Synthesis, characterization and vibrational properties of *p*-fluorosulfinylaniline
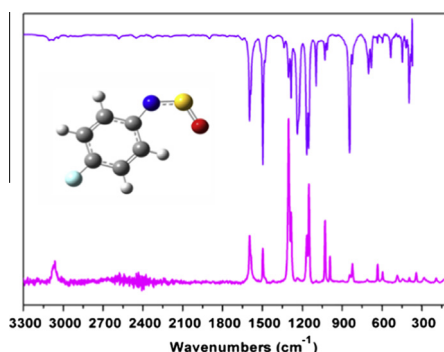
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HIGHLIGHTS

- A new fluorinated sulfinylaniline was prepared in good yield.
- IR, Raman and ^{1}H NMR spectra evidence the presence of a single *syn* configuration.
- The *syn* configuration adopted may be explained through donor–acceptor interactions.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The reaction of *p*-fluoroaniline and SOCl$_2$ rendered *p*-fluorosulfinylaniline in good yield. The obtained dark yellowish liquid compound was characterized by NMR, UV–visible, FT-IR and Raman spectroscopies. The observed features were consistent with the existence of only one conformer, belonging to the C_S symmetry group. A tentative assignment of the vibrational modes was performed on the basis of experimental spectra and quantum chemical calculations at different levels of theory (B3LYP and MP2 with 6-31+G(d), 6-311+G(d) and 6-311+G(df) basis sets). The conformational and vibrational properties of *p*-fluorosulfinylaniline were in good agreement with experimental data reported for other substituted sulfinylanilines and *p*-halogenanilines.

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Introduction

The study of structural, conformational and vibrational properties of R—N=S=O compounds is of considerable interest. Even though N-sulfinyl compounds can exist in two configurational forms (*syn* and *anti,* see Scheme 1), the gas phase structures for some members of this family showed only the presence of the sterically unfavorable *syn* (Z-) conformer [1–7]. The presence of a N=S=O group makes these compounds interesting respect to pre-resonant Raman properties due to π orbitals and their related double bond character, an effect that can be used for sensing molecular structure.

N-sulfinylaniline, O=S=N—C$_6$H$_5$, was first prepared by Michaelis et al. in 1890 [8] but its exact geometrical structure was not confirmed until 1999 [9]. According to the results obtained by low temperature X-ray crystallography, the ground state of O=S=N—C$_6$H$_5$ is planar with *syn* (Z) configuration, in agreement with earlier results. Although about 600 N-sulfinyl compounds are now known [10], only a few N-sulfinyl-aromatic-imines have been characterized and their reactivity has not been completely understood. While it

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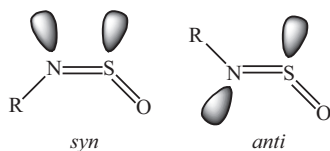
Scheme 1.

is assumed that steric hindrance could lead to kinetic stabilization, the electronic effects that substituents may cause on the aromatic N-sulfinyl compounds have not been determined [11]. The study of fluorinated substances is of considerable importance since they are widely used in industries [12]. Due to the small size of the fluorine atom and its high electronegativity, fluorinated compounds show entirely different physical and chemical properties compared to the other halogenated compounds [13]. In this context, we present now the study of structural, conformational and vibrational properties of *p*-fluorosulfinylaniline, a compound that will allow us to assess the effect of an halogen atom in *para* position of an aromatic ring respect to N=S=O properties.

Materials and methods

Experimental

Synthesis and characterization

According to the method proposed by Michaelis for the synthesis of R—N=S=O compounds [8], *p*-fluorosulfinylaniline was prepared using a 1:2:5 M relation of the corresponding fluorinated aniline, thionyl chloride and benzene as the reaction solvent respectively. *p*-fluoroaniline (3.52 g) and benzene (13.20 g) were allowed to warm up at *ca.* 60 °C in a closed three neck round bottom flask equipped with a Liebig condenser which was sealed with a CaCl$_2$ trap. Thionyl chloride (9.80 g) was added drop-to-drop to the warming mixture. To prevent the interaction with air humidity, the reaction was carried out in a nitrogen atmosphere. The mixture was continuously stirred for 6 h at 85 °C and subsequently purified by several distillation cycles in order to obtain a dark yellowish liquid as the final product with *ca.* 95% yield. Its purity was controlled by NMR, IR and Raman spectroscopies. The substance was highly hygroscopic and corrosive. NMR spectra were recorded using a Varian Unity 200 at 200 MHz for samples held at room temperature and dissolved in CCl$_4$ and CDCl$_3$. ^{1}H NMR: δ = 7.06 (H8), 7.10 (H10), 7.89 (H7), 7.94 (H11) ppm.

