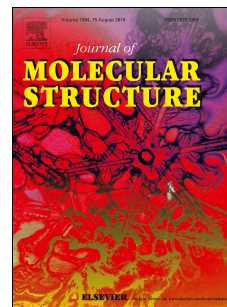


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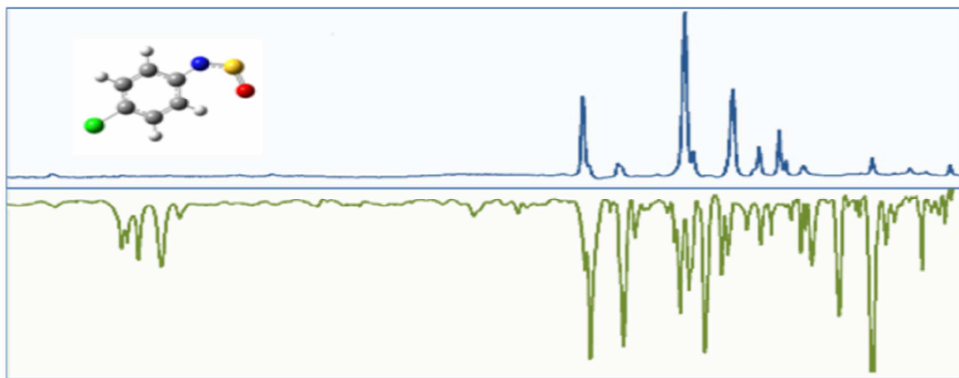
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Graphical Abstract



Synthesis, Characterization and Vibrational Studies of *p*-Chlorosulfinylaniline

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ABSTRACT

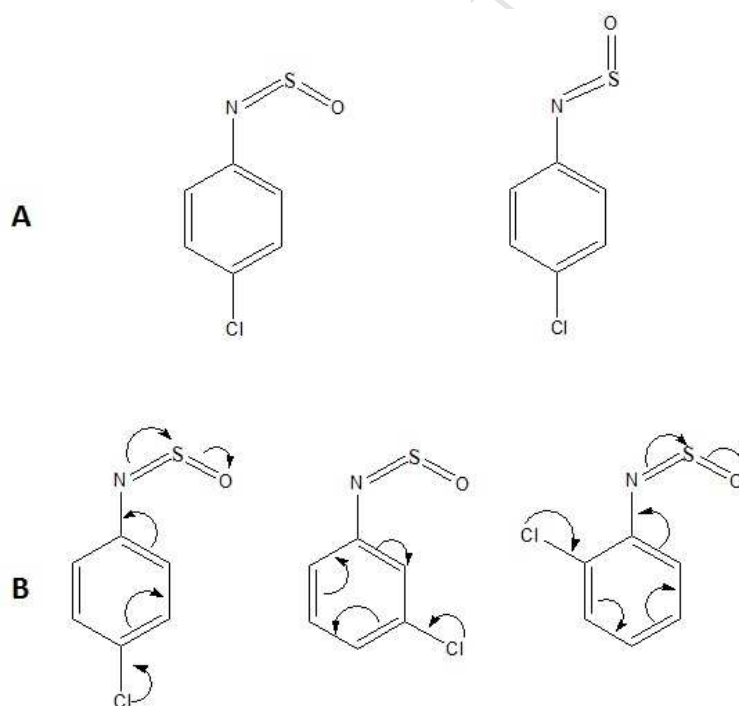
p-Chlorosulfinylaniline was prepared by the reaction of *p*-chloroaniline and SOCl₂. The structural, conformational and configurational properties of the obtained liquid compound were studied by Raman and infrared spectroscopy in the liquid state. The assignment of the vibrational spectra was carried out with the help of data obtained by quantum chemical calculations at the harmonic oscillator approximation and using anharmonic vibrational self-consistent field (VSCF) method as well. The ¹H and ¹³C NMR chemical shifts of the molecule were calculated by Gauge including orbital (GIAO) method (DFT/B3LYP approximation using 6-311+G(df), 6-311++G(df,pd) and cc-pVTZ basis sets) and compared to the experimental values. Natural Bond Orbital analysis provides an explanation of the stability of the molecule and its electronic properties upon charge delocalization.

Keywords *p*-Chlorosulfinylamine; vibrational spectroscopy; quantum chemical calculations; conformational properties.

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1. Introduction

The history of the discovery of N-sulfinylamines ($R-N=S=O$) can be traced back to the 1890's, when they were synthesized and investigated by Michaelis *et al.* [1, 2]. As this work proposed a general procedure for the quantitative obtention of these compounds, it constituted the initial step for the research of the structural properties, reactivity and applications of N-sulfinylamines. To this day, numerous N-sulfinylamines are still obtained through Michaelis' method. Although more than 600 N-sulfinyl compounds are known [3], only a few N-sulfinylamines were structurally characterized and their reactivity analyzed to some extent. Gas electron diffraction studies for ClNSO [4], CH_3NSO [5], SiH_3NSO [6], $FC(O)SNSO$ [7], $SiMe_3NSO$ [8], CF_3SNSO [9] and CF_3SSNSO [10] resulted in the presence of only the sterically unfavorable *syn* conformation of the $R-N=S=O$ skeleton (see Scheme IA).



Scheme I. A) *Syn* and *anti* forms around the N=S bond; B) Charge delocalization structures for *p*-, *m*- and *o*-chlorosulfinylaniline.

Furthermore, vibrational studies combined with quantum chemical calculations for CF₃NSO and SF₅NSO demonstrate the preference of the *syn* structure [11]. Quantum chemical calculations (B3LYP/6-311+G(df)) predict energy differences $\Delta E = (E_{anti} - E_{syn})$ of 7.1 kcal/mol for CINSO, 6.3 kcal/mol for CH₃NSO, 3.1 kcal/mol for CF₃NSO and 3.9 kcal/mol for SF₅NSO. The HF/6-31G(d) method results in $\Delta E = 10.7$ kcal/mol for CF₃SNSO [9].

