SPECTRAL AND ELECTROCHEMICAL STUDY OF THE REDUCTION BEHAVIOUR OF SOME BENZOYL SUBSTITUTED HETEROCYCLES

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abstract: The heteroaromatic compounds containing fragments with different donor-acceptor properties have large applications in many fields in which charge separation represents a required property. The present work is constituted in a spectral and electrochemical study of the benzoyl derivatives of the phenoxathiine and dibenzo-*par*a-dioxin. The reduction behaviour of the compounds was investigated using the cyclic voltametry and ESR technics. The experimental results were in agreement with the MO calculations.

Introduction

The heteroaromatic compounds containing fragments with different donor-acceptor properties have large applications in many fields in which charge separation represents a required property. The redox properties of these compounds are determined both by the character of the constituting moieties and the interaction between them. Experimental evidence on the predominance of the donor/acceptor character of the molecule can be furnished by coupled electrochemical and spectral ESR techniques.

This paper deals with the experimental and theoretical study of the benzoyl derivatives of two heterocycles with known donor character, phenoxathiine and dibenzo-p-dioxin. For the sake of comparison we have also included benzophenone, characterized by the presence of the same acceptor group. The compounds are presented in Figure 1
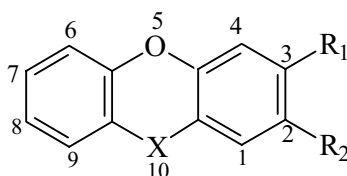
Ia X = S; R₁ = -H; R₂ = -COC₆H₅
Ib X = S; R₁ = -COC₆H₅ ; R₂ = -H
II X= O; R₁= -H ; R₂ = -COC₆H₅

Fig. 1: *Structure of Investigated Compounds.*

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Experimental

Cyclic voltammetry experiments with both stationary and rotating disc electrode (RDE) were performed in dimethyl sulphoxide (DMSO) with 0.1 M tetra buthyl ammonium tetrafluorborate ($TBABF_4$) as supporting electrolyte, at a VOLTALAB-32 electrochemical laboratory, with platinum working and counter electrodes and Ag- cuasi reference electrode [1]. The EPR spectra were recorded during the electrochemical reduction on JES-3B spectrometer in X-band frequency, using peroxylamine disulphonate as standard (a_N=1.3 mT, g=2.0055). The semiempirical MO calculations were performed using the AM1 hamiltonian in the AMSOL program package [2,3] and RHF (ROHF) formalism for closed and respectively open-shell structures.

Results and Discussion

Cyclic Voltammetry Results

The cyclic voltammograms of **Ia** and **Ib** in DMSO exhibit one redox couple in the range 0 to -1.9 V. A typical cyclic voltammogram is presented in Figure 2 and the relevant electrochemical data are presented in Table 1. The values of the peak potential for the first electron transfer (-1.4 – -1.5V/SCE) attest the reducibility of these molecules, comparable with that of benzophenone, and not influenced by the position of the substituent in the phenoxathiine ring. This wave was analysed according to the usual electrochemical criteria. The first wave presents a well shaped anodic counterpart, but the difference between the cathodic and anodic peak potentials is in the range 0.120 to 0.200 V. Using this difference and Nicholson's formula [4]:

$$\Psi = 28.6 k_s \big/ v^{1/2}$$

where v is the scan rate (the value 28.6 is obtained from the expression of the constant, $\gamma^\alpha (RT)^{1/2} / (nFD_O\pi)^{1/2}$, with n=1, $\gamma= D_O/D_R$ and considering $D_O=D_R = 1\times10^{-5}$ cm^2/s and T= 298K), the value of the standard electron transfer rate in Table 1, k_s, was estimated.

