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

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Trends between the Hammett's  $\sigma_p$  and related normal  $\sigma_p^n$ , inductive  $\sigma_l$ , resonance  $\sigma_R$ , negative  $\sigma_p^-$  and positive  $\sigma_p^+$ polar conjugation and Taft's  $\sigma_p^o$  substituent constants and the N—H···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 (HL<sub>1</sub>) and its *para*-substituted chloro (HL<sub>2</sub>), carboxy (HL<sub>3</sub>), fluoro (HL<sub>4</sub>) and nitro (HL<sub>5</sub>) derivatives were recognized. The best fits were found for  $\sigma_p$ and/or  $\sigma_p^-$  in the cases of  $d_{N\cdots O}$ ,  $\delta_{N-H}$  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 ( $\sigma_1$ ) are dominant. HL<sub>2</sub> exists in the hydrazo form in DMSO solution and in the solid state and contains an intramolecular H-bond with the N···O distance of 2.588(3) Å. It was also established that the dissociation process of HL<sub>1-5</sub> is non-spontaneous, endothermic and entropically unfavourable, and that the increase in the inductive effect ( $\sigma_1$ ) of *para*-substitutents (—H < —Cl < —COOH < —F < —NO<sub>2</sub>) leads to the corresponding growth of the N···O distance and decrease of the pK and of the changes of Gibbs free energy, of enthalpy and of entropy for the HL<sub>1-5</sub> acid dissociation process.

The electrochemical behaviour of HL<sub>1-5</sub> 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 © 2010 John Wiley & Sons, Ltd.

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**Keywords:** 3-(4-substituted phenylhydrazo)pentane-2,4-diones; correlation analysis; DFT calculations; redox potential; tautomers; thermodynamic parameters

# INTRODUCTION

Although azoderivatives of  $\beta$ -diketones (ADB, herein denoted as HL, Scheme 1) are known since long,<sup>[1-3]</sup> they still show a surprisingly modest impact in organic, coordination and organometallic chemistries. In spite of the relatively limited number of publications on this class of compounds, it has been shown that ADB can be potentially applied for optical storage,<sup>[4]</sup> spectrophotometric determination of some metal ions,<sup>[5-7]</sup> futher organic synthesis,<sup>[8]</sup> as spin-coating films,<sup>[9]</sup> liquid crystals,<sup>[10]</sup> self-assembled layers,<sup>[11]</sup> antineoplastics,<sup>[12,13]</sup> semiconducting materials,<sup>[14]</sup> antipyretic,<sup>[15]</sup> analgesic,<sup>[15,16]</sup> antibacterial<sup>[17-19]</sup> drugs, etc. Hence, the study of their physico-chemical properties and in particular of their tautomery is of interest from both theoretical and practical points of view.

All the structurally studied ADB have a characteristic conjugated heterodienic system forming a strong intramolecular resonance assisted N—H···O hydrogen bond (RAHB) linking one of the carbonyl groups to the NH-moiety of the hydrazo unit.<sup>[20–24]</sup> It was shown<sup>[22]</sup> that this hydrogen bond strongly influences the properties of ADB and that its strength is essentially determined by the degree of  $\pi$ -delocalization within the ketohydrazone hetero-conjugated system and is modulated by the factors that can affect the degree of conjugation, including inductive ones and non-bonding intermolecular interactions. On the other hand, it was assumed that there is a cooperative effect

between the H-bond strengthening and the  $\pi$ -electron delocalization of conjugated bonds linking the proton-donating and proton-accepting groups.<sup>[25,26]</sup> Since the interacting groups, N—H and C=O, can be considered as substituents, their electronic properties can be described by the Hammett's and Taft's  $\sigma$  substituent constants,<sup>[27-38]</sup> which express the degree of electron-donating or electron-accepting character of the substituent.<sup>[28-43]</sup>

In the RAHB systems, the proton-donating N—H group is an electron-donor when considered as a substituent (thus with a

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Scheme 1. Possible tautomeric equilibria in azoderivatives of  $\beta$ -diketones HL<sub>1-5</sub>

negative  $\sigma$  value), whereas the proton-accepting C=O group is an electron-acceptor substituent (hence with a positive  $\sigma$  value). They may interact via an intramolecular H-bond, forming a very stable cycle of conjugated bonds. As a result, the N—H bond length should elongate and the electron-donor properties of this group as a substituent should become stronger. On the other hand, the proton approaches C=O with formation of C=O···H and, as a consequence, the electron-attracting power, as a substituent, of C=O in C=O···H should increase in comparison with C=O itself.<sup>[44,45]</sup>

Another important feature of ADB is their tautomerism. The keto-enol tautomerism of β-diketones has been extensively studied during the past five decades<sup>[46]</sup> and still attracts attention,<sup>[47]</sup> showing that the relative amounts of the tautomers are connected with the intramolecular hydrogen bonding and depend on the substituents, temperature and media.<sup>[48]</sup> In the case of ADB one more conjugated N=N double bond is present, thus significantly increasing the number of possible tautomers: (E-, Z-) enol-azo, keto-azo and hydrazo (Scheme 1).<sup>[49,50]</sup> Furthermore, there are several possible conformers for each category of tautomers depending on the overall symmetry of the molecule.<sup>[49–52]</sup> For example, it has been observed that in ADB formed by unsymmetrical  $\beta$ -diketones, the six-membered H-bonded ring will be generated at the more sterically favourable side of the molecule.<sup>[3]</sup> Moreover, the substituent in the para position of the phenyl ring relative to the hydrazone function of ADB should provide another important factor to influence their structural properties.

Thus, the aim of this paper is to study in a quantitative way possible correlations among the physico chemical properties of *para*-substituted 3-(phenylhydrazo)pentane-2,4-diones (HL), i.e. (Scheme 1) 3-(phenylhydrazo)pentane-2,4-dione (HL<sub>1</sub>), 3-(4-chlorophenylhydrazo)pentane-2,4-dione (HL<sub>2</sub>), 3-(4-carboxyphenylhydrazo)pentane-2,4-dione (HL<sub>3</sub>), 3-(4-fluorophenylhydrazo) pentane-2,4-dione (HL<sub>4</sub>) and 3-(4-nitrophenylhydrazo) pentane-2,4-dione (HL<sub>5</sub>).

# **RESULTS AND DISCUSSION**

#### Synthesis of HL<sub>2</sub> and spectroscopic study

The *para*-substituted 3-(phenylhydrazo)pentane-2,4-diones (HL, Scheme 1) were prepared by aqueous diazotization and azocoupling. The synthesis and some properties of  $HL_{1,3-5}$  were reported before.<sup>[49,53-55]</sup> It has also been found that diazotized

aromatic amines couple successfully with a range of reactive methylene coupling components in an organic solvent and in the presence of sodium acetate.<sup>[1–3]</sup> However, attempts to prepare our *para*-substituted  $HL_{1,3-5}$  compounds using this base either failed completely or gave a low yield of a highly impure product.<sup>[49,53–55]</sup> Thus, we modified the reported procedure and found that good yields of HL could be obtained when the coupling was undertaken in a *sodium hydroxide* solution (described in Experimental section).

