

NMR Studies on N-sulfinylanilines:  
Solvent Effects and Complexation with Pyridine

Sanjun Li

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## Abstract

### NMR Studies on N-Sulfinylanilines: solvent effects and complexation with pyridine

Sanjun Li, Ph.D.

Concordia University, 2009

N-sulfinyl compounds RNSO show a wide range of reactivities to water with a change of the substituent R. For several N-sulfinylamines, Mironova and Konoplva proposed that the reaction of a pyridine-H<sub>2</sub>O complex with the N-sulfinylamine is the rate-determining step in its hydrolysis. And later, Cerioni et al. observed complexes of N-sulfinylamines with pyridine by <sup>13</sup>C and <sup>17</sup>O NMR spectroscopies and proposed an equilibrium between “free” and “complexed” N-sulfinylamines. Muchall proposed an anti-hydrogen bond, C–H...O, in N-sulfinylamines through an analysis of the calculated electron density. We are interested in whether the C–H...O interaction has an effect on the reactivity of the sulfur atom in RNSO compounds, especially in N-sulfinylanilines. Using <sup>1</sup>H and <sup>17</sup>O NMR spectroscopies we have obtained experimental evidence for the C–H...O interaction. The <sup>17</sup>O chemical shifts are more sensitive to the polarity or polarizability of a solvent rather than to its H-bonding capabilities, which support the fact that the oxygen atom is involved in an intramolecular C–H...O interaction. The small dependence of the <sup>17</sup>O chemical shift of all N-sulfinylanilines on the H-donating ability of a solvent supports the idea of planar molecules with intramolecular C–H...O bonds. The strength of the C–H...O interaction is dependent on the strength of the S...N interaction in the complexes of N-sulfinylanilines with pyridine. Temperature studies show an increasingly deshielded (shielded) <sup>17</sup>O (<sup>1</sup>H) nucleus upon an increase in temperature, and ortho <sup>1</sup>H

nuclei are deshielded as the pyridine concentration is increased. These changes can be interpreted to demonstrate a strengthening of the C–H...O interaction upon S...N complexation. Equilibrium constants show that an electron donating substituent leads to a weaker complex. It is also shown that a weaker complex possesses a stronger C–H...O interaction based on substituent effects on the temperature dependence of the  $^{17}\text{O}$  nucleus in a complex. It is deduced that a “strong” C–H...O interaction could inhibit complexation, and maybe lead to a reduced reactivity of a N-sulfinylaniline.

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## Dedication

I dedicate my PhD thesis to my parents, my brothers and sisters, to my wife and my sons.

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## List of Abbreviations and Symbols

$\alpha$	H-bond donor acidity scale for a solvent
$\beta$	H-bond acceptor basicity scale for a solvent
$\delta$	chemical shift
$\epsilon$	dielectric constant
$\nu$	stretching frequency
$\phi$	volume fraction
$\pi^*$	polarity-polarizability scale for solvents
$\rho$	density
$\sigma^+$	Hammett substituent constants
$\chi_M$	molar susceptibility
$\chi_V$	volume magnetic susceptibility
a	solvatochromic H-bond donating coefficient
b	solvatochromic H-bond accepting coefficients
b.p.	boiling point
c	concentration
DMSO	dimethyl sulfoxide
HMDS	hexamethyldisiloxane
IR	infrared
$K$	equilibrium constant
M	molar mass
m	medium

m.p.	melting point
n	number of moles
NMR	nuclear magnetic resonance
ppb	parts per billion
ppm	parts per million
Py	pyridine
s	solvatochromic polarity coefficient
s	strong
UV/Vis	ultraviolet/visible
$V_m$	molar volume
$x$	mole fraction



## 1 Introduction

### 1.1 N-sulfinylanilines

The formation of N-sulfinylaniline (**1**) was reported first by Bottiger<sup>[1]</sup> in 1878 and by Michaelis and Herz<sup>[2]</sup> in 1890. Michaelis and Herz used the reaction of aniline with thionyl chloride, SOCl<sub>2</sub>, to produce **1** (Figure 1.1), and later Michaelis used this procedure to prepare seventy five N-sulfinylamines.<sup>[3]</sup> Michaelis' work provided a solid foundation for the research of the structure, properties, reactions and applications of N-sulfinylamines. Even now, many N-sulfinylamines are still prepared by Michaelis' method.

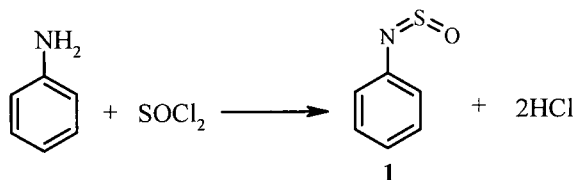


Fig. 1.1 Preparation of N-sulfinylaniline (**1**) from aniline

Although N-sulfinylaniline (**1**) was found so early, Romano et al. only determined its structure in 1999.<sup>[4]</sup> Earlier, there was a controversy about whether N-sulfinyl amines prefer the syn (shown in Figure 1.1, the CNSO torsional angle is 0°) or the anti configuration (the CNSO torsional angle is 180°). For example, Roberts et al. determined the <sup>15</sup>N NMR spectra for N-sulfinylaniline, N-sulfinylcyclohexaneamine, p-methoxy-N-sulfinylaniline and p-nitro-N-sulfinylaniline.<sup>[5]</sup> The <sup>15</sup>N NMR chemical shifts are 57.6 ppm for N-sulfinylaniline and 22.6 ppm for N-sulfinylcyclohexaneamine, relative to

external nitric acid in D<sub>2</sub>O. The deshielding effect on the nitrogen of the aromatic N-sulfinylaniline by 35 ppm was interpreted to show that the NSO group conjugates with the benzene ring, and the electron density of the nitrogen atom in N-sulfinylaniline would therefore be reduced more than that of the nitrogen atom in N-sulfinylcyclohexaneamine. Using <sup>1</sup>H and <sup>13</sup>C NMR, Stufkens et al. suggested that N-sulfinylaniline is planar with a syn configuration, while 2,4,6-trimethyl-N-sulfinylaniline still has a syn configuration, but the dihedral angle between the NSO group and the ring is 90°.<sup>[6]</sup> In contrast to this and based on the stereochemistry of the products from the cycloadditions of N-sulfinylanilines with 1,4-epoxy-1,4-dihydrophthalene, Hanson et al. suggested that N-sulfinylaniline has an anti configuration in the ground state or is in a syn/anti equilibrium.<sup>[7-11]</sup> Della Vedova et al. finally confirmed that N-sulfinylaniline is planar and has a syn configuration in the crystalline state by X-ray diffraction,<sup>[12]</sup> and later that this is also true for liquid and dissolved states by various (especially Raman) spectroscopies.<sup>[13]</sup>

For the electronic structure of the NSO group, it is known that the N=S bond is a four electron bond with the S atom as the positive and the N atom as the negative end of the dipole.<sup>[14]</sup> But for the SO bond, there was an uncertainty about its structure. The NSO group has been described as a “cumulated π-system”,<sup>[15]</sup> but the SO bond has also been described as S<sup>+</sup>-O<sup>-</sup>.<sup>[16-18]</sup> Further <sup>17</sup>O NMR studies on the SO bond showed it to be a “four electron bond” with double bond character, due to the fact that the trend of <sup>17</sup>O chemical shifts for these SO bonds in organic compounds is very similar to that for carbonyl CO bonds.<sup>[19]</sup>

Glass et al. reported the IR spectra for N-sulfinylaniline, N-sulfinylmethylaniline and N-sulfinylethylaniline.<sup>[20]</sup> Stephenson et al. determined the IR spectrum for N-sulfinylaniline,<sup>[21]</sup> and Stufkens et al. reported the IR spectra of <sup>15</sup>N labelled N-sulfinylaniline,<sup>[6]</sup> which allowed the characteristic vibrations of the NSO group to be determined. For example, the frequencies are 1284 cm<sup>-1</sup> for the NS and 1155 cm<sup>-1</sup> for the SO stretch in N-sulfinylaniline. For comparison, the symmetric and asymmetric stretches in SO<sub>2</sub> are found at 1151 and 1361 cm<sup>-1</sup>, respectively, whereas the SO stretch in compounds that have more single bond character for S–O, such as sulfoxides, is at about 1050 cm<sup>-1</sup>.<sup>[22]</sup>

Mironova et al. used pyridine as a catalyst in the hydrolysis study of N-sulfinylanilines (Figure 1.2).<sup>[23]</sup> The proposed mechanism for hydrolysis of N-sulfinylanilines includes the reaction of a pyridine–H<sub>2</sub>O complex with the N-sulfinylanilines in the rate-determining step (Figure 1.3, Py = pyridine). Cerioni et al. were able to observe the complex of N-sulfinylanilines with pyridine in the absence of water in <sup>13</sup>C and <sup>17</sup>O NMR spectra.<sup>[19]</sup> They suggested an equilibrium between “free” and “complexed” N-sulfinylanilines.

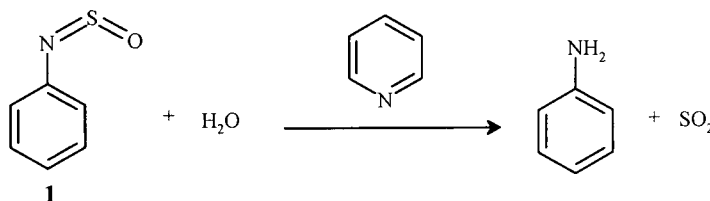


Fig. 1.2 Base-catalyzed hydrolysis of N-sulfinylaniline (1)

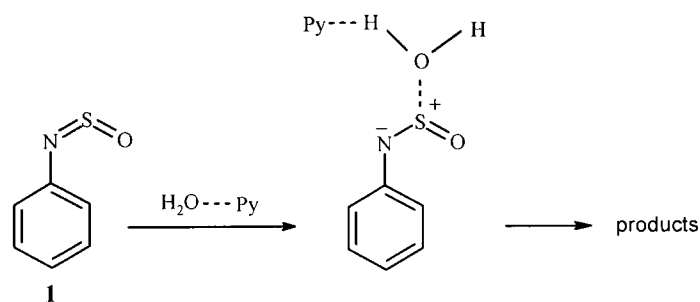


Fig. 1.3 Reaction of the pyridine–H<sub>2</sub>O complex with N-sulfinylaniline (**1**)

Our group is interested in the structure and reactivity of N-sulfinylamines. Muchall studied the electronic structure of the NSO group in CH<sub>3</sub>–NSO and CH<sub>3</sub>–NH–NSO by computational methods.<sup>[24]</sup> In comparison to the SO bond in SO<sub>2</sub>, it was found that the SO bond is best described as a polar double bond, similar to the CO bond in carbonyl compounds. It was also found that the oxygen of the NSO group can form an anti- (or blue-shifting) hydrogen bond (C–H...O interaction) with ortho hydrogen atoms of aromatic N-sulfinylamines.<sup>[25]</sup> Calculated (B3LYP/6-311+G(d,p)) geometrical parameters for the syn unit that lead to the short C–H...O distance are given in Figure 1.4.

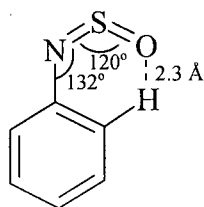


Fig. 1.4 Selected geometrical parameters of N-sulfinylaniline (**1**) from ref. 25

In an anti-hydrogen bond, the C–H stretching frequency is blue shifted, in contrast to the

red shift found for, e.g., the N–H stretching frequency in an N–H...O hydrogen bond.<sup>[26]</sup> According to the electron density, an anti-H bond behaves just like a H-bond. Other than the frequency shift, there is nothing special about it in terms of the H...O interaction.<sup>[27]</sup> Ivanova and Muchall have studied the complexes of N-sulfinylaniline (**1**) with one to three and five water molecules computationally.<sup>[28]</sup> It was shown that water attacks on the sulfur atom perpendicular to the NSO plane. Hydrolysis is concerted and shows two possible mechanisms, as **1** reacts across the N=S or the S=O bond. For a series of substituted N-sulfinylamines, the charge on sulfur correlates well with the activation enthalpy of hydrolysis.<sup>[28]</sup>

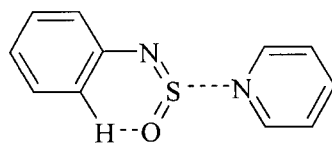


Fig. 1.5 C–H...O and S...N interaction in the complex of N-sulfinylaniline (**1**) and pyridine

In the hydrolyses, the S...O<sub>H<sub>2</sub>O</sub> interaction in the rate-determining step leads to a reaction and to the destruction of the NSO unit. In contrast, the S...N<sub>pyridine</sub> interaction in the complex of pyridine with **1** (Figure 1.5) does not lead to a reaction, and so these complexes can be studied spectroscopically to learn about the reactivity of the sulfur atom and the importance of the C–H...O interaction.

## 1.2 NMR spectroscopic studies on H-bonds

The hydrogen bond (H-bond) is a fundamental weak interaction in organic systems.<sup>[29, 30]</sup> Many physical methods have been used to study the H-bond. For H-bonded systems that involve hydrogen and oxygen atoms,  $^1\text{H}$  and  $^{17}\text{O}$  NMR spectroscopies can be used for direct observation of effects on hydrogen and oxygen atoms.<sup>[31, 32]</sup> Table 1.1 shows the properties of H-bonds,<sup>[30]</sup> and, as follows from the small energy value for a weak H-bond and in analogy to the small shift in IR frequencies, chemical shift changes in weak H-bonds are relatively small and potentially difficult to detect.

Table 1.1 Properties of H-bonds, from ref. 30

	Normal	Weak
Examples	O–H...O=C	C–H...O
Energy (kcal/mol)	4 – 15	< 4
IR $\nu_s$ shift ( $\text{cm}^{-1}$ )	5 – 25%	< 5%
d(H...A) (Å)	1.5 – 2.2	2.0 – 3.0

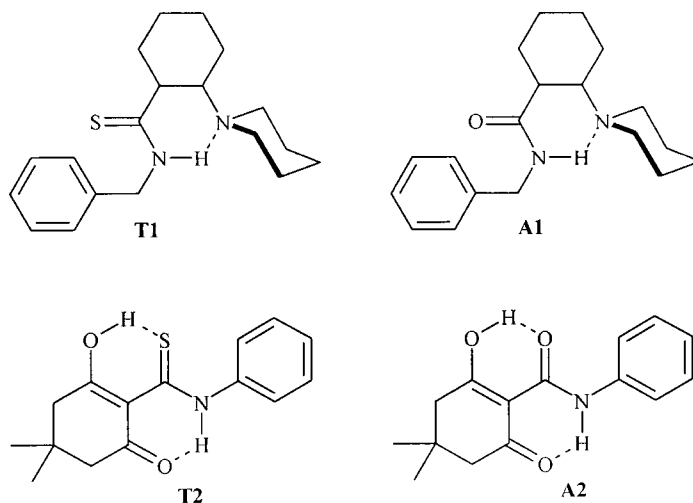
### 1.2.1 $^1\text{H}$ NMR spectroscopy

$^1\text{H}$  NMR spectroscopy is an extremely sensitive method for identifying H-bonds. In 1951 Liddel and Ramsey first identified H-bonds by  $^1\text{H}$  NMR spectroscopy.<sup>[33]</sup> Since then,  $^1\text{H}$  NMR spectroscopy has been widely applied in the study of H-bonds. If a proton is involved in an H-bond, it will be deshielded (shifted to lower field or higher ppm). For

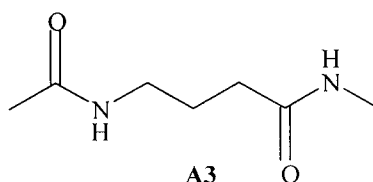
example, the hydroxyl proton in ethanol as a dilute solute in a non-hydrogen-bonding solvent such as  $\text{CCl}_4$  resonates at  $\delta$  0.7 ppm. But in pure ethanol with extensive H-bonding, it resonates at  $\delta$  5.3 ppm. In addition, there is a temperature dependence to the chemical shift.<sup>[34]</sup> Early on, temperature coefficients have been related to the extent of exposure of the H-bond donor atoms to the solvent.<sup>[35]</sup>

Temperature coefficients are known for  $^1\text{H}$ <sup>[34]</sup> and  $^{15}\text{N}$ <sup>[36]</sup> nuclei, and the proton is most well studied. When different types of H-bonds are considered, temperature coefficients are less negative for stronger H-bonds. In general, the signal shifts upfield as the temperature increases, because the hydrogen bond is weakened (lengthened on average). This is termed a negative temperature coefficient,  $\Delta\delta/\Delta T$ . Not surprisingly, temperature coefficients vary with structure (type of interaction, participating functional group, directionality, hybridization of the acceptor atom) and solvent.<sup>[34]</sup>

Temperature coefficients for the  $^1\text{H}$  signal in N–H...N range from  $-17$  to  $-7.5$  ppb/K in thioamides with intramolecular H-bonding; for comparison, the temperature coefficient of non-H-bonded N–H signals is more positive than  $-5$  ppb/K in non-H-bonding solvents.  $\Delta\delta/\Delta T$  for N–H...N in amides is in general smaller and reported as small as  $-4.8$  to  $-1$  ppb/K, even though these amides and thioamides are not comparable in structure.<sup>[34]</sup> Direct comparisons are provided for **T1** and **A1**, where  $\Delta\delta/\Delta T$  for the  $^1\text{H}$  signal in N–H...N in the thioamide is  $-14$  ppb/K, that in the amide is  $-9.3$  ppb/K; and for **T2** and **A2**, where  $\Delta\delta/\Delta T$  for  $^1\text{H}$  in N–H...O in the thioamide is  $-2$  ppb/K whereas that in the amide is  $-1$  ppb/K. Some  $\Delta\delta/\Delta T$  for  $^1\text{H}$  in N–H...O in thioamides range from  $-4$  to  $-2$  ppb/K.<sup>[34]</sup>



For diamides, the size of the temperature coefficient has been related to the change in IR intensity. For the two N–H in **A3**,  $^1\text{H}$  in N–H...O shows  $-9.8$  ppb/K that corresponds to a large decrease in IR intensity upon a raise in temperature, whereas the non-interacting N–H only shows  $-2.5$  ppb/K and the relative intensity of the IR band hardly changes.<sup>[37]</sup>



Temperature coefficients for  $^1\text{H}$  in intramolecular O–H...O interactions in complex alcohol structures in DMSO are about  $-1$  ppb/K.<sup>[38]</sup> While the literature contains many reports on N–H and O–H temperature dependences, not much is reported for C–H. In acetone/water mixtures of different composition, from the data reported for three different temperatures, the temperature coefficient for the methyl protons of acetone can



be estimated to be about  $-2$  ppb/K.<sup>[39]</sup> In t-butanol/water mixtures, it is about  $-3$  ppb/K for the methyl protons. The C–H...O interactions in both systems are anti-H bonds.<sup>[40]</sup>

### 1.2.2 $^{17}\text{O}$ NMR spectroscopy

There are three stable oxygen isotopes,  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ . As  $^{16}\text{O}$  and  $^{18}\text{O}$  both have a nuclear spin of  $I = 0$ ,  $^{17}\text{O}$  with  $I = 5/2$  is the only NMR active nucleus. In practice, the detection of  $^{17}\text{O}$  signals is often difficult because of the low natural abundance (0.037%) of  $^{17}\text{O}$ . The calculated receptivity of  $^{17}\text{O}$  nuclei is about  $10^{-5}$  that of protons. As the  $^{17}\text{O}$  nucleus ( $I = 5/2$ ) has a quadrupole moment, for diamagnetic species the quadrupole relaxation mechanism dominates and leads to short relaxation times  $T_1$  and  $T_2$ . These short relaxation times give rise to large linewidths. For small molecules these are from several tens to several hundred Hz (compared to  $< 1$  Hz for  $^1\text{H}$ ). To improve the signal to noise ratio (needed for accurate measurements of linewidths or intensities), isotopically enriched samples have been used.<sup>[41]</sup> But nowadays, with high field spectrometers, natural abundance samples are sufficient to record good  $^{17}\text{O}$  spectra for small molecules, especially for terminal (doubly bonded) oxygen systems.<sup>[42]</sup>

#### 1.2.2.1 Studies on intramolecular H-bonds

In the early 1960s, Christ et al. studied intramolecular H-bonds in the enol of acetylacetone ( $\text{A}$ ,  $\text{R} = \text{R}' = \text{CH}_3$ , Figure 1.5) by  $^{17}\text{O}$  NMR spectroscopy.<sup>[43]</sup> The fact that only one signal was observed at 269 ppm for the two oxygen atoms suggested an

intramolecular hydrogen bond and fast chemical exchange, so that only the average of the two extreme oxygen environments could be seen.

In 1967, Gorodetsky et al. studied the intramolecular H-bond in the two enol tautomers of nonsymmetric  $\beta$ -diketones (**A**, Figure 1.6).<sup>[44]</sup> For each enol pair with its two distinct oxygen atoms, only one  $^{17}\text{O}$  signal again indicated the existence of fast chemical exchange. While there are two H-bonds, only one average signal was observed. Two signals were observed for the enol of 1,2-cyclohexanedione (**B**, Figure 1.6) due to slow chemical exchange.<sup>[44]</sup> Boykin et al. also observed intramolecular H-bonds in the related 2,5-dihydroxybenzoquinone (**C**, Figure 1.6).<sup>[45]</sup>

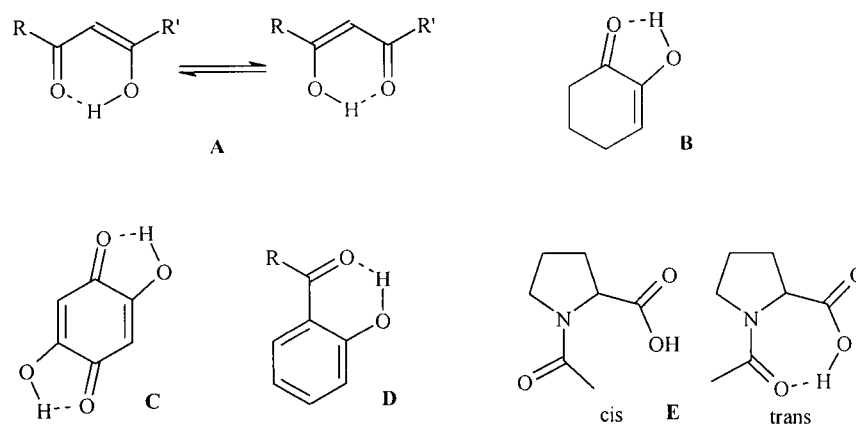


Fig. 1.6 Reference compounds for intramolecular H-bonds

In contrast to these equilibrating system, Fiat et al. studied acetophenones (**D**,  $\text{R} = \text{CH}_3$ ) Figure 1.6) and benzaldehydes (**D**,  $\text{R} = \text{H}$ , Figure 1.6).<sup>[46]</sup>  $^{17}\text{O}$  signals for the ortho-hydroxyl isomers were found at higher field, by about 24 ppm, than expected based on the signals in the para isomers, which was taken as evidence for intramolecular H-bonds.

