¹π→¹π* Ultraviolet Absorption Bands and Electronic Charge Transfers in Singlet Excited States of Sulfur Aromatic Heterocycles

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Abstract: Indoline-2-thione (BC), benzimidazole-2-thione (BN), benzoxazole-2-thione (BO), and benzothiazole-2-thione (BS) define an interesting series of aromatic compounds containing a NCS synthonic unit in a heterocyclic ring of five centers, substituted by atomic centers of the type C, N, O, or S, where the main electronic absorption bands are localized in the spectral range of ultraviolet A or B.

The first two singlet electronic transitions of this series, $^1S_0 \to {}^1S_1(n,\pi^*)$ and $^1S_0 \to {}^1S_2(\pi,\pi^*)$, determine the main spectroscopic characteristic of these compounds in order to be used as potential photochemical actinometers of solar ultraviolet radiation. Furthermore, the second electronic transition, localized in the 270–360 nm ultraviolet spectral range, presents a hipsochromic spectral shift as function of the electronic nature of the heteroatomic centers in the heterocyclic ring.

In order to determine a spectroscopic assignment of the main absorption bands in aqueous solution and analyze the effect of the substituent on the electronic charge distributions in the ground and the first two singlet excited electronic states, we have used a semiempirical molecular orbital calculation in the INDO/S-CIS approach. On the other hand, we have carried out a molecular orbital calculation in the AM1 framework, in order to determine the energetic stability of the thiones with respect to the thiol compounds.

INTRODUCTION

For many years, we have been interested in the electronic properties of the NCS synthonic unit,[1,2] with respect to the resonance and inductive effects that a π-electron-donor center induces on the sulfur atom through the nitrogen and carbon atoms, respectively. Furthermore, we have extended these studies to the proton transfer (PT) process between sulfur and nitrogen of the NCS structure.[3] In this work, we have explored a particular series of sulfur aromatic heterocyclic compounds containing a NCS synthonic unit in a heterocyclic ring of five centers after corroborating that indoline-2-thione (BC) presents an interesting photochemical behavior[4] due to the main electronic absorption band in the ultraviolet region. Therefore, we have prepared this molecular series as a means of introducing a heteroatomic center (N, O, and S) in the heterocyclic ring, in order to characterize the electronic absorption bands, as well as induce an electronic change in the molecular charge distribution in the excited state and the corresponding effect on the absorption spectra. Therefore, we have modified the molecular structure of indoline-2-thione (BC) by benzimidazole-2-thione (BN), benzoxazole-2-thione (BO), and benzothiazole-2-thione (BS) as can be seen in Fig. 1.

In the past, these molecular species have been used as polymer catalysts,[5] fungicides,[6] bactericides,[7,8] or molecular markers for urban environment[9] and present a good molecular stability in solution at room temperature and under visible light. However, after preparing an aqueous solution of indoline-2-thione and exposing this solution to solar radiation, we have found that this compound follows a typical behavior of photochemical actinometer of ultraviolet radiation; that is, these compounds present a simple isosbestic spectral pattern after ultraviolet irradiation or sunlight exposition.[4]

Therefore, we have extended this spectroscopic study to these molecular series, in order to analyze the substitution effect on the carbon center of the NCS group, in a first approximation, by means of the electronegativity trends that introduce the N, O, and S substitution with respect to the carbon atom in the heterocyclic ring of five centers.

Furthermore, we have analyzed the thione-thiol character of these molecular species, because it is a well-known fact that all these molecular
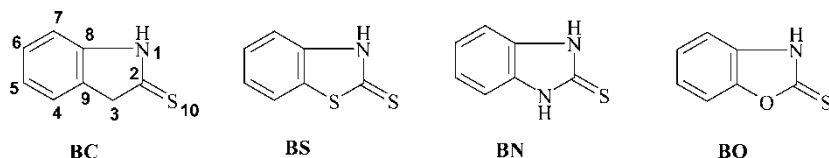
Figure 1. Indoline-2-thione (BC), benzimidazole-2-thione (BN), benzoxazole-2-thione (BO), and benzothiazole-2-thione (BS).
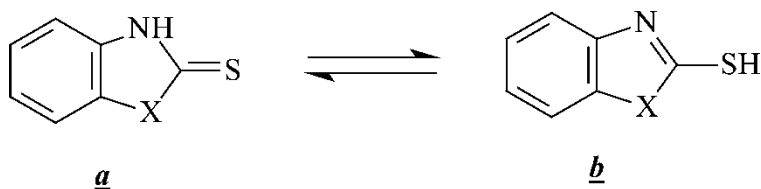
systems can show a thione (a)–thiol (b) tautomeric equilibrium in solution[10] according to the reaction in Scheme 1.

