B. L. Shapiro
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Symposium
First International Symposium on Organic Chemistry of Germanium, Tin and Lead,
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J. Prestien and H. Guenther
$^{12}$C-Labeling - A Novel Isotopic Substitution-Technique

R. T. Pajer and R. J. Cushley
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Deadline Dates: No. 188: 6 May 1974
No. 189: 3 June 1974

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Those who have been following our occasional statements concerning the TAMU NMR Newsletter finances will learn without surprise that as we approach the final quarter of our fiscal year, our financial picture continues to look more and more grim. The simple fact is that increased costs have not been met by increased income. Our Advertisers, Sponsors and Contributors have all come forward most generously, but there simply are not enough of them. It would be greatly appreciated if each Newsletter reader would review the list of Advertisers, Sponsors and Contributors, and take note of them as well as initiating such action as you deem appropriate to let these public spirited individuals and corporations know that their efforts and monies are appreciated. It would, of course, be most useful if you could encourage (or even extort?) additional financial participation in the Newsletter by other Advertisers, Sponsors and Contributors. I continue to feel that many organizations could help support the Newsletter for a microscopic fraction of their annual investment in, and use of, NMR spectroscopy.

If the Newsletter is to survive in its present, or an only slightly modified form, it is essential that we adopt some immediate economies. Therefore, the following:

1. Newsletter Mailing. The issue containing this notice will be the last to be sent by First-Class mail in the U.S. and Canada and by Air Mail-Printed Matter to overseas recipients. Significant economies can be effected by using Third Class (Printed Matter) for domestic and Canadian mailings, and Printed Matter-Surface mail for our overseas recipients. We will, however, continue to use the best possible First Class or Air Mail service for our Advertisers, Sponsors and Contributors, as well as any other recipients who would like to send us an additional amount of money for the extra postage involved.

2. Length of Technical Contributions to the Newsletter. Effective immediately, I feel it is essential that we limit any one contribution to a maximum of three pages, and to be fairly strict about enforcement of this policy. With due attention to keeping margins to a minimum size, single spacing, formatting figures and photographs for minimum space utilization, this should really impose little if any restrictions to the amount of subject matter actually purveyed. Needless to say, one- and two-page contributions are preferable. However, it must be emphasized that we do not wish these space restrictions to be used as an excuse to give an overly brief and less useful account of your work than you feel desirable.

Again, we call for constructive ideas on how we might either raise more money or cut our costs without sacrificing the apparently successful monthly format of the Newsletter. (We must continue to publish the Newsletter monthly, if only to justify our current level of advertising income.)

Should our financial situation be alleviated by some minor miracles, we will of course be most happy to rescind one or both of the above restrictions on the Newsletter. If on the other hand the situation grows worse, and even more of my time and effort are required to operate the Newsletter as at present, even more stringent measures will be adopted as necessary.

B. L. Shapiro
Recently we reported 100 MHz 1H studies of conformational transitions in solutions of heterogeneous oxidised-wool proteins while attempts to induce such transitions by temperature variation or addition of urea were unsuccessful in TFA/chloroform-δ and TFA/m-toluenesulphonic solvent systems. It was found that most resonances in the spectra of ac-keratose and urea-soluble3 sample U.3.3 broadened at room temperature when a CDCl3/DCDOD solvent system was used with as much as 50 w/w CDCl3. Taken with o.F.A. measurements, this was regarded as consistent with the notion that these wool protein fractions (which contain relatively low percentages of cysteic acid residues) gradually increase in degree of helicity with increase of CDCl3 in the solvent.

220 MHz 1H measurements have now been carried out (by B.J.D.) on aqueous solutions of some effectively homogeneous high-sulphur fractions of reduced wool, S-carboxymethyl keratin (J.K.) 3-III 3b (the first keratin protein to have been sequenced)4 and 30K d-III 8b, both samples kindly provided by Dr. T. Haylett.

For protein solutions both in D2O and in trifluoroacetic acid, peaks were assigned to resonances of constituent amino acids from a knowledge of the amino acid composition of the proteins and from known amino acid and peptide chemical shifts. Some confirmation of these assignments is provided by the agreement between the experimental spectrum for 30K 1-III 8b in D2O (Fig. 1) and that simulated by the m/Donald & Phillips5 procedure.

The absence of noticeable spectral changes when the temperature is raised from 295 to 351K is consistent with a predominance of unordered conformation for these proteins, which contain a relatively high proportion of sulphur-containing amino acids as well as of other amino acids known not to favour helical conformation.

Dr. B. J. Dale is now at Abbott Laboratories, Ltd., Queenborough, Kent, England.

Yours sincerely,

B. J. Dale

187-2
References

1. B.J. Dale and D.H. Jones, Polymer, 14, 523 (1973)

Fig. 1. Part of simulated (a) and (b) and experimental (c) 220 MHz spectra of SCHB-III B2 in D₂O. Chemical shifts are in p.p.m. downfield from 2,2-dimethyl-2-silapentane-5-sulphonic acid sodium salt (DSS).
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Dear Professor Shapiro,

In enolesters of 1,3-diketones (C=O-diacyl-enols) an intramolecular O\(\rightarrow\)O acyl migration can be observed by \(^1\)H NMR. We have now used \(^{13}\)C NMR to check these findings. At \(\sim 35^\circ\) the methyl signals at \(\delta = 21.7\) and \(30.5\) for \(^{22}\) are broadened, apparently as a result of an intermediate rate of acetyl migration. Accordingly, the sp\(^2\) carbon signals of \(^{22}\) at \(156.3\) and \(193.8\) and of \(^{42}\) at \(157.0\) and \(187.7\) are also broadened. \(^{32}\), however, does not show any broadening. Its acetyl groups are in the E arrangement which means that the O-acetyl group cannot migrate.

