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Newsletter

No. 216

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All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
 Department of Chemistry
 Texas A&M University
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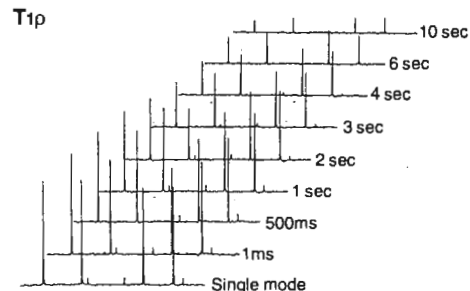
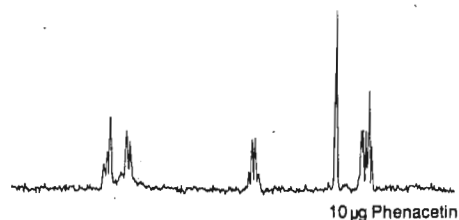
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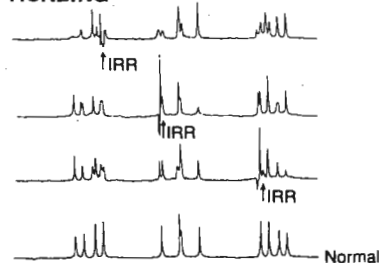
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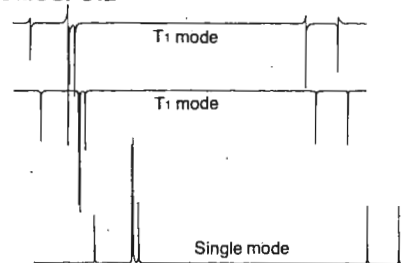
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PHYSICS DEPARTMENT

June 30, 1976.

Dear Barry;

 T_2 of Water in Wood

I am sorry to be late in replying to your reminders. Various perturbations, such as preparations to move to a new building and acquisition of a minicomputer, have delayed our contribution.

Together with M.T. Riggan and A.R. Sharp of this department, and with M.H. Schneider of the Forestry Department, we have studied the Carr-Purcell-Meiboom-Gill echo envelope of the proton signal from white spruce sapwood at moisture contents from 5% to 176%. Moisture content is the weight loss on drying a wood sample divided by the weight of the oven dried sample. Measurements were made at 5.0 and at 17.3 MHz with pulse spacings from 100 to 300 μ sec, but results (at room temperature) were unchanged in these ranges. At low moisture content, the echo envelope due to water is essentially a single exponential with time constant increasing from about 80 μ sec at 5% moisture to 900 μ sec at 30% moisture. Beginning at about 30% moisture, two exponentials can be distinguished with time constants plotted in figure 1 and amplitude ratio in figure 2.

The system was analysed with a 3-phase model:

- a) Hydrogen nuclei in the solid wood structure (not directly observed in this study) with $T_2 = 7 \mu$ sec;
- b) Hydrogen nuclei of water adsorbed on the wood cell walls with $T_2 = 10$ msec and with population P_b ;
- c) Hydrogen nuclei of mobile water in the wood cell cavities with $T_2 = \infty$. Its population P_c is zero at moisture contents below the fibre saturation point of about 33%.

Exchange is permitted between bound and mobile water at a rate of 90 sec^{-1} , and between bound water and hydroxyl protons of the wood fibre at a rate of 350 sec^{-1} . This model produces the solid curves drawn in figures 1 and 2.

Although the 3-phase model with the quoted parameter values appears to account for the echo measurements, it is certainly oversimplified. One piece of evidence comes from the linewidth of the water resonance in cw spectra of moist wood. The linewidth is considerably greater than would be expected from the above model. It appears that there is a distribution of magnetic environments resulting in an inhomogeneously broadened line for the mobile water in cell cavities. Indeed, the resonance peak is shifted from the line of pure water. Also, matters are not simplified by the presence of Mn^{3+} ions which were detected by ESR, but magnetic resonance methods should be able to provide further information on the wood-water system.

