



Conformational properties and spectroscopic characterization of *m*-chlorosulfinylaniline



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ABSTRACT

In the present work we report a combined experimental and theoretical study on the molecular structure and vibrational spectra of *m*-chlorosulfinylaniline. The substance was characterized by ¹H and ¹³C NMR and GC-mass spectrometry as well as by FT-IR and Raman spectroscopy. Experimental results were complemented with theoretical calculations at the B3LYP and MP2 levels of theory for electronic structure and harmonic oscillator and Vibrational Self-consistent Field levels of theory for vibrational structure. The observed and calculated frequencies were found to be in good agreement. Natural Bond Orbital analysis provides an explanation of the stability of the molecule and its electronic properties upon charge delocalization.

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1. Introduction

Our main interest in the study of N-sulfinylamines of general formula R–N=S=O (R = aromatic ring) is focused on their vibrational, structural and conformational properties. The parent compound N-sulfinylamine was synthesized in 1890 by Michaelis *et al.* [1,2] and its structure was determined in 1999 [3]. The conformational preferences, vibrational spectra and pre-resonant Raman properties of compounds including the –N=S=O group have been extensively studied [4]. Due to the nonlinearity of the N=S=O group, these compounds can in principle be found in one of two configurations, *syn* or *anti*. Interestingly however, all of the molecules studied so far have been experimentally observed only in the *syn* orientation [5–10].

The cumulated π system of the N=S=O group confers these molecules some interesting properties in pre-resonant Raman spectroscopy and it has been shown to be quite useful as a conformational sensor for excited states [4]. Spectroscopic analyses of this kind are relatively scarce, though, as their low stability usually comes in the way of this kind of experiments.

There is an interesting range of applications for this kind of molecules, as they can participate in cycloaddition reactions

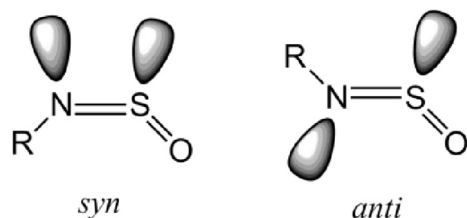
through their N=S bond. The hydrolysis of N-sulfinylamines is also quite interesting, as the kinetics of these reactions depend very strongly on the identity of the R substituent and can range from explosive, in the case of CINSO, for example, to quite mild in the case of N-sulfinylanilines [11].

There has been a considerable effort in the past decades directed to the study of R–N=S=O general family of molecules and a fair number of works have been published on this subject over the years [12]. However, there are comparatively few works on the N-sulfinylaniline family, with early work centered on N-sulfinylaniline (C₆H₅–N=S=O) [3] and the sterically hindered derivatives O=S=N–C₆H₃[(CH–CH₃)₂–2,6 and O=S=N–C₆H₃(CH₃–CH₂)₂–2,6 by Romano *et al.* [12], and more recently studies focusing on fluorine-substituted N-sulfinylanilines by our group [13–15] employing a wide variety of spectroscopic techniques. In all cases the N=S=O group was observed to acquire a *syn* configuration (see Scheme 1).

In this work we present the second part of an ongoing series featuring chlorosulfinylaniline isomers [16]. In this opportunity, we present a detailed analysis of the vibrational and structural properties of *m*-chlorosulfinylaniline, a member of the aromatic branch of the N-sulfinylamine family of compounds. A detailed characterization is performed on the basis of ¹H and ¹³C, NMR spectroscopy and GC-mass spectrometry, followed by a vibrational study using FTIR and Raman spectroscopies, supported by quantum chemical calculations at various levels of electronic and vibrational structure theories. These results complement those reported previously by

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Scheme 1. *Syn* and *anti* forms with respect to the C–N single and S=O double bonds.

several research groups [17–19]. We analyze the effect of the halogen substitution in the *meta* position with respect of the sulfinyl group of the aromatic ring, and compare it with the *para* isomer previously reported by our group, with particular attention to the NSO marker bands.

2. Computational details

The analyses of the potential energy surface of *m*-chlorosulfinylaniline and optimization of the structural parameters of stable minima found were performed by using the GAUSSIAN03 program [20]. Vibrational frequencies as well as Raman and IR intensities were calculated using a combination of several electronic and vibrational structure methodologies. In particular, for electronic structure calculations we used gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [21] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [22] in combination with 6-311 + G (df, pd), 6-311++G (df, pd) and cc-pVTZ basis sets, as well as second order Moller-Plesset Perturbation Theory (MP2), in combination with the cc-pVDZ basis set. Natural population analysis NBO [23], as implemented in the GAUSSIAN03 program, was performed together with the Gauge-including atomic orbital (GIAO) method [24]. In addition to these calculations for the *m*-chlorosulfinylaniline, the B3LYP/6-311 + G (df) method was applied also to the parent sulfinylaniline and to *p*-chlorosulfinylaniline compounds for the sake of comparison.

