

Structure and stereochemistry of electrochemically synthesized poly-(1-naphthylamine) from neutral acetonitrile solution

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Abstract: Poly-(1-naphthylamine) films were synthesized potentiodynamically and potentiostatically from 1-naphthylamine in neutral acetonitrile medium using a platinum electrode. These polymer films were investigated by infrared spectroscopy. Contrary to earlier published results neglecting the stereochemistry of the poly-(1-naphthylamine), we predict on the basis of quantum stereochemical analysis of the possible structural subunits of the polymer, that the ordinary N–C(4) coupled product is not predominant in the polymer because it is far removed from the expected planarity. Based on the results of IR investigations and semiempirical quantum chemical calculations, it is proposed that the polymer products are formed *via* mixed N–C(4), N–C(5) and N–C(7) coupling routes. The heats of formation of the oxidized 1-naphthylamine dimers and hexamers were calculated.

Keywords: coupling routes, infrared spectroscopy, polymer structure, poly-(1-naphthylamine) films, stereochemistry.

INTRODUCTION

In the last two decades, there have been many reports which describe the synthesis and properties of conducting aromatic polymers. Polyaniline has been extensively studied, due to its high electrical conductivity, pH-sensitivity, stability, as well as its various technological applications.^{1–4} Zhou *et al.*⁵ reported that polyaniline has a planar structure. As opposed to polyaniline, 1-naphthylamine, (1-NPA), has two condensed aromatic rings. To the best of our knowledge, there are only two articles in the literature which describe the structure of poly-(1-naphthylamine), (p-1-NPA)⁶ and oligonaphthylamine⁷ films synthesized by the electrochemical method. Huang *et al.*⁶ reported that a polymeric product was

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formed by cyclic voltammetry (CV) of 1-naphthylamine in acetonitrile acid solution. They reported that the polymerization of 1-NPA occurred at the *p*-position. Schmitz and Euler⁷ reported on colored electrochemically synthesized oligonaphthylamine films in an aqueous acidic solution containing KI. Based on CV and IR data they suggested that the oligonaphthylamine products are 1,4-coupled *via* amine/imine linkages.

The literature survey shows that there are no reports on the stereochemistry of *p*-1-NPA and electrodeposition of *p*-1-NPA from a neutral media. In the present work, 1-naphthylamine was polymerized potentiodynamically and potentiostatically from neutral acetonitrile solution onto a platinum surface and the obtained polymer films were characterized by infrared spectroscopy. Based on the basic stereochemical analysis, IR spectroscopy data and quantum chemical calculations, it is proposed that the polymer products were formed *via* mixed N-C(4), N-C(5) and N-C(7) coupling routes, which is quite different from that previously proposed in the literature^{6,7} when the stereochemistry of *p*-1-NPA was neglected. The heats of formation of oxidized 1-naphthylamine dimers and hexamers obtained by molecular-orbital calculations are also reported.

EXPERIMENTAL

1-Naphthylamine (purum $\geq 98\%$, Fluka Chemical Company) was used as purchased. Acetonitrile (puriss, p.a. ACS $\geq 99.5\%$, Fluka Chemical Company) was used as received, but molecular sieves were added to the solutions for further drying. LiClO₄ (purum p.a. $\geq 98\%$, Fluka Chemical Company) was vacuum dried overnight at 200 °C to reduce water content to $< 0.5\%$ before use. The working electrode was a platinum plate with an exposed area of 0.98 cm², or a platinum wire. Before each measurement, the electrodes were freshly polished by fine emery paper No. 1200. The counter electrode was a platinum foil. All the potentials reported here are referred to a saturated calomel electrode, SCE. A thermostated single-compartment cell containing 10 ml of the solution was used. A PAR (model 273) potentiostat/galvanostat was used for the electrochemical measurements. IR Spectra were recorded on a Perkin Elmer Infrared Spectrophotometer (model 983 G) using the KBr technique. All experiments were performed at room temperature.