In Scheme 1, where X (C, N, O, or S) is localized in position 3 of the heterocycle. Several studies have shown that BC and BN are thione tautomers in ethanol[11] and dioxane[12] solutions, respectively. Theoretical studies[13] developed on the benzimidazol-2-tione are in concordance with the experimental observation. On the other hand, it has been reported[2] that in solutions of protic or nonprotic solvents of BS, under normal conditions of temperature and pressure, the thione tautomer is the predominant species. The same conclusion was obtained by Koch[14] through electronic absorption spectroscopy of BS in benzene, chloroform, and ethanol solutions. Recently, gas-phase photoemission studies have determined that the BS thione with respect to the thiol form emerges as the stable tautomer species, an experimental determination developed without solvent.[15]

Therefore, in the current work we have analyzed the main spectral absorption band in the ultraviolet region from a spectroscopical and theoretical point of view. Furthermore, we have developed a molecular orbital study in the ground and singlet excited states in order to carry out an electronic characterization that permits us to establish the effect of the substituent along the molecular series. Finally, by means of a theoretical study of molecular orbital calculations on the stability of the thiones with respect to their thiol tautomers, we have corroborated the experimental evidence on BC, BN, and BS and extended this analysis to the BO compound of the series.

EXPERIMENTAL

Indoline-2-thione (BC) was synthesized as published,[16] by the reaction of Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide] (7.82 g) and oxindole (3.28 g) in 200 mL of toluene.[17] The final product was characterized by means of ^{1}H-NMR and ^{13}C-NMR spectroscopy, ultraviolet absorption spectroscopy, and elemental analysis. The remaining compounds were purchased from Aldrich Chemical Co. Every compound was recrystallized followed by vacuum sublimation. Fresh aqueous solutions were prepared at room temperature in bidistilled water.

Scheme 1.

The absorption spectra were registered in a UV-Vis Perkin-Elmer Lambda 11 spectrophotometer in a 10-mm quartz cell.

The molecular geometry of these thione and thiol tautomers have been obtained by molecular orbital theory calculations using the semiempirical AM1 approach,[18] under complete relaxation of the bond lengths and bond angles reaching the lowest energy condition. Furthermore, the electronic transition energies of the thiones, as well as the net charge density calculations of the atomic centers in the ground and excited states were obtained by Zerner INDO/S-CIS molecular orbital calculations,[19] that have been parameterized for gas-phase spectra at the singles-only configuration interaction (CIS).

A semiempirical molecular orbital package for spectroscopy (WinMOPAC 3.0,)[20] including AM1 and INDO/S-CIS approaches were used. The AM1 optimized geometries (SCFCRT = 1E-10 and Gnorm = 0.001) were used as input of the INDO/S-CIS calculations in order to determine the first two $^1S_0 \rightarrow {}^1S_1(n,\pi^*)$ and $^1S_0 \rightarrow {}^1S_2(\pi,\pi^*)$ singlet electronic transitions. Software INDO/S-CIS parameters such as Echarge CI = all, parm = type, G = NMW, and the k-NM = 0.75 were used.[21] In addition, heteroatomic center parameters were as follows: O (Es: 32.40; Ep: 15.88; Bsp: 34.0; G: 13.0), S (Es: 21.73; Ep: 11.92; Bsp: 15.0; G: 10.09) and N (Es: 25.69; Ep: 14.5; Bsp; G: MOS-F value), where Es is the ionization potential for *s*-type orbitals, Ep is the ionization potential for *p*-type orbitals, Bsp is the resonance integral of both *s*- and *p*-type, and G is one-center electron repulsion integral.

