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Synthesis, experimental and theoretical characterization of *m*-fluorosulfinylaniline

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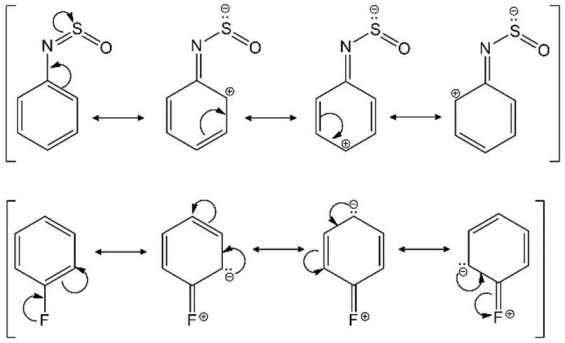
The synthesis of *m*-fluorosulfinylaniline together with a tentative assignment of the vibrational, NMR and mass spectra, are reported. Quantum chemical calculations predict two stable conformers, with very similar energies, both of which possess in the liquid phase *syn* structure of the –N=S=O moiety (*syn* of the S=O double bond relative to the C–N single bond). Both conformers belong to C_S symmetry group and differ by relative orientation of the fluorine atom and the NSO group. However, the FT-IR, FT-Raman and NMR spectra do not allow a distinction between these two conformers. The experimentally observed spectral data (FT-IR, FT-Raman, ^{1}H and ^{13}C and GC-Mass Spectrometry) of the title compound are compared with the spectral data obtained by quantum chemical calculations and gauge including atomic orbital (GIAO) method (DFT/B3LYP approximation using 6-311+G(df), 6-311++G(df,pd) and cc-pVTZ basis sets). Moreover, Natural Bond Orbital (NBO) analysis is applied for studying the stability of the molecule upon charge delocalization in order to provide an explanation of its electronic properties.

Introduction

N-sulfinylamines, R–N=S=O, constitute a vast family of organic compounds and despite the fact that they have been known since the end of the 19th century, they have not been studied intensively until the second half of the 20th century. The geometry of these compounds are controversial since earlier studies suggested a linear configuration of the heterocumulene unit [1], but subsequent studies predicted *syn*/*anti* structures for this group (*syn* (*Z*) or *anti* (*E*) of the S=O bond with respect to the R–N bond), the former one being more stable [2 – 5].

The first aromatic *N*-sulfinylamine, called *N*-sulfinylaniline or *N*-sulfinyl-benzenamine, C_6H_5–N=S=O was prepared by Michaelis *et al.* in 1890 [6]. For this compound, and later for other R–N=S=O compounds, the configurational controversy about the N=S=O geometry was clarified by the X-ray diffraction and vibrational studies in 1999 [7]. Although about 600 N-sulfinyl compounds are known today [8], only a few *N*-sulfinyl-aromatic-imines have been characterized and their reactivity has not yet been completely understood.

While it is assumed that steric hindrance could lead to kinetic stabilization, the electronic effects, which substituents may cause in the aromatic *N*-sufinyl compounds, have not been determined [9]. The inclusion of a substituent group/atom in *N*-sulfinylaniline leads to a variation of charge distribution in the molecule, with consequent effects on the structural, electronic and vibrational parameters. Being an electron withdrawing group [10], the presence of the N=S=O group could lead to the different mesomeric structures depicted on Scheme I. The electron withdrawing inductive effect of the fluorine atom is obvious, being the most electronegative element so far reported. The opposite effect, via mesomeric delocalization, is evident from the structures shown (see Scheme I).



Scheme I. Different mesomeric structures for monosubstituted benzene rings.

Our recent study of *p*-fluorosulfinylaniline evidences the combination of both effects [11] (see Scheme II). From Scheme II it can be noted that the influence of the halogen atom in a *para* position is negligible on the structural and therefore on the vibrational properties of the N=S=O group: the electron deficiency occurring for the N=S=O group in *para* position with respect to the halogen substituent is compensated by electron delocalization towards C1 and the experimental vibrational frequencies strongly resemble those belonging to the parent unsubstituted sulfinylaniline.

