

Scientific paper

Electrochemical and Spectroscopic Behaviors of 1-(*o*-, *m*-, *p*- Cl, or Br) Substituted Phenyl-3, 5-diphenylformazans in Dimethyl Sulfoxide

Habibe Tezcan* and Güler Ekmekci

Department of Chemistry, Gazi University, Faculty of Gazi Education, Teknikokullar, 06500 Ankara, Turkey

* Corresponding author: E-mail: habibe@gazi.edu.tr

Fax: +90-312-2228483

Received: 24-06-2009

Abstract

1-(*o*-, *m*-, *p*-Cl, -Br) substituted phenyl-3, 5-diphenylformazans were synthesized. Their structures were elucidated and spectral behaviours were investigated by elemental analysis, FT-IR, UV-vis spectral data. The electrochemical properties such as number of electrons transferred (n), diffusion coefficient (D) and heterogeneous rate constant (k_s) were determined and possible mechanisms were proposed using platinum and ultramicro platinum electrodes, cyclic voltammetry, linear sweep voltammetry and chronoamperometry. The oxidations were carried out at different electrochemical steps that were dependent upon the structure of formazans. The relation between their absorption properties with electrochemical properties was investigated. A suitable correlation was obtained between the absorption λ_{\max} with electrochemical properties, and between the oxidation peak potentials E_{ox1} with k_s values of formazans.

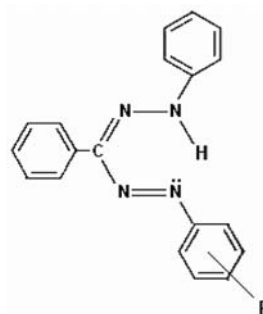
Keywords: Formazans; UV-vis spectra; IR spectra; Substituent effect; electrochemical behavior

1. Introduction

Formazans are colored compounds as they have π - π^* transitions of π -electrons in their structure. There are important fields of use for formazans such as analytical reagents, trace element determination, photos and thermochromic materials. Foremost, the most important fields of usage are as biochemical markers and antineoplastic properties which are based on spectral and redox reactions of tetrazolium/formazans systems.^{1,2} Since these fields of use are based on spectral and redox reactions, these features are quite important. That is why there is an increasing interest in the chemistry of formazans.

Since the first formazans were synthesized, there have been numerous formazans synthesized up to now and their structural features, tautomeric and photochromic isomers were investigated.³⁻⁷ Although, formazans have been extensively studied by many workers, a little has been reported about the electrochemical redox behavior. It was reported that formazans are oxidized either in a single two electron transfer followed by a deprotonation reaction forming corresponding tetrazolium cations or in two steps one apiece electron transfer followed by a deprotonation

reaction forming tetrazolium cations.⁸⁻¹¹ Also, the reduction of tetrazolium salts into formazans was carried out.¹²⁻¹⁴



Formazans (a)	R	Abbreviation
1	H	TPF
2	<i>o</i> -Cl	<i>o</i> -ClPF
3	<i>m</i> -Cl	<i>m</i> -ClPF
4	<i>p</i> -Cl	<i>p</i> -ClPF
5	<i>o</i> -Br	<i>o</i> -BrPF
6	<i>m</i> -Br	<i>m</i> -BrPF
7	<i>p</i> -Br	<i>p</i> -BrPF

Scheme 1. The structure of the formazan derivatives (1-7).

However, there is no systematic study concerning the effect of substituent, and there aren't any studies concerning the comparison between the electrochemical and spectral properties of these compounds in the literature. There are few systematic studies concerning the effect of substituent and some of them are complexes of formazans.^{11,15} As all the fields of use of the formazans are based on spectral and electrochemical properties, we focused in this study on synthesis, spectral and electrochemical behaviors of various substituted formazans.

In this study spectral and electrochemical properties of synthesized formazans [1-(*o*-, *m*-, *p*-Cl, -Br) substituted phenyl-3,5-diphenylformazans] were investigated and compared (Scheme 1). We intended to elucidate the influence of type and position of the substituents on electrochemical and spectral properties. It is also hoped that this study is suitable for all the fields of use of formazans.

2. Experimental

2.1. General

All starting reagents and solvents were purchased from Merck, Sigma-Aldrich Chemical Co. and used without further purification. For synthesis deionized water (Millipore, Milli-Q), for spectroscopic measurements the organic solvent, CH₃OH (99.9%), and for electrochemical measurements dimethyl sulfoxide (DMSO) (99.9%) were used. The infrared (IR) spectra were recorded on a UNICAM SP-1025 spectrophotometer between 4000 and 400 cm⁻¹ in KBr pellets. The ultraviolet-visible (UV-vis) spectra were obtained with PERKIN-ELMER 550 spectrophotometer using 1 cm quartz cell, in 10⁻⁴ mol L⁻¹ CH₃OH in the range of 200–650 nm. The elemental analysis studies were carried out by LECO-CHNS-932 elemental analyzer.

Electrochemical studies were carried out with a computerized CHI Instrument 660 B system in a conventional three-electrode cell. A platinum electrode (PE) (CHI102) and a 10 μm-platinum ultramicrodisc electrode (UME) (CHI107) were used as a working electrode. The electrodes were cleaned by electrochemical potential cycling and washing with excess DMSO. A platinum wire was used as an auxiliary electrode. The reference electrode was a silver wire in constant contact with 0.1 M AgNO₃ in dimethyl sulfoxide. All solutions were de-aerated for 10 min with pure argon and the measurements were taken at room temperature. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBA⁺BF₄⁻) was purchased from Fluka (21796-4) and was used without purification and stored in a desiccator. The voltammograms were scanned over the potential range (-2000)–0 mV (positive potential direction in forward mode), and the scan rate employed were 10, 100 and 1000 mVs⁻¹.

2.2. Synthesis of Formazans 1-7

2.2.1. Synthesis of 1,3,5- triphenylformazan (1)

1,3,5-triphenylformazan was synthesized by the reaction of benzaldehyde (1.06 g, 0.01 mol), phenylhydrazine (1.08 g, 0.01 mol), aniline (0.93 g, 0.01 mol) concentrated HCl (5 mL) and sodium nitrite (0.75 g) in a methanol, at 0–5 °C alike.^{4,7} The compound color is cheery-red; yield: 78%; m.p. 172–173 °C (in literature: 170–173 °C). Elemental analysis: for C₁₉H₁₆N₄ calculation (%): C; 76.00, H; 5.33, N; 18.66, found (%): C; 76.04, H; 5.31, N; 18.62.