The ADB prepared in this study potentially can exist in the enol-azo, keto-azo and hydrazo tautomeric forms (Scheme 1), but earlier it was shown experimentally that hydrazones formed from pentane-2,4-dione exist in the hydrazo form both in solution and in the solid state.<sup>[49,53-55]</sup> An intramolecular hydrogen bridge linking one of the carbonyl groups to the NH-moiety of the hydrazone unit and forming the six-membered hydrogen bonding ring was found to be a characteristic feature of the hydrazo form (Scheme 1) thus stabilizing this particular tautomer.

The infrared spectra of hydrazones based on a pentane-2,4dione and, in particular, the position of the carbonyl stretching vibration, have been of considerable importance in establishing that the compounds exist in the hydrazo form. The solid state IR spectrum of the hydrazone HL<sub>2</sub> shows two intense carbonyl bands assignable to the hydrazo form with intramolecular hydrogen bonding (N—H  $\nu$ (C=O),  $\nu$ (C=O···H) and  $\nu$ (C=N) are observed at 3449, 1668, 1627 and 1587 cm<sup>-1</sup>, respectively) in view of the agreement with published reports on its analogues HL<sub>1,3-5</sub>.<sup>[49,53-55]</sup>

In the <sup>1</sup>H NMR spectrum of HL<sub>2</sub>, the hydrazone proton appears as a broad singlet at  $\delta$  13.85, which is a clear indication of a protonated nitrogen atom adjacent to the aromatic unit. Moreover, the two methyl groups of the pentane-2,4-dione moiety yield separate singlets at  $\delta$  2.40 and 2.47. The stable six-membered H-bonded ring (Scheme 1) turns the hydrazone tautomeric structure unsymmetrical in accord with the non- equivalence of the two methyl groups.

Considering all the azoderivatives of pentane-2,4-dione of this study, i.e.  $HL_{1-5}$  (Scheme 1), one observes that the functional group (X) in *para* position of the aromatic part of the molecule influences  $\delta_{N-H}$ , although no clear linear relationship was found between the Hammett's or any related substituent constants (Tables S1–S3; Tables and figures indicated with the capital letter S are given as Supplementary Information) and that chemical shift, the latter taken from the following sources:  $HL_{1}$ ,<sup>[53]</sup>  $HL_{2}$  (this work, Experimental section),  $HL_{3}$ ,<sup>[54]</sup>  $HL_{4}$  (Supplementary Information),  $HL_{5}$ <sup>[55]</sup> (all data in CDCl<sub>3</sub>). The best (although rather

rough) 'correlation' was observed for the Hammett's  $\sigma_{\rm p}$  constant ( $\sigma_{\rm p} = -2.55\delta_{\rm N-H} + 37.67$ ,  $r^2 = 0.758$ , n = 5) (Fig. S1). An increase of the electron-acceptor character of the X substituent corresponds to a proton shift to higher field. The normal  $\sigma_{\rm p}^{\rm n}$  constant follows a similar trend, but the inductive ( $\sigma_{\rm I}$ ) and resonance ( $\sigma_{\rm R}$ ) constants do not correlate at all. Hence, both resonance and inductive substituent effects appear to operate significantly.

#### X-ray diffraction study

Compound HL<sub>2</sub> (Fig. 1) exhibits a nearly planar overall conformation with structural parameters, bond distances and angles similar to those found in  $HL_{1,3-5}^{[49,53-55]}$ , as presented in Tables S4–S6.

The crystal lattice of  $HL_2$  is stabilized by hydrogen bonding interactions. Indeed, while the chloride atoms act as acceptors of the H7C hydrogens of vicinal molecules leading to the formation of a 1D chain, the O2 carbonyl oxygens act as acceptors in both intramolecular (with N2—H2N) and intermolecular (with the aromatic C2—H2) hydrogen bondings to the nearest molecules in the same plane, which thus expand the structure to a second dimension. Due to the hydrogen bonding involving O2, the C10—O2 bond length is longer than that of 'free' C8—O1 (1.234(4) and 1.223(3) Å, respectively).

The most significant characteristic for this structure is the presence of the HN—N=C—C=O conjugated heterodienic system with formation of the heteronuclear N2—H2N···O2 RAHB. In particular, Table S5 compares the bond lengths and angles involved in the N—H···O RAHBs, as well as in other relevant hydrogen interactions.

In the six-membered H2N—N2—N1—C9—C10—O2 cycle the angles vary from 103.3(2) to 130.6(2)°, the widest value belonging to O2—H2N—N2. The *para*-Cl substituent (with  $\sigma_p = 0.23$ ) causes a significant shortening of the N—H bond and a slight elongation of the N···O distance, which falls in the N···O range for HL<sub>1,3-5</sub>, 2.580–2.603 Å.<sup>[49,53–55]</sup>

The plots of the Hammett's  $\sigma_{\rm p}$ , Taft's  $\sigma_{\rm p}^{\rm o}$  and related substituent constants *versus* the N···O distance (Tables S1–S3) show that this distance appears to tend to increase with an increase of the electron-acceptance of the substituent, though the  $d_{\rm N...O}$  changes in some cases are insignificant and a clear correlation cannot be established. The best 'relationships', with  $r^2 = 0.84-78$ , were found for  $\sigma_{\rm p}^-$  ( $\sigma_{\rm p}^- = 52.25d_{\rm N...O} - 135.01$ ,  $r^2 = 0.842$ , n = 5, Fig. S2) and Taft's  $\sigma_{\rm p}^{\rm o}$ . Hence, the functional group in *para* position of the ADB phenyl ring affects the  $d_{\rm N...O}$  distance and thus the tautomeric equilibrium, what can be particularly important for some applications of this class of compounds (Introduction Section).

#### Thermodynamic functions of the dissociation process

To determine the dissociation constants of the studied ADB, pH-metric titration in aqueous-ethanol media was used. The ionic strength was maintained constant (l = 0.1 M) by adding a calculated amount of KCI. The dissociation constant of HL<sub>5</sub> (Supplementary Information, Table S7) was calculated by the following equation:<sup>[56]</sup>

$$\mathsf{p}\mathsf{K} = -\mathsf{log}\mathsf{K} = \mathsf{p}\mathsf{H} + \mathsf{log}\,[\mathsf{HL}] - \mathsf{log}\,[\mathsf{L}^{-}]$$

and found to be  $pK = 8.10 \pm 0.02$ . For determination of the dissociation constants of the diprotic acid HL<sub>3</sub>, the Schwarzenbach algebraic method was used:<sup>[57]</sup>

$$\begin{split} & \mathcal{K}_{1} = \frac{[H^{+}]\{ac_{H_{2L}} + [H^{+}] - [OH^{-}]\}}{(1 - \alpha)c_{H_{2L}} - [H^{+}] + [OH^{-}]}; \\ & \mathcal{K}_{2} = \frac{[H^{+}]\{(\alpha - 1)c_{H_{2L}} + [H^{+}] - [OH^{-}]\}}{(2 - \alpha)c_{H_{2L}} - [H^{+}] + [OH^{-}]} \end{split}$$

where  $c_{H_2L}$  is total concentration of the diprotic acid (HL<sub>3</sub>) and a is neutralization point. The performed calculations (calculation details and Table S8 at Supplementary Information) gave  $pK_1 = 3.98 \pm 0.03$  and  $pK_2 = 8.24 \pm 0.02$ .

