



# Assessment of the molecular structure and spectroscopic properties of CF<sub>3</sub>-substituted sulfinylaniline derivatives

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## ABSTRACT

The presence of a perfluorinated functional group as a substituent of the aromatic ring in *m*- and *o*-trifluoromethylsulfinylaniline may provide conformational and vibrational properties of interest for the synthesis of compounds of pharmacological relevance, as it was observed for other *N*-sulfinylaniline derivatives previously reported. The air sensitive and highly reactive compounds under study were prepared by the reaction of the corresponding aniline derivatives and thionyl chloride. The liquid samples were characterized by FT IR, Raman and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopies and GC/MS spectrometry. The experimental spectra indicate the presence of a single conformer of *syn* geometry (*syn* of the C-N bond with respect to the S=O bond), in good agreement with results obtained by quantum chemical calculations derived from the Functional Density Theory. The stable conformation found as the global minimum of the potential energy surface was rationalized by considering intramolecular orbital interactions evinced by a Natural Bond Orbital (NBO) analysis and the quantum theory of Atoms In Molecules (AIM). Through this last approach, an intramolecular C-H...O interaction meeting the characteristics of an *anti*-hydrogen bond was found.

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## 1. Introduction

More than 100 years after the isolation of *N*-sulfinylaniline by Michaelis and Herz [1], there is little doubt about the structural and conformational properties of the NSO group in the large family of compounds of general formula R-N=S=O (R = phenyl group). Scheme 1 shows the most stable conformers predicted, but it is the *syn* form the conformation adopted by each and every compound of this type isolated so far [2]. This sterically unfavorable conformation is stabilized by conjugative  $\pi$  interactions between the NSO group and the phenyl ring [3]. If possible, an additional stabilizing intramolecular interaction of the type C-H...O is established between the oxygen atom of the sulfinyl group and an *ortho* hydrogen atom of the ring [4].

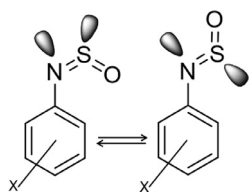
Among the different chemical reactions where sulfinylaniline derivatives might be involved, Diels-Alder cycloaddition reactions are the most interesting [5] not only because the compounds may act as diene or dienophiles, but also because the transition state involves an *anti* geometry of the NSO group [5–7]. The presence

of substituents in the aromatic ring modifies the electronic properties of the compound as a whole and influences the consequent reactivity, which is more considerable when electron withdrawing substituents are bonded to the ring [8]. Fluoro-substituted compounds were reported as relevant starting materials with great potential in the pharmaceutical industry [9–11]. Our recent studies regarding the conformational and vibrational properties of a series of fluorine [12–14] and chlorine [15,16] monosubstituted *N*-sulfinylanilines proved that the properties vary according to the position of the substituent in the aromatic ring and the prevalence of different electronic effects. These halogen atoms interact through mesomeric (+M) and inductive (-I) effects with different extents.

The present study addresses the conformational and vibrational study, together with a structural characterization of *m*- and *o*-trifluoromethylsulfinylaniline conformational isomers, abbreviated in the following text as *m*-CF<sub>3</sub>ArNSO and *o*-CF<sub>3</sub>ArNSO, respectively. The perfluorinated substituent CF<sub>3</sub> lacks the possibility of interacting with any other electronic effect but short-range inductive effect. In consequence, its influence over the vibrational frequencies of the NSO group are expected to be more pronounced in the *ortho* isomer than in *meta*. The trifluoromethyl group possesses a van

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**Scheme 1.** *Syn* and *anti* forms of N-sulfinylaniline derivatives (X = F, Cl, -C<sub>2</sub>H<sub>5</sub>).

der Waals radius larger than the corresponding for a methyl group and shows the same electronegativity than oxygen atom. The high electronegativity of fluorine atoms make the C-F bonds one of the strongest for organic compounds, conferring additional stability to the molecule as a whole [17]. The compounds were obtained through the reaction of the corresponding aniline derivatives and thionyl chloride and were characterized by using FT IR, Raman, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and GC/MS spectrometry. The assignment of the experimental spectra was achieved considering quantum chemical calculations derived from Density Functional Theory and data reported in literature for related compounds. In order to understand intramolecular orbital interactions which stabilize a given conformation a Natural Bond Orbital analysis (NBO), as implemented in the Gaussian 03 program package was performed. Additionally, a topological bond analysis of the most stable conformations was obtained based on Bader's theory through the Atom In Molecules (AIM) program.

## 2. Materials and methods

### 2.1. Synthesis

*m*-CF<sub>3</sub>ArNSO and *o*-CF<sub>3</sub>ArNSO were prepared according to the procedure reported in the literature [1]. The corresponding aniline derivative (*m*-trifluoromethylaniline (3.84 g, 23.83 mmol) or *o*-trifluoromethylaniline (3.85 g, 23.88 mmol), respectively) and benzene used as the reaction solvent (13.2 g, 169.3 mmol) were placed in a closed three neck round bottom flask equipped with a Liebig condenser sealed with a CaCl<sub>2</sub> trap. Thionyl chloride (9.84 g, 83.3 mmol) was added drop wise to the mixture with agitation. All the substances were purchased to Sigma-Aldrich Argentina and used without further purification. To prevent the interaction with air humidity, the reactions were carried out in nitrogen atmosphere. A vigorous reaction took place and aniline hydrochloride precipitated. The reaction mixture was continuously stirred and heated maintaining the reaction temperature in the range 80–85 °C for 8 h. The complete disappearance of the signals attributed to the NH<sub>2</sub> group (3400–3500 cm<sup>-1</sup> region) in the infrared spectrum of aliquots of the reaction mixture evidenced the final point of the reaction. The liquid products generated were purified by several simple and vacuum distillation cycles; a yield of 87% and of 89% was achieved for the *meta* and *ortho* isomers, respectively, obtained as dark green liquids.

The elemental analyses were conducted using an EXCETER CE-440 analyser. According to the molecular formula of *m*-CF<sub>3</sub>ArNSO and *o*-CF<sub>3</sub>ArNSO isomers the following abundances (expressed in %) are expected: C, 40.58; H, 1.94; N, 6.76. The elemental analyses for the obtained compounds gave the following abundances: C, 41.23; H, 1.87; N, 6.95 for the *m*-CF<sub>3</sub>ArNSO and C, 40.55; H, 2.19; N, 6.56 for isomer *o*-CF<sub>3</sub>ArNSO.

