Ab Initio and DFT Study of the Geometric Structures and Static Dipole (Hyper)polarizabilities of Aromatic Anions

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The geometries and the static dipole (hyper)polarizabilities (α, β, γ) of a series of aromatic anions were investigated at the ab initio (HF, MP2, and MP4) and density functional theory DFT (B3LYP) levels of theory. The anions chosen for the present study are the benzenethiolate ($Ph-S^-$), benzenecarboxylate ($Ph-CO_2^-$), benzenesulfinate ($Ph-SO_2^-$), benzenesulfonate ($Ph-SO_3^-$), and 1,3-benzenedicarboxylate ($1,3\text{-}Ph-(CO_2)_2^{2-}$). For benzenethiolate anion, additional α, β, and γ calculations were performed at the coupled cluster CCSD level with MP2 optimized geometries. The standard diffuse and polarized 6-31+G(d,p) basis set was employed in conjunction to the ab initio and DFT methods. Additional HF calculations were performed with the 6-311++G(3d,3p) basis set for all the anions. The correlated electric properties were evaluated numerically within the formalism of finite field. The optimized geometries were analyzed in terms of the few reports about the phenolate and sulfonate ions. The results show that electron correlation effects on the polarizabilities are very important in all the anion series. Was found that $Ph-SO_2^-$ is highly polarizable in terms of α and β, and the $Ph-S^-$ is the highest second hyperpolarizable in the series. The results of α were rationalized in terms of the analysis of the polarization of charge based in Mulliken atomic population and the structural features of the optimized geometries of anions, whereas the large differences in the β and γ values in the series were respectively interpreted in terms of the bond length alternation BLA and the separation of charge in the aromatic ring by effects of the substitution. These results allowed us to suggest the benzenesulfinate and benzenethiolate anions as promising candidates that should be incorporated in ionic materials for second and third-order nonlinear optical devices.

1. Introduction

The experimental method used to study the optical second-order nonlinearities of ionic species is the hyper-Rayleigh scattering techniques in solution.[1] The study of properties of aromatic anion species is of fundamental importance to understand the relationships between proton transfer in self-assembled monolayers on metal surfaces and nonlinear optical properties in solution[2] and in crystals.[3] However, the study of properties of isolated anions is only possible by quantum mechanic methods.[4] Despite the importance of the charged aromatic species, that can be present in many physical and chemical phenomena, few reports have been published dealing with aromatic anion properties,[5,6] and little is known about the performance of the standard theoretical methods for the characterization of the structural, spectral, electronic, and response properties of these anions.

The presence of polarizable organic ions (strong electron donor or acceptor) in crystal and solution has become an important strategy of research in nonlinear optics, mainly in problems of second-order and third-order effects characterization.[5,7] In particular, highly polarizable aromatic anions such as thiolates and carboxylates could be interesting candidates that can be incorporated in either polymer matrix or extended systems for nonlinear optical applications. In this context, we have started a theoretical research program with the aim of the characterization of the structural and electronic properties of a series of important (poly)aromatic (poly)anions, based on the presence of negative polarizable entities such as S, CO_2, SO_2, and SO_3. In the present work, we report a theoretical ab initio and density functional theory DFT study of the geometric structures, charge distribution, and static (hyper)polarizabilities (dipole polarizability α, first hyperpolarizability β, and second hyperpolarizability γ) of a series of isolated aromatic anions such as C_6H_5-G, with G = (S^-, CO_2^-, SO_2^-, SO_3^-) and $1,3\text{-}C_6H_4-(CO_2)_2^{2-}$, which will be referred as benzenethiolate (BT), benzenecarboxylate (BC), benzenesulfinate (BS), benzenesulfonate (BSO), and 1,3-benzenedicarboxylate (BDC), respectively. The α, β, and γ properties were evaluated within the finite field formalism by using energy differences. Additionally,

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CCSD coupled cluster higher level of theory is employed for the study of the BT anion properties, and the corresponding results are compared with those from other levels of theory. The calculated electrooptical properties of the series of aromatic anions are analyzed in terms of the structural and electronic variations in the aromatic ring due to the effects of the negatively charged G substituents.

2. Theory and Computational Methods

The total energy of a molecular species that interacts with an external electric field can be represented as a power series in terms of the components of the electric field:[8]

$$E(F) = E(0) - \sum_i \mu_i F_i - \frac{1}{2!}\sum_{ij}\alpha_{ij}F_iF_j - \frac{1}{3!}\sum_{ijk}\beta_{ijk}F_iF_jF_k - \frac{1}{4!}\sum_{ijkl}\gamma_{ijkl}F_iF_jF_kF_l + \ldots \tag{1}$$

where $E(0)$ is the energy of the isolated system and μ_i, α_{ij}, β_{ijk}, and γ_{ijkl} are the components of the dipole moment, dipole polarizability, first hyperpolarizability, and second hyperpolarizability tensors, respectively. We have evaluated these independent components at static regime for the studied anions by using numerical finite field FF methods,[9] and four invariants of experimental importance were obtained with the formulas

$$\alpha_{\rm ave} = \frac{1}{3}\sum_{i=1}^{3}\alpha_{ii} \tag{2a}$$

$$\beta_{\rm vec} = \beta_i = \sum_j(\beta_{ijj} + \beta_{jji} + \beta_{jij}) \tag{2b}$$

$$\beta_{zzz}^{2}({\rm HRS}) = \frac{1}{7}\sum_i \beta_{iii}^{2} + \frac{6}{35}\sum_{\substack{i,j\\ i\neq j}}\beta_{iii}\beta_{ijj} + \frac{6}{35}\sum_{\substack{i,j,k\\ i\neq j<k\neq i}}\beta_{iij}\beta_{jkk} + \frac{9}{35}\sum_{i\neq j}\beta_{iij}^{2} + \frac{17}{35}\beta_{xyz}^{2} \tag{2c}$$

$$\gamma_{\rm ave} = \frac{1}{5}\sum_{i,j=x,y,z}^{3}\gamma_{iijj} \tag{2d}$$

where $\alpha_{\rm ave}$, $\beta_{\rm vec}$, β_{zzz}^{2}(HRS), and $\gamma_{\rm ave}$ are the average of the dipole polarizability, vector of first hyperpolarizability, dominant component of the hyper-Raighley scattering first hyperpolarizability, and the scalar part of the second hyperpolarizability, respectively.

