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A monthly collection of informal private letters from laboratories involved with NMR spectroscopy. Information contained herein is solely for the use of the reader. Quotation of material from the Newsletter is not permitted, except by direct arrangement with the author of the letter, in which case the material quoted must be referred to as a "Private Communication". Results, findings, and opinions appearing in the Newsletter are solely the responsibility of the author(s). Reference to The NMR Newsletter or its previous names in the open literature is strictly forbidden.

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FORTHCOMING NMR MEETINGS

XIVth International Conference on Phosphorus Chemistry, Cincinnati, OH, July 12 - 17, 1998. For details, see Newsletter 468, 40.

NMR Symposium at the 40th Rocky Mountain Conference on Analytical Chemistry, Denver, CO, July 27 - 30, 1998. Contact: Dr. Robert A. Wind, Battelle/Pacific Northwest National Laboratory, P.O. Box 999, MS K8-98, Richland, WA 99352; (509) 376-1115; Fax: (509) 376-2303; Email: ra_wind@pnl.gov. See Newsletter 470, 8.

XVIIIth International Conference on Magnetic Resonance in Biological Systems, Tokyo Metropolitan University, August 23 - 28, 1998. Contact: Professor Masatsune Kainosho, Department of Chemistry, Tokyo Metropolitan University; +81-426-77-2544; Fax: +81-426-77-2525; e-mail: kainosho@raphael.chem.metro-u.ac.jp; http://icmrbs98.chem.metro-u.ac.jp

NMR Technologies: Development and Applications for Drug Design and Characterizations, Baltimore, MD, October 29-30, 1998; Contact: Jennifer Laakso, Cambridge Healthtech Institute, 1037 Chestnut St. Newton Upper Falls, MA 02164; 617-630-1300; Fax: 617-630-1325; chi@healthtech.com; http://www.healthtech.com/conferences/

"NMR of Polymers and Biopolymers," Symposium at the 54th SouthWest Regional ACS Meeting, Baton Rouge, LA, November 1-2, 1998; Contact: members.aol.com/ACKolbert/symposium.html or e-mail to: mailto:ackolbert@aol.com" Xiaolian Gao at xgao@uh.edu

NMR Spectroscopy of Polymers, Breckenridge, Colorado, January 24-27, 1999; an International Symposium Sponsored by the Division of Polymer Chemistry, American Chemical Society; Organizers: P. T. Inglefield and A. D. English. Registration contact: Neta L. Byerly, Division of Polymer Chemistry, Inc., Virginia Tech, 201 Hancock Hall, M.C. 0257, Blacksburg, VA 24061; 540-231-3029; Fax: 540-231-9452; email: nbyerly@vt.edu

40th ENC (Experimental NMR Conference), Clarion Plaza Hotel, Orlando, Florida, February 28 - March 5, 1999; immediately preceding Pittcon in Orlando. Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87505; (505) 989-4573; Fax: (505) 989-1073; Email: enc@enc-conference.org.

continued on inside back cover
Dr. B. L Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303.

Dear Barry,

(received 5/27/98)

We have been involved lately in characterizing numerous models of congestive heart disorders for evaluating efficacy of drug candidates. One of the critical issues in designing the studies is the necessity to evaluate the most relevant indices and how they relate to overall pharmacological actions of compounds. We have used cardiac-gated magnetic resonance imaging (MRI) as an interrogating tool for understanding physiological changes in heart structure and function serially.

The hemodynamic information (stroke volumes, etc) with appropriate estimates of blood pressure from the aortic arch, (i.e. afterload) can generate indices of (a) work done by the heart per beat to push a given stroke volume against the afterload i.e. the stroke-work (Joules/kg), (b) power required by the heart to achieve such stroke-work (Watts/kg) and (c) the intra-cardiac end-diastolic and peak systolic wall-tensions (DWT, SWT respectively; Newton/meter) that develop to pump such stroke volumes into the aorta. Using MRI, differences between normo- and hypertensive rats were determined to evaluate these measurements. SHR and WKY rats (n=3-5/group) were imaged using a BRUKER 4.7T/40 cm imaging system with local transcievers gated to appropriate cardiac phases. Blood pressure recordings were obtained from the same animals. Cross-sectional areas of mid-ventricular heart sections were measured from the same anatomical site for all animals using the MRI data. Wall tensions were calculated using the Laplace equation \( T=Pr \).

Calculated parameters for hypertensive rats expressed as a percentage of normotensive rats were: Stroke-Work (191%), Power (161%), Stroke volume (101%), Ejection Fraction (91%), SWT (240%*), DWT (206%*), Blood Pressure (sys/dias: 190%/186%) *p<0.005.

Results demonstrate that stroke-work, power requirements (both related to energy requirements of the heart), and intra-cardiac wall tensions between normotensive and hypertensive groups differ more than some of the hemodynamic parameters (stroke volume and ejection fraction).

Sincerely,

Sudeep Chandra and Susanta Sarkar

We acknowledge following members of CV pharmacology for valuable discussions: Drs. Robert Willette, Frank Barone, and Eliot Ohlstein
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These factors, along with computer driven automatic testing and environmental stress screening of the final product, ensure that the performance, quality and reliability meet AMT’s exacting standards.
May 22, 1998
(received 6/10/98)

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

The Application of DECRA to the solid state NMR spectra of mixtures.

Dear Dr. Shapiro:

We previously reported [1,2] the application of direct exponential curve resolution algorithm or DECRA to PGSE NMR data from multicomponent systems and shown that highly overlapped spectra can be resolved if the diffusivities of the components are different. The key to the success of DECRA is for the spectra of the individual components to decay exponentially, a condition fulfilled by typical PGSE data sets.

We have recently observed that DECRA can also be used in conjunction with a \(^1\)H T\(_1\) filter [3, 4] to cleanly separate the CP/MAS spectra of multicomponent solid mixtures. Efficient proton spin diffusion insures that each domain in a grossly phase-separated material or physical mixture has its own uniform \(^1\)H T\(_1\). The example given in figure 1 shows the separation of the \(^{13}\)C CP/MAS spectrum of a mixture of glycine powder and polystyrene pellets into individual component spectra. DECRA treatment of the data offers the advantage of spectral separation even when the \(^1\)H T\(_1\) values of the components differ by as little as 20%. This and other advantages and variants of the DECRA analysis as applied to solid state NMR will be discussed in a forthcoming publication.

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bantalek@kodak.com

Willem Windig
windig@kodak.com

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Selective Use of Selective Decoupling

Dear Barry,

The constant time $^1$H/$^{13}$C HSQC (CT-HSQC) experiment is a very useful tool in the assignment of protein resonances. The sign of the peaks is determined by whether the number of attached aliphatic carbons is odd or even. This enables peaks due to Gly $\alpha$, Thr $\beta$ and Met $\varepsilon$ to be readily identified as they produce negative peaks in regions otherwise dominated by positive ones.

