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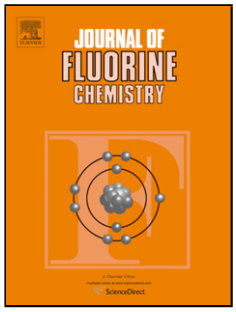

Title: On the search of the influence of substituents in the structural and vibrational properties of *p*-substituted sulfinylanilines: study of *p*-trifluoromethylsulfinylaniline

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On the search of the influence of substituents in the structural and vibrational properties of *p*-substituted sulfinylanilines: study of *p*-trifluoromethylsulfinylaniline

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Dedicated to Prof. Dr. Rüdiger Mews on occasion of his seventy-fifth birthday.

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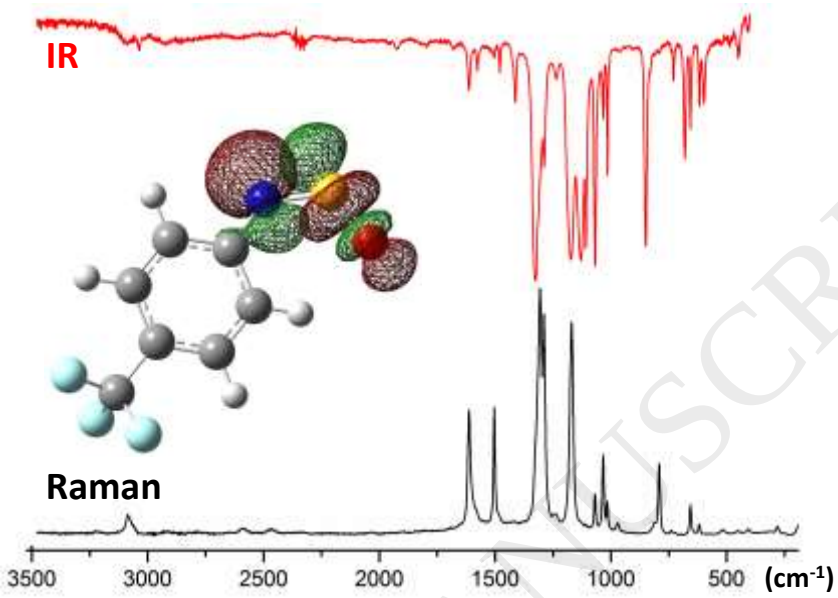
HIGHLIGHTS

Molecular properties of *p*-CF_3ArNSO were determined by the NMR, Raman, FTIR, GC-Mass methodologies.

PES scans and subsequent structural and vibrational characterization were performed by DFT methods.

The energetically preferred molecular geometry has the NSO group in s*yn* conformation and coplanar with the aromatic ring.

GRAPHICAK ABSTRACT



Abstract

The study of substitution effects on the structural and vibrational properties of *para* substituted sulfinylanilines proceeds a step forward with the study of *p*-trifluoromethylsulfinylaniline, synthesized and characterized by NMR, Raman, FTIR and mass spectra. The experimental spectra were compared and analyzed taking into account theoretical spectra obtained with quantum chemical calculations at different levels of theory. The spectroscopic results reveal the presence of a single form of this molecule which, according to the calculated molecular structure, possesses the NSO group coplanar with the ring plane. In addition, the *syn* conformation of the NSO group is also derived from both, experimental and theoretical data. The presence of the CF_3 group in the *para* position of the aromatic ring influences the properties of the N=S=O group, with the N=S bond more strongly affected than the S=O bond compared to results reported for other *para* substituted sulfinylanilines.

Keywords: sulfinylaniline; vibrational spectroscopy; structural analysis

1. Introduction

Reactivity and structural/chemical properties of several organic *N*-sulfinylimines compounds of the type R–N=S=O have been subject of studies since the first reports of their synthesis by Michaelis and co-workers [1, 2]. By using various experimental techniques such as gas electron diffraction, X-ray crystallography, UV-visible absorption spectroscopy, ^{17}O NMR spectroscopy, GC-Mass Spectrometry, and FTIR and Raman spectroscopies, as well as theoretical methods, it was demonstrated that all R–N=S=O compounds show *syn* conformation between the R–N single bond and the S=O double bond. The R group was benzene [3], ClC(O)S [4], CF_3SS [5], more recently CF_3 and SF_5 [6] and many others, as it was reviewed by Romano and Della Védova [7]. The stability of this sterically unfavorable conformation, where the electron lone pairs of nitrogen and sulfur eclipse each other, lies in the orbital interactions between each lone pair and the opposite S–O or N–R antibonding σ* orbital. This anomeric effect is absent in the *anti* form. As result, quantum chemical calculations predict the energy of *anti* conformation about 8 $kcal.mol^{-1}$ higher than *syn* for all mentioned compounds [7].

Particularly interesting are the N-sulfinylanilines since, due to the high reactivity of the aromatic sulfinylamine function (Ar-N=S=O), they are used as ligands in organometallic chemistry [8] and as precursors for obtaining cyclic sulfonamides with pharmacological properties [9-11]. The study of the influence of substituents in the aromatic ring on the properties of the –N=S=O group is therefore of significant relevance. Accordingly, we have focused on determining the structural and vibrational characteristics of monosubstituted halogen sulfinylanilines such as *o*-, *m* and *p*-fluorosulfinylaniline (FArNSO) [12-14], and *m*- and *p*-chlorosulfinylaniline (ClArNSO) [15, 16] by using FTIR and Raman spectroscopies and quantum chemical predictions together with NMR and GC-mass measurements. In these compounds, the *syn* conformation is characterized by a fully planar molecular structure. This geometry not only favors the formation of an intramolecular hydrogen bond between the oxygen and the H atoms in *ortho* position, but also the electronic delocalization through the aromatic ring and the sulfinylimine group [17].