In the particular case of vibrational structure calculations, in addition to the customary harmonic oscillator approximation for the vibrational energies and wavefunctions we performed advanced vibrational structure calculations using the vibrational self-consistent field (VSCF) ansatz, recently implemented in the QUMVIA software package [15], developed by our group. 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 [25–27].

The vibrational Schrödinger equation for a molecular system expressed in rectilinear normal coordinates $\{q_i\}$ can be formulated, neglecting rotational coupling, as follows:

$$\left(-\frac{1}{2} \sum_{i=1}^f \frac{\partial^2}{\partial q_i^2} + \mathbf{V}(\vec{\mathbf{q}}) \right) \psi_{\mathbf{n}}(\vec{\mathbf{q}}) = \mathbf{E}_{\mathbf{n}} \psi_{\mathbf{n}}(\vec{\mathbf{q}})$$

With

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

The vibrational wavefunction is represented as a Hartree product, this is, a product of one-dimensional, single-mode wavefunctions or “modals” $\{\phi_i\}$, (with $i = 1, \dots, f$) which in turn, are

functions of the mass weighted normal coordinates q_i , in analogy to orbitals in electronic structure theory. Using this assumption and the variational principle it is possible to obtain the VSCF equations for each modal.

$$[\mathbf{H}_i^0(\mathbf{q}_i) + \mathbf{v}_i(\mathbf{q}_i)] \phi_i(\mathbf{q}_i) = \epsilon_i \phi_i(\mathbf{q}_i)$$

$$\mathbf{v}_i(\mathbf{q}_i) = \prod_{j \neq i}^f \phi_j |\mathbf{V}_c(\vec{\mathbf{q}})| \prod_{j \neq i}^f \phi_j$$

\mathbf{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 [28]. The nuclear potential energy surface (PES) is approximated using a quartic force field (QFF) with a 3-mode coupling representation [29], 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 (GAUSSIAN03, in our case) at MP2/cc-pVDZ and B3LYP/6-311++G (df, pd) electronic structure level 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 GAUSSIAN03. 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 GAUSSIAN03. Finally these Hessian matrices were used to compute 3-mode coupling QFFusing QUMVIA. Sixteen distributed Gaussian basis functions positioned at 16 scaled Gauss-Hermite quadrature points were used for each normal mode. A VSCF energy convergence criterion of 10^{-9} Hartrees was used.

3. Experimental details

3.1. Synthesis

The preparation of R–N=S=O compounds follows the method proposed by Michaelis *et al.* [1]. *m*-Chlorosulfinylaniline was prepared using a 1:2:5 M relation of the corresponding chlorinated aniline, thionyl chloride and benzene as the reaction solvent, respectively. *m*-Chloroaniline (3.63 g; 28.48 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 CaCl₂ trap. Thionyl chloride (9.80 g; 82.30mmol) 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 the mixture was continuously stirred and heated for 8 h at 80–85 °C until a dark solution was obtained. The liquid mixture obtained was purified by several distillation cycles in order to get a dark green liquid as the final product with *ca.* 97% yield. Its purity was controlled by ¹H and ¹³C NMR spectroscopy (CDCl₃ solvent, TMS internal reference), GC-Mass Spectrometry, IR and Raman spectroscopy. The substance is highly hygroscopic and corrosive.

3.2. Raman and FT-IR measurement

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 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 4 cm^{-1} with a grating groove density of 900 lines/mm. A confocal aperture of $50\ \mu\text{m}$ slit was used and 60 expositions of 1 s were accumulated for the sample in order to achieve sufficient signal to noise ratio. The samples were handled in Pyrex capillaries at room temperature.

The FT-IR spectra of *m*-chlorosulfinylaniline were recorded between 3500 and 400 cm^{-1} at room temperature using a Perkin-Elmer GX1 Fourier Transform infrared instrument, by placing the liquid sample between KRS-5 windows (1 cm^{-1} spectral resolution).

3.3. NMR and GC/MS measurements

Varian Unity 200 spectrometer was used for NMR studies. ^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz, respectively (chemical shifts expressed in parts per million ppm or δ relative to tetramethylsilane, TMS). The number of scans was appropriate to generate good quality spectra for analysis.

