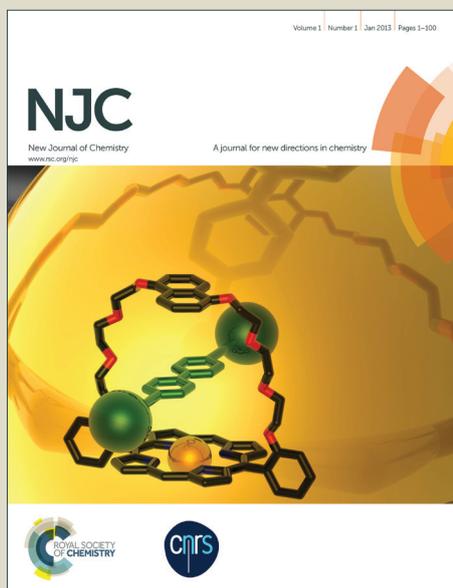


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ARTICLE

Synthesis and characterization of *o*-fluorosulfinylaniline.

A comparative vibrational study of fluorinated sulfinylanilines series

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

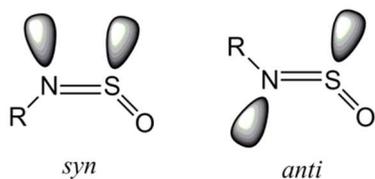
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The synthesis of *o*-fluorosulfinylaniline is reported with the aim to complete the fluorinated sulfinylanilines series. The FT-IR and Raman spectra of *o*-fluorosulfinylaniline are recorded and the fundamental modes of its vibrational frequencies are assigned together with a tentative assignment of the NMR and mass spectra. Quantum chemical calculations on the optimized geometry predict in the liquid phase a planar structure with *syn* orientation of the $-N=S=O$ moiety (*syn* of the S=O double bond relative to the C–N single bond), which belongs to C_s symmetry group. The experimentally observed spectral data (FT-IR, Raman, 1H and ^{13}C and GC-Mass Spectrometry) of the title compound are compared with those obtained theoretically from DFT calculations and gauge including atomic orbital (GIAO) method. Vibrational frequencies were assigned with the aid of anharmonic variational methods (VSCF) obtaining a significantly better agreement with experiment than with simple harmonic oscillator methods. Moreover, stability of the molecule arising from hyper conjugative interactions, charge delocalization has been analyzed using Natural Bond Orbital (NBO) analysis.

Introduction

The formation of N-sulfinylaniline was first reported by Bottiger in 1878¹ and by Michaelis and Herz in 1890.² Michaelis and Herz used the reaction of aniline with thionyl chloride, $SOCl_2$, to produce this compound and later Michaelis used this procedure to prepare seventy five N-sulfinylamine derivatives. Michaelis' work provided a solid foundation for the research of the structure, properties, reactions and applications of N-sulfinylamines. Even now, many N-sulfinylamines are still prepared by using Michaelis' method.

Organic N-sulfinyl compounds have drawn particular interest because of their geometry: the heterocumulene unit is not linear therefore *syn* and *anti* configurations are possible (*syn* or *anti* with respect to the C–N single and S=O double bond, see scheme I).



Scheme I. *Syn* and *anti* forms (*syn* or *anti* with respect to the C–N single and S=O double bond).

Although N-sulfinylaniline was found in 1890, its structure was determined a century later. Earlier, there was a controversy about whether N-sulfinyl amines prefer the *syn* or the *anti* configurations. Romano *et al.* finally determined by X-ray diffraction, that N-sulfinylaniline possesses in the crystalline state a planar structure with *syn* configuration.³ Later this was also confirmed for liquid and dissolved states using various spectroscopies.⁴

The $-N=S=O$ group has been described as a “cumulated π -system or cumulated double bond system”. It is known that the N=S bond is a four electron bond with the S atom as the positive and the N atom as the negative end of the dipole while the SO bond has been described as S^+-O^- . In comparison to SO_2 , it was found that the SO bond is best described as a polar double bond and further ^{17}O NMR studies showed it to be a four electron bond with double bond character, due to the fact that the trend of ^{17}O chemical shifts for these SO bonds in organic compounds is very similar to that for carbonyl CO bonds.⁵ Glass *et al.* confirmed that the $-N=S=O$ group is electron withdrawing in *p*-disubstituted benzenes, withdrawing electrons from the benzene ring.⁶

It was also found that the oxygen of the $-N=S=O$ group can form an anti-hydrogen bond (C–H \cdots O interaction) with *ortho* hydrogen atoms of aromatic N-sulfinylamines. Muchall proposed an anti-hydrogen bond, C–H \cdots O, in N-sulfinylamines based on an analysis of the calculated electron density.⁷ By using 1H and ^{17}O NMR spectroscopies, experimental evidence for this C–H \cdots O interaction was put forward.⁸

Grinninger *et al.* reported the ultraviolet spectra of some N-sulfinylanilines in ether and in several alcohols and discussed the effect of substituents on the spectra.⁹ Meanwhile, Roberts *et al.* obtained the ¹⁵N Nuclear Magnetic Resonance spectra of isocyanates, isothiocyanates and N-sulfinylamines.¹⁰

Stufkens *et al.* reported the IR and Raman spectra of the ¹⁵N labelled N-sulfinylaniline, which allowed the characteristic vibrations of the –N=S=O group to be determined. The results showed the N=S and S=O stretching modes to be largely independent. This assignment was achieved based on comparison with data reported for SO₂.¹¹ However, a subsequent study of the pre-resonant Raman spectra of N-sulfinylaniline concluded that both stretching modes are actually coupled.³

Finally, Muchall *et al.* reported a comparative study about the hydrolytic reactivity of R–N=S=O compounds. The hydrolytic mechanism proposed consists of hydroxylation of sulfur and protonation of the –N=S=O group. The reactivity with water varies dramatically depending on the substituent R attached to the –N=S=O group. The results suggest that electron-donating substituents stabilize N-sulfinylamines towards water. Accordingly, electron-withdrawing substituents increased the rate of hydrolysis.¹²

In this work, a clear-cut assignment of the available experimental spectra (FT-IR, Raman, NMR and GC-Chromatography) is made on the basis of the quantum chemical methods at different levels of theory. Previously, our group has reported studies of *p*-fluorosulfinylaniline¹³ and *m*-fluorosulfinylaniline.¹⁴ The purpose of this work is to complete the fluorinated sulfinylanilines series by investigating the effect of substituent by change of fluorine atom on *ortho*, *meta* and *para* positions of the aromatic ring on the vibrational spectra of sulfinylanilines, especially on the fundamental modes of the –N=S=O group. Also a comparative study between them is performed. The present research allows us to obtain more concise and accurate picture and to expand the scope of investigation of this family of compounds.

