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A Method for Easily Determining Coupling Constant Values: An Addendum to "A Practical Guide to First-Order Multiplet Analysis in ^{1}H NMR Spectroscopy"

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A systematic procedure to decipher first-order ^{1}H NMR multiplets is described. This method is a very practical tool for extracting coupling constant values. It requires only that one (a) learn to identify each of the 2^n (n = number of spin $^1/_2$ nuclei to which the proton is coupled) "units of intensity" of a multiplet and (b) then apply a clearly delineated sequence of iterative steps that allows the J's to be assigned in order (from smallest to largest). The approach is even easier to use than one described previously (*J. Org. Chem.* **1994**, *59*, 4096−4103).

Introduction

Several years ago, we described a method for deciphering the individual coupling constants from a complex, first-order multiplet in a ^{1}H NMR spectrum.[1] Anecdotal evidence makes it clear that many have found this discussion to be very helpful. We now present an alternative, complementary protocol for obtaining the same information. The method we describe here makes the task of extracting the individual J values from complex multiplets even easier.

In general,[2] a first-order multiplet with chemical shift δ, having coupling constants arising from interaction with n spin $^1/_2$ nuclei, will contain a maximum of 2^n peaks that are symmetrically arrayed about the midpoint (δ). The actual number of individual peaks is usually reduced by degeneracies arising from certain relationships among two or more J's (e.g., two identical J values or cases where a third J is the sum or difference of two other J values). Nonetheless, the total "units of intensity", hereafter called components, will always sum to 2^n regardless of the presence or absence of line degeneracy. A trivial example makes the point: a 1:1:1:1 doublet of doublets (dd) and a 1:2:1 triplet (i.e., a dd with identical J's in which components number 2 and 3 are superimposed) both contain a total of four (2^2) components.[3] The increasingly complex set of multiplets shown in Figure 1 reinforce this important point. Recognize that each of the 2^n individual components coincides with one of the following line positions in the multiplet: δ (Hz) + $^1/_2(\pm J_1 \pm J_2 \pm J_3 \ldots \pm J_n)$. The furthest downfield and upfield lines in the multiplet are δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 \ldots + J_n)$ and δ (Hz) + $^1/_2(-J_1 - J_2 - J_3 \ldots -J_n)$, respectively. It follows that the separation between the outermost peaks of a multiplet is the sum of the individual coupling constants.[4,2]

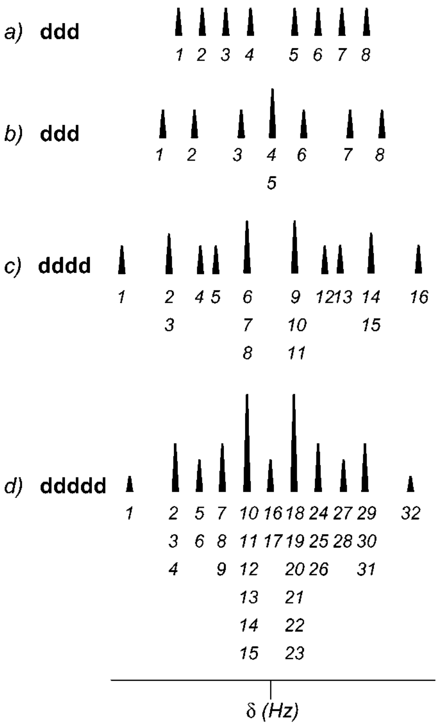

Figure 1. Four examples of assignment of all 2^n components to the individual lines in a first-order multiplet.

In what follows and for the sake of generality, we consider any multiplet arising from interaction with n protons to be a series of n doublets (e.g., dddd for $n = 4$) regardless of whether any of the protons are chemically and magnetically equivalent. In the case of equivalency,

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(1) Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem.* **1994**, *59*, 4096−4103.

