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www.chem.utk.edu/facilities/nmr

∗ Measuring molecular weights with DOSY.

An interesting application of the DOSY experiment is the possibility to measure molecular weights (MW) of chemical compounds in solution.

The translational diffusion coefficient (D) of a compound in liquid solution, depends on its shape and volume, as well as on the viscosity of the solvent.

Volumes can be transformed into molecular weights if the densities of the compounds are known. Thus, by measuring D on several compounds of similar shapes and densities, it is possible to generate a curve of log(D) against log(MW) as shown in the figure. In turn, the curve allows to calculate MWs given D measured on a molecule of unknown molecular weight.
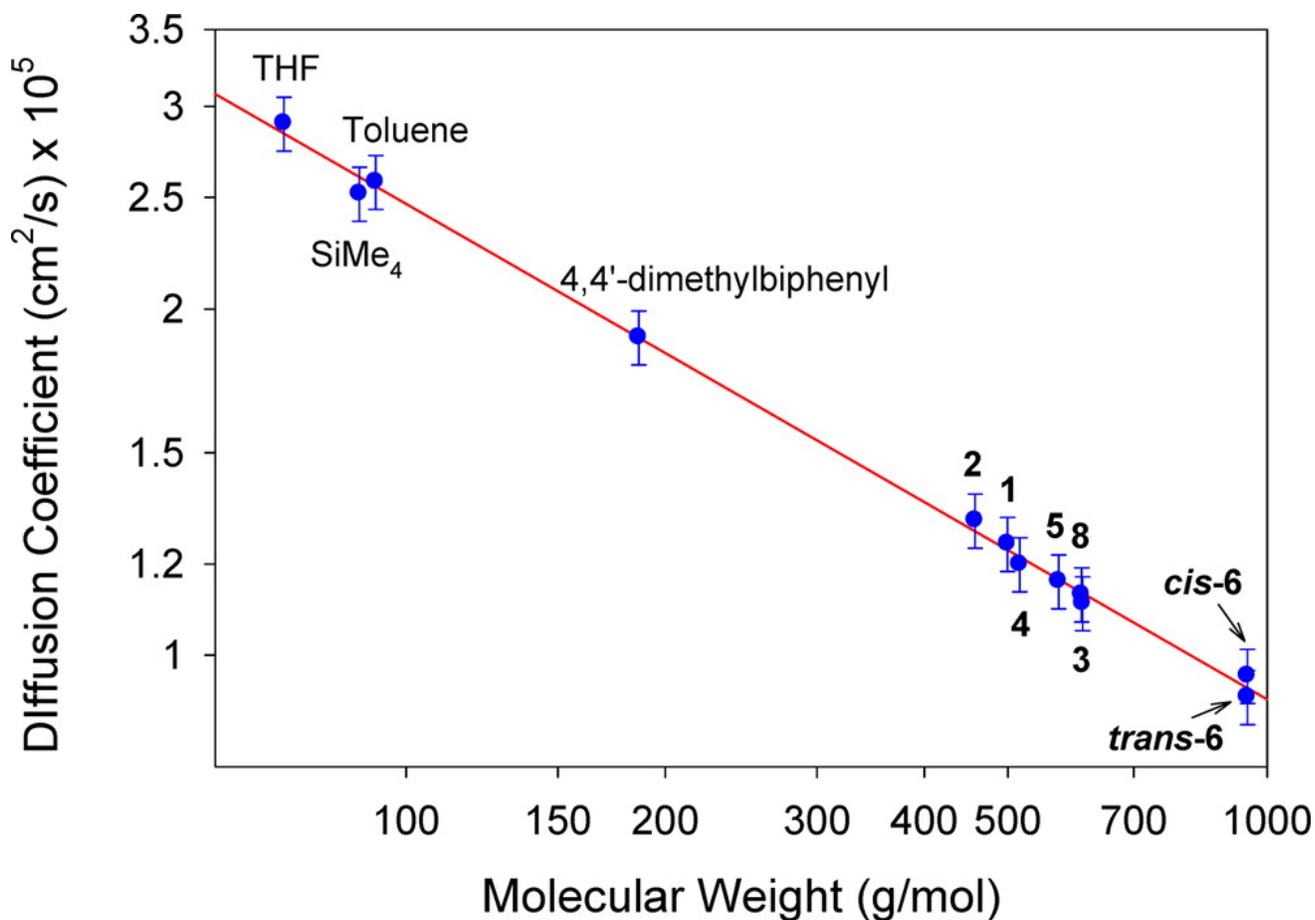
In the figure shown above, after measuring D in several known compounds, a calibration curve was generated. Then, D was measured on several compounds, labelled 1-6 and 8. Although the structure of these compounds were known, the interest was to determine whether they were monomers or dimers in solution. Compounds 1-5 and 8 were found to be monomers. Compounds cis-6 and trans-6 are dimers.

Interestingly, compound **1** is a monomer in solution as indicated by DOSY experiments, but it is a dimer in the solid state as shown by its X-Ray Crystal Structure.

The DOSY technique can be used to calculate MWs of small molecules, as well as polymers and proteins.