Materials and Methods

Synthesis

According to the method proposed by Michaelis for the synthesis of R–N=S=O compounds,² *o*-fluorosulfinylaniline was prepared using a 1:2:4 molar relation of the corresponding fluorinated aniline, thionyl chloride and benzene as the reaction solvent, respectively. *o*-fluoroaniline (3.45 g, 31 mmol) and benzene (10.56 g, 135.2 mmol) were placed in a closed three neck round bottom flask equipped with a Liebig condenser which was sealed with a CaCl₂ trap. Thionyl chloride (9.80 g, 82.3 mmol) was added drop wise to the mixture. To prevent the interaction with air humidity, the reaction was carried out in nitrogen atmosphere. A vigorous reaction took place and aniline hydrochloride precipitated. The reaction mixture was continuously stirred and heated for 7 hours at 80–85 °C until a clear solution was obtained. The dark yellow to green liquid mixture obtained was purified by several distillation cycles in order to obtain a green-yellowish liquid as the final product with *ca.* 98% yield. Its purity was controlled by ¹H and ¹³C NMR spectroscopy, GC-Mass Spectrometry, IR and Raman spectroscopy. The substance is highly hygroscopic and corrosive.

FT-IR measurements

The FT-IR spectrum of the liquid was recorded in the region 3500–400 cm⁻¹ at room temperature using a Perkin-Elmer GX1 Fourier Transform infrared instrument provided with KRS-5 windows (4 cm⁻¹ spectral resolution).

Raman measurements

The Raman spectrum of the liquid was recorded at room temperature in the range 3500–50 cm⁻¹ by employing a diode-pump, solid state green laser of 532 nm with 9.0 mW laser power at the sample for excitation in a Thermoscientific DXR Smart Raman instrument equipped with CCD detector. The spectral resolution was 5 cm⁻¹ with a grating groove density of 900 lines/mm. A confocal aperture of 50 μm slit was used and 10 expositions of 2 s were accumulated for the sample in order to achieve sufficient signal to noise ratio.

NMR and GC/MS measurements

NMR spectra were measured in CDCl₃ at 200 MHz for ¹H and 50 MHz for ¹³C on a Varian Unity 200 spectrometer. ¹H NMR: δ = 7.24 (C(3)H), 7.24 (C(5)H), 7.43 (C(4)H), and 8.34 (C(6)H) ppm. ¹³C NMR: δ = 116.6 (C5); 124.7 (C3); 128.4 (C6); 131.0 (C1); 131.9 (C4) and 155.0 (C2) ppm (for atom numbering, see Fig. 1).

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 using a DB-5 capillary column. Split-less injection was used for this study. The initial temperature of the oven was 60°C. After maintaining that temperature for 3 min, the oven temperature was increased at a rate of 15°C/min to reach a final oven temperature of 250°C. The final temperature was maintained for 5 min and the total run time was 20 min. Helium was used as carrier gas. The mass spectrometer was operated in the electron ionization scan mode (range, *m/z*: 40–200). Quantification of the peaks was based on peak area.

Computational details

All electronic structure calculations were performed using the GAUSSIAN 03 program.¹⁵ The methods employed are based on the gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3)¹⁶ for the exchange part and the Lee-Yang-Parr (LYP) correlation function.¹⁷ The calculations were carried out using 6-311+G(df) and 6-311++G(df,pd) basis sets. Natural Bond Orbital (NBO) analysis,¹⁸ as implemented in the GAUSSIAN 03 program, were performed together with the Gauge-including atomic orbital (GIAO) method.¹⁹

Additionally, vibrational structure calculations were performed using the vibrational self-consistent field (VSCF) ansatz recently implemented in the QUMVIA software package.²⁰ VSCF is a mean-field, variational iterative method for the calculation of the vibrational wavefunction, entirely analogous to the Hartree-Fock method in electronic structure theory. Following is a brief summary of VSCF theory. A more detailed account can be found elsewhere.^{21,22}

The vibrational Schrodinger equation for a molecular system expressed in rectilinear normal coordinates {*q*_{*i*}} can be formulated, neglecting rotational coupling, as follows:

$$\left(-\frac{1}{2} \sum_{i=1}^f \frac{\partial^2}{\partial q_i^2} + V(\vec{q}) \right) \psi_n(\vec{q}) = E_n \psi_n(\vec{q})$$

With

$$\psi_n(\vec{q}) = \prod_{i=1}^f \phi_{i,n}(\vec{q})$$

The vibrational wavefunction is represented as a Hartree product, this is, a product of one-dimensional, single-mode wavefunctions or “modals” (in analogy to orbitals in electronic structure theory).

Where ψ is the vibrational wavefunction, $\{\phi_i\}$, (with $i=1, \dots, f$) are the one-dimensional modals and q_i are the mass weighted normal coordinates. Using this assumption and the variational principle it is possible to obtain the VSCF equations for each modal.

$$[H_i^0(q_i) + v_i(q_i)]\phi_i(q_i) = \epsilon_i \phi_i(q_i)$$

$$v_i(q_i) = \left\langle \prod_{j \neq i}^f \phi_j \left| V_c(\vec{q}) \right| \prod_{j \neq i}^f \phi_j \right\rangle$$

H_i^0 is the core Hamiltonian for mode “i”, consisting of the kinetic energy and the diagonal potential and v_i is the mean field potential.

