



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

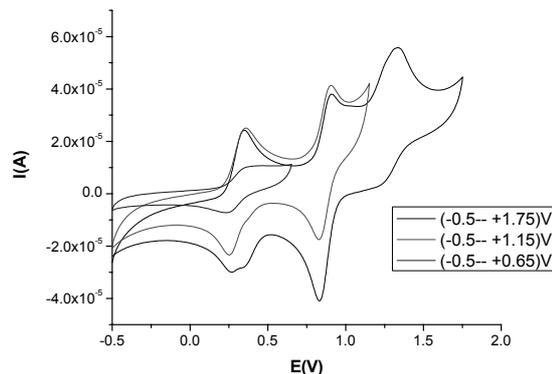
ELECTROCHEMICAL STUDY OF 2,2-DIPHENYL-1-(2,4-DINITROPHENYL)HYDRAZINE AND 2,2-DIPHENYL-1-(3,5-DINITROPYRIDIN-2-YL)HYDRAZINE

Cassiana Cristina ANDREI, Daniela BALA* and Constantin MIHAILCIUC*

Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta, 030018 Bucharest, Roumania

Received November 29, 2012

The CV and DPV behaviour is investigated for two hydrazine derivatives, 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (A), and 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine (B) which differ structurally by the presence of a nitrogen atom (in the pyridinyl moiety of B) instead of a carbon atom (in the phenyl moiety of A) in an aromatic ring. The studies take advantage of the presence of an acidic hydrogen atom which can be removed by the methoxide ion base. So that each compound is studied in the absence and in the presence of this hydrogen abstractor. In each case a mechanism of the electrode reaction is proposed. The structure of each compound allows the electronic conjugation (electron withdrawing and electron donating effects being present in different degrees) which leads to similar and/or different CV and DPV behaviour. The anodic and cathodic peak potentials, the half-wave potentials, the shape factor and the peak separation are found and used to explain electrochemical mechanisms.



INTRODUCTION

In the past years there is a special interest for the synthesis and characterization of some new organic free stable radicals. Such compounds can be used for production of materials with magnetic properties.¹⁻⁴ An important class of stable free radicals derived from hydrazine.

The hydrazyl stable free radical is 2,2-diphenyl-1-picrylhydrazyl (DPPH) synthesized by Goldschmidt in 1922.⁵ It is characterized by high chemical stability, able to change colour properties in different media. DPPH can participate to acid-

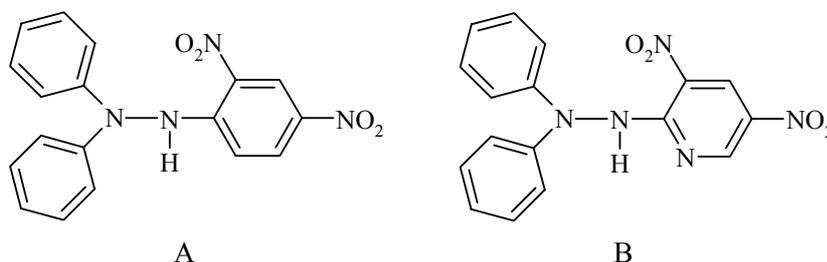
base processes being good hydrogen- or electron-abstractor.⁶ Due to its properties, DPPH has found many applications: it has been used as scavenger for many other radicals, as standard in ESR spectroscopy, but also as indicator for measuring the antioxidant capacity in human plasma.^{7,8} Some derivatives of DPPH like 2,2-*p*-nitrophenyl-1-picrylhydrazyl or the hybrid compound DPPH-PBN (PBN- *N-t*-butyl- α -phenylnitron) were used as spin-traps of free radicals in cigarette smoke.⁹

In this paper we study electrochemical behaviour of two compounds: 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine(A) and 2,2-diphenyl-1-

* Corresponding author: cmpaul@gw-chimie.math.unibuc.ro or dbala@gw-chimie.math.unibuc.ro

(3,5-dinitropyridin-2-yl)hydrazine(B) (Fig. 1). In order to obtain detailed information concerning the redox processes of these hydrazine-derivatives,

cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed.



Scheme 1 – Structure of compounds: (A) 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine, and (B) 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine.

EXPERIMENTAL

Apparatus: Electrochemical experiments were performed with a potentiostat-galvanostat system Autolab PGStat 12 controlled by General Purpose Electrochemical System (GPES) electrochemical interface for Windows (version 4.9.007). Three electrodes in one-compartment cell (10 mL) were used in all experiments: two disk-shaped platinum electrodes (Metrohm, 3 mm in diameter) as working electrode and counter electrode, respectively and Ag (wire) as pseudo-reference electrode.

The platinum electrode surfaces were polished with alumina slurry on a polishing pad, washed with distilled water and sonicated for 1 minute.