In order to improve the gas-phase electronic transition calculations with respect to the experimental spectra determined in water solutions, we have made use of the solvent effect option that the INDO/S-CIS software introduces by means of the classic Onsager reaction field model.[22] Therefore, we have used the dielectric constant and the refraction index of water as complementary input parameters of the INDO/S-CIS calculation software.[21]

Furthermore, the molecular cavity radii associated with the molecular systems in the ground electronic state were calculated by means of *ab initio* MO calculations in a 6-31G basis set.[23]

Oscillator strength (*f*) of the main absorption spectral bands, $^1S_0 \rightarrow {}^1S_2(\pi,\pi^*)$, was determined by means of the classical equation $f = 4.3 \times 10^{-9} \int \varepsilon d\bar{\nu}$. The absorption bands are well defined in the first three compounds (BS, BC, and BN): however, in the last compound (BO), we have extrapolated the trend of the spectral curve near 265 nm.

RESULTS AND DISCUSSION

In Fig. 2, we show the electronic absorption spectra of this molecular series in aqueous solutions at room temperature. From this figure, we can appreciate the main absorption band of the BN and BO compounds centered in the UV-B
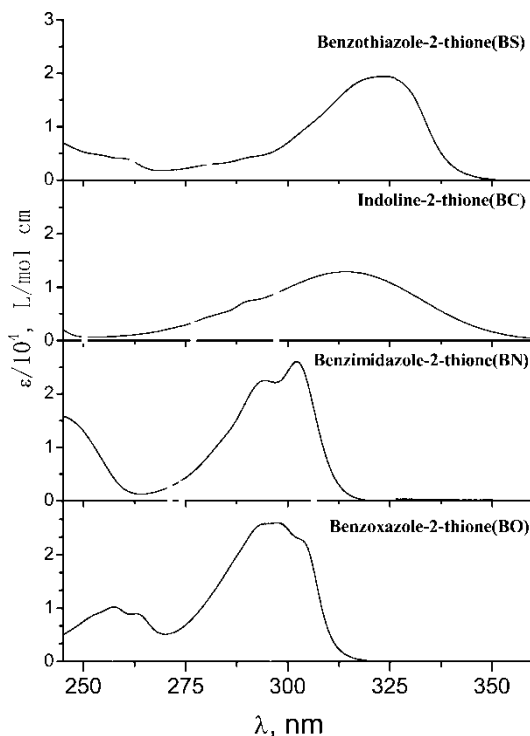
Figure 2. Electronic absorption spectra of thiones in aqueous solutions at room temperature.

range (280–320 nm), as well as the broad bands of the BS and BC compounds in the UV-A and UV-B range (270–360 nm). All these compounds present a relatively high molar absorption coefficient at the band maxima wavelength. The oscillator strengths[24] determined from these experimental bands are near 0.3 (Table 1). Based on the absorption spectral band positions as well as the spectral structure and the molar absorption coefficients, these results define a typical $^1\pi \to {}^1\pi^*$ electronic transition involving a charge transfer character, induced by the phenyl group on the thiocarbonyl group of the heterocyclic ring.

Furthermore, from the same figure, we can appreciate a hipsochromic spectral shift of the ultraviolet absorption band maxima when the X-substituent is interchanged in the heterocyclic ring. Therefore, in a first approximation, we have used the electronegativity of the X-substituent in order to parameterize the inductive effect on the NCS unit in the $^1\pi \to {}^1\pi^*$ absorption band shift. Thus, we can appreciate a blue shift given by the following sequence: BS < BC < BN < BO, according to the heteroatom electronegativity increase from 2.4 in BS (X=S) to 3.5 in BO (X=O). From this trend, we

observe a decrease of the charge transfer from the phenyl group to the NCS unit when the electronegativity increases in the heteroatomic substituent.

In Table 1, we present the electronic transitions for the four thiones in water solution and the main electronic configurations involved in the ground and excited state, obtained from our INDO/S-CIS molecular orbital calculations in the Onsager reaction field approach.[22] The cavity radii calculated from *ab initio* molecular orbital calculations[23] were $r_c(BC) = 4.28$ Å; $r_c(BN) = 4.39$Å; $r_c(BO) = 4.35$ Å; and $r_c(BS) = 4.49$ Å.