(2) Most of the concepts noted in this introductory paragraph are well established and accepted truths, the original statements of which are difficult to locate but the existences of which are evidenced in many of the early treatises in the field: e.g., (a) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon: Oxford, 1959. (b) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969. (c) Becker, E. D. *High-Resolution NMR.; Theory and Chemical Applications*; Academic Press: New York, 1969.

(3) The outermost peaks in the multiplet are always the smallest and should be assigned a relative intensity value of 1.

(4) I.e., the total width of the multiplet = δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 \ldots + J_n)$ − [δ (Hz) + $^1/_2(-J_1 - J_2 - J_3 \ldots -J_n)$] = $(J_1 + J_2 + J_3 \ldots + J_n)$.

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Chart 1. Steps for Identifying *J* Values in Sequence from Smallest to Largest (J_1 to J_n) ({1 to *x*} Represents the Distance between the Peak Corresponding to Component 1 to the Peak Corresponding to Component x)

i) {1 to 2} is J_1.[a]

ii) {1 to 3} is J_2.[b]

iii) remove from further consideration the *component*[c] corresponding to ($J_1 + J_2$).

iv) {1 to next higher *remaining* component (i.e., 4 or 5)} is J_3. Thus, if $J_1 + J_2$ is {1 to 4}, then {1 to 5} is J_3. Conversely, if $J_1 + J_2$ is not {1 to 4}, then {1 to 4} is J_3.[d]

corollary: one of {1 to 4} or {1 to 5} is J_3.

v) remove from further consideration the *components*[c] corresponding to the remaining combinations of the first three *J* values [i.e., ($J_1 + J_3$), ($J_2 + J_3$), and ($J_1 + J_2 + J_3$)].

vi) {1 to the *lowest remaining* component} is J_4.

corollary: one of {1 to 5} through {1 to 9} is J_4.

vii) remove from further consideration the *components*[c] corresponding to the remaining combinations of the first four *J* values [i.e., ($J_1 + J_4$), ($J_2 + J_4$), ($J_3 + J_4$), ($J_1 + J_2 + J_4$), ($J_1 + J_3 + J_4$), ($J_2 + J_3 + J_4$), and ($J_1 + J_2 + J_3 + J_4$)].

viii) {1 to the *lowest remaining* component} is J_5.

corollary: one of {1 to 6} through {1 to 17} is J_5.

ix) etc.

[a] {1 to 2} = δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 ... + J_n) - [\delta$ (Hz) + $^1/_2(-J_1 + J_2 + J_3 ... + J_n)] = J_1$. [b] {1 to 3} = δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 ... + J_n) - [\delta$ (Hz) + $^1/_2(+J_1 - J_2 + J_3 ... + J_n)] = J_2$. [c] Each peak in the multiplet may (and often will) contain more than one component; *each* component should be individually removed from consideration or associated with a *J* value. [d] For a ddd: {1 to 4} (or {1 to 5}) = δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 ... + J_n) - [\delta$ (Hz) + $^1/_2(-J_1 - J_2 + J_3 ... + J_n)] = J_1 + J_2$ and {1 to 5} (or {1 to 4}) = δ (Hz) + $^1/_2(+J_1 + J_2 + J_3 ... + J_n) - [\delta$ (Hz) + $^1/_2(+J_1 + J_2 - J_3 ... + J_n)] = J_3$.

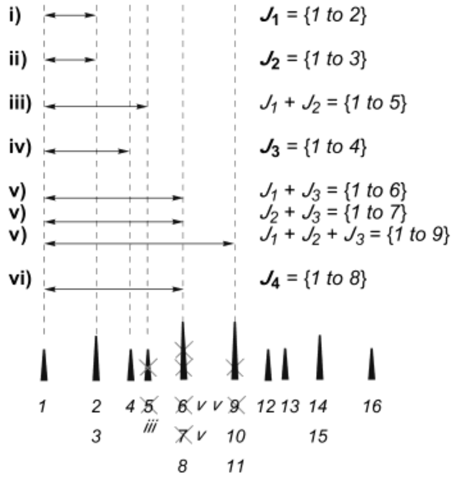

Figure 2. Assignment of $J_1 - J_4$ for a dddd by applying steps i−vi from Chart 1.

the multiplets are more commonly referred to, of course, as triplets, quartets, pentets, etc. (i.e., dd, ddd, dddd, etc. with identical *J*'s). Recognize then, that the method presented below for deducing the values of all *J*'s in, e.g., a dddd is applicable to *all* multiplets with 16 components: i.e., a pentet (p), a doublet of quartets (dq), a triplet of triplets (tt), or a doublet of doublet of triplets (ddt) in addition to a true doublet of doublet of doublet of doublets (dddd).