Chemicals: Compounds 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (A) and 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine (B), were prepared as described.^{10,11} The others reagents: acetonitrile (Fisher Chemicals), Bu_4NBF_4 (Fluka), sodium hydroxide (Sigma), methanol (Chimopar) were used as purchased.

Measurements: Two working solutions of 10 mL each were prepared and studied: one obtained by solving the electroactive compounds A or B (1 mM) in acetonitrile 0.1 M Bu_4NBF_4 as supporting electrolyte, and the other by adding 0.1 mL NaOH 0.11 M in methanol to the former solution in order to create a basic medium (the obtained effect was the hydrogen-atom abstraction from hydrazyl moiety). CV and DPV measurements were performed.

Cyclic voltammetry experiments were carried out in the potential ranges: between -0.50 V and +1.75 V, -0.50 V and +0.65 V and respectively -0.50 V and +1.15 V for compound A. For compound B the potential domains were: between -0.50 V and +1.85 V, -0.50 V and +0.75 V, and respectively -0.50 V and +1.15 V. To investigate the influence of scan rate several values were used (0.05 - 0.75 V s^{-1}). DPV curves were recorded using different parameters: step potential 10 mV, and two values for modulation amplitude 25 and 50 mV respectively.

The solution containing the electroactive hydrazine derivative and the supporting electrolyte, either without or with methoxide ion, was purged with Ar, and low pressure

inert gas atmosphere was maintained above the solution during the electrochemical experiments.

RESULTS AND DISCUSSION

Electrochemical study of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine CV study

Fig. 1 illustrates the cyclic voltammograms obtained for scan rates between 0.05 V s^{-1} and 0.75 V s^{-1} in the potential range from -0.5 V to 1.75 V. They are characterized by a complex morphological aspect, they reflecting multistep oxidation-reduction electrode reaction and protonation-deprotonation chemical reaction.

Thus, at small scan rates can be observed four anodic peaks (ap_1 , ap_2 , ap_3 , ap_4), first and second ones are not scan rate dependent but in the case of the third one is observed a decrease with increasing scan rate, at high scan rates it takes a shoulder appearance. So that, at high scan rates can be observed only 3 anodic peaks (ap_1 , ap_2 , and ap_{3-4}) at the potential values: 0.344 V, 0.904 V and 1.327 V, the peaks 3 and 4 becoming one single wave (ap_{3-4}) because the distance between them on the potential scale is too small. On the cyclic voltammogram can be observed as well two cathodic peaks (cp_I -left side, cp_{II} -right side) at the potential values: 0.289 V and 0.834 V. The cathodic peak from lower potential values (cp_I) is preceded by a shoulder.

The reversibility can be proved by the value of the shape factor,¹² potential domain (0.0 V --- + 1.75 V).

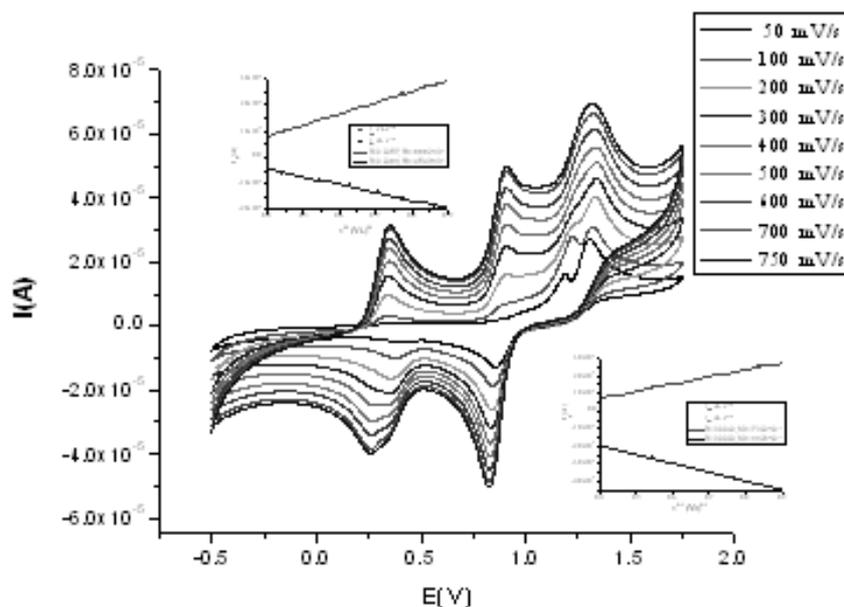


Fig. 1 – Cyclic voltammograms of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), potential domain (-0.50 V --- +1.75 V), for different values of scan rate between 0.05 and 0.75 V s^{-1} . Insets show the plots I_{pa} vs. $v^{1/2}$ (up) and I_{pc} vs. $v^{1/2}$ (down), respectively: upper-left for the first couple of peaks and bottom-right for the second couple of peaks.

