A First Principle Analysis of the Structure of Oligoanilines Doped with Alkylsulfonic Acids

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The interaction of polyaniline with alkylsulfonate dopants have been investigated at the atomic level using quantum mechanical methods. Calculations have been performed on complexes formed by dopant molecules with an alkyl group ranging from methyl to nonyl and model oligoanilines of different sizes. The stabilization provided by the formation of the alkylsulfonate···oligoaniline complexes (70−90 kcal/mol) is significantly higher than that found for conventional hydrogen bonds (5−12 kcal/mol) but lower than that obtained for methylsulfate···alkylammonium and methylsulfate···Na$^+$ systems (120−135 kcal/mol). On the other hand, the influence of size of the alkyl group contained in the dopant on the interaction is practically negligible, whereas, in opposition, the number of aniline units used to represent polyaniline significantly affects the energetics of the interaction. Specifically, the interaction energy of an alkyl-dopant molecule and an infinite polyaniline chain has been predicted to be around −65 kcal/mol. The overall results allow the conclusion that the interaction between alkylsulfonate dopants and polyaniline is a very local phenomenon.

Introduction

In recent years the investigation of conducting polymers (CPs) has attracted much attention because of their unique properties and promising applications. From a theoretical point of view, a relatively large number of papers have been dedicated to study the structural and electronic properties of CPs using quantum mechanical calculations, although many of such studies mainly concentrated on thiophene, pyrrole, and their derivatives. In contrast, the number of investigations devoted to understanding the more important electronic properties of polyaniline (PAni) using sophisticated, that is, ab initio or density functional theory (DFT), quantum methods is relatively scarce.[1−9] This is an amazing feature because quantum mechanical studies have demonstrated to be very useful to rationalize the experimental observations and, as a consequence, to design new conducting materials for subsequent development. Furthermore, the industrial use of PAni has increased significantly in the past decade because of its excellent properties: high chemical and environment stability, easy processability, remarkably high electrical conductivity in the doped state, and low cost.[10]

The emeraldine base (EB) structure of PAni (PAni-EB) consists of a series of phenyl-nitrogen (Ph-N) repeating units, where the nitrogen exists in either an amine or imine environment. PAni-EB is electrically insulating but doping with acids can protonate both nitrogens giving rise to the emeraldine salt form (PAni-ES), which has levels of conductivity approaching those of metals and a large variety of potential applications.[11−15] On the other hand, it is know that dopants constituted by functionalized protonic acids, as sulfonic acids, improve the solubility of PAni-ES in standard organic solvents allowing problems related to its processability to be overcome.[16] Furthermore, this kind of dopants also results in significant electrical conductivities, such as ∼10^3 S·cm^{-1} for PAni doped with camphorsulfonic acid (CSA).[17,18]

If sophisticated quantum mechanical calculations on PAni are relatively scarce, these kinds of studies applied to polymer/dopant complexes are practically nonexistent, the majority of investigations published being carried out using simple semiempirical techniques. Among the few papers dealing with the application of full ab initio or DFT methods to PAni-ES/dopant complexes, the works of Foreman and Monkman,[5] Valera-Álvarez et al.[6] and Yang et al.[7] stand out for different reasons. Foreman and Monkman[5] applied DFT methods on reduced model systems to investigate the influence of intermolecular hydrogen bonds between PAni and CSA on the molecular and electronic structure of the complex. Calculations showed that the hydrogen bond between the amine and sulfonic acid groups increases the ability of the phenyl−nitrogen−phenyl backbone to transfer electron density. On the other hand, Valera-Álvarez et al.[6] used DFT methods with periodic boundary conditions to explore the electronic mechanisms responsible for increasing the electrical conductivity of PAni upon protonation. Finally, in a very recent study, Yang et al.[7a] analyzed the electronic structure of oligoanilines after doping with hydrochloric acid and CSA. Results indicated that the latter dopant induces more charge transfer than the former one explaining the differences found in the electrical conductivity of PAni when it is doped