The strong preference of the sterically unfavorable *syn* structure has been rationalized by orbital interactions. The nitrogen lone pair delocalize electronic density towards vicinal antibonding σ^* (S–O) orbital, with a consequent decrease in the global energy of the conformer involved. A similar effect is showed by the sulfur lone pair and adjacent antibonding σ^* (C–N) orbital. These anomeric effects stabilize the *syn* conformation much more strongly than the *anti* structure, by 18.3 kcal/mol in CINSO, 17.4 kcal/mol in CH₃NSO, 16.2 kcal/mol in CF₃NSO and by 16.6 kcal/mol in SF₅NSO. Thus, these strong anomeric effects override the steric repulsion in the *syn* form. This steric repulsion is evident from the bond angles at nitrogen and sulfur, which increase according to the calculations by 7° to almost 10° when going from *anti* to *syn* conformation.

Several works with contradictory results concerning the structure of N-sulfinylaniline exist in the literature [12]. The indication for the presence of a *syn* conformation, based on NMR data [13, 14], was confirmed by an X-ray diffraction experiment [15]. This result for the solid state was confirmed also for the free molecule by vibrational spectra and quantum chemical calculations (B3LYP/6-311+G (df), and an energy difference ΔE of 8.1 kcal/mol was reported [16]. Also in sulfinylaniline anomeric effects, which are much stronger in the *syn* (25.4 kcal/mol) than in the *anti* structure (8.0 kcal/mol), stabilize the *syn* conformation. H. Muchall rationalized the preference of the *syn* conformation with an intramolecular C–H•••O bond involving the ortho hydrogen atom [17].

The inclusion of a substituent group/atom in N-sulfinylaniline leads to variation in the molecular charge distribution, and consequently greatly affects the electronic, structural and vibrational parameters.

The mass spectra of *p*-chlorosulfinylaniline were reported by Bowie *et al* [18]. Since no report of the vibrational properties of this substance was attempted so far, in the present investigation a conformational and vibrational analysis of *p*-chlorosulfinylaniline has been

undertaken on the basis of a detailed characterization and a tentative assignment of the vibrational spectra (FT-IR and Raman) supported by quantum chemical calculations at different levels of theory. The effect of a halogen atom in *para* position of an aromatic ring on the N=S=O properties has been analyzed.

2. Experimental details

2.1 Synthesis

p-Chlorosulfinylaniline was obtained with a 1:2:5 molar relation of the corresponding chlorinated aniline (3.14 g; 18 mmol), thionyl chloride (9.80 g; 82 mmol) and benzene (13.20 g; 169 mmol) as the reaction solvent, respectively. The chlorinated aniline used as precursor and the solvent were placed in a closed three neck round bottom flask equipped with a Liebig condenser sealed with CaCl₂. Thionyl chloride was added drop wise to the 50 – 60 °C heated mixture. As the expected reaction product was expected to be an air sensitive compound, the reaction was performed in nitrogen atmosphere.

The reaction mixture was continuously stirred and heated 8 hours at 80 – 85 °C until a dark solution was obtained. The liquid mixture was then purified by several distillation cycles until a dark green liquid with *ca* 93% yield was obtained. The purity of the substance was checked by ¹H and ¹³C NMR spectroscopy and GC-Mass spectrometry, together with IR and Raman spectroscopy. In contact with air humidity, the substance hydrolyses rapidly. It was also found to be a very corrosive compound for KBr windows, therefore KRS-5 windows had to be used to register infrared spectra.

2.2 FT-IR and Raman measurement

FT-IR spectra of *p*-chlorosulfinylaniline was registered between in the 3500 – 400 cm⁻¹ region at ambient temperature using a Perkin Elmer GX1 Fourier Transform infrared spectrometer by placing the liquid sample between KRS-5 windows (spectral resolution: 1 cm⁻¹).

Raman spectra of a liquid sample were registered at room temperature in the 3500 – 50 cm⁻¹ region by using a diode-pump solid state 532 nm green laser with 9.0 mW power at the sample for excitation available in a ThermoScientific DXR Smart Raman instrument equipped with CCD detector (spectral resolution: 4 cm⁻¹; grating groove density of 900

lines/mm). A confocal aperture of 25 μm slit was used and 40 expositions of 1 s were accumulated for the sample to improve signal to noise ratio. The samples were held in Pyrex capillaries at room temperature.

2.3. NMR and GC-MS measurements

NMR spectra were registered in CDCl_3 at 200 MHz for ^1H and 50 MHz for ^{13}C on a Varian Unity 200 spectrometer. The molecule was dissolved in chloroform-d solution (CDCl_3). The chemical shifts were reported in ppm relative to tetramethylsilane (TMS).

The GC/MS analysis was performed using a Model Trace GC Ultra gas chromatograph coupled to a Polaris Q mass spectrometer with a ion-trap analyzer using a DB-5 capillary column. Split-less injection was employed for the analysis. The oven was set initially at 60 $^\circ\text{C}$ and kept at this temperature for 3 min. The temperature was afterwards increased at a rate of 20 $^\circ\text{C}/\text{min}$ until a final 280 $^\circ\text{C}$ temperature was reached and kept for 5 min (total run time: 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.

3. Computational information

The theoretical predictions of the molecular structure, conformational properties, IR and Raman spectroscopy were achieved by using the GAUSSIAN03 program [19]. Based on the Density Functional Theory (DFT), the three-parameter hybrid functional for the exchange part [20] and the Lee-Yang-Parr (LYP) correlation function [21] together with the 6-311+G(df), 6-311++G(df, pd) and cc-pVTZ bases sets provide good approximations for the quantum chemical calculations required to characterize the system in study. For the study of the orbital interactions and nuclear magnetic shielding tensors, the natural population analysis (NBO) [22] and Gauge-including atomic orbital (GIAO) method [23] were used, respectively, as implemented in the GAUSSIAN03 program. In addition to these calculations for the *p*-chlorosulfinylaniline, the B3LYP/6-311+G(df) method was applied also to sulfinylaniline and to *p*-fluorosulfinylaniline for the sake of comparison.