### 2.2. Spectroscopic measurements

The GC/MS analyses were carried out using a Model Trace GC Ultra gas chromatograph coupled to a Polaris Q mass spectrometer with an ion-trap analyzer with a DB-5 capillary column. Split-

less injection and helium as carrier gas were used for these studies. For each experiment, the initial temperature of the oven was 60 °C. After maintaining that temperature for 3 min, the temperature was increased at a rate of 15 °C/min to reach a final value of 250 °C, which was then maintained for 5 min. The total run time was 20 min. The signals observed at 9.35 and 9.38 min (98% relative area) in the total ion chromatogram accounts for the presence of each of the compounds under study (*ortho* and *meta* conformational isomers, respectively). Quantification of the peaks was based on peak area. On the other hand, the mass spectrometer was operated in the electron ionization scan mode (range *m/z* = 50–250). The molecular ions were assigned to the peaks of *m/z* = 207 in the spectra of each conformational isomer.

### 2.3. Computational details

Molecular quantum chemical calculations were performed with Gaussian 03 program package [18]. Based on the Density Functional Theory (DFT), the Becke-style three parameter hybrid functional for the exchange part [19] with the Lee-Yang-Parr correlation function (B3LYP) [20] and the 6-311+G(df) and 6-311++G(df,pd) bases sets were applied for geometry optimization, conformational properties and vibrational frequency calculations of *m*-CF<sub>3</sub>ArNSO and *o*-CF<sub>3</sub>ArNSO conformational isomers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were calculated within a Gauge Invariant Atomic Orbital (GIAO) approach [21] which is one of the most common approaches for calculating nuclear magnetic shielding tensors. On the other hand, intramolecular orbital interactions were evaluated by the Natural Bond Orbital analysis NBO [22] while the nature of intramolecular hydrogen bonds was evaluated using the AIM approach by means of AIM2000 software [23]. The GIAO, NBO and AIM calculations were performed by using the B3LYP/6-311+G(df) approximation.

## 3. Results and discussion

### 3.1. Conformational analysis

#### 3.1.1. Potential energy surface analysis

As it was mentioned before, a *syn* configuration of the C-N and S=O bonds was already expected as the most stable geometry for the sulfinylaniline derivatives now studied (see Scheme 1) [12–16,24,25]. Accordingly, the potential energy surfaces were studied through the evaluation of energy potential curves for optimized structures with fixed values of the C-N=S=O dihedral angles obtained using the B3LYP/6-311+G(df) approximation (see Fig. 1). Full optimization of minima found predicted a rotational barrier  $\Delta G(\textit{anti-syn}) \sim 7 \text{ kcal.mol}^{-1}$  (by using 6-311+G(df) and 6-311++G(df,pd) bases sets) (see Fig. 2).

The angular geometry of the sulfinyl group determines that two different conformers may result upon rotation about the C-N bond (see Fig. 2). The corresponding potential energy curve obtained using the same theoretical approach for optimizing structures of *m*-CF<sub>3</sub>ArNSO conformational isomer with fixed values for the C-C-N=S dihedral angle determined a conformational equilibrium of *syn* I and II ( $\Delta E^\circ = 0.34 \text{ kcal.mol}^{-1}$ ), in agreement with results found for other *meta* sulfinylaniline derivatives [13,16], being the rotational barrier of *ca.* 5 kcal.mol<sup>-1</sup>. Only one *syn* form was feasible for the *ortho* isomer. Table 1 lists the structural parameters of the most stable conformers of *m*- and *o*-CF<sub>3</sub>ArNSO.

#### 3.1.2. Natural bond orbital (NBO) analysis and atom in molecules (AIM) topological analysis

The conformational preferences of stable molecular structures adopted by sulfinylamines, and in the present case, perfluorinated sulfinylaniline derivatives, may be understood on one hand by the

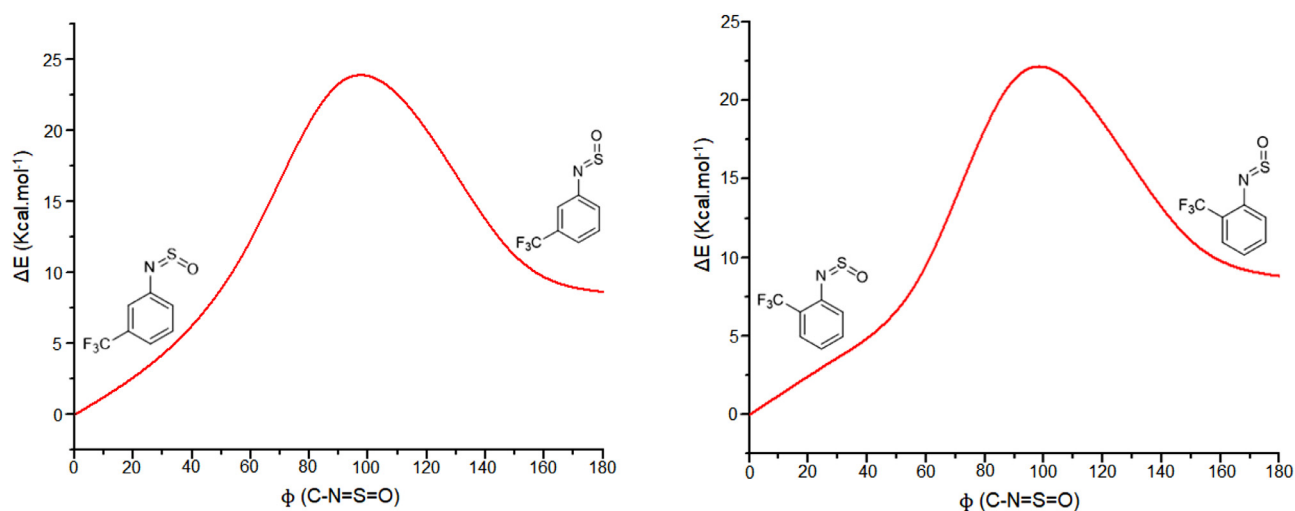


Fig. 1. Calculated rotational barrier around the N=S bond at B3LYP/6-311+G(df) level of theory for *m*-CF<sub>3</sub>ArNSO and *o*-CF<sub>3</sub>ArNSO.

Table 1

Calculated geometric parameters<sup>a</sup> for stable forms of trifluoromethylsulfinylaniline conformational isomers.

Structural Parameters	B3LYP/6-311+G(df)		B3LYP/6-311++G(df,pd)	
	<i>o</i> -CF <sub>3</sub> ArNSO	<i>m</i> -CF <sub>3</sub> ArNSO	<i>o</i> -CF <sub>3</sub> ArNSO	<i>m</i> -CF <sub>3</sub> ArNSO
O...H(1)	2.323	2.342	2.320	2.337
C(2)...O	3.097	3.097	3.094	3.093
C(2)-H(1)	1.080	1.081	1.080	1.080
C(6)-C(7)	1.514	-	1.514	-
C(5)-C(7)	-	1.508	-	1.508
N=S	1.536	1.539	1.537	1.539
S=O	1.483	1.484	1.483	1.484
C(1)-N	1.386	1.390	1.386	1.390
C(1)-N=S	133.0	132.2	133.0	132.1
N=S=O	119.6	119.5	119.6	119.5

<sup>a</sup> Bond lengths in Å and angles in degrees. For atom numbering see Fig. 3.

