J. Phys. Chem. A **1997,** *101,* 6945−6950

Substituents Effect on the Electronic Properties of Aniline and Oligoanilines

Mariana E. Vaschetto*[,†]

Fakultat fur Chemie, Universitat Konstanz, Postfach 5560, D-78434 Konstanz, Germany

Bernardo A. Retamal

Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 33040, Correo 33, Santiago, Chile

Received: December 13, 1996; In Final Form: April 7, 1997[⊗]

Aniline oligomers have been intensively studied in the past years. In particular, aniline oligomers substituted with electron-donor groups have been synthesized and its electronic properties calculated. However, when an electron-acceptor group is attached to the benzenoid ring of the oligoaniline, strong effects over its electronic properties are expected to happen. In this work some semiempirical quantum chemistry calculations of geometric structures, and energy level distribution of aniline and substituted anilines and its corresponding oligomer are presented. Geometry calculations of aniline and oligoanilines have been performed by using the PM3 and AM1 methods. Energy calculations and UV−vis spectra have been done by using the ZINDO/S-CI method. The studied substituents are methoxy, methyl, fluorine, nitro, and cyano groups, located at positions 2 or 3, in the benzenoid ring. This series of substituent groups involves a large range of $\sigma-\pi$ electron-donor−acceptor capability. The methoxy and the nitro substituted tetranilines show an interaction between the oxygen of the substitutent and the nitrogen of the oligomer through an hydrogen atom. These hydrogen bonds modify largely the structure of the oligomers. Particularly nitro groups show the strongest electrostatic attraction between hydrogen and oxygen. The cyano and the nitro groups ($\sigma-\pi$ acceptor) induce an increasing of the ionization potential. Theoretical analysis of the orbital energies of molecules substituted with electron-acceptor groups shows a lowering of the LUMO energy values larger than those in the HOMOs cases. A decreasing of the energy of the first optical transition when the electron acceptor capability of the substituent increases is shown. Tetranilines substituted with nitro groups display a band around 380 nm in the calculated UV−vis spectrum. Thus, oligoanilines substituted with electron-acceptor groups (especially nitro groups) show the lowest energy gap and they are the most encouraging material for semiconducting applications that we have studied.

Introduction

During the last decade, a great deal of research has been focused on materials containing extended π electron-systems.[1,2] In particular, the tuning of electronic and optical properties is an extraordinary challenge for materials science.[3,4] In this context, the investigation of low band gap organic systems, such as oligomers and polymers, becomes increasingly important. High intrinsic electrical conductivity, already in the reduced state, has been predicted for one-dimensional oligomeric and polymeric materials possessing a small HOMO−LUMO (highest occupied molecular orbital−lowest unoccupied molecular orbital) energy level difference (bandgap).[5,6]

Particularly, polyaniline has been studied for a long period because of its electronic properties. This compound shows an insulator to metal transition when its oxidation level increases. Although studies have been performed in polyaniline systems,[7−9] the present trend in the science of materials is concerned with the oligomeric materials. This is because these materials are easily processable and can reach crystalline states. Usually, the physicochemical properties of these compounds are able to be improved by modification in the backbone. These materials could be functionalized by adding side groups covalentely bonded.[6,10,11] Theoretical calculations permit the design of new organic systems with optimum physicochemical characteristics.

The desired characteristics for a conducting organic material are (i) small energy value of the first optical transition (ΔE HOMO−LUMO),[10] (ii) high stability,[6] (iii) good processability,[12] and (iv) large nonlinear optical response.[4] It is possible to improve these characteristics of oligoanilines in order to reach optimum values by adding side groups. Electron-acceptor groups should affect the LUMO orbital and in consequence change the ΔE HOMO−LUMO.[13] Also, this kind of substituents should increase the ionization potential (IP) and, in principle, increase the stability relative to oxidation reactions of the oligomer.[14] Usually, oligomeric systems present good processability compared to the polymeric ones.[6]

Accordingly, the first aim of this work is to explore a way to improve the electronic properties of aniline and oligoaniline in order to obtain molecules with low band gap even in the reduced state. Thus, in this work aniline monomers and oligoanilines are studied. The effect of the substituent groups placed at position 2 or 3 in the benzenoid ring are analyzed. Most of the previous calculations in oligoanilines have been performed considering symmetrical structures either by neglecting the amine terminal group or by adding a new one.[2] Although this consideration could be appropriate when the aim of the work is to calculate properties extrapolable to polymeric systems, we have demonstrated that asymmetrical chains are more realistic when the main interest is to evaluate physicochemical properties of aniline oligomers.[15]

To understand the extent of the substituents effect over the structure and electronic properties of aniline and oligoaniline, groups involving a large $\sigma-\pi$ electron-donor−acceptor capability range are studied.[16] The substituents analyzed are cyano,

---

[†] E-mail: mv1@chclu.chemie.uni-konstanz.de.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

