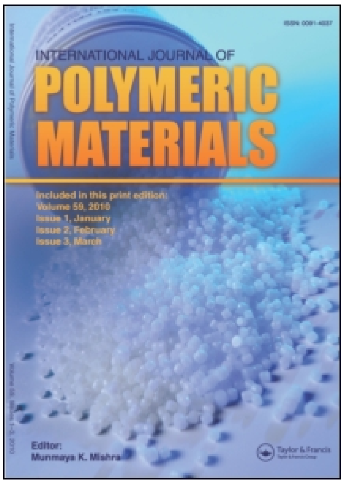

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Systematic Study of the Influence of Several Parameters on Physicochemical Properties of Oligoanilines and their Derivatives

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Systematic Study of the Influence of Several Parameters on Physicochemical Properties of Oligoanilines and their Derivatives

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In this work we study the influence of asymmetry, chain length, oxidation state, counterions and substituents groups over the physicochemical properties of oligoanilines.

We present some semiempirical quantum chemistry calculations of optimized structures, charge distributions, energy gaps and enthalpies of formation (ΔHf) for aniline oligomers in different oxidation states using the ***AM1 method***. Also, substituted structures are calculated. The substituents studied are methoxy, methyl and cyano groups located at positions 2 or 3 in the benzenoid ring. Methoxy substituted tetraanilines show hydrogen bridge formation; therefore, these are the most stable structures. The cyano group ($\sigma-\pi$ acceptor) induces a lowering of charge on the terminal amine group in all oxidation states. Our calculations show that a linear relationship exists between charge on terminal amine group and the IP, having different slope values depending on the substituents position. Theoretical energy gaps and experimental ones (from references) display a quite linear relationship. Tetraanilines substituted with cyano groups show the lowest energy gap and is the most interesting material that we have studied. Moreover, charged structures have been analyzed. Calculations on radical cation and dication structures are introduced. The influence of the counterions on the electronic properties of charged structures is presented.

Keywords: Aniline; oligoaniline; polyaniline; AM1; methoxy; cyano; methyl; counterion; electronic properties; energy levels

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INTRODUCTION

During the last decades, conjugated polymers have attracted great attention as organic conductors due to their unique electronic properties. Many theoretical and experimental works have been devoted to understand the relationship between chemical structures and electronic properties of the conjugated polymers [1, 2].

Recently, much interest has been devoted to polyaniline because of its electronic properties [2–4]. It is known that the reduced polyaniline displays a large band gap (about 4 eV) [5]. However, when the polyaniline is oxidized this energy gap value decreases abruptly [6]. Therefore, the reduced structure is an insulator, meanwhile, the oxidized forms display a semiconducting behaviour. This energy gap value could be reduced by adding positive charges on the chain, which induces structural defects on the chain. These positive charges (polarons) modify largely the energy levels, besides they are quite mobile and induce an increase of the conductivity [4–7]. Also, it is possible to improve the electrical properties of polymers (*i.e.*, polythiophene, polypyrrole or polyaniline) by adding side groups on the chain [8].

Consequently, in this area appear as an interesting topic to be analyzed the way to improve the electronic properties of oligoaniline and polyaniline. At this point several parameters (such as asymmetry, chain length, substitution, oxidation level and counterions) could influence the physicochemical properties of oligo or polyaniline. The main aim of this work is to analyze the global effect and the relative weight of these parameters over the electronic properties of oligoanilines.

In this work, we are studied the effect on the geometrical and electronic properties of the ground state of oligoaniline and its derivatives, considered in several oxidation states, and containing several substituent groups. We perform theoretical calculations on tetramers in order to farther understand physicochemical properties of polymers. In previous work we have demonstrated tetramer structures seem to be good model systems to calculate electronic properties of polymers (particularly in the polyaniline family) [9, 10]. Although, most of the previous calculations on oligoanilines are performed considering symmetrical structures by either neglecting the amine terminal group or by adding a new phenyl group [11, 12], we have demonstrated consideration of asymmetrical structures seems to be more adequate in calculations of physicochemical properties of aniline oligomers [9, 10].

In this paper we report theoretical studies performed on tetraaniline and tetraanilines substituted in position 2 or 3. In the first section, general considerations about physicochemical properties of aniline and its oligomers depending on the chain length and aysmmetry imposed by an amine terminal group will be analyzed. In the second part, the effect of several substituents over the electronic properties of tetraaniline will be examined at several oxidation levels. The substituents studied are cyano, methyl and methoxy groups. These substituents involve a large $\sigma-\pi$ electron capability range [13, 14]. In the last section we will analyze the effect displayed by positive charges on the structure and electronic properties of the oligomer molecules. Moreover, the interaction between the radical cation and the dication structures with several counterions such as SO_4H^-, CH_3COO^-, Cl^- and SO_4^{2-} will be analyzed. Geometries, ΔH of formation, Ionization Potentials, Gap Energies and Orbital Energy Levels of tetraaniline and its derivatives calculated by using the semiempirical method Hartree-Fock-Austin Model 1 (AM1) [15, 16] are presented and discussed.

METHODOLOGY

The geometry of the oligomers was optimized by using the semiempirical Hartree-Fock-Austin Model 1 (AM1) program [15, 16]. Most of the aniline and oligoanilines calculations have been performed in the framework of the Modified Neglected Differential Overlap (MNDO) method (from which one the AM1 method was originated). The AM1 method has been more carefully parametrized than MNDO. Therefore the obtained results by using AM1 method should be better than which one from MNDO method. In the last years PM3 (Parametrization Method 3) has been largely used to calculate organic molecules. There are discrepancies about which method (AM1 or PM3) gives better results. In our case we would use AM1 because it has proved to give accurate structural data compared with which one obtained by using X-ray crystallographic data for aniline oligomers [9]. Initially, the aniline molecule was optimized. Then, two optimized aniline molecules were coupled to generate the dimer (see Fig. 1). After that, dimer geometry optimization was performed with different fixed torsion angles between ring moiety and