Because the solutions (the modals) are necessary to compute the mean field potential, the VSCF equations must be solved iteratively until self-consistency.

Distributed gaussian functions are used as a basis set.²³ The nuclear potential energy surface (PES) is approximated using a quartic force field (QFF) with a 3-mode coupling representation²⁴ (i.e. three normal modes are allowed to couple simultaneously). Third and fourth order force constants are obtained by numerical differentiation of Hessian matrices calculated analytically using a separate electronic structure software (Gaussian 03, in our case) at a MP2/cc-pVDZ and B3LYP/6-311++G(df,pd) electronic structure levels of theory. Molecular structures were optimized using a “very strict” convergence criterion, following a frequency calculation to obtain normal modes, harmonic frequencies and hessian matrix in Gaussian 03. With these data, a series of conformations distorted along each normal mode were generated by QUMVIA, and hessian matrices were calculated for each of these using Gaussian 03. Finally these Hessian matrices were used to compute 3-mode coupling QFF using QUMVIA. 16 distributed Gaussian basis functions positioned at sixteen scaled Gauss-Hermite quadrature points were used for each normal mode. A VSCF energy convergence criterion of 10^{-9} Hartrees was used.²⁰

Results and Discussion

Quantum chemical calculations analysis

Compounds having the framework R–N=S=O can, in principle, adopt two stable conformers around the N=S double bond, defined as *syn* and *anti* (see Scheme I). However, calculations reported for the parent sulfinylaniline¹¹ and some others substituted sulfinylanilines³⁻⁵ demonstrate that only the *syn* form is observed in liquid phase. Theoretical calculations performed by our group for the fluorinated sulfinylanilines demonstrated that the most stable conformer possesses *syn* form and planar structure with C_s symmetry.

In order to describe the conformational properties of the *o*-fluorosulfinylaniline, the potential energy function for rotation around the N=S bond was determined by structure optimizations at fixed dihedral angles C–N=S=O in steps of 30°. Calculations at the B3LYP/6-311+G(df) approximation predicted the *syn* conformation as the global minimum and the *anti* conformation as a local minimum with ΔE° (*anti-syn*) = 7.90 Kcal.mol⁻¹ and ΔG° (*anti-syn*) = 7.35 Kcal.mol⁻¹. Due to the bent geometry of the –N=S=O group and taking into account the possible formation of an anti-hydrogen bond (C–H...O interaction),^{7,8} the structure proposed for the *o*-fluorosulfinylaniline shows the fluorine atom in opposite position to the –N=S=O group (see Fig. 1). The isomer with the fluorine atom closer to the oxygen atom was found to be 2.32 Kcal.mol⁻¹ (B3LYP/6-311+G(df)) less stable than the configuration depicted in Fig 1.

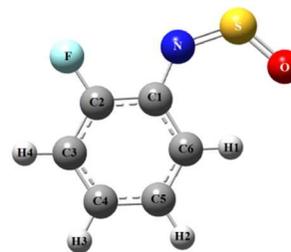


Fig. 1. Molecular model of the *syn* conformer of *o*-fluorosulfinylaniline.

The higher stability of the statically unfavorable *syn* conformation observed for all sulfinylanilines reported hitherto may be rationalized by orbital interactions. A Natural Bond Orbital (NBO) analysis of the B3LYP/6-311+G(df) wavefunction of *o*-fluorosulfinylaniline suggests that the formal S=O double bond possesses only σ -bond character, and therefore three lone-pair orbitals exist at the oxygen atom. Two of them (lp2 and lp3) show a pure p-type nature and possess low occupancies due to strong delocalization towards vicinal antibonding orbitals: lp2 (O) \rightarrow $\sigma^*(\text{N-S})$ and lp3 (O) \rightarrow $\pi^*(\text{N-S})$ with interaction energies of 19 and 63 kcal.mol⁻¹ in the *syn* conformer. In the *anti* form these interaction energies are lower, 18 and 54 kcal.mol⁻¹, respectively. Even larger energy differences, which stabilize the *syn* conformer, exist for interactions between nitrogen and sulfur lone pair orbitals with vicinal antibonding orbitals: lp (N) \rightarrow $\sigma^*(\text{S-O})$ and lp (S) \rightarrow $\sigma^*(\text{C-N})$ with interaction energies of 15 and 10 kcal.mol⁻¹. Corresponding interaction energies in the *anti* form are only 6 and 1 kcal.mol⁻¹, respectively. As these anomeric interactions decrease from *syn*

to *anti* configurations, the thermodynamic preference of the *syn* form can be rationalized by higher stabilizing anomeric interactions. An anti-hydrogen bond in *o*-fluorosulfinylaniline was evidenced through the AIM approach.⁷ The same was also evidenced now as a consequence of the orbital interaction of oxygen lone pairs towards the σ^* (C6-H1) orbital in the *syn* form (these interactions are absent in the *anti* configuration). Fig. 2 depicts the molecular orbitals involved in the relevant orbital interactions.

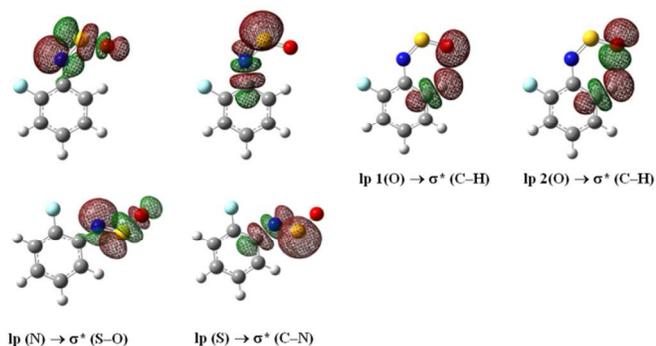


Fig. 2. Relevant NBO orbitals [B3LYP/6-311+G(df)] for the *syn* (upper) and *anti* (lower) conformers of *o*-fluorosulfinylaniline.

