Texas A & M University
N-M-R Newsletter
February, 1975

R. Knorr, H. Polke, and A. Weis
Spin Transmission into Rotating and Rigid Phenyl Groups: Angular Dependence and Conformational Analysis

J. Lutgenburg and C. A. G. Haasnoot
C1s- and Trans-Vinyl-Carbethoxy cyclopropanes

C. P. Beeman and K. L. Williamson
Additivity of Carbon-13 Spin-Lattice Relaxation Times

G. Hagle and J. Richter
Long-Range Coupling Constants in Fluorinated Aromatics

R. J. Goodfellow and M. Murray
Measurement of 1H and Some Other Less Commonly Studied Nuclei: 13C Spectra with 19F Noise Decoupling

E. H. Kohler
Paramagnetic Organometallics Investigated by 13C PFT NMR: Selective Proton Decoupling of Phenyl Resonances

G. A. Gray
J(CP) in a Three-Membered Phosphorus Heterocycle: J(NP) in (Me2N)3PX, X= : ,S, and O

R. J. Mynatt and E. G. Hoffmann
Isomeric and Steric Interaction Effects on 11B- and 13C-Chemical Shifts of Some Et2BO Compounds

J. D. Swalen
16th ENC, Asilomar, CA, April 20-24, 1975: Program and Notices

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Deadline Dates: No. 198: 3 March 1975
No. 199: 7 April 1975

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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 197
Beeman, C. P. . . . . 37 Kohler, F. H. . . . . 43
Beno, G. J. . . . . . 1 Luttenburg, J. . . . . 36
de Bie, M. J. A. . 6 Lundin, J. D. . . . . 49
Cushley, R. J. . . . . 29 Macmurchie, D. D. . . . . 29
Ditchfield, R. A. . 7 Murray, K. S. . . . . 3
Durr, H. . . . . . . . 20 Murray, M. . . . . 41
Froix, M. F. . . . . 25 Mynott, R. J. . . . . 47
Goodfellow, R. J. . 41 Oldan, N. . . . . 17
Gray, S. A. . . . . . 46 Polzer, H. . . . . 32
Gunther, H. . . . . . 28 Reilly, C. A. . . . . 13
Hassonat, C. A. G. . 35 Richter, J. . . . . 39
Hagele, G. . . . . . 39 Sheldon, R. . . . . 55
Happe, J. . . . . . . 15 Sudmeier, J. L. . . . . 10
Hoffmann, E. G. . 47 Tschudin, R. . . . . 56
Holler, B. . . . . . 15 Ward, R. L. . . . . 15
Ishibetsu, K. . . . . 17 Web, A. . . . . 32
Johnson, L. F. . . 53 Westley, M. . . . . 23
Knight, S. . . . . . . 23 Williams, D. J. . . . 25
Knorr, R. . . . . . . 32 Williamson, K. L. . . . 37
Kober, H. . . . . . 20

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Cher Professeur Shapiro,

Votre lettre de rappel du 10 décembre 1974 m'est bien parvenue et je vous en remercie. Je vous fais part des titres suivants :

1. Travaux récents en magnétisme nucléaire :

Communication au 18ème Congrès Ampère de Nottingham (D8) - sept.1974

"Shift of nuclear magnetic frequencies by non-resonant alternating or rotating RF fields" note de MM. G.J Béné, B. Borcard M. Guenin, E. Hiltbrand, C. Piron, R. Séchéhaye.

Résumé : The action of a non-resonant RF field on a system of nuclear moments, submitted to a constant magnetic field was investigated on proton resonances of liquid systems in the earth field range. The main effects experimentally observed by alternative field excitation (shift of the Larmor frequency, as a function of the amplitude and the frequency of the excitation RF field) were theoretically investigated below and above the Larmor frequency. A good agreement between theory and experiment is found. We give also first results obtained with a rotating RF field excitation, where an exact theoretical solution is known.

"Non-resonant pulse excitation of nuclear magnetic sublevels" note de MM. B. Borcard et G.J Béné.

Résumé : We report some new non-resonant pulse techniques in order to obtain :
- nuclear magnetic coherence - detected by free precession classical experiments -
Prof. B. L SHAPIRO,

- nuclear magnetic reversal of magnetization - detected by observation of the thermodynamical equilibre recovery
- spin-echoes by a succession of short non-resonant pulses.

A phenomenological theory is given in a qualitative agreement with the observed phenomena.


2. Meetings du Groupement Ampère,
- 18ème Congrès Ampère Nott-GB - septembre 1974. Le compte rendu sera publié très prochainement (janvier 1975) et peut être obtenu chez North Holland Publ. Co. à Amsterdam. Il comprend deux volumes : volume I contient la préface, etc. et les pages 1 à 294 ; volume II contient aussi la préface, etc. et les pages 295 à 589. (suite de travaux scientifiques et liste des participants)


The programme of the Colloque is intended to cover the applications of NMR, EST, Mössbauer and neutron spectroscopy in solid state physics. The main emphasis will be put on investigations in the field of
- metals and alloys liquid crystals and developments in NMR tech­nique.

If you wish to receive further informations, please, ask to the following address :

2nd Specialized Colloque AMPERE
c/o Prof. K. TOMPA
Central Research Institute for Physics
H-1525. Budapest 114. POB 49
Hungary

Avec mes sentiments les meilleurs et mes voeux pour la nouvelle année,

Prof. G. J. Béné
TELEGRAMS: MONASHUNI, MELBOURNE

MONASH UNIVERSITY
CLAYTON, VICTORIA, 3168

DEPARTMENT OF CHEMISTRY

January 8, 1975

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

Dear Professor Shapiro,

Most of the work described here was carried out on the Bruker WH 90 at Oxford with the very able help of Mrs. Eva Richards; it is continuing at Monash using a similar instrument. Drs. Ian Rae and Michael Heffernan kindly asked me to contribute the results to the newsletter.

Isotopic shifts of $^{13}$C in natural abundance have been measured on a series of binuclear oxo-bridged iron (III) salicylaldimine complexes. A typical spectrum is shown in Figure 1. A number of the carbons have been assigned by ring substitution and N-R-substitution as well as by off-resonance decoupling. The temperature dependence of the shifts was determined for the complex [Fe(5Me-sal-N-Prn 2 o]. The results were compared with the theoretical contact shift expression deduced using a $^\text{a}$J$^\text{S}$.s Hamiltonian for two weakly-coupled $S = 5/2$ centres.\(^1\) $\Delta \nu / \nu$, for the 5C and 5Me are strongly temperature dependent and give good fits to the theory, the resulting J (exchange-coupling constant) and $\Delta_\nu$ values are of the same order as those obtained for the attached protons.\(^1\) In contrast the 4CH carbon shift varies little with temperature and the best-fit J value is vastly different to that obtained for the 4CH proton. I'll come back to a possible reason for this later.

Bearing in mind the little that is known about hyperfine parameters and spin-delocalisation in polynuclear complexes I have calculated $\tau$-spin densities from proton hyperfine parameters by use of McConnell relations.\(^2\) From their $\rho_{CH}$ values it was then possible to use Karplus-Fraenkel expressions to obtain carbon-hyperfine parameters $A_C$, for comparison with those deduced from the temperature study. The results are shown in Table 1 for a limited number of nuclei. The calculated and 'best-fit' $A_C$ values for the 5C and 5CH$^3$ of the 5Me-sal-N-Prn$^2$ complex are in reasonable accord, whilst those for 4CH are certainly not. These agreements and differences are further confirmed in calculating shift ratios, $\Delta \nu / \Delta H$, the sign of the ratio however being always negative as predicted for $\pi$-delocalisation.

In summary, the proton shift study pointed to a predominant $\pi$-mechanism. The carbon study, which should be more sensitive to the transmission of unpaired spin-density, supports a $\pi$-delocalisation pathway to the 5-ring position but not to the 4-position. It is possible that $\sigma$-delocalization to this position is important. Different mechanisms for carbon and contiguous proton are also possible, as pointed out by Dodrell and Roberts for other paramagnetic complexes.\(^3\) Further $^{13}$C studies are in progress on monomeric metal salicylaldimines and other polynuclear complexes to try to tie up the various loose ends and uncertainties.

Yours sincerely,

Keith S. Murray

Keith S. Murray
2. e.g. in 'N.m.r. of Paramagnetic Molecules', ed. La Mar, Horrocks and Holm (Academic Press 1973) Chaps. 3, 4.