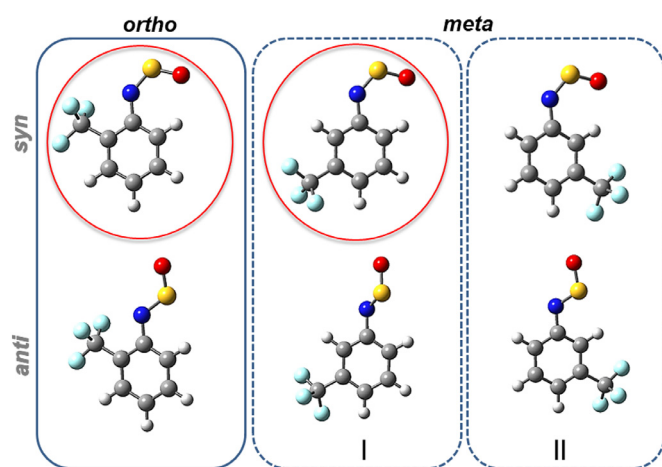


Fig. 2. Calculated stable conformational isomers of trifluoromethylsulfinylaniline (global minima shown in red circles).

examination of the most relevant orbital hyperconjugative interactions using the Natural Bond Orbital analysis (NBO) [22] and on the other, through bond characterization of the electronic charge density and the Laplacian value at the Bond Critical Point (BCP) (AIM) [23].

The NBO analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty'

(acceptor) non-Lewis NBOs and estimating their energetic importance by second order perturbation theory. The larger the energy value, the more intensive is the interaction between electron donors and acceptors and the most stable the evaluated conformation. Fig. 4 depicts hyperconjugative orbital interactions calculated by using the B3LYP/6-311+G(df) approximation between nitrogen and sulfur electron lone pair orbitals and corresponding vicinal anti-bonding orbitals. As it was evidenced by the study of the potential energy surface, for *syn* structures the delocalization energy values are larger than those obtained for *anti* structures.

According to the NBO analysis the S-O bond possesses only  $\sigma$ -bond character, therefore three lone-pair orbitals were associated to the oxygen atom. Only two of them (lone pairs 1 and 2, respectively) exhibit low occupancies, evidencing their being involved in orbital interactions as electron-donors towards  $\sigma^*(\text{C2-H1})$  orbitals (see Fig. 5).

The presence of the orbital interactions showed in Fig. 5 would lead to C-H bond lengthening because of electron density delocalization from oxygen lone pairs towards anti-bonding orbitals. However, the small energy delocalization values would only have minor effects on the C-H bond lengths and corresponding frequency values, according to the results obtained through the AIM approach. Fig. 3 shows the calculated H...O distance for the most stable conformational isomers found. As stated long ago by Desiraju [26], the C...O distance in a large variety of carbon acids with C-H...O interaction lay between 3.00 and 4.00 Å, as it was predicted for both conformational isomers analyzed in the present case (see Table 1). The evaluation of corresponding geometrical parameters for a set

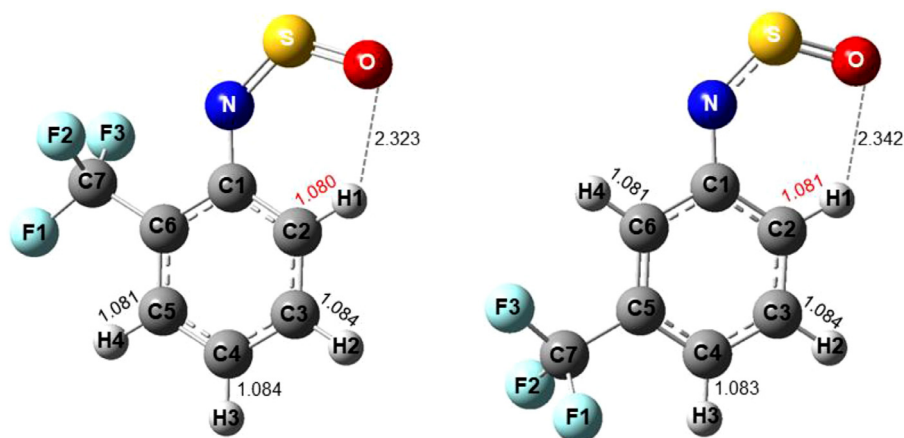


Fig. 3. Calculated geometrical parameters of stable conformational isomers of trifluoromethylsulfinylaniline.

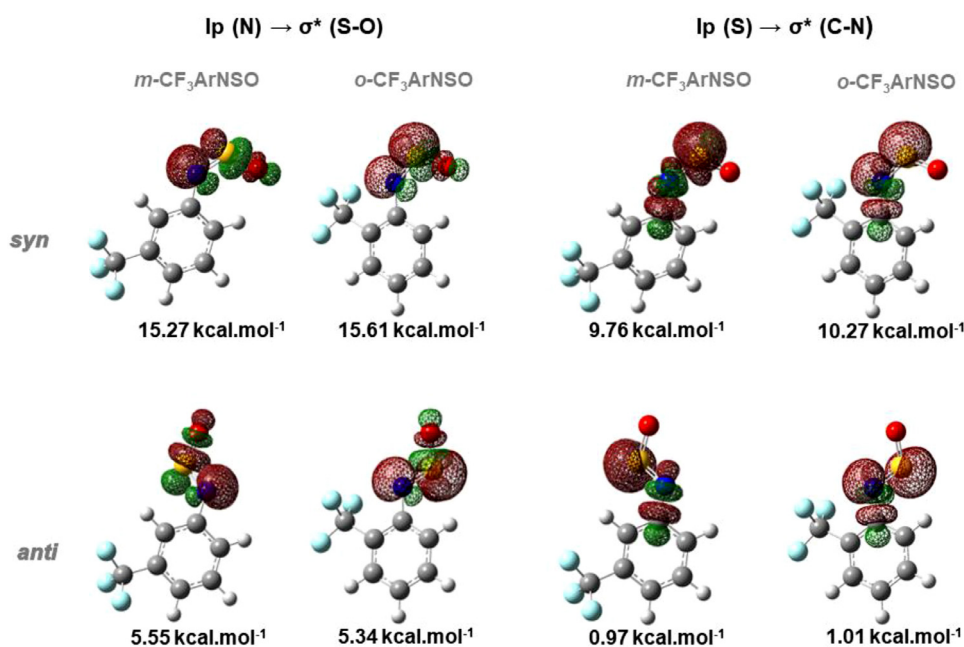


Fig. 4. Relevant NBO orbital interactions [B3LYP/6-311+G(df)] and corresponding energy delocalization values (kcal.mol<sup>-1</sup>) (isovalue for orbital plotting: 0.08).

of N-sulfinylamines with *ortho* H atoms by the quantum theory of Atoms In Molecules (AIM) proved that a so called anti-hydrogen bond would be present [4].

