

Solid State NMR Spectroscopy of Boron Compounds

Libor Kobera, Olivia Policianova, Martina Urbanova, Jiri Brus

Institute of Macromolecular Chemistry, Academy of Science of Czech Republic,
Heyrovského nám. 2, 162 06 Praha 6, Czech Republic



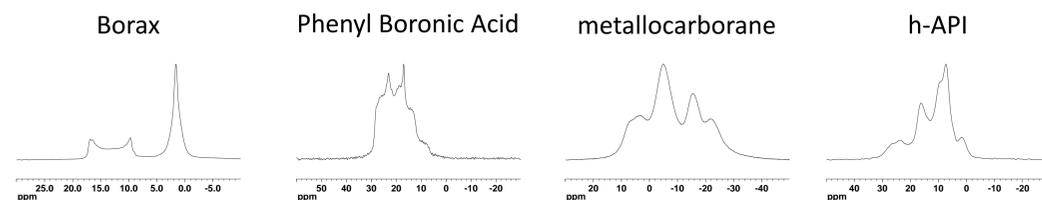
Introduction

Very important, for finally using as a medicinal product, is precise description of structural homogeneity and purity. Excellent tool for structural analysis is solid state NMR spectroscopy. Organoboron compounds description is possible by NMR measurements of included nuclei such as ^{13}C , ^{11}B etc.

High sensitivity and abundance of boron nucleus is suitable for measurement and consequently analysis of NMR spectra. On the other hand, the quadrupolar character of boron atoms complicates detail analysis. Typical 1D MAS NMR spectra are very complicated and difficult to interpret. However, the solution provides the MQ/MAS NMR experiment and using of relatively new techniques called biaxial shearing. This combination enhances the spectral resolution and thereby helps correctly analyze and describe structure units.



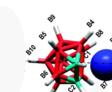
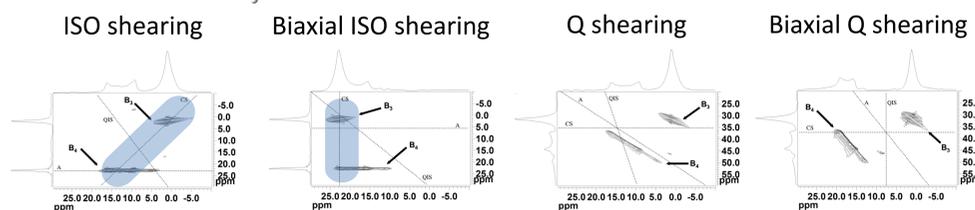
^{11}B MAS NMR