In a conformational analysis of N-acetyl-L-proline (**E**, Figure 1.6), Lauterwein et al. reported two sets of signals for the  $^{17}\text{O}$ -enriched carboxyl and amide groups, indicating the existence of cis and trans conformers obtained from rotation about the N–C bond.<sup>[47, 48]</sup> Upon dilution with acetone, downfield shifts were observed for both  $^{17}\text{O}$  amide signals, with the larger concentration dependence for the cis isomer. This was taken as evidence for an intramolecular H-bond in the trans conformer, where the amide  $^{17}\text{O}$  nucleus would not be experiencing large changes in environment upon dilution. In the cis isomer, on the other hand, the amide  $^{17}\text{O}$  nucleus would be exposed to the solvent and therefore report on a change in solvation.<sup>[47, 48]</sup>

More examples are given in a comprehensive account by Boykin.<sup>[49]</sup>

### 1.2.2.1 Studies on intermolecular H-bonds

Intermolecular H-bonds were studied by  $^{17}\text{O}$  NMR spectroscopy in the solutions of formamide (**F**, Figure 1.7),<sup>[50]</sup> N-methylformamide,<sup>[50]</sup> N,N-dimethylformamide,<sup>[50]</sup> 1-methyl-2-pyrrolidinone,<sup>[51]</sup> 1-ethyl-2-pyrrolidinone (**G**, Figure 1.7)<sup>[51]</sup> and substituted benzaldehydes.<sup>[52-56]</sup> Because inert solvents can disrupt the intermolecular interactions of the solute, dilution of the H-bonded systems caused downfield shifts of the  $^{17}\text{O}$  resonances.<sup>[50]</sup> Protic solvents could form new intermolecular H-bonds with solutes, which resulted in the carbonyl  $^{17}\text{O}$  resonances to shift upfield.<sup>[50]</sup> For example, for N-methylformamide, the downfield shift of its  $^{17}\text{O}$  resonance on dilution with acetone was taken to show that the intermolecular amide H-bonds are destroyed by acetone. The

upfield shift of the  $^{17}\text{O}$  resonance on dilution with water showed that stronger H-bonds formed between N-methylformamide and water.<sup>[50]</sup> The downfield shift for the carbonyl  $^{17}\text{O}$  signal of the N-methylformamide monomer (infinite dilution in diethylether) is 52 ppm compared to the fully H-bonded carbonyl signal in water solution.<sup>[50]</sup> For 1-ethyl-2-pyrrolidinone (**G**, Figure 1.7), the stronger the proton-donating ability of the solvent, the greater the upfield shift of the  $^{17}\text{O}$  signal.<sup>[51]</sup> For example, upfield shifts of 2.4 ppm in ethanol and 5.3 ppm in 2,2,2-trifluoroethanol were observed.<sup>[51]</sup>

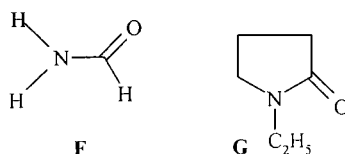


Fig. 1.7 Reference compounds for intermolecular H-bonds

From the above, it is obvious that the  $^{17}\text{O}$  signal is influenced by its environment, as has been acknowledged in the literature.<sup>[50-56]</sup> It is therefore not surprising that other solute-solvent interactions cannot be neglected in  $^{17}\text{O}$  NMR studies. The solvatochromic comparison method developed by Taft et al.<sup>[57]</sup> can be used to unravel multiple solvent effects on properties studied, such as  $^{17}\text{O}$  chemical shifts.

### 1.2.3 Solvatochromic comparison method

The solvatochromic comparison method<sup>[57]</sup> uses the change in position (and sometimes intensity) of a UV/Vis absorption band with a change of solvent with different polarity

and hydrogen bond properties. The solvatochromic equation in the solvatochromic comparison method is

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta$$

where XYZ usually stands for spectral shifts,<sup>[58-63]</sup> reaction rates<sup>[64-66]</sup> and equilibrium constants,<sup>[67]</sup> XYZ<sub>0</sub> is the intrinsic value,  $\pi^*$ <sup>[68]</sup>,  $\alpha$ <sup>[69]</sup> and  $\beta$ <sup>[70]</sup> are solvatochromic parameters for solvents, and s, a and b are solvatochromic coefficients and indicate the responses of the property to polarity and H-bonding.  $\pi^*$  is the polarity-polarizability scale for solvents and indicates the ability of a solvent to stabilize a charge and dipole by its dielectric effect.  $\alpha$  is the H-bond donor acidity scale for a solvent and measures the ability of the solvent to donate a proton to the solute.  $\beta$  is the H-bond acceptor basicity scale for a solvent and measures the ability of the solvent to accept a proton from the solute. Table 1.2 shows the solvatochromic parameters for a small selection of solvents; Table A13 in Appendix A shows the solvatochromic parameters for all the solvents used in these studies.<sup>[57]</sup> From Table 1.2, dimethyl sulfoxide ( $\pi^*$  of 1.00) has the strongest ability to stabilize a charge and dipole by its dielectric effect, and only methanol ( $\alpha = 0.98$ ) has the ability to donate a proton to the solute. The three solvents in Table 1.2 have almost the same ability to accept a proton from the solute.

Table 1.2 Solvatochromic parameters for a small selection of solvents

Solvent	$\pi^*$	$\alpha$	$\beta$
Methanol	0.60	0.98	0.62
Pyridine	0.87	0.00	0.64
Dimethyl sulfoxide	1.00	0.00	0.76

## 2 Objectives

The long-term question is: Does the C–H...O interaction in certain N-sulfinylanilines affect their reactivity? As this is not trivial to answer, we use complexation as a model for reactivity, in particular, we study the complexation of N-sulfinylanilines with pyridine. As the C–H...O interaction is very weak, the effects of this interaction on reactivity might be very small and hard to detect. However, the changes in the spectroscopic properties of the atoms involved in the C–H...O interaction can be used to monitor complexation and therefore reactivity.

We select substituted N-sulfinylanilines (**1** – **4**, Figure 2.1) to study substituent effects on the C–H...O and S...N interactions. As we know, in N-sulfinylaniline the phenyl ring is coplanar with the NSO group, giving an extended  $\pi$ -system with its resonance structures. Therefore, the chosen para-substituted N-sulfinylanilines with an electron donating substituent are expected to increase the electron density on the sulfur atom in the NSO group and the S...N interaction (complexation) should be weaker than that of N-sulfinylaniline. The reverse should be true for  $\pi$ -electron withdrawing groups, and stronger complexes due to a more electrophilic sulfur atom are expected. We also choose ortho-substituted N-sulfinylanilines, because these might be expected to be twisted, depending on the size and electronic nature of the substituent. A twisted conformation would reduce the conjugation of the phenyl ring with the NSO group, and so substituents should have smaller effects on the electron density of the sulfur atom than in the planar systems. While mono-ortho-substituted compounds still retain an ortho-hydrogen atom

for a C–H...O interaction, the substituent effects on this C–H...O interaction should be reflected in the NMR studies.

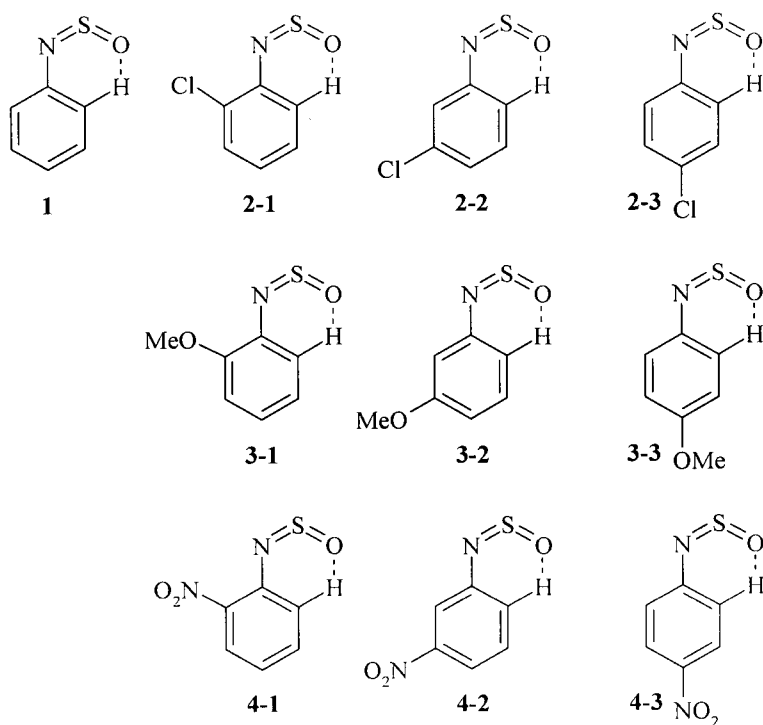


Fig. 2.1 N-sulfinylanilines 1 – 4 used in these studies

As  $^1\text{H}$  and  $^{17}\text{O}$  are directly involved in the C–H...O interaction, we take  $^1\text{H}$  and  $^{17}\text{O}$  NMR as the main methods in our studies. As the systems studied are in liquid phase or solution, we evaluate whether the solvent effects arise from the polarity or from H-bonding interactions. We use the solvatochromic comparison method to separate and analyze the polarity and H-bond effects of solvents. The range of solvents chosen are from H-bonding, protic and polar alcohols to apolar aprotic solvents such as cyclohexane or benzene. The solvatochromic coefficients ( $s$ ,  $a$  and  $b$ ) are expected to differ for the different compounds, and they are analyzed in terms of substituent effects.

Compounds **1** – **4** are complexed with pyridine. The presence of two signals around 400 ppm in the  $^{17}\text{O}$  NMR spectrum shows the presence of a complex.<sup>[19]</sup> At the same time, the  $^{13}\text{C}$  chemical shifts should change to those of the precursor anilines because of the anticipated loss of conjugation.<sup>[19]</sup> This is checked for **1**. Differences in the  $^{17}\text{O}$  chemical shifts in the “free” and the “complexed” species and temperature studies on the equilibria provide more data to find the source of the substituent effect on the S...N and C–H...O interactions. Equilibrium constants are determined to provide independent data on the strengths of the S...N interactions.

As both H and O atoms are involved in the C–H...O interactions,  $^1\text{H}$  NMR temperature studies are used in combination with  $^{17}\text{O}$  temperature studies to provide complementary data. Concentration studies on **1** are expected to give information on the strength of the C–H...O interaction and its dependence on the strength of the complexation.

We also use IR spectroscopy as a survey on **1**, because IR data are in general very useful in H-bonding studies. These studies establish whether the S=O stretching vibration is sensitive enough to report on changes in C–H...O and S...N interactions.

All compounds have to be synthesized, except N-sulfinylaniline (**1**) which is commercially available. All compounds are known and are prepared according to literature procedures.



### 3 Syntheses

The procedure for preparation (Figure 3.1) of N-sulfinylaniline (**1**) is that aniline is dissolved in dry benzene. The benzene has to be dry (dried over sodium metal), as N-sulfinylaniline is susceptible to base-catalyzed hydrolysis. With cooling (ice bath) and stirring, thionyl chloride is dripped into the solution. A large amount of aniline hydrochloride precipitates and the solution turns yellow to orange with the formation of **1**. The solution is heated under reflux until there is no more precipitate. After the excess thionyl chloride and benzene have been distilled off, the N-sulfinylaniline is vacuum distilled.<sup>[3]</sup> N-sulfinylaniline was not synthesized in our lab as it is commercially available.

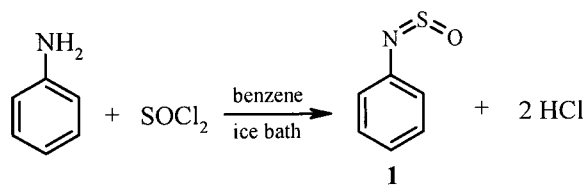


Fig. 3.1 Preparation of N-sulfinylaniline (**1**) from aniline

The general procedure above was followed for the substituted compounds as well. All substituted N-sulfinylanilines (**2** – **4**) were synthesized according to the literature methods.<sup>[3]</sup> On vacuum distillation, the fresh N-sulfinylanilines are bright yellow or orange liquids or solids. All compounds were freshly prepared and not stored for long (less than one week) for hydrolysis reasons. Details on the syntheses can be found in Chapter 8.

## 4 Substituent and solvent effects on $\delta^{17}\text{O}$ in N-sulfinylanilines

### 4.1 Substituent effects in 1 – 4

Figure 4.1 shows the  $^{17}\text{O}$  spectrum of N-sulfinylaniline (**1**), with its narrow signal (the half-width is 117 Hz) at 413 ppm, and Figure 4.2 the  $^{17}\text{O}$  spectrum of para-methoxy-N-sulfinylaniline (**3-3**), with its broader signal (half-width 613 Hz) at 398.64 ppm. For comparison, the  $^{17}\text{O}$  signals for sulfoxides ( $\text{R-SO-R}'$ ) are in the range of  $-10$  to  $70$  ppm,<sup>[49]</sup> those for  $\text{R-O-SO-O-R}$  and  $\text{R-O-SO-Cl}$  are in the range of  $170$  to  $225$  ppm,<sup>[49]</sup> and those for simple amides around  $300$  ppm.<sup>[50]</sup> The  $^{17}\text{O}$  chemical shifts for N-sulfinylanilines are therefore larger than those of related compounds with terminal oxygen atoms. Among the reasons for this is that a) the SO bond in **1** has more double bond character than that in sulfoxides, where oxygen carries a negative charge and b) the electron density on oxygen in the NSO group is lower than that of oxygen in a general  $\text{X=O}$  bond ( $\text{X} = \text{S}, \text{N}$ ), because of the conjugation of the NSO group and the phenyl ring in **1**.

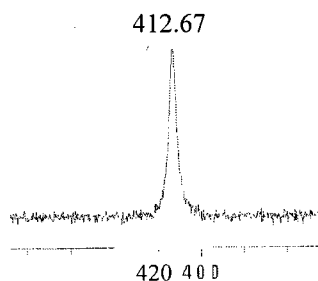


Fig. 4.1  $^{17}\text{O}$  spectrum of neat N-sulfinylaniline (**1**) at  $21\text{ }^{\circ}\text{C}$

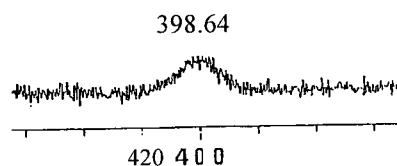


Fig. 4.2  $^{17}\text{O}$  spectrum of neat p-methoxy-N-sulfinylaniline (**3-3**) at 40 °C

Table 4.1 shows  $^{17}\text{O}$  chemical shifts and signal half-widths for N-sulfinylanilines (**1** – **4**). The  $^{17}\text{O}$  chemical shifts for ortho- and meta-chloro-N-sulfinylaniline (**2-1** and **2-2**) are at lower field compared to that for **1**, whereas the signal for the para-chloro-N-sulfinylaniline (**2-3**) shows a smaller chemical shift than that for **1**. Obviously, from the two opposing effects, i.e. electron donation by conjugation and electron withdrawal by induction, the inductive effect is important in the ortho- and meta-chloro-substituted N-sulfinylanilines and the conjugation effect is important in the para-chloro-N-sulfinylaniline. The electron density on the oxygen nucleus is decreased in the order ortho > meta > para and therefore shows a normal distance effect. In contrast to the ortho- and meta-chloro-N-sulfinylaniline, the  $^{17}\text{O}$  signals for methoxyl-substituted N-sulfinylanilines (**3-1**, **3-2** and **3-3**) appear at a higher field compared to that for **1**, due to the dominating  $\pi$ -electron donating effect of the methoxyl group. Finally, the  $^{17}\text{O}$  signals for the nitro-N-sulfinylanilines (**4-1**, **4-2** and **4-3**) are found again at a lower field compared to **1**, showing the strong  $\pi$ -electron withdrawing effect of the nitro group. Cerioni et al.<sup>[19]</sup> and Dans et al.<sup>[71]</sup> also showed these substituent effects for methoxyl and nitro groups in their studies. The substituent effect in the neat compounds is illustrated in Figure 4.3, where the  $^{17}\text{O}$  chemical shift is plotted against the Hammett  $\sigma^+$  constants<sup>[72]</sup> for the three substituents (Cl, OCH<sub>3</sub> and NO<sub>2</sub>) and for hydrogen in para position. The good linear

correlation shows that the substituent effect is transmitted effectively to the oxygen atom of the NSO group. In fact, with this small set of substituents, and for the neat compounds, a better correlation with  $\sigma^+$  is obtained than for a larger set (exactly which were used is unspecified) in chloroform.<sup>[19]</sup>

Table 4.1 <sup>17</sup>O chemical shifts (ppm) and half-widths (Hz) for neat N-sulfinylanilines **1** – **4** (at 40 °C)

	$\delta^{17}\text{O}$	$W_{1/2}$
<b>1</b>	413.75 <sup>a</sup>	117 <sup>b</sup>
<b>2-1</b>	419.16	329
<b>2-2</b>	418.44	322
<b>2-3</b>	410.88 <sup>a</sup>	133 <sup>b</sup>
<b>3-1</b>	409.80	510
<b>3-2</b>	411.60	456
<b>3-3</b>	398.64 <sup>a</sup>	613 <sup>b</sup>
<b>4-1</b>	422.76 <sup>a,c</sup>	136 <sup>c</sup>
<b>4-2</b>	424.20 <sup>a,c</sup>	109 <sup>c</sup>
<b>4-3</b>	424.20 <sup>a,c</sup>	112 <sup>b,c</sup>

<sup>a</sup> Values in chloroform at unknown concentration and 294K from ref. 19: **1** 406, **2-3** 408, **3-3** 391, **4-3** 432 ppm. <sup>b</sup> Values in chloroform from ref. 19: **1** 120, **2-3** 280, **3-3** 140, **4-3** 66 Hz. <sup>c</sup> In benzene solution at 40 °C.

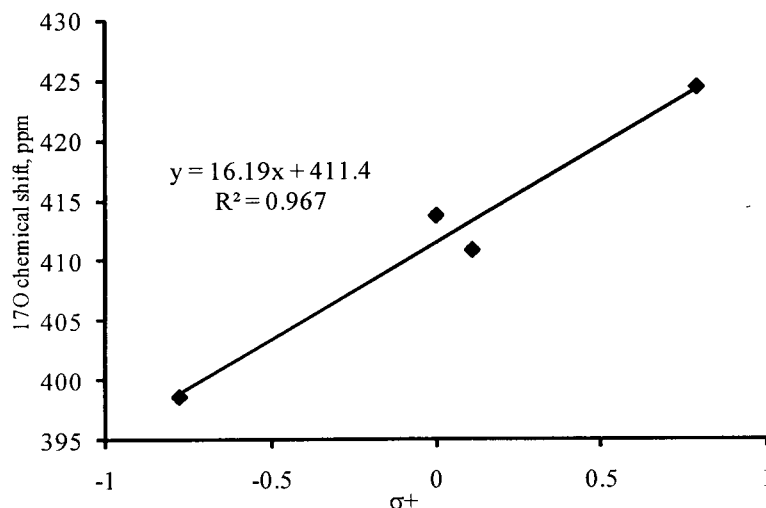


Fig. 4.3 Plot of the  $^{17}\text{O}$  chemical shift of the neat para-substituted compounds (**2-3**, **3-3** and **4-3**) and **1** at 40 °C as a function of the Hammett  $\sigma^+$  constant

The half-widths data in Table 4.1 do not show a substituent effect. They are similar in size or somewhat larger than those reported in chloroform,<sup>[19]</sup> or for  $^{17}\text{O}$  signals in amides, which are on the order of 150 Hz.<sup>[50]</sup>

#### 4.2 Solvent effects in 1 – 4

In these solvent studies, the  $^{17}\text{O}$  NMR measurements were performed with an external standard (water) in a capillary tube. Therefore, all raw  $^{17}\text{O}$  chemical shifts need to be corrected for the difference in volume magnetic susceptibility,  $\chi_v$ , of sample and standard (reference correction). In principle, this is possible, in practice it presents many problems, one of these being the magnetic susceptibility of the solution, which is derived from that of the solute (solvent correction). The following are attempts to address these corrections.

For a superconducting magnet, the correction is

$$\delta_{\text{corrected}} = \delta_{\text{observed}} + 4\pi/3(\chi_{\text{v,standard}} - \chi_{\text{v,sample}})$$

The problem is that  $\chi_{\text{v,sample}}$  is not known, because the sample is an equimolar mixture of solute and solvent. To address this problem, we are considering the following. The volume magnetic susceptibility is related to the molar susceptibility,  $\chi_{\text{M}}$ , through the density,  $\rho$ , and the molar mass,  $M$ , as in

$$\chi_{\text{M}} = \chi_{\text{v}} \cdot M / \rho$$

For a mixture of compounds 1 and 2, the molar susceptibility is given by

$$\chi_{\text{M,mixture}} = x_1 \cdot \chi_{\text{M1}} + x_2 \cdot \chi_{\text{M2}}$$

where  $x$  is the mole fraction ( $x_1$  and  $x_2$  here are 0.5). Experimental values for both  $\chi_{\text{M}}$  and  $\chi_{\text{v}}$  are compiled in, e.g., the CRC Handbook of Chemistry and Physics for many solvents and other compounds.<sup>[73]</sup> Unfortunately,  $\chi_{\text{M}}$  is not known for the N-sulfinylanilines, but it can be calculated quantumchemically. For the solvents used here, experimentally determined and calculated  $\chi_{\text{M}}$  are in very good agreement (see Table A1, Appendix A). Most compounds studied here have more than one conformer, and  $\chi_{\text{M}}$  can differ by as much as 4 ppm between conformers (see Table A2, Appendix A).<sup>[74]</sup> So  $\chi_{\text{M}}$  (as the weighted average for the conformers) can be obtained accurately for all N-sulfinylanilines studied, but as their densities are also not known, the conversion from  $\chi_{\text{M}}$  to  $\chi_{\text{v}}$  introduces an error. Densities are estimated as follows, based on the density changes for related aromatic systems (such as substituted anilines and benzenes). The density for the parent Ph-NSO is known ( $\rho$  1.236 g/mL), substitution of a hydrogen by a chlorine

atom adds 0.2 g/mL, a nitro group adds 0.3 g/mL and a methoxy group adds 0.1 g/mL. A final uncertainty is introduced by the fact that there could be a change in volume as the sample and the solvent are mixed; we are assuming that, if there is any, it is negligible, and so the density of the mixture is taken as the average of the densities of sample and solvent.

Here is a calculated example for the correction for the chloro series (**2-1** to **2-3**) in methanol; the correction is estimated using two different versions.

First version. The weighted average for  $\chi_M$  from Table B2 for o-chloro-N-sulfinylaniline is  $-82.3$  ppm, for m-chloro  $-77.2$  ppm, and  $\chi_M$  for p-chloro is  $-78.2$  ppm. For consistency, we also use the calculated, rather than the experimental,  $\chi_M$  for the solvent. An equimolar mixture in methanol would have a  $\chi_{M,mixture}$  of  $-51.9$  (ortho),  $-49.4$  (meta) and  $-49.9$  (para) ppm. With averages for density (1.1 g/mL) and molar mass (102.8 g/mol) for the mixture, these convert to  $\chi_{v,mixture}$ , or  $\chi_{v,sample}$ , of  $-0.56$  (ortho),  $-0.53$  (meta) and  $-0.53$  (para) ppm. The correction for the external standard, using the calculated  $\chi_v$  for the standard, is therefore  $-0.9$  (ortho),  $-1.0$  (meta) and  $-1.0$  (para) ppm.

Second version. The volume susceptibility can also be expressed by

$$\chi_{v,mixture} = \phi_1 \cdot \chi_{v1} + \phi_2 \cdot \chi_{v2}$$

where  $\phi$  is the volume fraction. The volume fraction is expressed through the calculated molar volume,  $V_m$ , by

$$\phi_1 = n_1 \cdot V_{m1} / (n_1 \cdot V_{m1} + n_2 \cdot V_{m2})$$

The weighted average for  $\chi_v$  for o-chloro-N-sulfinylaniline from Table A2 is  $-0.66$  ppm, for m-chloro  $-0.62$  ppm, and  $\chi_v$  for p-chloro is  $-0.63$  ppm; the weighted averages for the molar volumes are  $109$  mL/mol for o-chloro,  $107$  mL/mol for m-chloro, and  $V_m$  for p-chloro is  $106$  mL/mol. These give values for  $\chi_{v,mixture}$ , or  $\chi_{v,sample}$ , of  $-0.63$  (ortho),  $-0.60$  (meta) and  $-0.61$  (para) ppm, and the correction for the external standard is  $-0.6$  (ortho) and  $-0.7$  (meta and para) ppm.

Both versions employed here lead to similar corrections, and, even though the  $\chi_M$  in the chloro series differ by as much as  $5$  ppm, the necessary correction in each case amounts to only about  $1$  ppm.

Alternatively to the above, the influence of the solvent on the chemical shift can be standardized by extrapolation to infinite dilution. This was done in studies on solvent effects on amides, where  $^{17}\text{O}$  chemical shifts of amides were extrapolated to infinite dilution in water and in acetone.<sup>[50]</sup> Yet, chemical shifts are not always corrected in the literature, and this is the case in the solvent effect study on 2-pyrrolidinone.<sup>[75]</sup> This makes comparisons to literature values of solvent effects difficult. In our solvent studies, we therefore report uncorrected as well as corrected chemical shifts. Crude estimates of the “infinite dilution chemical shift” in the different solvents are gained by using the value of the neat sample and that in equimolar solution.

Tables A3-A12 in Appendix A give the original, experimentally determined  $\delta^{17}\text{O}$  for **1–4**,



the corrections calculated using both version 1 and version 2, and the corrected  $\delta^{17}\text{O}$  determined from the average of the two corrections. For **1**, the corrections are less than 2 ppm. The larger corrections are 1.50 ppm for acetone and 1.43 ppm for methanol. For **2** and **3**, the corrections are less than 1.2 ppm. The larger corrections for **2** and **3** are 1 ppm for acetone and methanol. For **4**, the corrections are less than 1.4 ppm. The larger corrections are 1.24 ppm for acetone. In the following, we will correlate uncorrected and corrected chemical shifts with the solvatochromic parameters for the solvents.