2.2.2. Synthesis of 1-(*o*-, *m*-, *p*-bromophenyl)-3.5-diphenylformazan Formazans (5,6,7)

Benzaldehyde-phenylhydrazone was prepared by adding in a dropwise manner phenylhydrazine solution (1.08 g, 0.01 mol) in CH₃OH (50 mL) into the benzaldehyde solution (1.06g, 0.01 mol) in CH₃OH (50 mL) at the 25 °C. The adding was completed in 30 min. It was kept stirred under the reflux for one hour and left on the bench for two days. A light yellow benzaldehyde-phenylhydrazone precipitated out. Then, the precipitate was filtered out and recrystallised from methanol and washed with methanol and water respectively. This product was dissolved in CH₃OH (100 mL) by constant stirring under reflux and solution was added into the basic buffer solution which was prepared of 2.50g NaOH and 3.50g CH₃COONa in 200 mL CH₃OH. The resulting mixture was lefted cooling.

On the other hand, the diazonium salt was prepared through known procedure^{4,7} using *o*-, *m*-, *p*-bromoaniline (1.7203g, 0.01 mol), concentrated HCl (2.5 mL) and sodium nitrite (0.75g) at -5–0 °C. In order to keep the temperature between -5–0 °C, iced cubes were added to the reaction medium. For the coupling reaction, this solution was added into the basic benzaldehyde phenylhydrazone solution in dropwise manner with constant stirring and keeping the temperature between -5–0 °C. The solution was stirred for 2 h at the same temperature and was kept in a refrigerator about a day and then on the bench for 4–5 days. Dark red-claret red colored formazans formed and each compound was recrystallised from methanol. The crystals were washed with methanol and then with water and dried in an oven at 40 °C.

Yield: 74%; m.p.: 189–190 °C (in literature 191 °C). Elemental analysis: C₁₉H₁₅N₄Br, for *o*- Br formazan calculation (%): C; 60.15, H; 3.96, N; 14.77, found: (%) C; 59.85, H; 3.92, N; 14.62.

1-(*m*-bromophenyl)-3.5-diphenylformazan (6): dark red color; yield 70%; m.p. 120–122 °C.

1-(*p*-bromophenyl)-3.5-diphenylformazan (7): bright red color; yield 74%; m.p. 189–190 °C.

2. 2. 3. Synthesis of 1-(*o*-, *m*-, *p*-chlorinephenyl)-3,5-diphenylformazan Formazans (2,3,4)

Formazans were synthesized by the reaction of benzaldehyde (1.06 g, 0.01 mol), phenylhydrazine (1.08 g, 0.01 mol), *o*-, *m*-, *p*-chlorineanilines (0.127 g, 0.01 mol) concentrated HCl (5 mL) and sodium nitrite (0.75 g) in a methanol, at 0–5 °C. The procedure was similar with the one stated earlier in section 2.2.2.

1-(o-chlorophenyl)-3,5-diphenylformazan (2): dark red color; yield 76%; m.p 142–143 °C. Elemental Analysis: C₁₉H₁₅N₄Cl, for *o*- Cl formazan Calc. (%): C; 68.26, H; 4.49, N; 16.76. Found: (%): C; 68.12, H; 4.35, N; 17.01.

1-(m-chlorophenyl)-3,5-diphenylformazan (3): red color; yield 74%; m.p 158 °C.

1-(p-chlorophenyl)-3,5-diphenylformazan (4): bright red color; yield 72%; m.p. 119 °C; (in literature: 117 °C).

3. Results and Discussion

The IR and UV-vis. spectral data of 1-(substitutedphenyl)-3,5-diphenylformazans are listed in Tables 1 and 2 respectively. Elemental analysis and IR data were corroborated suggested structure in Scheme 1. Also UV-vis data and broad peaks aspect of spectra are characteristics of formazan skeleton.

3. 1. IR Spectroscopy

The IR data of formazans (1-7) given in Table 1 the C=N stretching band appears at 1505–1535 cm⁻¹. When 1-phenyl ring is substituted with bulky groups such as -Cl, -Br, NO₂ these groups must push 5-phenyl rings. Therefore in formazans, the C=N stretching band appears at 1565–1551 cm⁻¹ in the case where there is no chelate structure present (excited state) and 1510–1500 cm⁻¹ in the case of chelation. The C=N stretching band occurs at the 1520–1530 cm⁻¹ chelate and non-chelate structures are in equilibrium.^{2, 7, 18} If so, our formazans' 1-7 chelate and non-chelate structures must be in equilibrium. Other IR data can be evaluated in a similar manner. It was observed vibration peaks at 3095–3100 cm⁻¹ for aromatic(Ar.)

C-H, at 1600–1610 cm⁻¹ for Ar. C=C, at 1505–1535 cm⁻¹ for C=N, at 1450–1455 cm⁻¹ for N=N, at 1240–1370 cm⁻¹ for C-N2, at 1160–1200 cm⁻¹ for C-N4, at 1030–1090 cm⁻¹ for N-N, at 825–935 cm⁻¹ for CNNC structure vibration, at 645–780 cm⁻¹ Ar.(C-H) plane out bending. All the data were as expected. Besides, the peaks which were observed in 825–935 cm⁻¹ fingerprint range are the proof of formazans structures (4-7).