According to these theoretical results, the $S_0 \rightarrow S_1(n,\pi^*)$ electronic transition is predicted in the UV-A and visible regions (365 to 425 nm), while the $S_0 \rightarrow S_2 (\pi,\pi^*)$ electronic transition is predicted in the ultraviolet-B spectral range (295 to 313 nm). Effectively, the theoretical electronic transitions ascribed to the $S_0 \rightarrow S_2 (\pi,\pi^*)$ band agree very well with the experimental absorption band maxima, as can be seen in Table 1. However, the $S_0 \rightarrow S_1$ (n,π^*) absorption bands were not detected at solution concentrations lower than 1.0×10^{-5} M and optical pathlength cells of 1 cm. These results agree with the low theoretical oscillator strength reported in Table 1. Furthermore, we have analyzed the spectral emission of these compounds and we have not evidenced fluorescence,[4] which is in agreement with the nature of the first $S_1(n,\pi^*)$ excited state.[24]

On the other hand, it is interesting to note that the theoretical calculations in aqueous solution with respect to the gas-phase agree better with the experimental data, because the reaction field scheme incorporated in the INDO/S-CIS calculations,[22] introduces a blue shift of 12 nm as mean value in the $S_0 \rightarrow S_1 (n,\pi^*)$, while in the $S_0 \rightarrow S_2 (\pi,\pi^*)$ transition we have observed a red shift of 11 nm as mean value. Moreover, because the theoretical mean deviation on the transition energy of the INDO/S-CIS calculations is close to 0.1 eV,[25] whereas the spectral range under study represents 7 to 10 nm, consequently, the theoretical data agree very well with the experimental measurements. Although hydrogen bonds are not involved in the computational calculations, the solvent effect defined by means of the reaction field is adequate enough to improve the spectral shift observed in the $^1S_0 \rightarrow {}^1S_2(\pi,\pi^*)$ singlet electronic transition in solution, with respect to the typical calculations in the gas phase. Evidently, the $^1S_0 \rightarrow {}^1S_1 (n,\pi^*)$ electronic transition must mainly be affected; however, we have not detected this particular absorption band at the concentration range used.

From Table 1 and Fig. 2, we can observe that the first two singlet–singlet electronic transitions, $S_0 \rightarrow S_1(n,\pi^*)$ and $S_0 \rightarrow S_2(\pi,\pi^*)$, have only one main electronic configuration, where the first transition involves the HOMO-1 (H-1) and LUMO (L) orbitals, and the second transition involves the HOMO (H) and LUMO (L) orbitals. Notwithstanding, the H-1 is a nonbonding molecular orbital (n) located in the molecular plane of the sulfur atom in the N–C=S unit, and L is a delocalized π^*-orbital, which involves important electronic contribution of the C and S atoms. Thus, the $S_0 \rightarrow S_1$ electronic transition corresponds to the typical $n \rightarrow \pi^*$ molecular orbital transition with strong

Table 1. INDO/S-CIS calculation of the $S_0 \rightarrow S_1$ (n,π^*) and $S_0 \rightarrow S_2$ (π,π^*) electronic transitions and $S_0 \rightarrow S_2$ (π,π^*) experimental data of BC, BN, BO, and BS in aqueous solution

	$S_0 \rightarrow S_1$ (n,π^*) (INDO/S-CIS)			$S_0 \rightarrow S_2$ (π,π^*) (INDO/S-CIS)			$S_0 \rightarrow S_2$ (π,π^*) (Experimental)[a]
	Wavelength, nm (Osc. strength)	CI[b] (%)	MO[c]	Wavelength, nm (Osc. strength)	CI[b] %	MO[c]	wavelength, nm (Osc. strength)
BC	414 (2E-4)	91	H-1 → L	297 (0.395)	88	H → L	314 (0.292)
BN	366 (4E-6)	80	H-1 → L	306 (0.373)	85	H → L	302 (0.306)
		20	H-2 → L + 2		7	H-2 → L + 1	
BO	374 (1E-6)	87	H-1 → L	296 (0.353)	81	H → L	297 (0.347)
					7	H-2 → L + 1	
BS	426 (7E-5)	92	H-1 → L	313 (0.414)	91	H → L	323 (0.292)

[a]Absorption band maxima.
[b]Main configuration interaction (CI).
[c]H, HOMO; H-1, HOMO-1; H-2, HOMO-2; L, LUMO; L + 1, LUMO + 1, L + 2, LUMO + 2.

charge transfer character from the sulfur atom to the carbon atom of the NCS structure, while the $S_0 \rightarrow S_2$ electronic transition determines a $\pi \rightarrow \pi^*$ molecular orbital transition involving a charge transfer contribution from the phenyl group to the NCS group. In Fig. 3 we have depicted the six main molecular orbitals involved in the corresponding first three singlet electronic transitions for the BC compound. The other three thiones under study present a similar MO pattern.

