

# Theoretical NMR Spectroscopic Analysis of the Intramolecular Proton Transfer Mechanism in *ortho*-Hydroxyaryl (Un-)Substitued Schiff Bases

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Both NMR spectroscopic parameters are calculated as a function of the distance  $d(\text{N-H})$  of the  $\text{O}\cdots\text{H}\cdots\text{N}$  subsystem of (un- or Z-) substituted *ortho*-hydroxyaryl Schiff bases, with Z = 4-OMe and 5-Cl. Typical patterns for NMR  $J$  couplings and magnetic shieldings,  $\sigma(\text{N})$  (or the chemical shift  $\delta(\text{N})$ ), are obtained showing that they are reliable sensors from which one can get a deeper insight on the intramolecular proton transfer mechanism. An inflection point is found by representing each NMR spectroscopic parameter as a function of  $d(\text{N-H})$  or when the correlation between both parameters is depicted. The analysis of these (cubic) functions shows whether the proton is bound to the oxygen or to the nitrogen atom or is shared by both atoms. In line with these findings, it is possible to predict the position of the proton in the bridge. These theoretical findings are supported by previous experimental measurements. It is shown that nitrogen chemical shift is quite sensitive to substituent effects though  $^1J(^{15}\text{NH})$  is not. This last parameter depends on  $d(\text{NH})$ . When correlating both spectroscopic parameters, a previous  $\delta(\text{N})$  vs  $^1J(^{15}\text{NH})$  linear dependence is generalized to a cubic dependence which seems to be more reliable. Calculations are based on two state of the art methodologies: DFT-B3LYP and polarization propagators at second order of approach (SOPPA) with large enough basis sets.

## 1. Introduction

During the past decade, a large amount of efforts were devoted to get experimental data which relate some NMR spectroscopic parameters, e.g., the imino  $\delta(^{15}\text{N})$  chemical shifts and indirect  $^1J(^{15}\text{NH})$  spin–spin couplings with tautomeric forms of substituted *ortho*-hydroxyaryl Schiff bases. The temperature dependence of tautomeric equilibria was clearly shown and also the way by which that NMR spectroscopic parameters can be used to learn about whether the compounds are in one or the other of their tautomers.

The analysis of the proton transfer mechanism in Schiff bases is important not only to understanding the chemical behavior of these interesting systems, but also due to its application in chemistry, biochemistry, and technology. It is known that proton transfer mechanism plays a central role in biological properties of Schiff bases,<sup>1</sup> as well as in their chemical and technological applications<sup>2</sup> like photochromic and thermochromic properties attributed to intramolecular proton transfer,<sup>3,4</sup> and its applications as optical switches or optical memory devices.<sup>5</sup> Thermochromism is associated with a change in the  $\pi$ -electron system due to proton transfer. This can take place in the ground-state and requires a planar molecular system.<sup>6</sup> Thermochromic (photochromic) properties of salicylideneanilines arise when their conformations are planar (nonplanar).<sup>2,7,8</sup> One of the key parameters that determine the properties of the Schiff bases is the position of the tautomeric equilibrium.

Long-term programs of research were developed to establish standar spectroscopic parameters, e.g., NMR spectroscopic parameters, vibrational frecuencies of IR spectra, and structural parameters, for the OH and NH tautomers of Schiff bases derived from salicylic aldehydes and aliphatic amines.<sup>2,9–17</sup> Different kinds of deuterium isotope effects on  $^{13}\text{C}$  chemical shifts and the correlations of these parameters with coupling

constants of intramolecularly hydrogen-bonded Schiff bases were widely studied by Hansen and co-workers.<sup>13,17</sup> Searching for a correlation between different NMR spectroscopic parameters, a linear dependence between the NMR nuclear magnetic shielding,  $\sigma(^{15}\text{N})$ , and  $^1J(^{15}\text{NH})$  was proposed recently.<sup>18,19</sup> It is worth mentioning that in the whole literature only the absolute value of  $^1J(^{15}\text{NH})$  was considered. Recently Filarowski<sup>18</sup> reported some studies on sterically modified *o*-hydroxyaryl Schiff bases with an intramolecular hydrogen bond made short owing to steric repulsion. He analyzed results taken from X-ray, IR, UV, and NMR spectroscopic methods.

From the above-mentioned NMR spectroscopic parameters of the Schiff bases, one can have physical evidence of the degree of residence of the proton in the bridge between both the oxygen and the nitrogen atom. In particular, the chemical shift of the imino nitrogen atom is sensitive to protonation effects as well as substituent effects and also to the hydrogen-bond formation.<sup>9,20</sup> This last effect was found to be the most important. Then, the chemical shift of the imino nitrogen and nitrogen–proton one bond coupling constants provides quantitative estimation of the proton position, compared with a qualitative estimation that can be obtained from carbon NMR studies.<sup>21</sup> Unfortunately experiments can give reliable information only on the extreme positions of the H-bond, i.e., which of the OH or NH tautomers is involved in the measurement. So one should resort to theoretical models in order to learn in more detail how the proton transfer takes place.

Ogawa, Harada and coauthors recently have shown that for salicylideneanilines, the NH form is predominantly zwitterionic in crystals but neutral in the gas phase.<sup>22,23</sup> They have also found that the OH form of salicylideneanilines is exclusively present at room temperature in the fluid solution of a saturated hydrocarbon solvent, and the NH form is almost exclusively present at low temperature.<sup>24</sup> Our research is based on these assumptions due to the fact that we treat all compounds in their gas phase.