3. 2. Substituents Effect on the UV-vis Absorption λ_{max} Values

As seen in Table 2, characteristic absorption peak of 1,3,5-triphenylformazan shows a maximum at 482.0 nm while 486, 486, 489 nm at the *o*-, *m*-, *p*-Cl formazans and 487, 487, 489 nm at the *o*-, *m*-, *p*-Br formazans. In the *o*-position Cl and Br substituted compounds the λ_{max} value shifted to less due to the fact that their inductive electron withdrawing and resonance electron donating effects impose an opposing effect on each other. There is *m*-position only decreased inductive effect. For this reasons, the bathochromic effects are the same at the *o*- and *m*-positions (2 with 3, and 5 with 6). It is natural that Cl shifted λ_{max} 1 nm less than Br which is due to the difference in their electronegativity values. At *p*-position both substituents (compounds 4, 7) shifted the λ_{max} as 2–3 nm and acted as more less electron withdrawing groups due to resonance effect and shown more bathochromic effects than *o*- and *m*-positions. These shifts are strikingly close to each other which are not surprising, because the Hammett constant

Table 2. Absorption spectral data for formazans 1-7 (in CH₃OH, 10⁻⁵ mol L⁻¹)

Comp.	λ _{max1} (nm)	Chemical shift Δλ _{max}	Hammett substituent constant σ
1	482.0		
2	486.0	-4	
3	486.0	-4	<i>m</i> -Cl = +0.37
4	489.0	-7	<i>p</i> -Cl = +0.23
5	487.0	-5	
6	487.0	-5	<i>m</i> -Br = +0.39
7	489.0	-7	<i>p</i> -Br = +0.23

Table 1. The IR spectral data of formazans (1-7) (KBr, cm⁻¹)

Comp.	Ar. C-H	Ar. C=C	C=N	N=N	C-N2	C-N4	N-N Vibr.	CNNC struc. vibr.	Ar.(C-H) plane outbending
1	-	1610	1505	1455	1365,1250	1200	1090-1035	930,905	775-650
2	3095	1610	1525	1450	1365,1245	1190,1160	1080-1030	925,825	775-645
3	3100	1600	1535	1455	1370,1260	1200	1085-1035	910,840	785-650
4	-	1610	1530	1455	1370,1260	1200	1100-1035	930,850	780-650
5	-	1610	1520	1455	1270,1240	1195,1170	1090-1030	930,825	770-650
6	3100	1610	1520	1455	1370,1240	1195,1170	1090-1030	900,840	770-650
7	3100	1605	1520	1450	1360,1240	1200,1180	1080-1030	935,840	780-650

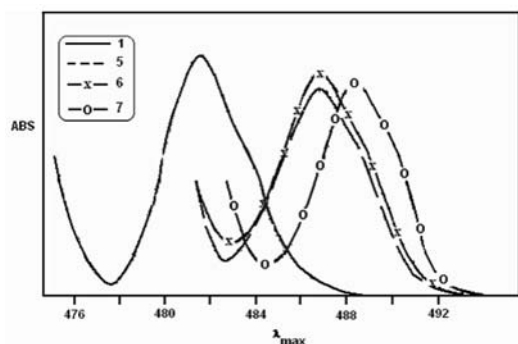


Fig. 1. Absorption spectra of 1.0×10^{-5} mol L $^{-1}$ CH $_3$ OH solutions of compounds **1**, **5**-**7**.

contributions of *m*-, *p*-Cl, Br are almost the same (Table 2). λ_{max} Values of formazans are shown in Fig. 1 (*o*-, *m*-, *p*-Br) in comparison to compound **1** as a sampling.

3. 3. Cyclic Voltammetry

Cyclic voltammetry method was used to propose the possible reaction mechanisms and to identify whether the

reaction is reversible, irreversible or quasi-reversible. The electrochemistry of formazans **1**-**7** was investigated in the anodic region by carrying out cyclic voltammetry experiments on 10^{-5} mol L $^{-1}$ solutions at the relevant compound dissolved in 0.1 mol L $^{-1}$ of TBA $^+$ BF $_4^-$ in anhydrous DM-SO at 25 °C. All the cyclic voltammetric data were tabulated in Table 3. Substituted formazans with -Cl and -Br at the *o*-, *m*-, *p*-positions of the 1-phenyl ring (**2**-**7**) were compared with **1** in Figs. 2, 3.

A cyclic sweep in the -1.60 to +0.00 V range is shown two anodic peaks and two cathodic peaks for compound **1**. There were two major anodic peaks in the cyclic voltammogram of compound **1**, corresponding to the formation of formazan radical TPF $^{\bullet}$ at -1390.3 mV and tetrazolium cation TPT $^+$ at -688.9 mV. Also two cathodic peaks E_{red1} , E_{red2} were observed at -426.0 mV, -815.1 mV for **1** (Fig. 2). From these results, the following stepwise electron transfer reactions are given. These results are compatible with the literature.^{11, 12}