The geometries of the studied aromatic anions, whose structures and label notation are shown in Figure 1a, were fully optimized at HF/6-31+G(d,p), HF/6-311++G(3d,3p), MP2/6-31+G(d,p), and B3LYP/6-31+G(d,p) with the Gaussian 98 program.[10] Symmetry restriction was used for these optimizations (see Figure 1). To evaluate the convergence of the geometric results with respect to the employed methods and basis sets, the root-mean-square (rms) was calculated for each set of bond length values of each anion structure. The rms values are reported in the corresponding tables of the optimized geometric parameters in the section of results and discussion.

The (hyper)polarizabilities were calculated by using numeric finite field method from the energy differences at the HF/6-31+G(d,p), HF/6-311++G(3d,3p), MP2/6-31+G(d,p), and MP4/6-31+G(d,p)//MP2/6-31+G(d,p) with the GAMESS[11] program and the B3LYP/6-31+G(d,p) ones with the Gaussian 98 package and using default finite electric fields from each program. The electric field intensity used for the Gamess calculations are on the order of ±0.010 au, while the corresponding for the Gaussian program are on the order of ±0.015 au. To test the finite field method employed in this work, we also evaluated the (hyper)polarizabilities of the aromatic anions with the analytic time-dependent-Hartree–Fock (TDHF/6-31+G(d,p)) method as implemented at the GAMESS program. These TDHF calculations are coincident with those from HF/6-31+G(d,p) finite field ones. For the HF and correlated hyperpolarizability calculations performed with Gamess and Gaussian packages, the accuracy of the energy was chosen to be of 1.0×10^{-8} au. Consistency between the set of results of hyperpolarizability values from MP2 and MP4 (from Gamess with field intensities of ±0.010) and from B3LYP (from Gaussian with field intensities of ±0.015) was found, where the dependence of these results in terms of the electric field is negligible at the level of the used intensity. In fact, we are confident that the present finite field calculations are able to give accurate values for the (hyper)polarizability of aromatic anions. Additional CCSD/6-31+G(d,p) hyperpolarizability calculations were computed with the Gaussian program for the benzene thiolate $Ph-S^-$ anion. These CCSD calculations were performed in order to test the performance of the ab initio and DFT methods in the theoretical evaluation of the (hyper)-polarizabilities of charged species in the gas phase.

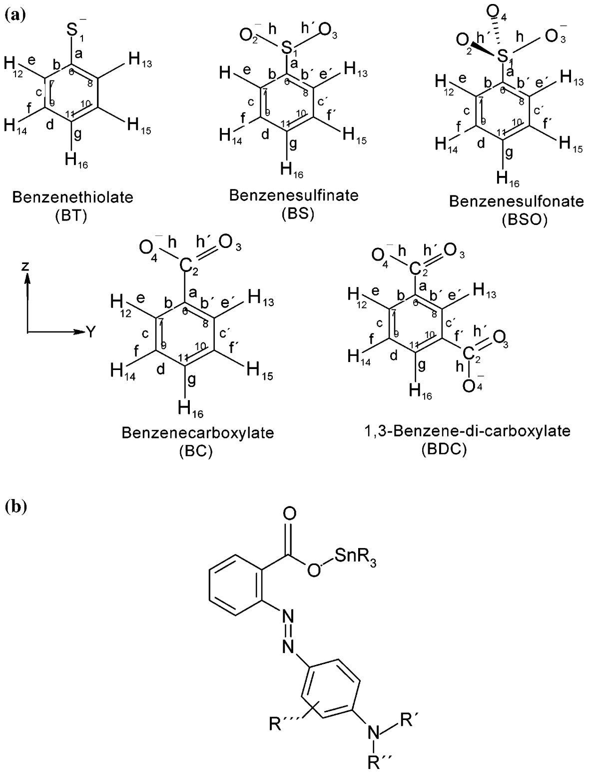


Figure 1. (a) Molecular geometries, geometric parameter labels, and orientation axis of the studied aromatic anions. (b) General schematic structure for organostannylarylazobenzecarboxylates.

3. Results and Discussion

3.1. Optimized Geometries. The benzenethiolate species $C_6H_5-S^-$ (BT) is the anion of the aromatic benzenethiol (C_6H_5-SH). The thiols are compounds that are able to interact with metal surfaces to form self-assembled monolayers (SAMs).[12] Experimentally, it has been shown that benzenethiol can be adsorbed in metal surfaces through the S atom to give an

TABLE 1: Optimized Geometric Parameters of $[C_6H_5-S]^-$, $[C_6H_5-CO_2]^-$, $[C_6H_4-(CO_2)_2]^{2-}$, $[C_6H_5-SO_2]^-$, and $[C_6H_5-SO_3]^-$, with the MP2 and B3LYP Methods the 6-31+G(d,p) Basis Set