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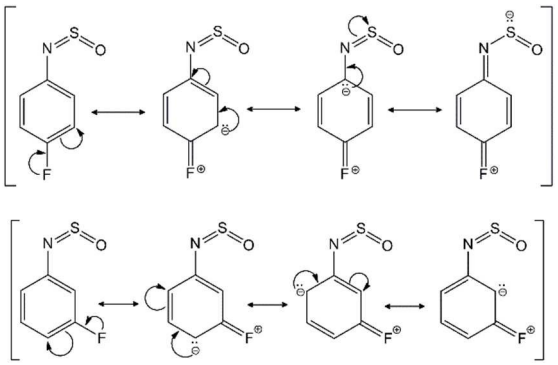
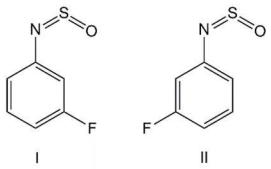


Scheme II. Different mesomeric structures for p- and m- fluoro substituted sulfinylaniline.

In this work, we present the structural, conformational and vibrational analysis of *m*-fluorosulfinylaniline on the basis of a detailed characterization (^{1}H and ^{13}C NMR, COSY, HSQC and GC-Chromatography) and a tentative assignment of the vibrational spectra (FT-IR and FT-Raman) supported by quantum chemical calculations at different levels of theory. The present study allows us to demonstrate the effects of both, N=S=O moiety and fluorine substituents, on the properties of the compound by placing the fluorine atom *meta* with respect to the sulfinyl group. Due to the bent geometry of the N=S=O group, I and II structures would be equal only if the C–N=S=O moiety were linear. Therefore, two different conformers with very similar energies can be expected (see Scheme III).



Scheme III. Structures I and II of m-fluorosulfinylaniline.

Materials and Methods

Experimental

Synthesis and characterization. According to the method proposed by Michaelis for the synthesis of R−N=S=O compounds [6], *m*-fluorosulfinylaniline was prepared using a 1:2:5 molar relation of the corresponding fluorinated aniline, thionyl chloride and benzene as the reaction solvent, respectively. *m*-fluoroaniline (3.47 g , 31 mmol) and benzene (13.20 g , 169 mmol) were placed 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 , 82 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.* 92% yield. Its purity was controlled by ^{1}H and ^{13}C NMR spectroscopy, GC-Mass Spectrometry, IR and Raman spectroscopy. The substance is highly hygroscopic and corrosive. NMR spectra were measured in $CDCl_3$ at 200 MHz for ^{1}H and 50 MHz for ^{13}C on a Varian Unity 200 spectrometer. ^{1}H NMR: δ = 7.10 (C(4)H), 7.38 (C(5)H), 7.58 (C(6)H), and 7.62 (C(2)H) ppm. ^{13}C NMR: δ = 113.97 and 114.43 (C6); 117.39 and 117.82 (C4); 122.92 and 122.98 (C2); 130.22 and 130.40 (C5); 159.93 (C1) and 164.88 (C3) ppm.

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 10.1 min. Helium was used as carrier gas. The mass spectrometer was operated in the electron ionization scan mode (range, *m/z*: 40-160). Quantification of the peaks was based on peak area.

Vibrational spectra. Fig. 1 shows the experimental vibrational spectrum of *m*-fluorosulfinylaniline. 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). The FT-Raman spectrum of the liquid was recorded at room temperature in the range 3500–50 cm^{-1} by employing a diode-pump, solid state 532 nm green laser with 9.0 mW power at the sample for excitation in a Thermoscientific DXR Smart Raman instrument equipped with CCD detector. The resolution was 1.9285 Raman shift (cm^{-1}) with a grating groove density of 900 lines/mm. A confocal aperture of 50 μm slit was used and 80 expositions of 6 s were accumulated for the sample in order to achieve sufficient signal to noise ratio.

