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C-F Coupling in 2-Fluoro-Naphthalenes

Rate Processes in an Alkoxycarbonyl Complex

Magnetic and Non-Magnetic Relaxation: A Comparison

Comments on J. Shoolery's Letter in TAMU #211.

Homoallylic Coupling Constants and Dihydroaromatics—Carbon-Proton Coupling Constants

Comparison of Long Range 13C-13C Coupling Constants in Homoadamantane Derivatives

Slightly Off-Course from the 'Topic of Cancer'

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Magic-Angle C-13 NMR Analysis of Coal

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1H and 13C NMR Spectra of Nitrobenzene-15N

Select - A - Spin

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## CHART PAPER

First grade NMR Chart Paper made to be used in every model spectrometer. All charts have been updated to coincide with the newest instrument techniques... Fourier Transformation, Hetero-Decoupling, and Time-Averaging.

**NOTE:** All charts packaged 1000 sheets to a box except roll charts or as otherwise noted.

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| WCN-60/1000 | A-60, HA-100, A-56/60 | Cal. | $35.00 |
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DEADLINE DATES: No. 215: 2 August 1976
No. 216: 6 September 1976

All Newsletter Correspondence, Etc. Should Be Addressed To:
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843 U.S.A.

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- 10 sec
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- 2 sec
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T2 mode

Single mode

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201-272-8820
June 8, 1976

Professor B. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Professor Shapiro:

Fourier Transform Double-Quantum NMR

We have shown recently\(^1\) that our new technique Fourier Transform Double-Quantum (FTDQ) NMR can be used to eliminate the broadening from electric quadrupole couplings (\(\sim 100 \text{ KHz}\)) in ordered deuterium systems so that small effects, i.e., chemical shieldings (\(\sim 100 \text{ Hz}\)), can be observed. As an example of this technique we determined the carboxyl deuteron shielding anisotropy in a single crystal of partially deuterium labeled oxalic acid dihydrate.

The extension of high resolution FTDQ spectroscopy to powders would allow direct determination of shielding anisotropies for deuterium. The experiments are complicated by the fact that the intensity of double-quantum coherence observed is dependent upon the quadrupole splitting for a particular nucleus or orientation. However, application of an appropriate sequence of pulses\(^2\) allows one to map out the double-quantum coherence for all orientations simultaneously. After Fourier Transformation this gives a powder pattern with a predictable lineshape. In such a spectrum all quadrupole splitting has been completely removed. As an example of this we measured the shielding anisotropy of deuterons for 10% benzene d-1 doped into normal protonated benzene. From the powder pattern we derived an anisotropy of \(\Delta \sigma \approx -6.5 \text{ ppm}\). This measurement was performed on our home-built spectrometer operating at 28 MHz for deuterium, with high power proton decoupling. A complete description of this and other FTDQ work will be coming out soon.

Sincerely,

David Wennmer
Shimon Vega

Please credit to the account of Professor Alex Pines

2. S. Vega, D. Wennmer and A. Pines, to be published.
Dear Barry:

SUBJECT: C-F Coupling in 2-Fluoro-Naphthalenes

Some time ago I had the opportunity to measure the $^{13}$C nmr spectra of the three 2-fluoro-naphthalenes in the Table attached. From the results obtained on II and III, I felt the necessity of remeasuring I. The spectrum obtained supported the assignments of II and III, but disagreed with the literature$^{1,2}$ available at that time. A 1974 paper$^{3}$ agreed with the others$^{1,2}$ but not my results. My results do, however, agree with those of Ernst$^{4,5}$ and I believe that considerable revision of the assignments of 2-fluoro-naphthalene derivatives$^{6}$ and their analogs are necessary. Characteristic coupling patterns in fully coupled spectra provide a useful method for assigning peaks in the naphthalene series$^{6}$ and selective $^{13}$C-{H} double resonance should be used to remove any remaining ambiguities.

Sincerely,

Michael L. Maddox, Ph.D.

June 1, 1976
AR/1187
TABLE Ia

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<tr>
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<th>δc</th>
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<td>1.2</td>
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</table>

a) Spectra measured on Bruker WH-90 in CCl₃ using 6 KHz or 2 KHz sweep width and 16 K data tables. δc reported in ppm to high frequency from internal TMS coupling constants in Hz ± 0.2 Hz.

4L. Ernst, Z. Naturforsch, 30b, 800 (1975)
5L. Ernst, J. Magn. Resonance, 20, 544 (1975)
Title: Rate Processes in an Alkoxyboran Complex

Dear Professor Shapiro,

We have studied the dynamic behaviour of the alkoxyboran complex 1 with the aid of variable temperature NMR. The following processes A, B, and C have been observed simultaneously.

A: \[ \text{proton exchange} \]

B: \[ \text{nitrogen inversion} \]

C: \[ \text{ligand exchange} \]

The OH-signal in the \(^1\text{H}-\text{NMR}\) spectra is strongly shifted upfield on raising the temperature and is coalescing due to process A with the almost non-shifted NH-signal at 4.9 ppm (see figure).

Starting from low temperatures the very complex spectrum of the methylene protons first coalesces to a broadened 4 line spectrum...
(disappearance of the gem. methylene proton nonequivalence by nitrogen inversion B) and finally at high temperature only two triplets for the O-methylene and N-methylene protons are observed (fast ligand exchange C). The processes B and C can also be followed in the $^{13}$C-NMR spectrum. B leads to coalescence of the two non-equivalent sets of aromatic carbon signals$^{1}$). The coalescence phenomena of the signals between 50 and 63 ppm are caused by ligand exchange C.

The data are listed in the table and rough estimation of the free enthalpy of activation is added.

1) The broadening of the $^{13}$C-signals at higher temperatures is due to the quadrupol relaxation and coupling of the boron nuclei.

Table: Kinetic Data for the Rate Processes of $^{1}$ in CD$_2$Cl$_2$

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<th>Process</th>
<th>Nucleus</th>
<th>exchanging groups</th>
<th>$T_c$ [K]$^a$</th>
<th>$\Delta v_c$ [Hz]</th>
<th>$\Delta G^+_c$ [kcal/mol]$^a$</th>
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<tr>
<td>A</td>
<td>$^1$H</td>
<td>OH, NH</td>
<td>290 ± 10</td>
<td>94</td>
<td>13.9 ± 0.5</td>
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<td>B</td>
<td>$^{13}$C</td>
<td>C-2, C-2', C-3, C-3'</td>
<td>260 ± 5</td>
<td>56.6</td>
<td>12.6 ± 0.3</td>
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<tr>
<td></td>
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<td>H-8, H-8', H-9, H-9'</td>
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<td>16</td>
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<td>$^1$H</td>
<td>H-7, H-7'</td>
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<td>260 ± 5</td>
<td>38</td>
<td>12.8 ± 0.3</td>
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<tr>
<td>C</td>
<td>$^{13}$C</td>
<td>C-8, C-9</td>
<td>308 ± 5$^b$</td>
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<td>14.8 ± 0.3</td>
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<td>C-7, C-10</td>
<td>313 ± 5$^b$</td>
<td>122</td>
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<td>$^1$H</td>
<td>H-8, H-9</td>
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<td>H-7, H-10</td>
<td>297 ± 5</td>
<td>43</td>
<td>14.7 ± 0.3</td>
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a) rough estimated values
b) observed in C$_2$D$_2$Cl$_4$

Sincerely yours,

(Prof. Kessler) (G. Zimmermann)
Magnetic and Non-Magnetic Relaxation: A Comparison

Dear Barry,

As you know, I have been collaborating with Prof. M. B. Comisarow here at the University of B.C., in the development of Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy. Part of that development has been inspired (and occasionally nurtured) by analogies to prior FT-NMR theory, which is in turn based on long-known linear response theory. Similarly, there have recently appeared a number of line-narrowing experiments in optical spectroscopy which bear strong analogy to pulsed NMR "echo" techniques.

In trying to gain further physical insight into any phenomenon, one can often progress more easily by analogy than by deduction. We have therefore been led to examine a number of correspondences between relaxation in NMR and ICR in work which will shortly be published, some of which are listed on the next page. While the various processes listed in the NMR (or ICR) column are certainly known to those in NMR (or ICR), the close parallels between NMR and ICR shown in the table should facilitate future cross-fertilization between theory and experiment in the two types of spectroscopy.

