



On the search of cumulative effect of fluoro-substituents in the structural and vibrational properties of sulfinylanilines: Study of 3,4-difluorosulfinylaniline and 2,3,4-trifluorosulfinylaniline

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ABSTRACT

The study of substitution effects on the structural and vibrational properties of a series of recently reported mono fluoro-substituted sulfinylanilines proceeds a step forward with the present study of 3,4-difluorosulfinylaniline and 2,3,4-trifluorosulfinylaniline. These substances were synthesized and characterized by FTIR, Raman and NMR spectra, which were subsequently compared with theoretical spectra, obtained by quantum chemical calculations at different levels of theory. The number of signals in the vibrational spectra, together with the analysis of the potential energy surface of both compounds reveal the presence of stable conformers possessing the angular N=S→O group in a *syn* conformation of the C–N and S→O bonds and coplanar with the ring plane. According to the Natural Bond Orbital analysis performed, the prevalence of a given structure of the stable *syn* conformer over other local minima of the potential energy surface obtained upon rotation around the N=S and C–N bonds is a consequence of different orbital interactions. The planar conformation predicted for stable minima are stabilized by conjugation between the π -systems of the N=S→O group and the ring and by a weak orbital interaction between oxygen and the *ortho* hydrogen closest to it.

1. Introduction

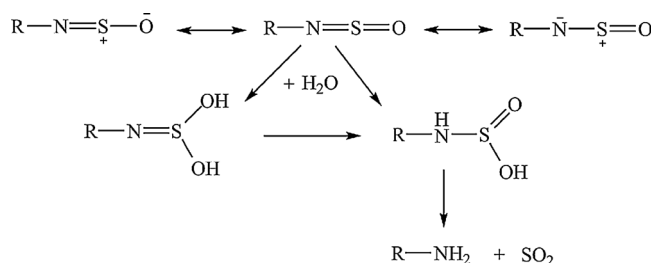
As a substituent, fluorine is rarely ineffective and produces interesting effects not only on chemical properties but also on biological activities of fluorinated compounds. A recent review deals with the significant fluorine effects in nucleophilic, electrophilic, radical and transition metal-mediated fluoroalkylation reactions in comparison with either non-fluorinated or fluorinated counterparts with different numbers of fluorine atoms [1]. Wiberg and Rablen determined that the effect of fluorine on the structural parameters of benzene ring is mainly related to polarization. The only cases in which fluorine was found to be a π -donor were those where a full positive charge may be stabilized. They observed that an increase in electronegativity of X leads to a decreased C–X bond length (X: substituent), an increase in the C–C–C bond angle and a decrease in the C–C bond lengths adjacent to the substituent [2]. Chambers et al. discussed the effect of fluorine as a substituent on nucleophilic aromatic substitution. They found that a fluorine atom located in the *ortho* and *meta* positions with respect to a given functional group may be of variable activating influence, whereas a fluorine located in *para* position is slightly deactivating [3]. In addition, Siodla et al. introduced a few quantum-chemical models for the

interpretation of the substituent effect acting on fluorine atom or a CF₃ group attached to ethene or benzene [4]. Leyva et al. investigated the effects of fluorine substituent on naphthoquinones by NMR spectroscopy; since fluorine is both electron-attracting (σ acceptor) and electron-donating (π donor), the effect of fluorine substituent will depend on its position in the ring. According to ¹H chemical shifts, they observed that a fluoro substituent in *meta* or *para* position behaves as a σ acceptor, while a fluoro substituent in *ortho* position actually acts as a π donor [5].

On the search of the influence of fluorine on structural and vibrational properties of substituted sulfinylanilines, our group recently reported the results for a series of monosubstituted derivatives of parent *N*-sulfinylaniline, i.e. *o*-, *m*- and *p*- isomers of fluorosulfinylaniline (FArNSO) [6–8]. This family of fluorine substituted compounds is supplemented in the present article by the joint study of the di- and tri-substituted derivatives 3,4-difluorosulfinylaniline (3,4-diFArNSO) and 2,3,4-trifluorosulfinylaniline (2,3,4-triFArNSO), respectively. As members of the sulfinyl compounds family, they possess the NSO functional group. The non-linear configuration of this group can possess *syn* and *anti* forms (*syn* or *anti* of the SO bond relative to the CN bond). All studies performed up to date demonstrated that the *syn* form is the most

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Scheme 1. Hydrolysis of *N*-sulfinylanilines.

stable isomer [9,10]. These compounds are generally liquids or low-melting solids and are extremely reactive. Due to their extreme sensitivity towards water these compounds are very prone to decomposition through hydrolysis reactions with the formation of amine derivatives and sulfur dioxide [11] (see Scheme 1).

The outstanding reactivity of the sulfinyl group makes them also suitable for several chemical processes of synthetic utility, particularly cycloaddition reactions, producing four-membered heterocycles with interesting biological activities [12]. Within this context, Veremeichik reported the synthesis of fluorinated sulfonamides via heteroatomic Diels-Alder reaction of 4-fluoro-*N*-sulfinylaniline with bicyclic [2.2.1] heptanes [13] and Makarov et al. performed a detailed structural study of a number of new fluorinated derivatives of benzodithiadiazine obtained by a general method starting from 3,5- and 3,4-difluorosulfinylanilines and 2,3,4-trifluorosulfinylaniline through electrophilic cyclisation reactions [14]. In general, the reactivity of *N*-sulfinylanilines depends on the substituent R attached to the NSO group. It has been demonstrated that electron-withdrawing substituents, such as fluorine and the trifluoromethyl group, increase the reactivity of *N*-sulfinylanilines since the electrophilicity of sulfur atom increases and the majority of the reactions proceeds across the N=S bond [15].

In addition to the structural, conformational and vibrational studies of *o*-, *m*- and *p*- isomers of fluorosulfinylaniline mentioned before, similar studies were performed by our group for *m*- [16] and *p*-chlorosulfinylaniline (ClArNSO) [17] and recently, *p*-trifluoromethylsulfinylaniline (*p*-CF₃ArNSO) [18]. Since the NSO group constitutes the key functional group in several reaction paths [11–15], these studies were devoted to the analysis of the influence of substituents attached to the aromatic ring on the structural and vibrational properties of this functional group. From our findings we concluded that although the vibrational stretches involving the NSO group are coupled in symmetric and antisymmetric modes, the former shows a higher character of SO stretching while the stretching of the NS bond is dominant in the antisymmetric vibration. From these studies it was clear that the effect exerted by the substituent was stronger in the NS bond of the NSO group than in the SO bond. The present work allows us to rationalize similarities and differences among the different fluoro-substituted compounds considering now the increase in the number of fluorine atoms, with the consequent better understanding of the effects involved. Despite the difference in the electron donor-acceptor properties of the NH₂ and NSO groups, it is worth mentioning that for the 2,3- and 2,4-difluoroaniline isomers as well as for the 2,3,4- and 2,3,6-trifluoroanilines an elaborated study of the effect of fluorine atoms on the geometries and normal modes of the aniline derivatives were reported [19,20]. The analysis of the vibrational spectra of these compounds reveals that the presence of the fluorine atoms modifies the wavenumbers of different vibrational fundamental modes and these changes depend on their position in the aromatic ring.