Sincerely yours,

R. Kaiser
Professor

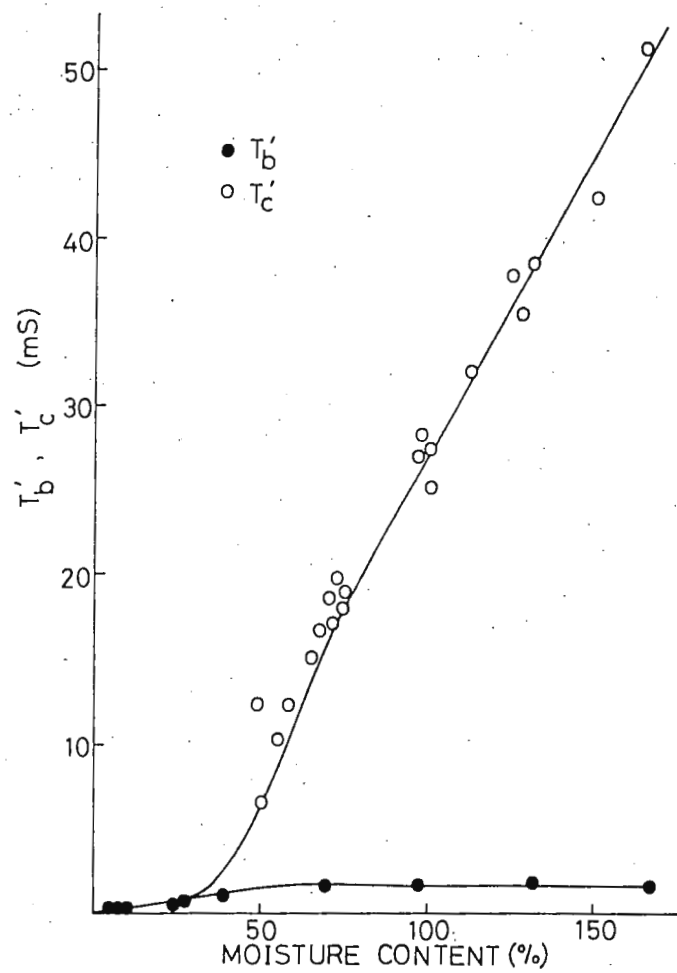


Figure 1

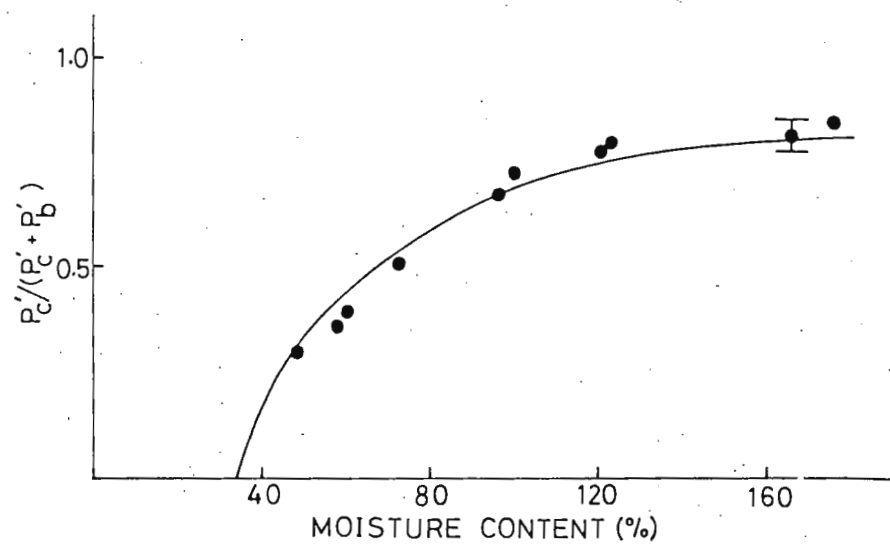


Figure 2

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der Universität Düsseldorf

Direktor: Professor Dr. L. Birkofer

4 Düsseldorf, den August 4, 1976

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Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

DNMR Progress Article. ^{13}C Chemical Shift Calculations

Dear Professor Shapiro:

I am sorry to be late with my contribution. The delay is partly due to a just finished progress article "Application of Dynamic NMR Spectroscopy to the Mechanistic Study of Rearrangements and Exchange Reactions" which will appear in the series "NMR - Basic Principles and Progress". In this article the feature of mechanistic analysis by band shape calculations is illustrated for representative examples. Emphasis is laid on the derivation of kinetic exchange matrices for "uncoupled" and coupled - first-order as well as non-first-order - spin systems. In addition, permutational analysis of the rearrangements of phosphoranes is performed to show the problems encountered in DNMR studies of polytopal rearrangements.

In this note I want to call attention on the calculation and theoretical interpretation of ^{13}C chemical shifts, the progress of which is rather slow compared to the experimental developments in ^{13}C -NMR spectroscopy. The fundamental relations are well known since the early theory of Ramsey. For instance, the z-component of the chemical shielding tensor is given as the sum of the two terms

$$\sigma_{zz}^d = \frac{e^2}{2mc^2} \sum_i^{\text{occ}} \langle \psi_i | \frac{x^2 + y^2}{r^3} | \psi_i \rangle$$

$$\sigma_{zz}^p = - \frac{e^2}{2mc^2} \sum_i^{\text{occ}} \sum_n^{\text{unocc}} \frac{2}{\Delta E_{in}} (\langle \psi_i | l_z | \psi_n \rangle \langle \psi_n | \frac{1}{r^3} | \psi_i \rangle + \langle \psi_i | \frac{1}{r^3} | \psi_n \rangle \langle \psi_n | l_z | \psi_i \rangle)$$

The corresponding x and y components of the tensor are given similarly with the respective operators. Here I only want to discuss the evaluation of the bracket term of σ_{zz}^p for acetylene as an example by using the ab initio wave function of $\alpha\alpha$ Palke and Lipscomb (JACS 88, 2384 (1966)). If the origin of the vector potential of the magnetic field is chosen as one of the carbon nuclei labeled 1 and 2, it is easily shown that the angular momentum operator l_α affects the p-type atomic orbitals of both carbon atoms in the same way, i.e.

$$l_x | p_x^{1(2)} \rangle = l_y | p_y^{1(2)} \rangle = l_z | p_z^{1(2)} \rangle = 0,$$

$$\begin{aligned}
1_x | p_y^{1(2)} \rangle &= i \hbar p_z^{1(2)}, & 1_x | p_z^{1(2)} \rangle &= -i \hbar p_y^{1(2)}, \\
1_y | p_x^{1(2)} \rangle &= -i \hbar p_z^{1(2)}, & 1_y | p_z^{1(2)} \rangle &= i \hbar p_x^{1(2)}, \\
1_z | p_x^{1(2)} \rangle &= i \hbar p_y^{1(2)}, & 1_z | p_y^{1(2)} \rangle &= -i \hbar p_x^{1(2)},
\end{aligned}$$

while the application on s-type orbitals leads to zero values. Thus the only integrals which can give final values are of the type $\langle \pi_{y(x)} | O_{x(y)} | \sigma \rangle$, $\langle \sigma | O_{x(y)} | \pi_{y(x)} \rangle$, and $\langle \pi_{x(y)} | O_z | \pi_{y(x)} \rangle$ with O being 1 or $1/r^3$ (CC bond in z-direction!). To estimate the values for the different pairs of occupied and unoccupied mo's, the Mulliken coefficients \bar{c}_{ik} of the p orbitals have been calculated from $\bar{c}_{ik}^2 = c_{ik}^2 + \sum_{l \neq k} c_{ik} c_{il} S_{kl}$:

MO	Orbital energy (a.u.)	Mulliken coefficients					
		p_z^1	p_z^2	p_x^1	p_x^2	p_y^1	p_y^2
$1\sigma_g$	-11.2978	0.000	0.000				
$1\sigma_u$	-11.2951	0.000	0.000				
$2\sigma_g$	-1.0048	-0.262	0.262				
$2\sigma_u$	-0.7513	0.401	0.401				
$3\sigma_g$	-0.6563	0.561	-0.561				
$1\pi_{ux}$	-0.4056			0.707	0.707		
$1\pi_{uy}$	-0.4056					0.707	0.707
$1\pi_{gx}$	0.3058			0.707	-0.707		
$1\pi_{gy}$	0.3058					0.707	-0.707
$3\sigma_u$	0.4758	0.000	0.000				
$4\sigma_g$	0.6541	0.338	-0.338				
$4\sigma_u$	1.3426	-0.583	-0.583				

The integrals now are easily evaluated since no cross terms have to be considered and the effect of the r^{-3} operator is taken in account by using the expectation value for carbon 2p orbitals (1.4303).

From the signs of the π mo's it is seen that there is no paramagnetic contribution to the chemical shielding if the magnetic field is in the CC bond direction (cp. Pople Proc. Roy. Soc. A 239, 541 (1957)).

The pairs of mo's which contribute to the y and x components of σ^P are seen to be $2\sigma_g/1\pi_{gx}(y)$, $3\sigma_g/1\pi_{gx}(y)$, and $1\pi_{ux}(y)/4\sigma_u$, for which the value of the bracket term of the σ^P expression amounts to $0.195\hbar^2$, $0.899\hbar^2$, and $0.978\hbar^2$, respectively.