#### 4.2.1 Unsubstituted N-sulfinylaniline (**1**)

As mentioned above, solutions were prepared equimolar in **1** and the solvent. Table 4.2

Table 4.2  $^{17}\text{O}$  chemical shift ( $\delta$  in ppm, original) of N-sulfinylaniline (**1**) neat and in various solvents (1:1 mol%)<sup>a</sup> and their dielectric constants  $\epsilon$

solvent	$\epsilon$	$\delta^{17}\text{O}$	solvent	$\epsilon$	$\delta^{17}\text{O}$
Neat		412.67	Dimethyl sulfoxide	46.45	409.07
1-Butanol	17.51	412.31	Methylene chloride	8.93	410.87
2-Propanol	19.92	412.31	Chloroform	4.89	411.23
1-Propanol	20.45	411.95	Carbon tetrachloride	2.24	414.83
Ethanol	24.55	410.87	Toluene	2.38	414.83
Methanol	32.66	411.59	Benzene	2.27	413.75
Acetone	20.56	412.31	Cyclohexane	2.02	416.27
Pyridine	12.91	411.23; <sup>b</sup> 426.41 <sup>b,c</sup>	Hexane	1.88	416.27
Acetonitrile	35.94	409.79			

<sup>a</sup> At 21 °C. <sup>b</sup> 406 and 413 ppm at unknown concentration and 294K from ref. 19. <sup>c</sup> Signal for the complex of **1** with pyridine.

shows the experimentally determined  $^{17}\text{O}$  chemical shifts of N-sulfinylaniline (**1**), neat and in various solvents, as well as the dielectric constants for each solvent.<sup>[76]</sup> Table A3 in Appendix A lists the corrected chemical shifts.

A clear solvent effect is observed, and the largest changes in  $^{17}\text{O}$  chemical shifts are 3.6 ppm towards lower field for cyclohexane and 3.6 ppm towards higher field for dimethyl sulfoxide (DMSO), both compared to neat N-sulfinylaniline. These solvent-induced changes compare well in size to those observed for 1-ethyl-2-pyrrolidinone (**G**, Figure 1.6), with 26 ppm and 2 ppm towards higher field for trifluoroethanol and DMSO, respectively, compared to neat 1-ethyl-2-pyrrolidinone,<sup>[51]</sup> where the solvent effect mainly stems from H-bonding interactions with the solvents. For 2-pyrrolidinone, which can in addition interact through its N-H bond, solvent effects are observed by 14 (towards higher field) and 9 (towards lower field) ppm shifts for trifluoroethanol and DMSO, respectively, both compared to neat 2-pyrrolidinone.<sup>[75]</sup> Here the solvent effect stems from both the dielectric and H-bonding interactions of 2-pyrrolidinone with the solvents. As has been done for 2-pyrrolidinone,<sup>[75]</sup> the changes for **1** can be explained through small changes in the electronic structure. For example, while the NSO group can,

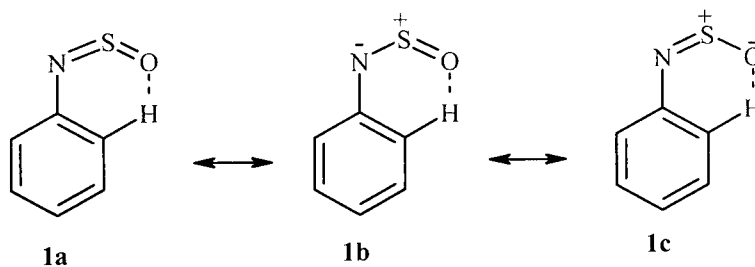


Fig. 4.4 Resonance in the NSO group of **1**

in general, be described through three resonance structures (Figure 4.4), in DMSO **1c**, with its higher electron density on oxygen, seems to have more weight.

The same is true for the other aprotic, polar solvents, acetone and acetonitrile, and the  $^{17}\text{O}$  chemical shifts follow the polarities of these solvents. The protic, polar alcohols can interact strongly with **1** due to their hydrogen bonding ability in addition to their high polarity. From Table 4.2 we can see that  $\delta^{17}\text{O}$  for **1** in alcohols moves to higher field compared to the neat **1**. This is expected, because a) in general, H-bonding induces a shielding of the  $^{17}\text{O}$  atom as the electron density at the nucleus increases,<sup>[29]</sup> and b) we have already mentioned that polar solvents lead to shielded  $^{17}\text{O}$  nuclei. There are two additional observations. First, the extent of shielding follows the dielectric constants of

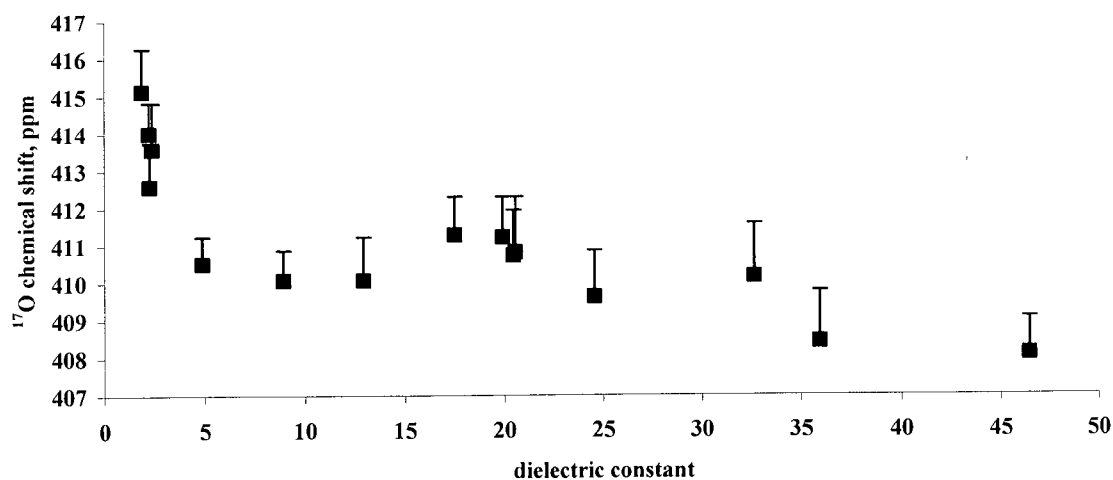


Fig. 4.5 Plot of the  $^{17}\text{O}$  chemical shift (corrected average from the two calculations) of N-sulfinylaniline (**1**) in various solvents (1:1 mol%) against their dielectric constants. The half-error bar shows the range between the uncorrected and the corrected averaged chemical shift

the alcohols except for methanol. And second, comparing the shielding in alcohols and DMSO, we can see that polarity has a larger effect on the  $^{17}\text{O}$  chemical shifts of **1** than H-bonding. From Figure 4.5 we can see that a general agreement is observed between the change in dielectric constant of the solvent and the change in the  $^{17}\text{O}$  chemical shift, but there is no obvious correlation.

In order to quantify the above observation we made on the influence of DMSO, we have used the solvatochromic comparison method<sup>[57]</sup> to analyse the solvent effect on the  $^{17}\text{O}$  chemical shifts further. In Table A13 we show the solvatochromic parameters for the solvents used in our studies. We have used a multiple linear regression analysis to obtain the solvatochromic equation for the  $^{17}\text{O}$  chemical shifts of **1**. We used the original, corrected for external reference, and corrected for solvent (that is, for infinite dilution) from Table A3 in Appendix A. For N-sulfinylaniline (**1**), the solvatochromic equations are as given in Equations 1 – 3.

$$\text{From the original values:} \quad \delta^{17}\text{O} = 417 - 6.7\pi^* - 1.8\alpha - 0.4\beta \quad (1)$$

$$\text{From external reference correction:} \quad \delta^{17}\text{O} = 417 - 7.4\pi^* - 3.5\alpha - 1.2\beta \quad (2)$$

$$\text{From infinite dilution:} \quad \delta^{17}\text{O} = 421 - 13.2\pi^* - 2.5\alpha - 2.4\beta \quad (3)$$

Because the calculated reference corrections were only small, Equations 1 and 2 are similar and both are somewhat different from Equation 3, but while the absolute values in these three equations obviously differ, it is important to note that trends do not change.

For example, all corrections enter the three equations with negative signs, and the  $\pi^*$  contribution is largest for all three. Figures 4.6, 4.7 and 4.8 show the correlations for the original, corrected for external reference and corrected for solvent values with the corresponding calculated (from the solvatochromic equations)  $^{17}\text{O}$  chemical shifts for **1** in various solvents. We can see that the  $R^2$  values increase from the original (0.9018) over the corrected for external reference (0.9154) to the corrected for solvent (0.9204)  $^{17}\text{O}$  chemical shifts. Following Equation 3, the  $^{17}\text{O}$  chemical shift of **1** is therefore more responsive to the polarity or polarizability (factor of -13.2) than to the H-bonding abilities (factor of -2.5 for  $\alpha$  and -2.4 for  $\beta$ ) of a solvent. It is interesting to note that the  $^{17}\text{O}$

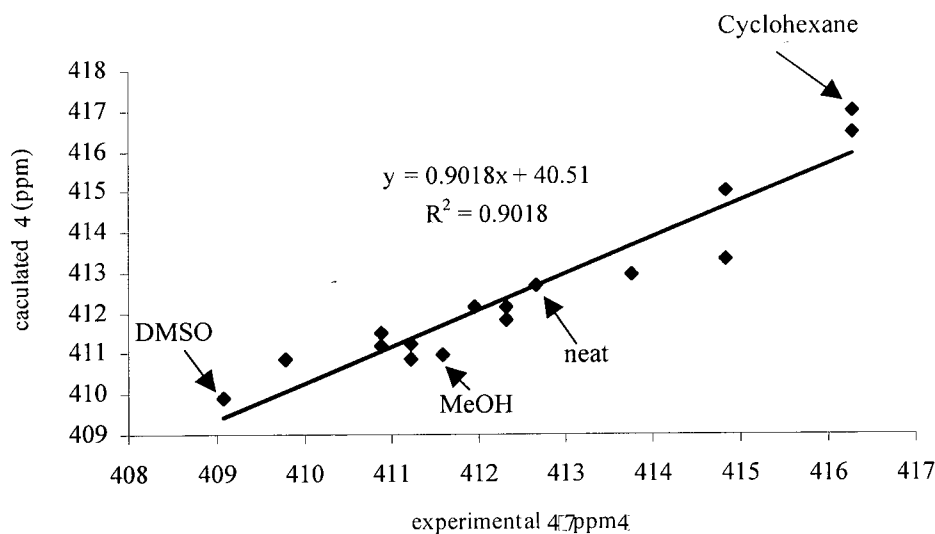


Fig. 4.6 Correlation between original experimental and calculated (from the solvatochromic equation)  $^{17}\text{O}$  chemical shifts for N-sulfinylaniline (**1**) in different solvents at a 1:1 molar ratio

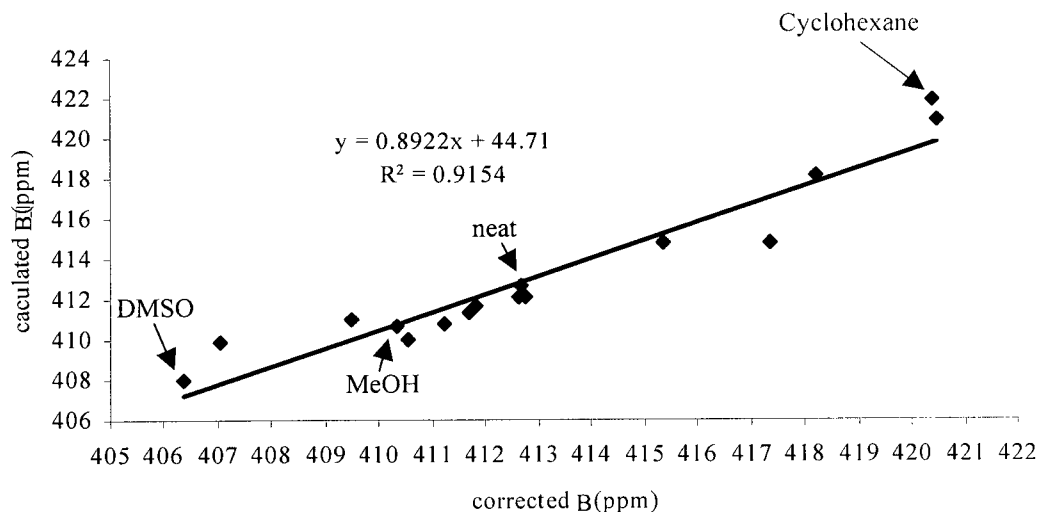


Fig. 4.7 Correlation between corrected for external reference and calculated (from the solvatochromic equation)  $^{17}\text{O}$  chemical shifts for N-sulfinylaniline (1) in different solvents at a 1:1 molar ratio

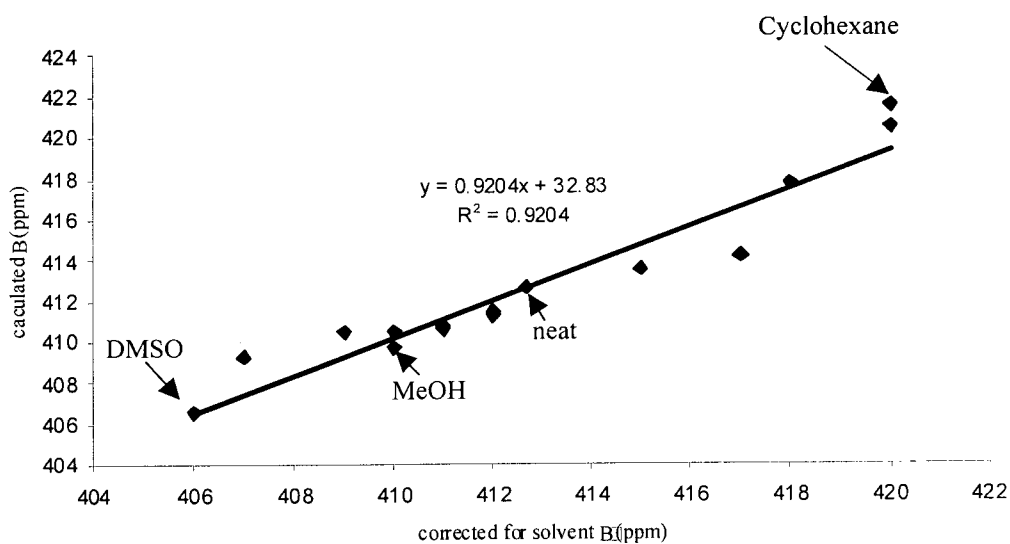


Fig. 4.8 Correlation between corrected for solvent and calculated (from the solvatochromic equation)  $^{17}\text{O}$  chemical shifts for N-sulfinylaniline (1) in different solvents at a 1:1 molar ratio

chemical shift of **1** has about the same sensitivity to the H-donating and accepting ability of a solvent, because **1** does not possess active H-atoms. But because the H-accepting ability of a molecule (here the solvent) is related to its basicity or nucleophilicity, the  $\beta$  value in these equations is an indication of the complexing ability of **1**, which will be addressed in Chapter 5.

Ruostesuo and coworkers also proposed solvatochromic equations for  $^{17}\text{O}$  chemical shifts of sulfinamide (Figure 4.9)<sup>[77]</sup> (Equation 4) and pyrrolidinone<sup>[75]</sup> (Equation 5) in various solvents.

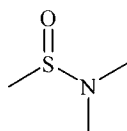


Fig. 4.9 Structure of sulfinamide

$$\text{sulfinamide:} \quad \delta^{17}\text{O} = 78.9 - 0.526\pi^* - 4.35\alpha \quad (4)$$

$$\text{pyrrolidinone:} \quad \delta^{17}\text{O} = 280.3 + 8.1\pi^* - 14.3\alpha + 3.5\beta \quad (5)$$

They chose 1:1 mixtures and did not use any corrections on their chemical shifts. In comparison, Equations 1, 2 and 3 for N-sulfinylaniline have coefficients for both  $\alpha$  and  $\beta$ , whereas for the sulfinamide that is not the case, because it does not possess active H-atoms (and unlike **1** can also not complex on sulfur), and so the value for  $\beta$  is zero. Also, all coefficients for **1** are negative, while those for  $\pi^*$  and  $\beta$  are positive for pyrrolidinone and therefore deshielding for the oxygen nucleus. In contrast to **1** and not unexpected,

pyrrolidinone is more susceptible to the H-bond donating ability of the solvent than to its polarity or polarizability. This could be due to oxygen in **1** already being involved in an intramolecular C–H...O interaction.

#### 4.2.2 Substituted N-sulfinylanilines **2** – **4**

The same analysis as for **1** was done for **2** – **4**. The original data are given in Tables A3 – A12 of Appendix A. Table 4.3 shows the solvatochromic coefficients for original, corrected for external reference and corrected for solvents  $^{17}\text{O}$  chemical shifts of N-sulfinylanilines **1** – **4** in different solvents. For comparison, we discuss the corrected for solvent (infinite dilution) correlation, because this showed the best correlation for **1**. For the nitro-substituted N-sulfinylanilines (**4-1**, **4-2** and **4-3**), because there is no “neat”  $^{17}\text{O}$  chemical shift (the compounds are solids), the correlation for corrected external reference will be compared.

Table 4.3 shows that the correction for solvent can be large, and so **4-1** to **4-3** cannot be discussed reliably. But in addition, we are using crude corrected chemical shifts, obtained from a two-point (100% and 50% **1**) linear extrapolation to infinite dilution, when it is known that the dependence of the  $^{17}\text{O}$  chemical shift on the molar fraction can be somewhat curved.<sup>[78]</sup> For a more reliable analysis, more accurate chemical shifts at infinite dilution should be employed, as they would be obtained from an extensive dilution study.



Nevertheless, some general statements can be made from Table 4.3. All solvatochromic parameters enter the equations with either negative or close to zero coefficients (only two  $\beta$  coefficients are close to zero). This leads in all cases to a decrease in the intrinsic  $^{17}\text{O}$  chemical shift upon interaction with a solvent, and therefore to a more shielded  $^{17}\text{O}$  nucleus, unlike in the loosely related amide, pyrrolidinone (Chapter 4.2.1). The solvatochromic parameters for meta-substitution do not vary substantially from those for **1**, as would be expected because electronic effects cannot be transmitted to the  $^{17}\text{O}$  nucleus effectively. With the strongly electron-donating methoxyl-substituent in ortho- and para-position, there is no dependence on the H-bond accepting properties of the solvent (the value for  $b$  is close to zero). For **1**, we interpreted the  $\beta$  contribution to indicate complexation on sulfur, and this interpretation is supported and strengthened by the equations determined for **3-1** and **3-3**. A nucleophile would not as readily attack a more electron-rich sulfur atom. In contrast, we would expect to see a larger  $b$ -value for the nitro-substituted N-sulfinylanilines **4-1** and **4-3** than for **1**, because the sulfur atom should be electron-poor. This seems to be suggested by the large  $b$ -values for **4-1**, but as mentioned above, confirmation will have to wait for an extensive dilution study of

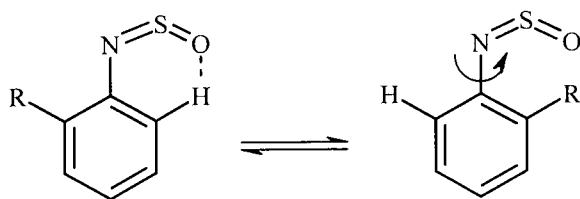


Fig. 4.10 The two possible conformations for ortho-substituted N-sulfinylanilines: planar with a C-H...O interaction or twisted by  $180^\circ$

Table 4.3 Solvatochromic coefficients for N-sulfinylanilines 2 – 4

		XYZ <sub>0</sub>	s	a	b	R <sup>2</sup>
<b>1</b>	original	417	-6.7	-1.8	-0.4	0.9018
	Corrected for reference	417	-7.4	-3.5	-1.2	0.9154
	<b>Corrected for solvent</b>	<b>421</b>	<b>-13.2</b>	<b>-2.5</b>	<b>-2.4</b>	<b>0.9204</b>
<b>2-1</b>	original	419	-2.8	-0.2	-1.0	0.7933
	Corrected for reference	418	-2.8	-0.2	-1.2	0.8195
	<b>Corrected for solvent</b>	<b>419</b>	<b>-5.6</b>	<b>-0.3</b>	<b>-2.5</b>	<b>0.835</b>
<b>2-2</b>	original	422	-6.3	-2.5	-1.8	0.9161
	Corrected for reference	422	-6.2	-2.8	-2.1	0.9233
	<b>Corrected for solvent</b>	<b>427</b>	<b>-12.5</b>	<b>-5.5</b>	<b>-3.9</b>	<b>0.9233</b>
<b>2-3</b>	original	418	-2.7	-8.8	-5.5	0.7311
	Corrected for reference	417	-2.8	-8.2	-5.6	0.7575
	<b>Corrected for solvent</b>	<b>424</b>	<b>-5.5</b>	<b>-16.5</b>	<b>-11.1</b>	<b>0.9477</b>
<b>3-1</b>	original	413	-4.1	-2.2	-0.3	0.8328
	Corrected for reference	412	-4.0	-2.2	0.1	0.8455
	<b>Corrected for solvent</b>	<b>416</b>	<b>-8.0</b>	<b>-4.3</b>	<b>0.1</b>	<b>0.8455</b>
<b>3-2</b>	original	413	-3.8	-0.6	-1.0	0.5453
	Corrected for reference	412	-3.7	-0.6	-1.2	0.5658
	<b>Corrected for solvent</b>	<b>412</b>	<b>-7.5</b>	<b>-1.1</b>	<b>-2.5</b>	<b>0.5658</b>
<b>3-3</b>	original	402	-3.8	-2.7	0.4	0.8412
	Corrected for reference	401	-3.7	-2.6	0.1	0.8513
	<b>Corrected for solvent</b>	<b>404</b>	<b>-7.4</b>	<b>-5.2</b>	<b>0.2</b>	<b>0.8513</b>
<b>4-1</b>	original	430	-13.2	-3.2	-6.6	0.9793
	<b>Corrected for reference</b>	<b>429</b>	<b>-12.3</b>	<b>-3.7</b>	<b>-7.4</b>	<b>0.9678</b>
<b>4-2</b>	original	426	-10.1	-1.8	-4.5	0.865
	<b>Corrected for reference</b>	<b>424</b>	<b>-9.2</b>	<b>-2.3</b>	<b>-0.8</b>	<b>0.6097</b>
<b>4-3</b>	original	424	-5.3	-14.2	-2.7	0.6396
	<b>Corrected for reference</b>	<b>424</b>	<b>-7.2</b>	<b>-8.8</b>	<b>-2.2</b>	<b>0.5477</b>

compounds 4. Finally, most a-values for the substituted 2 – 4 are small, as was found for 1. The small response to the H-donating ability of a solvent agrees with the fact that all substituted N-sulfinylanilines possess a C–H...O interaction, even upon ortho-

substitution, and are therefore planar (Figure 4.10). The only exception to this is the large negative  $\rho$ -value for the meta-chloro substituted **2-3**, but there is no reason to assume that this molecule would be twisted and its oxygen atom more accessible to the solvent.

### 4.3 Summary

We have determined the  $^{17}\text{O}$  chemical shifts for the parent N-sulfinylaniline (**1**) and its ortho-, meta- and para-substituted derivatives (substituents Cl,  $\text{OCH}_3$  and  $\text{NO}_2$ ) neat and in various solvents.

For all chloro-substituted N-sulfinylanilines, the dominant substituent effect seems to be inductive. The dominant substituent effects are electron donating for all methoxyl-substituted N-sulfinylanilines and electron withdrawing for all nitro-substituted N-sulfinylanilines. The neat  $^{17}\text{O}$  chemical shifts for the para substituted N-sulfinylanilines correlate well with Hammett  $\sigma^+$  constants.

For **1** and the chloro- and methoxy-N-sulfinylanilines, with one exception, the  $^{17}\text{O}$  chemical shifts are most sensitive to the polarity or polarizability of the solvents rather than to their H-bonding capabilities.

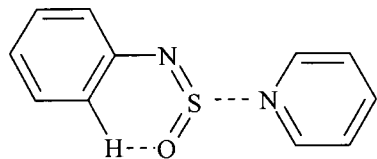
In general, the small dependence of the  $^{17}\text{O}$  chemical shift of all N-sulfinylanilines on the H-donating ability of a solvent supports the idea of planar molecules with intramolecular C–H...O bonds that decrease the solvent accessibility for intermolecular H-bonds. The

presence of a small dependence of the  $^{17}\text{O}$  chemical shift on the H-accepting ability of a solvent is attributed to its nucleophilicity, and therefore its ability to complex with the electropositive sulfur atom.

