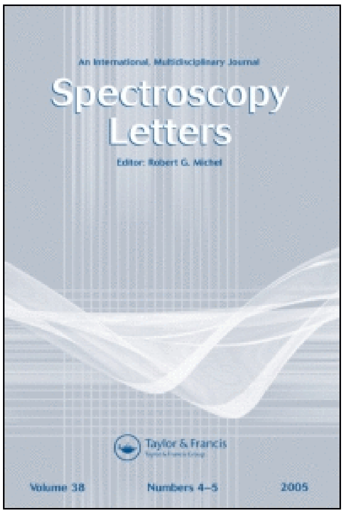

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Atria, Ana María , Valenzuela, Jorge , Contreras, Martín and Zolezzi, Santiago(2002) 'AN ELECTRON SPIN RESONANCE (ESR) INVESTIGATION OF POTENTIAL LIGANDS OF INORGANIC INTEREST WITH NITRO SUBSTITUENTS', Spectroscopy Letters, 35: 5, 633 — 642

To link to this Article: DOI: 10.1081/SL-120014936

URL: http://dx.doi.org/10.1081/SL-120014936

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SPECTROSCOPY LETTERS
Vol. 35, No. 5, pp. 633–642, 2002

AN ELECTRON SPIN RESONANCE (ESR) INVESTIGATION OF POTENTIAL LIGANDS OF INORGANIC INTEREST WITH NITRO SUBSTITUENTS

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ABSTRACT

Electron Spin Resonance spectra were obtained of the salicyliden-2-imino-5-nitropyrimidine ($1^{\bullet -}$), N,N-bis(5-nitro-salicyliden) ethylendiamine ($2^{\bullet -}$), 2-hydroxy-5-nitro-benziliden-5-iminoquinoline ($3^{\bullet -}$) anion radicals produced by electro chemical reduction in DMSO. Hyperfine splitting constants were assigned by comparison with radical anions of similar structure and in some cases with the help of INDO method. For the ($2^{\bullet -}$) and ($3^{\bullet -}$) the substitutions in position meta affect greatly some proton coupling constants.

Key Words: Anion radicals; Schiff bases; ESR

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DOI: 10.1081/SL-120014936 0038-7010 (Print); 1532-2289 (Online)

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INTRODUCTION

The study of Schiff bases reductions has been of great interest during the last years due, in part, to their use as ligands in the synthesis of transition metal complexes utilized in many electrocatalytic processes.[1–4] In this type of processes a key factor is the reduction of the transition metal to a low oxidation state. In certain cases a preferential reduction of the ligand takes place. For example, Koch and Dessy studied the electrochemical reductions of diimines in DMSO and 1,2-dimethoxyethane. They found a dependence of the solvent and the structure of Schiff base with the open-chain diamines or two cyclic diamines resulting from intramolecular coupling of radical species. These authors also reported the isolation of stable radical anions.[5] There is also literature concerning chemical reductions of Schiff bases in relation to the reduction products and mechanistic studies.[6–8]

In this context this paper describes the ESR characterization of the anion radicals derived by electrochemical reductions from the following Schiff bases ligands: salicyliden-2-imino-5-nitropyrimidine (**1**), N,N-bis(5-nitrosalicyliden)ethylendiamine (**2**), and 2-hydroxi-5-nitro-benziliden-5-iminoquinoline (**3**) (Scheme 1).