Table 1 lists the structural parameters calculated for the fluorinated sulfinylanilines series depicted in Fig. 3 by the B3LYP method with 6-311+G(df) basis set and the experimental data for the parent N-sulfinylaniline obtained by X-ray crystallography.³ The results demonstrate good agreement between them. By using this theoretical approximation the stability decrease in the following order *p*- > *m*- > *o*-. The most important conclusions that may be inferred from the comparison, together with the results obtained from the QUMVIA software package²⁰ will be discussed in the Vibrational Study section.

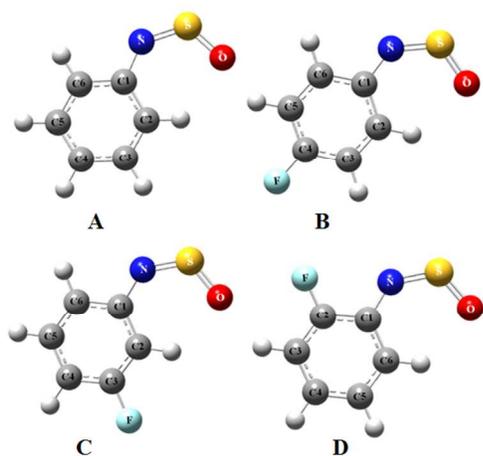


Fig. 3. Schematic representation of the N-sulfinylaniline and the fluorinated sulfinylanilines series. A: N-sulfinylaniline, B: *p*-fluorosulfinylaniline, C: *m*-fluorosulfinylaniline and D: *o*-fluorosulfinylaniline.

Table 1. The structural parameters calculated for the fluorinated sulfinylanilines series by B3LYP method with 6-311+G (df) basis set and experimental data for N-sulfinylaniline obtained by X-ray crystallography.^a

Structural Parameters	B3LYP/6-311+G(df)			X ray diffraction
	B ¹³	C ¹⁴	D	A ³
S=O	1.486	1.484	1.485	1.4584(10)
N=S	1.541	1.540	1.539	1.5160(11)
N-C(1)	1.387	1.398	1.381	1.401(2)
C(1)-C(2)	1.410	1.408	1.409	1.4059(14)
C(2)-C(3)	1.386	1.381	1.381	1.386(2)
C(3)-C(4)	1.387	1.387	1.391	1.392(2)
C(4)-C(5)	1.388	1.393	1.394	1.395(2)
C(5)-C(6)	1.383	1.385	1.386	1.382(2)
C(1)-C(6)	1.406	1.405	1.410	1.402(2)
N=S=O	119.4	119.6	119.4	120.61(6)
C(1)-N=S	132.2	132.3	132.2	131.23(8)
NC(1)C(2)	124.8	124.3	116.8	124.23(10)
NC(1)C(6)	115.9	115.9	125.6	115.98(9)
C(6)C(1)C(2)	119.3	119.8	117.6	119.80(10)
C(1)C(2)C(3)	119.9	118.0	122.2	119.35(10)
C(2)C(3)C(4)	119.1	123.0	119.0	120.68(11)
C(3)C(4)C(5)	122.4	118.4	120.4	119.94(12)
C(4)C(5)C(6)	118.4	120.5	120.4	120.07(11)
C(5)C(6)C(1)	120.8	120.2	120.4	120.15(10)
C-F	1.344	1.347	1.337	
C-H	1.083	1.082	1.083	

^a Bond lengths in Å and angles in degrees. Mean values are given for parameters that are not unique. For atom numbering see Fig. 3.

Vibrational Study

A tentative assignment of the $3N - 6 = 36$ vibrational modes expected for the C_s configuration of *o*-fluorosulfinylaniline are listed on Table 2. Fig. 4 depicts the experimental IR and Raman spectra of *o*-fluorosulfinylaniline. The vibrational analysis of the liquid sample was supported by Density Functional Theory calculations with the 6-311++G(df,pd) basis set and by MP2 wavefunction theory with the cc-pVDZ basis set. In addition, theoretical ¹⁵N substitution was used to help identifying the vibrational modes expected for the -N=S=O group. Reported data for the parent sulfinylaniline,¹¹ *p*-fluorosulfinylaniline,¹³ *m*-fluorosulfinylaniline¹⁴ and the fluoroanilines series²⁵ were also taken into account. However, the best correlation was provided by anharmonic vibrational structure calculations at the VSCF vibrational level of theory using an electronic potential

energy surface (PES) at the B3LYP/6-311++G(df,pd) electronic level of theory. Mean absolute deviation (MAD) over the whole spectra was only 22 cm^{-1} for VSCF with a B3LYP/6-311++G(df,pd) and 26 cm^{-1} of VSCF calculations at MP2/cc-pVDZ level of theory, a substantial improvement over harmonic oscillator method predictions, which produced MADs of 39 and 49 cm^{-1} for B3LYP and MP2 potential energy surfaces, respectively. VSCF calculations also predicted changes in the energy ordering of some vibrational states. Most strikingly in the case of C–H stretching transitions, where the ordering predicted by VSCF/B3LYP/6-311++G(df,pd) calculations was $\nu_3 > \nu_2 > \nu_1 > \nu_4$, while VSCF//MP2/cc-pVDZ predicted $\nu_2 > \nu_3 > \nu_1 > \nu_4$. The cause of the discrepancies in the order of ν_2 and ν_3 states in VSCF//MP2 and VSCF//B3LYP is due to the fact that both states are very close in energy. This, taken together with the prediction of similar IR and Raman intensities for ν_1 , ν_2 and ν_3 , suggests the possibility that ν_2 and ν_3 are almost degenerate and may appear as one band in the vibrational spectra. Transitions corresponding to ν_{23} and ν_{24} also exchange positions in VSCF under both potential energy surfaces, while ν_{17} and ν_{18} also do so but only in VSCF//MP2, while VSCF//B3LYP predicts these two states to be almost degenerate. Another interesting feature can be observed in the lower portion of the spectra, where anharmonic transitions are predicted to have higher frequencies than their harmonic counterparts. This is because potential energy surfaces along low frequency normal modes tend to be flatter near the equilibrium geometry than in more displaced geometries, which produces quadratic approximations that are too flat compared to the real, fully anharmonic PES. Taken as a whole, VSCF calculations proved to be a very valuable asset in the assignment of the vibrational spectra. When compared to popular *ad hoc* methodologies, such as scaling the spectra using one or more empirical factors, the VSCF methodology is clearly superior, as it is capable not only of producing overall absolute frequencies of similar or better precision as scaled spectra, but also is capable of handling more difficult cases, where the assignment is not straightforward. This is clear for the C–H stretchings mentioned above and the lower frequencies, where the tendency of anharmonicity is contrary to the effect of scaling factors. In summary, we propose the use of anharmonic variational methods such as those presented here, to be highly desirable and advantageous when compared to the use of *ad hoc* scaling factors.