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 $60\text{ }^\circ\text{C}$. After maintaining that temperature for 3 min, the oven temperature was increased at a rate of $15\text{ }^\circ\text{C}/\text{min}$ to reach a final oven temperature of $250\text{ }^\circ\text{C}$. 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 : 60–180). Quantification of the peaks was based on peak area. In the total-ion chromatogram and the mass spectra of *m*-chlorosulfinylaniline were observed an intense signal at 9.56 min (97% relative area) and a m/z 173 relation (base peak of molecular ion), respectively, which account for the presence of the studied molecule.

4. Results and discussion

4.1. Molecular geometry, structural properties and NBO analysis

As it was already observed for the fluorinated isomer of *m*-chlorosulfinylaniline [14] and previously for *m*-chlorosulfinylaniline itself [30], the geometry adopted by the $\text{N}=\text{S}=\text{O}$ group determines that two different structures with very similar energy might be feasible, one with the chlorine atom closer to the oxygen atom of the $\text{N}=\text{S}=\text{O}$ group than the other, which shows an opposite disposition of the *meta* substituent. The relative energy values predicted with the B3LYP/6-311 + G (df) approximation confirms this assumption, with $\Delta E = 0.16\text{ kcal mol}^{-1}$. A $5.48\text{ kcal mol}^{-1}$ energy barrier for rotation around the C–N bond was predicted between both forms by this approximation. The optimized molecular structure of the most stable conformer of *m*-chlorosulfinylaniline obtained at this level of theory is shown in Fig. 1. Such small energy difference between both forms would prevent their being identified separately in the vibrational and NMR spectra. The optimized molecular structure reveals that the *meta*-substituted $\text{N}=\text{S}=\text{O}$ group is coplanar with the benzene ring.

The structural parameters calculated using different basis sets are presented in Table 1. In order to confirm the assumption that the most stable conformer possesses *syn* geometry, the potential energy function for the coordinate of rotation around the $\text{N}=\text{S}$ bond was determined by a relaxed scan of the C–N=S=O dihedral angle in steps of 30° at the B3LYP/6-311 + G (df) level of theory. The results predicted a *syn* conformer with C_s symmetry as the global minimum of the potential energy surface and the *anti* conformation as a local minimum with ΔE° (*anti-syn*) = $7.26\text{ kcal mol}^{-1}$ and ΔG° (*anti-syn*) = $6.78\text{ kcal mol}^{-1}$. Fig. 2 shows the calculated potential

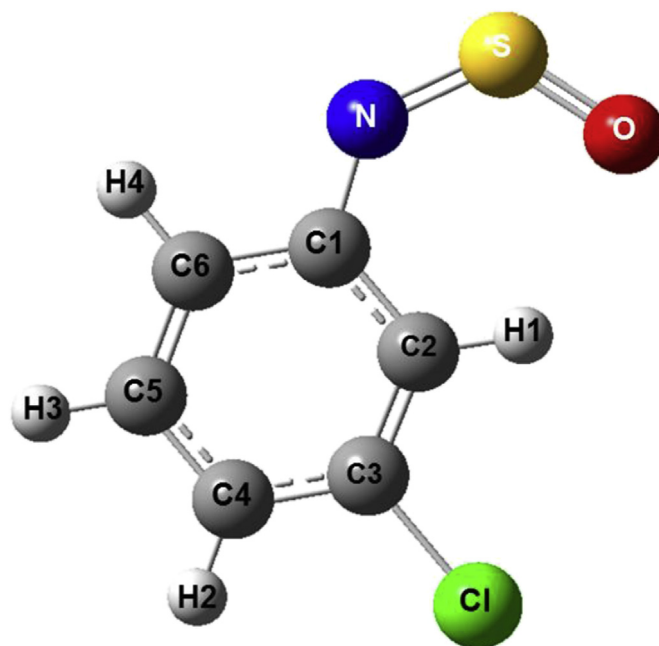


Fig. 1. Molecular model of the *syn* conformer of *m*-chlorosulfinylaniline.

Table 1

Calculated geometric parameters for the *m*-chlorosulfinylaniline.