2. Results and discussion

Figs. 1 and 2 show the FTIR and Raman spectra in the 1800–400 cm⁻¹ (or 100 cm⁻¹) spectral ranges, for the liquid samples of

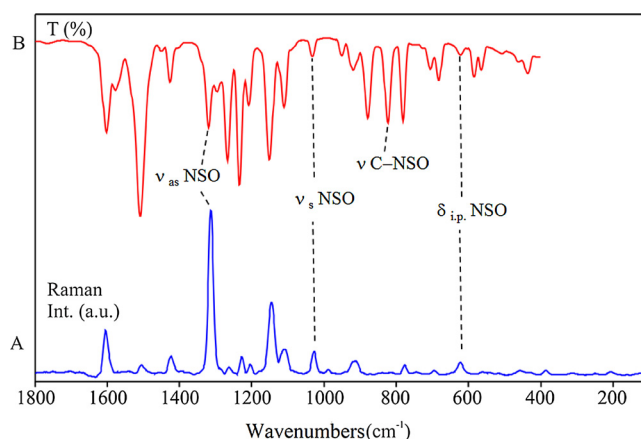


Fig. 1. Experimental spectra of 3,4-difluorosulfinylaniline (3,4-diFArNSO). A) Raman spectrum of the liquid sample recorded in the region of 1800–100 cm⁻¹ at room temperature. B) Infrared spectrum of the liquid sample held between KRS-5 windows recorded in the region of 1800–400 cm⁻¹ at room temperature.

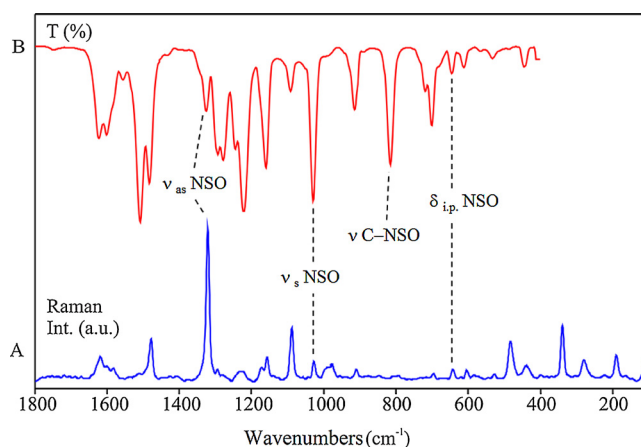


Fig. 2. Experimental spectra of 2,3,4-trifluorosulfinylaniline (2,3,4-triFArNSO). A) Raman spectrum of the liquid sample recorded in the region of 1800–100 cm⁻¹ at room temperature. B) Infrared spectrum of the liquid sample held between KRS-5 windows recorded in the region of 1800–400 cm⁻¹ at room temperature.

3,4-diFArNSO and 2,3,4-triFArNSO, respectively, obtained after purification. The absence of bands attributable to the NH₂ group (between 3500 and 3400 cm⁻¹, region not shown) indicates that the amine precursor has been completely eliminated.

2.1. Conformational analysis and structural characterization

As it was reported for all R-NSO compounds studied so far, the potential energy function for rotation around the NS bond determined by structure optimizations at fixed CNSO dihedral angles for the di- and tri-fluoro-substituted *N*-sulfinylanilines under investigation demonstrated that the most stable conformers possess *syn* configuration of the carbon nitrogen and sulfur oxygen bonds. Theoretical calculations for the studied molecules with the B3LYP/6-311+G(df) approximation predict a local minimum for the *anti* conformation of these bonds and ΔE° (*anti-syn*) = 8.00 kcal mol⁻¹ (ΔG° (*anti-syn*) = 7.42 kcal mol⁻¹) and ΔE° (*anti-syn*) = 6.37 kcal mol⁻¹ (ΔG° (*anti-syn*) = 5.25 kcal mol⁻¹) for 3,4-diFArNSO and 2,3,4-triFArNSO, respectively. These large energy differences indicate that only the *syn* form of both studied molecules would be observed in the experimental spectra. In this context, Lee et al. studied Diels-Alder reactions involving sulfinyl dienophiles and observed that the *syn* forms of X-substituted sulfinyl dienophiles O⁻-S⁺=N-X are more stable than the *anti* ones, and even though the

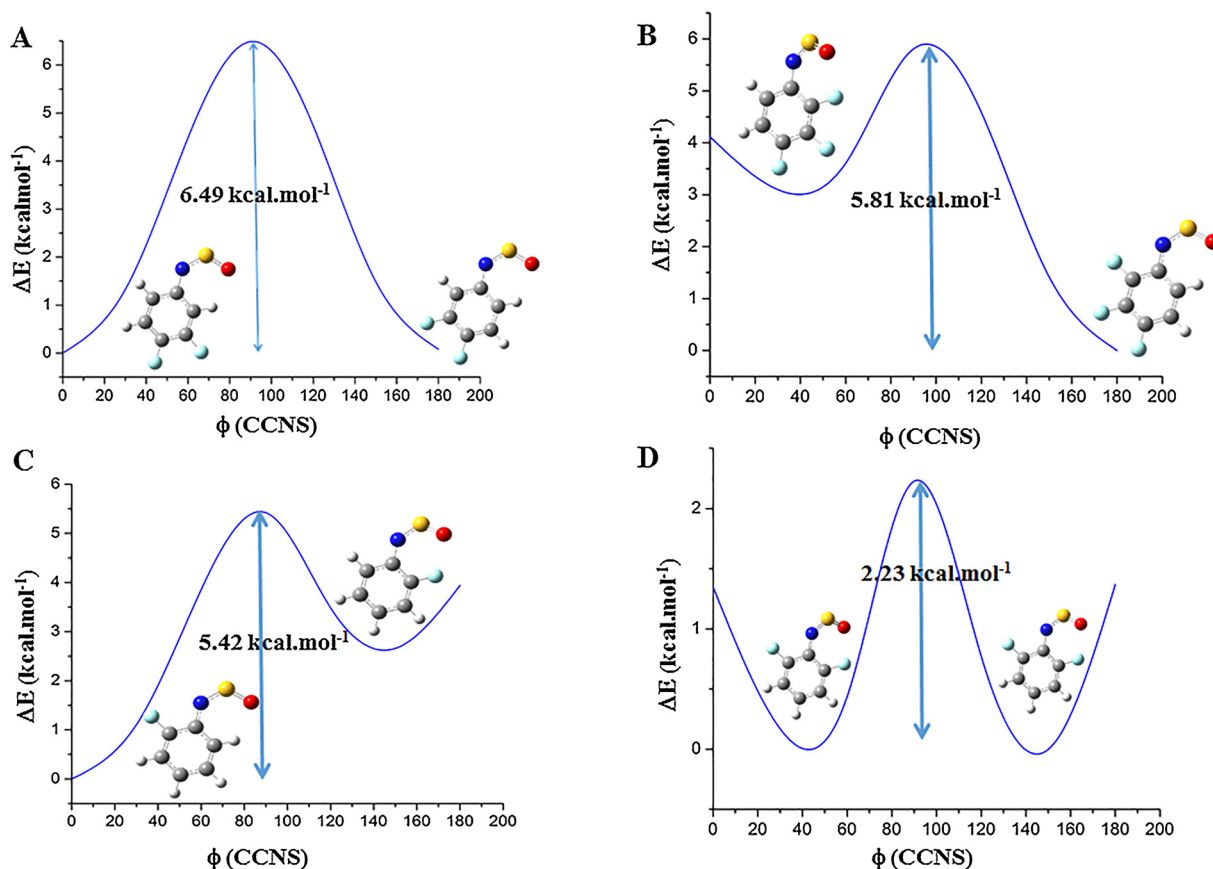


Fig. 3. Calculated rotational barrier around the C–N bond at B3LYP/6-311+G(df) level of theory for: A) 3,4-diFArNSO; B) 2,3,4-triFArNSO; C) *o*-fluor-sulfinylaniline and D) 2,6-difluorosulfinylaniline.

energy difference between the two forms decreases when X becomes more electron-withdrawing, the cycloaddition reactions always start from the *syn* form [21].