## 5 Complexation of N-sulfinylaniline (**1**)

Cerioni et al.<sup>[19]</sup> proposed complexes of N-sulfinylaniline (**1**) and a series of para-substituted N-sulfinylanilines in pyridine (py) solution from  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR spectroscopic studies (Figure 5.1). Two sets of  $^{13}\text{C}$  NMR signals for the phenyl carbon atoms arise from the complexed (**1-py**) and uncomplexed **1**. There are also two  $^{17}\text{O}$  resonance signals, that at lower field for the complexed **1-py** and that at higher field for the “free” or uncomplexed **1**. Muchall<sup>[25]</sup> proposed from a computational study that there is an anti-hydrogen bond (C–H...O) in **1**. Thus, there are S...N and C–H...O interactions in the complexes. Chapter 4 shows that structural and medium effects influence the  $^{17}\text{O}$  chemical shift, and in particular that the nucleophilicity of a solvent has an effect on the electron density at the  $^{17}\text{O}$  nucleus. We would therefore expect that there is an interplay between the strength of the S...N interaction and that of the C–H...O interaction.

a)



b)

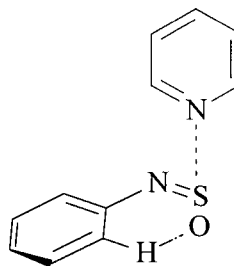


Fig. 5.1 The complex of **1** and pyridine, denoted **1-py**, with C–H...O and S...N interactions. a) Taken from ref. 19; b) Representation showing the perpendicular attack.<sup>78</sup>

To confirm the existence of complex **1-py**, we repeated the  $^{13}\text{C}$  NMR study on **1** in pyridine. To study the interplay of the two interactions, we monitored both  $^{17}\text{O}$  and  $^1\text{H}$  nuclei in temperature (21 to 70 °C) or concentration studies.

### 5.1 $^{13}\text{C}$ NMR spectra

In order to confirm the presence of the complex of N-sulfinylaniline (**1**) in a pyridine solution, we repeated the  $^{13}\text{C}$  NMR studies of Cerioni et al.<sup>[19]</sup> From Table 5.1 we can indeed see the two sets of  $^{13}\text{C}$  chemical shifts for the carbon nuclei in **1** and one set of  $^{13}\text{C}$

Table 5.1  $^{13}\text{C}$  chemical shifts for **1** (uncomplexed) and **1-py** (complexed) in pyridine and chloroform solution.<sup>a</sup>

% <b>1</b>	1	1'	2	2'	3	3'	4	4'	C $\alpha^b$	C $\beta^b$	C $\gamma^b$
97.5 <sup>c</sup>	140.6	146.8	124.1	112.3	127.8	127.8	128.2	115.9	146.9	121.9	133.5
96.8 <sup>c</sup>	140.8	147.8	125.4	112.6	127.4	127.3	128.3	115.9	147.9	121.9	133.8
79.2 <sup>c</sup>	140.6	147.9	125.3	112.5	127.4	127.4	128.3	115.8	147.8	121.9	133.4
55.1 <sup>c</sup>	140.8	148.0	124.5	112.3	127.8	127.8	128.3	115.6	147.9	121.8	133.4
30.9 <sup>c</sup>	140.8	148.0	124.4	112.2	127.8	127.8	128.3	114.5	147.9	121.8	133.4
35 <sup>d</sup>	142.3	-----	126.7	---	128.5	----	130.5	----	-----	----	-----

<sup>a</sup> Internal reference for the pyridine solution: Hexamethyldisiloxane. Signals for nuclei in the complex **1-py** are denoted with a prime. <sup>b</sup> Pyridine carbons. <sup>c</sup> In pyridine. <sup>d</sup> In chloroform.

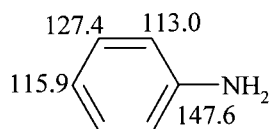


Fig. 5.2 <sup>13</sup>C chemical shifts (ppm) in aniline

chemical shifts for the pyridine carbon atoms. The <sup>13</sup>C chemical shifts for aniline from our lab are shown in Figure 5.2 for comparison. The differences for the two sets of <sup>13</sup>C chemical shifts in **1** are ipso (entries 1 and 1') 7.0 ppm, ortho (2 and 2') 12.4 ppm, meta (3 and 3') 0 ppm and para (4 and 4') 12.7 ppm. These are comparable to those in the earlier study, where differences for ipso 6.3 ppm, ortho 12.6 ppm, meta 0 ppm and para 13.5 ppm were reported.<sup>[19]</sup> For comparison, one experiment was run in chloroform, to show the absence of the second set of signals for **1**.

As Cerioni et al. already noted,<sup>[19]</sup> the aromatic <sup>13</sup>C chemical shifts in **1-py** (the "prime" entries in Table 5.1) are similar to those of aniline carbon atoms (Figure 5.2). One possible reason for this is the possible hydrolysis of **1**, where aniline and SO<sub>2</sub> are the products. However, SO<sub>2</sub> has a <sup>17</sup>O chemical shift (513 ppm) that is not observed. And if SO<sub>2</sub> reacts with pyridine, different <sup>13</sup>C signals for pyridine should be observed, which is also not the case. A second possible reason is the complexation of N-sulfinylaniline with pyridine. The interaction between the S atom and pyridine (S...N) would cut the π-system in **1** into two parts. In the complex, only the N atom of the NSO group would conjugate with the phenyl ring, not the S=O part, which would lead to aniline-like <sup>13</sup>C chemical shifts (**1-py-b** in Figure 5.3). An equilibrium between complexed and uncomplexed **1** would therefore have two sets of <sup>13</sup>C signals for **1** in solution. In the

complex, a fast exchange of pyridine would lead to only one set of signals for pyridine.<sup>[19]</sup>

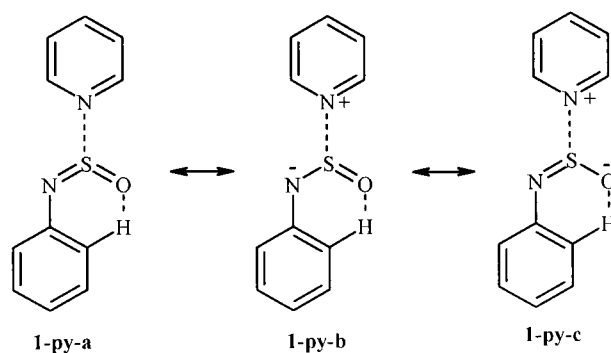


Fig. 5.3 Resonance in the NSO group of **1-py**, from ref. 19

## 5.2 <sup>17</sup>O NMR spectra

The two sets of <sup>17</sup>O signals that are observed for the oxygen in the NSO group of **1** in pyridine confirm the second scenario given in Chapter 5.1. Figure 5.4 shows the spectrum we obtained at 21 °C.

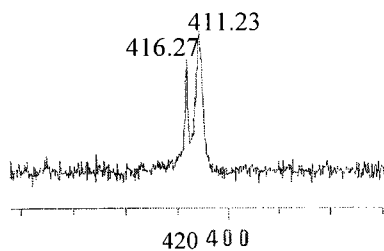


Fig. 5.4 <sup>17</sup>O NMR spectrum of **1** in pyridine at 21 °C

Cerioni et al.<sup>[19]</sup> proposed a complex of **1** with pyridine, suggesting that one signal



belongs to the free **1** (411.23 ppm; 406 ppm in ref. 19) while the other belongs to the complexed **1** (416.27 ppm; 413 ppm in ref. 19). The  $^{17}\text{O}$  chemical shift for the free N-sulfinylaniline is found at slightly higher field compared to that of the neat **1** (412.67 ppm) as pyridine is an aprotic, polar solvent. The signal for the complexed N-sulfinylaniline, at the temperature chosen (21 °C), is found at lower field. The explanation given for this was that resonance structure **1c** loses weight, and **1b** becomes more important (Figure 4.3).<sup>[19]</sup> The results from the  $^{13}\text{C}$  NMR study support structure **1-py-b** (Figure 5.3) for the complex of **1** and pyridine, because the  $^{13}\text{C}$  chemical shifts become aniline-like upon complexation, indicating loss of conjugation across the C–N bond, as discussed above.<sup>[19]</sup>

Table 5.2 addresses the temperature dependence of the  $^{17}\text{O}$  chemical shifts (given in graphical form in Figure 5.5) and integration ratios of a 1:1 (molar ratio) N-sulfinylaniline-pyridine solution.

Table 5.2  $^{17}\text{O}$  chemical shifts (ppm) and integration ratios for N-sulfinylaniline (**1**) in pyridine (1:1 molar ratio) at various temperatures (°C)

Temperature	$\delta^{17}\text{O}$	Integration ratio
21	411.23, 416.27	3:1
32	411.59, 421.67	14:1
40	411.95, 426.35	24:1
50	412.67, 432.12	35:1
60	413.75, 437.88	20:1
70	414.83, 444.36	18:1

The  $^{17}\text{O}$  chemical shifts in this temperature study are uncorrected. There will of course be errors for the reported chemical shifts, but because all spectra have two sets of signals and the analyses are comparative ( $^{17}\text{O}$  in the complex **1-py** versus that in the uncomplexed **1**), the errors should cancel out. For example, in the temperature study, the volume susceptibility is temperature dependent, because it has the density in it. We are not correcting for changes in density, because the two sets of data ( $^{17}\text{O}$  signals) lead to one graph with two different slopes (Figure 5.5), so a change in density should affect the two signals alike. Also, between different samples, the density dependence on the temperature should be comparable.

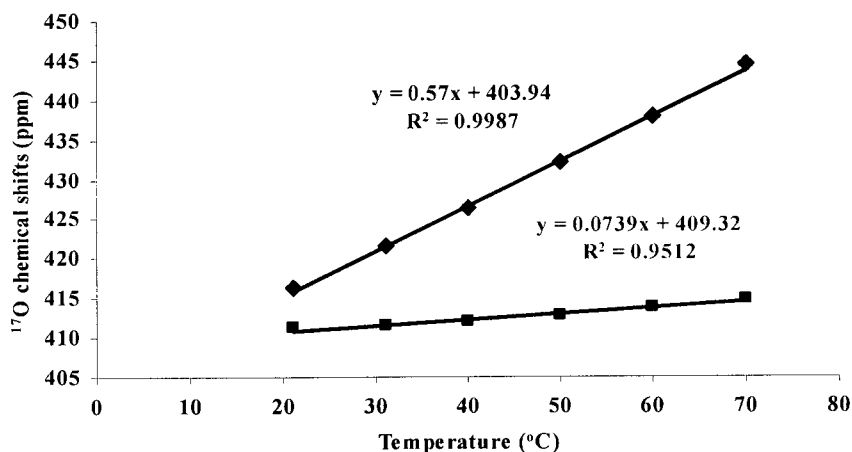


Fig. 5.5 Temperature effect on the  $^{17}\text{O}$  signal of free (♦) and complexed (■) N-sulfinylaniline (**1**) in pyridine (1:1 molar ratio)

From Figure 5.5, the  $^{17}\text{O}$  chemical shifts for both free and complexed **1** move to lower field with an increase in temperature, by 3.6 ppm and 28.1 ppm, respectively, from 21 to 70 °C. We can assume that, with a temperature increase, the C–H...O interaction in **1** will

be increasingly disrupted by rotation about the C–N bond. As the oxygen atom is shielded in a C–H...O interaction, it therefore will be increasingly deshielded. Figure 5.5 shows that this is the case, therefore supporting the presence of a C–H...O interaction, and it can be seen that the effect is larger in the complex. The temperature coefficients  $\Delta\delta/\Delta T$  that can be seen from the slopes in the equations are 0.57 ppm/K for  $^{17}\text{O}$  in the complex and 0.074 ppm/K for that in the free **1**. If the change with temperature for the uncomplexed **1** is taken as “normal” (ab initio calculations give a maximum change from 503 ppm in the planar **1** to 511 ppm in the  $90^\circ$  twisted **1**),<sup>[79]</sup> then the much larger dependence for the oxygen nucleus in the complex must be due to S...N complexation. This could be indicating a stronger C–H...O than in the free **1** due to the S...N interaction, as suggested from resonance structure **1-py-c** (Figure 5.3). In support of this interpretation, the calculated maximum changes in  $^{17}\text{O}$  chemical shift upon a twist in N-sulfinylpyrrole (Figure 5.6) are 90 ppm for loss of the C–H...O interaction and 150 ppm for loss of the stronger N–H...O interaction.<sup>[79]</sup>



Fig. 5.6 C–H...O and N–H...O interactions in N-sulfinylpyrrole

A linear regression was chosen in Figure 5.5, and seems to fit very well over the relatively small temperature range. The plot suggests a crossover of the two straight lines below  $10^\circ\text{C}$ , and this is supported by the  $^{17}\text{O}$  chemical shifts that can be calculated with

ab initio methods for **1** and **1-py**. At 0K in the gas phase, these are 503 and 477 ppm, respectively.<sup>[79]</sup> Obviously, this suggests that a regression similar to that in Figure 5.5 should not be linear over the 0K to 340K range.

The change of the integration ratio reflects the changes in the relative amounts of free and complexed N-sulfinylaniline, and, as expected, the relative amount of the complex is largest at the lowest temperature.

### 5.3 <sup>1</sup>H NMR spectra

A change of temperature and concentration is expected to shift the equilibrium between free and complexed N-sulfinylaniline (**1**), and spectral changes are expected due to changes in S...N interaction and C-H...O strength. Because a proton is involved in the C-H...O interaction, we obtained additional information from the <sup>1</sup>H NMR spectra of **1** in pyridine, especially from the <sup>1</sup>H chemical shifts for the ortho-protons of the phenyl ring.

Table B1 in Appendix B shows the phenyl <sup>1</sup>H chemical shifts for different concentrations of **1** in pyridine at various temperatures. As in Chapter 5.2, the values are not corrected, because we can compare changes in the  $\delta^1\text{H}$  for the ortho-protons to those of the meta- and para-protons, and so any deviations arising from temperature changes (e.g. in the density of the solution) should affect all signals equally. Two representative plots for the data listed in Table B1 are given in Figure 5.7. Figure 5.7a shows the graphical

representation of the temperature effect on the ortho-protons of **1** in a 10 mol% solution. Figure 5.7b is the corresponding plot for a 40 mol% solution and shows that the temperature effect for the ortho-protons is linear, rather than exponential as might be suggested from Figure 5.7a. Figure 5.8 shows phenyl meta- and para-protons in the 10 mol% solution.

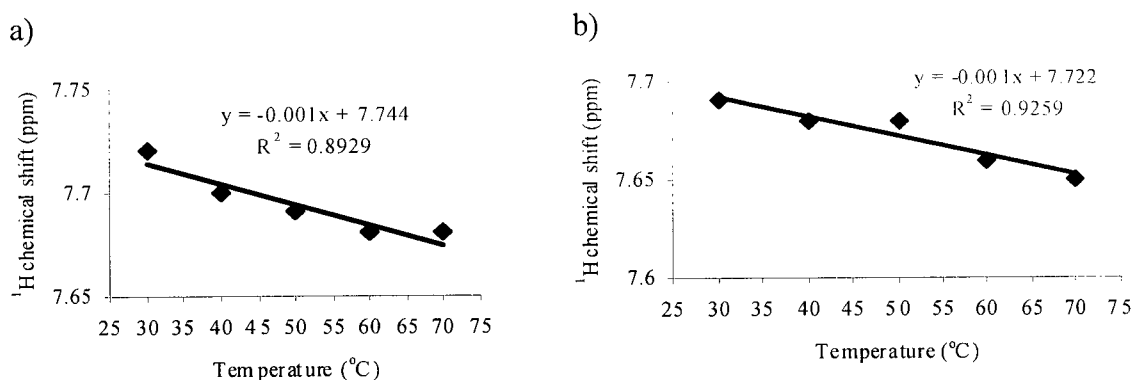


Fig. 5.7 Temperature effect on  $\delta^1\text{H}$  of the ortho-protons in **1**. a) 10 mol% and b) 40 mol%

#### **1** in pyridine

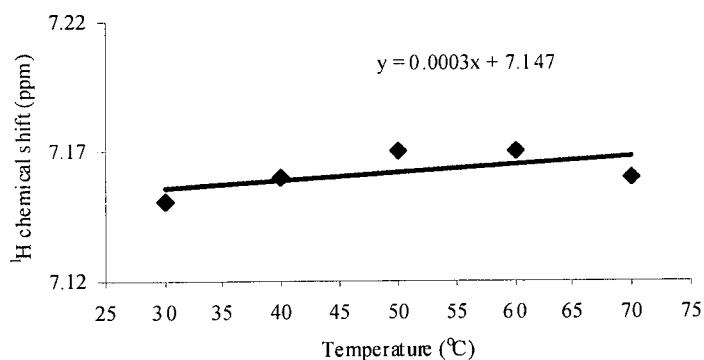


Fig. 5.8 Temperature effect on  $\delta^1\text{H}$  of the meta- and para-protons in **1** (10 mol% in pyridine)

Opposite to what was found for the  $^{17}\text{O}$  chemical shift (Chapter 5.2), the  $^1\text{H}$  chemical shift for the ortho-protons moves to higher field for all solutions as the temperature is

increased. In contrast, the  $^1\text{H}$  chemical shifts for meta- and para-protons show only small irregular changes that are not significant. The value of the temperature coefficient  $\Delta\delta/\Delta T$  for the ortho-protons ( $-1.0$  ppb/K) is clearly higher than that for meta- and para-protons ( $-0.3$  ppb/K), which supports the conclusion drawn from the  $^{17}\text{O}$  study above that there is indeed a C–H...O interaction in **1**. As an ortho-proton in **1** forms a C–H...O interaction with the oxygen atom of the NSO group,<sup>[25]</sup> the electron density of the proton is decreased and the  $^1\text{H}$  chemical shift is found at lower field.<sup>[29]</sup> As discussed above, the C–H...O interaction is increasingly disrupted as the temperature is increased. As the ortho-proton is increasingly released from the C–H...O interaction with a raise in temperature, its electron density increases and its  $^1\text{H}$  chemical shift moves to higher field. Because the meta- and para-protons do not take part in weak interactions, they are largely unaffected by the temperature change.

To put the above into context, temperature coefficients for  $^{15}\text{N}$  signals in N–H...O interactions of amide-modified oligosaccharides are on the order of  $-0.015$  to  $-0.020$  ppm/K. That for the  $^1\text{H}$  signal in these N–H...O interactions is about  $-0.007$  ppm/K, so the  $^{15}\text{N}$  coefficients are more sensitive and show a larger dynamic range.<sup>[35]</sup> The same is found for  $^{17}\text{O}$  and  $^1\text{H}$  signals in the C–H...O interaction of N-sulfinylanilines (**1**). As the C–H...O interaction is much weaker than the N–H...O interaction, the temperature coefficient for  $^1\text{H}$  in the weaker interaction is, not surprisingly, much smaller.

Table 5.3 shows the  $^1\text{H}$  chemical shifts of the phenyl ring for different concentrations of **1** in pyridine, and Figure 5.9 shows the concentration effect on the phenyl ortho-protons

graphically. Figure 5.10 shows the dependence for the meta- and para-protons of **1**. From Figure 5.9 we can see that the ortho-protons become deshielded as the neat N-sulfinylaniline (100 mol%) is diluted with pyridine. The concentration coefficient  $\Delta\delta/\Delta c$  is 1.3 ppb/mol%. The  $^1\text{H}$  chemical shift difference for the ortho-protons is 0.13 ppm from “no complex” (100 mol% **1**) to “all complexed” (“0” mol%, or infinite dilution). From Figure 5.10, we can see that the meta- and para-protons of **1** also shift in the same direction as the concentration of pyridine increases, but that the concentration coefficient with 0.8 ppb/mol% is smaller. The  $^1\text{H}$  chemical shift difference for meta- and para-protons is only 0.07 ppm over the full range of complexation. The values in Table 5.3 are again uncorrected, and so the small concentration coefficient for meta- and para-protons can probably be attributed to the change in magnetic susceptibility of the solution as the

Table 5.3 Phenyl  $^1\text{H}$  chemical shifts (ppm) for different concentrations of N-sulfinylaniline (**1**) in pyridine at ambient temperature

mol%	ortho-H	meta-H	para-H
100	7.62	7.10	7.10
90	7.63	7.10	7.10
80	7.64	7.11	7.11
70	7.67	7.11	7.11
60	7.67	7.12	7.12
50	7.67	7.13	7.13
40	7.71	7.13	7.13
30	7.71	7.15	7.15
20	7.73	7.15	7.15
10	7.73	7.17	7.17

composition is changed. With this as calibration, the almost twice as large concentration coefficient for the ortho-protons should be a real effect. Because in the complex the ortho-proton is deshielded compared to the uncomplexed, neat N-sulfinylaniline, the C–H...O interaction might be considered stronger in the complex. This interpretation is thus the same from  $^{17}\text{O}$  and  $^1\text{H}$  studies.

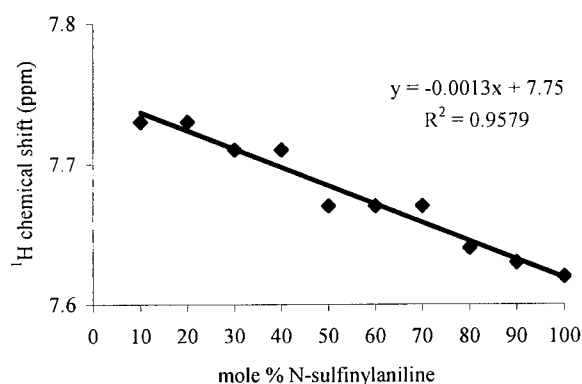


Fig. 5.9 Concentration effect on the ortho-protons of N-sulfinylaniline (**1**) in pyridine

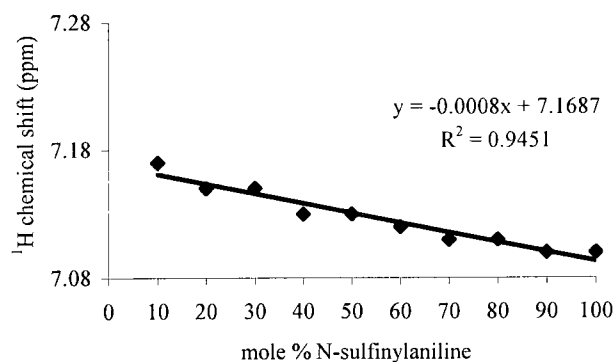


Fig. 5.10 Concentration effect on meta- and para-protons of N-sulfinylaniline (**1**) in pyridine



## 5.4 IR studies

Stufkens et al. assigned the characteristic vibrations of N-sulfinylamines in the IR spectra of  $^{15}\text{N}$  labelled N-sulfinylamines.<sup>[6]</sup> For the NSO group in N-sulfinylaniline (**1**), the frequencies are reported as  $1155\text{ cm}^{-1}$  for the SO stretch ( $\nu(\text{S}=\text{O})$ ) and  $1284\text{ cm}^{-1}$  for the NS stretch ( $\nu(\text{N}=\text{S})$ ), both with strong (“s”) intensities, which makes the bands easy to identify. The frequency for C–N stretching ( $\nu(\text{C}-\text{N})$ ) was reported as  $1299\text{ cm}^{-1}$ , with a medium (“m”) intensity.<sup>[6]</sup> We focus here on the vibrational frequencies for S=O, N=S and C–N of N-sulfinylaniline in pyridine, because with changing concentration, we might expect to observe shifts of the vibrational frequencies and intensity changes that reflect

Table 5.4 Concentration effect on  $\nu(\text{S}=\text{O})$ ,  $\nu(\text{N}=\text{S})$  and  $\nu(\text{C}-\text{N})$  ( $\text{cm}^{-1}$ ) of N-sulfinylaniline (**1**) in pyridine<sup>a</sup>

mol%	$\nu(\text{S}=\text{O})$	$\nu(\text{N}=\text{S})$	$\nu(\text{C}-\text{N})$
100	1161s	1283s	1298m
90	1160s	1283s	1298m
80	1160s	1283s	1298m
70	1160s	1283s	1298m
60	1161s	1283s	1298m
50	1160s	1283s	1298m
40	1160s	1283s	1298m
30	1160s	1283s	1298m
20	1160m	1283m	1297m
10	1161m	1283m	1297m

<sup>a</sup> The entries “s” and “m” refer to the relative band intensities.

the strength of the S...N or C-H...O interactions in the N-sulfinylaniline-pyridine complex.

