



Electrochemical characterization of (1E)-1-N-{[4-(4-[(E)-N-(3-aminophenyl) carboxyimidoyl] phenoxy) butoxy] phenyl] methilidene} benzene -1,3-diamine

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Abstract: Oxido-reduction properties of a newly synthesized Schiff base were investigated by cyclic voltammetry and differential pulse voltammetry. Measurements were conducted in a three electrode voltammetric cell in a non-aqueous media. Glassy carbon was used as a working electrode, platinum wire as counter electrode and non-aqueous Ag/Ag⁺ electrode as a reference electrode. Inert atmosphere was accomplished by system purging with high purity argon Ar 5 ($\phi_{Ar} = 99,999\%$), before each measurement. Cyclic voltammograms revealed one oxidation peak of the investigated Schiff base ($E_{p,a} = 0.69$ V), which increased with increasing concentration ($c = 3.1 \cdot 10^{-5}$ mol dm⁻³- $1.25 \cdot 10^{-4}$ mol dm⁻³) and scan rate ($v = 50$ - 300 mV/s). Differential pulse voltammetry showed one oxidation peak $E_{p,a} = 0.69$ V, which also increased with increasing concentration.

INTRODUCTION

Symmetrical bis-Schiff bases have been widely studied due to their pronounced biological and pharmacological activity (Liang, Xia, Lei, et al., 2014), optical (Fang, Cao, Chen, et al., 2014), photochromical (Zhao, Zhao, Liu, et al., 2001), thermochromical (Minkin, Tsukanov, Dubonosov, et al., 2011) properties and other outstanding material properties. Furthermore, they can easily form different types of polydentant ligands and because of their diversified donor groups (or atoms) are suitable as chelating agents. Complex compounds of Schiff bases are considered to be a transition state between simple coordination compounds and metalloproteins (Chandra and Pundir, 2008). Recently, symmetrical bis-Schiff bases were used in design of liquid crystals (Iwan, Janeczek, Jarzabek, et al., 2009). These compounds are often used as building blocks for synthesis of liquid crystal polymers or oligomers (Iwan and Sek, 2008).

In this study, we have synthesized a novel symmetrical bis-Schiff base (1E)-1-N-{[4-(4-[(E)-N-(2-aminophenyl) carboxyimidoyl] phenoxy) butoxy] phenyl] methilidene} benzene-1,3-diamine. The

synthesized molecule is a rare example of a symmetrical bis-Schiff base with uncondensed primary amino group (there are only few known examples of similar structures (Shakir, Abbasi, Azam, et al., 2011)). The compound was characterized by means of IR spectroscopy, NMR spectroscopy and TG/DSC analysis. In addition we have studied oxido-reduction properties of the synthesized compound. Preliminary information acquired from this study is very useful as indicators of potential application of the synthesized Schiff base (i.e. potentiometric sensor, organic semiconductor, liquid crystal, etc.).

EXPERIMENTAL

Chemicals and apparatus

All commercially available chemicals were of reagent grade and used as purchased from commercial sources. Dialdehyde 4-[4-(4-formylphenoxy) butoxy]benzaldehyde was prepared by previously reported method (Balić, Marković and Balić, 2013). All solvents were purchased commercially. N,N-dimethylformamide (DMF) was purchased from Fischer Chemical and lithium chloride (LiCl) from BDH Prolabo and were used without further purification.

IR spectrum was recorded on a Shimadzu FTIR 8400S spectrophotometer using the DRS 8000 attachment, in the 4000-400 cm^{-1} region. The sample was mixed with KBr (IR grade). Thermogravimetric analysis was performed using a simultaneous TGA-DSC analyser (Mettler-Toledo TGA/DSC 1). The compound was placed in aluminium pan (100 μL) and heated in nitrogen atmosphere (200 mL min^{-1}) up to 590 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$. The data collection and analysis were performed using the program package STAR^e Software 10.0 (STAR^e, Software 10.0 (2809), Mettler-Toledo GmbH). The ^1H NMR and ^{13}C NMR were recorded on NMR (300 MHz) Bruker instrument, using deuterated chloroform as solvent at NMR Laboratory of the Ruđer Bošković Institute, Zagreb.