Method of calculation

The structures of compounds were generated by PC MODEL, version 4.0,⁸ that involves an MMX force field^{9,10} and were saved as MOPAC^{11,12} files for PM3 semiempirical calculations.^{13,14} In this work the MNDO-PM3 method, which has proved to be highly reliable for investigating the molecular properties of molecules and ions was used. The MOPAC program package, Version 7.01 was used for calculating the properties of the dimers and Hyperchem program package, Version 4.0 for the tetramers and hexamers. The geometries of all molecular species correspond to the energy minima in a vacuum and were optimized by the PM3 method.

RESULTS AND DISCUSSION

Poly-(1-naphthylamine) film formation

a) Under potentiodynamic condition. 1-Naphthylamine was electropolymerized at a platinum electrode by cycling the potential between -0.8 and 0.9 V during seven cycles from 0.1 M 1-naphthylamine/ 0.5 M LiClO₄ acetonitrile solution, at a scan rate of 50 mV/s. An adherent black-blue film of the polymer was obtained.

b) Under potentiostatic condition. The electrosynthesis of poly-1-naphthylamine was also done using a potentiostatic pulse of 1.3 and 1.6 V from a solution containing 0.05 M 1-NPA,

0.5 M LiClO₄ acetonitrile solution. The potentiostatic pulse duration was 600 s. Black-blue adherent deposits were obtained at the platinum plate working electrode. The current decreased during the first 10 seconds of synthesis and then becomes approximately constant.

Infrared spectroscopy of poly-(1-naphthylamine) films

The IR spectra of p-1-NPA films prepared: (a) by cyclic voltammetry (film A); (b) potentiostatically at 1.3 V (film B); (c) potentiostatically at 1.6 V (film C), at a platinum electrode are shown in Fig. 1. The principal absorption bands observed in the IR spectra of monomer 1-NPA and the p-1-NPA films (A, B and C) are given in Table I.

TABLE I. Characteristic IR frequencies (cm⁻¹) of monomer 1-NPA and polymer p-1-NPA films

Compound	Vibration mode/cm ⁻¹									
	$\nu(\text{NH})$	$\nu(\text{CH})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\delta(\text{NH})$	$\nu(\text{C}-\text{N})$	$\nu(\text{B}-\text{NH}-\text{Q})^*$ $\nu(\text{B}-\text{NH}-\text{B})$	$\delta(\text{CH})$	$\gamma(\text{CH})$	$\nu(\text{ClO}_4^-)$
1-NPA			1624			1402				956
	3416	3041	1511		1574	1373		1012	856	
	3343		1465			1287		1085	792	
									770	
p-1-NPA										
Film A										938
			[1622]							900
						1401	1140			1087
	3453		1510	1622	1573				767	
					1301	1108				
		1455						710	627	
Film B										897
										810
			[1623]			1400	1142			1083
	3434			1623				1035	761	
		1510			1300	1119		685	626	
Film C										896
			[1638]			1399	1145			1080
	3427			1638				1035	815	
			1510			1300	1120			625
									762	

*B-benzene ring, Q-quinoid ring

Absorption peaks due to N-H stretching vibrations are observed at 3416 cm⁻¹ and 3343 cm⁻¹ for 1-NPA. The two absorption peaks are characteristic of primary amines.

