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Article

Electrochemical and Spectroscopic Study of 4-(Phenyldiazenyl)-2-{[tris-(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one. Mechanism of the Azo and Imine Electroreduction

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O composto 4-(fenildiazenil)-2-{[tris(hidroximetil)metil]aminometileno}ciclohexa-3,5-dien-1(2H)-ona foi sintetizado e caracterizado por análise elementar, espectroscopia infravermelho, ressonância magnética nuclear, espectro eletrônico e voltametria cíclica. O equilíbrio tautomérico do 4-(fenildiazenil)-2-{[tris(hidroximetil)metil]aminometileno} ciclohexa-3,5-dien-1(2H)-ona em dimeteilsulfóxido deuterado é comprovado por dados de ^{1}H RMN. A natureza do processo eletroquímico do 4-(fenildiazenil)-2-{[tris(hidroximetil)metil]aminometileno} ciclohexa-3,5-dien-1(2H)-ona em solução tampão de Britton-Robinson (pH 2-9) foi estudada com o eletrodo gotejante de mercúrio utilizando voltametria de onda quadrada, onda quadrada adsortiva e voltametria cíclica. Os parâmetros eletroquímicos do composto (I_p/E_p, I_p/v, I_p/pH, I_p/t_{acc}) foram determinados.

Newly synthesized 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one was characterized by elemental analysis, FT-IR, NMR, electronic spectra, voltammetry. Tautomeric equilibrium of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one in $DMSO_d$ is supported by ^{1}H NMR data. The nature of electrochemical process of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one in Britton-Robinson buffer (pH 2–9) was studied on the HMDE by square-wave (SWV), adsorptive stripping square-wave (AdSWV) and cyclic voltammetry (CV). The electrochemical parameters (I_p/E_p, I_p/v, I_p/pH, I_p/t_{acc}) of the compound were determined.

Keywords: 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one, FT-IR, electronic spectra, voltammetry

Introduction

Azo compounds are the largest class of industrial synthesized organic dyes. Although some azo dyes have been reported to be toxic, dozens of additional monoazo dyes are permitted in drugs and cosmetics.[1] The pharmaceutical importance of compounds including an arylazo group has been extensively reported in the literature.[2] The oxidation-reduction behaviors of these compounds play an important role in its biological activity.[3]

There is considerably interest in Schiff base ligands and their complexes due to their antitumour activities.[4] *o*-Hydroxy Schiff bases exist as enol,[5] keto[6] or enol/keto mixtures.[7] The proton tautomerism plays an important role in many fields of chemistry and especially biochemistry. Knowledge of which of the tautomeric structures is dominant under certain conditions is important in respect of colouristic and technological properties of dyes.[8] About 50% of commercially disclosed structures of azo dyes contain a naphthol ring and therefore have a potential tautomeric structure.[9]

The voltammetric behaviours of the synthesized azo compounds have been extensively reported in the literature.[3,10-13] The present study describes the synthesis, characterization and voltammetric behavior of the newly synthesized 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one.

Experimental

Synthesis

A mixture of aniline (0.93 g, 10 mmol), water (50 mL) and concentrated hydrochloride acid (2.5 mL, 30 mmol) was

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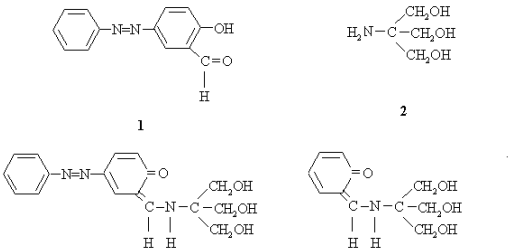
heated while stirring until a clear solution was obtained. This solution was cooled to 0-5 °C and a solution of sodium nitrite (0.96 g, 14 mmol) in water was then added dropwise, maintaining the temperature below 5 °C. The resulting mixture was stirred for 30 min in an ice bath. The salicylaldehyde (1.22 g, 10 mmol) solution (pH 9) was gradually added to the solution of the cooled benzenediazonium chloride prepared as described above and the resulting mixture was continually stirred at 0-5 °C for 60 min in an ice bath. The resulting product was recrystallized from ethyl alcohol to give a solid 5-phenylazosalicylaldehyde of m.p. 128-129 °C (Literature: [14] 128 °C).