Fig. 1 shows the Ca/Ha region of the 500MHz gradient $^1$H/$^{13}$C CT-HSQC on a sample of 2mM $^{13}$C/$^{15}$N ubiquitin pH 5.1 in D$_2$O at 298K. The data was acquired on a Bruker DRX500 with a Nalorac z-gradient 5mm triple resonance probe. Negative peaks are shown as a single contour. The Gly $\alpha$ resonances are clearly visible between 44 and 46 ppm, and the Thr $\beta$ resonances between 68 and 73 ppm. The remaining resonances are due not only to non-Gly $\alpha$, but also to Ser $\beta$ and Pro $\delta$.

![Fig. 1: Expansion of lowfield region of $^1$H/$^{13}$C CT-HSQC of ubiquitin with Seduce decoupling of carbonyl region.](image-url)
A simple method to identify the Ser β and Pro δ resonances is to re-run the experiment without Seduce decoupling of the carbonyl region. This leaves the \( J_{\text{COC}} \) coupling of \(~55\text{Hz}\) visible as a splitting in the \( ^{13}\text{C} \) dimension. Carbons that are more than 1 bond away from a carbonyl do not exhibit a splitting due to the smaller long-range coupling constants.

Fig. 2 shows a CT-HSQC acquired without Seduce decoupling. Three times as many scans per FID were acquired so the lowest contour level is 3 times higher. The majority of the resonances are clearly split by the coupling to the carboxyls. However, the resonances due to the 3 Ser βs are now readily identifiable at 62.3, 63.2 and 64.8ppm. In addition, the resonances due to the 3 Pro δs are also easily picked out at 50.4, 51.0 and 51.05ppm.

**Fig. 2:** Same region as fig. 1 without Seduce decoupling of the carbonyl region and showing splitting of resonances except Thr/Ser β and Pro δ.

This is a simple method for the identification of the chemical shifts of certain residue types, and provides useful starting points for the analysis of other datasets. It is equally applicable to the identification of other carbons adjacent to carbonyls in Asn, Asp, Gln and Glu residues.

Duncan M Smith

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Dear Barry:

Recently, we have applied one- and two-dimensional \(^{129}\)Xe NMR methods to investigate the morphology of reinforcement carbon blacks. Interestingly, we observe a wide range in chemical shifts among different samples, and we attribute these differences primarily to variations in aggregate structure.

Figure 1 shows the \(^{129}\)Xe NMR spectrum of a physical mixture of three “normal” ASTM fillers: N110 (1.89 g), N347 (3.00 g), and N472 (1.00 g). The blend quantities represent the amounts necessary to yield equal surface areas of each component according to their ASTM D3037 \(N_2\) adsorption values. The peak at \(\delta=0\)ppm corresponds to xenon atoms which are very weakly adsorbed. The next farthest upfield peak (\(\delta=53\) ppm) corresponds to N347 adsorbed \(^{129}\)Xe atoms, followed by N110 (\(\delta=68\) ppm) and N472 (\(\delta=94\) ppm) adsorbed xenon.

We interpret the observed variations in \(^{129}\)Xe NMR chemical shift in terms of the relative pore sizes within the aggregate structure. Thus, the aggregate voids of sample N472 are smallest, followed by fillers N110 and N347. Additionally, we use the integrated NMR peak intensities of each sample as a measure of their relative unoccupied aggregate volume. It is therefore possible to calculate the relative aggregate density of each sample, and the so called “structure” of the aggregate (which depends primarily on aggregate density). Figure 2 shows a plot of relative aggregate volume (from \(^{129}\)Xe NMR peak intensity) versus aggregate “structure” (ASTM D2414 dibutyl phthalate absorption) for each sample. The ratio of aggregate volume:aggregate surface area is also used to calculate the relative linear void dimensions, and found to be consistent with our assignment based on chemical shift.

Finally, using two-dimensional \(^{129}\)Xe NMR exchange spectroscopy, we calculate the approximate exchange times of xenon atoms between filler samples. Figure 3 shows the 2D spectrum obtained with an exchange time of 100 ms, where exchange is apparent between all filler pairs except N472 and N110. The absence of exchange between these two samples is attributed to their relatively small aggregate void size (as indicated by their downfield \(^{129}\)Xe NMR chemical shifts and volume:surface area ratios). When the exchange time is reduced to 6 ms, no evidence of exchange between any of the samples is apparent.

Please credit this contribution to the Naval Research Laboratory.

With best regards,

Ken

K.J. McGrath
Code 6122
Naval Research Lab
Washington, DC 20375-5342
mcgrath@ccf.nrl.navy.mil
Figure 1: $^{129}$Xe NMR Spectrum of CB Blend

Figure 2: $^{129}$Xe NMR vs. ASTM "Volume"

Figure 3: 2D $^{129}$Xe NMR Exchange Spectrum
(100 ms exchange time)
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Comparison of the first $^1$H-1H plane of NOESY-HSQC experiment on labeled protein in 95% H$_2$O / 5% D$_2$O with buffer. Spectra courtesy of T. J. H. Miller, University of Minnesota.

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Cryostat Assembly
Re: 13C NMR Spectral Simplifications of Fluoralkyl Chains from 19F decoupling at High Field

Dear Barry,

We have recently explored heteronuclear 19F decoupling capabilities on our Varian Unity 600 spectrometer to obtain 13C NMR data on fluoroalkyl compounds. Heteronuclear 19F decoupling is currently not in general use as many NMR spectrometers are not equipped with this capability. Ideally, 13C NMR spectral simplification from heteronuclear 19F decoupling could be accomplished at low decoupler power levels so that heating of the sample is minimized. Early NMR studies (90MHz or lower B0 Zeeman field) on fluoroalkanes using noise decoupling recorded two separate 13C spectra, first with the 19F decoupler set at the CF3 resonance and then at the midpoint of the CF2 resonances (1). Wide-band heteronuclear 19F decoupling for the recording of a single 13C spectrum required the use of very high power (50W) decoupler units (2,3). At 50 W decoupler power, a rapid stream of nitrogen gas was used to cool the decoupling coil (3). It is unclear to what extent sample heating affected the data.

There is ~60 ppm separation between CF3 and CF2 19F signals in fluoroalkyls, and Fig. 1A shows the 564 MHz 19F NMR spectrum of the fluorinated alcohol CF3-(CF2)4-CF2-CH2CH2OH recorded using a 5mm Varian triple resonance probe with high band coil tuned for 1H detection. 60 ppm is ~34 kHz at 600 MHz B0 field, or ~6X the 6 kHz needed to span a 10 ppm 1H window. The fully coupled 600 MHz 13C NMR spectrum (Fig. 1B) reveals a complex pattern of ~50 resolved lines between 106 and 122 ppm with 1JCF and 2JCF couplings of ~280 and 33 Hz for the six fluorinated carbons (C3-C8). Since 1JCF is ~2X 1JCH and 19F shifts span ~6X 1H shifts, complete wide-band heteronuclear 19F decoupling of fluoroalkyl chains is taken to be ~12 times more difficult to achieve than complete 1H decoupling of alkyl compounds.