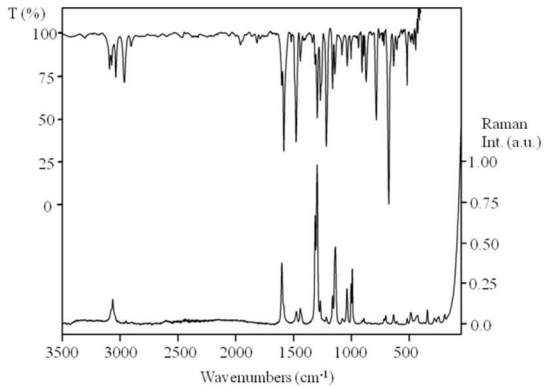


Fig. 1. Experimental infrared and Raman spectra of *m*-fluorosulfinylaniline. Top: infrared spectrum of a liquid sample held between KRS-5 windows; bottom: room temperature Raman spectrum of a liquid sample.

Computational details

All quantum chemical calculations were performed using the GAUSSIAN03 program [12]. The methods employed are based on the gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [13a] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [13b]. The calculations were carried out using 6-311+G(df), 6-311++G(df, pd) and cc-pVTZ basis sets. Natural population analyses NBO [14], as implemented in the

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GAUSSIAN03 program, were performed together with the Gauge-including atomic orbital (GIAO) method [15].

Results and Discussion

Quantum chemical calculations analysis

Stable conformers with different orientation around the N=S double bond are expected for *m*-fluorosulfinylaniline, defined as *syn* and *anti* according to the orientation of the S=O bond with respect to the C–N bond. However, calculations reported for the parent sulfinylaniline and some other substituted sulfinylanilines [2–7] demonstrate that only the *syn* form is observed in the liquid phase. The potential energy function for rotation around the N=S bond of *m*-fluorosulfinylaniline 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) and B3LYP/cc-pVTZ approximations predicted the *syn* structure as the global minimum and a local minimum with *anti* geometry, about 7 Kcal.mol^{-1} higher in energy. Subsequent full optimizations and frequency calculations at these two minima resulted in ΔG° (*anti* – *syn*) = 6.87 and 6.64 Kcal.mol^{-1} for both basis sets, respectively.

Considering the orientation of the fluorine atom with respect to the N=S=O group, two different *syn* isomers of the title compound may be obtained from the reaction of *m*-fluoroaniline and $SOCl_2$ (see Scheme III). The potential energy function for rotation around the C–N bond shows two minima with very similar energies for structures I and II with a rotational barrier of *ca*. 5 kcal.mol^{-1}. Subsequent full optimizations and frequency calculations of these two minima resulted in ΔG° (*II* – *I*) = 0.04 Kcal.mol^{-1}.

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

Structural parameters	*m*-fluorosulfinylaniline B3LYP/ 6-311++G(df,pd)	B3LYP/ cc-pVTZ
C–F	1.347	1.347
C–H	1.081	1.080
C1–C2,6	1.406	1.405
C2,5–C3,6	1.383	1.382
C4–C3,5	1.390	1.389
C1–N	1.389	1.391
N=S	1.540	1.535
S=O	1.484	1.478
N=S=O	119.6	119.9
C1–N=S	132.2	131.8
C2–C1–C6	119.8	119.7
C3–C4–C5	118.4	118.4
C2–C1–N	124.3	124.3
C6–C1–N	115.9	116.0
F–C3–C2,4	118.5	118.5
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.

With this small energy difference both conformers are expected to be present in almost equal amounts. Table 1 lists the structural parameters of the *syn* (*I*) form of *m*-fluorosulfinylaniline. Parameters of the *syn* (*II*) conformer are very similar. (see Fig. 2).