Vibrational spectra

Fig. 1 shows the vibrational spectrum of *p*-fluorosulfinylaniline. The FT-IR spectrum of this compound was recorded in the region 4000–400 cm^{-1} at room temperature using a Perkin Elmer GX1 Fourier Transform infrared instrument provided with KRS5 windows (4 cm^{-1} spectral resolution). The Raman spectrum of the liquid was recorded at room temperature in the range 3350–50 cm^{-1} by employing a diode-pump, solid state 532 nm green laser with 9.2 mW power at the sample for excitation in a Thermoscientific DXR Smart Raman instrument equipped with CCD detector. The resolution was between 2.7 and 4.2 cm^{-1} with a grating groove density of 900 lines/mm. A confocal aperture of 25 μm pinhole was used and 40 expositions of 8 s were accumulated for the sample in order to achieve sufficient signal to noise ratio.

Computational details

All quantum chemical calculations were performed using the GAUSSIAN03 program [14]. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [15a] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [15b] has been employed, together with the Rayleigh–Schrödinger perturbation theory developed by Møller and Plesset at second order (MP2) [16]. 6-31+G(d), 6-311+G(d) and 6-311+G(df) basis sets were used. Natural population analyses NBO [17], as implemented in the GAUSSIAN03 program, were performed. Gauge-including atomic orbital (GIAO) [18] and ^{1}H chemical shift calculations were done at the B3LYP/6-311+G(df) level of theory.

Results and discussion

Quantum chemical calculations

Two stable conformers around the N=S double bond are expected for *p*-fluorosulfinylaniline (see Scheme 1). However, calculations reported for the parent sulfinylaniline [9] and some other substituted sulfinylanilines [1–7] demonstrate that only the *syn* form will be observed in the fluid phases. The potential energy function for rotation around the N=S bond of *p*-fluorosulfinylaniline was determined by structure optimizations at fixed dihedral angles C—N=S=O in steps of 30°. Calculations at the B3LYP/6-31+G(d) and MP2/6-31+G(d) approximations predicted a *syn*
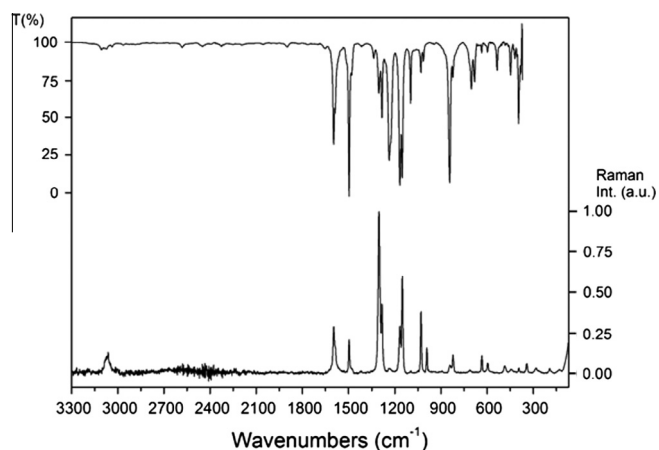

Fig. 1. Experimental infrared and Raman spectra of *p*-fluorosulfinylaniline. Top: infrared spectrum of a liquid sample held between KRS5 windows; bottom: room temperature Raman spectrum of a liquid sample.