Table 5.4 shows the wavenumbers for  $\nu(\text{S}=\text{O})$ ,  $\nu(\text{N}=\text{S})$  and  $\nu(\text{C}-\text{N})$  for different concentrations of **1** in pyridine. We could not observe a concentration dependence for the three vibrations. Ab initio calculations predict a wavenumber difference for  $\nu(\text{S}=\text{O})$  between neat N-sulfinylaniline and the complex of only  $5 \text{ cm}^{-1}$  in the gas phase.<sup>[79]</sup> Obviously, we cannot detect this small wavenumber change that would reflect the S...N interaction. From Table 5.4, we can see that the intensities for  $\nu(\text{S}=\text{O})$  and  $\nu(\text{N}=\text{S})$  change from strong to medium for dilute samples, which is relatively arbitrary and not significant.

## 5.5 Summary

We were able to observe the complex formation between N-sulfinylaniline and pyridine by  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR spectroscopies, as had already been reported in the literature.<sup>[19]</sup>

The  $^{17}\text{O}$  chemical shift for N-sulfinylaniline is temperature dependent. With an increase in temperature, the  $^{17}\text{O}$  chemical shift for both the “free” and the “complexed” N-sulfinylaniline is observed to be progressively deshielded, in line with a loss of the C-H...O interaction. Over the range from 21 – 70 °C, the signal for **1-py** shows a much larger temperature coefficient than that for **1**, and this is interpreted to reflect a stronger C-H...O interaction upon complexation.

The  $^1\text{H}$  chemical shift for the ortho-protons of **1** in pyridine is more sensitive to temperature variation than those of meta- and para-protons, because the ortho-protons are involved in a C–H...O interaction. With an increase in temperature, this is disrupted, and  $\delta^1\text{H}$  for the ortho-protons moves to higher field. The  $^1\text{H}$  chemical shifts also show a concentration dependence upon dilution of **1** with pyridine. All  $^1\text{H}$  signals of N-sulfinylaniline are observed to be progressively deshielded as the amount of pyridine is increased, but the effect is larger for ortho- than for meta- or para-protons. These changes upon temperature and concentration variation provide information on the interplay between S...N and C–H...O interactions in **1** and can again be interpreted to imply a stronger C–H...O interaction upon complexation.

We did not observe a concentration dependence for the characteristic stretching vibrations of N-sulfinylaniline in pyridine due to the very small changes upon complexation.

## 6 Complexation of substituted N-sulfinylanilines 2 – 4

### 6.1 $^{17}\text{O}$ NMR spectra

From the complexation study on N-sulfinylaniline (**1**) in Chapter 5, we saw that  $^{17}\text{O}$  NMR spectroscopy gives information about the complexation (S...N<sub>pyridine</sub> interaction). From the substitution study in Chapter 4, we saw that the  $^{17}\text{O}$  nucleus reports on the change in substitution on the aromatic ring. We will now investigate how the substituents affect the S...N interaction by again monitoring the  $^{17}\text{O}$  chemical shift. We also investigate how temperature changes affect the S...N interaction in the complexes of **2** – **4**.

#### 6.1.1 Substituent effects

As deduced in Chapter 4.2.2, in all N-sulfinylanilines **1** – **4** the phenyl ring is coplanar with the NSO group, giving an extended  $\pi$ -system with its resonance structures. For N-sulfinylanilines **3-1**, **3-2** and **3-3**, the methoxyl group with its electron donating ability increases the electron density on the sulfur atom in the NSO group, and the S...N interaction should therefore be weaker than that with **1**. The reverse should be true for N-sulfinylanilines **4-1**, **4-2** and **4-3**. Stronger complexes could be expected due to a more electrophilic sulfur atom caused by the electron withdrawing nitro group. This conclusion was also reached by Cerioni et al. from the fact that only one  $^{17}\text{O}$  signal was obtained in their “complexations” of para-dimethylamino-N-sulfinylaniline and **4-3** with pyridine.<sup>[19]</sup>

This was interpreted to reflect a lack of complexation for the electron rich para-dimethylamino compound and complete complexation for the electron poor **4-3**.<sup>[19]</sup> It is at this point unclear whether the larger density on oxygen for methoxyl-substitution also suggests a stronger C–H...O interaction, but this will be addressed again in Chapter 6.1.2.

In this study, complexes are observed for all substituted N-sulfinylanilines. Table 6.1 shows the <sup>17</sup>O chemical shifts of N-sulfinylanilines **2** – **4** in pyridine, those for **1** are included for comparison, as are the neat values from Table 4.1 for easy comparison. Within a series, the change in <sup>17</sup>O chemical shift is similar for the uncomplexed and the neat compounds. And so, for example,  $\delta^{17}\text{O}$  for the uncomplexed ortho-, meta- and para-chloro-N-sulfinylanilines (**2-1** to **2-3**) in pyridine reflects the normal distance effect of the substituent that was already discussed for the neat compounds in Chapter 4. The presence of pyridine also does not change the fact that the <sup>17</sup>O nucleus is still shielded for methoxyl-substitution and deshielded for nitro-substitution on the aromatic ring. This is true for the uncomplexed as well as the complexed N-sulfinylanilines. But upon complexation with pyridine, in the **2**- and **3**-series, the <sup>17</sup>O chemical shift for the complexed N-sulfinylanilines is almost insensitive to the substituent position, again supporting resonance structure b in Figure 5.3. The para-nitro substituent in **4-3-py** is the only one that increases the range of <sup>17</sup>O chemical shifts in the complexes. Upon closer inspection, for the chloro-substituted N-sulfinylanilines **2-py** a reversal in distance effect is observed, which suggests that multiple, contrasting electronic effects are at play that are hard to interpret without the help of ab initio calculations.

While Cerioni et al. also observed a similar electron donating effect for para-methoxy-N-sulfinylaniline in pyridine as well as the complex of para-chloro-N-sulfinylaniline, they did not observe the complex for para-nitro-N-sulfinylaniline in pyridine.<sup>[19]</sup> We believe that the reason for this might be found in the temperature dependence of the <sup>17</sup>O chemical shift, as discussed in Chapter 6.1.2.

Table 6.1 <sup>17</sup>O chemical shifts (ppm) of N-sulfinylanilines **1** – **4**, in pyridine (1:1 molar ratio, complexed and uncomplexed) and in the neat compounds at 40 °C.

	$\delta^{17}\text{O}$		
	complexed	uncomplexed	neat
<b>1</b>	426.35 <sup>a</sup>	411.95 <sup>a</sup>	410.88 <sup>b</sup>
<b>2-1</b>	428.52	417.00	419.16
<b>2-2</b>	429.24	416.28	418.44
<b>2-3</b>	430.68 <sup>a</sup>	413.76 <sup>a</sup>	410.88 <sup>b,c</sup>
<b>3-1</b>	420.96	410.52	409.80
<b>3-2</b>	422.04	409.80	411.60
<b>3-3</b>	421.68 <sup>a</sup>	400.44 <sup>a</sup>	398.64 <sup>b</sup>
<b>4-1</b>	417.72	417.72	422.76 <sup>d</sup>
<b>4-2</b>	415.56	411.00	424.20 <sup>d</sup>
<b>4-3</b>	431.05 <sup>a</sup>	416.28	424.20 <sup>b,d</sup>

<sup>a</sup> Values at unknown concentration and 294K from ref. 19: **1** 413, 406 ppm; **2-3** 415, 406.5 ppm; **3-3** 413, 395.5 ppm; **4-3** 409.4 ppm. <sup>b</sup> Values in chloroform at unknown concentration and 294K from ref. 19: **1** 406, **2-3** 408, **3-3** 391, **4-3** 432 ppm. <sup>c</sup> **2-3** is liquid at 40 °C. <sup>d</sup> In benzene.

### 6.1.2 Temperature effects

As for **1**, a temperature dependence of the  $^{17}\text{O}$  chemical shift was found for all substituted N-sulfinylanilines in pyridine. The temperature  $^{17}\text{O}$  NMR data for **1** – **4** are shown in Tables C1 – C3 in Appendix C. Figure D1 in Appendix D shows the plot for the temperature effect on the  $^{17}\text{O}$  signal of neat **1**, Figure D2 repeats the plot for the temperature effect on the  $^{17}\text{O}$  signal of free and complexed **1** in pyridine. Figures D3, 5, 7, 9, 11, 13, 15, 17, 19 show the data for the neat N-sulfinylanilines **2** – **4** (**2-3** at 20 °C was taken in hexane and data for the solid **4** were taken in benzene) and Figures

Table 6.2 Temperature coefficients (ppm/K) for the  $^{17}\text{O}$  chemical shift of N-sulfinylanilines **1** – **4**, in pyridine (1:1 molar ratio, complexed and uncomplexed) and in the neat compounds

	$\Delta\delta/\Delta T$		
	complexed	uncomplexed	Neat
<b>1</b>	0.570	0.074	0.058
<b>2-1</b>	0.641	0.108	0.086
<b>2-2</b>	0.531	0.064	0.086
<b>2-3</b>	0.491	0.060	0.090
<b>3-1</b>	0.609	0.068	0.121
<b>3-2</b>	0.802	0.104	0.032
<b>3-3</b>	0.633	0.051	0.208
<b>4-1</b>	0.559	0.127	0.054 <sup>a</sup>
<b>4-2</b>	0.476	0.141	0.069 <sup>a</sup>
<b>4-3</b>	0.534	0.111	0.065 <sup>a</sup>

<sup>a</sup> In benzene.

D4, 6, 8, 10, 12, 14, 16, 18, 20 those for N-sulfinylanilines **2** – **4** in pyridine. Table 6.2 summarizes the temperature coefficients for the  $^{17}\text{O}$  chemical shifts of N-sulfinylanilines **1** – **4**, neat, uncomplexed in pyridine and in the complex.

As was already noted for **1** in Chapter 5.2, from Table 6.2 it is obvious that the temperature coefficients ( $\Delta\delta/\Delta T$ ) in the complexes are larger than those in the uncomplexed and in the neat species. The temperature coefficients in the complexes range from 0.476 (**4-2-py**) to 0.802 (**3-2-py**) ppm/K. Temperature coefficients in the uncomplexed and in the neat N-sulfinylanilines are rather similar and range from 0.050 (**3-3**) to 0.141 (**4-2**) ppm/K and from 0.054 (**4-1**) to 0.121 (**3-1**) ppm/K, respectively. As in the  $^{17}\text{O}$  temperature study for **1**, because even the ortho-substituted N-sulfinylanilines **2** – **4** retain an ortho-hydrogen atom, with a temperature increase, the C–H...O interaction will be increasingly disrupted and therefore  $\delta^{17}\text{O}$  will be shifted downfield. The stronger the C–H...O interactions in the N-sulfinylanilines are, the larger the deshielding is, which means larger temperature coefficients. With this reasoning, we can see that the C–H...O interaction is strengthened in all pyridine complexes of N-sulfinylanilines, showing a cooperative effect between C–H...O and S...N interactions.

At the beginning of Chapter 6.1.1, we made a prediction for the strength of the complexation for methoxyl- and nitro-substituted N-sulfinylanilines, based on the findings from the solvent study. Table 6.2 shows that larger  $\Delta\delta/\Delta T$  are found for methoxyl substitution (**3-series**) than for **1**, while the nitro-substituted **4-2** has the smallest  $\Delta\delta/\Delta T$ . While it seems that these temperature coefficients cannot be correlated



with the strength of the complexation, they do show the expected trend as to the strength of the C–H...O interaction. In Chapter 6.1.1 we commented on the larger electron density on the  $^{17}\text{O}$  nucleus in the methoxyl-substituted **3**. As the **3**-series also shows the larger temperature coefficients, it seems safe to state that their C–H...O interaction is indeed stronger.

Because the temperature coefficients for the free and complexed species in pyridine are different, the two lines in the temperature plots cross at one point (the actual crossover point is not shown in Figure 5.5). The crossover temperatures, calculated from the intercept of the two straight lines, are listed in Table 6.3. Obviously, at these crossover points, the  $^{17}\text{O}$  chemical shifts of free and complexed N-sulfinylanilines are identical. This does not necessarily mean that the two C–H...O interactions are of the same strength or that the two oxygen nuclei experience the same environment, though. The environments could be quite dissimilar, but different shielding or deshielding effects on the two nuclei could simply sum up to the same observed chemical shift. From Table 6.3, the temperature at the crossover point in the **2**- and **4**-series is related to the distance between the oxygen atom and the substituent. In general, the crossover temperature is lowest for para-substitution (as well as for no substitution in **1**). This could be a manifestation of the inductive effect on the oxygen nucleus that should be greater the closer the substituent is. So far, it is unclear of whether any other physical relevance should be attributed to the crossover point and the change in its position in the temperature plots for the different N-sulfinylanilines.

There is one practical significance to the crossover point, though. For **2-1**, **3-1** and **3-2**, the crossover temperatures are at just about room temperature. If someone takes  $^{17}\text{O}$  NMR spectra at room temperature only, he might only see one signal instead of two, and the complexation might be missed entirely. Cerioni et al., for example, did not see all complexes (for example, that for **4-3** was not found),<sup>[19]</sup> maybe for just this reason.

Table 6.3 Crossover temperature ( $^{\circ}\text{C}$ ) and  $\delta^{17}\text{O}$  (ppm) for N-sulfinylanilines in pyridine (1:1 molar ratio)

	Temperature	$\delta^{17}\text{O}$
<b>1</b>	10.8	410.00
<b>2-1</b>	18.9	414.72
<b>2-2</b>	11.9	415.13
<b>2-3</b>	-1.1	411.73
<b>3-1</b>	19.7	409.65
<b>3-2</b>	26.0	408.09
<b>3-3</b>	2.1	397.98
<b>4-1</b>	34.2	415.21
<b>4-2</b>	29.9	411.77
<b>4-3</b>	6.3	412.57

To finally establish a link between the strength of the C–H...O interaction, as discussed above, and the strength of the S...N interaction in the complexes, we determined the equilibrium constants ( $K$ ) for complex formation.  $K$  for complex formation can be calculated according to the equation in Figure 6.1.<sup>[80]</sup>

$$A + B \rightleftharpoons A \cdots B$$

$$\frac{1}{\Delta_{obs}} = \frac{1}{K * x * \Delta_{comp}} + \frac{1}{\Delta_{comp}}$$

Fig. 6.1 Determination of the equilibrium constant for complexation from the chemical shift

In the equation,  $K$  is the equilibrium constant, and  $x$  is the molar fraction of B. The  $\Delta$ -values are  $\Delta_{obs} = \delta_{obs} - \delta_{free}$ ,  $\Delta_{comp} = \delta_{comp} - \delta_{free}$ , where  $\delta_{obs}$  is the chemical shift of the uncomplexed A,  $\delta_{comp}$  is the chemical shift of the complexed A, and  $\delta_{free}$  is the chemical shift of the neat A. Here A is a N-sulfinylaniline and B is pyridine. The chemical shifts are the  $^{17}\text{O}$  chemical shifts.

The equilibrium constants for complexes of N-sulfinylanilines **1** – **4** and pyridine are shown in Tables C1, C2 and C3 of Appendix C. The  $K$  values show that the complexes weaken as the temperature is increased, as was found from the integration of the  $^{17}\text{O}$  signals for **1** and **1-py** in Table 5.2. Earlier we found for all N-sulfinylanilines that the C–H...O interactions are increasingly disrupted with a raise in temperature. Therefore, both weak interactions are disrupted with an increase in temperature, as might have been expected.

The equilibrium constants for 20 °C are summarized in Table 6.4.  $K$  for **1-py** formation is smaller than that for chloro-substitution **2-py**. Upon chloro-substitution, the equilibrium shifts closer to a 1:1 composition. The interesting complexes are again **3-py** and **4-py**,

because of the contrasting electronic effects of their substituents. Table 6.4 shows equilibrium constants for the methoxyl-substituted **3**-series that are much smaller than those for the nitro-substituted **4**-series (where  $K$  values are now larger than 1, showing the equilibria shifted far to the side of the complexes), finally confirming the predicted stronger complexes for nitro-substitution, due to the electron withdrawing effect on the sulfur atom.

Table 6.4 The  $K$  values for N-sulfinylanilines at 20 °C

	$K$
<b>1</b>	0.57
<b>2-1</b>	0.77
<b>2-2</b>	0.63
<b>2-3</b>	0.76
<b>3-1<sup>a</sup></b>	0.36
<b>3-2<sup>a</sup></b>	0.33
<b>3-3<sup>a</sup></b>	0.40
<b>4-1</b>	15.35
<b>4-2</b>	14.15
<b>4-3</b>	3.47

<sup>a</sup> Because solutions of **3-2** and **3-3** at 20 °C were highly viscous, temperature data were measured at 30 °C.

## 6.2 Summary

All substituted N-sulfinylanilines studied here show complexes with pyridine, in contrast to what was reported in the literature.<sup>[19]</sup> In the complexes, the substituent effect on the

$^{17}\text{O}$  nucleus is vastly reduced in comparison to that in the neat N-sulfinylanilines, which indicates a disruption of the  $\pi$ -conjugation between the aromatic ring and the S=O group.

As for the parent compound **1**, for all substituted N-sulfinylanilines, the temperature coefficient for the  $^{17}\text{O}$  signal in the complex is larger than that in the uncomplexed and in the neat species. Again we attribute this to stronger C–H...O interactions in the complexes, which demonstrates a cooperative effect between C–H...O and S...N interactions.

The difference in temperature coefficients of  $\delta^{17}\text{O}$  for an uncomplexed and a complexed N-sulfinylaniline leads to a crossover point, at which the  $^{17}\text{O}$  chemical shifts of free and complexed N-sulfinylanilines are identical. This is of practical importance, in that care must be taken if, upon addition of pyridine, only one  $^{17}\text{O}$  signal is obtained and therefore seemingly complexation is not observed.

Equilibrium constants for complexation show the expected trend with temperature, that is, lower temperatures shift the equilibrium to the side of the complexes. More of interest is that equilibrium constants confirm that the electron donating methoxyl substituent leads to weaker complexes. For the electron withdrawing nitro substituent, the equilibrium is decidedly on the side of the complexes.

## 7 Summary, conclusions and outlook

### 7.1 Summary and conclusions

The here presented studies were prompted by a lack of understanding to which extent a weak bonding interaction can influence reactivity. Even though the NSO group of N-sulfinylanilines should be considered a heterocumulene,  $N=S=O$ , resonance contributors with a positive charge on sulfur can be formulated that show its electrophilic nature. Accordingly, most reactions of N-sulfinylanilines are initiated by a nucleophilic attack on the sulfur atom of the NSO group. In hydrolysis, for example, an initial attack of the water oxygen on sulfur, a S...O interaction, is followed by a proton transfer from the water molecule. Tertiary amines such as pyridine are able to initiate a similar S...N interaction, but further reaction is not possible due to missing active hydrogen atoms on nitrogen of the amine. Complexation of a N-sulfinylaniline, therefore, can be used as a model for the initial step of its reactions. Complexation on sulfur causes changes in the electronic structure of the NSO group, and these changes can be probed spectroscopically. The oxygen atom of the NSO group is a particularly good probe, because it not only is directly connected to the complexing sulfur, but, according to computational studies, it is also involved in a C-H...O interaction with available ortho-H atoms on the aromatic ring of the N-sulfinylaniline.

Based on the above, we set out to determine whether the intramolecular C-H...O interaction could influence N-sulfinylaniline reactivity as modeled by S...N

complexation with pyridine. Our main tool was  $^{17}\text{O}$  NMR spectroscopy, but  $^{13}\text{C}$  and  $^1\text{H}$  NMR, and IR spectroscopies were also employed. In addition to the unsubstituted parent N-sulfinylaniline (Ph-NSO, **1**), we chose a selection of substituted (Cl, OCH<sub>3</sub>, NO<sub>2</sub>) N-sulfinylanilines **2** – **4** with substituents on the aromatic ring that would allow for a wide range of electron donating and withdrawing abilities to tune the electron density on the NSO group. Except for **1**, all compounds were synthesized according to literature procedures.

To begin with, it was important to determine how sensitive the NSO oxygen nucleus is to changes in its environment that are caused by changes in solvent and nature and position of substituents on the aromatic ring. The  $^{17}\text{O}$  chemical shift lies around 400 ppm, and a chemical shift range of about 25 ppm was determined for the different neat compounds. Chemical shifts for the para-substituted compounds follow Hammett substituent constants, which illustrates the extent of conjugation in the system. But overall, substituent effects are hard to interpret, because of multiple influences on the  $^{17}\text{O}$  nucleus:  $\sigma$ - and  $\pi$ -effects directly through the aromatic ring but also  $\sigma$ -effects on the ortho C–H bonds and therefore indirectly through the C–H...O interaction. Solvent induced chemical shift changes are in general somewhat smaller. While they follow the solvent dielectric constants only loosely, they can be described well with solvatochromic equations. In general, the  $^{17}\text{O}$  chemical shifts are more sensitive to the polarity or polarizability of a solvent rather than to its H-bonding capabilities, in line with the fact that the oxygen atom is involved in an intramolecular C–H...O interaction. Interestingly, though, a dependence on the H-bond accepting properties of a solvent is found, which is

interpreted as the complexing ability of the solvent with the sulfur atom. This dependence is largest for nitro-substitution, and therefore the most electropositive sulfur.

One more change in environment for the NSO oxygen nucleus was brought about by a change in temperature, because the oxygen is thought to be involved in a hydrogen-bonding interaction. Upon an increase in temperature, a downfield shift of the  $^{17}\text{O}$  signal was observed in all N-sulfinylanilines, signalling that the oxygen was increasingly released from an intramolecular C–H...O interaction. This was seen even for mono-ortho-substitution. For the parent N-sulfinylaniline (**1**) only, we also probed the temperature dependence of the  $^1\text{H}$  signals. The small shifts for  $^1\text{H}$  signals from meta and para protons provided a calibration, and the larger temperature coefficient for the ortho protons was found to be significant. Upon an increase in temperature, the signal for the ortho protons shifted upfield, again signalling that the hydrogen was increasingly released from its C–H...O interaction.

We were unable to show the complex of N-sulfinylaniline (**1**) with pyridine through IR spectroscopy due to very small changes in band positions upon complexation, but NMR spectroscopy proved sensitive enough. We observed a small concentration dependence of the meta and para protons as **1** was diluted with pyridine, and again this was taken as calibration. The larger deshielding of the ortho protons not only showed complex formation, but also suggested a stronger C–H...O interaction in the complex. Complex formation in **1** was also shown through the appearance of a second set of  $^{13}\text{C}$  signals for the aromatic ring of **1** upon addition of pyridine. That all N-sulfinylanilines form



complexes with pyridine was shown from two sets of signals in their  $^{17}\text{O}$  NMR spectra. In the complexes, there was a reduced substituent effect on the  $^{17}\text{O}$  chemical shift, which demonstrated the change in electronic structure of the NSO group upon complexation of sulfur and the loss of conjugation with the aromatic ring. The  $^{17}\text{O}$  nucleus was deshielded with an increase in temperature, and temperature coefficients for the complexed N-sulfinylanilines were greater than those for the free species, which can lead to an accidental degeneracy of the two signals. The observed deshielding was in line with a gradual loss of an intramolecular C–H...O interaction upon a raise in temperature, and the larger changes in the complexes implied stronger C–H...O interactions in the complexes. Equilibrium constants for complexation corroborated the conclusion drawn from the solvent study, in that the strongly electron withdrawing nitro group gave rise to stronger complexes.

In conclusion, we were able to demonstrate experimentally the intramolecular C–H...O interaction in N-sulfinylanilines, which formerly had only been predicted computationally, and the dependence of its strength on the S...N interaction in the complexes of N-sulfinylanilines with pyridine. From the different temperature dependences of a  $^{17}\text{O}$  nucleus in a N-sulfinylaniline and in its complex, it seems safe to state that the C–H...O interaction is strengthened upon complexation. Equilibrium constants indicate that an electron donating substituent leads to a weaker complex. Finally, substituent effects on the temperature dependence of the  $^{17}\text{O}$  nucleus in a complex seem to indicate that a weaker complex possesses a stronger C–H...O

interaction. If this is phrased the other way around, a “strong” C–H...O interaction could inhibit complexation, and maybe lead to a reduced reactivity of a N-sulfinylaniline.

## 7.2 Outlook

Several questions follow logically from the various studies performed here, which should be addressed in the future.

First of all, for temperature coefficients, computational results suggest that the selection of reference compounds for which intramolecular H-bonds strengths are known would be useful. Not much is known on the temperature dependence of  $^{17}\text{O}$  signals in simple terminal oxygen systems, and these studies would complement this work on N-sulfinylanilines. Also, a system such as N-sulfinylpyrrole, with the possibility of both C–H...O and N–H...O interactions should provide additional valuable insight as to the size of temperature coefficients.

Secondly,  $^1\text{H}$  NMR studies, for both temperature and concentration dependences, should be carried out for the substituted N-sulfinylanilines. While changes in  $^1\text{H}$  chemical shifts are naturally smaller than those for  $^{17}\text{O}$ ,  $^1\text{H}$  chemical shifts are more “robust” and suffer less from environmental changes as do  $^{17}\text{O}$  chemical shifts. Substituent effects might be more easily interpreted with these sets of data available, even though they are expected to be complementary to the  $^{17}\text{O}$  results.

