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ScienceDirect
Polymer 48 (2007) 5431−5439
polymer
www.elsevier.com/locate/polymer

Electronic structure and conformations of *ortho*-, *meta*-, and *para*-aminobenzensulfonic acid and its dimers

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Received 21 December 2006; received in revised form 18 June 2007; accepted 19 June 2007
Available online 28 June 2007

Abstract

Geometric and electronic structures of some aniline derivatives have been obtained, aimed at a microscopic explanation of the observed electropolymerizability of these compounds. Monomers, dimers and their corresponding free radicals and ionic species, with the sulfonic acid group substituent located at various positions on the benzenoid ring, are considered. In this work we present an ab initio post-Hartree−Fock and density functional study of the *ortho*-, *meta*- and *para*-isomer of aminobenzenesulfonic acid (*ortho*-, *meta*-, and *para*-ABSA). To envisage a possible coupling scheme between ABSA molecules, we have obtained the equilibrium geometry and the electronic structure for monomers and dimers of ABSA as well as for the corresponding free radicals and ions.

Based on the monomer-optimized geometries, atomic charges, bond orders and spin densities, a coupling scheme in the electrochemical polymerization is suggested. We have also calculated band gaps and ionization potentials. Some comments concerning the different theoretical methods used are made.

Keywords: Aminobenzenesulfonic acid; Polymerization; Band gap

1. Introduction

Since 1980, when Díaz and Logan reported the electrooxidation of aniline which gives rise to an electroactive polyaniline [1], additional research has indicated that polyaniline exhibits an increase in its electrical conductivity by 10 orders of magnitude, either by simple protonation [2] or by electrochemical doping [3]. Furthermore, this material exhibits electrochromic effects, changing color from yellow to green, to blue-violet [1,2]. The reversibility of these unusual electrical and optical properties and the low cost of fabrication make this polymer very attractive for implementation in various technological devices, such as biosensors [4], light-emitting diodes [5], molecular devices [6], conducting photoresists [7], optical switches [8], smart windows [9] and others. The oxidatively activated polymerization is an efficient way of head-to-tail bond formation, in other words, a chemical bond between the nitrogen atom and the ring carbon atom at the *para* position [10].

In order for a material to be conductive, electrons must be able to flow through it. Highly conjugated polymers such as poly(acetylene) have been shown to be good conductive materials. Additional attention has been given to several classes of conductive polymers such as poly(aniline) (PANI), and many applications have been explored for them. Some aromatic polymers hold more promise as conducting polymers for commercial applications. However, their widespread use has not been successful because of low mechanical properties, poor thermal oxidative stabilities, low solubility and poor processability.

To overcome these drawbacks, two main routes have been followed. First, blending conductive and nonconductive polymers; second, by synthesizing new conductive polymers from

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doi:10.1016/j.polymer.2007.06.054

monomer analogous to those used in preparation of typical conductive polymers. In this second line of research, analogous to PANI have been obtained by polymerizing mono- and disubstitued anilines, which frequently show a low reactivity. Indeed, it has been reported that *meta*-chloroaniline could not be polymerized efficiently in the acid media [11]. More recently, it has been reported that the electrochemical synthesis of poly(*meta*-chloroaniline) (PmCLANI) films [12] and the conductive properties of PmCLANI are highly dependent on the acid–base conditions during polymerization.

A considerable amount of work related to the synthesis and application of polyaniline has been published [13]. Quantum chemistry studies on PANI have been carried out at several levels of theory, in contrast to substituted analogs which have received less attention [14]. One example of a substituted aniline is the molecule of *para*-aminobenzenesulfonic acid (*para*-ABSA) also known as sulfanilic acid. It is an important substance in the manufacture of dyes (one of which is the familiar indicator methyl orange) and medical agents as sulfanilamide, and other "sulfa" drugs. On the other hand, it has been observed that the incorporation of $-SO_3H$ groups on the aniline molecule gives specific properties to the resulting polymer such as solubility in aqueous media, electroactivity in neutral or alkaline pHs and corrosion resistance [15,16]. Also, it has been found that the electroxidation of *para* substituted anilines by the group $-SO_3H$ can form polymeric deposits on the electrode surface. This last result is apparently in opposition with that for other *para* substituted anilines with chlorides or methyl groups [12,14]. It is well established that the coupling reactions occurring during the polymerization of the aniline are head-to-tail [17] so when the *para* position is occupied, it is expected that this polymerization is inhibited.

In this work we present an ab initio study of the *ortho*-, *meta*- and *para*-isomer of aminobenzenesulfonic acid (*ortho*-, *meta*-, and *para*-ABSA) (Fig. 1). To envisage a possible coupling scheme between ABSA molecules, we have obtained the equilibrium geometry and the electronic structure for monomers and dimers of ABSA as well as for the corresponding free radicals and ions. Also reported in Fig. 1 are the energies relative to *para*-ABSA, which is the more stable isomer at the HF level.

A coupling scheme in the electrochemical polymerization is suggested based on the monomer-optimized geometries, atomic charges, bond orders and spin densities. Band gaps and ionization potentials are also calculated.