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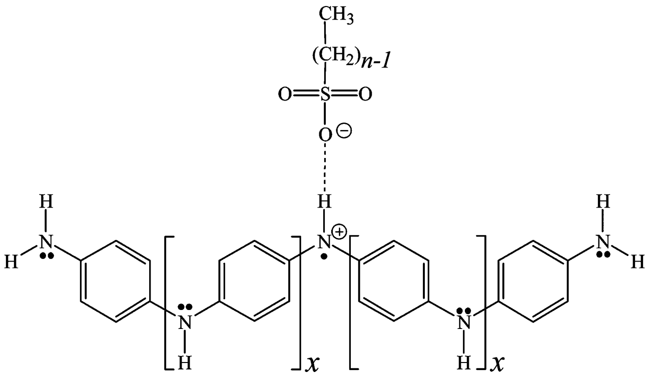
SCHEME 1



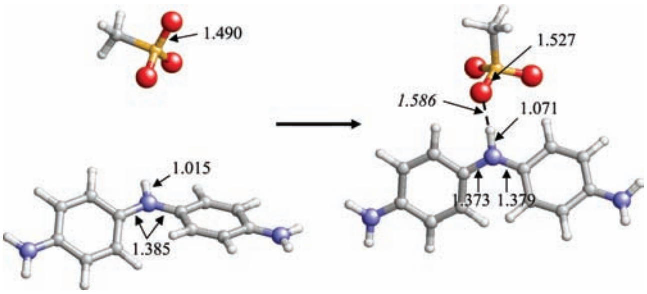


Figure 1. Molecular geometries optimized at the UB3LYP/6-31G(d) level of the methylsulfonate···2-PAni complex and the corresponding isolated fragments. The more relevant bond lengths (in Å; plain text) and the intermolecular distances (in Å; italic) are explicitly indicated.

with hydrochloric acid or CSA. On the other hand, it should be mentioned that the interaction of PAni with alkylsulfante anions parallels some chemical coloring processes observed in organic dyes, even though the aims of the theoretical investigations reported on such topics were mainly concentrated on the interpretation of the absorption spectra.[19]

Following our recent work about the molecular and electronic properties of the different forms of PAni[8] and taking into account the lack of theoretical studies on complexes, we are motivated to deal with the study of the interaction between different alkylsulfonate anions and PAni-ES. Specifically, we have examined the influence of the dopant in the complexation process, particularly in charge transfer, applying first principle quantum chemical methods on model oligomers. Furthermore, results have allowed the determination of the influence of both the length of the alkyl group of the dopant and the size of the model used to describe the polymer chain on the properties of the complex. To address these topics, we considered different alkylsulfonate anions, in which the alkyl group ranged from methyl to nonyl, and oligoanilines involving from two to six phenyl rings in the chain. We hope that these findings will contribute to get a deeper insight into the properties of this important CP when is doped with protonic acids.

Methods

To model the interaction between PAni-ES and alkylsulfonate anions, polymer chains were described using model molecules in the radical cation state that involved two, four, or six Ph cycles blocked at the ends by nitrogen atoms in the amine form (Scheme 1). These structures, which correspond to $x = 0$, 1, and 2 in Scheme 1, have been denoted as 2-, 4-, and 6-PAni, respectively, that is, $(2x + 2)$-PAni. The dopant anions considered in our calculations were the methyl-, ethyl-, propyl-, pentyl-, heptyl-, and nonyl-sulfonate anions, which correspond to the chemical structures with $n = 1$, 2, 3, 5, 7, and 9 in Scheme 1, respectively.

Initially, all the oligoanilines and alkylsulfonate anions were submitted separately to complete geometry optimizations in the gas-phase, frequency analyses being carried out to verify the nature of minimum state of the resulting stationary points. Next, the interaction between dopant and the PAni-ES model molecules was considered by approaching the anions to the reactive center of oligoanilines and performing full geometry optimizations without symmetry restrictions of these complexes. All calculations were performed at the DFT level of theory using the Becke's three-parameter hybrid functional (B3)[20] combined with the expression developed by Lee, Yang, and Parr (LYP) for the nonlocal correlation.[21] The unrestricted formalism of this exchange-correlation functional (UB3LYP) was combined with the 6-31G(d) basis set.[22] This theoretical level is able to describe accurately the structural characteristics of the doped and undoped forms of PAni.[8]

The geometric parameters used to define the nonbonding interaction between the alkylsulfonate anions and $(2x + 2)$-PAni, i.e. S−O···H−N interaction, are the O···H distance ($d_{O\cdots H}$) and the ∠O···H−N angle. The interaction energies, ΔE_{int}, were evaluated as the difference between the energy of the complex and the sum of the energies calculated for the isolated fragments. The basis set superposition error (BSSE) derived from the use of a limited basis set was taken into account by correcting the ΔE_{int} values with the counterpoise method,[23] which gave rise to the counterpoise corrected interaction energies, $\Delta E_{int,CP}$.