From the molecular orbital analysis, it can be observed that the H-orbital has a node plane on the C atom of the NCS unit. This orbital is delocalized on the phenyl group and localized on the sulfur atom of the NCS group. On the other hand, the LUMO orbital shows a nodal plane perpendicular to the C=S bond (see Fig. 3), but this orbital has a significant electronic character of the C atom of the NCS unit. Then, the $S_0 \rightarrow S_2$ electronic transition has a $\pi \rightarrow \pi^*$ character, and a charge transfer comes from the phenyl ring to the NCS carbon atom, in good agreement with the experimental considerations. In addition,
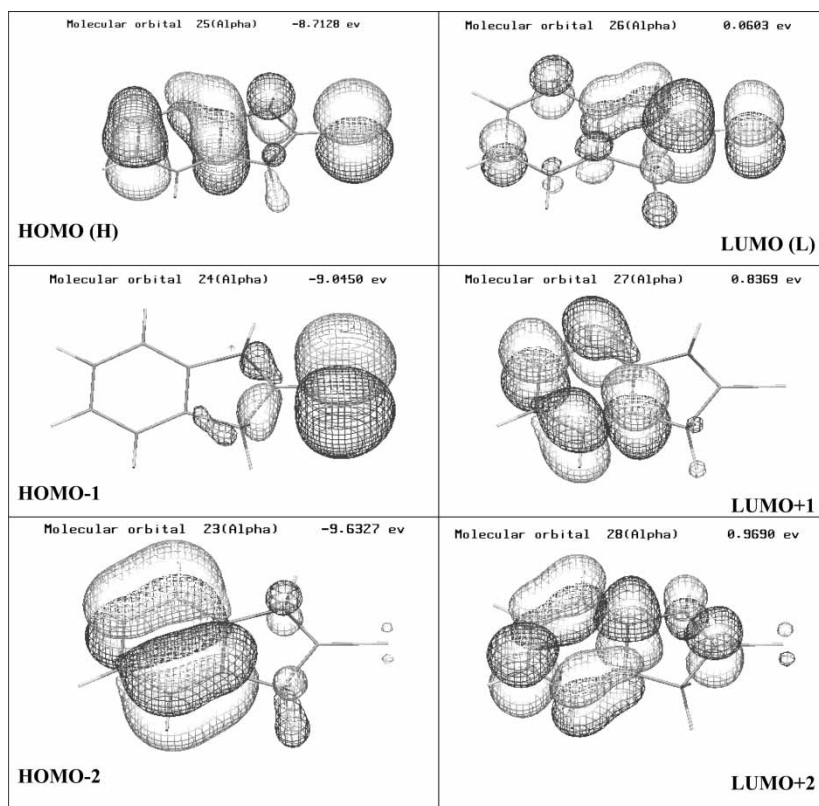

Figure 3. INDO/CIS molecular orbitals of indoline-2-thione (BC): the six main molecular orbitals involved in the first two singlet electronic excited states.

this last result agrees very well with our preliminary experimental observation of the photochemical desulfuration of BC.[4] Therefore, the nature of the LUMO orbital can provide us with a first explanation about how the photolytic rupture in the thioketo bond occurs after the charge transfer process.

In particular, O and N atoms emerge as the main centers perturbing the NCS carbon center, subsequently inducing a decrease of the charge transfer from the phenyl group. Therefore, while the carbon center of the NCS group receives the same perturbation effect from the X atoms, the $S_0 \rightarrow S_1(n,\pi^*)$ and $S_0 \rightarrow S_2(\pi,\pi^*)$ electronic transitions follow an opposite direction of the charge transfer phenomena given by the nature of the electronic orbitals involved in the optical process.

In addition to the molecular orbital characterization, we have developed an analysis of the electronic charge transfers distributed in the atomic centers of the NCS and phenyl groups for every thione according to the electronegativity of the heteroatom in the heterocyclic ring (Fig. 4).