Table 1

<table>
<thead>
<tr>
<th>X</th>
<th>Ring 4</th>
<th>Ring 5</th>
<th>Ring 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_H (a)</td>
<td>-215,696</td>
<td>+142,488</td>
<td>-52,046</td>
</tr>
<tr>
<td>( \rho_{C\pi} ) (b)</td>
<td>+0.0034</td>
<td>-0.0023</td>
<td>-0.0012 ((Q=44.6))</td>
</tr>
<tr>
<td>A_C (calc) (c)</td>
<td>-437,000</td>
<td>+766,000</td>
<td>+44,000</td>
</tr>
<tr>
<td>5Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_H</td>
<td>+219,066</td>
<td>+152,142</td>
<td>+214,656</td>
</tr>
<tr>
<td>( \rho_{C\pi} )</td>
<td>-0.0034</td>
<td>-0.0024</td>
<td>+0.0042 ((Q=51.1))</td>
</tr>
<tr>
<td>A_C (calc)</td>
<td>-687,000</td>
<td>+650,000</td>
<td>-159,600</td>
</tr>
<tr>
<td>( \Delta \nu / \nu ) (d)</td>
<td>-49,600</td>
<td>+363,800</td>
<td>-135,438</td>
</tr>
<tr>
<td>J (cm(^{-1}))</td>
<td>-416</td>
<td>-300</td>
<td>-288</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A_H</td>
<td>+223,038</td>
<td>-218,878</td>
<td>+120,099</td>
</tr>
<tr>
<td>( \rho_{C\pi} )</td>
<td>-0.0035</td>
<td>+0.0035</td>
<td>-0.0019</td>
</tr>
<tr>
<td>A_C (calc)</td>
<td>-437,000</td>
<td>+551,000</td>
<td></td>
</tr>
</tbody>
</table>

(a) From ref. 1 (corrected).
(b) From McConnell's equation.
(c) From Karplus-Fraenkel equation.
(d) From \( \Delta \nu / \nu \) vs. temp. fits.
ORGANISCH CHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT TE UTRECHT
CROESESTRAAT 79
POSTBRIQO 63985 - TEL. 8 32311

UTRECHT, January 13, 1975

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

Dear Professor Shapiro,

I would greatly appreciate if the following announcement
could be made in TAMU:

Announcement

The second European Experimental NMR Conference, dealing with new or
improved instrumentation, techniques and experimental methods in high
resolution NMR will be held at the Twente University of Technology,
Enschede, The Netherlands from 12 - 14 November 1975.
The Conference is the continuation of an initiative of the British NMR
discussion group which organised the first conference on experimental
techniques in Europe in April 1974. The conference is organised by the
Dutch NMR Discussion Group, an affiliate of the Analytical Chemistry
Section of the Royal Dutch Chemical Society. The organising committee
consists of M.J.A. de Bie, F.W. van Deursen and R. Visser. The committee
is assured of the assistance of an advisory board, consisting of
Dr. G. Gatti, Prof. Dr. R. Kosfeld, Prof. Dr. J.M. Lehn, Prof. Dr. W. von
Philipsborn, Prof. Dr. E.W. Randall and Prof. Dr. K. Schaumburg.
Further details on the conference are available from F.W. van Deursen,

Yours sincerely,

Dr. M.J.A. de Bie
THEORETICAL STUDIES OF MAGNETIC SHIELDING AT HYDROGEN-BONDED PROTONS

January 9, 1975

Dear Barry:

In response to your recent missive we'd like to report some of our preliminary theoretical studies of magnetic shielding at hydrogen-bonded protons. The main aim of this work is to obtain a better understanding of how geometrical features of hydrogen-bonding influence magnetic shielding at the atoms in the hydrogen-bonded system.

For this purpose we have examined magnetic shielding in the water monomer and the water dimer using the GIAO method we developed recently. Although the water dimer may be a somewhat idealized hydrogen-bonded system, it should provide a useful model for identifying those features of electronic structure which are important for an understanding of magnetic shielding in hydrogen-bonded systems.

In the Table we present the calculated elements of the symmetric part of the shielding tensor $\sigma$ for hydrogen atom $H_3$ in $H_2O$ and $(H_2O)_2$ using the axis system indicated. These values indicate a deshielding of 2.9 ppm for the hydrogen-bonded proton. It is worth noting that the magnitude of the change in $\Delta \sigma$ is significantly greater than that in $\sigma_{iso}$. This suggests that proton shielding anisotropies may be more sensitive measures of features of hydrogen bonding than are isotropic values of proton shielding.

[Diagram of monomer and dimer geometries]

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

Dartmouth College
HANOVER • NEW HAMPSHIRE • 03755
Department of Chemistry • TEL. (603) 646-2301
Ari analysis of the contributions to $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ using the procedure described elsewhere,1 yields the following result: -4.7 ppm of the -7.5 ppm change in $\sigma_{xx}$, -4.6 ppm of the -6.5 ppm change in $\sigma_{yy}$ and 5.0 ppm of the 5.1 ppm change in $\sigma_{zz}$ are due to deshielding effects of the currents on oxygen O4. Thus, these results suggest that the features of magnetic shielding at the hydrogen bonded proton are determined to a large extent by the currents induced on oxygen O4 by the external magnetic field. This appears to be contrary to the interpretation often given.3

Yours sincerely,

RoBERT DITCHFIELD


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You can update a T-60 for $^{13}$C measurements at a fraction of the cost of a new, dedicated system with the Nicolet TT-7 pulsed FT nmr accessory. The sensitivity provided by this combined system is comparable to that of instruments specifically designed for $^{13}$C spectroscopy. Features offered with the TT-7/T-60 combination include:

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Phone: 415/969-2076
Dear Barry:

Although several structural studies of nucleotides (e.g., 5'-AMP\(^1\) and 3',5'-cyclic AMP\(^2,3\)) in aqueous solution have been reported by nmr using lanthanide nitrates or halides as shift reagents, there has been no conformational analysis of a nucleotide undergoing rapid averaging among two or more species. We report here the results of a proton nmr study of cyclic-2',3'-AMP in D\(_2\)O (pD = 2.3) which was carried out with R.J.P. Williams at Oxford and my student Tim Dunn here at UCR.

In contrast to previous studies, our analysis searched for solutions in which several conformers are in rapid equilibrium, and has made full use of vicinal H-C-C-H and P-O-C-H spin coupling constants and corresponding Karplus equations. Cyclic-2',3'-AMP was chosen for this study because a) (unlike 5'-AMP) it is a diester which greatly reduces the number of possible modes of Ln\(^3+\) binding to the phosphate group over that found for monoesters, b) unlike cyclic-3',5'-AMP, the ribose ring is largely free to undergo pseudo-rotation, providing a more conformationally interesting system, and c) the closer distance and more favorable angle of the phosphate group to the adenine group should lead to sensitive monitoring of adenine conformations. As in previous studies, \(^1-3\) there are systematic variations in the lanthanide-induced shift (LIS) ratios of certain proton resonances (as large as 12%) obtained for various metal ions, e.g., Eu\(^3+\), Pr\(^3+\), and Dy\(^3+\). Average LIS ratios were weighed according to the agreement found, and spin coupling constants were used as a pre-filter to reduce the number of conformers.
Atomic coordinates for various conformers of the fused ribose and phosphate ring systems were generated (24 species in all) by careful measurement from precision large scale (5 cm/A) metallic models, assembled using bond distances and angles available from closely related crystal structures. Additional conformers involving simple rotations of groups (e.g., adenine) about a particular axis were generated by computer.

The observed spin-coupling constants ($J_{1'2'} = 3.4$, $JP2' = 9.0$, $JP3' = 9.3$ Hz) could be fit within experimental error only by the use of roughly equal parts of species generally categorized as 2'-endo and 3'-endo, the mixture slightly favoring the former. Out of 276 possible binary combinations, about twenty yielded acceptable fits to the spin-coupling constant assuming $J_g = 2.0$ and $J_t = 11.7$ Hz for vicinal protons in ribose, and $J_g = 1.8$ and $J_t = 20.9$ Hz for vicinal P-O=C-H couplings.

Of these twenty cases, the best fit to the LIS ratios (and coincidentally to the $J$'s) arises from a 55% mixture of the 2'-endo species in Fig. 1A with 45% of the 3'-endo species shown in Fig. 1B. Both have the phosphate atom puckered "down" 12 degrees about the O2'-O3' axis in contrast to an equal pucker "up" in the crystal, protons H2' and H3' are staggered rather than eclipsed as in the crystal, C2' and C3' are not coplanar with C1' and C4' as in the crystal, and adenine is "anti" with a torsion angle of -30 degrees. The principal magnetic axis was assumed to lie in the O2'-P-O3' plane and along the bisector of that angle. The best Ln-P distance is 2.5A. The proposed solution fits the LIS ratios with a weighted $R$ value of about 6%, arising almost exclusively from rather poor fits at H8 and H5", and the $J$'s fit to within $\pm 0.8$ Hz. The inclusion of orthorhombic terms provided little improvement in the $R$ value.

Yours sincerely,

James L. Sudmeier
Associate Professor of Chemistry

JLS/nc

7) R. D. Lapper and I. C. P. Smith, ibid., 95, 2880 (1973).
Fig. 1A  Stereo Views of 2'-endo cyclic-2',3'-AMP (55%)

Fig. 1B  Stereo Views of 3'-endo cyclic-2',3'-AMP (45%)
Professor B. L. Shapiro  
College of Science  
Texas A&M University  
College Station, Texas 77843

Dear Barry:

I finally found out that your pink letter really means what it says! I hope this contribution will reinstate my subscription and put me in your good graces again.

For some time now we have been adding Cr(acac)_3 to solutions of various materials in order to quench the NOE (most of it anyway) and, equally as important, to shorten T1's (particularly of completely substituted carbons) for more efficient acquisition of spectra. We have noted that the Cr(acac)_3 added always broadens the center line (due to 13C coupling with the 0 spin state of D) from the CDCl_3 solvent more than it does the outer two lines (coupling to +1 and -1 spin states of D). An example with CDCl_3 alone is shown in the enclosed Figure.

