Measuring Non-Bonded $^{14}N/^{13}C$ Distances with the R-RESPDOR Experiment

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Introduction

Solid-state NMR (SSNMR) provides a powerful and general method for characterizing materials unsuitable for conventional crystallography. Recently, molecular structures and even complete crystal structures have been characterized using SSNMR data.[1] Isotope labeling enhances SSNMR characterizations and analysis of unlabeled materials is significantly more challenging. The SSNMR method R-RESPDOR[2] allows characterization of unlabeled materials by measuring multiple I > ½, S = ½ distances via dipole couplings. Here R-RESPDOR is used to study $^{14}N/^{13}C$ couplings in a previously uncharacterized pyranose at natural abundance.

Experimental

All $^{14}N/^{13}C$ R-RESPDOR data were acquired using a 600 MHz widebore NMR system with a 3.2 mm magic-angle spinning triple-resonance low-*E* probe at the NHMFL in Tallahassee. The $^{14}N/^{13}C$ dipolar dephasing curves are fit in the time domain using the universal REDOR curves described in [2] to obtain couplings and to extract the associated distance information.

Results and Discussion

An R-RESPDOR analysis of the pyranose shown in Figure 1 provided 8 $^{14}N/^{13}C$ couplings in a single experiment including 6 involving one or two bond couplings. These short-range data are extremely valuable for shift assignment but less useful in structural analysis. Two of the observed couplings represent longer-range interactions of ^{14}N sites with C2' and C4'. Modeling all possible conformations at C2 and C3 indicates that these couplings are not consistent with intramolecular interactions. Instead the long-range couplings appear to arise from non-bonded interactions with a neighboring molecule having the azide group positioned within 3 Å of the C4' position. Modeling is currently underway to identify structures consistent with this feature. The positioning of a second molecule will establish a portion of the crystallographic unit cell and aid in the determination of a complete crystal structure in this difficult-to-crystallize material.

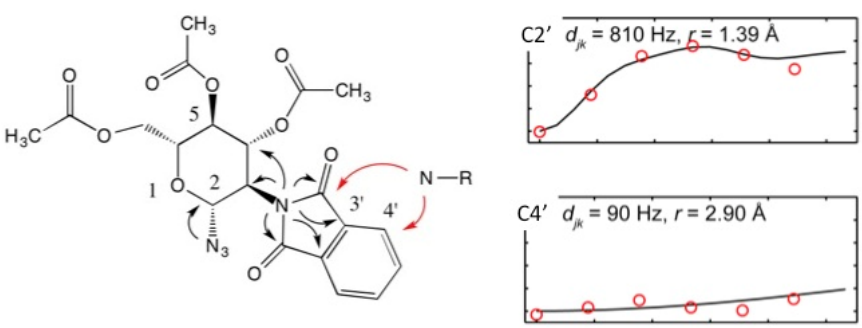

Figure 1. Structure of the pyranose studied here with arrows showing the $^{14}N/^{13}C$ interactions measured using the RESPDOR experiment. Two of these couplings (shown in red) arise from non-bonded interactions and thus provide significant crystallographic structural information. The dipolar dephasing curve at C2' (top plot) is 200 Hz larger than the symmetry related C=O site, indicating contributions from at least 2 ^{14}N's. Ongoing modeling work seeks to identify feasible structures.

Conclusions

This R-RESPDOR analysis described herein establishes crystallographic lattice features solely from NMR in a previously uncharacterized solid. Recent work has demonstrated that complete crystal structures can be obtained using long-range NMR constrains.[3] The R-RESPDOR $^{14}N/^{13}C$ data compliments these alternative NMR crystallographic methods and extends them to unlabeled organic structures containing ^{14}N.

Acknowledgements

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References

[1] Brouwer, D. H., *et al*., J. Am. Chem. Soc., **135**, 5641-5655 (2013). (b) Baias, M., *et al.,* J. Am. Chem. Soc., **135**, 17501-17507 (2013). (c) Kalakewich, K., *et al*., Cryst. Growth Des., **13**, 5391–5396 (2013).
[2] Gan, Z., Chem. Commun., 4712-4714 (2006).
[3] Luchinat, C., *et al*., J. Am. Chem. Soc., **134**, 5006-5009 (2012).