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

	B3LYP/6-311+G(df)	MP2/6-311+G(d)
C—F	1.344	1.349
C—H	1.083	1.086
C4—C3,5	1.388	1.392
C1—C2,6	1.408	1.411
C2,5—C3,6	1.385	1.395
C1—N	1.387	1.406
N=S	1.541	1.556
S=O	1.486	1.486
N=S=O	119.4	120.7
C1—N=S	132.2	129.1
C2—C1—C6	119.3	119.7
C3—C4—C5	122.4	122.3
C2—C1—N	115.8	115.0
C6—C1—N	124.8	125.3
F—C—C	118.8	118.8
C1—N=S=O	0.0	0.0

[a] Bond lengths in Å and angles in degrees. Mean values are given for parameters that are not unique. For numbering atoms see Fig. 2.

structure as global minimum and a local minimum for *anti* geometry, about 10 kcal mol^{-1} higher in energy. Subsequent full optimizations and frequency calculations at these two minima resulted in $\Delta G°$ (*anti–syn*) = 7.54 and 6.29 kcal mol^{-1} with the B3LYP/6-311+G(df) and MP2/6-311+G(d) approximations, respectively. Table 1 lists the structural parameters of the *syn* form of *p*-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 *p*-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 (lp1 and lp2) show a pure p-type nature and possess low occupancies due to strong delocalization towards vicinal antibonding orbitals: lp2(O) → σ^* (N–S) and lp2 (O) → π^* (N–S) with interaction energies of 19 and 62 kcal mol^{-1} in the *syn* conformer. In the *anti* form these interaction energies are lower, 18 and 55 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) → σ^* (S–O) and lp (S) → σ^* (C–N) with interaction energies of 15 and 10 kcal mol^{-1}. Corresponding interaction energies in the *anti* form are only 8 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. Fig. 3 depicts the molecular orbitals involved in the relevant orbital interactions.
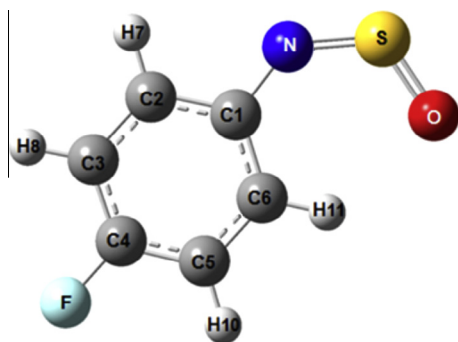

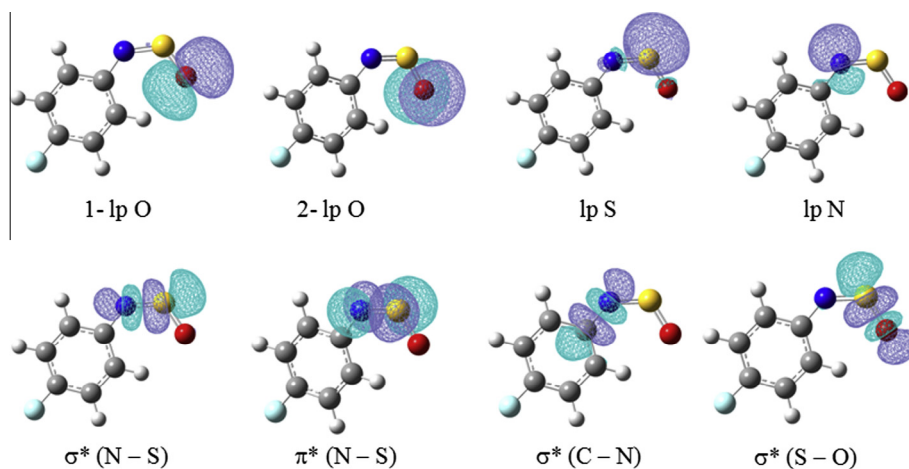**Fig. 2.** Molecular model of the *syn* conformer of *p*-fluorosulfinylaniline.