The quantum theory of “Atoms In Molecules” (AIM) is considered an excellent tool for undertaking in-depth characterization of bonds through a topological analysis of the electronic charge density [23,27]. The formation of hydrogen bonds is associated with the presence of a Bond Critical Point (BCP) between the hydrogen atom of a donor group and an acceptor atom, which are linked by the associated bond path. At the bond critical point several properties might be evaluated, such as the electronic charge density  $\rho$  and the Hessian matrix of the charge density whose diagonalization renders the eigenvalues  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ . Two derived quantities are the Laplacian of the charge density at the bond critical point  $\nabla^2\rho$  and the bond ellipticity,  $\varepsilon$ , which provide a measure of the extent to which charge is preferentially accumulated in a given plane, in other words, a quantitative measure of the bond p-character [28,29]. Table 2 shows that the concentration of the charge density has a value close to zero and the Laplacian function  $\nabla^2\rho$  of the charge density is positive. These features suggest the existence of weak hydrogen bonds in the structures depicted

in Fig. 3 [4,29,30]. A direct consequence of this type of interaction would be evidenced as an increase in the frequency of the C-H bond stretching involved (Fig. 6).

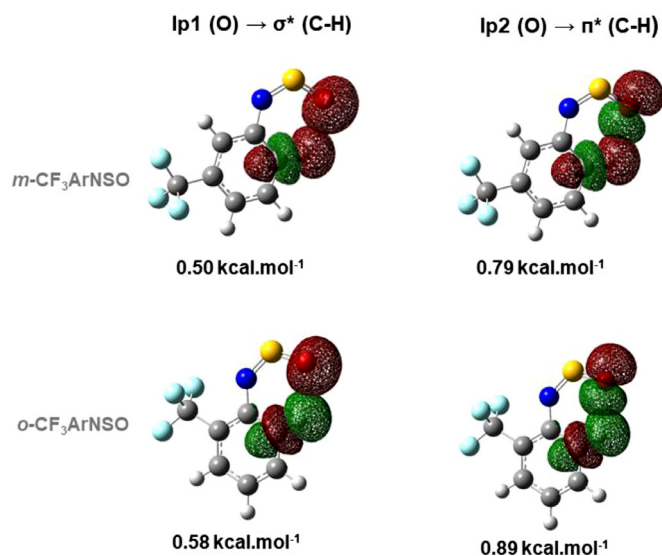
### 3.2. Vibrational analysis

The  $3N - 6 = 45$  vibrational modes expected for the conformational isomers of trifluoromethylsulfinylaniline under study were analyzed considering data reported for compounds possessing the NSO and CF<sub>3</sub> functional groups [12–16,25]. In addition, other studies performed for related compounds were also considered [31]. Besides, the assignment was supported by theoretical calculations with the B3LYP/6-311++G(df,pd) approximation. Additional calculations were performed with the same purpose using the same theoretical approach and a less extended basis set (6-311+G(df)) for <sup>13</sup>C and <sup>15</sup>N isotopically substituted versions of the compounds. The present discussion focus on the vibrational signals observed in Figs. 7 and 8 and wavenumbers values listed in Table 3. The tentative assignment of all fundamental vibrational modes was provided as supplementary material (see Tables S1 and S2). In general, the theoretical vibrational frequencies predicted are overestimated,

**Table 2**  
Topological parameters of the bond critical points for trifluoromethylsulfinylaniline conformational isomers calculated with the B3LYP/6-311+G(df) approximation.<sup>a</sup>

Compound	$r(\text{H}\cdots\text{O})$	$\rho$	$\nabla^2\rho$	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\varepsilon$
<i>m</i> -CF <sub>3</sub> ArN=S=O	2.337	0.0131	0.0474	-0.0126	-0.0109	0.0709	0.1504
<i>o</i> -CF <sub>3</sub> ArN=S=O	2.320	0.0135	0.0489	-0.0132	-0.0115	0.0738	0.1458

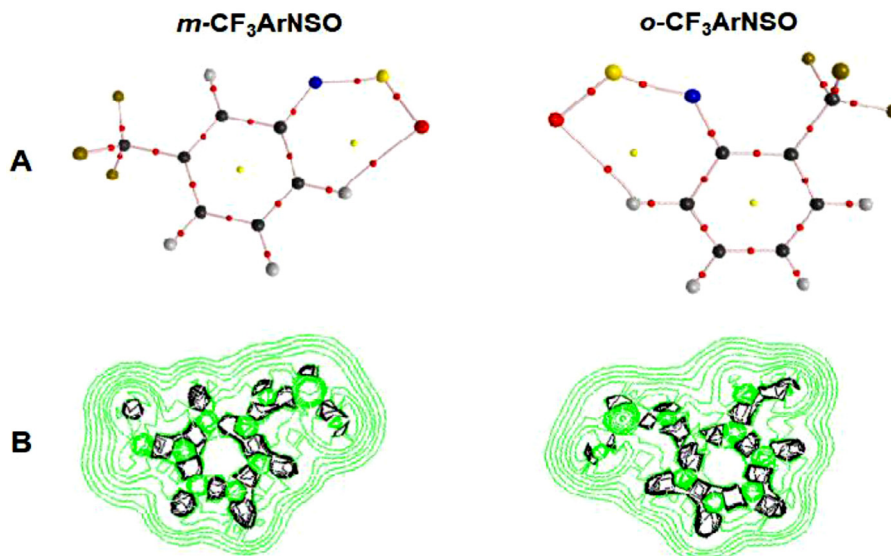
<sup>a</sup>  $\rho$ : electron density (a.u.);  $\nabla^2\rho$ : Laplacian of electron density at the BCP (a.u.);  $r$ : Distances H $\cdots$ O in Å;  $\varepsilon$ : ellipticity.



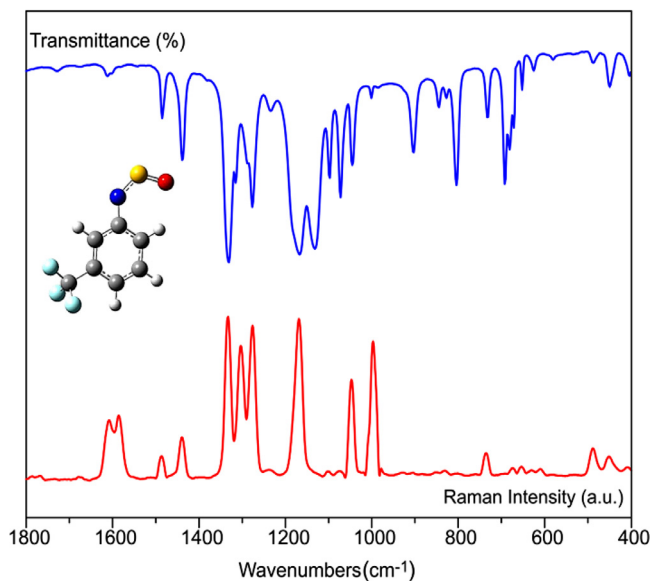
**Fig. 5.** Relevant NBO orbital interactions [B3LYP/6-311+G(df)] and corresponding energy delocalization values (kcal.mol<sup>-1</sup>) (isovalue for orbital plotting: 0.04).

since no anharmonicity deviations are considered in the oscillator model of the program [18], therefore the frequency values had to be scaled by a given factor in order to get a better match with the experimental frequency values observed [32]. In the present study, two different scaling factors were used [32,33]. The main characteristic vibrational modes are discussed below.