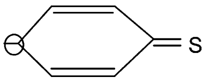
	$[C_6H_5-S]^-$ (BT)		$[C_6H_5-CO_2]^-$ (BC)		$[C_6H_4-(CO_2)_2]^{2-}$ (BDC)		$[C_6H_5-SO_2]^-$ (BS)		$[C_6H_5-SO_3]^-$ (BSO)	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
					Bond Lengths/Å					
a	1.735	1.750	1.543	1.553 1.55[a]	1.544	1.551	1.666	1.691	1.809	1.830
b	1.420	1.424	1.401	1.402 1.50[a]	1.403	1.404	1.432	1.432	1.395	1.396
b′					1.406	1.408			1.399	1.400
c	1.395	1.395	1.397	1.398 1.35[a]	1.398	1.399	1.387	1.388	1.398	1.400
c′					1.406	1.408			1.395	1.396
d	1.401	1.403	1.399	1.403 1.35[a]	1.398	1.399	1.406	1.408	1.398	1.398
d′					1.403	1.404			1.400	1.401
e	1.084	1.087	1.082	1.086	1.083	1.086	1.082	1.084	1.082	1.085
e′					1.081	1.084			1.082	1.086
f	1.086	1.090	1.085	1.089	1.088	1.092	1.086	1.089	1.084	1.088
f′					1.544	1.551			1.084	1.088
g	1.084	1.088	1.084	1.088	1.083	1.086	1.083	1.086	1.084	1.088
h			1.267	1.259 1.17[a]	1.275	1.269	1.530	1.540	1.490	1.492
h′					1.268	1.261			1.491	1.492
rms	1.334	1.339	1.293	1.296	1.323	1.324	1.350	1.357	1.344	1.348
					Bond Angles/deg					
ab	122.5	122.3	120.7	120.8 121.0[a]	119.3	119.4	120.9	120.7	120.5	120.6
ab′					122.1	122.3			119.2	119.6
bb	115.0	115.3	118.6	118.4 119.0[a]			118.2	118.5		
bb′					118.6	118.3			120.0	119.8
bc	122.6	122.2	120.8	120.9 117.0[a]	120.3	120.5	119.9	119.7	119.9	120.0
b′c′					121.6	121.9			120.0	120.1
be	117.8	117.8	117.5	117.3	117.8	117.5	118.9	119.0	118.3	118.3
b′e′					119.2	119.0			119.1	119.1
ce	119.6	119.9	121.7	121.7	121.9	121.8	121.2	121.3	121.7	121.7
c′e′					119.2	119.0			120.9	120.8
cd	120.9	121.1	120.3	120.1 124.0[a]	120.5	120.2	122.1	122.1	120.3	120.2
c′d′					118.6	118.3			120.2	120.2
cf	119.2	119.2	120.0	120.0	119.7	119.8	118.2	118.3	119.8	119.8
c′f′					122.1	122.3			119.8	119.8
df	119.9	119.7	119.8	119.8	119.7	119.8	119.7	119.6	119.9	120.0
d′f′					119.3	119.4				
ah			115.2	115.4	115.7	115.8	117.8	117.8	103.6	104.0
ah′					116.5	116.8			114.6	114.5
f′h					115.7	115.8				
f′h′					116.5	116.8				
hh			129.5	129.2 126.4[a]			124.4	124.3		
hh′					127.8	127.3			114.2	113.9

[a] Experimental from X-ray crystallographic data for tri-*n*-butylstannyl-2[4(diethylamino)arylazo]benzenecarboxylate compound.[17] The rest of geometry optimizations are reported as Supporting Information.

adsorption complex that is able to dissociate to the BT anion.[13] A great variety of theoretical reports have been published with information about the geometric features of the BT adsorbed on metallic structures.[14,15] However, detailed information about the accurate structure of the isolated BT anion has not been reported so far.

In the present work, we are interested in the study of the structural and electronic properties of the isolated aromatic anions, and for this reason we have carried out fully optimizations of the geometry of the ionic species at different levels of theory for the calculations of the response properties. In Table 1 are reported the main results of the MP2/6-31+G(d,p) and B3LYP/6-31+G(d,p) optimization of the geometric parameters of all the series of studied aromatic anions according to the labels of Figure 1a. Additionally, the values of the rms for the optimized bond lengths at the different methods and basis sets are reported in Table 1. We will also compare these optimized parameters with the reported geometry of the oxygenated analogue of BT, the phenolate anion.[16] At the HF level, the 6-31+G(d,p) (A) and 6-311++G(3d,3p) (B) basis sets have been used for the optimizations of BT (C_{2v} symmetry), and the corresponding C−S (a) bond length (reported as Supporting Information) varies between 1.757 and 1.750 Å, where the effect of the basis sets reduces this bond in 0.007 Å. Likewise, a further reduction to 1.735 Å occurs in this bond when the MP2 correlation effect is taken into account. Nevertheless, the DFT: B3LYP correlation effect increases this bond to 1.750 Å, and all these values of the C−S bond in BT lie in the range of the partial CS double bond, like in thiophene molecule. It is important to note that when the BT is bonded to Au cluster surfaces, the C−S bond distance increases in the range of 1.740−1.790 Å, and the character of double partial bond is

SCHEME 1



reduced by coordination effects.[17] The CC (*b* and *c* parameters) bond length show that due to the substitution by the $-S^-$ anion, the geometry of the benzene ring is derived to the quinoid structure according to the differences in the CC double bond distances as shown in Scheme 1. In general, the results show that electron correlation increases the CC bonds in BT anion. For these optimized bond lengths of BT, the corresponding rms values at the HF, MP2, and B3LYP methods lie in the range 1.329−1.339, and it can be observed that electron correlation increases these rms values for the BT structure.

With respect to the optimized bond angles, the predicted internal CCC (bb) angle of the ring varies from 115.8° (at HF level with the 6-31+G(d,p) basis set) to 115.0° (at MP2). The inclusion of the B3LYP increases this angle to 115.3°. The tendency of these results of BT optimization geometries are similar to those observed for the predicted phenolate anion geometry in ref 16, where the quinoid character dominates the structure of the aromatic ring.