The quantum-chemical calculations at the B3LYP level of theory indicate that in CH<sub>3</sub>CN solution the hydrazo-form of HL<sub>1</sub> (Scheme 1) is the most stable one followed by the *Z*-enol-azo, *E*-enol-azo and keto-azo forms (less stable by 7.5, 9.2 and 15.4 kcal/mol, respectively). The deprotonated hydrazo-form of HL<sub>3</sub> with the proton removed from the COOH group (HL<sub>3</sub><sup>-</sup>**a**) is more stable than the deprotonated form HL<sub>3</sub><sup>-</sup>**b** with the proton abstracted from the NH group (Table S9 in Supplementary Information). This indicates that the COOH moiety in HL<sub>3</sub> is more acidic than the NH unit, and the experimentally determined pK<sub>1</sub> and pK<sub>2</sub> values correspond to the proton elimination from the COOH and NH groups, respectively.

The dissociation constants of  $HL_{3,5}$  have been evaluated at 308 and 318 K and the thermodynamic functions for the dissociation process were calculated using the following well known relationships:<sup>[58,59]</sup>

$$\begin{split} \Delta G^{0} &= 2.303 RT pK; \\ \Delta H^{0} &= \left[ -R \big( pK_{(T_{3})} - pK_{(T_{1})} \big) \right] / \left[ (1/T_{3}) - (1/T_{1}) \right]; \\ \Delta S^{0} &= \left( \Delta H^{0} - \Delta G^{0} \right) / T. \end{split}$$

The thermodynamic parameters of the dissociation process of  $HL_{1,2,4}$  were described earlier<sup>[49,60,61]</sup> and will be considered herein for comparative purposes (Table 1). The data thus obtained testify that with the increase of temperature the acidity



**Figure 1.** Molecular structure of HL<sub>2</sub> with atom numbering scheme and hydrogen bond interactions. Ellipsoids were drawn at 30% probability. Symmetry operations used to generate equivalent atoms: (i) 1/2 + x, -1/5 + y, +z; (ii) 1/2 - x, 1/2 - y, -z; (iii) -1/2 + x, 1/2 - y, -z

Table 1. Thermodynamic characteristics of dissociation of HL <sub>1-5</sub> in water–ethanol solution									
$HL_{1-5}$	Т (К)	p <i>K</i>	$\Delta G^{0}$ (kJ mol $^{-1}$ )	$\Delta H^0$ (kJ mol $^{-1}$ )	$\Delta S^{0}~(\mathrm{Jmol^{-1}K^{-1}})$				
$HL_{1}^{[60]}$	$298\pm0.5$	$8.54\pm0.02$	$48.72\pm0.10$		$-7.98\pm2.53$				
·	$308\pm0.5$	$8.30\pm0.03$		$\textbf{46.34} \pm \textbf{2.43}$					
	$318\pm0.5$	$\textbf{8.03} \pm \textbf{0.04}$							
$HL_{2}^{[61]}$	$298 \pm 0.5$	$8.36\pm0.02$	$\textbf{47.70} \pm \textbf{0.10}$		$-35.06\pm2.09$				
	$308 \pm 0.5$	$\textbf{8.15} \pm \textbf{0.04}$		$\textbf{37.25} \pm \textbf{1.99}$					
	$318\pm0.5$	$\textbf{7.95} \pm \textbf{0.05}$							
$HL_3^a$	$298\pm0.5$	$8.24\pm0.02$	$\textbf{47.02} \pm \textbf{0.10}$		$-44.97\pm1.88$				
	$308\pm0.5$	$8.06\pm0.06$		$\textbf{33.62} \pm \textbf{1.78}$					
	$318\pm0.5$	$\textbf{7.87} \pm \textbf{0.05}$							
HL <sub>4</sub> <sup>[49]</sup>	$298\pm0.5$	$8.12\pm0.01$	$\textbf{46.33} \pm \textbf{0.09}$		$-48.72\pm1.76$				
	$308\pm0.5$	$\textbf{7.95} \pm \textbf{0.03}$		$31.81 \pm 1.67$					
	$318\pm0.5$	$\textbf{7.77} \pm \textbf{0.05}$							
HL₅	$298\pm0.5$	$8.10\pm0.02$	$\textbf{46.22} \pm \textbf{0.11}$		$-51.40\pm1.81$				
	$308 \pm 0.5$	$\textbf{7.95} \pm \textbf{0.03}$		$\textbf{30.90} \pm \textbf{1.70}$					
	$318\pm0.5$	$\textbf{7.76} \pm \textbf{0.05}$							
<sup>a</sup> For HL <sub>3</sub> , the values of $pK_2$ were used.									

of  $HL_{1-5}$  increases (pK decreases); hence the deprotonation is endothermic.

The introduction of a functional group in the *para* position of the aromatic ring of the molecule influences the thermodynamic characteristics of the dissociation process of HL<sub>1-5</sub>, i.e. with an increase of the inductive effect (Table S1) of that substituent ( $-H < -Cl < -COOH < -F < -NO_2$ ) the O--H and N--H bonds weaken and as result the values of  $\Delta H^0$  decrease and  $\Delta S^0$  becomes more negative (see below), i.e. the acidity and the number of ions in the system increase. A large positive value of  $\Delta G^0$  indicates that the dissociation process is not spontaneous, i.e. it should be forced by a base if the deprotonation is needed (e.g. for coordination).

The Hammett's inductive  $\sigma_1$  substituent constant provides the best relations with the thermodynamic functions of the dissociation process of HL<sub>1-5</sub> ( $\sigma_1 = -1.19 pK + 10.27$ ,  $r^2 = 0.806$ ;  $\sigma_{\rm I} = -0.21\Delta G^0 + 10.29, r^2 = 0.805; \sigma_{\rm I} = (-3.71) \times 10^{-2} \Delta H^0 + 1.75,$  $r^2 = 0.927$ ;  $\sigma_1 = (-1.33) \times 10^{-2} \Delta S^0 - 0.08$ ,  $r^2 = 0.941$ , n = 5; Table S2, Fig. S3). An increase in  $\sigma_1$  (i.e. in the substituent electronacceptance by inductive effect) leads usually to a decrease of pK, of  $\Delta G^{0}$  and of  $\Delta H^{0}$ , while  $\Delta S^{0}$  becomes more negative. Thus, a strong electron-withdrawing substituent can significantly shift the tautomeric equilibrium to the enol-azo form, allowing its isolation in solid phase what can be useful in some applications.<sup>[8-26]</sup> Also an electron-acceptor substituent tends to promote the acidity of ADB (Fig. S3a), allowing their complexation with metals in more acidic conditions, what can favour the analytical selectivity of ADB reagents.<sup>[5–7]</sup> Hence, one can regulate some practically important properties of ADB by inclusion of a suitable functional group with a certain substituent constant.