To a solution of this 5-phenylazosalicylaldehyde (**1**) (1.07 g, 5 mmol) in 75 mL butane-1-ol was added a solution of tris(hydroxymethyl)aminomethane (**2**) (0.605 g, 5 mmol) in 25 mL butane-1-ol. The mixture was stirred at reflux temperature and the occurring water in the reaction was distilled out of reaction mixture. Resulting orange precipitate was filtered, recrystallized from ethyl alcohol and good-shaped crystals were obtained by slow evaporation from acetonitrile after 2 days. Yield: 90%, m.p. 169-171 °C. Anal. Calc. for 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one (**3**): C, 62.00; H, 5.77; N, 12.76. Found: C, 60.95; H, 5.85; N, 12.58%. Compound **4** was prepared as previously reported.[15]



Vibrational spectra

The FT-IR spectra in the 4000-400 cm^{-1} region were recorded from KBr pellets with a Shimadzu FT-IR 8800 interferometer.

NMR spectra

Proton (200 MHz) NMR spectra were recorded with a AC-200 Bruker FT-NMR spectrometer ($DMSO_d$ as internal standart).

Electronic spectra

The electronic absorption spectra in the 800–200 nm range were recorded on Unicam V2–100 UV-Vis spectrophotometer, using 1 cm quartz cells.

Voltammetry

Electrochemical measurements were performed with a hanging mercury drop electrode (HMDE, controlled growth mercury electrode, EG&G PARC Model 303A) controlled by a EG&G PAR 384B polarographic analyzer. A HMDE with a surface area of 0.01765 cm^2 was used for measurements. Experiments were carried out with an HMDE in a three-electrode cell equipped with a Pt counter electrode an $Ag/AgCl/KCl_{sat.}$ reference electrode. All experiments were conducted at 25 ± 1 °C.

4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one was dissolved in 50% (v/v) ethanol/water mixture. Ten milliliters of the supporting electrolyte solution were added into the cell and deoxygenated with nitrogen for ten minutes prior to each experiment. The addition of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one to the cell containing supporting electrolyte was carried out and then the voltammograms were recorded.

Results and Discussion

Infrared spectra

The (FT-IR) spectrum of 4-(phenyldiazenyl)-2-{[tris (hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one complex is presented in Figure 1. The most important infrared data are reported in Table 1. As can be seen in Figure 1, C=O carbonyl group is visible at 1635 cm^{-1}.

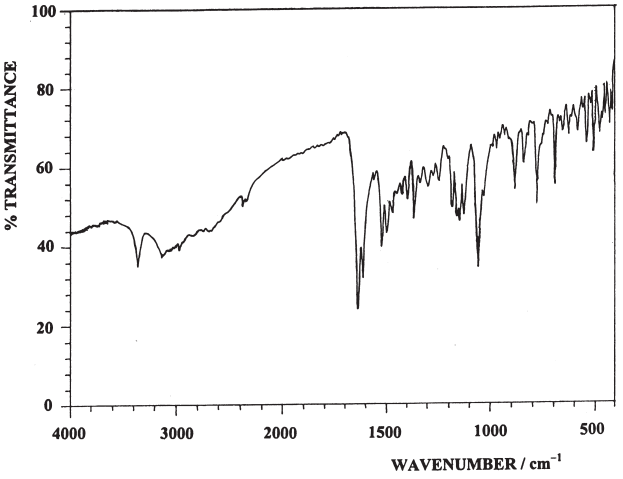


Figure 1. The FT-IR spectrum of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one.

Table 1. Assignments of the most characteristic FT-IR bands of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]amino-methylene} cyclohexa-3,5-dien-1(2H)-one (band positions in cm^{-1})

4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one	Assignments
3356	ν (N-H)
2966	ν (C-H)
1635	ν (C=O)
1612	ν (C=C)
1429	ν (N=N)
1396	ν (C-N)
968	ν (C-C)
883	ν $(C-H)_{ring}$

Others: 655, 690, 775, 1053, 1145, 1180, 1558.