Structural parameters ^a	<i>m</i> -chlorosulfinylaniline	
	B3LYP/6-311++G (df,pd)	B3LYP/cc-pVTZ
C–Cl	1.753	1.751
C–H	1.081	1.077
C1–C2 (6)	1.408	1.406
C2 (5)–C3 (6)	1.385	1.384
C4–C3 (5)	1.391	1.390
C1–N	1.380	1.391
N=S	1.530	1.535
S=O	1.483	1.478
N=S=O	119.8	119.7
C1–N=S	132.4	132.0
C2–C1–C6	119.1	119.0
C3–C4–C5	121.1	121.1
C2–C1–N	124.3	1.243
C6–C1–N	115.9	116.0
Cl–C–C	119.1	119.1
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 atom numbering see Fig. 1.

function for rotation around the $\text{N}=\text{S}$ bond obtained with the B3LYP/6-311++G (df,pd) approximation. The higher stability of the sterically unfavourable *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 also 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. $\text{lp}(\text{N}) \rightarrow \sigma^*(\text{S}-\text{O})$ and $\text{lp}(\text{S}) \rightarrow \sigma^*(\text{C}-\text{N})$ (anomeric effects) stabilize the *syn* conformer relative ($15.34\text{ kcal mol}^{-1}$ and $9.84\text{ kcal mol}^{-1}$) to the *anti* structure ($5.57\text{ kcal mol}^{-1}$ and $0.73\text{ kcal mol}^{-1}$).

4.2. Vibrational assignment

Table 2 and Fig. 3 show vibrational spectral assignment and experimental FT-IR and Raman spectra of a liquid sample of *m*-

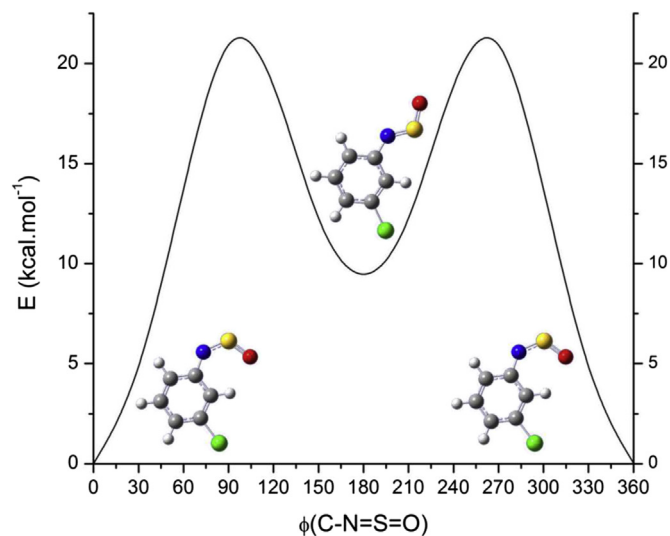


Fig. 2. Calculated potential function for rotation around the N=S bond (B3LYP/6-311++G (df,pd)).

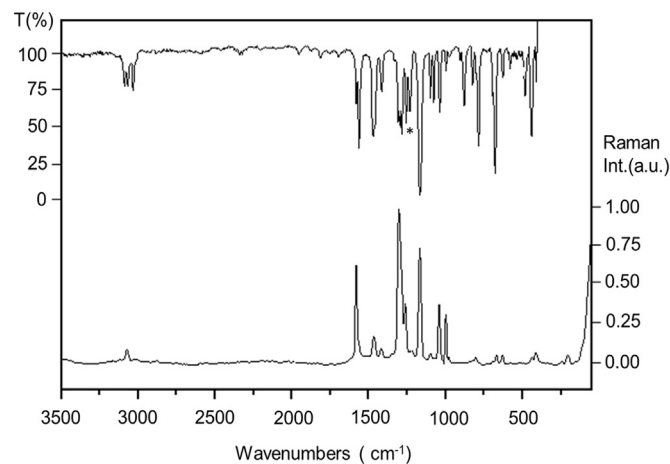


Fig. 3. Experimental infrared and Raman spectra of *m*-chlorosulfinylaniline. Top: infrared spectrum of a liquid sample held between KRS-5 windows; bottom: room temperature Raman spectrum of a liquid sample (* impurity).

Table 2

Experimental and calculated wavenumbers of the *m*-chlorosulfinylaniline and tentative assignments of fundamental vibrational modes.