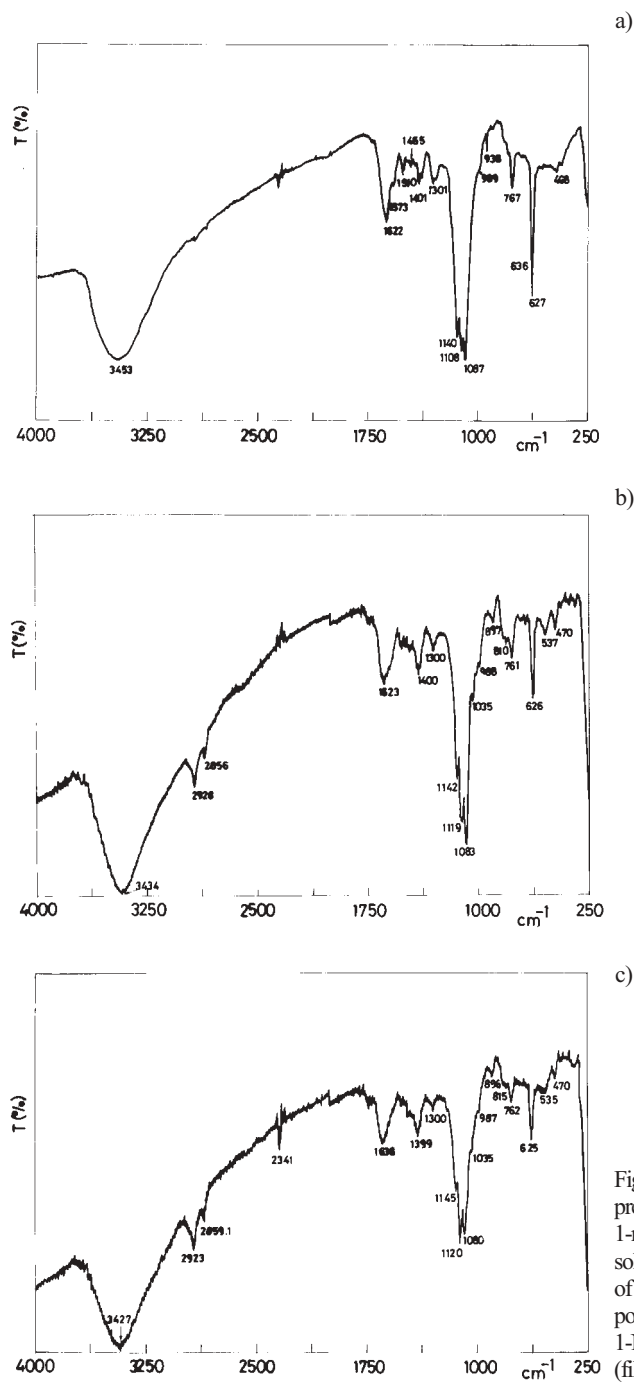


Fig. 1. IR spectra of: (a) p-1-NPA (film A) prepared by cyclic voltammetry of 0.1 M 1-naphthylamine in 0.5 M LiClO₄/ACN solution during seven cycles, at a scan rate of 50 mV/s; (b) p-1-NPA (film B) prepared potentiostatically at 1.3 V from 0.05 M 1-NPA /0.5 M LiClO₄/ACN; (c) p-1-NPA (film C) prepared potentiostatically at 1.6 V from the solution given in (b).

Polymer films spectra show only one absorption peak due the N–H stretching vibrations, $\nu(\text{N–H})$, observed at *ca.* 3400 cm^{-1} , characteristic of secondary aryl-amines. This observation means that the $-\text{NH}_2$ groups play a role in the polymerization.

In the region $1465\text{--}1624\text{ cm}^{-1}$ of the monomer spectrum, bands due to stretching vibrations of the aromatic C=C bonds, $\nu(\text{C=C})$, and deformation vibration in plane of the N–H bonds (scissoring), $\delta(\text{N–H})$, are observed. In the same region, for the polymer films, the vibration modes $\nu(\text{C=C})$ are observed. The band at 1573 cm^{-1} for N–H bending vibrations,³ $\delta(\text{N–H})$, is found only for film A. It arises from termination of the polymer chains. This fact indicates that the degree of the polymerization is higher when the electropolymerization is performed at constant potential. The broad peak centered at $\approx 1620\text{ cm}^{-1}$ is observed for all three polymer films. It has to be concluded that this band is a composite of two contributions, the aromatic ring C=C stretching mode and (particularly 1638 cm^{-1} in the spectrum of film C) the imine C=N– stretching mode, $\nu(\text{C=N})$.⁷ This indication of imine bonds hints of C–N or head-to-tail coupling during the electrooxidation of 1-NPA.

