NMR: FREQUENT ERRORS and USEFUL FOOTNOTES

1. FREQUENT DANGEROUS ERROR

Coupling constants are very useful for assignments. However, **the magnitude of the coupling constant does not automatically correlate to "how far" two atoms are apart** (how many atoms they are separated by). Also, coupling constants have signs (plus / minus), but this is always ignored in reporting raw data.

Examples from "Carbon-13 NMR Spectroscopy" by Kalinowski, Berger, and Braun (1988)

PPh_3 J_{CP} values: $^1J/^2J/^3J/^4J$ = 12.5, **19.7**, 6.8, 0.3
$P(nBu)_3$ J_{CP} values: $^1J/^2J/^3J/^4J$ = 10.9, 11.7, **12.5**, 0
$O{=}PPh_3$ J_{CP} values: $^1J/^2J/^3J/^4J$ = 104.4, 9.8, **12.1**, 2.8
$O{=}P(nBu)(OEt)_2$ J_{CP} values: $^1J/^2J/^3J/^4J$ = 140.9, 9.8, **12.1**, 2.8

2. ERRORS: a little PHILOSOPHY

2.1 It is important to avoid any error in NMR data presented in a thesis or manuscript

2.2 It is perfectly acceptable to leave a peak unassigned, or (for example) to group three peaks and assign them to a group of three atoms. In this format, mistakes are avoided.

2.3 If you put in a footnote that "this assignment is tentative", perhaps with a few extra words "based upon...", you can never be accused of making a mistake.

2.4 If you make an assignment based upon a 2D NMR technique, you must add a footnote to every peak so assigned.

2.5 Why is it necessary to assign any NMR peaks at all? If the structure has been "proved" by other criteria, the assignment is only an exercise. The editorial policy of *J. Org. Chem.* forbids making assignments except under certain restricted conditions. However, it is always a good idea to make sure there are no "extra peaks" that would indicate impurities or equilibrating species.

2.6 Many journals are now requiring that original spectra be submitted as supplementary material, with the peak list output (replacing the peak list/assignments in the text). This will be required for all Texas A&M dissertations.

3. CHEMICAL SHIFTS of RESIDUAL SOLVENT SIGNALS

A "scholarly reference" is always preferable to some handout given away at a trade show. An official technical manual of a manufacturer could be considered a scholarly reference, but they are not commonly available in libraries and therefore are "second choice". The best journal article I know of is:

Gottlieb, H. E.; Kotlyar, V.; Nudelman *J. Org. Chem.* **1997**, *62*, 7512

Additional data is given in by Kalinowski, Berger and Braun (see above). Summaries of shifts are also available on the web, but are not as reliable. We favor the data from Cambridge Isotopes, from whom a PDF file can be downloaded (see 06.12)

4. HOW THE META (and other) ^{13}C SIGNAL of a PHENYL RING is ASSIGNED

[53] The ^{13}C NMR signal with the chemical shift closest to benzene is assigned to the meta aryl carbon: Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

5. GOT SATELLITES?

Here is the footnote for you.

[61] This coupling represents a satellite (d; ^{195}Pt = 33.8% or ^{183}W = 14.3%), and is not reflected in the peak multiplicity given.

6. VIRTUAL COUPLING?

What is virtual coupling? At the first mention of the phenomenon in the text, I cite this paper:

[11] Hersh, W. H. *J. Chem. Educ.* **1997**, *74*, 1485.
an older but not as informative ref: Pregosin, P. S.; Venanzi, L. M. *Chem. Brit.* **1978**, 276.

Don't get into the sticky issue of the true value of the coupling constant. Use this footnote:

[23] The *J* values given represent the *apparent* coupling between adjacent peaks of the triplet.

An NMR lab supervisor has formulated this concise description of the most frequently encountered version of this phenomenon: "When a ^{13}C nucleus couples to a ^{31}P nucleus which in turn couples to a chemically equivalent ^{31}P, a "triplet" is observed in the ^{13}C-spectrum (typically for the ipso, ortho and meta carbons of an aryl phosphine or analogous signals of an alkyl phosphine). This is termed in the literature "virtual coupling", a poor expression since it is merely a consequence of a spin system where first order rules no longer apply. The phenomenon can be conveniently simulated by appropriate software, e.g. "gNMR"

7. CAN'T SEE THE COUPLING THAT SHOULD BE THERE?

One approach is to measure the width of the peak at half height, $w_{1/2}$. If this is greater than the expected coupling, this explains everything. Report as: x.xx ppm (br s, $w_{1/2}$ = zz Hz).
In other cases, footnotes of the following types may be applicable:
[15] A satellite would be expected based upon other spectra in this paper, but could not be discerned above background noise.
[16] These ^{13}C signals are assigned by analogy to those of the more soluble *p*-tol_3P analog, for which additional diagnostic couplings (J_{CP}, J_{CPt}) could be observed and ^{1}H-*un*decoupled spectra were recorded [6].
[63] The C_6F_5 signals were too weak for complete assignment.

8. ONLY ONE LINE of a DOUBLET VISIBLE?

If you have a good idea of what the coupling should be (e.g., the 400th chiral rhenium compound with PPh_3), and the second line is exactly coincident with another signal, you can "extract" the chemical shift and coupling constant. If you are only 80-90% certain, you put in a footnote about this being a "tentative chemical shift/coupling constant value due to an overlapping signal" (it is *not* a tentative assignment). If the second line is "buried like hell" use a footnote along these lines:
[34] This represents the chemical shift of the upfield line of doublet. The other line was obscured.

9. CAN'T SEE THE SIGNAL?

If there is an obvious signal missing, and an obvious reason why it should be weak, just put in a footnote:
[48] The *ipso* PC signal was not observed.

10. TOO MUCH COUPLING?

If it doesn't pay to do further 2D experiments to resolve the coupling, just describe the spectrum in words in the experimental text. You would start to list signals, then formulate something like: 4.67-5.10 (overlapping unresolved multiplets, specific atoms, integration).

However, it would be an error to designate a region of overlapping ^{13}C signals as a "multiplet". A multiplet desciptor can only be applied to a single signal.

11. RANDOM COLLECTION of OTHER USEFUL FOOTNOTES

[57] The $PCH_2CH_2CH_2$ ^{13}C NMR signals were assigned from chemical shift and coupling constant patterns established previously: Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A. *J. Chem. Soc., Perkin 2*, **1982**, 327.

12. MOST COMMONLY NEEDED DYNAMIC NMR EQUATIONS

from Sandström, J. "Dynamic NMR Spectrometry" Academic Press: New York, 1982

Calculation of DG≠ for Systems with Two-site Exchange

A. Simple (50:50)

$$k = \frac{pdn}{\sqrt{2}} \qquad dn = (n_A - n_B)$$

$$DG^{\neq} = (4.575 \times 10^{-3})T_c\,[\,10.319 + \log(T_c / k)]$$

B. Unequal populations (p_A and p_B are partial fractions of the major and minor components respectively)

1. $k_A = k_{(\text{major to minor})} = p_B / t_{max} = 2pdnp_B$

2. $k_A = k_{(\text{major to minor})} = p_B / t_c$

$$t_c = X / 2pdn$$

where X is graphically related to $p_A - p_B$
(see Table 6.1 on page 82)