Mode	Approximate description ^a	Experimental ^b		Theoretical ^c					
		IR (liq.)	Raman (liq.)	B3LYP/cc-pVTZ		B3LYP/6-311++G (df,pd)		MP2/cc-pVDZ	
				HO	HO	VSCF	HO	VSCF	
ν_1 (A')	C–H Stretch.	3088 m	–	3239 (5) [<1]	3233 (4) [3]	3042	3278	3077	
ν_2 (A')	C–H Stretch.	–	3073 m	3210 (2) [56]	3211 (1) [40]	3070	3254	3121	
ν_3 (A')	C–H Stretch.	3068 m	–	3205 (1) [23]	3206 (<1) [17]	3038	3247	3075	
ν_4 (A')	C–H Stretch.	3034 m	–	3183 (5) [26]	3185 (3)[19]	3012	3228	3059	
ν_5 (A')	C–C Stretch. + C–H Def.	1581 m	1582 vs	1621 (<1) [78]	1619 (<1) [66]	1595	1634	1608	
ν_6 (A')	C–C Stretch. + C–H Def.	1563 s	1564 sh	1596 (34) [6]	1593 (28) [4]	1570	1615	1590	
ν_7 (A')	C–C Stretch. + C–H Def.	1472 s	1467 m	1504 (29) [20]	1502 (21) [16]	1484	1501	1480	
ν_8 (A')	C–C Stretch. + C–H Def.	1416 m	1419 w	1446 (8) [9]	1442 (6) [8]	1426	1473	1445	
ν_9 (A')	C–C Stretch.	1334 vw	–	1350 (4) [49]	1349 (1) [32]	1338	1443	1424	
ν_{10} (A')	N=S=O Asym. Stretch.	1298 s	1304 vs	1312 (38) [86]	1310 (24) [63]	1295	1307	1294	
ν_{11} (A')	C–H Def. i.p.	1286 s	1284 s	1298 (9) [100]	1299 (8) [100]	1284	1279	1265	
ν_{12} (A')	C–C Stretch.	1168 vs	1169 vs	1190 (16) [<1]	1191 (4) [2]	1188	1203	1198	
ν_{13} (A')	Ring Def. i.p.	–	–	1176 (100) [43]	1162 (100) [28]	1148	1173	1171	
ν_{14} (A')	C–H Def i.p.	1100 m	1100 w	1122 (11) [<1]	1122 (10) [<1]	1116	1128	1121	
ν_{15} (A')	C–H Def. i.p.	1077 m	–	1099 (14) [2]	1098 (10) [1]	1092	1098	1092	
ν_{16} (A')	N=S=O Symm. Stretch.	1039 m	1043 s	1058 (22) [24]	1051 (21) [22]	1041	1016	1006	
ν_{17} (A')	Ring Def. i.p.	998 w	999 s	1016 (4) [17]	1013 (3) [16]	1003	1001	992	
ν_{18} (A'')	C–H Def. o.o.p.	–	982 w	1005 (<1) [<1]	1006 (<1) [<1]	1029	956	995	
ν_{19} (A'')	C–H Def. o.o.p.	906 w	–	943 (9) [<1]	939 (6) [<1]	969	895	926	
ν_{20} (A'')	C–H Def. o.o.p.	880 s	–	931 (6) [<1]	927 (7) [<1]	952	877	900	
ν_{21} (A')	C–Cl Stretch.	825 m	825 w	836 (45) [3]	835 (37) [3]	828	824	816	
ν_{22} (A'')	C–H Def. o.o.p.	804 sh	806 w	814 (27) [<1]	810 (26) [<1]	845	781	830	
ν_{23} (A')	C–N Stretch	786 m	–	702 (16) [<1]	694 (11) [<1]	711	674	669	
ν_{24} (A')	Ring Def.	–	–	682 (3) [6]	681 (2) [5]	676	643	691	
ν_{25} (A')	N=S=O Def. i.p.	–	–	641 (5) [2]	638 (5) [2]	633	634	631	
ν_{26} (A'')	C–H Def. o.o.p.	677 vs	670 w	608 (2) [<1]	606 (2) [<1]	598	575	600	
ν_{27} (A'')	C–H Def. o.o.p.	484 m	–	461 (1) [<1]	461 (<1) [<1]	468	444	458	
ν_{28} (A')	Ring Def.	–	–	447 (10) [1]	446 (8) [1]	444	434	433	
ν_{29} (A'')	N=S=O Def. o.o.p.	440 s	441 w	410 (3) [2]	411 (2) [2]	406	414	412	
ν_{30} (A'')	C–N Skeletal Def.	410 m	413 m	375 (5) [<1]	371 (5) [<1]	377	360	362	
ν_{31} (A')	C–Cl Def. i.p.	–	–	369 (3) [<1]	368 (3) [<1]	370	356	360	
ν_{32} (A')	Skeletal Def.	–	243 w	240 (6) [2]	237 (4) [15]	237	240	239	
ν_{33} (A'')	C–Cl Def. o.o.p.	–	207 m	201 (<1) [<1]	200 (<1) [<1]	207	199	208	
ν_{34} (A'')	Torsion N=S=O	–	–	142 (2) [<1]	141 (<1) [<1]	157	141	156	
ν_{35} (A')	Skeletal Def.	–	–	114 (1) [1]	112 (<1) [1]	114	123	123	
ν_{36} (A'')	Def. C–N=S	–	–	57 (<1) [<1]	56 (4) [<1]	80	51	73	