Table 1. Cyclic voltammetry results for the first wave of compounds Ia and Ib.

v (Vs^{-1})	Ia				Ib			
	-E_{pc} (V)	-ΔE_p (V)	I_{pa}/I_{pc}	$I_p/v^{1/2}$x10^4 (AV$^{-1/2}$s$^{1/2}$)	-E_{pc} (V)	-ΔE_p (V)	I_{pa}/I_{pc}	$I_p/v^{1/2}$x10^4 (AV$^{-1/2}$s$^{1/2}$)
0.100	1.460	0.120	0.740	0.652	1.460	0.150	1.350	0.386
0.200	1.501	0.150	1.020	0.640	1.461	0.150	1.150	0.362
0.400	1.520	0.180	1.070	0.604	1.480	0.180	1.190	0.348
0.600	1.510	0.190	1.040	0.591	1.470	0.170	1.130	0.347
0.800	1.540	0.200	0.990	0.572	1.480	0.200	1.090	0.335
	k_s~3.72 x 10^{-3} cm/s				k_s~3.73 x 10^{-3} cm/s			

The I_{pa} /I_{pc} ratio is in the range 0.74÷1.35 for the first wave of both compounds, if the scan is reversed after the first peak. The plot of the peak current *vs* the square root of the sweep

rate, $I_{pc} = f(\nu^{1/2})$, is fairly linear (correlation coefficient r ~ 0.998), attesting to diffusional control for the first wave of both compounds. As the standard transfer rate for both compounds is at the lower limit of the rapid transfer, this process was assigned to the quasireversible monoelectronic reduction of the neutral compound to a rather stable anion-radical.
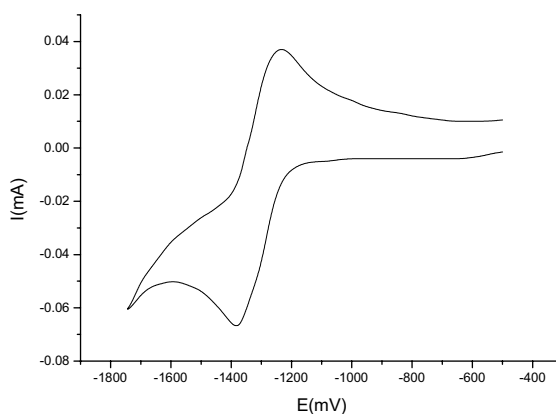
Fig. 2: *Cyclic voltammogram of compound **Ib**.*

RDE linear voltametry

The analysis of the RDE electrochemical data allows the determination of *n*, the number of electrons involved, the electron transfer rate k_f, the transfer coefficient α and the diffusion coefficient D_O, using the dependences E= f $(\ln(I_l\text{-}I)/I)$, I = f$(\omega^{1/2})$, I^1 = f$(\omega^{-1/2})$ as expressed by the equations [1, 5]:

$$I = 0.620\ n\ FAD_O^{2/3}\ \omega^{1/2}\nu^{-1/6}c_O{}^* \tag{1}$$

$$1/I = 1/I_k + 1/\ (\ 0.620\ n\ FAD_O^{2/3}\ \omega^{1/2}\nu^{-1/6}c_O{}^*) \tag{2}$$

$$I_k = nFAk_f(E)\ c_O{}^* \tag{3}$$

In these relationships *A* is the electrode area, D_O is the diffusion coefficient , ω the rotation rate, ν the kinematic viscosity of the solvent ($\nu = 0.01896$ cm^2/s for DMSO) and $c_O{}^*$ is the bulk substrate concentration. From the analysis of the first wave, values of 0.63×10^{-5} cm^2/s for **Ia** and 3.25×10^{-5} cm^2/s for **Ib** in DMSO were obtained. Both waves are monoelectronic and the values of the electron transfer rate in the range 3×10^{-3}- 1×10^{-2} cm/s are in reasonable agreement with those obtained by cyclic voltammetry.