2. Theoretical details and results

The electronic structure calculations required for this study were performed utilizing the suite of programs known as Gaussian 98 [18]. To optimize the geometry of the molecules studied we use the Hartree–Fock method with a split valence basis set including d-orbitals for all the non-hydrogen atoms, 6-31G* [19]. To obtain a better estimation of the electronic properties, we include electronic correlation, first through a single point calculation with the HF geometry, using the many body Moller–Plesset theory to second order of

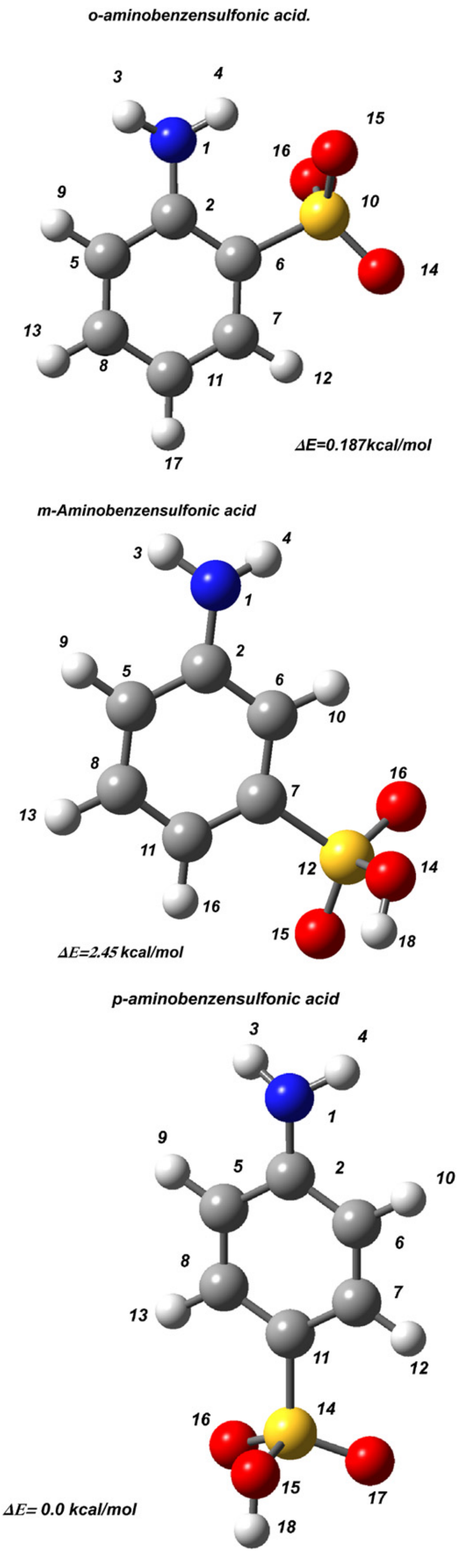


Fig. 1. Optimized equilibrium geometry of the *ortho*-, *meta*-, and *para*-isomer of aminobenzensulfonic acid, also are shown the relative energies obtained at the MP2/6-31G*//HF/6-31G* level of theory, and the atom numbering.

perturbation [20], with the same basis set 6-31G*. The terminology used to indicate a calculation of this kind is MP2/6-31G*//HF/6-31G*. To confirm our results we made fully optimized calculations with MP2/6-31G* and also density functional theory with the B3LYP functional [21] and the same basis set. Density functional theory also involves the effects of electronic correlation.

It is known that the lowest excitation energy of monomer units is related to the energy band gap between the valence and conducting bands of a polymer. Therefore, in order to design conducting polymers with low band gap, it is desirable to start with monomer units having small excitation energies. One method of estimating excitation energies is to compute it as energy difference between the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO. The dipole moment, HOMO, LUMO, gap and total energies for monomers at the MP2/6-31G*//UHF/6-31G* levels of theory are listed in Table 1.

The first molecules studied were the *ortho*-, *meta*- and *para*-isomer of the aminobenzenesulfonic acid. We report in Table 1 the minimum energy values for each isomer as calculated with and without electronic correlation. One notes that there is not a large difference between the energies of the three isomers. At the HF level, the more stable isomer is the *para* by 2.646 and 0.187 kcal with respect to the *meta* and *ortho*. The DFT highest occupied molecular orbital energy values are larger than the corresponding MP2 values by around 30%, however, they follow the same order, $ortho > meta > para$. The DFT lowest unoccupied molecular orbital energies have smaller values than the corresponding MP2 values by around 40%. Even with different sign, the MP2 and DFT LUMO energies do not follow the same order. This mismatch between MP2 and B3LYP is similar to that found before [22], and in general with the well-known fact that the DFT methods underestimates band gaps. When the electronic correlation is included in single point calculations, the isomer with minimum energy is the *ortho* by 1.518 and 1.4018 kcal relative to the *meta* and *para*, respectively. Calculations with correlation and full optimization show the same energy sequence obtained in the single point MP2 calculations, $ortho < para < meta$. The energy difference between the *ortho* and *para* conformations calculated with MP2 and DFT are 1.14 and 0.936 kcal/mol, respectively. The minimum energy conformation obtained for the *ortho*-isomer is shown in Fig. 1. There, we can see that one amine-hydrogen is near to one oxygen atom from the $-SO_3H$ group forming a stabilizing interaction. The bond distance $O_{16}\cdots H_4$ 2.057 and 2.103 Å is obtained when the geometry is optimized with B3LYP and MP2 methods, respectively. The electronic population between $O_{16}\cdots H_4$ is 0.064 and 0.032 at the B3LYP and MP2 levels, respectively. That is, with the MP2 method a smaller electronic population between O_{16} and H_4 makes the bond longer. These values suggest the existence of an intramolecular hydrogen bond between O_{16} and H_4.

From the Mulliken population analysis charges and electronic populations (in boldface) on atoms calculated without geometry restrictions and the MP2/6-31G*//HF/6-31G* method are reported in Table 2. There we observe that the carbon atoms have negative charge except C_2 to which the amine group is attached. The effect provoked by the $-SO_3H$ group is observed on the carbon atom to which the sulphur is bonded. It has the more negative atomic charge and the greater atomic population. In the *ortho*- and *para*-isomer H_9 has the smallest charge and largest atomic population with respect to the other hydrogen atoms. In the *meta*-isomer H_9 and H_{13} have similar values.