In the present work we address a conformational and vibrational analysis of *para*-trifluoromethylsulfinylaniline, (*p*-CF_3ArNSO). The inclusion of this compound in our series of halogen substituted-sulfinylanilines is based on the popularity of the trifluoromethyl group in pharma and agrochemical molecules, due to its capacity to exert significant changes on

neighboring active centers as well as to increase lipophilicity of the molecules that contain it [18]. *p*-CF_3ArNSO preparation was reported previously, as part of a study of the reactivity of N-sulfinyl compounds with thioborane [19]. Further studies, based on comparative analyses by ^{17}O and ^{13}C NMR spectroscopy of several sulfinylanilines, were focused in the nature of the S-O bond and the influence of substituents on its properties [20]. Now we present a more complete approach of the structural properties of the *p*-CF_3ArNSO molecule, for which FTIR, Raman and NMR (^1H and ^{13}C) spectroscopies, together with measurements by GC-mass spectrometry, were used. Quantum chemical calculations at various levels of theory supported the analysis of the experimental data. A comparison with the results previously obtained for *p*-halogen substituted sulfinylanilines allowed us to establish a correlation between specific vibrational frequencies and hence to infer about the effect produced by the substituent at structural level according to its inductive and mesomeric characteristics. It is well known that many efforts have been invested in studying the biological aspects of new fluorine or trifluoromethyl-containing compounds [21]. Then, we expect that our results contribute to a better understanding of the reactivity of this kind of molecules.

2. Results and discussion

Figure 1 presents the FTIR and Raman spectra in the 4000–400 and 3500–300 cm^{-1} spectral ranges, respectively, of the green liquid obtained after purification. The absence of bands attributable to the NH_2 group (between 3500 and 3400 cm^{-1}) indicates that the amine precursor has been completely eliminated.

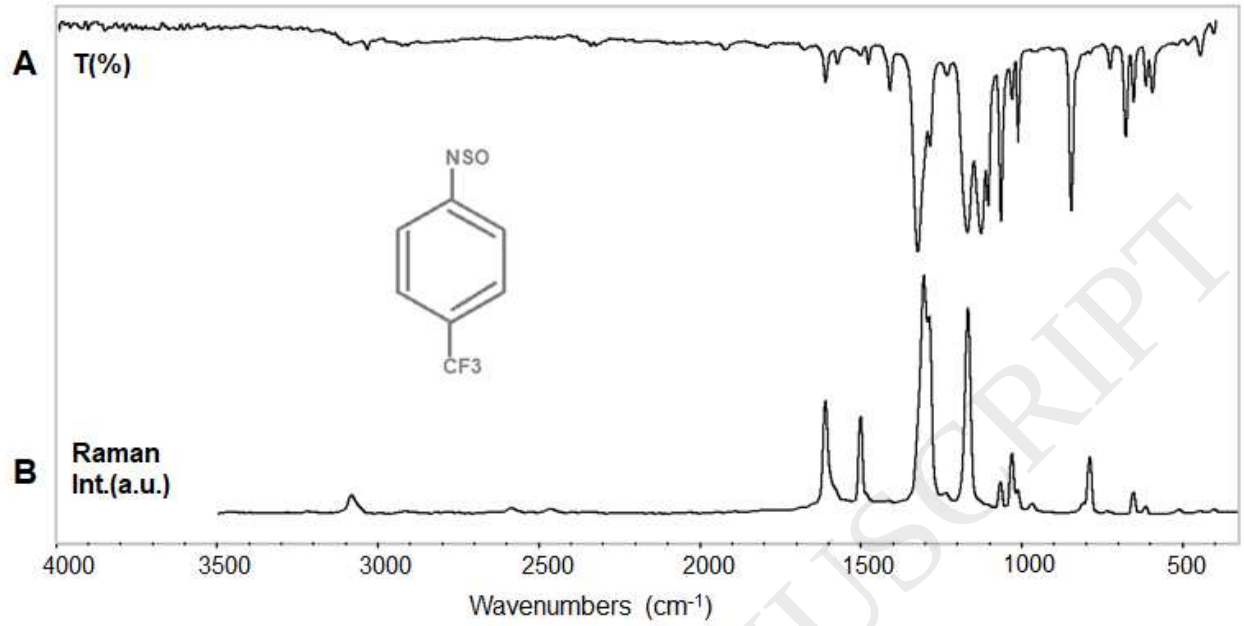


Figure 1. Experimental infrared (A) and Raman (B) spectra of *p*-CF_3ArNSO.

2.1. *Conformational analysis and structural characterization*

The evaluation of the most stable conformations adopted by the *p*-CF_3ArNSO molecule was performed by exploring the potential energy surface (PES) as a function of two dihedral angles that were modified independently. Figure 2 shows the relaxed PES scans done at the B3LYP/6-311+G(df) level for the dihedral angles ϕ(C-N=S=O) and ϕ(C-C-N=S), varied from 0° to 180° in steps of 30°. As it was observed for all *N*-sulfinylimines reported so far, the global minimum obtained for the first scan corresponds to the *syn* conformation regarding the orientation of the C–N and the S=O bonds, ϕ(C-N=S=O) = 0°, while a considerably high barrier to rotation around the N=S double bond was predicted. A previous PES study of HNSO, the simplest N-sulfinylimine, indicated that the *syn* conformer is 4.58/4.97 kcal.mol^{-1} (B3LYP/MP2, respectively) than the *anti* form, and that the interconversion between them solely involves a planar nitrogen inversion [22]. However, in a recent article on the generation and characterization of the OSNSO species, conformational interconversions of the type *syn-syn*→ *syn-anti* and *syn-syn* → *anti-anti* were analyzed by considering the explicit N=S bond rotation [23].The scan around the C-N bond of *p*-CF_3ArNSO indicated that the planar conformation was adopted by the whole molecule, since two

equivalent minima were obtained for the variable ϕ(C-C-N=S) = 0°/180°. The barrier to internal rotation at the perpendicular conformation was calculated to be 5.06 kcal.mol^{-1}.