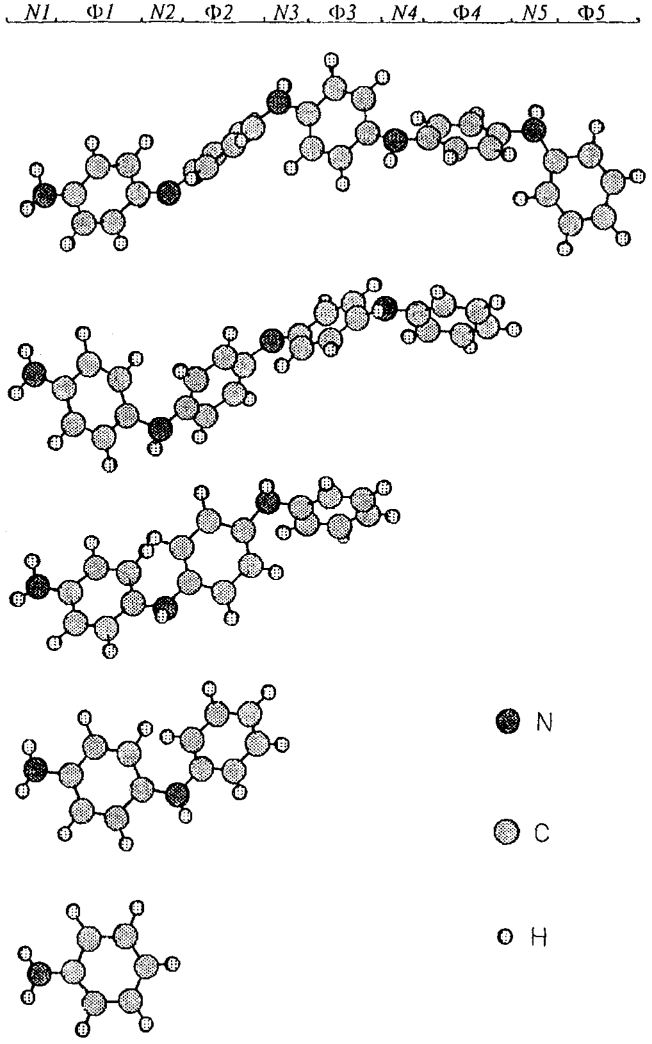


FIGURE 1 Optimized structures of aniline and oligoanilines. (Adapted from Ref. [9]).

the adjacent N—C—C backbone (θ_1 or θ_2 in Fig. 2). Torsion angle values used were varied 15° each time among 0 and 90°. The following structures were generated by the successive addition of one optimized aniline molecule to the most stable dimer, trimer and tetramer structure resulting from previous calculations. For the oxidized oligomers

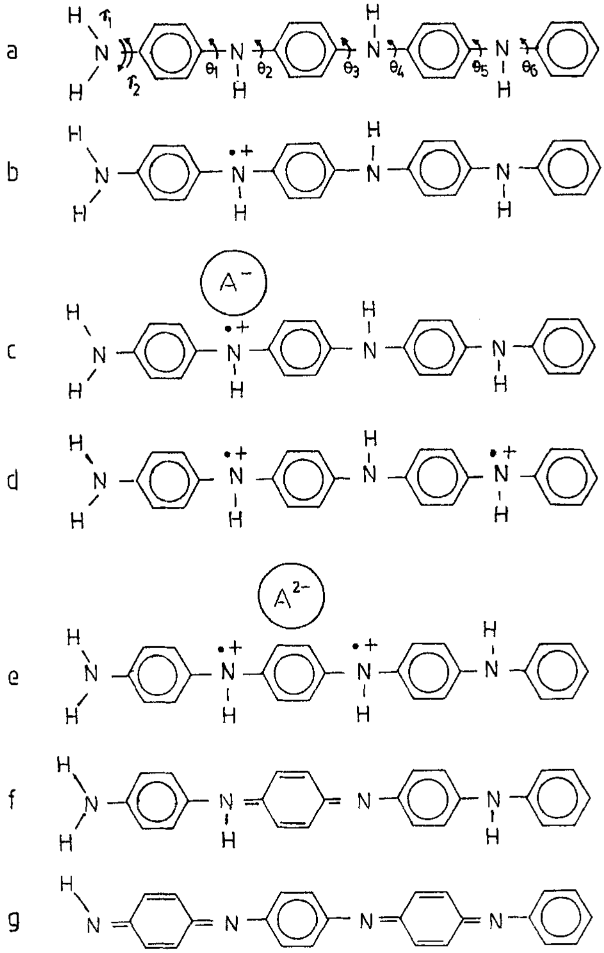


FIGURE 2 Schematic representation of studied tetraanilines. (a) Reduced, (b) radical cation, (c) radical cation + counterion, (d) dication, (e) dication + counterion, (f) 50% oxidized and (g) 100% oxidized. Substituents are placed at position 2 or 3 in benzenoid rings.

we have considered the reduced tetramer as the initial structure from which electrons were removed to give the radical cation and dication forms. Hydrogen atoms were removed accordingly for generating the diimine structures, called quinone type structures (see Fig. 2). A final total optimization of each structure was done.

For radical cation plus chloride (as a counterion) two initial positions were chosen to be optimized. One of these displays the chloride ion at a distance of 6 Å from nitrogen in the same plane of the oligomeric structure. The other initial position shows the chloride counterion located at 5 Å distance from nitrogen but over the plane of the structure. These distances (5 Å or 6 Å) were chosen at values larger than the value corresponding to tetraaniline electrostatic potential surface.

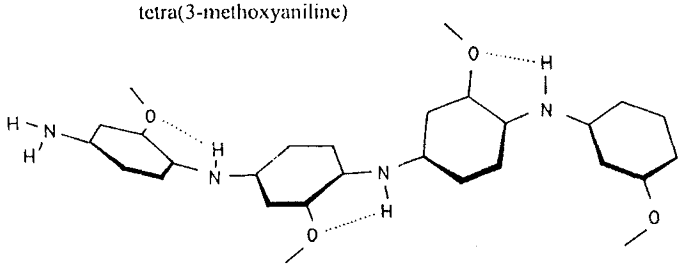
The substituted structures were generated by removing one hydrogen from position 2 or 3 of the ring and replacing it with the corresponding substituent. After that, these structures were totally optimized without geometry restrictions. When the substituent studied is methoxy a rotation around carbon (from the ring) oxygen (from methoxy group) bond is possible. Therefore, several initial positions were adopted and after that optimized. The most stable structure is that one where hydrogen bridges are present between oxygen from methoxy groups and hydrogen from amine groups (in the reduced, and emeraldine states) (see. Fig. 3).

AM1 results presented in this work consider calculations for these final optimized structures.