Electrochemical experiments were performed on PalmSens potentiostat/galvanostat (PalmSens BV, Utrecht, The Netherlands) driven by PSTrace 4.2 software. A conventional three-electrode cell was used with a glassy carbon as a working electrode, non-aqueous Ag/Ag^+ (Ag wire in acetonitrile solution of 0.01 M AgNO_3 and 0.1 M Tetrabutylammonium perchlorate) as a reference electrode and a platinum wire as a counter electrode. The glassy carbon working electrode was polished with coarse diamond polish (1 μm , ALS, Japan) and with polishing $\alpha\text{-Al}_2\text{O}_3$ (0.05 μm , ALS, Japan) before each measurement. Cyclic voltammetry scan rate was 100 mVs^{-1} . The differential pulse voltammetry conditions were: scan increment 5 mV, pulse amplitude 25 mV, pulse width 70 ms and scan rate 5 mV s^{-1} .

Synthesis of the title compound

Dialdehyde, 4-[4-(4-formylphenoxy)butoxy]benzaldehyde (0.6 g, 2 mmol) was dissolved in 40 mL of methanol and 0.274 mL (2 mmol) triethylamine was added to this solution. The solution was brought to brisk reflux and 0.49 g (4.5 mmol) of *m*-phenylenediamine dissolved in 25 mL of methanol was gradually added. The mixture was heated at reflux temperature for 3 hours. After the reaction was completed, the resulting mixture was left at room temperature for 24 hours. The white yellow product was filtered and washed with cold ethanol and diethyl ether. Yield: 62%.

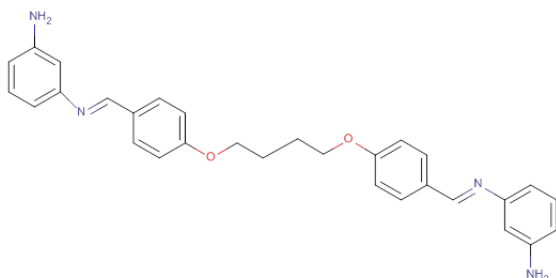


Figure 1: Structure of the title compound.

RESULTS AND DISCUSSION

Cyclic voltammetry studies

A cyclic voltammogram of the investigated Schiff base is shown in **Fig. 2**. One anodic peak is visible at a potential of 0.690 V when the potential was scanned from -0.2 V to 0.8 V vs. Ag/Ag^+ reference electrode. No reduction wave can be observed, indicating that the oxidation reaction is totally irreversible.

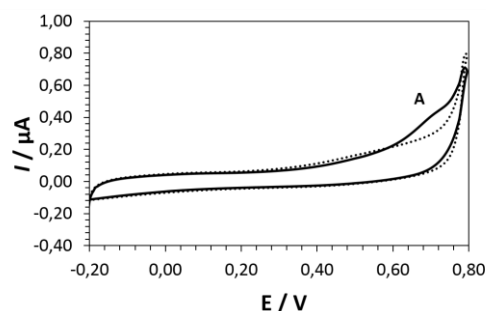


Figure 2. Cyclic voltammogram of the title compound ($c = 1.1 \cdot 10^{-4} \text{ mol dm}^{-3}$) at a glassy carbon electrode ($I_c = 0.1 \text{ M LiCl}$ in DMF). Scan rate: 100 mV/s . a) 0.1 M LiCl (supporting electrolyte), dashed line and b) title compound, solid line.

The influence of scan rate and the effect of concentration of the investigated Schiff base on anodic peak current and anodic peak potential were examined. It was observed that both anodic peak potential and anodic peak current increase with the increase in Schiff base concentration and scan rate. **Fig. 3** shows that at concentrations under $c \sim 1.1 \cdot 10^{-4} \text{ mol dm}^{-3}$ anodic peak current is a linear function of the Schiff base concentration, which indicates that oxidation products are adsorbed on the glassy carbon electrode surface. At higher concentrations of Schiff base (above $c \sim 1.1 \cdot 10^{-4} \text{ mol dm}^{-3}$), the increase of peak current slows down, which could be explained by increase of interactions between molecules adsorbed on the electrode surface and by diffusion current (Zeng, Wei, Xiao, *et al.*, 2006; Medvidović-Kosanović, Šeruga, Jakobek, *et al.*, 2010). Oxidation peak current increases linearly with the title product concentration in the concentration range ($c = 3.1 \cdot 10^{-5} \text{ mol dm}^{-3} \dots 1.25 \cdot 10^{-4} \text{ mol dm}^{-3}$).