Vibrational spectroscopy

A tentative assignment of the 3N − 6 = 36 vibrational modes expected for the title compound is presented in Table 2. The analysis of the experimental infrared and Raman spectra of a liquid sample of *p*-fluorosulfinylaniline (see Fig. 1) was supported by theoretical calculations using B3LYP and MP2 methods with the 6-311+G(d) and 6-311+G(df) basis sets. Reported data for the parent sulfinylaniline [9,19] and the reactant *p*-fluoroaniline [20] were also taken into account. Wojciechowski et al. demonstrated that the MP2 method was very limited in predicting the experimental vibrational wavenumbers of several modes in aromatic molecules (aniline and phenol) despite the use of extended basis sets. The same could be stated for *p*-fluorosulfinylaniline through the comparison of calculated wavenumbers obtained with B3LYP/6-311+G(d) and MP2/6-311+G(d) approximations (see Table 2). The same authors published a good concordance between DFT predicted wavenumbers for *p*-halogenanilines after applying suitable scale factors, and the corresponding experimental values [21]. The same scale factors proposed in the study of *p*-halogenanilines were applied to the B3LYP/6-311+G(df) calculated wavenumbers for the title compound: 0.958, for the C–H stretchings and 0.983 for the remaining vibrational fundamentals (see Table 2). In addition, theoretical ^{15}N substitution was used to help identifying the vibrational modes expected for the N=S=O group. Figs. 4 and 5 show graphical comparisons between the experimental and theoretical spectra obtained for *p*-fluorosulfinylaniline. The theoretical Raman spectrum was simulated considering irradiation of the sample with a 532 nm laser, according to the method reported [21].

So far, the vibrational modes belonging to the −N=S=O group were analyzed for more than 600 compounds [10]. According to the data reported in a review article summarizing the spectroscopic and vibrational properties of the R–N=S=O compounds, the asymmetric stretching mode occurs in a wide spectroscopic region: from 1145 cm^{-1} in Cd(N=S=O)$_2$ to 1302 cm^{-1} in Si(CH$_3$)$_3$ N=S=O. Similarly, the corresponding symmetric mode was found between 990 cm^{-1}, in K–N=S=O and 1174 cm^{-1}, in 2,6-diethyl-sulfinylaniline [1]. Thus, it is obvious that the substitution at the nitrogen atom plays an important role in determining the strength of the considered bonds, which in turn accounts for the orbital interactions manifested in this group, as it was discussed above. On the other hand, an early study on the parent sulfinylaniline described the stretching modes as two independent N=S and S=O stretchings, placed at 1284 and 1155 cm^{-1}, respectively [22]. This assignment was achieved based on comparison with data reported for SO$_2$, therefore the last fundamental was assigned to


Fig. 3. Relevant NBO orbitals [B3LYP/6-311+G(df)] for the *syn* conformer of *p*-fluorosulfinylaniline.

Table 2
Experimental and calculated wavenumbers (cm^{-1}) and tentative assignments of the fundamental modes for p-fluorosulfinylaniline.