S1089-5639(97)00029-7 CCC: $14.00

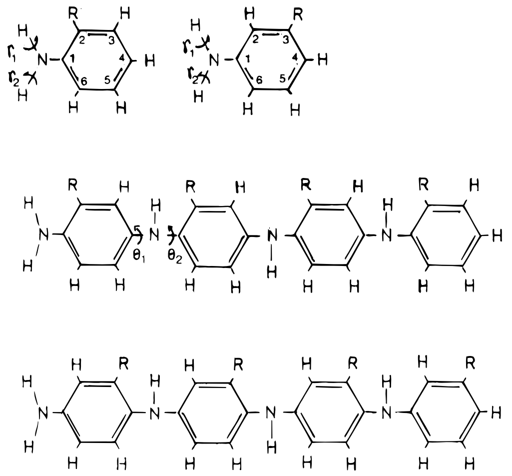

Figure 1. Schematic representation of aniline substituted at position 2 (a) or 3 (b) and tetraniline substituted at position 2 (c) or 3 (d).

nitro, methyl, fluorine, and methoxy groups. Theoretical studies performed on tetraniline and tetranilines substituted in position 2 or 3 are reported in this work. In a previous paper we have demonstrated tetranilines are good model systems in order to represent larger oligomers. Geometries of these systems are calculated by using the semiempirical PM3 method. Moreover, some data from AM1 calculations are included. Energy levels, ionization potentials, orbital picture, and UV−vis spectra of the monomers and oligomers are calculated by using the ZINDO/S-CI method. To the best of our knowledge, this kind of analysis on aniline, oligoaniline, and its derivatives has not yet been reported.

Methodology

The gas phase experimental geometries for aniline derivatives and their oligomers are not available. However, some theoretical ab inito calculations for aniline have been performed.[17] Also, some crystallographic data have been reported for the monomer and some symmetrical diphenylamines and triphenylamines in their salt form.[18] These experimental data are very useful in order to compare the obtained geometrical results from calculations to point out the quality of theoretical method employed.

Geometries of the monomers and oligomers have been optimized by using the semiempirical parametrization method 3 (PM3).[19] Also, results obtained from the Austin Model 1 (AM1)[20] method have been included in order to compare some data obtained from PM3 calculations. Both methods are based on the NDDO aproximation. The qualities of these methods have been largely proved.[21−23] Initially, an aniline molecule was optimized. Then, two optimized aniline molecules were coupled to generate the dimer. After that, the geometry optimization of the dimer was performed considering different fixed torsion angles between ring moiety and the adjacent N−C−C backbone (θ_1 or θ_2 in Figure 1). Torsion angle values were varied 15° each time among 0 and 90°. The following structures were generated by the consecutive addition of one optimized aniline molecule to the most stable dimer, trimer, and tetramer structure resulting from previous calculations. The substituted structures were generated by removing one hydrogen from position 2 or 3 respectively of the ring and replacing it with the corresponding substituent (see Figure 1). After that, these structures were totally optimized without geometry restrictions. When the substituent studied is the nitro group, a rotation around carbon (from the ring) nitrogen (from nitro group) bond is possible. Therefore, several initial positions were adopted and then optimized. This consideration was also performed with methoxy group. The most stable structure is the one where hydrogen bonds (mainly due to an electrostatic attraction) are present between the oxygen of the substituent groups and the hydrogen from amine groups (see Figure 2). Once obtained, the optimized geometrical structures, calculation of energy orbital distribution, and UV−vis spectra are performed by using Zerner's intermediate neglect differential overlap (ZINDO/S-CI) method[24] with up to 160 singlet configurations. ZINDO/S-CI has been specifically parametrized to describe the UV−vis optical transition of organic molecules. The theoretically obtained wavelengths were broadened with Gaussians of width = 14 nm to yield a comparison with the experimental data.

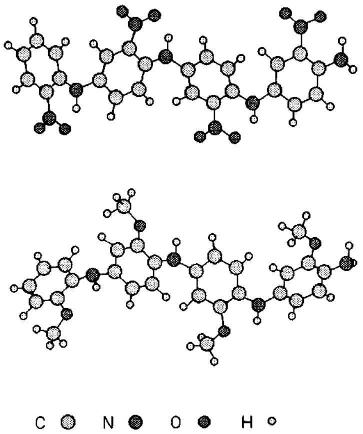

Figure 2. Tetrakis(2-methoxyaniline)- and tetrakis(2-nitroaniline)-optimized structures. Dotted lines indicate hydrogen bridges.

Results and Discussion

In the literature, most of the molecular orbital calculations reported for aniline oligomers have been performed on the basis of symmetrical model systems.[2,25] Also, a systematic theoretical study for substituted oligoanilines has not yet been performed. This kind of studies is very important in the material design field. Calculations of aniline, oligoanilines, and its derivatives (without symmetry constraints) should provide relevant information about the influence of the substituent groups on their physicochemical properties.