The results of geometry optimizations of the benzenecarboxylate (BC) and benzene 1,3-benzenedicarboxylate (BDC) anion structures, according to atomic label notation of Figure 1a and following the C_{2v} symmetry and the rms values for the bond lengths of BC, as shown in Table 1, indicates that these species are dominated by the interaction of the C═O double bond (*h* parameter) and the C_6H_5 moiety that are linked by a CC partial double bond. In fact, the predicted C═O bond lengths for the BC anion varies from the 1.234 Å (HF/6-31+G(d,p)) to 1.267 Å (MP2/6-31+G(d,p)). For the BDC species, all of these C═O bonds are not symmetric, and two sets of values were found (*h*, *h′*), where the first (*h*) varies from 1.243 Å (HF) to 1.275 Å (MP2) and the other one (*h′*) varies from 1.235 Å (HF) to 1.268 Å (MP2). It is observed that MP2 increases the C═O bond length more than B3LYP. The comparison of all these values with the C═O pure double bond (1.21 Å) indicates that the nature of carbon−oxygen bonds in the carboxylate groups, both in BC and BDC, are mainly of double bond character, although somewhat weakened by the expected electron delocalization within each carboxylate group. Likewise, the neighbor CC bond (a), whose values range from 1.543 Å (MP2) to 1.553 Å (B3LYP), is larger in BC than the known C−C alkyl single bond which length oscillates around 1.530 Å. The aromatic (b) bond is larger than in the benzene ring but shorter than in the BT anion, and the (c) CC and (d) bonds have similar distances to the CC bond in isolated benzene, suggesting that in BC the phenyl group behaves as a benzene group with small quinoid character. These features are valid also for the geometric parameters of the dicarboxylate anion. The bond angles are also similar in both anions as shown in Table 1. However, the steric effects of the two CO_2 negative groups in the ring plane induce a closing of the O═C═O bond angle that goes from 129.2° (B3LYP) in the monocarboxylate BC anion to 127.3° (B3LYP) in the dicarboxylate BDC one structure.

Table 1 also reports the experimental geometric parameters of the benzenecarboxylate moiety from the experimental X-ray structural characterization of tri-*n*-butylstannyl-2[4(diethylamino)arylazo]benzenecarboxylate compound,[17] whose structure is displayed in Figure 1b. From the results we can see that there is a good agreement between experimental and theory for the geometry of the BC anion. However, differences are observed and the larger discrepancies are for geometric parameters involved in the carboxylate region, where the theoretical (B3LYP) C═O bond length and the O═C═O bond angle are 0.8 Å and 3° shorter than in the crystal, respectively.

The substitution of the negative SO_2^- and SO_3^- groups in the phenyl ring leads to the formation of the benzenesulfinate (BS) and benzenesulfonate (BSO) anions, respectively. These species can be formed by the exposition of thiol SAMs adsorbed on Au metal surface to air, where the oxidation of the S atom can occurs.[18] For these aromatic anions, the only structure theoretically known is that of the isolated BSO anion, which has been calculated with DFT methods with the BLYP and B3LYP hybrid approaches in conjunction with 6-31+G(d,p) standard basis set,[19] and no report has been published so far for the structure of the BS anion. Table 1 displays the results of geometry optimization with C_{2v} symmetry for BS and Cs symmetry restriction for BSO. The theoretical values found in ref 19 are not presented in Table 1 since they coincide with the present B3LYP/6-31+G(d,p) calculations. Table 1 also reports the rms values of the optimized bond lengths of the BS and BSO optimized structures.

The benzenesulfinate structure has been considered planar, where the O−S−O angular group lies in the plane of the aromatic ring. The predicted geometry, as presented in Table 1, indicates that the S−O bond length is larger than the corresponding to the BSO anion. In fact, the S−O bond length in BS values range from 1.468 Å (HF/extended basis set (Supporting Information)) to 1.540 Å (B3LYP), whereas these bonds in the BSO anion varies from 1.431 Å (HF/extended basis set (Supporting Information)) to 1.492 Å (B3LYP). These results show that the bond order of the S−O bond is less in sulfinate than in sulfonate species. In the same context, we can see that the neighbor C−S bond is shorter in BS (1.691 Å at B3LYP) than in BSO (1.830 Å at B3LYP), indicating that its partial double bond character is larger in BS than in BSO. Furthermore, this C−S bond (a) in the benzenesulfinate species is shorter also in BS than in benzenethiolate BT structure (see Table 1), suggesting that this bond has stronger double-bond character in BS than in BT and BSO species. For the CC bond (b) in the aromatic ring, the values in BS go from 1.419 Å (HF) to 1.432 Å (MP2, B3LYP) and are larger than in BSO, BT, and BC (see Table 1) anions. For example, the CC (b) bond length values in BSO range from 1.381 Å (HF) to 1.396 Å (B3LYP). In the same way, the CC (c) bond is reduced drastically in the sulfinate anion, being lower than in the BSO, BT, and BC anions. These values indicate that the aromatic BS moiety resembles a like-quinoid structure, where the double and single bonds are clearly depicted and in the conjugation predominate the O−S(single)···C−S(double)···C−C(single)···C−C(double)···CC(single) picture. These effects on the structure are more strongly marked in the sulfinate species than in the rest of studied anions, indicating that electron conjugation is strongest when the BS group is the G substituent one.

We have analyzed the main structural features of the aromatic anions from the rationalization of the relevant C−C, C−S, C−O, and S−O bonds and for the analysis of the corresponding C−H bonds; we can see in Table 1 (and the Supporting Information) that in general the C−H bond lengths tend to be larger in the anions than in isolated benzene. As can be concluded, the structures of the studied anions can be easily obtained by using a DFT:B3LYP geometry optimization, producing geometries that are structurally comparable with those optimized with MP2. However, expected small differences there exist between the DFT and MP2 optimized geometries.

TABLE 2: Polarization Charges $\delta q/e$ of the Relevant Bonds, Charges in the Susbtituents (q_G/e), and Ring (q_ϕ/e) Groups of the Aromatic Anions

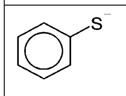
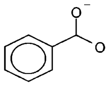
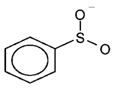
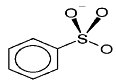
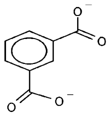
	$[C_6H_5{-}S]^-$ (BT)		$[C_6H_5{-}CO_2]^-$ (BC)		$[C_6H_5{-}SO_2]^-$ (BS)		$[C_6H_5{-}SO_3]^-$ (BSO)	
$\delta q/e$	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
$C_6{-}C_7$	+0.312	+0.020	−0.074	+0.164	−0.503	−0.368	−1.405	−1.196
$C_7{-}C_9$	−0.144	−0.127	+0.176	−0.060	−0.135	−0.185	+0.131	+0.004
$C_9{-}C_{11}$	+0.217	+0.188	−0.047	−0.005	+0.366	+0.265	+0.302	+0.102
$S_1{-}C_6$	−0.995	−0.540			+1.709	+1.595	+3.149	+2.696
$C_2{-}C_6$			+0.744	+0.626				
$O_3{-}C_2$			+1.392	+1.222				
$O_2{-}S_1$					−2.009	−1.718	−2.804	−2.155
q_G/e	−0.901	−0.688	−0.894	−0.686	−0.421	−0.319	−0.552	−0.469
q_ϕ/e	−0.099	−0.312	−0.106	−0.314	−0.579	−0.681	−0.448	−0.531