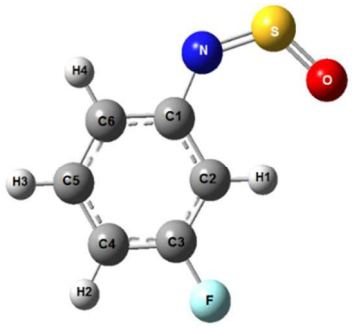

Fig. 2. Molecular model of the *syn* conformer of *m*-fluorosulfinylaniline.

The higher stability of the sterically unfavorable *syn* conformation of the C–N=S=O group observed for all sulfinylanilines reported hitherto may be rationalized by orbital interactions. A Natural Bond Orbital (NBO) analysis performed at the DFT/B3LYP/6-311+G (df) level of theory suggests that two orbital interactions between nitrogen and sulfur lone pairs with vicinal antibonding orbitals, i.e. lp (N) →σ* (S–O) and lp (S) →σ* (C–N) (anomeric effects) stabilize the *syn* conformer relative to the *anti* structure. The interaction energies of 15.3 and 9.8 kcal.mol^{-1} in the *syn* conformer are much stronger than the corresponding interaction energies in the *anti* form of only 6.8 and 1.2 kcal.mol^{-1}, respectively. These anomeric interactions override the higher steric interactions in the *syn* form and lead to a thermodynamic preference of the *syn* conformer. Fig. 3 depicts the molecular orbitals involved in the relevant orbital interactions.

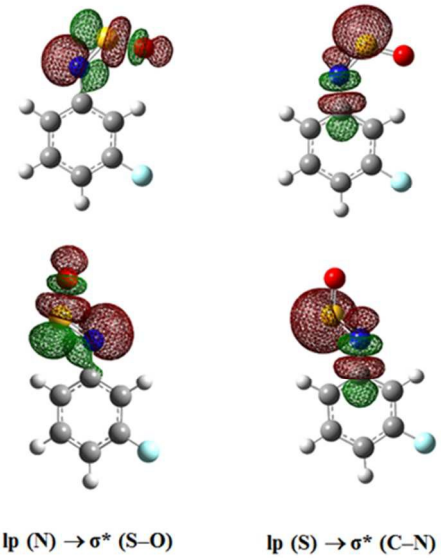

Fig. 3. Relevant NBO orbitals [B3LYP/6-311+G(df)] for the syn (upper) and anti (lower) conformers of m-fluorosulfinylaniline.

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Vibrational Analysis

Table 2 shows a tentative assignment of the 3N – 6 = 36 normal vibrational modes expected for *m*-fluorosulfinylaniline. The analysis of the experimental infrared and Raman spectra of a liquid sample was supported by Density Functional Theory calculations with the 6-311++G(df,pd) and cc-pVTZ basis sets using suitable scale factors to improve the theoretical frequencies predicted, according to the results reported by Wojciechowski *et al* [16] (see Fig. 1). In addition, theoretical ^{15}N substitution was used to help identifying the vibrational modes expected for the N=S=O group. From the experimental and theoretical spectra, the distinction between conformers I and II could not be established because the differences in vibrational frequencies are too small to confirm a given particular structure. Reported data for the parent sulfinylaniline [7], p-fluorosulfinylaniline [11] and the reactant *m*-fluoroaniline [17] were also taken into account. Figs. 4 and 5 show graphical comparisons between the experimental and theoretical vibrational spectra.