The very strong band at 1108 cm^{-1} in the spectrum of polymer film A (shifted to 1119 cm^{-1} and 1120 cm^{-1} in the spectra of polymer film B and C, respectively) having a shoulder at 1140 cm^{-1} can be assigned as the characteristic mode of benzene ring –NH– quinoid ring, or benzene ring –NH– benzene ring fragments.^{2,16}

The very strong band at 1087 cm^{-1} – film A (1083 cm^{-1} – film B and 1080 cm^{-1} – film C) can be assigned to ClO_4^- ion stretching vibrations.

In the region $700\text{--}960\text{ cm}^{-1}$, the IR spectrum of 1-NPA and of the p-1-NPA films show bands due to aromatic C–H out of plane deformation modes, $\gamma(\text{C–H})$.

In the spectrum of the polymer film A, the set of peaks at $938, 900, 767$ and 710 cm^{-1} is observed. It can be assigned to two contributions, 1,2,3-trisubstitution ($900, 767$ and 710 cm^{-1}) and 1,2,4-trisubstitution ($938, 900$ and 767 cm^{-1}).¹⁷ 1,2,3-Trisubstitution is consistent with the N–C(5) coupling route, while the combination of 1,2,3- and 1,2,4-trisubstitution is present in the N–C(7) linkages. So, polymer film A is a mixture of polymer structures obtained *via* the N–C(5) and N–C(7) coupling routes.

In the spectrum of the polymer film B, a set of peaks at $897, 810, 761$ and 685 cm^{-1} is observed. Consideration of this set shows that it can be assigned to contributions of 1,2,3-trisubstitution ($897, 761$ and 685 cm^{-1}), 1,2,4-trisubstitution (897 and 761 cm^{-1}), and 1,2-disubstitution (761 and 810 cm^{-1}).¹⁷ The peak at 810 cm^{-1} is also indicative of two adjacent H atoms in a ring, *i.e.*, it is consistent with a 1,2,3,4-substitution pattern.¹⁷ The combination of 1,2- and 1,2,3,4-substitution corresponds to N–C(4) linkages of the 1-naphthylamine molecules. So, the poly-(1-naphthylamine) film B is a mixture of the structures obtained *via* the N–C(5), N–C(7) and N–C(4) coupling routes. The set of peaks from the spectrum of film C in the region $700\text{--}960\text{ cm}^{-1}$ can be explained in the same manner as for film B.

Hence, spectral data from the $700\text{--}900\text{ cm}^{-1}$ region suggest that the p-1-NPA films are coupled *via* N–C(4), N–C(5) or N–C(7) linkages. Films B and C were obtained *via* the N–C(4), N–C(5) and N–C(7) coupling routes, while the set of peaks of film A in this region is most consistent with the N–C(5) and N–C(7) coupling routes. These results differ from

those in earlier works^{6,7} which suggested that the oligonaphthylamine products are 1,4-coupled, *i.e.*, that the polymerization of 1-NPA occurred only at the *p*-position.

Quantum-chemically assisted stereochemical analysis of poly-(1-naphthylamine)

The conductivity of poly-(1-naphthylamine)⁶ is very low compared to polyaniline. The main reason seems to be the stereochemical differences between these two conducting polymers. Oxidized polyaniline has an almost planar structure⁵ with low ionization potential due to strong delocalization of the π -electrons. For poly-(1-naphthylamine), it is presumed that the planarity of the oligomeric and polymeric oxidized (conducting) forms of 1-NPA, coupled by the N-C(4) coupling route, is prevented on a account of steric van der Waals repulsion interactions (Fig. 2). Stereoisomer A is predominant because it has considerably weaker van der Waals repulsions, similar to polyaniline. When the number of oxidized A dimer units exceeds 3 (hexamer), it is impossible to obtain a stable planar structure. Planar geometry is possible only for oxidized *p*-1-NPA, which consists of dimers coupled *via* N-C(5) (Fig. 3. scheme C), and N-C(7) (Fig. 3. scheme D) linkages.