RESULTS AND DISCUSSION

Analysis of Physicochemical Properties of Aniline and Oligoanilines. Effect of the Number of Units in the Chain (*n*)

Aniline and its oligomers have been largely studied in order to obtain the electronic and structural parameters [2–12, 17, 18]. It is well described the influence of the ring torsional angle on the electronic properties of aniline oligomers (and polyaniline) [19]. As well as the evolution of their electronic properties with the oxidation level [18]. In previous works, usually, a consideration about aniline oligomers has tetra(3-methoxyaniline)



tetra(2-methoxyaniline)

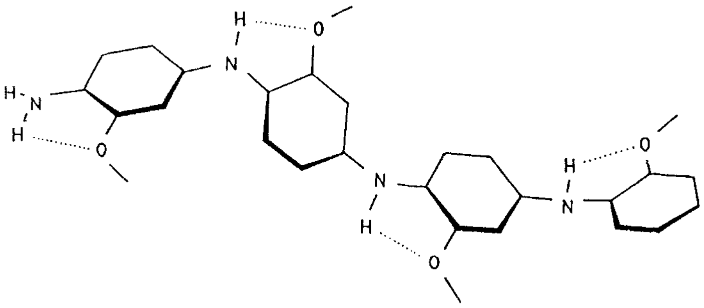


FIGURE 3 Optimized structures of tetra(3-methoxyaniline) and tetra(2-methoxyaniline).

been performed: these oligoanilines are considered as symmetrical structure [18, 19]. This condition is obtained either by suppressing or by adding an amine terminal group. Usually, the calculated structures are diphenylamine, triphenyldiamine, *etc.* types. In our case we are interested into understand the effect of the amine terminal group in the electronic properties of the oligoanilines. Therefore we performed studies of asymmetrical structures (see Fig. 1).

The reduced structures showed in Figure 1 display all the benzenoid ring having an aromatic like structures (with $\Delta r < 0.030$ Å, being Δr the difference between the largest and the shortest carbon—carbon bond length of the benzenoid ring). The torsional angles ($|\theta 1| + |\theta 2|$) *increase* with the distance from the amine terminal group [9].

Charge on the terminal amine group (hydrogen charges are summed up to nitrogen one) increases from the monomer (0.0373 $|e|$) to the pentamer (0.0405 $|e|$); reaching a quasi constant value at the tetramer (0.0403 $|e|$). This fact indicates the amine terminal group does not induce significative changes in the charge distribution after four units.

Figure 4a shows the IP and gap energy values of the aniline and its oligomers against $1/n$, being n the number of mers. The gap energy values and $1/n$ display a quite linear relationship between them. However, the IP reaches a quasi constant value for $n \cong 4$ or 5. Figure 4b shows the relationship between the charge on amine terminal group and the IP for aniline and oligoanilines in the reduced state. The obtained linear relationship could be indicating that the electron corresponding to the first ionization potential is probably removed from the nitrogen of the terminal amine group. Results have shown a decrease of IP against $1/n$ until reach a constant value for the tetramer structure. These data are in agreement with electrochemical measurements, which indicate the monomer is oxidized around 0.8 V *vs* SCE and this value decrease until it reach 0.2 V *vs* SCE for polyaniline in aqueous acid medium [20].

From the obtained results it is possible to establish the use of tetraaniline as model system in order to understand the electronic properties of polyaniline constitute a good approximate treatment [9, 10].

Effect of the Substituent Over the Electronic Properties of the Tetramers

Systematic studies of substituents effect on physicochemical properties of oligomers could be an important tool in order to design new materials [8]. In this work we introduce calculations of the influence of several substituent groups, covalentely bonded to the chain, over physicochemical properties of oligoanilines. Chains containing aniline units have been chosen to be studied. The substituent groups analyzed are cyano, methyl and methoxy. These have been located at position 2 or 3 in the benzenoid ring.

Geometry optimizations were performed by using AM1 method [15, 16]. Reduced oligoanilines show $\Delta r < 0.030$ Å; therefore, all studied oligomers have aromatic like rings. However, a special case is displayed by the cyano group. In this case Δr is approximately

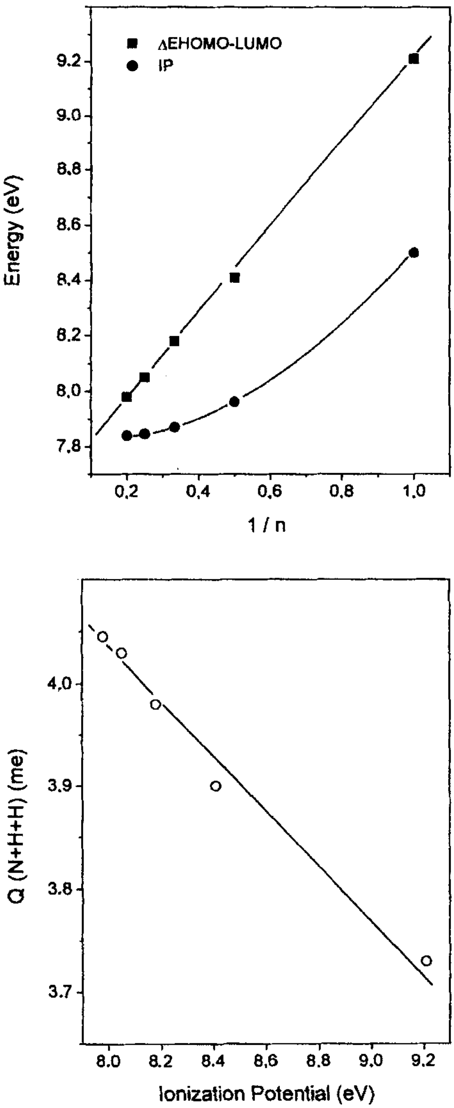


FIGURE 4 a. - Plot of calculated Δ*E*(HOMO-LUMO) (eV) and Ionization Potential (eV) against 1/*n*. (Reproduced from Ref. [9] by permission of Plenum. Pub. Corp.). b. Plot of the charge on terminal amine group (hydrogens charges are summed up nitrogen one) against the Ionization Potential (eV).

0.040 Å, and this value indicates this substituent induces a lowering in the aromaticity of the benzenoid ring. This breakdown of the benzenoid ring aromaticity would be caused by a develop of positive charge over this ring induced by the cyano group [21]. According with the classification of substituents considering their σ and π electron behaviour performed by Jug *et al.*, the cyano group is a strong σ acceptor and π acceptor [13, 14]. The large Δr observed in this case could be explained by the capacity of this group to accept electrons. Furthermore, this fact could be confirmed by a detailed charge distribution analysis.