The title compound consists of a benzene ring substituted with –N=S=O group and a fluorine atom in *ortho* position with regard to that group, the vibrational modes are therefore grouped and discussed as: i) –N=S=O group vibrations; ii) C–F vibrations and iii) C–N vibrations.

i) –N=S=O group vibrations. The vibrational modes belonging to the sulfinyl group were analysed for more than 600 compounds so far. According to the data reported in a review article for R–N=S=O compounds, the asymmetric stretching mode occurs in a wide spectroscopic region: from 1145 cm^{-1} in $\text{Cd}(\text{N}=\text{S}=\text{O})_2$ to 1302 cm^{-1} in $\text{Si}(\text{CH}_3)_3\text{N}=\text{S}=\text{O}$. Similarly, the corresponding symmetric mode was observed between 990 cm^{-1} in $\text{K}-\text{N}=\text{S}=\text{O}$ and 1174 cm^{-1} in 2,6-diethylsulfinylaniline.⁴ The vibrational spectra of the parent sulfinylaniline were extensively discussed by several authors.

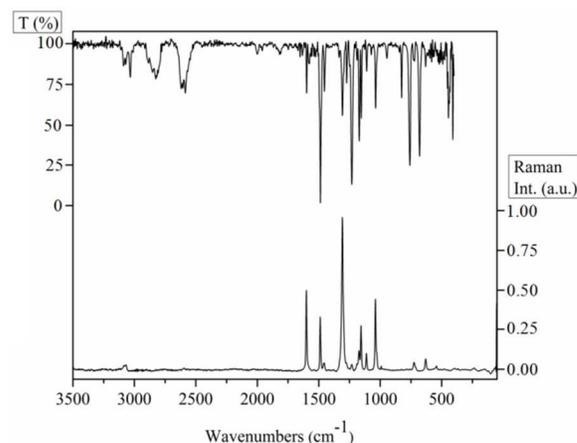
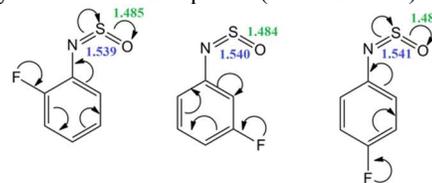


Fig. 4. Experimental infrared and Raman spectra of *o*-fluorosulfinylaniline. Top: infrared spectrum of a liquid sample held between KRS-5 windows; bottom: room temperature Raman spectrum of a liquid sample.

Stufkens *et al*¹¹ analysed the ¹⁵N isotopomer and concluded that for –N=S=O group the stretching modes must be assigned to a N=S stretching (1284 cm^{-1}) and a S=O stretching (1155 cm^{-1}). In this article the authors rule out a coupling between both vibrations, in contrast to the description of these stretching modes as out of phase and in phase given by other authors. Romano *et al.* carried out quantum chemical calculations and the analysis of the resonance Raman scattering effect revealing two –N=S=O stretching modes: an out of phase and in-phase stretching modes, appearing at 1298 cm^{-1} and 1163 cm^{-1} , respectively.³ In our study of the vibrational spectra of *p*- and *m*-fluorosulfinylaniline, the bands at 1303 and 1030 cm^{-1} (IR) and 1314 and 1036 cm^{-1} (IR) were assigned to the –N=S=O asymmetric and symmetric stretching, respectively. In the present work, the –N=S=O asymmetric and symmetric stretching of *o*-fluorosulfinylaniline was observed at 1307 and 1037 cm^{-1} (IR) and 1308 and 1039 cm^{-1} (Raman), respectively. This assignment may be understood as a result of a partial contribution of resonance structures representing effective charge delocalization when the fluorine atom is placed in *ortho* and *para* position and the shortening and elongation of the N=S and S=O bonds. As we postulated in a previous paper on *m*-fluorosulfinylaniline,¹⁴ the *o*-derivative follows a similar trend as the *p*-substituted compound, while the corresponding modes for the *m*-isomer appear at higher frequencies since the lone pair of fluorine atom does not resonate with the –N=S=O group and the N=S and S=O bonds do not acquire partial single bond character, as the *o*- and *p*-derivative do. A greater partial double bond character in *m*-derivatives accounts, then, for the higher frequency observed in the spectra (see Scheme 2).