Several questions need to be answered, e.g.,

Why does this happen?
How general is the phenomenon?
Are the T1's of all spin states shortened similarly?

It seems unlikely that I shall have the time to pursue this matter further in the near future. I would be grateful for any contribution your readers can make toward an understanding of this phenomenon.

Sincerely yours,

C. A. Reilly

P.S. Suggested caption: Effect of Cr(acac)_3 on the Spin States of CDCl_3.
2 mL CDCl₃
+ x mg Cr(acac)₃

NO. DATA PTS:
= 6k/5000 Hz

PULSE WIDTH
= 6μs (= 30°)

PULSE SPACING
= Y SEC

NO. PULSES
= Z

X = 63.4
Y = 2.0
Z = 5000

X = 32.3
Y = 2.0
Z = 5000

X = 0
Y = 5.0
Z = 2500
Dr. B. L. Shapiro  
Texas A & M University  
College of Science  
College Station, Texas, 77843

Dear Dr. Shapiro:

Title: $^{35}$Cl-NMR Studies of Anion Binding Sites in Proteins

In response to your pink sheet we submit the following note of our activities.

We have continued to explore the use of Cl$^-$ ion probes to examine anion binding sites in proteins. Although the technique was originally devised to take advantage of the complex formation between Cl$^-$ and protein bound metal ions such as Hg$^{2+}$ or Zn$^{2+}$, nonmetallo anion binding sites in proteins can also be examined.

We have used $^{35}$Cl nmr line width measurements to study anion binding sites in pig heart lactate dehydrogenase. Lactic dehydrogenase catalyzes the conversion of pyruvate to lactate. The enzyme requires NAD as a co-factor and consists of four subunits of 47,000 molecular weight. Each subunit contains an active catalytic site. Each active site acts independently of the others and requires an obligatory order of binding of coenzyme followed by substrate.

Our NMR studies reveal two types of sites; one is intimately associated with the active site, the other is not. The nonactive site has been ascribed to a subunit site in analogy with crystallographic results from the dogfish $M_4$ enzyme. The binding of either the reduced or oxidized form of NAD results in an increase in the $^{35}$Cl nmr line width by a factor of 1.8-2 (Fig. 1). The enhanced nmr line broadening of the binary LDH-NAD complex is however reduced on binding of the substrate inhibitor molecules oxalate or oxamate. Further studies are planned to examine the mechanism for the enhanced line broadening on binding of NAD.

Sincerely yours,

Raymond L. Ward
James Happe
Bert Holder

RLW: gw
Figure 1 - The change of the net $^{35}$Cl nmr line width, $\Delta \nu_{\text{net}} = \Delta \nu_{\text{obs}} - \Delta \nu_{\text{CIs}}$, for various concentrations of NAD$^+$. After the maximum $\Delta \nu_{\text{net}}$ was obtained, the solution was titrated with oxalate. The solution contained 6.14 mg/ml of pit heart lactate dehydrogenase and $10^{-4}$M EDTA in 0.5 M NaCl, pH 7.4.
January 16, 1975

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

Simple Way to Reduce the Unnecessary Broad Signal

Dear Barry:

When we observe the silicon-29 or Boron-11, we are afflicted by the broad signal from the sample tube which includes $^{29}\text{Si}$ and $^{11}\text{B}$. Sometimes, this kind of broad signal makes the spectrum analysis difficult.

In order to reduce the broad signal, we must use some special technique (special sample tube, special window function, etc.); and recently, in our laboratory, we have found a simple way to reduce this broad signal. This procedure is done by the following subtraction:

[Original spectrum] - [100 points or more smoothed spectrum]

100 points or more smoothed spectrum show only broad signal because all sharp signals are smoothed out. We show the typical example of $^{29}\text{Si}$ spectrum.

We think we will be able to apply this simple technique to other type of broad signal problems.

Sincerely yours,

K. Ishibitsu

N. Odan

"Bringing the Scientist Tomorrow's Capabilities Today."
Sample
$\text{C}_2\text{F}_5\text{SiF}_3$
30000 scans
1 KHz width

The Original Spectrum

The spectrum after subtraction
WP 60

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- High resolution magnet for proton FT
- 10 mm variable temp for C¹³
- Superior sensitivity

FOR DETAILS, PLEASE CONTACT YOUR NEAREST BRUKER REPRESENTATIVE.
Er liebt das Muster}

Dear Professor Shapiro:

The valence isomerism of cycloheptatrien-Norcaradiene is an interesting, widely studied problem in organic chemistry. In the last decade, a new technique, the 13C-NMR spectroscopy, is applied to study the equilibrium of cycloheptatrien-Norcaradiene isomers, besides Gunthert's technique. With this technique, the individual spectra of both valence isomers can be observed. We report here about the first example of a cycloheptatrien-Norcaradiene isomer, in which the 13C-NMR valence isomerism is observed. This further allows the determination of the energy barrier between the two valence isomers.

[2.3]-Spirene 1 represent a fascinating class of compounds, as they have the possibility of valence isomerism as models for spiroconjugation, as well as precursors for bisnorcaradienes, of great interest. 7,8)
Die Synthese von \(1a \leftrightarrow 2a\) ist in l.c. 5) publiziert worden. \(1b \leftrightarrow 2b\) wurde durch Photolyse von Diazopoly in Benzol6) erhalten.

Die Messung der \(13C\)-NMR-Spektren bei verschiedenen Temperaturen bestätigt eindeutig die Existenz fluktuierender Strukturen für \(1a \leftrightarrow 2a\), wie wir bereits durch \(^1H\)-NMR-Spektroskopie zeigen konnten.5)

In Abbildung 1 sind die \(13C\)-NMR-Spektren bei schnelllem und langsamen Austausch wiedergegeben. Die für eine Auswertung entscheidenden \(C\)-Signale für \(1a\) treten bei 160°K bei δ 56.0 (s, C-7) und δ 128.3 (d, C-1,6) ppm auf. Die chemische Verschiebung der C-1,6-Atome stimmt gut mit den Werten von Cycloheptatrien (C-1,6:120.4 ppm6) überein. Die Signale für die Norcaradienform \(2b\) werden bei 160°K bei δ 56.0 (s, C-7) und 38.6 (d, C-1,6) ppm beobachtet. Diese C-1,6-Verschiebungen liegen im gleichen Bereich wie die von \(3^1\). Mit fallender Temperatur erfahren die C-7-bzw. die C-1,6-Signale bei \(1a,b \leftrightarrow 2a,b\) eine Hochfeldverschiebung (s. Tab. 1). Dies deutet darauf hin, dass die SpiroNorcaradienform 2 das stabileren Valenzisomere darstellt, wie bereits unsere \(^1H\)-NMR-Spektroskopie-Studien ergeben hatten).

**Tabelle 1.** \(13C\)-NMR-Daten für die Valenzisomeren \(1a,b \leftrightarrow 2a,b\) (\(\delta_{TMS}\)

<table>
<thead>
<tr>
<th>Verbindung</th>
<th>(T) [°K]</th>
<th>C-7</th>
<th>C-1,6</th>
<th>C-2,5,3,4 (+ arom.C)</th>
<th>(\Delta G^\circ) [kcal/Mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a \leftrightarrow 1b)</td>
<td>290</td>
<td>47.1</td>
<td>108.4</td>
<td>153.0;138.9;128.9;127.5;127.0;124.5</td>
<td>10 ((T_c=235^\circ))</td>
</tr>
<tr>
<td>(1a)</td>
<td>160</td>
<td>56.0</td>
<td>128.3 (s)</td>
<td>(\Delta H)</td>
<td>8 ((T_c=190^\circ))</td>
</tr>
<tr>
<td>(2a)</td>
<td>160</td>
<td>56.0</td>
<td>38.6 (d)</td>
<td>(\Delta S)</td>
<td></td>
</tr>
<tr>
<td>(1b \leftrightarrow 2b)</td>
<td>270</td>
<td>38.9</td>
<td>73.3</td>
<td>150.7;143.5;134.4;128.8;127.4;126.4;126.4;125.5;121.4;119.4</td>
<td></td>
</tr>
<tr>
<td>(1b)</td>
<td>160</td>
<td>26.0</td>
<td>36.7 (d)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Alle Spektren wurden mit der FT-Technik unter Breitbandentkopplung in einem Bruker HX-90-Gerät aufgenommen.
b) In Klammern sind die Multiplizitäten des "off resonance"-Spektrums angegeben.
Abb. 1: C^{13}-NMR-Spektren bei 290°K und 160°K

Mit freundlichen Grüßen

(H. Dürr)

(H. Kober)

4) R. Wehner und H. Günther, ibid 107, 3149 (1974).
6) D. Rewicki und C. Tuchschereir, Angew. Chem. 84, 31 (1972); Int. Ed. 11, 44 (1972).
Gated proton decoupling is a most useful technique for producing carbon-13 spectra with a good signal-noise ratio which retains the carbon-proton spin coupling information. Early models of pulse spectrometers were not fitted with the necessary instrumentation to utilise this technique.