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Usual  $^{15}\text{N}$  chemical shift of Schiff bases are reported with respect to external nitromethane as a standard and appears within  $-60$  to  $-250$  ppm.<sup>15,25</sup> This huge upfield effect on  $^{15}\text{N}$  chemical shift is the main reason for applying this parameter to quantitative tautomeric equilibrium calculations.<sup>21</sup> It is known that for the OH- tautomer there is no measurable  $^1J(^{15}\text{NH})$ . Several studies show that when the temperature goes down an effective proton transfer appears for some substituted Schiff bases.<sup>20,25</sup> When the hydrogen atom becomes slightly bonded to the nitrogen atom there starts to be a nonvanishing value of  $^1J(^{15}\text{NH})$  coupling that increase as the temperature falls though not for all substituted Schiff bases.<sup>20</sup>

Searching for another structural parameter that could give information about the equilibrium position of the transferred proton, Filarowski suggested that the CO bond length reflects the proton transfer process. The HOMA (harmonic oscillator measure of aromaticity) index increase from 0.8 to 1.00 when  $d(\text{CO})$  increase from 1.28 to 1.35 Å. The proton is located somewhere in the bridge, and the whole system should have two stationary states: one with the proton close to the proton donor (O) and the other with the proton close to the proton acceptor (N). Several theoretical papers have shown that there is a potential barrier which confirms the existence of a transition state.<sup>26</sup> If this is the case, one may argue that the NMR spectroscopic parameters should also have typical patterns showing the existence of that transition state. The characterization of these possible patterns is one of the main aims of this article. Studying the intermediate states one may explain how the proton transfer mechanism occurs. So one can ask about (i) when is it possible to consider that the proton start to be bonded to the imine nitrogen atom; (ii) which are the typical values of ( $\delta(^{15}\text{N})$  and  $^1J(^{15}\text{NH})$ ) in the whole process or, in other words, is it possible to obtain typical patterns for both parameters; (iii) is it possible to quantify the dependence of both parameters with substituents; and (iv) is the previously found linear dependence between both NMR parameters a general rule? Our goal is to answer all these enquires and to obtain a theoretical understanding on the way the hydrogen bond behaves for these molecular systems and how the position of the hydrogen in the bridge is related to the NMR spectroscopic parameters. Our results are in line with previous findings, though we are able to generalize them. It will be shown that the low barrier of the hydrogen bond (LBHB) obtained from the calculation of potential functions is in coincidence with the OH and NH tautomers we find, and the fact that the inflection point that arises when both NMR spectroscopic parameters are depicted as a function of N–H distances can be related to the maximum value of that potential curves. Another step forward on the physical insights and the quantification of the intermediate steps of the proton transfer mechanism which have such importance in the electronic behavior of Schiff bases is given.

In section 2, we give a brief description of the theoretical model we propose to get the transition path from OH to NH tautomers. This model is within the nonadiabatic approximation. Converged results of NMR spectroscopic parameters for nitromethane as reference compound are given in the first part of the section with results. Differences between basis set requirements of DFT-B3LYP and SOPPA methods applied on the reference compound are analyzed. Calculated geometrical parameters and  $\sigma(^{15}\text{N})$  and  $^1J(^{15}\text{NH})$  are then shown. A comparative analysis of theoretical results and also a comparison of them with experiments is given. We show the functional

dependence of  $\sigma(\text{N})$  and  $^1J(\text{NH})$  with  $d(\text{NH})$ . From them an inflection point is obtained. Concluding remarks are finally stressed.

## 2. Theoretical Model and Computational Details

Ramsey's electronic mechanisms<sup>27</sup> which underlies both NMR spectroscopic parameters,  $\sigma$  and  $J$ , are, for  $J$  couplings, of two types: (i) electron spin-dependent [the Fermi contact (FC) and the spin dipolar (SD)] and (ii) electron spin-independent [paramagnetic spin-orbital (PSO) and diamagnetic spin-orbital (DSO)]. For nuclear magnetic shieldings, ( $\sigma$ ), they are also of two types: paramagnetic and diamagnetic. This last parameter is never measured directly. In experiments one usually measures what is known as the chemical shift of a given nucleus by comparing the resonance of the same nucleus in that compound of interest with its resonance in an arbitrary reference compound.<sup>28</sup> On the other side, from theoretical models one usually calculates the nuclear magnetic shieldings. The relationship between both parameters belonging to a given nucleus X is

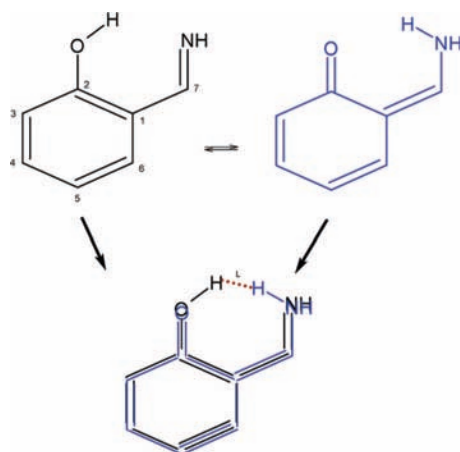
$$\delta(\text{X}) = \frac{\sigma_{\text{ref}} - \sigma}{1 - \sigma_{\text{ref}}} \quad (1)$$

Given that  $\sigma_{\text{ref}} \ll 1$ , one can set the denominator equal to one. In order to compare chemical shifts  $\delta(\text{X})$  with  $\sigma(\text{X})$ , we have calculated the nitrogen magnetic shieldings of nitromethane as the reference compound.

Gauss has shown that one must include electron correlation in order to obtain accurate shielding tensors in molecules with multiple bonds.<sup>29</sup> This is specially so for magnetic shieldings of  $^{15}\text{N}$  and  $^{17}\text{O}$ . It is known that the correlation contributions are relatively small for carbons involved in single bonds while they are considerably larger for multiply bonded carbons, especially when bonded to nitrogen or oxygen.<sup>30</sup> A similar statement is applied for  $J$  coupling calculations.<sup>31</sup> Several schemes were developed to include electron correlation. The implementations of the density-functional theory (DFT)<sup>32</sup> show that the choice of the exchange-correlation functional is critical. Recent studies<sup>33</sup> show that calculations of  $^1J(\text{NH})$  for  $\text{NH}_3$  and  $^2J(\text{NH})$  for HCN with the semiempirical hybrid B3LYP<sup>34</sup> functional give closer results to experiments when compared with some other nonempirical functionals. In the case of H-bonded systems, there is clear evidence that DFT can reproduce accurately magnetic shieldings but not in all cases.<sup>35</sup> There are no definite conclusions about it and specially for Schiff bases for which there are no theoretical studies reported in the literature. The overall pattern of both NMR spectroscopic parameters from DFT-B3LYP calculations will be shown; they will be compared with results from one of the most reliable ab initio methods we have at hand for NMR  $J$  coupling calculations, the second-order polarization propagator approach (SOPPA),<sup>36</sup> and also with experiments. Studies of its accuracy for calculations of shielding constants were recently published.<sup>37,38</sup>