Sincerely,

Alan G. Marshall
Associate Professor


<table>
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<tr>
<th>Process</th>
<th>Manifestation in NMR</th>
<th>Manifestation in ICR</th>
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<tr>
<td>Circular motion due to magnetic field:</td>
<td>precession of nuclear magnetic moment</td>
<td>orbiting of electrically charged ion</td>
</tr>
<tr>
<td>Source of coherent radiation excitation:</td>
<td>linear or circularly polarized r.f. magnetic field (from r.f. current in one or more coils)</td>
<td>linear or circularly polarized r.f. electric field (from r.f. voltage to one or more plates)</td>
</tr>
<tr>
<td>Coupling between resonances detected by &quot;double&quot; irradiation:</td>
<td>Scalar or chemical coupling between two or more nuclei</td>
<td>kinetic (chemical reaction) coupling between 2 or more ions</td>
</tr>
<tr>
<td>Exchange between 2 different resonant frequencies:</td>
<td>Chemical exchange</td>
<td>Charge exchange (ion-molecule reaction; charge-transfer)</td>
</tr>
<tr>
<td>Signal amplitude proportional to:</td>
<td>Difference in population between two nuclear spin states</td>
<td>Number of ions of a given charge-to-mass ratio</td>
</tr>
<tr>
<td>Signal saturation due to:</td>
<td>depletion of spin state population difference due to stimulated (by applied r.f.) transitions</td>
<td>depletion of number of excited ions of a given (q/m)-ratio, due to ion removal on reaching the charged plates of the sample container</td>
</tr>
<tr>
<td>Inhomogeneous line-broadening:</td>
<td>Spatial inhomogeneity in $H_0$ or $H_1$</td>
<td>Spatial inhomogeneity in $H_0$ or $E_1$</td>
</tr>
<tr>
<td>Homogeneous line-broadening</td>
<td>$T_2$ phenomena: spin state transitions between states differing in energy by approximately the Larmor frequency, due to temporal magnetic field fluctuations near Larmor freq.</td>
<td>Ion-molecule reactions: loss of ICR signal due to loss of ion identity</td>
</tr>
<tr>
<td>Secular relaxation:</td>
<td>$T_1$ phenomena: transitions at frequencies of about zero or about the Larmor frequency, due to field fluctuations at those frequencies</td>
<td>Non-reactive or reactive ion-molecule collisions: loss of ICR signal due either to loss of coherence in orbital ion motion or to loss of ion identity</td>
</tr>
<tr>
<td>Homogeneous line-broadening</td>
<td>$T_1 = T_2$: Time-dependent perturbations fluctuate rapidly compared to the Larmor frequency--NMR line width determined wholly by $T_1$ (&quot;lifetime&quot;) broadening</td>
<td>All ion-molecule collisions are reactive--ICR line width determined wholly by reactive collision rate</td>
</tr>
<tr>
<td>Non-secular relaxation:</td>
<td>Sample is spun externally</td>
<td>Sample &quot;spins itself&quot; by inherent cyclotron orbital motion</td>
</tr>
</tbody>
</table>
Professor Shapiro,

I was interested in Jim Shoolery's letter entitled "Carbon-13 NMR for the Micro-Chemist". He remarks about the slow appreciation and utilization of carbon-13 NMR, as it is currently practised, by many chemists. However, I should like to comment that the blame for this situation does not entirely lay with the chemist. One of the main reasons for this can be seen on the back page advertisement of the TAMU newsletter containing Jim Shoolery's letter. Many chemists still associate carbon-13 NMR with an entire room full of very expensive electronics which only a relatively few institutions or companies can afford. The point that ought to be now made is that it does not require a room full of electronics to produce high quality carbon-13 NMR spectra. It does not require a 15T (or 18T) magnet to produce a highly uniform magnetic field of 2.3T over the kind of sample volume used to obtain the spectra shown by Jim Shoolery. In fact the magnet need only be a fraction of the size (and cost) of the XL100 magnet. The developments that have taken place in RF pulse amplifiers and in low noise RF signal amplifiers over the last two decades or so now make the manufacture of these units not a particularly difficult or expensive business. True one is left with the mini-computer (soon micro-computer) to control and order the various instrument and data collecting functions, but anyone who has looked behind the front panel of a typical modern mini-computer will know how much can be packed into such a small space and at such modest cost. Thus the point I should like to make is that the stage is now set for the production of literally a 'table top' carbon-13 NMR spectrometer with a very high performance. Such an instrument would be greatly welcomed by the majority of organic chemists and could augment the existing range of simple 60 MHz cw instruments now in such wide use. As pioneer in so many new NMR ventures perhaps Varian could lead the way in such an exciting development.

Yours sincerely,

S.A. Knight

S. Knight
June 29, 1976

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Title: We Aim to Please

Dear Barry:

Thank you for sharing the comments by Dr. Knight regarding the possibility of using a smaller (and presumably less expensive) spectrometer system than the XL-100 to obtain $^{13}$C spectra from small samples similar to those in my letter "Carbon-13 NMR for the Micro-Chemist" (TAMU 211). Anticipating this point, we had gone ahead with the development of 1.7 mm $^1$H and $^{13}$C microprobes for the CFT-20 with very gratifying results. Many of your readers may have seen some of these spectra at the last ENC meeting, but for those who did not I offer Figures 1 and 2 which are the $^1$H spectrum of 1.0 µg of Cortisone Acetate and the $^{13}$C spectrum of 500 µg of Ethyl Vanillin respectively, both obtained with an overnight run. The prophecy is thus fulfilled, at least in some degree, although I must admit that a very strong table is needed to support a CFT-20. (Available as an optional accessory.)

Sincerely,

James N. Shooley
Applications Chemist
NMR Applications Laboratory
Instrument Division

JNS:¢
Figure 1

Figure 2
Dear Barry:

For lecithin lamellar liquid crystalline phases the shape of the proton resonance signal is determined by static dipolar couplings, and is very broad with little structure. On sonicating lecithin-water systems vesicles 25 - 30 nm in diameter are formed, which give proton spectra with typical high resolution features. The way in which the sonication leads to this narrowing has been argued in the literature for some time. The mechanisms proposed are (i) rotational Brownian motion of the vesicles, (ii) rapid lateral diffusion and (iii) more structural disorder in the fluid state of the lipids in vesicle bilayers than in lamellar systems. Recently we have analyzed theoretically the PMR bandshape of vesicles using a detailed density matrix description of the transverse relaxation process. The analysis is based on the following:

1) The vesicle rotation is fast enough to give an effective zero average value for the dipolar couplings, and these couplings give only relaxation effects.
2) The molecular motion can be divided into two independent parts, a fast local motion within the bilayer that is assumed to be the same in sonicated and unsonicated systems and a slow motion due to vesicle rotation and/or lateral diffusion in the bilayer.

The total bandspe is then a superposition of Lorentzians with different widths. Figure (a) shows an experimental spectrum and (b) the corresponding simulated spectrum. The fit between the two spectra is very good even far out in the wings of the spectrum. This shows that is is not possible to assign a single $T_2$ to any one of the peaks. It also follows that the width at half height $\Delta\nu_{1/2}$ is not at all sufficient to characterize a signal and should be used with care when analyzing spectral changes.

Sincerely yours,

Sture Forsén
Jan Ulmius
Håkan Wennerström
Fig a: A 100 MHz $^1$H NMR spectrum of dimyristoyl lecithin vesicles with a diameter of approximately 27 nm recorded at 30°C.

Fig b: A simulated spectrum. The small peaks at $\delta = 2.33$ and 3.64 ppm in the experimental spectrum have not been included in the simulation.
From: Dr. R.K. Harris and Mr. R.H. Newman

School of Chemical Sciences
The University of East Anglia
Norwich NR4 7TJ, ENGLAND.
Telephone Norwich (0603) 56161
Telegraphic Address UEA NOR NORTHC

10th June 1976

SILICON-29 N.M.R. OF TRIMETHYLSILYLATED MINERALS

Dear Barry,

When silicate anions are leached from acid-soluble minerals, the silicic acids rearrange too rapidly for isolation and identification. Lentz overcame this problem by trimethylsilylating the silicic acids during leaching. The trimethylsilyl derivatives are stable, and the major product retains the structure of the original silicate in the mineral. Trimethylsilylation is a valuable technique for analysis of poorly-crystallised specimens that cannot be satisfactorily analysed by X-ray diffraction; e.g. it has been possible to follow polymerisation of silicates during curing of cement pastes. The volatile trimethylsilyl derivatives are identified by g.l.c., the residue being classified as "unidentified polysilicates".

We have been investigating the possibility of using $^{29}$Si to identify the trimethylsilyl derivatives. Silicon-29 chemical shifts for the trimethylsilyl groups are not sufficiently dispersed to be useful, but chemical shifts for the silicate $^{29}$Si's are spread over about 5 p.p.m. We have run $^{29}$Si spectra of four of the smaller structures. The solvent was benzene, and chemical shifts (for the silicate $^{29}$Si only) are given below in p.p.m. from TMS (positive shifts are to high frequency):

\[
\begin{align*}
&\text{(Me}_3\text{Si)\text{SiO}_4} \quad \text{monomer} \quad -104.1 \\
&\text{(Me}_3\text{Si)\text{Si}_2\text{O}_7} \quad \text{dimer} \quad -106.5 \\
&\text{(Me}_3\text{Si)\text{Si}_3\text{O}_{10}} \quad \text{linear trimer} \quad -109.2 \quad \text{(central)} \\
&\text{[Me}_3\text{Si)\text{SiO}_3]}_4 \quad \text{cyclic tetramer} \quad -107.8
\end{align*}
\]

The monomer and dimer were obtained from I.C.I. Ltd. (Organics Division) and the Paint Research Association, and we are grateful for the help of these organisations. The linear trimer and cyclic tetramer were prepared by trimethylsilylation of the appropriate minerals (natrolite and laumontite, respectively).

The trends of the $^{29}$Si shifts are qualitatively similar to trends observed for silicate anions in aqueous solutions: e.g. increasing condensation results in low frequency shifts by steps of about 2.6 p.p.m. (monomer + end units + chain units) compared with steps of about 7 p.p.m. for aqueous silicates. Cyclisation results in a high frequency shift.
of 1.4 p.p.m. (linear chain + cyclic tetramer) compared with a shift of about 2 p.p.m. for aqueous silicates.