The distribution of charges in the alkylsulfonate···$(2x + 2)$-PAni complexes was evaluated by applying full natural bond orbital analyses[24,25] to the calculated UB3LYP/6-31G(d) wave functions. The occupation numbers of the natural atomic orbitals led to the NBO charges, which are more realistic than the Mulliken ones. Furthermore, partial electrostatic charges (ESP) were obtained by fitting the rigorously defined quantum mechanical molecular electrostatic potential to the Coulombic electrostatic potential. All calculations were carried out using the Gaussian 03 computer program.[26]

Results and Discussion

Dopant···PAni-ES Interaction. Initially, we analyzed the complex formed by the interaction between the smallest model molecules used to represent the alkylsulfonate anion and PAni-ES, that is, methylsulfonate and 2-PAni ($n = 1$ and $x = 0$ in Scheme 1), respectively, their more relevant structural parameters being compared with those obtained for the isolated fragments. Geometry optimizations of the complex and the fragments at the UB3LYP/6-31G(d) level led to the results displayed in Figure 1. On the other hand, the values of the interaction energies, ΔE_{int} and $\Delta E_{int,CP}$, and the intermolecular geometric parameters, $d_{O\cdots H}$ and ∠N−H···O, are listed in Table 1.

As can be seen, the strength of N−H···O−S interaction in methylsulfonate···2-PAni is significantly higher than that usually found in conventional hydrogen bonds that show $\Delta E_{int,CP}$ values typically ranging from −4 to −12 kcal/mol.[27−29] Thus, the electrostatic attraction involved in this interaction enhances the stabilization to about −85 kcal/mol. However, this value is ∼33 and ∼51 kcal/mol less attractive than those found for the methylsulfate···methylammonium and methylsulfate···$^+$Na complexes at a similar level of theory, respectively,[30] that is, the values of ΔE_{int} calculated for the latter complexes at the

TABLE 1: Relevant Intermolecular Parameters ($d_{O\cdots H}$ and ∠N−H···O in Å and deg, Respectively), Noncorrected and Counterpoise Corrected Interaction Energies (ΔE_{int} and $\Delta E_{int,CP}$ in kcal/mol), and NBO and ESP Charges of the Dopant (Q_{NBO} and Q_{ESP} in Atomic Units) for the Alkylsulfonate···2-PAni Complexes Obtained at the UB3LYP/6-31G(d) Level. In the First Column *n* Refers to the Length of the Alkyl Chain (See Scheme 1)

n	$d_{O\cdots H}$	∠N−H···O	ΔE_{int}	$\Delta E_{int,CP}$	Q_{NBO}	Q_{ESP}
1	1.586	169.9	−90.2	−85.1	−0.852	−0.804
2	1.586	169.7	−89.6	−84.6	−0.851	−0.804
3	1.586	169.9	−89.3	−84.3	−0.854	−0.809
5	1.587	169.3	−89.0	−84.0	−0.855	−0.800
7	1.588	169.6	−88.9	−83.9	−0.851	−0.798
9	1.587	169.3	−88.8	−83.9	−0.850	−0.798

MP2/6-31G(d) level were −118.5 and −135.8 kcal/mol, evidencing that the electrostatic component is smaller in methylsulfonate···2-PAni. The strength of the interaction in this complex is also reflected in the intermolecular geometric parameters, $d_{O\cdots H}$ = 1.586 Å and ∠N−H···O = 169.9°, the value of $d_{O\cdots H}$ being remarkably small.

Comparison between the geometry of the complex and that of the isolated fragments reveals that the structural changes associated to bring closer the fragments and to form the interaction are relatively small but not negligible. Specifically, the bond lengths of the N−H and S−O groups involved in the interaction increase 0.056 and 0.037 Å, respectively, that is consistent with the fact that some electrons are removed from these bonds to form the N−H···O−S interaction. Furthermore, the dihedral angle between the Ph rings and the N−Ph bond length decreases 3.7° and 0.009 Å (in average), respectively. These changes indicate that the electronic structure of 2-PAni is altered upon the formation of the complex: the N−C bond becomes intermediate between σ and π enhancing the planarity of the Ph−N−Ph backbone. These results suggest that the π-conjugation of PAni increases after interaction with the dopant ions, which is in excellent agreement with the conclusions reached by Foreman and Monkman,[5] and Yang et al.[7]

