

Density Functional Theory/GIAO/CSGT Studies of the ^{13}C NMR Chemical Shifts in 1-Chlorosilatrane

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Ab initio NMR calculations are now attainable and accurate enough to be useful exploring the relationship between chemical shift and molecular structure. The calculated ^{13}C chemical shifts, in particular, appear to be accurate enough to aid in experimental peak assignments. Density functional theory (DFT) has emerged in recent years as a promising alternative to conventional *ab initio* methods in quantum chemistry. It therefore seems reasonable to investigate in detail how well DFT predicts magnetic response properties, in particular shielding tensors.

The interest in silatranes $-\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$, 1-organyl-2,8,9-trioxa-5-aza-1-silabicyclo [3.3.3] undecanes- is due to their intriguing molecular structure, biological activity, and patterns of chemical reactivity.¹⁻³ The most intriguing aspect of this structure is the existence and influence of a "transannular bond" between the silicon and nitrogen atoms. The transannular Si-N donor-acceptor bond makes these molecules especially interesting and challenging for theoretical and experimental studies.⁴⁻¹²

Recently, we reported on ^{13}C , ^{15}N , and ^{29}Si NMR chemical shifts¹³ that were computed for several silatranes using Gauge-Including Atomic Orbitals (GIAO)¹⁴ and Continuous Set of Gauge Transformations (CSGT)¹⁵ at the Hartree-Fock level of theory. Both of the results for ^{13}C isotropic chemical shifts at the HF/6-31G* level are sufficiently accurate to aid in experimental peak assignments. But they are about 5 ppm from the experimental values because silatranes are strongly correlated molecules that have electronegative atoms attached directly to carbons. Thus, we need to perform higher-quality calculations than Hartree-Fock level.

In this study, to describe the electron correlation effect we have calculated the ^{13}C chemical shift in 1-Chlorosilatrane¹³ using the GIAO and the CSGT methods at DFT level of theory. We use functionals that do not include a specific magnetic field dependent term, but which have yielded good accuracy for other chemical properties. In addition, several functionals, including hybrid functionals, are investigated for their ability to predict NMR ^{13}C chemical shifts. The molecular geometry of the 1-chlorosilatrane was fully optimized at B3LYP/6-31G(d) level of theory. The 6-31G(d) basis set used Cartesian d functions. All these calculations were carried out with Gaussian 94 package of programs.¹⁶

For the DFT methods, the combinations of functionals considered in this study are defined as follows: The LSDA (Local Spin Density Approximation) uses Slater exchange^{17,18} and the VWN correlation functional.¹⁹ BLYP uses the Becke exchange functional²⁰ and the LYP correlation functional.²¹

BPW91 uses the Becke exchange functional²⁰ and Perdew and Wang's 1991 gradient-corrected correlation functional.²² The B3PW91 functional is Becke's three parameter hybrid functional.²³ The B3LYP hybrid functional is a slight variation of Becke's three parameter functional.

Calculations performed with GIAO/DFT and CSGT/DFT methods were used the geometry optimized at the B3LYP/6-31G(d) level of theory. In all ^{13}C NMR chemical shift calculations with GIAO/DFT and CSGT/DFT methods, 6-31G(d) basis set was employed on all atoms. To compare the results of DFT-method with those of HF-method, NMR chemical shift calculations were also performed with GIAO/DFT and CSGT/DFT methods using the optimized geometry.

The chemical shift δ is obtained from σ by

$$\delta = \sigma_{\text{ref}} - \sigma,$$

where σ_{ref} is the shielding tensor of the reference compound, in our case, tetramethylsilane (TMS) for ^{13}C . A negative value of δ indicates a stronger shielding in the silatranes than in TMS (equivalent to an upfield or low-frequency shift), while a positive value of δ indicates less shielding than in TMS.

GIAO and CSGT theoretical isotropic ^{13}C chemical shifts are given in Table 1 for 1-Chlorosilatrane obtained at the Hartree-Fock and DFT levels of theory. In Table 1, calculated ^{13}C values are relative to TMS and compared with experimental values. Differences between experimental and calculated data are given in the fourth (for OCH_2 carbons) and sixth (for NCH_2 carbons) columns. Experimentally, the OCH_2 carbons of the 1-Chlorosilatrane framework have isotropic ^{13}C chemical shift of 60.1 ppm, and the NCH_2 carbons have isotropic ^{13}C chemical shift of 52.7 ppm, as shown in Table 1. These assignments and the peak assignments for this molecule are based on variable-field high-resolution solid-state ^{13}C NMR results.²⁴ Also, all of the calculated isotropic ^{13}C chemical shifts for the OCH_2 carbons of the 1-Chlorosilatrane framework are larger than those of NCH_2 . Their assignment, therefore, was verified by calculated isotropic ^{13}C chemical shifts.