We are now working on the possibility of identifying structural units in the benzene-soluble non-volatile polymers.

We hope this letter keeps us on the TAMU N.M.R. mailing list.

With best wishes,

Yours sincerely,

Robin

R.K. Harris
R.H. Newman

Professor B.L. Shapiro,
Department of Chemistry,
Texas A&M University,
College of Science,
College Station,
Texas 77843,
U.S.A.

RKH/RHN/DB

References

Before you order a Fourier transform accessory for your nmr spectrometer you should consult Transform Technology Inc. The name is new but the personnel have many years experience in the spectroscopy field. Write or call collect to discuss your requirements.

We ran this ad in mid-1972 when six of us formed Transform Technology Incorporated with the help of Nicolet Instrument Corporation. Now, less than four years later we have over three dozen employees and are now a Nicolet operating division, known as Nicolet Technology Corporation.

What has happened since our first ad? Well, we don’t mind tooting our horn by pointing out that NTC has become established as a leader in the development of FT NMR equipment. We have developed, produced and installed scores of FT accessories for use on instruments such as the XL-100, HR-220, T-60, R-12 and R-32. In fact, for over a year we have been the leader in U.S. sales of FT data systems. Now we’re working on becoming the leader in overseas sales as well.

Why the success story? We feel it’s because we’re responsive to customers’ needs. Being a relatively small group of dedicated souls we can move quickly in the development of equipment which utilizes the latest techniques.

Consider some of our “firsts” in commercial equipment:

FIRST to employ a single sideband crystal filter for improved signal-to-noise ratio,
FIRST to provide phase shifted rf pulses for high resolution $T_1$ studies,
FIRST to use Quadrature Phase Detection,
FIRST to provide plots of relaxation recovery curves with data points, and
FIRST to develop a complete software package which includes provision for five methods of measuring $T_1$ values and three methods for $T_2$ values.

You can be sure that we are actively working on new “firsts.” For example, we’ll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another “first.”
Gadolinium Salts for Reduction of Long $^{15}$N Relaxation Times in Polar Solvents

Dear Barry,

We have been taking natural-abundance $^{15}$N spectra of several nucleosides, using dimethyl sulfoxide (DMSO) as solvent. A major problem in this study has been the very long time (up to nine hours) required to obtain spectra of even 0.7 - 1.0 M solutions. For this reason, we have tried several different metals and metal complexes in the hope of reducing the observed $T_1$'s of these and other, similar compounds. Because we wished a reagent soluble in both DMSO and water, the classical relaxation reagents such as Cr(AcAc)$_2$ were not suitable. The best results were obtained with the rather implausible combination of Gd(NO$_3$)$_3$ with an equal molar amount of inositol. The inositol was essential because of the prohibitive line broadening which resulted with Gd(NO$_3$)$_3$ alone. As an example of the use of this relaxation reagent, we ran 0.7 M solutions of adenosine in DMSO—with and without the relaxing reagent. Without the relaxation reagent, the S/N was 2.2, using a 90° pulse, 10-second delay, and proton decoupling during acquisition only. * The sample with the reagent (4 x 10$^{-5}$ M, or 6 x 10$^{-4}$ mole ratio of Gd(NO$_3$)$_3$ to adenosine) gave a S/N of 5.4 with the same instrumental parameters. The improvement in S/N corresponded to a six-fold saving in time. The spectra obtained with and without the relaxing reagent had the same line shapes and chemical shifts. Similar results have been obtained with formamide in both DMSO and in water as solvents.

Other ligands besides inositol may give still better results; but, at least, the Gd(NO$_3$)$_3$-inositol combination is very useful for DMSO and water.

With all good wishes,

Very truly yours,

William H. Bearden
Glenn R. Sullivan

*Gated decoupling was used, because the small negative NOE produced by full decoupling resulted in a reduction in the signal intensity.
Dr. Barry Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas  77843

Dear Dr. Shapiro,

I would like to pass along some information which might be useful to those of your readers using capillary inserts with their NMR spectrometers. In my particular case, the one millimeter insert used with the Varian XL-100, the normal commercially available capillary tubes which are supplied are coagulation capillary tubes sealed at one end which are 75 mm long and vary from 0.5-0.9 mm I.D. These tubes are not of precision quality to begin with, and their length has proved to be a severe drawback. The 75 mm length is just long enough that the tube may be sealed by melting the end shut rather than by the more desirable "pull-seal" method, and we have had occasional problems with imperfect seals resulting in ultimate evaporation of the sample from the capillary tube. I have located a commercial source which will produce precision open-ended capillary tubes of 1.0 mm O.D. and 0.8 mm I.D. at a length of 100 mm. The tubes are made of SF glass and are custom order items available at a cost of about $3 per hundred from Drummond Scientific Company, 500 Parkway, Broomall, Pa. 19008; phone (215) 353-0200.

These tubes may be "pull-sealed" at both ends to produce excellent seals relative to the end melting technique. Perhaps the most useful application I have found for these tubes is in preparing samples of microgram quantities of materials in hygroscopic solvents such as DMSO, where the introduction of what would normally be considered negligible amounts of water can cause problems. The sample is made by preparing five microliters of solution under dry nitrogen in a glove bag, transferring the solution into a one millimeter tube by capillary action, plugging the ends of the tube with corks, and removing the sample from the glove bag and "pull-sealing" both ends. This procedure prevents introduction of water into the sample from either the atmosphere or the sealing flame, and we have achieved good results in minimizing the water content of our samples. I hope this information will be of use and would be happy to discuss the details further if anyone wants to.

Very truly yours,

David G. Westmoreland

DGW:pt
It works, it must be a Fluke

Dear Barry:

We have recently begun a series of heteronuclear decoupling experiments on our new XL-100 using an unusual configuration. We use a Fluke 6160 synthesizer for our decoupling frequency and an ENI 320L linear amplifier to provide the power for broad band decoupling. We have used standard matching networks on the V-4415 probe. Proton noise decoupled 13C spectra are as good as expected. The modulation is provided by NTG's adaptation of one of their decoupler networks.

We have been so anxious to observe 1H decoupled from 31P that we performed the following experiment: The Fluke synthesizer output was amplified by the ENI to about 5 W and applied to the decoupling coils by the standard match-box. The frequency of the synthesizer was set to the 31P frequency (ca. 40.45 MHz), and the whole thing worked. In addition we found no birdies or other problems in the 1H spectrum. The total time to set up the experiment was about ten minutes.

We are now building match-boxes for other frequencies to see if the spectral purity of the Fluke synthesizer will permit other easy decouplings. Details on request.

With best regards.

Sincerely yours,

M. R. Willcott
Professor of Chemistry

MRW: dar
June 11, 1976

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

Titration Behavior of Individual Tyrosine Residues of Myoglobin from Sperm Whale, Horse and Red Kangaroo.

My co-worker Dr. David J. Wilbur has studied the titration behavior of individual tyrosine residues of myoglobins by observing the pH dependence of the chemical shifts of $^{13}$C and C$^\gamma$ of these residues in natural abundance $^{13}$C Fourier transform NMR spectra (at 15.18 MHz, in 20-mm sample tubes, at 37°C) of cyanoferrimyoglobin from sperm whale, horse, and red kangaroo (Figure 1). These three species were chosen, because the myoglobin from sperm whale contains three tyrosine residues (at positions 103, 146, and 151), the protein from horse has tyrosines only at positions 103 and 146, and the kangaroo myoglobin has a single tyrosine at position 146 in the sequence.

A comparison of the pH dependence of the spectra of the three proteins (Figures 2-4) yielded specific assignments for the resonances of Tyr-151 (sperm whale) and Tyr-103 (sperm whale and horse). Selective proton-decoupling yielded specific assignments for $^{13}$C of Tyr-146 of the cyanoferrimyoglobin from horse and kangaroo, but not the corresponding assignment for sperm whale. The pH dependence of the chemical shifts indicated that only Tyr-151 and Tyr-103 are titratable tyrosine residues. The titration behavior of $^{13}$C and C$^\gamma$ of Tyr-151 of sperm whale cyanoferrimyoglobin yielded a single pK value of 10.6. The pH dependence of the chemical shift of each of the resonances of Tyr-103 of the cyanoferrimyoglobin from horse and sperm whale could not be fitted with the use of a single pK value, but was consistent with two pK values (about 9.8 and 11.6). Furthermore, the resonances of $^{13}$C and C$^\gamma$ of Tyr-103 broadened at high pH.

The titration behavior of the tyrosines of sperm whale carbon monoxide myoglobin and horse ferrimyoglobin was also examined. A comparison of all the experimental results indicated that Tyr-151 is exposed to solvent, Tyr-146 is not exposed, and Tyr-103 exhibits intermediate
behavior. These results for myoglobins in solution are consistent with expectations based on the crystal structure.

A preprint is available upon request.