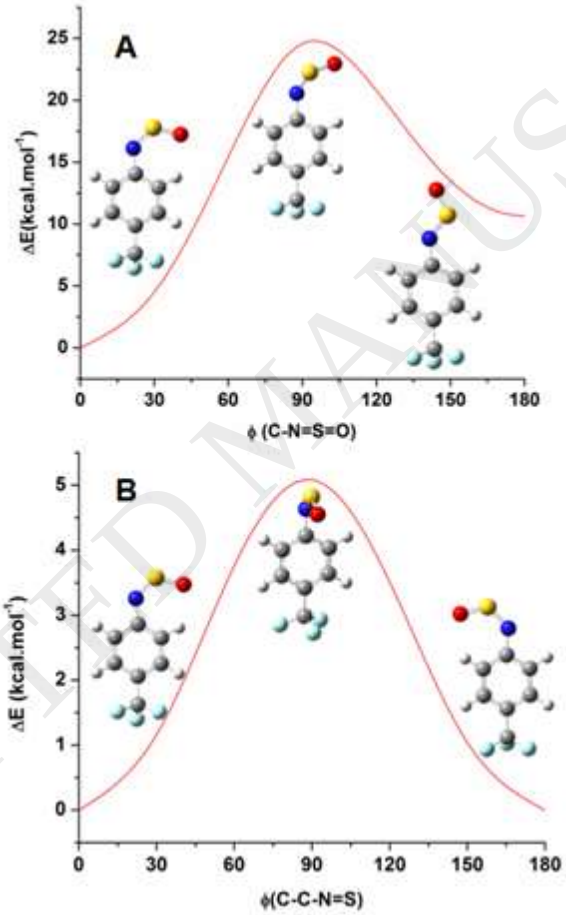


Figure 2. Calculated relaxed PES scans for rotation around the N=S bond (A) and the C–N bond (B). A): the *syn* cornformation (ϕ CNSO = 0°) of the NSO group is the most stable one; the second local minimum predicted corresponds to the *anti* form (ϕ CNSO = 180°). B): similarly, coplanarity between the NSO group with the aromatic ring (ϕ CCNS = 0° or 360°) is the preferred arrangement. Calculations were performed at the B3LYP/6-311+G(df) level of theory.

Subsequent full optimization and frequency calculation for the planar molecule in both the *syn* and *anti* conformations were performed at the B3LYP/6-311+G(df) and MP2/cc-pVTZ levels of theory. Since no imaginary vibrational frequencies were predicted, both forms correspond to stable structures, but the *syn* form was the preferred one according to ΔE° (*anti-syn*) = 5.06/8.14 kcal.mol^{-1} and ΔG° (*anti-syn*) = 6.63 /8.52 kcal.mol^{-1} (B3LYP/MP2 methods, respectively).

The higher stability of the sterically unfavorable *syn* conformation of the N=S=O group is explained by anomeric effects. The NBO analysis performed with the B3LYP/6-311+G(df) approximation showed orbital interactions between the nitrogen and sulfur lone pairs with vicinal antibonding orbitals. Figure 3 represents the lp (N) →σ* (S–O) and lp (S) →σ* (C–N) orbital interactions that contribute with 15.33 and 5.61 kcal.mol^{-1}, respectively, to the stabilization of the *syn* conformation, while the contributions for the *anti* form amount only 9.90 and 1.01 kcal.mol^{-1}, respectively.

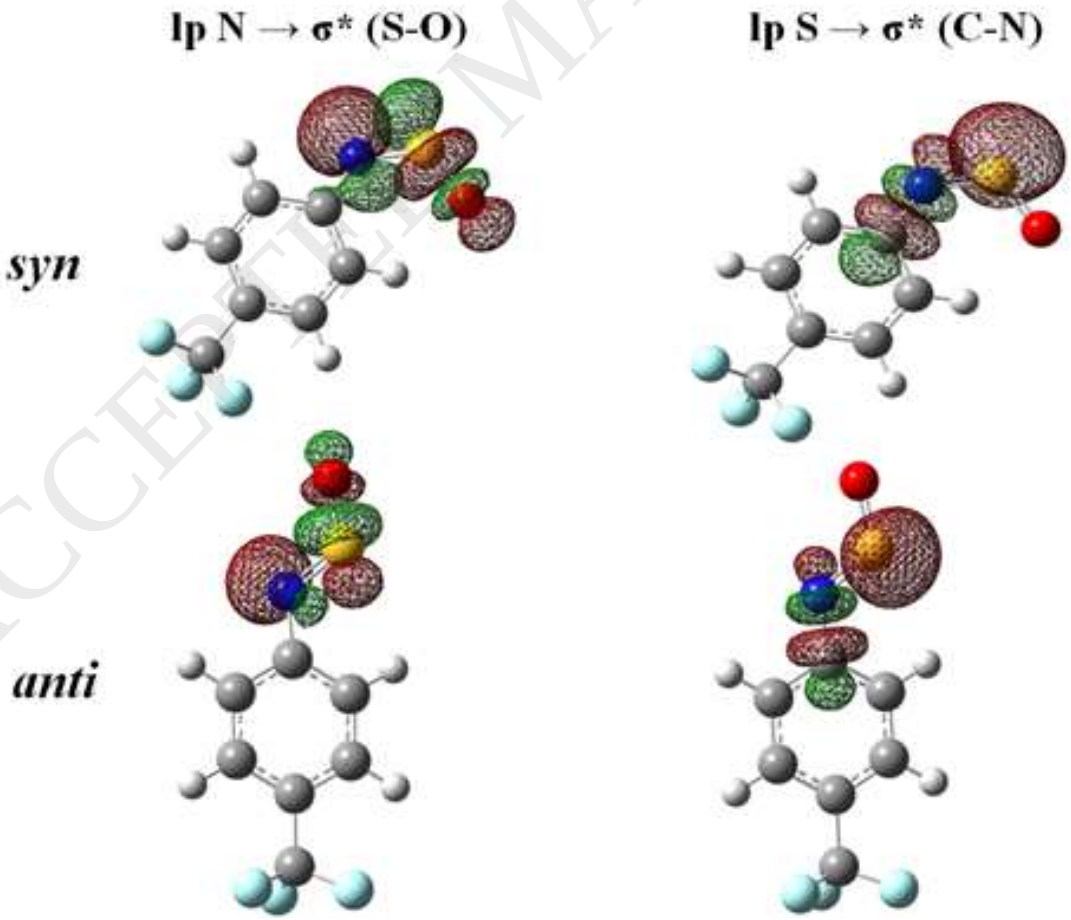


Figure 3. Relevant NBO orbital interactions calculated with B3LYP/6-311+G(df) approximation for *syn* and *anti* conformations of *p*-CF_3ArNSO.

The planar conformation predicted for the molecule facilitates a weak orbital interaction between oxygen and the *ortho* hydrogen closest to it. This interaction is called *anti*-hydrogen bond, and a distinctive consequence of it is the shortening of the C–H bond involved and the consequent blue shift of its stretching frequency. Additionally, the C---O distance is generally found to be in the 3.00 – 4.00 Å range [24]. This interaction was already observed in the parent *N*-sulfinylaniline [17]. According to MP2/cc-pVTZ calculation the overlap population for this O---H interaction is +0.02 au, about 5% of the C–H overlap (0.42 au). The O---H distance (2.27 Å) is shorter than the Van der Waals distance of 2.60 Å while the C---O distance is predicted to be 3.05 Å.