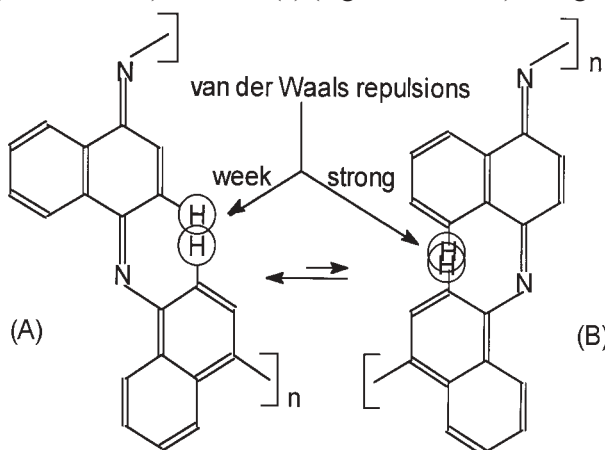


Fig. 2. Stereoisomers of oxidized 1-naphthylamine [N-C(4)] dimer units.

These simple stereochemical considerations have been checked by molecular-orbital calculations (semiempirical MNDO-PM3) of the oxidized dimers and hexamers of 1-NPA. The heats of formation, ΔH_f , of the oxidized dimers are listed in Table II. The most stable oxidized form of 1-NPA dimer has a N-C(4) type of coupling and nonplanar *anti* orientation. Its heat of formation, ΔH_f , and ionization potential, E_i , were calculated to amount to 523.67 kJ/mol and 8.61 eV, respectively. Oxidized 1-NPA dimer [N-C(4)] with a partial planar structure has a somewhat higher heat of formation. The oxidized dimer of 1-NPA with N-C(5) coupling has a much higher value of the heat of formation ($\Delta H_f = 529.86$ kJ/mol), and smaller ionization potential ($E_i = 8.21$ eV) by reason of the nearly planar molecular geometry. A similar heat of formation and a similar ionization potential were calculated for oxidized 1-NPA, N-C(7) coupled dimer.

TABLE II. Heat of formation, ΔH_f , of the oxidized dimers of 1-naphthylamine

Type of coupling	Molecular geometry	$\Delta H_f/\text{kJ mol}^{-1}$
N-C(4)	Nonplanar <i>anti</i> orientation	523.67
N-C(4)	Partial planar	529.86
N-C(5)	Nearly planar	593.88
N-C(7)	Nonplanar	592.41

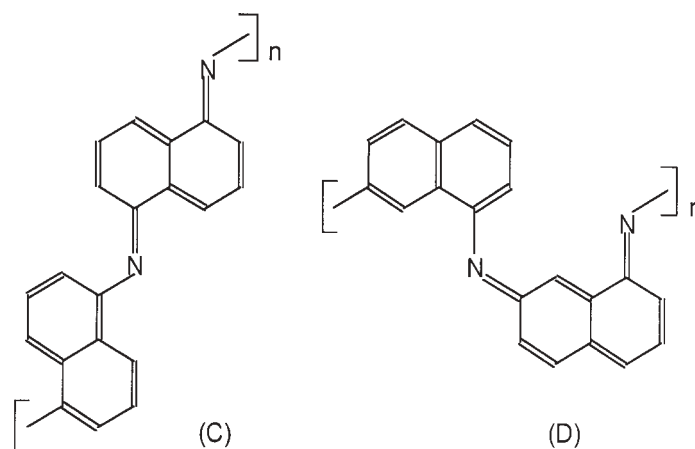


Fig. 3. Oxidized 1-naphthylamine [N-C(5)] (C) and [N-C(7)] (D) dimer units.