Taking the non-linear geometry of the NSO group into account, two possible *syn* conformers for the two compounds are possible, with the oxygen atom of the sulfinyl group closer or further away from fluorine atoms. By using the same quantum chemical approximation mentioned before, the rotational barrier around the C–N bond was calculated first by structure optimizations at fixed CCNS angles in steps of 30°. For 3,4-diFArNSO, a 6.49 kcal mol⁻¹ energy barrier for rotation around the C–N bond is predicted. Subsequently, the minima with planar structures were fully optimized at the same level of theory. The conformer with the oxygen atom further away from the fluorine atom at *meta* position is slightly higher in energy by 0.064 kcal mol⁻¹ (see Fig. 3A). Since no imaginary vibrational frequencies were predicted, both forms correspond to stable structures. The high rotational barrier indicates that the free rotation around the C–N bond would be restricted; the small energy difference between both stable minima does not allow us to distinguish which conformer would be present. The corresponding theoretical analysis for 2,3,4-triFArNSO was also performed with the same theoretical approximation; a rotational barrier of 5.81 kcal mol⁻¹ and a considerably higher energy difference of 2.65 kcal mol⁻¹ is predicted between the planar conformer with the NSO group rotated away from the *ortho* fluorine and the non-planar conformer with the NSO group towards the *ortho* fluorine atom (see Fig. 3B). The less stable form possesses a torsional angle of 41°. This large energy difference between the two minima suggests in this case that only a planar *syn* conformer will be observed.

The planar conformations predicted for the minima conformers of 3,4-diFArNSO and 2,3,4-triFArNSO are stabilized by conjugation between the π -systems of the NSO group and the ring and by a weak

orbital interaction between oxygen and the *ortho* hydrogen closest to it (see Section 2.2). The highest energy barrier for rotation around the C–N bond was observed for 3,4-diFArNSO, where both minima are planar, and all stabilizing interactions are feasible. In contrast, the conformers of 2,3,4-triFArNSO (Fig. 3B) and *o*-FArNSO (Fig. 3C) with the oxygen atom close to *ortho* fluorine possess a non-planar orientation of the NSO group due to O...F steric repulsion and considerably higher energies and lower barriers for internal rotation. For 2,6-diFArNSO with fluorine atoms in both *ortho* positions both conformers are non-planar and the energy barrier decreases even more (see Fig. 3D) [22]. Although intramolecular interactions between oxygen and the *ortho* hydrogen closest to it contribute to stabilization of planar conformations, other effects are more important (see below). In the present cases, these particular hydrogen bonding interactions might be better assessed as *anti*-hydrogen bonds, already observed in *N*-sulfinylanilines by Mucchall [23] and also noticed in *o*-fluorosulfinylaniline [8]. A feature of such an interaction is the shortening of the C–H bond involved and the consequent blue shift of its stretching frequency.

Fig. 4 shows the optimized molecular structure of the most stable conformer of 3,4-diFArNSO and 2,3,4-triFArNSO; the C–H bond lengths and O...H distance calculated at the B3LYP/6-311+G(df) level are included. The remaining structural parameters are presented in Table 1. Comparing the theoretical structural parameters of the molecules studied in this work with those reported for *p*-fluorosulfinylaniline [6], *m*-fluorosulfinylaniline [7] and *o*-fluorosulfinylaniline [8] (from now *p*-, *m*- and *o*-FArNSO, respectively) at the same level of theory, no remarkable differences were found among them. Zibarev et al. also observed that the geometry of the NSO group in ArNSO compounds is practically independent of the conformation (planar or twisted) as well as of the nature of the substituents [24].

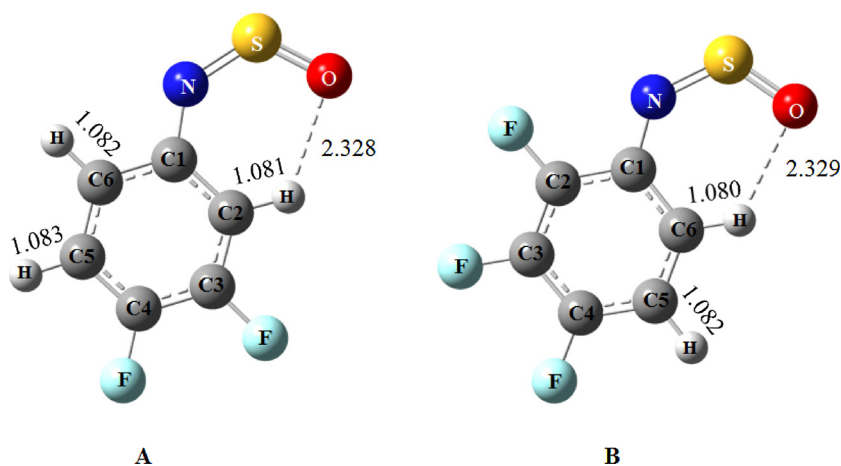


Fig. 4. Molecular models for the most stable conformers of: A) 3,4-diFArNSO and B) 2,3,4-triFArNSO. All C–H bond lengths (Å) and H...O distances (Å), calculated at the B3LYP/6-311+G(df) level of theory, are included in order to show the shortening of the C–H bond as consequence of the formation of the *anti*-hydrogen bond.

Table 1

Structural parameters (Bond lengths (Å) and angles (°)) of 3,4-diFArNSO and 2,3,4-triFArNSO calculated at B3LYP/6-311+G(df) level. For atom numbering, see Fig. 4.

| Structural Parameters | B3LYP/6-311+G(df) | |
|-----------------------|-------------------|-----------------|
| | 3,4-diFArNSO | 2,3,4-triFArNSO |
| S=O | 1.484 | 1.484 |
| N=S | 1.541 | 1.540 |
| N–C1 | 1.387 | 1.379 |
| C1–C2 | 1.410 | 1.409 |
| C2–C3 | 1.379 | 1.385 |
| C3–C4 | 1.393 | 1.391 |
| C4–C5 | 1.386 | 1.386 |
| C5–C6 | 1.384 | 1.385 |
| C1–C6 | 1.405 | 1.410 |
| C2–F | – | 1.327 |
| C3–F | 1.338 | 1.332 |
| C4–F | 1.336 | 1.334 |
| N=S=O | 119.2 | 119.1 |
| C1–N=S | 131.9 | 131.8 |
| N–C1–C2 | 124.4 | 116.0 |
| N–C1–C6 | 116.0 | 125.9 |
| C6–C1–C2 | 119.6 | 118.0 |
| C1–C2–C3 | 118.9 | 121.2 |
| C2–C3–C4 | 121.0 | 119.2 |
| C3–C4–C5 | 120.5 | 121.0 |
| C4–C5–C6 | 119.3 | 119.7 |
| C5–C6–C1 | 120.6 | 120.8 |
| C1–N=S=O | 0.0 | 0.0 |