#### Electrochemical behaviour of HL<sub>1-5</sub>

The electrochemical reduction of hydrazone compounds has been the subject of a number of investigations and the presence of the electro-active group C=N-NH has been shown, e.g. by polarographic methods.<sup>[62,63]</sup> For instance, the aromatic

compounds of the type ArRC=N-NR'R" can follow different electrochemical reduction and also oxidation routes in aprotic solvents, depending on the substituents<sup>[63]</sup> which also strongly influence the redox potentials.<sup>[37,38,41,42,64]</sup>

To search for correlations of the reduction or oxidation potentials of HL<sub>1-5</sub> with the nature of the substituent X, a cyclic voltammetric study was performed, at a Pt disk electrode, in 0.2 M [<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe or THF (or [<sup>n</sup>Bu<sub>4</sub>N][ClO<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> for HL<sub>5</sub>), at room temperature. Compounds HL<sub>1-5</sub> exhibit one irreversible oxidation wave (l<sup>ox</sup>) and one irreversible reduction wave (l<sup>red</sup>) (Fig. 2 for HL<sub>4</sub>) at half-peak potential ( $E_{p/2}^{ox}$  and  $E_{p/2}^{red}$ ) values (vs. the ferrocene/ferricinium redox couple) given in Table 2. In the case of HL<sub>5</sub>, the reduction wave of the nitro group is observed at  $E_p^{red} = -1.53$  V. Exhaustive controlled potential electrolysis (CPE) at a potential slightly anodic (or cathodic, for the reduction) to that of the peak potential indicates the occurrence of a single-electron oxidation or of a two-electron reduction at the corresponding waves, during the extended time scale of CPE.



**Figure 2.** Cyclic voltammogram ( $\nu = 0.2 \text{ V s}^{-1}$ ) of a 5.2 mM solution of HL<sub>4</sub>, initiated by the anodic sweep, in 0.2 M [<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe, at a platinum disk electrode (d = 0.5 mm)

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<b>Table 2.</b> Cyclic voltammetric data <sup>a</sup> and theoretical vertical						
ionization potential and electron affinity for $HL_{1-5}$						

HL	х	$E_{p/2}^{ox}$	1P <sup>b</sup>	$E_{p/2}^{red}$	EA <sup>c</sup>
HL₁	Н	1.07	6.44	-1.77	2.71
$HL_2$	Cl	1.02	6.46	-1.68	2.78
HL <sub>3</sub>	COOH <sup>d</sup>	1.18	6.68	-1.76	2.99
$HL_4$	F	1.06	6.46	-1.76	2.73
HI 🖉	NO <sub>2</sub> e	1.31	6.89	-1.82	3.34

<sup>a</sup> Values given in  $V \pm 0.03$  relative to the [Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> redox couple, measured in 0.2 M [<sup>*n*</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe (unless stated otherwise), at the scan rate = 0.2 V s<sup>-1</sup>.

<sup>b</sup> Vertical ionization potentials in eV.

<sup>c</sup> Vertical electron affinities in eV.

<sup>d</sup> In THF.

<sup>e</sup> In [<sup>*n*</sup>Bu<sub>4</sub>N][ClO<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub>; an irreversible reduction wave is also observed at  $E_p^{\text{red}} = -1.53$  V due to the reduction of the nitro group.

Since the redox processes are irreversible, the redox potentials are not determined only by thermodynamic factors and thus it would not be surprising if good correlations with the Hammett's and related constants would not be found. Nevertheless, one observes that the oxidation potential values ( $E_{p/2}^{ox} = 1.31$  and 1.18 V) for the ADB with the strongest electron-acceptor substituents, NO<sub>2</sub> and COOH ( $\sigma_p = 0.78$  and 0.45, or  $\sigma_p^- = 1.27$  and 0.77, respectively), are higher than those with the other substituents which fall in a narrow range ( $E_{p/2}^{ox}$  at 1.07–1.02 V). The best fit ( $r^2 = 0.903$ ) is found for  $E_{p/2}^{ox}$  versus  $\sigma_p^-$  (Fig. 3), suggesting



**Figure 3.** Plot of the  $\sigma_p^-$  substituent constant versus  $E_{p/2}^{ox}$  for HL<sub>1-5</sub>

the significance of the polar conjugation effects of the substituent, namely in the HOMO of  $HL_{1-5}$ .

Correlations of the oxidation potential with Hammett's  $\sigma_p$  and related substituent constants have been reported in other systems, namely for series of coordination compounds bearing different substituents.<sup>[37,38,41,64–68]</sup> In contrast, the reduction potential values do not vary appreciably with a change of the substituent, being rather close ( $-1.75 \pm 0.07$  V), what suggests an insignificant involvement of the substituent in the LUMO of HL<sub>1-5</sub>.

Aiming to interpret the experimental electrochemical results and to give an insight into the possible mechanisms of the oxidation and reduction irreversible processes, theoretical calculations at the B3LYP level of theory were performed.

The calculations reveal that the HOMOs of HL<sub>1-5</sub> are mainly localized on the C9 and N2 atoms of the C=N-N moiety and on the C atoms of the phenyl group (Fig. 4). Furthermore, an orbital of the aromatic CI atom also gives a noticeable contribution to the HOMO of HL<sub>2</sub>. The delocalized composition of the HOMO is consistent with the expected (see above and Fig. 4) mesomeric effect of the substituent. Moreover, the calculated vertical ionization potentials (IP) of HL<sub>1-5</sub> are the highest ones for HL<sub>5</sub> and HL<sub>3</sub> (bearing the NO<sub>2</sub> and COOH substituents, respectively) and follow the trend of the experimental oxidation potential values (Table 2). In the oxidized species  $HL_{1-5}^+$ , the spin density is delocalized along several atoms and has the highest values on the aromatic C4 atom and on the N2 and C9 atoms of the C= N—N moiety (0.35, 0.30 and 0.26, respectively) and noticeable values on the aromatic C2 and C6 atoms (0.16). The corresponding resonance structures of  $HL_{1-5}^+$  (A–D) are shown in Scheme 2. Such a distribution provides the possibility of  $HL_{1-5}^+$ dimerization (eventually via H<sup>+</sup> loss) through those atoms (in the case of C4, for the unsubstituted  $HL_1$ ), as reported<sup>[69]</sup> for some arylhydrazones. The occurrence of any of such single-electron anodically induced chemical reactions can account for the observed irreversibility of the anodic process.[41,70-72]

The LUMOs of  $HL_1-HL_4$  (Fig. 4) are mostly centred on the N1, N2, C9 and C10 atoms of the H-bonded C—C=N—N fragment, with noticeable contributions coming also from orbitals of the oxygen atoms. Hence, resonance substituent effects are not expected to play a relevant role. However, for  $HL_5$  (with the nitro substituent), orbitals of the C4 atom and the NO<sub>2</sub> group also give a significant contribution to the LUMO.

The N1C9, N1N2 and CO combinations of the LUMO have antibonding character (Fig. 4) and hence the one- and, in particular, two-electron reductions of  $HL_{1-5}$  result in a significant elongation of the N1C9 and N1N2 bonds (by 0.088 and 0.079 Å, respectively, for the two-electron reduction of  $HL_1$ ). This correlates with experimental results<sup>[69,73-76]</sup> indicating that the cleavage of the N1N2 bond is possible as a result of the



Figure 4. Plots of the HOMO and LUMO of HL<sub>1</sub>



Scheme 2. Possible reduction and oxidation processes of HL<sub>1-5</sub>

reduction, and thus also can account<sup>[77–79]</sup> for the irreversibility of the cathodic process. This irreversible character conceivably is the basis of the lack of correlation of the experimental reduction potentials with the calculated electron affinities (EA) (Table 2), the



Figure 5. Distribution of negative electrostatic potential for  $HL_1^{2-}$ 

latter predicting a substantial variation with the change of the substituent (an increase of its electron-withdrawing character leads to an increase of the EA, thus favouring the reduction), in contrast with the former data (similar  $E_{p/2}^{red}$  values for all the HL<sub>1-5</sub>). For the mono-reduced species HL<sub>1-5</sub>, the highest spin density

For the mono-reduced species  $HL_{1-5}^-$ , the highest spin density is localized at the N1 atom, and the most stable resonance structures of the doubly-reduced compounds  $HL_{1-5}^{2-}$  are shown in Scheme 2 (in accord with results of the natural bond orbital (NBO) analysis, see computational details).