The heats of formation, ΔH_f , of the oxidized hexamers are listed in Table III. Molecular-orbital calculations show that the most stable oxidized hexamer of 1-NPA is nonplanar, with N-C(4) bonding between the monomer units (Fig. 4). Its heat of formation was calculated to be 1627.49 kJ/mol. Spirally twisted oxidized 1-NPA [N-C(4)] hexamer (Fig. 5) with some degree of planarity has a slightly higher value of the heat of formation. The heat of formation of oxidized 1-NPA [N-C(5)] hexamers with spiral twisting (Fig. 6) and flip-flop geometry (Fig. 7) is considerably higher. Planar geometry is possible for oxidized 1-NPA [N-C(5)] hexamer, with extremely low ionization potential (Fig. 8).

TABLE III. Heat of formation, ΔH_f , of the oxidized hexamers of 1-naphthylamine

Type of coupling	Molecular geometry	$\Delta H_f/\text{kJ mol}^{-1}$
N-C(4)	Nonplanar	1627.49
N-C(4)	Spirally twisted	1641.21
N-C(5)	Spirally twisted	1817.82
N-C(5)	Flip-flop	1818.53
N-C(5)	Planar	1839.83

Molecular-orbital calculations of the oxidized dimers and hexamers, of 1-naphthylamine clearly show the influence of the bonding pattern between the oxidized 1-NPA

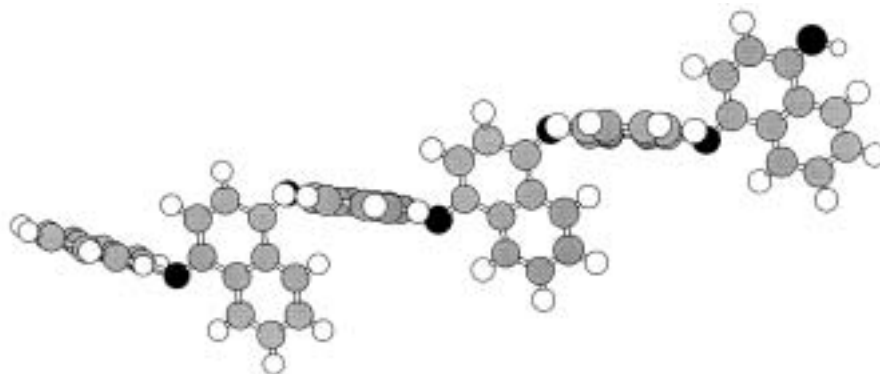


Fig. 4. Nonplanar oxidized 1-naphthylamine [N-C(4)] hexamer (the white spheres represent the hydrogen atoms, the black spheres represent the nitrogen atoms and the grey spheres represent the carbon atoms).

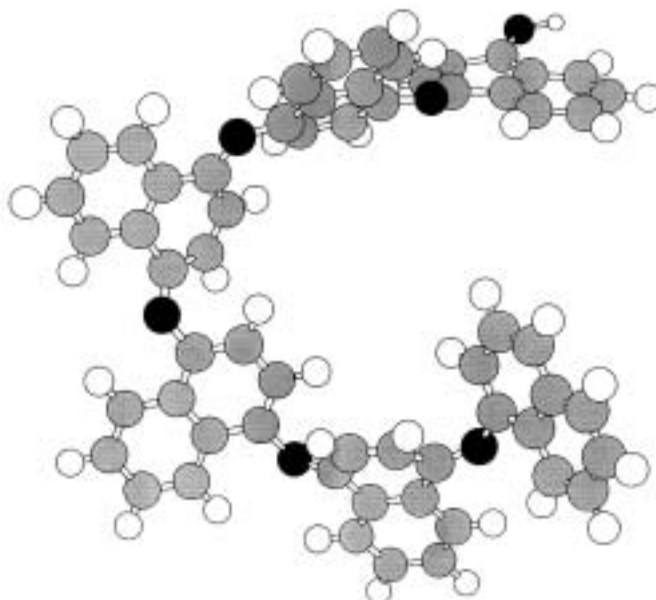


Fig. 5. Spirally twisted oxidized 1-naphthylamine [N-C(4)] hexamer (the spheres have the same meaning as in Fig. 4).