On the other hand, the charge transfer process between the dopant anion and the oligoaniline backbone was examined by summing the NBO atomic charges of methylsulfonate atoms in the complex (Q_{NBO}). Results, which are included in Table 1, indicate that the formation of the S−O···H−N interaction in the methylsulfonate···2-PAni complex involves a net transference of 0.148 e^- from the dopant to the oligoaniline (Q_{NBO} = −0.852 e^-). Similar conclusions are reached when the ESP atomic charges are considered (Q_{ESP}), the predicted net transference being 0.196 e^- (Q_{ESP} = −0.804 e^-) in this case.

Influence of the Alkyl Chain. The length of the alkyl side chain is expected to produce small but non-negligible changes in both the strength of the interaction and the charge transfer process. Thus, previous studies on ion pairs containing alkyl groups in the cation and/or the anion evidenced that the strength of the interaction decreases when the size of such groups increases.[30,31] In this work the influence of the size of the alkylsufonate dopant in the interaction with PAni-ES has been examined considering complexes formed by 2-PAni (x = 0 in Scheme 1) and dopant molecules involving methyl, ethyl, propyl, pentyl-, heptyl-, and nonyl alkyl groups (n = 1, 2, 3, 5, 7, and 9 in Scheme 1). Table 1 summarizes the results obtained for these complexes at the UB3LYP/6-31G(d) level.

The intermolecular geometric parameters for the S−O···H−N interaction were very similar for the six optimized complexes. Thus, the largest difference in the values of $d_{O\cdots H}$ and ∠N−H···O is 0.002 Å and 6°, respectively. This feature is reflected in Figure 2, which shows the nonylsulfanate···2-PAni complex. As can be seen, no significant differences are found with respect to the complex with methylsufonate. On the other hand, it should be emphasized that the relative orientation of the nonylsulfonate with respect to the 2-PAni molecule in the optimized complex is completely different from that used as starting point, in which the alkyl chain of the former was arranged perpendicularly to the backbone of the latter. Thus, long alkyl groups adopted a tilted arrangement upon geometry optimization, which was not detected in the complexes involving methyl- and ethylsulfonate.

Inspection to the ΔE_{int} and $\Delta E_{int,CP}$ values, which are listed in Table 1, indicates that the strength of the interaction decreases by less than 1.5 kcal/mol when the size of the alkyl group grows from methyl to nonyl. This behavior is consistent with that found for alkylsulfate···ethylammonium complexes, in which the energetic of the binding did not undergo any significant alteration upon increasing the size of the alkyl group from methyl to heptyl.[30] In contrast, the strength of the interaction in methylsulfate···alkylammonium complexes was predicted to decrease 4.0 kcal/mol at the MP2/6-31G(d) level when the alkyl group increases from methyl to butyl.[30] Similarly, the interaction energy calculated for acetate···trimethylalkylammonium complexes decreases 2.4 kcal/mol when the alkyl group increases from methyl to butyl.[31] The overall of these results indicate that the influence of the alkyl group in the strength of the interaction is lower when it is attached to the anion, as in the present case. On the other hand, comparison between ΔE_{int} and $\Delta E_{int,CP}$ values shows that the BSSE energy represents ~5.6% of the interaction energy. Interestingly, this correction is almost constant, that is,

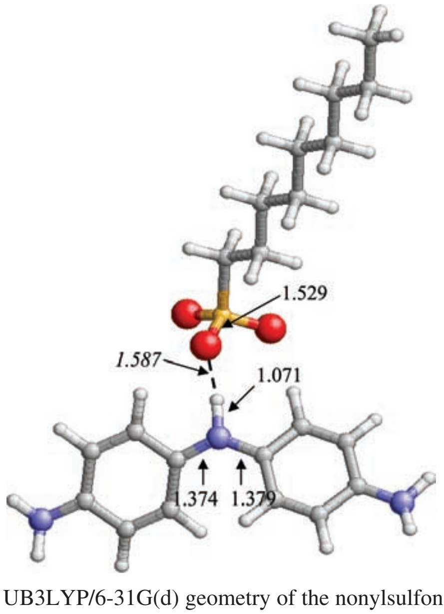


Figure 2. UB3LYP/6-31G(d) geometry of the nonylsulfonate/2-PAni complex. Some bond lengths (plain text) and the hydrogen bond distance (italics) are explicitly indicated in Å.