As it was expected, the CF_3 group attached in *para* position is freely rotating. In the equilibrium orientation, one C–F bond is perpendicular to the phenyl ring and the barrier of this 6-fold potential with one C–F bond in the plane of the phenyl ring is only 0.04 kcal/mol.

Figure 4 shows the optimized molecular structure of the most stable conformer. C–H bond lengths and O--H distance, calculated at the B3LYP/6-311+G(df) level are included. The remaining structural parameters are presented in Table 1, together with those obtained with the MP2/cc-pVTZ approximation.

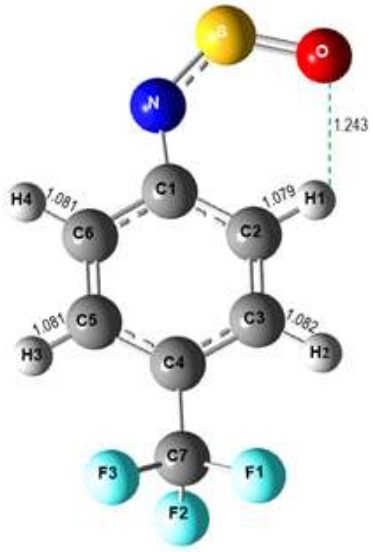


Figure 4. Optimized molecular structure of *p*-trifluoromethylsulfinylaniline. All the C–H distances, calculated with the B3LYP/6-311+G(df) method, are included in order to show the shortening of the C2-H1 bond as consequence of the *anti*-Hydrogen bond interaction.

2.2. *Vibrational analysis*

The vibrational analysis of *p*-CF_3ArNSO was based on the evaluation of the experimental FTIR and Raman bands and on the corresponding theoretical predictions. Experimental and calculated vibrational behaviors for related systems such as the parent sulfinylaniline [3] and the reactant *p*-trifluoromethlyaniline [25], as well as reported experimental and calculated data for *p*-FArNSO [14] and *p*-ClArNSO [16] were also taken into account.

Figure 5 shows the spectral region between 1500 and 500 cm^{-1} of the experimental FTIR and Raman and the calculated spectra (B3LYP/6-311++G(df,dp)) of *p*-CF_3ArNSO. A tentative assignment of all the fundamental vibrational modes expected for the title compound is presented in Table 2. As can be seen in Table 2, vibrational frequencies calculated at B3LYP/6-311++G(df,dp) and B3LYP/cc-pVTZ levels of theory show similar accuracy compared to the experimental bands. Nevertheless, while both basis sets are of triple zeta level, the former is split valence, which makes it significantly less expensive in terms of computational cost. In order to check the performance of the variational approach attained with B3LYP, MP2 calculations were also performed. It is well known that electronic self-interaction (among other deficiencies) may sometimes be a serious problem in DFT-based calculations, so we consider good practice to

perform wavefunction (post-Hartree-Fock) calculations in order to check for serious discrepancies in the predictions, whenever possible. In this occasion, MP2 and DFT predictions did not differ in any significant (qualitative) way, although DFT methods produced frequencies that were better correlated with the experimental data than MP2 [26].

Although the vibrational spectra of the parent sulfinylaniline have been extensively studied, some controversies were detected a few years back regarding the coupling of N=S and S=O bonds in the stretching vibrations. A detailed work published by Meij *et al.* on the Raman spectra of sulfinylaniline [27] concluded that the stretching modes of the N=S=O group should be described as two independent modes placed at 1284 cm^{-1} and 1155 cm^{-1} and assigned to the N=S and S=O bonds, respectively. Romano *et al.* reported later the resonance Raman spectra and quantum chemical calculations of this compound revealing a strong coupling between both modes, which were defined as antisymmetric (at 1298 cm^{-1}) and symmetric (at 1163 cm^{-1}) stretching vibrations [3]. More recently, our group reported the analysis of the vibrational spectra and theoretical frequencies of *p*-FArNSO [14]. This analysis pointed out that the bands centered at 1303 cm^{-1} and 1030 cm^{-1}in the IR spectrum could be attributed to the N=S=O antisymmetric and symmetric stretching modes, respectively. A similar interpretation of the IR bands at 1297 cm^{-1} and 1031 cm^{-1} of *p*-chlorosulfinylaniline was later proposed [16]. A preliminar comparison with results for *m*-, *o*-, and *p*- isomers of FArNSO [13,12,14] showed that the antisymmetric stretching of the N=S=O group is the most affected vibration upon substitution at different ring locations, with a frequency blue shift of up to 11 and 4 cm^{-1} for the *meta* and *ortho* isomers, respectively. These shifts may be rationalized by taking into account the electronic effects derived from the position of the substituent in the aromatic ring. As it was stated for this fluorosulfinylaniline series, the small size of the fluorine atom may help in supplying the aromatic ring with electronic density upon mesomeric delocalization of lone pair orbitals. In contrast, it may withdraw electronic density from the aromatic ring due to its strong inductive effect. In the present case, the CF_3 group in *para* position of the aromatic ring would not represent a source of electronic density towards the aromatic ring either through mesomeric or inductive effects. The bands observed at 1289 and 1033 cm^{-1} in both vibrational spectra were attributed to the antisymmetric and symmetric stretching modes of the N=S=O group (see Table 2). When comparing different *p*-substituted compounds, the evaluation of the contribution of the

electronic effects involved did not help to understand the frequency of the stretching vibrations. In the series: *p*-FArNSO, *p*-CF_3ArNSO and *p*-ClArNSO, the N=S distance was predicted to be 1.541, 1.539 and 1.507 Å, respectively (B3LYP/6-311++G(df,pd)). The corresponding antisymmetric N=S=O stretching mode was assigned to the signals at 1303, 1289 and 1297 cm^{-1}, respectively (IR), suggesting this vibration to be sensitive to the substituent although it did not show correlation with the bond lengths. The S=O bond distance was rather constant in this series, being 1.486, 1.483 and 1.485 Å, respectively (B3LYP/6-311++G(df,pd)). The N=S=O symmetric stretching mode was found to be similar for all studied substituted sulfinylanilines; this mode was assigned to the signals centered at 1030, 1033 and 1031 cm^{-1}, respectively in the mentioned series. It is clear then that the effect exerted by the substituent was stronger in the N=S bond of the N=S=O group than in the S=O one. The low sensitivity of the S=O bond to the ring substitution in *para* position would be a consequence of the *anti*-H bond interaction in which it is involved. The assignment of these stretching vibrations was further supported by additional calculations: theoretical ^{15}N substitution evidenced significant downshifts of the bands attributable to the N=S=O antisymmetric and symmetric stretchings (1267 and 1017 cm^{-1}, respectively, with B3LYP/6-311++G(df,pd)), allowing a confident identification of these modes in the experimental spectra. The C–N stretching appeared to be involved in several fundamental stretching and bending vibrations, making difficult its assignment to a unique signal. However, the C-N stretching was associated with the band observed at 730 cm^{-1} and calculated at 723 cm^{-1} based on the downshift, albeit small, predicted upon ^{15}N substitution (720 cm^{-1}).