In Table 3 the total overlap population derived from the Mulliken analysis and the bond distances (in boldface) obtained with the MP2/6-31G*//HF/6-31G* model chemistry are presented. The bond distances C_2-C_5 and C_2-C_6 are similar to the experimental and theoretical values reported for benzene [23]. In the *meta*- and *para*-isomer the bonds C_5—

Table 1
Different energy values (a.u.) and dipolar moment (Debye) calculated for the isomers of the aminobenzenesulfonic acid with HF, MP2 and B3LYP methods and the 6-31G* basis set

Method	Property	*ortho*-ABSA	*meta*-ABSA	*para*-ABSA
HF	μ (D)	4.7480	5.0210	5.2970
MP2		4.8749	5.3327	5.1019
B3LYP		4.0917	4.9639	5.4487
HF	HOMO	−0.315	−0.318	−0.323
MP2		−0.318	−0.319	−0.327
B3LYP		−0.222	−0.224	−0.228
HF	LUMO	0.101	0.096	0.112
MP2		0.094	0.089	0.106
B3LYP		−0.037	−0.039	−0.027
HF	Gap	0.416	0.414	0.435
MP2		0.412	0.408	0.433
B3LYP		0.185	0.185	0.201
HF	Energy	−907.757612	−907.753694	−907.757910
$MP2_{(SP)}$		−909.353088	−909.350669	−909.350854
$MP2_{(Opt)}$		−909.360294	−909.358031	−909.358474
$B3LYP_{(Opt)}$		−911.397992	−911.394054	−911.396501

Table 2
MP2/6-31G* total atomic charges and (**atom population**)

	ortho-ABSA		*meta*-ABSA		*para*-ABSA	
1	N	−0.937 (**7.090**)	N	−0.891 (**7.038**)	N	−0.901 (**7.045**)
2	C	0.395 (**4.403**)	C	0.301 (**4.492**)	C	0.342 (**4.438**)
3	H	0.378 (**0.331**)	H	0.367 (**0.348**)	H	0.377 (**0.334**)
4	H	0.434 (**0.274**)	H	0.371 (**0.343**)	H	0.377 (**0.334**)
5	C	−0.261 (**4.996**)	C	−0.228 (**4.948**)	C	−0.260 (**4.497**)
6	C	−0.423 (**5.554**)	C	−0.222 (**4.984**)	C	−0.260 (**4.497**)
7	C	−0.154 (**4.858**)	C	−0.301 (**5.353**)	C	−0.137 (**4.832**)
8	C	−0.158 (**4.831**)	C	−0.186 (**4.873**)	C	−0.137 (**4.832**)
9	H	0.207 (**0.469**)	H	0.212 (**0.465**)	H	0.211 (**0.463**)
10	S	1.665 (**12.796**)	H	0.254 (**0.416**)	H	0.211 (**0.463**)
11	C	−0.238 (**4.946**)	C	−0.210 (**4.928**)	C	−0.363 (**5.432**)
12	H	0.264 (**0.406**)	S	1.634 (**12.793**)	H	0.261 (**0.409**)
13	H	0.218 (**0.458**)	H	0.218 (**0.454**)	H	0.261 (**0.409**)
14	O	−0.666 (**8.285**)	O	−0.765 (**8.441**)	S	1.606 (**12.789**)
15	O	−0.763 (**8.441**)	O	−0.671 (**8.293**)	O	−0.767 (**8.444**)
16	O	−0.668 (**8.295**)	H	0.254 (**0.413**)	O	−0.656 (**8.274**)
17	H	0.213 (**0.458**)	O	−0.635 (**8.236**)	O	−0.656 (**8.274**)
18	H	0.497 (**0.240**)	H	0.497 (**0.239**)	H	0.494 (**0.246**)

Table 3
Total overlap population and (**bond distances**)

Bond	*ortho*-ABSA	*meta*-ABSA	*para*-ABSA
N1–C2	0.692 (**1.371**)	0.622 (**1.391**)	0.636 (**1.378**)
N1–H3	0.666 (**0.995**)	0.664 (**0.997**)	0.670 (**0.996**)
N1–H4	0.632 (**0.997**)	0.670 (**0.997**)	0.670 (**0.996**)
C2–C5	1.094 (**1.402**)	1.127 (**1.395**)	1.115 (**1.398**)
C2–C6	0.972 (**1.404**)	1.099 (**1.390**)	1.115 (**1.398**)
C5–C8	1.128 (**1.375**)	1.116 (**1.381**)	1.093 (**1.377**)
C6–C7	1.010 (**1.395**)	1.008 (**1.385**)	1.093 (**1.378**)
C7–C11	1.114 (**1.375**)	1.051 (**1.383**)	1.011 (**1.389**)
C8–C11	1.114 (**1.392**)	1.070 (**1.387**)	1.011 (**1.389**)
C–S	0.598 (**1.735**)	0.570 (**1.766**)	0.602 (**1.744**)
S–O	1.058 (**1.588**)	1.052 (**1.589**)	1.083 (**1.595**)
S–O	0.463 (**1.426**)	0.469 (**1.427**)	0.490 (**1.426**)
S–O	1.048 (**1.425**)	1.103 (**1.419**)	1.083 (**1.426**)
O–H	0.507 (**0.953**)	0.509 (**0.953**)	0.505 (**0.956**)
C5–H9	0.762 (**1.076**)	0.758 (**1.076**)	0.762 (**1.075**)
C8–H13	0.762 (**1.075**)	0.766 (**1.075**)	0.756 (**1.073**)

H_9 and C_8–H_{13} have smaller electronic population. These hydrogen atoms are candidates which really leave molecule and result in ionic or free radical species. In this form the molecules can readily polymerize. Experimental results have shown that the *meta*-isomer polymerizes easily [24].