We should like to describe a simple decoupler switching circuit which can be fitted to virtually any spectrometer. The switching element used is the Signetics NE/SE 555. This is a very versatile monolithic timing circuit which has the advantage of having an output stage capable of driving other switch circuits such as ring modulators. In the construction of a gated proton decoupling device three times are important — the overall experiment time, the decoupler 'on' time and the following delay time to allow the output of the decoupler power stage to fall to zero. These times linked as shown in the circuit below enable the three times indicated above to be determined. The negative going edge of the output of the last stage is used to trigger the Nicolet 1074 (and hence the Bruker pulse unit). If Bruker ring modulators are used then it is preferable to switch the \((30+\Delta f_2/3)\) MHz at “eingang f_2” on the transmitter (sender) unit rather than the \((90+\Delta f_2)\) MHz output. A typical result (ethyl benzene alkyl carbons) is shown in Figure 1. As can be appreciated, gated decoupling gives a S/N improvement that enables undecoupled spectra useful for interpretation studies to be obtained from relatively small samples.

S. Knight
FIG 1 ETHYL BENZENE
ALKYL CARBON

CH₃

CH₂

WITH GATED DECOUPLING

EACH SPECTRUM 128 PULSES

WITHOUT GATED DECOUPLING

T 6588 / BW
January 15, 1975

Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station Texas

Dear Professor Shapiro:

Nmr Relaxation Time Studies of Poly(N-vinylcarbazole).

We have recently measured proton $T_1$ and $T_2$ values for Poly(N-vinylcarbazole) (PVK) and observed some unusual results. The measurements were made in O$_2$, N$_2$, and ambient atmospheres and in vacuo on a highly purified sample (A) with a broad molecular weight distribution ($M_w$=240,000 and $M_w/M_n$=5.1). A second sample B with a much higher molecular weight and narrow distribution ($M_w/M_n$=1.25) was also examined. $T_1$ results for sample A in vacuo are shown in Fig. 1. Virtually identical results were obtained for sample (B) under similar conditions as well as for both samples in the presence of N$_2$. In an O$_2$ atmosphere the behavior in figure 2 is exhibited. A general lowering of $T_1$ and the appearance of a minima with three $T_1$ components is seen. The behavior is very similar for sample (B). $T_2$ data for sample (A) is shown in figure 3. The non-exponential FID analyzes to two components. In sample (B) only the short $T_2$ component is seen.

We attribute the multiple $T_2$ behavior in sample A to the presence of low molecular weight fractions which have a higher degree of conformational freedom and therefore a shorter $T_2$. The multiple $T_2$ behavior, however, is much less straightforward.

The general lowering of $T_1$ is attributable to a paramagnetic effect from O$_2$. The fluctuating magnetic field provided by the relaxing O$_2$ molecule provides an efficient route for thermal equilibration of the nuclear spin system with the lattice via the spin diffusion mechanism. The multiple $T_1$ behavior is probably the consequence of variations in O$_2$ concentration in the surface and bulk of the powdered polymer samples. This is more apparent from an examination of the equation for rapid spin diffusion

$$\frac{1}{T_1} = \frac{n^2}{4N\pi} b^3 \gamma_p \gamma_n^2 \frac{1}{r^6} \tau/(1+\tau^2)$$

where $\omega$ is the proton resonance frequency, $N$ is the concentration of O$_2$, $\gamma_p$ and $\gamma_n$ are the magneto-gyric ratios of the electron and nuclear spins, $r$ is the distance between paramagnetic nuclei, $\tau$ is the electron spin-lattice relaxation time, and $b$ is a characteristic radius inside of which the dipolar field of the electron is greater than the dipolar field of the protons. A minimum in $T_1$ will occur
when \( \omega = \tau \). The shortest \( T_1 \) component with the lowest temperature minimum probably corresponds to protons on or near the surface where the concentration \( N \) of \( O_2 \) is the highest and where \( \tau \) is likely to be smaller than in the bulk. The higher \( T_1 \) values would then correspond to the bulk. The multiple \( T_1 \) behavior in the bulk may be an artifact of the analysis caused by a non-uniform concentration of \( O_2 \) in the bulk.

These results will be discussed in more detail in a forthcoming publication.

Sincerely,

David J. Williams
Michael F. Froix
Webster Research Center, Xerox Corp.
800 Phillips Rd., Bldg. 114
Webster, N. Y. 14580


Enclosures

Figure 1.
Dear Barry:

In the course of our work on the assignment of the cycloheptatriene spectrum (1) we synthesized a mixture of the two deuterated hydrocarbons 1 and 2. An obvious extension was the synthesis of the corresponding chromium tricarbonyls and the assignment of their C-13 spectra. Our findings (table) confirm the tentative assignment for 5(2) and 5(3) given by Kreiter and Lang (2).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>Δσ</th>
</tr>
</thead>
<tbody>
<tr>
<td>5(1,6)</td>
<td>58.20</td>
<td>58.04</td>
<td>0.16</td>
</tr>
<tr>
<td>5(2,5)</td>
<td>102.1</td>
<td>102.1</td>
<td></td>
</tr>
<tr>
<td>5(3,4)</td>
<td>99.45</td>
<td>99.63</td>
<td></td>
</tr>
<tr>
<td>5(7)</td>
<td>24.43</td>
<td>24.06</td>
<td>0.37</td>
</tr>
<tr>
<td>5(CO)</td>
<td>232.88</td>
<td>232.88</td>
<td></td>
</tr>
</tbody>
</table>

An earlier assignment for C-2 and C-4 in quinazoline (3), however, must be reversed according to information we obtained from the undecoupled spectrum. The one bond J(C,H) values are J(2,H) = 20.4 and J(4,H) = 181 Hz. Both resonances are well distinguished by the additional splitting present only for C-4 due to vicinal coupling. As a consequence, our assignment of C-2 and C-4 in pteridine (4), which was based on increments derived from the quinazoline spectrum, must also be reversed.


Sincerely yours,
January 16, 1975

Dear Barry,

Rubidium NMR

We have observed $^{87}$Rb at 15.58 MHz using Ted's pulsed spectrometer (1). We find, in agreement with Robb and Smith (2), that the relaxation rate of the RbCl/H$_2$O solution is constant ($T_2^* = 2.7$ msec) from 1M to 60 mM; however we do find a shift of approximately 6 ppm to higher field. The linewidth is sensitive to the nature of the counter-ion being 10% greater for SCN$^-$ than Cl$^-$. The resonance line broadens further when D$_2$O is substituted for H$_2$O but no shift is discernable.

Rb$^+$ is isoelectronic with K$^+$ and additionally is similarly complexed by the antibiotic Valinomycin. The association constants for K$^+$ and Rb$^+$ are $8 \times 10^4$ M$^{-1}$ and $1.8 \times 10^5$ M$^{-1}$, respectively (3). Rb$^+$ is thus seen to be a much better choice of cation than Na$^+$ ($K = 4.7 \times 10^{-4}$) by several orders of magnitude.

In the accompanying figure using MeOH solution, the $^{87}$Rb$^+$ (Cl$^-$) line is shifted 24 ppm upfield and broadened by approximately 170 Hz with respect to the resonance in aqueous solution. The addition of Valinomycin produces broadening as shown, but no significant shifts.

A complete discussion of these results and results in
other solvent systems will be reported shortly.

Sincerely,

D. D. Macmurchie  
R. J. Cushley,  
Associate Professor

RJC/PL

References:


Legend to Figure:

Rb-5 (lower trace) 44mM RbCl in methanol.  
Rb/V-39 (upper trace) 64mM RbCl 25mM Valinomycin in methanol.
Spin Transmission into Rotating and Rigid Phenyl Groups:

Angular Dependence and Conformational Analysis

Dear Professor Shapiro:

'H nmr shifts of nickel complexes of the chelate type \( \text{I} \) obey the Curie 
\((1/\text{T}) \) law. \(^1,2\) This will become evident from the temperature independence 
of isotropic reduced \(^1,2\) shifts, \( \delta \). Figure 1 exhibits this expected in-
variance of \( \delta \) for the meta and para protons of the anilino groups in 
\( \text{Ia} \) as a representative example. However, the positive shifts (caused by 
spin polarization) of the 2- and 4-hydrogen atoms in the phenyl group 
bound to \( \text{C}^6 \) show an "abnormal" temperature dependence which we ascribe 
to thermally excited rotation about the \( \text{C}^6 \) bond.

\[
\delta = \delta_0 + \delta_2 \cos^2 \theta \quad (I)
\]

We suppose that transmission of positive \(^1,2\) spin density from the 2p 
orbital at \( \text{C}^6 \) into the phenyl substituent depends on the \( \cos^2 \) of the 
interplanar angle, \( \theta \) in eq I, between the phenyl ring and the chelate 
plane. The thermal expectation value, \( \langle \cos^2 \theta \rangle \), may be computed in the 
usual way, \(^1,2\) assuming the \( \sin^2 \) shaped potential energy function of eq 
II. The heavy traces through \( \delta (2-\text{H}) \) and \( \delta (4-\text{H}) \) in Figure 1 represent 
theoretical temperature dependences. Table I is a collection of the pa-
rameters used in eq II for these calculations. The angular dependent 
\( \delta_2 \) and independent \( \delta_0 \) shift contributions for \( \text{Ia-\text{g}} \) agree reasonably 
well with relative coupling constants from an INDO calculation \(^3\) on the 
twisted benzyl radical. A very small temperature dependence of \( \delta (3-\text{H}) \) 
in Figure I is also consistent with the INDO results, \(^3\) but the value of 
\( \delta (3-\text{H}) \) is much less negative than predicted (a usual failure of 
INDO).