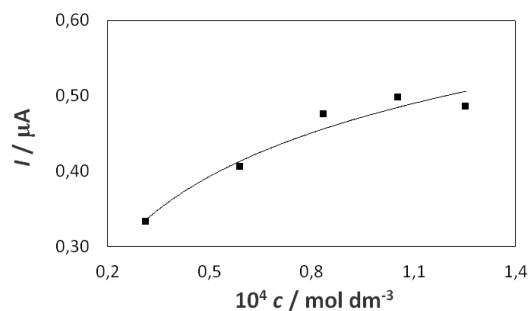


Figure 3. Anodic peak current as a function of the title compound concentration ($I_c = 0.1 \text{ M LiCl}$ in DMF). Scan rate: 100 mV/s .

Our research has shown that the Schiff base oxidation is controlled by diffusion since linear dependence (**Fig. 4a**) was found between anodic peak current and the square root of scan rate (Medvidović-Kosanović, Šeruga, Jakobek, et al., 2010; Simić, Manojlović, Šegan, et al., 2007). Logarithm of anodic peak current is also a linear function of logarithm of scan rate, with slope 0.40 (**Fig. 4b**) which also confirms that the oxidation process is diffusion controlled (Yagmur, Yilmaz, Saglikoglu, et al., 2014; Yagmur, Yilmaz, Saglikoglu, et al., 2013)

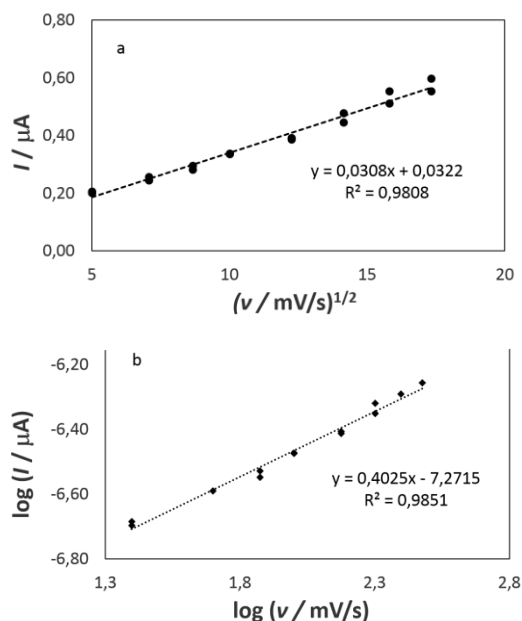


Figure 4. a) Anodic peak current, I , as a function of the square root of scan rate, $v^{1/2}$, b) Logarithm of anodic peak current, $\log I$ as a function of logarithm of scan rate, $\log v$, at a glassy carbon electrode in solution of the title compound ($c = 8.4 \cdot 10^{-5} \text{ mol dm}^{-3}$, $I_c = 0.1 \text{ M LiCl}$ in DMF).

Differential pulse voltammetry studies

Differential pulse voltammogram in **Fig. 5** also reveals one oxidation peak of the investigated Schiff base at the potential of 0.690 V. The oxidation peak decreases with successive scans which confirms adsorption of the Schiff base oxidation products on the glassy carbon electrode surface.

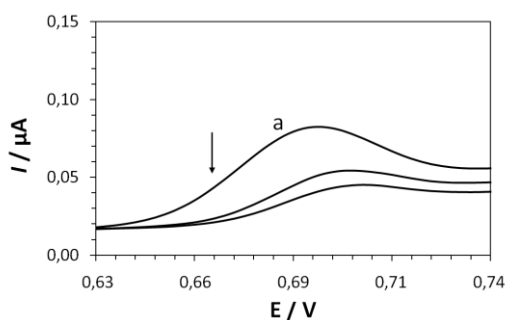


Figure 5. Differential pulse voltammogram of the title compound ($c = 1.1 \cdot 10^{-4} \text{ mol dm}^{-3}$) at a glassy carbon electrode ($I_c = 0.1 \text{ M LiCl}$ in DMF). Scan rate: 5 mV/s. First scan (a).

Peak current and peak potential also increases with increasing Schiff base concentration (**Fig. 6**) which could be explained by kinetic limitation in the reaction between the redox sites of a glassy carbon electrode and the investigated Schiff base (Menati, Azadbakht, Taeb, et al., 2012).