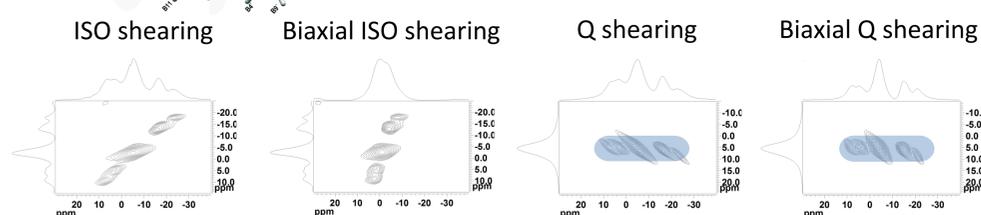
Classical & biaxial shearing



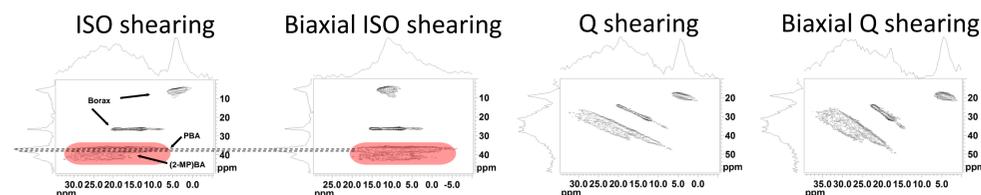
^{11}B MQ/MAS NMR of borax



^{11}B 3Q/MAS NMR of metallocarborane



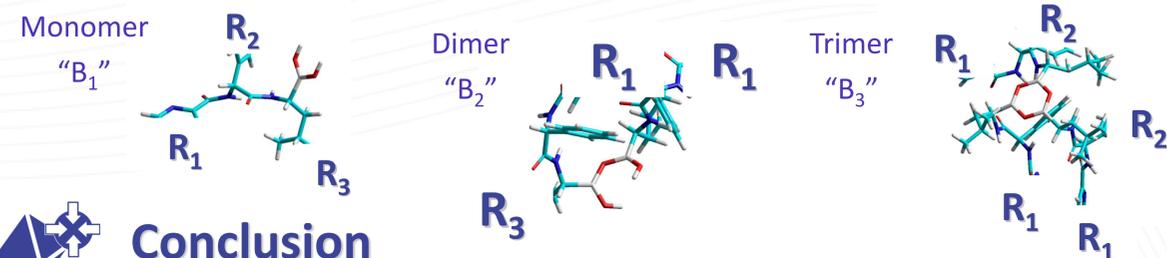
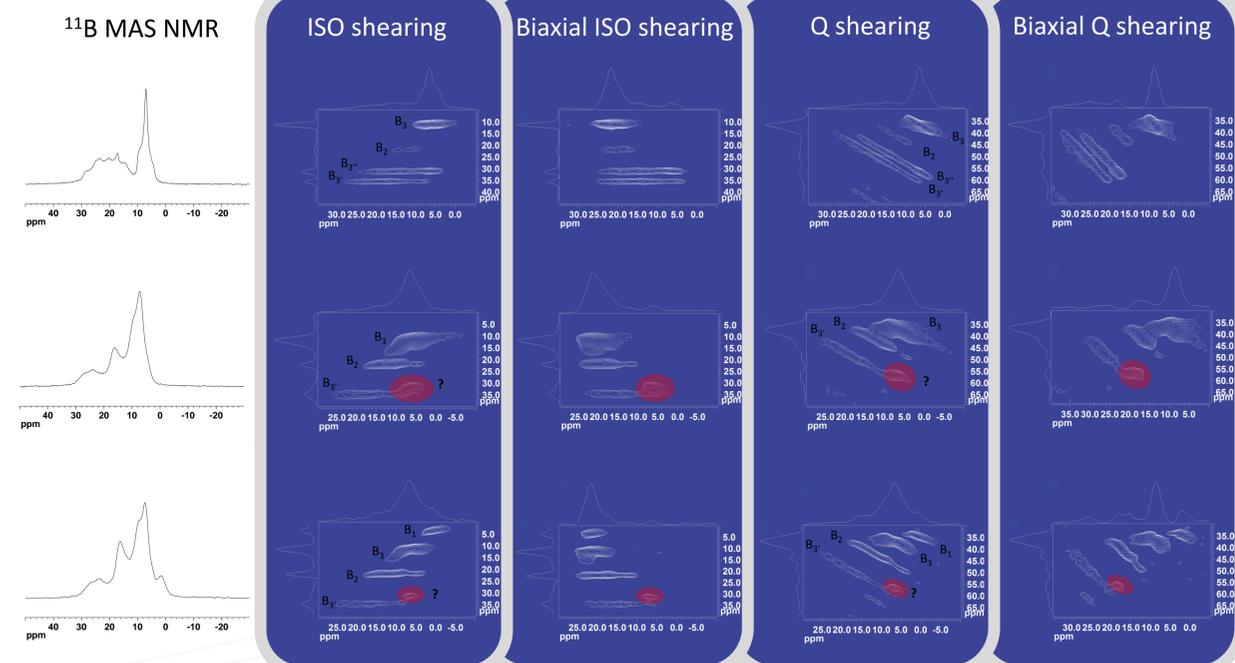
^{11}B 3Q/MAS NMR of Borax + Phenyl Boronic Acid + (2-methylpropyl) boronic acid physical mixture



Results

^{11}B 3Q/MAS NMR of high Active Pharmaceutical Ingredients

These proteasome inhibitors systems, exhibits not only extensive polymorphism, but boronic acid fragments can spontaneously undergoes condensation and dehydration forming thus various oligomers.



Conclusion

Four possible schemes was demonstrated on this poster which may be valuable for shearing 2D MQ/MAS NMR spectra. Examination of peaks contours under different shearing schemes helps to interpret the 2D MQ/MAS NMR spectra. The suggestion arises that the choice of shearing factor should be made on a case-by-case basis. Where distinct chemical sites are well resolved, as for many model compounds, **ISO-shearing** is the best choice. Amorphous or disordered materials, on the other hand, typically give a distribution of chemical shift and/or quadrupolar parameters, and it can be more difficult to interpret MQMAS spectra to identify distinct chemical sites. Where the distribution of chemical shifts leads to greater inhomogeneous linewidths than the second-order quadrupolar broadening, eliminating chemical shift in the indirect dimension by **Q-shearing** can lead to apparently sharper spectra and therefore enhanced ability to distinguish dissimilar sites. Additional shearing in the directly detected dimension (**biaxial shearing**) can provide further cosmetic modifications of the spectra which may aid interpretation by helping to identify and characterize independent chemical sites.

Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