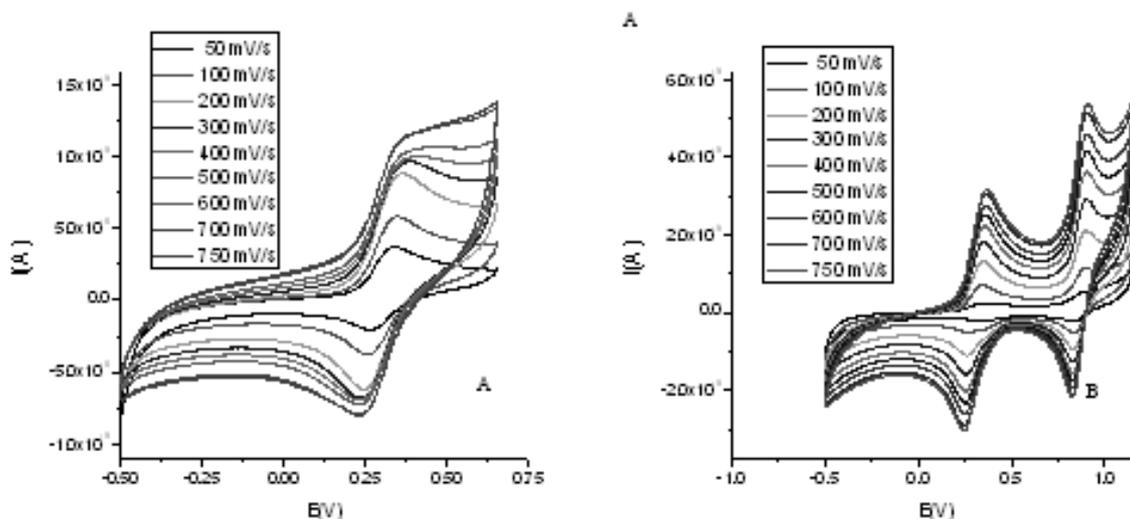


Fig. 2 – Cyclic voltammograms of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), potential domains -0.50 V---+0.65 V (A), and -0.50 V---+1.15 V, (B), for different values of scan rate between 0.05 and 0.75 V s^{-1} .

$E_{\text{pa}} - E_{\text{pa}/2}$: 0.063 V corresponding to the ap_1 and 0.055 V to the ap_2 but also by the values of the peak separation, $E_{\text{pa}} - E_{\text{pc}}$: 0.056 V corresponding to the first couple of peaks (ap_1 and cp_1) and 0.069 V for the second couple of peaks (pa_2 and pc_{II}). Taking into account their heights as well as the values obtained for the shape factor and peak separation, one may say that both of them correspond to one-electron electrode reaction.

The usual plots I_{pa} vs. $v^{1/2}$ and I_{pc} vs. $v^{1/2}$, respectively, lead to straight lines having the following parameters: i) for the first couple of peaks $R=0.9957$, $\text{SD}=6.662 \cdot 10^{-7}$, and the equation of the line $I_{\text{pa}} = -9.147 \cdot 10^{-6} + 4.266 \cdot 10^{-5} v^{1/2}$ and $R=0.9961$, $\text{SD}=4.540 \cdot 10^{-7}$, and the equation of the line $I_{\text{pc}} = 7.655 \cdot 10^{-6} - 3.017 \cdot 10^{-5} v^{1/2}$ and ii) for the second couple of peaks $R=0.9943$, $\text{SD}=7.393 \cdot 10^{-7}$,

and the equation of the line $I_{pa} = -9.249 \cdot 10^{-6} + 4.100 \cdot 10^{-5} v^{1/2}$ and $R=0.9999$, and the equation of the line $SD=1.120 \cdot 10^{-7}$ $I_{pc} = 8.179 \cdot 10^{-7} - 5.087 \cdot 10^{-5} v^{1/2}$.

The genetic link between the ap_1 and cp_1 , on one hand, and pa_2 and pc_{II} , on the other hand, is proved by the CV studies in the Fig. 2.A (recorded in the potential range -0.5 V --- $+0.65$ V, at all scan rates used) and Fig. 2.B (recorded in the potential range -0.5 V --- $+1.15$ V, at all scan rates used). The cyclic voltammograms, recorded on shorter potential domains, put in evidence the above assigned correspondence, which can be also seen in Fig. 4, for a particular scan rate of 0.5 V s^{-1} . Using the half-wave potential, defined as

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2}, \text{ one obtains the value } 0.316 \text{ V}$$

for the first couple of peaks and 0.869 V for the second couple of peaks.

Fig. 3 illustrates the excellent concordance between waves: the characteristic peaks are recorded at the same values of peak potentials no matter the domain. Comparing the voltammograms recorded on different domains but at the same scan rate (0.5 V), it can also be emphasized the almost reversible behaviour of the first and the second redox couple of peaks. The absence of a reverse peak corresponding to third anodic peak (ap_{3-4}) can be explained by an EC mechanism, electron transfer step followed by a chemical reaction.