Figure 1 shows some of the studied systems. Structures **A** and **B** correspond to the aniline monomer and its derivatives substituted in position 2 or 3, respectively, and structures **C** and **D** correspond to the tetramers substituted at the same positions. Also dimer and trimer structures have been calculated.

The electronic and optical properties of a conducting compound are intimately related to its geometrical arrangement.[15−17,26] In Table 1 some geometrical parameters for *aniline and its derivatives* calculated by using PM3 and AM1 methods are introduced. Geometrical parameters are strongly affected by the electronic characteristics and the exclusion volume of the substituents. In previous work[15] we have defined a parameter called "bond alternation" (Δr). It corresponds to the difference between the bond lengths, of the largest and the shortest, C−C bonds in the benzenoid rings. When Δr is smaller than 0.030 Å, the ring is considered an aromatic-like structure. If Δr is larger than 0.080 Å, this ring is considered a quinoid-like structure. Zerbi et al.[26] have extensively studied the relationship between the electronic delocalization length, the structure, and the vibrational spectra of several oligomers that contain a network of delocalized π electrons. They have introduced an "effective conjugation coordinate" (ECC) instead of the param-

TABLE 1: Amine Terminal Group Torsion Angles ($\gamma 1$ and $\gamma 2$) and Bond Alternation (Δr) of Monomers Calculated by Using PM3 Method, Except when Indicated (see Figure 2)

	$\gamma 1$(deg)	$\gamma 2$(deg)	Δr (Å)
aniline	29.98	154.95	0.0136
2-methylaniline	31.72	156.38	0.0210
3-methylaniline	29.84	154.4	0.0118
2-methoxyaniline	16.99	147.84	0.0352
2-methoxyaniline[a]	16.50	146.98	0.0360
3-methoxyaniline	30.47	155.33	0.0165
2-fluoraniline	30.25	155.7	0.0235
3-fluoraniline	29.48	156.05	0.0159
2-cyanoaniline	27.97	155.09	0.0235
3-cyanoaniline	28.31	154.50	0.0156
2-nitroaniline	20.61	156.00	0.0667
2-nitroaniline[a]	8.31	174.34	0.0549
3-nitroaniline	25.15	154.21	0.0164

[a] Data obtained from AM1 calculations.

eter u (dimerization parameter). They labeled the ECC as R mode. The corresponding vibrational parameter F_R gives a measure of the effective conjugation, and it has been shown to be directly related to the parameter λ (pinning parameter) and indirectly to the phonon−electron coupling. Their calculations have indicated that F_R is linear with energy gap for oligomers. The parameter F_R could be directly related to the Δr introduced by us. In general, reduced structures show aromatic characteristics, $\Delta r < 0.030$ Å (in agreement with data obtained form ab initio calculations and microwave spectroscopy[17,18]), except when the substituent is a nitro group which displays $\Delta r > 0.040$ Å (nitro is a strong electron-acceptor group).[2] In this case, the benzenoid ring remains as a quasi-charged structure and large distortions in the C−C bond lenghts are displayed.

Figure 2 shows the optimized geometries of tetramers substituted with nitro and methoxy groups. When these substituents are placed at position 2 in the benzenoid ring, it is possible to observe an interaction between the hydrogen of amine group and the oxygen of the substituent. This interaction is remarkable in tetrakis(2-nitroaniline). Calculated geometrical parameters show a distance between −O and −H approximately of 1.8 Å; meanwhile the angle N−H···O is around 135° and finally the torsion angle is near 10°. In an hydrogen bond the partial charges of the participating nitrogen and oxygen atoms affect the length and the strength of these bonds. Thus, hydrogen bonding is primarily an electrostatic phenomenon, and quantum mechanics calculation provides good geometries and energies for such systems.[21,22,27] Because this phenomenon in tetrakis(2-nitroaniline) the oxygen interacting whith the hydrogen displays more negative charge than the second oxygen of the nitro group. For tetrakis(2-methoxyaniline), an interaction through an hydrogen bond is also present. *However, in that case it seem to be favorless than in the tetrakis(2-nitroaniline).* For oligoanilines substituted with methoxy, geometrical parameters show a distance between −O and −H around 2.3 Å; meanwhile, the angle N−H···O is around 108° and finally the torsion angle is near 18°. Intramolecular hydrogen bonds have already been reported.[21,22,27] Particularly, Khalil et al.[21] have described the formation of intermolecular and intramolecular hydrogen bonds of the form $X \cdots H \rightarrow Y$ (X, $Y = N, O$), which exert profound conformational influences on organic molecules. They have presented a comparison between MNDO/M (version of MNDO which has an improved core−core repulsion term for H···O and H···N) and AM1 method. These calculations suggest the AM1 method closely reproduces the experimental geometry of molecules showing intramolecular hydrogen bonds, while MNDO/M overestimates the hydrogen bond distance and underestimates the angle. In our case, AM1 results are introduced in order to compare the data obtained by using PM3 method. When intramolecular hydrogen bonds are present, differences between the calculated structural parameters by using AM1 and PM3 methods are observed (see Table 1).