\(^{32}\) is converted to itself by an O\(\rightarrow\)O acyl migration. In the case of \(^{52}\) this process should give rise to a constitutional isomer \(^6\). \(^1\)H NMR measurements between \(+60^\circ\) and \(-35^\circ\) yield only one set of resonances for a CDCl\(_3\) solution. Therefore, such solutions contain predominantly either \(^{52}\) or \(^6\). The \(\delta\)-values assigned to formula \(^{52}\) are consistent with the results for \(^{22}\), \(^{42}\), \(^{4E}\), \(^{42}\), and \(^{52}\), whereas the assignment of these same \(\delta\)-values to constitution \(^6\) fails completely for the signal at 19.5 (see formula). Apparently, the O-acyl group prefers to be fixed to the "methyl side" (\(^{52}\)), not to the "phenyl side" (\(^6\)) of the parent C\(^2\)-acyl-enol system.

It has been proposed\(^3\) that the ground-state of such diacyl-enols undergoes a special attractive interaction (e.g. dotted...
The numbers appearing with the formulae are $\delta$-values (TMS, $CDCl_3$) at $\sim 35^\circ$ (except for $\delta_{42}$, measured at $\sim 10^\circ$). For $\delta_{22}$, $\delta_{32}$, and $\delta_{6}$ the $\delta$-values for the carbonyl groups might be interchanged.
line in formula \( \frac{3}{2} \) between the \( \ce{C^2} \) and the \( \ce{O-acyl} \) groups. Our IR measurements do not support this hypothesis. The \( \ce{^{13}C} \) spectra might reveal this attractive interaction by unusual shifts of the two participating carbonyl groups. However, the \( \delta \)-values of \( \frac{2}{2} \) (\( \ce{C^2-acyl} 193.8, \ce{O-acyl} 166.7 \)) and \( \frac{2}{2} \) (\( \ce{C^2-acyl} 196.4, \ce{O-acyl} 167.4 \)) are very similar. Therefore, at this moment we are not convinced of the above mentioned special arrangement of carbonyl groups.

In addition to the investigation of acyl migrations, we are continuing our \( \ce{^1H} \) NMR studies on non-planar butadienes\(^4\) and on diastereomeric and enantiomeric association complexes\(^5\), including some \( \ce{^{13}C} \) work.

A postdoctoral position in our group has to be filled, June 1974 being the earliest possible date at which the position is available. Anyone interested should write to A.M. By the way, Ratisbona (Bavaria) is an old, interesting town with a new university, founded in 1965.

Sincerely yours,

Albrecht Mannschreck
Hans Dvořák
Thomas Burgemeister

2) A. Mannschreck, H. Dvořák, and T. Burgemeister, Tetrahedron Lett. 1974, to be published; preprints available. Measurements carried out on Varian XL-100 in the PFT mode. Some of the spectra provided by Drs. B. Kolb, Regensburg, and J. Müller, Marburg.
Title: An Inexpensive Gas Thermostat

Dear Professor Shapiro,

Please accept this letter as our first contribution for your newsletter.

We have recently developed this circuit for thermostatting a gas flow system in a Varian A56/60D spectrometer. It uses the original probe heater (or a 24W/24V soldering iron heater in other systems), and a thermocouple attached to a Comark Electronic thermometer (Type 1625 Comark Electronics Ltd., Brookside Avenue, Rushington, Sussex, G.B.), which registers temperature in 10°C ranges from -100°C to +290°C and gives a 0-1V output within each range. The difference between this output and a 0-1V variable source (SET TEMP) is used to drive a heater in the gas stream, so that we have a closed loop servo system. The SET GAIN control is used to adjust the loop gain of the system so that the temperature does not hunt. Control is better than ±0.1°C. To protect the heater power is turned off if the gas pressure drops, and the maximum heater current is limited.

Some recent $^{31}$P investigations by one of us (K. Dillon) into halide scrambling in $^{\text{III}}$ halides has led to the assignment of the PCl$_3$/PBr$_3$/PI$_3$ spectrum shown overleaf. It illustrates the use of quadrupolar broadening in assignment.

Yours sincerely,

K.B. Dillon.
R.S. Matthews.
A. Royston.
FIG. 2  $^{31}$p NMR Spectrum of a PCl$_3$-PBr$_3$-PI$_3$ Mixture
TEMPERATURE CONTROLLER - Circuit Diagram

- System Connections

[Diagram of the temperature controller circuit with various components and connections.]

Power Supplies
+15V, 25mA each
-15V, regulated
+23V/2A unregulated
Dear Professor Shapiro,

we feel it is time to renew our subscription of TAMUN NMR NEWSLETTERS before receiving one of these red reminders. During the year passed we did some line shape analytical work for spectral analysts using a BRUKER 60 spectrometer. We added extra outputs for the Y-component and the trigger impulse of the digitized X-axis of our H 60 DIGITAL recorder. Using a SCHNEIDER digital-voltmeter in connection with a DIEHL interphase and paper tape punch leads to a series of digitized Y-values punched in SBCDE-code. A SIEMENS computer 4004 reads these tapes in machine-code, transforms the data to FORTRAN-accessible values, processes an error-analysis and finally sets up with the aid of some external informations—a correct set of X/Y-pairs for transition frequencies and relative intensities.

Experimental spectra are compared with theoretical ones, generated in problem-specific subroutines, to find the optimal parameter set by the criterion of least squares. The non-linear-optimization problem is solved by two subroutines QCPE 59 and 61 working according to POWELL 1). The complete set of master-program and subroutines is supposed to be fairly general.—Some simple electronic modifications on the H 60 enabled us to read in optically arbitrary spectra to make use of "old spectra" in addition to on-line spectra. Please credit this contribution to the benefit of the NMR group in Düsseldorf.