In addition to these calculations, the recently implemented vibrational self-consistent field (VSCF) ansatz in the QUMVIA software package [24] was used for the vibrational

calculations. VSCF is a mean-field, variational iterative method for the calculation of the vibrational wavefunction similar to the Hartree-Fock method in the electronic structure theory. Following is a summary of the main postulates of this theoretical approach; further details can be found elsewhere [25–28].

Neglecting rotational couplings, the vibrational Schrödinger equation for a molecule depicted in rectilinear normal coordinates $\{q_i\}$ may be formulated as:

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

With

$$\Psi_n(\vec{q}) = \prod_{i=1}^f \Phi_{i,n}(q_i)$$

The vibrational wavefunction is represented as a Hartree product, i.e. a product of one-dimensional, single-mode wavefunctions, usually called modals, that play a similar role as orbitals do in the electronic structure theory. Ψ is the vibrational wavefunction, $\Phi_{i,n}$ are the one-dimensional modals and q_i are the mass weighted normal coordinates. By using this assumption and taking into account 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”, which involves the kinetic energy and the diagonal potential; v_i is the mean field potential. Since the solutions are required to compute the mean field potential, the VSCF equations must be solved iteratively until self-consistency is reached.

Distributed Gaussian functions are employed as a basis set [29]. The nuclear potential energy surface (PES) was approximated by using a quartic force field (QFF) with a 3-mode coupling representation [30]. Third and fourth order force constants were obtained by numerical differentiation of Hessian matrices calculated analytically by using a different electronic structure software (GAUSSIAN03, in this case) with the MP2/cc-pVDZ and B3LYP/6-311++G(df, pd) approximations. By using a “very strict” convergence criterion, the optimization of the molecular structures followed by the frequency calculation to obtain the harmonic frequencies and hessian matrices was achieved. These results were used to build a set of distorted conformations along each normal mode using QUMVIA, and Hessian matrices were calculated for each conformation using GAUSSIAN03. At last, these Hessian matrices were used to calculate 3-mode coupling QFF using QUMVIA.

4. Results and Discussion

4.1 Molecular geometry, structural properties and NBO analysis

Calculations for the *syn* conformer of *p*-chlorosulfinylaniline depicted in Fig. 1 result in a planar structure and calculated properties are listed in Table 1 (geometric parameters) together with experimental values in Table 2 (vibrational frequencies), Table 3 (¹H NMR shifts) and in Table 4 (¹³C NMR shifts). B3LYP/6-311+G(df) calculations for the *anti* conformer of sulfinylaniline and the *p*-fluoro and *p*-chloro derivatives result in non-planar structures with the NSO group rotated out of the phenyl plane by $\varphi(\text{C-N-S=O}) = 36.5^\circ$, 33.0° and 34.3° , respectively. The predicted energy differences $\Delta E = (E_{anti} - E_{syn})$ are 7.5, 8.1 and 7.9 kcal/mole, respectively. The value for the parent compound differs slightly from that reported in Ref. 16 (8.1 kcal/mol), since a planar structure for the *anti* conformer was used. As in the case of the N-sulfinylamines (see Introduction), the adoption of the sterically unfavorable *syn* conformation may be understood primarily with anomeric effects $\text{lp}(\text{N}) \rightarrow \sigma^*(\text{S-O})$ and $\text{lp}(\text{S}) \rightarrow \sigma^*(\text{N-C})$. The interaction energies involved in these delocalizations are higher in the *syn* structure by 18.8 and 18.3 kcal/mol, respectively. The formation of an intramolecular C-H \cdots O bond involving the ortho hydrogen atom proposed in Ref.17 may contribute additionally to the stabilization of the *syn* conformer.

4.2 Vibrational assignment

The experimental FT-IR and Raman spectra have been assigned on the basis of their calculated vibrational frequencies and intensities. Table 2 lists the experimental and theoretical wavenumbers together with a tentative assignment of the fundamental transitions expected for *p*-chlorosulfinylaniline. The analysis of the experimental vibrational spectra was performed taking into account vibrational spectra obtained by using the harmonic oscillator (HO) approximation and also at the anharmonic vibrational self-consistent field (VSCF) level of theory. Two potential energy surfaces (PES), B3LYP/6-311++G(df,pd) and MP2/cc-pVDZ were used for HO and VSCF vibrational levels of theory. To facilitate the identification of vibrational modes belonging to the N=S=O group and C–Cl bond, theoretical ¹⁵N and ³⁷Cl substitution were used, together with data reported for sulfinylaniline [14 – 16], *p*-fluorosulfinylaniline [31] and the reactant *p*-chloroaniline [32]. Figures 2 and 3 show experimental and theoretical spectra of *p*-chlorosulfinylaniline. Although HO-based calculations furnished us with quite useful theoretical predictions, a better correlation was given by anharmonic vibrational frequency calculations at the VSCF level of theory. Mean absolute deviations (MAD) over the entire spectra were of 38 and 48 cm⁻¹ for HO//B3LYP/6-311++G(df,pd) and HO//MP2/cc-pVDZ PES, respectively, while only 24 and 23 cm⁻¹ for VSCF// B3LYP/6-311++G(df,pd) and VSCF// MP2/cc-pVDZ levels of theory, respectively. Notice that VSCF calculations increased average accuracy by a factor of almost two relative to the HO approximation. Moreover, although B3LYP PES produced substantially better results than MP2 at the HO level, it is the later that produced the best results at the VSCF approximation, despite the fact that a significantly bigger basis set was used for B3LYP than for MP2. In other words, although B3LYP appears to produce a better approximation for the potential energy function at the HO level, this apparent advantage vanishes when anharmonicity is taken explicitly into account. Moreover, VSCF calculations predicted modifications in the energy order of several vibrational states, a result of the fact that anharmonicity affects different states by differing degrees, sometimes modifying the assignments made by the HO approximation. In particular, C–H stretching modes are very good examples of this. As shown in Table 2, the energy order predicted for these fundamentals at the VSCF level are $\nu_2 > \nu_1 > \nu_4 > \nu_3$ and $\nu_2 > \nu_1 > \nu_3 > \nu_4$ for MP2 and B3LYP PESs, respectively. Notice that although in B3LYP states ν_3 and ν_4 do not exchange

