

## RESEARCH ARTICLE

# One-bond $^1J(^{15}\text{N},\text{H})$ coupling constants at $\text{sp}^2$ -hybridized nitrogen of Schiff bases, enaminones and similar compounds: A theoretical study

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## Abstract

$^1J(^{15}\text{N},\text{H})$  coupling constants for enaminones and NH-forms of intramolecularly hydrogen-bonded Schiff bases as model compounds for  $\text{sp}^2$ -hybridized nitrogen atoms are evaluated using density functional theory (DFT) to find the optimal functionals and basis sets. Ammonia is used as a test molecule and its one-bond coupling constant is compared with experiment. A methylamine Schiff base of a truncated molecule of gossypol is used for checking the performance of selected B3LYP, O3LYP, PBE, BHandH, and APFD density functionals and standard, modified, and dedicated basis sets for coupling constants. Both in vacuum and in chloroform, modeled by the simple continuum model of solvent, the modified basis sets predict significantly better the  $^1J(^{15}\text{N},\text{H})$  value in ammonia and in the methylamine Schiff base of a truncated molecule of gossypol than the standard basis sets. This procedure is then used on a broad set of intramolecularly hydrogen-bonded molecules, and a good correlation between calculated and experimental one-bond NH coupling constants is obtained. The  $^1J(^{15}\text{N},\text{H})$  couplings are slightly overestimated. The calculated data show for hydrogen-bonded NH interatomic distances that the calculated values depend on the NH bond lengths. The shorter the bond lengths, the larger the  $^1J(^{15}\text{N},\text{H})$ . A useful correlation between  $^1J(^{15}\text{N},\text{H})$  and NH bond length is derived that enables realistic predictions of one-bond NH coupling constants. The calculations reproduce experimentally observed trends for the studied molecules.

## KEYWORDS

DFT calculations, NH-forms, one-bond NH coupling constants, Schiff bases, SSCC, Tautomerism

## 1 | INTRODUCTION

$^1J(^{15}\text{N},\text{H})$  indirect spin–spin coupling constants (SSCCs) have been used extensively to estimate mole fractions for tautomeric systems such as Schiff bases of *o*-hydroxyacyl aromatics and salicylaldehydes<sup>[1–6]</sup> (see Figure 1).

They have been measured in a few cases in enaminones.<sup>[7,8]</sup> However, one of the problems of using

$^1J(^{15}\text{N},\text{H})$  in studies of Schiff bases is that very few have been determined for compounds fully at the NH-form.<sup>[9,10]</sup>  $^1J(^{15}\text{N},\text{H})$  has typically been estimated using model compounds such as enaminones<sup>[5,7,8]</sup> or even hydrazones.<sup>[11]</sup> Some general observations have been made. One-bond coupling constants can be correlated to the bond order of the N–H bond.<sup>[12]</sup> The larger the bond order, the larger  $^1J(^{15}\text{N},\text{H})$ . It has also been observed that