We have obtained independent support for our parameters from the reduced 
shifts denoted for complexes \( \text{Ig} \) and \( \text{I} \). No temperature dependence is ob-
erved for \( \delta \) of the perpendicularly locked phenyl groups in \( \text{I} \). \( \delta (2-\text{H}) \) 
and \( \delta (4-\text{H}) \) have dropped quite closely to the respective \( \delta_0 \) in Table I, 
as expected for \( \cos^2 90^\circ = 0 \). On the other hand, the shifts \( \delta (2-\text{H}) \) 
and \( \delta (4-\text{H}) \) (slightly extrapolated toward \( 0^\circ \)) denoted for the almost 
coplanar phenyl group in \( \text{I} \) (\( \cos^2 0 = 1 \)) agree perfectly with \( \delta_0 + \delta_2 \) from 
Table I. Note that the 2-, 3-, and 4-H shift pattern disagrees with the 
relative coupling constants of most radicals with reportedly twisted 
aryl groups. \(^4\)

A rotational barrier of 1.3 kcal/mol in eq II for \( \text{Ia-g} \) appears reason-
able because biphenyl as a model for \( \text{Ia} \) is thought to possess a very 
shallow potential curve. The equilibrium angle, \( 5^\circ \) \((\pm 5^\circ) \) in eq II (i.e. 
almost coplanar arrangement at \( 0^\circ \)), is also in accord with seemingly 
contradicting values for biphenyl if apparent interplanar angles, \( \langle \theta \rangle \), 
are computed from the experimental shifts \( \delta \) and the tabulated \( \delta_0 \) and \( \delta_2 \) 
parameters. These implications for conformational analysis will be dis-
credited elsewhere. \(^5\)

Positive spin density transmitted from the 2p orbital at \( \text{C}^6 \) into a 
methyl group in \( \text{Ig} \) and \( \text{I} \) will result in a downfield methyl shift (part-
ly by hyperconjugation). Likewise, the 3-CH₃ groups of 18 have a positive \( \delta^r(CH_3) \) because negative spin density resides at C3. The experimental temperature dependences were simulated as before with the parameters of 1C-1G in Table I. It will now be interesting to see that methyl shifts also indicate a weak leakage of \( \tilde{\pi} \) spin density into the twisted phenyl substituent. The positive 3-CH₃ shift of 1G has strongly diminished in 6. Small negative 4-CH₃ and 4-CH₂ shifts remain in 6 and 5, respectively; compare these with \( \delta^r(CH_3) \) of 1G and 1J in Table I.

Complete orthogonality is only achieved in 7 where the 4-CH₃ shift becomes positive and agrees with \( \delta^r(CH_3) \) for 1E in Table I, as expected from eq I if \( \cos^2 \Theta \approx 0 \). We shall discuss later whether \( \delta^r \) is a measure of spin transmission in the \( \pi \)-system. Can we interpret \( \delta^r \) as the con-
Table I. Parameters of angular dependent (δ₂) and independent (δ₀) shift contributions for 1a-g from -50° to +140°.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ₀(2-H) (±1 ppm)</th>
<th>δ₂(2-H) (±3 ppm)</th>
<th>δ₀(4-H) (±0.5 ppm)</th>
<th>δ₂(4-H) (±1 ppm)</th>
<th>δ₀(CH₃) (±0.5 ppm)</th>
<th>δ₂(CH₃) (±1 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>4.65</td>
<td>18.0</td>
<td>1.95</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>5.0</td>
<td>18.0</td>
<td>2.35</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>5.25</td>
<td>18.0</td>
<td>2.65</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>5.55</td>
<td>17.5</td>
<td>2.55</td>
<td>17.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>3.5</td>
<td>19.5</td>
<td></td>
<td>0.5</td>
<td>-14.0</td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>3.8</td>
<td>19.5</td>
<td></td>
<td>0.15</td>
<td>-14.0</td>
<td></td>
</tr>
<tr>
<td>1g</td>
<td>4.25</td>
<td>19.0</td>
<td>2.8</td>
<td>16.0</td>
<td>1.1</td>
<td>+6.5</td>
</tr>
</tbody>
</table>

Contribution of π-delocalization?

Please credit this letter to the account of Prof. Gerhard Binsch with whom we have arranged for informing and contributive partnership in these Newsletters. Sincerely yours,

Rudolf Knorr
Heinz Polzer
Alfons Weiss

References:

Figure 1. Isotropically reduced shifts δ as a function of temperature.
Dear Professor Shapiro,

Cis- and trans vinyl-carbethoxy cyclopropanes.

The reaction of butadiene with $\text{N} = \text{N} = \text{OET}$ at $110^0\text{C}/8$ atm. gives two primary products which were separated by preparative G.L.C. have structures $^a$ (I) and (II). We were interested in these molecules for natural product syntheses.

To check the configurations of the two isomers the $^1$H-NMR-spectra were recorded. Both isomers gave very complicated spectra, which were simplified by adding Eu (FDO)$_3$ in small portions. From these "LIS-Reagent-Added"-spectra the coupling constants were extracted and based on the later the configuration of the two isomers was established.

The found coupling constants were:

<table>
<thead>
<tr>
<th>$^a$</th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>6.3 Hz</td>
<td>8.6</td>
</tr>
<tr>
<td>13</td>
<td>4.2</td>
<td>8.0</td>
</tr>
<tr>
<td>14</td>
<td>8.4</td>
<td>5.9</td>
</tr>
<tr>
<td>23</td>
<td>8.5</td>
<td>8.3</td>
</tr>
<tr>
<td>24</td>
<td>4.1</td>
<td>7.1</td>
</tr>
<tr>
<td>25</td>
<td>6.4</td>
<td>9.1</td>
</tr>
<tr>
<td>34</td>
<td>-5.3</td>
<td>-4.8</td>
</tr>
<tr>
<td>56</td>
<td>17.0</td>
<td>16.9</td>
</tr>
<tr>
<td>57</td>
<td>11 Hz</td>
<td>11 Hz</td>
</tr>
</tbody>
</table>
The chemical shifts in CDCl₃ (without Eu (FOD)₃) were approximated to be:

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ₁</td>
<td>1.0 ppm</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₂</td>
<td>2.0</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₃</td>
<td>1.3</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₄</td>
<td>1.6</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₅</td>
<td>5.4</td>
<td>5.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₆</td>
<td>5.1</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ₇</td>
<td>4.9</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


I trans-vinyl carboxy-cyclopropane
II cis-vinyl carboxy-cyclopropane
ADDITIVITY OF CARBON-13 SPIN-LATTICE RELAXATION TIMES

We have measured the $T_1$'s of all 108 carbon atoms in the 18 isomeric six carbon aliphatic monohydric alcohols. The relaxation times of the 95 magnetically non-equivalent carbon atoms in these alcohols were subjected to multiple linear regression analysis, and were found to follow an additivity relationship similar to that which allows the calculation of $^{13}$C chemical shifts where $T_1(k)$ is the spin-lattice relaxation time of the $k$th carbon,

$$T_1(k) = B + \sum A_i n_i + C + D$$

lattice relaxation time of the $k$th carbon, $B$ is a constant, $n_i$ is the number of carbon atoms in the $i$th position relative to the $k$th carbon atom, $A_i$ is the additive spin-lattice relaxation parameter assigned to the $i$th carbon atom, $C$ is the additive spin-lattice relaxation parameter describing the relationship of the $k$th carbon to the hydroxyl group ($\alpha$, $\beta$, etc.) and $D$ is the term which describes the relationship of the $k$th atom to its most highly branched neighbor, e.g. $3^0(2^3)$ means that each secondary carbon adjacent to a tertiary carbon will add 1.77+0.35 sec to the $T_1$ of the tertiary carbon (see Table). Using the parameters of the Table the $T_1$ of a given carbon within these 18 alcohols may be estimated with a surprising degree of success.

For example for 2,3-dimethyl-2-butanol:

$$C-C-O-C_1 \text{ for } C_2 = (5.21)+3(-0.71)+(-3.05)+(16.29) = 16.3 \text{ sec calc.}$$

$$15.0+1.5 \text{ sec found}$$

We are presently refining the analysis and investigating the generality of this additivity relationship in other systems.

Sincerely yours,

Curt P. Beeman
Postdoctoral Fellow

Kenneth L. Williamson
Professor of Chemistry
Regression Analysis of Spin-Lattice Relaxation Times in Six-Carbon Alcohols

Number of observations: 95
Number of independent variables: 14
Multiple correlation coefficient R squared: 0.968
Standard deviation in predicted T₁: ± 0.59 sec.
Constant term B: 5.21 ± 0.43 sec.