We measured the continuous-wave (CW) decoupler output on our Unity 600 using a Bird Thruline Wattmeter terminated with a 50 ohm load and fitted with either 1W 425-850 MHz or 5W 400-1000 MHz crystals. As decoupler power increased from 28 to 49db (maximum recommended by Varian), the wattmeter readings increased from 20 mW to 1.6W. Calibration of the decoupler field strength in the triple resonance probe by off-resonance decoupling gave \( \gamma H2=5753 \text{ Hz at 49 db, i.e. an effective decoupler bandwidth of ~23 kHz, which is obviously less than the 34 kHz between CF3 and CF2 signals at 600 MHz field. When the decoupler is set at the midpoint between CF3 and CF2 signals and broadband WALTZ-16 decoupling is applied, only a partial simplification of the fluoroalkyl 13C NMR spectrum is achieved (Fig. 1C).}

GARP-1 decoupling (4) programmed through the waveform generator at lower power (47db, 1.1W) however sufficed to simultaneously decouple the CF3 and CF2 regions and all fluorinated carbon signals collapse to singlets (Fig. 1D), except for the C5 signal at 118.8 ppm which is a triplet with a small 1JCF coupling (Fig. 1G). C7 at 109.4 ppm removes the 1JCF coupling (Fig. 1E). This identifies the 118.1 ppm signal as the CF3 (C8) resonance, and also confirms that the most upfield 19F resonance which now collapses to a simple quartet with a 2JCF coupling from the C4 CF2 which is now identified at 111.7 ppm.

Single frequency CW decoupling of the -85 ppm CF3 19F resonance removes the 1JCF coupling from the 118.1 ppm resonance which now collapses to a simple quartet with a 1JCF coupling (Fig. 1G). C7 at 109.4 ppm now appears as a "triplet-of-triplets" with its own 1JCF coupling and a 2JCF coupling from the C6 CF2. On limiting the decoupler (42db, 320mW power) to excite only the -120 to -130 ppm CF2 region, two simple quartets result at 118.1 and 109.4 ppm with 1JCF and 2JCF couplings. These quartets clearly arise from the terminal CF3 and adjacent CF2 groups.

The 13C NMR resonances shown (Fig. 1B-H) have linewidths ~4Hz, digital resolution of 0.59 Hz/pt, and are processed with 1 Hz line broadening. The 1W level for heteronuclear 19F decoupling appears to be reasonable to minimize heating effects in the sample. The selective 19F decoupling exploiting two- as well as one-bond effects for the 13C NMR spectral simplification achieves a complete 13C NMR assignment for the fluorinated alcohol.

Regards,

Tony

Anthony A. Ribeiro (A² R)
ribeiro@tweety.mc.duke.edu
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1996 Varian publishes the definitive "High-Resolution NMR Spectra of Solid-Phase Synthesis Resins."

1997 Varian announces the innovative NMS, bringing automation to Nano Probes.

1998 Varian announces the gHx Nano Probe which goes even further by offering indirect detection capabilities for even the most demanding experiments.
Re: MAS-NMR of Solvent-Swollen Plant Polymers

Dear Barry:

In recent years, magic-angle spinning (MAS) $^1$H and $^{13}$C NMR techniques have been used to examine peptides and drug candidates bound to solvent-swollen solid-phase synthesis resins; these methods offer significant potential for applications in combinatorial chemistry and drug discovery.$^{[1,2]}$ The use of solvent swelling to enhance mobility and MAS to minimize magnetic susceptibility line-broadening can dramatically improve the resolution of the resulting NMR spectra, making it possible to monitor the syntheses in situ, without time-consuming purification steps. Rather than examining the small molecules, we have drawn upon prior $^1$H spectral studies of the resins themselves$^{[3]}$ to focus on solid biopolymer supports with intrinsic mobility and significant interactions with various solvents. In particular, we are seeking to obtain high-resolution spectra of swelled plant cuticular polymers using MAS methods.

Presented below are preliminary results for suberin, a solid biopolymer blend isolated from wound-healing potatoes.$^{[4]}$ This agriculturally important protective material is thought to possess spatially separated domains that consist of polysaccharides, aromatics (phenolics) and aliphatics (fatty acids). Each constituent is blended or connected to the others, in ways not yet established. As expected, the traditional $^1$H NMR spectrum of suberin is broad and featureless even with MAS at 8 kHz, as shown in Fig. 1a. The rigidity of the dry polymer is confirmed by the retention of large dipolar coupling effects and consequent breadth of the spectral pattern.

What happens after swelling the suberin sample for a day in chloroform? Without spinning, the $^1$H NMR spectrum remains broad (Fig. 1b), but with 8-kHz MAS there appears a forest of sharper peaks (Fig. 1c). Though well short of the resolution typical in a solution-state NMR spectrum, these data make it straightforward to distinguish the three domains in suberin: aliphatics at 0.9-2.4 ppm; polysaccharides at 3.5-5.3 ppm; and aromatics at 6.2-8.0 ppm. The sharpest singlet has a linewidth of 24 Hz, compared with 1-2 Hz for liquid water in our Doty XC5 CPMAS probe. So far, we have obtained the best resolution enhancements across the spectrum with CDCl$_3$ as the swelling solvent.

A variety of other useful $^1$H NMR experiments are also feasible with this approach. COSY and NOESY results in the CDCl$_3$-swollen suberin sample are shown in Figs. 2a and 2b. With COSY, through-bond correlations within each structural type are clearly observable and may be analyzed in detail. The NOESY spectrum shows correlations between the aliphatic and polysaccharide domains, but none of the anticipated cross peaks$^{[4]}$ are found between aromatic protons and the other two chemical types. This anomaly is attributable to preferential swelling of different domains by the solvent. For instance, CDCl$_3$ will solvate the aliphatics readily and the polysaccharides to some degree, but the solvent may fail to penetrate the heavily crosslinked

---

networks in which the phenolic suberin moieties are thought to be located. This hypothesis is supported by the relative peak intensities in the MAS $^1$H NMR spectrum (Fig. 1c), since the aliphatic peaks are large and sharp whereas aromatics that are known to be compositionally important in suberin$^9$ can barely be seen. Under these conditions, it becomes more difficult to observe NOESY crosspeaks that involve aromatics.

Our current efforts to improve this protocol include the use of solvent mixtures and variation of the temperatures for solvent swelling and NMR spectral acquisition, respectively. Suggestions are also welcome from the readership of the Newsletter.

Sincerely yours,

Ruth E. Stark
Professor of Chemistry
Email: stark@postbox.csi.cuny.edu

Figure 1. 300 MHz $^1$H NMR of suberin samples. (a) dry, MAS=8 kHz; (b) swollen in CDCl$_3$, static; (c) swollen in CDCl$_3$, MAS=8 kHz. All spectra were obtained using a 5 mm XCS probe from Doty Scientific Inc.

Figure 2. 2D NMR of swollen suberin (MAS at 8 kHz). (a) COSY; (b) NOESY (mixing time 150 ms).