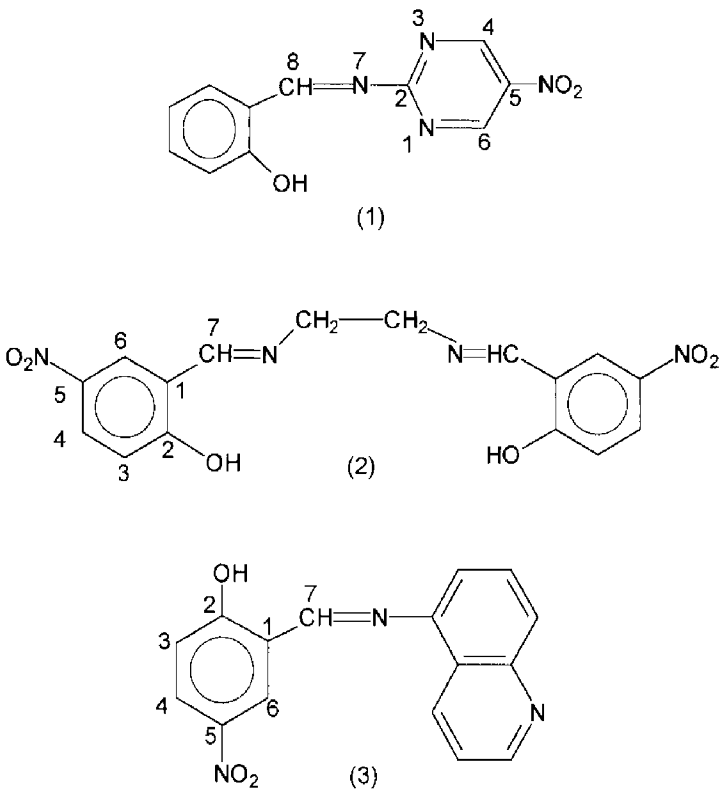
EXPERIMENTAL

Reagents

DMSO was obtained from Aldrich. Tetrabutylammonium perchlorate (TBAP) used as supporting electrolyte was obtained from Fluka. All reagents employed in the synthesis were analytical grade.

Synthesis

The Schiff bases were prepared following the procedure described in the literature.[9,10] Equimolar solutions of the selected amine and salicyldehyde and 2-hidroxy-5-nitro benzaldehyde in methanol were mixed. The resulting solution was maintained at the boiling point for the one hour. A yellow crystalline precipited was rapidly formed on cooling, in high yield. Satisfactory elemental analyses (C,N,H) were obtained. No absorption bands corresponding to amine and carbonilic groups were observed in



Scheme 1.

the IR spectrum of the Schiff bases, but a band was located in the vicinity of 1610 cm^{-1}. This band is ascribable to C=N stretching vibration of the Schiff bases.

ESR Measurements

The nitro radical anions of the Schiff bases were generated by electrochemical reduction in situ at room temperature using DMSO as solvent. The anion radicals are moderately stable. ESR spectra were recorded on an X-band spectrometer Bruker ECS 106, using a rectangular cavity with 50 kHz field modulation. The hyperfine coupling constants are reported in gauss and are estimated to be accurate within 0.05 G.

RESULTS AND DISCUSSION

ESR Spectra

Electrochemical reductions to the radical form (in situ) in DMSO were carried out applying the corresponding potential to the first wave for the Schiff bases as obtained from cyclic voltammetry experiments.

The analysis of the ESR spectra and the assignments of the hyperfine coupling constants were done by comparison with similar radicals and confirmed by computer simulations. In a few cases some assignments were confirmed with the help of INDO molecular orbital calculations using Hyperchem 6.0.

The electrochemical reduction of **(1)** produced a dark yellow solution in DMSO. Well-resolved ESR spectrum of 36 lines has been recorded and interpreted in terms of a triplet due to a nitrogen nucleus, a triplet due to a pair of equivalent protons, a septet due to three nitrogens, and a doublet due to a proton (Fig. 1). The assignment of the hyperfine coupling constants was done by inspection and by comparison with the 5-nitropyrimidine anion radical spectrum.[11] The assignment was verified by computer simulation of the experimental spectrum (Fig. 1). The values of the hyperfine coupling constants are shown in Table 1. By examining the hyperfine patterns, the largest coupling constant of 11.70 G can be assigned to the nitrogen nucleus of the pyrimidine nitro group. There is also no doubt to assign a triplet of 3.2 G to two-equivalent ring protons in positions 4 and 6. The assignment of a septet generated by three nitrogens (two from the heterocyclic ring in positions 1 and 3, and the other from imine nitrogen in position 7), which appear accidentally equivalents for the ESR, it is supported by computer simulation. Finally there is a doublet as a contribution of an imine proton. These assignments were supported in some cases with the help of spin density calculated by means of the INDO method. The assignments and the INDO calculations are given in Table 1.