Our laboratory recently reported the conformational and vibrational properties of *p*-fluorosulfinylaniline [11]. Its vibrational spectra showed no remarkable influence of the fluorine atom on the frequencies of the N=S=O group in comparison with the parent sulfinylaniline. In contrast, previous calculations performed for *o*- and *m*-fluorosulfinilaniline indicated that the influence of a fluorine atom depends on its position in the aromatic ring and on the vibrational mode considered. The asymmetric stretching of the N=S=O group in the *o*-derivative was predicted in close agreement with that belonging to the *p*-substituted compound, around 1334 cm^{-1} (B3LYP/6-311+G(df)), while the corresponding mode for the *m*-isomer was predicted about 14 cm^{-1} higher in frequency terms. From the hypothetic resonance structures depicted in Scheme II it is possible to visualize that a fluorine atom in para position might contribute to compensate the electronic deficiency due to the electron withdrawing N=S=O group. Some of the structures contributing to the hybrid show partial single N–S bonds, consequently, the N=S=O vibrational modes for the *p*-, and possibly *o*-, substituted isomers were expected at lower frequencies than those corresponding to the *m*-fluorosulfinylaniline. We are now able to confirm part of that assumption, since the experimental spectra obtained for the title compound show bands at 1314 and 1036 cm^{-1} (IR) and 1313 and 1038 cm^{-1} (Raman), which were assigned to the N=S=O asymmetric and symmetric stretchings, respectively. Theoretical calculations confirmed this assignment, predicting a 5 cm^{-1} downshift upon isotopic substitution with ^{15}N atom. It still remains to be confirmed that the experimental vibrational spectra of *o*-fluorosulfinylaniline agree with the assumptions stated above [18].

The in-plane deformation of the N=S=O group was assigned to the signal placed at 634 and 636 cm^{-1} in the infrared and Raman spectra, respectively, in agreement with frequencies reported for *p*-fluorosulfinylaniline.

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 [17]. Consequently, the shoulder observed at ca. 1227 cm^{-1} in the infrared spectrum of *p*-fluorosulfinylaniline was attributed to that fundamental.

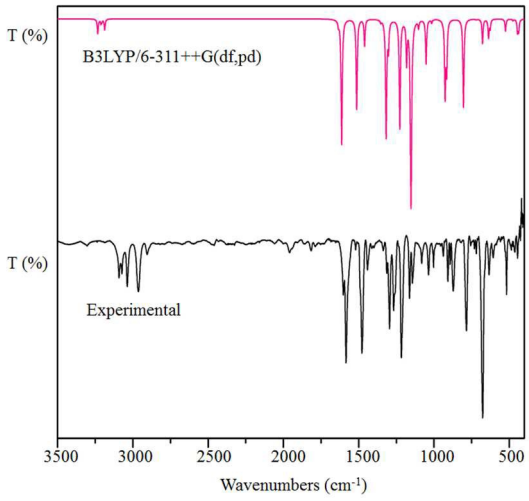

Fig. 4. Experimental and theoretical infrared spectra of *m*-fluorosulfinylaniline. Top: theoretical gas phase spectrum calculated at the B3LYP/6-311++G(df,pd) level of theory; bottom: room temperature infrared spectrum of a liquid sample.

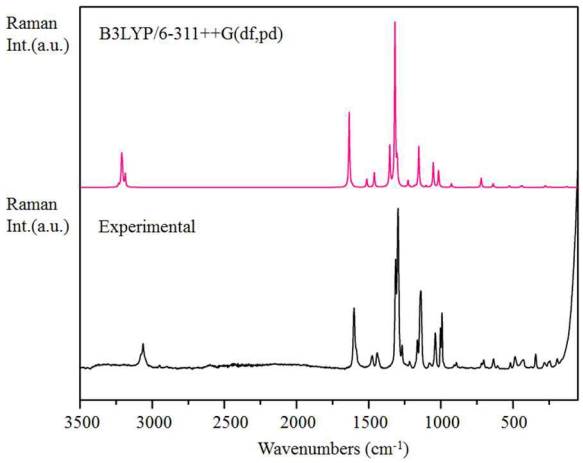

Fig. 5. Experimental and theoretical Raman spectra of *m*-fluorosulfinylaniline. Top: theoretical gas phase Raman spectrum calculated at the B3LYP/6-311++G(df,pd) level of theory (532 nm excitation laser); bottom: room temperature spectrum of a liquid sample.