^a Stretch.: stretching; Def.: deformation; Asym.: asymmetric; Sym.: symmetric; sh: shoulder; i.p.: in phase; o.o.p.: out of phase.

^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%.

chlorosulfinylaniline, respectively. For the assignment of the vibrational bands we used a combination of several theoretical techniques for the prediction of vibrational spectra. Harmonic oscillator (HO) vibrational frequencies and intensities were obtained using potential energy surfaces at the B3LYP/6-311++G(df,pd), B3LYP/cc-pVTZ and MP2/cc-pVDZ electronic levels of theory, whereas Vibrational Self-Consistent Field vibrational energies and wavefunctions were obtained using potential energy surfaces at the B3LYP/6-311++G(df,pd) and MP2/cc-pVDZ electronic levels of theory. In addition, theoretical ^{15}N substitution was used to help identifying the vibrational modes expected for the $\text{N}=\text{S}=\text{O}$ group. As it was already observed for molecules containing the $\text{N}=\text{S}=\text{O}$ group, the $\text{N}=\text{S}$ and $\text{S}=\text{O}$ stretching modes are strongly coupled, therefore the vibrations will be described as symmetric and antisymmetric stretching modes for the $\text{N}=\text{S}=\text{O}$ group.

Previous studies showed that there is a strong dependence between the vibrational frequencies of this group and the substituent bonded to the N atom [4], so the assignment must be carefully considered. Many studies have focused in the past on the vibrational aspects of the related sulfinylaniline molecule [18, 31–34]. In particular, Stufkens [33] reported a very detailed analysis on the Raman spectra of sulfinylaniline and its ^{15}N isotopologue, and found that 7 bands (at 1299, 1284, 1161, 1034, 1020, 747 and 638 cm^{-1}) had significant nitrogen contributions. Building on this work, Romano *et al.* [3] used a combination of higher resolution IR, pre-resonant and normal Raman spectroscopies, and assigned the antisymmetric and symmetric stretching modes to the 1298 cm^{-1} and 1163 cm^{-1} bands, respectively. Moreover, equivalent assignments were made at $1298/1174\text{ cm}^{-1}$ for the $\text{O}=\text{S}=\text{N}-\text{C}_6\text{H}_3(-\text{CH}_2-\text{CH}_3)_2-2,6$ derivative and more tentatively at $1287/1173\text{ cm}^{-1}$ for the $\text{O}=\text{S}=\text{N}-\text{C}_6\text{H}_3[\text{CH}(\text{CH}_3)_2]_2-2,6$ derivative. In all cases these bands showed medium to strong intensity in both Raman and IR spectra. It is to be expected that the equivalent bands for *m*-chlorosulfinylaniline will not be observed far from these values. However, some differences were already observed for the symmetric $\text{N}=\text{S}=\text{O}$ stretching mode in the halogen substituted derivatives *p*-, *m*- and *o*-fluorosulfinylaniline series [13–15] and recently for *p*-chlorosulfinylaniline [16]. In the present study, theoretical calculations at the harmonic oscillator level predict $\text{N}=\text{S}=\text{O}$ group stretching modes at $1312/1058\text{ cm}^{-1}$ (B3LYP/cc-pVTZ potential), $1310/1051\text{ cm}^{-1}$ (B3LYP/6-311++G(df,pd) potential) and $1307/1016\text{ cm}^{-1}$ (MP2/cc-pVDZ) for the antisymmetric and symmetric modes, respectively. More advanced theoretical calculations at the vibrational self-consistent field (VSCF) vibrational structure level of theory, using a 3-mode coupling quartic force field predict these bands at $1295/1041\text{ cm}^{-1}$ (B3LYP/6-311++G(df,pd) potential) and $1294/1006\text{ cm}^{-1}$ (MP2/cc-pVDZ potential). The $\text{N}=\text{S}=\text{O}$ antisymmetric and symmetric stretching modes of *m*-chlorosulfinylaniline were therefore assigned to the 1298 and 1039 cm^{-1} (IR) and 1304 and 1043 cm^{-1} (Raman) bands, respectively. A slight blue shift of the $\text{N}=\text{S}=\text{O}$ stretching modes in the *meta* with respect to the *para* isomer ($1297/1031\text{ cm}^{-1}$, respectively) is to be expected, due to mesomeric effects of the chlorine lone pair with the $-\text{N}=\text{S}=\text{O}$ group (See Scheme 2).