Mode	Approximate description[a]	Experimental[b]		Calculated			
		IR (liq.)	Raman (liq.)	B3LYP/6-311+G(df)		B3LYP/6-311+G(d)	MP2/6-311+G(d)
				Calculated values	Scaled values[c]		
v_1	C—H Stretch.	3106 vw	–	3238 (1) [7]	3102	3232 (2) [5]	3253 (2) [16]
v_2	C—H Stretch.	3091 vw	3071 m	3217 (1) [37]	3082	3210 (2) [26]	3237 (<1) [59]
v_3	C—H Stretch.	3072 vw	3063 m	3206 (1) [27]	3071	3200 (1) [19]	3229 (<1) [39]
v_4	C—H Stretch.	–	–	3203 (1) [13]	3068	3197 (2) [9]	3221 (1) [16]
v_5	C—C Stretch.	1597 m	1597 m	1636 (73) [67]	1609	1638 (95) [48]	1649 (49) [57]
v_6	C—C Stretch.	1587 m	1587 sh	1610 (6) [5]	1583	1611 (7) [3]	1629 (4) [10]
v_7	C—C Stretch. + C—H Def.	1497 vs	1497 m	1531 (37) [23]	1505	1530 (47) [15]	1535 (87) [25]
v_8	C—C Stretch. + C—H Def.	–	–	1452 (1) [1]	1427	1451 (1) [1]	1476 (<1) [3]
v_9	N=S=O Asym. Stretch.	1303 m	1302 vs	1334 (5) [75]	1311	1332 (5) [34]	1413 (<1) [9]
v_{10}	C—C Stretch. + C—H Def.	1283 m	1283 m	1330 (2) [34]	1307	1326 (1) [11]	1323 (3) [10]
v_{11}	C—C Stretch.	1236 s	1236 w	1312 (16) [100]	1290	1304 (24) [100]	1316 (20) [100]
v_{12}	C—F Stretch.	1227 sh		1261 (67) [5]	1240	1248 (83) [4]	1256 (100) [4]
v_{13}	C—H Def.	1167 s	1167 m	1186 (15) [11]	1166	1181 (27) [12]	1200 (61) [72]
v_{14}	C—H Def.	1152 s	1151 s	1155 (100) [39]	1135	1139 (100) [15]	1189 (17) [7]
v_{15}	C—H Def. + C—C Def. i.p.	1097 m	1095 vw	1128 (19) [2]	1109	1123 (53) [3]	1126 (10) [<1]
v_{16}	N=S=O Sym. Stretch.	1030 m	1029 s	1037 (6) [22]	1019	1029 (1) [2]	1030 (20) [<1]
v_{17}	C—H Def. + C—C Def. i.p.	1013 w	–	1030 (3) [3]	1012	1023 (18) [19]	1017 (8) [<1]
v_{18}	C—H Def. o.o.p. + Ring torsion	–	–	1000 (<1) [<1]	983	983 (<1) [<1]	878 (<1) [<1]
v_{19}	C—H Def. o.o.p. + Ring torsion	–	–	979 (1) [<1]	962	965 (<1) [<1]	857 (<1) [<1]
v_{20}	Ring Def.	876 sh	–	874 (40) [<1]	859	862 (53) [<1]	836 (15) [11]
v_{21}	C—H Def. o.o.p.	843 s	842 w	843 (4) [18]	829	839 (6) [13]	804 (67) [<1]
v_{22}	C—N Stretch.	822 m	821 m	837 (<1) [<1]	823	825 (<1) [<1]	789 (3) [<1]
v_{23}	C—H Def. o.o.p.	702 m	712 w	717 (14) [<1]	705	717 (20) [1]	707 (16) [4]
v_{24}	C—H Def.	681 m	–	714 (<1) [<1]	702	711 (<1) [<1]	642 (<1) [2]
v_{25}	N=S=O Def. i.p.	635 w	634 m	648 (1) [5]	637	646 (2) [3]	602 (2) [1]
v_{26}	Ring Def.	598 w	596 m	604 (1) [2]	594	603 (1) [2]	498 (8) [<1]
v_{27}	Ring Def.	535 m	–	548 (3) [<1]	539	544 (4) [<1]	489 (1) [1]
v_{28}	Ring Def.	484 vw	486 w	450 (5) [<1]	442	448 (7) [<1]	417 (3) [<1]
v_{29}	C—F Def. i.p.	448 m	446 vw	430 (<1) [<1]	423	428 (<1) [<1]	404 (1) [<1]
v_{30}	Ring Def.	420 w	–	425 (2) [<1]	418	422 (2) [<1]	395 (15) [1]
v_{31}	C—F Def. o.o.p.	396 m	393 vw	401 (12) [1]	394	400 (16) [1]	388 (3) [1]
v_{32}	Skeletal Def.	–	342 w	282 (3) [1]	277	281 (4) [1]	275 (5) [1]
v_{33}	N=S=O Def. o.o.p.	–	281 w	268 (4) [<1]	263	268 (5) [<1]	249 (6) [1]
v_{34}	Ring Def.	–	193 w	135 (1) [<1]	133	137 (1) [<1]	145 (1) [1]
v_{35}	Ring Def.	–	130 w	117 (<1) [<1]	115	117 (<1) [<1]	110 (<1) [<1]
v_{36}	Ring Def.	–	–	63 (<1) [<1]	62	64 (1) [<1]	30 (<1) [<1]