Table 1 displays some geometrical parameter of the studied monomers. $\gamma 1$ and $\gamma 2$ are the corresponding torsion angles of hydrogens of the amine terminal group. These are defined as the angle described by H−N−C1−C2 (see Figure 1). In aniline, the nitrogen atom is located out of the benzene plane and the torsion angle defined by N−C1−C2−C3 has a value of 5.37°. Table 1 shows there exists a twisting of $\gamma 1$ and $\gamma 2$ in 2-methoxyaniline and 2-nitroaniline. This effect is associated with the intramolecular hydrogen bond formation. When the substituents (nitro or methoxy) are rotated with respect to the benzenoid ring, a torsion barrier of energy appears. The energy values of these barriers are lower than 6 kcal/mol in both cases.

Also, most of the *oligoanilines* shows $\Delta r < 0.030$ Å. Consequently, all studied oligomers show aromatic-like rings. The obtained results are in agreement with the diphenylamines crystallographic data introduced by Hlavata et al.[18] who pointed out that the average lengths of the shorter C−C bonds (1.38 Å) and the longer ones (1.41 Å) are closer to the C−C benzene bonds (1.395 Å) than to the C−C bond lengths in benzoquinone (1.32 and 1.48 Å), respectively. Similar data have been reported by Shacklette et al.[18] From our calculations, in oligoanilines special geometric features take place when the considered substituents are the nitro or the methoxy groups (as in the monomer case). In these cases Δr's > 0.030 Å are displayed. Therefore, these substituents induce a reduction in the aromaticity of the benzenoid ring. According to the classification of substituents performed by Jug et al.,[16] the nitro group is a strong σ and π electron-acceptor. Therefore, the large Δr observed in this case could be explained by the capability of this group to accept electrons. (Rings can stand larger positive charge density; this fact produces the C−C bond length distortion.) Also, the hydrogen bond formation between the oxygen of the substituent group and the hydrogen of the related amine group could contribute to this distortion.[21,22,27,28] The methoxy and the nitro groups show an arrangement of a five-member-ring (methoxy) or six-member-ring (nitro) fused to the benzenoid ring (see Figure 2a,b). Therefore, distortions in their Δr and in their torsion angles are evidenced. Although in crystalline arrangements these quasi-rings fused to the chain could be less important by interactions in the solid state, in gas phase these hydrogen bonds should be observed.

From torsion angles of hydrogen of the amine terminal groups ($\gamma 1$ and $\gamma 2$), it is possible to deduce the contribution from the p_z orbital of the nitrogen to the π system of the aniline. The nitro group induces an additional reduction of about 5−7° (cyano group induces one of about 4°) in these torsion angles. In these cases, due to the deficiency of electronic density on the benzenoid ring, the p_z orbital of the amine nitrogen atom must interact with the π electronic system of the benzenoid ring (see Figure 2 and Table 1).

Toman et al. have shown experimental values for dihedral angle between the planes of benzene rings for neutral diphenylamines between 61 and 65°.[18] Previous theoretical studies of oligoaniline show torsion angles between adjacent benzenoid rings ($|\theta 1| + |\theta 2|$) around 60°. These studies have been performed considering all nitrogens in the same plane.[25] However, if this restriction is eliminated, the obtained values are larger than in previous cases.[25,29,30] This is because the most stable structure of tetraniline presents amine nitrogen atoms defining a quarter of helix. In most of the cases these torsion angles change when a substituent is added to the chain. This

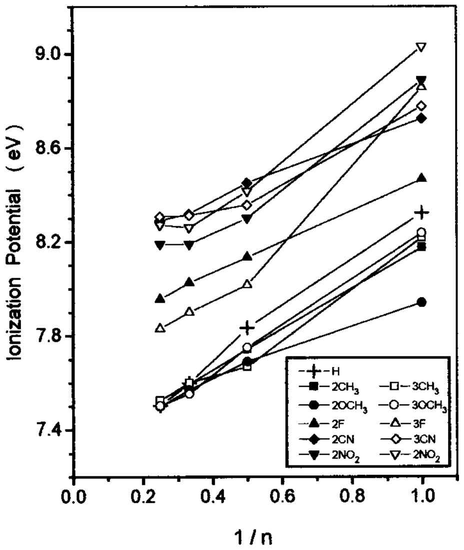

Figure 3. Calculated ionization potential for reduced structures plotted against 1/*n* (where *n* is the number of the mers in the chain). A following nomenclature is used (*i.e.*, 2-CH3, aniline (or oligoaniline) substituted with methyl group at position 2, and so on).

effect could 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.