Third. To get a less crude idea of the solvent influence, one might want to conduct detailed “infinite dilution” studies, especially towards very dilute solutions, because it is known that there can be a curvature in that region in a plot of chemical shift versus concentration. Studies on solvent effects in ortho-disubstituted N-sulfinylanilines, where there is no C–H...O interaction, and on N-sulfinylpyrrole, where there is possibility of both C–H...O and the stronger N–H...O interactions, should provide important additional results. In ortho-disubstituted N-sulfinylanilines, a twisted conformation would a) reduce the conjugation of the phenyl ring with the NSO group, and so substituents should have smaller effects on the electron density of the sulfur atom than in the planar systems, and b) expose the oxygen atom to the solvent more than a planar system.

Finally, even from the limited computational data provided here, it is obvious that, in order to interpret the data fully, quantum chemical results are needed.

## 8 Experimental

### 8.1 NMR spectroscopy<sup>[81-87]</sup>

The  $^1\text{H}$  NMR spectra were run on a Varian UNITY *INOVA*-300 NMR spectrometer. For the proton spectra, a 5 mm probe was used and spectra were referenced to an internal standard, hexamethyldisiloxane (HMDS). For variable temperature  $^1\text{H}$  NMR spectra, air was used for a requested temperature between 15 and 70 °C. The air flow was adjusted to about 10 L/min. A standard methanol sample was used to calibrate the probe temperature.

As  $^{17}\text{O}$  spectra are not routine spectra, there are no standard parameters in NMR instruments. After the selection of many parameters, we set up the  $^{17}\text{O}$  NMR parameters in the Varian UNITY *INOVA*-300 NMR spectrometer.<sup>[88-89]</sup> A 5 mm broadband probe was operated at 40.687 MHz, 29.9 kHz spectral width, 90° pulse and 0.1  $\mu\text{s}$  acquisition delay. The pulse width was 11.3  $\mu\text{s}$ . Acquisition time was 0.05s. Spectra were not proton-decoupled. The number of transients was from 40,000 to 80,000. External  $\text{D}_2\text{O}$  ( $\delta = 0$  ppm) in a concentric tube was the reference. All experiments were performed with materials of natural isotopic abundance. A molar ratio of 1:1 N-sulfinylaniline with the various solvents was used. The half-widths for  $^{17}\text{O}$  signals were measured with the command “res”.

### 8.2 IR spectroscopy

Infrared spectra of samples at room temperature were recorded in the 500 – 4000  $\text{cm}^{-1}$

region with a Magna 550 spectrometer from Nicolet. Two NaCl plates were used. Each spectrum was composed of 32 scans. Infrared spectra of liquid samples were recorded for the pure liquids. Infrared spectra of solid samples were measured with mulls. A mull was prepared by grinding the sample with mineral oil. The paste was sandwiched between NaCl plates.

### **8.3 NMR sample preparation<sup>[90]</sup>**

Good-quality NMR tubes were selected. Used tubes were carefully cleaned and dried before using again. The NMR tube was filled to a height of 5 cm with sample and deuterated solvent not to complicate shimming. Samples were fully mixed. Solid particles remaining in the sample were filtered off by a small amount of glass wool in a pipette.

## **8.4 Syntheses**

### **8.4.1 o-Chloro-N-sulfinylaniline (2-1)**

In a 50 mL flask fitted with a water condenser, 15.5 g (0.122 mol) of o-chloroaniline and 17 mL of sodium-dried benzene were placed. Thionyl chloride (14.5 g, 0.122 mol) was added dropwise with magnetic stirring and ice bath cooling. A vigorous reaction took place and aniline hydrochloride precipitated. As a result of the exothermic reaction, benzene reflux temperature was reached. The reaction mixture was stirred and heated until the solids gradually disappeared (5 hours), after which 0.5 mL thionyl chloride were

added. The reaction mixture was heated for an additional 2 hours. A clear solution without residue in the flask was obtained. The benzene and excess thionyl chloride were evaporated using a rotary evaporator under reduced pressure at 50 °C. Then the residual brownish-yellow liquid was distilled under vacuum. Yield 17.12 g (80.8 %, lit. 83 %<sup>[91-93]</sup>), yellow liquid, b.p. 68-77 °C/0.4-0.5 mmHg (lit. 76-80 °C/0.5-0.6 mmHg<sup>[91-93]</sup>). <sup>1</sup>H NMR: 8.1 (1H, m), 7.3 (1H, m), 7.1 (1H, m), 7.0 ppm (1H, m). <sup>13</sup>C NMR: 139, 131, 130, 129, 128, 127 ppm. IR: 1168  $\nu$ (S=O), 1218  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.2 m-Chloro-N-sulfinylaniline (2-2)

Same procedure as in 8.4.1.

Yield 15.1g (71.3 %, lit. 79 %<sup>[93]</sup>), yellow liquid, b.p. 78-86 °C/0.4-0.5 mmHg. (lit. 79-85 °C/0.4-0.5 mmHg<sup>[93]</sup>). <sup>1</sup>H NMR: 7.6 (1H, m), 7.5 (1H, m), 7.2 (1H, m), 7.1 ppm (1H, m). <sup>13</sup>C NMR: 142, 133, 129, 127, 125, 124 ppm. IR: 1167  $\nu$ (S=O), 1219  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.3 p-Chloro-N-sulfinylaniline (2-3)

In a 50 mL flask fitted with a water condenser were placed 10.2 g (0.244 mol) of p-chloroaniline and 15 mL of sodium-dried benzene. 9.49 g (0.244 mol) of thionyl chloride were added dropwise to the flask. The contents were heated to reflux until the material in the bottom of the flask disappeared. After 5 hours of reflux, a dark solution was obtained with a big lump of black solid in the bottom of the flask. The liquid was decanted. The benzene and excess thionyl chloride were evaporated using the rotary evaporator under

reduced pressure at 50 °C. Then the residual black liquid (p-chloro-N-sulfinylaniline in benzene) was distilled under vacuum by fractional distillation apparatus. We obtained the yellow p-chloro-N-sulfinylaniline, which solidified readily at room temperature. Yield 9.11 g (21.5 %, lit. 41 %<sup>[91, 92, 94]</sup>), yellow solid, b.p. 78-86 °C/0.4-0.5 mmHg (lit. 108-109 °C/1.5 mmHg<sup>[91, 92, 94]</sup>) m.p. 22-23 °C. <sup>1</sup>H NMR: 7.8 (2H, dd), 7.3 ppm (2H, dd). <sup>13</sup>C NMR: 140, 136, 129, 128 ppm. IR: 1160  $\nu$ (S=O), 1221  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.4 o-Methoxy-N-sulfinylaniline (3-1)

Same procedure as in 8.4.1.

Yield 16g (78 %, lit. 87 %<sup>[93]</sup>), orange liquid, b.p. 93-95 °C/3 mmHg (lit. 94 °C/3 mmHg<sup>[93]</sup>). <sup>1</sup>H NMR: 8.1 (1H, m), 7.3 (1H, m), 7.2 (1H, m), 6.8 (1H, m), 3.7 ppm (3H, s). <sup>13</sup>C NMR: 152, 132, 131, 127, 120, 111, 55 ppm. IR: 1160  $\nu$ (S=O), 1221  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.5 m-Methoxy-N-sulfinylaniline (3-2)

Same procedure as in 8.4.1.

Yield 17.5g (85 %, lit. 90 %<sup>[95]</sup>), orange liquid, b.p. 132-135 °C/17 mmHg (lit. 133-134 °C/17 mmHg<sup>[95]</sup>). <sup>1</sup>H NMR: 7.3 (1H, m), 7.2 (1H, m), 7.0 (1H, m), 6.7 (1H, m), 3.5 ppm (3H, s). <sup>13</sup>C NMR: 159, 142, 129, 119, 116, 111, 54 ppm. IR: 1162  $\nu$ (S=O), 1230  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.6 p-Methoxy-N-sulfinylaniline (3-3)

Same procedure as in 8.4.1.

Yield 16.9g (82 %, lit. 91 %<sup>[96]</sup>), orange liquid, b.p. 142-144 °C/17 mmHg (lit. 144 °C/15 mmHg<sup>[96]</sup>). <sup>1</sup>H NMR: 7.8 (2H, dd), 6.8 (2H, dd), 3.8 (3H, s). <sup>13</sup>C NMR: 160, 137, 129, 114, 116, 111, 55 ppm. IR: 1147  $\nu$ (S=O), 1218  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.7 o-Nitro-N-sulfinylaniline (4-1)

In a 50 mL flask fitted with a water condenser were placed 10.2 g (0.122 mol) of ortho-nitro aniline and 15 mL of sodium-dried benzene. 9.49 g (0.122 mol) of thionyl chloride were added dropwise to the flask. The contents were heated to reflux until the material in the bottom of the flask disappeared. After 5 hours of reflux, a dark solution was obtained with a big lump of black solid in the bottom of the flask. The benzene and excess thionyl chloride were evaporated using the rotary evaporator under reduced pressure at 50 °C. A residual oil was obtained that solidified. Recrystallization from a mixture of benzene and petroleum ether gave yellow crystals. Yield 4.1g (24 %, lit. 51 %<sup>[91]</sup>), yellow crystals, m.p. 51-54 °C (lit. 52 °C<sup>[91]</sup>). <sup>1</sup>H NMR: 8.0 (1H, m), 7.4 (1H, m), 7.0 (1H, m), 6.6 ppm (1H, m). <sup>13</sup>C NMR: 136, 128, 125, 122, 121, 116 ppm. IR: 1220  $\nu$ (S=O), 1260  $\text{cm}^{-1}$   $\nu$ (N=S).

#### 8.4.8 m-nitro-N-sulfinylaniline (4-2)

Same procedure as in 8.4.7.



Yield 10.2g (60 %, lit. 71%<sup>[97, 98]</sup>), yellow crystals, m.p. 62-65 °C (lit. 63.5 °C<sup>[97, 98]</sup>). <sup>1</sup>H NMR: 8.5 (1H, m), 8.2 (1H, m), 8.1 (1H, m), 7.7 ppm (1H, m). <sup>13</sup>C NMR: 143, 134, 124, 118, 124, 121 ppm. IR: 1176 v(S=O), 1217 cm<sup>-1</sup> v(N=S).

#### **8.4.9 p-Nitro-N-sulfinylaniline (4-3)**

Same procedure as in 8.4.7.

Yield 11g (65 %, lit. 77 %<sup>[97, 98]</sup>), yellow crystals, m.p. 69-71 °C (lit. 70 °C<sup>[97, 98]</sup>). <sup>1</sup>H NMR: 8.1 (2H, dd), 6.7 ppm (2H, dd). <sup>13</sup>C NMR: 143, 134, 124, 118, 124, 121 ppm. IR: 1176 v(S=O), 1217 cm<sup>-1</sup> v(N=S).

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## Appendix A

**Computational data in Tables A1 and A2 were provided by Dr. Heidi Muchall, private communication.**

Table A1 Experimental<sup>a</sup> and calculated<sup>b</sup> molar ( $\chi_M$ ) and volumetric ( $\chi_V$ ) susceptibility in cgs-ppm, density<sup>a,c</sup> ( $\rho$ , g/mL), molar mass (M, g/mol) and molar volume<sup>b</sup> ( $V_m$ , mL/mol) of solvents.

Table A2 Calculated<sup>a</sup> molar ( $\chi_M$ ) and volumetric ( $\chi_V$ ) susceptibility in cgs-ppm, density<sup>b</sup> ( $\rho$ , g/mL), molar mass (M, g/mol), molar volume ( $V_m$ , mL/mol) and population (%) of the rotamers<sup>c</sup> of N-sulfinylanilines **1-4**.

Table A3 Experimental and corrected <sup>17</sup>O chemical shifts (ppm) for N-sulfinylaniline (**1**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution.

Tables A4-A12 Same as Table A3, for N-sulfinylanilines **2 – 4**

Table A13 Solvatochromic parameters of the solvents used.<sup>a</sup>

Table A1 Experimental<sup>a</sup> and calculated<sup>b</sup> molar ( $\chi_M$ ) and volumetric ( $\chi_v$ ) susceptibility in cgs-ppm, density<sup>a,c</sup> ( $\rho$ , g/mL), molar mass (M, g/mol) and molar volume<sup>b</sup> ( $V_m$ , mL/mol) of solvents

	$-\chi_{M,\text{exp}}$	$-\chi_{M,\text{calc}}$	$\rho$	M	$V_m$	$-\chi_{v,\text{exp}}$	$-\chi_{v,\text{calc}}$
water	12.97	14.0	0.998	18.0	16	0.719	0.776
methanol	21.40	21.5	0.7914	32.0	30	0.530	0.532
ethanol	33.60	34.2	0.7893	46.1	44	0.575	0.586
1-propanol	45.176	45.9	0.8035	60.1	61	0.6047	0.614
2-propanol	45.794	47.4	0.7855	60.1	61	0.5985	0.620
1-butanol	56.536	57.4	0.8098	74.1	72	0.6176	0.627
methylene chloride	46.6	47.9	1.325	84.9	44	0.733	0.748
chloroform	59.30	59.4	1.492	119.4	66	0.740	0.742
tetrachloro methane	66.60	66.6	1.5867	153.8	79	0.691	0.687
acetone	33.7	33.7	0.7899	58.1	57	0.460	0.458
acetonitrile	28.0	28.0	0.7857	41.1	41	0.534	0.535
DMSO	43.7 <sup>d</sup>	45.9	1.1014	78.1	64	0.616 <sup>e</sup>	0.647
pyridine	49.21	47.9	0.9819	79.1	71	0.611	0.595
benzene	54.84	54.4	0.8765	78.1	74	0.611	0.611
toluene	66.11	64.0	0.8669	92.1	92	0.6179	0.602
hexane	74.6	75.5	0.6603	86.2	99	0.565	0.578
cyclohexane	68.13	67.3	0.7785	84.2	90	0.627	0.622

<sup>a</sup> From the CRC Handbook of Chemistry and Physics, 63<sup>rd</sup> edition, CRC Press, 1983.

<sup>b</sup> Geometry optimization with B3LYP/6-31+G(2d,2p). GIAO isotropic susceptibilities ( $\chi_M$ ) with OPBE/6-311++G(2df,pd). Molar volume to the 0.001 e/bohr<sup>3</sup> density.

<sup>c</sup> Density mostly given at 20 °C.

<sup>d</sup> From the volumetric susceptibility.

<sup>e</sup> From A.B. Kudrzavtsev, W. Linert, Physico-chemical applications of NMR, World Scientific, Singapore, 1996.

Table A2 Calculated<sup>a</sup> molar ( $\chi_M$ ) and volumetric ( $\chi_V$ ) susceptibility in cgs-ppm, density<sup>b</sup> ( $\rho$ , g/mL), molar mass (M, g/mol), molar volume ( $V_m$ , mL/mol) and population (%) of the rotamers<sup>c</sup> of N-sulfinylanilines 1-4

	$-\chi_M$	$\rho$	M	$V_m$	$-\chi_V$	Population
Ph-NSO	64.4	1.236	139.2	88	0.572	100
2-Cl	75.5	1.4	173.6	107	0.61	<1
6-Cl	82.3	1.4	173.6	109	0.66	>99
ortho average <sup>d</sup>	82.3			109	0.66	
3-Cl	78.8	1.4	173.6	103	0.64	49
5-Cl	75.7	1.4	173.6	110	0.61	51
meta average <sup>d</sup>	77.2			107	0.62	
4-Cl	78.2	1.4	173.6	106	0.63	100
2-NO <sub>2</sub>	61.9	1.5	184.2	110	0.50	11
6-NO <sub>2</sub>	62.4	1.5	184.2	113	0.51	89
ortho average <sup>d</sup>	62.3			113	0.51	
3-NO <sub>2</sub>	67.0	1.5	184.2	121	0.55	46
5-NO <sub>2</sub>	63.7	1.5	184.2	108	0.52	54
meta average <sup>d</sup>	65.2			114	0.53	
4-NO <sub>2</sub>	70.4	1.5	184.2	111	0.57	100
2-OCH <sub>3</sub>	78.5	1.3	169.2	122	0.60	3
6-OCH <sub>3</sub>	76.2	1.3	169.2	110	0.59	97
ortho average <sup>d</sup>	76.3			110	0.59	
3-OCH <sub>3,syn</sub> <sup>e</sup>	79.0	1.3	169.2	132	0.61	57
3-OCH <sub>3,anti</sub> <sup>e</sup>	77.9	1.3	169.2	129	0.60	9
5-OCH <sub>3,syn</sub> <sup>e</sup>	74.4	1.3	169.2	115	0.57	24
5-OCH <sub>3,anti</sub> <sup>e</sup>	75.9	1.3	169.2	116	0.58	10
meta average <sup>d</sup>	77.5			126	0.60	
4-OCH <sub>3,syn</sub> <sup>e</sup>	81.7	1.3	169.2	113	0.63	51
4-OCH <sub>3,anti</sub> <sup>e</sup>	77.9	1.3	169.2	118	0.60	49
para average <sup>d</sup>	79.8			115	0.62	

<sup>a</sup> Geometry optimization with B3LYP/6-31+G(2d,2p). GIAO isotropic susceptibilities ( $\chi_M$ ) with OPBE/6-311++G(2df,pd). Molar volume to the 0.001 e/bohr<sup>3</sup> density.

<sup>b</sup> Estimated density upon substitution: chloro 1.236 + 0.2 g/mL, nitro 1.236 + 0.3 g/mL, methoxy 1.236 + 0.1 g/mL.

<sup>c</sup> Given for a set of rotamers in equilibrium: ortho (2 and 6), meta (3 and 5), para methoxy (4<sub>syn</sub> and 4<sub>anti</sub>). Calculated from the difference in total energy.

<sup>d</sup> Weighted average.

<sup>e</sup> Syn has the CH<sub>3</sub> group oriented towards the SO oxygen, anti away from it.

Table A3 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for N-sulfinylaniline (**1**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	412.67					
methanol	411.59	410.48	409.85	410.16	-1.43	410
ethanol	410.87	409.88	409.38	409.63	-1.24	409
1-propanol	411.95	411.05	410.42	410.73	-1.22	411
2-propanol	412.31	411.45	410.99	411.22	-1.09	412
1-butanol	412.31	411.48	411.07	411.28	-1.04	412
methylene chloride	410.87	410.30	409.84	410.07	-0.80	410
chloroform	411.23	410.70	410.33	410.51	-0.72	411
tetrachloro methane	414.83	414.22	413.80	414.01	-0.82	418
acetone	412.31	411.15	410.48	410.82	-1.50	411
acetonitrile	409.79	408.72	408.13	408.42	-1.37	407
DMSO	409.07	408.28	407.88	408.08	-0.99	406
pyridine	411.23 426.41	410.37 425.41	409.77 424.81	410.07 425.11	-1.16 -1.30	410 440
benzene	413.75	412.93	412.22	412.58	-1.18	415
toluene	414.83	414.01	413.14	413.58	-1.26	417
hexane	416.27	415.48	414.78	415.13	-1.14	420
cyclohexane	416.27	415.48	414.68	415.08	-1.19	420

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

Table A4 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for o-chloro-N-sulfinylaniline (**2-1**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	416.64					
methanol	415.20	414.25	414.17	414.21	-0.99	412
ethanol	416.28	415.46	415.33	415.40	-0.89	414
1-propanol	417.72	416.98	416.82	416.9	-0.82	417
1-butanol	416.28	415.63	415.42	415.53	-0.76	414
methylene chloride	415.56	415.20	414.78	414.989	-0.57	413
chloroform	416.64	416.32	415.95	416.14	-0.51	415
tetrachloro methane	419.52	419.12	418.78	418.95	-0.57	421
acetone	417.72	416.77	416.61	416.69	-1.03	416
acetonitrile	415.56	414.66	414.53	414.59	-0.97	413
DMSO	413.04	412.47	412.18	412.32	-0.72	408
pyridine	413.76 426.72	413.07 426.03	412.86 425.82	412.96 425.72	-0.80 -0.80	409
benzene	417.00	416.35	416.10	416.25	-0.78	416
toluene	419.88	419.06	418.98	419.02	-0.86	421
hexane	417.72	417.11	416.77	416.94	-0.78	417
cyclohexane	416.64	416.04	415.78	415.91	-0.73	415

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

Table A5 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for m-chloro-N-sulfinylaniline (**2-2**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	417.00					
methanol	414.58	413.45	413.45	413.45	-1.03	409
ethanol	415.92	415.02	414.97	415.00	-0.93	413
1-propanol	415.56	414.74	414.66	414.70	-0.86	412
1-butanol	417.00	416.26	416.14	416.20	-0.80	415
methylene chloride	417.36	416.87	416.58	416.73	-0.64	416
chloroform	416.28	415.84	415.59	415.72	-0.57	414
tetrachloro methane	420.60	420.11	419.86	419.99	-0.62	423
acetone	417.72	416.65	416.61	416.63	-1.09	416
acetonitrile	416.28	415.29	415.25	415.27	-1.01	414
DMSO	413.76	413.07	412.10	412.98	-0.78	409
pyridine	416.28 424.92	415.50 424.14	415.38 424.02	415.89 424.08	-0.39 -0.84	415 431
benzene	419.52	418.79	418.62	418.71	-0.82	420
toluene	420.24	419.42	419.34	419.38	-0.86	422
hexane	422.40	421.71	421.45	421.58	-0.82	426
cyclohexane	421.32	420.63	420.46	420.55	-0.78	424

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

Table A6 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for p-chloro-N-sulfinylaniline (**2-3**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	410.16 <sup>d</sup>					
methylene chloride	413.40	413.04	412.62	412.83	-0.57	416
chloroform	413.40	413.08	412.71	412.89	-0.51	416
tetrachloro methane	417.72	417.32	416.98	417.15	-0.57	424
acetonitrile	411.96	411.06	410.93	410.99	-0.97	412
DMSO	411.24	410.67	410.38	410.52	-0.72	411
pyridine	415.92 422.76	414.50 422.19	415.02 421.86	414.76 422.03	-1.16 -0.90	413 427
benzene	415.20	414.55	414.30	414.42	-0.78	419
toluene	416.64	415.82	415.74	415.78	-0.86	421
hexane	417.36	416.75	416.41	416.58	-0.78	423
cyclohexane	417.72	417.12	416.86	416.99	-0.73	424

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

<sup>d</sup> Solid sample. hexane solution.

Table A7 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for o-methoxy-N-sulfinylaniline (**3-1**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	409.80					
methanol	408.36	407.25	407.54	407.39	-0.97	406
ethanol	408.72	407.73	407.94	407.83	-0.89	407
1-propanol	409.44	408.54	408.70	408.62	-0.82	409
1-butanol	409.77	408.98	409.06	409.02	-0.78	410
methylene chloride	408.36	407.79	407.79	407.79	-0.57	407
chloroform	409.08	408.59	408.55	408.57	-0.51	409
tetrachloro methane	411.24	410.67	410.63	410.65	-0.59	413
acetone	409.44	408.33	408.49	408.41	-1.03	408
acetonitrile	408.72	407.65	407.90	407.77	-0.95	407
DMSO	408.72	407.94	408.03	407.98	-0.74	408
pyridine	409.44	408.58	408.66	408.62	-0.82	409
	415.56	414.70	414.78	414.74	-0.82	421
benzene	411.96	411.14	411.22	411.18	-0.78	414
toluene	411.59	410.77	410.85	410.81	-0.78	413
hexane	412.32	411.50	411.50	411.50	-0.82	415
cyclohexane	412.32	411.54	411.58	411.56	-0.76	415

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.