SOPPA calculations of the shielding constants of H-bonded systems is given here for the first time. Then an analysis of the basis set dependence is needed because there is not enough experience on this matter. A local dense basis set scheme was used for all calculations of N chemical shift and  $^1J(^{15}\text{NH})$  on Schiff bases. This is due to restrictions on the maximum number of functions of the basis set that can be applied for actual SOPPA calculations. Converged results are qualitatively compared with experiments, because there are no experimental values available for the NMR spectroscopic parameters of the model compounds we used in these studies.

## SCHEME 1: OH and NH Tautomers of Schiff Bases



Our DFT calculations were performed employing both gauge-including atomic orbitals GIAO/London orbitals to guarantee origin-independence<sup>39</sup> and also the single-origin gauge scheme with the gauge origin placed at the site of nitrogen atom. This last scheme was applied in all of our SOPPA calculations.

In Scheme 1 the neutral tautomers of unsubstituted *o*-hydroxyaryl Schiff bases are shown. The hydrogen atom is transferred from its position close to the O atom (OH tautomer) to its position close to the N atom (NH tautomer). We considered first both tautomers without any substituent and then those cases with the following substituted compounds: 5-Cl and 4-OMe. The procedure to obtain the intermediate steps (the reaction path) between both tautomers is as follows: the geometry of each tautomer, OH and NH, was first theoretically optimized. Then the straight line “L” that connects the position of the H-bonded atom in each tautomer was obtained. That line was then divided in five equidistant points. Starting from the position of the H atom in the OH tautomer, its position was then displaced to the next point of the above-mentioned five points. The whole molecular geometry was optimized with the new O–H and H–N bond distances fixed. The next step consisted in moving the H atom to the next point within the line L and the same procedure was repeated again and again until the transferred hydrogen atom reached its corresponding position in the NH tautomer. Our way to get the proton-transfer reaction path is close to the nonadiabatic approximation suggested quite recently by Filarowsky and coauthors [published a few weeks before the submission of this work].<sup>40</sup>

All calculations of NMR spectroscopic parameters and the geometry optimization of all molecular structures were performed with the DALTON suite of programs.<sup>41</sup> We worked mostly with standard correlated-consistent basis set of Dunning and collaborators: the correlation-consistent polarized valence basis sets or cc-pVXZ (X = D and T)<sup>42</sup> and their improvements via the flexibility in the outer valence region (augmented-cc-pVXZ, X = D and T)<sup>43</sup> or their improvement via the flexibility in the core region (cc-pCVXZ, X = D and T).<sup>44</sup>

### 3. Results and Discussion

Recent calculations of *J*-coupling parameters for H-bonding containing molecules show that SOPPA level of approach give reliable results for these kind of systems.<sup>45</sup>

The molecule of nitromethane is used as a external reference for <sup>15</sup>N shieldings. Calculations for nitromethane are given with a different Gaussian basis set centered at the nucleus under study and the nuclei bounded to them. The comparative analysis of

TABLE 1: Calculated NMR  $\sigma(N)$  for Nitromethane (in ppm)

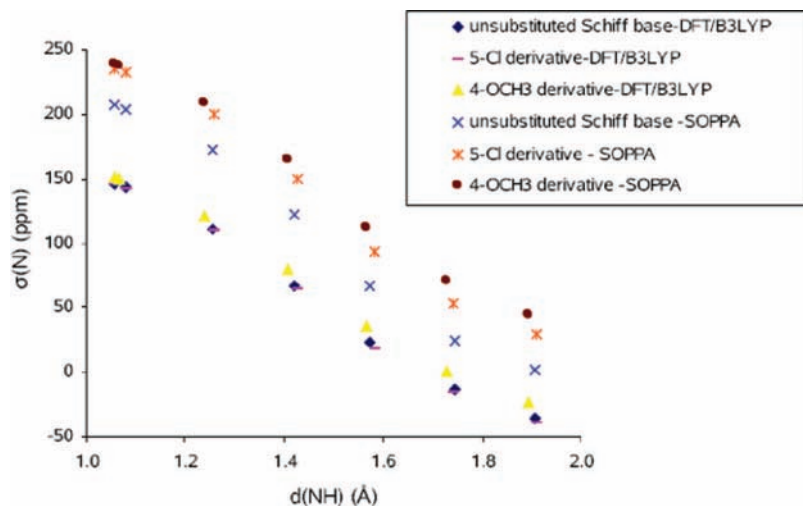
| basis set <sup>a</sup> | DFT <sup>b</sup><br>(DFT) <sup>c</sup> | SOPPA <sup>c</sup> | basis set   | DFT <sup>b</sup><br>(DFT) <sup>c</sup> | SOPPA <sup>c</sup> |
|------------------------|--|--------------------|---|--|--------------------|
| pD                     | -94.81<br>(-45.48)                     | -45.27             |   |  |                    |
| pT: N, O, C<br>m: H    | -120.47<br>(-93.64)                    | -106.77            | pCT: N<br>pT: O, C, H                             |  | -114.02            |
| pT                     | -119.99<br>(-96.13)                    | -108.30            | apCT: N<br>pT: O, C, H<br>apCT: N<br>apT: O, C, H |  | -118.63            |
| apT: N, O<br>pD: C, H  | -123.27<br>(-97.43)                    | -112.65            | apCT: N, O<br>pT: C, H                            | -129.72                                | -135.23            |
| apT: N, O<br>apD: C, H | -123.36<br>(-98.07)                    | -113.48            | pCT: N, O<br>pT: C, H                             |  | -128.21            |
| apT: N, O<br>pT: C, H  | -123.14<br>(-102.05)                   | -115.47            | apCT: N, O<br>pD: C, H                            | -129.81<br>(-118.09)                   | -132.45            |
| apT                    | -123.27<br>(-102.47)                   | -115.87            | apCT: N, O<br>pT(D): C (H)                        | -129.62<br>(-121.80)                   | -134.26            |
|                        |  |                    | apCT: N, O, C<br>pD: H                            | -129.52<br>(-127.21)                   | -139.53            |
|                        |  |                    | exp <sup>d</sup>                                  |  | -135.8             |