monomer units on the stability and planarity (conductivity) of 1-NPA oligomers. The most stable oligomeric structures [N-C(4)] obviously have low conductivity due to nonplanarity. As one goes to the more planar structures of the 1-NPA oligomers [N-C(5)], the forms of poly-(1-naphthylamine) with low ionization potentials and increased conductivity could be found. However, these planar 1-NPA oligomers are of low stability. The produced polymer is most probably a mixture of several structures. It is difficult to obtain coplanarity of the naphthalene rings in the polymer. Because of this fact, the diminished electronic conductivity of poly-(1-naphthylamine) compared to polyaniline and its deriva-

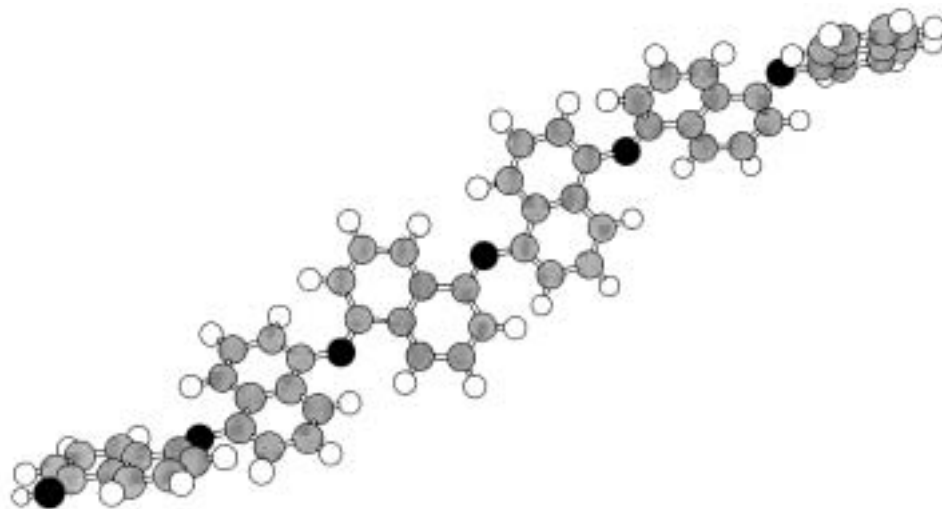


Fig. 6. Spirally twisted oxidized 1-naphthylamine [N-C(5)] hexamer (the spheres have the same meaning as in Fig. 4).

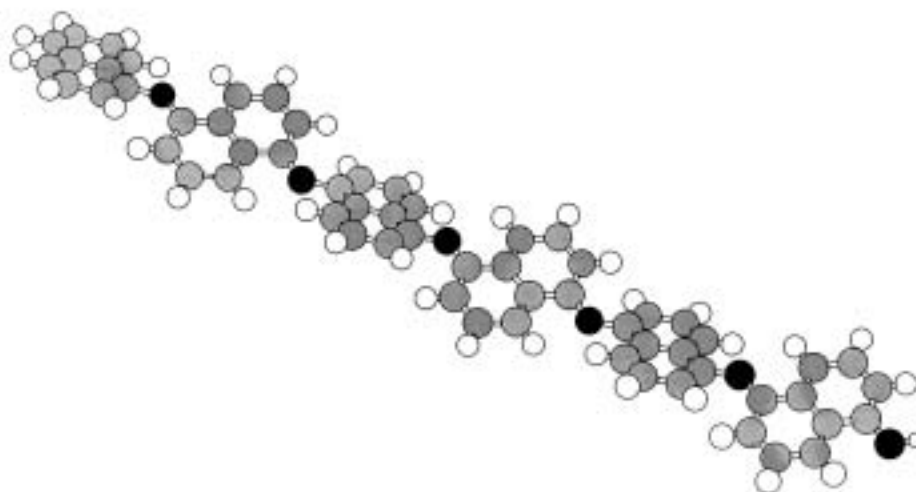


Fig. 7. Flip-flop oxidized 1-naphthylamine [N-C(5)] hexamer (the spheres have the same meaning as in Fig. 4).
tives it to be expected. However, it should be kept in mind that the possible interaction of the polymer film with the electrode surface might abolish steric hindrance.