3.2. Electronic Population Analysis. The analysis of absolute atomic populations gives an idea about the degree of charge concentration in an atomic position only; however, we have considered more interesting to discuss these atomic charges in terms of the bond charge polarization δq. Table 2 reports the bond charge polarization for the studied anions, calculated with MP2 and B3LYP methods. For a particular AB bond, bond charge polarization can be defined as $\delta q_{AB} = q_B - q_A$ and gives a degree of the charge contained in the studied bond as well as an estimation of the polarization of charge in the region of that bond. These values were calculated using Mulliken atomic population MAP (q/e) of the relevant atoms, which values and the total energy (−ET/au) of the studied aromatic anions are reported as Supporting Information. The validity of these electronic populations is only of qualitative value, and they are useful for comparing charge distribution in similar molecular ensembles. Additionally, we have estimated the charge of the phenyl ring q_ϕ/e and the substituent groups q_G/e G (S, CO_2, SO_2, and SO_3) to seek the degree of sharing of the negative charge between the aromatic part and the groups in the overall anion structure. The corresponding MP2 and B3LYP results of q_ϕ/e and q_G/e are also reported in Table 2. The analysis of these values indicates that the degree of concentration of charge in the substituents groups follow the BT > BC > BSO > BS order, where the thiolate substituent (S^-) concentrates almost all the negative charge of the anion, leaving the phenyl ring with low negative charge. For the rest of the aromatic anions, the negative charge is shared between the aromatic ring and the elements of the susbtituent groups. This tendency is hold at both MP2 and B3LYP levels of theory.

In this same context, the dipole moment is an important property for analyzing a molecular charge distribution; however, in the present study it was not taken into consideration because this property is dependent on the origin for charged species.

3.3. Static Dipole (Hyper)polarizabilities. *Dipole Polarizability.* The results of the main α_{ii} components and the average α_{ave} of the static dipole polarizability tensor of BT, BC, BDC, BS, and BSO aromatic anions are collected as Supporting Information, with a summary of the relevant results presented in Table 3. It is important to note that, with the exception of the BC anion, the extension of the basis at HF level set reduces the values of α_{ii} components in the anions, whereas for all the studied anions the MP2 electron correlations increase these properties. This behavior is reflected in the final values of the average polarizability α_{ave}, where the MP2 effects with respect to HF are 5.4%, 4.8%, 7.9%, 6.9%, and 9.7% for BT, BC, BS, BSO, and BDC, respectively. With respect to MP2 effects, the MP4 level affects randomly this property, where the relative differences range from ±1.02 to ±2.20% in the series of anions. These differences are too small to be meaningful. To seek a higher order of electron correlation effects on the polarizability of aromatic anions, we have explored the performance of the coupled clusters with the single and double excitations CCSD method and the same 6-31+G(d,p) basis set on the benzenethiolate anion by using the MP2/6-31+G(d,p) optimized geometry. The results displayed in Table 3 show that CCSD adds the same effects as MP2 on the α values of BT, but with smaller value. We have also explored the performance of the density functional theory DFT methods by using the B3LYP hybrid approach, which has shown to give good values of these properties in molecules of different sizes and nature.[21] With respect to HF/6-31+G(d,p) values, the B3LYP/6-31+G(d,p) α_{ave} values are increased in the 6.1%, 7.9%, 5.3%, 6.2%, and 13.1% for the BT, BC, BS, BSO, and BDC anions, respectively. These B3LYP effects are slightly larger than MP2 for the BT, BC, and BDC anions, and in most of the cases the B3LYP α_{ave} values are similar to the MP4/6-31+G(d,p) ones, except for the BC, where

TABLE 3: Summary of the Studied Properties: Average Dipolar Polarizability α_{ave}, First Hyperpolarizability β_{zzz}^{HRS}, Second Hyperpolarizability γ_{ave} of the Monocyclic Anions (Basis Sets: A = 6-31+G(d,p); B = 6-311++G(3d,3p))

Aromatic anions	Property	HF/A	HF/B	MP2/A	MP4/A	B3LYP/A
 $C_6H_5\text{-}S^-$ (BT)	α_{ave}/au	109.52	102.66	115.39	116.62 (112.88)[a]	116.21 67.25[b]
	$\lvert\beta_z\rvert$/au	300.4	167.5	642.7	952.3 (819.7)[a]	400.8
	β_{zzz}^{HRS}/au	407.0	343.2	702.9	897.2 (804.5)[a]	583.4
	γ_{ave}/au	65,670.	74,537.	93,810.	138,633. (109,201.)[a]	123,488.
 $C_6H_5\text{-}CO_2^-$ (BC)	α_{ave}/au	89.49	93.74	93.80	91.76	96.56
	$\lvert\beta_z\rvert$/au	267.0	239.9	286.8	339.3	644.9
	β_{zzz}^{HRS}/au	96.8	87.0	102.1	125.9	258.9
	γ_{ave}/au	20,020.	20,971.	33,889.	33,530.	60,321.
 $C_6H_5\text{-}SO_2^-$ (BS)	α_{ave}/au	118.57	111.62	127.99	125.16	124.89
	$\lvert\beta_z\rvert$/au	2,944.8	2,441.7	3,680.8	3,685.1	2,846.4
	β_{zzz}^{HRS}/au	1,481.9	1,131.5	1,776.9	1,712.3	1,333.9
	γ_{ave}/au	50,785.	71,152.	49,293.	68,946.	77,386.
 $C_6H_5\text{-}SO_3^-$ (BSO)	α_{ave}/au	95.98	91.88	102.59	100.56	105.96
	$\lvert\beta_z\rvert$/au	334.7	338.1	453.2	378.3	730.4
	β_{zzz}^{HRS}/au	126.0	128.8	176.5	141.5	315.5
	γ_{ave}/au	17,777.	18,195.	31,069.	31,025.	40,653.
 $C_6H_4\text{-}(CO_2)_2^{2-}$ (BDC)	α_{ave}/au	112.84	107.3	123.82	125.54	127.67
	$\lvert\beta_z\rvert$/au	250.6	223.2	186.9	318.8	495.9
	β_{zzz}^{HRS}/au	188.5	178.3	254.9	306.2	339.6
	γ_{ave}/au	31,476.	33,530.	50,720.	73,903.	113,107.