CASE Programs and the Mysteries of Free Valences

Dear Barry,

I will continue my discussion of Computer Assisted Structure Elucidation (CASE) programs with a discussion of free valences and the difference in the ways in which the DENDRAL programs and MolGen handle them.

In the DENDRAL programs, free valences could be satisfied by attachment to "heavy atoms" only. That is, attachment to hydrogen was forbidden. Thus, substructure P4 in Figure 1 could not become an O-methyl or a hydroxymethyl group during structure generation. There was a bit of a trap here. By default with this definition, specifying the location of one free valence implied that all other sites in the substructure were to be "filled out" with protons. This was sometimes easy to forget, especially since the "drawings" presented by these programs did not explicitly show these protons. For example, the DENDRAL representation of P4 would be "-C-O-". However, once one got used to this convention it was very convenient, since it fit very neatly the NMR spectroscopist's view of substructures.

![Figure 1: Substructures from Last Contribution](https://example.com/figure1.png)

Of course there were occasions when this rather rigid definition was not appropriate. Especially before the days of the DEPT experiment there were times when one wasn't entirely sure just how many protons were attached to each site of a substructure. In such cases one used the tool HRANGE to specify the range of protons possible at each site. With large substructures the specification of the number of protons at each site could become tiresome and also provided the user with ample opportunity to make mistakes. Because I am pretty good at making mistakes, I used the free valence definition whenever possible, but the flexibility afforded by the HRANGE tool was convenient at times.

Flexibility is also available in MolGen, but the defaults are different. In MolGen free valences can be satisfied by any atom, including hydrogen atoms. In the example from last month we had defined ch2ch2-1 (Figure 1) as one of the GoodList substructures in the MolGen analysis. MolGen can in principle expand ch2ch2-1 to an O-propyl or a hydroxyethylene group. In fact there were too few remaining protons to fill out the quaternary carbon of ch2ch2-1 to make a methyl group, but attachment of the oxygen atom to hydrogen was possible, and because of this we got twice as many candidate structures (6) from MolGen as we got (3) from GENOA.

The problem is solved, in both GENOA and MolGen, by simply telling the programs everything that we know about the substructure. For example, we know that the oxygen atom of ch2ch2-1 is not attached to a hydrogen atom. We can probably assume that it is not attached to oxygen, since that would lead to a peroxide. Therefore, with the constraints inherent in the molecular formula, it must be attached to carbon.

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1 See NMR Newsletter, March 1998, #474, p. 5.
2 See NMR Newsletter, April 1998, #475, p. 29.
We don't know how many protons are attached to that carbon, or even its hybridization, but with the default free valence definition of MolGen the substructure \texttt{ch2ch2-2} provides the constraint we want. With this substructure added to GoodList, MolGen gets the same final three structures that GENOA does.

Let's go through another example of free valences. One of my favorite compounds for testing these programs is borneol. If one inputs the molecular formula of borneol (C\textsubscript{10}H\textsubscript{18}O) into MolGen and hits the "start" button, one gets a total of 95,312 structures.

If you put in the multiplicities of all the carbon resonances, which is very easy to input in version 3.5 with the "H-distribution" window, the number of structures is reduced to 8,295. If one uses the carbon chemical shift data to forbid MolGen from forming any multiple bonds (again, easy to do in MolGen) one gets 2191 structures. If one looks at some of these structures, one sees some strained bicyclic systems that one could probably safely put on BadList, and perhaps other substructures that could be ruled out on the basis of chemical shifts. But again it is more efficient to put in positive evidence if we have it.

For example, we know from the proton spectrum that the three methyl carbons must be attached to quaternary carbons, so let's try to explain that to the program (Figure 2).

![Figure 2: Ways to Represent Singlet Methyl Groups](image)

By now we know that \texttt{sCH\textsubscript{3}-1} will not work. Since free valences can be satisfied by protons as well as other atoms, \texttt{sCH\textsubscript{3}-1} can be seen to represent methyl singlets, doublets, or triplets. Thus we should not be surprised by the fact that putting three \texttt{sCH\textsubscript{3}-1} groups on GoodList has no effect on the number of structures generated. \texttt{sCH\textsubscript{3}-2} uses X atoms, which by definition can be anything but proton. But putting three \texttt{sCH\textsubscript{3}-2} substructures on GoodList leads to no structures passing the constraints! I am not sure why this happens, and neither is anyone I have asked. I suspect that this results from pushing the overlapping capabilities of substructures on GoodList in MolGen too far. The DEPT data tell us that there are three quaternary carbons and three methyl groups in borneol. Thus, two of the methyls must be attached to one of the quaternary carbons. Putting three \texttt{sCH\textsubscript{3}-2} groups on GoodList implies three methyls and three quaternary carbons, and perhaps the program is unable to recognize the necessity to overlap a couple of the latter.

But with a program as powerful as MolGen, there is always a work-around. The one I chose was to define \texttt{sCH\textsubscript{3}-3} and put it on BadList. \texttt{sCH\textsubscript{3}-3} specifies that the methyl is attached to a carbon bearing at least one proton; i.e., a doublet methyl. Since free valences can be satisfied by hydrogen atoms, \texttt{sCH\textsubscript{3}-3} could also represent a methyl triplet. By putting this substructure on BadList, one rules out all methyls except those attached to quaternary carbons. Structure generation with this constraint leads to 306 structures.

MolGen is a good CASE program, but it is of the type that I have begun to call a "classical" CASE program. It leaves all the spectrum interpretation to the molecular structure chemist. In addition, even after the human has a clear idea of the constraint he wants to give to the program, there can still be problems "translating" this information to the program, as we saw in the example above with borneol. In my next contribution I will describe an alternative program, one that I call a "non-classical CASE program."

---

\[ \text{Doug Dorman} \\
\text{doug_dorman@lilly.com} \]

3 Don't try to look at these structures by hitting the "Results" button. With this many structures, this crashes the program.

4 With "only" 2,191 structures the program does not crash.
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### Specifications for Vertical Bore, High Resolution NMR Magnet Systems

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Deuterium-induced carbon-13 isotope shifts in cross-conjugated systems

Dear Professor Shapiro:

The deuterium induced $^{13}$C isotope shifts for a structurally varied group of 21 nitrogen-containing benzo-heterocyclic systems, labeled at the NH position, have been measured in DMSO-$d_6$. The analyzed compounds included bridged diphenylamines, benzolactams, 4-quinolinone, acridinones, carbazoles and indoles (Scheme). The variations of two-bond isotope effects ($2\Delta$) are function of the competitive nitrogen lone-pair delocalization into the two neighboring unsaturated systems ($\alpha$ and $\alpha'$) [1-4]. A dependence between the $\delta$NH with the arithmetic mean of $2\Delta\alpha$ and $2\Delta\alpha'$ is evidenced (Figure). Exclusion of 5—for which the formation of an azepine ring anion with $\delta$-electrons on deprotonation makes the NH proton less acidic—and 13 improves considerably the quality of the correlation, to give $r = 0.90$. The least-squares equation is $2\Delta(C\alpha + C\alpha')/2$ (ppb) = -25.53 $\delta$NH (ppm) + 146.5.