As concerns the mechanism of the electrode reaction in the absence of methoxide ion, the reaction steps in Scheme 2 might be proposed.

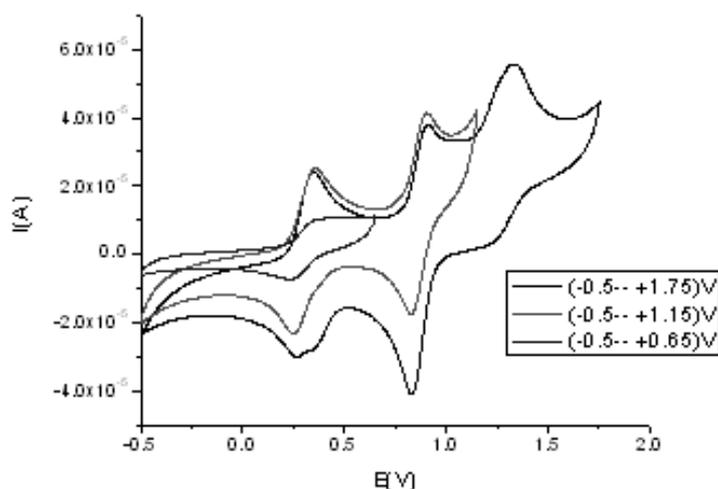
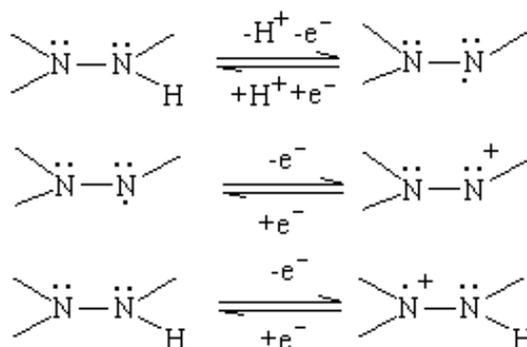
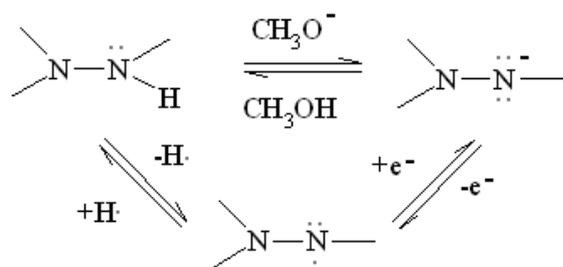


Fig. 3 – Cyclic voltammograms of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), for different potential domains, scan rate 0.5 V s^{-1} .



Scheme 2 – Reaction mechanism proposed for CV and DPV behaviour of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M) in the absence of methoxide ion.

The first couple of peaks, at $E_{1/2}=0.316$ V, is given by the first electron transfer in Scheme 2. This involves besides the electron transfer a deprotonation-protonation intervention. The anodic peak occurring at $E_{pa_3}=1.327$ V and leading to the formation of the nitrogen cation is given by the second electron transfer in Scheme 2. This anodic peak is accompanied by a cathodic counterpeak shoulder-shaped. The third electron transfer, occurring at the tertiary nitrogen atom (numbered with 2), gives rise to the couple of peaks appearing at $E_{1/2}=0.869$ V. The above mechanism of the entire electrode reaction is located on the hydrazyl moiety and the assignment of the first and third peaks was based on interpretation of the behaviour of similar compounds.^{13,14} The increase of the peak potentials for the oxidation of nitrogen from NH-group firstly at nitrogen radical (first anodic wave) and secondly at nitrogen cation (third wave), comparing to those previously reported in the literature, is due to the influence of the strongly deactivating nitro groups in 2- and 4- position in the phenyl located at N1. Regarding the second wave, the de-electronation reaction occurring at tertiary nitrogen from hydrazyl moiety involves the lone pair of electrons participating at two different conjugation processes with phenyl groups. As a consequence, the de-electronation process occurs at a more positive potential.



Scheme 3 – Generic mechanism illustrating the redox and acidic-basic behaviour of hydrazine moiety.

The hydrazyl moiety of the compound is characterized by acidity (being able to lose the proton in basic media as shown in Scheme 3 – horizontally), but it can also lead to a radical in one-step process (left side) by directly losing the hydrogen atom or in two-step process losing at first the proton in an acid-base process, and then losing an electron (right side). Thus, it makes

sense to perform an electrochemical study of the hydrazyl moiety in basic media (in the presence of the methoxide ion).

In order to create a basic media, 100 μ L of 0.11 M NaOH in methanol (solution containing methoxide ion) has been added to the solution of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine in acetonitrile.