[a] CCSD/6-31+G(d,p) results. [b] Benzene: B3LYP/A, ref 20.

a difference of 4.7 au is observed. With respect to the CCSD, the polarizability of benzenethiolate is overestimated in less than 3% by the B3LYP method.

In general, at the level of the employed basis set and the considered quantum mechanical techniques, the convergence of the predicted static polarizability calculations for the chosen aromatic anions is obtained. Furthermore, linear relationships with correlation coefficient larger than $r = 0.98$ were found for all the fitting between the HF and MP2, MP4, and B3LYP α_{ave} values. Also, it is worth mentioning that the absolute DFT α_{ave} values are consistent with those calculated at MP2 and MP4 levels of theory.

The studied anions are very polarizable in comparison to benzene, whose α_{ave} value is 66.53 au (B3LYP, ref 20), also reported in Table 3. In fact, the negative substituent increases the polarizability by a factor of 2 with respect to the benzene in all the studied cases. Taking the B3LYP/6-31+G(d,p) values as reference, the order of polarizability is the following: BC < BSO < BT < BS < BDC. The larger value of α_{ave} for BDC is expected due to its larger molecular size. However, the interpretation of the tendencies in these dipole polarizabilities is not apparent from the analysis of the structural and electronic charge distribution discussed above and cannot be understood only in terms of the separation of the negative charge from the aromatic ring and the substituent groups, since the pattern of the atomic charges of Table 2 does not follow the pattern of polarizabilities of Table 3. For instance, among the monosubstituted species the benzenesulfinate BS is the anion with larger polarizability, and in this compound the aromatic ring has the larger negative charge from the series. However, BT and BC anions possess similar charge separation but very different charge distribution, and the differences between their polarizabilities are significant. Likely, the explanation for the tendencies in the α values lies in the charge distribution of the internal bonds of the phenyl ring. In fact, BC and BSO are the anions with lower polarizabilities from the series, and the corresponding values of the charge polarization for the C_7-C_9 bond (DFT level) approach to zero for both anions. We can expect that when the polarization of charge in a bond approaches zero, it indicates that the flux of charge is minimal and the response of the electronic cloud to the perturbation of the electric field is low. Furthermore, in BC the C_9-C_{11} is an additional bond with very low charge separation. This fact reinforces the statement about the lower polarizability in terms of lower polarization of internal bonds. In contrast, for BT the polarization of the C6−C7 bond is positively low; however, the charge of the S atom is very negative, and a transfer from the S atom to this bond can explain why the polarizability of BT is larger than BC and BSO. Other important feature in the anions with large polarizability is the alternation of bond with defined charge separation, indicating a marked degree of bond order where the positive and negative signs change according to the conjugation of the bonds; effects that are very well-defined in BT, BS, and BSO anions. This interpretation is also in agreement with the analysis of the structure of the aromatic anions where the lengths of the bonds alternate according to the expected bond order from the picture of the charge separation in the most of the cases.

First Hyperpolarizability. The components of the first hyperpolarizability tensor β of the studied anions are reported as Supporting Information, and a summary of these results are displayed in Table 3. The independent components of β are β_{zxx}, β_{zyy}, and β_{zzz} labels, where the last term corresponds to the longitudinal one. We also calculated the magnitude of the $|\beta_z|$ vector and the response of the HRS scattering denoted as β_{zzz}^{HRS} in au. These properties, which are very important for the comparison with experimental measurements, have been calculated at the same levels of theory as the dipole polarizability calculations, where the electron correlation effects are accounted through the MP2, MP4, and B3LYP methods. Additionally, particular attention was taken to the evaluation of the β tensor of the benzenethiolate anion at the CCSD/6-31+G(d,p) level to estimate the convergence of this property with the employed basis set and a comparison with the other methods. Further extension of this CCSD method with larger basis set is out of our computing resources.

The HF/6-31+G(d,p) (HF/A) and HF/6-311++G(3d,3p) (HF/B) β results indicate that the studied anions show significant values of first hyperpolarizability, where the order of β values follows the same tendency as the average of the dipole polarizability α. These HF/A and HF/B calculations show that the effect of basis sets is relatively low with the exception of the BT, where at HF level the β_z value decreases in about 45% by effect of the 6-31+G(d,p) extended basis set. The most relevant result from these hyperpolarizabilities is the relatively high value of the β components for the benzenesulfinate anion, whose β_{zzz} value at the HF/6-31+G(d,p) level is 4, 8.8, 11, and 11.7 times the corresponding to BT, BSO, BC, and BDC anions, respectively. Owing to the high value in the β_{zzz} component, BS has large values in the $|\beta_z|$ vector and β_{zzz}^{HRS} ones. This tendency is followed at all the levels of theory. We have performed linear fitting between both sets of values ($|\beta_z|$ and β_{zzz}^{HRS}) at the different levels of theory, and the correlation coefficient values are of $r = 0.80$, 0.92, 0.98, 0.99, and 1.0 for BDC, BC, BS, BT, and BSO, respectively, indicating that good linear correlation there exists between them. Therefore, we use β_{zzz}^{HRS} for analyzing the hyperpolarizability of anions and the electron correlation in the results of first hyperpolarizability. Electron correlation affects the HF values significantly. In particular, MP2 effects increases β_{zzz}^{HRS} from 20% for BSO to 161% in BT anion, while MP4 reduces the MP2 values of β_{zzz}^{HRS} in a range of 20% and 25% for BDC and BC, respectively; whereas for BT and BDC, these effects are positive on the order of 27% and 20%, respectively. For BS, the anion with higher hyperpolarizability, these MP4 effects are very low in about −4%. At this point it is worth considering the BT CCSD β_{zzz}^{HRS} results, whose comparison with the MP2 and MP4 results indicates that the highly correlated β values of benzenthiolate lies between the MP2 and MP4 values. In this sense we are confident with our MP4 results for the rest of anions.