Scheme 2. Structures representing the charge delocalization on the molecule. Calculated values in Å (B3LYP/6-311+G(df)) are given for the N=S (blue) and S=O (green) bond lengths, respectively.

ii) C–F vibrations. For the series of *p*-, *o*- and *m*-substituted fluoroaniline the C–F stretching was assigned to the signals at 1225, 1270 and 1288 cm^{-1} , respectively in the infrared spectra.²⁵ The vibrational spectra of fluorinated sulfinylaniline series showed an opposite trend, with the C–F bond belonging to the *p*- and *o*- derivative being stronger than that of the *m*-isomer, appearing at 1227, 1231 and 1216 cm^{-1} (IR), respectively. This matter was raised in a previous work.¹⁴ These different trends may be understood in terms of the opposite withdrawing effects of the $-\text{NH}_2$ and $-\text{N}=\text{S}=\text{O}$ groups. The last group is a stronger electron acceptor, and T. Siodla *et al.* reported that the C–F bond in fluorobenzenes is shortened by resonance when the ring is attached to an electron withdrawing group in *para* position with regard to fluorine atom. The same conclusion is valid when the electron withdrawing group is found in *ortho* position, but such interaction is weaker in an *m*-derivative.²⁶ The calculated magnitudes of the shortening of the C–F bond in the fluorinated sulfinylanilines is: *o*- < *p*- < *m*-. Accordingly the corresponding stretching frequencies order are predicted to be: *o*- > *p*- > *m*- (see Scheme 3).

iii) C–N vibrations. Following a similar reasoning and considering the structures depicted in Scheme 3, the shortening of the C–F bond is accompanied by a shortening of the C–N bond. Therefore the C–N stretching in *o*-fluorosulfinylaniline can be assigned to the signal placed at 826 cm^{-1} (IR) and 827 cm^{-1} (Raman). The corresponding fundamental transitions were observed at 822 cm^{-1} (IR) and 785 cm^{-1} (IR) in the *p*- and *m*-substituted derivative, respectively.

Fig. 5 shows a graphical comparison of the main modes discussed above for fluorinated sulfinylaniline compounds.

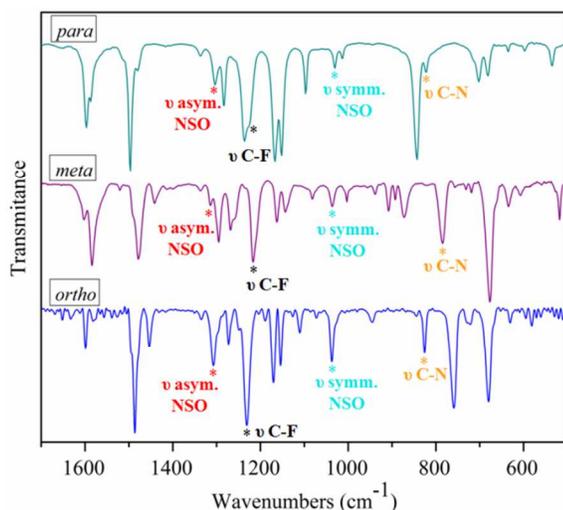
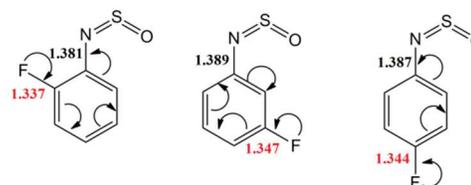


Fig. 5. Experimental IR spectra of the three fluorosulfinylanilines recorded in the region 1700–400 cm^{-1} . The red, black, sky-blue and orange asterisks correspond to $-\text{N}=\text{S}=\text{O}$ asymmetric stretching, C–F stretching, $-\text{N}=\text{S}=\text{O}$ symmetric stretching and C–N stretching modes, respectively.



Scheme 3. Structures representing the charge delocalization on the molecule. Calculated values in Å (B3LYP/6-311+G(df)) are given for the C–F (red) and C–N (black) bond lengths, respectively.

We now turn our attention to the broad bands centered at 2850 and 2600 cm^{-1} . Neither *para* nor *meta* isomers showed bands of similar intensity in this region. They are most certainly not due to impurities, as the mass and NMR spectra show without question. The only possibility that remains is that they are actually overtones and/or combination bands borrowing intensity from the C–H stretching allowed transitions through Fermi resonance. The broad profiles of these bands are probably due to liquid bulk effects, as Fermi resonant states are conspicuously sensitive to the environment. In any case, the upcoming studies on other monosubstituted derivatives will probably shed some light over the identity of these bands. Additionally, more accurate vibrational structure calculations that take into account vibrational correlation explicitly, such as vibrational configuration interaction (VCI)²¹ are currently into intense development by our group and may be able to provide more certitude in the near future about these puzzling spectral features.

NMR Spectra Analysis

The experimental and theoretical ^1H and ^{13}C chemical shifts recorded in CDCl_3 for the *o*-fluorosulfinylaniline are presented in Tables 3 and 4 (TMS was used as internal reference). The assignment proposed was based on results reported for other similarly substituted aromatic molecules, as well as on data reported for unsubstituted sulfinylaniline,¹¹ *p*-fluorosulfinylaniline¹³ and *m*-fluorosulfinylaniline.¹⁴ Furthermore, the observed resonance signals were compared with those predicted by using optimized molecular structure at DFT/B3LYP/6-311+G(df) level of theory using the GIAO method which is one of the most common approaches for calculating nuclear magnetic shielding tensors. The spectra are complicated because there is coupling not only between protons but also between protons and fluorine atom.

The chemical shifts of aromatic protons and carbon atoms of organic compounds are usually recorded in the range of 7.00–8.00 ppm and 100–150 ppm, respectively. However, the attachment of more than one electron withdrawing and electron realising substituents lead to deshielding of the protons and carbon atoms and the consequent expansion of the range of aromatic chemical shifts. The four protons attached to the aromatic ring of *o*-fluorosulfinylaniline give resonance signals at 7.24 (C(3)H and C(5)H), 7.43 (C(4)H) and 8.34 ppm (C(6)H). Meanwhile, ^{13}C NMR spectrum showed signals at 116.6 (C(5)), 124.7 (C(3)), 128.4 (C(6)), 131.9 ppm (C(4)), 131.0 (C(1)) and 155.0 ppm (C(2)).

Table 2. Experimental and calculated wavenumbers of the *o*-fluorosulfinylaniline and tentative assignments of main fundamental vibrational modes.