To our knowledge, there has been not a polymerization mechanism proposed for the polyaminobenzenesulfonic acid electrochemically obtained. This is to the fact that it is necessary to investigate different coupling possibilities for the monomers, thus, we have to consider different ionic and free radical species for each isomer. To study the cations there are two possibilities to simulate them. The first when a carbon–hydrogen bond is broken in a heterolytic way with the electronic pair remaining on the hydrogen atom, a carbonium ion ($\cdots C^+$) is formed. For the *para*-isomer there are two possibilities to form a carbonium ion by this way, namely, when the hydrogen is moved away from the *ortho* or from the *meta* position with respect to the $-NH_2$ group. Another

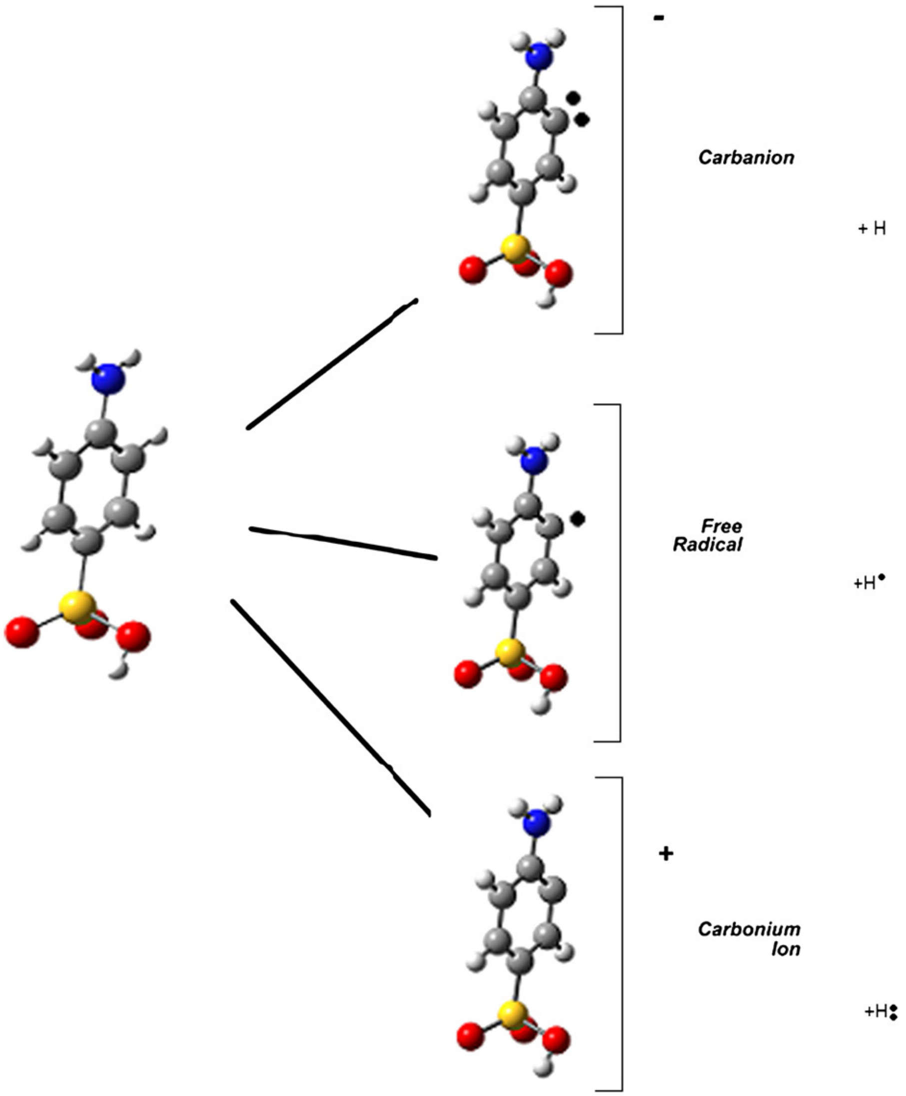


Fig. 2. Schematic representation of different possibilities of a C–H bond breaking, forming a carbonium, free radical or a carbonium ion of the *para*-aminobenzenesulfonic acid.

possibility to simulate a cation is by removing an electron from the corresponding isomer. Only the first possibility is considered in this work.

Rupture of a carbon–hydrogen bond can also occur in a homolytic way and a free radical (an unpaired (odd) electron) may in theory be produced from a molecule by loss of a hydrogen atom ($H^{\bullet}$), which, itself, may be considered as a radical because of its ‘‘odd’’ electron. If a proton is removed from the molecule, the remaining entity is a negative ion ($\cdots C:^{-}$), a carbanion. In Fig. 2, it is represented in a schematic form the rupture of a C–H bond forming three different species of the *para*-ABSA in the *ortho* position with respect to the $-NH_2$ group. We have investigated in which position is more stable for the formation of each species of *para*-ABSA. That is, from the *para*-ABSA isomer it is possible to obtain a carbanion, free radical or carbonium ion in *ortho*-NH_2 or in *meta*-NH_2 positions. For the *ortho*-ABSA and *meta*-ABSA there exists four positions where it is possible to form the ionic or free radicals species. In total, there are 10 different possibilities to form every one of the three species, however, from these possibilities, we have discarded the *ortho*-NH_2 and *ortho*-SO_3H in *meta*-ABSA, because of steric hindrance due to the presence of both groups near the site of interaction.

We report in Table 4 the total HF and MP2 (in boldface) energies obtained for the different species of *ortho*-, *meta*-, and *para*-isomer of the aminobenzenesulfonic acid (first line). In the first column are the positions where a C–H bond was broken to form a free radical, anion, or cation. These results indicate that the minimum energy conformation corresponds to the anions of *ortho*-, *meta*-, and *para*-ABSA when localized in an *ortho* position with respect to the $-SO_3H$ group, respectively, and from these results it is found that the anion of the *ortho*-ABSA is more stable. The order of stability is $E_{\text{anion}} < E_{\text{free radical}} < E_{\text{cation}}$.