places, they are predicted to be almost degenerate in energy, so the tendency is similar in both PES. It is also noteworthy the fact that the absolute transition frequencies for these states is greatly improved, with absolute deviations (only considering C–H stretching modes) going from 186 cm^{-1} at the HO approximation to only 10 cm^{-1} at VSCF level of theory for the MP2 PES and from 141 to 32 cm^{-1} for B3LYP PES, where the frequencies in this region are somewhat underestimated. Other vibrational states also exchange places. Particularly pairs of states ν_{17} and ν_{18} are predicted to exchange places in both PES, while a similar trend is predicted by VSCF//MP2 calculations for pairs ν_{23}/ν_{24} , and pairs ν_{26}/ν_{27} and ν_{32}/ν_{33} by VSCF//B3LYP. The lower portion of the spectra exhibits an interesting feature, since the anharmonic transitions were predicted to have higher frequencies than their harmonic counterparts. This may be understood taking into account that potential energy surfaces along low frequency normal modes are usually flatter near the equilibrium geometry than in other more displaced geometries. As a consequence, quadratic approximations are too flat compared to the real, fully anharmonic PES. In general terms, VSCF calculations proved to be very useful for the assignment of the vibrational spectra. In comparison with common *ad-hoc* methodologies, which ordinarily use empirical scaling factors, the VSCF methodology allows the prediction of overall absolute frequencies of similar or better accuracy with respect to experimental values. In addition, it is able to handle more complicated assignments, as in the C–H stretchings mentioned above or the lower part of the spectra, where the trend of anharmonicity is opposite to the effect of scaling factors. For these reasons, we conclude that the use of anharmonic variational methods is a very good alternative in comparison with the use of current *ad-hoc* scaling factors.

We now address some issues regarding the –N=S=O moiety. Previous analysis showed a marked correlation between the stretching vibrations of this group and the atom bonded to the N atom. An early study on the parent sulfinylaniline described the stretching modes as two independent modes placed at 1284 cm^{-1} and 1155 cm^{-1} for N=S and S=O respectively [14]. Later, the study of the pre-resonant Raman spectra of sulfinylaniline evidenced a strong coupling of the N=S and S=O stretching modes [16]. According to the data reported for *p*-fluorosulfinylaniline, the signals centered at 1303/1302 cm^{-1} and 1030/1029 cm^{-1} in the IR and Raman spectra were attributed to the asymmetric and symmetric stretching

modes of the N=S=O group, respectively [31]. Consequently, in the present work the signals observed at 1297 and 1031 cm^{-1} in the infrared spectra and at 1296 and 1031 cm^{-1} in the Raman spectra were assigned to the asymmetric and symmetric stretching respectively of *p*-chlorosulfinylaniline. The vibrational spectra evidenced no significant influence of the chlorine atom in the vibrational modes of the N=S=O group compared to the corresponding signals for *p*-fluorosulfinylaniline. Preliminary calculations performed for *o*- and *m*-chlorosulfinylaniline indicate that the effect of the chlorine atom on the frequencies of the N=S=O group depends on its place in the aromatic ring. The asymmetric stretching of the N=S=O group in *o*-chlorosulfinylaniline was calculated at 1320 cm^{-1} , 4 cm^{-1} lower in frequency terms, with respect to *p*-fluorosulfinylaniline, while the corresponding mode for the *meta* substituted compound was predicted at 1308 cm^{-1} at the B3LYP/6-311++G(df,pd) level. The resonance structures depicted on Scheme IIB (should be Scheme IB) show the effective charge delocalization for the chlorine atom in *ortho*, *meta* and *para* position. The assignment proposed may be rationalized linking the shortening and elongation of the N=S and S=O bonds with the partial contribution of these structures to the resonance hybrid.

The in-plane bending of the N=S=O group was attributed to the signals at 618 cm^{-1} in the vibrational spectra while the out-of-plane bending mode for this group was assigned to the signal centered at 486 cm^{-1} in the infrared spectrum. This is not completely comparable to the assignment proposed for the corresponding modes in *p*-fluorosulfinylaniline, for which signals at 634 cm^{-1} and 281 cm^{-1} (Raman) were observed [31].

Depending on the configuration and conformation of the aromatic compound the C–Cl stretching vibration was observed in the region between 850 and 550 cm^{-1} [30]. For this molecule the band at 836 cm^{-1} (Raman) was assigned to the C–Cl stretching while the C–Cl in-plane bending vibration was assigned at 354 cm^{-1} in the Raman spectra, in agreement with harmonic and anharmonic calculations (see Table 2). The C–N stretching mode was observed at 785 cm^{-1} in the infrared spectrum of the *p*-fluoro derivative [31], while in this study, this vibration was assigned to the band observed at 770 cm^{-1} in the infrared and Raman spectrum.

We finally focus on the bands centered at 1484 cm^{-1} which were labeled as ν_7 in this work. These bands are actually complex bands, with two weaker features centered at 1479 and 1473 cm^{-1} in IR and only one companion observed at 1473 cm^{-1} in Raman spectra. When

comparing equivalent bands of *p*-fluorosulfinylaniline [31], we observed a similar set of bands in the same region. Since the mass and NMR spectra would not evidence the presence of relevant amount of impurities, it is possible to attribute these signals to overtones and/or combination bands, borrowing intensity from ν_7 dipole-allowed transition through Fermi resonance. The exact identity of the resonant overtones or combination bands is quite hard to determine, because of the high density of "dark" vibrational states in this region and the low symmetry of the molecule. More accurate vibrational structure calculations considering vibrational correlation explicitly, as in the vibrational configuration interaction approach (VCI) [26] are now in development by our research group. We trust they shall be able to provide a more solid foundation about these interesting spectra features in the near future.