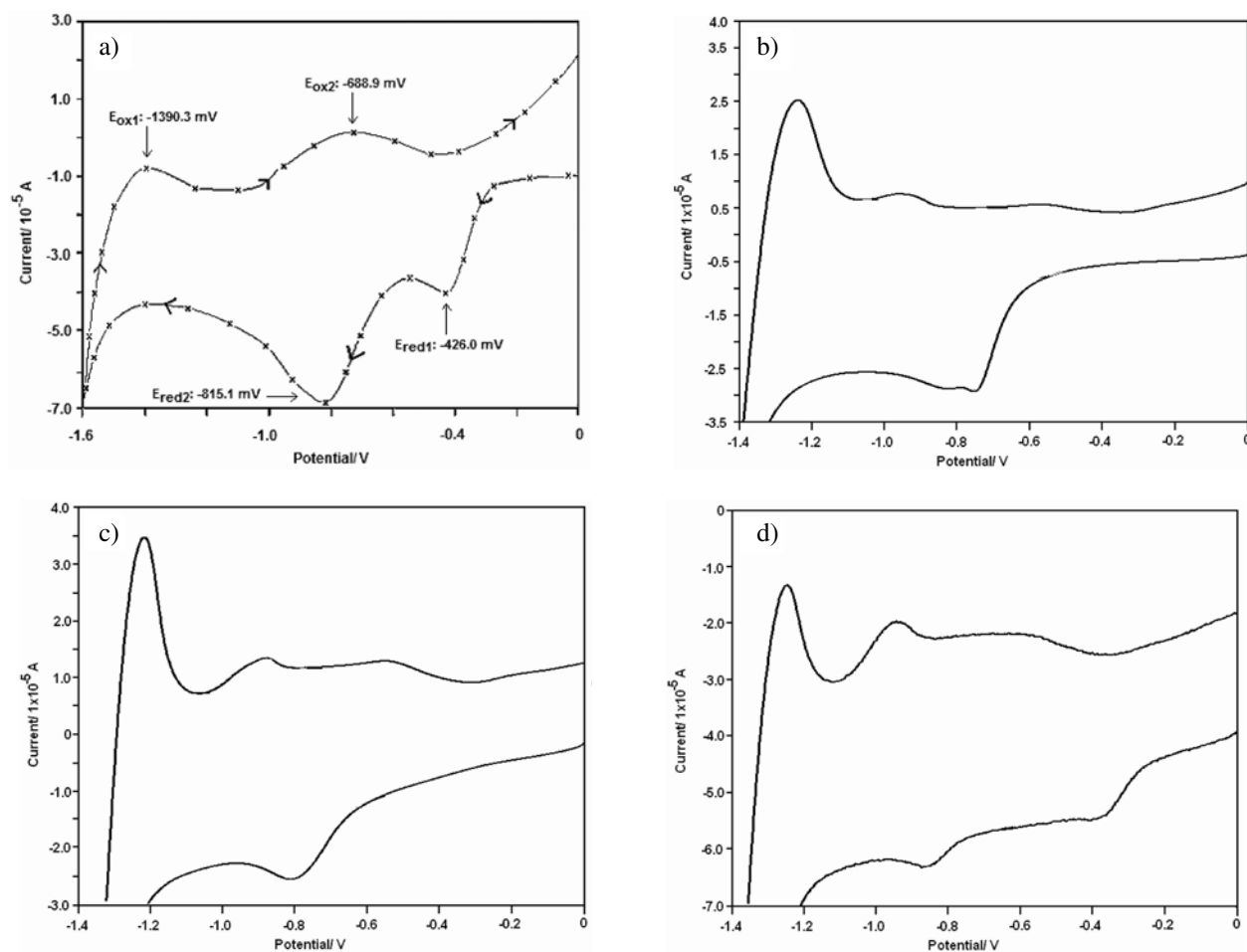
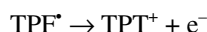


Fig. 2. Representative cyclic voltammogram of compound: (a) **1**; (b) **2**; (c) **3**; (d) **4**, in DMSO (25 °C, ionic strength: 0.1 mol L $^{-1}$ TBATFB, V : 100 mV s $^{-1}$),

Table 3. Voltamperometric results of formazans (1-7)

Comp.	E_{ox1} (mV)	E_{ox2} (mV)	E_{red1} (mV)	E_{red2} (mV)	ΔE_p (mV)	k_s (cm s^{-1})
1	-1390.3	-688.9	-426.0	-815.1	-964.3	7.722×10^{-3}
2	-1234.8	-964.0	-752.0	–	-482.8	21.960×10^{-3}
3	-1212.0	-881.0	-814.0	–	-398.0	3.544×10^{-3}
4	-1243.9	-942.1	-873.0	–	-370.9	1.158×10^{-3}
5	-1202.9	-884.8	-781.9	–	-421.0	1.893×10^{-3}
6	-1335.5	-1024.2	-794.2	–	-541.3	4.374×10^{-3}
7	-1280.4	-1021.7	-935.5	–	-344.9	3.772×10^{-3}

Column 6: ΔE_p : $E_{ox1} - E_{red1}$ (mV).

Electrochemical studies were carried out in DMSO at 25 °C at platinum electrode, ionic strength 0.1 mol L⁻¹ (TBATFB), sweep speed: 100 mV s⁻¹. E_{ox} : oxidation; E_{red} : reduction, k_s /cm s⁻¹ values