Another special case is presented by oligoanilines substituted with the methoxy group [22]. This kind of groups show the ability to build a hydrogen bridge between the oxygen of methoxy group and the hydrogen of amine group. This fact creates a five member ring (fused to the benzenoid ring) (see Fig. 3). Therefore, distortions in the Δr and in the torsion angles would be expected to happen. In 50% oxidized cases, the hydrogens from N2 and N3 are removed and the benzenoid ring $\Phi2$ becomes a quinoid-type structure ($\Delta r > 0.135$ Å) (see Fig. 2-f). Also the length of C —N bonds next to this ring are lower than in the reduced form [2]. As in the reduced case, cyano group produces the most important increases on Δr values. For totally oxidized structures all hydrogens (except one) from amine groups are removed (see Fig. 2-g). This fact implies the generation of two quinoid-like rings ($\Phi1$ and $\Phi3$; $\Delta r > 0.139$ Å). As in the other oxidation states, the most important inductive effect is displayed by the cyano group. Besides, the loss of hydrogens from amine groups implies the breakdown of hydrogen bridges of oligoanilines substituted with the methoxy group. Therefore, the forced benzenoid ring bond length distortions in these oligoanilines are lost.

From the torsional angles of hydrogen of the terminal amine groups ($\gamma1, \gamma2$, see Fig. 2), it is possible to deduce the degree of aromaticity of the benzenoid ring next to it [9]. The most important fact is the reduction of these angles when the quinoid character of the benzenoid ring number 1 increases. In the reduced structures only the cyano group induces additional lowering by about 5–7 degrees in these torsion angles.

In most of the cases torsion angles ($|\theta1| + |\theta2|$, see Fig. 2) change when a substituent is added. These torsional angle variations depend strongly on the substituent position. $\theta 1$ presents the most important changes for molecules substituted at position 3 and $\theta 6$ for ones substituted in position 2. Due to $\theta 1$ and $\theta 6$ are the less constrained torsional angles which have been able to modify their initial conformations. These changes can be originated either by steric effects due to the substituent groups, or by electronic changes induced in the backbone by these groups, or by both effects acting together.

The asymmetry imposed by the presence of the terminal amine group lead to a strong effect over the charge distribution. Also, charges on several molecular fragements are altered by the substituent position. Positive charges on the terminal amine group for molecules substituted at position 2 are larger than for ones substituted at position 3. This is a consequence of inductive and resonance effects produced by a substituent depending on its ring positions. For tetranilines substituted at position 3, the positive charge on benzenoid rings increases when distance from the terminal amine group increases. However, for tetramers substituted at position 2, charges on the benzenoid ring have the maximum values for benzenoid rings number 2 and 3. *All systems show an increase of negative charge on amine groups when the distance of the amine terminal group increases.* Molecules substituted at position 2 show a dipole moment higher than ones substituted on 3 because of these charge distributions. The studied substituents show charges in agreement with their $\sigma-\pi$ acceptor donor capabilities. The cyano group ($\sigma-\pi$ acceptor) shows a very large negative charge, meanwhile, methyl group ($\sigma-\pi$ donor) creates a positive one. If $\sigma-\pi$ compensated effects exist, the extent (absolute value) of the charge on substituents is smaller than in cyano case. It is clear from these results, that an induced charge by substituents could be the main source of geometry distortions showed above, especially in tetraanilines substituted with cyano groups. For 50% oxidized structures substituted at position 2, more positive charges are shown on the terminal amine group than for ones substituted in 3. Nevertheless, the total charge distribution in the first cases induces larger dipole moments than in the second ones. This relation between dipole moments and substituent positions in the benzenoid ring changes for 100% oxidized tetraanilines. This fact could be explained in terms of different substituents capacities to interact with the orbitals of the benzenoid rings. These capabilities for conjugation depend on whether the benzenoid ring aromaticity [13, 14]. Therefore, since there is a gradual increase of the quinoid-like benzenoid ring when the oxidation level increases, large changes in the properties that depend on π electrons are expected to happen.

From our results it is possible to find two linear relationships between the IP and the charge on the terminal amine group, one for molecules substituted at position 2 and another for molecules substituted at position 3 (see Fig. 5). In general, charges and IPs for molecules substituted at position 2 are lower than for those substituted at position 3. This is because the largest inductive and resonance effect due to the terminal amine group exists in the first case. The trends between experimental oxidation potentials and theoretical IP results are in agreement [23–25]. For oxidized structures, as in the reduced ones, substituent at position 2 displays stronger effects on the IP than which ones located at position 3. A possible explanation of this fact is

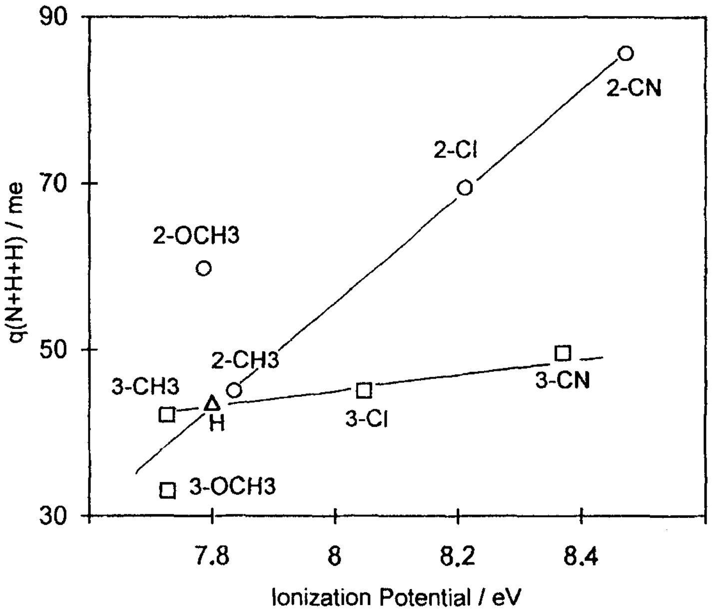


FIGURE 5 Plot of the charge on terminal amine group (hydrogens charges are summed up nitrogen one) against the Ionization Potential (eV) for tetraanilines substituted at position 2 or 3.

the first electron could be removed from the terminal amine group, and the effect on its charge will be stronger when substituents are located at position 2. This effect is in agreement with the changes on the HOMO produced by several substituents.

Tetraanilines substituted at position 2 or 3 with a cyano group show the largest heat of formation (ΔHf). Meanwhile, tetraaniline substituted with methoxy groups show the smallest, because of hydrogen bridge formations. As the oxidation state of the tetramer increases, ΔHf increases as well (see Tab. I). These values are consistent with those determined through electrochemical experiments, which indicate that the oxidation of anilines and its oligomers is an endergonic process when it is considered as a half-reaction [9]. In general, complete oxidation implies a ΔHf around of 100 kcal/mol.