Table A8 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for m-methoxy-N-sulfinylaniline (**3-2**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	411.32					
methanol	410.52	409.41	409.74	409.57	-0.95	408
ethanol	408.00	407.01	407.26	407.13	-0.87	403
1-propanol	411.24	410.38	410.50	410.44	-0.80	410
1-butanol	407.28	406.46	406.59	406.52	-0.76	402
methylene chloride	409.08	408.55	408.51	408.53	-0.55	406
chloroform	408.36	407.87	407.83	407.85	-0.51	404
tetrachloro methane	412.68	412.11	412.07	412.09	-0.59	413
acetone	409.08	407.97	408.18	408.07	-1.01	405
acetonitrile	410.52	409.45	409.70	409.57	-0.95	408
DMSO	407.64	406.90	406.98	406.94	-0.70	403
pyridine	408.36 422.04	407.64 421.32	409.42 421.30	408.53 421.33	0.17 -0.71	406 431
benzene	410.16	409.34	409.42	409.38	-0.78	407
toluene	410.52	409.70	409.78	409.74	-0.78	408
hexane	410.88	410.10	410.10	410.10	-0.78	409
cyclohexane	413.40	412.62	412.70	412.66	-0.74	414

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

Table A9 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for p-methoxy-N-sulfinylaniline (**3-3**) in different solvents. Corrections for external standard from two correction versions,<sup>a</sup> final corrected value and value upon infinite dilution

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error	infinite dilution shifts <sup>c</sup>
neat	398.64					
methanol	397.19	396.16	396.45	396.31	-0.89	394
ethanol	398.28	397.33	397.59	397.46	-0.82	396
1-propanol	398.27	397.45	397.62	397.54	-0.74	396
1-butanol	398.27	397.49	397.62	397.56	-0.72	396
methylene chloride	398.64	398.15	398.15	398.15	-0.49	398
chloroform	397.92	397.48	397.43	397.45	-0.47	396
tetrachloro methane	401.16	400.63	400.63	400.63	-0.53	403
acetone	400.44	399.37	399.58	399.47	-0.97	400
acetonitrile	397.55	396.53	396.81	396.67	-0.88	395
DMSO	397.91	397.22	397.30	397.26	-0.65	396
pyridine	397.55 415.20	396.77 414.42	397.36 415.01	397.07 414.71	-0.48 -0.49	383 418
benzene	400.08	399.30	399.43	399.36	-0.72	400
toluene	400.44	399.62	399.75	399.68	-0.76	401
hexane	401.16	400.42	400.42	400.42	-0.74	402
cyclohexane	401.52	400.78	400.87	400.82	-0.70	403

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Crude estimate from the neat and the equimolar value.

Table A10 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for o-nitro-N-sulfinylaniline (**4-1**) in different solvents. Corrections for external standard from two correction versions<sup>a</sup> and final corrected value

	original	correction version 1	correction version 2	corrected <sup>b</sup>	Error
neat	- <sup>c</sup>				
methylene chloride	418.44	417.61	417.61	417.61	0.00
chloroform	419.52	418.78	418.77	418.77	-0.01
acetone	416.64	415.29	415.45	415.37	0.08
acetonitrile	415.56	414.23	414.47	414.35	0.12
DMSO	412.32	411.32	411.41	411.36	0.05
pyridine	417.36 423.48	418.43 423.48	418.34 424.46	418.39 423.97	1.03 0.49
benzene	421.68	420.65	420.74	420.69	0.04
toluene	422.40	422.40	421.46	421.52	-0.06

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Solid sample, no dissolution with nonpolar aliphatic solvents.

Table A11 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for m-nitro-N-sulfinylaniline (**4-2**) in different solvents. Corrections for external standard from two correction versions<sup>a</sup> and final corrected value

	original	correction version 1	correction version 2	corrected <sup>b</sup>	Error
neat	- <sup>c</sup>				
methylene chloride	417.72	416.96	416.89	416.92	-0.80
chloroform	419.52	418.84	418.77	418.80	-0.72
acetone	417.36	416.07	416.17	416.12	-1.24
acetonitrile	412.68	411.41	411.59	411.50	-1.18
DMSO	418.08	417.14	417.17	417.16	-0.92
pyridine	410.88 413.00	409.86 411.98	409.90 412.02	409.88 412.00	-1.00 -1.00
benzene	419.16	418.18	418.21	418.20	-0.96
toluene	422.04	421.22	421.10	421.16	-0.88

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Solid sample, no dissolution with nonpolar aliphatic solvents.

Table A12 Experimental and corrected  $^{17}\text{O}$  chemical shifts (ppm) for p-nitro-N-sulfinylaniline (**4-3**) in different solvents. Corrections for external standard from two correction versions<sup>a</sup> and final corrected value

	original	correction version 1	correction version 2	corrected <sup>b</sup>	error
neat	- <sup>c</sup>				
methylene chloride	416.28	415.63	416.89	416.26	-0.02
chloroform	416.28	415.71	418.77	417.24	0.96
acetone	416.28	415.09	416.17	415.63	-0.65
acetonitrile	412.68	411.52	411.59	411.56	-1.12
DMSO	418.08	417.25	417.17	417.21	-0.87
pyridine	415.56 425.64	414.65 424.73	414.58 424.66	414.62 424.70	-0.94 -0.94
benzene	419.16	418.28	418.21	418.25	-0.91
toluene	422.04	422.04	421.10	421.57	-0.47

<sup>a</sup> See text for correction versions 1 and 2 used.

<sup>b</sup> Using the average of the two corrections.

<sup>c</sup> Solid sample, no dissolution with nonpolar aliphatic solvents.

Table A13 Solvatochromic parameters of the solvents used<sup>a</sup>

solvent	$\pi^*$	$\alpha$	$\beta$
1-butanol	0.46	0.79	0.88
2-propanol	0.46	0.78	0.95
1-propanol	0.51	0.80	0.95
ethanol	0.54	0.86	0.77
methanol	0.60	0.98	0.62
acetone	0.72	0.07	0.48
pyridine	0.87	0.00	0.64
acetonitrile	0.85	0.15	0.31
dimethyl sulfoxide	1.00	0.00	0.76
methylene chloride	0.80	0.22	0.00
chloroform	0.76	0.34	0.00
carbon tetrachloride	0.29	0.00	0.00
toluene	0.54	0.00	0.11
benzene	0.59	0.00	0.10
cyclohexane	0.00	0.00	0.00
hexane	0.08	0.00	0.00

<sup>a</sup> From reference [44].

## Appendix B

Table B1. Phenyl  $^1\text{H}$  chemical shifts (ppm) for N-sulfinylaniline (**1**) in pyridine at various temperatures.

Table B1 Phenyl <sup>1</sup>H chemical shifts (ppm) for N-sulfinylaniline (**1**) in pyridine at various temperatures<sup>a</sup>

T (°C)	<i>ortho</i>	<i>meta</i>	<i>para</i>
10 mol% <i>N</i> -sulfinylaniline			
30	7.72	7.15	7.15
40	7.70	7.16	7.16
50	7.69	7.17	7.17
60	7.68	7.17	7.17
70	7.68	7.16	7.16
30 mol% <i>N</i> -sulfinylaniline			
30	7.72	7.16	7.16
40	7.69	7.14	7.14
50	7.69	7.15	7.15
60	7.66	7.16	7.16
70	7.68	7.15	7.15
50 mol% <i>N</i> -sulfinylaniline			
30	7.69	7.14	7.14
35	7.68	7.14	7.14
40	7.67	7.14	7.14
45	7.67	7.14	7.14
50	7.67	7.14	7.14
55	7.67	7.12	7.12
60	7.66	7.13	7.13
65	7.65	7.12	7.12
70	7.65	7.14	7.14
70 mol% <i>N</i> -sulfinylaniline			
40	7.64	7.11	7.11
50	7.63	7.1	7.1
60	7.64	7.11	7.11
70	7.62	7.11	7.11
80 mol% <i>N</i> -sulfinylaniline			
30	7.67	7.12	7.12
40	7.65	7.12	7.12
50	7.66	7.11	7.11
60	7.65	7.11	7.11
70	7.63	7.11	7.11

T (°C)	<i>ortho</i>	<i>meta</i>	<i>para</i>
20 mol% <i>N</i> -sulfinylaniline			
30	7.72	7.17	7.17
40	7.71	7.17	7.17
50	7.69	7.17	7.17
60	7.69	7.16	7.16
70	7.67	7.16	7.16
40 mol% <i>N</i> -sulfinylaniline			
30	7.69	7.14	7.14
40	7.68	7.14	7.14
50	7.68	7.15	7.15
60	7.66	7.15	7.15
70	7.65	7.13	7.13
60 mol% <i>N</i> -sulfinylaniline			
30	7.67	7.14	7.14
40	7.66	7.13	7.13
50	7.65	7.13	7.13
60	7.65	7.13	7.13
70	7.65	7.12	7.12
90 mol% <i>N</i> -sulfinylaniline			
30	7.66	7.10	7.10
35	7.66	7.10	7.10
40	7.64	7.11	7.11
45	7.64	7.09	7.09
55	7.62	7.08	7.08
60	7.65	7.10	7.10
65	7.65	7.09	7.09
70	7.63	7.09	7.09

<sup>a</sup> Reference HMDS.



## Appendix C

Table C1 Temperature  $^{17}\text{O}$  NMR data for N-sulfinylaniline (**1**) and chloro-N-sulfinylanilines **2-1**, **2-2**, **2-3**

Table C2 Temperature  $^{17}\text{O}$  NMR data for methoxy-N-sulfinylanilines **3-1**, **3-2**, **3-3**

Table C3 Temperature  $^{17}\text{O}$  NMR data for nitro-N-sulfinylanilines **4-1**, **4-2**, **4-3**

Table C1 Temperature (°C) <sup>17</sup>O NMR data for N-sulfinylaniline (**1**) and chloro-N-sulfinylanilines **2-1**, **2-2**, **2-3**. Chemical shifts (ppm), half-widths (Hz)

T	complexed		uncomplexed		δ <sup>17</sup> O	W <sub>1/2</sub>	K
	δ <sup>17</sup> O	W <sub>1/2</sub>	δ <sup>17</sup> O	W <sub>1/2</sub>			
	<b>1</b>				<b>1</b> Neat		
20	416.27 <sup>a</sup>	58	411.23 <sup>a</sup>	113	412.67	160	0.57
30	421.67 <sup>b</sup>	51	411.59 <sup>b</sup>	102	413.39	141	0.36
40	426.35	51	411.95	96	413.75	117	0.25
50	432.12	43	412.67	92	414.47	101	0.18
60	437.88	42	413.75	68	414.48	87	0.06
70	444.36	41	414.83	64	415.92	76	0.07
	<b>2-1</b>				<b>2-1</b> Neat		
20	414.84	167	414.84	167	416.64	385	0.77
30	422.76	44	415.92	122	418.44	329	0.70
40	428.52	43	417.00	110	419.16	249	0.33
50	434.29	42	418.08	108	419.52	199	0.20
60	440.41	42	419.16	107	420.60	174	0.13
70	448.00	38	420.24	104	421.32	149	0.09
	<b>2-2</b>				<b>2-2</b> Neat		
20	420.00	109	415.92	200	415.92	455	0.63
30	424.92	67	416.28	167	417.00	322	0.24
40	429.24	51	416.28	133	418.44	247	0.17
50	435.01	33	417.72	113	418.44	236	0.13
60	440.77	29	418.44	109	419.88	195	0.12
70	446.53	25	418.80	89	420.24	155	0.11
	<b>2-3</b>				<b>2-3</b> Neat		
20	423.14	56	413.04	233	409.80 <sup>c</sup>	211	0.76
30	426.72	54	413.76	211	410.16	133	0.46
40	430.68	51	413.76	194	410.88	118	0.32
50	436.45	44	414.84	144	411.96	89	0.24
60	441.85	39	415.56	122	413.04	83	0.19
70	447.25	39	415.92	113	414.12	67	0.15

<sup>a</sup> Shifts at 21 °C.

<sup>b</sup> Shifts at 32 °C.

<sup>c</sup> **2-3** is solid at 20 °C. Determined from a 0.9 mol% hexane solution.

Table C2 Temperature (°C) <sup>17</sup>O NMR data for methoxy-N-sulfinylanilines **3-1**, **3-2**, **3-3**.  
Chemical shifts (ppm), half-widths (Hz)

T	complexed		uncomplexed		OMe	NSO	W <sub>1/2</sub>	OMe	K
	δ <sup>17</sup> O	W <sub>1/2</sub>	δ <sup>17</sup> O	W <sub>1/2</sub>	δ <sup>17</sup> O	δ <sup>17</sup> O		δ <sup>17</sup> O	
	<b>3-1</b>				<b>3-1 Neat</b>				
20	410.88	233	410.88	233	17.65	407.64	720	16.57	0.36
30	415.56	119	409.44	231	17.65	408.36	510	16.93	0.21
40	420.96	56	410.52	220	18.37	409.80	399	17.65	0.14
50	427.44	55	411.24	129	18.73	410.88	377	18.37	0.04
60	434.65	51	412.32	122	19.81	411.24	304	18.37	0.10
70	440.77	47	413.76	109	20.53	414.14	441	19.45	0.03
	<b>3-2</b>				<b>3-2 Neat</b>				
30	409.12	113	408.36	234	35.78	412.32	456	36.73	0.33
40	422.04	68	409.80	211	35.61	411.60	432	36.57	0.29
50	428.16	61	410.52	167	36.73	412.68	345	36.63	0.24
60	433.92	31	411.60	123	36.73	413.60	234	36.11	0.16
70	443.29	30	412.68	97	37.45	413.04	210	36.45	0.02
	<b>3-3</b>				<b>3-3 Neat</b>				
30	415.21	144	397.55	455	17.65	393.11	613	17.34	0.40
40	421.68	101	400.44	344	18.37	398.64	551	18.73	0.17
50	428.16	87	399.36	231	19.09	401.52	498	18.37	0.15
60	434.65	57	400.80	210	19.45	401.16	346	19.09	0.02
70	441.13	49	402.24	153	20.17	402.24	257	20.17	0.27

Table C3 Temperature (°C)  $^{17}\text{O}$  NMR data for nitro-N-sulfinylanilines **4-1**, **4-2**, **4-3**.  
Chemical shifts (ppm), half-widths (Hz)

T	complexed		uncomplexed		NO <sub>2</sub>	NSO	NO <sub>2</sub>		K
	$\delta^{17}\text{O}$	$W_{1/2}$	$\delta^{17}\text{O}$	$W_{1/2}$	$\delta^{17}\text{O}$	$\delta^{17}\text{O}$	$W_{1/2}$	$\delta^{17}\text{O}$	
	<b>4-1</b>				<b>4-1 Neat<sup>a</sup></b>				
20	408.72	89	414.48	456	580.49	422.04	155	579.41	15.35
30	411.97	344	411.96	344	575.45	422.40	136	580.49	7.06
40	417.72	256	417.72	256	580.85	422.76	109	579.77	4.23
50	423.48	94	417.36	224	577.61	423.48	107	582.65	2.81
60	429.60	79	418.44	218	580.85	424.20	99	581.21	1.03
70	436.09	78	419.52	210	581.21	424.56	87	583.01	1.38
	<b>4-2</b>				<b>4-2 Neat<sup>a</sup></b>				
20	406.97	93	412.00	467	571.84	422.76	124	576.89	14.15
30	413.00	91	410.88	338	579.05	423.84	109	579.05	8.23
40	415.56	59	411.00	189	577.25	424.20	89	585.53	5.79
50	420.96	57	415.56	122	579.41	424.92	84	583.73	3.47
60	426.00	56	416.28	109	582.65	425.64	67	582.31	1.93
70	431.41	39	417.72	107	581.57	426.36	65	584.09	1.26
	<b>4-3</b>				<b>4-3 Neat<sup>a</sup></b>				
20	419.16	112	413.76	234	577.97	423.12	134	576.17	3.47
30	425.64	56	415.56	134	576.53	423.48	112	577.25	1.57
40	431.05	43	416.28	133	578.69	424.20	110	581.93	1.07
50	436.45	46	417.72	112	580.13	424.92	111	580.13	0.77
60	441.13	45	418.44	113	580.49	425.64	109	581.93	0.63
70	446.17	43	419.52	112	580.85	426.36	109	583.73	0.51

<sup>a</sup> Solid sample, no dissolution with nonpolar aliphatic solvents. Determined from a 0.8 mol% benzene solution.

## Appendix D

Fig. D1 Temperature effect on the  $^{17}\text{O}$  signal of N-sulfinylaniline (**1**)

Fig. D2 Temperature effect on the  $^{17}\text{O}$  signal of free (■) and complexed (◆) N-sulfinylaniline (**1**) in pyridine (1:1 molar ratio).

Figs. D3, 5, 7, 9, 11, 13, 15, 17, 19: Same as D1, for N-sulfinylanilines **2** – **4**

Figs. D4, 6, 8, 10, 12, 14, 16, 18, 20: Same as D2, for N-sulfinylanilines **2** – **4**

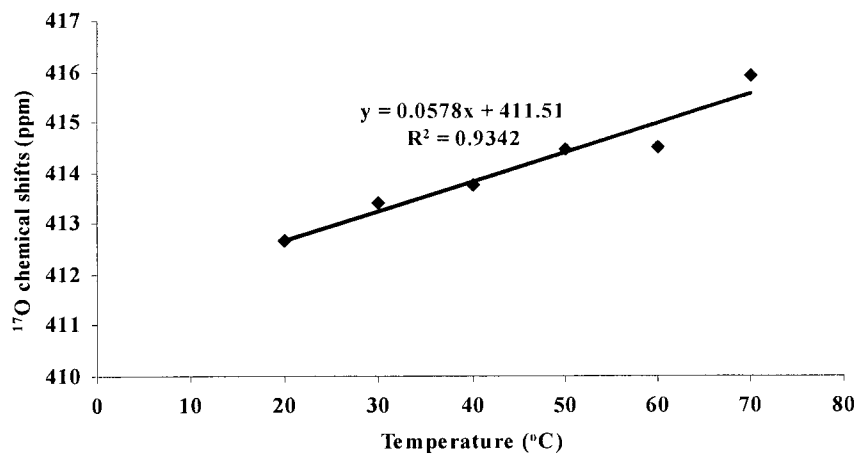


Fig. D1 Temperature effect on the <sup>17</sup>O signal of neat N-sulfinylaniline (1)

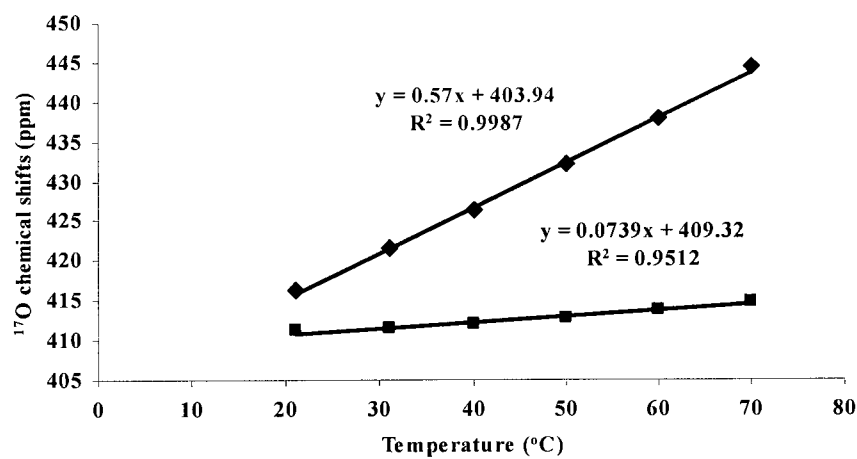


Fig. D2 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) N-sulfinylaniline (1) in pyridine (1:1 molar ratio)

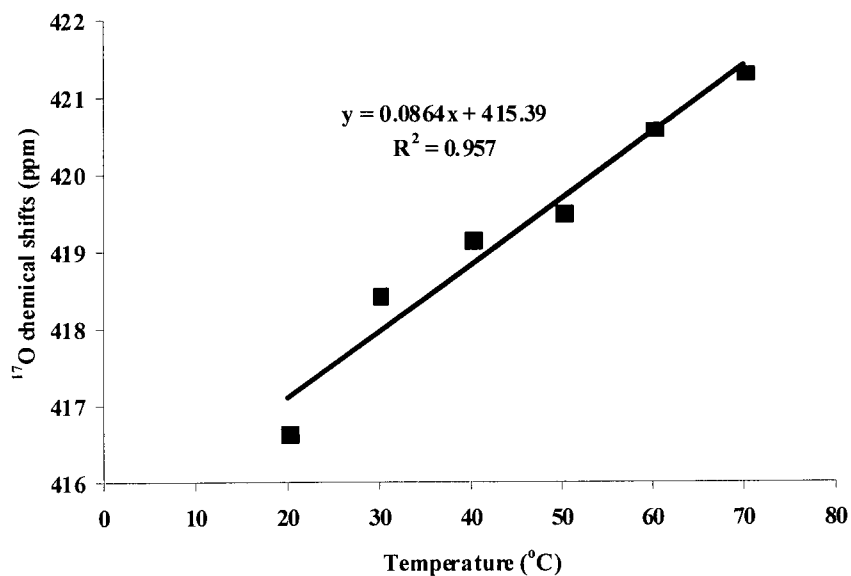


Fig. D3 Temperature effect on the  $^{17}\text{O}$  signal of o-chloro-N-sulfinylaniline (2-1)

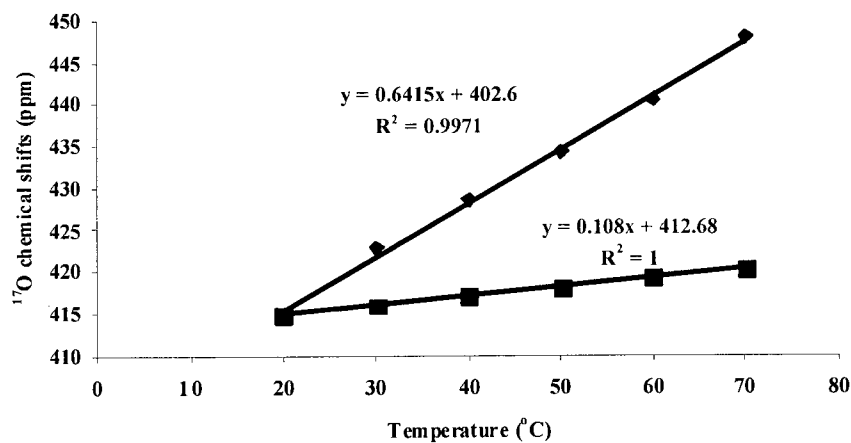


Fig. D4 Temperature effect on the  $^{17}\text{O}$  signal of free (■) and complexed (◆) o-chloro-N-sulfinylaniline (2-1) in pyridine (1:1 molar ratio)

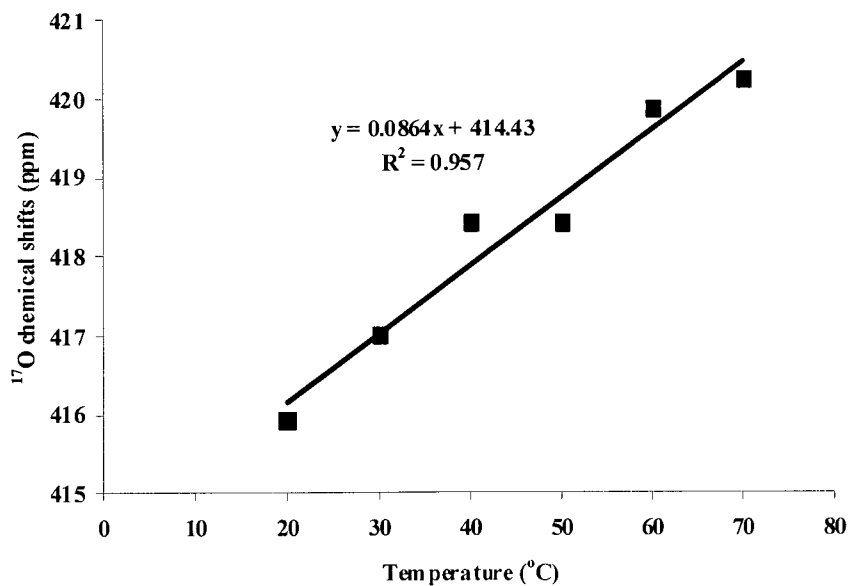


Fig. D5 Temperature effect on the <sup>17</sup>O signal of m-chloro-N-sulfinylaniline (2-2) in hexane (1:1 molar ratio)

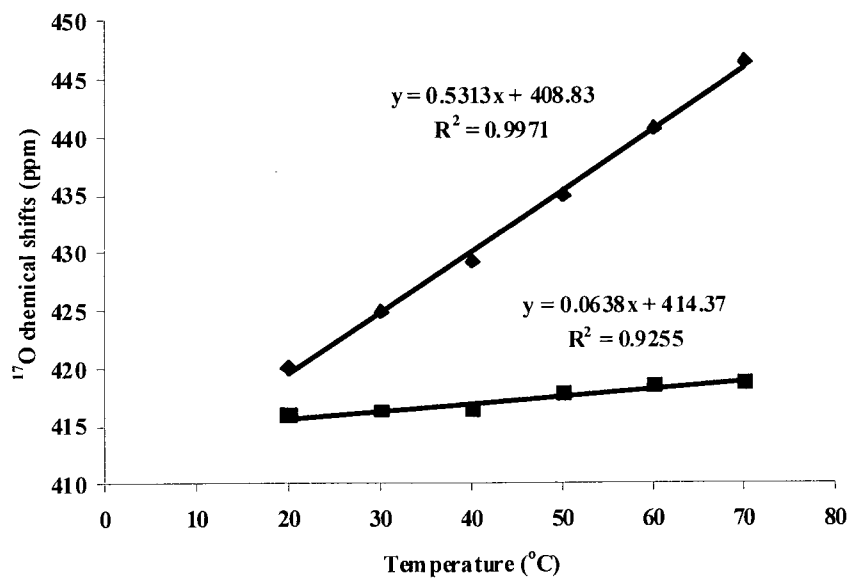


Fig. D6 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) m-chloro-N-sulfinylaniline (2-2) in pyridine (1:1 molar ratio)