ZINDO/S-CI calculations were performed in order to compute the orbital energy distribution. It is possible to estimate the IP by using Koopman's theorem.[31] The energy of the HOMO corresponds to the approximated IP values. The analysis of the IP has great importance because of their capability to predict the correct trends of the experimental oxidation potential.[6] The increase of the IP values is remarkable when anilines are substituted with cyano and nitro groups. This effect is a consequence of the strong $\sigma-\pi$ acceptor capabilities of these groups. The disadvantage of large IP values in oligoanilines concerns to the difficulty to arrive at oxidized states. Usually, that oxidized molecules display better electronic properties than the reduced ones. However, these large IP values obtained could prevent the degradation, produced by overoxidation, of these organic molecules. Also, fluorine substituent induces an increase of the IP. When anilines substituted with methyl group are analyzed, a decreasing of the IP is observed, in agreement with $\sigma-\pi$ donor effect showed by the methyl group. In anilines substituted with methoxy groups the expected value of IP is modified by the hydrogen bond formation.[16,21,22,27,32]

Figure 3 shows the variation of the IP with 1/*n* (being *n* the number of the mers in the chain). The effect of the substituents on the IP values in the oligomer is similar to which one displayed by them on the monomer. Zotti et al. have determined the oxidation potential of several monomers by using electrochemical measurements. They have obtained 1.03 V vs SCE for aniline, 0.88 V vs SCE for 2-methylaniline and 0.75 V vs SCE for 2-methoxyaniline.[11] These experimental results are in agreement with the trend of the IP values showed in Figure 3. As before, oligoaniline substituted with electron-withdrawing groups show the largest IP values. Therefore, their stability (vs oxidation reaction) should be the largest ones. From Figure 3 it is possible to extract the IP of the associated polymer ($1/n \rightarrow \infty$). The calculated theoretical IP values showed in Figure 3 are in agreement with experimental oxidation potentials obtained through electrochemical measurements (most of the systems have been synthesized except oligonitroaniline ones).[11,33–36] The good correlation between experimental electrochemical oxidation potentials and theoretical IP values confirms the ability of the AM1 and the PM3 methods to predict correct structures and the aptitude of the ZINDO/S to predict electronic properties. Performed calculations have shown charges on amine terminal groups are deeply influenced by the substituents added to the chain. The value of this charge density increases or decreases following the electron-acceptor or -donor capability of the substituent groups. Electronic density on amine terminal group and IP for molecules substituted at position 2 are lower than for that substituted at position 3. This is because of the largest inductive and resonant effect on the amine terminal group exists in the first case.

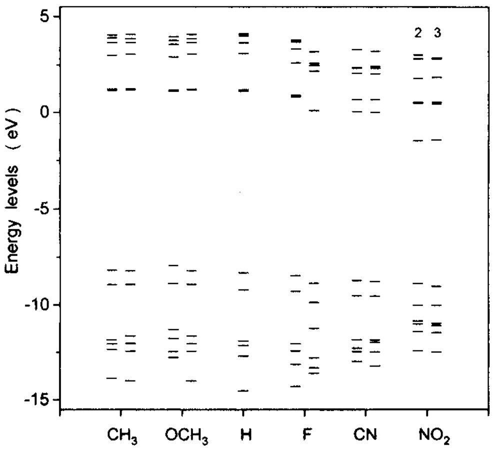

Figure 4. One-electron energies of aniline and substituted anilines. Two columns for each substituent is presented. The left one (2) correspond to the monomer substituted at position 2 and the right one (3) corresponds to the monomer substituted at position 3. The corresponding nomenclature was introduced in Figure 3.

Figure 4 shows a diagram of the six highest occupied molecular orbitals (HOMO) and the six lowest unoccupied molecular orbitals (LUMO) of the studied **monomers**. We first analyze the HOMO and the LUMO spatial distribution patterns for the monomers. Aniline HOMO shows a large contribution from the amine terminal group and from the HOMO of the benzenoid ring. Meanwhile its LUMO corresponds mainly to the benzene one.[37] These orbital patterns changes depending on the substituent added to the monomer. It is remarkable the lowering of the LUMO of cyanoaniline and nitroaniline in relation to the aniline ones. *The nitro group depicts a strong LUMO interaction between its LUMO and those from benzene.* These both two orbitals have similar energies. Therefore, perturbation between them produces a LUMO at very low energy. Similar behavior is produced by cyano substituent and to a minor extent by fluorine group. The HOMO orbital is less affected by these groups compared to the LUMO one. Our results indicate a lowering of the first optical transition. Electron-donor groups (as methyl) act over the HOMO. The p_z orbital of the carbon atom from methyl and methoxy groups interact with the aniline π system. However, this interaction is weak. It is important to point out the relevance of the hydrogen bond formation. This effect changes the values of the first optical transition because of the entire structural modification produced by them. It is known that, usually, the addition of a fused ring to the chain produces a lowering of the first optical transition.[5,38,39]

Figure 5 shows the energies of the first optical transition (from HOMO to LUMO, $\pi \rightarrow \pi^*$) of the all studied systems (monomer to tetramer). There is experimental evidence for aniline systems that shows a shift of the UV–vis band from 4.3 eV for aniline to 4.0 eV for tetraniline, achieving 3.8 eV in polyaniline.[36] That trend is in agreement with the results displayed in Figure 5. From this figure it is possible to deduce the energy of the first