1) M.J.D.POWELL, Comp.J.7,155(1964)

Yours sincerely

(Gerhard Hägele)
Recently Gus Lienhard (Dartmouth Medical School) and I have been using $^{11}$B FT NMR to study the binding of phenylethane boronic acid (PEBA) to $\alpha$-chymotrypsin. During these studies we were confused for a long time (although many readers may say I could have told you so) by a resonance which turned out to come from the Wilmad 12 mm NMR tubes and I was surprised when reminded that pyrex is a borosilicate glass containing ~10-20% $B_2O_3$. This resonance is shown on the enclosed figure underneath the sharper resonance corresponding to 2x$10^{-3}$ M PEBA. This spectrum is 10,240 transients, spectral width shown approximately 9000 Hz, with acquisition time 0.01 sec acquired on a Varian XL-100 NMR spectrometer. The chemical shift of the pyrex peak is ~1000 Hz downfield from $B(OH)_4^-$ at pH ~10 and the linewidth is ~2500 Hz. This seems relatively narrow and might then reflect a relatively symmetric environment for the quadrupolar relaxed boron in pyrex. We have now switched to plastic NMR tubes!

With best regards.

Yours sincerely,

Brian D. Sykes

Enc.
March 7, 1974

Dear Professor Shapiro,

Double Inversion at Two Nitrogen of A Bicyclic Hydrazine.

As a means to investigate the rate process involved in organic compounds, C-13 n.m.r. spectroscopy has some advantage over p.m.r. in that the C-13 spectra are much less susceptible to effects other than structural change (if any) caused by the rate process.

An example is the C-13 study of the double inversion at two nitrogens of 2,3-dimethyl-2,3-diazabicyclo[2.2.1]heptane. At 76°C, four sharp singlets are observed, indicating that the inversion is rapid in n.m.r. timescale. As the temperature lowers, peaks other than C-7 singlet gradually broaden, and coalesce at about -10°C. Upon further cooling, three sets of doublets, of equal intensity, appear again. At -39°C the freezing seems complete.

The fact that the C-7 peak remains a sharp singlet throughout the temperature range investigated clearly indicates that the double inversion is trans(a) → trans(a') rather than cis(b) ↔ cis(c). If the latter is the case C-7 should give two peaks at lower temperature since an accidental degeneracy of C-7 peaks for (b) and (c) is highly unlikely.

A similar investigations were attempted with the aid of p.m.r. spectroscopy (1,2). In these cases, however, the possibility of cis ↔ cis inversion was a priori excluded.


Sincerely yours,

Yujiro NOMURA, Naruhito MASAI, and Yoshito TAKEUCHI
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Dear Professor Shapiro,

Once again my contribution to TAMU-NMR Letters is overdue. First of all I should like to inform you that for the past six months Dr. Richard Mynott has been working here with us. Dr. Mynott has worked in the field of NMR for several years; his Ph.D. work was in the field of phosphine complexes of the platinum metals, and since then he has worked on NMR studies of biochemical and organometallic compounds. I expect that he will be sending a contribution to your Letters himself before long.

On p. 28 of Issue Number 174 of TAMU-NMR Letters, I wrote that we are no longer dependent upon our PDP-10 main computer for the acquisition of data in FT spectroscopy, but that we still use it for Fourier transformation and for storing the data from pulsed spectra for later evaluation. We are now expanding the system further (presently PDP-11 with 16K core and Dec-tape system) by incorporating a moving head disk (2.4 million bytes).

A Tektronix 4012 Display Unit has proved itself very valuable for the measurement of line positions. I consider that this method of measuring with a cursor is more reliable (error < 0.07 ppm for a spectrum 150ppm wide) and at least as fast as with an automatic peak searching program with the computer. Furthermore, one does not have to wade through long rolls of paper, matching peaks with the printout! The enclosed hard copies illustrate the method of programming and the mode of input of parameters, and also the convenience of the output of the spectra with a table of the signal locations.

Best wishes,

E. Hoffmann
$\text{Zn}^{(sBu)}_2$

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DAR - DATENRATE
ORD - ORDNUNG DER RECHNUNG
EXP - EXPONENTIELLE FALTUNG
LIN - LINEARE FALTUNG
PNT - ANZAHL DER PUNKTE
IFA - PHASENDREHUNG
PHI - PARAMETER FUER PHI
DPH - PARAMETER FUER DPHI
AUS - ANZAHL DER AUSZUSCHNEIDENDEN PUNKTE

NGL - ANZAHL DER GLETTUNGEN
INT - INTEGRATION
SNR - SPEKTRENNUMMER
FRQ - MESSFREQUENZ
EXT - ENDE DER EINGABE
HLP - SCHREIBE DIESEN TEXT
TYP - SCHREIBE DIE MOMENTANEN PARAMETER
TRA - TRANSFORMATION
PUL - PULSAUSSCHNITT

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LAUFZEIT RECHNUNG (MSEC.) 853
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AMPHIPHILE DIFFUSION IN CUBIC LIOTROPIC MESOPHASES

Dear Prof. Shapiro,

X-ray diffraction studies have been successfully used to determine the structure of various liquid crystalline phases in systems composed of surface-active agents and water. However, the diffraction patterns obtained from the optically isotropic cubic mesophases which form in many binary and ternary soap systems often do not contain a sufficient number of reflections to unambiguously index the diffraction pattern. Even for those cases where the space group has been identified there has been considerable controversy about the structure. Two types of structures for these cubic phases have been proposed: to wit 1) structures based on networks of rod-like units extending over macroscopic distances and 2) structures based on spherical or globular aggregates of small extension.

If we assume that the amphiphile diffusion is much faster within a continuous structure than is the diffusion from one structure to another or of the structure itself, then we may be able to use NMR self-diffusion measurements to distinguish between the two possibilities. In particular, we would expect considerably faster amphiphile diffusion in structures of type 1) than of type 2).

In order to test this possibility, we have measured the self-diffusion coefficient of dodecyltrimethyl-
ammonium chloride (C₁₂TAC) in three isotropic phases of the binary system C₁₂TAC-D₂O at 29°C. These phases are a) the micellar aqueous solution (denoted S₁), b) the phase between S₁ and the normal hexagonal phase or middle soap (denoted S₁c), and c) the phase between the normal hexagonal phase and the lamellar phase (denoted V₁). Due to the isotropy of these phases and the consequent lack of direct dipole-dipole coupling in C₁₂TAC, we have been able to measure the diffusion coefficient using the standard 90°-t-180°-t-echo technique with field gradient pulses placed between the 90° and 180° pulses and between the 180° pulse and the echo.