Best regards,

Adam Allerhand
Professor of Chemistry

FIGURE CAPTIONS

Fig. 1. Region of aromatic carbons and $C^\beta$ of arginine residues in convolution-difference natural abundance $^{13}$C Fourier transform NMR spectra of cyanoferrimyoglobins in H$_2$O (0.1 M KCl) at pH 10.5 (complete aromatic region) and pH 7.9 (155-165 ppm only), recorded at 15.18 MHz, under conditions of noise modulated off-resonance proton decoupling [see Oldfield, Norton, and Allerhand, J. Biol. Chem. (1975) 250, 6368-6380 and 6381-6402]. (A) 10 mM sperm whale cyanoferrimyoglobin at 36°, after 32,768 accumulations with a recycle time of 0.555 s (pH 10.5) or 1.055 s (pH 7.9). (B) Horse cyanoferrimyoglobin at 36°, after 32,768 accumulations with a recycle time of 1.045 s (at both pH values). Protein concentration was 12 mM at pH 10.5 and 7 mM at pH 7.9. (C) About 12 mM red kangaroo cyanoferrimyoglobin at 36°, after 65,536 accumulations with a recycle time of 1.045 s at pH 10.5, and after 32,768 accumulations with a recycle time of 0.555 s at pH 7.9.

Fig. 2. Effect of pH on the chemical shifts of some nonprotonated aromatic carbons and $C^\beta$ of arginine residues of sperm whale cyanoferrimyoglobin at 36°. Observed nonprotonated aromatic carbon resonances which are not shown (105-115 ppm and 130-145 ppm) have chemical shifts which are practically pH independent above pH 8. Peak numbers are those of Fig. 1A. Open circles, closed circles, triangles and squares indicate peaks that arise from 1, 2, 3, and 4 carbons, respectively. Figure 1A gives typical sample and spectral conditions. The solid lines are best-fit theoretical titration curves, with one pK for Tyr-151 and two pK values for Tyr-103. Dashed lines are best-fit single pK titration curves for Tyr-103. Below pH 10.5, the dashed curves for $C^\beta$ of Tyr-103 coincides with the solid curve for $C^\beta$ of Tyr-151.
Fig. 3. Effect of pH on the chemical shifts of some nonprotonated aromatic carbons and C^6 of arginine residues of horse cyanoferrimyoglobin at 38°. Peak numbers and typical sample and spectral conditions are given in Fig. 1B. The behavior of omitted resonances and the meaning of symbols and curves are given in the caption of Fig. 2.

Fig. 4. Effect of pH on the chemical shifts of some nonprotonated aromatic carbons and C^6 of arginine residues of red kangaroo cyanoferrimyoglobin at 36°. Peak numbers and typical sample and spectral conditions are given in Fig. 1C. The behavior of omitted resonances and the meaning of symbols are given in the caption of Fig. 2.

Figure 1
Indirect Observation of Bloch-Siegert Shifts (or Where are the Protons) in $^{13}$C-$^{1}$H Multiple Resonance Experiments;

3rd EENC

Dear Barry,

In connection with our work on determination of relative signs of $^{13}$C-X coupling constants using various selective $^{13}$C-$^{1}$H double resonance methods (1) we came across some examples which required selective irradiation at two or more positions in the $^{1}$H spectrum in order to remove simultaneously the multiplet structure caused by one-bond ($^{1}$JC-$^{1}$H) and long-range $^{13}$C-$^{1}$H couplings in the observed $^{13}$C spectrum. These experiments are complicated by the fact that the power of the coherent rf field needed to collapse a one-bond $^{13}$C-$^{1}$H splitting completely (using on-resonance conditions) causes extraordinarily large Bloch-Siegert shifts for other protons in the $^{1}$H spectrum. An indirect observation of these Bloch-Siegert shifts is illustrated in the $^{13}$C-$^{1}$H-$^{1}$H triple resonance experiment on toluene in Fig. 1b. The $^{13}$C-$^{1}$H double resonance spectrum of the aromatic carbon atoms obtained with strong $^{1}$H irradiation ($\nu_{H}/2\pi = 486$ Hz) at the exact decoupling frequency for the ortho (H2) and para (H4) protons ($\nu_{H2} = 484.5$ Hz, $\nu_{H4} = 493.4$ Hz and $\nu_{H4} = 484.8$ Hz relative to the methyl protons, $\nu_{CH}$, in the $^{1}$H spectrum at 100.1 MHz) is shown in Fig. 1a. Under these conditions the C1 and C2 carbon signals display residual quartet splittings of approximately 3-5 Hz (2a), whereas much smaller quartet splittings may be observed for the C4 carbon. C3 shows mainly a residual one-bond splitting, $^{1}$JC3-$^{1}$H3. These observations are in agreement with the magnitudes determined for the long-range $^{13}$C-$^{1}$H couplings between the ring carbons and methyl protons in toluene (2b). In order to remove the residual quartet splittings from the spectrum observed in Fig. 1a a second coherent rf field $^{1}$H of weaker amplitude ($\nu_{H}/2\pi = 58$ Hz) was applied to the methyl proton resonance. However, from the $\nu_{H}$ decoupling frequency it was empirically observed that these protons experienced a Bloch-Siegert shift of 195 Hz to lower frequency due to the strong $^{1}$H field. The experiment was performed using various $^{1}$H decoupling amplitudes and the results in Table 1 show that even moderate decoupling amplitudes in coherent $^{13}$C-$^{1}$H off-resonance decoupling experiments may easily shift the proton resonances completely outside the frequency range of the normal $^{1}$H spectrum.
The Bloch-Siegert shifts observed in the experiments described above \((\nu_A - \nu_s \neq 0)\) may be accounted for (Table 1) using the formula

\[
\text{B.-S. shift} = (\nu_A - \nu_s) \left[ \frac{\nu_H}{2\pi} \right]^2 \frac{(\nu_A - \nu_s)^2 + 1}{1 - 1}
\]

which includes the sign of the frequency shift. The high-frequency Bloch-Siegert shift of a methyl proton resonance line of weaker intensity is not considered here. A full account on these results, some experimental applications, and experimental details has been submitted for publication.


Table 1. Experimentally Observed and Calculated Bloch-Siegert Shifts of the Methyl Protons in Toluene from the Experiments Described in the Text.

<table>
<thead>
<tr>
<th></th>
<th>(\nu_H/2\pi) (Hz)</th>
<th>Calc. B.-S. Shift (Hz)</th>
<th>Exp. B.-S. Shift (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
<td>486 ± 12</td>
<td>200 ± 9</td>
<td>195 ± 3</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>930 ± 15</td>
<td>559 ± 13</td>
<td>562 ± 3</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>1330 ± 20</td>
<td>922 ± 19</td>
<td>939 ± 3</td>
</tr>
</tbody>
</table>

Figure 1.

a) \(^{13}\text{C}-(1\text{H})\) double resonance spectrum of the aromatic carbons in toluene with coherent irradiation of \(H_2\) and \(H_4\), \(\nu_H/2\pi = 486\) Hz (Exp. 1).

b) Same as in a but with coherent irradiation, \(\nu_H/2\pi = 58\) Hz, of the B.-S. shifted strong methyl proton resonance line (see text).
The 3rd EENC (European Experimental NMR Conference) will be held in Elsinore, Denmark


Elsinore, the city of Shakespeare's Hamlet, is located on the coast 25 miles from Copenhagen.

Based on the experience from the previous conferences an incomplete list of tentative subjects would be:

- Magnet developments;
- $T_1$ and $T_2$ measurements;
- Elimination of dipole broadening in solids and liquid crystals;
- NMR detection of quadrupole transitions;
- Spatial resolution of NMR signals;
- Development of pulse techniques for weak signals and less common nuclei;
- On-line and off-line data handling;
- "Unexpected results and unexplainable phenomena"

All correspondence concerning the conference should be addressed to

Dr. Kjeld Schaumburg
3rd EENC
University of Copenhagen
The H. C. Ørsted Institute
Kemisk Laboratorium 5
Universitetsparken 5
DK-2100 KØBENHAVN Ø
Denmark

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Mississauga, Ontario, Canada L4W1E4
Phone 416-625-2375
Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843  

SUBJECT: Whatever turns you on.

Dear Barry:

When one encounters a variety of chemical structure problems simultaneously, it becomes attractive to consider systems for coping with the more routine aspects of interpretation on a more organized basis, which involves some thought about the strategy by which one derives a chemical structure from NMR evidence alone. This is not only remarkably consistent from problem to problem (differing mainly in the shortcuts provided by evidence from other sources), but lends itself to a natural hierarchy of experiments that increase in difficulty as they become more specific in purpose. We are presently restricting our standard formats to molecules containing only carbon, hydrogen, oxygen, and nitrogen atoms for which the empirical formula is known. These are conveniently divided into peripheral (surface) and framework types, based on the number of atoms to which they are attached by arbitrary bond multiplicities. This division is natural for NMR spectroscopy, since PMR and CMR (excepting isocyanides) each deal exclusively with atoms of a single type. One begins by attempting to define the set of basic structure units, consisting of each framework atom plus its attached peripherals, using such observables as the chemical shift ranges of the framework atom, the number of protons on the unit, and dynamic and isotopic exchange characteristics. This may or may not require the direct observation of additional nuclei, depending on the number of types encountered. The structure units are topographically classified into terminals (T), links (L), branches (B) and intersections (I), which are related by the rule

\[ T = B + 2(I + 1 - R) \]

from which the number of rings, \( R \), in the structure can be determined.

Our standard format for summarizing the essential data and listing the basic structure units is illustrated in Figure 1, using a simple molecule with empirical formula \( \text{C}_6\text{H}_6\text{O}_2 \). In this instance there are no nitrogen atoms or peripheral (carbonyl) oxygen, the latter fact being apparent from the CMR shifts; one hydroxyl unit is evident from its exchangeable proton, and one other unit is assignable by elimination. The structure is therefore deduced to contain three rings and four double bonds, all between carbon.