The energy of formation of the free radical, ΔE, was calculated from the energetic barriers obtained by the homolytic dissociation of the bonds C_5-H_9 and C_8-H_{13} in *para*-ABSA (Fig. 3a and b). To obtain the energetic barrier the bond distance was increased by 0.1 Å from 0.85 to 1.3 Å. From there the stepsize was changed to 0.4 Å and the energy calculated in each point includes the energy of the H radical. The scan was realized with full geometry optimization at each point using the MP2/6-31G*//HF/6-31G* model chemistry. From these

Table 4
Total HF and MP2 (in boldface) energy in Hartrees calculated for the *ortho*-, *meta*-, and *para*-isomer of ABSA (first line)

		ortho-ABSA	*meta*-ABSA	*para*-ABSA
ortho-NH_2	Radical	−907.1156 **−908.6430**	−907.1136 **−908.6358**	−907.1125 **−908.6404**
	Anion	−907.1249 **−908.7354**	−907.1128 **−908.7146**	−907.1142 **−908.7190**
	Cation	−906.7943 **−908.3640**	−906.7892 **−908.3639**	−906.7924 **−908.3648**
meta-NH_2	Radical	−907.1157 **−908.6477**	−907.1138 **−908.6370**	−907.1142 **−908.6423**
	Anion	−907.1106 **−908.7058**	−907.1048 **−908.7069**	907.2298 **−908.8291**
	Cation	−906.8035 **−908.3898**	−906.7980 **−908.3864**	−906.7950 **−908.3804**
para-NH_2	Radical	−907.1139 **−908.6442**	−907.1114 **−908.6318**	
	Anion	−907.1002 **−908.7058**	−907.2302 **−908.8308**	
	Cation	−906.7989 **−908.3714**	−906.7888 **−908.3589**	
ortho-SO_3H	Radical	−907.1144 **−908.6451**		
	Anion	−907.2357 **−908.8392**		
	Cation	−906.8015 **−908.3869**		

In the first column are the positions where the C–H bond is broken to form a free radical, anion or cation. Example, the *para*-ABSA can form one of each species in the *ortho*-NH_2, and one of each species in the *meta*-NH_2 positions (last column).

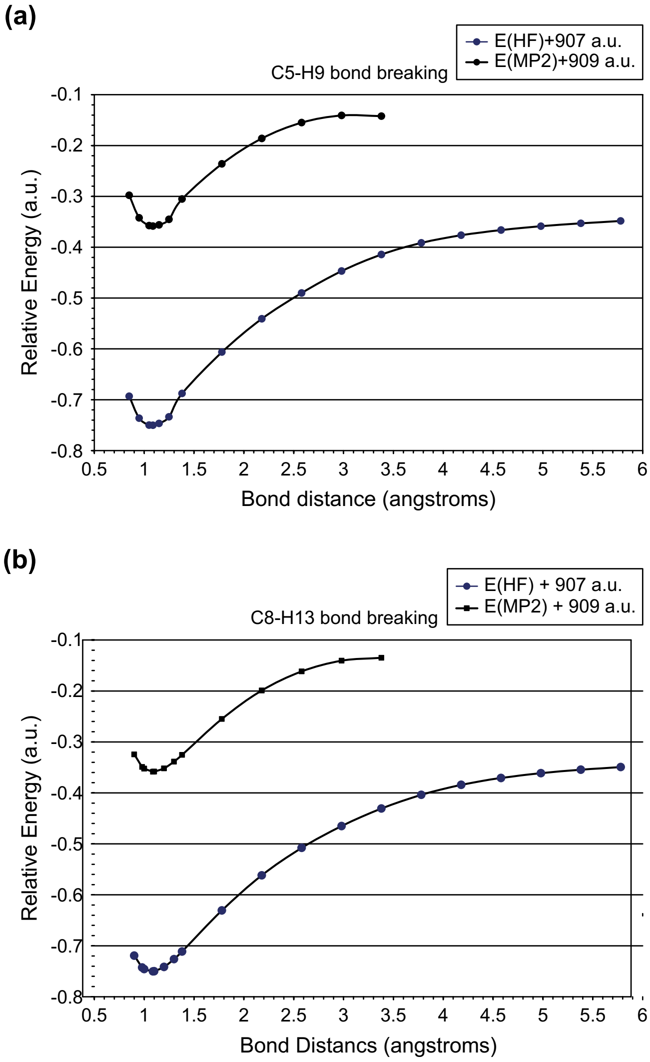
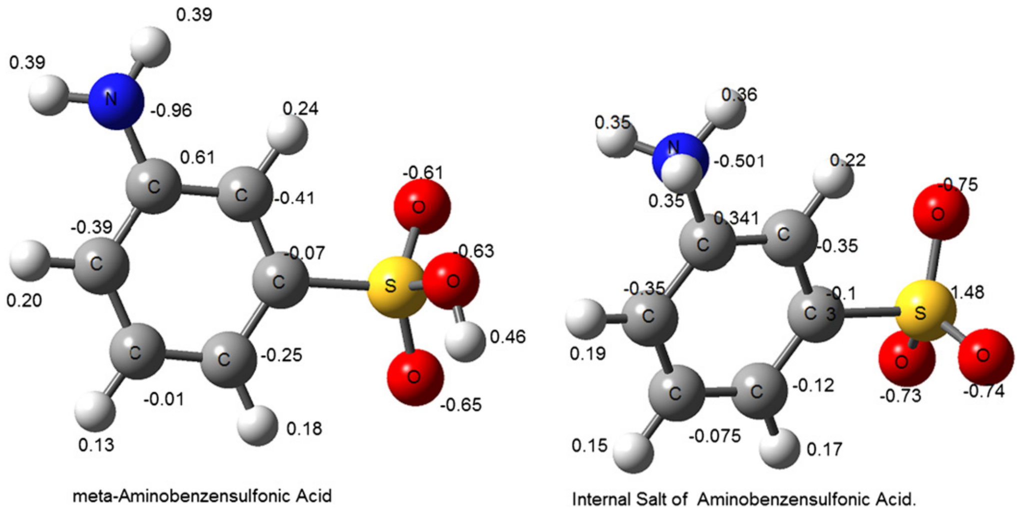