2.2. NBO analysis

Natural Bond Orbital (NBO) analysis provides an efficient method for studying intra- and inter-molecular interactions and provides information about charge transfer and/or conjugative interactions in molecular systems. The second-order perturbation theory is employed in the NBO analysis to evaluate the donor-acceptor interactions associating a stabilization energy value for each donor \rightarrow acceptor delocalization. For larger values of this energy the donating tendency from electron donors to electron acceptors increases, and the extent of conjugation of the whole system is greater. Delocalization from electron density between occupied Lewis-type (bonding or lone pair) NBO orbitals to formally unoccupied (antibonding or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. These interactions are observed as an increase in electron density in the corresponding antibonding orbital, with the consequent weakening of the bond and its elongation [25]. In the present case NBO analysis was performed on the title molecules with the DFT/B3LYP/6-311+G(df) approximation with the aim of explaining the conformation of the

stable minima. The interactions between the nitrogen and sulfur lone pair orbitals with vicinal antibonding orbitals, *i.e.* $lp(N) \rightarrow \sigma^*(S-O)$ and $lp(S) \rightarrow \sigma^*(C-N)$ orbital interactions for 3,4-diFArNSO contributed 15.03 and 9.67 kcal mol⁻¹, respectively, to the stabilization of the *syn* conformation, whereas the corresponding contributions for the *anti* form amount only to 5.73 and 1.01 kcal mol⁻¹, respectively. The same orbital interactions were 14.91 and 9.47 kcal mol⁻¹ for the *syn* form, and 7.10 and 1.32 kcal mol⁻¹, for the *anti* form of 2,3,4-triFArNSO. This confirms the well-known conformational preferences of R–NSO compounds. Moreover, the evident reason for the ubiquitous *syn*-bent CNSO geometry is due to the strong preference for the anti-periplanar orientation of nitrogen lone pair and the highly polar $\sigma^*(S-O)$ antibonding orbital. Therefore, the first referral to N=S=O as a cumulated π -system should be denoted by N=S \rightarrow O with a dative single bond to oxygen atom (S \rightarrow O) [26]. This would also be consistent with the resonance structures shown in Scheme 1 in which the left most resonance structure has significantly higher weight than the well-known N=S=O moiety and the right one because of the larger electronegativity of the oxygen atom.

The relative energy of minima in the potential energy surface for rotation around the C–N bond demonstrates, that a single conformer is expected for 2,3,4-triFArNSO and that both forms shown in Fig. 3A might be present in the case of 3,4-diFArNSO (see Section 2.1). These conformations are stabilized primarily by conjugation between the π -systems of NSO and the ring, and additionally by the formation of intramolecular *anti*-hydrogen bonds. Fig. 5 shows relevant orbital interactions together with the corresponding delocalization energies values. By using the quantum theory of atoms in molecules (AIM) Muchall reported the formation of such an unusual kind of hydrogen bonds in aromatic *N*-sulfinylamines with *ortho* H atoms, with a C...O distance in the range 3.00–4.00 Å [23]. Later, Alabugin et al. explained the electronic basis of such improper hydrogen bonding, as called by the authors, as a result of a subtle balance of hyperconjugation and rehybridization [27]. In a series of complexes of trifluoromethane and different hydrogen-acceptor species the authors claimed that there are no fundamental differences between classical and improper (*anti*-) hydrogen bonding. Adapting their findings to our systems under study, improper hydrogen bonding would likely be observed when the C–H bond lengthening and $lp(O) \rightarrow \sigma^*(C-H)$ hyperconjugative interaction were relatively weak. In addition, the occurrence of improper H-bonding is connected to a natural feature in the molecular structure itself which should allow significant rehybridization of the C–H bond upon formation of the intramolecular interaction. If the molecular structure inhibits rehybridization, a red-shift in the C–H stretching frequency would be observed (classical H-bonding); the opposite effect would be noticeable for improper (*anti*-) H-bonding. By analyzing the proportion of s and p orbitals involved in the formation of the hybrid orbital responsible for the C–H bond, it was proposed that the

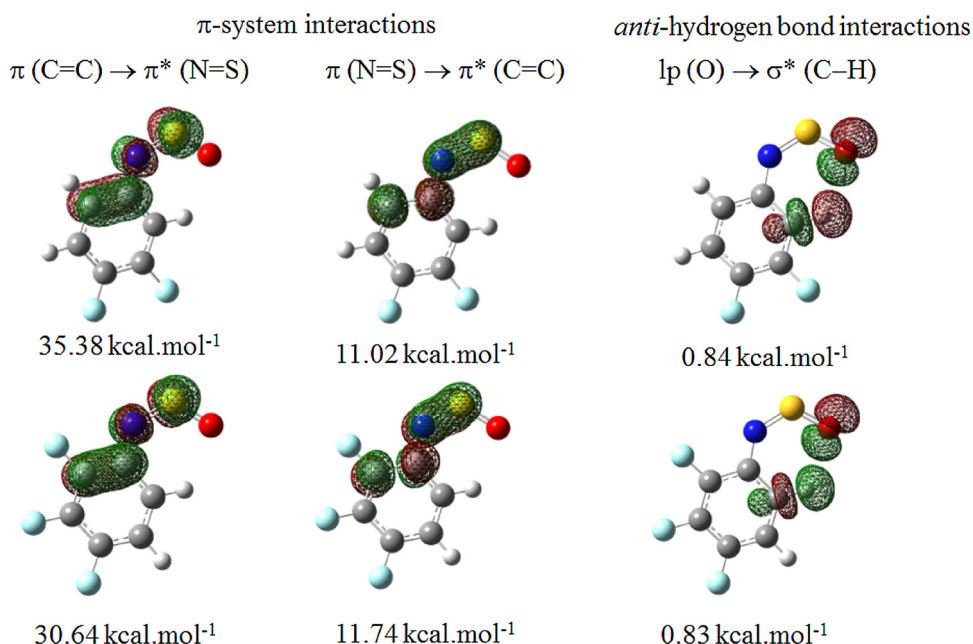


Fig. 5. Relevant orbital interactions together with the corresponding delocalization energies values calculated at B3LYP/6-311+G(df) level of theory for 3,4-diFArNSO and 2,3,4-triFArNSO.

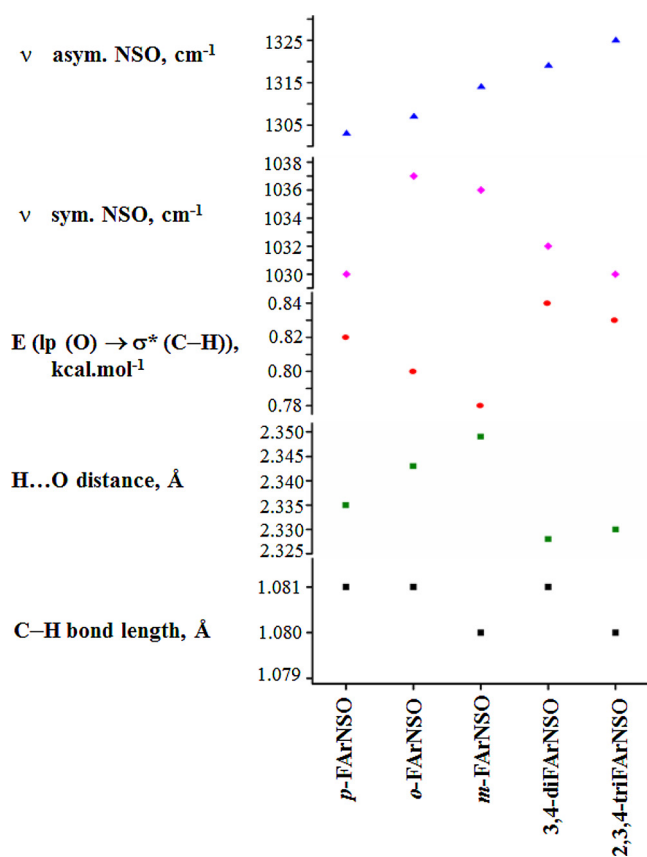


Fig. 6. Correlation of representative parameters of intramolecular hydrogen bonding for mono- and polysubstituted fluoro derivatives of sulfinylaniline.

characteristic C–H strengthening effect, and the consequent blue-shift in the frequency of this bond, is a consequence of an increase in s-character of carbon hybrid orbital in the C–H bond. In order to confirm that, the same kind of phenomenon was also performed in our systems, although in this case it would involve an intramolecular interaction.