B3LYP exchange-correlation effects have been also considered, and we can see that these effects increases the values of the properties calculated at HF level, and furthermore these effects are large with respect to MP2, which relative differences are for BSO (+80%), BC (+54%), BDC (+30%), BT (−17%), and BS (−25%). Similar tendencies are observed with respect to the MP4 values. The comparison of B3LYP β responses with the CCSD results for BT indicates that the DFT hyperpolarizabilities are subestimated significantly in about 27.5%. Despite these discrepancies in the absolute values of the first hyperpolarizability of aromatic anions, the B3LYP β_{zzz}^{HRS} values parallel the corresponding MP2 and also the MP4 ones, and a linear relationship for MP2 is depicted in Figure 2, with correlation coefficient of $r = 0.98$.

To rationalize the tendencies of hyperpolarizabilities in monosubstituted aromatic anions and understand the large values of β for BS and BT with respect to the BSO and BC, we have analyzed the Mulliken atomic population and the bond length alternation BLA[22] in the aromatic ring by effect of the

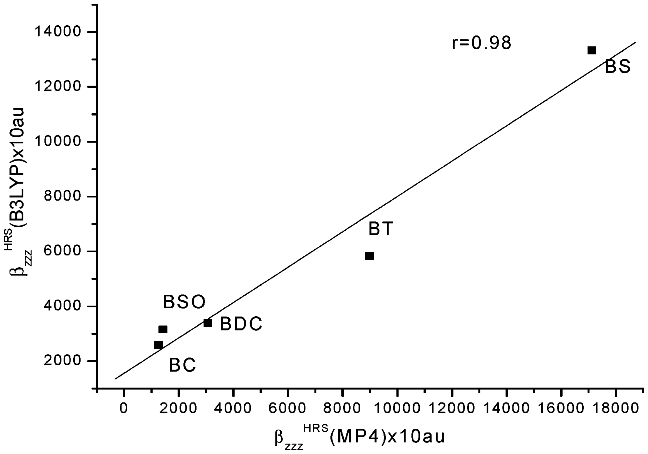


Figure 2. Relationship between the $\beta_{zzz}^{\mathrm{HRS}}$/au at the B3LYP level with respect to $\beta_{zzz}^{\mathrm{HRS}}$/au at MP4. The correlation coefficient is $r = 0.98$.

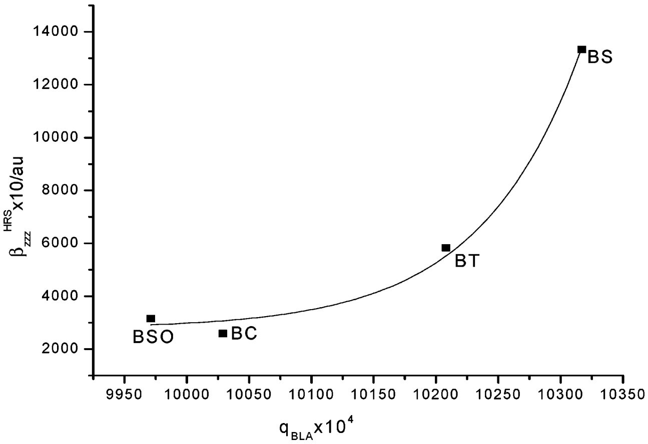


Figure 3. Function of the $\beta_{zzz}^{\mathrm{HRS}}$/au at the B3LYP level in terms the ratio of the bond length alternation q_{BLA} at the B3LYP level. The correlation coefficient is $r = 0.995$.

substitution. We have found that the first hyperpolarizability of anions cannot be interpreted directly from the electronic distribution and the separation of charge. From the structural results we can see significant variations in the adjacent C_6-C_7 "single" and C_7-C_9 "double" bond lengths that represent the response of the π-aromatic system to the chemical interaction of the substituted negative group. Analysis of these bonds in the phenyl ring shows a defined bond length alternation BLA, and therefore, a property-structural relationship should exist between the first hyperpolarizability and these BLA. A quotient between these two bonds, denoted as $q_{\mathrm{BLA}} = d(C_6 - C_7)/d(C_7 - C_9)$, can be used as structural descriptor of BLA in order to explain the first hyperpolarizabilities in anions and in a push-pull molecular system. Figure 3 shows the relationship between the $\beta_{zzz}^{\mathrm{HRS}}$ (B3LYP) and q_{BLA} that is of an exponential growth fitting. A similar relationship there exists for the corresponding MP4 results. These results indicate that anions with lower value of q_{BLA} have low β value and anions with high q_{BLA} show high first hyperpolarizability. Similar behavior there exists between the $\beta_{zzz}^{\mathrm{HRS}}$ and the dipole polarizability α in the monosubstituted aromatic anions. In this context, we are exploring further extension of these finding to different push-pull systems, such as cations, neutral, and excited molecules.

To summarize, the studied aromatic anions show a relatively high response of first dipole hyperpolarizability that can be interpreted in terms of the bonds length alternations. Similar tendencies in these β calculations can be achieved at low computational cost methods such as DFT instead of the high computational costs of MP4 methods. From the studied anions, the benzenesulfinate shows the largest value of β. At this point, it is also important to consider the range of the calculated β values of the studied anions in the context of push-pull molecules. For instance, we have evaluated at the B3LYP/6-31+G(d,p) level the $\beta_{zzz}^{\mathrm{HRS}}$ of *p*-nitroaniline (PNA) molecule, which is a model for NLO applications, to be 645 au (5.57×10^{-36} esu), which is 50% of the corresponding value of the BS anion.