CONCLUSIONS

Electrochemical polymerization of 1-naphthylamine from neutral acetonitrile/LiClO₄ solution was carried out by cyclic voltammetry and potentiostatically onto a platinum substrate. The resulting black-blue polymer films adhered to the platinum electrode surface. They were characterized by infrared spectroscopy. The IR data and quantum chemical calculations are consistent and suggest that the polynaphthylamine products are mixture of

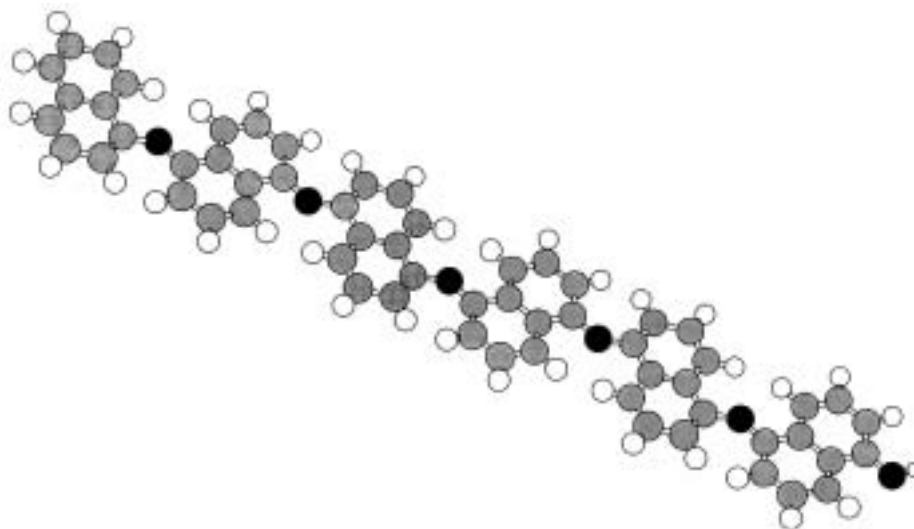


Fig. 8. Planar oxidized 1-naphthylamine [N-C(5)] hexamer (the spheres have the same meaning as in Fig. 4). several possible structures obtained *via* the N-C(4), N-C(5) or N-C(7) coupling route. Based on the IR spectroscopic investigations of p-1-NPA films correlated with quantum-chemically-assisted stereochemical analysis of poly-(1-naphthylamine), it can be concluded, contrary to earlier reports, that the N-C(4) coupled product is not predominant in this polymer because it is far away from the expected planarity.

ИЗВОД

СТРУКТУРА И СТЕРЕОХЕМИЈА ПОЛИ-(1-НАФТИЛАМИНА) ЕЛЕКТРОХЕМИЈСКИ СИНТЕТИСАНОГ У НЕУТРАЛНОМ АЦЕТОНИТРИЛНОМ РАСТВОРУ

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Поли-(1-нафтиламински) филмови синтетисани су потенциостатски и потенциодинамички из неутралног ацетонитрилног раствора 1-нафтиламина на платинској електроди. Ови полимерни филмови испитивани су ИР спектроскопијом. За разлику од раније публикованих резултата који су занемаривали стереохемију поли-1-(нафтиламина), у овом раду се предвиђа на основу квантне стереохемијске анализе могућих структурних јединица полимера, да уобичајени N-C(4) купловани продукт није преобладајући у полимеру, јер његова структура није планарна. На основу резултата ИР испитивања и семиемпиријских квантно-хемијских прорачуна ми претпостављено је да се полимерни продукти формирају комбинацијом N-C(4), N-C(5) и N-C(7) начинима везивања 1-нафтиламина. У овом раду су такође израчунате топлоте настајања оксидованих димера и хексамера 1-нафтиламина.

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