In effect, in Fig. 4a we can appreciate an important charge transfer from the sulfur atom to the carbon of the NCS group as well as to the phenyl group. This is an expected process in a typical $S_0 \rightarrow S_1(n,\pi^*)$ transition, where the local dipole moment centered on the CS bond experiences a diminution due to the charge transfer process between the sulfur and the carbon center.
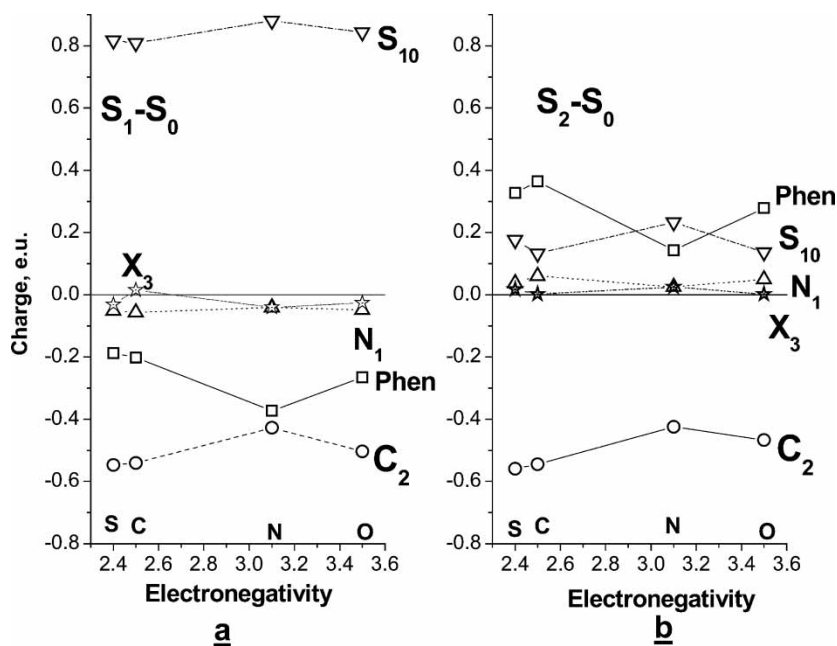

Figure 4. Electronic charge transfer (in excited states) as function of the electronegativity of the heteroatom X at position 3. X = S(2,4), C(2,5), N(3,1), and O(3,5). (a) $S_0 \rightarrow S_1(n,\pi^*)$ and (b) $S_0 \rightarrow S_2(\pi,\pi^*)$.

Table 2. AM1 heats of formation of thione and thiol tautomers (kcal/mol)

	In vacuum		In water	
Compounds	Thione	Thiol	Thione	Thiol
BC	53.5	61.2	31.6	45.1
BN	65.7	72.8	37.4	50.5
BO	35.0	37.9	13.7	23.8
BS	53.7	58.6	30.2	43.5

This last effect can be effectively observed after comparing the LUMO and HOMO-1 orbital nature. Therefore, if the hydrogen bonds of the solute–solvent interaction are explicitly considered in the theoretical calculations, we can expect a slight blue-shift improvement in the prediction of the electronic transitions.

On the other hand, from Fig. 4b we can appreciate how the $S_0 \rightarrow S_2(\pi, \pi^*)$ electronic transition induces a charge transfer from the phenyl group to the carbon center of the NCS group, where this process is mainly favored in the S and C with respect to the N and O substituents. In fact, in this case the charge transfer process does not follow the inductive effect trend defined by the electronegativity of the atomic substituents. Therefore, we must expect that the π-donor character of these atomic centers are controlling the charge transfer process on the carbon center of the NCS group.

Finally, by means of the same molecular orbital study, we have corroborated the molecular stability of the thiones with respect to their corresponding thiols. Thus, we have determined the heat of formation of the thione and thiol tautomers by means of the AM1 molecular orbital approach (Table 2). Our theoretical calculations in all these thione tautomers are 3 to 8 kcal/mol more stable than the thiol tautomers in vacuum. However, the same phenomenon was observed in aqueous solution, under the same approximation previously described, where the bulk of solvent was simulated by the Onsager reaction field, without considering the hydrogen bond links. In both cases, our calculations show that this energy gap increases at least twice. Therefore, whenever we consider the hydrogen bond contribution expected in the thiol compounds relative to the thione compounds, the observed trends are big enough to maintain the current energy gap between thiones and thiols. Thus, from Table 2 we can appreciate that all thione tautomers are the stable species. These results agree very well with early works developed in BO and BS compounds in gas-phase[1] and we have corroborated the thiones as the predominant molecular species in aqueous solutions. On the other hand, our results agree very well with those obtained from preliminary experimental data of the ^{1}H-NMR spectral type, where BO and BS thione tautomers are the main species in polar solvents.[22]

ACKNOWLEDGMENTS

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