The dianionic  $HL_{1-5}^{2-}$  may be protonated,<sup>[73]</sup> and the O and N1 atoms are the most probable sites of proton attack. Indeed, (i) the effective NBO charges on these atoms are strongly negative (-0.79, -0.75 and -0.57, respectively in  $HL_1^{2-}$ ), (ii) the regions of the most negative electrostatic potential are located near these atoms (Fig. 5) and (*iii*) the proton attack at such atoms is not sterically hampered. However, the corresponding diprotonated structure  $H_3L_1a$  of the enol type (Schemes 2 and 3) is relatively unstable and should undergo tautomerization. The geometry optimization of possible diprotonated species showed that the



**Scheme 3.** Calculated  $H_3L_1$  structures derived upon reduction ( $2e^-/2H^+$ ) of  $HL_1$ . Gibbs free energies in MeCN solution relative to the most stable structure are indicated in kcal/mol

most stable is that of the iminoalcohol type  $H_3L_1b$  followed by the keto-amino structure  $H_3L_1c$ ,  $H_3L_1a$  and two structures with protonated phenyl group ( $H_3L_1d$  and  $H_3L_1e$ ) (Scheme 3). The calculations also indicate that the experimentally proposed N1N2 bond cleavage (Scheme 2) to give the imine (CH<sub>3</sub>CO)<sub>2</sub>C=NH and phenylamine C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> <sup>[73-76,80]</sup> is thermodynamically favourable. The Gibbs free energy in MeCN solution of the reaction  $H_3L_1b \rightarrow$ (CH<sub>3</sub>CO)<sub>2</sub>C=NH + C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> is -18.9 kcal/mol.

In the case of HL<sub>5</sub>, with the electroactive nitro substituent that is shown to contribute to the LUMO (see above), the reduction of this group occurs at a more favourable potential ( $E_{p/2}^{red} = -1.53 \text{ V}$ ) than that of the ADB moiety ( $E_{p/2}^{red} = -1.82 \text{ V}$ ). This is consistent with the reported<sup>[73–75]</sup> redox chemistry of some aromatic nitro compounds which in aprotic media undergo a one-electron reduction giving a delocalized radical that is further reduced to a dianion which finally converts to the nitroso anion radical.

# CONCLUSIONS

Trends between Hammett's  $\sigma_p$ , normal  $\sigma_p^n$ , inductive  $\sigma_l$ , resonance  $\sigma_{\rm R}$ , negative  $\sigma_p^-$  and positive  $\sigma_p^+$  polar conjugation and Taft's  $\sigma_p^0$  substituent constants and some properties (N—H···O distance,  $\delta_{\rm N-H}$  chemical shift, redox potentials and thermodynamic functions of the dissociation process) of series of *para* substitued aryl ADB [ $\sigma_p$  vs.  $\delta_{\rm N-H}$  ( $r^2$ =0.76);  $\sigma_p^-$  vs.  $d_{\rm N-O}$  ( $r^2$ =0.84),  $E_{p/2}^{\rm ox}$  ( $r^2$ =0.90);  $\sigma_l$  vs. pK ( $r^2$ =0.81),  $\Delta G^0$  ( $r^2$ =0.81),  $\Delta H^0$  ( $r^2$ =0.93) and  $\Delta S^0$  ( $r^2$ =0.94)] were found. An increase of the electron-acceptance by inductive effect of the *para* substituent (H < Cl < COOH < F < NO<sub>2</sub>) of HL<sub>1-5</sub> enhances the acidity and the N···O distance, whereas  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  of HL<sub>1-5</sub> dissociation decrease in the same order, the process being unspontaneous, endothermic and entropically unfavourable.

IR, NMR and X-ray diffraction analyses showed that  $HL_2$  exists in DMSO solution and in the solid state in the hydrazo form containing an intramolecular H-bond, similary to the reported analogs  $HL_{1,3-5}$ .<sup>[49,53–55]</sup>

The electrochemical behaviour of  $HL_{1-5}$  was studied using CV and the results were interpreted by theoretical calculations at the DFT/HF hybrid level. The substituent at the aromatic ring has a stronger influence on the oxidation potential than on the reduction one, as shown by CV and in accord with the HOMO and LUMO compositions, the former with an important contribution of the aromatic component and the latter being essentially localized at the ADB part. Theoretical studies can account for the irreversibility of the redox processes and allow proposing conceivable mechanisms involving single-electron anodically induced dimerization and two-electron cathodically induced protonation followed by N—N bond cleavage.

The obtained correlations or trends should be used to tune various properties of ADB such as acidity, coordination ability, biological activity, etc., what can be important for fundamental studies and for practical applications.

### **EXPERIMENTAL**

#### Materials and methods

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Bruker Avance II+300 (UltraShield<sup>TM</sup> Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton

and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference. The infrared spectra (4000–400 cm<sup>-1</sup>) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. The acidity of the solutions was measured using an I-130 potentiometer with an ESL-43-07 glass electrode and an EVL-1M3.1 silver-silver chloride electrode adjusted by standard buffer solutions. The pH-metric titration was carried out in water-ethanol mixtures (see below) with consideration of the Bates correction<sup>[81]</sup> at temperatures of 298, 308 and 318 K. The temperature was maintained constant within 0.5 K by using an ultrathermostat (Neslab 2 RTE 220). The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. CV studies were undertaken at room temperature using a two-compartment three-electrode cell with Pt disc working (d = 0.5 mm) and Pt wire counter electrodes. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the abovementioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential, and a Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by CV, thus assuring no significant potential drift occurred along the electrolyses. The solutions were saturated with dinitrogen by bubbling this gas before each run. The redox potentials of the HL<sub>1-5</sub> were measured in 0.2 M ["Bu<sub>4</sub>N][BF<sub>4</sub>]/ NCMe or THF (or ["Bu<sub>4</sub>N][ClO<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> for HL<sub>5</sub>), using ferrocene as an internal potential reference and all reported potentials (measured at a scan rate of  $0.2 \text{ V s}^{-1}$ ) are given versus the redox potential for the ferrocene/ferricinium couple (Fc/Fc<sup>+</sup>).<sup>[82]</sup>

# Synthesis of the 3-(4-chlorophenylhydrazo) pentane-2,4-dione

The synthesis and X-ray study of  $HL_{1,3-5}$  were reported earlier,<sup>[49,53-55]</sup> and hence will not be discussed in detail here. The arylhydrazone  $HL_2$  was synthesized via the modified Japp– Klingemann reaction<sup>[1-3]</sup> between the aromatic diazonium salt of 4-chloroaniline and pentane-2,4-dione in water solution containing sodium hydroxide. The same method, using NaOH as base, was also applied in the current study to the synthesis of the other HL compounds, in good or reasonable yields that are better than those previously achieved when using sodium acetate.