ESR results

The ESR spectra obtained at the electrochemical reduction of the investigated compounds in DMSO are presented in Fig. 3 and the relevant parameters (hyperfine splitting constants hfs, g-factor values, line widths) are contained in Table 2.
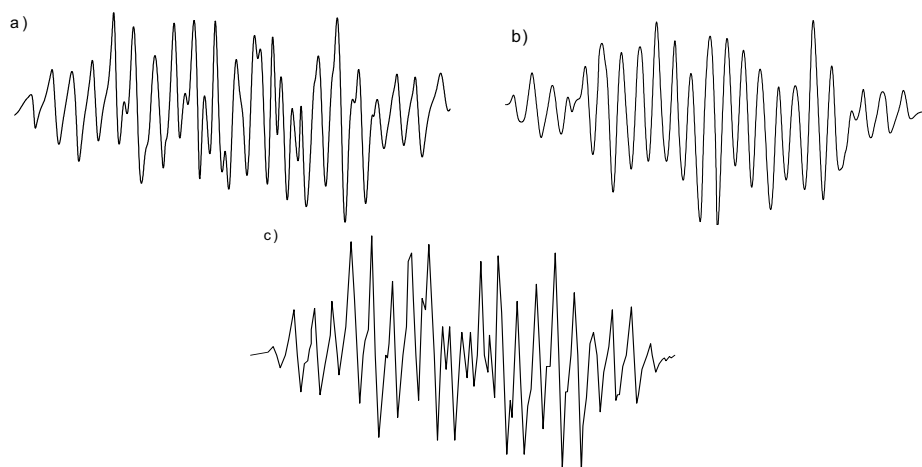
Fig. 3: *RPE spectra of investigated compounds:* **Ia** *(a),* **Ib** *(b) and* **II** *(c),*
electrochemical reduction in DMSO/ 0.1 M TBAP (in-situ technique)

Table 2. EPR parameters for investigated compounds and the benzophenone.

Compound	1	2	3	4	o	o'	m/m'	p	δ (mT)	g-factor
Ia	0.247	-	0.247	0.082	0.277	0.310	0.082	0.330	0.025	2.0037
Ib	0.080	0.210	-	0.210	0.294	0.310	0.080	0.350	0.030	2.0035
II	0.255	-	0.255	0.086	0.255	0.307	0.086	0.337	0.025	2.0035
Benzophenone*	-	-	-	-	0.260	0.260	0.088	0.345	-	2.0037

* values from reference [6].

Both g-factor values and hfs. constants attest an odd electron distribution similar to that of the anion-radical of benzophenone and other benzoyl derivatives [6, 7], *i.e.* mainly determined by the benzoyl moiety and not by the parent heterocycle. This is further supported by the similitude of the hf splittings of anion-radicals **Ia**, 2-benzoyl phenoxathiine, and **II,** 2-benzoyl dibenz-p-dioxin. Somewhat greater differences are observed in function of the substitution site in the heterocycle. Substitution in site 3 (anion-radical **Ib**) determines a greater delocalization of the unpaired electron on the benzoyl moiety, as attested by the slightly higher hf.coupling constants for anion-radical **Ib**.

MO calculations

The electronic structure of the investigated compounds is dependent on the relative position of the substituent and the heterocycle. The configurations are mainly dependent on two torsion angles, the torsion around the heteocycle-benzoyl bond, hereafter labelled as τ_1, and a second torsion, τ_2, between the carbonyl group and the phenyl ring of the benzoyl fragment. An *in vacuo* conformational search performed on the compounds attests that a lot of conformations within 1 kcal/mol are possible, the presence of the two torsions conferring to the molecule an enhanced flexibility. In order to select the minimum energy