The electrochemical reduction of **(2)** produced a dark yellow solution in DMSO. Well-resolved ESR spectrum of 30 lines has been recorded and analyzed in terms of a triplet due to a nitrogen, two doublets due to two non-equivalent protons, and a triplet due to two equivalent protons (Fig. 2). It is reasonable to assume that the hyperfine interaction is therefore restricted to one moiety of the radical anion. The assignment of the nitro group nitrogen is straightforward with a coupling constant of 12.90 G However, the assignments of the coupling constants due the protons are not straightforward and can be done by comparison with p-nitrophenol anion radical and other anion radicals with similar structure.[12–17] From this comparison, positions 4 and 6 should have the biggest hydrogen coupling

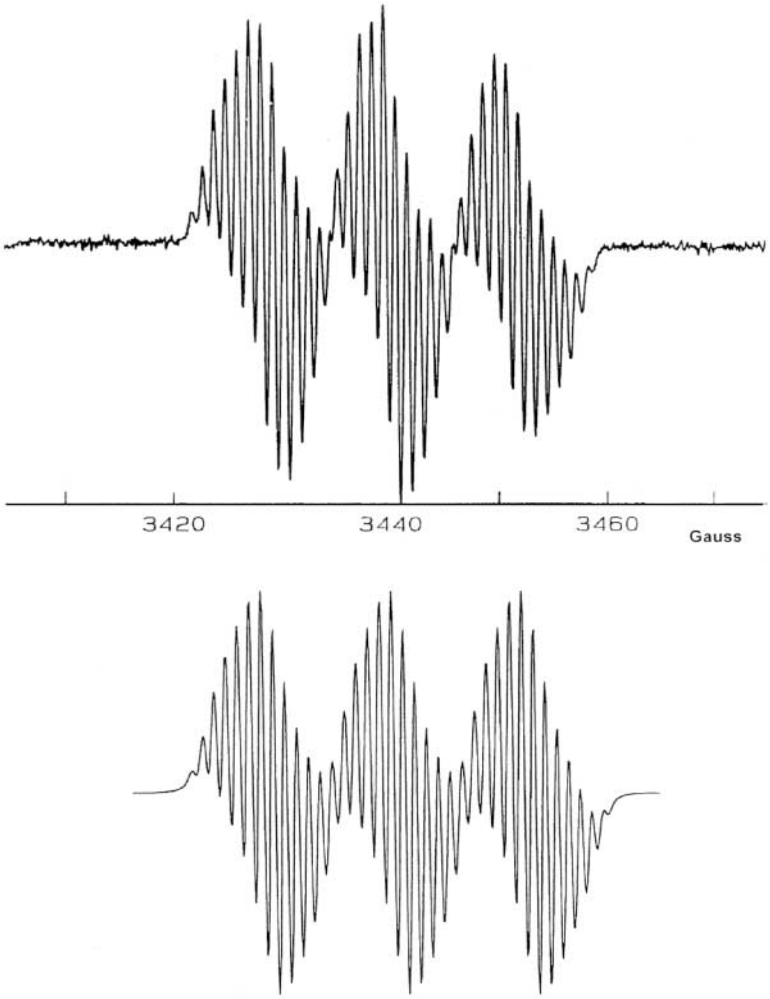


Figure 1. Top: ESR spectrum of the salicyliden-2-imino-5-nitropyrimidine anion radical (**1**$^{\bullet -}$). Bottom: Computer simulation of the same spectrum.

constants. However, the meta substitution greatly affects the values of the coupling constants in positions 4 and 6 as compared with anion radicals with similar structure. It can be assigned to the position 4 a coupling constant of 4.97 G and to position 6 the value of 1.37 G. It is also observed a triplet with a coupling constant of 0.60 G, which can be assigned to the protons of positions 3 and 7, which appear accidentally equivalents. These

Table 1. Experimental and Calculated Hyperfine Coupling Constants (G)

