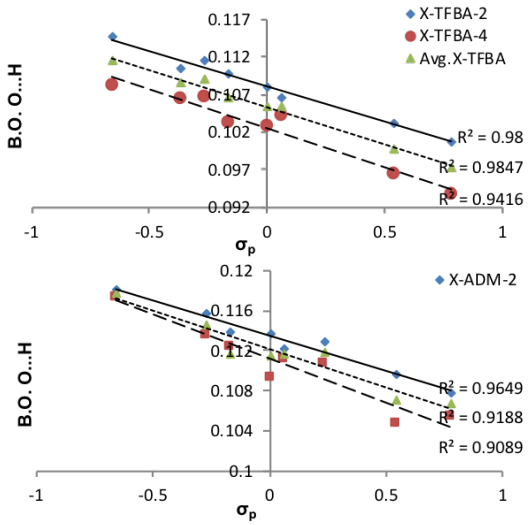


Figure S6. The linear correlations between bond orders of O-H and O...H with σ_p.