The results of these measurements are shown in Fig. 1. Although the transverse relaxation time (T₂) for C₁₂TAC decreases monotonically with soap concentration (indicating a progressively inhibited short time motion), the diffusion coefficient for diffusion over macroscopic distances increases by a factor of 10 in going from the S₁c to the V₁ phase. The behaviour in phases S₁ and S₁c can be explained by taking into account the increasing fraction of aggregated soap and decreasing micellar translational mobility with concentration; however, our data greatly favor (perhaps even require) a structure involving units which extend over macroscopic distances for the V₁ phase.

These data show that, under certain circumstances, NMR self diffusion measurements can be used to help distinguish between various types of liquid crystalline structures.

Best wishes

T.E. Bull

Björn Lindman

Fig. 1. Diffusion coefficient, $D$, of dodecyltrimethylammonium chloride ($C_{12}$TAC) at 29° in the $C_{12}$TAC-$D_2O$ system as a function of the mole fraction of $C_{12}$TAC. $S_1$ denotes amorphous isotropic solutions and $S_{1c}$ and $V_1$ optically isotropic mesophases.
March 7, 1974

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

Title: "Request for Nmr Computer Preprints - Apologia for SW Discrepancy"

Dear Barry:

I am preparing an article on the use of the computer in Fourier transform Nmr, which will include discussions of various advanced techniques in which computers can play a useful role. I would appreciate receiving any preprints on these topics that might be available. I am operating under a rather tight deadline and will need this data before the beginning of May.

I am indeed sorry that Dr. Bremser has found problems with the Nicolet - Bruker BNC-12 Nmr program. I would like to take this opportunity to emphasize that Nicolet corporately and I personally stand behind these programs and that we are always glad to assist workers in both performing new experiments and in correcting problems in standard programs and techniques.

We were not previously aware that the problem of accurate Spectral Width calculation existed in BNC-FT 1973 before Dr. Bremser brought it to our attention. We have corrected it and will be glad to send copies to anyone who requests it. Copies have also been forwarded to Bruker Physik and Spectrospin. Again, we apologize for the error.

Sincerely,

James W. Cooper, Ph.D.  
Applications Manager

JWC/tab
Positive $^1J_{CP(III)}$: Both Positive and Negative $^1J_{CP}$ to the Same Phosphorus

March 12, 1974

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

Dear Barry,

The phosphines continue to provide us with surprises. In a study of ring size effects on $^{13}$C shifts and $^{13}$C-$^{31}$P couplings we have determined signs of the latter using the convenient methods outlined by Jakobsen et al. for a series of compounds including:

![Chemical structure diagrams showing $^1J_{CP}$ values for different phosphorus compounds.](image)
These contain the first observed positive \( ^1J_{CP(III)} \) (relative to the \( ^2J_{PH} \) which are positive by virtue of their dihedral angle dependence with respect to the phosphorus lone pair). Opposite double-resonance behavior is noted for the 5- and 6-membered ring alpha carbons, even though one might expect very similar behavior.

The substituted phenyl carbon must have a negative coupling since a smooth trend is observed from the reported negative value in triphenylphosphine to those above as two phenyls are serially replaced by n-butyls, and ring formation allowed to the 6-membered ring. These are the first instances of having a positive and negative one-bond coupling to the same atom. This is unexplainable within the model of a simple hybridization scheme for a phosphorus with mild substituent distortions.

The alpha methyl carbons show the previously reported \( ^5 \) dihedral angle dependence but in this case it is showed that the pseudoequatorial methyl carbon has a negative coupling. The above is treated in more detail in a submitted paper.

Sincerely yours,

George A. Gray
Senior Applications Chemist

gag:egt

1 See, for example T. Bundgaard and H. J. Jakobsen, Acta. Chem. Scand., 26, 2548 (1972)
Cher Professeur Shapiro,

Je vous remercie de votre lettre de rappel du 5 mars, et vous fais part des titres suivants :

1. Travaux récents dans le domaine du magnétisme nucléaire :

"Interactions électromagnétiques non résonantes sur des spins nucléaires dans l'état condensé."
Note de MM. E.Hiltbrand, R.Sechehaye, B.Borcard et G.-J.Béné, Département de Physique de la Matière Condensée, Genève.
Résumé : Un champ de radiofréquence non résonant déplace la fréquence de Larmor de spins nucléaires sur les systèmes soit résonants soit en précession libre. Ce déplacement de fréquence s'accompagne d'un élargissement de la raie correspondante.

"Determination de la fréquence de Larmor de spins nucléaires soumis à un champ constant et à un champ RF non résonnant."
E.Hiltbrand, R.Sechehaye, B.Borcard, G.-J.Béné, Département de Physique de la Matière Condensée, Genève, et C.Piron, Département de Physique Théorique, Genève.
Résumé : Nous donnons les résultats expérimentaux obtenus par l'action d'un champ magnétique non résonnant sur un système de spins nucléaires soumis à l'action d'un champ magnétique statique homogène.
"Déplacement de la fréquence de Larmor de spins nucléaires sous l'effet d'un champ de radiofréquence non resonnant."
Note de MM. E.Hiltbrand, B.Borcard, R.Sechehaye, G.-J.Béné, Département de Physique de la Matière Condensée, Genève, et C.Piron, Département de Physique Théorique, Genève.
Résumé : Le déplacement observé est interprété quantitativement avec une bonne précision pour les fréquences du champ de radiofréquence, inférieures à celle de la précession de Larmor — même pour des valeurs assez élevées de l'amplitude — en ne considérant que la composante tournant dans le même sens que la précession de Larmor.

2. Travaux en cours :

Communications à la session de printemps de la Société Suisse de Physique — Berne, mai 1974.