The method we now describe for deducing the individual *J* values from any first-order multiplet requires two principal operations: (i) assignment of each of the individual 2^n components (cf. Figure 1) and (ii) systematic identification of the individual *J*'s (cf. Chart 1 and the example in Figure 2).[5]

For the first operation, assign every peak in the multiplet one or more component numbers from 1 to 2^n from left to right (arbitrarily) by analogy to the examples shown in Figure 1. This involves assigning the relative intensities among all peaks of the multiplet, an operation that for some complex resonances (cf., Figure 1d) might require an iterative approach but that is usually straightforward for multiplets having 4, 8, 16, and even 32 components.

The second operation requires systematic identification of the *J*'s by the series of steps outlined in Chart 1. Adopt the convention that $J_1 \leq J_2 \leq J_3 \leq J_4 \leq ... J_n$. Appreciate that for J_3 and beyond it is necessary to have first determined the previous coupling constants (e.g., both J_1 and J_2 must be known before J_3 can be determined). In other words, one must deduce the *J*'s in order, from smallest to largest. Assign individual coupling constant values starting with step i (Chart 1), where {1 to *x*} is the distance in Hz between component 1 (which, necessarily, corresponds to the lefthandmost peak) and component *x*. The task is complete (all *J*'s identified) following step iv for a ddd, vi for a dddd, and viii for a ddddd. In practice, for some complex, slightly non-first-order (leaning/distorted), and/or partially overlapped multiplets, it is advantageous to work synergistically from both extremities of the multiplet.

Consider the dddd, whose component numbers were assigned in Figure 1c. In Figure 2, the determination of

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[5] The process requires practice at the outset, but it is well worth learning. Once familiar with the technique, people have deduced the six individual *J* values in the multiplet shown in Figure 3e (a dddddd) in 1−2 min.