Fig. 3. Energetic barrier involved in the free radical formation of the *para*-aminobenzensulfonic acid, obtained with full MP2/6-31G* optimization in each point. (a) Rupture of the C_5-H_9 bond. (b) Rupture of the C_8-H_{13} bond.



meta-Aminobenzensulfonic Acid

Internal Salt of Aminobenzensulfonic Acid.

Fig. 4. Total atomic charges obtained from an electrostatic potential calculation, we present the *meta*-isomer of the aminobenzensulfonic acid, and its zwitterionic form.

calculations it is observed that at the HF level both bonds have an almost equal barrier, however, at the MP2 level the C_8-H_{13} bond is slightly easier to break, that is, this bond has a small energy barrier, 135.74 kcal/mol, than the corresponding C_5-H_9 bond, 140.28 kcal/mol. In a polymerization process by free radicals, the first step is the free radical formation. Thus the energetic barrier obtained in this way corresponds to an initiation step in a free radicals polymerization process for ABSA. Also in Fig. 3a and b it is observed that H_9 and H_{13} could be released with almost the same ease, the MP2 curves becomes asymptotic around 3 Å while the curves at the HF level becomes asymptotic after 5 Å. This could be because the electronic correlation is important when a bond breaks homolytically, this is in agreement with the well-known fact that the HF theory is inadequate to describe this kind of dissociation.

One factor in the bonding of two units of *para*-aminobenzenesulfonic acid could be the director character of the $-NH_2$ and $-SO_3H$ groups [25]. From this point of view *para*-aminobenzenesulfonic acid is an important and interesting compound. The presence of two substituents on the ring makes the problem of orientation complicated since the group $-NH_2$ is a strongly activating *ortho* and *para* director, while the group $-SO_3H$ is a deactivating *meta* director. It is known that the strongly activating groups generally win out over weakly activating groups [26], both groups direct to the *ortho*-NH_2 position, the $-NH_2$ activating while $-SO_3H$ deactivating. Apparently the deactivating action of the $-SO_3H$ group dominates the activating action of the $-NH_2$ group, remaining as an interaction site the *ortho*-SO_3H (*meta*-NH_2) position for the dimer formation. This is in accord with the results shown in Table 4 where the more stable species are in *meta*-NH_2 position for the *para*-isomer. For the *ortho*-isomer of ABSA, the director character of both groups compete and as a result the *ortho*-SO_3H position is favored in the formation of ionic and free radical species. In the case of the *meta*-isomer, the anion is the more stable species. In this case the orientation pattern is followed, however, the

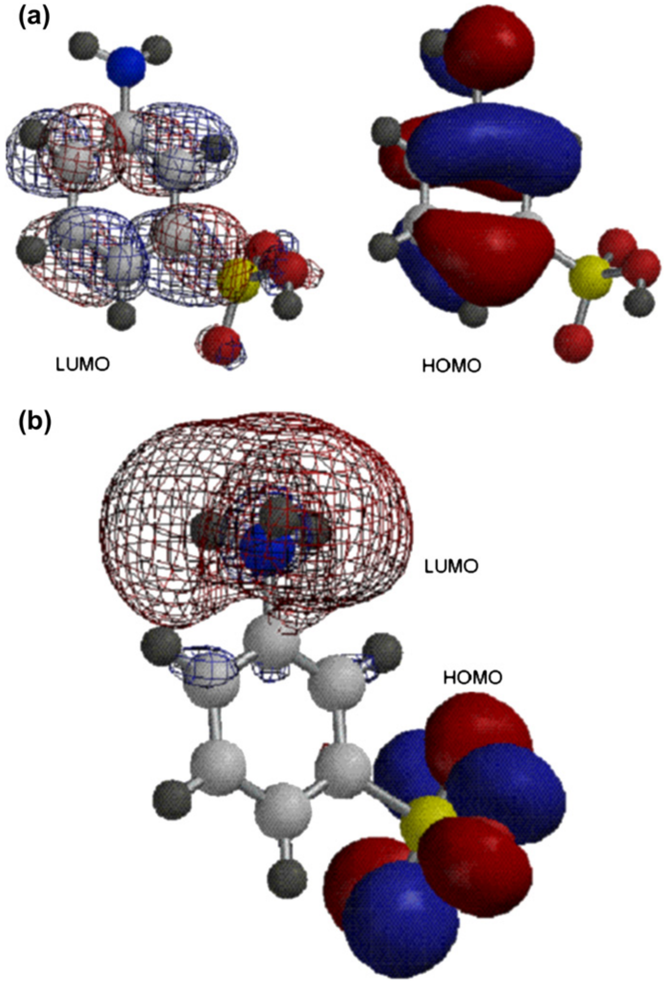


Fig. 5. (a) The lowest unoccupied molecular orbital, LUMO, (mesh) and the highest occupied molecular orbital, HOMO, (solid lines) calculated for the *meta*-aminobenzensulfonic acid. (b). HOMO (solid lines) and LUMO (mesh) calculated for the zwitterionic form of *meta*-aminobenzensulfonic acid.

minimum energy conformation for the cation and free radical is on the *meta*-NH_2 position. Both HF and MP2 methods coincide and show the same minimum energy isomers.