Yours sincerely,

Alfred Steigel

(A. Steigel)

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

Relative Signs of $^2J_{31P-13C}$ Coupling Constants in Chromium
and Tungsten Complexes.

Dear Professor Shapiro,

we are using ^{13}C FT nmr to study the
static and dynamic stereochemistry of octahedral diene complexes.
One complex type under investigation is $M(CO)_3[P(OCH_3)_3](diene)$
with $M = Cr, W$. I.R. and low temperature ^{13}C nmr spectra
strongly support a facial arrangement of the three carbonyl
ligands. For the 1,3-butadiene complexes two carbonyl signals
with the approximate intensities 1:2 (2:1) are observed, each
split by $^{31}P-^{13}C$ -coupling:

Carbonyl signals, chemical shifts rel. i. TMS, δ ppm, $^{31}P-^{13}C$ -
coupling constants [cps] at two different temperatures.

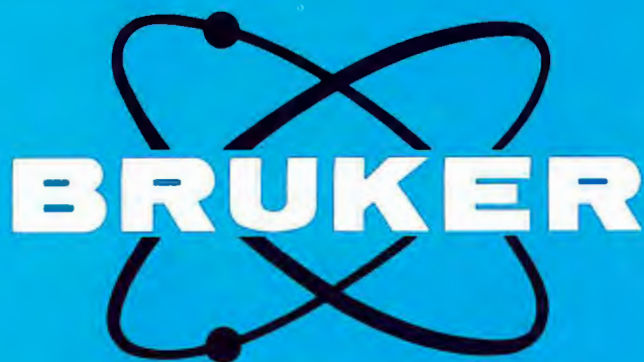
$Cr(CO)_3[P(OCH_3)_3](C_4H_6)$	237.34 (d,1) [+14.65]	234.32 (d,2) [+39.06]	212 K
	234.86 (d) [+29.30]		301 K
$W(CO)_3[P(OCH_3)_3](C_4H_6)$	216.41 (d,2) [+14.65]	212.69 (d,1) [+17.09]	246 K
	215.55 (d) [+ 4.88]		297 K

Resolution: ± 2.44 cps, ± 0.11 ppm

When the temperature is raised a scrambling of the carbonyl
ligands causes the usual broadening and collapse of their ^{13}C
nmr signals. The high temperature carbonyl signal of the
chromium complex forms a doublet, its splitting corresponds
well to the average splitting of the low temperature signals
with 30.93 cps. Surprisingly the equivalent signal of the tung-
sten complex must be explained on the basis of opposite signs
of the $^{31}P-^{13}C$ -coupling constants, average value 4.07 cps.

Sincerely
C. G. Kreiter
C. G. Kreiter

Saim Ozkar
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216-8

Professor E.I. Shwiro,
Department of Chemistry,
Texas A&M University,
College Station,
Texas 77843,
U.S.A.

Your reference

Our reference

Date *20 Aug 1976*

Title: Computer Matching of ^{13}C NMR Spectra

Dear Professor Shapiro:

Like many other FTNMR owners, we frequently generate ^{13}C spectra of pure, or nearly pure, materials of known structure in order to determine the structure of "unknown" materials. We can manually match spectra against commercially available files for compounds to which we have no access. However, the spectral collections of which we are aware (Johnson and Jankowski, Sadtler and Atlas of ^{13}C NMR Data) have only a thousand or so spectra apiece and do not permit computer matching.

From our experience with computer infra-red spectral matching using a data base of 110,000 spectra, we are sure that large, computer searchable, ^{13}C files would be the optimum way to go. While we see papers on ^{13}C searching in the literature, we would much appreciate any of your correspondents telling us of more extensive ^{13}C schemes, commercial or otherwise, to which we may have access.

Yours sincerely,

Ian O'Neill

I. K. O'NEILL

August 19, 1976

313.01

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

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

Dear Barry:

A full membership vote of ASTM has approved the revised standard E 386, "Standard Definitions of Terms, Symbols, Conventions, and References Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy". Copies are available from ASTM, 1916 Race Street, Philadelphia, PA 19103 for a small fee. I expect to have a small number of copies available gratis for distribution later on. I enclose a copy for your information, although I recognize that it is too long to reproduce in the Newsletter.

Yours truly,

Rolf

Rolf B. Johannesen, Chairman
ASTM Subcommittee E 13.07



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Prof. B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science
College Station Texas
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U.S.A.

Genève, le 4 août 1976

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 16 juillet 1976.

1. Interactions non résonantes en magnétisme nucléaire.

Cette ligne de recherche, entreprise dès l'automne 1973 dans le domaine des champs faibles, a déjà permis l'étude de l'excitation des moments nucléaires par une onde de radiofréquence non résonante, mais d'intensité appréciable, en présence d'un champ homogène et constant : le champ magnétique terrestre.

Ont été examinées l'influence d'un champ tournant, perpendiculaire au champ terrestre et celle d'un champ alternatif d'orientation quelconque.

Une synthèse des résultats expérimentaux les plus importants et leur interprétation à l'aide du formalisme de P. Fontana et P. Thomann (Phys. Rev. A13, 1512, 1976) feront l'objet de deux conférences à l'Ecole d'Eté de Pula (Yougoslavie) du 13 au 23 septembre 1976 et seront probablement publiés dans les actes de ce meeting.

Les résultats les plus importants de cette étude sont :

- l'existence d'un déplacement de la fréquence propre du système de spins lorsqu'ils sont soumis à une irradiation non résonante. Ce déplacement peut atteindre des valeurs importantes et on doit en tenir compte dans les expériences classiques de double irradiation, surtout à forte intensité.
- l'intérêt d'impulsions non résonantes pour produire soit la précession libre soit des échos de spins. Cette technique évite la saturation du circuit de réception par l'impulsion et supprime le temps-mort après cette impulsion.

2. XIXème Congrès Ampère - Heidelberg

(27 septembre - 2 octobre 1976)

Nous donnons ci-après, à l'intention des participants

éventuels à cette rencontre, la liste des
"conférences invitées" à ce meeting.

- Dr. BLOOR "Electron Spin Resonance of One-Dimensional Conjugated Polymers"
- J. CHRISTIANSEN "Hyperfine Interactions Investigated with Isomeric Nuclear States"
- S. CLOUGH "Tunnerlin Effects in Molecular Solids"
- E.I. FEDIN "NMR Investigations of Order Disorder Phenomena in Mixtures of Chiral Liquids"
- V.A. GOLENISHCHEV-KUTUZOV "Acoustic Nuclear and Electron Spin Echo in Crystals"
- V.S. GRECHISHKIN "The Peculiarities of S- Signal in Time-Sharing Programs"
(not definitely confirmed)
- S. NAGAKURA "Electronic Structure and Dynamic Behavior of the Triplet States of Some Electron Dono-Acceptor Complexes"
- C. RICHARDSON "Magnetism in Superfluid ^3He "
- J. SCHMIDT "Optically Detected Magnetic Resonance in Photo-Excited Triplet States of Poly-Atomic Molecules"
- C.P. SLICHTER "Nuclear Resonance Studies of the Kondo Effect"
- B. SAPOVAL "Optical Detection of Magnetic Resonances and Giant Fields in Semiconductors"
- F. WALDNER "Electron Paramagnetic Resonance, Ferro-Magnetic Resonance, and Mössbauer Studies of Quasi-Two-Dimensional Magnets" .