Taking into account data reported for the *p*-trifluoromethylaniline, the assignment of the fundamental vibrational modes belonging to the CF_3 group in *p*-CF_3ArNSO was straightforward. In general, all benzene derivatives containing a trifluoromethyl group show a broad and strong band near 1330 cm^{-1} in the infrared spectrum, while in the Raman its counterpart possesses variable intensity [25]. In the present case, an intense and broad IR signal with maximum at 1326 cm^{-1} and a shoulder at *ca* 1314 cm^{-1} were assigned to the CF_3 antisymmetric and symmetric stretching modes, respectively. The totally symmetric CF_3 stretching was observed at 1173 cm^{-1}. The features observed at 1328 and 1170 cm^{-1} in the Raman spectrum were associated to these vibrations. In agreement with the assignment proposed for several other species containing the

CF_3 functional group, the symmetric CF_3 bending was associated to the medium intensity signal centered at 792 cm^{-1} in the Raman spectra.

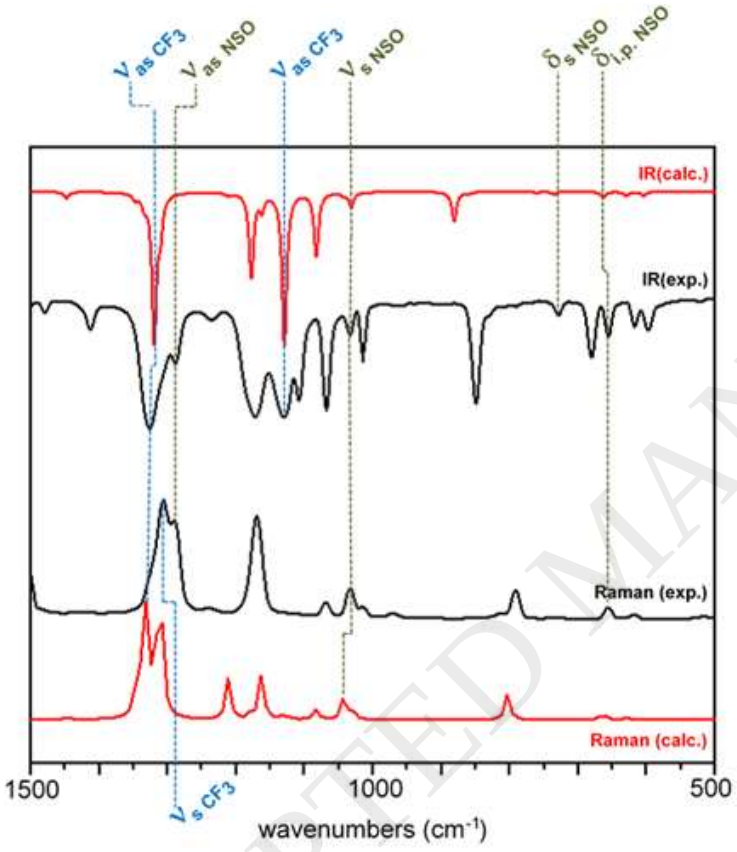


Figure 5. Experimental and theoretical spectra of *p*-trifluoromethylsulfinylaniline in the region between 1500 and 500 cm^{-1}. Red lines: spectra calculated with the B3LYP/6-311++G(df,pd) approximation for the isolated molecule in vacuum. Black lines: experimental spectra of the liquid sample at room temperature.

2.3. *NMR analysis*

Table 3 shows the experimental ^{1}H and ^{13}C chemical shifts of *p*-CF_3ArNSO in $CDCl_3$ (TMS was used as internal reference) and the corresponding calculated values with the B3LYP/6-311+G(df) approximation and the *gauge*-invariant atomic orbital (GIAO) method. According to reported values for benzene derivatives and taking into account the theoretical predictions, the four

protons attached to the aromatic ring, labeled as H1, H4, H3 and H2 in Figure 4, showed signals at 7.88, 7.84, 7.61, and 7.66 ppm, respectively, and appear as two doublets. The highest shielding was experienced by H1 since it was closest to the S=O group; H4 was also affected, although in a lesser extent, indicating that the NSO group was able of a 180° rotation to give an equivalent conformation. This conformational interconversion was in agreement with the potential energy scan presented in Fig. 2B. However, such H4 chemical shift was not predicted by the calculations (see Table 3) due to the limitation of the theoretical method (no rotations are allowed during calculation). The magnitude of the shielding experienced by the H atoms in *ortho* position could also be related to the presence of the CF_3 substituent, since experimental NMR results previously obtained for *p*-FArNSO and *p*-ClArNSO have shown higher (7.94/7.89 ppm) [14] and lower (7.12/7.07 ppm) [16] shielding, respectively, compared with the title molecule. This behavior would be in line with the N=S bond length mentioned above. On the other hand, the signals observed at 144.40, 126.98, 126.36, 127.71, 126.31, 126.89, and 131.57 ppm were assigned to the carbon atoms from C1 to C7. The high chemical shifts observed for C1 and C7 with respect to the other carbon atoms were attributed to the shielding exerted by the nitrogen and the fluorine atoms, respectively.