para-Aminobenzenesulfonic acid exists largely in the form of an internal salt but a rather special kind of salt, called a dipolar ion or zwitterion. This is a neutral valence structure which incorporates both a formal positive charge and a formal negative charge. This kind of compounds is also known as autodoped because when the $-NH_2$ group releases electrons, the $-SO_3H$ group withdraws electrons. We also studied the internal salt of the *ortho*-, *meta*- and *para*-isomer. In Fig. 4 we present the total atomic charges obtained from the electrostatic potential for the *meta*-isomer and its internal salt, with the HF/6-31G* model chemistry. The more significant changes occur

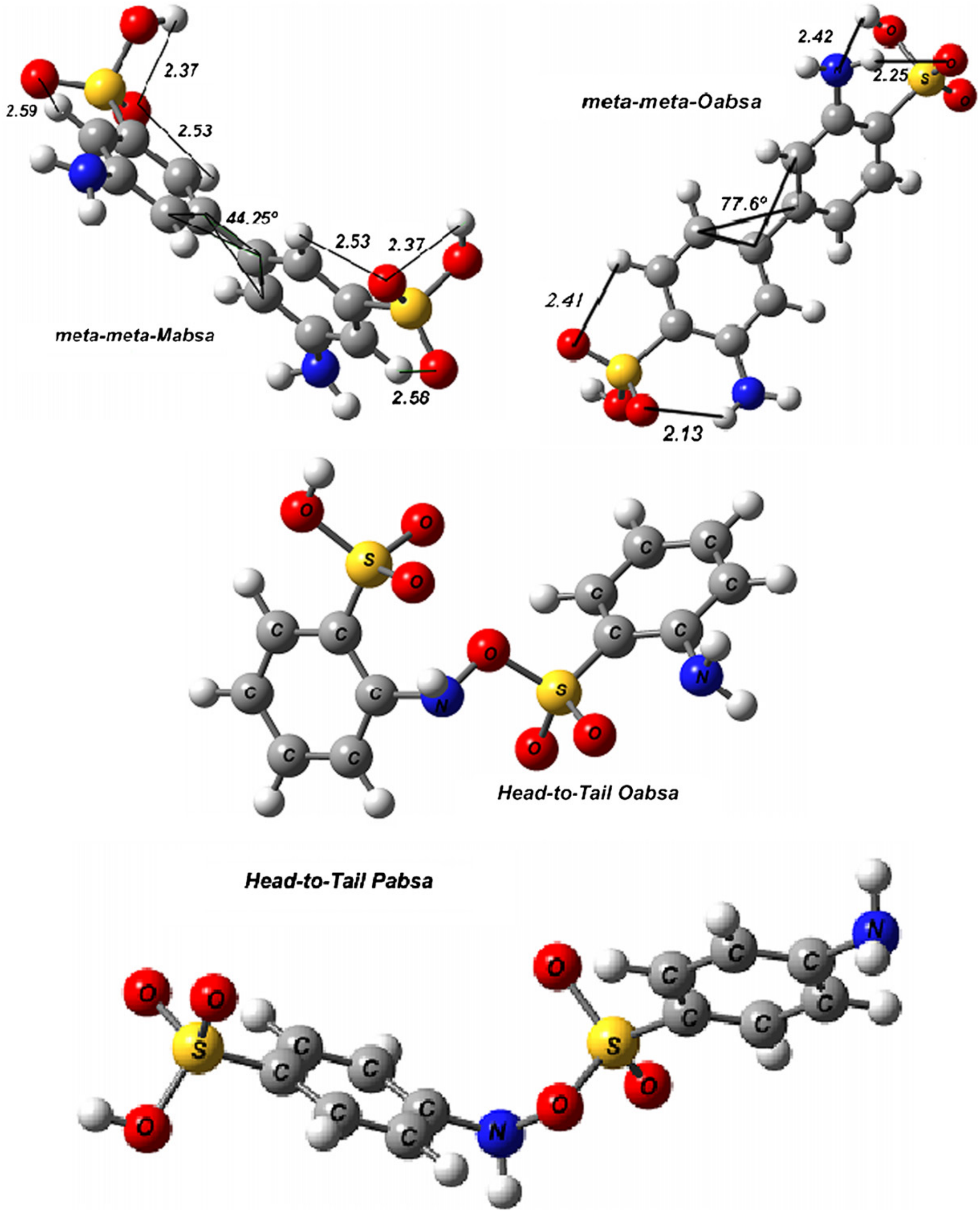


Fig. 6. Models of coupling between monomers of aminobenzensulfonic acid, each one was obtained with full optimization at the MP2/6-311G*//HF/6-31G* level of theory. (a) and (b) are dimers of the *ortho*- and *meta*-monomers bonded through the *meta* position, also are shown some bond distances in angstroms, and the dihedral angle in degrees formed between the carbon rings.

on the N−C−C−C−S−O sequence of atoms. It is also interesting to note the small negative charge on the ring atom in *meta* position in both molecules. In Fig. 5 the surfaces of the HOMO (solid lines) and LUMO (mesh) frontier orbitals, calculated for *meta*-isomer and its salt are plotted. There is a notorious difference between both plots. The HOMO of the *meta*-isomer is mainly on the ring and the nitrogen atom and the LUMO is principally on the ring and the sulphur atom. In the internal salt both orbitals are completely separated forming two regions where possible reactions with electrophilic or nucleophilic agents could occur. However, the band gap for the salt is slightly greater (0.330 and 0.222). A drastic change occurs in the dipole moment which goes from 5.36 to 21.63 D in the salt. The isomer is energetically favored by 42.6 kcal/mol with respect to their internal salt. Based on this information, the internal salt could be a candidate for two types of coupling, that is, through the *meta* carbon atom and through a head-to-tail coupling scheme. Energetically, the more stable salt is the *meta*-isomer which also has smaller band gap. The C−H bonds in the *meta* position posses the smaller electronic density.