				INDO		
Radical Anion	Nucleus	Position	a_{exp}[a]	ρ_{π}[b]	ρ_{tot}[c]	a_{theor}[d]
$\mathbf{1}^{\bullet -}$	N	1	1.02	−0.116	−0.132	−1.98
	N	3	1.02	−0.116	−0.132	−1.98
	H	4	3.20		−0.0067	−3.62
	$N(NO_2)$	5	11.70	0.427	0.481	9.99
	H	6	3.20		−0.0067	−3.62
	N(–N=)	7	1.02	0.00125	−0.0031	−1.78
	H	8	1.02		0.00065	0.35
$\mathbf{2}^{\bullet -}$	H	3	0.60		0.0045	2.42
	H	4	4.97		−0.0075	−4.04
	$N(NO_2)$	5	12.90	0.363	0.415	8.18
	H	6	1.37		−0.0072	−3.86
$\mathbf{3}^{\bullet -}$	H	3	0.85		0.00443	2.39
	H	4	5.15		−0.00791	4.27
	$N(NO_2)$	5	12.90	0.327	0.403	7.96
	H	6	1.42		−0.00727	−3.92
	H	7	0.85		−0.00193	−1.04

[a] Experimental coupling constants.
[b] π–spin density.
[c] Total spin density.
[d] Theoretical coupling constants.

assignments were verified by computer simulation of the experimental spectrum (Fig. 2). In some cases the hyperfine splitting constants were assigned with the help of INDO molecular orbital. The hyperfine coupling constant assignments and the INDO calculations are given in Table 1. It is not observed further contribution from the rest of the molecule.

The electrochemical reduction of **(3)** generated a dark yellow solution in DMSO. Well-resolved ESR spectra of 30 lines has been recorded and interpreted on the basis of a triplet due to a nitrogen, two doublets due to two non-equivalent protons and a triplet due to two equivalent protons (Fig. 3). The assignment of nitro group nitrogen is straightforward with a coupling constant of 12.90 G As the results are very similar to those obtained in ($\mathbf{2}^{\bullet -}$), we follow the same procedure to assign the coupling constants, that is to compare with the spectra of radical anions of similar structure. Here the meta substitution also affects greatly the values of the coupling constants in positions 4 and 6 as compared with anion radicals with similar structure.[12–17] Then the following coupling constants are

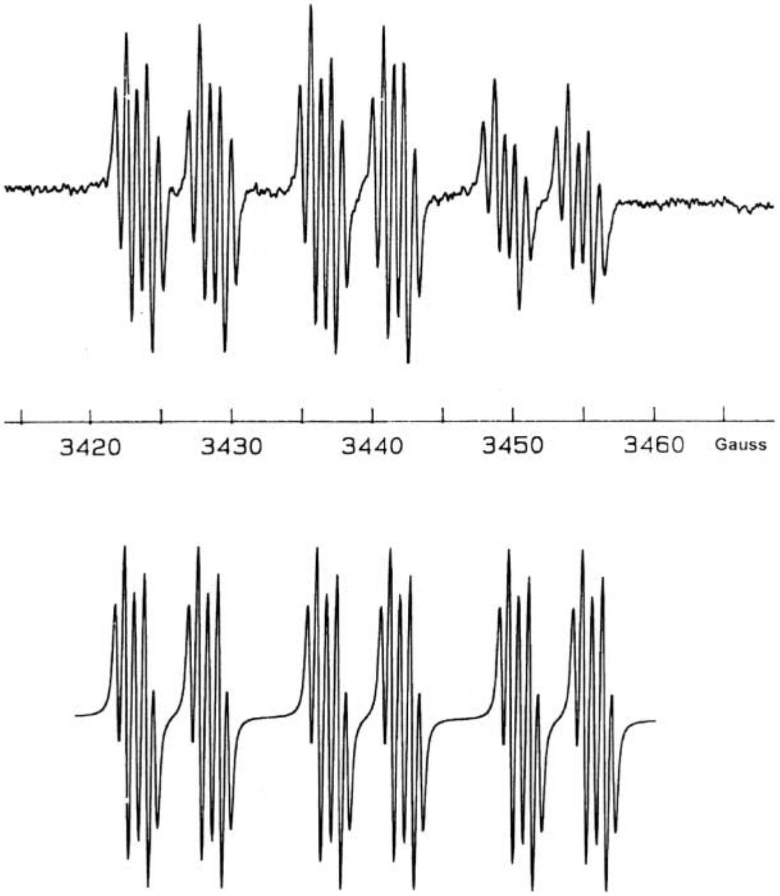


Figure 2. Top: ESR spectrum of the N,N-*bis*(5-nitrosalicyliden) ethylendiamine anion radical (**2**$^{\bullet-}$). Bottom: Computer simulation of the same spectrum.