conformations the potential energy surfaces (PES) were built for all the compounds, in term with τ_1. As an example, the PES for 2-benzoylphenoxathiine is presented in Fig. 4 and the main results for all the compounds are listed in Table 3.
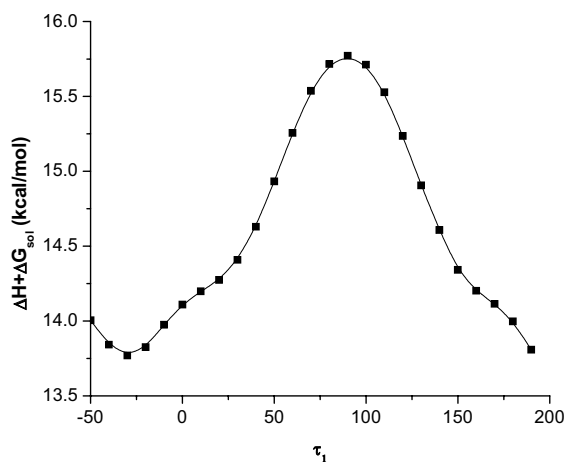

Fig. 4: *Potential energy surface (PES) of compound Ib.*

Table 3. Main theoretical parameters for the neutral, ΔG (kcal/mol), compounds and the anion radicals

Compound	τ_1 (deg)	τ_2 (deg)	$\Delta H + \Delta G_{solv}$ (kcal/mol)	ΔG_{solv} (kcal/mol)
Ia	-28.7	145.4	13.78	-16.68
Ia(⁻•)	-6.2	122.0	-64.31	-
Ib	-31.5	149.9	13.98	-17.072
Ib(⁻•)	-4.0	123.6	-67.16	-
II	-30.2	147.3	14.35	-15.781
II(⁻•)	-1.5	123.0	-93.11	-

The results predict nonplanar conformations, even if the barrier to rotation are about 2 kcal/mol. The highest point on the PES corresponds to the values of 90 deg for both torsions, that means for those conformations in which the conjugation is totally interrupted. Considering the equilibrium conformations the vertical and adiabatic electronegativity were calculated. The results are presented in Table 4 and are in good agreement with the experimental observations. The vertical and adiabatic electronegativities are not too different reflecting the slight changes in the geometry in going from the neutral to the charged species. Due to the high donor character of the phenoxathiine ring, known for its low ionisation potential and its ability to give cation radicals even in the presence of electron acceptors, the presence of the benzoyl fragment confer some reducibility but lower than that of dibenzo-*p*-dioxin a poorer electron donor. However, both substituted heterocycles are less electronegative than benzophenone.

Table 4. DMSO Calculated vertical^1,χ_V , adiabatic^2, χ_{ad} (eV).

Compound	ε_{homo}	ε_{lemo}	I_{ad}	A_{ad}	χ_V	χ_{ad}
Ia	-8.368	-1.134	5.88	3.40	4.75	4.64
Ib	-8.462	-1.222	5.96	3.53	4.84	4.75
II	-9.007	-1.103	6.79	3.42	5.06	5.10
Benzophenone	-9.755	-0.818	7.35	3.16	5.41	5.26

^{1} $\chi_V = -\frac{1}{2}(\varepsilon_{homo} + \varepsilon_{lemo})$

^{2}$\chi_{ad} = \frac{1}{2}(I_{ad} + A_{ad})$; I_{ad} is given by the enthalpy of the process, $M \longrightarrow M^+ + e^-$; A_{ad}, the adiabatic electron affinity, is given by the negative of the enthalpy of the process, $M + e^- \longrightarrow M^-$.

In order to obtain some information on the charged species restricted Hartree-Fock calculations were performed on the anion radicals. The main geometric features for the minimum energy conformations are given in Table 3. The theoretical results predict a tendency to planarity of the heteroring with the carbonyl group of the substituent and a twisted position of the phenyl ring. For these conformations, the conjugation heterering-CO is enhanced and a larger delocalisation on the odd electron on the substituted phenyl ring of the heterocycle was obtained. However, as for the neutral parent compounds, several conformations with close energy were found implying that an average of the spin distribution is obtained experimentally.

Conclusions

Both electrochemical and EPR data attest that, in spite of the donor properties of the two heterocycles, the elecon acceptor character of the benzoyl group is sufficient to ensure the formation of stable anion radicals. The calculated vertical and adiabatic electronegativity reflect well the experimental behaviour.

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