[a] Stretch.: stretching; Def.: deformation; Asym.: antisymmetric; Sym.: symmetric; sh: shoulder; i.p.: in phase; o.o.p.: out of phase; and tors.: torsion.
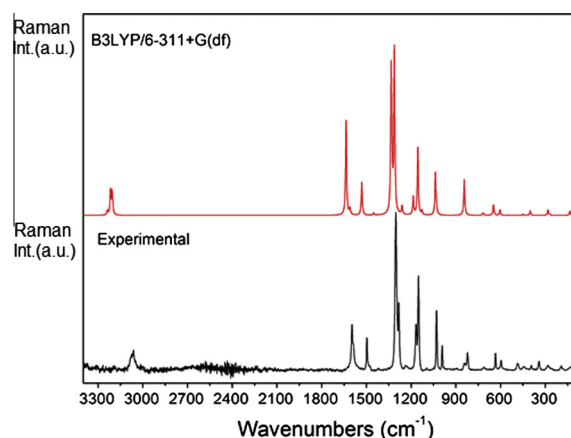[b] s: Strong; vs: very strong; m: medium; w: weak; and vw: very weak.
[c] Values scaled according to scaling factors in Ref. [21].
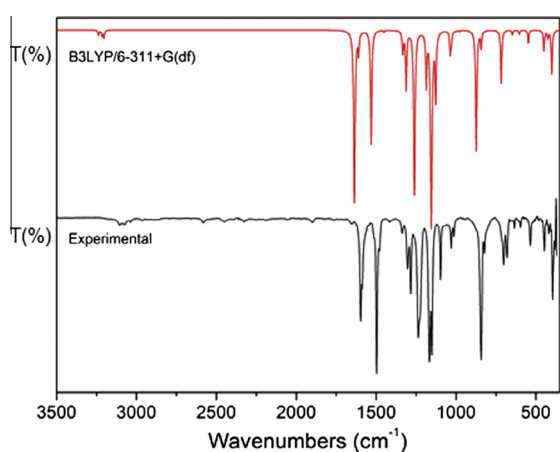
Fig. 4. Experimental and theoretical infrared spectra of p-fluorosulfinylaniline. Top: theoretical gas phase spectrum calculated at the B3LYP/6-311+G(df) level of theory; bottom: room temperature infrared spectrum of a liquid sample.

Fig. 5. Experimental and theoretical Raman spectra of p-fluorosulfinylaniline. Top: theoretical gas phase Raman spectrum calculated at the B3LYP/6-311+G(df) level of theory (532 nm excitation laser); bottom: room temperature spectrum of a liquid sample.

the S=O symmetric stretching. However, a subsequent study of the pre-resonant Raman spectra of sulfinylaniline concluded that both stretching modes are actually coupled and appear at 1298 cm^{-1} (NSO asym) and 1163 cm^{-1} (NSO sym.), tough no frequency shift was observed for the bands upon isotopic substitution of the

nitrogen atom [19]. In the vibrational spectra of p-fluorosulfinylaniline the bands at 1303 and 1030 cm^{-1} (IR) and 1302 and 1029 cm^{-1} (Raman) were assigned to the NSO asymmetric and symmetric stretchings, respectively. The downshift of 6 cm^{-1} predicted for the 1037 cm^{-1} feature, while no changes were predicted

Table 3
Tentative assignments of ^{1}H NMR experimental and calculated chemical shifts for p-fluorosulfinylaniline.

Atoms[a]	Chemical shift (δ) (ppm)	
	Experimental	Theoretical[b]
H8	7.06	6.785
H10	7.10	6.873
H7	7.89	7.206
H11	7.94	8.911

[a] For atom numbering see Fig. 2.
[b] Calculated chemical shifts (GIAO method) using B3LYP/6-311+G(df) approximation.

for neither the 1186 cm^{-1} nor the 1155 cm^{-1} bands, allowed us to propose these assignments.