Avec mes sentiments très cordiaux.

Prof. G.-J. Béné



Gesellschaft für Molekularbiologische Forschung mbH

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D-3300 Braunschweig-Stöckheim, West-Germany

Telefon (0531) 7008-1 - Telex 9-52667

Bahnhstation: Expresgut Braunschweig Hbf-Selbstabholer
Stückgut Braunschweig HGBf

Prof. Dr. Bernhard L. Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843
USA

Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen
VW/caTel. Durchwahl:
7008 362..Datum
August 4th, 1976Additivity of substituent effects upon J_{FF}

Dear Professor Shapiro,

We have recently established the additivity of substituent effects upon J_{FH} in polysubstituted fluorobenzenes¹ by the use of a collection of fluorine-coupling constant data². A similar treatment for J_{FF} has allowed us to show that substituent effects upon J_{FF} are additive, enabling us to re-evaluate Abraham *et al*'s substituent constants by taking into account the larger number of J 's now available.

A substituent constant is defined as the change that occurs in the value of J_{FF} upon substitution of a proton by a substituent X, (i.e. $\Delta J_{FF}^X = J_{FF}^{X\text{Benzene}} - J_{FF}^{H\text{Benzene}}$). The calculated coupling, $n_{J_{FF}}^{\text{Calc}}$, is then evaluated by

$$n_{J_{FF}}^{\text{Calc}} = n_{J_{FF}}^{H\text{Benzene}} + \sum_{i=1}^4 \Delta J_{FF}^X$$

A linear regression analysis, for a total of 183 J_{FF} 's, gave the substituent constants in the table.

Yours sincerely,

Victor Wray
Victor Wray

1. V. Wray and D.N.Lincoln, J.C.S. Perkin II, in press.
2. J.W.Emsley, L.Phillips and V.Wray, Progr. N.M.R. Spectroscopy, in press.
3. R.J.Abraham, D.B. Macdonald and E.S. Pepper, J.Amer.Chem.Soc., 1968, 90,147.

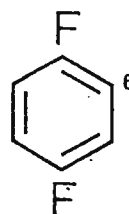
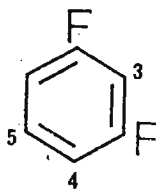
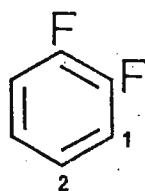
Substituent constants^{a)} ΔJ_{FF}^x and calculated unperturbed couplings, nJ_{FF}^H , of 1,2-, 1,3- and 1,4-difluorobenzene

Substituent	Substituent constants ^{b) c)}					
	1	2	3	4	5	6
NH ₂	0.06 (9)	-1.31 (9)	7.06 (5) 7.2	-8.61 (6) -8.7	-0.46 (5) 0.5	-2.98 (11) -2.9
OH	0.49 (4)	-1.79 (3)	2.81 (3) 4.7	-4.24 (2) -7.7	-2.05 (1) -0.8	-2.78 (7) -3.0
F	0.39 (66)	-0.60 (59)	-0.60 (37) -0.1	-3.85 (81) -3.8	-1.62 (37) -0.3	-3.29 (78) -3.2
Cl	0.14 (8)	-0.38 (11)	-3.32 (10) -3.2	-0.41 (13) -0.4	-0.16 (4) 0.7	-1.99 (17) -2.0
Br	-1.10 (2)	-0.20 (7)	-3.12 (1) -3.4	0.48 (3) -0.5	-0.28 (2) 0.1	-1.97 (4) -2.1
I	-1.67 (1)	-0.40 (5)	-4.65 (1) -3.1	-1.94 (2) 0.5	3.60 (2) 0.7	-1.12 (3) -1.4
CF ₃	1.19 (6)	0.55 (7)	-5.30 (2) -5.5	4.81 (6) 4.2	1.52 (3) 2.0	0.24 (11) 0.0
CN	0.32 (3)	-0.27 (3)	-5.83 (2) -5.7	5.00 (3) 4.3	2.27 (2) 1.9	-0.78 (3) -0.3
NO ₂	-0.05 (6)	-0.38 (5)	-7.67 (3) -8.2	5.61 (7) 5.6	1.48 (7) 2.3	-0.73 (10) -0.6

nJ_{FF}^H	n = 3	-19.95 (63)	RMS 0.69
	4	6.95 (76)	Correl. Coeff. 0.999
	5	18.30 (44)	

Footnotes:

- a) The number of times each constant appeared in the analysis is^{shown} in parentheses.
- b) Substituent constants are for the disposition of substituents as shown below:



- c) Substituent constants of Abraham et al are shown under the ones found here.

FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

August 12, 1976

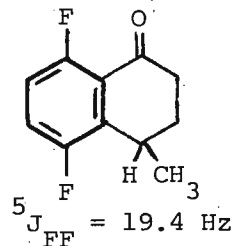
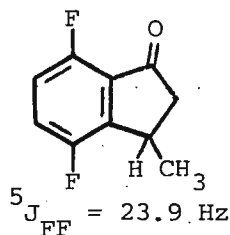
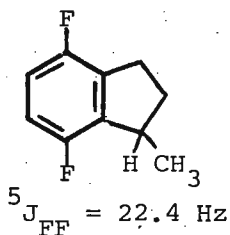
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
UNITED STATES OF AMERICA

Dear Barry,

⁵J in p-Difluorobenzenes

The coupling between para-fluorines on a benzene ring can be expressed as the parent value for p-difluorobenzene (18.1 Hz) plus a substituent correction (Abraham, Macdonald and Pepper, J. Am. Chem. Soc., 1968, 90, 147).

In Abraham's original work most of the compounds were very heavily substituted. The substituent corrections are negative (NH₂, OH, CH₃, Ph, F, Cl, Br, I, CN, NO₂) or zero (CF₃) and their relative magnitudes do not seem to be related to any of the usual substituent sets. We have looked at 2-substituted-1,4-difluorobenzenes and find that Abraham's substituent constants give good estimates for the observed coupling constants in these simpler systems. Some new substituents, however, produced higher values: 2-COOH, 18.2; 2-COCH₃, 18.9 Hz. Even greater effects were attributable to annelation.