assigned: for position 4 a value of 5.15 G and for position 6 a value of 1.41 G For positions 3 and 7 the same coupling constant : 0.85 G These assignments were verified by computer simulation of the experimental spectrum (Fig. 3). Coupling constants were assigned in some cases with the help of INDO method. The coupling constant assignments and the INDO calculations are given in Table 1.

In the case of (**2**$^{\bullet-}$) and (**3**$^{\bullet-}$) the substitutions by big groups in position meta greatly affect proton coupling constants of positions 4 and 6 as compared with similar radicals and predictions of INDO MO calculations.

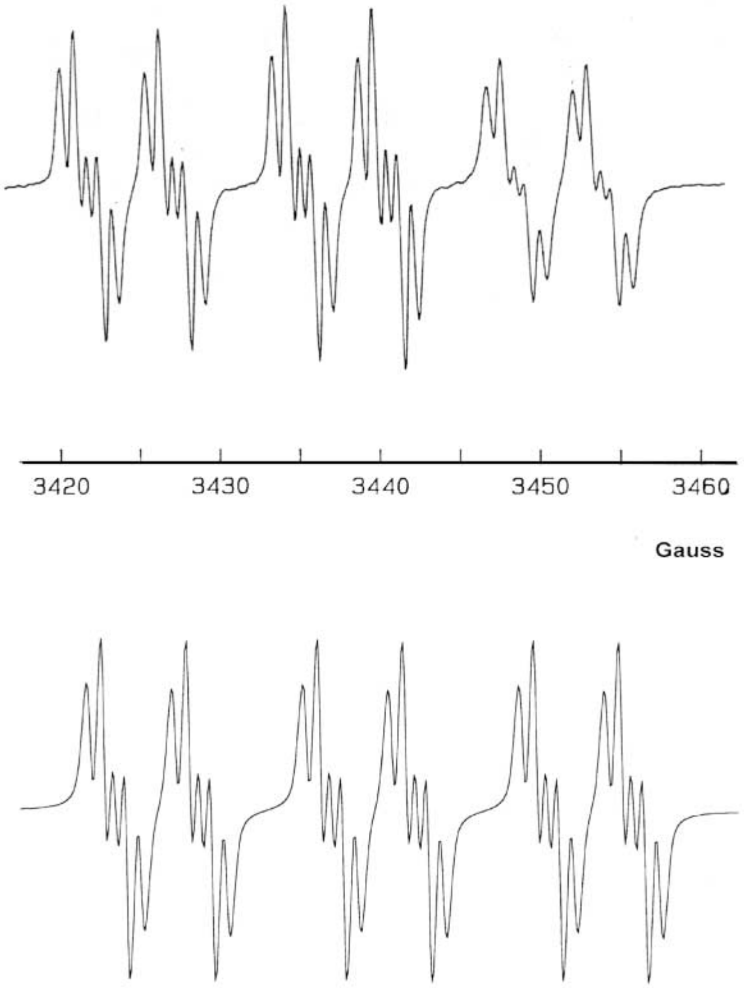


Figure 3. Top: ESR spectrum of 2-hydroxy-5-nitro-benziliden-5-iminoquinoline anion radical ($\mathbf{3}^{\bullet -}$). Bottom: Computer simulation of the same spectrum.

In all spectra it is observed that the line widths are affected by asymmetric variations due to the electron spin relaxation as it is found in some aromatic nitro anion radicals.[18]

The INDO calculations only showed a rather qualitative relation to experimental results due perhaps to the sensibility of the method to the different possible conformations produced by to free rotations around the some specific σ-bonds of these molecules.

ACKNOWLEDGMENT

The authors acknowledge support from Project FONDAP 11980002.

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Received January 14, 2002
Accepted March 15, 2002