However, calculations performed for this series with the B3LYP/6-311+G(df) approximation predict an opposite trend, being the C–F bond belonging to the *p*-and *o*-derivatives being stronger than that of the *m*-isomer, 1261, 1262 and 1228 cm^{-1}, respectively . Therefore, the strong signal observed at 1216 cm^{-1} in the infrared spectra of the title compound was assigned to this stretching, in good agreement with calculations performed now with larger basis sets. This assignment may be rationalized in terms of the opposite withdrawing effects of the $–NH_2$ and –N=S=O groups [19]. Following the same reasoning, the C–N stretching was assigned to the medium/strong signal placed at 785 cm^{-1} in the infrared spectrum. The corresponding fundamental was observed at 822 cm^{-1} in the infrared spectrum of the *p*-substituted derivative.

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

Mode	Approximate description[a]	Experimental [b]		Theoretical values[c]		
		IR(liq.)	Raman(liq.)	B3LYP/ 6-311++G(df,pd)	Scaled values[d]	B3LYP/ cc-pVTZ
ν_1	C–H Stretch.	3091 m	-	3233(4)[3]	3097	3237(6)[4]
ν_2	C–H Stretch.	3072 m	3078 sh	3212(1)[28]	3077	3210(3)[35]
ν_3	C–H Stretch.	-	3063m	3206(1)[16]	3071	3204(2)[19]
ν_4	C–H Stretch.	3037 m	-	3187(3)[12]	3053	3185(5)[15]
ν_5	C–C Stretch.	1602 m	1601 m	1635(1)[50]	1607	1638(2)[52]
ν_6	C–C Stretch.	1584 s	1583 sh	1613(49)[1]	1586	1616(67)[1]
ν_7	C–C Stretch. + C–H Def.	1478 s	1476 w	1513(32)[5]	1487	1516(46)[6]
ν_8	C–C Stretch. + C–H Def.	1442 w	1442 w	1461(8)[9]	1436	1465(12)[10]
ν_9	N=S=O Asym. Stretch.	1314 m	1313 s	1354(1)[26]	1331	1354(1)[32]
ν_{10}	C–C Stretch. + C–H Def.	1295 s	1297 vs	1318(46)[100]	1296	1320(67)[100]
ν_{11}	C–C Stretch.	1268 m	1268 m	1302(8)[15]	1280	1302(14)[15]
ν_{12}	C–F Stretch.	1216 s	1216 vw	1227(41)[4]	1206	1231(57)[3]
ν_{13}	C–H Def.	1163 m	1163 m	1182(13)[1]	1162	1184(39)[3]
ν_{14}	C–H Def.	1143 m	1140 s	1153(100)[25]	1133	1163(100)[31]
ν_{15}	C–H Def. + C–C Def. i.p.	1082 w	1082 vw	1103(2)[1]	1084	1104(4)[1]
ν_{16}	N=S=O Sym. Stretch.	1036 w	1038 m	1053(14)[14]	1035	1057(13)[13]
ν_{17}	C–H Def. + C–C Def. i.p.	1003 w	1003 m	1016(1)[9]	999	1020(<1)[9]
ν_{18}	Ring Def.	992 sh	992 m	995(<1)[<1]	978	1000(<1)[<1]
ν_{19}	C–H Def. o.o.p. + Ring torsion	938 w	-	926(26)[2]	910	930(10)[<1]
ν_{20}	Ring Def.	908 w	908 vw	923(1)[<1]	907	930(34)[1]
ν_{21}	C–H Def. o.o.p.	872 m	-	915(16)[<1]	899	922(15)[<1]
ν_{22}	C–N Stretch.	785 s	-	804(31)[<1]	790	811(32)[<1]
ν_{23}	Ring Def.	719vw	719 vw	720(<1)[5]	708	722(<1)[5]
ν_{24}	C – H Def. i.p.	676 vs	-	678(7)[<1]	666	703(16)[<1]
ν_{25}	N=S=O Def. i.p.	634 w	636 w	638(5)[2]	627	642(7)[2]
ν_{26}	Ring Def.	607 w	607 vw	627(3)[<1]	616	634(3)[<1]
ν_{27}	Ring Def.	518 m	517 w	525(4)[1]	516	526(5)[1]
ν_{28}	Ring Def.	486 w	486 w	475(<1)[<1]	467	479(1)[<1]
ν_{29}	C – F Def. i.p.	444 w	445sh	445(4)[<1]	437	446(6)[1]
ν_{30}	Ring Def.	426 w	427 w	437(3)[1]	430	438(4)[1]
ν_{31}	C–F Def. o.o.p.	-	343 w	372(5)[<1]	366	380(6)[<1]
ν_{32}	Skeletal Def.	-	283 w	276(6)[1]	271	279(8)[1]
ν_{33}	N=S=O Def. o.o.p.	-	245 w	244(<1)[<1]	240	247(<1)[1]
ν_{34}	Ring Def.	-	194 w	148(1)[<1]	145	150(2)[<1]
ν_{35}	Ring Def.	-	-	127(1)[<1]	125	131(1)[<1]
ν_{36}	Ring Def.	-	-	60(<1)[<1]	59	59(<1)[<1]