To understand the electronic processes in oligoanilines it is necessary to know the electronic properties, particularly the energy levels, of the grounds state of these systems. The first optical transition is a $\pi \rightarrow \pi^*$ one (around 4 eV), from the level that corresponds to N interacting with the benzenoid ring, to the benzenoid antibonding one [4]. Because of experimental data from tetramers of aniline or substituted tetraanilines are scarce we have analyzed the polyaniline ones. When polyaniline is oxidized the experimental spectrum shows two electronic transitions in the energy range 0 to 5 eV [5, 6, 18]. One is around 2 eV and another near 4 eV. Stafstrom *et al.* [18] interpreted the low energy absorption in terms of the orbital pictures of polyemeraldine (or its oligomeric equivalents). The absorption around 2 eV was found to be due to the transition from a π state of benzene (πb) to a LUMO that is π quinoid-like (πq). The HOMO, πb is a delocalized

TABLE I ΔHf for tetraanilines in several oxidation states (kcal/mol). 2-CH3 means tetra(2-methylaniline), 3-CH3 means tetra(3-methylaniline) and so on

	Red.	50%*ox.*	100%*ox.*
H	124.26	169.27	220.92
2-CH_3	97.28	142.04	192.55
2-OCH_3	−22.51	23.99	77.72
2-CN	250.53	299.13	355.78
3-CH_3	97.68	140.44	191.60
3-OCH_3	−22.92	24.24	107.82
3-CN	253.07	300.48	355.13

orbital, whereas the LUMO πq is strongly localized on the quinoid ring and the two surrounding imine nitrogens. This means that the new level in the gap region (πq) is responsible for the low energy (2 eV) of the electronic process.

In general, substituents contributes to frontier orbitals. In the reduced state, it is well known the cyano group depicts a strong π^* interaction between its π^* orbitals and benzene ones. These both two orbitals have similar energies, therefore, perturbations between them produce a very low energy π^* orbital [21, 26]. pz orbitals of carbon from methyl and methoxy groups interact with the π orbital of tetraaniline. However, this interaction is weak. Substitution effects on the oxidized structure energy levels are similar to that of the reduced ones. It is important to point out that the energy gap depends on the substituents position. For 50% oxidized structures the lowest ΔE(HOMO-LUMO) is obtained. In this case tetraanilines substituted with a methoxy group show different values of ΔE(HOMO-LUMO)

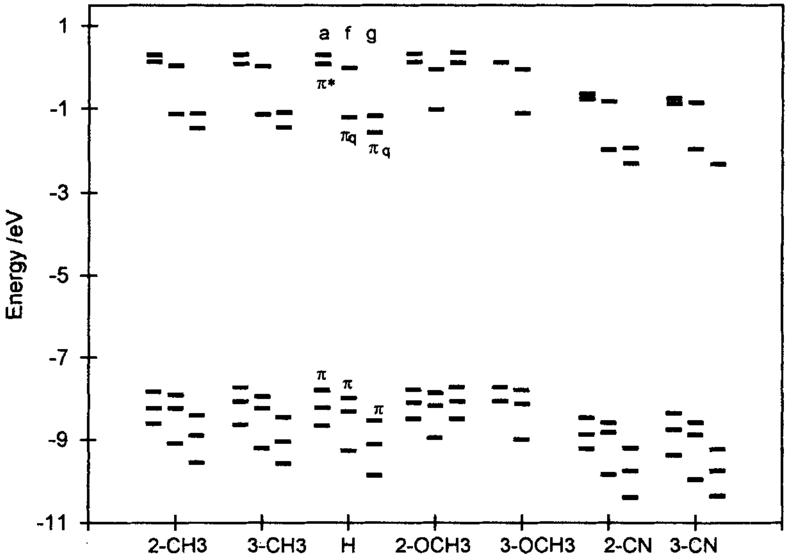


FIGURE 6 Energy level distribution of frontier orbitals of tetraanilines substituted in position 2 or 3. In all cases the left values (a) correspond to the reduced state, the middle value (f) to the 50% oxidized and the right values (g) to the 100% oxidized. 2-CH3 means tetra(2-methylaniline), 3-CH3 means tetra(3-methylaniline) and so on.

according to the substituent position. The large gap energy showed when the methoxy is at position 2 is due to a strong interaction between the lone pair of oxygen and one hydrogen from the terminal amine group. This behaviour changes the energy levels. The cyano group shows the strongest perturbation between its π^* levels and the πq levels. In spite of the values of these orbitals are not so close as in the reduced form; therefore a perturbation between them is smaller than in the reduced case. For 100% oxidized structures the energy gap is larger than for 50% oxidized ones. From the obtained results it is possible to establish that the cyano substituted oligoanilines are the most encouraging material in order to be used as a semiconductor.

Effect of Charges Over the Electronic Properties of the Tetramers. Analysis of the Counterion Influence

It is well known, the first step in the oxidation process of reduced tetraaniline is the removing of one electron. This originates a radical cation structure (see Fig. 2-b). After that, a second electron is removed to give a dication structure (see Fig. 2-d). These charged structures should display significant interactions with counterions present in the reaction medium. In this section we will try to evaluate the interaction between these cation structures and several counterions.

As was introduced below, reduced tetraaniline presents an aromatic-like structure for all benzenoid rings [9, 12, 18]. Radical cation tetraanilines without counterion show the benzenoid ring Φ2 having a predominantly quinoid character, meanwhile rings Φ1 and Φ3 have an intermediate (between aromatic and quinoid) character.

Figure 7 shows the optimized geometry for the different structures. The final optimized position of the chloride counterion using the AM1 method depends on its initial location. If initial position is over the molecule, after the optimization process, the Cl^- counterion is located at 2.3 Å above the second benzenoid ring, Φ2, shifted to the nitrogen N2 neighborhood. If the initial position is in the same plane that the molecule (in a side), the final obtained structure yields a chloride counterion forming a hydrogen bond with the nitrogen N_2 ($Cl^- \ldots N$ distance was 3.2 Å). This result shows that Cl^- has a great ability to interact with one hydrogen atom of the amine group from the