Mode	Approximate description ^a	Experimental ^b		Theoretical ^c			
		IR	Raman	B3LYP/6-311++G(df,pd)		MP2/cc-pVDZ	
		(liq.)	(liq.)	HO	VSCF	HO	VSCF
v ₁	C–H Stretch.	3087m	3086w	3218(2)[5]	3032	3275(4)[19]	3084
v ₂	C–H Stretch.	3070m	3067w	3195(1)[39]	3037	3254(2)[100]	3100
v ₃	C–H Stretch.	-	-	3184(4)[21]	3048	3242(9)[54]	3098
v ₄	C–H Stretch.	3033m	-	3170(<1)[10]	3011	3227(2)[30]	3065
v ₅	C–C Stretch.	1599m	1601s	1636(22)[50]	1613	1658(16)[30]	1632
v ₆	C–C Stretch.	1579w	-	1605(8)[<1]	1580	1636(17)[4]	1610
v ₇	C–C Stretch. + C–H Def.	1486vs	1488m	1517(40)[25]	1497	1529(100)[40]	1510
v ₈	C–C Stretch. + C–H Def.	1454m	1457w	1486(8)[7]	1466	1485(19)[5]	1465
v ₉	N=S=O Asym. Stretch.	1307s	1308vs	1335(6)[100]	1316	1461(11)[3]	1436
v ₁₀	C–C Stretch. + C–H Def.	1296sh	-	1329(3)[39]	1316	1318(26)[70]	1301
v ₁₁	C–C Stretch.	1273m	1276sh	1303(9)[11]	1288	1295(41)[2]	1283
v ₁₂	C–F Stretch.	1231vs	1231w	1259(51)[6]	1244	1257(88)[6]	1245
v ₁₃	C–H Def.	1170s	1172w	1191(<1)[5]	1185	1201(33)[41]	1196
v ₁₄	C–H Def.	1154s	1156m	1162(100)[10]	1150	1170(<1)[5]	1169
v ₁₅	C–H Def. + C–C Def. i.p.	1110m	1113m	1136(2)[6]	1129	1125(38)[1]	1120
v ₁₆	N=S=O Symm. Stretch.	1037m	1039s	1058(8)[16]	1051	1060(12)[8]	1054
v ₁₇	C–H Def. + C–C Def. i.p.	1026sh	1028sh	1039(7)[14]	1028	999(33)[5]	988
v ₁₈	C–H Def. + C–C Def. i.p.	-	992w	1013(<1)[<1]	1025	959(1)[<1]	999
v ₁₉	C–H Def. o.o.p. + Ring torsion	945m	-	982(2)[<1]	988	941(6)[<1]	974
v ₂₀	Ring Def.	844w	-	893(<1)[<1]	915	871(<1)[1]	904
v ₂₁	C–N Stretch.	826m	827vw	845(8)[<1]	837	831(16)[7]	827
v ₂₂	C–H Def. o.o.p.	759s	758vw	789(41)[<1]	820	775(83)[<1]	814
v ₂₃	C–H Def. o.o.p.	725m	724w	761(<1)[<1]	714	730(17)[5]	723
v ₂₄	C–H def.	-	-	742(9)[7]	736	689(1)[<1]	726
v ₂₅	C–H def.	679s	-	637(4)[3]	632	632(9)[3]	628
v ₂₆	N=S=O Def. i.p.	631m	630w	573(1)[<1]	552	548(1)[<1]	571
v ₂₇	Ring Def. i.p.	595w	-	551(2)[2]	547	540(5)[4]	537
v ₂₈	Ring Def.	-	543w	508(<1)[<1]	503	500(<1)[<1]	496
v ₂₉	Ring Def.	530w	-	498(<1)[<1]	501	483(<1)[<1]	495
v ₃₀	C–F Def. i.p.	445s	-	399(9)[1]	398	383(22)[1]	383
v ₃₁	C–F Def. o.o.p.	410s	-	383(3)[<1]	383	373(6)[<1]	377
v ₃₂	Ring Def.	-	367vw	240(1)[<1]	246	240(2)[1]	248
v ₃₃	N=S=O Def. o.o.p.	-	234vw	236(1)[1]	235	230(2)[1]	229
v ₃₄	Ring Def.	-	-	140(2)[1]	142	160(4)[1]	161
v ₃₅	Ring Def.	-	-	133(2)[<1]	147	133(3)[2]	149
v ₃₆	Skeletal Def.	-	-	62(1)[<1]	82	53(<1)[<1]	74

^a Stretch.: stretching; Def.: deformation; Asym.: antisymmetric; Sym.: symmetric; sh: shoulder; i.p.: in phase; o.o.p.: out of phase; tors.: torsion; ^b s: strong; vs: very strong; m: medium; w: weak; vw: very weak. ^c Relative infrared intensities in parentheses, normalized to 100%; Relative activities between brackets, normalized to 100%; HO: Harmonic oscillator method; VSCF: Vibrational Self-consistent Field method.

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Experimental spectra show good agreement with theoretical predictions. COSY, HSQC and HMBC experimental NMR spectra of *o*-fluorosulfinylaniline were useful for the assignment, showing H–H, single C–H and multiple C–H correlations, respectively. The electronic nature and position of the fluorine substituent on the fluorinated sulfinylanilines series determined the different signals observed in each case.

Table 3. ^1H NMR experimental (200 MHz, CDCl_3 , TMS) and calculated data of the *o*-fluorosulfinylaniline.

H ^a	δ [ppm], multiplicity, J [Hz] Experimental	δ [ppm] Theoretical ^b
C(3)H	7.24, m, 8.0	6.86
C(5)H	7.24, m, 8.0	6.91
C(4)H	7.43, m, 7.0	7.14
C(6)H	8.34, m, 7.7	8.80

^a For atom numbering see Fig. 1; ^b Calculated chemical shifts (GIAO method) using B3LYP/6-311+G(df) approximation.

Table 4. ^{13}C NMR experimental (50 MHz, CDCl_3 , TMS) and calculated data of *o*-fluorosulfinylaniline.