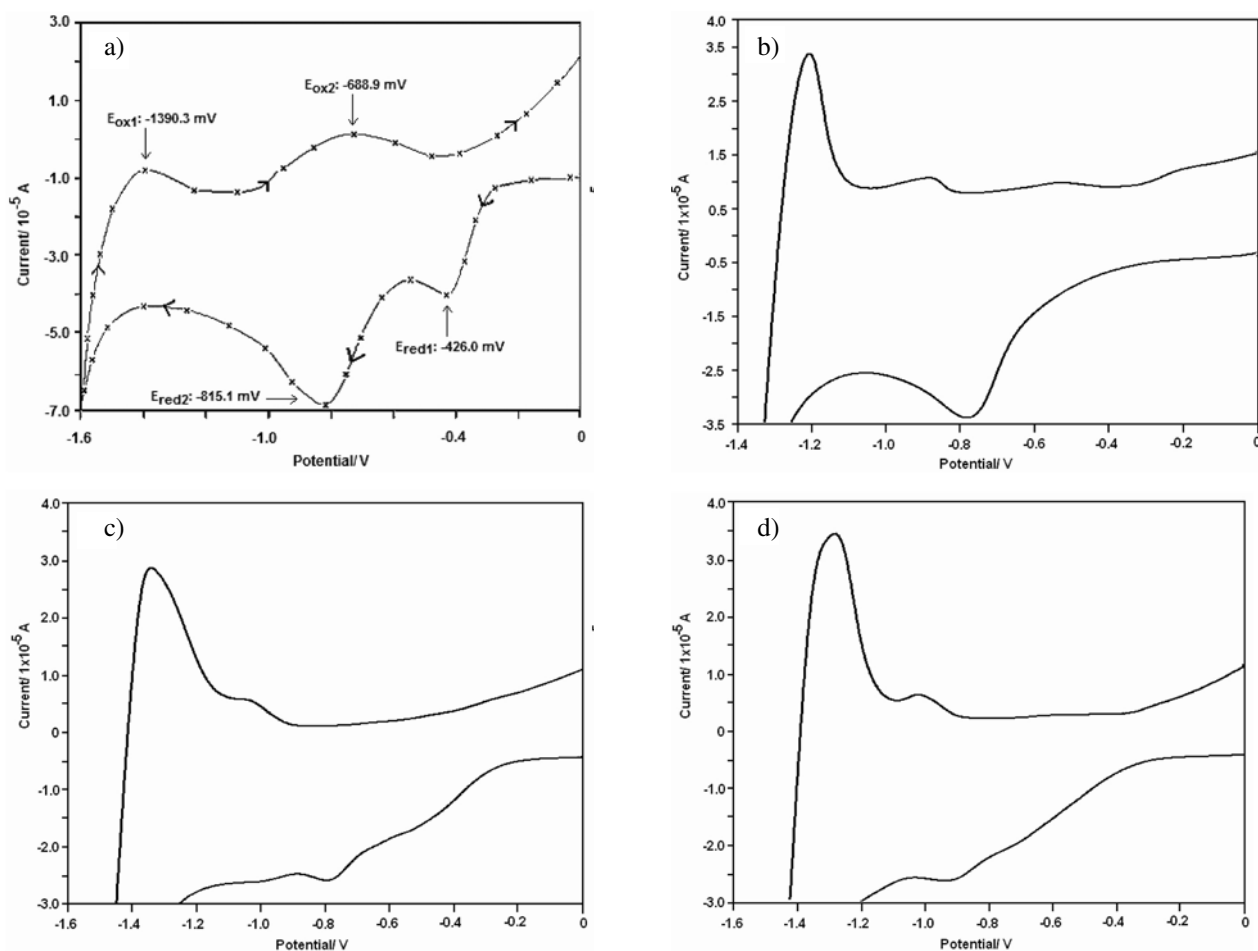


Fig. 3. Representative cyclic voltammogram in DMSO (25 °C, ionic strength: 0.1 mol L⁻¹ TBATFB, V: 100 mV s⁻¹): (a) compound 1; (b) 5; (c) 6; (d) 7.

Oxidation of Cl formazans: As seen in Table 3, the substitution of the 1-phenyl ring with Cl, at the *o*-, *m*-, *p*-positions (2-4) caused amount changes in both the peak potential and the peak currents as compared to 1. A cyclic sweep in the -1.60 to +0.00 V range has shown two anodic and one cathodic peak for 2-4. E_{ox1} values shifted to more anodic, E_{ox2} and E_{red} values shifted to more cathodic values when compared to 1. The first oxidation peak po-

tentials E_{ox1} were observed at -1234.8 mV, -1212.0 mV and -1243.9 mV for 2-4, respectively. It is obvious that there is anodic shift in potential in the order of *p*-<*o*-<*m*-substitutions, as it is known that the resonance is the least in *m*-position. Since there is no resonance effect at *m*-position they act as an electron withdrawing group due to a weak inductive effect and shifted anodic potential value slightly to a higher value when compared to others. The

second oxidation peak potentials $E_{\text{ox}2}$ were observed at -964.0 mV, -881.0 mV, and -942.1 mV for **2-4**, respectively. It is obvious that there is cathodic shift in potential compared to **1**. However, all the Cl substitute formazans $E_{\text{ox}2}$ are more anodic than $E_{\text{ox}1}$. Hence, oxidation rate may be dependent on the first step.

Reduction of Cl formazans: The first reduction peak potentials $E_{\text{red}1}$ of the *o*-, *m*-, *p*-Cl substituted formazans **2-4** were observed at -752.0 mV, -814.0 mV, -873.0 mV, respectively. It is obvious that there is a cathodic shift in potential and in the order of *o*-< *m*-< *p*- Cl substituted formazans. The second reduction peak potentials $E_{\text{red}2}$ were not observed well. This order is compatible with inductive effect.

Oxidation of Br formazans: As seen from Table 3, the substitution of the 1-phenyl ring with Br at the *o*-, *m*-, *p*-positions (**5-7**) caused amount changes in both the peak potential and the peak currents when compared to **1**. A cyclic sweep in the -1.60 to $+0.00$ V range has shown two anodic peaks. These $E_{\text{ox}1}$ are shifted to more anodic potential, second oxidation peaks are shifted to more cathodic potentials in the Br substituted formazans **5-7** when compared to **1**. The peak potentials $E_{\text{ox}1}$ corresponding to the oxidation of formazan to formazan radical TPF[•] were -1202.9 mV, -1335.5 mV, -1280.4 mV for **5-7**, respectively. The peak potentials $E_{\text{ox}2}$ corresponding to the oxidation of formazan radicals to tetrazolium cations TPT⁺ were observed at -884.8 mV, -1024.2 mV, -1021.7 mV for **5-7**, respectively Fig. 3.

In the first oxidation peak potentials $E_{\text{ox}1}$ Cl substituted formazans **2-4** shifted to more anodic potential values when compared to Br substituted formazans **5-7**. It is natural that Cl shifted to more anodic than Br which is due to the difference in their electronegativity. Results are compatible with their electronegativity values and spectral values.

Reduction of Br formazans: The reduction peak potentials of tetrazolium cations corresponding to formazans were observed at -781.9 mV, -794.2 mV, -935.5 mV for **5-7**, respectively. The second reduction peak potentials $E_{\text{red}2}$ were not observed.

The oxidation of TPF (**1**) and its Cl and Br derivatives appear to be quasi-reversible because $\Delta E_p = E_{\text{ox}1} -$

$E_{\text{red}1}$ mV (Table 3) is larger than $59/n$ mV. These results are consistent with a quasi-reversible behavior.^{18,19}

Also, peak potentials' shifts of Cl and Br are strikingly close to each other, as are absorption λ_{max} values. This is not surprising, because the Hammett substituent constant's contributions of Cl and Br are almost equal (in Table 2).

3. 4. Ultramicrodisc Electrode and Chronoamperometry

Ultra microelectrode CV technique of Baranski¹⁶ was used to determine the number of electron transferred (*n*) and the diffusion coefficients (*D*). The diffusion coefficients (*D*) were calculated from the Cottrell equation after the *n* values were calculated and tabulated in Table 4. The heterogeneous rate constants k_s were calculated with the use of Klingler-Kochi Method¹⁷ as the potential difference for the anodic and cathodic peak currents for the second peak was more than 350 mV. The resulting data was tabulated in Table 3. The k_s values under these circumstances are dependent on the scan rate, diffusion coefficient, oxidation and reduction peak potential.