4.3 NMR profile

Nuclear magnetic resonance (NMR) spectroscopy has evolved as one of the most powerful analytical techniques. It allows the visualization of single atoms and molecules in various media in solution as well as in solid state. NMR is nondestructive and gives molar response that allows structure elucidation and quantification simultaneously. The experimental and theoretical data of the spectra of ^1H and ^{13}C NMR in chloroform-*d* (CDCl_3) solution solvent are shown in Table 3 and 4. The atom positions were arranged based on number of Fig. 1. The assignment proposed for the title molecule was performed on the basis of data reported for substituted aromatic molecules with electron withdrawing groups in *para* position [31] and the unsubstituted sulfinylaniline [14]. For the calculation of nuclear magnetic shielding tensor with the gauge-including atomic orbital (GIAO) method [23] an optimized structure at the B3LYP/6-311+G(df) level of theory was used. As it is well known, the chemical shifts of aromatic protons and carbon atoms of organic compounds are usually observed in the 7.00 – 8.00 ppm and 100 – 150 ppm range, respectively. Therefore, the signals centered at 7.12, 7.78, 6.58 and 6.62 ppm in the ^1H NMR spectra were assigned to the four aromatic protons of *p*-chlorosulfinylaniline. Meanwhile, the ^{13}C NMR spectrum showed signals at 128.53 (C (1)), 128.58 (C (2)), 128.43 (C (3, 5, 6)) and 128.44 ppm (C (4)). These results confirmed 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 chlorine atom and the N=S=O group must be considered. The increase in chemical shift observed for C1 and C4 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. The assignment proposed took into account the well known fact that electron withdrawing atoms/groups attract electronic density, with the consequent de-shielding of nearby nuclei and the increment of their chemical shift value.

4.4 GC/MS profile

It is well known that aromatic halogenated compounds generally show an intense signal for the molecular ion. This fact, together with the common feature of isotopic patterns of chlorinated molecules in the mass spectra made the assignment of the observed signals quite straightforward. In agreement with a previous analysis of the mass spectra of chlorosulfinylaniline [32], the intense signal at 5.77 min (93.4 % relative area and 173 molecular weight) in the total-ion chromatogram and the accompanying peak found at 175 m/z were attributed to the $^{35}\text{Cl}/^{37}\text{Cl}$ substituted molecular ion, respectively (see Fig 4). Therefore the peak at m/z 174 was assigned to the protonated form of the base peak at m/z 173. Another common feature of halogen substituted aromatic compounds is the presence of a signal accounting for the halogen loss, observed in our experience at 138 m/z.

The additional peak found at time retention 5.16 min (0.38 % relative area and m/z 127) was assigned to the reactant *p*-chloroaniline, while the signals at m/z 110 and 63 were attributed to the $[\text{C}_6\text{H}_4\text{Cl}]^+$ and $[\text{H}-\text{N}=\text{S}=\text{O}]$ fragments, respectively. Fig. 5 depicts a scheme of the fragmentation pattern with the most relevant fragments of interest.

5. Conclusions

It is well known that the presence of substituents attached to a parent unsubstituted compound of acknowledged properties may modify those characteristics to such an extent that may compel us to evaluate the resulting compound as new specie. *p*-Chlorosulfinylaniline was obtained through the reaction of *p*-chloroaniline and SOCl_2 and characterized by using nuclear magnetic resonance spectroscopy, gas chromatography/mass spectrometry, vibrational spectra and quantum chemical calculations with the purpose

of adding one more step in the knowledge of the influence that the presence of halogen substituents exert on sulfinylanilines. Compared to the parent sulfinylaniline and *p*-fluorosulfinylaniline, the closest analogue so far reported, the vibrational fundamentals modes of the sulfinyl group, as well as the C–N and C–Cl stretching modes do not account for differences of considerable interest. However, taking into account preliminary theoretical calculations performed for the *m*- and *o*- isomers, it is expected that more significant changes would be observed in relation with the position of the substituent in the aromatic ring. These changes would reflect, as in the *p*-, *m*- and *o*-fluorosulfinylaniline [31, 33, 34] series, the joint action of electronic effects from the N=S=O and chlorine substituents.

With regard to the theoretical approaches employed in the analysis of the vibrational spectra, it is interesting to highlight that the vibrational self-consistent field method was found to be a very valuable tool for the assignment of the vibrational spectra. Its predictions not only significantly improved the overall accuracy of the theoretical spectra, but they also showed that the effects of anharmonicity cannot be mimicked by using simple *ad-hoc* scaling factors. Considering the relative ease of use and good cost-benefit ratio of VSCF methodology, when analytical Hessians are available, we propose that a more extended use of such is advisable.

We also identified a set of bands centered at 1484, 1479 and 1483 cm^{-1} in *p*-chlorosulfinylaniline spectra and at 1479, 1496 and 1513 cm^{-1} at *p*-fluorosulfinylaniline, which we propose are possible Fermi resonances. A more detailed study must await, however, the availability of more advanced post-VSCF methods suitable for the study of molecules of this size, which are in active development by our group.-

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Figure Captions

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

Fig. 2. Experimental and theoretical infrared spectra of *p*-chlorosulfinylaniline. 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 held between KRS-5 windows.

Fig. 3. Experimental and theoretical Raman spectra of *p*-chlorosulfinylaniline. 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.

Fig. 4. Mass spectra (mass numbers (m/z) versus relative abundance) obtained for *p*-chlorosulfinylaniline.

Fig. 5. Major fragmentation patterns of m/z peaks for *p*-chlorosulfinylaniline.

Scheme I. A) *Syn* and *anti* forms around the N=S bond; B) Charge delocalization structures for *p*-, *m*- and *o*-chlorosulfinylaniline.

Table 1. Calculated geometric parameters for the *p*-chlorosulfinylaniline.

Structural parameters ^a	<i>p</i> -chlorosulfinylaniline	
	B3LYP/ 6-311++G(df,pd)	B3LYP/ cc-pVTZ
C–Cl	1.748	1.746
C–H	1.080	1.078
C1–C2(6)	1.408	1.407
C2(5)–C3(6)	1.385	1.385
C4–C3(5)	1.391	1.390
C1–N	1.387	1.389
N=S	1.507	1.536
S=O	1.485	1.479
N=S=O	119.4	119.8
C1–N=S	132.2	131.8
C2–C1–C6	119.3	119.1
C3–C4–C5	121.1	121.1
C2–C1–N	124.8	124.9
C6–C1–N	116.0	116.1
C1–C–C	119.5	119.5
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. 1.