This band correlates with protonated imines, which usually exhibit a variable band in the region 1690-1640 cm^{-1}.[16] The weak absorption band at 3356 cm^{-1} may be due to a hydrogen bonded ν (O-H) in the enolate form or ν (N-H). The band at 1396 cm^{-1} attributed to ν (C-N). Band at 2966 cm^{-1} indicates the presence of aromatic ring. In addition, the band at 1612 cm^{-1} assigned to $\nu(C=C)_{ring}$ and band at 1429 cm^{-1} attributed to ν(N=N).

NMR spectra

In solution, the existence of intramolecular hydrogen bonding (N-H···O) in Schiff base ligands has been conformed by NMR spectroscopy.[6,17] The ^{1}H-NMR data for 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one show the tautomeric equilibrium in DMSO (δ = 14.47 ppm doublet N<u>H</u>-CH=, d = 8.63 ppm doublet =C<u>H</u>-N).

Electronic spectra

The electronic spectra of 4-(phenyldiazenyl)-2-{[tris (hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one were recorded in both DMF and EtOH between 200 and 600 nm (Figure 2). These solvents are selected in order to give a difference in the position of the tautomeric equilibrium (*ketoamine – enolimine*). The λ_{max} values of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one in DMF and EtOH are 393 (with shoulder at about 430 nm) and 339 nm, respectively. This tautomeric shift may be inferred from: selective solvation or the ability of the solvent to form stronger intermolecular H-bonds with a particular tautomeric form.[8] Also, the absorption spectra of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one at

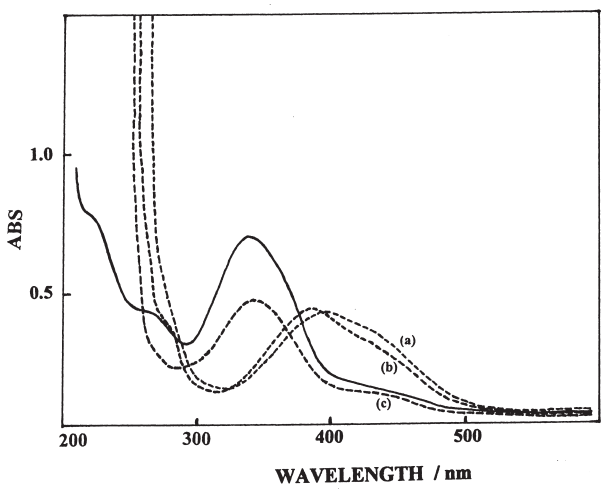


Figure 2. Absorption spectra of 4-(phenyldiazenyl)-2-{[tris (hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one in ethanol C=3.2x10^{-5} mol L^{-1} (———) and in DMF, C=1.6x10^{-5} mol L^{-1} (-------) (a) 0% ; (b) 45% and (c) 60% water.

different volume ratios of the applied pair of solvents DMF/water were recorded. It was observed that the absorption of the band at 393 nm (probably *enolimine* form) increased and shifted to 340 nm, while that of the other form (*ketoamine* at 430 nm) decrease with increasing of the volume content of water (Figure 2). H_2O lead to an increase of the H form.[8]

Voltammetry

The nature of electrochemical process of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene} cyclohexa-3,5-dien-1(2H)-one was studied by cyclic voltammetry (CV) square-wave voltammetry (SWV) and adsorptive stripping square-wave voltammetry (AdSWV). 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one gave three reduction waves at –0.206, –1.002 and –1.490 V in Britton-Robinson buffer (pH 4.09) for the potential range from 0.0 to –1.7 V (Figure 3). To determine the electroactive site, responsible from these peaks, the voltammogram of 4-(phenyldiazenyl)-2-{[tris(hydroxy-methyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one (**3**) was compared with those of other compounds (**1**, **2** and **4**). Tautomerism for compound **4** was developed by spectroscopic and voltammetric methods. The peak potential values of these compounds in Britton-Robinson buffer (pH 4.09) are presented in Table 2.