As it was reported previously [2,34–37] N=S and S=O stretching modes are strongly coupled therefore, these vibrations may be



**Fig. 6.** (A) Topological graphs for trifluoromethylsulfinylaniline conformational isomers obtained with B3LYP/6-311+G(df) by using AIM software package. Red dots represent BCP, yellow dots represent ring critical points and solid lines represent bonds; (B) Contour map of the Laplacian, showing the same orientation for molecules in (A).



**Fig. 7.** Experimental infrared and Raman spectra of *m*-CF<sub>3</sub>ArNSO in the region 1800–400 cm<sup>-1</sup>. Top: infrared spectrum of a liquid sample held between KRS-5 windows; bottom: room temperature Raman spectrum of a liquid sample.

better described as antisymmetric and symmetric stretching modes of the sulfinyl group. The series of compounds studied by our research group showed that for halogen monosubstituted sulfinylaniline derivatives (X = F [12–14] and Cl [15,16]), the characteristic stretching modes of the NSO group change in a larger or smaller degree according to the position of the substituent in the aromatic

**Table 3**

Experimental and calculated wavenumbers of trifluoromethylsulfanyl aniline conformational isomers and tentative assignment of selected fundamental vibrational modes.

Mode	Approximate description <sup>a</sup>	Experimental <sup>b</sup>		Theoretical values B3LYP/6-311+G(df)		
		IR (liq)	Raman (liq)	$\nu_{\text{cal}}$ (cm <sup>-1</sup> ) <sup>c</sup>	IR Intensity <sup>d</sup>	Raman Activity <sup>e</sup>
<i>m</i> -CF <sub>3</sub> ArN=S=O						
$\nu_9$	CF <sub>3</sub> Sym. Stretch.	1332 vs	1332 vs	1333	26	100
$\nu_{11}$	N=S=O Asym. Stretch.	1290 m	1303 s	1301	59	3
$\nu_{14}$	CF <sub>3</sub> Asym. Stretch.	1184 sh	-	1157	42	6
$\nu_{16}$	CF <sub>3</sub> Asym. Stretch.	1131 vs	-	1111	81	<1
$\nu_{19}$	N=S=O Sym. Stretch.	1045 m	1048 m	1038	3	20
$\nu_{26}$	C-N Stretch.	732 m	735 w	729	3	3
$\nu_{28}$	CF <sub>3</sub> Sym. Def.	681 m	-	665	7	<1
$\nu_{30}$	N=S=O Def. i.p. + C-H Def. i.p.	652 w	653 vw	625	1	1
$\nu_{31}$	CF <sub>3</sub> Asym. Def.	580 vw	-	568	<1	<1
$\nu_{34}$	CF <sub>3</sub> Asym. Def.	450 w	451 w	450	2	1
<i>o</i> -CF <sub>3</sub> ArN=S=O						
$\nu_9$	CF <sub>3</sub> Sym. Stretch.	1320 vs	1311 s	1321	10	100
$\nu_{10}$	N=S=O Asym. Stretch.	1298 s	1299 vs	1309	3	33
$\nu_{16}$	CF <sub>3</sub> Asym. Stretch.	1139 vs	1139 sh	1129	100	<1
$\nu_{17}$	CF <sub>3</sub> Asym. Stretch.	1116 vs	1116 vw	1111	52	<1
$\nu_{19}$	N=S=O Sym. Stretch.	1035 s	1035 sh	1036	28	6
$\nu_{27}$	C-N Stretch.	737 vw	737 vw	734	<1	6
$\nu_{28}$	CF <sub>3</sub> Sym. Def.	681 m	-	647	11	1
$\nu_{30}$	N=S=O Def.i.p. + C-H Def.i.p.	-	642 w	588	2	<1
$\nu_{31}$	CF <sub>3</sub> Asym. Def.	594 m	-	563	1	<1
$\nu_{34}$	CF <sub>3</sub> Asym. Def.	443 sh	443 vw	468	2	2

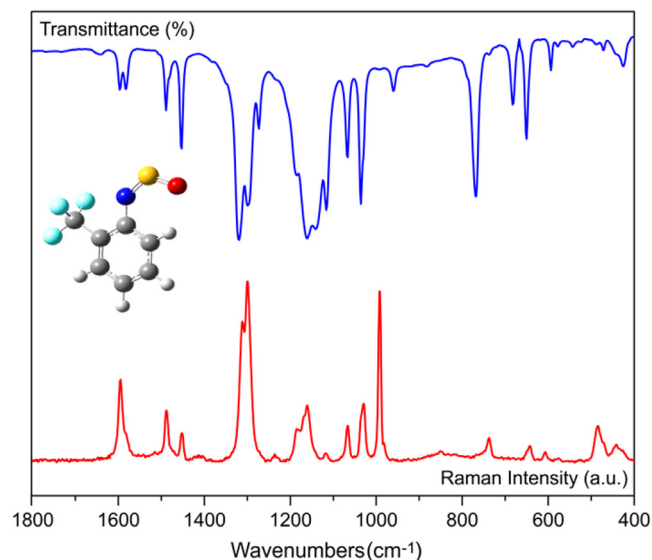
<sup>a</sup> Stretch.: stretching; Asym.: antisymmetric; Sym.: symmetric; Def.: deformation; i.p.: in phase;

<sup>b</sup> s: strong; vs: very strong; m: medium; w: weak; vw: very weak; sh: shoulder.

<sup>c</sup> Values scaled by 0.983, according to scaling factors in Ref. [33].

<sup>d</sup> Relative infrared intensities normalized to 100%.

<sup>e</sup> Raman activities normalized to 100%.