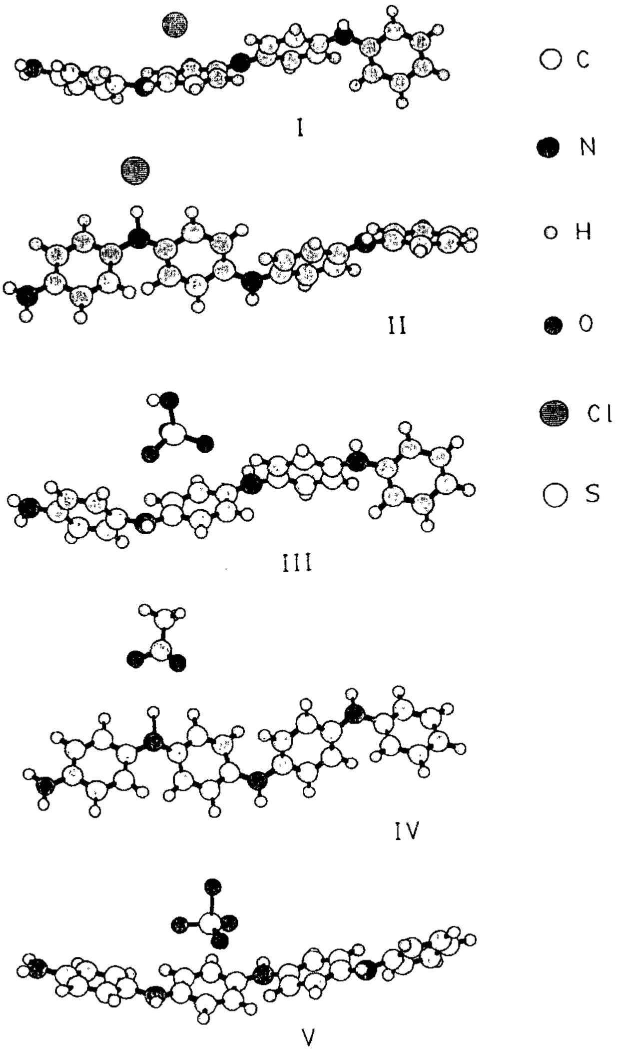


FIGURE 7 Optimized final structures of: (I and II) radical cation + Cl^-, (III) radical cation + HSO_4^-, (IV) radical cation + CH_3COO and (V) dication + SO_4^{2-}. (Reproduced from Ref. [10] by permission of Plenum. Pub. Corp.).

oligomer generating a kind of hydrogen bond. The second phenyl ring (Φ2) increases its quinoid character, meanwhile rings Φ1 and Φ3 become more aromatic [10]. However, final locations for the HSO_4^- and CH_3 COO^- (obtained after the optimization procedure) were independent of its initial position. HSO_4^- final position was 2.8 Å over the second benzenoid ring and also shifted to the nitrogen N2. Meanwhile, CH_3COO^- ion was forming a hydrogen bond with the amino group (see Fig. 7).

Δr values for dication tetramer show a large quinoid character for rings $\Phi 1$ and $\Phi 3$. However, ring $\Phi 2$ of the dication structure displays the largest quinoid character in the presence of a SO_4^{2-} counterion. Figure 7 shows the final optimized structure obtained for the dication in the presence of a SO_4^{2-}. It is possible to observe a distortion of the tetramer induced by the SO_4^{2-} ion, due to its double negative charge. This distortioned final structure (consequence of the bivalent character of this ion) could explain the experimentally determined dependence of the morphology obtained on the nature of the anion present in the electrolyte. When polymers are synthesized electrochemically fibrilar morphologies are obtained by using Cl^- or ClO_4^- and globular morphologies are obtained when SO_4^{2-} is employed (because of the possibility to coordinate two radical cations simultaneously, which are not necessarily present in the same chain) [27, 28].

On the other hand the evolution of dihedral angles of the terminal amine group is strongly dependent on the oxidation state. In the reduced state, nitrogen atom of the terminal amine group shows an sp^3 hybridization, meanwhile N bonded to a quinoid ring displays a sp^2 hybridization. When the oligoaniline changes from the totally reduced to the radical cation state the dihedral angles (γ_1 and γ_2 defined in Fig. 2) change from 157.9° and 26.7° to 167.8° and 16.2°, respectively. The amine terminal group becomes approximately 10° more planar. The presence of the counterion (Cl^-) induces the dihedral angles to be similar to those of the reduced polyaniline. In the dication state the terminal amine group is located at the same plane of the benzenoid ring [9].

Effects of counterions over the geometry of radical cation and dication structures could be explained as follows:

(i) There is a charge transfer from a negatively charged group to the chain (in this way the chain would become as a quasi-reduced).
(ii) There is a strong localization of the positive charge in some region of the chain (forming an adduct between the counterion and the tetraaniline).

(iii) Both effects could be associated to the influence of the counterion. Some of the counterions could favor charge transfer and others a localization of the positive charge.

The relevance of any of the above mentioned counterion effects over the physicochemical properties of the aniline oligomer could be better evaluated through a detailed charge distribution analysis. The terminal amine group influences strongly the charge distribution on the reduced structures. For the radical cation without any counterion, the charge is centered mainly over the benzenoid rings Φ2 and Φ3 with the largest value for ring Φ2 due to the chain asymmetry: terminal amine group induces an electrical field on the chain. This effect is not found for symmetrical structures [11, 17]. For radical cation structures in presence of counterions, our calculations are shown the charge distribution significantly depends on the nature of the counterion involved.

The first evidence of the behaviour of chlorine as a counterion was introduced for the case of polyacetylene neutral radical species chloride ion has shown about 15% of charge transfer [29]. Our calculations are shown, for the radical cation the charge on the phenyl Φ_2 in the absence of counterion is 273 me. In the presence of the Cl^- that value decreases by about 100 me [9] independent of the counterion location. The ability to transfer charge from the Cl^- to the oligomer has the property of keeping the aromaticity of the whole structure excepting the ring Φ2.

These results explain the tendency of the terminal amine group to remain tetrahedral as in the reduced structure. This large charge transfer results probably because counterion solvation is not considered. *Kang et al.* [30–33] have conducted XPS studies using conducting polymer systems in the presence of several counterions. Their experimental data suggest that a large charge transfer (ca. 50%) from a chloride to the polymer chain takes place. Chloride ion is the only one that shows this effect. Due to its large charge transfer, same authors have labeled this kind of chloride species as 'Cl^*' [31]. On the bases of the hardness of chloride ion, charge transfer should not be expected. However experimental XPS results and our calculations show that it is possible to find and evaluate this effect [30].

On the other hand, when CH_3COO^- and HSO_4^- are considered the charge transfer from counterion to the chain is small (less than 10% in both cases). For tetraaniline interacting with CH_3COO^- counterion, due to its basicity and to the presence of the COO^- group, formation of hydrogen bonds between the amine group and the COO^- of the anion is induced (see Fig. 7). For these cases a strong charge localization over benzenoid ring Φ2 (ring over which counterion is localized after optimization takes place) is displayed. Therefore, in these cases the tendency of the terminal amine group to remain tetrahedral could be explained by considering that a charge localization effect exists over a fragment of the chain (*i.e.*, ring Φ2) given by the counterion.

