^{31}P NMR SPECTROSCOPY IN STEREOCHEMICAL ANALYSIS

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Phosphorus is a fascinating element playing a crucial role in nature. It is a key component in nucleic acids (DNA, RNA), in energy storage (ATP/ADP system), or signal transduction. The P-containing compounds are also important in medicinal chemistry, e.g. nucleoside prodrugs with antiviral effects or drug delivery systems based on phosphate self-immolative linkers. The compounds with chiral center on phosphorus atom, so called P-chirogenic molecules, are crucial for enantioselective catalysis and in coordination chemistry. The correct determination of stereochemistry (configuration, conformation) is substantial for structure-activity relationship studies.

^{31}P isotope is a magnetically active nucleus with a high natural abundance, therefore, incorporation of ^{31}P NMR parameters into the analysis can provide the key structural information when the conventionally used NMR methods based on ^{1}H, ^{13}C NMR parameters fail.

In this work, we prepared model P-containing compounds, extracted ^{31}P NMR parameters, such as chemical shifts and internuclear interactions, and correlated them with quantum-chemical calculations. ^{31}P chemical shift is rather sensitive to even minor structural changes (e.g. solvation), which may be confusing in some cases. Spin-spin interactions of ^{31}P with the neighbouring nuclei (^{1}H, ^{13}C) provided the key connectivity and geometry information due to Karplus-like dependence of *J*-couplings on dihedral angles. Residual dipolar couplings were investigated as additional parameters used to obtain the stereochemical information. [1]

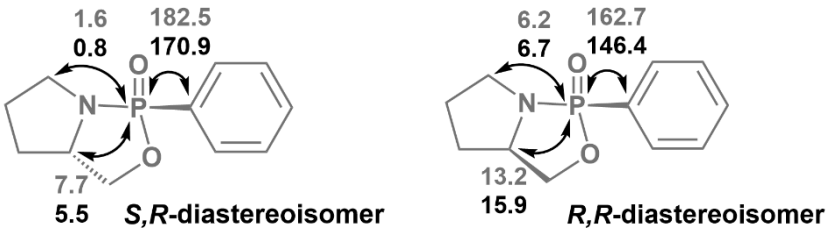

Figure 1. Experimental (grey) and DFT-calculated (black) ^{13}C-^{31}P *J*-couplings used for determination of relative configuration. The absolute configuration was confirmed by X-ray diffraction data.

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REFERENCES

[1] M. Tichotová, A. Ešnerová, L. Tučková, L. Bednárová, I. Císařová, O. Baszczyňski, E. Procházková, *J. Magn. Reson.* **2022**, *336*, 107149, 1–9.