Fig. 4 illustrates a comparison between the cyclic voltammograms obtained in the two different conditions already discussed: by using a solution of the compound dissolved in acetonitrile and after the addition of 0.11 M solution of sodium methoxide. In the presence of the methoxide ion as de-protonating agent, an anodic shift of all anodic peaks is recorded. The first couple of peaks, at $E_{1/2}=0.431$ V, is given by the first electron transfer in Scheme 4. This process is preceded by a proton extraction made by the methoxide ion. The anodic peak occurring at approximately $E_{pa_3}=1.327$ V and leading to the formation of the nitrogen cation is given by the second electron transfer in Scheme 4. This anodic peak has now the appearance of a shoulder and its cathodic counterpeak is almost absent in the CV study but very visible in the DPV study. The third electron transfer, occurring at the tertiary nitrogen atom (numbered with 2), gives rise to the couple of peaks appearing at $E_{1/2}=0.999$ V. The above mechanism of the entire electrode reaction is located on the hydrazyl moiety and the assignment of the first and third peaks was based on interpretation of the behaviour of the anions of similar compounds.^{13,14}

The increase of the peak potentials for the oxidation of nitrogen from NH-group firstly at nitrogen radical (first anodic wave) and secondly at nitrogen cation (third wave), comparing to those previously reported in the literature, is due to the influence of the strongly deactivating nitro groups in 2- and 4- position in the phenyl located at N1. Regarding the second wave, the de-electronation reaction occurring at tertiary nitrogen from hydrazyl moiety involves the lone pair of electrons participating at two different conjugation processes with phenyl groups. As a consequence, the de-electronation process occurs at a more positive potential.

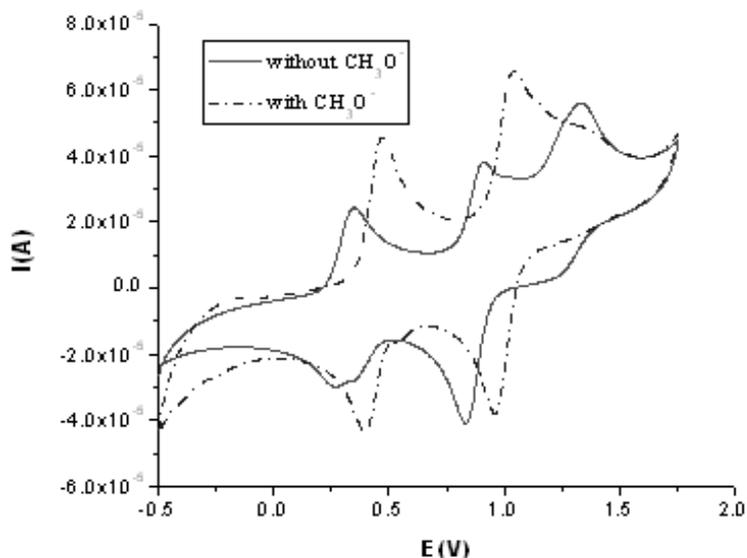
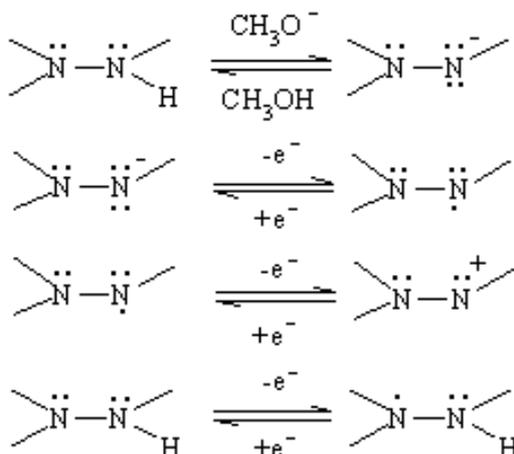


Fig. 4 – Cycling voltammograms of 2,2-diphenyl-(2,4-dinitrophenyl)hydrazine (0.001 M) with (blue) or without (red) methoxide ion added, potential domain (-0.50 V --- + 1.75 V), scan rate 0.5 Vs⁻¹.



Scheme 3 – Reaction mechanism proposed for CV and DPV behaviour of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu₄NBF₄ (0.1 M) in the presence of methoxide ion.

Comparing the cyclic voltammograms it can be emphasized that the characteristic peaks are not situated at the same value of peak potentials. In case of first two couples of peaks it can be observed a shift towards more anodic potentials: with 0.115 V for the first couple of peaks and 0.130 V for the second one (comparing the values of $E_{1/2}$ in the presence and in the absence of methoxide ion), as shown in Table 1. The reason for such a behaviour, in the presence of the methoxide ion, could be the increased conjugation process of the nitrogen anion (possessing two lone pairs of electrons) with the 2,4-dinitrophenyl

moiety in comparison with the case in the absence of the methoxide ion, when a nitrogen anion is not obtained. This increased conjugation leads to a decreasing electron density on the whole hydrazyl moiety having repercussion on the ease of the two electron transfer (*i.e.*, first and second anodic peaks) involving the hydrazyl moiety. As concerns the third anodic peak in both cases, it is the result of the same electron transfer step. So that the third anodic peak, denoted as ap_{3-4} , does not suffer a noticeable displacement on the potential scale, but it changes its shape becoming a shoulder with a decreased current peak.