<sup>a</sup> The following nomenclature was applied: apCT: aug-cc-pCVTZ; pCT:cc-pCVTZ; apT: aug-cc-pVTZ; pT: cc-pVTZ; apCD: aug-cc-pCVDZ; pCD: cc-pCVDZ; apD: aug-cc-pVDZ; pD: cc-pVDZ; m: minimal basis constituted by only one s-type orbital with coefficient 1.159. <sup>b</sup> GIAO/London orbital method. <sup>c</sup> Gauge origin at nitrogen atom. <sup>d</sup> See ref 46.

geometrical parameters obtained for our model compounds and those taken from the literature is given. The main contribution of this paper refers to the analysis of NMR spectroscopic parameters: their dependences with the NH distances and also the relation between both of them.

**3.1. References for Chemical Shifts of <sup>15</sup>N.** In Table 1, we include an study of the convergence of correlated-consistent type of basis set for  $\sigma(^{15}\text{N})$  of nitromethane. There is no enough experience on the accuracy and performance of both schemes adopted in this work: SOPPA and B3LYP for shieldings of nitrogen atoms belonging to multiply bonded molecules. The size of the molecules we are interested in will restrict the final option, which would not be the best set arising from this study. For SOPPA calculations, we are restricted to choose the higher quality basis set that the size of Schiff bases do permit us to apply. From several options we selected the basis set written in italics in Table 1. For B3LYP we adopted polarized triple- $\zeta$  basis sets for N and O which gives results close enough to the higher augmented-cc-pCVTZ basis for N, O and C atoms.

The basis set dependence of  $\sigma(^{15}\text{N})$  is different for both methodologies. B3LYP calculations converge to values that are always below the experimental ones and SOPPA calculations converge from above and are closer to experiments. Rovibrational effects are not included; we may guess a correction of no less than 2–3 ppm from accurate shielding calculations of C on multiply bonded molecules published by Auer et al.<sup>30</sup> They also showed that DFT-B3LYP systematically underestimates absolute shielding constants of C. Our comparative results between B3LYP and SOPPA show a similar behavior for nitrogen in nitromethane though only for valence-triple- $\zeta$  basis sets. When triple- $\zeta$  quality of basis set is included also in the core (i.e., cc-pCVTZ) the relative numbers change that behavior to the opposite.



**Figure 1.** Nitrogen NMR magnetic shielding calculations of (un)-substituted Schiff bases.

One should include triple- $\zeta$  rather than double- $\zeta$  quality basis set in order to get quantitative results as noted by Ligabue et al.<sup>37</sup> This last statement is valid for both methodologies: SOPPA and B3LYP. For B3LYP calculations of nitromethane, convergence is almost reached when the basis set for N atom is aug-cc-pCVTZ with independence of the basis set centered on the other vicinal nuclei. On the other hand the basis set convergence for SOPPA calculations needs the inclusion of polarized basis functions in the core of vicinal atoms. As observed in Table 1 there is a large modification (around 16 ppm) of  $\sigma(^{15}\text{N})$  when the basis set aug-cc-pCVTZ is replaced by aug-cc-pVTZ in both atoms, N and O. This effect is also observed for  $\sigma$  on C of  $\text{CH}_4$  but much less pronounced.<sup>37</sup>

The gauge origin dependence is also observed in Table 1. There are a clear pattern arising from both DFT schemes: all calculations taken with the gauge origin at the nitrogen atom are below the calculations taken with GIAO/London orbital scheme. The closest value between both is obtained when the largest basis set is applied, though this improvement of the basis set modifies the first kind of calculations.

**3.2. Schiff Bases: (un- or Z-) Substituted Compounds; Z = 4-OMe or 5-Cl.** We first optimized the geometric parameters and then studied the dependence of NMR spectroscopic parameters with the process of a hydrogen atom being transferred from the OH to NH tautomer following the procedure outlined in section 2.

**3.2.1. Optimized Geometry.** Geometric parameters of all Schiff bases we studied theoretically were optimized at Hartree-Fock level. We found that they are close to experimental data, even though these data in some cases belong to different substituted Schiff bases.<sup>6</sup> As an average, our theoretical findings fits well with experiments.

Tendencies are reproduced and in some cases our numbers are quite close to experiments. For instance from an X-ray studies of 3,5-dinitro-*N*-salicylidenoethylamine,<sup>6</sup> it was found that  $d(\text{NH})$  [ $d(\text{OH})$ ] for the OH tautomer is 1.665 [0.97] Å and 1.030 [1.869] Å for the NH tautomer. Our calculations on unsubstituted Schiff bases give 1.858 [0.958] Å and 1.006 [1.921] Å, respectively.

In the case of salicylideneanilines, Ogawa and coauthors reported selected geometrical parameters which were measured by X-ray or calculated at DFT-B3LYP/6-31G\*\* level.<sup>47</sup> For the OH tautomer they found  $d(\text{X}-\text{Y})$  distances like,  $d(\text{O}-\text{C}_2) = 1.34$  Å,  $d(\text{C}_1-\text{C}_7) = 1.45$  Å, and  $d(\text{C}_7-\text{N}) = 1.29$  Å. Our results are 1.33, 1.47, and 1.26 Å, respectively. For the NH tautomer

they have found some differences between calculated and measured distances. For the particular distance  $d(\text{O}-\text{C}_2)$ , they calculated a distance of 1.26 Å which is close to our result of 1.22 Å. This is also near the standard length of a C=O bond. In line with these results, they showed DFT calculations (measured) of  $d(\text{C}_7-\text{N}) = 1.33$  (1.31) Å. Our calculations give  $d(\text{C}_7-\text{N}) = 1.32$  Å. All of these analysis show that the NH tautomer should be quinoidal in the gas phase.