Second Hyperpolarizability. Table 3 also displays the γ_{ave} for the investigated anions with the components of the second hyperpolarizability γ_{ijkl} reported in the Supporting Information. The HF results show that all the studied anions have high second-hyperpolarizability responses. The γ_{zzz} component dominates the scalar property of the tensor. At this level of theory, the value of γ_{ave} of benzenethiolate is comparable to the benzenesulfinate, whose values are much higher than those of the rest of anions. The effects of the basis sets are about of 10% in the anion series. However, the MP2 electron correlation effects are very important in the order of 42%, 68%, −16%, 72%, and 62% for BT, BC, BS, BSO, and BDC, respectively. The MP4 effects with respect to the MP2 can be summarized as 48%, −1%, 40%, 0%, and 46% for these anions. It is important to note that the MP4 effect is almost zero for BC and zero for the BSO anion. For BS, the MP2 effect is negative, whereas the MP4 one is large and positive. The anions with the largest electron correlation effects are the BT (110%) and the BDC (134%), and they present the largest values of γ_{ave} at this level of theory. However, the difference in second polarizability between both of these anions is very significant. For instance, the γ_{ave} value for BT is 138 633 au while for BDC is 73 903 au. The fact that BDC shows large γ_{ave} can be understood by the cooperative effect of two substituent groups in the phenyl ring. However, the fact of the large hyperpolarizability in the monosubstituted anion (BT) is not easy to rationalize. To evaluate the real electron correlation effects on this property, we also calculated γ_{ave} with the CCSD/6-31+G(d,p) method, and the results are displayed in Table 3. The CCSD/6-31+G-(d,p) results that correlation effects are on the order of 66% with respect to HF/6-31+G(d,p) ones, and the γ_{ave} has a value of 109 201 au. This value is relatively very high for a monosubstituted phenyl ring if we consider that the value of γ_{ave} of isolated benzene is about 23 000 au[10] at MP2.

Table 3 also shows the B3LYP/6-31+G(d,p) results of second hyperpolarizability of the aromatic anions. With respect to MP4, the B3LYP effects are about of −11%, 80%, 12%, 31%, and 53% for BT, BC, BS, BSO, and BDC anions, respectively. It is worth noting that these B3LYP effects are negative for BT (the most second hyperpolarizable anion) and positive for the rest of anions. Another interesting aspect of these values is that there exists a linear relationship between the B3LYP and the MP4 ones with correlation coefficient of $r = 0.89$.

Turning out to the large second hyperpolarizability of benzenethiolate, which value at B3LYP is 2, 1.5, and 3 times the γ_{ave} of BC, BS, and BSO anions, we consider that the factor that is able to explain these tendencies is the excess of negative charge by atom of the substituent group, whose values (q_G/N) are $-0.688e$, $-0.229e$, $-0.106e$, and $-0.117e$ for BT, BC, BS, and BSO, respectively. See Table 2 for the corresponding q_G values. Figure 4 shows that for second hyperpolarizability calculations the excess of electron in a polarizable atom is an important parameter to understand the tendencies in nonlinear third-order optical properties of aromatic anions.

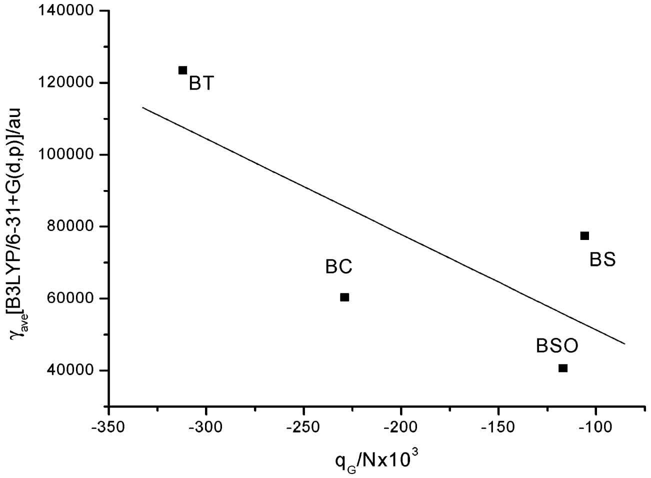


Figure 4. Relationship between the γ_{ave} at B3LYP and the q_G/N parameter. The correlation coefficient is $r = 0.70$.

4. Conclusions

Geometries, static dipole (hyper)polarizabilities α_{ave}, β_{vec}, β_{zzz}^{HRS}, and γ_{ave} of benzenethiolate (BT), benzenecarboxylate (BC), benzenesulfinate (BS), benzenesulfonate (BSO), and 1,3-benzenedicarboxylate (13BDC) aromatic anions were systematically evaluated by HF, MP2, and MP4 ab initio and density functional theory DFT:B3LYP methods with standard (polarized and diffuse) basis sets. The results have shown that these anions possess great (hyper)polarizability, and important variations between these electrooptical properties are observed due to the effects of the charged susbtituent on the aromatic ring. The results of α_{ave}, β, and γ are rationalized in terms of the structural and electronic polarization of the phenyl ring, bond length alternation (BLA), and excess of negative charge by atom in the substituent group, respectively. In fact, there exists an exponential relationship between the first hyperpolarizability and BLA, while a linear relationship exists between the γ_{ave} and the excess of negative charge of the anion. Electron correlation is very important in the (hyper)polarizability calculations in aromatic anions, and an excellent linear fitting exists between the MP4 and B3LYP (hyper)polarizability results.

Results of polarizabilities of aromatic anions also have shown that benzenesulfinate is an anion with exceptional values for β and that the benzenethiolate shows large values of γ compared with the rest of anions. We conclude that these anions could be incorporated in structural materials for non-second- and third-order nonlinear optical devices, respectively.

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Supporting Information Available: Tables of optimized geometric parameters and electronic properties of $[C_6H_5-S]^-$, $[C_6H_5-CO_2]^-$ and $[C_6H_4-(CO_2)_2]^{2-}$, and $[C_6H_5-SO_2]^-$ and $[C_6H_5-SO_3]^-$; tables of dipole polarizability as well as first and second hyperpolarizabilities of anionic monocyclic molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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