Table 1

The values of E_{pa} , E_{pc} , $E_{1/2}$ for the first two couples of peaks considering the situations: with or without methoxide ion added and the shift of the half-wave potential (denoted as $\Delta E_{1/2}$).

couples of peaks	without methoxide added			with methoxide added			displacement ($\Delta E_{1/2}$)
	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	
1	0.344	0.289	0.316	0.468	0.393	0.431	0.115
2	0.904	0.834	0.869	1.036	0.961	0.999	0.130

DPV study

To confirm the conclusions obtained using cyclic voltammetry technique, the compound has also been studied using DPV technique. The study was made considering the same working conditions: using two different solutions (with or without methoxide ion added), at different potential domains or at different value of parameters SP and MA.

Fig. 5 illustrates the correspondence between anodic and cathodic peaks as shown using CV technique at different potential domains. It can be observed that the peaks appear at the same potential value, no matter the potential domain investigated which is in very good agreement with the CV conclusions for 2,2-diphenyl-(2,4-

dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), in the absence of the methoxide ion. As concerns the study of 2,2-diphenyl-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), in the presence of the methoxide ion, the agreement between the anodic peak potentials is also enough good.

By adding methoxide ion in the solution of 2,2-diphenyl-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), an anodic shift of the peak potentials appear which is apparent in Fig. 6. The potential shift recorded is 0.081 V for the first anodic peak, 0.089 V for the second anodic peak, and 0.070 V for the third one, as given in Table 2.

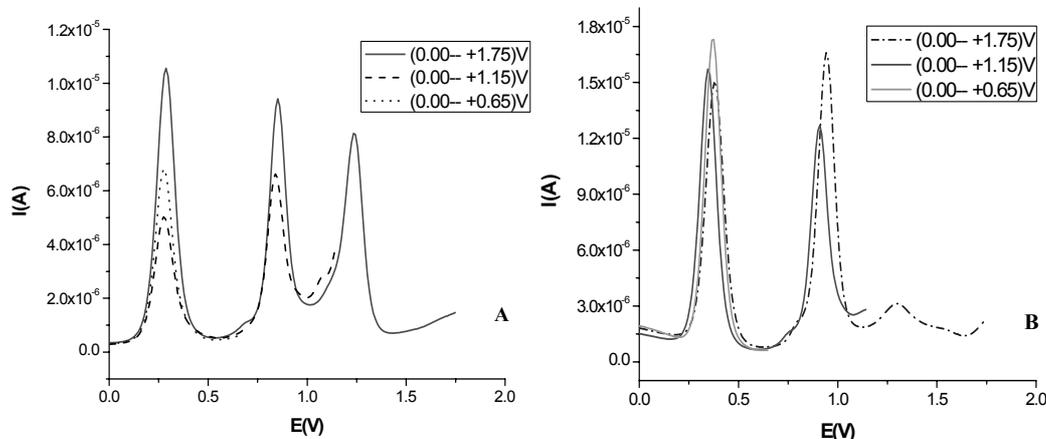


Fig. 5 – DPV traces of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M), without methoxide ion added (A) or with methoxide ion added (B) for different potential domains, DPV parameters being SP=10 mV and MA=25 mV.

Table 2

The displacement of peaks recorded using DPV technique for the compound A.

E_{pa} (V)	ap_1	ap_2	ap_3
$E_{pa, no CH_3O^-}$	0.289	0.852	1.234
$E_{pa, with CH_3O^-}$	0.370	0.941	1.304
$\Delta E_{pa} = E_{pa, no CH_3O^-} - E_{pa, with CH_3O^-}$	0,081	0,089	0,070

