

Theoretical Calculations of Proton-Proton NMR Indirect Spin-Spin Coupling Constants in Heterocyclic Three-Membered Rings

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Abstract: The remarkable potential of nuclear spin-spin coupling constants as probes for the study of electronic molecular structures is notably enhanced if experimental values are adequately complemented with theoretical analysis. In non-relativistic quantum mechanics, the indirect nuclear spin-spin coupling constant for two nuclei K and L consists of four terms. Thus, Fermi contact (FC) and spin-dipolar (SD) terms describe the interaction of the two nuclear spins via the spin of electrons, whereas dia- and paramagnetic spin-orbital contributions (DSO and PSO) are due to the interaction of nuclear spins with the magnetic moment associated with the electronic orbital angular momentum. In this work, the experimental and theoretical proton-proton coupling constants have been determined to provide the study of the effect of heteroatoms (O and S) in coupling pattern and pathway in 2-methyloxirane and 2-methylthiirane. In 2-methylthiirane, the hyperconjugative interactions affecting ${}^2J_{HH}$ should be between ($n_S \rightarrow \sigma^*_{CH}$) and for 2-methyloxirane between ($n_O \rightarrow \sigma^*_{CH}$). In 2-methylthiirane, the hyperconjugative interactions affecting ${}^2J_{HH}$ should be between ($n_S \rightarrow \sigma^*_{CH}$) and in 2-methyloxirane, between ($n_O \rightarrow \sigma^*_{CH}$). Those involving O instead of S are stronger, as was observed for NBO analysis. The interaction between the lone pair and C-H antibonding ($LP \rightarrow C-H^*$) for 2-methyloxirane is $5.3 \text{ kcal mol}^{-1}$ and those for 2-methylthiirane is $2.9 \text{ kcal mol}^{-1}$. For vicinal ${}^3J_{HH}$ couplings electron delocalizations into the (C-H)* antibonds cause important reductions in such couplings. This trend is nicely observed in ${}^3J_{H_1H_3}$ and ${}^3J_{H_2H_3}$. The theoretical NMR coupling constants, together with NBO analysis, allowed us to show the effects and interactions present in ${}^2J_{HH}$ and ${}^3J_{HH}$ coupling pathway.

The remarkable potential of nuclear spin-spin coupling constants as probes for the study of electronic molecular structures is notably enhanced if experimental values are adequately complemented with theoretical analyses.¹ However, obtaining accurate calculations of coupling constants proved to be a non-trivial task for quantum chemistry. In non-relativistic quantum mechanics, the indirect nuclear spin-spin coupling constant for two nuclei K and L consists of four terms. The

Fermi contact (FC) and spin-dipolar (SD) terms describe the interaction of the two nuclear spins via the spin of the electrons, whereas the dia- and paramagnetic spin-orbital contributions (DSO and PSO) are due to the interaction of nuclear spins with the magnetic moment associated with the electronic orbital angular momentum. The indirect nuclear spin-spin coupling constant is a second derivative of electronic energy, and the four contributions

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can therefore be derived in the wave function formalism.²

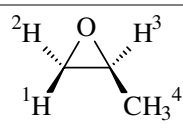
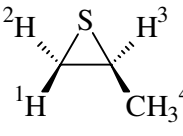
In this work, the experimental and theoretical proton-proton coupling constants have been determined to provide the study of the effect of heteroatoms (O and S) on coupling pattern and pathway for 2-methyloxirane (**1**) and 2-methylthiirane (**2**). The experimental ¹H NMR spectra of **1** and **2** were performed in a Varian INOVA 500MHz; the samples were prepared with *ca.* 10mg in 0.7 mL of CDCl₃ as solvent. Typical conditions were 48 transients, spectral width 5000 Hz with 32 K data points and zero filled to 128 K to give a digital resolution of 0.07 Hz. The coupling constants taken directly from the spectra are shown in Table 1.