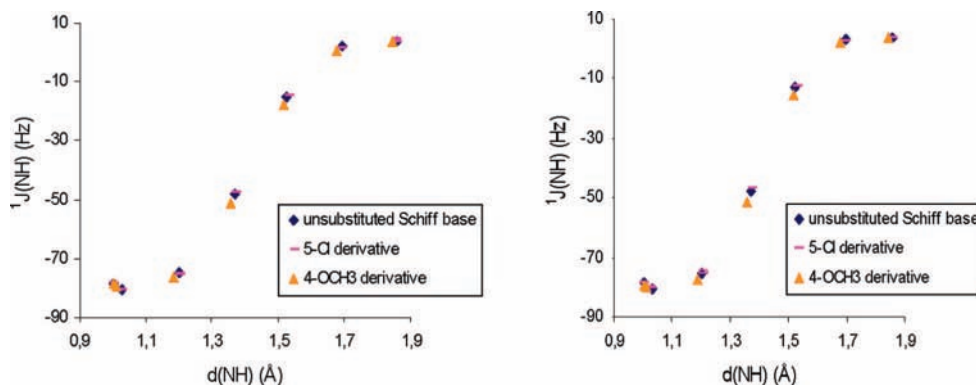
Calculations of adiabatic potential functions for proton displacement using B3LYP/6-31G(d,p) on 2-(*N*-methylimino methyl) phenol show that there are two relative minima.<sup>48</sup> The absolute minimum is found for the OH-form when  $d(\text{O}-\text{H})$  is close to 1.00 Å and a second relative minimum is located at  $d(\text{O}-\text{H})$  close to 1.80 Å. Both values are close to ours.

Structural data obtained by X-ray method for 2-(*N*-methylimino methyl)-4-Cl-phenol (OH tautomer)<sup>5,6</sup> and calculated at B3LYP 6-31G\*\* level for 2-(*N*-methylimino)-5-Cl-phenol (OH tautomer)<sup>5,18</sup> fit well with our results. Finally we stress the finding that our calculated distances are not much dependent on the substituents.

**3.2.2. Nuclear Magnetic Shieldings, Chemical Shifts and J Couplings  $^1J(\text{NH})$ .** From previous measurements<sup>49</sup> a typical value reported for  $\delta(\text{N})$  in pure imine structure is  $\approx -50$  ppm. Our DFT B3LYP calculations with the OH bond rotated 90 degrees, i.e., out of its planar position, gives a value of  $-25.80$  ppm, which is in line with experiments.

Our first analysis focus on the dependence of  $\sigma(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  with the distance between the imino nitrogen with the proton being transferred,  $d(\text{NH})$ , applying the theoretical model given in section 2. Theoretical results for unsubstituted Schiff bases as well as 5-Cl and 4-OMe-Schiff bases are shown in Figures 1 and 2. We applied different basis sets depending on the parameter, the model compound analyzed and the theoretical scheme used. In all cases, the atoms much involved in the H-bonding were described in the best way we could, and the others were described with smaller basis set.

For calculations of  $\sigma(\text{N})$  at DFT-B3LYP level, the basis set was: aug-cc-pVTZ for O, N, and  $\text{H}_1$ , and aug-cc-pVDZ for all other nuclei. For calculations at SOPPA level and for different model compounds we selected the following basis sets: (a) unsubstituted compound: cc-pCVTZ for N, cc-pVTZ for O,  $\text{C}_7$ , and  $\text{H}_1$ , and cc-pVDZ for all other nuclei; (b) 5-Cl-substituted: cc-pVTZ for N, O,  $\text{C}_7$ , and  $\text{H}_1$ , cc-pVDZ for all other carbon nuclei, minimal for all other hydrogen nuclei, and 6-31G for Cl; and (c) 4-OMe-substituted: cc-pVTZ for N, O,  $\text{C}_7$ , and  $\text{H}_1$ ,



**Figure 2.** Nitrogen NMR  $J$  coupling calculations of (un)-substituted Schiff bases at DFT (left) and SOPPA (right) levels of approximation.

cc-pVDZ for all other carbon nuclei, minimal for all other hydrogen nuclei, and 6-31 G for the oxygen and carbon of the methoxy substituent.

For calculations of  $^1J(^{15}\text{N},\text{H})$  at DFT-B3LYP level, the basis set was: cc-pVTZ for O, N, C<sub>7</sub>, and H<sub>1</sub>, 6-31G\*\* for all other C atoms and minimal for all other H atoms. For 5-Cl substituted compound the basis for Cl nucleus was 6-31G\*\* and for 4-OMe Schiff base the oxygen of the substituent was described with 6-31G\*\*. For calculations at SOPPA level and for different model compounds we selected the following basis sets: (a) unsubstituted compound: cc-pVTZ for O, N, C<sub>7</sub>, and H<sub>1</sub>, 6-31G for all other C atoms and minimal for all other H atoms; b) 5-Cl-substituted: cc-pVTZ for N, O, C<sub>7</sub>, and H<sub>1</sub>, minimal for all other hydrogen nuclei, and 6-31G for Cl and all other carbon nuclei; and (c) 4-OMe-substituted: cc-pVTZ for N, O, and H<sub>1</sub>, cc-pVDZ for C<sub>7</sub>, minimal all other hydrogen nuclei, 6-31 G all other carbon nuclei and the oxygen of OMe<sup>-</sup>.