It is interesting to note that no remarkable influence of this group was revealed in both, the experimental and theoretical vibrational spectra between the p-fluorosulfinylaniline and the parent unsubstituted compound. However, calculations performed for o- and m-fluorosulfinylaniline, indicate that the influence of a fluorine atom depends on its position in the aromatic ring and on the vibrational mode considered. Thus, the asymmetric stretching of the N=S=O group in o-fluorosulfinylaniline was calculated at 1335 cm^{-1}, in close agreement with that belonging to the title molecule (1334 cm^{-1}), while the corresponding mode for the meta substituted compound was predicted at 1348 cm^{-1} (B3LYP/6-311+G(df)). In turn, the symmetric N=S=O stretching was calculated at 1037, 1059 and 1056 cm^{-1} for p-, o- and m-sulfinylaniline, respectively [23].

The in-plane deformation of the N=S=O group was assigned to the signal placed at 635 and 634 cm^{-1} in the infrared and Raman spectra, respectively.

Data reported for the p-fluoroaniline allowed a straight assignment of the signal belonging to the C—F stretching in the title compound [20]. This signal was observed as a strong feature at 1225 cm^{-1} in the IR spectrum, therefore it was safely attributed to the shoulder ca. 1227 cm^{-1} in the infrared spectrum of p-fluorosulfinylaniline. It is worth mentioning that this fundamental mode has shown to be sensitive towards substitution of the benzene ring, since it was found at 1270 and 1288 cm^{-1} in the infrared spectrum of o-fluoroaniline and m-fluoroaniline, respectively [24]. The study of the corresponding o-fluorosulfinylaniline and m-fluorosulfinylaniline will allow us to determine if the N=S=O group exerts a similar influence on the C—F stretching on these compounds [23].

NMR spectroscopy

The optimized structure for the syn conformer of p-fluorosulfinylaniline at the B3LYP/6-311+G(df) level of theory was used for the gauge-including atomic orbital (GIAO) and ^{1}H chemical shift calculations with the same approximation. The GIAO method is one of the most common approaches for calculating nuclear magnetic shielding tensors. The results obtained were subsequently compared with the experimental values (see Table 3). The ^{1}H NMR spectrum of p-fluorosulfinylaniline showed two groups of signals centered approximately at 7.10 and 7.90 ppm, in agreement with results reported for the parent sulfinylaniline with signals located at 7.20 and 7.70 ppm, respectively [22]. It is well known that the presence of electron withdrawing groups/atoms lead to deshielding of the protons in resonance and the consequent increase in the chemical shift values, therefore the influence of the fluorine atom and the N=S=O group must be considered. At first sight, the presence of the fluorine atom in p- position of the aromatic ring may produce a similar deshielding in the H8 and H10 pair of atoms, and in the H7 and H11 pair, being the former the

strongest affected. However, the particular symmetry of the N=S=O group in the stable syn conformer of p-fluorosulfinylaniline breaks the expected equivalence of the aromatic protons, therefore, each of the expected signals show to be rather complex. Taking into account the theoretical ^{1}H NMR spectrum obtained, H7 and H11 (see Fig. 2) show to be the most influenced by the presence of the electron withdrawing N=S=O group, therefore, the signals observed at 7.94 and 7.89 ppm were assigned to those protons, respectively. Therefore, the remaining features observed belong to the H8 and H10 atoms.

Conclusions

A new member of the sulfinylaniline family of compounds has been prepared by reacting p-fluoroaniline and SOCl$_2$. The obtained highly reactive and corrosive liquid compound was characterized by using ^{1}H NMR and vibrational spectra. Although at least two stable conformers might be expected (syn and anti with respect to the C—N and S=O bonds), all experimental spectra evidence the presence of a single conformer, since no additional signals were observed to account for several forms in equilibrium at room temperature. Theoretical calculations using B3LYP and MP2 methods confirmed that only the syn conformer is present in the fluid phases, predicting a local C_1 symmetry for the N=S=O group, although a global C_S symmetry may be safely assumed in agreement with the properties observed for the parent sulfinylaniline. The unexpected syn configuration adopted by all R-N=S=O compounds reported so far might be rationalized in terms of orbital interactions. In fact, larger interaction energies were predicted for the syn configuration of p-fluorosulfinylaniline compared to the anti structure, according to Natural Bond Orbital analysis. Thus, the thermodynamic preference of the syn form can be rationalized as a result of the influence of stabilizing anomeric interactions.

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