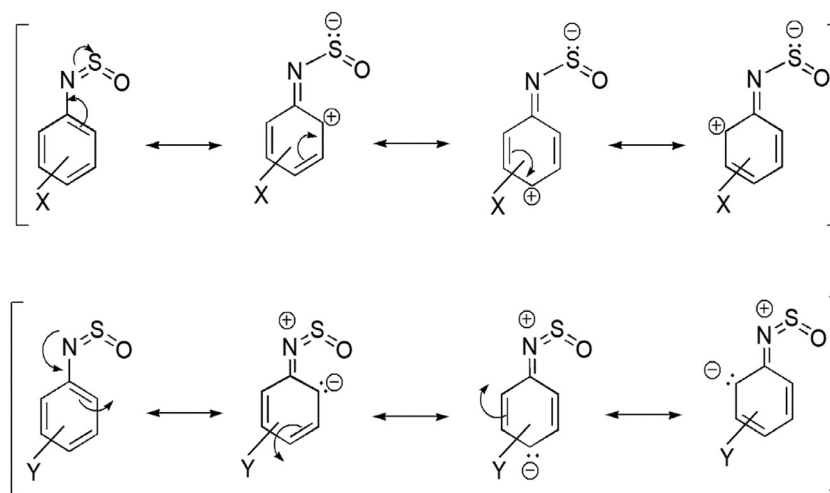
**Fig. 8.** Experimental infrared and Raman spectra of *o*-CF<sub>3</sub>ArNSO in the region 1800–400 cm<sup>-1</sup>. Top: infrared spectrum of a liquid sample held between KRS-5 windows; bottom: room temperature Raman spectrum of a liquid sample.

ring. Not only frequency values modify according to the position of the substituent, but they also change in response to the electronic density in the aromatic ring itself. According to the literature, the sulfinyl group may act as electron donor or electron withdrawing substituent depending on the possibility of electronic delocalization of the substituents [38]. Scheme 2 shows mesomeric structures for both opposite scenarios: while most of the structures with NSO as an electron withdrawing group show simple N-S bonds (X = F, Cl, Br), double N-S bonds might be present in all structures with NSO as an electron donor group (Y = CH<sub>3</sub>, OCH<sub>3</sub>)

[38]. As expected, the frequency values would modify accordingly. Halogen substituents in sulfinylaniline derivatives were found to provide electron density to the aromatic ring through mesomeric effects; in contrast, the CF<sub>3</sub> group behaves as a mild electron withdrawing substituent of the ring through inductive effect. Despite the differences in the electronic effects showed by halogen substituents and the CF<sub>3</sub> group, in each case the sulfinyl group behaves as an electron withdrawing substituent.

For *m*- and *o*-CF<sub>3</sub>ArNSO the antisymmetric stretching modes were assigned to the signals at 1290/1303 and 1298/1299 cm<sup>-1</sup> in the infrared/Raman spectra, respectively (see Figs. 7 and 8). The symmetric fundamentals were attributed to the signals at 1045/1048 (*meta* isomer) and 1035/1035 cm<sup>-1</sup> (*ortho* isomer), respectively. The in plane bending mode characteristic for this functional group is frequently observed as a medium to weak signal in the vibrational spectra in the region 600–660 cm<sup>-1</sup> and therefore was assigned to the features observed at 653 and 642 cm<sup>-1</sup> in the Raman spectra registered for *m*- and *o*- conformational isomers, respectively.

As a trait of vibrational modes belonging to the trifluoromethyl group the symmetric fundamentals are usually found at higher wavenumbers than the antisymmetric ones. The former ones are frequently found in the region 1300–1350 cm<sup>-1</sup> while the last ones are mostly observed in the range 1100–1200 cm<sup>-1</sup> [39]. Thus, the signals at 1332 and 1320 cm<sup>-1</sup> in the infrared spectra of *meta* and *ortho* conformational isomers, would account for the symmetric stretching modes while the antisymmetric fundamentals were observed at 1184 and 1131 cm<sup>-1</sup> (FTIR, *m*-CF<sub>3</sub>ArNSO) and 1139 and 1116 cm<sup>-1</sup> (FT Raman, *o*-CF<sub>3</sub>ArNSO). Similarly, the symmetric bending modes for both conformational isomers were observed as medium intensity signals centered at 681 cm<sup>-1</sup> in the infrared spectra. The antisymmetric deformation modes appeared at 580 and 450 cm<sup>-1</sup> (*m*-CF<sub>3</sub>ArNSO) and at 594 and 443 cm<sup>-1</sup> (*o*-CF<sub>3</sub>ArNSO). The remaining group bending modes characteristic of this group were assigned by taking into account data reported pre-



**Scheme 2.** Feasible mesomeric structures for sulfinylaniline derivatives (X = F, Cl, Br; Y = CH<sub>3</sub>, OCH<sub>3</sub>).

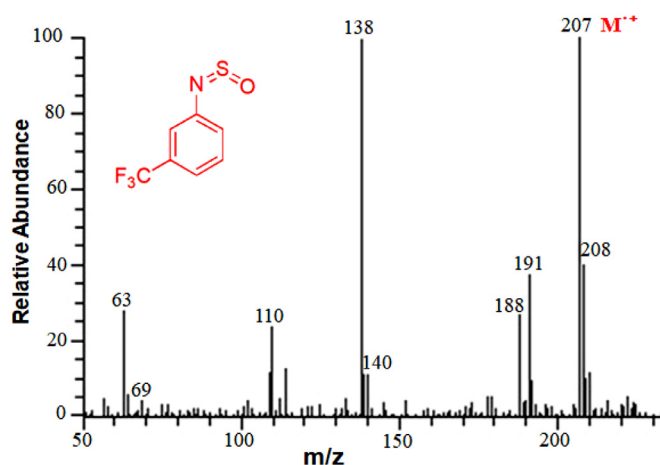
viously [31,40,41] and are available as supplementary material (see Tables S1 and S2).

The vibrational spectra of substituted benzene rings are among the most complicated to assign since the experimental features observed modify according to the type and position of the substituents bonded to the aromatic ring. For *meta* and *ortho* conformational isomers characteristic vibrations involving some C-H in-plane bending are found throughout the 1000 - 1600 cm<sup>-1</sup> region. These in-plane C-H bending vibrations interact, sometimes strongly, with vibrations involving ring C-C stretching modes. Figs. 7 and 8 show two features with similar shape at 1601 - 1611 cm<sup>-1</sup> (*meta*) and 1596-1581 cm<sup>-1</sup> (*ortho*) with different intensity pattern which allow to distinguish between both conformational isomers. Another region suitable to differentiate between these forms extends from 700 to 1000 cm<sup>-1</sup>, the C-H out-of-plane bending vibrations region. In the present study, the signals centered at 903 and 959 cm<sup>-1</sup> were attributed to the corresponding bending modes for *meta* and *ortho* conformational isomers, respectively with characteristic intensity patterns [42].