![Chemical structures](image)
Scheme. Structural formulae of bridged diphenylamines 1-5, benzolactams 6-13, 4-quinolinone 14, acridinones 15, 16, carbazoles 17-19 and indoles 20, 21.

Figure a): Plot of $^2\Delta$ vs. $\delta$NH. Symmetrical molecules ($\triangle$), $\alpha\alpha'$ (○), $\alpha\alpha'$ (■). b): Plot of $^2\Delta(C\alpha + C\alpha')/2$. The plot includes data for indole (a), tetrahydrocyclopent[b]indole (b) and tetrahydrocarbazole (c).


Sincerely yours,

Martha S. Morales-Ríos

Pedro Joseph-Nathan
Re: MRI Investigation of Anomalous Solvent Diffusion in Polymers

Dear Barry,

In recent years, MRI methods have proved useful for studying solvent transport behavior in polymers and coals. For instance, time-resolved MRI has been used in our lab to distinguish between Fickian and Case II swelling dynamics [Cody & Botto, TAMU nmr Newsletter, 424, 25 (1994)]. Recently we have observed anomalous swelling behavior in cross-linked rubber samples, for which the swelling dynamics are found to be intermediate between Fickian and Case II diffusion. Our results are unusual given that swelling of rubbers in typically Fickian in nature. The samples were cross-linked copolymers of poly(isobutylene)-co-poly(paramethyl-styrene) (PIB/PMS), kindly provided by Jeff White at Exxon Chemical. The mole % concentrations of PIB and PMS in the polymers were 97% and 3%, and Tg = -73°C and 101°C for PIB and PMS, respectively. Thus, the samples have largely 'rubber-like' properties at room temperature.

Images of cyclohexane uptake in samples were recorded in situ. The sample was contained inside a glass cross that was constructed from 5mm NMR tubes and held in place with Kel-F holders. The holders were free to slide leaving the samples unconstrained as they swelled. Samples were cut longer than they were wide with approximate dimensions 1 x 1 x 10 mm. By imaging a slice perpendicular to the long axis, swelling in two dimensions could be observed.

Front velocity and concentration profiles are diagnostic of the type of swelling behavior. Fickian transport is characterized by an exponentially decreasing solvent front that moves as the square root of time, while a sharp solvent front moving linearly with time is characteristic of Case II diffusion. Figure 1 shows the progression of cyclohexane in three PIB/PMS samples having different cross-link densities. Sample 1 is the most cross-linked while sample 3 is the least cross-linked. The points were fitted to the equation \( p = v \cdot t^n \), where \( p \) is position of solvent front, \( t \) is time and \( n \) is an exponent (\( n = 0.5 \) for Fickian and \( n = 1.0 \) for case II). The fits gave values for \( n \) of 0.70, 0.86 and 0.87 for samples 1, 2 and 3, respectively. These values are indicative of anomalous swelling behavior.

Figure 2 presents MRI images and the corresponding front profiles for sample 2. Brighter pixels indicate greater signal intensity. Diffusion weighting was employed in the images on the right as a means of eliminating signal from bulk cyclohexane. The diffusion coefficient of cyclohexane imbibed in the polymer was found to be smaller (by a factor of ca. 2) than that in the bulk solution. The relatively sharp front profiles observed indicate non-Fickian swelling.

Valtier and coworkers [Valtier, M.; Tekely, P.; Kiene, L.; Canet, D. Macromolecules, 1995, 28, 4075-4079] noticed another difference between Fickian and Case II swelling. They found that the 2D contour of the diffusion front reflects the initial shape of the object if the swelling is Case II. However, the diffusion contour quickly becomes circular in the case of Fickian swelling. In our samples, 2D contours retained the original object shape until the end of the swelling process. This indicates that swelling dynamics are closer to case II.

Observation of bright regions near the solvent front in the diffusion-weighted images is also interesting. The profiles obtained reflect gradients in the self-diffusion coefficients of cyclohexane across the sample. The data imply that the polymer network is relaxing slowly behind the solvent front. We intend to explore this property in more detail in the future.

Sincerely,

David M. Gregory
Robert E. Botto
Chemistry Division
Chemistry Division
Figure 1

Front Position (μm) vs Time (min)

- Sample 1
- Sample 2
- Sample 3

Figure 2

No spectral editing vs Diffusion weighted images

- 10 min.
- 28 min.
- 46 min.
- 21 min.
- 44 min.
- 83 min.
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- L-Aspartic Acid-$^{13}$C$_6$-$^{15}$N
- L-Glutamic Acid-$^{13}$C$_6$-$^{15}$N
- L-Glutamine-$^{13}$C$_6$-$^{15}$N$_2$
- Glycine-$^{13}$C$_6$-$^{15}$N
- L-Isoleucine-$^{13}$C$_6$-$^{15}$N
- L-Leucine-$^{13}$C$_6$-$^{15}$N
- L-Lysine-$^{13}$C$_6$-$^{15}$N$_2$
- L-Phenylalanine-$^{13}$C$_6$-$^{15}$N
- L-Serine-$^{13}$C$_6$-$^{15}$N
- L-Threonine-$^{13}$C$_6$-$^{15}$N
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Emerging Figures of Merit for NMR: Choosing the Right Probe for the Job

Dean L. Olson, Paul F. Molitor, Michael E. Lacey, Jonathan V. Sweedler
School of Chemical Sciences, University of Illinois at Urbana-Champaign

Dear Barry and NMR Newsletter Readers,

In light of recent advances and applications in NMR for trace analysis [1-4], new figures of merit are emerging [4] for users to evaluate and compare relative probe performance for a particular application [5]. Here, we present a few helpful definitions and interpret them with respect to common NMR experiments.

NMR users are accustomed to an expression of $S/N$ for a given analyte concentration, such as 0.1% ethylbenzene in CDCl$_3$, or 40% dioxane in C$_6$D$_6$. This performance parameter can be more explicitly defined as the concentration sensitivity

$$S_c = \frac{S/N}{C \cdot t^{1/2}}$$

where $C$ is the sample concentration, and the $t^{1/2}$ term normalizes for the total experiment time by incorporating into a single variable the acquisition time, number of transients, pre-delay, etc. Such a definition, however, may not tell the whole story for a probe which has been designed for mass-limited samples. In such a case, a more relevant indicator of probe performance is the mass sensitivity

$$S_m = \frac{S/N}{mol \cdot t^{1/2}}$$

where the mole amount is the portion of the sample which lies within the NMR coil observe volume, $V_{obs}$. The $V_{obs}$ and sample concentration are used to compute the moles of observed sample.

We now consider some cases where sample mass is and isn’t limiting to the analysis. The first example derives from product literature for a probe designed for trace analysis. In a recently received advertisement for the Nalorac SMIDG SUBMICRO™ probe, a proton spectrum is included which was acquired on a total sample of 172 µg of sucrose in 23 µL of D$_2$O (21.8 mM) in the 1.7 mm o.d. sample tube. The single-scan $S/N = 193$ for the anomeric proton on a 600 MHz spectrometer with an acquisition time of 4.1 sec. Since the total sample volume equals the observe volume in this example, the sensitivities (with appropriate units) are easily computed and appear in Table 1.