Results shown are from Dr. Xue's Inorganic group.
Seth C. Hunter et al.; Organometallics, in press.
http://pubs.acs.org/doi/full/10.1021/acs.organomet.5b00558

* ^{29}Si HMBC NMR

Sensitivity is a major issue in NMR. Even more when dealing with nuclei like ^{29}Si and ^{15}N. The reason for this is that these nuclei have negative gyromagnetic ratios. Thus, signals on a 1D experiment cannot be enhanced by NOE like in the case of ^{13}C 1D-NMR. The option then, in order to enhance the ^{29}Si or ^{15}N signals is to run a DEPT experiment with a set of parameters appropriate for that particular compound.

Although most users prefer direct detection methods (1D), indirect detection experiments (2D) are always more sensitive.

The figure below shows a ^{29}Si gHMBCAD spectrum of TaMe$_2$(=NSiMe$_3$)[N(SiMe$_3$)$_2$]. The HMBC is more sensitive than the ^{29}Si DEPT experiment and there is no need for any special set up.
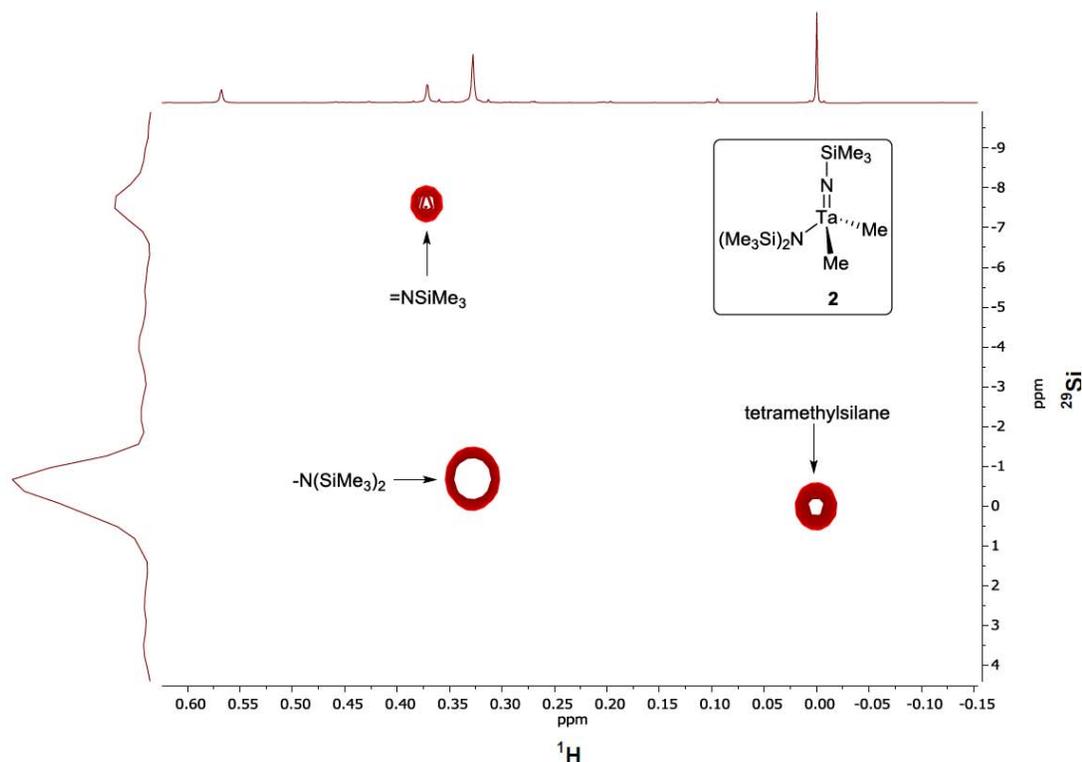
Figure S3. ^{1}H-^{29}Si HMBC NMR spectrum of **2** in benzene-d_6 at 25 °C with SiMe$_4$ as the internal standard.

Results shown are from Dr. Xue's Inorganic group.
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∗ Quantum Espresso and Gipaw. NICS Supercomputers.

I have opened an account for the NMR Facilities on the supercomputer Darter, of the National Institute for Computer Science (NICS). The main intention for this is to be able to run the programs Quantum Espresso (QE) and Gipaw. These programs allow to calculate chemical shifts of samples in the Solid State.

Quantum Espresso can also be used to calculate the relaxed state of a crystal at room temperature, using X-ray Crystallography data. Crystal structures are typically resolved at ~173 K. Therefore, at room temperature crystal structures can be slightly different from those determined by X-Ray Crystallography. This differences can be detected on the Chemical Shifts measured in Solid State NMR.

∗ WFGs boards installed in SSNMR Varian 400.

Wave Form Generators (WFGs) boards were installed in the Varian 400 MHz console. WFGs allow more advance features in Solid State NMR. Particularly, the ^1H Dipolar Decoupling (DD) sequences, TPPM and Spinal. These DD sequences are more efficient that the standard one available before.

Also, WFGs allow ramped and tangent Cross Polarization (CP), as well as CP FSLG (Frequency Switch Lee-Goldberg) sequences.

∗ Software updates.

Varian 600 MHz: The VNMRJ software was updated to version-4.2. **DOSY** package was also installed.

Varian 400 MHz: The VNMRJ software was updated to version-4.2.