As observed in Figure 1 DFT and SOPPA calculations as a function of  $d(\text{NH})$  follow a similar pattern. Calculations of  $\sigma(\text{N})$  are almost indistinguishable at DFT-B3LYP level but SOPPA calculations are sensitive to the electronic effect of substituents: nitrogen atom is less shielded for unsubstituted Schiff bases in both tautomers; there is a  $\Delta\sigma(\text{N})$  of around 30 ppm. For the NH tautomer there are no difference of  $\sigma(\text{N})$  for both substituents analyzed. This last behavior change in the way the proton becomes bounded to the oxygen. A clear difference is observed for the OH tautomer of all three model compounds analyzed.

What are the relations between calculations and experiments? DFT-B3LYP calculations of chemical shift are closer to experiments for both tautomers as observed in Table 2, with the exception of 4-OMe substituted compound. SOPPA calculations are such that they show a clear dependence with substituents. The  $\delta(\text{N})$  shielding as a function of  $d(\text{NH})$  follows a downfield displacement from the OH- to the NH- tautomers. The amount of this effect is such that it follows the rule: unsubstituted  $\geq$  5-Cl- substituted  $\geq$  4-OMe- substituted. As directly observed in Figure 1 DFT-B3LYP calculations are less sensitive to this dependence.

In ref 18, it was suggested that the coupling constant  $^1J(^{15}\text{N},\text{H})$  between the bridge proton and the nitrogen atom is the most accurate magnitude in terms of measurements and physical evidence that depicts the degree of residence of the bridge proton on the nitrogen atom; and also the fact that by using an equilibrium constant, one can obtain the following values for  $^1J(^{15}\text{N},\text{H})$ : 92.5 Hz for zwitterionic form and 2 Hz for enol-imine form of salicylideneimines compound. In Figure 2, we depicted calculations of  $^1J(^{15}\text{N},\text{H})$  at B3LYP and SOPPA levels. They give completely equivalent results which are not dependent

**TABLE 2: Chemical Shift,  $\delta(\text{N})$  for OH and NH Tautomers of (un- or Z-) Substituted *o*-Hydroxyaryl Schiff Bases, with Z = 5-Cl and 4-OMe**

| compound          | method             | OH-            | NH-              |
|-------------------|--------------------|----------------|------------------|
| unsubstituted     | SOPPA <sup>a</sup> | -115.49        | -320.94          |
|                   | B3LYP <sup>b</sup> | -86.78         | -269.40          |
| 5-Cl substituted  | SOPPA <sup>c</sup> | -137.03        | -343.76          |
|                   | B3LYP <sup>b</sup> | -83.40         | -268.56          |
|                   | exp. <sup>d</sup>  | -90.7 to -93.4 |                  |
| 4-OMe substituted | SOPPA <sup>e</sup> | -152.61        | -346.96          |
|                   | B3LYP <sup>b</sup> | -99.04         | -274.12          |
|                   | exp. <sup>d</sup>  | -130 to -186.5 | -226.9 to -244.2 |

<sup>a</sup> Value of reference: -114.02 ppm. Basis set for the model compound: cc-pCVTZ for N, cc-pVTZ for O, C<sub>7</sub>, and H<sub>1</sub>; cc-pVDZ for all other nuclei. <sup>b</sup> Value of reference: -123.27 ppm. Basis set for the model compound: aug-cc-pVTZ for O, N, and H<sub>1</sub> and aug-cc-pVDZ for all other nuclei. <sup>c</sup> Value of reference: -108.30 ppm. Basis set for the model compound: cc-pVTZ for N, O, C<sub>7</sub>, and H<sub>1</sub>; cc-pVDZ for all other C nuclei, minimal for all other H nuclei and 6-31G for Cl. <sup>d</sup> See ref 20. For the NH tautomeric form the values are taken from the 4, 6-di-OCH<sub>3</sub> substituent. <sup>e</sup> Value of reference: -108.30 ppm. Basis set for the model compound: cc-pVTZ for N, O, C<sub>7</sub>, and H<sub>7</sub>; cc-pVDZ for all other C nuclei; minimal for all other H nuclei and 6-31G for both the oxygen and carbon atoms of the substituent.

on the substituent. It is also observed that the  $J$ -coupling change its sign when the proton is completely bounded to the nitrogen atom.

Once we theoretically obtained the intermediate states, we searched for experimental evidence that could give support to our results. In Table 3, a clear correspondence between the calculated distances, chemical shifts and  $J$  couplings with experimental results are observed. As shown by Schilf and coauthors,<sup>20</sup> when the temperature of the 4-OMe substituted compound is diminished, its nitrogen chemical shift goes upfield, which implies that the tautomeric equilibrium of the Schiff base is displaced from the OH to its corresponding NH tautomeric form. It is remarkable the way in which theoretical and experimental values fits together, and the rationalization that arise from these results. Theoretical NMR spectroscopic parameters are obtained for fixed values of the distance between the proton and the acceptor nitrogen atom. In Table 3 theoretical calculations of  $\delta(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  corresponding to different  $d(\text{NH})$  are shown. They fits quite well with experimental values which corresponds to substituted Schiff bases at different temperatures. The first row value correspond to the OH tautomer, and the value in the 4th row is close to that corresponding to the NH tautomer.

For the OH tautomer of the 4-OMe substituted compound there is no measured  $^1J(^{15}\text{N},\text{H})$ . When the temperature falls

**TABLE 3: Chemical Shifts (in ppm) and  $J$  Couplings (in Hz) Calculated at DFT-B3LYP Level as a Function of  $d(\text{XH})$ ;  $X = \text{N, O}$  and Measured at Different Temperatures for Substituted Schiff Bases<sup>a</sup>**

| Compound                       | $d(\text{NH})$ | $d(\text{OH})$        | $\delta(\text{N})$   | $J(\text{NH})$ | Temp (K) |
|--------------------------------|----------------|-----------------------|----------------------|----------------|----------|
| 4-OMe substituted <sup>b</sup> | 1.678          | 1.144                 | -122.91              | 0.82           | 302      |
|                                |                |                       | (-130.5)             | (-)            |          |
|                                | 1.516          | 1.330                 | -158.46              | -17.69         | 266      |
|                                |                |                       | (-147)               | (24)           |          |
|                                | 1.357          | 1.519                 | -202.46              | -51.16         | 205.5    |
|                                |                | (-186.5)              | (53)                 |                |          |
| 1.188                          | 1.717          | -243.37               | -76.61               | 266            |          |
|                                |                | (-226.9) <sup>c</sup> | (76.4) <sup>c</sup>  |                |          |
|                                |                | (-242.5) <sup>c</sup> | (82.5) <sup>c</sup>  | 217            |          |
|                                |                | (-244.2) <sup>c</sup> | (85.7) <sup>c</sup>  |                |          |
| 5-Cl substituted <sup>b</sup>  | 1.859          | 0.959                 | -83.40               | 3.70           | 302      |
|                                |                |                       | (-90.7)              |                |          |
|                                |                |                       | (-84.8) <sup>d</sup> |                | 303      |
|                                |                |                       | (-94.1)              | (6.0)          |          |

