

Q-DEPT: A Powerful Experiment for Facilitating the NMR Analysis of Dendrimers

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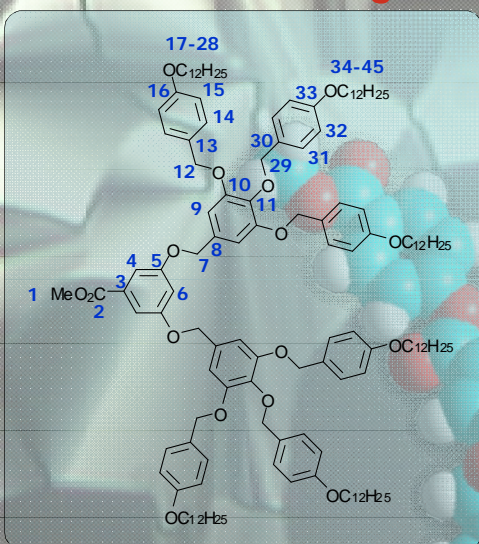
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Introduction

NMR spectroscopy has become a major tool for analyzing dendrimers at an atomic level. Dendrimers are usually highly symmetrical compounds, as they are built up from the same repetitive unit which is successively coupled as the generation of the dendrimer increases. In spite of the symmetry, ¹³C and DEPT NMR spectra of large-size dendrimers may readily contain tens of resonances, from which it is unlikely to get a full and unequivocal attribution. Consequently, the complete and unequivocal attribution of all ¹H and ¹³C NMR resonances requires recording the full battery of multidimensional and multinuclear NMR experiments currently available, as well as extensive data analysis. Dendrimers, however, produce very characteristic one dimensional ¹³C and DEPT spectra. Very often, the main building unit generates as many distinct sets of ¹³C resonances as the number of generations.

The full and unambiguous attribution of the resonances can be done in two steps



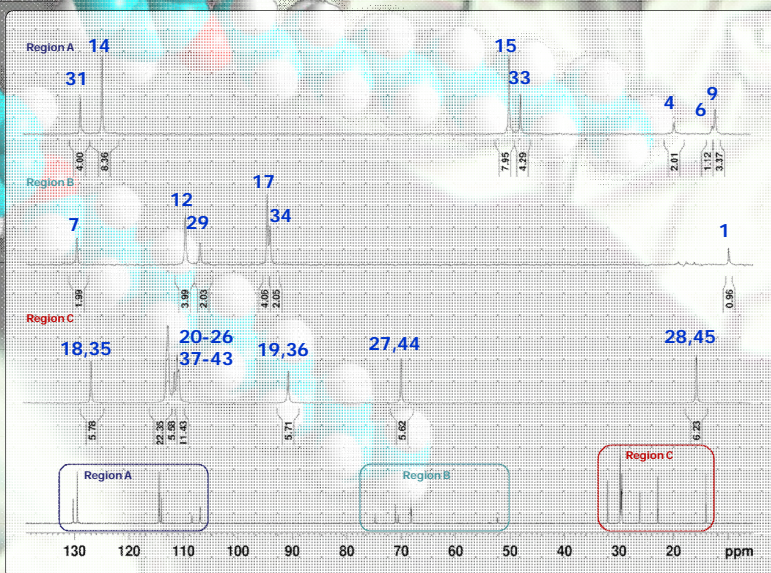
Step 1

Q-DEPT

Q-DEPT

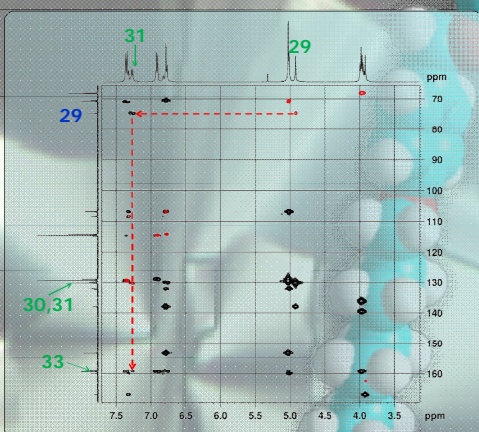
The usual quantitative ¹³C experiment is extremely time-consuming and cannot be applied for such molecules. The temptation to integrate the resonances in the DEPT spectra is great, but not reliable. The polarization-transfer efficiency is highly dependent on one-bond coupling constant (¹J_{CH}), spin systems (CH, CH₂, CH₃), and the transfer delay (Δ), the sensitivity enhancement is not uniform for ¹³C spins with different attached protons and ¹J_{CH} values, which restricts the application of polarization transfer to quantitative analysis. For simplifying and accelerating the attribution process of dendrimers, we propose to use the Q-DEPT¹ experiment, which provides integrable ¹³C resonances. The experiment has proven to be suitable for all spin systems over a large J-coupling range, and the ¹³C signals are nearly equally enhanced with standard deviation of less than 5%. In this way, a full and unequivocal attribution of all NMR resonances of dendrimers becomes straightforward, as extensive analyses of two-dimensional NMR experiments are no longer required.

Experimental verification



Step 2

HMBC+HSQC



Red cross peaks are from HSQC and black from HMBC.

The numbers in blue have been attributed with the Q-DEPT spectrum, while the green numbers are attributed with the HSQC and HMBC spectra.

The full and unambiguous attribution can be done easily and without extensive data analysis.

Conclusion

We have shown that the Q-DEPT method can be advantageously used for analyzing structures of dendrimers. All protonated carbons can be very easily assigned using one single Q-DEPT experiment, and the remaining quaternary carbons can be subsequently easily attributed using standard HSQC and HMBC experiments. The usual way for obtaining a full and unambiguous attribution requires using the full battery of multidimensional and multinuclear NMR experiments and extensive data analysis. The combination Q-DEPT - HMBC facilitates the attribution procedure and is much less time consuming.

Reference

(1) Jiang, B.; Xiao, N.; Liu, H.; Zhou, Z.; Mao, X.-a.; Liu, M. *Anal. Chem.* **2008**, *80*, 8293.

Acknowledgment

Financial support of this work by the Swiss National Science Foundation is gratefully acknowledged.