Several parameters were analyzed for monofluoro-substituted derivatives of sulfinylaniline and for the present molecules under study. The correlation of these parameters for this series of compounds is shown in Fig. 6.

From the comparison of the theoretical values predicted for the C–H bond lengths involved in the C–H...O interactions and those in other positions in the aromatic ring in all compounds mentioned in Fig. 6 was observed a clear, though small, shortening of this structural parameter. The consequent blue-shift of the stretching frequency was also predicted by the theoretical calculations (see Tables 2 and 3, Vibrational Analysis section). These two features account for the formation of an improper H-bonding, according to the literature mentioned. An average C...O distance of 3.09 Å was found for the series, in agreement with the expected range 3.00–4.00 Å typical for this kind of interaction [23]. Since these two features of the improper hydrogen bonding interaction are fulfilled, it follows that lp (O) \rightarrow σ^* (C–H) hyperconjugative interactions should be weak. This is clear from the delocalization energy values in Fig. 6, which decreased in the mono-substituted series in the *p*- > *o*- > *m*- order and change into larger values for the di- and tri-substituted derivatives. All in all, the values are rather small when compared with typical delocalization values predicted for this type of interaction in systems with classical H-bonding (values larger than 3–5 kcal mol⁻¹, which was the threshold range for the complexes reported in Ref. [27]). The s character in the carbon hybrid orbital in the C–H bond in *p*-, *o*- and *m*-FArNSO was 29.76%, 29.63% and 30.67%, respectively. With an additional fluorine atom, a 30.69% of s character was predicted for this orbital in 3,4-diFArNSO. Since no remarkable difference was observed in the percentage of s character upon increase of fluorine substituents from *m*-FArNSO to 3,4-diFArNSO, no change in the hybridization of the orbital must have occurred. However, the O...H distance decreases slightly (from 2.349 to 2.328 Å) and the delocalization energy accounting for the lp (O) \rightarrow σ^* (C–H) hyperconjugative interaction increased (from 0.78 to 0.84 kcal mol⁻¹). Therefore, it could be postulated that the addition of a fluorine substituent, though remote from the place where the hydrogen bonding takes place, had the effect of modifying the intramolecular interaction by turning it into a “less improper” kind. The addition of a third fluorine atom, as in 2,3,4-triFArNSO, lowered slightly the s character of the carbon hybrid orbital (30.01%) and

Table 2
Experimental and calculated vibrational frequency (cm^{-1}) of 3,4-difluorosulfinylaniline and tentative assignment of main fundamental vibrational modes.

| Mode | Approximate description ^a | Experimental ^b | | Theoretical ^c | |
|------------|--------------------------------------|---------------------------|--------------|-----------------------------|---------------------------|
| | | IR (liq.) | Raman (liq.) | B3LYP/ 6-311 + +G(df,pd) | B3LYP/ 6-311 + +G(d,p) |
| ν_1 | C2–H Stretch. | 3091 w | – | 3229(4)[3] | 3225(4)[4] |
| ν_2 | C–H Stretch. | 3064 w | 3062 w | 3216(< 1)[21] | 3213(< 1)[27] |
| ν_3 | C–H Stretch. | 3032 w | – | 3203(< 1)[12] | 3200(< 1)[15] |
| ν_4 | C–C Stretch. | 1608/1599 m | 1604 m | 1639(37)[50] | 1637(39)[62] |
| ν_5 | C–C Stretch. | 1581/1570 m | – | 1616(22)[1] | 1615(18)[2] |
| ν_6 | C–C Stretch. + C–H Def. | 1510 vs | 1504 w | 1539(100)[6] | 1532(100)[7] |
| ν_7 | C–C Stretch. + C–H Def. | 1427 m | 1424 w | 1449(8)[9] | 1445(8)[10] |
| ν_8 | N=S=O Asym. Stretch. | 1319 m | 1314 vs | 1350(50)[100] | 1343(40)[100] |
| ν_9 | C–C Stretch. + C–H Def. | 1300 w | – | 1321(14)[14] | 1319(26)[42] |
| ν_{10} | C–F Stretch. | 1268 s | 1265 w | 1293(37)[3] | 1284(32)[2] |
| ν_{11} | C–F Stretch. | 1234 s | 1228 m | 1256(21)[32] | 1246(22)[44] |
| ν_{12} | C–C Stretch. + C–H Def. | 1208 m | 1204 w | 1224(5)[< 1] | 1209(5)[1] |
| ν_{13} | C–H Def. | 1152 s | 1145 m | 1157(52)[13] | 1143(27)[5] |
| ν_{14} | C–H Def. | 1120s/1109sh | 1110 m | 1129(64)[17] | 1119(92)[24] |
| ν_{15} | N=S=O Sym. Stretch. | 1032 w | 1028 m | 1044(5)[9] | 1034(10)[14] |
| ν_{16} | C–H Def. o.o.p. + Ring tors. | 951 w | – | 969(1)[< 1] | 962(1)[< 1] |
| ν_{17} | Ring Def. | 924/912 w | 920/912 w | 940(9)[8] | 933(9)[12] |
| ν_{18} | C–H Def. o.o.p. | 877 m | – | 913(16)[< 1] | 909(16)[< 1] |
| ν_{19} | C–NSO | 825 m | – | 841(11)[< 1] | 937(16)[< 1] |
| ν_{20} | C–H Def. o.o.p. | 782 m | 776 w | 796(19)[5] | 791(21)[6] |
| ν_{21} | Def. o.o.p. | 708 w | 694 w | 710(3)[3] | 709(3)[4] |
| ν_{22} | Def. o.o.p. | 681 m | – | 691(0)[< 1] | 697(< 1)[< 1] |
| ν_{23} | N=S=O Def. i.p. | 622 w | 623 w | 634(1)[< 1] | 632(1)[< 1] |
| ν_{24} | Ring Def. | 585 m | – | 632(< 1)[3] | 629(< 1)[4] |
| ν_{25} | Ring Def. | 563 | – | 570(5)[1] | 567(5)[1] |
| ν_{26} | Def. o.o.p. | – | – | 481(< 1)[< 1] | 479(< 1)[1] |
| ν_{27} | C–F Def. i.p. | 461 m | 456 w | 472(< 1)[< 1] | 471(< 1)[< 1] |
| ν_{28} | C–F Def. i.p. | 436 w | – | 441(4)[< 1] | 440(4)[< 1] |
| ν_{29} | C–F Def. o.o.p. | – | 386 w | 399(10)[1] | 397(10)[1] |
| ν_{30} | C–F Def. o.o.p. | – | 307 w | 307(3)[< 1] | 306(3)[< 1] |
| ν_{31} | Skeletal Def. | – | – | 292(< 1)[< 1] | 289(< 1)[< 1] |
| ν_{32} | N=S=O Def. o.o.p. | – | 250 w | 270(3)[1] | 269(3)[1] |
| ν_{33} | Ring Def. | – | 207 w | 204(< 1)[< 1] | 203(< 1)[< 1] |
| ν_{34} | Ring Def. | – | – | 123(< 1)[< 1] | 126(< 1)[1] |
| ν_{35} | Ring Def. | – | – | 118(< 1)[< 1] | 118(< 1)[< 1] |
| ν_{36} | Ring Def. | – | – | 57(< 1)[< 1] | 58(< 1)[< 1] |

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

^b s: strong, vs: very strong; m: medium; w: weak.

^c Relative infrared intensities in parentheses, normalized to 100%; relative activities between brackets, normalized to 100%.

consequently decreased the delocalization energy value of the hyperconjugative interaction (see Fig. 5). This effect might be rationalized if the place where the new fluoro-substituent bonds to the aromatic ring is taken into account: the presence of an electronegative atom with strong electron withdrawing effect close to the functional NSO group might acquire relevance in the electronic effects involved in the C–H...O interaction. The effect of the improper H-bonding on the vibrational symmetric and antisymmetric stretching frequencies of the NSO group for the series of compounds mentioned may be seen from data in Fig. 6 and will be further discussed in the next section.