"Non-resonant excitation of nuclear magnetic sublevels?"
G.-J.Béné, B.Borcard, E.Hiltbrand, R.Sechehaye, Département de Physique de la Matière Condensée, Université de Genève, and M.Guenin, C.Piron, Département de Physique Théorique, Université de Genève.
Résumé : We report on the action of a non-resonant RF field on a system of nuclear moments submitted to a constant magnetic field. The effect has been experimentally and theoretically investigated for the whole range of amplitudes and RF-frequencies, below and above the Larmor frequency corresponding to the constant magnetic field. A good agreement between theory and experiment is found, except for very low RF-frequencies. The connection with other measurements is discussed.

"Précession libre et échos de spins à l'aide d'impulsions non résonnantes".
G.-J.Béné, B.Borcard, Département de Physique de la Matière Condensée, Genève.
Résumé : Sur la base de travaux antérieurs (séance d'automne de la Société Suisse de Physique, Lugano, oct.1973) se rapportant à l'influence d'un rayonnement EM non resonnant sur la distance des sous-niveaux magnétiques de spins nucléaires, les auteurs étudient de nouvelles techniques d'impulsion pour provoquer la précession libre ou réaliser des échos de spins par excitation non résonnante.

Avec mes sentiments les meilleurs,

Prof. G.-J. Béné
WP 60

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Toronto, Canada
Tel. (416) 486-7907
Tlx. 02-2771
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College of Science  
College Station, Texas  77843

Dear Barry:

Tungsten Locks (to keep the Wolfram the door )

While just about everybody nowadays seems to have settled on deuterium locks for high resolution work, a note on fluorine locks might still be appropriate. We don't like C6F6, or any other organic fluorine lock for that matter, since most of the unknowns we look at for carbon-13 have a diabolical way of resonating near the carbons in the lock. If one is annoyed by this to the extend of settling on an external (i.e., capillary) lock system, we have found tungsten hexafluoride to be an excellent choice for ambient temperature work. Apart from the 14.3% 183W (spin 1/2, JWF = 48 Hz), the line is sharp, and the T1 very favorable. It appears to be indefinitely stable in sealed tubes, and the suspended solids that do occur are evidently close enough in magnetic susceptibility not to cause any homogeneity problems. The only real problem is that its 19F chemical shift from C6D6 (~ 109 upfield) is outside the normal offset range of the Bruker spectrometer, which we solve by using an available synthesizer to offset the F0 channel appropriately.

Sincerely yours,

E. B. Whipple

R. L. Bujalski
March 15, 1974

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

CMR SPECTRA OF 7-HYDROXYALKYL GUANOSINIUM ACETATES

Dear Dr. Shapiro:

In the TAMU Newsletter No. 178 we described some of the pmr spectral features of 7-hydroxyalkylguanosinium acetates (IVA and IVb) from the reactions of guanosine (I) in glacial acetic acid with variously substituted epoxides (II and III). We now wish to describe some of the features of CMR spectra of these compounds.

\[
\begin{align*}
&\text{CMR SPECTRA OF 7-HYDROXYALKYL GUANOSINIUM ACETATES} \\
&\text{Dear Dr. Shapiro:} \\
&\text{In the TAMU Newsletter No. 178 we described some of the pmr spectral features of 7-hydroxyalkylguanosinium acetates (IVA and IVb) from the reactions of guanosine (I) in glacial acetic acid with variously substituted epoxides (II and III). We now wish to describe some of the features of CMR spectra of these compounds.}
\end{align*}
\]

Comparison of the CMR spectra of IVA and IVb with the CMR spectrum of guanosine (I) reveals that C5 and C4 are shifted upfield by about 8 ppm and 1 ppm respectively; C2, C6, and C8 are shifted downfield by about 4 ppm, 1 ppm and 2 ppm respectively. The chemical shifts of the methyl carbon and
and carboxylate carbon of the acetate anions occur at about 24ppm and 182ppm respectively. The C_5, C_6 and C_7 chemical shifts of the ribosyl group occur at a lower field than in guanosine; the chemical shifts of C_7 and C_8 are unchanged from their values in guanosine. The chemical shifts of the carbons of the hydroxyalkyl groups vary as would be expected from the compilations of substituent effects found in Carbon-13 NMR Spectroscopy by J. B. Stothers, Academic Press, 1972. We have not yet rationalized the downfield shifts of C_8 and the downfield shifts in C_3, C_4 and C_5 in the ribosyl groups of IVa and IVb. The chemical shifts of C_8 in these compounds were expected to occur upfield from C_8 in guanosine. In an earlier study by R. J. Pugmire and D. M. Grant, J. Am. Chem. Soc., 90:4232,(1968), it was found that the chemical shifts of the 2, 4, and 5 carbons of protonated imidazole occur upfield from their respective positions in imidazole. These upfield protonation shifts in protonated imidazole were reported to be related to a decrease in the order of the N-C_6 bonds. The downfield shifts in the C_5, C_6 and C_7 in IVa and IVb may be due to either the effect of the positive charge in the imidazole ring or a change in the orientation of the purine ring with respect to the ribosyl group due to rotation about the N_9-C_3 bonds. In order to determine whether a change in the orientation of the ribosyl groups occur with respect to guanosine. We plan to do an NOE experiment in which H_3 of IVa and IVb and guanosine is observed as the ring protons of the ribosyl group are successively irradiated.

We wish to thank Drs. R. J. Pugmire and D. K. Dalling of the Chemistry Department of the University of Utah for providing CMR spectra of a series of IVa and IVb type compounds.