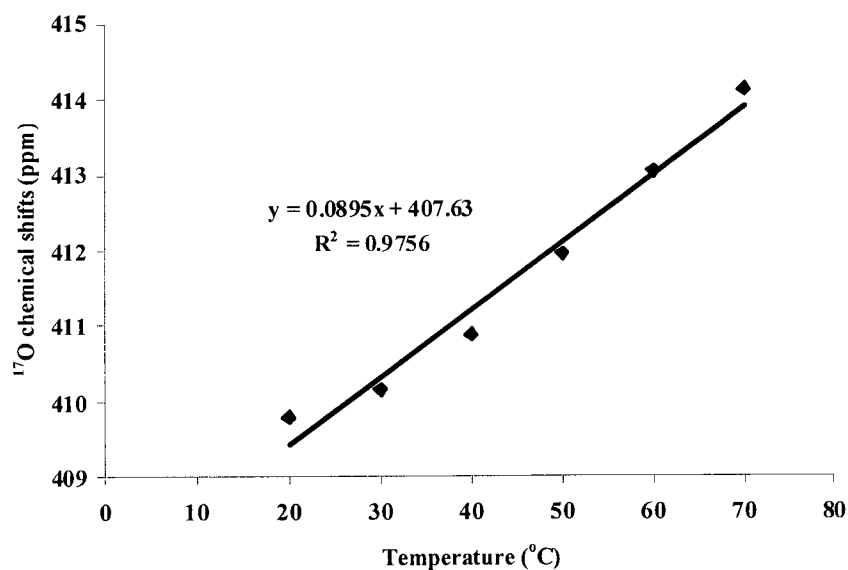


Fig. D7 Temperature effect on the  $^{17}\text{O}$  signal of p-chloro-N-sulfinylaniline (2-3) in hexane (1:1 molar ratio)

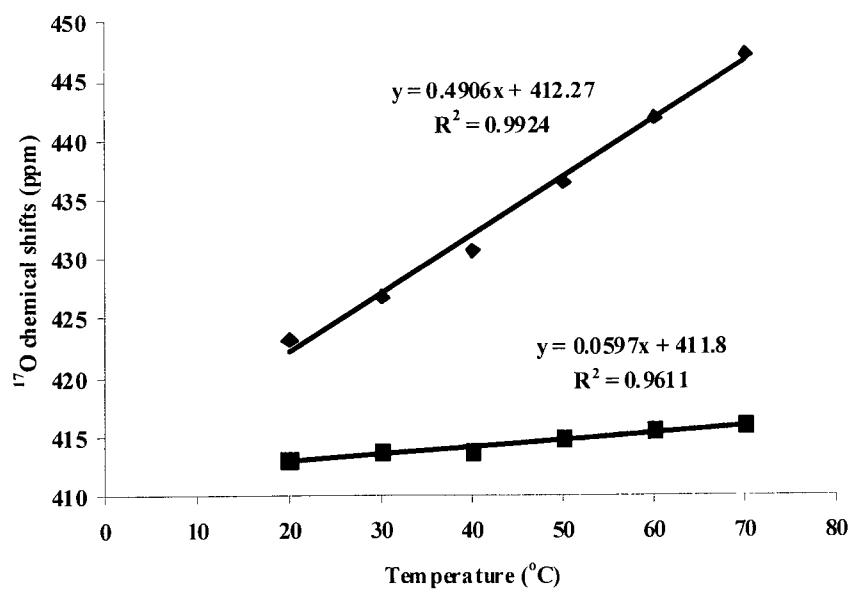


Fig. D8 Temperature effect on the  $^{17}\text{O}$  signal of free (■) and complexed (◆) p-chloro-N-sulfinylaniline (2-3) in pyridine (1:1 molar ratio)

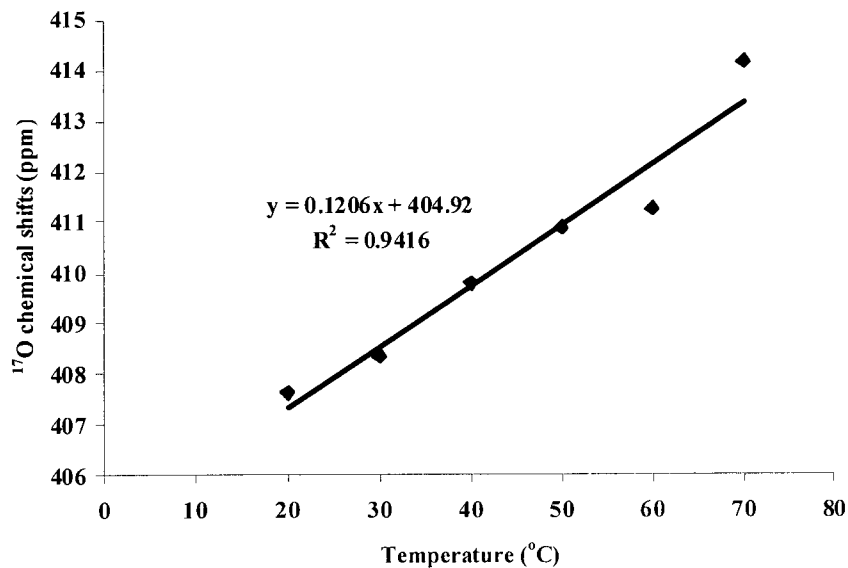


Fig. D9 Temperature effect on the <sup>17</sup>O signal of o-methoxy-N-sulfinylaniline (3-1)

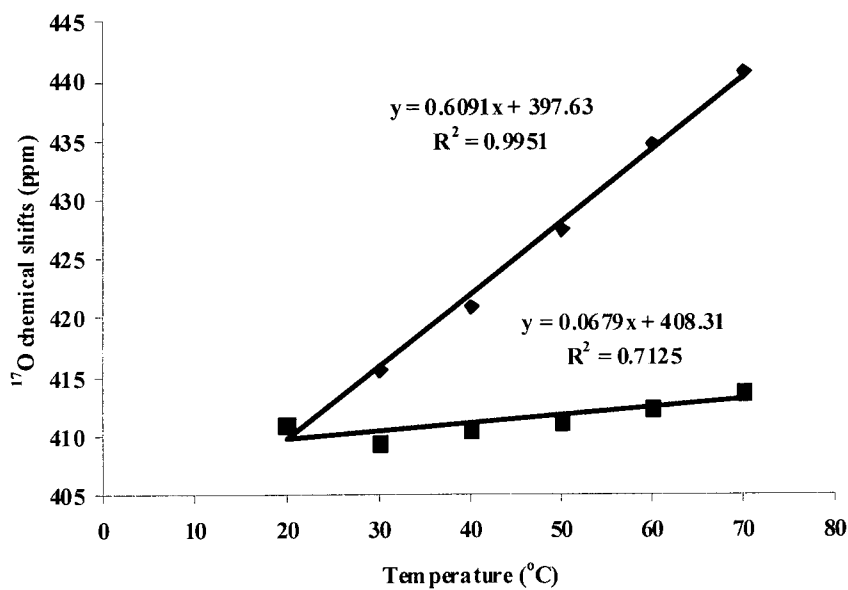


Fig. D10 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) o-methoxy-N-sulfinylaniline (3-1) in pyridine (1:1 molar ratio)

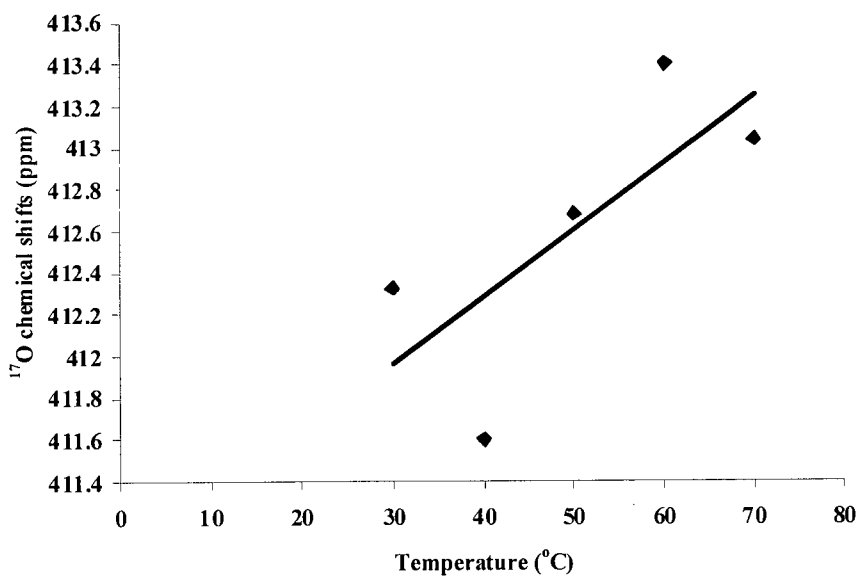


Fig. D11 Temperature effect on the <sup>17</sup>O signal of m-methoxy-N-sulfinylaniline (3-2)

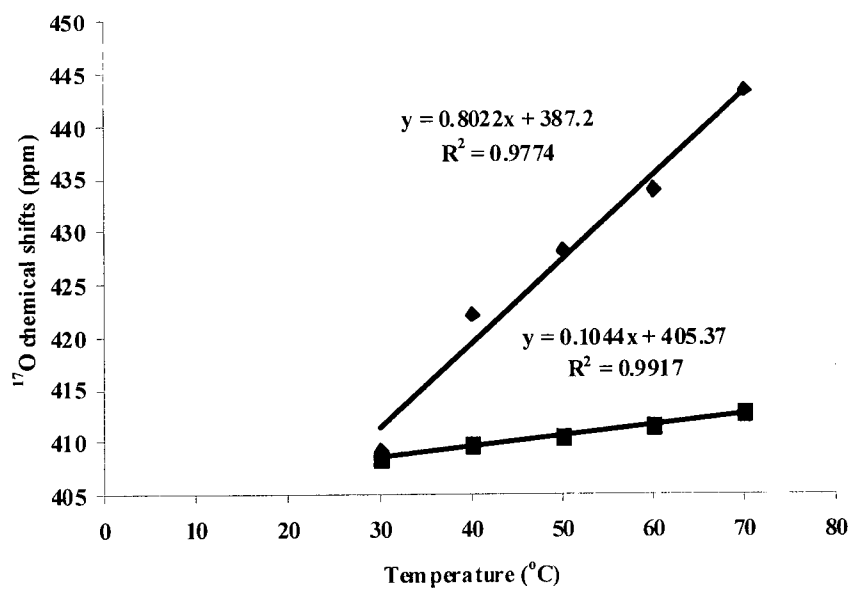


Fig. D12 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) m-methoxy-N-sulfinylaniline (3-2) in pyridine (1:1 molar ratio)

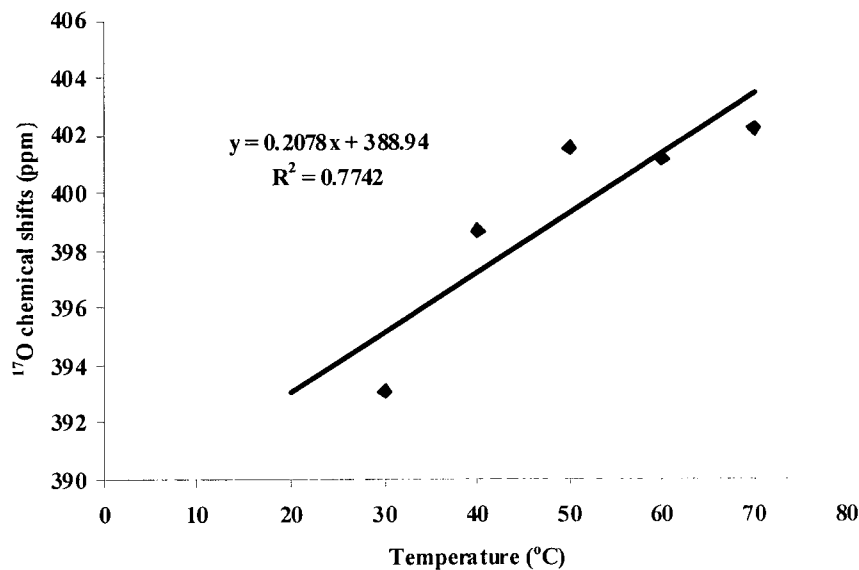


Fig. D13 Temperature effect on the <sup>17</sup>O signal of p-methoxy-N-sulfinylaniline (**3-3**)

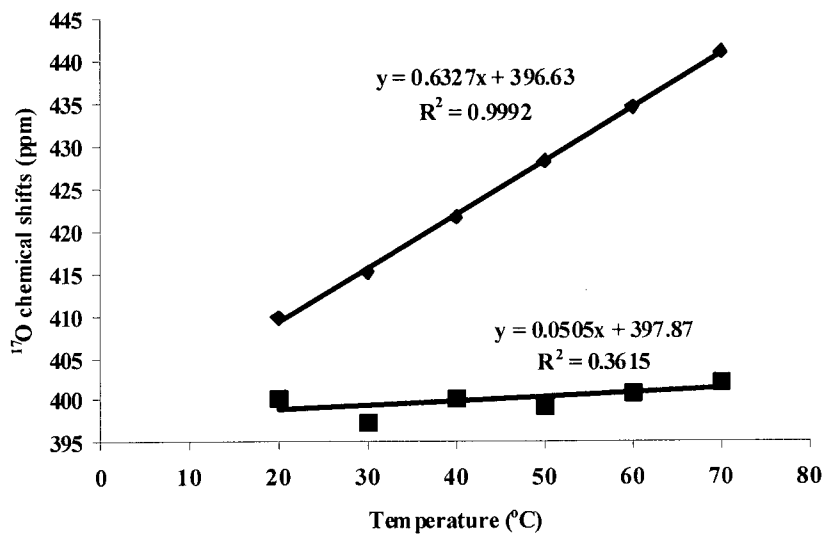


Fig. D14 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) p-methoxy-N-sulfinylaniline (**3-3**) in pyridine (1:1 molar ratio)

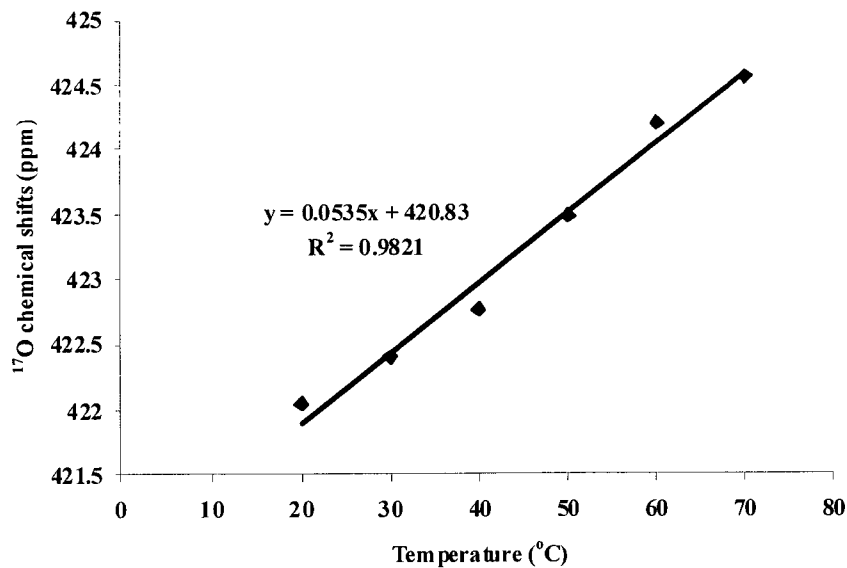


Fig. D15 Temperature effect on the  $^{17}\text{O}$  signal of o-nitro-N-sulfinylaniline (4-1) in benzene

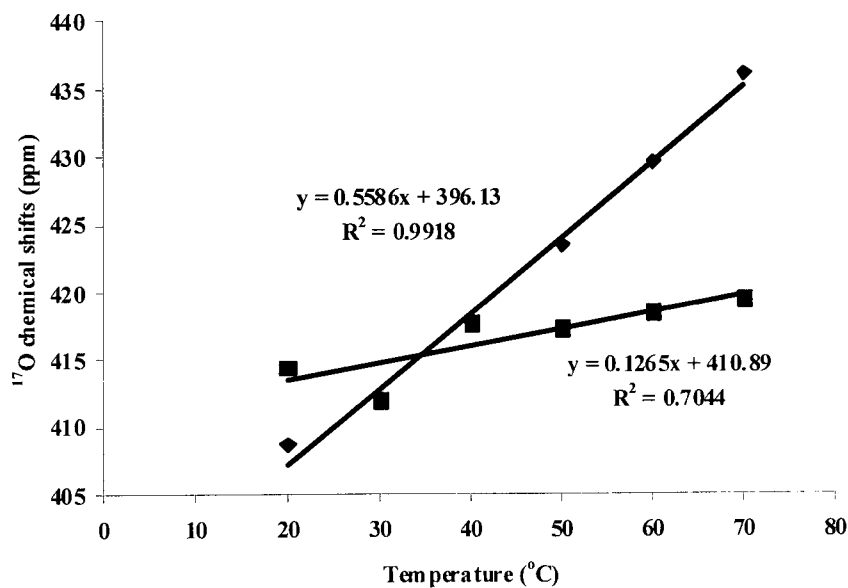


Fig. D16 Temperature effect on the  $^{17}\text{O}$  signal of free (■) and complexed (◆) o-nitro-N-sulfinylaniline (4-1) in pyridine (1:1 molar ratio)

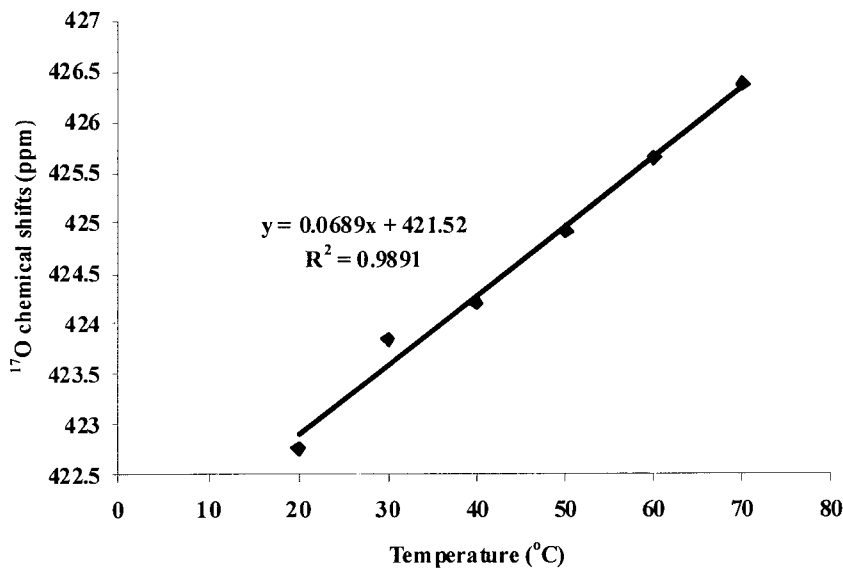


Fig. D17 Temperature effect on the <sup>17</sup>O signal of m-nitro-N-sulfinylaniline (4-2) in benzene

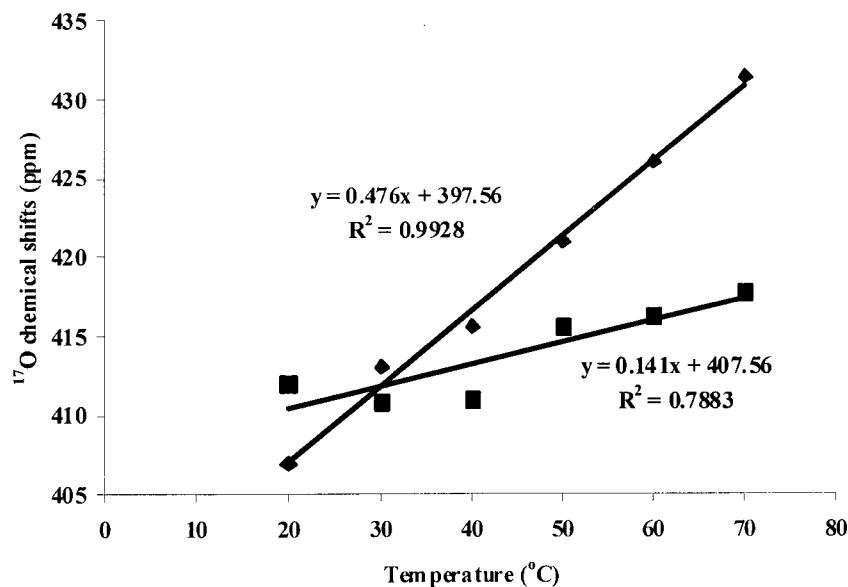


Fig. D18 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) m-nitro-N-sulfinylaniline (4-2) in pyridine (1:1 molar ratio)

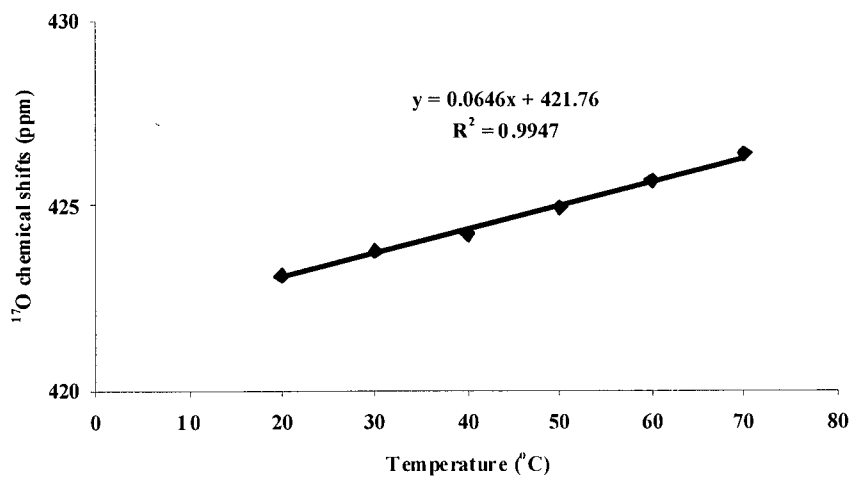


Fig. D19 Temperature effect on the <sup>17</sup>O signal of p-nitro-N-sulfinylaniline (4-3) in benzene

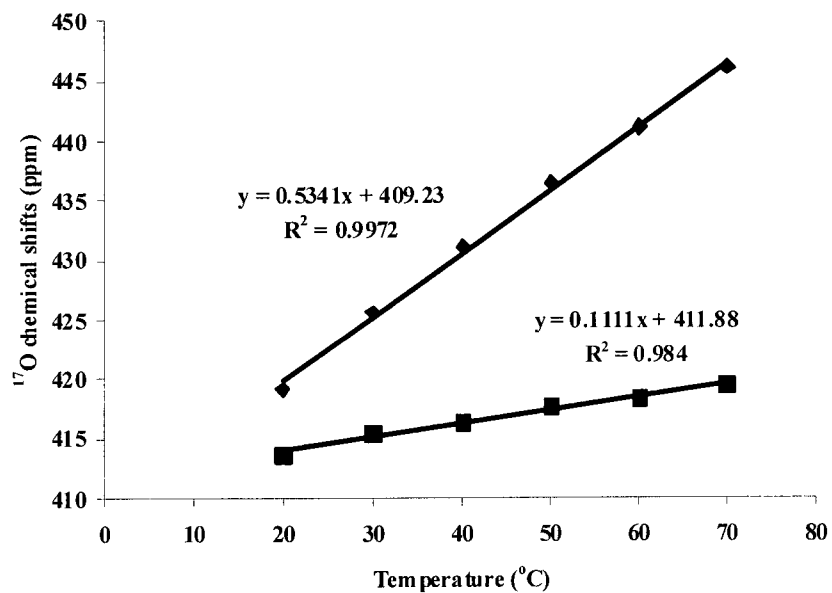


Fig. D20 Temperature effect on the <sup>17</sup>O signal of free (■) and complexed (◆) p-nitro-N-sulfinylaniline (4-3) in pyridine (1:1 molar ratio)