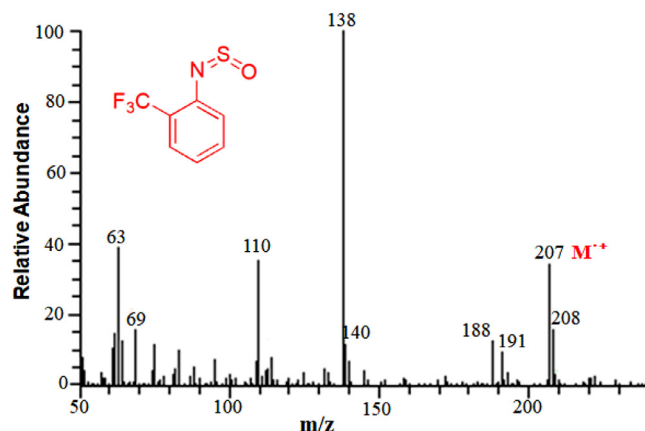
In general, the assignment of the signal corresponding to the C-N stretching is not direct, since not only this vibration is frequently involved in several fundamental stretching and bending modes, but also its intensity is quite variable, making difficult to identify it unambiguously. In the present study the C-N stretching was attributed to the band at 732/735 cm<sup>-1</sup> (*m*-CF<sub>3</sub>ArNSO) and at 737/737 cm<sup>-1</sup> (*o*-CF<sub>3</sub>ArNSO) in the infrared/Raman spectra, respectively. The same fundamental mode was observed at higher wavenumber values for a series of halogen substituted sulfinylaniline derivatives [33]. Presumably the mesomeric effects exerted by the halogen atoms are more effective to strengthen the C-N bond.

### 3.3. GC/MS analysis

Figs. 9 and 10 show the mass spectra obtained for *m*- and *o*-CF<sub>3</sub>ArNSO conformational isomers. According to the literature [43], parent sulfinylaniline fragments by two distinct pathways on electron impact, the first of them starting with SO loss from the molecular ion while the second initiates after atom reordering of the NSO group. In the present case, the corresponding molecular fragments would have the CF<sub>3</sub> functional group as well. Nevertheless, the signals observed as a consequence of any of these processes show relative abundance below 10% of the base peak. Fig. 11 shows a common tentative fragmentation pattern for both conformational isomers which accounts for the main signals observed.



**Fig. 9.** 70 eV Electron ionization mass spectrum of *m*-CF<sub>3</sub>ArNSO.



**Fig. 10.** 70 eV Electron ionization mass spectrum of *o*-CF<sub>3</sub>ArNSO.

The signal attributed to the molecular ion of  $m/z = 207$  shows different relative abundance for different conformational isomers. For *p*-trifluoromethylsulfinylaniline [25] and *m*-CF<sub>3</sub>ArNSO it was found as an intense peak, while in the *ortho* conformer, it would only amount up to ca 40%. In general, the stability of the molecular ion increases if  $\pi$ -bonding electrons for the delocalization of the charge are available and it decreases in the presence of preferred

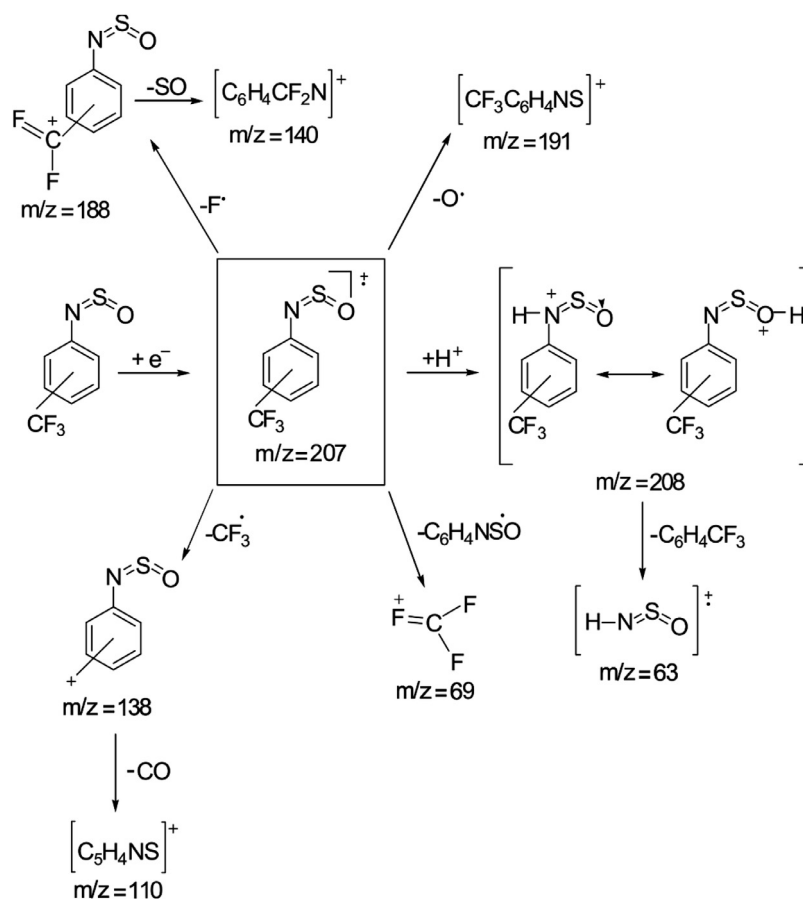


Fig. 11. Main fragmentation paths of trifluoromethylsulfinylaniline conformational isomers upon electron ionization.

sites for bond cleavage [44]. A similar pattern was found for *o*-, *m*- and *p*-halogen substituted *N*-acylanilines when the halogen atoms were chlorine, bromine and iodine, whereby an *ortho* effect was observed. In contrast, for corresponding fluorinated compounds the molecular ion would exhibit similar relative abundance [45]. As it was observed for this last series, the mass spectra of perfluorinated positional isomers of sulfinylaniline now under study, and that reported for *p*-trifluoromethylsulfinylaniline [25] differ only in the relative abundance of the peaks observed. The loss of the  $\text{CF}_3$  functional group is responsible for the base peak of the mass spectra for both isomers ( $m/z = 138$ ), and its stability was rationalized through several feasible resonance structures. In turn, one of the most evident differences between *o*- and *m*- mass spectra lay in the relative abundance of the peak attributed to the trifluoromethyl fragment itself ( $m/z = 69$ ), which is more abundant for the *ortho* isomer than for the corresponding *meta* and *para* [25] conformers. Additionally, the signal of  $m/z = 110$  results from CO loss as a consequence of internal atom reordering of the sulfinylaniline ion ( $m/z = 138$ ).

The signals of  $m/z = 191$  and  $m/z = 188$  result from oxygen and a single fluorine atom loss from the molecular ion, respectively. They were assigned taking into account similar fragmentation patterns previously reported [43,46]. The later specie would produce an additional fragment of  $m/z = 140$ , as a result of SO loss. Finally, as it was also found for *p*-trifluoromethylsulfinylaniline [25], both the MS spectra of corresponding *m*- and *o*- conformational isomers evidenced the formation of the  $\text{HNSO}^+$  fragment by the signal of  $m/z = 63$ .

### 3.4. NMR analysis

Table 4 lists experimental  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift values observed for liquid samples of *m*- and *o*- $\text{CF}_3\text{ArNSO}$  conformational isomers solved in  $\text{CDCl}_3$  at room temperature (TMS was used as internal reference) together with those obtained using GIAO method with the B3LYP/6-311+G(df) approximation.