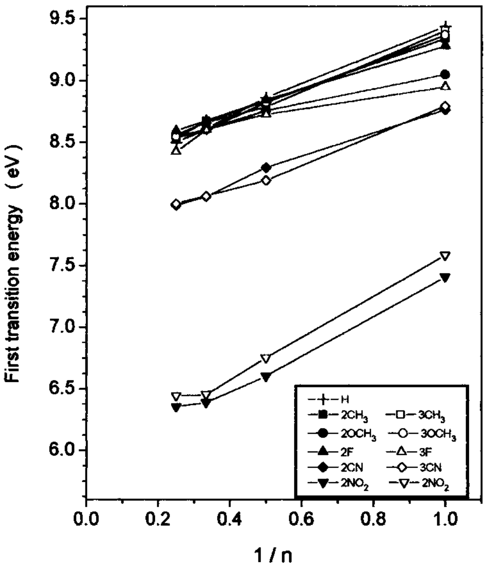

Figure 5. Calculated energies of the first electronic transition of aniline and derivatives plotted against 1/*n*, *n* being the number of mers of the chain. The attached nomenclature is introduced in Figure 3.

optical transition of the corresponding polymer. Electron-acceptor groups attached to the chain produce a lowering of the first optical transition. Orbitals involved in tetraniline transitions greatly resemble the aniline ones. General trends displayed by the monomers are kept in the oligomer cases. When the substituent is an electron withdrawing group, there is a lowering of the LUMO orbital energies larger than that in the HOMO ones. Meanwhile, if an electron-donor group is added to the chain, the first optical transition remains similar to that the oligoaniline one. The asymmetry of the tetramers under analysis (created by the presence of the only one amine terminal group) produces a breakdown of degeneracy of the HOMOs and the LUMOs (present in diphenylamine, triphenylamine, etc.).[15]

Figure 6 depicts the simulated UV−vis spectra of the aniline, its oligomers, and substituted tetranilines. Calculated aniline oligomers spectra show good correlation with the experimental ones.[36] When the number of units in the chain increases, an expected lowering of the energy of the transition located around 250 nm is displayed (see Figure 6a). The most significant result of this work is obtained when electron-withdrawing groups are added to the chain. Particularly, with nitro groups a new band around 370 nm is observed. This band is a consequence of a totally different spatial electronic distribution in these molecules. Therefore, even in the reduced state these molecules could achieve semiconductor behavior.

The obtained results for aniline and its oligomers are in agreement with experimental results reported previously by Cao et al.[36] displaying a quite good trend between both two. However, there are several parameters that hinder a quantitative relationship. Particularly, electrolyte effects existing when an experimental UV−vis measurements are performed.

In conclusions, our calculations have shown there exists a direct influence of the tetramer geometry over its electronic properties. Oligoanilines substituted with nitro and methoxy groups show hydrogen bond formation, which induces large structural distortions. Molecules having strong electron-acceptor group substituent groups display the largest quinoid character. Oligomers having the largest ring distortion show the most remarkable lowering on their Δ*E* HOMO−LUMO. Therefore, oligoanilines substituted with nitro group depict exceptional

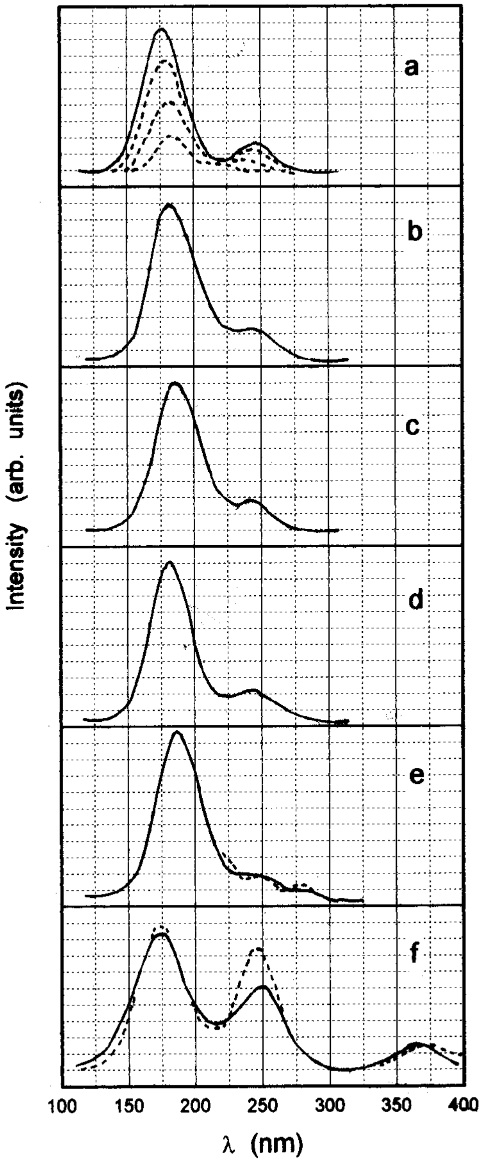

Figure 6. Calculated UV−vis spectra of tetraniline and its derivatives: (a) tetraniline (solid line), trianiline, dianiline, and aniline (dotted line); (b) tetrakis(2-methylaniline); (c) tetrakis(2-methoxyaniline); (d) tetrakis(2-flouroaniline); (e) tetrakis(2-cyanoaniline) (solid line) and tetrakis(3-cyanoaniline) (dotted line); (f) tetrakis(2-nitroaniline) (solid line) and tetrakis(3-nitroaniline) (dotted line).