A general solution to the structure problem now consists of defining all binary sequences of basic structure units. The second stage of a problem therefore involves the systematic linking of basic structure units into extended sequences. Spin coupling information is most naturally suited to this purpose, and can be augmented by chemical shift correlations of
all observable nuclei in a unit with model systems. As an example, our previous structure can be systematically shown to have the extended structure units tabulated in standard form in Figure 2. Units A, C, and D were in this instance established on the basis of straightforward parameter correlations, and unit B by homonuclear proton decoupling. The details are available for the asking.

The final stage of a problem occurs if and when the set of extended structure units becomes small enough to permit the delineation of a manageable set of alternative structures, and its accomplishment depends on one's ability to devise a critical series of experiments to differentiate among them. Relaxation times, Overhauser effects, and shift-reagent studies are examples of experiments best suited to this level of attack.

In our present example, only two structural arrangements of the extended units are possible, and one can show that II with \( m = 1, \beta = 0 \) is correct on the basis of CMR relaxation rates related to the length of the alkyl chain:

\[
\text{I (} m, n \geq 1, p_{\text{max}} = 1) \quad \quad \quad \quad \quad \quad \quad \text{II (} m \geq 1, p_{\text{max}} = 2) \]

We thereby arrive at structure III, with its trans ring juncture also evident from PMR coupling data.

While none of this is really new, we find it useful, and at the least propose that our old preoccupation with ethyl alcohol be replaced with an example more suited to the times. I wonder if the hospitality suites will go along?

Sincerely yours,

E.B. Whipple
### NMR SUMMARY AND BASIC STRUCTURE UNITS

**Compoond:** Mary Jane

<table>
<thead>
<tr>
<th>UNIT</th>
<th>ATTACHED H</th>
<th>TOTAL H</th>
<th>L</th>
<th>S</th>
<th>CH</th>
<th>TOTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>H</td>
<td>5</td>
<td>3</td>
<td></td>
<td>8</td>
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<tr>
<td>9</td>
<td>H</td>
<td>1</td>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
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<tr>
<td>16-21</td>
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<td>2</td>
<td>2</td>
<td>4</td>
<td>12</td>
<td>27</td>
</tr>
</tbody>
</table>

**TOTALS:** 21 6 6 4 27 121 30

**Formula:** \( \text{C}_{21}\text{H}_{59} \text{O}_{3} \)

### STRUCTURE UNITS

**Compoond:** Mary Jane  \( \text{C}_{21}\text{H}_{59} \text{O}_{3} \)

<table>
<thead>
<tr>
<th>UNIT</th>
<th>BASIC UNITS</th>
<th>EXTENDED UNITS</th>
<th>R±</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH</td>
<td>T 1 0 1 1</td>
<td>1 0 0 0</td>
<td>3</td>
</tr>
<tr>
<td>-CH3</td>
<td>4 4 12 0 0</td>
<td>2 1 0 0</td>
<td>3</td>
</tr>
<tr>
<td>-CH</td>
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<tr>
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<td>1 0 0 0</td>
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<td>3</td>
</tr>
<tr>
<td>-CH</td>
<td>8 2 2 0</td>
<td>0 2 0 0</td>
<td>3</td>
</tr>
<tr>
<td>-( \gamma )</td>
<td>5 5 0 0</td>
<td>4 1 0 0</td>
<td>3</td>
</tr>
</tbody>
</table>

**TOTALS:** 23 21 30 21 11 6 2 1

**KEY:**
- (A) \( \text{CH}_3-\text{CH}-(\text{R}) \)
- (B) \( \text{CH}_3-\text{CH}-(\text{A}) \)
- (C) \( \text{CH}_2-\text{CH}-(\text{R}) \)
- (D) \( \text{CH}_2-\text{CH}-(\text{A}) \)
Une méthode d’analyse quantitative de mélange d’hydrocarbures aromatiques monocycliques utilisant la résonance magnétique nucléaire du carbone-13 (R.M.N13C) est proposée. Cette méthode permet de déterminer le pourcentage en mole des constituants du mélange par mesure de l’intensité des signaux R.M.N des carbones aromatiques seulement ; ainsi le pourcentage d’un composé A, du mélange d’aromatiques men-nucléaires est donné par la relation : 

\[ \% A = \frac{\sqrt{y} - 100}{\sqrt{x} - 100} = \frac{0}{y} \]

 où, n représente l’intensité relative l’un des carbones du cycle du composé A par rapport aux raies de tous les carbones cycliques (x étant donné en pourcentage) et y représente le nombre de carbones aromatiques identiques de la molécule A.

L’application de cette technique a permis la détermination des pourcentages en moles des constituants de mélanges d’aromatiques, issus des fractions (50 --> 180°C) de 4 bruts de pétrole tunisiens, monocycliques : preuve obtenue par chromatographie de partage en phase vapeur (C.P.P.V.) et par découplage C.P.P.V. - spectrométrie de masse. Dans ce but, nous avons enregistré les spectres R.M.N13C des différents échantillons à l’aide d’un appareil Bruker HX90 (22,63 MHz) équipé d’un accessoire pour transformée de Fourier en adoptant la technique du découplage avec annulation de l’effet Overhauser nucléaire et en choisissant un temps "trigger" de 300 s (temps d’attente entre 2 interféromètres) tel qu’il soit égal au moins à 5 fois le temps de relaxation le plus élevé.
Ainsi nous avons pu mettre en évidence sans ambiguïté approximativement les 3/4 des constituants des différents mélanges. Ce travail nous a révélé que le pseudocumène et le m-xylène représentent les pourcentages les plus élevés dans le mélange I, alors que dans l'échantillon II le m-xylène constitue le 1/5 du total. De même, cette technique a montré l'importance quantitative du télène et du m-xylène dans le mélange III et a révélé que le quart de l'échantillon IV est constitué de télène.

La méthode, mise au point dans ce travail, est à notre avis susceptible d'être étendue à l'étude d'autres mélanges de composés aromatiques substitués par n'importe quels substituants, ce qui permettrait par exemple, d'analyser et qualitativement et quantitativement des mélanges d'isomères.

Nous tenons à signaler que ce travail a été réalisé grâce à l'aimable concours de M. le Prof. J. J. Delpeuch (Nancy) et l'assistance de M. P. Rubinì.

Croyez cher M. Shapire à nos sentiments cordiaux.

Titre : Étude par RMN du Carbone-13 des fractions aromatiques des coupes légères des bruts de pétrole tunisiens.
The University of Liverpool

Professor B.L. Shapiro,
Texas A and M University,
Department of Chemistry,
College of Science,
College Station,
Texas 77843,
U.S.A.

18th June, 1976.

Dear Barry,

A cautionary tale, or when did you last check your CDCl3?

TAMUNMR readers may be interested in a little problem which fooled us for some time recently. We were investigating the complex formed in CDCl3 solution between benzyl alcohol and ClCH2CH2CH2NHMeCl (I), in which we propose that the interaction is due to a) the attraction of the benzene ring with the N part and b) a hydrogen bond between the OH and the Cl part of the ion-pair.

To test this hypothesis, we made the tetraphenyl borate salt of (I). However, on dissolving this in CDCl3, we failed to get reproducible spectra; eventually we obtained the dilution curve shown which at first we thought was due to dissociation of the ion-pair. However, the shape of the curve is incorrect for a dissociation curve, and the correct answer was quite revealing.

\[
\begin{align*}
\delta_{\text{N-Me}} & \quad \text{conc. (M)} \\
2.7 & \quad 0.01 \\
2.6 & \quad 0.02 \\
2.5 & \quad 0.03 \\
2.4 & \quad 0.04 \\
\end{align*}
\]
The curve shown is a titration curve in which we are titrating the DCl in the CDCl₃ against the solute, following the equation shown.

\[
\text{R} \quad \text{NHMe₂} \quad \text{BPh₃} \quad + \quad \text{HCl} \quad \rightarrow \quad \text{R} \quad \text{NHMe₂Cl} \quad + \quad \text{BPh₃} \quad + \quad \text{C₆H₆}
\]

The infinite dilution shift is that of the hydrochloride but as the acid in the chloroform is used up the shift changes to that of the tetraphenyl borate.

Addition of HCl to the concentrated solution produced the ∞ diln. shifts, thus confirming this hypothesis.

This effect was seen despite considerable attempts to remove all acid by passing the CDCl₃ through alumina and storage over molecular sieves and silver foil. The problem was that the tetraphenyl borate was not very soluble in CDCl₃, and to achieve the required solution the mixture was usually warmed and shaken; precisely the right conditions for the formation of HCl.

With best wishes,

Yours sincerely,

Dr. R.J. Abraham.

'R. J. Abraham, K. Lewtas and W.A. Thomas, manuscript in preparation.
The Absence of Long Range $^{13}\text{C}^{13}\text{C}$ Coupling Constants in Homoadamantan Derivatives.