<sup>a</sup> Experimental values are given between parenthesis and distances in angstrom. <sup>b</sup> Experimental values taken from ref 20. <sup>c</sup> Experimental value corresponding to 4, 6-OMe substituted Schiff base and taken from ref 20. <sup>d</sup> Experimental value taken from ref 21.

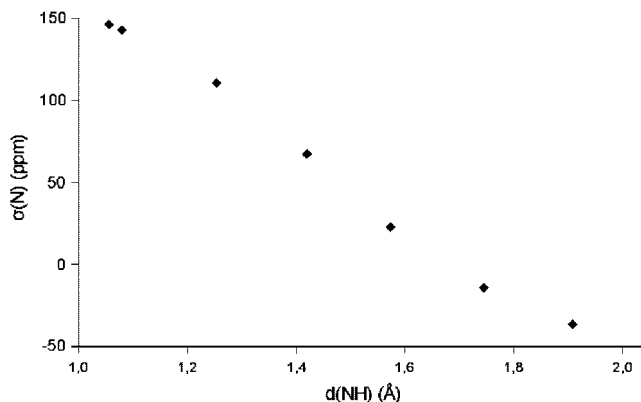
down there appears a growing  $J$  coupling. At the same time the chemical shift is shifted upfield when the  $d(\text{NH})$  is such that the molecular structure is close to its NH tautomer, our theoretical findings are close to experimental values corresponding to 4,6-OMe substituted compound at temperatures equal or below 266 °K. It is known by experiments that in such a case an NH tautomer is found.<sup>20</sup> In the case of 5-Cl-substituted compound there is only an OH tautomeric form at different temperatures. For this last substituent, calculations of  $\delta(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  are close to experiments. We must stress here that  $^1J(^{15}\text{N},\text{H}) = 6$  Hz when  $T = 195$  °K and our calculations give  $^1J(^{15}\text{N},\text{H}) = 3.7$  Hz, so we can expect nonvanishing values of  $^1J(^{15}\text{N},\text{H})$  for the OH tautomer.

Looking for correlations between different NMR spectroscopic parameters, Hansen and coauthors have found the following linear dependence  $\delta(\text{N}) = -1.93 ^1J(^{15}\text{N},\text{H}) - 83.23$ .<sup>19</sup> On the other hand, in a study of both nondeuterated and deuterated related Schiff bases<sup>13</sup> they found the following linear dependence:  $\delta(\text{N}) = -1.29 ^1J(^{15}\text{N},\text{H}) - 79.5$  with a correlation coefficient,  $R^2 = 0.971$ . Considering the first linear dependence one can obtain limited conditions for the chemical shift of nitrogen:  $\delta(\text{N})_{\text{OH}} \approx -85$  ppm and  $\delta(\text{N})_{\text{NH}} \approx -245$  ppm. Our theoretical calculations show that the functional dependence of  $\sigma(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  with  $d(\text{NH})$  are cubic. They are shown in Figures 3 and 4. From them it is possible to get the inflection point,  $x$ . For DFT (SOPPA) calculations, from  $\delta(\text{N})$  vs  $d(x)$  function,  $x = 1.403$  (1.418) Å and from  $^1J(^{15}\text{N},\text{H})$  vs  $d(x)$  function,  $x = 1.424$  (1.420) Å.

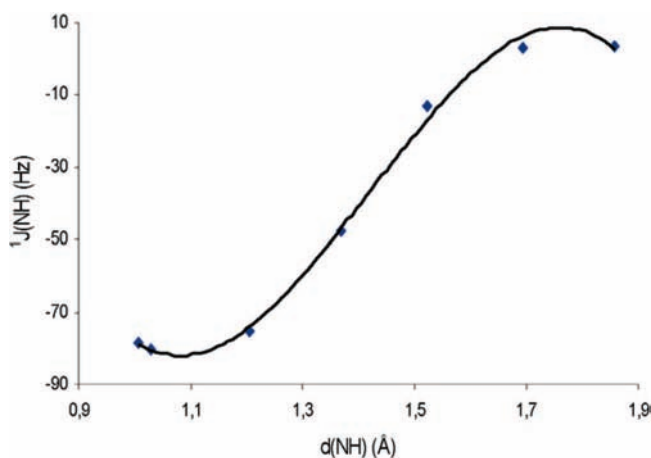
Based on our calculations it is also possible to find a relationship between  $\delta(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  that is not linear: it is cubic. In Figure 5 the polynomial which correspond to the fitting of  $\delta(\text{N})$  vs  $^1J(^{15}\text{N},\text{H})$  for 5-Cl-substituted Schiff base is shown. The  $R^2$  coefficient is close to 1. When one restrict the points to that belonging to a reduced domain, say, for  $-240$  ppm  $\leq \delta(\text{N}) \leq -100$  ppm, one obtain Figure 6. In this case the slope coefficient is 1.644 and the linear relation between  $\delta(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$  may be related with its experimental counterpart.