C ^a	Chemical shift δ [ppm]	
	Experimental	Theoretical ^b
C(5)	116.6	127.2
C(3)	124.7	119.0
C(6)	128.4	134.1
C(1)	131.0	140.5
C(4)	131.9	137.2
C(2)	155.0	163.5

^a For atom numbering see Fig. 1; ^b Calculated chemical shifts (GIAO method) using B3LYP/6-311+G(df) approximation.

GC/MS Analysis

The only intense signal observed at time retention 8.22 min (98.3% relative area and 157 molecular weight) in the total-ion chromatogram accounts for the presence and high purity of the studied molecule. Fig. 6 shows the mass spectra of the *o*-fluorosulfinylaniline. The mass spectra (mass numbers (m/z) versus relative abundance) exhibits the base peak at a m/z 157 relation, which was attributed to the molecular ion $[\text{M}^+]$, accompanied of peaks at m/z 158 $[\text{M}^++\text{H}]$ (protonated form of

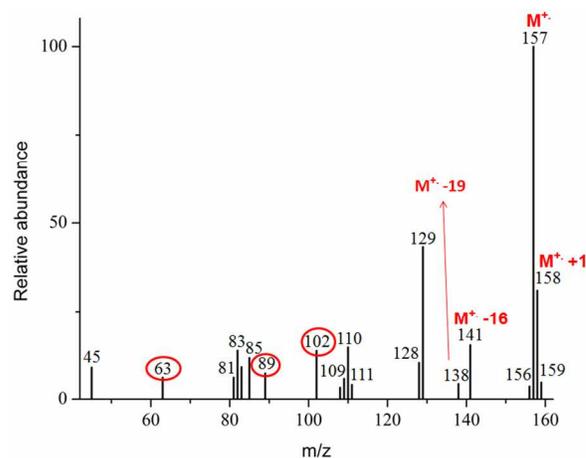


Fig. 6. Mass spectra (mass numbers (m/z) versus relative abundance) of *o*-fluorosulfinylaniline recorded in the range m/z 40–160.

the molecular ion), m/z 141 $[\text{M}^+-16]$ (loss de oxygen atom), m/z 138 $[\text{M}^+-19]$ (loss of fluorine atom). The clusters of ions found at m/z 102, 89 and 63 are well-known fragments arising from the decomposition of aromatic structures.²⁷

Conclusions

The present article concludes the study of the monosubstituted fluorosulfinylaniline series of compounds by analysing the conformational and vibrational properties of *o*-fluorosulfinylaniline. The highly hygroscopic and corrosive substance was obtained with 98% yield through the reaction of *o*-fluoroaniline and SOCl_2 and characterized by using nuclear magnetic resonance spectroscopy (^1H and ^{13}C), gas-chromatography/mass spectrometry, vibrational spectra and quantum chemical calculations at different levels of theory. As it was observed for the *p*- and *m*- isomers, the title compound adopts a *syn* conformation of the $\text{N}=\text{S}=\text{O}$ group (*syn* of the C–N bond with respect to the S=O bond). Theoretical calculations slightly favor the conformer possessing the fluorine atom in the *ortho* position further from the oxygen atom of the $-\text{N}=\text{S}=\text{O}$, in agreement with the formation of an intramolecular anti-hydrogen bond, evidenced now by Natural Bond Orbital Analysis. The analysis of the vibrational spectra of monosubstituted fluoroanilines reveals that the presence of a fluorine atom modifies the frequency of different vibrational modes in an extent related to its position in the aromatic ring. Similar behaviour trends may be found for the *p*- and *o*- isomers, as it may be expected taking into account the electronic effects of fluorine and $-\text{N}=\text{S}=\text{O}$ as substituents attached to the aromatic

ring. A complete assignment of the fundamental vibrational modes was proposed on the basis of present and reported experimental result and supported by theoretical calculations at different levels of theory. With regard to this point, the vibrational structure calculations performed using the vibrational self-consistent field (VSCF) ansatz recently implemented in the QUMVIA software package proved to be rather useful in the assignment of the fundamental and possible overtones and combination bands, using the B3LYP/6-311++G(df,pd) and MP2/cc-pVDZ potential energy surfaces. Important anharmonicity effects were found for many vibrational transitions, in ways that suggested, in some cases, a different assignment than the harmonic oscillator method. Compared to the widespread practice of scaling spectra using one or more *ad hoc* factors, the VSCF provides superior results, as it is capable of handling non-trivial cases in which a simple scaling factor is of little use, as well as improving the overall accuracy of theoretical predictions. The vibrational spectra of *o*-fluorosulfinylaniline reveal a more complex picture of the experimental signals in comparison with the spectra of the *p*- and *m*- isomers, particularly regarding the highest frequency region of the spectra. The broad profiles of several unexpected signals are still to be thoroughly understood, it is expected that the study of other monosubstituted derivatives, for example the chlorosulfinylaniline and trifluorosulfinylaniline serie might assist the interpretation of fundamental and non-fundamental vibrational modes characteristic for the sulfinyl family of compounds.

Acknowledgements

Authors acknowledge CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and UNT (Universidad Nacional de Tucumán) for the financial support. Authors also kindly acknowledge staff from LISA (Laboratorio de Investigación y Servicios Analíticos) for NMR and GC/MS measurements.

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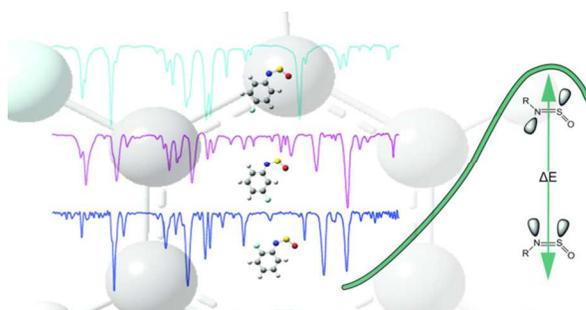
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TEXT

A complete vibrational study of a new fluoro substituted sulfanyl aniline was performed in comparison with *m*- and *p*- isomers.