TABLE 2: NBO Charges (in Atomic Units) Calculated at the UB3LYP/6-31G(d) Level of Calculation for the Different Fragments of Alkylsulfonate (See Text) in Both the Isolated State (Plain Text) and Complexed with 2-PAni (italics). In the First Column *n* Refers to the Length of the Alkyl Chain (See Scheme 1)

n	CH_3-	$-(CH_2)_{n-1}-$	$-CH_2-$	$-SO_3$	total
1	−0.278/*−0.189*	–	–	−0.722/*−0.663*	−1.0/*−0.852*
2	−0.018/*0.016*	–	−0.266/*−0.206*	−0.716/*−0.661*	−1.0/*−0.851*
3	−0.031/*0.001*	0.005/*0.010*	−0.269/*−0.208*	−0.707/*−0.657*	−1.0/*−0.854*
5	−0.014/*0.002*	−0.014/*0.002*	−0.264/*−0.204*	−0.704/*−0.655*	−1.0/*−0.855*
7	−0.007/*0.004*	−0.025/*0.004*	−0.264/*−0.203*	−0.704/*−0.656*	−1.0/*−0.851*
9	−0.002/*0.005*	−0.031/*−0.001*	−0.264/*−0.204*	−0.703/*−0.655*	−1.0/*−0.850*

~5 kcal/mol, for all the alkylsulfonate···2-PAni complexes investigated in this work. It should be noted that the B3LYP functional used in this work provides a reliable qualitative description of the interaction energies, as was recently demonstrated by comparing MP2 and B3LYP interaction energies for similar complexes.[32]

Without doubt an important question related to the doping process is the amount of charge transferred between the interacting systems. The total charge, Q_{NBO} and Q_{ESP}, of the alkylsulfonate molecules, once complexes are formed, is gathered in Table 1. In all cases Q_{NBO} and Q_{ESP} are around −0.85 and −0.80 units of electron, respectively, indicating that the length of the alkyl group does not affect the charge transfer, that is, the dopant transmit ca. −0.15 to −0.20 units of electron to 2-PAni independently of the size of the alkyl group. As can be seen, the concordance between Q_{NBO} and Q_{ESP} is very remarkable. To get a deeper understanding of this somehow surprising feature we computed not only the total charge of the alkylsulfonate molecules, but also the charge on the different chemical fragments contained in these anions in both the isolated state and in the complexes with 2-PAni. For this analysis we considered it convenient to rewrite the formula of alkylsulfonates as $CH_3-(CH_2)_{n-1}-CH_2-SO_3^-$, the following fragments being examined separately: the SO_3, the $-CH_2-$ unit next to the SO_3 moiety, the terminal CH_3-, and the central aliphatic segment $-(CH_2)_{n-1}-$. The NBO charges calculated in these fragments for the complexed and isolated dopants are listed in Table 2. As can be seen, results for $n \geq 1$ reveal that the negative charge of the isolated alkylsulfonate molecules is mainly concentrated in the SO_3 and the adjacent $-CH_2-$, the charge on the remaining fragments being small. Specifically, the SO_3 and the $-CH_2-$ accumulate 97−98% of the negative charge. In complexes these groups transfer ca. −0.06 and −0.05 units of electron, respectively, whereas the charge on the remaining fragments is practically zero. These results indicate that the SO_3 and $-CH_2-$ fragments are not only responsible for the accumulation of charge in alkylsulfonates but also of the charge transfer process, the role of the groups that are far from the hydrogen bond with the 2-PAni being negligible. This distribution of charges explains the small influence of the alkyl group size on both the strength of the interaction and the charge transfer. In contrast, the aliphatic segments contained in cations, rather than anions, were found to participate in these two phenomena.[30,31] It should be mentioned that ESP charges (data not shown) led to the same conclusions.

Influence of Oligoaniline Length. In the previous section we concluded that the charge transferred from alkylsulfonates to 2-PAni does not depend on the size of the alkyl group contained in the dopant. However, the influence of the size of the oligomer used to represent the polymer was not examined in such analysis. To address this aspect of the doping process, we extended calculations to complexes formed by the interaction of methylsulfonate with both 4-PAni and 6-PAni ($x = 1$ and 2 in Scheme 1).