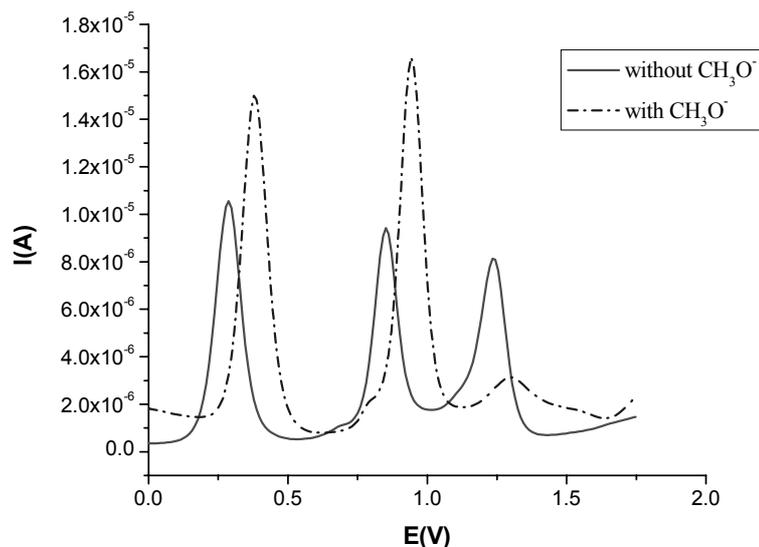


Fig. 6 – DPV traces of 2,2-diphenyl-(2,4-dinitrophenyl)hydrazine (0.001 M) in acetonitrile/ Bu_4NBF_4 (0.1 M) with (blue) or without (red) methoxide ion added, potential domain (0.0 V --- +1.75 V), DPV parameters being $\text{SP}=10$ mV and $\text{MA}=25$ mV.

Electrochemical study of 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine CV and DPV studies

Cyclic voltammetry measurements were performed on solution of the compound in acetonitrile with tetrabutylammonium tetrafluoroborate as supporting electrolyte. The study (both cyclic voltammetry and differential pulse voltammetry) of 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine followed the same steps like the study of 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine. Thus it was demonstrated the reversibility of the first two couples of peaks.

The aspect of the cyclic voltammograms obtained for 2,2-diphenyl-1-(3,5-dinitropyridin-2-

yl)hydrazine emphasizes a complex mechanism of the electrode reaction too. The shape of them is not too clear, as can be seen in Fig. 7.A, so that the DPV traces, which are very clear (Fig. 7.B), are used in the following. Comparing the cyclic voltammograms obtained for the solution of 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine without and with methoxide ion added (Fig. 7.A) it can be observed that is not observed a displacement of the peaks like it was recorded in case of 2,2-diphenyl-1-(2,4-dinitrophenyl) hydrazine. Another visible difference is the appearance of a supplementary peak comparing with the case of the compound 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine.

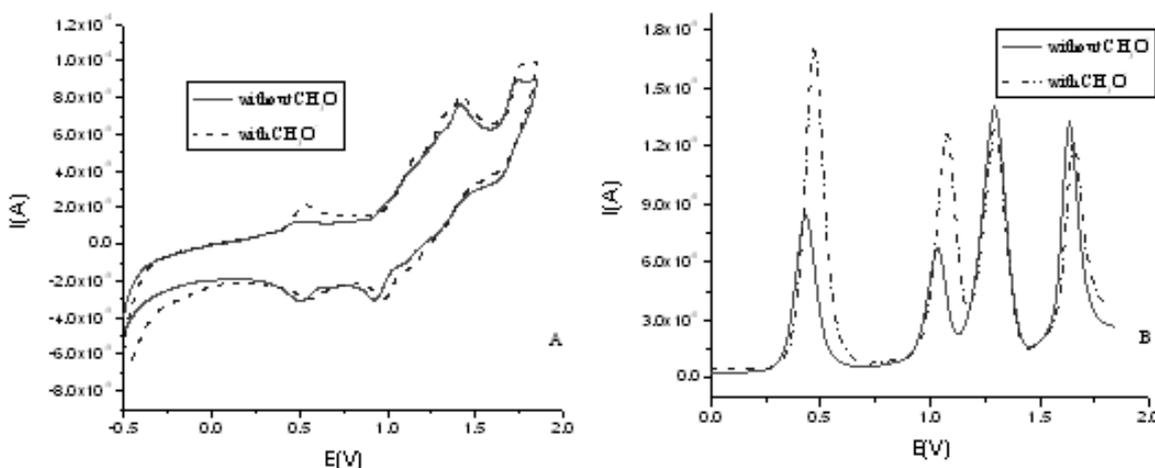
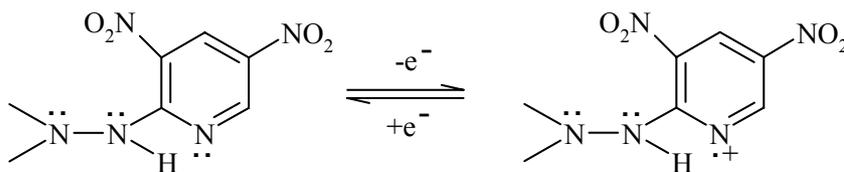


Fig. 7 – Cyclic voltammograms (A) and DPV-traces (B) of 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine (0.001 M) with (blue) or without (red) methoxide ion added, potential domain (0.0 V --- +1.85 V), CV: scan rate 0.5 Vs^{-1} , DPV parameters: $\text{SP}=10$ mV and $\text{MA}=25$ mV.



Scheme 4 – Additional electrode reaction proposed for CV and DPV behaviour of 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine (0.001 M) in acetonitrile/ Bu₄NBF₄ (0.1 M) in the presence of methoxide ion.

Table 3

The displacement of peaks recorded using DPV technique for the compound B.