<table>
<thead>
<tr>
<th>Variable and coefficients $A^a$</th>
<th>Observations affected by variable, no.</th>
<th>Student T ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ $-0.71 \pm 0.24$</td>
<td>95</td>
<td>-3.0</td>
</tr>
<tr>
<td>$\gamma$ $0.26 \pm 0.11$</td>
<td>75</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Corrective terms$^a$

$$
\begin{align*}
\alpha & = -3.08 \pm 0.30 \\
\beta & = -1.94 \pm 0.31 \\
\gamma & = -1.28 \pm 0.29 \\
\delta & = -0.97 \pm 0.29 \\
1^\circ (3^\circ) & = -0.76 \pm 0.23 \\
1^\circ (4^\circ) & = -1.08 \pm 0.32 \\
3^\circ (2^\circ) & = 1.77 \pm 0.35 \\
3^\circ (3^\circ) & = 1.83 \pm 0.34 \\
3^\circ (4^\circ) & = 3.08 \pm 0.50 \\
4^\circ (2^\circ)b & = 15.33 \pm 0.66 \\
4^\circ (2^\circ)c & = 14.79 \pm 0.64 \\
4^\circ (3^\circ) & = 16.29 \pm 0.64
\end{align*}
$$

$^a$In seconds

$^b$Quaternary carbon adjacent to one methylene group

$^c$Quaternary carbon adjacent to two methylene groups (see Ref 3).
Dear Prof. Shapiro

I do apologize for being late with our contribution!

We continue to look at long-range coupling constants $J_{FH}$ and $J_{FF}$ in fluorinated aromatics. We think, we found a nice example to demonstrate the interannular coupling $J_{FF}$ in a biphenylic compound $[C_6F_2(SCH_3)_3]_2$ (fig. 1-3).

Corresponding NMR data are:

- $\delta_H (X_3) = 2.593$ ppm, $J_{MX} = 1.91$ Hz
- $\delta_H (Y_3) = 2.511$ ppm, $J_{AY} = 1.99$ Hz
- $\delta_H (Z_3) = 2.360$ ppm, $J_{AZ} = 0.85$ Hz
- $\delta_F (A) = 60.327$ ppm, $J_{AA'} = 0.00$ Hz
- $\delta_F (M) = 55.376$ ppm, $J_{MM'} = 2.53$ Hz = $5J_{FF}$
- $\delta_F$ vs. $\delta_F$
  - $J_{AM} = 15.37$ Hz
  - $J_{A'M} = 0.23$ Hz

$^1H$, $^{19}F$- and $^{19}F(^{1}H)$-NMR spectra were obtained at 100 MHz and 94 MHz.

We wish to thank Dr. R. K. Harris for making available his equipment at Norwich during a pleasant summer research period.
We wish to inquire TAMUNN-readers about some computing problems with LAOCOON III:

It was not possible to obtain converging solutions by iterative calculations on the 100 MHz proton NMR spectra of P - O - CH₂ - CH₃ compounds. Appropriate spectra are close to first order. We are grateful for hints to overcome the mathematical problem inside the optimization process.

Yours sincerely,

(G. Hägele)

(J. Richter)
Dear Professor Shapiro,

As part of our studies on platinum complexes, we have prepared some dimethyl telluride derivatives with the object of obtaining some values for J(PtTe)\( ^{195}\text{Pt},\ 33\% ,\ ^{125}\text{Te},\ 7\% \). This proved possible by H\( ^{125}\text{Te} \) INDDOR on strong solutions of \([\text{PtX}_3\text{TeMe}_2]\), \(X\) = Cl or Br but not for \([\text{PtX}_3\text{TeMe}_2]\)²⁻ because we could not find the \(^{125}\text{Te} \) satellites in the proton spectrum. The latter disappointment led us to notice that the frequency for \(^{125}\text{Te} \) is close (31.6 MHz at 2.3 Tesla) to that of \(^{19}\text{F} \) (32.1 MHz). Accordingly, we used our JEOL PFT-100 / \( ^{19}\text{F} \) system to obtain \(^{125}\text{Te} \) resonances with moderate success yet very little readjustment. The \(^{125}\text{Te} \) frequency was provided by a Schomandl ND100M frequency synthesizer via the usual JEOL wide-band amplifier, and the pulse amplifier readjusted to give a 90° pulse of 12 μsec. The only other adjustment was of the 'Anal. Tuning' of the receiver preamplifier. A very strong solution of tellurium tetrachloride in HCl/D₂O i.e. H₂TeCl₄ was used to set up the spectrometer. For solutions of 200 mg of (Bu₄N)₂[TeCl₆] in an 8 mm tube, some 10,000 pulses were used but for the platinum complexes stronger solutions and more pulses were required to find the satellites. For the halo-anions, the line width at half height was ca. 20 Hz and the \(^{125}\text{Te} \) seemed to relax quite rapidly.

J(PtTe) is much larger (5923 Hz) in \([\text{PtCl}_3\text{TeMe}_2]\)²⁻ where both lone pairs are coordinated than in \([\text{PtCl}_3\text{TeMe}_2]\)⁻ (1553 Hz) where one lone pair remains free.

These measurements seem to be the first direct \(^{125}\text{Te} \) observations and hence provide the first values for the chemical shift in \([\text{TeCl}_6]\)²⁻ to complement the \(^{1}H \) \(^{125}\text{Te} \) double resonance values for a range of organic tellurium compounds. Tellurium shifts, seen relatively insensitive to change of halide in contrast to metal nuclei such as \(^{195}\text{Pt} \) (e.g. [MCl₆]²⁻ vs. [MBr₆]²⁻ ref. 2) but show a rather notable response to oxidation state and/or coordination number.
The principle used to measure $^{125}$Te spectra can be applied to several other nuclei and we have also observed $^{27}$Al (using the $^{13}$C system) and $^7$Li (using the $^{31}$P system). In these cases, observation is much easier as the concentrations of the nuclei are far higher than for $^{125}$Te ($^{27}$Al, 100%; $^7$Li, 92.6%). The cost of these adaptations is, of course, zero though signal: noise is not optimized. Improvements could be made by retuning the receiver coil and then the only loss of sensitivity would be in the main receiver amplifier which is not retunable.

We have recently been observing $^{13}$C with $^{19}$F noise decoupling, for which the JEOL system is excellently suited. The spin decoupler will provide around 50 watts of 94.1MHz R.F. power and retuning of the decoupler coils is achieved in a minute or so. This power is sufficient for adequate decoupling over a bandwidth of 5MHz giving linewidths of <2Hz; better decoupling being possible on smaller noise bandwidths. The 5MHz bandwidth is sufficient to cover the aromatic fluorine region and we have used the technique to obtain spectra of a number of C$_6$F$_n$ compounds, particularly phosphorus derivatives. The table below gives a few results.

13C n.m.r. data for

<table>
<thead>
<tr>
<th></th>
<th>$^4$C</th>
<th>$^2$C</th>
<th>$^3$C</th>
<th>$^4$C</th>
<th>$^4$XC</th>
<th>$^2$XC</th>
<th>$^3$XC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$F$_5$H</td>
<td>100.4</td>
<td>146.5</td>
<td>137.7</td>
<td>142.0</td>
<td>170.4</td>
<td>7.3</td>
<td>9.3</td>
</tr>
<tr>
<td>C$_6$F$_5$Br</td>
<td>94.7</td>
<td>145.3</td>
<td>138.1</td>
<td>141.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C$_6$F$_5$)$_3$P</td>
<td>104.9</td>
<td>148.0</td>
<td>138.0</td>
<td>143.5</td>
<td>35.1</td>
<td>12.2</td>
<td>0</td>
</tr>
<tr>
<td>(C$_6$F$_5$)$_3$PO</td>
<td>107.2</td>
<td>147.7</td>
<td>138.2</td>
<td>145.7</td>
<td>114.5</td>
<td>1.6</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Shifts in ppm from T.M.S. Coupling constants in Hz.

The most interesting feature is the difference in the JCP values for ortho- and meta - carbons in the three and five valent phosphorus species. This behaviour is common to all the phosphorus compounds we have measured.

Yours sincerely,

Robin Goodfellow

R.J. Goodfellow M. Murray

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

Paramagnetic organometallics investigated by $^{13}$C PFT NMR: selective proton decoupling of phenyl resonances.

Lieber Professor Shapiro!

Chrom(III)acetylacetonat ist zum Handwerkszeug der $^{13}$C-Spektroskopiker geworden. Diesen Vorzug verdankt es der Tatsache, daß die erwünschte Verringerung von $T_2$ nicht durch stark verbreiterte Signale und verfälschte Verzögerungen erkauft werden muß. Mit zunehmender Konzentration der paramagnetischen Zentren bzw. mit deren abnehmenden Abstand vom beobachteten C-Atom verschlechtern sich die Beobachtungsmöglichkeiten drastisch. Ein Grenzfall ist erreicht, wenn das paramagnetische Zentrum direkt eingebaut wird in das Molekül, dessen $^{13}$C-Resonanzen beobachtet werden sollen. Daß auch dann noch informationsreiche $^{12}$C-Spektren aufgenommen werden können, dafür ist Bis(h-1,3-diphenylcyclopentadienyl)kobalt ein Beispiel.

Während die Fünfring-C-Atome extrem schwer zu ermitteln sind, wird für die Phenylsignale sogar $J$ (CH) aufgelöst. Im $^{12}$C-wie auch im $^1$H-Spektrum wird zugleich ein erheblicher paramagnetischer Beitrag zur Signalverschiebung sichtbar. Das paramagnetische Metallzentrum wirkt als "eingebautes Verschiebungsreagenz" und trennt z.B. o-, m- und p-Phenyl- $^1$H-Signale (Abb. A). Dieses Verhalten ermöglicht eine selektive Protonen-entkopplung der Phenyl-$^{13}$C-Signale, welche bei diamagnetischen Phenylverbindungen bisher nicht möglich ist.