Very truly yours,

Robert Roe, Jr.
Joseph S. Paul
Measurement of P-P couplings by $^1\text{H} \{ ^{31}\text{P} \} \text{INDOR};$

Experience of JEOL PFT 100

We have continued our investigations of PP coupling in phosphine complexes using $^1\text{H} \{ ^{31}\text{P} \} \text{INDOR}$ which were mentioned in our last contribution. Firstly, we looked at some cis palladium complexes of trimethylphosphite since \( \text{PdCl}_2\{\text{P(O}Me\}_3\}_2 \) is reported to have \( 2J_{PP} = +79.9\text{Hz} \) in contrast to the couplings in cis phosphine complexes which are much smaller and negative. The larger value of \( J_{PP} \) places the 'outer' lines in the \(^{31}\text{P} \) spectrum well clear of the 'inner' lines. Monitoring a line of the strong doublet in the proton spectrum, the \( ^1\text{H} \{ ^{31}\text{P} \} \text{INDOR} \) spectrum reveals a central group of lines and, when the irradiating power is increased by ca. 15dB, outer lines on one side only. Monitoring the other strong proton line gives the outer lines on the other side, of course. The relationship between the signs of the couplings is similar to that for the more usual type of double resonance determinations namely, if the line monitored and the outer line found lie to the same side of \( \nu_X \) and \( \nu_A \) respectively, \( (J_{AX} + J_{AX'}) \) and \( J_{AA} \) have the same sign. \( 2J_{PP} \) was positive for cis \( \text{PdX}_2\{\text{P(O}Me\}_3\}_2, X = \text{Cl, Br and I}; \) a feature which we still find very surprising.

For trans isomers, \( 2J_{PP} \) is usually greater than \( 300\text{Hz} \) and the outer lines in the \( X \) spectrum are generally too weak to be found. However, the results on the phosphite complexes suggested that the outer lines in the \( ^1\text{H} \{ ^{31}\text{P} \} \) spectrum might be found if even more irradiating power was used. This is illustrated in the Figure. A series of runs like these at various powers seems the safest way to identify the outer lines (the 'features' on the central band are due to 50Hz interference). The larger the value of \( 2J_{PP} \), the more power is required to bring up the outer lines but although this increases the width of the central band, the two processes seem to be balanced such that the central resonance never interferes too seriously with the observation of the outer bands. The latter are not similarly broadened since the effective irradiating power is proportional to the transition moment as well as the power of the irradiating field. For complexes of trimethylphosphine and trimethylphosphite, the inner and outer bands can be
'resolved' into similar multiplets of splitting $\frac{1}{2}(J_{AX} + J_{AX'})$. We have obtained values for $2J_{pp}$ up to +1145 Hz (trans PdI$_2$(P(OMe)$_3$)$_2$) without noticeable difficulty using this method. The method also works for complexes of PMe$_2$Ph, PMePh$_2$, and PET$_3$ (using the methyl resonances) although the results are less accurate because the fine structure of the INDO R bands is not resolved. Although some trans complexes have $2J_{pp}$ less than 250 Hz, only trans complexes seem to have values greater than 250 Hz. Hence, finding the value of $2J_{pp}$ to be greater than 250 Hz provides a convenient proof of a trans arrangement of phosphine ligands.

Our JEOL PFT 100 system has now been operational for 5 months, and has been used successfully for the following nuclei: $^{13}$C, $^1$H, $^{19}$F, $^{31}$P, $^{11}$B. 24 hr. operation is usual, and presents no problems, as the stability of the system, despite only moderate air conditioning in the room, is excellent. The slight drifts in the oscillators (~2 Hz in 12 hrs.) are compensated for by the use of a trigger peak in the frequency domain accumulation routine.

The outstanding features of the system, compared to others of which we have experience, are the EC-100 computer interface and the deuterium lock channel sensitivity. The former compensates fully for the lack of CW facilities on our system, since the analytical signal can be presented on the scope as frequently as a normal CW oscilloscope scan. We have used this facility for such purposes as correcting field drift and resolution on samples which contain no deuterium signal for locking.

Most of the measurements we have done have been on various transition metal complexes, particularly of platinum and rhodium, and we have collected a large amount of data on $J_{pt-C}$ and $J_{Rh-C}$, which we hope to report on more fully in a later communication.

Yours sincerely,

Robin Goodfellow
R.J. Goodfellow
M. Murray
Brian Taylor
B.F. Taylor
$^1$H($^{31}$P) INDO spectrum of trans Pd(CN)$_2$(PMe$_3$)$_2$

(a) observing $\alpha\alpha$(m,p) line using various power levels of the irradiating field (dB below a nominal lv into 50Ω)

(b) observing $\beta\beta$(m,p) line

Dear Professor Shapiro,

In our investigations of structure and complexing-properties of maleic hydrazide, potassium maleic hydrazide, N-methyl-maleic hydrazide and N-acetyl-maleic-hydrazide we recently studied the hydrogen bonds of the anhydrous solids at room temperature. Here our results in brief:

1) In solid state there are considerable hydrogen bonds in all cases.

2) The peak shapes can be interpreted in terms of a potential function for the proton motion with two minima of potential energy.

3) The relative intensities of the peaks of the bridging protons and of the "fixed" protons give a relation of the number of the exchanging protons, which is important for the estimate of the relation of the tautomeric structures.

We interpret the experimental results as follows (cf. the added table!)

a) N-methyl-maleic hydrazide has a nearly ideal dimeric structure, which is probably centrosymmetric as in solution

b) Potassium maleic hydrazide and N-acetyl-maleic hydrazide have only to some extent the ideal centrosymmetric dimeric structure.
c) Maleic hydrazide either exists to a very small extent only in a polymeric structure with two exchanging protons per molecule or nearly completely in a polymeric structure with one exchanging proton per molecule. The latter can be interpreted as a polymeric structure with two different types of hydrogen bonds, one being strong with exchanging protons, the other being only weak without proton exchange.

Sincerely yours

[Signature]

Bernhard Lippert
Proton Exchange in Solid State

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**\(^1\)H-NMR spectra**

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**Theor. Values for complete exchange**

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Dear Professor Shapiro,

We have studied the kinetics of an intramolecular cation exchange process within the molecular cavity of ligand L using variable temperature $^{13}$C NMR spectroscopy.

L forms cryptate type inclusion complexes with various metal cations. The $^{13}$C spectrum of the complex with the calcium cation is temperature dependent (see figure). The low temperature spectrum shows that the cation is located dissymmetrically in the molecule, giving a doubling of all $^{13}$C lines. Coalescence occurs at higher temperatures. The data are in agreement with the exchange process shown below. The corresponding exchange rates and free energy of activation at +30° are respectively 58 sec$^{-1}$ and 15.3 kcal/mole. Intermolecular Ca$^{2+}$ exchange is also present but is much slower (rate of about 47 sec$^{-1}$ at +105°).