TABLE 3: Relevant Intermolecular Parameters ($d_{O\cdots H}$ and ∠N−H···O in Å and deg, Respectively), Noncorrected and Counterpoise Corrected Interaction Energies (ΔE_{int} and $\Delta E_{int,CP}$ in kcal/mol) and NBO Charge of the Dopant (Q_{NBO} in Atomic Units) for the Methylsulfonate···2-PAni, Methylsulfonate···4-PAni and Methylsulfonate···6-PAni Complexes ($x = 0$, 1, and 2, Respectively, in Scheme 1) Obtained at the UB3LYP/6-31G(d) Level. In the First Column *n* Refers to the Length of the Alkyl Chain (See Scheme 1)

x	$d_{O\cdots H}$	$<N-OH\cdots O$	ΔE_{int}	$\Delta E_{int,CP}$	Q_{NBO}
0	1.586	169.9	−90.2	−85.1	−0.852
1	1.609	169.3	−81.4	−76.3	−0.861
2	1.627	167.3	−76.4	−71.3	−0.865

Results obtained for methylsulfonate···2-PAni, methylsulfonate···4-PAni and methylsulfonate···6-PAni complexes at the UB3LYP/6-31G(d) level are compared in Table 3, while Figure 3 shows the optimized geometry of the latter complex. The bond lengths around the interacting groups obtained for the methylsulfonate···6-PAni complex are very similar to those displayed in Figure 1 for methylsulfonate···2-PAni. Moreover, the dihedral angle between the phenyl rings next to the intermolecular interaction varies less than 1° when the oligoaniline increases from 2-PAni to 6-PAni. Indeed, the largest geometrical change appears in the intermolecular distance $d_{O\cdots H}$, which is 0.023 and 0.041 Å larger in 4-PAni and 6-PAni, respectively, than in 2-PAni (Table 3). The enlargement of the intermolecular distance was found to affect the transference of charge between the dopant and the oligoaniline. Thus, the transferred charge calculated for methylsulfonate···4-PAni and methylsulfonate···6-PAni is 0.139 and 0.135 units of electron, respectively, that is, a reduction of 0.009 and 0.013 units of electron with respect to methylsulfonate···2-PAni.

On the other hand, the enlargement of $d_{O\cdots H}$ with the size of the oligoaniline involves a significant reduction in the energetic stability of the complexes. Specifically, the ΔE_{int} ($\Delta E_{int,CP}$) values are 9.6% (10.3%) and 15.3% (16.2%) higher in methylsulfonate···4-PAni and methylsulfonate···6-PAni, respectively, than in methylsulfonate···2-PAni. Thus, the strength of the interaction decreases 8.8 and 13.8 kcal/mol when the oligonaniline increases from 2-PAni to 4-PAni and 6-PAni, respectively. It is worth noting that the $\Delta E_{int,CP}$ values displayed in Table 3 suggest a linear variation ($y = a + bx$) with the inverse of the number of phenyl rings, the value of $\Delta E_{int,CP}$ derived from such regression for a polymer chain of infinite length being −65.2 kcal/mol.

The geometric and energetic characteristics of the systems under study suggest that the interaction between alkylsulfonate dopants and PAni-ES is a very local phenomenon. This fact is also reflected by the distribution of charges in the oliganilines in complexes with methylsulfonate. Figure 4a represents the distribution of charge in the central Ph−NH−Ph fragment and adjacent Ph−NH units for 2-, 4- and 6-PAni. As can be seen,

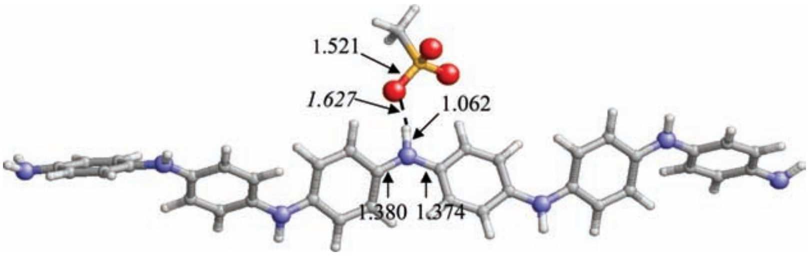


Figure 3. UB3LYP/6-31G(d) geometry of the methylsulfonate⋯6-PAni complex. Some bond lengths (plain text) and the hydrogen bond distance (italics) are explicitly indicated in Å.