2.4. *GC/MS analysis*

Figure 6 shows the mass spectrum of the *p*-CF_3ArNSO. The peak at m/z 207 was attributed to the molecular ion [$M^{+\cdot}$], therefore the peak at m/z 208 was assigned to the protonated form of the molecular ion [$MH^{+\cdot}$]. The feature at m/z 138 [$M^{+\cdot}$-69] was the base peak and was assigned to the fragment resulting from the loss of the trifluoromethyl group; the intensity of this signal was consistent with the high stability of the aromatic ion. The weaker peaks at m/z 191 [M^{+}-16] and 188 [M^{+}-19] were attributed to the loss of the O atom and a single fluorine atom, respectively. Taking into account general fragmentation schemes reported for several substituted arylsulphinylamines [28], the unstable species with 188 mass to charge ratio might subsequently experience an SO loss, being the evidence of this fragmentation path the signal at 140 m/z. By following these reported fragmentation schemes, the peak at m/z 63 might account for the formation of a $C_5H_3^+$ species which would be originated by the $C_6H_4N^+$ fragment (90 m/z), both appearing with significant relative abundance in the spectra presented [28]. However, the peak

associated to this last species showed very low abundance in the spectra registered for *p*-CF_3ArNSO. Then, an alternative interpretation of the feature at 63 m/z in the spectrum of the title molecule is proposed. Intramolecular interactions between oxygen and ortho hydrogen atoms in *p*-CF_3ArNSO would result reinforced upon loss of CF_3, favoring the fragmentation and subsequent loss of a $HNSO^+$ specie. Since HNSO was recently suggested to be the most stable isomer of S-nitrosothiols [29] its formation may be feasible. The base peak would be also responsible for the feature at 110 m/z, assigned to the $C_5H_4NS^+$ fragment that results from the loss of the CO group after an intramolecular rearrangement, in concordance with the reported fragmentation scheme for substituted arylsulphinylamines [28].

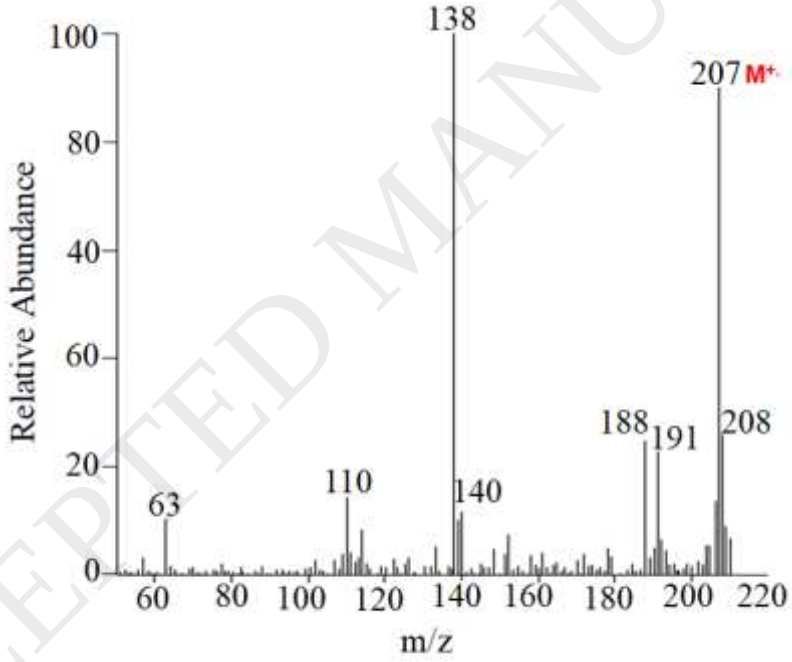


Figure 6. Mass spectrum of *p*-trifluoromethylsulfinylaniline, represented as relative abundance versus mass to charge ratio (m/z). The peak at m/z 207 is attributed to the molecular ion [$M^{+\cdot}$]. The loss of the CF_3 group results in the base peak at m/z 138, indicating that the resulting aromatic fragment is stable by charge delocalization.

3. Conclusions

By adjusting the general protocol for the synthesis of sulfinylanilines it was possible to obtain the product *p*-trifluoromethylsulfinylaniline. This compound enlarges the series of *para*

substituted aromatic-NSO compounds studied by our group, already integrated by the *p*-fluorosulfinylaniline and the *p*-chlorosulfinylaniline. Molecular properties were studied by ^{1}H and ^{13}C NMR and GC/MS measurements. A vibrational characterization was performed by using the FTIR and Raman spectroscopies and quantum-chemical calculations at different levels of theory.

According to energy calculations for the possible conformers and taking into account the number of vibrational bands observed in the experimental spectra, the presence of a single form of this molecule in the liquid phase was assumed. As was already demonstrated by previous studies of related sulfinylimines, the *syn* conformation of the NSO group was also the dominant form in this case. In addition, calculations predicted coplanarity between the NSO group and the aromatic ring, which was supported by the experimental ^{1}H NMR analysis.

Special attention was paid to the vibrational assignment of the N=S=O group, since this has been object of some discrepancies in the past. In the context of our serial studies, we proposed a consistent and reliable assignment of the infrared and Raman features for this kind of compounds: the vibrational stretches involving the NSO group are coupled in symmetric and antisymmetric modes, but the former shows a higher character of S=O stretching while the stretching of the N=S bond is dominant in the antisymmetric vibration. This interpretation was based on the frequency shifts that were observed upon ring substitution in *para* position. This, in turn, impacted on the experimentally observed chemical shifts of the protons attached to the aromatic ring in *ortho* position. In addition, GC-MS spectrum showed features that would be consistent with a molecular structure that favors the hydrogen-bonding interaction between the oxygen and one of the *ortho*-H atoms.

4. Experimental Details

4.1.1. *Synthesis*: Obtaining *p*-CF_3ArNSO was achieved by following the traditional method proposed by Michaelis that consists in treating amines with thionyl chloride in benzene or ether [1]. In the present case, a 1:3:7 molar relation of *p*-trifluoromethylaniline, thionyl chloride and benzene was used. All the substances were purchased to Sigma-Aldrich Argentina and used without further purification. *p*-Trifluoromethylaniline, (3.85 g, 24 mmol) and benzene (13.2 g, 170 mmol) were first placed in a three-neck round-bottom flask equipped with a Liebig

condenser which was sealed with a $CaCl_2$ trap. Then, thionylchloride (9.80 g, 82 mmol) was added drop wise to the mixture. To prevent the interaction with air humidity, the loading of the three components was carried out under nitrogen atmosphere. Since a vigorous reaction took place while thionyl chloride was added, the mixture was continuously stirred. Then, the flask was closed and the mixture was heated for 8 hours at 80–85 °C. The evolution of the reaction was followed by IR spectroscopy: the complete disappearance of the bands between 3400 and 3500 cm^{-1}, attributed to the NH_2 group of the reagent, was determinant. Once the reaction was over, the dark liquid obtained (yield: 4.54 g (92%)) was subsequently purified by several distillation cycles in order to get the pure final product (yield: 4.24 g (86%)). The resulting green liquid is highly hygroscopic and corrosive. It was subjected to elemental analyses and further purity control was performed by using several experimental techniques, as it is detailed.