Sorry for being so late with our contribution.

Yours sincerely,

Jean-Marie Lehn

JML:ga

Enclosure
$^{13}$C FT-nmr spectra of the Ca$^{2+}$ complex of L at different temperatures (D$_2$O solution of L + excess CaCl$_2$). At 4°C, the chemical shifts are: 23.3, 25.2 (C$_R$-N); 26.1, 27.2 (C$_B$-N); 33.2, 39.6 (C$_B$-O); 37.9, 38.5 (C$_R$-O) ppm (downfield from internal _ter_-butanol) (R= ring; B= bridge).
The TT-7 pulsed RF Fourier transform accessory benefits NMR operation by dramatically increasing sensitivity over that obtained in the normal CW mode of operation. Typically, samples five to ten times smaller than those now being handled can be run in the same amount of analysis time. Signal input, accumulated free induction decay, or transformed spectra can be displayed on the TT-7's cathode ray tube for visual monitoring. The spectra can be plotted using the T-60 recorder. Digital integrations of spectra can be viewed or plotted as well.

Not only will the TT-7 enhance the sensitivity and increase sample throughput of your T-60 but it will also provide an excellent Fourier transform training facility. Its ease of use is incomparable. In addition, spin-lattice relaxation times can be determined from a series of runs using the progressive saturation technique. Optional automatic T1 measurements are available using the inversion-recovery technique as well as other multi-pulse experiments. In addition to sensitivity improvement and T1 measurement applications, the basic TT-7 system will provide computer calculations of theoretical NMR spectra of up to six spins (seven spins with 12K core memory and disk memory systems).

Phone or write for more details.
March 25, 1974

Shift Reagents and Bicyclic Azoxy Compounds

Jim Snyder (Copenhagen) has shared a number of bicyclic azoxy compounds with us for quantitative lanthanide induced shift studies. We unhesitatingly applied the PDIGM computational method to the shifts observed by Yb(DPM)$_3$ in the compounds shown at the bottom of the page.

Since the free electron spin density at oxygen and nitrogen are essentially identical according to several different molecular orbital calculations, we tried to fit the LIS data with the principal magnetic axis of the lanthanide passing through either the oxygen or nitrogen centers. Even the most casual inspection of the results in the table show that a reasonable interpretation occurs only when the coordination site is assumed to be nitrogen. We even investigated a few cases in which the principal magnetic axis was oriented between the nitrogen and oxygen atoms and found that the agreement factor was worse. Obviously LIS computer programs in which the orientation of the principal magnetic is varied during computation would find an optimum orientation. We feel the agreement factors of 6-8% are already low enough to provide a satisfactory interpretation and we have not tried to find the best orientation.

If there are any readers who have thoughts to share on the causes of coordination of the shift reagent at the nitrogen we would like to hear from them. We still have the intuitive feeling that coordination at oxygen would benefit enough for reduced steric interactions that it should be the best center. Any and all arguments to the contrary will be welcome. With the greatest reservation, I am not enclosing any Aggie jokes, and I remain

Sincerely yours,

M. Robert Willcott

[Signatures]
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Rho of 0° is collinear N-O-Lam Array for Ox Entry in the table.
Rho of 60°, Phi=270° is a coplanar C_2 for the N entry in the table.
Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Title: $^{13}$C NMR Spectra of Some Imines and Oxaziranes

Dear Professor Shapiro:

Please excuse us for being slow in submitting this to you, but we have been very busy with our new CFT-20 spectrometer. It seems to be operating perfectly; we are certainly pleased.

One group of compounds which we synthesized for use in a mechanism problem seemed amenable to a $^{13}$C NMR study. The following imines and oxaziranes were investigated and their $^{13}$C NMR spectra are enclosed.

The imine spectra are quite straightforward. Off-noise decoupling enabled us to assign the resonances at 17.76 and 29.30 ppm to the geminal methyl carbons of compound III. By analogy to the oximes one can suggest that the carbon cis to the unshared pair of electrons is the more disfavored. [G.C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonances for Organic Chemists, Wiley-Interscience, New York, 1972, p. 131.] The imines I and II are formed as single geometrical isomers, this is consistent with their $^1$H spectra.

Compound VI, shows your different methyl carbons in its $^{13}$C NMR spectrum. Again, off-noise decoupling allows us to
assign the 17.25 and 26.53 5 absorptions to the non-equivalent ring methyl carbons and the 19.20 and 22.12 to the carbons of the iso-propyl group. The non-equivalence of the two carbons of the iso-propyl group is due to the chiral nitrogen of the three membered ring. The fact that oxaziranes are configurationally stable is well known. [A. Mannschreck et al. Ann., 727, 224 (1969).]

Sincerely yours,

Dorothy Z. Denney
Research Associate

Steven P. Tanis
Henry Rutgers Scholar

sb
Encl.
Title: Inaccurate Chemical Shift Values in $^{13}$C CW Spectra on the XL-100 System and the Effect This has on Other Nuclei

March 22, 1974

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

Please credit this contribution to the Purdue University subscription.

We recently observed that certain chemical shift data in $^{13}$C CW spectra taken on our XL-100 system did not agree with our own FFT data or literature values. A casual inspection of the system would have lead one to conclude that the recorder was out of calibration, however, we were getting quite accurate shift data at frequencies for all other nuclei on the system. The actual problem proved to be both subtle and insidious.

With reference to Varian schematic #87-126-846 for the $^{13}$C frequency control module, it will be noted that a feedback binary counter is used to divide the audio reference frequency ("magic offset numbers") by 124 for comparison to an audio signal derived from the 15.4MHz master oscillator and the $^{13}$C XVCO. If this counter fails in any of its feedback gates (U-6, U-7 or U-8), it will free run at a division ratio of 1/128. Unlike the other high frequency XVCO loops in the XL-100, this free running ratio is well within the lock range of the $^{13}$C observe transmitter frequency synthesizer. As a result, the system appears to operate properly with the exception that the actual CW sweep widths are too large by 4/128. If the recorder sweep VCO is adjusted to correct for this error, then the CW sweep widths for all other nuclei on the system will be too small by the same factor. In FFT operation this failure will not affect chemical shift data but will change the offset numbers required to produce a given centerband frequency compared to a properly operating XL-100 by the factor stated above divided by 2.