3. 5. The Relation Between the $E_{\text{ox}1}$, $E_{\text{ox}2}$ and $E_{\text{red}1}$ / mV (Ag/AgCl) and k_s (cm^{-1}) values

There was a good correlation between oxidation peak potentials $E_{\text{ox}1}$, $E_{\text{ox}2}$, and $E_{\text{red}1}$ of *o*-, *m*-, *p*-Cl **2-4** and *o*-, *m*-, *p*-Br **5-7** substituted formazans and their standard heterogeneous rate constants k_s values (Fig. 4, 5, 6). Because, already the k_s values are dependent on the scan rate, diffusion coefficient, oxidation and reduction peak potential.

Also, k_s values give another indication that oxidation reactions of TPF and its Cl and Br derivatives are quasi-reversible. The case $2 \times 10^{-5} \text{V}^{1/2} < k_s < 0.3 \text{V}^{1/2}$ corresponds to a quasi-reversible situation. The k_s values obtained in this study fall into this range.

On the other hand, k_s values of the oxidation reaction of *o*-Cl position formazan (**2**) is higher than others' k_s values. If so it may be explained by the higher oxidation reaction rate of formazan (**2**) when compared to others.

Table 4. Some of the parameters calculated for formazans (1-7)

Comp.	Abbreviation	C* (m mol L ⁻¹)	i_{ss} (A)	Cottrell Slope (S × 10 ⁻⁵)	<i>n</i>	<i>n</i> _{net}	<i>D</i> (cm ² s ⁻¹)
1	TPF (peak 1)	7.3	9.081×10^{-10}	1.599	0.75	1	4.297×10^{-6}
1	TPF (peak 2)	7.3	1.621×10^{-9}	2.109	0.73	1	7.880×10^{-6}
2		6.7	6.233×10^{-9}	5.883	1.61	2	1.205×10^{-4}
3		6.3	4.644×10^{-9}	4.879	1.58	2	9.548×10^{-6}
4		7.3	0.713×10^{-9}	6.844	1.75	2	1.265×10^{-5}
5		5.6	4.217×10^{-9}	5.056	2.10	2	9.757×10^{-6}
6		8.2	1.312×10^{-9}	3.419	2.11	2	2.072×10^{-6}
7		7.6	2.649×10^{-9}	4.120	1.63	2	4.515×10^{-6}

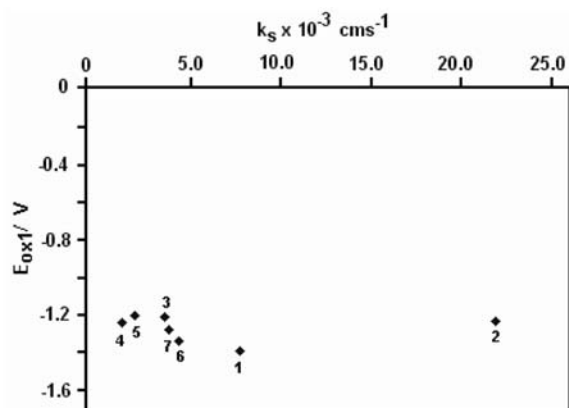


Fig. 4. The correlation between the $E_{\text{ox1}} / \text{V}$ (Ag/AgCl) and k_s (cm s^{-1}) values of 1-7.

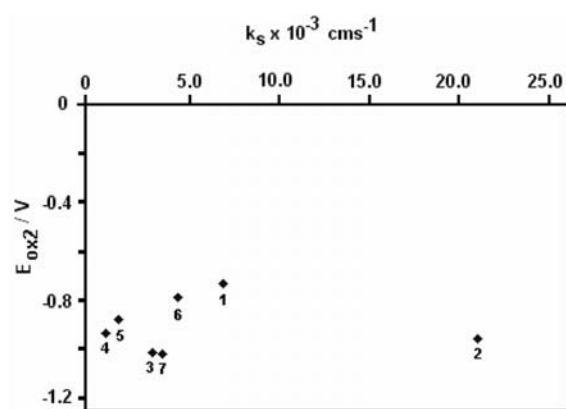


Fig. 5. The correlation between the $E_{\text{ox2}} / \text{V}$ (Ag/AgCl) and k_s (cm s^{-1}) values of 1-7.

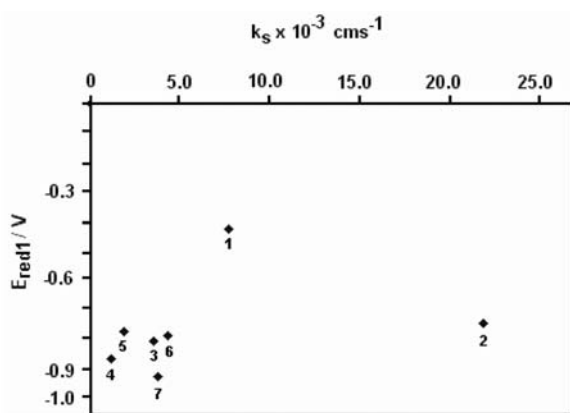


Fig. 6. The correlation between the $E_{\text{red1}} / \text{V}$ (Ag/AgCl) and k_s (cm s^{-1}) values of 1-7.

3. 6. The Calculation of the Number of Electrons Transferred and Reaction Mechanisms

The number of electrons transferred n was obtained with the use of chronoamperometric Cottrell equation and

ultramicro Pt disc electrode (UME) steady state current¹⁶. The real surface area of the Pt electrode was found 2.58 cm^2 with the use of ferrocene. If i_s values are plotted against $t^{-1/2}$ the resulting slope will be from which n could be calculated (in Table 4).

As seen in Table 4 and Fig. 7 there were two steps and one electron transfer in each step. Waves for compound 1 suggest that the compound gives (e^-) one electron and becomes a formazan radical which is followed by giving (e^-) a second electron and turns into tetrazolium cations. Possible mechanism of the oxidation of compound 1 is shown in Scheme 2a. Also, there were two steps and one electron transfer in each step for the case of *m*-, *p*-Cl and *o*-, *p*-Br the substituted formazans 3-5, 7. Possible mechanism of the oxidation of compounds 3-5, 7 is shown in Scheme 2a. These results are in agreement with^{11, 12}.