Im $^1$H-Spektrum in Abb. A sind die jeweiligen Entkopplungs frequenzen der nachfolgenden $^{13}$C-Spektren (Abb. B-D) vermerkt. Man erkennt, daß präzises Treffen (D) der $^1$H-Resonanz nicht notwendig ist. Vielmehr kann das off-resonance-Experiment selektiv geführt werden (B und C).
Mehr über $^{13}$C-Multiplettspektren paramagnetischer Komplexe erscheint demnächst im J. Organometal. Chem.

Ich bitte, den Beitrag zugunsten von Prof. H.P. Fritz zu vermerken, und bleibe mit besten Grüßen

F.H. Köhler
Stingy

Fisher Deuterated Solvents have such outstanding isotopic and chemical purity, it's against their nature to make NMR spectrum contributions.

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Fisher Scientific Company
January 28, 1975

Dr. Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas

J(CP) in a Three-membered Phosphorus Heterocycle;
J(NP) in (Me₂N)₃PX, X = :, S, and O

Dear Barry,

We've been extending our series of saturated phosphorus heterocycles in both directions and now have results for the smallest case (courtesy of the synthetic efforts of Dorothy Denney and Ms. Terry Wanus, Rutgers):

J = \[\begin{array}{c}
\text{CP} \\
-39.7 \\
\text{(-)38.7} \\
\text{(+)} 7.0 \\
0
\end{array}\]

As you might recall (TAMNMRN, 187-26) we had examined 6,5, and 4-membered rings. A few numbers there were incorrectly reported and should be revised for the 6- and 5-membered rings:

2.5

2.5

The very large, and negative, ring coupling in the three-membered ring is unusual, especially in view of the very small coupling for the 4-membered case. We've since done experiments on a 2,2,3,3,4-pentamethyl 4-membered ring case. We've found a positive coupling again (+4.4) for the C-4 methine. The phenyl one-bond couplings seem to proceed uneventfully throughout the series.

Our coupling interests are now including PN couplings in natural-abundance N¹⁵ spectra. So far we've determined J(PN) = +59.1 for X = :, 6.0 for X = S, and -26.9 for X = O. The sign change for P(III) → P(V) is reminiscent of the PC situation.

See you at Asilomar,

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

Dear Professor Shapiro,

In order to maintain our subscription to TAMU NMR Newsletters, we thought it appropriate to write about some of our recent $^{13}$C measurements on boron esters. These are best illustrated by a couple of examples.

(i) We routinely examine $^{11}$B spectra to determine ring size in cyclic boron esters. Recently, we examined a compound thought to be I, but in which the ring boron had a shift of 34.4 ppm (relative to ext. Et$_2$OBF$_3$), which is in the range we find characteristic for ethylborolans. (ethylborolans, 34-35 ppm; ethylborirans, 30-31 ppm)

\[ \text{Et}_2\text{B} \quad \text{I} \]

$^{13}$C cleared the matter up quite nicely, since in the lower field range there were three signals, at 76.3, 67.6 and 67.1 ppm (relative to int. TMS), confirming that the structure was II. The interesting feature of this spectrum was that the resonances of the carbon atoms directly bonded to boron were broadened greatly due to scalar relaxation. The methylene carbon resonance of $^{2}$OEt was found at approximately 3.8 ppm, and that of $^{3}$OEt$_2$ was at 12.1 ppm (half-width ca. 60Hz). The methyl carbons gave sharp signals at 8.0 and 7.8 ppm respectively.

The broadening of the $^{13}$C signals in a number of similar compounds showed the expected variation with the linewidths of the $^{11}$B signals - as these become broader, the $^{13}$C resonances become a sharper singlet, and when the boron lines are relatively sharp, $^{13}$C - $^{11}$B coupling can be discerned.

(ii) In the following example, with an OEt$_2$ group directly bonded to a double bond, $\text{Z}$ and $\text{E}$ isomers are possible (III and IV)
The $^{13}$C nmr spectra of a pure isomer and of a mixture of both isomers were recorded. Once again, the methylene carbons of the $\text{OBEt}_2$ give a very broad peak. Separate signals for the two isomers are seen for carbons 1-5. As expected, the resonance of $C_1$ in $\text{E}$ lies well upfield of the corresponding signal in $\text{Z}$; the chemical shift difference between these signals is 5.0 ppm, compared with 5.1 ppm for the corresponding carbons in the cis and trans 2-hexenes.\(^{(1)}\)

$C_4$ in the $\text{E}$ isomer has practically the same shift (29.5 ppm) as in cis 2-hexene (29.6 ppm), while in the $\text{Z}$ isomer, $C_4$ is shifted by 7.5 ppm to higher field relative to the olefin. The resonances of the olefinic carbons of the more crowded $\text{Z}$ isomer are found upfield of the corresponding signals for the $\text{E}$ isomer.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Z}$</th>
<th>$\text{E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>12.1</td>
<td>17.1</td>
</tr>
<tr>
<td>$C_2$</td>
<td>148.1</td>
<td>149.0</td>
</tr>
<tr>
<td>$C_3$</td>
<td>109.8</td>
<td>111.0</td>
</tr>
<tr>
<td>$C_4$</td>
<td>28.0</td>
<td>28.5</td>
</tr>
</tbody>
</table>

\(^{(1)}\)D. Dorman, M. Jautelat, J.D. Roberts; \textit{J. Org. Chem.} \textbf{36}, 2757 (1971)

Yours Sincerely

\textit{Richard J. Mynott}  
Dr. Richard J. Mynott

\textit{Professor Ernst G. Hoffmann}
The tentative program of the 16th ENC is given below. Anyone not already on the mailing list or who wishes to make further inquiries should address his requests to the Secretary, Dr. K. L. Williamson (address given above). Information concerning accommodation and other local arrangements' matters may be obtained directly from the Local Arrangements Chairman, Dr. R. E. Lundin (address given above).

**Poster Session**: In addition to the presentations listed below, papers may be submitted for inclusion in a Poster Session to be held on an informal basis Monday afternoon, April 21, under the Co-Chairpersons'hip of Drs. L. J. Durham* and C. G. Moreland. Anyone wishing to have a paper included in this session should submit a substantial abstract, along with any other material to be posted, directly to either of the Chairpersons. Anyone wishing to do so may contact either of the Chairpersons by telephone in advance of submitting an abstract, to discuss any questions of suitability of topic, results, etc. For papers accepted for this session, abstracts and other material must be received by one of the Chairpersons no later than April 7, in order to allow sufficient time for the preparation of copies for distribution at the Conference.

* Dr. Lois J. Durham  
Department of Chemistry  
Stanford University  
Stanford, CA 94305  
(415)497-1610

** Dr. Charles G. Moreland  
Department of Chemistry  
North Carolina State University  
Raleigh, NC 27607  
(919)737-2998

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**TENTATIVE PROGRAM 16TH ENC**

**CHAIRMAN**: J. D. SWALEN

**LOCAL ARRANGEMENTS CHAIRMAN**: R. E. LUNDIN

**Monday, April 21 (Morning)**

"New Digital Techniques", Chairman: T. C. Farrar

J. Cooper  
G. Samuelson  
D. Ziessow  

"Use & Misuse of Computers in FT/NMR"

"Application of Digital Phase Lock Techniques in FT/NMR Spectroscopy"

"NMR Spectroscopy: Saturation Behavior and Applications"
"New Experimental Techniques", Chairman: L. F. Johnson

M. P. Klein  "Fourier Internuclear Difference Spectroscopy (FINDS): A Sensitive Method for Observing $^{15}$N, Etc. at Natural Abundance"

D. M. Wilson  "Applications of Double Decoupled $^{13}$C($^1$H) NMR"

L. F. Johnson  "Quadrature FT NMR with a Four Pulse Cycle"

D. D. Traficante  "The Effective Utilization of Pulsed RF Power in FT NMR"

W. S. Hinshaw  "NMR Image Formation Using Time Dependent Gradients"

Monday, April 21 (Afternoon)

Poster Session, Co-Chairpersons: L. J. Durham and C. G. Moreland

Monday, April 21 (Evening)

"Biomolecules I", Chairman: S. I. Chan

J. Richards  "Catalysis by Serine Proteases"

R. D. Brown  "The Magnetic Field Dependence of $T_1$ of Solvent Water Protons by Field Cycling: Application to Paramagnetic Metalloproteins"

J. Seelig  "Deuterium and Phosphorus Magnetic Resonance of Lipid Membranes—Chain Flexibility and Head Group Motion"

"Biomolecules II", Chairman: F. A. L. Anet

S. I. Chan  "Use of Deuterated Phosphate Lipids to Elucidate Lipid-Lipid Interaction in Bilayer Membrane"

S. B. Roeder  "Application of Solid State NMR Techniques to the Study of Ordered Fluids and Membrane Models"

S. H. Smallcombe  "Temperature Jump NMR Study of Intermediates in Refolding of Ribonuclease"

Tuesday, April 22 (Morning)