Aromatic protons are usually observed in the 6.50 – 8.50 ppm region of the  $^1\text{H}$  NMR spectra [47] showing *J* *ortho* coupling constants in the range 7 – 9 Hz. In the present study, those values are in the range 7.3 – 8.3 Hz. The presence of the sulfinyl group nearby H1 proton (for atom numbering, see Fig. 3) produces the strongest effect on the chemical shift values for both conformational isomers (see Table 4), being the corresponding signals the least shielded in the aromatic proton region. Room temperature rotational barrier for rotation around the C-N bond for *m*- $\text{CF}_3\text{ArNSO}$  is low (see Section 3.1.1) therefore at first sight H1 and H4 protons would experience the effects of the sulfinyl group in the same extent. As a consequence, the experimental chemical shifts values corresponding to H1 and H4 would be similar, in agreement with data reported for *meta* substituted fluorosulfinylaniline [13]. However, calculated chemical shift value for H1 was overestimated with respect to the ones obtained for the other protons, as well as for the experimental features observed. In contrast, for the *ortho* isomer the theoretical chemical shift value predicted for H1 shows better correlation with the corresponding experimental one. The assignment is in good agreement with data reported for related compounds [31].



**Table 4**

Comparison between experimental and calculated chemical shift values for trifluoromethylsulfinylaniline conformational isomers with B3LYP/6-311+G(df) approximation.

	Chemical shift, $\delta$ (ppm) and Coupling constants, J (Hz)			
	<i>m</i> -trifluoromethylsulfinylaniline		<i>o</i> -trifluoromethylsulfinylaniline	
	Theoretical <sup>a</sup>	Experimental <sup>b</sup>	Theoretical <sup>a</sup>	Experimental <sup>b</sup>
<sup>13</sup> C NMR				
C(1)	151.23	142.50 (s)	148.60	139.17 (q) <sup>3</sup> J=4.9 Hz
C(2)	135.29	130.03 (s)	133.58	128.52 (s)
C(3)	133.05	128.47 (s)	135.95	132.88 (s)
C(4)	133.55	126.78 (q) <sup>3</sup> J=3.7 Hz	134.98	129.74 (s)
C(5)	137.22	131.92 (q) <sup>2</sup> J=33.1 Hz	129.98	126.88 (q) <sup>3</sup> J=5.2 Hz
C(6)	129.73	123.77 (q) <sup>3</sup> J=3.8 Hz	133.27	125.08 (q) <sup>2</sup> J=30.7 Hz
C(7)	133.37	123.52 (q) <sup>1</sup> J= 272.6 Hz	133.01	123.20 (q) <sup>1</sup> J=273.5 Hz
<sup>1</sup> H NMR				
H(1)	8.94	7.96 (d) J <sub>H1-H2</sub> = 7.3 Hz	8.81	8.47 (d) J <sub>H1-H2</sub> = 7.9 Hz
H(2)	7.37	7.44 (t) J <sub>H2-H1</sub> = 8.0 Hz; J <sub>H2-H3</sub> = 8.0 Hz	7.38	7.65 (t) J <sub>H1-H2</sub> = 7.9 Hz; J <sub>H2-H3</sub> = 7.6 Hz
H(3)	7.44	7.55 (d) J <sub>H3-H2</sub> = 7.6 Hz	7.29	7.51 (t) J <sub>H3-H4</sub> = 8.2 Hz; J <sub>H3-H2</sub> = 7.7 Hz
H(4)	7.46	7.98 (s)	7.61	7.80 (d) J <sub>H4-H3</sub> = 7.7 Hz

Signals belonging to aromatic carbon atoms in the <sup>13</sup>C NMR spectra are usually found in the 100 – 150 ppm range [47]. The presence of the CF<sub>3</sub> group was essential for the unambiguous assignment of the signals since the fluorine atoms couple with aromatic carbon atoms with characteristic coupling constants [48]. As expected, the signals attributed to the carbon atoms bonded to the NSO group were found at the lowest fields in both conformational isomers. Besides, the CF<sub>3</sub> group determines differences in the multiplicity of these signals. For the *ortho* isomer, a C-F coupling was evidenced by the presence of a quartet with the characteristic <sup>3</sup>J value. In contrast, a singlet was observed for the *meta* isomer since no coupling was expected being C1 and CF<sub>3</sub> group far away from each other, in complete agreement with data reported for benzotrifluorides derivatives [49,50]. The carbon atom of the CF<sub>3</sub> group and the corresponding aromatic C atom to which it is bonded are evidenced in the NMR spectra as quartet signals of very low intensity with characteristic <sup>1</sup>J and <sup>2</sup>J coupling constants. Since the coupling constants are so large and the signals so weak, if they are not looked for, they would not be easily found as they are barely noticeable [48]. The remaining features observed were assigned according to data reported in the literature for related compounds [31,49,50] and the theoretical chemical shift values obtained.

#### 4. Conclusions

By adjusting the general protocol for the synthesis of sulfinylaniline it was possible to obtain the products *m*- and *o*-CF<sub>3</sub>ArNSO. These compounds complete the series of mono trifluoromethyl substituted aromatic-NSO compounds studied by our group. The highly hygroscopic and corrosive substances were obtained with high yield through the reaction of *m*- and *o*-trifluoromethylaniline and SOCl<sub>2</sub> and were characterized by vibrational and <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy, gas chromatography/mass spectrometry and quantum chemical calculations. The potential energy surfaces obtained revealed two and one global minima with *syn* geometry and coplanar disposition of the NSO group and the aromatic ring for *m*- and *o*- conformational isomers, respectively. The coplanar disposition observed in each case is a consequence of stabilizing intramolecular interactions of the type C(2)–H(1)···O, defined as anti-hydrogen bonds [4] and predicted by AIM. The strengthening of the C-H bond involved in this interaction was not discernable through vibrational spectroscopy, as this fundamental vibrational mode is coupled with other bonds of this type of the ring. On the other hand, the symmetric N=S=O stretching mode does not change remarkably upon ring substitution with different halogen atoms (F, Cl) or with a CF<sub>3</sub> group, as in

the present case. Only subtle changes were observed for antisymmetric N=S=O stretching modes of monosubstituted sulfinylaniline derivatives with halogen or CF<sub>3</sub> group. Nevertheless, experimental <sup>1</sup>H NMR spectra do help discerning between different conformational isomers. Since the anti-hydrogen bond is feasible in both isomers, it is the presence of the CF<sub>3</sub> substituent which mostly affects the chemical shift values observed. Even though this group interacts in the molecule by different electronic effects than the halogen substituents, it does not change the electron withdrawing nature of the NSO group.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Doly M. Chemes:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **José O.G. Lezama:** Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Edgardo H. Cutin:** Writing - original draft, Writing - review & editing, Visualization, Funding acquisition. **Norma Lis Robles:** Conceptualization, Formal analysis, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.129879.

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