[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 Raman activities between brackets, normalized to 100%. [d] Values scaled according to scaling factors in Ref. [16].

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NMR Spectra Analysis

Since the barrier of rotation around the C–N single bond is low (about 5 Kcal/mol, see above) the change of conformers I and II due to rotation around this bond is much faster than the NMR time scale and only mean shift values are observed. Complex signals exist in the 7.00 and 7.70 ppm, and 113 and 165 ppm regions of the ^{1}H NMR and ^{13}C NMR spectra of *m*-fluorosulfinylaniline, respectively. The assignment proposed (see Tables 3 and 4) was based on results reported for other similarly substituted aromatic molecules containing fluorine and electron withdrawing groups in *meta* position, as well as on data reported for unsubstituted sulfinylaniline [7]. It is well known that the presence of electron withdrawing groups/atoms lead to deshielding of the protons in resonance and the consequent increase of the chemical shift values. Therefore, the influence of the fluorine atom and the N=S=O group must be considered. Thus, the signals observed at 7.10, 7.38, 7.58 and 7.62 ppm of the ^{1}H NMR spectrum were attributed to C(4)H, C(5)H, C(6)H and C(2)H, respectively (see Fig. 2). This assignment was supported by theoretical calculations at the B3LYP/6-311+G(df) level of theory with the gauge-including atomic orbital (GIAO) method, one of the most common approaches for calculating nuclear magnetic shielding tensors [15]. HSQC and COSY experimental spectra of *m*-fluorosulfinylaniline were useful for the assignment, showing H–H and C–H correlations, respectively. The HSQC spectrum of *m*-fluorosulfinylaniline showed cross-peaks between the signals assigned to C(5)H and C5, C(6)H and C6, C(4)H and C4 and C(2)H and C2 meanwhile the COSY spectrum showed cross-peaks between the signals assigned to C(4)H and C(5)H, and C(5)H with C(6)H. The characteristic time scale of NMR spectroscopy does not allow discerning between conformers I and II in the experimental spectra.

GC/MS Analysis

The intense signal observed at 7.81 min (91.8% relative area and 157 molecular weight) in the total-ion chromatogram accounts for the presence of *m*-fluorosulfinylaniline while the additional peak found at time retention 7.02 min (3.91% relative area and 111 molecular weight) belongs to the reactant *m*-fluoroaniline. The major fragmentation patterns of fragments of interest are proposed in Fig. 6. The base peak of the mass spectra of *m*-fluorosulfinylaniline (mass numbers (m/z) versus relative abundance) accounts for a m/z 157 relation, which was attributed to the molecular ion. Consequently, the peak at m/z 158 was assigned to the protonated form of the molecular ion. No evidence of the fragmentation of the C–halogen bond was found in the spectrum (ca. m/z 138 peak), possibly due to C–F bond is stronger than any other bond. The weak peak at m/z 95 was assigned to the $[C_6H_4F]^+$ fragment while that observed at m/z 76 may be attributed to $[C_6H_4]^+$ fragment. The clusters of ions found in the region of m/z 51, 52, 63, 65, 77, 78, 89-92 are well-known fragments arising from the decomposition of aromatic structures [20].