Dear Dr. Shapiro,

We have recently measured the long range $^{13}\text{C}^{13}\text{C}$ coupling constants in 2-substituted adamantanes labelled at the a-carbon atom. (J.C.S. Chem. Comm., in press). The conformational and substituent dependence of $^{2}\text{J}_{\text{CC}}$ and $^{3}\text{J}_{\text{CC}}$ in these compounds caused us to investigate a similar system with slightly different bond angles. However, we were not able to detect any three bond coupling constants in a series of homoadamantanes labelled at carbon atom 3. Two bond coupling constants could only be detected in $^{2}\text{g}$, $^{3}\text{g}$ and $^{4}\text{g}$ between carbon atoms 1 and 3 where carbon atom 2 has sp$^2$ hybridization.

At present, we have no satisfactory explanation for the different behaviour of adamantanes and homoadamantanes. To obtain more experimental results we are currently trying to synthesize some labelled noradamantane systems.

Sincerely yours,

Stefan Berger
Klaus Peter Zeller
(Institut für Organische Chemie der Universität Tübingen)
Professor B.L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas  77843 U.S.A.

SLIGHTLY OFF-COURSE FROM THE 'TOPIC OF CANCER'

June 22, 1976

Dear Barry:

NMR studies in our group here at the Cancer Center include investigations of tumor scanning agents, carcinogens, and cancer drugs. It is perhaps also interesting to look at something structurally more simple and hopefully, non-carcinogenic -- the ammonium ion.

Employing a Bruker HX-90 modified to accommodate a wide band Traficante insert, we have recently obtained $^{14}$N spectra of NH$_4^+$ and ND$_4^+$ in the lyotropic mesophase composed of decyl ammonium chloride, ammonium chloride and H$_2$O or D$_2$O (1). The ensuing spectra show partially resolved coupling between nitrogen and protons (sum of the scalar and the dipole-dipole coupling $|J_{\text{NN}}| + |D_{zz}|$) as well as very small $^{14}$N quadrupole splittings $(\Delta Q)$. The ND$_4^+$ samples were also used to study the deuterium quadrupole splittings of the same ion (under condition of identical probe temperature and almost identical history of sample orientation in the magnetic field). From the ratio of the $^{14}$N and the $^2$H splittings, the distortion model for tetrahedral species of Bailey et al. (2) yields a $^{14}$N quadrupole coupling constant of 3.1 MHz (assuming $e^2qQ/h = 175$ KHz and $\eta = 0$ for deuterium). This seems to be a reasonable value, and in general supports the simple distortion model. This is in contrast to a recent report (3) in which the same model apparently yielded results which
differ by one to two orders of magnitude from those obtained experimentally. A more detailed description of this study is being communicated to J. Amer. Chem. Soc.

Please credit this contribution to Dr. Robert Lenkinski's subscription.

Sincerely yours,

[Signature]

Douglas M. Chen, Ph.D.

[Signature]

Jerry D. Glickson, Ph.D.

REFERENCE

Some of your readers have been concerned with the utilization of homoallylic coupling constants in the conformational analysis of 1,4-cyclohexadienes. There has been some disagreement (too expansive to reference here) whether homoallylic coupling constants reflect the extent of puckering in dihydroaromatic compounds. A further complication is the possibility of rapidly interconverting conformers (e.g., boat ↔ boat), giving rise to averaged nmr parameters.

The fact that carbon-proton coupling constants can be related to proton-proton coupling constants in a wide variety of systems (slope = 0.62, correlation coefficient = 0.98, in 2-, 3-, 4-, and 5-bonded olefinic, aromatic, acetylenic, and aliphatic systems for $^{13}$C-labeled carboxylic acids; Organic Magnetic Resonance, in press) suggested to us that carbon-proton coupling constants could be used in the conformational analysis of dihydroaromatic compounds. Accordingly, we have synthesized the appropriate $^{13}$C-labeled, deuterium labeled compounds to get the parameters listed below for 1,4-dihydronaphthalene (1), 1,4-dihydronaphthalic acid (2), and 9,10-dihydro-9-anthracic acid (3). Several interesting observations can be made from this data.

First, for flat 1, the CH coupling constants seem to correlate with the HH coupling constants: the ratio of $J(CH-cis)/J(CH-trans)$ is the same as the ratio $J(HH-cis)/J(HH-trans) = 1.23 ± 0.01$. Further, the ratio of $J(CH-cis)/J(HH-cis)$ and of $J(CH-trans)/J(HH-trans)$ is the same as noted above $0.62 ± 0.01$.

Second, if 2 were rapidly interconverting between two boat conformations, the two ratios $J(CH-cis)/J(CH-trans)$ and $J(HH-cis)/J(HH-trans)$ would be the same -- but they are not. Clearly, 2 is not a rapidly interconverting pair of conformers (we also tried to "freeze out" conformers at low temperature but were unsuccessful).

Third, there is a monotonic trend in $J(CH-cis)/J(CH-trans)$ and in $J(HH-cis)/J(HH-trans)$ through the series 1-3 (increase and decrease, respectively). We believe that these two ratios can fairly accurately reflect the extent of puckering in these, and in other, compounds. Sufficient space does not exist here to allow this comparison with literature cases.

Fourth, we have done SCF-INDO-FPT calculations on 1,4-cyclohexadiene itself at various conformations, and the ratio of $J(cis)/J(trans)$ obtained from these calculations match up with the empirical values (e.g., for flat cyclohexadiene the calculated value of 1.29 compares with the empirical values of 1.22 (HH) and 1.24 (CH)).

Fifth, these studies point out the clear need to distinguish between the ratios $J(eq-eq)/J(ax-eq)$ and $J(ax-ax)/J(ax-eq)$ when applying the $J(cis)/J(trans)$ ratio to the conformational analysis of cyclohexadienes. The data shown below illustrate what to expect for $J(eq-eq)/J(ax-eq)$ ratios (viz., $J(HH-cis)/J(HH-trans)$) and for
\( \frac{J(ax-ax)}{J(ax-eq)} \) ratios (viz., \( \frac{J(CH-cis)}{J(CH-trans)} \)). We feel that "anomalies" in the literature can be explained once this distinction is recognized.

Sixth, and sufficient space does not exist here to tabulate this data, the calculated values in 1,4-cyclohexadiene show clearly that the expected values in this system are not just "doubled" values of the mono-path 2-butene. Instead, several changes can be noted. For example, the diaxial cis coupling does not simply increase throughout all possible conformers from a flat system to a highly puckered one (where the axial nuclei are parallel to the atomic \( p \) orbitals); instead, about half-way through these two extremes, the diaxial coupling starts to drift as the system continues to pucker further. Thus, claims to the "maximum degree of puckering" based on the "largest observed homoallylic coupling constant" can be misleading.

The main conclusion we have drawn from all this is that individual homoallylic coupling constants may be misleading in the conformational analysis of dihydro aromatics, but cis/trans ratios are more reliable. We further feel that ax-ax/ax-eq ratios are more reliable than eq-eq/ax-eq ratios.

<table>
<thead>
<tr>
<th>Compound</th>
<th>cis-( \frac{J}{\Delta HH} )</th>
<th>trans-( \frac{J}{\Delta HH} )</th>
<th>cis-( \frac{J}{\Delta CH} )</th>
<th>trans-( \frac{J}{\Delta CH} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.19</td>
<td>7.56</td>
<td>5.75</td>
<td>4.65</td>
</tr>
<tr>
<td>2</td>
<td>3.84</td>
<td>4.36</td>
<td>5.44</td>
<td>2.86</td>
</tr>
<tr>
<td>3</td>
<td>&lt;0.5</td>
<td>0.9</td>
<td>3.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Sincerely,

James L. Marshall
Professor of Chemistry
June 22, 1976.

Dear Barry:

Antiperiplanar deshielding effects in $^{13}$C spectra can mislead the unwary.

The receipt of your pink note has prompted me to bring my "subscription" up-to-date and I hope that the following finding will be of interest to some of the TAMU newsletter readers.

In collaboration with Bill Ayer (University of Alberta) I have been involved in the stereochemical assignment for a fungal metabolite, cybullol, isolated from one of the birds' nest fungi, Cyathus bulleri. This material was fairly readily shown to be a di-methyldecalin-diol and, at the outset of my involvement in the project, the prime problem was its stereochemistry. Since eight of the nine possible 10-methyl-trans-decalols, as well as a few cis-decalols, had been examined in an earlier study, it seemed to be a straightforward project, simply the distinction between A and B below:

Since 10-methyldecalin itself has a methyl signal at 15.7 ppm and the effects of the equatorial secondary hydroxyl and methyl were not expected to be large, perhaps 1 ppm each. One need only estimate the effect of the tertiary hydroxyl group to arrive at a prediction for the methyl carbon shielding for A and it was originally thought that this effect would be small and possibly slightly shielding. Thus, $\delta_C$ for the angular methyl was estimated to be <18 ppm. For B, on the basis of available models, it was estimated that the effects of the secondary hydroxyl and methyl groups would approximately cancel and the tertiary hydroxyl group would shield the C-10 methyl by ca. -6 ppm. This led to a prediction of -22 ppm. Cybullol exhibited methyl signals at 15.2 and 21.1 ppm and the latter was shown to be the angular methyl absorption by selective decoupling. This result indicated a cis ring junction but degradation of cybullol $\rightarrow$ geosmin (i.e. reduction of the secondary hydroxyl to $\text{-C}^\text{=O}$), whose structure had been established by synthesis as a trans-decalin derivative, pointed to the trans stereochemistry for cybullol. Subsequently a number of model compounds was prepared and examined to look at the effect of the 5a hydroxyl group in more detail for trans-fused 10-methyl-decalins and related systems. From these results it is apparent that the antiperiplanar arrangement of the hydroxyl and methyl groups at the ring junction leads to pronounced deshielding of the methyl carbon. Several examples are listed in the
accompanying Table. This effect has also been found for other substituents in steroids and some examples are included in the Table. Apparently the degree of substitution of the carbons bearing the substituents has a marked effect on the direction of the anti-periplanar \( \gamma \) shift since it has been known for some time that in less highly substituted systems the antiperiplanar hydroxyl, for example, shields the \( \gamma \) carbon by a few ppm. At the present time, there seems to be no simple interpretation of these observations but it is an interesting challenge for theoreticians. For stereochemical assignments from \( ^{13} \)C spectra, however, it reemphasizes the need for caution and the use of good model compounds before leaping to conclusions drawn from data for new systems.