E_{pa} (V)	ap_1	ap_2	ap_3	ap_4
$E_{pa, no CH_3O^-}$	0.437	1.031	1.293	1.635
$E_{pa, with CH_3O^-}$	0.467	1.071	1.293	1.655
$\Delta E_{pa} = E_{pa, no CH_3O^-} - E_{pa, with CH_3O^-}$	0.030	0.040	0.000	0.020

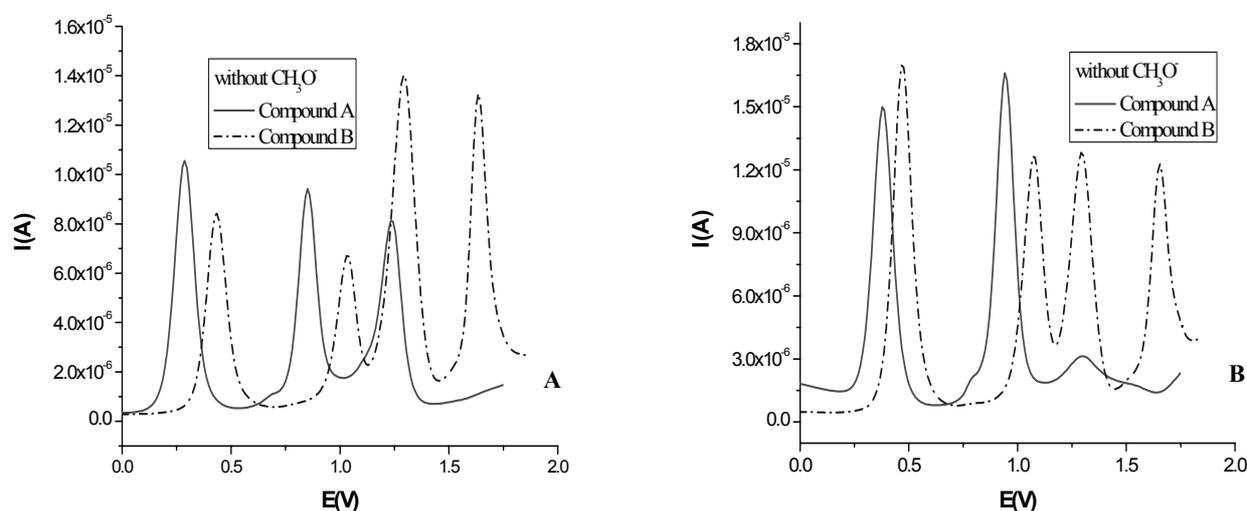


Fig. 8 – DPV-traces of 2,2-diphenyl-(2,4-dinitrophenyl)hydrazine (0.001 M) (red) and 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine (0.001 M) (blue) in acetonitrile/ Bu₄NBF₄ (0.1M), without methoxide ion added (A) or with methoxide ion added (B).

To explain the first three anodic peaks, exhibited by 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine, the same mechanism of electrode reaction can be invoked, Scheme 2, in the absence of methoxide ion, and Scheme 3, in the presence of methoxide ion. The fourth anodic peak, appearing at $E_{pa, no CH_3O^-} = 1.635$ V and $E_{pa, with CH_3O^-} = 1.655$ V, as shown Table 3, is generated by the electron transfer taking place at the nitrogen atom belonging to the pyridinyl moiety.

Comparison

Besides the different number of peaks, three 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine and

four for 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine, coming from the presence of the nitrogen atom in the pyridinyl moiety, both CV and DPV put in evidence a shift of the anodic peak potentials in the anodic direction in the case of the latter compound in comparison with the former one. This happens irrespective of the absence or the presence of the methoxide ion, as can be noticed in Fig. 8. Another difference between voltammograms recorded for 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine comparing to 2,2-diphenyl-1-(3,5-dinitropyridin-2-yl)hydrazine concerns the magnitude of the peak currents in the absence and in the presence of methoxide ion, as can be remarked in Fig. 8: the first two anodic peaks of the former compound are higher while the last two current

peaks of the latter are higher in the absence of the methoxide ion. In the presence of the methoxide ion, for the latter compound the last two anodic peaks decrease, while the first two anodic peaks increase comparing with the same anodic peaks obtained in the absence of the methoxide ion.

CONCLUSIONS

Each compound was studied both in the absence and in the presence of methoxide ion. Both CV and DPV studies allow finding the genetic link between the anodic and cathodic peaks, and also of the mechanism of the electron transfer in each case. The peak potentials were determined and an electron transfer reaction was assigned to each of them. The shift of the peak potential in the presence of the methoxide ion comparing with the absence of the methoxide ion was determined and explained by structural reasons and considering the electron withdrawing groups (nitro groups) and the electron releasing group (nitrogen atom) existing in the molecule. The peak potential shift found between the two hydrazine derivatives was also explained by using the same influences aforementioned.

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