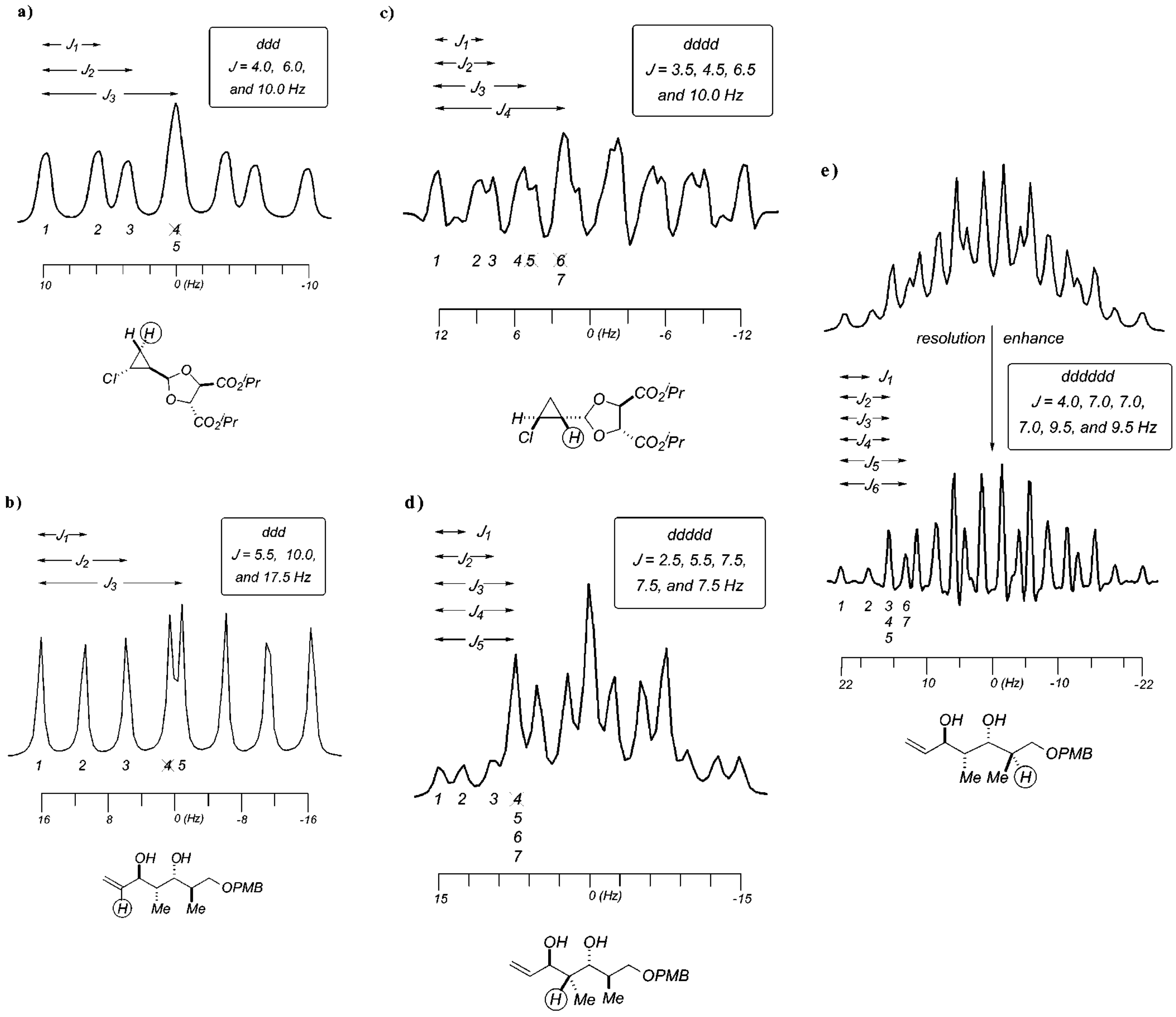

Figure 3. Examples of experimental multiplets for which the complete set of *J* values has been determined.

the *J*'s, arrived at by sequential application of steps i–vi, is shown.

This method has proven to be very practical. Commonly encountered first-order multiplets can be quickly analyzed.[6] Some selected multiplets from actual spectra are presented in Figure 3 to further demonstrate the power of this method. Notice that resolution enhancement/line broadening (vertical arrow in Figure 3e) can sometimes make the assignment of the 2^n component numbers more straightforward. Finally, it should not be overlooked that coupling constant values are valuable because they convey information about geometry.[7,8]

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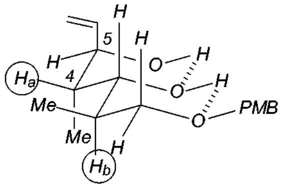
(6) **Note Added in Proof.** For a very recently described, complementary "approach to automated first-order multiplet analysis", see: Golotvin, S.; Vodopianov, E.; Williams, A. *Magn. Reson. Chem.* **2002**, *40*, 331–336.

(7) Karplus, M. *J. Chem. Phys.* **1959** *30*, 11–15.

(8) For example, the *vicinal* coupling constants for the two protons shown in Figure 3d,e suggest that the hydrogen-bonded conformation **1** (with two gauche relationships between H_a and its methine neighbors and one gauche and two anti arrangements between H_b and its three neighbors) is a major contributor in $CDCl_3$ to the family of conformers that define the solution structure of this polyol fragment. This is not necessarily to be expected because of the steric congestion flanking the C(4)–C(5) bond and would be a very difficult issue to assess by any method other than the *magnitudes* of coupling constants.



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