Bob Brownlee at La Trobe University (who shares our Newsletter) pointed out that our simple cases were quite well described by the dual substituent parameter equation:

$$J = -2.1\sigma_I + 5.6\sigma_R \quad (\text{SD} = 0.18 \text{ Hz})$$

While it is comforting to have an equation, it hasn't brought us much insight since a theoretical treatment for coupling of this type is lacking.

Please credit this contribution to Mike Heffernan's Monash subscription. Cheryl Kerr did all the work, Mike worried about the deadline and I wrote the letter!

With kind regards,

Ian D. Rae

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August 16, 1976

RIER/bl

Professor B. L. Shapiro
Department of Chemistry
Texas A + M University

College Station, Texas 77843

U.S.A.

SATURATION IN STOCHASTIC RESONANCE

Dear Barry,

The theoretically predicted saturation behavior of resonance lines in stochastic NMR experiments has remained a puzzle for a long time. The theory, which has been used up to now to treat stochastically perturbed spin systems and which has been based on Wiener's functional expansion of the stochastic response, predicts saturation without line broadening (J. Magn. Resonance, 3, 10 (1970)). There are some experimental results which seem to contradict this theoretical behavior, although, due to many experimental artifacts, no conclusive experiment has yet been made.

To clarify this unsatisfactory situation, we attempted to develop a completely new theory of a system under the influence of a random perturbation. The credits for finding an elegant solution are entirely due to Dr. Enrico Bartholdi. He showed that the density operator equation including a random perturbation must be interpreted as a stochastic differential equation in Stratonovich's sense. By means of a conversion formula, it is then possible to utilize the convenient Itô calculus to obtain an analytic solution, at least in simple cases.

And indeed, this new theory predicts a saturation broadening proportional to the strength of the stochastic perturbation. To verify this theoretical result, we performed a computer simulation of a stochastic resonance experiment on a one-spin system with a Gaussian random perturbation.

Eidg. Technische Hochschule Zürich
Laboratorium für Physikalische Chemie

August 16, 1976

Professor B.L. Shapiro

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Some of the results are shown in the following figures. Peak height and line width are plotted as functions of the stochastic rf field amplitude. It is seen that the results of the computer experiment (+, 0, Δ) agree well with the theoretical curves.

It should be pointed out that many aspects of a stochastic perturbation are predicted correctly by the old Wiener expansion theory, e.g. the features of noise decoupling (J. Chem. Phys. 45, 3845 (1966)) and the spectral features of stochastic resonance. But this theory has clearly its limitations whereas the stochastic differential equation approach seems always to lead to correct predictions. A full account of this story will be published shortly in Chemical Physics.

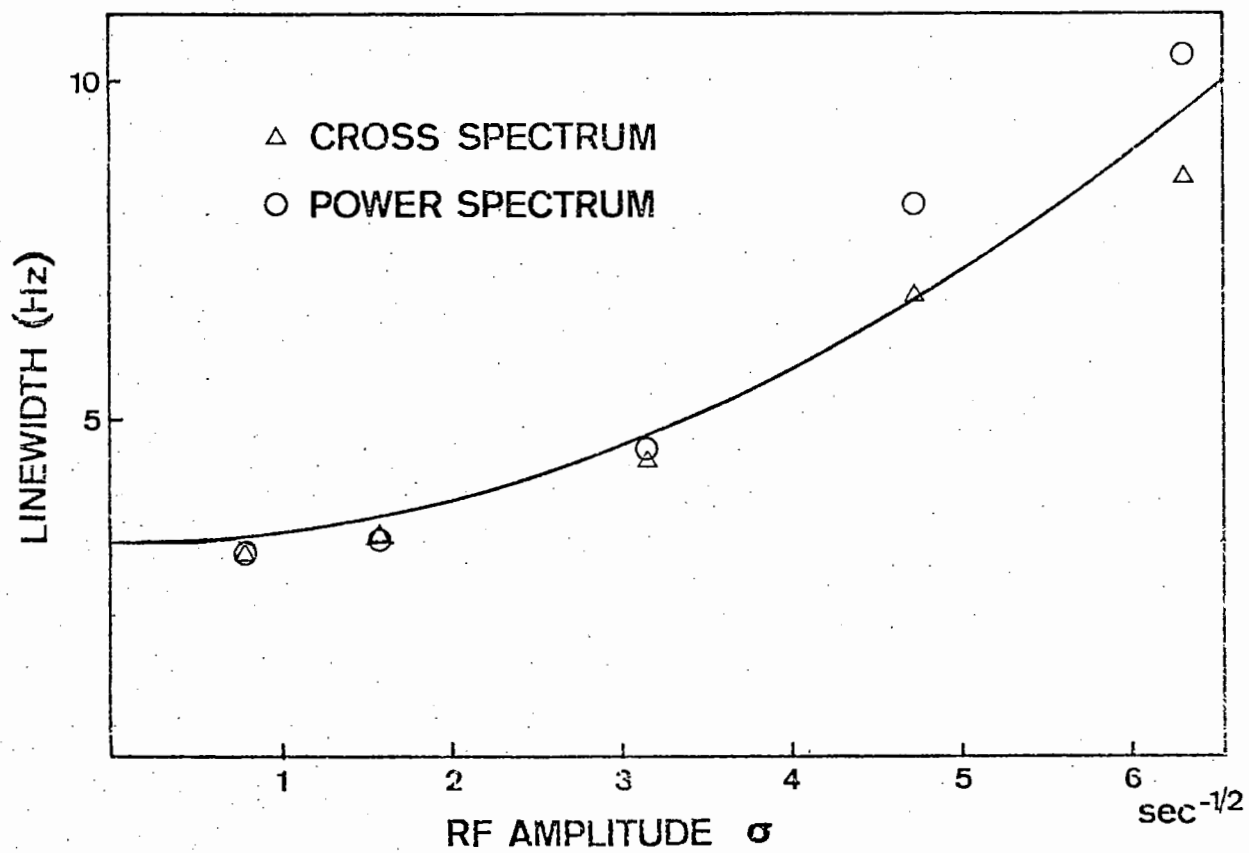
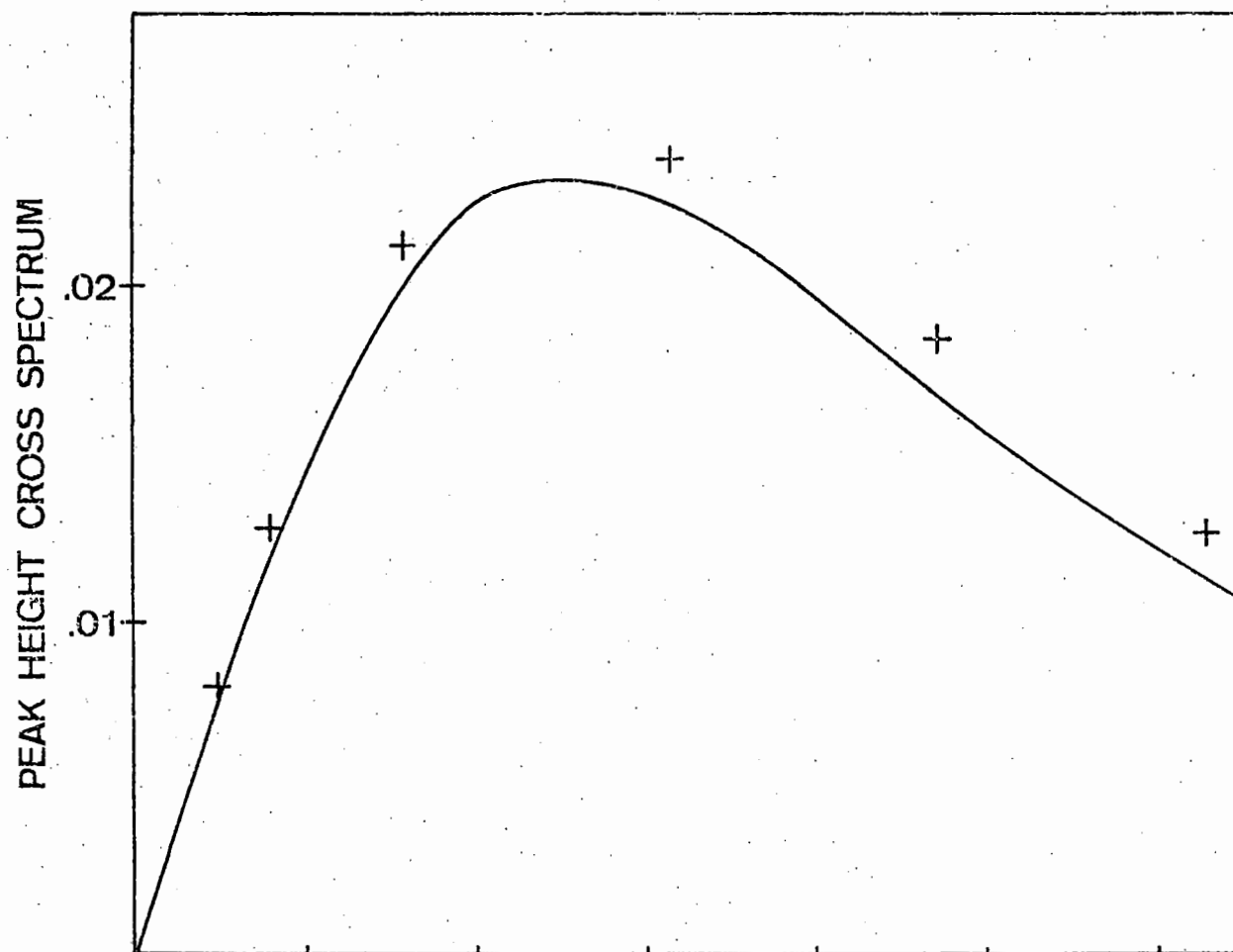
Sincerely yours,



