

## Conférence - CEISAM - UMR CNRS 6230

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**Pr. Paul G. Williard**

Department of Chemistry, Brown University, Providence, Rhode Island, USA 02912

### *Structure and Aggregation State of Organolithium Compounds - Size Matters*

The background and use of diffusion techniques in NMR spectroscopy known as PGSE and DOSY will be reviewed with emphasis on illustrating how NMR diffusion experiments such as DOSY can and should be used routinely. Examples in which x-ray diffraction combined with DOSY NMR experiments lead to the hypothesis that the most important factor controlling aggregation state and solvation state of organolithium compounds is their size and steric interactions. Hence, a progression of solvation and aggregation states from trisolvated monomers through hexasolvated hexamers will be shown in which the only explanation possible is that the size of the substituents in the aggregate dictate their overall structure.

Other examples of group 1A metal cations such as Li, Na or K enolates and amide anions form aggregates with Lewis bases such as THF or a tertiary amines or phosphoramidate have been characterized in solution and by x-ray diffraction analyses. Comparison of the structural features of a sequence of homologous compounds in which the size of chemically similar substituents will be presented where a systematic increase in size clearly shows that the steric bulk of the components is responsible for the dominant solvation state and aggregation state of the major complex formed. A priori predictability of these latter two features for new compounds seems attainable; hence size matters.

<https://vivo.brown.edu/display/pwilliar>

1. Guang J, Liu QP, Hopson R, Williard PG. Lithium Pinacolone Enolate Solvated by Hexamethylphosphoramidate. *Journal of the American Chemical Society*. 2015;137(23):7347-56. doi: 10.1021/jacs.5b01906. PubMed PMID: 2015:757421.
2. Su C, Hopson R, Williard PG. Influence of Steric Factors on Chiral Lithium Amide Aggregates. *Journal of the American Chemical Society*. 2014;136(8):3246-55. doi: 10.1021/ja4123957. PubMed PMID: 2014:123185.