The in plane deformation of the $\text{N}=\text{S}=\text{O}$ group had been described as a very weak signal in the vibrational spectra of the fluorosulfinylaniline series and also for *p*-chlorosulfinylaniline. For the *meta* isomer this signal was no discernible in the experimental spectra, but the theoretical calculations predicted it at 641 , 638 and 634 cm^{-1} according to B3LYP/cc-pVTZ, B3LYP/6-311++G(df,pd) and MP2/cc-pVDZ, respectively, in good agreement with the observed values for those related compounds. On the other hand, the out of plane deformation was observed at 440 cm^{-1} in the IR spectrum with theoretical calculations predicting it at 410 , 411 and

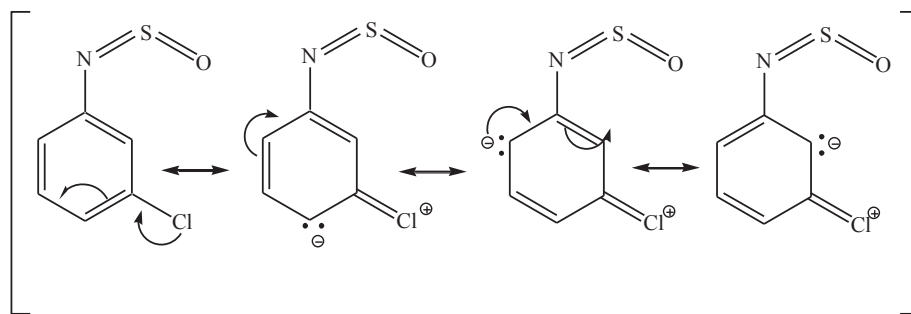
414 cm^{-1} HO//B3LYP/cc-pVTZ, HO//B3LYP/6-311++G(df,pd) and HO//MP2/cc-pVDZ, respectively, and at 406 and 412 cm^{-1} for VSCF//B3LYP/6-311++G(df,pd) and VSCF//MP2/cc-pVDZ levels of theory, respectively.

We now address the analysis of the C–N stretching mode, assigned at 786 cm^{-1} in the infrared spectra, with theoretical calculations predicting it at 702 , 694 and 674 cm^{-1} at the HO//B3LYP/cc-pVTZ, HO//B3LYP/6-311++G(df,pd) and HO//MP2/cc-pVDZ levels of theory respectively and at 711 and 669 cm^{-1} for VSCF//B3LYP/6-311++G(df,pd) and VSCF//MP2/cc-pVDZ, respectively for anharmonic vibrational calculations. A comparison with the corresponding mode in the *para* isomer (770 cm^{-1} , IR) shows that it is slightly blue-shifted in the *meta* compound with respect to the former. This trend is different from the observed for the corresponding isomers in the fluorinated series, where the red-shift shown in the vibrational spectra for the band belonging to the C–N stretching mode accounts for mesomeric effects of the fluorine atom, which are now proved to be different in the chlorinated specie. The different trend may be explained through orbital interactions, as evidenced by the Natural Bond Orbital analysis performed for the present study. Mesomeric effects affect predominantly *o*- and *p*-positions with respect to the halogen atom. By simply writing the resonance structures for the molecules, we can see that it confers a partial double bond character over the C–N bond when it is situated at those positions with respect to the halogen. In our calculations, this effect is observed to be far more important in the case of the fluorinated series than in the chlorinated series. In the *p*- and *o*-fluoro substituted isomers the C–N stretching signal was observed at larger frequency values with respect to the *m*-isomer, while for the chlorinated series, the opposite was true. We explain these differences by invoking the stronger mesomeric effects observed for the fluorinated series as explained above. In other words, the strong mesomeric effects in fluorinated compounds blue-shift the C–N frequencies for *o*- and *p*-isomers so much, that they appear at higher frequency than the *m*-isomer, but when these effects become weaker, as in the chlorinated series, C–N stretching bands for *o*- and *p*-isomers appear at lower frequencies than for the *m*-isomer.