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

Mode	Approximate description ^a	Experimental ^b		Theoretical			
		IR (liq.)	Raman (liq.)	B3LYP/6-311++G(df,pd)		MP2/cc-pVDZ	
				HO	VSCF	HO	VSCF
v ₁	C–H Stretch.	3091w	-	3224 (2) [4]	3039	3273(4) [27]	3083
v ₂	C–H Stretch.	-	3075vw	3210(1) [16]	3063	3252(<1) [95]	3100
v ₃	C–H Stretch.	3071vw	3071vw	3202(<1) [77]	3023	3243(<1) [51]	3054
v ₅	C–C Stretch.	1583s	1582s	1620(67) [64]	1594	1638(29) [95]	1613
v ₆	C–C Stretch.	1563vw	1563vw	1586(3) [3]	1563	1610(<1) [13]	1585
v ₇	C–C Stretch. + C–H Def.	1484s	1484w	1514(29) [11]	1495	1511(100) [23]	1492
v ₈	C–C Stretch.	1406w	-	1440(3) [<1]	1425	1489(2) [4]	1462
v ₉	C–H Def. i.p.	1336w	-	1330(<1) [<1]	1319	1405(5) [2]	1385
v ₁₀	N=S=O Asym. Stretch.	1297s	1296vs	1324(6) [100]	1306	1305(4) [17]	1295
v ₁₁	C–C Stretch.	1273s	1272w	1305(17) [38]	1290	1297(41) [100]	1279
v ₁₂	C–H Def. i.p.	1234vw	-	1202(3) [15]	1199	1204(52) [80]	1200
v ₁₃	C–H Def.	1176s	-	1160(100) [18]	1146	1188(4) [2]	1184
v ₁₄	C–H Def.	1162 vs	1161s	1133(21) [1]	1133	1129(68) [27]	1118
v ₁₅	C–Cl Stretch.	1102s	1102w	1101(89) [17]	1091	1117(17) [<1]	1117
v ₁₆	Ring Def.	1087s	1087m	1039(4) [12]	1029	1022(52) [4]	1015
v ₁₇	N=S=O Symm. Stretch.	1031w	1031s	1028(26) [7]	1017	990(19) [8]	979
v ₁₈	C–H Def. o.o.p.	1013s	1013w	1005(<1) [<1]	1025	957(<1) [<1]	992
v ₁₉	C–H Def. o.o.p.	-	963w	984(<1) [<1]	1016	931(<1) [<1]	979
v ₂₀	C–Cl Stretch.	836vs	-	864(44) [<1]	899	838(39) [1]	867
v ₂₁	C–H Def. o.o.p.	815vw	-	844(1) [<1]	882	833(35) [2]	864
v ₂₂	C–N Stretch.	770w	770w	784(3) [6]	782	773(26) [7]	768
v ₂₃	Ring Def.	679vs	684vw	734(<1) [<1]	717	671(31) [8]	666
v ₂₄	Ring Def.	665m	664w	673(16) [1]	667	639(<1) [<1]	707
v ₂₅	N=S=O Def. i.p.	618w	618vw	631(5) [1]	627	620(4) [2]	615
v ₂₆	C–H Def. o.o.p.	551vw	551w	554(<1) [2]	551	554(4) [<1]	551
v ₂₇	C–H Def. o.o.p.	529w	-	548(3) [<1]	560	519(5) [<1]	546
v ₂₈	N=S=O Def. o.o.p.	486vw	-	427(1) [<1]	429	413(3) [<1]	423
v ₂₉	Skeletal Def.	419m	-	425(10) [<1]	430	407(13) [<1]	411
v ₃₀	C–Cl Def. i.p.	-	354vw	361(9) [<1]	364	348(21) [4]	348
v ₃₁	Skeletal Def.	-	340vw	345(7) [<1]	344	342(2) [<1]	343
v ₃₂	C – Cl Def. i.p. + N=S=O Def. i.p.	-	-	242(2) [<1]	242	240(5) [<1]	239
v ₃₃	Torsion N=S=O	-	-	238(2) [<1]	244	234(5) [<1]	239
v ₃₄	Def. C–N=S	-	-	124(1) [<1]	126	139(1) [2]	139
v ₃₅	Torsion Skeletal	-	-	99(<1) [<1]	108	99(<1) [<1]	106
v ₃₆	Torsion Skeletal	-	-	57(<1) [<1]	79	52(<1) [<1]	72

^a Stretch.: stretching; Def.: deformation; Asym.: antisymmetric; Sym.: symmetric; 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.

Table 3. Experimental and calculated ^1H NMR chemical shifts for *p*-chlorosulfinylaniline (200 MHz, CDCl_3 , TMS).

H^{a}	δ [ppm], multiplicity J [Hz]	δ [ppm],
	Experimental ^a	Theoretical ^b
C(2)H	7.12, m $J_{1,2}=6.36$	8.78
C(3)H	7.07, m $J_{2,1}=6.36$	7.31
C(5)H	6.62, m $J_{3,4}=6,78$	7.06
C(6)H	6.58, m $J_{4,3}=6,78$	7.03

^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 (CDCl_3 , 50 MHz) and calculated data of *p*-chlorosulfinylaniline.

C ^a	Chemical shift (δ) (ppm)	
	Experimental	Theoretical ^b
C(1)	128.53	128.86
C(2)	129.58	133.56
C(3)	128.43	132.95
C(4)	128.44	151.14
C(5)	128.43	132.04
C(6)	128.43	133.26

^a For atom numbering see Fig. 1.