"NMR Solids", Chairman: R. W. Vaughn

E. L. Hahn  "Deuter-anomaly"

I. J. Lowe  "Short Time Behavior of Free Induction Decay"

C. S. Yannoni  "Polarizing Nuclei by Cross-Relaxation with Quadrupolar Spins in High Magnetic Fields"

"Spin Polarization", Chairman: J. Bargon

M. Cocivera  "NMR Spectroscopy of Flowing Liquids Applied to Studies of Chemical Reactions"

W. Veeman  "Optically Induced Spin Polarization"

J. P. Wolfe  "Dynamic Polarization by Optical Excitation of Molecular Vibrations"
Tuesday, April 22 (Afternoon)

"Lanthanide-Induced Shifts", Chairman: B. L. Shapiro

K. L. Williamson  "Conformation Analysis of Optically Active Alcohols Using Optically Active Shift Reagents and $^{13}$C NMR"

M. R. Willcott III  "SIMPLEX Optimization of LIS Parameters"

J. L. Sudmeier  "Conformational Analysis of Cyclic-2',3'-adenosine Monophosphate in D$_2$O Using Lanthanide Shift Reagents"

R. M. Wing  "Structure and Conformation of Vitamin D Analogs in Solution"

"NMR in Paramagnetic Molecules", Chairman: G. N. LaMar

W. DeW. Horrocks, Jr.  "Lanthanide Porphyrin Complexes: Potential Dipolar Probes for Biological Systems"

G. N. LaMar  "Proton Relaxation Times as Structural Probes for the Dimerization of Porphyrins"

G. C. Levy  "(Mis) Understandings of Spin-Lattice Relaxation in Solutions Containing Somewhat Inert Paramagnetic Relaxation Reagents"

I. Morishima  "NMR Studies of Ferric and Ferrous Hemoproteins and Hemoenzymes with Various Ligand Molecules"

Wednesday, April 23 (Morning)

"Wide-Line NMR and Surfaces", Chairman: W. S. Brey

W. Derbyshire  "Frequency Dependence Effects in Interfacial Systems"

D. Woessner  "Pulsed NMR for the Determinations of Proton Exchange Rates in Preferentially Oriented Water Molecules"

I. Gay  "Carbon-13 Spectroscopy of Adsorbed Molecules"

"High Resolution NMR of Solid Polymers", Chairman: J. Schaefer

A. C. Lind  "Multiple Pulse High Resolution Proton NMR of Solid Polymers"

D. L. Vander Hart  "Studies of Anisotropic Molecular Motion in Solid Polymers by Line Shape Analysis of Proton Decoupled Carbon-13 Spectra"

J. Schaefer  "Cross Polarization Carbon-13 NMR Studies of Solid Amorphous Polymers"

Wednesday, April 23 (Evening)

"Planetary Session", Chairman: E. D. Becker

R. Freeman  "Carbon-13 Spin-Spin Relaxation"

R. E. Richards  "Phosphorus Resonances in Intact Biological Tissues"

E. Lippert  "Relations Between NMR Solvent Shifts and..."
"Other Nuclei", Chairman: G. E. Maciel

R. R. Sharp  "Nuclear Relaxation of Some Less Common Resonances: $^{207}$Pb, $^{119}$Sn, $^{111}$Cd, $^{81}$Br and $^{127}$Tl"

R. R. Vold  "Relaxation of $^{170}$, $^{97}$Mo and $^{95}$Mo in Aqueous Molybdate and Related Systems"

P. D. Ellis  "Recent Progress in $^{113}$Cd NMR"

J. J. Dechter  "$^{205}$Tl NMR as a Probe of Binding Sites in Systems of Biological Interest"

R. L. Lichter  "New Experimental Aspects of $^{15}$N NMR"

Thursday, April 24 (Morning)

"Relaxation", Chairman: R. L. Vold

J. H. Noggle  "$T_1O$ Measurement with FT NMR Spectrometers"

D. M. Grant  "Coupled Relaxation Involving Carbon-13"

H. D. W. Hill  "Selective Relaxation Measurements in Proton NMR"

"Experimental Aspects of Carbon-13 Magnetic Resonance", Chairman: D. M. Grant

J. B. Grutzner  "Coherent Broad Band Decoupling in Carbon-13 NMR"

F. E. Fagerness  "Versatile Proton Decoupler for Carbon-13 NMR Studies"

J. D. Gust  "The New Bruker WH180 Spectrometer in Carbon-13 and Nitrogen-15 Studies"

J. D. Roberts  "The New Bruker WH180 Spectrometer in Carbon-13 and Nitrogen-15 Studies"

A. Allerhand, et al.  "Pros and Cons of Large Sample Probes"
Dear Barry,

We have been running our TT-14 system observe several different nuclei at 15.09 MHz. So far, spectra have been obtained from 13.40, 13.60, and 14.15 K Gauss, respectively, using a strong sample, rapid pulsing, and come in as the resonance field is TT-14 console are made, and therefore, no lower field strengths. For most applica-adequate stability for short runs, and scheme, whereby a peak in the transformed serves as a register peak for addition of.

Shown here is a 1000 Hz plot of the available biological fluid. Nine tran- and the measured line width is 14 Hz. of course, related to measurement.

Shown on the next page is a set of an aluminum sulfate (Mallinckrodt AR were collected for each D1 (τ) value, f.i.d.'s were stored on disc and the T1 value for the major peak turns out to around 40 msec. I have no assignment relative to the major peak, upon dilut-when a new bottle of aluminum sulfate

at reduced magnetic field strength to MHz, using the Allerhand 20 mm probe. 31p, 23Na, 27Al, and 79Br at 8.76. The field strength is adjusted readily an audio monitor to hear the f.i.d. approached. No modifications of the deuterium lock channel exists at the tions the flux stabilizer provides for longer runs we use a "computer lock" spectrum of the first block of f.i.d.'s subsequent blocks of data.

23Na resonance from a common, readily sients were collected in 1.8 seconds, The significance of this measurement is, or other factors. inversion-recovery 27Al spectra from grade)-H2O solution. Eight f.i.d.'s which ranged from 10-300 msec. The total experiment time was 52 seconds. The be 61 msec, and for the minor peak for the minor peak which doesn't change, ing the sample. I intend to try again arrives.

Best regards,

LeRoy F. Johnson
>LP
LFJ  2JAN75
"ALR<(SO4)3 IN H2O DIL SOLN

T/IR
P1 = 64.0000
P2 = 32.0000
D5 = .000000
DI = .010000
ACQ = 5
SIZE = 1024
AT = .512000 SEC
ADC = 0
DE = 0
SU = 1030.03
OF = -672.126
SF = 15.0905
LB = 1.30002
PA = 24.2596
PH = -42.7375

>DI
#  1 = 0.02000
#  2 = 0.02000
#  3 = 0.03000
#  4 = 0.04000
#  5 = 0.05000
#  6 = 0.06000
#  7 = 0.07000
#  8 = 0.08000
#  9 = 0.09000
# 10 = 0.10000
# 11 = 0.29999
January 23, 1975

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

Dear Barry:

NMR SYSTEM FOR SALE

We have for sale a Varian HR-300 Superconducting NMR Spectrometer. The system is equipped for Variable temperature, 5-mm Proton, Frequency Sweep operation. Included in the selling price of $110,000 will be complete factory reconditioning, warranty and installation.

Interested parties please contact Robert Sheldon at Varian Associates, 611 Hansen Way, Box D-421, Palo Alto, CA 94303 - Telephone: (415) 493-4000 extension 3047.

Sincerely,

Robert Sheldon

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

Subject: Varian V-2100 and V-2200 Magnet Power Supplies.

Dear Dr. Shapiro

Some of these power supplies have successfully been converted to Solid State pass banks and rectifiers to save the cost of future tube replacements and cut down on the power dissipation.

I would like to make such a Solid State conversion kit commercially available, provided there is a demand.

To obtain some idea on the number of these supplies still in use, what they are used for and if the user might be interested in such a kit, please fill in the lower part of this page and send it to me.

Sincerely

Rolf Tschudin

>Name:
>Institute:
>Street:
>City: State: Zip:
>I own a V-2100 ( ) used on a HR/HA-60 ( ) ,WL/BPR ( )
>V-2200 ( ) HR/HA-100( ) other ( )
>I am interested ( ) have already converted ( )
>not interested ( )
Now the XL-100A NMR Spectrometer lets you think small.

Thanks to another Varian first, a 1-mm Insert Accessory for the XL-100A Pulsed-Fourier Transform NMR Spectrometer, scientists such as biochemists and pharmaceutical chemists who have to work with limited sample quantities can obtain rapid proton NMR analysis of microgram samples.

Using the insert, it's possible to run spectra of 50 µg or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of δ9-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 µg of sample in a 1-mm tube) and Spectrum C (20 µg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

The sample volume in the 1-mm Insert is so much less than the 400 µl required for 5-mm tubes that use of deuterated species becomes more economical.

The 1-mm capillary has its own spinner turbine attached. Unlike other existing techniques designed to accommodate small quantities of samples, there are no plugs to adjust and no sample positioning is necessary. Proper positioning is automatic thereby assuring reproducible homogeneity.

Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.

The spectrum of 20 µg of δ9-THC (tetrahydrocannabinol) in a 1-mm capillary with 5 µl CDC3. Total time was 16.25 minutes (1000 pulses at 1-second intervals). The spectrum of a concentrated sample is partially reproduced above for comparison. Assignments are written over peaks.

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Spectra: $^1$H of ODCB; $^{13}$C of ODCB with proton spin-coupling.