2.3. Vibrational analysis

The experimental FTIR and Raman spectra of both liquid samples are presented in Figs. 1 and 2. Observed and calculated frequencies (cm^{-1}), together with a tentative assignment for the $3N - 6 = 36$ fundamental modes are listed in Tables 2 and 3. The vibrational spectra were assigned by comparison with the spectra of related molecules, particularly *p*-FArNSO [6], *m*-FArNSO [7], *o*-FArNSO [8], 3,4-difluoroaniline [28] and 2,3,4-trifluoroaniline [19], and on the basis of calculated vibrational frequencies and intensities computed by DFT-B3LYP method with the 6-311 + +G(df,pd) and 6-311 + +G(d,p) basis sets. In addition, theoretical ^{15}N substitution was used to help identifying the vibrational modes expected for the NSO group. Although quantum chemical methods overestimate the force constants at the

exact equilibrium geometry, which results in higher values of calculated harmonic vibrational frequencies than the corresponding experimental ones, the comparison between them shows adequate agreement.

As it was stated in the structural analysis section, the calculated geometric parameters belonging to the NSO group were found to be unmodified with respect to those predicted for *p*-, *m*- and *o*-FArNSO at the same level of approximation. Therefore, no remarkable changes in the vibrational frequencies might be expected. However, the NSO antisymmetric stretching mode frequency increases when the number of fluorine atoms increases. In fact, the NSO antisymmetric stretching was reported in the infrared spectra at 1303 cm^{-1} in *p*-FArNSO, at 1307 cm^{-1} in *o*-FArNSO, at 1314 cm^{-1} in *m*-FArNSO, and assigned now to the signals observed at $1319/1314 \text{ cm}^{-1}$ (FTIR/Raman) and at $1325/1322 \text{ cm}^{-1}$ (FTIR/Raman) in the experimental spectra of 3,4-diFArNSO and 2,3,4-triFArNSO, respectively. For the monosubstituted series the change in the frequency values for this vibrational fundamental mode was attributed to electronic effects regarding the position of the fluorine atom in the aromatic ring [8]. Although the theoretical calculations failed in predicting noticeable differences in the N=S bonds for the mono-substituted series and the compounds analyzed in the present study, from the frequency values predicted it is clear that this bond strengthens as the number of fluorine atoms attached to the aromatic ring increases. This trend might have relevant consequences in reactions where R–NSO compounds participate, particularly those mentioned in the Introduction where the first steps in cycloaddition

Table 3
Experimental and calculated vibrational frequencies (cm^{-1}) of 2,3,4-trifluorosulfinylaniline and tentative assignment of main fundamental vibrational modes.

| Mode | Approximate description ^a | Experimental ^b | | Theoretical ^c | |
|------------|--------------------------------------|---------------------------|--------------|------------------------------|--------------------------|
| | | IR (liq.) | Raman (liq.) | B3LYP/ 6-311 + + G(df,pd) | B3LYP/ 6-311 + G(d,p) |
| ν_1 | C6–H Stretch. | 3093 w | – | 3234(2)[3] | 3230(3)[4] |
| ν_2 | C–H Stretch. | – | 3060 m | 3209(< 1)[12] | 3207(< 1)[12] |
| ν_3 | C–C Stretch. | 1622 m | 1618 m | 1643(39)[32] | 1643(39)[35] |
| ν_4 | C–C Stretch. | 1599 m | 1599 m | 1617(22)[3] | 1617(22)[4] |
| ν_5 | C–C Stretch. + C–H Def. | 1508 vs | – | 1535(100)[2] | 1528(100)[2] |
| ν_6 | C–C Stretch. + C–H Def. | 1482 s | 1478 m | 1503(46)[20] | 1498(50)[20] |
| ν_7 | N=S=O Asym. Stretch. | 1325 m | 1322 vs | 1347(23)[100] | 1339(29)[100] |
| ν_8 | C–C Stretch. + C–H Def. | 1298 m | 1294 w | 1334(8)[7] | 1332(2)[13] |
| ν_9 | C–F Stretch. | 1277 m | – | 1305(28)[9] | 1297(36)[5] |
| ν_{10} | C–F Stretch. | 1244 m | – | 1270(6)[4] | 1260(5)[3] |
| ν_{11} | C–F Stretch. + C–C Stretch. | 1222 s | – | 1239(67)(1) | 1228(62)[< 1] |
| ν_{12} | C–H Def. | 1159s | 1157 w | 1165(61)[2] | 1151(65)[1] |
| ν_{13} | C–H Def. + C–C Def. i.p. | 1092 m | 1089 m | 1106(9)[18] | 1092(15)[18] |
| ν_{14} | N=S=O Sym. Stretch. | 1030 s | 1027 m | 1050(40)[10] | 1038(46)[12] |
| ν_{15} | C–H Def. | – | – | 973(< 1)[< 1] | 969(< 1)[< 1] |
| ν_{16} | Ring Def. | 924/912 m | 909 w | 926(14)[4] | 918(16)[5] |
| ν_{17} | C–NSO | 816 s | – | 840(18)[< 1] | 836(19)[< 1] |
| ν_{18} | C–H Def. o.o.p. | 719 m | – | 731(5)[< 1] | 749(< 1)[< 1] |
| ν_{19} | C–H Def. o.o.p. | – | – | 729(< 1)[< 1] | 727(6)[< 1] |
| ν_{20} | C–H Def. o.o.p. | 701 m | 697 w | 713(10)[2] | 713(10)[3] |
| ν_{21} | N=S=O Def. i.p. | 646 m | 642 w | 653(2)[2] | 649(3)[3] |
| ν_{22} | Ring Def. | 611 m | 605 w | 629(1)[< 1] | 632(1)[< 1] |
| ν_{23} | Ring Def. | 566 w | – | 566(< 1)[< 1] | 567(< 1)[< 1] |
| ν_{24} | Ring Def. | 531 w | 527 w | 532(1)[1] | 529(1)[1] |
| ν_{25} | C–F Def. i.p. | – | 483 m | 487(< 1)[1] | 485(< 1)[1] |
| ν_{26} | C–F Def. i.p. | 445 m | 439 w | 451(3)[< 1] | 448(3)[< 1] |
| ν_{27} | C–F Def. i.p. | – | – | 407(8)[1] | 405(9)[1] |
| ν_{28} | C–F Def. o.o.p. | – | 339 m | 313(2)[< 1] | 312(1)[< 1] |
| ν_{29} | C–F Def. o.o.p. | – | – | 311(1)[< 1] | 311(2)[< 1] |
| ν_{30} | N=S=O Def. o.o.p. | – | 279 w | 283(< 1)[< 1] | 281(< 1)[< 1] |
| ν_{31} | Skeletal Def. | – | – | 261(2)[< 1] | 260(2)[< 1] |
| ν_{32} | C–F Def. o.o.p. | – | – | 229(< 1)[1] | 229(1)[1] |
| ν_{33} | Ring Def. | – | 190 w | 153(< 1)[< 1] | 153(< 1)[< 1] |
| ν_{34} | Ring Def. | – | – | 130(1)[< 1] | 134(1)[< 1] |
| ν_{35} | Ring Def. | – | – | 107(< 1)[< 1] | 107(< 1)[< 1] |
| ν_{36} | Ring Def. | – | – | 55(1)[< 1] | 57(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 activities between brackets, normalized to 100%.