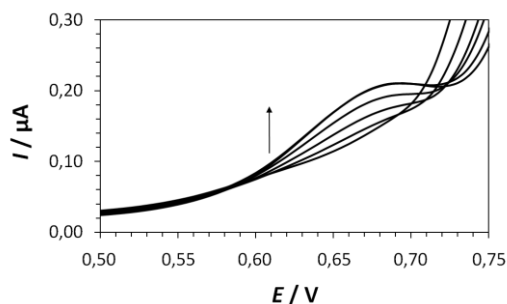


Figure 6. Differential pulse voltammograms in the solutions of the title compound with concentrations ($c = 0.7 \cdot 10^{-5}$; $0.9 \cdot 10^{-5}$; $1.1 \cdot 10^{-4}$; $1.3 \cdot 10^{-4}$; $1.5 \cdot 10^{-4}$ and $1.6 \cdot 10^{-4} \text{ mol dm}^{-3}$) at a glassy carbon electrode ($I_c = 0.1 \text{ M LiCl}$ in DMF). Scan rate: 5 mV/s

A linear relationship can be established between peak current and Schiff base concentration in the range of $0.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ to $1.6 \cdot 10^{-4} \text{ mol dm}^{-3}$ (**Fig. 7**). A linear regression equation, $I_p = 10.969 c + 0.4095$ with a correlation coefficient $R^2 = 0.9876$, is obtained, where I_p is the oxidation peak current and c is the Schiff base concentration

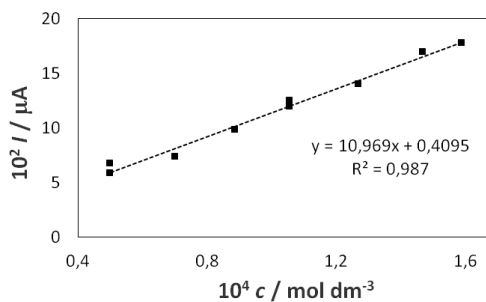


Figure 7. Anodic peak current as a function of the title compound concentration ($c = 0.5 \cdot 10^{-5}$; $0.7 \cdot 10^{-5}$; $0.9 \cdot 10^{-5}$; $1.1 \cdot 10^{-4}$; $1.3 \cdot 10^{-4}$; $1.5 \cdot 10^{-4}$ and $1.6 \cdot 10^{-4} \text{ mol dm}^{-3}$) at a glassy carbon electrode ($I_c = 0.1 \text{ M LiCl}$ in DMF). Scan rate: 5 mV/s.

CONCLUSION

The electrochemical results have shown that the oxidation of the Schiff base title compound is irreversible and controlled by diffusion at the investigated experimental conditions. Adsorption of the oxidation products on the glassy carbon electrode occurs and this process is kinetically limited. A linear relationship between peak current and Schiff base concentration in the range $0.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ to $1.6 \cdot 10^{-4} \text{ mol dm}^{-3}$ was established.

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Summary/Sažetak

Ispitivana su oksido-redukcijska svojstva novosintetizirane Schiffove baze uporabom cikličke i diferencijalne pulsne voltametrije. Mjerenja su izvedena u troelektrodnoj ćeliji u nevodenom mediju pri sobnoj temperaturi, a inertna atmosfera je postignuta propuhivanjem sustava argonom visoke čistoće Ar 5 ($\phi_{Ar} = 99,999\%$), prije svakog mjerenja. Kao radna elektroda korištena je elektroda od staklastog ugljika, protuelektroda je bila platinska žica, a kao referentna elektroda je korištena Ag/Ag⁺ elektroda za nevodeni medij. Rezultati cikličke voltametrije su pokazali da se ispitivana Schiffova baza oksidira (uočen je jedan oksidacijski strujni vrh u anodnom dijelu voltamograma na potencijalu $E_{p,a} = 0.69$ V, a visina oksidacijskog strujnog vrha raste s povećanjem koncentracije ($c = 3.1 \cdot 10^{-5}$ mol dm⁻³... $1.25 \cdot 10^{-4}$ mol dm⁻³) i brzine promjene potencijala ($v = 50$... 300 mV/s). Diferencijalnom pulsnom voltametrijom je također uočen jedan oksidacijski strujni vrh pri $E_{p,a} = 0.69$ V, koji se povećavao s povećanjem koncentracije ispitivane Schiffove baze.