Since the –N=N– group (compounds **1** and **3**) is more susceptible to reduction than the –C=N– (compounds **3** and **4**) or C=O groups (compound **1**), –N=N– group is reduced at less negative potential than other sites.[11,12] At the voltammogram of 4-(phenyldiazenyl)-2-{[tris

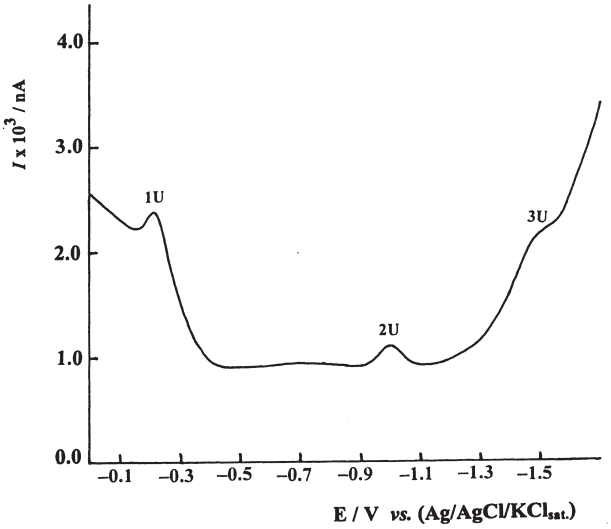


Figure 3. Square-wave voltammogram of 9.7×10^{-6} mol L^{-1} 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one in Britton-Robinson buffer (pH 4.09). Experimental conditions: scan rate, 200 mV s^{-1}; drop size, medium; equilibrium time, 5 s. 1U, the reduction of azo group; 2U, the reduction of azomethine group; 3U, catalytic hydrogen wave.

Table 2. The voltammetric characteristics of some compounds in Britton-Robinson buffer (pH 4.09)

Compound	E_{p1} / V	E_{p2} / V	E_{p3} / V
1	–0.256	–1.038	–1.628
2	-	–1.046	-
3	–0.206	–1.002	–1.490
4	-	–1.244	–1.636

(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one, the first peak (–0.206 V) can be therefore attributed to the reduction of the –N=N–. Second peak (–1.002 V) can also attributed to reduction of azomethine (–C=N–) group due to probably the *ketoamine – enolimine* tautomeric equilibrium in aqueous solution. The last peak may be also attributed to the catalytic hydrogen reduction. The influence of pH on the reduction process was examined (Figure 4). As can be seen in Figure 4, the reduction peaks shift towards more negative values with increase in pH. In the cases of azo and azomethine groups, the peak potentials give a linear relationship with pH. However, unlike the cases of azo and azomethine groups, the peak potential of catalytic hydrogen wave fails to give a linear relationship with pH. It was obtained that the peak currents are also dependent on pH. The reversibility of the electrode process was characterized by cyclic voltammetry (Figure 5). From the cyclic voltammograms (Figure 5), it was determined that the electrode process of azo group was quasi-reversible ($\Delta E_p = E_{pa} - E_{pc}$ = 35 mV for 400 mV s^{-1}) while

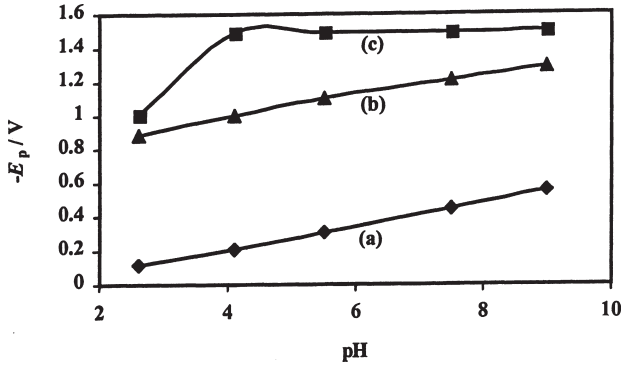


Figure 4. Variation of E_p with pH for the reduction of a) azo group, b) azomethine group, c) catalytic hydrogen wave of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one.