4.1.2. ***Elemental analysis:*** These studies were conducted using an EXCETER CE-440 analyzer. According to the molecular formula of *p*-CF_3ArNSO the following abundances (expressed in %) are expected: C, 40.58; H, 1.93; N, 6.76. The elemental analyses for the obtained compound gave the following abundances (in %): C, 40.64; H, 1.69; N, 7.13, which indicated a yield of *ca*. 98%.

4.1.3. ***Spectroscopic measurements*****:** FTIR spectra of *p*-CF_3ArNSO between 3500 and 400 cm^{-1} were recorded with a Perkin-Elmer GX1 Fourier Transform infrared instrument (1 cm^{-1} spectral resolution). A film of the liquid sample was placed between KRS-5 windows. A DXR Smart Raman instrument (Thermo Fisher Scientific) equipped with a diode-pump, solid state laser emitting at 532 nm was used for the Raman measurements (5 cm^{-1} of spectral resolution). The liquid sample was handled in glass tubes of 0.5 cm of internal diameter. Spectra between 3500 and 50 cm^{-1} were acquired from accumulation of 60 expositions of 1 s each one with a laser power of 9 mW at the sample. All FTIR and Raman measurements were carried out at room temperature.

^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, for the *p*-trifluoromethylsulfinylaniline dissolved in $CDCl_3$. Tetramethylsilane (TMS) was used as internal standard for chemical shift calibration.

The GC-MS analysis was 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 this study. 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 signal observed at 4.38 min (98% relative area) in the total-ion chromatogram accounts for the presence of the molecule under study. 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, 40–160 *m/z*). The molecular ion was assigned to the peak with m/z 207.

4.2. Computational Details

GAUSSIAN 03 program package [30] was used for geometry optimization, conformational properties, ^{15}N isotopic substitution and vibrational frequency calculations of *p*-CF_3ArNSO. Based on the Density Functional Theory (DFT), the three-parameter hybrid functional for the exchange part [31] and the Lee-Yang-Parr (LYP) correlation function (B3LYP) [32] was used. Calculations at the level of Rayleigh-Schrödinger perturbation theory developed by Møller and Plesset at second order (MP2) [33] were also performed. Both methods were used with the 6-311+G(df), 6-311++G(df,pd) and cc-pVTZ bases sets. The methods provided good approximations for the quantum chemical calculations required to characterize the system under study. In addition, by using the same approximations, a natural population analysis (NBO) [34] was performed. On the other hand, the ^{1}H and ^{13}C NMR chemical shielding were evaluated for *p*-CF_3ArNSO by using the GIAO method [35]at the B3LYP/6-311+G(df) level of theory.

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Table 1. Calculated geometric parameters for *p*-trifluoromethylsulfinylaniline[a].

Structural parameters	B3LYP/ 6-311++G(df,pd)	B3LYP/ cc-pVTZ	MP2/ cc-pVTZ
C(1)–C(2)	1.407	1.405	1.405
C(1)–C(6)	1.404	1.403	1.403
C(2)–C(3)	1.386	1.389	1.389
C(6)–C(5)	1.383	1.386	1.386
C(3)–C(4)	1.393	1.393	1.393
C(5)–C(4)	1.395	1.395	1.395
C(4)–C(7)	1.507	1.499	1.499
C(1)–N	1.390	1.399	1.399
N=S	1.539	1.549	1.549
S=O	1.483	1.480	1.480
C(2)–H(1)	1.079	1.078	1.078
O••••H(1)	2.341	2.274	2.274
C(7)–F(1,3)	1.346	1.340	1.340
C(7)–F(2)	1.352	1.344	1.344
N=S=O	119.6	121.1	121.1
C(1)–N=S	132.2	129.3	129.3
C(2)–C(1)–C(6)	119.4	119.8	119.8
C(3)–C(2)–C(1)	119.7	119.5	119.5
C(3)–C(4)–C(5)	120.3	120.4	120.4
C(6)–C(5)–C(4)	119.7	119.6	119.8
C(2)–C(1)–N	127.7	124.8	124.8
C(6)–C(1)–N	115.8	115.4	115.4
C(4)–C(7)–F(2)	115.5	112.2	111.2
C(4)–C(7)–F(1)	112.2	112.0	112.0
C(4)–C(7)–F(3)	112.1	111.8	111.8
C(1)–N=S=O	0.0	0.0	0.0

[a] Bond lengths in Å and angles in degrees. For atom numbering see Fig. 4.

Table 2. Experimental and calculated vibrational frequencies of *p*-trifluoromethylsulfinylaniline. Tentative assignment of fundamental vibrational modes.