The DFT calculation at the B3LYP/aug-cc-pVTZ level was applied for geometries optimization. The DFT calculations of FC and SD terms were carried out using the FPT scheme,² which was implemented into the Gaussian 98 package program.³ The PSO term was calculated using the coupled perturbed DFT framework. To this end, the necessary modifications were introduced into Gaussian 98 package.³ The DSO term was obtained from the contraction of the ground-state one-electron density matrix and corresponding integrals. In both cases (PSO and DSO) the one-electron integrals were evaluated with the DALTON program.⁴ The B3LYP method was chosen to carry out DFT calculations. For FC, SD and PSO, aug-cc-pVTZ-J basis sets⁵ were used for hydrogen and carbon atoms and aug-cc-pVTZ were used for sulfur and oxygen atoms. For the DSO term the cc-pVTZ basis set was applied for all atoms. These (aug-cc-pVTZ-J) are essentially the aug-cc-pVTZ basis sets, but

have been augmented with four *s*-type functions with very large exponents, which are crucial for a correct description of FC interactions. The theoretical calculations were performed in an Athlon PC with FreeBSD system, 1.7 MHz of processor, 80GB of hard disc and 1.5 GB of RAM. The results for proton-proton calculated coupling constants are shown in Table 1. According to the data from Table 1, it can be observed that the geminal couplings (²J_{H₁H₂) for **1** are bigger (5.38Hz) than those for **2** (0.85 Hz). This behaviour is supported by theoretical coupling constants calculations and originates in the trend of the FC term. The question is: What is the effect of sulfur and oxygen on coupling pathway? In short, we can say that, for geminal couplings, hyperconjugative interactions that put charge into the antibonding orbitals of the coupling pathway yield a positive increase in ²J_{HH} coupling, as the FC term is sensitive to electrons in *s* orbitals.⁶ In 2-methylthiirane, the hyperconjugative interactions affecting ²J_{HH} should be between (n_S→σ*_{CH}) and for 2-methyloxirane between (n_O→σ*_{CH}). For 2-methylthiirane, the hyperconjugative interactions affecting ²J_{HH} should be between (n_S→σ*_{CH}) and for 2-methyloxirane, between (n_O→σ*_{CH}). Those involving O instead of S are stronger, as was observed performing NBO analysis. The interaction between the lone pair and C-H antibonding (LP→C-H*) for 2-methyloxirane is 5.3 kcal mol⁻¹ and those for 2-methylthiirane is 2.9 kcal mol⁻¹. The theoretical NMR coupling constants, together with NBO analysis, allowed us to show the effects and interactions present in ²J_{HH} coupling pathway. For *vicinal* ³J_{HH} couplings, electron delocalizations into the (C-H)* antibonds cause}

important reductions in such couplings.⁶ This trend is nicely observed in ${}^3J_{H_1H_3}$ and ${}^3J_{H_2H_3}$.

Table 1. Comparison between calculated and experimental ${}^nJ_{HH}$ couplings (Hz) in 2-methyloxirane and 2-methylthiirane.

Compounds	${}^nJ_{HH}$	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}	$J_{cal.}$	$J_{exp.}$	ΔJ
 1	${}^2J_{H_1H_2}$	5.46	0.35	3.15	-3.10	5.86	5.38	0.48
	${}^3J_{H_1H_3}$	2.40	0.02	3.03	-3.11	2.34	2.57	-0.23
	${}^3J_{H_2H_3}$	4.06	0.12	0.38	-0.42	4.14	4.28	-0.14
	${}^3J_{H_3H_4}$	5.82	0.05	1.39	-1.46	5.80	5.26	0.54
 2	${}^2J_{H_1H_2}$	-1.37	0.36	3.34	-2.92	-0.59	-0.85	0.26
	${}^3J_{H_1H_3}$	6.09	0.00	2.76	-2.80	6.05	5.64	0.41
	${}^3J_{H_2H_3}$	7.13	0.16	0.24	-0.10	7.43	6.41	1.02
	${}^3J_{H_3H_4}$	6.52	0.05	1.41	-1.34	6.64	6.11	0.53

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