electronic properties. Aditional relevant conclusions could be derivate from an analysis of oligomers at superior oxidation level.

Summary

The incorporation of substituent groups in the backbone of aniline and its oligomers (or polyaniline) creates a completely new class of compounds. These kinds of materials have shown new geometrical characteristics and electronic properties.

Strong effects exerts by the terminal amine group and the substituents over the physicochemical properties of anilines and oligoanilines are displayed. The electronic distribution and the geometrical structure of aniline and oligoanilines depend deeply of the substituent attached to the chain. In this work we present theoretical calculations of aniline substituted with cyano, methyl, methoxy, nitro, and fluorine groups. Also its corresponding oligomers are studied. Particularly three of the studied substituent are displayed the strongest effects on the physicochemical properties of aniline and aniline oligomers: (i) the first one

is the methoxy group. In this case, an hydrogen bond between the nitrogen of the terminal amine group and the oxygen of the methoxy group is generated. Therefore a five-member ring fused to the benzenoid is displayed. This effect induces large geometrical distortion of the benzenoid ring. (ii) The second substituent which displays some especial effects on these properties is the cyano group. Due its electron-acceptor capability, the benzenoid ring becomes quasi-charged. This system shows an increasing of the IP (associated with the HOMO energy). Besides, the LUMO orbitals of the benzenoid ring interacts strongly with which one from cyano group. The final consequence is a lowering of the first optical transition in this compound. (iii) The third substituent that exerts a large influence on the aniline systems is the nitro group. It displays (a) formation of hydrogen bonds between the nitrogen of the terminal amine group and the oxygen of the nitro group and (b) strong perturbation LUMO (of the nitro group)−LUMO (of the ring). Results show that oligoanilines substituted with nitro groups display excellent electronic properties. From the calculated UV−vis spectrum of this compound, a first optical transition around 380 nm is displayed. This compound would be displays semiconducting properties, even in the reduced state.

In general, substitution is a successful way to obtain new materials with useful electronic properties. The main aim of material design is to save time and effort. Consequently, this research field becomes more important every day. This paper constitutes the first theoretical approach in the evaluation of the substituents effect, like methyl, methoxy, nitro, fluorine and cyano groups, on the geometric characteristics and electronic properties of tetranilines. In our next work we will be pleased to introduce several data of these systems at superior oxidation levels.

Acknowledgment. M.V. and B.R. acknowledge the financial support of FONDECYT-CHILE. (Projects 2940001 and 2950052). The authors are largely grateful to Universitat Konstanz (Germany) facilities B.R. was a recipient of a CONICYT a doctoral fellowship. The authors thank Prof. M. L. Contreras for the critical useful suggestions. Also, we are very grateful for referees' comments and critically useful suggestions.

References and Notes

(1) Springborg, M. *Int. Rev. Phys. Chem.* **1993**, *12*, 241.

(2) Libert, J.; Brédas, J. L.; Epstein, A. J. *Phys. Rev. B* **1995**, *51*, 5711.

(3) Wan, M.; Yang, J.; Jiang, Q.; Mi, X.; Ye, P. *J. App. Polym. Sci.* **1993**, *47*, 1263.

(4) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341.

(5) Kertesz, M. *Synth. Met.* **1995**, *69*, 641.

(6) Hong, S. Y.; Kwon, S. J.; Kim, S. C.; Marynick, D. S. *Synth. Met.* **1995**, *69*, 701.

(7) Sjögren, B.; Stasftröm, S. *J. Chem. Phys.* **1988**, *88*, 3840.

(8) Huang, W. S.; MacDiarmid, A. G. *Polymer* **1993**, *34*, 1833.

(9) Lux, F. *Polymer* **1994**, *35*, 2915.

(10) Zális, S.; Kertesz, M. *Synth. Met.* **1992**, *47*, 179.

(11) D'Aprano, G.; Leclerc, M.; Zotti, G. *J. Electroanal. Chem.* **1993**, *351*, 145.

(12) For example, see: Gustafsson, G.; Inganäs, O.; Salaneck, W. R.; Laakso, J.; Loponen, M.; Taka, T.; Österholm, J.-E.; Stubb, H.; Hjertberg, T. in *Conjugated Polymers: Novel Science and Technology of Conducting and Nonlinear Optically Active Materials*; Brédas, J. L., Silbey, R., Eds.; Kluwer Academic Publishing: The Netherlands, 1991; p 315.