Table 3. ^{1}H NMR experimental (200 MHz, $CDCl_3$, Me_4Si) and calculated data of *m*-fluorosulfinylaniline.

H[a]	Chemical shift (δ) (ppm) Experimental	Theoretical[b]
C(4)H	7.10 (1H, m, $J_{2,F}$ 9.20, $J_{2,3}$ 6.34, $J_{2,4}$= $J_{2,1}$ 2,30)	6.89
C(5)H	7.38 (1H, dd, $J_{3,2}$=$J_{3,4}$ 6.34)	7.14
C(6)H	7.58 (1H, ddd, $J_{4,3}$ 6.34, $J_{4,2}$=$J_{4,1}$ 2,30)	6.94
C(2)H	7.62 (1H, m, $J_{1,F}$ 6.91, $J_{1,2}$=$J_{1,4}$ 2.30)	8.53

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

Table 4. ^{13}C NMR experimental (50 MHz, $CDCl_3$, Me_4Si) and calculated data of *m*-fluorosulfinylaniline.

C [a]	Chemical shift (δ) (ppm) Experimental	Theoretical[b]
C(6)	113.97, 114.43	128.0
C(4)	117.39, 117.82	122.7
C(2)	122.92, 122.98	119.05
C(5)	130.22, 130.40	133.1
C(1)	159.93	152.3
C(3)	164.88	169.9

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

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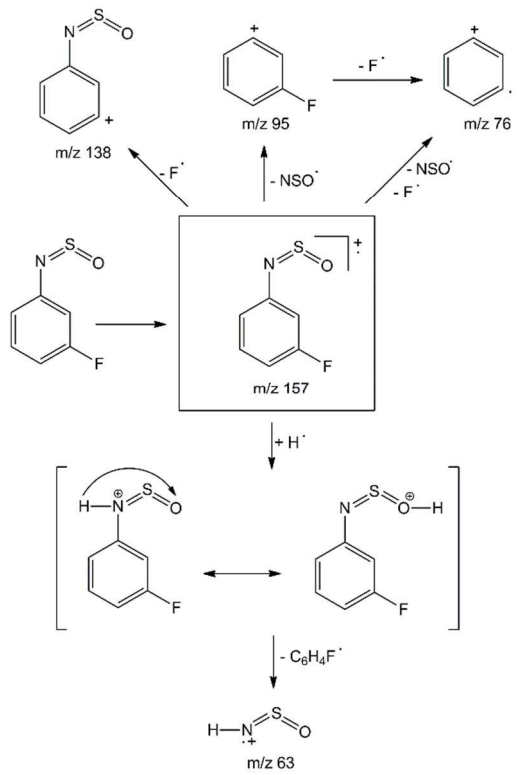

Fig. 6. Major fragmentation patterns of m/z peaks for *m*-fluorosulfinylaniline.

Conclusions

A new member of the sulfinylaniline family of compounds has been prepared by reacting *m*-fluoroaniline and $SOCl_2$. The highly reactive and corrosive liquid compound obtained was characterized by using nuclear magnetic resonance spectroscopy (^1H and ^{13}C), gas-chromatography/mass spectrometry, vibrational spectra and quantum chemical calculations. Although at least two stable conformers might be expected around the N=S bond (*syn* and *anti* of the C–N bond with respect to the S=O bond) and also two stable structures were predicted taking into account the orientation of the N=S=O and fluorine substituents, 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 with different basis sets confirmed that only the *syn* conformation of the N=S=O moiety can be observed in the liquid phase, predicting global C_S symmetry of this compound 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 *m*-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.

From the analysis of the vibrational frequencies of the *p*- and *m*-fluorosulfinylaniline compounds reported up to the moment, we may state that the influence of a fluorine atom on the frequency shifts of functional groups in an aromatic ring depends on its position in the aromatic ring and on the vibrational mode considered.

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