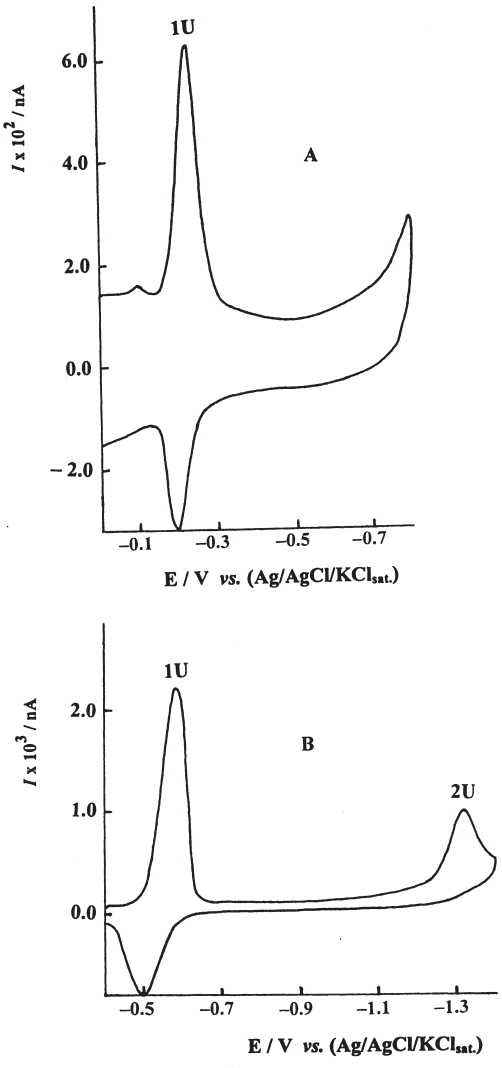


Figure 5. Cyclic voltammograms of 4-(phenyldiazenyl)-2-{[tris (hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one in Britton-Robinson buffer A) (1.9×10^{-5} mol L^{-1}) pH 4.09; B) (9.9×10^{-6} mol L^{-1}) pH 9.00. Experimental conditions: scan rate, 400 mVs^{-1}; drop size, medium; equilibrium time, 5 s; working electrode, HMDE. 1U, the reduction of azo group; 2U, the reduction of azomethine group

Table 3. Voltammetric results of the first peak of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one in Britton-Robinson buffer, using HMDE

	pH 4.09[a]			pH 9.00[b]		
v / V s^{-1}	$-E_{pc}$ / V	I_{pc} / $v^{1/2}$ / μAV$^{-1/2}$s$^{1/2}$	ΔE_p / mV	$-E_{pc}$ / V	I_{pc} / $v^{1/2}$ / μAV$^{-1/2}$s$^{1/2}$	ΔE_p / mV
0.050	0.210	0.313	0	0.540	1.552	5
0.100	0.214	0.462	5	0.552	1.964	15
0.200	0.220	0.668	15	0.556	2.638	45
0.250	0.222	0.790	20	0.572	2.920	50
0.333	0.226	0.965	25	0.580	3.223	70
0.400	0.228	0.985	35	0.586	3.463	85
0.500	0.234	1.176	45	0.595	3.790	95

[a] 1.9x10^{-5} mol L^{-1}; [b] 9.9x10^{-6} mol L^{-1}.

other peaks (azomethine and catalytic hydrogen wave) were irreversible because the anodic peaks are absent. Also the charge transfer coefficients of the electrode process of N=N group are dependent on both pH and scan rate (Table 3). A constant scan rate of 400 mV s^{-1}, αn values (ΔE_p (V) = E_{pa}–E_{pc} = 0.0591/αn) for pHs 4.09 and 9.00 are 1.688 and 0.695, respectively. Azo compounds are reduced in a two-electron step to hydrazo derivatives.[12] Assuming n=2 (for N=N) the charge transfer coefficients can be evaluated as 0.844 and 0.348, respectively. As can be seen in Table 3, with increasing scan rate, the difference between anodic and cathodic peaks potentials for electrode process of azo group increases.