(13) Yumatov, V. D.; Salakhutdinov, N. F. *Russ. Chem. Bull.* **1994**, *43*, 1186.

(14) Wolf, J. F.; Forbes, C. E.; Gould, S.; Shacklette, L. W. *J. Electrochem. Soc.* **1989**, *136*, 2887.

(15) (a) Vaschetto, M. E.; Retamal, B. A.; Contreras, M. L.; Zagal, J. H.; Bulhoes, L. O. S. *Struct. Chem.* **1995**, *6*, 129. (b) Vaschetto, M. E.; Retamal, B. A.; Contreras, M. L.; Zagal, J. H. *Struct. Chem.* **1997**, *8*, 121.

(16) (a) Jug, K.; Matuschewski, M.; Köster, A. M. *J. Phys. Org. Chem.* **1993**, *6*, 645. (b) Jug, K.; Matuschewski, M. *Int. J. Quantum Chem.* **1994**, *49*, 197.

(17) Wang, Y.; Saebø, S.; Pittman, C. U. *J. Mol. Struct. (THEOCHEM)*, **1993**, *281*, 91.

(18) (a) Lister, D. J.; Tyler, J. K.; Hog, J. H.; Larsen, N. W. *J. Mol. Struct. (THEOCHEM)* **1974**, *23*, 253. (b) Hlavata, D. *Acta Crystallogr., Sect. B; Struct. Sci.* **1971**, *27*, 1483. (c) Schaklette, L. W.; Wolf, J. F., Gould, S.; Baughman, R. H. *J. Chem. Phys.* **1988**, *88*, 3955. (d) Toman, K.; Ocenaskova, D. *Acta Crystallogr.* **1966**, *20*, 514. (e) Toman, K.; Ocenaskova, D.; Huml, K. *Acta Crystallogr.* **1967**, *22*, 32.

(19) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(20) (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1993**, *113*, 5348.

(21) Khalil, M; Woods, R. J.; Weaver, D. F.; Smith, V. H., Jr. *J. Comput. Chem.* **1991**, *12*, 584.

(22) Weaver, D. F.; Khalil, M.; Smith, V. H., Jr. *J. Mol. Struct. (THEOCHEM)* **1991**, *226*, 73.

(23) Bahceci, S.; Toppare, L.; Yurtsever, E. *Synth. Met.* **1994**, *68*, 57.

(24) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223.

(25) (a) Libert, J.; Brédas, J. L. *Synth. Met.* **1993**, *55*−*57*, 4314. (b) Brédas, J. L.; Quatrocchi, C.; Libert, J.; MacDiarmid, A. G.; Ginder, J. M.; Epstein, A. J. *Phys. Rev. B* **1991**, *44*, 6002.

(26) Zerbi, G.; Gussoni, M.; Castiglioni, C. In *Conjugated Polymers: Novel Science and Technology of Conducting and Nonlinear Optically Active Materials*; Brédas, J. L., Silbey, R. Eds.; Kluwer Academic Publishing: Amsterdam, The Netherlands, 1991; p 435.

(27) Woods, R. J.; Smith, V. H., Jr.; Szarek, W. A.; Farazdel, A. *J. Chem. Soc., Chem. Commun.* **1987**, 937.

(28) Toshima, N.; Yan, H.; Gotoh, Y.; Ishiwatari, M. *Chem. Lett.* **1994**, 2229.

(29) Stasftröm, S.; Sjögren, B.; Weneström, O.; Hjertberg, T. *Synth. Met.* **1986**, *16*, 31.

(30) Ginder, J. M.; Epstein, A. J. *Phys. Rev. B* **1990**, *41*, 10674.

(31) Koopman, T. *Physica (The Hague)* **1933**, *10*, 104.

(32) Sautet. P.; Joachim, C. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Brédas, J. L., Chance, R. R., Eds.; Kluwer Academic Publishing: Amsterdam, The Netherlands, 1990; pp 531.

(33) Cattarin, S.; Doubova, L.; Mengoli, G.; Zotti, G. *Electrochim. Acta* **1988**, *33*, 1077.

(34) Leclerc, M.; D'Aprano, G.; Zotti, G. *Synth. Met.* **1993**, *55*−*57*, 1527.

(35) Sato, M.; Yamanaka, S.; Nakaya, J.; Hyodo, K. *J. Chem Soc., Chem. Commun.* **1991**, 650.

(36) Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth. Met.* **1986**, *16*, 305.

(37) Stasftröm, S.; Sjögren, B.; Brédas, J. L. *Synth. Met.* **1989**, *29*, E219.

(38) Kürti, J.; Surján, P. R.; Kertész, M.; Frapper, G. *Synth. Met.* **1993**, *55*−*57*, 4338.

(39) Kürti, J.; Surján, P. R.; Kertész, M. *J. Am. Chem. Soc.* **1991**, *113*, 9865.