Sincerely,

J.B. Stothers.

Angular methyl shieldings in some 10-methyl-decalins

<table>
<thead>
<tr>
<th>Substitution</th>
<th>( \delta_{C-10} )</th>
<th>( \Delta \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>nil</td>
<td>15.7</td>
<td>28.2(^b)</td>
</tr>
<tr>
<td>5-OH</td>
<td>20.4 +4.7</td>
<td>22.4 -5.8</td>
</tr>
<tr>
<td>4(\alpha)-Me-5-OH</td>
<td>20.3 +4.6</td>
<td>22.3(^c) -5.9</td>
</tr>
<tr>
<td>2(\alpha)-OH</td>
<td>76.6</td>
<td>21.0 +4.4</td>
</tr>
<tr>
<td>2(\alpha), 5-(OH)(_2)</td>
<td>14.9</td>
<td>21.5 -6.7</td>
</tr>
<tr>
<td>3-oxo-4(\alpha)-Me-5-OH</td>
<td>20.8 +5.9</td>
<td>20(\alpha)-5-OH</td>
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</table>

C-19 shieldings in some steroids

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<th>Cholestanes</th>
<th>Substitution</th>
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<th>( \Delta \delta )</th>
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<td>5(\alpha)-N(_3)</td>
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<td>e</td>
</tr>
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<td>5(\alpha)-NH(_2)</td>
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<td>f</td>
</tr>
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<td>5(\alpha)-CN</td>
<td>19.5</td>
<td>+8.0</td>
<td>f</td>
</tr>
</tbody>
</table>

a Ring junction stereochemistry.
c This compound was kindly provided by Prof. J.A. Marshall.
f These compounds were kindly supplied by Prof. J. Levisalles.
Monsanto

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

June 22, 1976

Professor B. L. Shapiro
Chemistry Department
Texas A&M University
College Station, TX 77843

MAGIC-ANGLE C-13 NMR ANALYSIS OF COAL

Dear Barry,

In collaboration with Vic Bartuska and Gary Maciel (MHPL, Colorado State University at Fort Collins), we have established the practicality of performing cross-polarization C-13 nmr experiments on coal powders, with 3-kHz mechanical spinning at the magic angle. Typical spectra of a lignite and an anthracite are shown in the figure. Magic-angle spinning removes from the determination of the relative concentrations of aromatic and aliphatic carbons, any ambiguity in the spectra arising from the overlap of chemical shift anisotropies.

These experiments were performed using hollow rotors, specifications for which have appeared earlier (JCP, 61, 2351 (1974)). The sample volume available in these rotors is about one-fourth of the effective sample volume that is realized by filling a 10-mm thin-wall nmr tube to a height equal to that of the C-13 coil, and is about one-half that of the total volume of the rotor. Naturally, when we perform magic-angle spinning experiments on solids which are not powders, but can be machined, we prefer to use a solid rotor and take advantage of the gain in sensitivity.

Sincerely,

Jacob Schaefer E. O. Stejskal
CP C-13 NMR spectra of coals

anthracite (USGS 61722S)

lignite

spinning at the magic angle

without spinning

100 ppm
June 29, 1976

Professor Bernard L. Shapiro
Chemistry Department
Texas A and M University
College Station, Texas 77843

Dear Barry:

Ion Pairing with TMS and TMAC Salts

In the May 1976 issue of the TAMU NMR Newsletter, 212-48, W. A. Thomas illustrates some unusual shifts found for TMS salts compared to t-BuOH, acetone, or dioxane internal references with a series of aryl ethanolamine hydrochlorides in aqueous solutions.

Of the reference compounds employed, only the TMS salts are negatively charged and may hence undergo ion pairing with the positively charged aryl ethanolamine hydrochlorides. Similar ion pairing of negatively charged TMS salts with cations probably occurs more frequently than recognized. The ion pairing becomes especially evident when a properly positioned aryl group provides the anisotropy to produce an evident chemical shift in the internal TMS reference.

Another ion pairing example was reported by H. Donato, Jr. and R. B. Martin in J. Am. Chem. Soc., 94, 4129 (1972) where the positively charged internal reference \((\text{CH}_3)_4\text{N}^+\) (TMAC) interacted with the trinegatively charged complexes of tris 2,6-dipicolinate and several lanthanides. No shifts were observed with bis nitrilotriacetate complexes, also with three negative charges on the complex, attesting again to the importance of an aryl group to produce an evident shift.

Other examples of ion pairing with charged internal reference compounds must exist in the literature. Analysis of the chemical shifts provides an opportunity to determine equilibrium constants for ion pair formation in such systems.

Sincerely yours,

R. Bruce Martin
Professor of Chemistry

RBM/dhw
Dear Barry,

This paper created quite some confusion and I would like to comment on a few points:

1) We used some years ago the 3N200 Dual-Gate Fet as input stage because of its excellent overall performance and the measured noise figure of the complete Amplifier turned to be about 3.5 dB.

2) Since for the past two years we have been using a very low noise silicon transistor with a noise figure of typ. 1dB and the measured NF of the complete amplifier (including input match and second stage) is less than 2dB. This gave a signal to noise improvement of about 20 % which corresponds to the NF-difference of about 2dB.

3) We tried to replace all old version amplifiers in the field and if anyone still own's an old one or a defective one we would like him to call the nearest Bruker Office and not to write a new paper.

With best regards

SPECTROSPIN AG

W. Schittenhelm
Discrete Frequency Artifacts in FT NMR Spectra of High Dynamic Range Samples

There are in the literature excellent discussions of random noise introduced into FT NMR spectra by digitization of either the incoming free induction decay or truncation of the data at intermediate stages of the fourier transformation process (see J.W. Cooper in "Topics in 13C NMR Spectroscopy, Vol. 2," G. Levy ed.). We wish to point out that for high dynamic range samples, dilute \( H_2 O \) samples of proteins for example, there are also discrete frequency artifacts. These discrete frequency artifacts can be illustrated by simply transforming a mathematically generated decaying sine wave and observing the resulting spectrum at high amplification. The artifacts are indicated with arrows in figure 1a.

The artifacts originate from imperfect representation of the FID by the digitization process. The frequencies at which they occur for a slowly decaying signal can be predicted by a simple qualitative analysis. If there are an integral number of data points per cycle of the incoming signal it is clear that the only errors in representation will be such that they recur with a frequency which is an integral multiple of the FID frequency, i.e., artifacts will appear at higher harmonics. If there are a non integral number of points per cycle of the FID one will have additional errors which will recycle after a sufficient time to have accumulated deviations from a perfect period which is an integral multiple of the dwell time. Artifacts can then appear at \( N F \) where \( F \) is the deviation of the true FID frequency from the spectrum's nearest integral frequency and will look like modulation sidebands.

The qualitative analysis of the artifacts suggests a simple means for their elimination, that is, adjusting the transmitter frequency so the most intense peak in the spectrum, the water resonance for example, is exactly in the center. With 4 data points per cycle for single phase detection harmonics will appear only at the edges of the spectrum and \( \Delta F \) for sidebands will be zero. The elimination of artifacts is illustrated in figure 1b.

J.H. Prestegard, W. Krol and P. Demou
Southern New England High Field NMR Facility
Yale University, Department of Chemistry
New Haven, Connecticut 06520
Dear Dr. Shapiro:

The Stanford Magnetic Resonance Laboratory wishes to announce:

The Second Annual

STANFORD CONFERENCE ON MOLECULAR STRUCTURAL
METHODS IN BIOLOGICAL RESEARCH

October 3 thru 6, 1976

At Stanford University

The Conference will be devoted to recent advances in the solution of biological structural problems by spectroscopic and crystallographic techniques, with a special emphasis on problems of protein and membrane structure and function.

A Partial List of Speakers
Includes:

Y. Arata (Tokyo)  J. Markley (Purdue)
R. L. Baldwin (Stanford)  H. M. McConnell (Stanford)
E. Blout (Harvard)  D. Patel (Bell Labs)
M. Bloom (British Columbia)  M. Raftery (Cal Tech)
F. W. Dahlquist (Oregon)  A. Redfield (Brandeis)
W. Hubbell (Berkeley)  E. Reich (Rockefeller)
O. Jardetzky (Stanford)  R. G. Shulman (Bell Labs)
M. P. Klein (Berkeley)  J. S. Waugh (MIT)

The Conference is sponsored by the Biotechnology Resources Branch of the National Institutes of Health. Participation in the conference is limited to 120. A registration fee of $30 is required which covers luncheons on October 4, 5 and 6 and a banquet dinner in the evening of October 6. For further information and registration forms, contact me at the letterhead address (Phone: 415/497-6270).

