Calculations of ^{31}P NMR chemical shifts in phosphorus compounds: correlations between theory and experiment

Mayrla L. A. de Oliveira*(PG¹), Brenda K. de Almeida², Leonardo M. da Costa (PQ²), José Walkimar de M. Carneiro(PQ²).

¹Programa de Pós-graduação em Química, Universidade Estadual do Piauí, Rua João Cabral, 2231 64002-150.

²Departamento de Química Inorgânica e Departamento de Química Orgânica, Universidade Federal Fluminense, Outeiro de São João Batista s/n 24020-14.

*Corresponding author: E-mail: mayrla-oliveira@hotmail.com

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Introduction

^{31}P NMR chemical shifts (CS) calculations using quantum chemical methods have been used to predict structures of several phosphorus compounds, helping rationalize their application in biological studies and in organic and inorganic phosphorous chemistry. The search for the optimal combination of optimization method and CS calculations continues to be a requirement to attain an acceptable agreement between theoretical and experimental data.²⁻⁴

Methodology

All the theoretical data were obtained with the local meta-GGA functional M06L and the Def2tzvp basis set (geometry optimization and magnetic shielding calculations). The calculated absolute shielding values in the gas phase and in implicit solvents were converted into chemical shifts relative to 85% solution of phosphoric acid using the absolute shielding of 328.35 ppm. In total 33 compounds were investigated, covering a chemical shift range over 500 ppm. Some examples are illustrated in Fig.1.

Fig. 1 Structures of representative compounds.

Results and discussion

Fig.2a summarizes the calculated and experimental ^{31}P NMR chemical shifts of trivalent phosphorus compounds. The correlation between computed (M06L/def2tzvp) and experimental data is 0.99. Critical outliers (deviation around or above 10 ppm) were found for: CH_3PF_2 and CH_3PCl_2 .

Fig. 2 Correlation of calculated versus experimental ^{31}P CSs for the phosphorus compounds: (a) trivalent and (b) pentavalent.

For the pentavalent compounds (Fig. 2b) the agreement is much lower (correlation coefficient 0.71). Several reports on divergences from theoretical to experimental data for pentavalent phosphorous compounds have been presented. Relativistic effects, particularly in the cases where phosphorous is bonded to heavier atoms, and extra coordination of solvent to the phosphorous atom was indicated as the possible origin for the divergence. In our computation the highest deviations were found for compound containing a P-X (X = halogen) bond. Previous studies have shown that the deviations for the multi-chloro compounds are higher when the number of chlorine atoms increases, pointing out the importance of relativistic effects.¹ However, we show that the result can be considerably improved even without inclusion of relativistic contribution. This and other aspects will be discussed in our contribution.¹

Conclusion

The use of the M06L/def2tzvp combination of functional and basis set considerably improved the description of ³¹P NMR chemical shifts, although some critical cases, particularly for pentavalent phosphorous compounds, still requires a deeper investigation.

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