#### Diazotization

A 3.20 g (0.025 mol) portion of 4-chloroaniline was dissolved in 50 mL water. The solution was cooled in an ice bath to 273 K and 1.725 g (0.025 mol) of NaNO<sub>2</sub> was added; then 5.00 mL HCl were added in 0.5 mL portions for 1 h. The temperature of the mixture should not exceed 278 K.

#### Azocoupling

One gram (0.025 mol) of NaOH was added to a mixture of 2.55 mL (0.025 mol) of pentane-2,4-dione with 50 mL of water. The solution was cooled in an ice bath to *ca*. 273 K, and a suspension

of 4-chloroaniline diazonium (see above) was added in three portions under rigorous stirring for 1 h.

Yield 92% (based on pentane-2,4-dione), yellow powder soluble in DMSO, methanol, ethanol and acetone, and insoluble in water. Elemental analysis: C<sub>11</sub>H<sub>11</sub>Cl<sub>1</sub>N<sub>2</sub>O<sub>2</sub> (*M* = 238.67); C 55.53 (calc. 55.36); H 4.58 (4.65); N 11.69 (11.74) %. IR (KBr): 3449  $\nu(\rm NH),$ 1668  $\nu$ (C=O), 1627  $\nu$ (C=O···H), 1587  $\nu$ (C=N) cm<sup>-1</sup>. <sup>1</sup>H NMR (300.130 MHz) in DMSO- $d_6$ , internal TMS,  $\delta$  (ppm): 2.40 (s, 3H, CH<sub>3</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 7.45, 7.47 (m, 2H, J = 9.0 Hz, Ar—H), 7.58, 7.61 (m, 2H, J = 9.0 Hz, Ar—H), 13.85 (s, 1H, N—H). <sup>13</sup>C-NMR (75.468 MHz) in DMSO- $d_{6r}$  internal TMS,  $\delta$  (ppm): 26.34 (CH<sub>3</sub>), 31.20 (CH<sub>3</sub>), 117.91 (Ar-H), 117.91 (Ar-H), 128.97 (Ar-NH-N), 129.42 (Ar-H), 129.42 (Ar-H), 133.81 (C=N), 140.91 (Ar-Cl), 196.27 (C=O), 196.81 (C=O). <sup>1</sup>H NMR (300.130 MHz) in CDCl<sub>3</sub>, internal TMS, δ (ppm): 2.39 (s, 3H, CH<sub>3</sub>), 2.51 (s, 3H, CH<sub>3</sub>), 7.17, 7.23 (m, 2H, J = 18.0 Hz, Ar—H), 7.27, 7.29 (m, 2H, J = 6.0 Hz, Ar—H), 14.60 (s, 1H, N—H). <sup>13</sup>C-NMR (75.468 MHz) in CDCl<sub>3</sub>, internal TMS,  $\delta$  (ppm): 26.73 (CH<sub>3</sub>), 31.80 (CH<sub>3</sub>), 117.46 (Ar-H), 117.46 (Ar-H), 129.90 (Ar-NH-N), 131.12 (Ar-H), 131.12 (Ar-H), 133.60 (C=N), 140.31 (Ar-Cl), 197.02 (C=O), 198.29 (C=O).

#### X-ray measurements

The X-ray quality single crystals of HL<sub>2</sub> were grown by slow evaporation at room temperature of its ethanol solution. They were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT<sup>[83]</sup> on all the observed reflections. Absorption corrections were applied using SADABS. Structures were solved by direct methods by using the SHELXS-97 package<sup>[84]</sup> and refined with SHELXL-97.<sup>[85]</sup> Calculations were performed using the WinGX System-Version 1.80.03.<sup>[86]</sup> All hydrogens were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC (766556) for compound HL<sub>2</sub>. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033. E-mail: data\_request@ ccdc.cam.ac.uk. Web page: http://www.ccdc.cam.ac.uk.

#### **Potentiometric measurements**

The following mixtures, (i)–(iii), were prepared and titrated potentiometrically against standard 0.01 M NaOH (for  $HL_3$  0.04 M NaOH) in a 40/60% (v/v) water–ethanol mixture at 298 K.

- (i) 5 mL of 0.001 M HCl + 5 mL of 1 M KCl + 30 mL ethanol;
- (ii) 5 mL of 0.001 M HCl+5 mL of 1 M KCl+25 mL ethanol+5 mL 0.01 M HL<sub>5</sub>;
- (iii) 5 mL of 0.001 M HCl + 5 mL of 1 M KCl + 25 mL of ethanol + 5 mL of 0.02 M HL\_3.

For each mixture (i)–(iii) the volume was made up to 50 mL with bidistilled water before the titration process. These titrations were also repeated at temperatures of 308 and 318 K.

#### DFT computational details

The full geometry optimization of all structures has been carried out at the DFT/HF hybrid level of theory using the B3LYP functional<sup>[87,88]</sup> and 6-311+G(d,p) basis set with the help of the Gaussian-98<sup>[89]</sup> program package. Restricted approximations for the structures with closed electron shells and unrestricted methods for the structures with open electron shells have been employed. No symmetry operations have been applied. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies), and to estimate the thermodynamic parameters, the latter being calculated at 25 °C.

Total energies corrected for solvent effects ( $E_s$ ) were estimated at the single-point calculations on the basis of gas-phase geometries using the polarizable continuum model<sup>[90]</sup> in the CPCM version<sup>[91]</sup> with CH<sub>3</sub>CN as solvent. The entropic term in CH<sub>3</sub>CN solution ( $S_s$ ) was calculated according to the procedure described by Wertz<sup>[92]</sup> and Cooper and Ziegler<sup>[93]</sup> using Eqns. (1)–(4)

$$\Delta S_1 = R \ln V_{m,liq}^s / V_{m,gas}$$
<sup>(1)</sup>

$$\Delta S_2 = R \ln V_{\rm m}^{\circ} / V_{\rm m, liq}^{\rm s}$$
<sup>(2)</sup>

$$\alpha = \frac{S_{\text{liq}}^{0,\text{s}} - \left(S_{\text{gas}}^{0,\text{s}} + R \ln V_{\text{m,liq}}^{\text{s}} / V_{\text{m,gas}}\right)}{\left(S_{\text{gas}}^{0,\text{s}} + R \ln V_{\text{m,liq}}^{\text{s}} / V_{\text{m,gas}}\right)}$$
(3)

$$\begin{split} S_{\rm s} &= S_{\rm g} + \Delta S_{\rm sol} = S_{\rm g} + [\Delta S_{\rm 1} + \alpha (S_{\rm g} + \Delta S_{\rm 1}) + \Delta S_{\rm 2}] \\ &= S_{\rm g} + [(-12.21\,\text{cal/mol}\,\text{K}) - 0.23(S_{\rm g} - 12.21\,\text{cal/mol}\,\text{K}) \\ &+ 5.87\,\text{cal/mol}\,\text{K}] \end{split} \tag{4}$$

where  $S_g$  – gas-phase entropy of solute,  $\Delta S_{sol}$  – solvation entropy,  $S_{iga}^{0.s}$  gas and  $V_{m,liq}^s$  – standard entropies and molar volume of the solvent in liquid or gas phases (149.62 and 245.48 J/mol K and 52.16 mL/mol, respectively, for CH<sub>3</sub>CN),  $V_{m,gas}$  – molar volume of the ideal gas at 25 °C (24 450 mL/mol),  $V_m^o$  – molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The enthalpies and Gibbs free energies in solution ( $H_s$  and  $G_s$ ) were estimated using the expressions (5) and (6)

$$H_{\rm s} = E_{\rm s} + H_{\rm g} - E_{\rm g} \tag{5}$$

$$G_{\rm s} = H_{\rm s} - T \cdot S_{\rm s} \tag{6}$$

where  $E_{s}$ ,  $E_{g}$  and  $H_{g}$  are the total energies in solution and in gas phase and gas-phase enthalpy.