Sincerely,

Alice Walker
Conference Coordinator
25 June 1976

Professor B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

Your pink slips are only slightly more ominous than those expected by some of our people during the recent closing (lockout?) here. The latter event is a partial explanation for our tardiness in maintaining our subscription obligation, and with this contribution we request reinstatement.

In the course of our $^{13}$C studies of some alkaloids (Org. Magn. Reson., 8, 198 (1976)) we noted changes in the resonance positions of carbon nuclei in the vicinity of amide functions on addition of one equivalent of trifluoroacetic acid (TFA). Since there appeared to be no systematic study of this effect to determine its diagnostic value, we decided to examine some simple amides under these conditions. We have included for comparison the changes in $^{15}$N resonance positions. The results for some representative types of amides are given in the attached figure.

As is generally known, the carbonyl resonance moves downfield, reflecting partial protonation or extensive hydrogen bonding. Consistent with this change is the substantial downfield shift of the nitrogen resonance position. In the acyclic compounds N-alkyl carbons also move downfield, those cis to the carbonyl displaying larger changes than those trans. This contrasts with the upfield shifts experienced by the $\alpha$ carbons of amines on protonation. Alkyl groups attached to the carbonyl consistently move upfield. The same trends do not hold in the lactams, and at the moment we are playing with conformational influences as a working hypothesis. In all cases the changes in the resonance positions appear to level off at about four equivalents of TFA.

More detailed results and discussion will be submitted for publication shortly.

Sincerely yours,

P.R. Srinivasan

Robert L. Lichter
Associate Professor
Figure. Chemical shift changes of amides in trifluoroacetic acid. Values are in ppm relative to the resonance positions in the absence of acid. Positive values denote shifts to lower applied field. Carbon spectra were run in CDCl₃ containing the amides in ca. 2M concentration, with TMS as internal reference and with successive addition of one, two, and three equivalents of trifluoroacetic acid. Nitrogen spectra were determined on ca. 4M solutions of the amides in CDCl₃, with subsequent addition of one equivalent of TFA. Chemical shifts were determined with respect to external t-NH₄Cl in 1M HCl.
June 28, 1976

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77840

Dear Professor Shapiro:

Recently, we have prepared $^{15}$N-labeled meso-tetrphenylporphyrin
free base as part of a series of NMR studies of $^{15}$N-labeled metallo-
porphyrins. We have found that variation of temperature has an
intriguing effect on the imino proton spectrum of the $^{15}$N-labeled
compound (Figure 1). At $-49^\circ$, the resonance of N-H proton ($\delta$ -2.82)
appears as a doublet with peak seperation of 97 Hz attributing to a
typical one bond $^{15}$N-H coupling in pyrrole, suggesting that the
residence time of the imino proton on a given $^{15}$N atom is relatively
long in comparison to the nmr time scale. As the temperature is
raised, the spectrum changes and finally shows a quintet with a
observed coupling constant of 24.2 Hz, resulting from an intramolecular
rapid exchange of the imino protons among four $^{15}$N atoms. The quintet
arises from the random spin orientations of four $^{15}$N and the observed
average coupling constant of 24.2 Hz ($\sim$ 97 Hz/4) arises from the
fact that a jumping proton spends only $\frac{1}{4}$ of its time spin coupled
to a given $^{15}$N. We think that the result is a good example of four
site exchange process which may be used as a homework problem in the
first year NMR course.

Sincerely yours,

Herman Yeh, Mitsuo Sato
Isao Morishima

SUBJECT: Example of intramolecular four site exchange

Please give credit to H.Y.
Natural Abundance $^{13}$C SPT Experiment on a Basic WH-90

We made sign determinations of some two-bond $^{13}$C-H coupling constants using the "selective population transfer (SPT)" technique$^1$ with our Bruker WH-90 equipped with a B-SV broad band proton decoupler.

The decoupler frequency was read to 1 Hz using a Heath-Kit frequency counter (model 115-1103). One minor modification to the decoupler was that the one-turn potentiometer (500 Ω) to vary the power was replaced by a ten-turn pot so that low power levels could be reproduced precisely.

The accompanying figure shows a typical set of SPT $^{13}$C spectra obtained, using a 1,2:5,6-di-O-isopropylidene-D-glucose-3rd in CDCl$_3$ ($\nu$1 M). The procedure was as follows:

1. The H-2 resonant frequency was determined by observing the maximum collapse of the $^{13}$C-2 signal with the lowest possible decoupler power (0.2 W on meter).

2. From the proton NMR spectrum and this frequency, all four H-2 transition frequencies were located.

3. Each of these lines was irradiated, in turn, with much weaker power (no meter deflection) for a short period (0.2 sec.) just prior to every $^{13}$C pulse, 500 signals were accumulated for each spectrum.

In this example the sign was seen to be positive (+ 5.6 Hz).

Using the same technique, the signs of other two-bond coupling constants have also been determined:

$^2J_{C(1)-H(2)}$ (in β-D-glucopyranose) = - 5.7 Hz

$^2J_{C(2)-H(3)}$ (in methyl α-D-glucopyranoside) = - 4.7 Hz.

These and related stereochemical aspects of two-bond coupling constants will be discussed elsewhere$^2$.$^3$.

References:

3. N. Cyr, G.K. Hamer and A.S. Perlin, to be published.

Yours sincerely,

[Signature]

N. Cyr

NC/mtn

Enclosure
Dear Barry:

Recently Kelvin Chum and I completed an analysis of the $^1$H and $^{13}$C nmr spectra of nitrobenzene-$^{15}$N. The observed and simulated $^1$H spectra are shown in Figures A and B respectively. The RMS deviation between observed and calculated $^1$H transitions was 0.015 Hz; 119 transitions were assigned. The spectra shown in Figures C and D are observed and simulated double resonance spectra which help confirm the relative signs of the $^{15}$N,H coupling constants. The observed $^{15}$N,H and $^{15}$N,$^{13}$C coupling constants are given below and compared with those observed for aniline-$^{15}$N.

<table>
<thead>
<tr>
<th>Coupling Constants</th>
<th>Nitrobenzene-$^{15}$N</th>
<th>Aniline-$^{15}$N (1-3)</th>
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<tr>
<td>$^3J(N,H)$</td>
<td>$-1.921 \pm 0.005$ Hz</td>
<td>$-1.94$ Hz</td>
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<tr>
<td>$^4J(N,H)$</td>
<td>$-0.837 \pm 0.005$ Hz</td>
<td>$-0.48$ Hz</td>
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<td>$^5J(N,H)$</td>
<td>$-0.303 \pm 0.008$ Hz</td>
<td>$0.0$ Hz</td>
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<tr>
<td>$^1J(N,^{13}C)$</td>
<td>$-14.6 \pm 0.1$ Hz</td>
<td>$-11.47$ Hz</td>
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<tr>
<td>$^2J(N,^{13}C)$</td>
<td>$\pm 1.7 \pm 0.1$ Hz</td>
<td>$-2.68$ Hz</td>
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<td>$^3J(N,^{13}C)$</td>
<td>$\pm 2.5 \pm 0.1$ Hz</td>
<td>$-1.29$ Hz</td>
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<tr>
<td>$^4J(N,^{13}C)$</td>
<td>$\pm 0.7 \pm 0.1$ Hz</td>
<td>$0.27$ Hz</td>
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</table>

The observed coupling constants (Fermi contact contribution) have been compared with those calculated using FPT and semi-empirical MO theory at the INDO level of approximation. INDO predicts $^1J(N,^{13}C)$ in nitrobenzene and aniline to be $-29.8$ Hz and $-16.3$ Hz respectively.

I am presently writing a review for "Annual Reports on NMR Spectroscopy" on $^{13}$C-X nuclear spin-spin coupling constants where X is a first row element. I would appreciate any preprints of papers on this topic. Thank you.

References

Yours sincerely,

[Signature]
Select - A - Spin

The word is out - the periodic table has spins, and they are accessible to most multinuclei spectrometers. In our search for things bright and beautiful we have often needed a nuclear table arranged according to frequency. Using a series of controlled scissors pulses, Kathy has transformed the Lee and Anderson table into this new dimension. Fear prompted us to restrict ourselves to the non-radioactive nuclei. Frequencies for 23.5 Kg field should act as an appropriate page filler.


Yours sincerely,

Kathy

John Grutzner

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<td>Natural abundance (%)</td>
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Note: The table contains columns for the isotope, natural abundance, magnetic moment, and electric quadrupole moment.
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</table>

Free electron with

$\mu = 1.919 \times 10^{-22} A m$.
New 18-mm Probe for the XL-100

13C Spectra
10 Times Faster

Now Varian XL-100 users can run natural abundance 13C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose—clearly this new probe could extend the application of 13C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs 13C spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10—with results second to none.

Not only is the absolute sensitivity of the V-4418 Probe outstanding, it also offers excellent sensitivity per milliliter of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.

For further information contact your local Varian representative or write to:
Varian Instruments, 611 Hansen Way,
Box D-070, Palo Alto, CA 94303.

Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D2O, one using an 18-mm sample, the other the standard 12-mm sample. Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.
If you’re considering the purchase of an FT NMR System. Consider JEOL’s FX Spectrometer Series.

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