The dication structure shows a larger charge localization on rings Φ1 and Φ3 with respect to the rest of the molecule. However when a SO_4^{2-} is added, the counterion transfers about 50% of its charge.

The tetraaniline radical cation (without any counterion) shows larger IP than the reduced structure. The presence of a counterion reduces the IP. This is in agreement with the fact that *loosing* one electron from a positively charged system (radical cation without counterion) is energetically less favorable than loosing one electron from a neutral system (radical cation with counterion). The diradical cation structure shows the largets IP value but if SO_4^{2-} is added to the system, the IP decreases significantly. This fact is in agreement with the behaviour showed by a radical cation with counterions as discussed above. Data from electrochemical measurements show that there is a strong dependency of the oxidation potential with the number of counterions present in the medium and the pH. If there are no counterions in the reaction medium the electrochemical oxidation of polyaniline is energetically less favorable [34, 35].

The reaction:

$$\text{reduced tetramer} + HA \rightarrow \text{radical cation tetramer} + A^- + (1/2)H_2$$

displays a total enthalic cost that depends on the counterion. Calculated isolated counterions show negative ΔH_f($\Delta H_f Cl^- = -37$ kcal/mol, $\Delta H_f CH_3COO^- = -115.5$ kcal/mol, $\Delta H_f HSO_4^- = -234.0$ kcal/mol). Tetraaniline radical cation without counterion displays a $\Delta H_f = 282.2$ kcal/mol. Radical cation structure optimized in the presence of a counterion displays a lowering of the ΔH_f. The obtained values after the optimization are: for Cl^-, $\Delta H_f \approx 136.9$ kcal/mol; for CH_3COO^-,

$\Delta H_f \approx 79$ kcal/mol; and for HSO_4^-, $\Delta H_f \approx -24.1$ kcal/mol. That could be associated to the stabilizing capacity each counterion provides. The stabilizing effect of Cl^-, (−108.3 kcal/mol) is larger than that of CH_3COO^- (−87.7 kcal/mol) or HSO_4^- (−72.3 kcal/mol). These results are in agreement with the pKa values of the acids. From the three analyzed counterions, it is possible to speculate that a better stabilization in these cases is achieved principally due to charge transfer as compared to charge localization. When the counterion transfers a large percentage of its charge to the chain, the oligomer would actually remain as a reduced species (124 kcal/mol [9]). To analyze the influence of HSO_4^- it is necessary to consider that this ion stabilizes charges by localization of them into a molecular fragment. This fact could provide a possible explanation for the stabilization of the radical cation in the presence of HSO_4^-. For the CH_3COO^-, formation of a hydrogen bond gives additional stabilization. Diradical cation has the largest value of ΔH_f of all studied species. If a bivalent counterion (SO_4^{2-}) is added to this system there is a large decrease of the ΔH_f.

The enthalpy difference in the reaction:

$$\text{reduced tetramer} + H_2SO_4 \rightarrow \text{dication tetramer} + SO_4^{2-} + H_2$$

is about 112.7 kcal/mol.

As the oxidation state of the tetramer increases, ΔHf changes, passing through the maximum value for the dication form. From these results, one could deduce that the dication (Fig. 2-e) is a "high energy intermediate state" whose energy is about 360.0 kcal/mol above the reduced structure (Fig. 2-a). Consequently, the minimum "activation energy" for the transformation of the reduced tetramer to the intermediate oxidized form (Fig. 2-e) is about 360.0 kcal/mol.

Frontier orbitals energy values of the reduced, radical cation and dication tetraanilines are shown in Table II. For reduced structures the HOMO corresponds to the π orbital of the benzenoid ring interacting with the pz nitrogen orbital. Meanwhile, the LUMO corresponds to the π^* benzenoid orbital [4]. When this structure is oxidized to give a radical cation, the energy levels associated with the frontier orbitals are more negative [4, 18]. Therefore, for radical cation and dication structures new intermediate levels in the gap region appear. Similar

TABLE II Energy levels of tetraaniline in different oxidation states. Effect of the counterion. (Reproduced from Ref. [10] by permission of Plenum. Pub. Corp.)

	Reduced	*Radical cation without counterion*	*Radical cation + Cl^- (I)*	*Radical cation + CH_3COO^-*	*Radical cation + HSO_4^-*	*Dication*	*Dication $+SO_4^{2-}$*
EHOMO/eV	−7.67	−10.61	−7.69	−8.11	−8.61	−13.97	−8.54
ESOMO1/eV	–	−8.18	−4.21	−5.41	−5.67	−10.82	−6.27
ESOMO2/eV	–	–	–	–	–	−10.53	−5.63
ELUMO/eV	0.02	−3.17	0.13	−0.69	−0.90	−5.87	−0.61

levels have been defined for polyaniline by Stafstrom *et al.*, as polaron (in our case radical cation) level. These "mid gap levels" are semi-occupied, therefore constitutes SOMOs of the systems [30]. The energy levels corresponding to HOMO, SOMO, and LUMO of the radical cation state in the presence of counterions are destabilized in relation to the energy levels of the radical cation without any counterion. This is possible due to either charge localization (CH_3COO^- and HSO_4^-) or charge transfer (Cl^-).

The energies of the 'mid gap levels' (SOMO) for the dication structure are smaller than those in the radical cation. They are splited in two new levels. This stabilization could probably be associated with the charge delocalization on the oligomer due to the absence of the counterion. If a counterion like SO_4^{2-} is added, the frontier orbitals are destabilized. This destabilization could probably be associated to the charge localization.

In order to make the oligomer model system comparable or extrapolable to a polymer, it is essential that oligomer radical cation will be studied in the presence of counterions. That is because of counterions help to localize the effect of the positive charge over a short fragment of an oligomer as proposed in this work. In this way oligomers and polymers do have corresponding πb and πq levels.

CONCLUSIONS

In this work we are describing the effects of several factors over the geometrical and electronic parameters of oligoaniline. Was demonstrated that the terminal amine group exerts a strong influence over the charge distribution and the energy levels distribution. The decrease in the IP in relation with $1/n$ can be associated with the oligomer polarization that increases with the chain length.