Vertical ionization potentials were calculated as the difference of the total energies in solution of the oxidized species with an unrelaxed geometry and the neutral structure  $HL_{1-5}$ . Vertical electron affinities were calculated as the difference of the total energies in solution of the neutral structure  $HL_{1-5}$  and the reduced species with an unrelaxed geometry. The nature of the chemical bonds, electron structures, and effective atomic charges were calculated and analyzed using the NBO partitioning scheme.<sup>[94]</sup>

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- [1] F. R. Japp, F. Klingemann, Liebigs Ann. Chem. 1888, 247, 190-225.
- [2] H. C. Yao, P. Resnick, J. Am. Chem. Soc. 1962, 84, 3514–3517.
- [3] H. C. Yao, J. Org. Chem. 1964, 29, 2959–2963.
- [4] Z. M. Chen, F. X. Huang, Y. Q. Wu, D. H. Gu, F. X. Gan, Inorg. Chem. Comm. 2006, 9, 21–24.
- [5] R. A. Aliyeva, F. M. Chyragov, K. T. Mahmudov, J. Anal. Chem. 2005, 50, 137–140.
- [6] S. R. Gadjieva, T. M. Mursalov, K. T. Mahmudov, F. H. Pashaev, F. M. Chyragov, J. Anal. Chem. 2006, 61, 550–555.
- [7] K. T. Mahmudov, R. A. Aliyeva, S. R. Gadjieva, F. M. Chyragov, J. Anal. Chem. 2008, 63, 435–438.
- [8] E. V. Shchegolkov, Ya. V. Burgart, O. G. Khudina, V. I. Saloutin, O. N. Chupakhin, *Rus. Chem. Bul. Inter. Ed.* **2004**, *53*, 2584–2590.
- [9] Z. M. Chen, Y. Q. Wu, D. H. Gu, F. X. Gan, Spectrochim. Acta A 2007, 68, 918–926.
- [10] M. J. Jeong, J. H. Park, C. Lee, J. Y. Chang, Org. Lett. 2006, 8, 2221–2224.
- [11] J. Marten, A. Erbe, K. Critchley, J. P. Bramble, E. Weber, S. D. Evans, Langmuir 2008, 24, 2479–2486.
- [12] H. G. Garg, R. A. Sharma, J. Med. Chem. 1969, 12, 1122-1124.
- [13] H. G. Garg, R. A. Sharma, J. Med. Chem. 1970, 13, 763–765.
- [14] H. B. Hassib, Y. M. Issa, W. S. Mohamed, J. Therm. Anal. Cal. 2008, 92, 775–782.
- [15] E. V. Shchegol'kov, O. G. Khudina, L. V. Anikina, Ya. V. Burgart, V. I. Saloutin, *Pharm. Chem. J.* **2006**, 40, 373–376.
- [16] E. E. Oruch, B. Kochyigit-Kaymakchoglu, B. Oral, H. Z. Altunbas-Toklu, L. Kabasakal, S. Rollas, Arch. Pharm. Chem. Life Sci. 2006, 339, 267–272.
- [17] S. C. Nigam, G. S. Saharia, H. R. Sharma, Def. Sci. J. 1982, 32, 87–94.
- [18] G. Sh. Kuchukguzel, S. Rollas, I. Kuchukguzel, M. Kiraz, Eur. J. Med. Chem. 1999, 34, 1093–1100.
- [19] E. S. H. El Ashry, L. F. Awad, E. I. Ibrahim, O. Kh. Bdeewy, Chin. J. Chem. 2007, 25, 570–573.
- [20] V. Bertolassi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 1991, 113, 4917–4925.
- [21] V. Bertolasi, V. Ferretti, P. Gilli, G. Gilli, Y. M. Issa, O. E. Sherif, J. Chem. Soc. [Perkin 2] 1993, 11, 2223–2228.
- [22] V. Bertolasi, L. Nanni, G. Gilli, V. Ferretti, P. Gilli, Y. M. Issa, O. E. Sherif, New J. Chem. **1994**, 18, 251–261.
- [23] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, Acta Crystallogr. B 1994, 50, 617–625.
- [24] P. Gilli, V. Bertolasi, L. Pretto, A. Lyčka, G. Gilli, J. Am. Chem. Soc. 2002, 124, 13554–13567.
- [25] G. Gilli, F. Belluci, V. Ferretti, V. Bertolasi, J. Am. Chem. Soc. 1989, 111, 1023–1028.
- [26] G. Gilli, P. Gilli, J. Mol. Struct. 2000, 552, 1-15.
- [27] L. P. Hammett, J. Am. Chem. Soc. 1937, 59, 96-103.
- [28] L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, **1940**.
- [29] H. C. Brown, Y. Okomoto, J. Am. Chem. Soc. 1957, 79, 1913–1917.
- [30] H. Van Bekkum, P. E. Verkade, B. M. Wepster, *Recl. Trav. Chim.* 1959, 78, 815–863.
- [31] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, **1953**.
- [32] B. Galabov, S. Ilieva, H. F. Schaefer, J. Org. Chem. 2006, 71, 6382–6387.
- [33] C. Hansch, A. Leo, W. R. Taft, Chem. Rev. 1991, 91, 165–195.
- [34] C. Laurence, B. Wojtkowiak, Ann. Chim. 1970, 5, 163–191.
- [35] B. P. Mcdaniel, H. C. Brown, J. Org. Chem. 1958, 23, 420-427.
- [36] V. A. Pal'm, Rus. Chem. Rev. **1961**, 30, 471–498.
- [37] A. J. L. Pombeiro, Eur. J. Inorg. Chem. 2007, 11, 1473–1482.
- [38] A. J. L. Pombeiro, J. Organometal. Chem. 2005, 690, 6021–6040.
- [39] J. Shorter, Pure Appl. Chem. **1994**, 66, 2451–2468.
- [40] J. Shorter, *Pure Appl. Chem.* **1997**, *69*, 2497–2510.
- [41] A. J. L. Pombeiro, *New J. Chem.* **1997**, *21*, 649–660.
- [42] M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, N. Deus, T. J. Castilho, M. F. C. G. da Silva, *J. Organometal. Chem.* **1991**, *421*, 75–89.