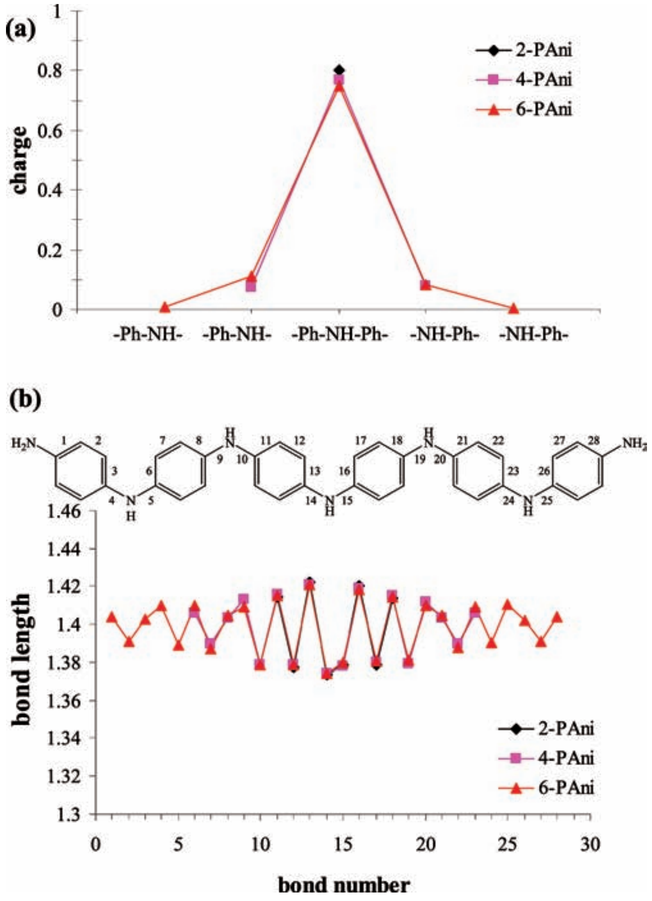


Figure 4. For the methylsulfonate⋯2-PAni, methylsulfonate⋯4-PAni, and methylsulfonate⋯6-PAni complexes calculated at the UB3LYP/6-31G(d) level: (a) NBO charges (in units of electron) of the −Ph−NH−Ph− fragment and adjacent Ph−NH− units; (b) backbone bond length pattern of the oligomers.

when going from 2-PAni to the longer oligomers the charge does not spread about the molecular chain, being localized in the central Ph−NH−Ph fragment (∼80%) without significant difference between 4-PAni and 6-PAni. This feature is also evidenced by the backbone bond length pattern (BBLP), which is provided in Figure 4b for the oligoanilines complexed with methylsulfonate. As can be seen, the BBLP of 2-PAni corresponds to a quinoid-like form that is perfectly reproduced in the central part of 4-PAni and 6-PAni, the maximum difference between the bond lengths of 2-PAni and those of 4-PAni and 6-PAni being of 0.002 Å only. Accordingly, the molecular geometry of the Ph−NH−Ph block responsible of the interaction with the dopant is not affected by the size of the oligoaniline. These results corroborate our previous investigations on different forms of PAni.[8] Thus, we concluded that the extension of the cationic defect in PAni-ES is lower than that found in other conducting polymers, such as polythiophene derivatives. In this work, in which counterions have been considered explicitly, we concluded that the doping effect in PAni-ES is more localized than it was previously predicted.[8]

Conclusions

The DFT calculations provided in this work allow us reach important conclusions about the microscopic details of the interaction between PAni-ES and alkylsulfonate dopants. First, we found that the strength of such interaction is not affected by the size of the alkyl group contained in alkylsulfonates. These results together with those reported in previous studies indicate that the role of the alkyl group in electrostatic interactions is important when it is attached to the positively charged molecule but it is negligible when it is contained in the negatively charged one. In contrast, the strength of the interaction depends significantly on the size of the model oligoaniline used to describe PAni-ES. Thus, the interaction energy decreases from −85.1 to −71.3 kcal/mol when the number of phenyl rings contained in the model compound increases from 2 to 6. Analysis of the results allows us to establish that the strength of the interaction between PAni-ES and alkylsulfonate dopants, which involves a charge transfer from the dopant to the polymer of around 0.15 units of electron, is around −65 kcal/mol. Furthermore, the distribution of the charges and intermolecular geometries indicate that the effects associated to the doping process are localized around the binding site.

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Supporting Information Available: Coordinates and energies of the complexes calculated in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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