

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

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Source: Journal of Physical Organic Chemistry

Volume: 24 **Issue:** 9 **Pages:** 764-773 **DOI:** 10.1002/poc.1824 **Published:** Sep 2011

Document Type: Article

Language: English

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 $d(N \text{ center dot center dot center dot } O)$, $\delta(N-H)$ 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)Å. 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-substituted (-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.

Author Keywords: 3-(4-Substituted Phenylhydrazo)Pentane-2,4-Diones; Correlation Analysis; DFT Calculations; Redox Potential; Tautomers; Thermodynamic Parameters

Keywords Plus: Structure-Reactivity Parameters; Ruthenium Anticancer Drugs; Substituted Benzoic-Acids; Beta-Diketones; Crystal-Structure; Redox Properties; Potential Antineoplastics; Coordination-Compounds; Ferrocene Derivatives; Electron-Transfer

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Funding:

Funding Agency	Grant Number
Foundation for Science and Technology (FCT), Portugal	
PPCDT (FEDER)	
'Science 2007' programs	

Publisher: Wiley-Blackwell

Publisher Address: Commerce Place, 350 Main St, Malden 02148, MA USA

ISSN: 0894-3230

Citation: KOPYLOVICH, Maximilian N.; MAHMUDOV, Kamran T.; GUEDES DA SILVA, M. Fátima C.; MARTINS, Luísa M. D. R. S.; KUZNETSOV, Maxim L.; SILVA, Telma F. S.; FRAÚSTO DA SILVA, João J. R.; POMBEIRO, Armando J. L. - Trends in properties of para-substituted 3-(phenylhydrazo)pentane-2,4-diones. Journal of Physical Organic Chemistry. ISSN 0894-3230. Vol. 24, n.º 9 (2011) p. 764-773.