The incorporating of substituent groups on the backbone of tetraaniline (or polyaniline) opens a completely new class of compounds (polymers). These kinds of materials have new electronic and geometrical properties. The substituent effects on physicochemical properties of tetraaniline (or polyaniline) depend on its electronic and geometrical attributes. Two of the studied substituents present strong effects on these properties. The first one is the methoxy group that originates a five member ring fused to the benzenoid one through hydrogen bridges (see Fig. 3). This particularity gives to this kind of compound a special conformation that produces strong effects on the electronic properties. The second one is due to the cyano group and its strong $\sigma-\pi$ acceptor electronic capabilities. This fact implies a large positive charge on benzenoid rings that induces strong distortions on it. The LUMO of the cyano substituted tetraanilines is located at quite low energy value. This is because of it is originated by a strong perturbation between π^* of benzenoid (or quinoid for oxidized structures) and the π^* of the cyano group. In general, substitution could be a successful way to obtain new materials with useful electronic properties.

From this work we can conclude that counterions can produce, at least two different effects over the physicochemical properties of tetraaniline radical cation and dication, depending on the nature of the counterion studied. One of them is the charge transfer from the anion to the oligomer chain. This kind of effect is displayed by chloride. The second effect is the charge localization in a fragment of the chain. This effect was observed mainly in the presence of HSO_4^- and CH_3COO^-. The chloride charge transfer to the chain was predicted in our previous work [9], which constitutes the first theoretical approximation in the evaluation of the effect of the counterions in these sysems [9]. This unexpected effect has been verified by comparison with experimental results from XPS studies obtained by Kang *et al.* [30–33]. The agreement between the experimental and the theoretical values demonstrates that the AM1 program is appropriate for calculating this kind of systems. The energy level distribution and the shape of the frontier orbitals in tetraaniline radical cation plus counterion are analogous to the polymer energy band distribution. In order to compare the energy levels of charged tetraaniline systems to those of polyaniline, it is essential that oligomer radical cation be studied in the presence of a counterion.

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References

[1] Springborg, M. (1993). *Int. Rev. Phys. Chem.*, **12**, 241.
[2] André, J. M., Delhalle, J. and Brédas, J. L. (1991). Quantum Chemistry Aided Design of Organic Polymers (World Scientific Pub.: Singapur).
[3] Lux, F. (1994). *Polymer*, **35**, 2915.
[4] Sjögren, B. and Stasftröm, S. (1988). *J. Chem. Phys.*, **88**, 3840.
[5] Masters, J. G., Sun, Y., MacDiarmid, A. G. and Epstein, A. J. (1991). *Synth. Met.*, **41**–**43**, 715.
[6] Huang, W. S. and MacDiarmid, A. G. (1993). *Polymer*, **34**, 1833.
[7] Epstein, A. J. (1991). In: Brédas, J. L. and Silbey, R. S. (Eds.), Conjugated Polymers. The Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials (Kluwer Acad. Pub., Netherlands), p. 211.
[8] Zális, S. and Kertesz, M. (1992). *Synth. Met.*, **47**, 179.
[9] Vaschetto, M. E., Retamal, B. A., Contreras, M. L., Zagal, J. H. and Bulhoes, L. O. S. (1995). *Struct. Chem.*, **6**, 129.
[10] Vaschetto, M. E., Retamal, B. A., Contreras, M. L. and Zagal, J. H., *Struct. Chem.*, in press.
[11] Libert, J., Brédas, J. L. and Epstein, A. J. (1995). *Phys. Rev. B.*, **51**, 5711.
[12] Brédas, J. L., Quatrocchi, C., Libert, J., MacDiarmid, A. G., Ginder, J. M. and Epstein, A. J. (1991). *Phys. Rev. B.*, **44**, 6002.
[13] Jug, K., Matuschewski, M. and Köster, A. M. (1993). *J. Phys. Org. Chem.*, **6**, 645.
[14] Jug, K. and Matuschewski, M. (1994). *Int. J. Quantum Chem.*, **49**, 197.
[15] Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. (1985). *J. Am. Chem. Soc.*, **107**, 3902.
[16] Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P. (1993). *J. Am. Chem. Soc.*, **113**, 5348.
[17] Libert, J. and Brédas, J. L. (1993). *Synth. Met.*, **55**–**57**, 4314.
[18] Stasftröm, S., Sjögren, B. and Brédas, J. L. (1989). *Synth. Met.*, **29**, E219.
[19] Ginder, J. M. and Epstein, A. J. (1990). *Phys. Rev. B.*, **41**, 10674.
[20] Johnson, B. J. and Park, S.-M. (1996). *J. Electrochem. Soc.*, **143**, 1269.
[21] Yumatov, V. D. and Salakhutdinov, N. F. (1994). *Russ. Chem. Bull.*, **43**, 1186.
[22] Toshima, N., Yan, H., Gotoh, Y. and Ishiwatari, M. (1994). *Chem. Lett.*, p. 2229.
[23] D'Apranov, G., Leclerc, M. and Zotti, G. (1993). *J. Electroanal. Chem.*, **351**, 145.
[24] Cattarin, S., Doubova, L., Mengoli, G. and Zotti, G. (1988). *Electrochim. Acta*, **33**, 1077.
[25] Leclerc, M., D'Aprano, G. and Zotti, G. (1993). *Synth. Met.*, **55**–**57**, 1527.

[26] Sautet, P. and Joachim, C. (1990). In: "Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics"; Brédas, J. L. and Chance, R. R., Eds. (Kluwer: The Netherlands), p. 531.

[27] Lapkowski, M. (1990). *Synth. Met.*, **35**, 183.

[28] Koziel, K. and Lapkowski, M. (1993). *Synth. Met.*, **55–57**, 1005.

[29] Tanaka, Ch. and Tanaka, J. (1993). *Bull. Chem. Soc. Jpn.*, **66**, 357.

[30] Kang, E. T., Neoh, K. G., Ong, Y. K., Tan, K. L. and Tan, B. T. G. (1991). *Macromol.*, **24**, 2822.

[31] Kang, E. T., Neoh, K. G. and Tan, K. L. (1993). *Adv. Polym. Sci.*, **106**, 135.

[32] Kang, E. T., Neoh, K. G., Woo, Y. L., Tan, K. L., Huan, C. H. A. and Wee, A. T. S. (1993). *Synth. Met.*, **53**, 333.

[33] Kang, E. T., Neoh, K. G. and Tan, K. L. (1994). *Synth. Met.*, **64**, 77.

[34] Genies, E. M. and Lapkowski, M., In: Electronic Properties of Conjugated Polymers, Kuzmany, H., Mehring, M. and Roth, S., Eds. (Springer-Verlag, 1987), pp. 223–227.