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

Figure 1

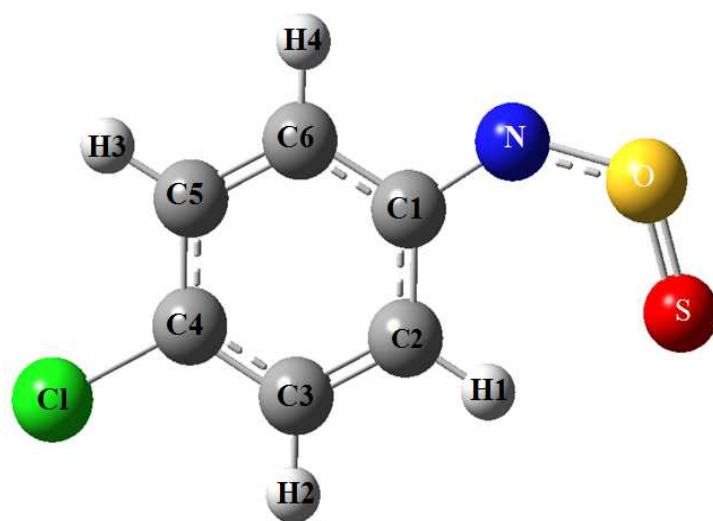


Figure 2

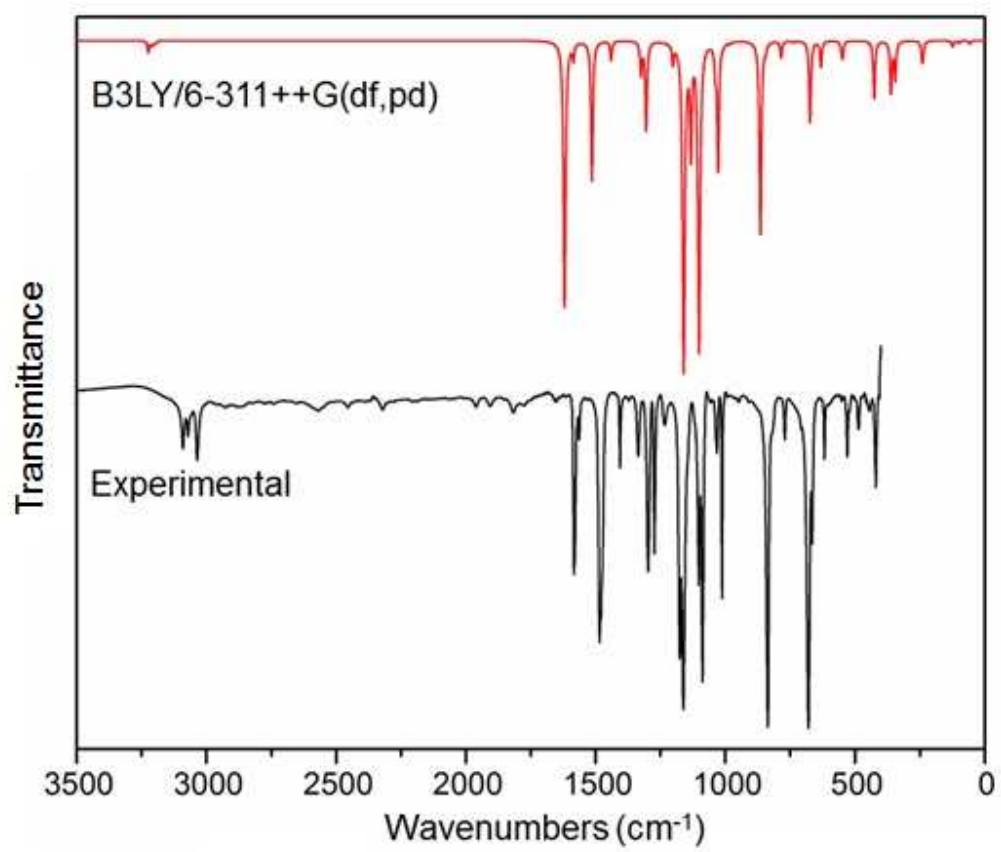


Figure 3

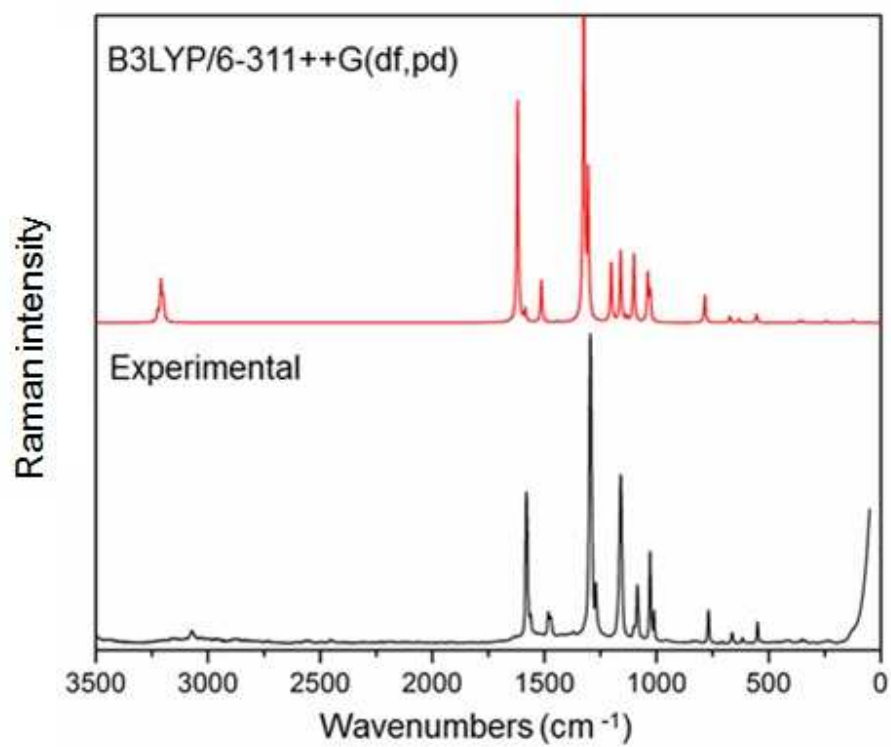


Figure 4

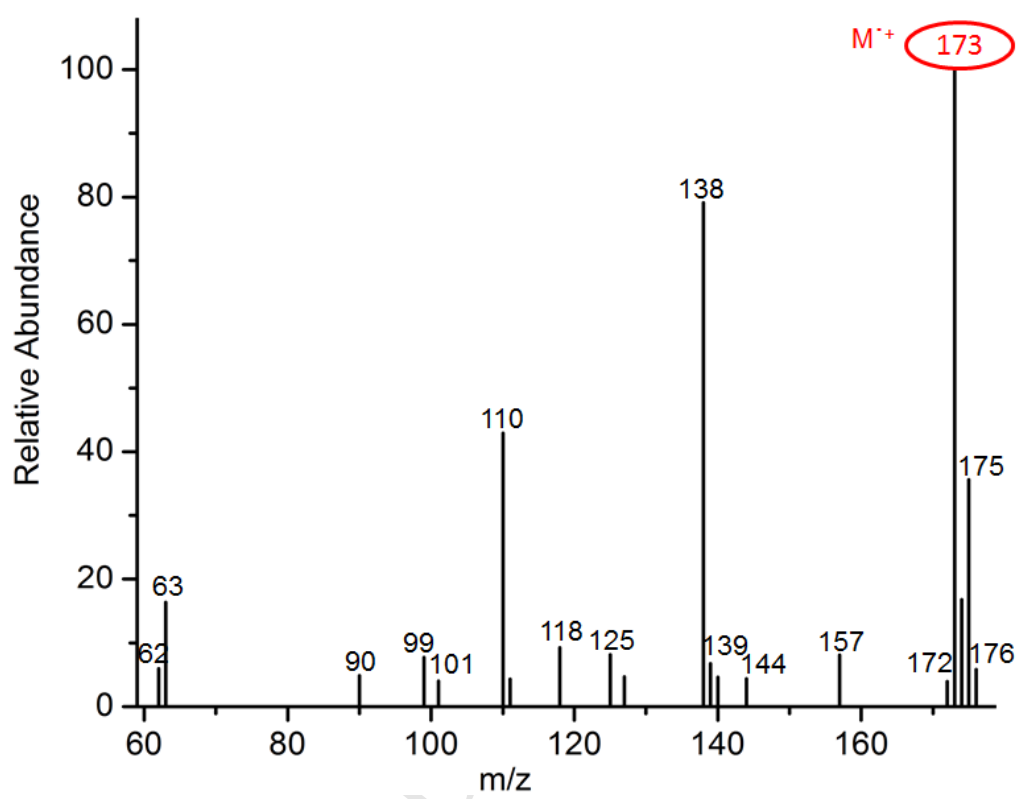
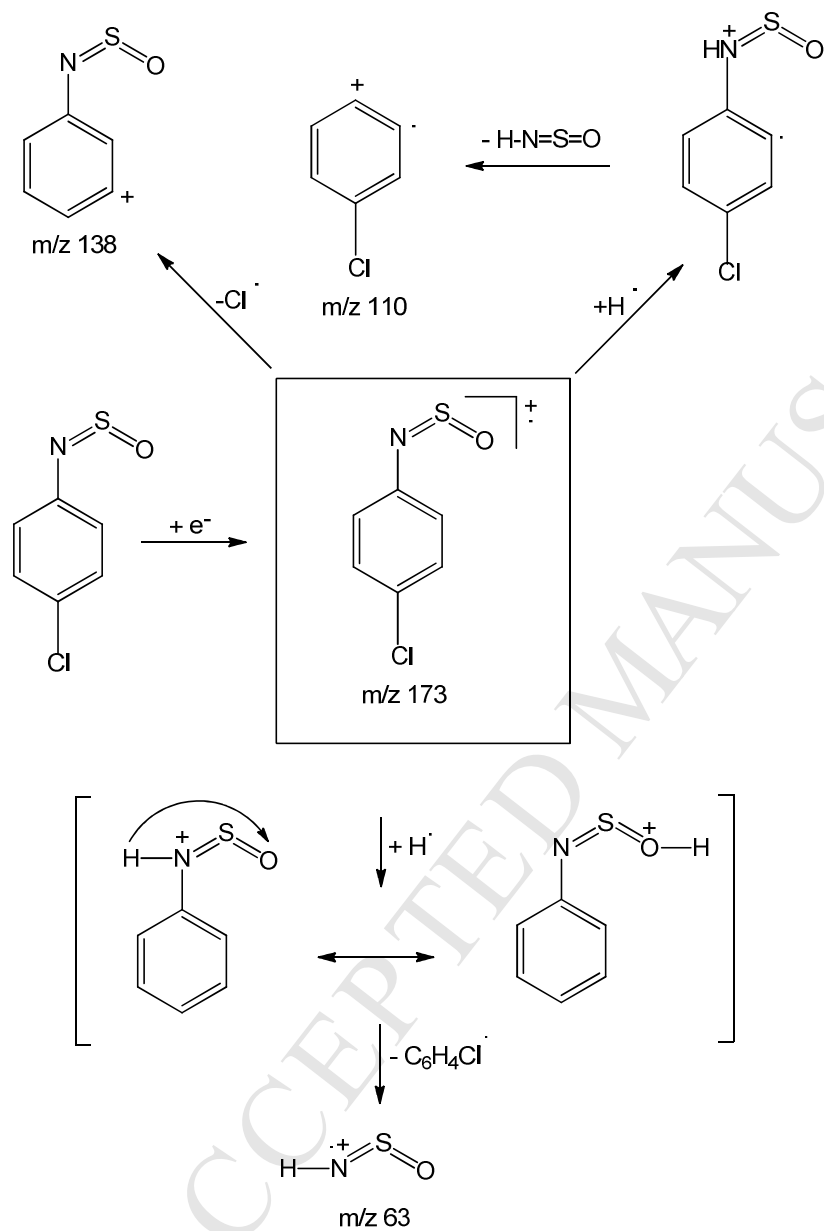


Figure 5



Highlights

- Theoretical calculations predict the *syn* form.
- Chlorinated sulfinylaniline was prepared in good yield.
- The spectroscopic properties of the compound were examined by FT-IR, NMR and Mass techniques.
- Vibrational, NMR and Mass assignments were provided by using experimental and theoretical data.