reactions involve an attack to the sulfur center [12–15]. From the results obtained by our group for a series of mono-substituted sulfinylanilines [18] we have recently concluded that even though the vibrational stretching modes that involve the NSO group are coupled in symmetric and antisymmetric modes, the former shows a higher character of SO stretching while the NS stretching is dominant in the antisymmetric vibration. Being this last one the most affected, it is therefore straightforward that frequency shifts upon multiple substitutions in the aromatic ring (fluorine atoms in this case), should be expected. On the other hand, just as it was observed for the NSO symmetric stretching mode in the mono-substituted derivatives, observed at 1030, 1036 and 1037 cm^{-1} in the infrared spectra of *p*-, *o*- and *m*-fluorosulfinylaniline, no remarkable differences in the frequency values were found for this vibration in the present study. This fundamental vibrational mode was attributed to the signals placed at 1032 cm^{-1} (FTIR) and 1028 cm^{-1} (Raman) in 3,4-diFArNSO and 1030 cm^{-1} (FTIR) and 1027 cm^{-1} (Raman) in 2,3,4-triFArNSO. The assignment of these stretching vibrations was further supported by additional calculations: theoretical ^{15}N substitution evidenced significant downshifts of the bands attributable to the NSO antisymmetric and symmetric stretching (8 and 7 cm^{-1} , and 8 and 3 cm^{-1} , for 3,4-diFArNSO and 2,3,4-triFArNSO, respectively, calculated at B3LYP/6-311 + + G(df,pd)), allowing a confident identification of these modes in the experimental spectra.

From the assignment of the vibrational spectra of the title compounds and those reported previously [6–8], the C–N stretching

frequency values were found to be quite independent of the number of fluorine atoms attached to the aromatic ring; it is rather the location of the substituent in the aromatic ring which might exert some influence. In effect, this mode was observed as a medium band placed at 825 cm^{-1} and 816 cm^{-1} in the IR spectra of 3,4-difluorosulfinylaniline and 2,3,4-trifluorosulfinylaniline, respectively, and as an inactive signal in the Raman spectra of both molecules. The corresponding mode was reported at 826 cm^{-1} (FTIR), 822 cm^{-1} (FTIR) and 785 cm^{-1} (FTIR) in *o*-, *p*- and *m*-fluorosulfinylaniline, respectively. Unfortunately, the C–N stretching appears to be involved in several fundamental stretching and bending vibrations, making its assignment to a unique signal and further discussion about the shifts observed difficult.

The C–F stretching mode in aromatic compounds are expected and observed in the region 1000–1360 cm^{-1} [29]. Therefore, the C–F stretching modes were assigned to the strong signals placed at 1268/1265 cm^{-1} (FTIR/Raman) and 1234/1228 cm^{-1} (FTIR/Raman) in the vibrational spectra of 3,4-diFArNSO and to the signals observed in the infrared at 1277 cm^{-1} , 1244 cm^{-1} and 1222 cm^{-1} for 2,3,4-triFArNSO. These frequencies values are higher than those observed in the infrared spectra for the corresponding fundamental vibrational modes in the *ortho*, *para* and *meta* mono-fluorinated derivatives reported (1231 cm^{-1} , 1227 cm^{-1} and 1216 cm^{-1} , respectively).

Table 4
Experimental vs. calculated values at B3LYP/6-311 + G(df) of chemical shifts for 3,4-difluorosulfinylaniline.

| Atoms ^a | Chemical shift δ (ppm) | |
|--------------------|---------------------------------------|------------|
| | Experimental | Calculated |
| (C2)H | 7.84 (1H, m, J = 9, 2.5 Hz) | 8.71 |
| (C6)H | 7.65 (1H, m, J = 2.5, 0.5 Hz) | 6.94 |
| (C5)H | 7.21 (1H, m, J = 9 Hz) | 6.83 |
| C1 | 138.89 (1C, dd, J = 7.54 Hz) | 147.54 |
| C2 | 116.58 (1C, d, J = 18.86 Hz) | 121.84 |
| C3 | 149.73 (1C, dd, J = 252.15, 13.83 Hz) | 156.90 |
| C4 | 150.97 (1C, dd, J = 252.15, 13.83 Hz) | 159.78 |
| C5 | 117.58 (1C, d, J = 18.86 Hz) | 120.04 |
| C6 | 124.27 (1C, d, J = 6.92, 3.14 Hz) | 129.28 |
| C(3)F | -134.20 (1F, d, J = 21 Hz) | -140.83 |
| C(4)F | -130.70 (1F, d, J = 21 Hz) | -131.94 |

^a For atom numbering see Fig. 4.

2.4. NMR analysis

The optimized structures for the *syn* conformers of 3,4-diFArNSO and 2,3,4-triFArNSO at the B3LYP/6-311 + G(df) level of theory were used for the gauge including/invariant atomic orbital (GIAO) in combination with the same approach for calculating ¹H, ¹³C and ¹⁹F chemical shifts [30]. The chemical shifts of aromatic protons and carbon atoms of organic compounds are usually recorded in the range of 7.00–8.00 ppm and 100–150 ppm, respectively; fluorine substituents on a benzene ring absorb in the general region of fluoroalkenes (range between -50 and -220 ppm) and the chemical shifts of fluorobenzenes depend on solvent effects and the position of the fluorine atom in the aromatic ring [31]. Tables 4 and 5 list the characteristic chemical shifts proposed for each studied molecule, respectively. The assignments were performed taking into account the tabulated chemical shifts and coupling constants for these compounds and the ¹³C chemical shifts for the sulfinyl group as a substituent in benzenes [32] and on the basis of the chemical shifts for mono-fluorinated sulfinylanilines previously reported [6–8]. Moreover, theoretical calculations supported this; there is good agreement between the hypothetical and experimental values. It is interesting to notice that the tri-fluorinated sulfinylaniline depicted the lowest chemical shift of the carbon attached to the sulfinyl group (C1). In the mono-fluorinated sulfinylanilines series, the C1 chemical shift increases in the order *ortho* > *para* > *meta*. Therefore, the lowest value found for the tri-fluoro-substituted compound was not unexpected. The fluorine atoms in *ortho* and *para* feature a shielding effect in C1 in 2,3,4-triFArNSO.

Previously, Zibarev et al. observed that the introduction of the sulfinyl group into *para* position of fluorobenzene resulted in a 10 ppm

Table 5
Experimental vs. calculated values at B3LYP/6-311 + G(df) of chemical shifts for 2,3,4-trifluorosulfinylaniline.

| Atoms ^a | Chemical shift δ (ppm) | |
|--------------------|---------------------------------------|------------|
| | Experimental | Calculated |
| (C6)H | 8.15 (1H, m, J = 8.25 Hz) | 8.55 |
| (C5)H | 7.03 (1H, m, J = 8.25 Hz) | 6.64 |
| C1 | 128.53 (1C, dd, J = 8.80 Hz) | 138.14 |
| C2 | 145.20 (1C, dd, J = 260.95, 14.46 Hz) | 153.81 |
| C3 | 140.49 (1C, tt, J = 252.78 Hz) | 147.88 |
| C4 | 151.77 (1C, dd, J = 257.18, 12.58 Hz) | 161.44 |
| C5 | 112.07 (1C, dd, J = 18.86, 3.77 Hz) | 114.60 |
| C6 | 122.82 (1C, dd, J = 8.17, 4.40 Hz) | 128.10 |
| C(2)F | -134.10 (1F, dd, J = 20, 9.4 Hz) | -133.32 |
| C(3)F | -157.30 (1F, t, J = 20 Hz) | -167.10 |
| C(4)F | -127.80 (1F, dd, J = 20, 9.4 Hz) | -129.00 |

^a For atom numbering see Fig. 4.

downfield shift of the ¹⁹F NMR signal. For this reason, they concluded that the NSO group already acts as a strong acceptor with respect to the 4-fluorophenyl ring [33]. The ¹⁹F NMR chemical shifts for both compounds were calculated from the isotropic shielding (σ) as $\delta = \sigma_{\text{ref}} - \sigma + \delta_{\text{ref}}$, using C₆F₆ as reference (calculated $\sigma_{\text{ref}} = 333.6$ ppm at the same approach, tabulated $\delta_{\text{ref}} = -164.9$ ppm) [34]. Hence, experimental values are in general agreement with the calculated ones.