Suppose an analyst wants to know what the result would be for the same sample mass in a 5 mm probe. A good comparison is to acquire an identical spectrum on a sucrose concentration which
corresponds to the same mass of sucrose (172 µg) dissolved in the observe volume of the 5 mm probe. Based on a coil length of 16 mm and a tube i.d. of 4.2 mm, $V_{\text{obs}} = 222$ µL (2.26 mM sucrose). The anomic proton $S/N = 136$ for a single scan on our 600 MHz Varian INOVA™ spectrometer using the Varian 5 mm proton detection probe. We used the same data acquisition and processing parameters and have presumed that line width and shape are comparable; the resultant sensitivities appear in Table 1. Clearly, the mass sensitivity is better for the SMIDG probe, but the concentration sensitivity is better for the 5 mm Varian probe.

An additional figure of merit to consider especially when comparing NMR probes for use as detectors in separations like LC-NMR, CE-NMR, and CEC-NMR [6], is the limit of detection ($LOD$) defined in terms of the concentration or mass of sample which yields a $S/N = 3$. These values are affected by the experiment time as well, so that

$$LOD_c = \frac{3 \cdot C \cdot t^{1/2}}{S/N} \quad \text{and} \quad LOD_m = \frac{3 \cdot \text{mol} \cdot t^{1/2}}{S/N}$$

where the mole quantity again refers to that amount of sample in the observe volume. These values appear in Table 1 for the two previous probes. The $LODs$ are consistent with the earlier conclusions, but also allow the user to compute the approximate mass or concentration of sample needed to acquire a given $S/N$ in a particular probe.

Our research focuses on developing sensitive NMR detectors for mass-limited conditions using solenoidal microcoils fabricated directly on capillaries. For a microcoil wound on capillary with a 357 µm o.d. and $V_{\text{obs}} = 5$ nL [7], the $S/N = 32$ for the sucrose anomic proton. The data were acquired on a 300 MHz spectrometer using acquisition and analysis conditions different from the previous two examples. Though the total experiment time is 60 sec, a time-normalized comparison can still be made. The figures of merit for sucrose in the microcoil are included in Table 1. In comparison to the other two probes, these performance indicators show that the microcoil achieves the highest $S_m$ and requires the smallest sample size, but is limited in $S_c$. It should be noted that a significant improvement in $S_c$ and a proportionate decrease in $LOD_c$ for the microcoil can be attained by increasing $V_{\text{obs}}$ [8]. Users should bear in mind that the possibility of radiation damping becomes greater in a more mass-sensitive probe.

To conclude, performance comparisons for NMR probes employed under different analytical situations are easily rendered using the figures of merit described here. These performance criteria are readily obtained and quite useful in choosing a probe for a particular analysis. An additional consideration is the total sample amount available to the analyst and how it can be most effectively prepared to generate an acceptable result. For instance, in the cases of the 5 mm probe and the microcoil, only a fraction of the total sample (the observe factor) lies within $V_{\text{obs}}$. Consequently, this may require the use of a speciality tube, susceptibility matched plugs, or additional sample. A mass-limited condition probably calls for the greatest $S_m$, which is usually the probe with the smallest coil. A situation which is not mass-limited, or where the sample already exists in a relatively large volume and can't be concentrated, would benefit by using the probe with the largest $S_c$, which will usually have the biggest $V_{\text{obs}}$. Determination of the figures of merit described here help guide the user in choosing the most appropriate NMR probe for the job.
References


Table 1.

<table>
<thead>
<tr>
<th>Figure of Merit</th>
<th>Varian 5 mm</th>
<th>Nalorac SMIDG</th>
<th>Microcoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_e ) (S/N • mM(^{-1} ) • sec(^{-1/2} ))</td>
<td>30</td>
<td>4.4</td>
<td>0.0083</td>
</tr>
<tr>
<td>( S_m ) (S/N • µmol(^{-1} ) • sec(^{-1/2} ))</td>
<td>134</td>
<td>190</td>
<td>1660</td>
</tr>
<tr>
<td>LOD(_e) (mM • sec(^{1/2} ) • S/N(^{-1} ))</td>
<td>0.10</td>
<td>0.69</td>
<td>360</td>
</tr>
<tr>
<td>LOD(_m) (nmol • sec(^{1/2} ) • S/N(^{-1} ))</td>
<td>22</td>
<td>16</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Please credit this contribution to Dr. Vera Mainz, Director of the Varian-Oxford Instruments Center for Excellence in NMR (VOICE Lab) at the School of Chemical Sciences, University of Illinois.

Best regards,

Dean L. Olson          Paul F. Molitor          Michael E. Lacey          Jonathan V. Sweedler
June 10, 1998  
(received 6/16/98)

Dr. B. L. Shapiro  
The NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Dear Barry,

Recently, I decided to expand my horizons a little and do $^{39}$K NMR as well as $^{23}$Na relaxation experiments, in spite of the 200-fold loss in sensitivity. Potassium is an extremely important biomedical ion (as well as sodium) but researchers have reported a decrease in $^{39}$K NMR "visibility" with lowering B$_0$. With this in mind, I decided to set up $^{39}$K experiments. Because of the short T$_2$ of the satellite transition (spin I = 3/2), I decided to use the wideline probe on our Bruker MSL-200 with 4.7 T super-wide-bore (15 cm) vertical magnet. Later on, if our new Varian INOVA 300 MHz console ever achieves $^{39}$K functionality, I hope to check the B$_0$ dependence reported for biological tissue.

I had expected a weak signal, but the initial S/N was unexpectedly low. By tweaking the electronics, such as the duplexer, I achieved "reasonable" signal strength; but, the signal was just too noisy, with a noise level that changed hourly. Because the $^{39}$K signal is at 9.339 MHz, it was in the range of my portable short wave radio. With it, I found extremely intense noise around 9.3 MHz all over the lab, but especially strong at the magnet and even stronger at the console. I went next door to the new clinical Phillips MRI machine and found that one of the monitors emits very strong 9.3 MHz noise. I found the same noise at the two GE/Omega consoles in two other labs, at the monitor of my office PC (486, 66 MHz), and at the monitor of my home PC (Pentium II, 266 MHz). However, I did not find such noise (either at 9.3 MHz or at 14 MHz) at the SUN computers of the two Varian INOVA consoles or at the monitor of a Dell 90 MHz Pentium computer in the computer room. Because such r.f. noise is so prevalent and extremely strong, it is a real problem. I had similar problems twenty years ago with the TI Silent Writer terminal on the Nicolet computer used to control a home-made NMR spectrometer, but that noise was around 13.3 MHz.

Obviously, shielding/filtering is important for the probe, pre-amp, r.f. cables (RG-58 cables are leaky), power leads to the pre-amp, cables to the magnet shims, etc. I am making headway on the problem, but I would appreciate advice from others who may have had similar problems.