In the case of 1-phenyl ring is substituted with *o*-Cl and *m*-Br, the substituted formazans 2, 6 give two electrons in one step and proton (H^+) transfers giving directly tetrazolium cations. Possible mechanism of the oxidation

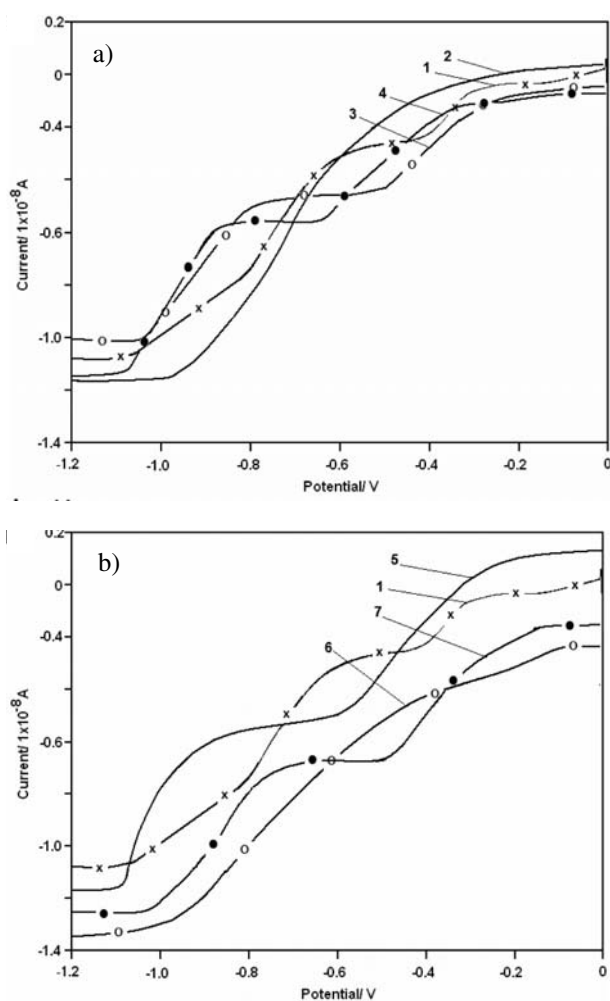
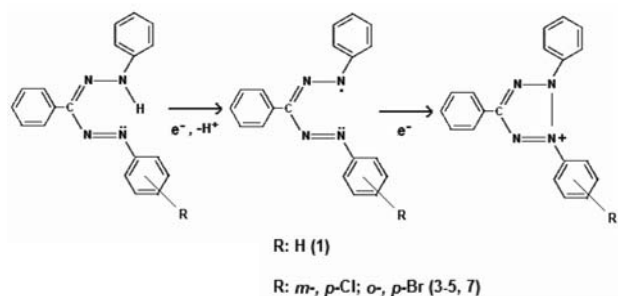


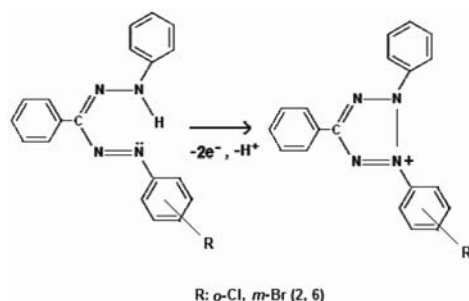
Fig. 7. UME curves of DMSO solutions of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ 1-4 (a); 1, 5-7 (b) in the presence of 0.1 mol L^{-1} TBATFB at $10 \mu\text{m}$ -platinum ultramicro electrode. Potential scan rate: 10 mV s^{-1} .

of **2**, **6** are shown in Scheme 2b. These results are in agreement with.^{9,10}

When the scan rate was increased, anodic peak potentials E_{ox1} were shifted towards anodic values, both Cl and Br substituted formazans. According to these results oxidation reactions may be EC mechanism.



Scheme 2a. Possible oxidation mechanism of **1**, **3-5**, **7**.



Scheme 2b. Possible oxidation mechanism of **2**, **6**.

4. Conclusions

In these study spectral and electrochemical properties of the 1-(*o*-, *m*-, *p*-Cl, and *o*-, *m*-, *p*-Br) substituted phenyl-3,5-diphenylformazans were investigated.

The peak potentials E_{ox1} of compound **2-7** were observed to shift towards more anodic potentials, but E_{ox2} and E_{red} shifted towards more cathodic potentials according to compound **1**. However, among all the substitute formazans E_{ox2} more anodic than E_{ox1} . Hence, oxidation rate may be dependent on the first step.

Shifts of Cl and Br-formazans are strikingly close to each other. These results are also in accordance with the spectroscopic data. This is not surprising, because the Hammett substituent constant contributions of Cl and Br are almost equal.

The oxidation of formazans **1**, **3-5**, **7** was observed to take one electron each at two steps and two electrons were transferred one step in formazans **2**, **6**. We reported previously a similar study, but there were two substituents in the same structure which are Cl and Br at the *o*-, *m*-, *p*-positions of the 1-phenyl ring and NO_2 group at the *m*-position of 3-phenyl ring. We obtained similar result in it as well¹¹.

The oxidation of TPF (**1**) and its Cl and Br derivatives appear to be quasi-reversible because $\Delta E_p = E_{\text{ox1}} - E_{\text{red1}}$ mV (Table 3) is larger than $59/n$ mV. These results are consistent with a quasi-reversible behavior. Also, k_s values are another indication that the system is quasi-reversible, because the condition $2 \times 10^{-5} \text{ v}^{1/2} < k_s < 0.3 \text{ v}^{1/2}$ is met in this study.

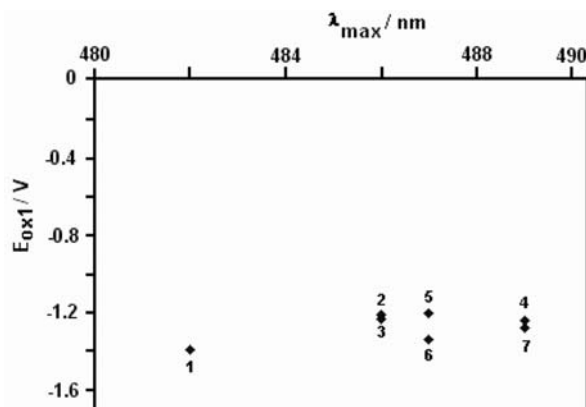


Fig. 8. The correlation between the λ_{max} and the E_{ox1}/V (Ag/AgCl) values of **1-7**.