Richard R. Ernst



Alexander Wokaun





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Division of Biological
Sciences

Division des sciences
biologiques

File Référence

6 August 1976

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

Dear Barry,

Microsecond Pulse Delays on the XL-100. A Cure for Jitters

Our application of deuterium NMR to the study of biological membranes has led to the need for increasingly wider spectral windows for the observation of very broad lines (1,2,3). The presence of a finite spectrometer dead time causes severe spectral distortions and phase aberrations which cannot be corrected. Consequently, we have recently attempted a Fourier transform solid echo experiment as a means of overcoming the spectrometer dead time. This involves a $(90^\circ_x, \tau, 90^\circ_y, \tau, \text{F.I.D.})_n$ pulse sequence where τ is slightly longer than the dead time (a few tens of microseconds). During the implementation of this sequence, we discovered a serious jitter in the pulse spacing τ which turned out to be a direct consequence of Varian's approach to maintaining phase coherence in the R.F. pulse.

The R.F. gating pulse is generated in a timing loop in the acquisition program and the leading edge of this pulse must be phase coherent with the R.F. The gating pulse is synchronised with the R.F. by a sense loop in the program (locations 1115 to 1125 in 994100-D) which detects a zero crossing to a 40.96 kHz sine wave present in the FT control module and phase locked to the R.F. When a zero crossing is detected, the gating pulse is started. Unfortunately, the zero crossing sense loop creates jitter in the pulse spacing τ . The jitter can be several multiples of the period of the reference signal (25 μsec). This will of course have serious consequences for any multiple pulse experiment with short τ values.

This problem is easily overcome by increasing the reference frequency to a value where its period creates insignificant jitter. The 40.96 kHz signal is normally present at pin 20 of the logic board (ASSY. No. 931590, Schematic 87-109-753)

Professor B.L. Shapiro


6 August 1976

in the FT control module. The connection to pin 20 was removed and stored. A 3.85 MHz sine wave is present at the BNC connector J1820 at the rear of the FT control module and it was jumpered to pin 20 on the logic board. The period of the reference signal is thus reduced to 0.26 μ sec. The sense loop in the program was eliminated by changing the value in location 1115 to 1000, 1116 to 1166, and locations 1117-1125 to 5000 (NOP's). In consequence, R.F. phase coherence is maintained, the jitter in τ is reduced to 0.26 μ sec, and a jitter of 0.26 μ sec is introduced into the pulse width representing a variation of 1.4° in the 90° pulse, which has no deleterious effect on the spectrum. Note that this modification should be used only with heteronuclear lock.

Best wishes,


Gerald W. Stockton


Leo Turner


Ian C.P. Smith

GWS:cg

1. Gerald W. Stockton, A.R. Quirt, L. Turner and Ian C.P. Smith, TAMUNMR, 200, 6 (1975).
2. Gerald W. Stockton, Carl F. Polnaszek, A.P. Tulloch, Fariza Hasan and Ian C.P. Smith, Biochem., 15, 954-966 (1976).
3. Gerald W. Stockton and Ian C.P. Smith, Chem. Phys. Lipids (In Press).

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The Nicolet 1090A EXPLORER **Digital Oscilloscope**, the other kind of oscilloscope, is in service testing hockey helmets for **shock absorption**, analyzing pulsed nmr signals in **liquid crystal research**, searching out leaks in nuclear reactor coolant systems, capturing **stress and strain data** in materials

testing and making measurements in hundreds of other applications that require its accuracy, resolution, and ability to interface to other instruments for data recording or modification.