Sincerely,

Donald E. Woessner  
dwoess@mednet.swmed.edu
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- GE QE-300, including dual 1H/13C electronics, ¹H/¹³C switchable probe. $45,000.
- Varian VXR-300, including broadband electronics, ¹H/¹³C switchable probe. $58,000.

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June 1, 1998
(received 6/6/98)

Dr. B. L. Shapiro,
The NMR Newsletter,
966 Elsinore Court,
Palo Alto, CA 94303, USA.

title:  **NMR of fluoroboron cations including $^{11}$B,$^{19}$F HETCOR**

Dear Barry:

Our $^{19}$F and $^{11}$B nmr studies of the formation of fluoroboron cations ($D_2B$F$_2^+$ and $D_3B$F$_2^{2+}; D =$ various Lewis bases$^1$) have recently been given a major boost from the capabilities of McMaster University’s Bruker DRX-500 instrument. Its full $^{19}$F capability, which allows a wide range of X nucleus-fluorine 2D experiments, was installed to extend the work of Gary Schrobilgen’s research group at McMaster, which is a leader in inorganic fluorine chemistry and has many interesting multinuclear nmr studies to its credit. We do our routine work at Brock University on our “workhorse” 12-year-old Bruker AC-200 (for solution work) and our 2-year-old Bruker DPX-300 (for MAS), and have access to the McMaster DRX-500 when necessary. One very simple advantage of the DRX-500 is that we can obtain 1D $^{19}$F and $^{11}$B spectra in rapid succession: important because many of our systems are highly reactive and change with time.

We have been working on the synthesis of fluoroboron cations involving chelating donors, few of which are known. These are best made by ligand displacement from easier-to-prepare fluoroboron cations such as pyr$_2$BF$_2^+$ (readily isolable as its PF$_6$ salt$^1$) or ligand and Cl$^-$ displacement from adducts such as pyr.BF$_2$Cl. Two displacements by a single bidentate ligand give the desired chelated-donor difluoroboron cations. Similar approaches starting from pyr$_3$BF$_2^{2+}$, pyr$_2$BFCl$^+$, or pyr.BFCl$_2$ and involving three displacements should give fully chelated BF$_2^{2+}$ cations of tridentate ligands such as pentamethyldiethylenetriamine (I).

\[ \text{I} \quad \text{II} \quad \text{III} \]

The Figure shows a portion of the $^{11}$B,$^{19}$F HETCOR spectrum of the complex system resulting from reaction of I with the adduct system 4-methylpyridine.BF$_3$ + BCl$_3$, which was already complex and contained species such as 4-Mepyrr.BFCl$_2$ (formed by halogen
Redistribution) and 4-MepyrlBF$_2^+$ (formed by displacement of Cl$^-$ from 4-MepyrlBF$_2$Cl by further 4-Mepyrl. Adding I causes further displacements, and new species incorporating I appear. Of particular interest is the $^{11}$B signal at 3.5 ppm which correlates with two $^{19}$F signals at -152.2 and -154.1 ppm. This is consistent with the tridentate ligand coordinating to boron via its centre N and one of its terminal N’s to give II in which the centre N is chiral, making the BF$_2$ fluorines prochiral and magnetically nonequivalent. This is confirmed by the F,F COSY spectrum: of all of the many $^{19}$F signals, arising from many different species, only these give cross peaks, confirming that the two fluorines are present in the same molecule. The one-bond $^{11}$B-$^{19}$F coupling constants of the magnetically nonequivalent fluorines are appreciably different (32.9 and 37.6 Hz). The two-bond $^{19}$F-$^{19}$F coupling constant of 61.2 Hz is consistent with the relatively few reported examples of two-bond FBF coupling (e.g. B$_2$F$_7^-$, 95 ± 10 Hz$^{2a}$; (PhCH$_2$NMeEt)$_2$BF$_2^+$, 72 Hz$^{2b}$, D$^*$BF$_2$X (X = Br, I), 33-49 Hz$^{2b}$). The Figure also shows the emergence of what we believe to be the first fully-chelated tridentate-ligand fluoroboron species, III.
We thank Dr. Don Hughes and Mr. Brian Sayer for assistance and the Department of Chemistry, McMaster University, for instrument time. We also thank Prof. Alex Janzen, University of Manitoba, for discussions leading to our work on these systems.

Yours sincerely,

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graduate student
js94cx@badger.ac.brocku.ca

References


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Dear Barry,

The structures of organometallic reagents important in synthetic procedures are continually studied under the assumption that a better knowledge of the ground state structures of the reagents will lead to improved control in the reactivity (e.g. selectivity) of their reactions. We have studied by NMR spectroscopy $^{13}$C- and $^6$Li-labeled methyl cuprates to address further the much debated topic of "higher order" organocuprates vs. "lower order" organocuprates. 1 An identical coupling pattern is observed in the $^1$H and $^1$H-coupled $^{13}$C spectra for all three of the $^{13}$C labeled organocuprates $\text{Me}_1^1\text{CuLi}$ (1), $\text{Me}_3\text{CuLi}_2$ (2), and $\text{Me}_2\text{Cu(CN)}\text{Li}_2$ (3) with the following coupling constants: $^1\text{JCH} = 109.5$ Hz, $^2\text{JCC} = 21$ Hz, $^3\text{JCH} = -0.8$ Hz, and $^4\text{JHH} = 0$ Hz (see Figure 1a). We have recently published results2 indicating that the predominant solution structures of organocuprates 2 and 3 are lower-order in nature, and the dimethyl-cuprate core resembles that found for 1.

Our attention has now turned to the homologous zinc reagents. 3 The neutral $\text{Me}_2\text{Zn}$ (4) reagent shows a similar coupling pattern ($^1\text{JCH} = 116.1$ Hz, $^2\text{JCC} = 15.3$ Hz, $^3\text{JCH} = -0.1$ Hz, and $^4\text{JHH} = 0$ Hz) to isoelectronic 1 (see Figure 1b). However, unlike the copper system, treatment of $\text{Me}_2\text{Zn}$ with another equivalent of $\text{MeLi}$ results in formation of a higher-order zincate $\text{Me}_3\text{ZnLi}$ (5) as evidenced by the change in the proton coupled $^{13}$C NMR spectrum (Figure 2a). This coupling pattern was simulated (Figure 2b) using the WINDAISY simulation program and refined on the experimental spectrum to give the following coupling constants: $^1\text{JCH} = 110.9$ Hz, $^2\text{JCC} = 14.0$ Hz, $^3\text{JCH} = 0.6$ Hz, and $^4\text{JHH} = 0.4$ Hz. We are currently further investigating this zinc system.

Sincerely yours

T. A. Mobley

Prof. Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CAL. 94303
USA

Leipzig, 17.06.98
(received 6/24/98)


Figure 1. $^1$H-coupled $^{13}$C NMR of fully $^{13}$C-labeled (a) Me$_2$CuLi (1) and (b) Me$_2$Zn (4)

Figure 2. $^1$H-coupled $^{13}$C NMR of fully $^{13}$C-labeled Me$_3$ZnLi (5) (a) experimental and (b) calculated.