In agreement to the previous reasoning, the C–Cl stretching mode follows this trend as it was observed in the present study at 825 cm^{-1} in comparison with the 836 cm^{-1} frequency found in the *p*-isomer.

4.3. NMR profile

We used a combination of nuclear magnetic resonance (NMR) spectroscopy and mass-spectrometry for the molecular structure determination using theoretical methods to help in the assignments. The molecular structure of *m*-chlorosulfinylaniline was optimized at the B3LYP/6-311+G(df) level of theory followed by ^{13}C and ^1H chemical shift calculations through the GIAO method which were subsequently compared to the experimental chemical shift values (see Tables 3 and 4). The GIAO method is one of the most common approaches for calculating nuclear magnetic shielding tensors. Aromatic carbons show signals in the 100 – 150 ppm range [35] while signals belonging to aromatic protons are usually found around 7.00 – 8.00 ppm . In a correlative order, the signals observed for C1 to C6 were 142.90 , 130.10 , 134.71 , 130.42 , 129.90 and 125.10 ppm ; on the other hand, the hydrogen atoms H1, H4, H3 and H2 showed signals at 7.80 , 7.70 , 7.32 and 7.32 ppm , respectively. The external magnetic field experienced by carbon nuclei is affected by the electronegativity of atoms/groups bonded therefore the influence of the chlorine atom and $\text{N}=\text{S}=\text{O}$ group must be considered. The assignment proposed is based on shifts reported for similar molecules [13–16]. The increase in the chemical shift observed for



Scheme 2. Different mesomeric structures for *m*-chlorosulfinylaniline.

Table 3

¹³C NMR experimental (50 MHz, CDCl₃, TMS) and calculated data of *m*-chlorosulfinylaniline.

C ^a	Chemical shift δ [ppm]	
	Experimental	Theoretical ^b
C (6)	125.10	129.85
C (5)	129.90	132.09
C (4)	130.42	136.17
C (3)	134.71	148.77
C (2)	130.10	132.56
C (1)	142.90	151.88

^a For atom numbering see Fig. 1.

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

Table 4

¹H NMR experimental (200 MHz) and calculated data of the *m*-chlorosulfinylaniline.

H ^a	δ [ppm] Experimental	δ [ppm] Theoretical ^b
H1	7.80	8.84
H4	7.70	7.06
H3	7.32	7.04
H2	7.32	6.95

^a For atom numbering see Fig. 1.

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

C1 and C3 with respect to the other carbon atoms might be attributed to the presence of the chlorine and the N=S=O group attached to the aromatic ring.

5. Conclusions

The present article features the study of the conformational and vibrational properties of *m*-chlorosulfinylaniline, and is the second in an ongoing series dedicated to chlorine monosubstituted sulfinylaniline series of compounds. In the present work we performed the conformational analysis and characterization of *m*-chlorosulfinylaniline by nuclear magnetic resonance spectroscopy (¹H and ¹³C), gas chromatography/mass spectrometry, vibrational spectra and quantum chemical calculations at different levels of theory, thus complementing partial results reported previously. The title compound was obtained through the reaction *m*-chloroaniline and SOCl₂, obtaining a highly hygroscopic and corrosive substance.

As observed with all sulfinylamine derivatives, theoretical calculations strongly indicate that only the *syn* conformation of the N=S=O moiety can be observed in the gas phase, implying a global C_s symmetry, in agreement with the properties observed for the parent sulfinylaniline. Moreover, Natural Bond Orbital analysis

showed that this thermodynamic preference is due to strong stabilizing anomeric interactions for the *syn* configuration that are lower in the *anti* conformer.

In comparison with the parent sulfinylaniline and *p*-chlorosulfinylaniline, previously reported, the vibrational fundamentals of the N=S=O group, as well as the C–N and C–Cl stretching modes, show some interesting shifts that offer some clues on the effect of substitution on the molecular electronic structure, and some possible rationalizations are explored in this work. A complete assignment of the fundamental vibrational transition bands is proposed on the basis of present and previous experimental work, and strongly supported by theoretical calculations at harmonic and anharmonic vibrational levels of theory. With regard to this later point, the vibrational self-consistent field (VSCF) ansatz as implemented in the QUMVIA software package, developed by our group, proved to be quite useful in the assignment of fundamental bands, as well as for the identification of possible overtones and combination bands, and presents itself as a much more physically motivated method than the widespread practice of using simple *ad-hoc* scaling factors for harmonic oscillator vibrational frequencies, as the former is capable of handling non-trivial effects of anharmonicity, that cannot be modeled by more traditional techniques.

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