As shown in (Figure 6a) the voltammetric curves registered at low scan speeds (v) for 1.3x10^{-5} mol L^{-1} 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one solutions present the typical behavior of irreversible diffusion controlled voltammograms, while for scan speed values higher than 100 mV s^{-1} the corresponding anodic peak became more visible to that at low scan speeds which is indicative of electrolysis product consumption by a slow homogeneous chemical reaction that follows the electron transfer step. With increasing $v^{1/2}$, cathodic peak current

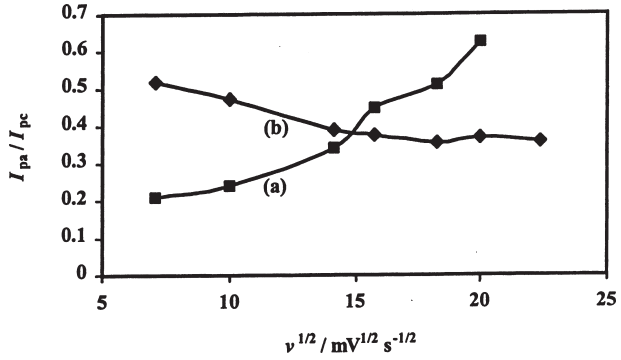


Figure 6. Variation of I_{pa}/I_{pc} ratio with $v^{1/2}$ for the reduction of azo group of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one at a) pH 4.09; b) pH 9.00.

also increased and the I_{pa}/I_{pc} ratio tended to be unity. These results revealed that the reduction of the –N=N– bond is quasi-reversible. In contrast to these results, with increasing scan rate the increase in current of anodic peak is less than that of cathodic peak at pH 9 (Figure 6b). This behavior in basic medium shows that the absorption of reactant[18] is more effective than that of acidic medium.

The voltammetric parameters measured over the range of scan rates investigated are presented in Table 3. At irreversible systems, the current function (I_{pc} / $v^{1/2}$) can be scan rate independent.[19] On the other hand, the peak potential of a reversible system is independent from scan rate.[18] As can be seen in Table 3, the current function (I_{pc} / $v^{1/2}$) for azo group depends on the scan rates while E_{pc} varies negatively as the scan rate increases. At Table 3, the presented results are an additional evidence for the quasi-reversible electrode process of azo group.

On the other hand, in the cyclic voltammograms of the compound small adsorption peaks are seen. The effect of the accumulation time (5-60 s) on the reduction peak intensity (I_{pc}) was evaluated for 3.3x10^{-6} mol L^{-1} 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one solution (Figure 7). From Figure 7, one can see that the responses of first and second peaks preceded by adsorption and increase dramatically (up to the accumulation time of 25 s for azo group; of 40 s for azomethine group). This behavior suggests a higher rate of adsorption.

For the azo and azomethine groups, the dependence of the peak intensity of reduction process (I_{pc}) at HMDE on the scan rate (v) was examined at different pH values (Figure 8). A linear plot of I_p *vs.* $v^{1/2}$ should be obtained when the electrode process is diffusion-controlled whereas the adsorption-controlled process should result in linear plot of I_p *vs.* v.[20] When the potential was scanned at increasing rates from 50–500 mV s^{-1} a linear relationship was observed between the first peak intensity I_{pc} and scan rate v (Figure 8 and Table 4), suggesting the adsorption of 4-(phenyl-

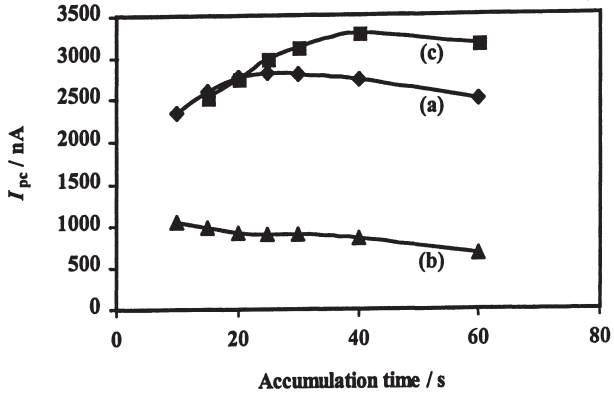


Figure 7. The effect of the accumulation time on the reduction peak intensity (I_{pc}) of a) azo group, b) azomethine group, c) catalytic hydrogen wave for $3.3x10^{-6}$ mol L^{-1} 4-(phenyldiazenyl)-2-{[tris (hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2H)-one solution in Britton-Robinson buffer (pH 4.09).

diazenyl)-2-{[tris(hydroxymethyl)methyl] amino-methylene}cyclohexa-3,5-dien-1(2H)-one on the electrode surface, although the dependence of peak intensity I_{pc} with square root of the scan rate ($v^{1/2}$) was not completely linear (Figure 9).