The repair of this problem usually involved the replacement of IC package U7. We have not observed an outright failure of this package, but rather the risetime of the gate degrades to the point that the down counter is not reset at the 124 count. We therefore advise that the replacement package be selected with care to avoid further difficulty. After repairs are complete, a reliable down count of 124 must be verified by direct measurement with a digital frequency counter that can be gated for a full ten second accumulation.
It must be emphasized that, even in this failure mode, the basic stability of the system is not degraded. As a result it is possible to exactly correct any erroneous data. In cases where this failure seems to have occurred in systems other than our own, it is usually mis-diagnosed as stated above. The resulting adjustments only further mask the problem while affecting the CW chemical shift data for any other nuclei run on the system.

Sincerely yours,

Robert E. Santini

John B. Grutzner

FIRST INTERNATIONAL SYMPOSIUM ON ORGANIC CHEMISTRY
OF GERMANIUM, TIN AND LEAD

The first International Symposium on Organic Chemistry of Germanium, Tin and Lead will be held from October 15-19, 1974, at the "Universite de Droit, d'Economie et des Sciences d'Aix-Marseille, Marseille, France". An international advisory committee has been established to draw up the program of the symposium. A number of invited major lectures and contributed papers will be presented.

All persons interested in receiving further details, including Final Registration Forms, and housing information are asked to write to:

First International Symposium on Organic Chemistry of Germanium, Tin and Lead
Laboratoire des Organometalliques
Faculte des Sciences et Techniques de St-Jerome
13397, Marseille Cedex 4, FRANCE
Dear Barry,

The availability of $^{12}$C-enriched materials, mostly solvents for
$^{13}$C n.m.r. spectroscopy (Merck, Darmstadt, Germany), has led us to
propose and apply a new isotopic substitution technique that may
be used in combination with $^{13}$C n.m.r. spectroscopy for the elu­
cidation of reaction mechanisms: $^{12}$C-LABELING.

The technique is fully equivalent to the widespread $^2$H-labeling
used in proton n.m.r. Compared to $^{13}$C-labeling it has several ad­vantages:

1) No complications due to $^{13}$C-$^{13}$C coupling constants arise
2) In the absence of scrambling, the still problematic integration
of $^{13}$C signals is not necessary
3) $^{12}$C is at present (!) much less expensive than $^{13}$C.

The first successful application of this new method will appear in
the 2nd March issue of "Angewandte Chemie"; a short account was al­ready given in Nachr. Chem. Techn. 21, 541 (1973) included in the
German issue of Angew. Chem. No. 24, 1973. We were able to establish
the correct mechanism for the formation of benzocyclopropene from

The enclosed spectra clearly show that the label, introduced via
$^{12}$CCl$_2$ (from $^{12}$CDCl$_3$), stays at the 7-position, thereby ruling out
any skeletal rearrangement.

With best regards

J. Prestien
H. Günther
$^{13}$C-n.m.r. spectra of benzocyclopropene; (a) normal isotopic distribution; (b) $^{12}$C-labeled in the 7-position.
Professor B. L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77843

Dear Barry,

We have noticed communications lately on the subject of line intensities in Fourier transform NMR spectroscopy. One cause of this problem lies in the fact that spectral resolution is determined by the size of the data set.

In the accompanying Figure we show the Fourier transform spectrum of three $^{13}$C resonance lines due to a four carbon fragment (two of the carbons being equivalent). In the top spectrum, using a 4K data set ($N = 4096$), the line intensities are seen to be approximately equal. In the spectrum at bottom, where an 8K data set is used, intensities are seen to reflect the nature of the four carbon fragment.

We have developed a scheme whereby we can improve the line intensities by resolution enhancement of the 4K data set. This work has been submitted for publication and we have named the technique, "Resolution Improved Fourier Transform (RIFT) Spectroscopy".

Sincerely yours,

Raymond T. Pajer

Robert J. Cushley*

*As of May 1, 1974 my new address will be:

Department of Chemistry  
Simon Fraser University  
Burnaby 2, British Columbia  
Canada
4K Data Set

8K Data Set
KONTES GLASS COMPANY

KONTES GLASS COMPANY
VINELAND, NEW JERSEY, 08360
TELEPHONE: (609) 692-8500

KONTES QUALITY COMES TO NMR...

K-897265 NMR TUBE, QUARTZ, 5 mm., GRADE I
K-897266 NMR TUBE, QUARTZ, 5 mm., GRADE II

Fabricated from thin wall, precision bore, clear fused quartz tubing, and highly polished for maximum spectral resolution, and optimum sensitivity. These tubes are especially useful in all-quartz optical systems for 1H Fourier Transform studies of CIDNP in Photochemical reactions.

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K-897085 PIPET, LONG TIP, NMR

Special long tip pipet for transferring solutions in NMR studies. Overall length is 9", with 1½" body, and 7½" tip. Body O.D. is 7.0 to 7.5 mm; tip O.D. is 1.5 to 2.0 mm. Manufactured from standard flint glass. Packed 100 per package.

Per Package 15.75

K-611680 EPR COLD FINGER DEWAR, QUARTZ

A high performance Liquid Nitrogen dewar. Designed to minimize conduction through the walls while assuring wall parallelism in the sample zone. Reservoir is solid silvered. Please specify size when ordering.

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K-611690 ESR-EPR DEWAR, FLOW THROUGH, QUARTZ

Fabricated from high grade Amersil quartz for use in variable low temperature applications. Base of dewar body is solid silvered for more efficient operation. Size 0001 Dewar fits Varian E-Line and Brucker spectrometers. Size 0002 fits the Varian V-Line Spectrometer. Please specify size when ordering.

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