#### 4. Concluding Remarks

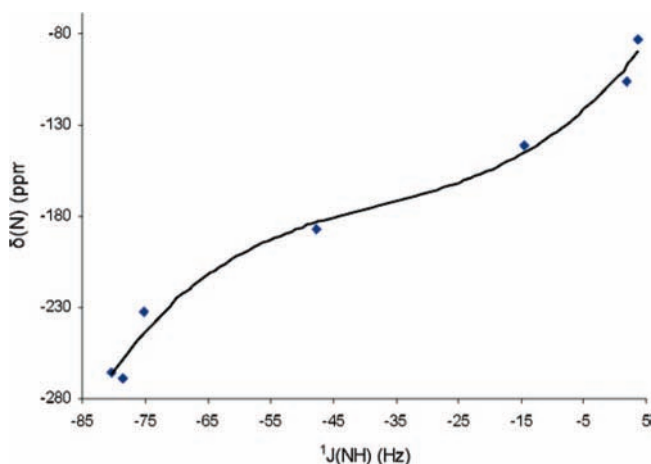
A theoretical analysis based on two state of the art theoretical models, DFT-B3LYP and SOPPA, of the proton transfer



**Figure 3.** Polynomial fit of  $\sigma(\text{N})$  vs  $d(\text{NH})$  of unsubstituted Schiff base (DFT calculation);  $\sigma(\text{N}) = 359.16x^3 - 1512.2x^2 + 1842.4x - 542.75$  where  $x = d(\text{NH})$ ;  $R^2 = 0.9999$ .

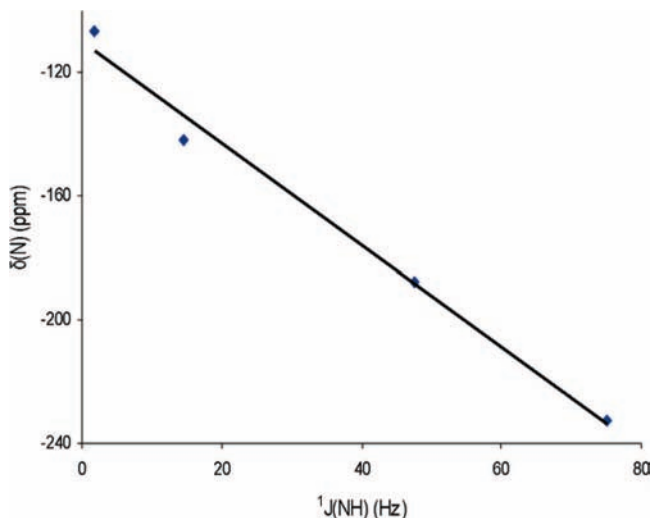


**Figure 4.** Polynomial fit of  $J$  coupling vs  $d(\text{NH})$  of unsubstituted Schiff base. SOPPA calculation.  $^1J(\text{NH}) = -573.45x^3 + 2443.4x^2 - 3270.3x + 1322.2$  where  $x = d(\text{NH})$ ;  $R^2 = 0.9971$ .



**Figure 5.** Polynomial fit of  $\delta(\text{N})$  vs  $^1J(\text{NH})$  for 5-Cl derivative;  $\delta(\text{N}) = 0.0007x^3 + 0.078x^2 + 3.7899x - 104.91$  where  $x = ^1J(\text{NH})$ ;  $R^2 = 0.9887$ .

mechanism in OH and NH tautomers of *ortho*-hydroxyaryl Schiff bases is presented. Three different *ortho*-hydroxy Schiff bases were studied: unsubstituted, 5-Cl- and 4-OMe-substituted. A relationship between the spatial position of the hydrogen atom that is being transferred with both NMR spectroscopic parameters,  $\sigma(\text{N})$  and  $^1J(^{15}\text{N},\text{H})$ , is found. Given that by experiments one is used to consider chemical shifts instead of nuclear magnetic shieldings, the magnetic shielding of nitromethane as a reference compound for the nitrogen atom is also analyzed.



**Figure 6.** Polynomial fit of  $\delta(N)$  vs  ${}^1J(NH)$  for 5-Cl derivative with restriction on the range of  ${}^1J(NH)$  values.  $\delta(N) = -1.6435 J(NH) - 109.94$ ;  $R^2 = 0.9885$ .

Basis set based on Dunning correlated-consistent scheme were applied. In the case of nitromethane it was found that SOPPA calculations of magnetic shieldings are quite sensitive to basis set centered on vicinal atoms and one need to consider also polarized functions for the core region of the atom of interest. For DFT-B3LYP calculations these considerations are much less important. As a rule the nitrogen atom and its vicinal atoms were described by a basis set larger or equal to cc-pVTZ for all SOPPA calculations. For nitromethane the basis set augmented-cc-pCVTZ for the heavy atoms is good enough to get convergence for both theoretical methods. Unfortunately it is not possible to use that basis set in calculations of Schiff bases, so one must work with smaller basis set. Different schemes of local dense basis set were designed to get reliable results.

DFT-B3LYP calculations gives chemical shifts that are closer to experimental values when compared with SOPPA calculations, though this last method is quite more sensitive to substituent effects. There is a downfield displacement in  $\sigma(N)$  which follows the rule: unsubstituted  $\geq 5$ -Cl- substituted  $\geq 4$ -OMe- substituted. On the other hand, the calculated couplings  ${}^1J({}^{15}N,H)$  with both schemes are close each other, and they are also independent of the substituent.

One of the main goals of these studies is the fact that we can predict the position of the transferred proton whence any of both NMR spectroscopic parameters,  $\sigma(N)$  or  ${}^1J({}^{15}N,H)$  is known. Predictions are based on calculations which were confronted with experimental measurements of similar Schiff bases. Another important finding is the appearance of an inflection point from which one can infer to which atom the proton being transferred is bounded. That inflection point arise in the study of both NMR spectroscopic parameters and is such that  $d(NH)$  is  $\cong 1.42 \text{ \AA}$ .

The linear dependence of  $\delta(N)$  with  ${}^1J({}^{15}N,H)$  proposed from experimental results seems to be cubic. This function becomes linear when the range of chemical shift is restricted to  $-240 \text{ ppm} \leq \delta(N) \leq -100 \text{ ppm}$ .

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