To obtain an indication of the reversibility of electrode processes, cyclic voltammograms of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one were taken in different pHs (Figure 5). As can be seen in Figures 5 and 10, the reversibility degree of the electrode process of first peak depends on both supporting electrolyte and pH. The reversibility of the electrode process of azo group is well seen in acetate buffer (pH 4.5) (Figure 10).

It should be also note that the reversibility of first peak depends on the experimental parameters such as scan rate,

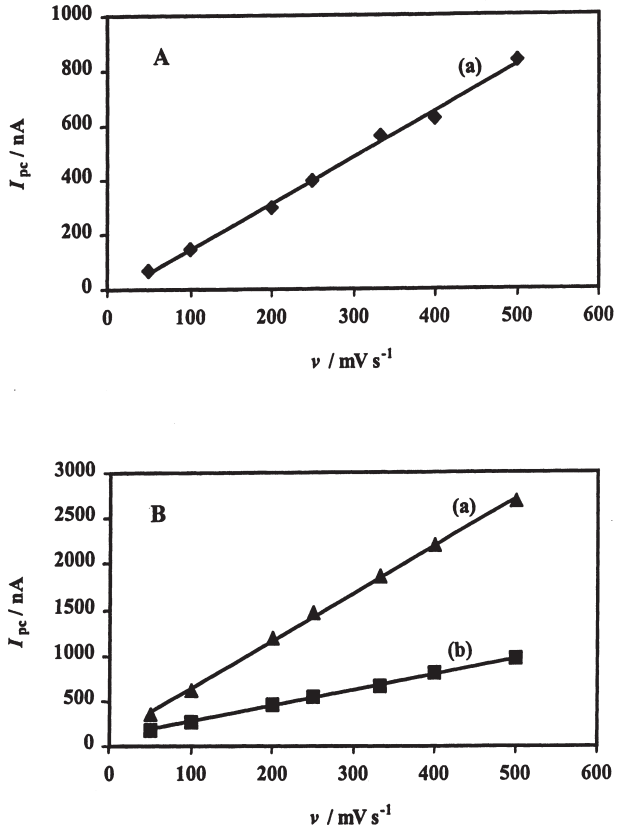


Figure 8. The dependence of peak intensity (I_{pc}) of a) azo group, b) azomethine group with the scan rate (v) for 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one solution in A) ($1.9x10^{-5}$ mol L^{-1}) pH 4.09; B) ($9.9x10^{-6}$ mol L^{-1}) pH 9.00.