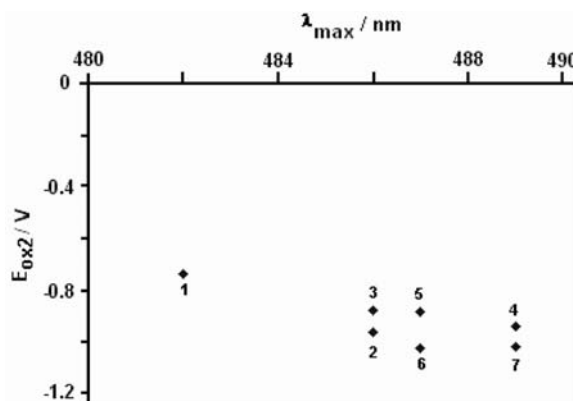


Fig. 9. The correlation between the λ_{max} and the E_{ox2}/V (Ag/AgCl) values of **1-7**.

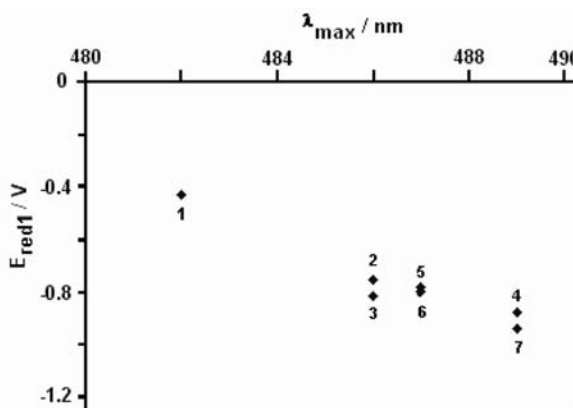


Fig. 10. The correlation between the λ_{max} and the E_{red1}/V (Ag/AgCl) values of **1-7**.

In addition, there was a good correlation between absorption λ_{\max} values of Cl, Br substituted formazans **2-7** and their oxidation and reduction peak potentials E_{ox1} , E_{ox2} , E_{red1} (Fig. 8-10). These results are expected because; both spectral and electrochemical behaviors are dependent on the abundance of electrons of system, which were dependent on the type and position of the substituent in the structure.

5. Acknowledgements

We are very grateful to Prof. Dr. M. Levent Aksu for his kind permission of using the computerized CHI Instrument and the Gazi University Research fund for providing financial support for this Project (No. 04/ 2004-13).

6. References

1. V. S. Misra, S. Dhar, B. L. Chowdhary. *Pharmazie*, **1978**, *33*, 790–792.
2. J. A. Plumb, R. Milray, S. B. Kaye. *Cancer Research* **1989**, *49*, 4435–4440.
3. J. W. Lewis, C. Sandorfy. *Can. J. Chem.* **1983**, *61*, 809–816.
4. A. R. Katritzky, S. A. Belyakov, D. Cheng, H. D. Durst, *Synthesis*, **1995**, *5*, 577–581.
5. L. Hunter, C.B. Roberts, *J. Chem. Soc.* **1941**, *9*, 820–823.
6. G. McConnachie, F. A. Neuqebauer, *Tetrahedron* **1975**, *31*, 555–560.
7. H. Tezcan, Ş. Can, R. Tezcan, *Dyes and Pigments*, **2002**, *52*, 121–127.
8. V. C. Schiele, *Ber.* **1964**, *30*, 308–318.
9. G. M. Abou Elenien, S. O. Allah, N. A. Ismail, W. M. Hosny, *J. Indian Chem. Soc.* **1988**, *65*, 253–257.
10. G. M. Abou Elenien, *J. Electroanal. Chem.* **1994**, *375*, 301–305.
11. H. Tezcan, E. Uzluk, M. L. Aksu, *J. Electroanal. Chem.* **2008**, *105*, 619–620.
12. T. Oritani, N. Fukuhara, T. Okajima, F. Kitamura, T. Ohsaka, *Inorg. Chim. Acta.* **2004**, *357*, 436–442.
13. K. Umemoto, *Bulletin of the Chemical Society of Japan* **1989**, *62*, 3783–3789.
14. G. Gokce, Z. Durmus, H. Tezcan, E. Kilic, H. Yilmaz, *Analytical Science* **2005**, *21*, 1–4.
15. a) H. Tezcan, E. Uzluk, M. L. Aksu, *Spectrochimica Acta Part A. Molecular and Biomolecular Spectroscopy*, **2008**, *70*, 973–982. b) H. Tezcan, E. Uzluk, M.L. Aksu, *Electrochimica Acta*, **2008**, *53*, 5597–5607.
16. A. S. Baranski, W. R. Fawcett, C. M. Gilbert, *Anal. Chem.* **1985**, *57*, 166–170.
17. R. J. Klingler, J. K. Kochi, *J. Phys. Chem.* **1981**, *85*, 1726–1731.
18. J. Wang, *Analytical Electrochemistry* 2nd. Ed, Wiley-VCH, **2000**.
19. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and applications*, John Wiley and sons, New York, **2001**
20. E. Erdik, *Spectroscopic methods in Organic Chemistry*, Gazi Kitabevi, Ankara, **1993**.
21. D. H Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill Publishing Company Limited, London, **1966**.

Povzetek

Sintetizirali smo 1-(*o*-, *m*-, *p*-Cl, -Br) substituirane fenil-3,5-difenilformazane. Njihovo strukturo smo določili s elementno analizo ter FT-IR in UV-vis spektroskopijo. S ciklično voltometrijo, linearno »sweep« voltometrijo ter kronoamperometrijo smo proučevali njihove elektrokemijske lastnosti. Ugotovili smo, da oksidacija posameznih formazanov poteka v različnih elektrokemijskih stopnjah, ki so odvisne od strukture spojin. Očitno je, da obstaja zveza med valovno dolžino maksimalne absorpcije λ_{\max} , položajem potenciala oksidacijskega vrha E_{ox1} ter konstanto reakcijske hitrosti k_s .