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18th August, 1976

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

Dear Professor Shapiro,

¹³C Longitudinal Relaxation Times of Carboxylic Acids

As background information for our ¹³C nmr studies on membrane lipids we have measured the longitudinal relaxation times of the individual carbon atoms in a series of carboxylic acids. A selection of T₁'s from 20% weight/volume solutions in CDCl₃, using a π-t-π/2 pulse sequence on a Varian CFT20 are shown in Table 1.

TABLE 1

¹³C Longitudinal Relaxation Times (sec.) of n-Carboxylic Acids in CDCl₃

Acid	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈
C4	5.5	6.2	6.7														
C5	3.5	4.8	5.6	5.6													
C8	1.9	2.3	2.6	3.1	4.1	5.0	5.3										
C12	1.2	1.5	1.5	1.8	2.0	2.2 ⁺	2.2 ⁺	2.5	3.9	5.0	5.5						
C18	0.8	1.0	1.0	1.1	1.2	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.4 ⁺	2.2	3.4	4.6	5.4
C18 ^{Δ9}	1.0	1.2	1.3 ⁺	1.4	1.3 ⁺	1.5	1.6	2.3	2.3	1.8	1.9	2.5 ⁺	2.4	2.5 ⁺	4.2	5.0	5.2
C18 ^{Δ9,12}	1.1	1.2	1.4 ⁺	1.4 ⁺	1.4 ⁺	1.8	2.4 ⁺	2.8	2.7	3.0	3.5	3.6	2.4 ⁺	4.0	5.0	6.5	6.5
+ Unresolvable signals.																	

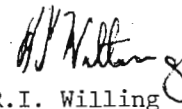
Maximum NOE values for all the carbons except those of butanoic acid show that the ¹H - ¹³C dipole-dipole interaction is the sole relaxation mechanism. The T₁ values indicate that all the acids are associated at the carboxylic acid groups, probably in the form of inverted micelles, and that the dynamics of the longer chain acids are dominated by segmental motion. The relaxation times and hence the motions of the terminal carbon atoms become greater with increased unsaturation, a property of structural importance in the lipid composition of natural membranes.

Please credit this contribution to Dr. D.P. Kelly's subscription.

Yours sincerely,



S.R. Johns



R.I. Willing

Stain, Barry

August 15, 1976

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

TRITIUM SPECTRA AND T_1 MEASUREMENTS FOR MULTIPLY TRITIATED COMPOUNDS
 POSITIONS AVAILABLE

Dear Barry:

As we indicated in an earlier letter, we are setting up a national facility for NMR studies on radioactive samples, with emphasis on tritium NMR spectroscopy. We continue to welcome inquiries about possible collaborative projects. During the past year, we have concentrated our efforts on the analytical uses of tritium NMR in studies of the locations and stereochemistry of tritium atoms in labeled molecules. In particular we have been able to determine, in several instances, the relative amounts of various mono- and polytritiated species in compounds of high specific activity.

As an example of such an analysis, Figure 1 displays a spectrum of L-proline-(2,3- ^3H) $\cdot\text{HCl}$ obtained on our XL-100-12 spectrometer with proton noise decoupling. Careful scrutiny reveals the presence of at least five isotopically different molecular species: proline-2-T (1); proline-3 α -T (2); proline-3 β -T (3); proline-2,3 α -T₂ (4); and proline-3 α ,3 β -T₂ (5), as shown schematically on the spectrum. Also given are the T_1 values, which are slightly but significantly shorter in a ditritiated molecule than in the corresponding monotritiated species. NOE measurements (H-T) indicate that dipole-dipole relaxation is responsible for the differences.

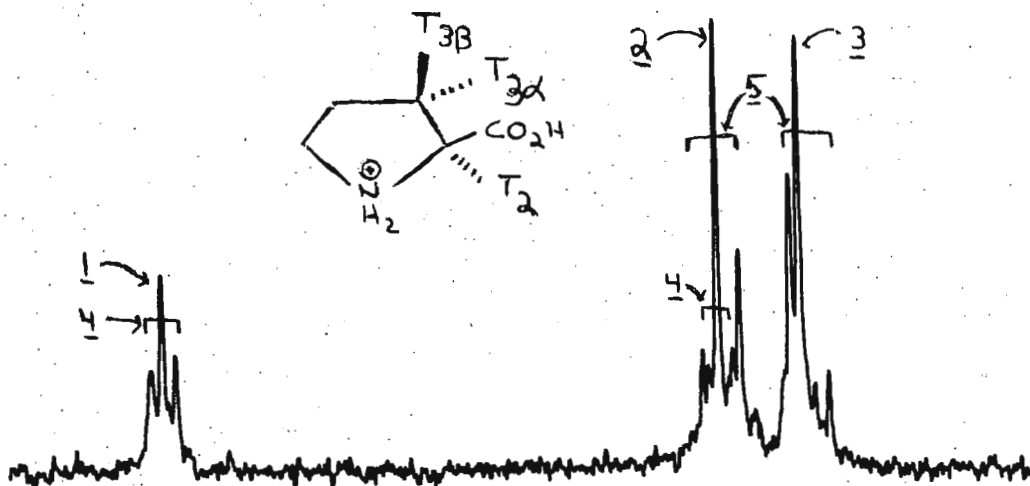


Figure 1 - Tritium NMR spectrum of mixed tritiated prolines

Professor B. L. Shapiro

August 15, 1976

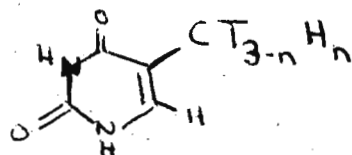
Table 1 - T_1 's and NOE of various tritiated Prolines

Compound	Position of Tritium	Percentage in Mixture*	T_1 (position) ⁺	NOE(position)
1	2	12.2%	1.40	.27
2	3 α	24.2%	1.18	.35
3	3 β	24.2%	1.25	.30
4	2,3 α	14.2%	-	.17 (2)
5	3 α ,3 β	25.1%	0.98 (3 α) 0.95 (3 β)	.13 (3 α) .17 (3 β)

* - percentages are based upon peak heights in the NOE suppressed, decoupled spectrum

+ - the errors associated with the T_1 's are approximately 0.15 seconds

Similar observations made on the methyl-labeled thymine were presented at the 17th ENC, and are summarized below.

Table 2 - T_1 's and NOE of Methyl-labeled thymine

n	T_1	NOE
0	1.18	0.03
1	1.33	0.19
2	1.84	0.37

We should also like to announce two openings within the Department of Chemistry. The first, available immediately, is for an experienced technical support person whose primary responsibility would be the maintenance of magnetic resonance spectrometers and their associated computers in the Department. The second, available in January, is for a postdoctoral research associate to engage in Tritium NMR studies.