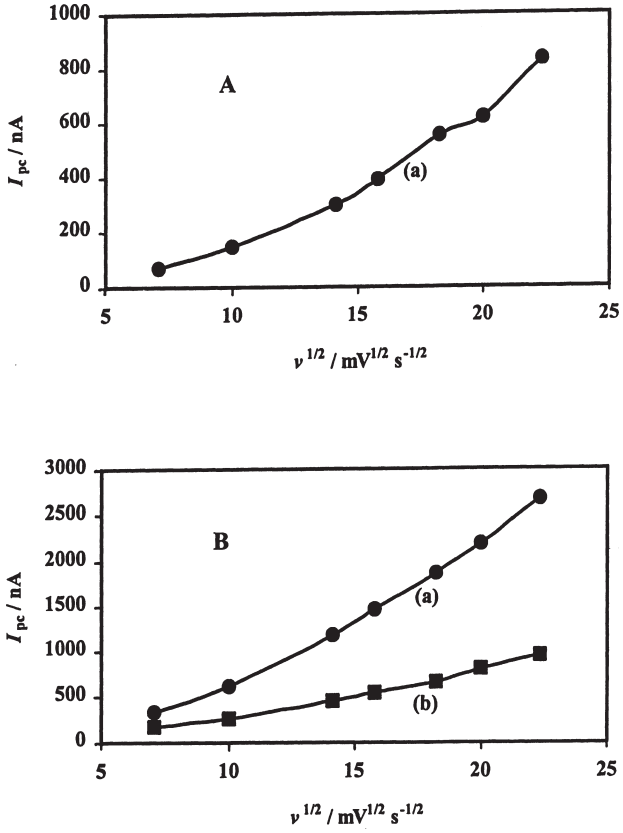


Figure 9. The dependence of peak intensity (I_{pc}) of a) azo group, b) azomethine group with square root of the scan rate ($v^{1/2}$) for 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl) methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one solution in A) ($1.9x10^{-5}$ mol L^{-1}) pH 4.09; B) ($9.9x10^{-6}$ mol L^{-1}) pH 9.00.

Table 4. The relationships between the peak intensity I_{pc} and scan rate v in different pH values

Group	pH 4.09	pH 9.00
N=N	I_{pc} (nA) = 1.6815 v – 22.957 r^2 = 0.9964	I_{pc} (nA) = 5.1868 v + 118.44 r^2 = 0.9988
C=N	-	I_{pc} (nA) = 1.7359 v + 100.71 r^2 = 0.9978

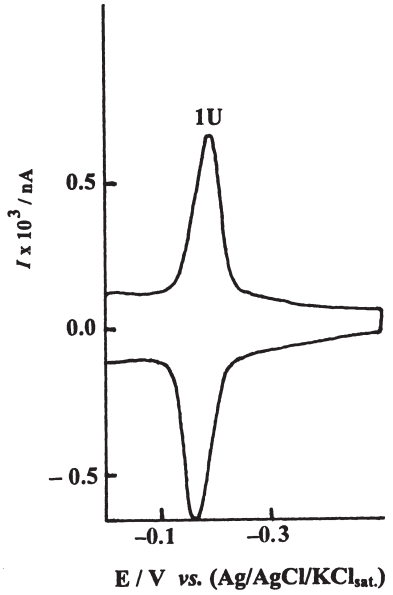


Figure 10. Cyclic voltammograms of 1.48×10^{-5} mol L^{-1} 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene} cyclohexa-3,5-dien-1(2H)-one in acetate buffer (pH 4.50). Experimental conditions are as in Figure 5. 1U, the reduction of azo group.

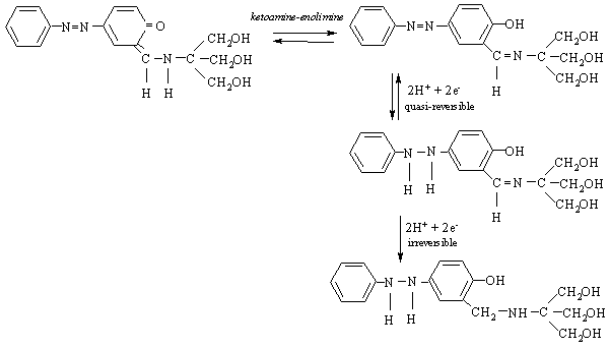
initial and final potentials, concentration, pH of the buffer solution.

For the reversible process, the peak current i_p is proportional to the scan rate v, equation 1;

$$i_p = n^2F^2A\,\Gamma v / 4RT \qquad (1)$$

As regards to the above equation, the amount of reactant adsorbed on the mercury electrode surface, Γ is calculated as 0.9×10^{-11} mol cm^{-2} for acetate buffer (pH 4.5). Because the cathodic current is bigger than that of anodic current for other buffer solutions, the amount of reactant adsorbed on the mercury electrode varies according to the above mentioned experimental parameters.

Finally, the electrode reaction mechanism of 4-(phenyldiazenyl)-2-{[tris(hydroxymethyl)methyl] aminomethylene}cyclohexa-3,5-dien-1(2H)-one can be suggested as following mechanism:



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