3. Conclusions

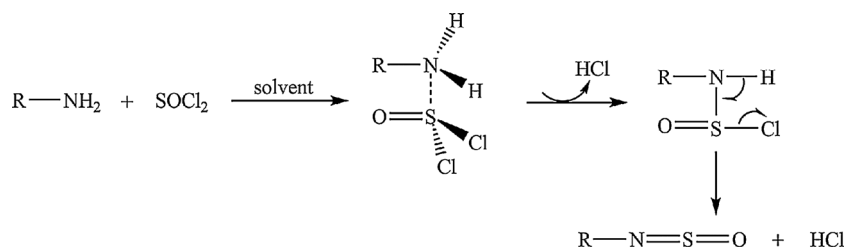
By adjusting the general protocol for the synthesis of sulfinylanilines it was possible to obtain the products 3,4-difluorosulfinylaniline and 2,3,4-trifluorosulfinylaniline. These compounds enlarge the series of fluoro-substituted aromatic NSO compounds studied by our group, already represented by the *o*-, *m*- and *p*-fluorosulfinylaniline. Experimental characterization was achieved by using ¹H, ¹³C and ¹⁹F NMR, together with FTIR and Raman spectroscopies. The experimental spectra were compared and analyzed taking into account those predicted by quantum chemical calculations at different levels of approximation.

The analysis of the potential energy surface revealed the presence of a single observable conformer for 2,3,4-triFArNSO and two conformers with very similar energies for 3,4-diFArNSO. In each case, the global minimum possesses a *syn* configuration of the CN and SO bonds, with planar orientation of the NSO group with respect to the aromatic ring. In both cases, the most stable structure allows an intramolecular interaction between the oxygen atom of the sulfinyl group and the closest hydrogen atom involved in a C–H bond of the aromatic ring. This C–H bond shows features consistent with the so called *anti*-hydrogen bond or improper H-bond, to emphasize its differences with a classical hydrogen bond. Taking into account the results found for the series of mono-substituted fluorosulfinylanilines, a correlation of representative data to evaluate changes upon increase of the number of fluorine substituents in the aromatic was proposed. From this correlation the formation of improper hydrogen bonding was evident for all compounds belonging to the series, demonstrated not only by the effect on the C–H bond length and vibrational frequency but also in the low delocalization energies of the lp (O) \rightarrow σ^* (C–H) hyperconjugative interactions and the increase of the s character of the carbon hybrid orbitals. From the results obtained by the quantum chemical calculations, the effect of the increase of the number of fluorine substituents in the aromatic ring may affect the character of hydrogen bonding as a function of its proximity to the NSO functional group. This statement agrees with our previous results with regard to the NSO stretching modes, *i.e.* even though these stretching modes are coupled in symmetric and antisymmetric modes, the former shows a higher character of SO stretching while the stretching of the NS bond is dominant in the antisymmetric vibration. In other words, being the SO bond involved in the intramolecular interaction as the improper hydrogen bonding in all compounds of the series, the low dispersion of the frequency values found for this vibration is quite expected.

4. Experimental details

4.1. Synthesis

3,4-diFArNSO and 2,3,4-triFArNSO were prepared according to the procedure reported in the literature with some modifications [14,35]. The corresponding aniline derivative (3,4-difluoroaniline (3.12 g, 24.2 mmol) and 2,3,4-trifluoroaniline (2.79 g, 19.0 mmol), respectively) and benzene used as the reaction solvent (13.2 g, 169.2 mmol) were placed in a closed three neck round bottom flask equipped with a Liebig condenser sealed with a CaCl₂ trap. Thionyl chloride (9.84 g, 83.3 mmol) was added drop wise to the mixture with agitation. All the substances were purchased to Sigma-Aldrich Argentina and used without further purification. To prevent the interaction with air



Scheme 2. General mechanism for the synthesis of sulfinylamines.

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 maintaining the reaction temperature in the range between 80 °C and 85 °C for 11 h. The complete disappearance of the signals attributed to the NH₂ group (3400–3500 cm⁻¹ region) in the infrared spectrum of aliquots of the reaction mixture evidenced the final point of the reaction. The liquid products generated were purified by several simple and vacuum distillation cycles in order to facilitate removal of HCl and the excess of SOCl₂ and benzene obtaining a pure liquid as final product: dark green for 3,4-diFArNSO (yield: 91%) and dark purple for 2,3,4-triFArNSO (yield: 92%). The general mechanism of this reaction, which was not described in detail in the literature, probably involves the interaction of the electrophilic sulfur of thionyl chloride with the nitrogen atom of the amine (see Scheme 2).

4.2. Elemental analysis

These studies were conducted using an EXCETER CE-440 analyzer. According to the molecular formula of 3,4-diFArNSO the following abundances (expressed in %) are expected: C, 41.14; H, 1.73; N, 7.99. The elemental analyses for the obtained compound gave the following abundances (in %): C, 41.50; H, 2.06; N, 7.20, which indicated a yield of ca. 91%. Whereas for 2,3,4-triFArNSO, according to its molecular formula, the following abundances (expressed in %) are expected: C, 37.31; H 1.04; N 7.25. The elemental analyses for the obtained compound gave the following abundances (in %): C 38.61; H 1.27; N 7.22, which indicated a yield of ca. 92%.

4.3. Spectroscopic measurements

FTIR spectra of both liquid compounds were recorded at room temperature in KRS-5 windows within the 3500–400 cm⁻¹ range using a Perkin-Elmer GX1 Fourier Transform infrared instrument with a spectral resolution of 4 cm⁻¹. The Raman spectra of both liquid samples were measured at room temperature in the spectral interval from 3500 to 50 cm⁻¹ with a LABRAM-HR Horiba Jobin-Yvon confocal microscope Raman system using a 514.5 nm laser. Raman spectra were carried out with a 100 × objective lens (0.7 NA) and 5.88 mW laser power.

The ¹H, ¹³C and ¹⁹F nuclear magnetic resonance (NMR) spectra of both samples were measured in chloroform-d solution (CDCl₃) with a Bruker Avance 500 spectrometer at frequencies of 500.13, 125.76 and 470.52 MHz, respectively. The chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ¹H, ¹³C spectra and referenced to CFCl₃ for ¹⁹F spectra.

4.4. Computational details

All calculations were performed using the GAUSSIAN 03 program [36]. The method employed is based on the gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [37] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [38]. The optimization calculations were carried out using 6-311+G(df) basis set, the structural parameters after obtaining the

optimized geometries corresponding to the minima on the potential energy surface were employed to calculate the vibrational frequencies and ¹⁵N isotopic substitution by using 6-311 + G(df,pd) and 6-311 + G(d,p) basis sets. The ¹H, ¹³C and ¹⁹F NMR isotropic chemical shielding were obtained by using the gauge-invariant atomic orbital (GIAO) with B3LYP/6-311 + G(df). The GIAO method is one of the most prevalent approaches for calculating nuclear magnetic shielding tensors useful for reliable studies of magnetic properties [30]. Natural population analysis NBO [39], as implemented in the GAUSSIAN 03 program, was performed by using the B3LYP/6-311 + G(df) approximation.

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