Mode	Approximate description [a]	Experimental [b] (cm^{-1})		Theoretical values [c] (cm^{-1})			
		IR (liq)	Raman (liq)	B3LYP/6-311++G(df, pd) Calculated values	B3LYP/6-311++G(df, pd) Scaled values [d]	B3LYP/cc-pVTZ	MP2/cc-pVTZ
ν_1	C–H Stretch.	-	-	3229 (1)[8]	3093	3234 (1)[8]	3264 (1)[17]
ν_2	C–H Stretch.	3092 vw	3084 w	3212 (<1)[33]	3077	3211 (<1)[37]	3248 (<1)[54]
ν_3	C–H Stretch.	3061 vw	3065 sh	3202 (<1)[17]	3068	3202 (<1)[20]	3239 (<1)[28]
ν_4	C–H Stretch.	3039 w	-	3199 (<1)[11]	3065	3197 (<1)[12]	3232 (<1)[16]
ν_5	C=C Stretch.	1612 m	1612 m	1647 (<1)[100]	1619	1649 (<1)[98]	1653 (1)[54]
ν_6	C=C Stretch. + C–H Def.	1576 w	1577 sh	1598 (1)[2]	1571	1601 (<1)[<1]	1614(<1)[3]
ν_7	C=C Stretch.+ C–H Def.	1503 vw	1503 m	1532(<1)[32]	1506	1536 (<1)[32]	1535(<1)[27]
ν_8	C=C Stretch.+ C–H Def.	1413m	-	1448 (4)[1]	1423	1450 (4)[1]	1485 (1)[5]
ν_9	CF_3 Asym. Stretch.	1326 vs	1328 sh	1347 (4)[13]	1324	1349 (5)[15]	1425(3)[1]
ν_{10}	CF_3 Sym. Stretch.	1314 sh	-	1334 (7)[99]	1311	1334 (12)[100]	1366(100)[20]
ν_{11}	C=C Stretch + C–H Def.	-	1305 vs	1320 (100)[36]	1298	1323 (100)[20]	1326(1)[1]
ν_{12}	N=S=O Asym. Stretch.	1289 m	1289 s	1311 (23)[93]	1289	1314 (14)[99]	1317(10)[100]
ν_{13}	C–C Stretch. + C–H Def. i.p	1184 sh	-	1211 (2)[28]	1190	1211 (3)[20]	1222(46)[2]
ν_{14}	CF_3 Asym Stretch.	1173 vs	1170 vs	1178 (57)[4]	1158	1183 (57)[30]	1212(6)[25]
ν_{15}	C–C Stretch.	1130 vs	-	1163 (10)[32]	1143	1173 (4)[18]	1199(3)[20]
ν_{16}	C–H Def. +C–C Stretch.	1108 s	1108 vw	1130 (49)[<1]	1111	1135 (63)[2]	1190(56)[3]
ν_{17}	C–H Def. +C–C Stretch.	-	-	1129 (57)[3]	1110	1130 (29)[1]	1127(8)[<1]
ν_{18}	C=C Stretch. +C–H Def.	1069vs	1069 m	1083 (43)[7]	1065	1084 (38)[7]	1094(22)[4]
ν_{19}	N=S=O Sym. Stretch.	1033m	1033 m	1043 (2)[13]	1025	1050 (1)[14]	1035(11)[1]
ν_{20}	C–H Def.	1015 m	1015w	1032 (10)[7]	1014	1035 (9)[4]	1022(<1)[<1]
ν_{21}	C–H Def. o.o.p.	1007sh	-	1013 (<1)[<1]	996	1011 (<1)[10]	979(<1)[<1]
ν_{22}	C–H Def. o.o.p.	-	971 w	995(<1)[<1]	978	1001 (<1)[<1]	963(<1)[<1]
ν_{23}	C–H Def. o.o.p.	849 vs	-	881 (20)[<1]	866	886 (7)[<1]	867(15)[<1]
ν_{24}	C–H Def. o.o.p.	830 sh	-	860(1)[<1]	845	860 (<1)[<1]	852(<1)[<1]
ν_{25}	Ring Def.	-	810 w	803 (<1)[17]	789	805 (<1)[15]	804 (<1)[10]
ν_{26}	CF_3 Sym. Def.	-	792 m	761 (<1)[<1]	748	768 (<1)[<1]	742(<1)[<1]

ν_{27}	C–N Stretch.	730 m	-	736 (1)[<1]	723	737 (1)[<1]	739(3)[1]
ν_{28}	C–H Def.i.p.+ N=S=O Def.i.p.	680 m	-	664 (3)[4]	653	666 (3)[4]	661(4)[2]
ν_{29}	N=S=O Def.i.p. + C–H Def.i.p.	656m	656w	630 (3)[1]	619	632 (2)[1]	619 (2)[2]
ν_{30}	C–H Def. o.o.p.	618m	619 w	604 (3)[<1]	594	607 (3)[<1]	608(3)[<1]
ν_{31}	CF_3 Asym. Def.	598 m	-	574 (<1)[<1]	564	575 (<1)[<1]	587(<1)[<1]
ν_{32}	C–H Def. o.o.p.	-	-	534 (<1)[<1]	525	536 (<1)[<1]	533(<1)[<1]
ν_{33}	CF_3 Asym. Def.	-	516 vw	519 (<1)[1]	510	521 (<1)[1]	520(1)[<1]
ν_{34}	C–H Def. o.o.p.	449vw	453vw	451 (1)[<1]	443	454 (1)[<1]	453(1)[<1]
ν_{35}	C–H Def. o.o.p.	-	-	421 (<1)[<1]	414	423 (<1)[<1]	416(<1)[<1]
ν_{36}	C–H Def. i.p.	406vw	406vw	407 (1)[<1]	400	408 (1)[<1]	408(<1)[<1]
ν_{37}	C–H Def. o.o.p.	-	-	323 (2)[<1]	318	326 (2)[<1]	322(1)[<1]
ν_{38}	N=S=O Def. o.o.p.	-	-	317 (4)[<1]	312	319 (3)[<1]	311(3)[1]
ν_{39}	C–H Def. i.p.	-	281w	283 (1)[<1]	278	284 (1)[<1]	284(1)[<1]
ν_{40}	Ring Def.i.p.	-	183 vw	186 (1)[1]	183	188 (1)[1]	186(1)[1]
ν_{41}	Ring Def. o.o.p.	-	-	181 (<1)[<1]	178	184 (<1)[<1]	182(<1)[1]
ν_{42}	C–N=S Def.	-	116 sh	112 (<1)[1]	110	114 (<1)[<1]	116 (<1)[1]
ν_{43}	N=S=O Def. i.p. + C–H Def. o.o.p.	-	-	83 (<1)[<1]	82	84 (<1)[<1]	80(<1)[1]
ν_{44}	N=S=O Def. i.p. + C–H Def. o.o.p.	-	-	49 (<1)[<1]	48	50 (<1)[<1]	41 (<1)[<1]
ν_{45}	Torsion CF_3	-	-	18 (<1)[1]	18	19 (<1)[1]	15 (<1)[1]

[a] Stretch.: stretching; Def.: deformation; Asym.: antisymmetric; Sym.: symmetric; i.p.: in phase; o.o.p.: out of phase; sh: shoulder.[b] s: strong; vs: very strong; m: medium; w: weak; vw: very weak. [c] Relatives infrared intensities in parentheses, normalized to 100% ;Relative Raman activities between brackets, normalized to 100%. [d] Values scaled according to the scaling factors in Ref. [26].

Table 3. Experimental and calculated chemical shifts for ^{1}H (200 MHz) and ^{13}C (50 MHz) of *p*-trifluoromethylsulfinylaniline dissolved in $CDCl_3$. TMS was used as internal reference.

Assignment [a]	Chemical shift (δ) (ppm)	
	Experimental	Theoretical [b]
H1	7.88	8.90
H2	7.84	7.51
H3	7.66	7.51
H4	7.61	7.19
C2	126.98	132.69
C3	126.36	130.54
C4	127.71	133.96
C5	126.31	129.84
C6	126.89	132.25
C7	131.57	139.16
C1	144.40	152.94

[a] For atom numbering see Fig. 4.

[b] Calculated chemical shifts (GIAO method) using B3LYP/6-311+G(df) approximation.