- [43] M. E. N. P. R. A. Silva, A. J. L. Pombeiro, J. J. R. Fraústo da Silva, R. Herrmann, M. Deus, R. E. Bozak, J. Organometal. Chem. 1994, 480, 81–90.
- [44] T. M. Krygowski, J. E. Zachara-Horeglad, M. Palusiak, S. Pelloni, P. Lazzeretti, J. Org. Chem. 2008, 73, 2138–2145.
- [45] T. M. Krygowski, J. E. Zachara-Horeglad, Tetrahedron 2009, 65, 2010–2014.
- [46] U. Casellato, M. Vidali, P. A. Vigato, Coord. Chem. Rev. 1977, 23, 31–117.
- [47] G. Aromi, P. Gamez, J. Reedijk, Coord. Chem. Rev. **2008**, 252, 964–989.
- [48] P. A. Vigato, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* 2009, 253, 1099–1201.
   [40] A. M. Makamara and D. A. Aliman and A. Aliman and A. M. Makamara and D. A. Aliman and A. Alima
- [49] A. M. Maharramov, R. A. Aliyeva, I. A. Aliyev, F. H. Pashaev, A. G. Gasanov, S. I. Azimova, R. K. Askerov, A. V. Kurbanov, K. T. Mahmudov, *Dyes Pigm.* **2010**, *85*, 1–6.
- [50] K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, P. J. Figiel, Y. Yu. Karabach, A. J. L. Pombeiro, J. Mol. Catal. A: Chem. 2010, 318, 44–50.
- [51] A. M. Maharramov, R. A. Aliyeva, K. T. Mahmudov, A. V. Kurbanov, R. K. Askerov, *Rus. J. Coord. Chem.* **2009**, *35*, 704–709.
- [52] R. A. Aliyeva, F. M. Chyragov, K. T. Mahmudov, M. B. Babanly, *Rus. J. Inorg. Chem.* 2005, *50*, 131–134.
- [53] J. Marten, W. Seichter, E. Weber, U. Bohme, J. Phys. Org. Chem. 2007, 20, 716–731.
- [54] J. Marten, W. Seichter, E. Weber, Z. Anorg. Allg. Chem. 2005, 631, 869–877.
- [55] C. Bustos, C. Sanchez, R. Martinez, R. Ugarte, E. Schott, C. D. Mac-Leod, M. T. Garland, L. Espinoza, *Dyes Pigm.* 2007, 74, 615–621.
- [56] D. Harvey, Modern Analytical Chemistry, Wiley, New York, 2000.
- [57] N. M. Dyatlova, V. Y. Temkina, I. D. Kolpakova, Complexones, Khimiya, Moscow, 1970.
- [58] P. Atkins, De. J. Paula, Physical Chemistry, Oxford Univ., Oxford, 2002.
- [59] I. N. Levin, *Physical Chemistry*, Pashupati Printers Pvt. Ltd., New Delhi, 2002.
- [60] S. R. Gadjieva, T. M. Mursalov, K. T. Mahmudov, F. M. Chyragov, *Rus. J. Coord. Chem.* 2006, 32, 304–308.
- [61] R. A. Aliyeva, F. H. Pashaev, A. G. Gasanov, K. T. Mahmudov, Rus. J. Inorg. Chem. 2009, 54, 1407–1411.
- [62] W. Malik, R. N. Goyal, V. K. Mahest, *Electroanal. Chem.* 1975, 62, 451–458.
- [63] Y. P. Kitaev, G. K. Budnikov, L. Maslova, *Izv. Akad. Nauk SSSR Ser. Khim.* 1967, 9, 1906–1911.
- [64] A. J. L. Pombeiro, C. J. Pickett, R. L. Richards, J. Organomet. Chem. 1982, 224, 285–294.
- [65] T. El-Shihi, F. Siglmüller, R. Herrmann, M. F. N. N. Carvalho, A. J. L. Pombeiro, J. Organomet. Chem. 1987, 335, 239–247.
- [66] S. Lu, V. V. Strelets, M. F. Ryan, W. J. Pietro, A. B. P. Lever, *Inorg. Chem.* 1996, 35, 1013–1023.
- [67] R. Steudel, K. Hassenberg, J. Pickardt, E. Grigiotti, P. Zanello, Organometallics 2002, 21, 2604–2608.
- [68] P. Zanello, S. Fedi, F. F. de Biani, G. Giorgi, T. Amaya, H. Sakane, T. Hirao, Dalton Trans. 2009, 42, 9192–9197.
- [69] G. M. Abou-Elenien, N. A. Ismail, T. S. Hafez, Bull. Chem. Soc. Jpn. 1991, 64, 651–654.
- [70] M. A. N. D. A. Lemos, A. J. L. Pombeiro, J. Organomet. Chem. 1987, 332, C17–C20.
- [71] S. S. P. R. Almeida, M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, J. Chem. Soc. Dalton Trans. 1999, 467–472.
- [72] A. I. F. Venâncio, M. L. Kuznetsov, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 6456–6467.
- [73] B. Soucase-Guillous, H. Lund, Electroanal. Chem. 1997, 423, 109–114.
- [74] T. N. Tropol'skaya, E. N. Martin, Yu. P. Kitaev, *Izv. Akad. Nauk SSSR Ser. Khim.* **1979**, *20*, 982–989.
- [75] Yu. P. Kitaev, T. V. Troporskaya, L. V. Ermolaeva, E. N. Munin, *Izv. Akad. Nauk SSSR Ser. Khim.* **1985**, *27*, 736–741.
- [76] A. V. Il'yasov, M. Yu. Kitaeva, A. A. Vafina, R. M. Zaripova, Yu. P. Kitaev, Rus. Chem. Bul. **1993**, 42, 1020–1023.
- [77] E. Reisner, V. B. Arion, M. F. C. Guedes da Silva, R. Lichtenecker, A. Eichinger, B. K. Keppler, V. Yu. Kukushkin, A. J. L. Pombeiro, *Inorg. Chem.* 2004, 43, 7083–7093.
- [78] A. Venâncio, M. F. C. Guedes da Silva, L. M. D. R. S. Martins, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, Organometallics 2005, 24, 4654–4665.
- [79] E. Reisner, V. B. Arion, A. Eichinger, N. Kandler, G. Geister, A. J. L. Pombeiro, B. K. Keppler, *Inorg. Chem.* **2005**, 44, 6704–6716.

- [80] R. Jain, P. Padmaja, S. Gupta, Can. J. Chem. 1997, 75, 567-574.
- [81] R. G. Bates, *Determination of pH: Theory and Practice*, Wiley, New York, **1973**.
- [82] A. J. L. Pombeiro, M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, Coord. Chem. Rev. 2001, 219-221, 53–80.
- [83] Bruker, APEX2 & SAINT. Bruker, AXS Inc., Madison, Wisconsin, USA, 2004.
- [84] G. M. Sheldrick, Acta Crystallogr. A **1990**, 46, 467–473.
- [85] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112-122.
- [86] L. J. Farrugia, J. Appl. Crystal. 1999, 32, 837-838.
- [87] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [88] C. Lee, W. Yang, R. G. Parr, Phys. Rev. 1988, B37, 785-789.
- [89] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C.

Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Peterson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh, PA, **1998**.

- [90] J. Tomasi, M. Persico, Chem. Rev. 1997, 94, 2027–2033.
- [91] V. Barone, M. Cossi, J. Phys. Chem. 1998, 102, 1995–2001.
- [92] G. H. Wertz, J. Am. Chem. Soc. 1980, 102, 5316-5322.
- [93] J. Cooper, T. Ziegler, Inorg. Chem. 2002, 41, 6614-6622.
- [94] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.