Continued from p. 40

Top trace: $^2$H NMR spectrum of Benzene in the natural abundance oriented in phase ZLI-1114

Bottom trace: $^1$H NMR spectrum of Benzene oriented in phase ZLI-1114 under identical condition
Dear Barry,

In the last decade, the field of NMR of oriented molecules appeared to have reached a saturation point as far as the structural studies are concerned with only a few significant applications. This is essentially due to spectral complexity with increase in the number of interacting nuclei. Now it has once again become an active field due to several recent developments such as the discovery of thermotropic liquid crystals of low order parameter (1), the use of lyotropic liquid crystals as solvents for large biomolecules (2) and the use of high magnetic fields for aligning molecules (3). Another development in this direction is the possibility of recording natural abundance $^2$H NMR spectra of pure liquid crystals (4). We have recently extended this method to record the natural abundance deuterium NMR spectra of dissolved molecules (5). These latter developments may be expected to aid the analyses of complex proton spectra.

The top trace of Fig. 1 shows the $^2$H NMR spectrum of benzene in the natural abundance oriented in MERCK phase ZLI-1114. The spectrum was obtained on a Bruker AMX-400 NMR spectrometer using a 10 mm diameter sample tube in about 18 hours. A quadrupole split doublet with a separation of 31.952 KHz is observed. This corresponds to an order parameter in the plane of the benzene ring equal to 0.1084 (obtained using a value of 196.5 KHz for the $^2$H-quadrupole coupling constant). From this information, the dipolar coupling between the ortho protons of benzene was derived as $-852.1$ Hz.

The proton spectrum of the same sample under identical conditions is shown in *Fig. 1 (bottom trace). The analysis of the spectrum using the standard techniques also gives a value of $-852.1$ Hz for the ortho H-H dipolar coupling in benzene.

The results demonstrate that the natural abundance deuterium NMR spectra of molecules dissolved in liquid crystals can be obtained within reasonable time on the present day spectrometers. Such studies can be used to derive information which can enhance the utility of the NMR spectroscopy of oriented molecules particularly when applied to complicated systems.

References:

* The figure is on p. 39.
"NMR Spectroscopy: Processing Strategies"
(an interactive course)

by

Peter Bigler

VCH Verlagsgesellschaft, Weinheim, Germany, 1997; 249 pages, ISBN 3-527-28812-0
$99.00 (hardcover); A CD-ROM for working with sample spectra is provided.

Distributed processing of NMR data is widespread, which means that the chemist obtains or collects FIDs, and has her/his own software to process these files. Some manufacturers have integrated spectral processing, analysis and interpretation tools. It means different programmers, different philosophies, different layouts, etc. This programmed learning book by Peter Bigler is clearly written for the novice, the non-specialist, although experts may also find useful hints on matters hidden by the usual users manual. The book fulfills a real need for an up-to-date introduction to NMR data processing, and provides an in-depth understanding of the advanced processing strategies necessary for a fruitful application of modern multidimensional NMR. Clearly the book can be welcomed by Bruker instrument users. It is written for explaining the sometimes bewildering and diverse software tools which lack an easy-to-learn, but still sufficiently detailed, users' manual. The practitioners who read this book and proceed with the worked examples "Check It's" as they occur in the text, will be rewarded with a proper functional understanding of NMR data processing/analysis at a level that will allow them to derive full benefit of this spectroscopic method.

Software facilities are, of course, always being upgraded, and for this reason any text can be easily outdated. Anticipation of forthcoming books in this series (e.g. Modern Spectral Analysis, Data Acquisition and Intelligent Data Management, in part written by Bruker people) makes this piece of work valuable for those who wish to learn the whole game from zero knowledge to full structure elucidation.

The practical summaries of basic 1D and 2D experiments typical for applications by organic chemists are very useful. Since this is a programmed introduction, first you have to install the software, then proceed with tasks of increasing complexity. This explains for example the reverse order of processing and display/plot chapters. The book can be used also for educational purposes, most efficiently in combination with the Bruker's manual. However, to a certain extent, the half-German/half-English abbreviated commands, e.g., StrukEd. are annoying. The same is true for mixed language snapshots of the Windows screens.

Continued
The book consists of six Chapters, as follows:

1. Introduction: Outlines the specific aims of the book, providing the readers with basic theoretical and practical knowledge, as well as expert guidance on processing strategies in NMR spectroscopy.

2. Your Personal "PC NMR Processing Station": Includes hints for installation of 1D/2D WIN-NMR and the GETFILE file transfer protocol. However, it seems that network problems, if such arise, should be deferred to the expert.

3. Modern Homo- and Heteronuclear 1D and 2D NMR Experiments: A short overview: Simplified theoretical descriptions, pulse sequence figures (as plotted by the NMRSIM module), application field, examples of spectra, and a useful collection of recommended readings are provided.

4. How to Display and Plot 1D and 2D Spectra: Assuming that processed spectra are available, a step-by-step description is given, based on pull-down menus and commands.

5. How to Process 1D and 2D NMR Data: Provides the fundamental concepts of NMR data processing. Many examples of 1D and 2D applications are presented at both basic and advanced levels to help the readers assess an overall mastery of the processing strategies.

6. NMR Data of an Unknown Oligosaccharide: For a self-test, a real situation of structure elucidation is provided. At this final stage, the reader can check her/his skill with the different processing tools in applying them to the structure determination of an unknown oligosaccharide.

Following Chapter 6 are a glossary and a subject index.

A few items of practical importance deserve be mentioned, such as explanation of linear prediction, multiplet analysis (which can be useful for teaching first order analysis), diagonal removal from 2D spectra, and efficient 1D WIN-NMR serial processing. Some things seem to be missing, however, such as preferred settings for ftp in Getfile, or are not explained clearly enough. In the Open menu, for example, how the Hosts should be defined: is it the NFS the remotely defined Host? Also, in T1 analysis, if you are not aware that the variable delay list format is different in UXNMR and WIN-NMR, you are lost.

In summary, we believe that the book provides a very useful and practical treatise of data processing strategies employed in modern NMR spectroscopy, and is a very welcome addition to existing software manuals. Practical NMR courses organized at universities, technical schools, etc., can derive full benefit of the material presented in the book.

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Forthcoming NMR Meetings, continued from page 1:

Spin Choreography - a symposium in appreciation of Ray Freeman, Cambridge, England, April 8-11, 1999; web site: http://mchsg4.ch.man.ac.uk/mcmr/RF.html; fax: c/o M.H.Levitt +46-8-15 2187; email: mhl@physc.su.se.

41st ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, CA, April 9-14, 2000; Contact: ENC, 1201 Don Diego Avenue, Santa Fe, NM 87505; (505) 989-4573; Fax: (505) 989-1073; Email: enc@enc-conference.org.

Additional listings of meetings, etc., are invited.
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