Greater improvement should be expected in the isotropic ^{13}C chemical shift of silatranes calculated using DFT than in the calculations based on the Hartree-Fock approach because they are strongly correlated molecules composed of electronegative atoms. Both results using GIAO and CSGT methods at HF/6-31G(d) level diverge by about 5 ppm from the experimental values, as shown in Table 1. In the DFT method, as we expected, the isotropic ^{13}C chemical shifts

Table 1. Comparison of ^{13}C Chemical Shifts (δ , in ppm) Calculated at the Hartree-Fock and DFT Levels of Theory

Method	Basis Set	OCH ₂ (Cal-Expt) ^d	NCH ₂ (Cal-Expt) ^d	
GIAO	HF	3-21G ^a	50.07 -10.03 45.28 -7.42	
	HF	6-31G ^a	55.42 -4.68 48.07 -4.63	
	HF	6-31G(d) ^b	55.07 -5.03 48.32 -4.38	
	HF	6-31G(d) ^b	54.54 -5.56 48.56 -4.14	
	LSDA	6-31G(d) ^b	60.85 0.75 54.18 1.48	
	BPW91	6-31G(d) ^b	60.68 0.58 53.31 0.61	
	BLYP	6-31G(d) ^b	60.25 0.15 53.32 0.62	
	B3PW91	6-31G(d) ^b	59.58 -0.52 52.59 -0.11	
	B3LYP	6-31G(d) ^b	59.17 -0.93 52.53 -0.17	
	CSGT	HF	3-21G ^a	43.14 -16.96 37.31 -15.39
		HF	6-31G ^a	52.91 -7.19 44.66 -8.04
HF		6-31G(d) ^b	55.17 -4.93 47.52 -5.18	
HF		6-31G(d) ^b	54.41 -5.69 47.50 -5.20	
LSDA		6-31G(d) ^b	61.99 1.89 54.49 1.79	
BPW91		6-31G(d) ^b	61.95 1.85 53.79 1.09	
BLYP		6-31G(d) ^b	60.95 0.85 53.30 0.60	
B3PW91		6-31G(d) ^b	60.63 0.53 52.80 0.10	
B3LYP		6-31G(d) ^b	59.78 -0.32 52.36 -0.34	
Expt ^c			60.10 52.70	

^aHartree-Fock results from Ref. 13. ^bOptimized with B3LYP/6-31G(d). ^cExperimental ^{13}C values taken from Ref. 24. ^dDifference of ^{13}C chemical shift between the calculated and experimental values.

calculated at DFT/6-31G(d) levels improved by about 5 ppm over those of HF/6-31G(d). In the DFT calculation, all the ^{13}C chemical shifts for 1-Chlorosilatrane are in good agreement with the experimental values. These results indicate the importance of including electron correlation in the GIAO and CSGT calculations.

It is observed that the gradient-corrected DFT functionals provide improvement. Differences between the gradient-corrected DFT functional and experimental values, with the exception of BPW91 with CSGT, are less than 1 ppm. When we use especially hybrid functionals (B3PW91 and B3LYP) with the CSGT method, the differences are in excellent agreement with the experimental values. On the other hand, the calculated CSGT results for all carbons are greater than those of GIAO by an average of 0.28 ppm.

To investigate the theoretical value depending on geometry, e.g., the transannular Si-N donor-acceptor bond, we have also calculated the ^{13}C chemical shifts for 1-Chlorosilatrane, using the GIAO-HF/6-31G(d) and B3LYP/6-31G(d) optimized geometries. In this calculation, the OCH₂ carbons of the 1-Chlorosilatrane framework in the GIAO-HF/6-31G(d)/HF/6-31G(d) and GIAO-HF/6-31G(d)/B3LYP/6-31G(d) calculations have isotropic ^{13}C chemical shift of 55.07 ppm and 54.54 ppm, respectively. This difference (0.53 ppm) reflects the observation that the isotropic ^{13}C chemical shift of this molecule appears to be nearly independent of the level of optimized geometries. The calculated isotropic ^{13}C chemical shifts of 1-Chlorosilatrane depend on mainly the method (or level) of calculation for NMR chemical shift.

Comparisons of the GIAO/SCF and GIAO/DFT (or CSGT/SCF and CSGT/DFT) isotropic ^{13}C chemical shifts of

1-Chlorosilatrane clearly show that electron correlation effects must be considered when calculating NMR chemical shifts of strongly correlated molecules that have electronegative atoms attached directly to carbons. In the CSGT/DFT calculation, the ^{13}C chemical shifts for 1-Chlorosilatrane are in very good agreement with the experimental values, especially when we use hybrid functionals. There is no clear trend in the calculated ^{13}C NMR chemical shifts that depends on whether the geometry is optimized at the HF or DFT levels.

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