Title: Trends in properties of para-substituted 3-(phenylhydrazo)pentane-2,4-diones

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Abstract: Trends between the Hammett's sigma(p) and related normal sigma(n)(p), inductive sigma(I), resonance sigma(R), negative sigma(-)(p) and positive sigma(+)(p) polar conjugation and Taft's sigma(o)(p) substituent constants and the N-H center dot center dot center dot O distance, delta(N-H) NMR chemical shift, oxidation potential (E-p/2(ox), measured in this study by cyclic voltammetry (CV)) and thermodynamic parameters (pK, Delta G(0), Delta H-0 and Delta S-0) of the dissociation process of unsubstituted 3-(phenylhydrazo)pentane-2,4-dione (HL1) and its para-substituted chloro (HL2), carboxy (HL3), fluoro (HL4) and nitro (HL5) derivatives were recognized. The best fits were found for sigma(p) and/or sigma(-)(p) in the cases of d(N center dot center dot center dot O), delta(N-H) and E-p/2(ox), showing the importance of resonance and conjugation effects in such properties, whereas for the above thermodynamic properties the inductive effects (sigma(I)) are dominant. HL2 exists in the hydrazo form in DMSO solution and in the solid state and contains an intramolecular H-bond with the N center dot center dot center dot O distance of 2.588(3)angstrom. It was also established that the dissociation process of HL1-5 is non-spontaneous, endothermic and entropically unfavourable, and that the increase in the inductive effect (sigma(I)) of para-substitutents (-H < -Cl < -COOH < -F < -NO2) leads to the corresponding growth of the N center dot center dot center dot O distance and decrease of the pK and of the changes of Gibbs free energy, of enthalpy and of entropy for the HL1-5 acid dissociation process. The electrochemical behaviour of HL1-5 was interpreted using theoretical calculations at the DFT/HF hybrid level, namely in terms of HOMO and LUMO compositions, and of reactivities induced by anodic and cathodic electron-transfers. Copyright (C) 2010 John Wiley & Sons, Ltd.

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