Fig. 6 shows the equilibrium geometry of neutral dimers of ABSA after complete optimization at the MP2/6-311G*//HF/6-31G* level of calculation. These dimers could be considered as the termination step in the polymerization process. It is the result of the interaction between two free radical units. To calculate the energy of dimerization, the C−C bond between monomeric units was broken. This was done by changing the bond distance in steps of 0.04 Å from a slightly smaller value than the equilibrium distance to 4.64 Å. All the geometrical parameters were optimized at each point. The potential energy curve obtained for the dissociation of the *para*-ABSA dimer is shown in Fig. 7. For this step we calculate the energy as 123 kcal/mol. The energy of dissociation obtained in this way must be equal to the negative value of the energy calculated for the termination step. It can be seen that the energy is maximum around a distance of 3.4 Å after this value is possible considerer the bond as broken and the energy of the system is relaxed to the value of two radicals. This means that the dimer is dissociated and that the C−C bond is almost broken, the process in the opposite direction must be a dimerization process, which may be interpreted as a final step in a polymerization mechanism. On the basis of our results it can be considered that two units can be bound by their carbon ring atoms, we have considered five different types of coupling to form dimers. The joining point of both monomers is named by the position with respect to the $-NH_2$ group to which both are bonded. Moreover, the electronic structure of the internal salt suggests the possibility of strong electrostatic interactions between positive and negative regions from different monomeric internal salts leading to the dimer formation by a head-to-tail mechanism. We optimize at the HF/6-31G* level the geometry of three head-to-tail dimers obtained from two *ortho*-, *meta*-, or *para*-isomer. There is also the possibility of the coupling between different isomers, however, these will be discussed later.

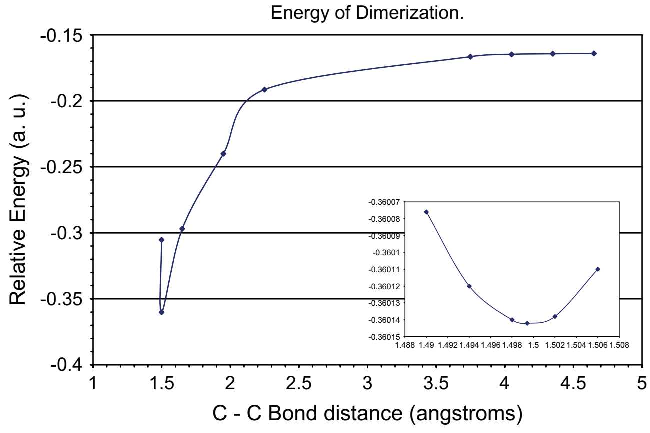


Fig. 7. Energy barrier obtained for the rupture of the C−C bond between two units of aminobenzensulfonic acid, obtained by gradually increasing the bond distance with full optimization at each distance with the MP2/6-31G* level of theory.

From the eight dimers calculated the most stable was that where the bond between units of *para*-ABSA occurs through the *ortho*-NH_2 position. The small band gap corresponds also to this dimer. The head-to-tail dimers are energetically less probable. Table 5 presents the relative energy, the dipole moment and their corresponding band gap, calculated for the head-to-tail dimers at the MP2/6-311G*//HF/6-31G* level.

3. Conclusions

Ions, free radical, internal salt, and dimers of *ortho*-, *meta*-, and *para*-aminobenzensulfonic acids have been studied using ab initio HF, MP2, and DFT theory. The molecular structure of these compounds has been obtained by means of full geometry optimization. We have simulated the initiation, dimerization and termination steps in a mechanism of polymerization. Our results show that the *ortho*-aminobenzenesulfonic acid as the minimum energy conformer independently of the model chemistry utilized, and suggest that, the *meta* conformer may be a better conductor material than the *ortho* because of its small band gap. This fact is in agreement with the experimental evidence. For the *ortho*-, *meta*-, and *para*-isomer of ABSA the anions are the more stable species. An anionic mechanism seems to be the most possible one.

Table 5
Relative HF/6-31G* and MP2/6-311G* energy of dimers, band gap and dipolar moment values are from MP2 calculations, the nomenclature followed is coupling site 1-coupling site 2-monomer unit

DIMER	ΔE_{HF} (kcal/mol)	ΔE_{MP2} (kcal/mol)	Band gap (a.u.)	Dipolar moment (D)
ortho-ortho-para-ABSA	0.0	0.0	0.370	0.827
para-para-ortho-ABSA	7.586	27.610	0.387	4.202
meta-meta-ortho-ABSA	8.365	30.898	0.379	2.451
meta-meta-para-ABSA	14.784	32.441	0.412	4.588
meta-meta-meta-ABSA	13.867	34.952	0.384	0.926
Head-to-tail-*ortho*-ABSA	45.914	80.260	0.406	9.506
Head-to-tail-*meta*-ABSA	58.084	84.344	0.401	6.044
Head-to-tail-*para*-ABSA	46.340	84.670	0.422	8.708

The dimer with the minimum energy conformation is formed when the *para*-aminobenzenesulfonic acid is bonded through the *ortho* position. This dimer also presents the small band gap and polarity. The energy of dimerization of *para*-ABSA is calculated as 123 kcal/mol, and a critical distance between monomeric free radicals of 3.4 Å. From an energetic point of view the head-to-tail polymeric coupling is less probable.

Many possibilities may be suggested for the reaction pathway followed by a monomer free radical in their approach to other free radical, but only one path is possible in the dissociated process.

The results enable us to postulate that dimerization can be reasonably studied by ab initio quantum mechanical calculations.

Acknowledgment

The authors are grateful to Dr. Robin Sagar for valuable discussions and reading of the manuscript.

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