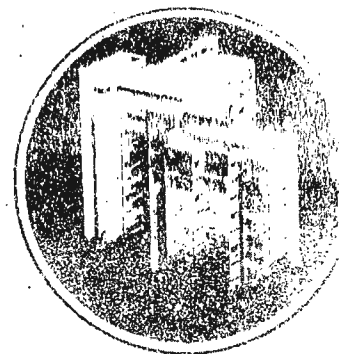
Sincerely yours,

Lawrence J. Altman
Associate Professor of Chemistry

P.S. Please credit this letter to the Newsletter subscription of Paul C. Lauterbur

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AT CHAPEL HILL



Department of Chemistry

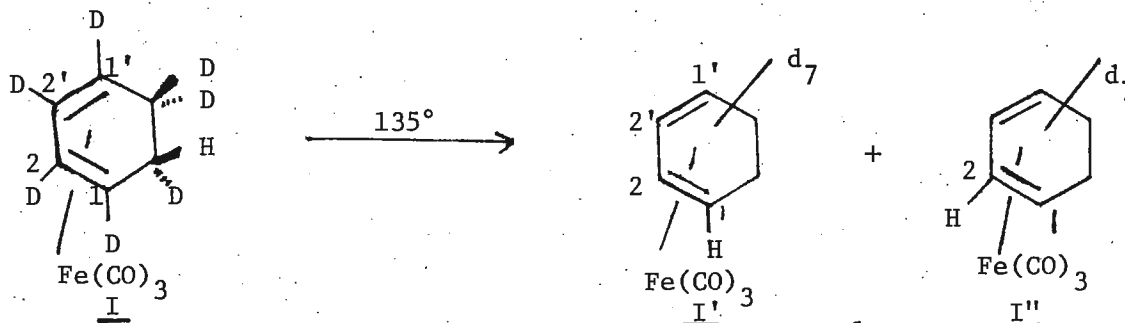
August 17, 1976

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

Title: Spurious ^1H Integrals noted During FT-NMR Rate Studies
 in Highly Degassed Solvents

Dear Professor Shapiro:

We have recently been using ^1H FT-NMR to study the thermally induced deuterium shifts in the d_7 -cyclohexadieneiron tricarbonyl complex, I. In general, endo-deuterium shifts occur, presumably through π -allyliron hydride intermediates, to scramble the single exo hydrogen to positions 1 and 2. By following the rate of decrease of the allylic exo-H signal we intended to measure the rate of the isomerization. In addition,



by following the initial relative rates of incorporation of ^1H into position 1 and 2 (i.e., the initial rates of formation of I' and I'') certain conclusions can be drawn regarding the precise nature of the π -allyliron hydride intermediates.

Experiments were initially carried out in d_8 -toluene as solvent in nmr tubes which were rigorously degassed and vacuum sealed. Concentrations of I were adjusted so that the residual proton signal of d_8 -toluene would serve as our integration standard. The following unusual results were noted. As the tubes were heated and monitored by ^1H FT-NMR, signals emerged at the expected positions for H_1 and H_2 ; however, the total integration of the ^1H resonances of the complex showed a marked decrease relative to the residual aromatic and methyl proton resonances of d_8 -toluene with increasing time. In addition we noted that the ratio of the aromatic: methyl resonances decreased from 5:2.5 to 5:3.0.

We felt it was not chemically reasonable to postulate H-D exchange between I and toluene. Further, it has been our experience that iron (0) complexes on decomposition often produce traces of paramagnetic impurities. We felt the following explanation might apply in this case: In the initial stages of the experiment the residual protons of the toluene may have longer relaxation times and thus be more easily saturated than the protons of I. As the sample is heated, traces of paramagnetic impurities develop and thus gradually level all ^1H T_1 's to similar values. This would result in the observed increase in an intensity of the toluene proton signals relative to I. Indeed, measurement of the T_1 's of a rigorously degassed d_8 -toluene solution by the fast inversion-recovery FT method revealed amazingly large values of 42 seconds for the $-\text{CHD}_2$ proton and ca. 225 seconds for the residual ring protons.

If this explanation is correct, the obvious way to cure this troublesome integration problem was to add tris-dipivaloylmethanatochromium(III) to level all ^1H T_1 's to similar values.¹ Indeed when this was done we observed a smooth decrease in the exo-H integral with time, no change in the total integration of ^1H signals of I relative to the residual ^1H signals of d_8 -toluene with time and a constant ratio of the ring:methyl integrals of the d_8 -toluene of 5:3.5 in good agreement with the ratio measured by CW-NMR.

Please credit this contribution to David Harris, our NMR expert and operator of our XL-100, who has taken over the UNC Chemistry Department subscription from Charles Johnson.

Sincerely yours,

Maurice S. Brookhart

Maurice S. Brookhart

Karin J. Karel

Karin Karel

MSB/KK/psc

REFERENCE

1. G.C. Levy, U. Edlund and J.G. Hexem, J. Magn. Resonance, 10, 231 (1973).



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Prof. B.L. Shapiro
Texas A and M University
Department of Chemistry
College of Science
College Station
TEXAS 77843

U.S.A.

Dear Prof. Shapiro,

August 26, 1976

A new FT-16-T₁ program for a Varian 620-f computer.

The original FT-16 program (No. 994100-02-E) for our Varian 620-f computer in connection with an XL-100-15 and a Sykes-Compucorder has been modified to a FT-16-T₁ program. We introduced scope display during acquisition and used ten 620-f instructions, all Jump (A-B-X) Not Zero or Jump SS1 Not Set. However we think that at least most parts of the program can be applied by 620-1,1 users.

By removing the absolute-value, BL and OK routines we could create a VCT-exit and the necessary read-in, test and read-out procedures for an automatic T₁-measurement. If SS₁ is set, the automatic way of accumulating, writing and restarting the next spectrum is followed. The VCT-exit is used too in (overnight) runs when after NK(NT) or NB(NT) transients with GG=σP=0 the F.I.D. or FT-spectrum is written automatically on tape and the acquisition restarted with GG=1 and NK (or NB)=0. The NK- routine is working with blocks of NT-transients.

With the commands DM and AI we can perform the following pulse sequences:

1. DM=0, AI=- : | -HS-PD-90°-HS-σD-90°-AT |_N
2. DM=0, AI=1 : | PD-180°-σD-90°-AT |_N
3. DM=1, AI=1 : | PD-90°-AT-PD-180°-σD-90°-AT |_N

A homo-spoil pulse (HS) is applied to the Z-axis and the decoupler is gated simultaneously.

For read-in of "-" (minus) the flag-routine was rewritten.

AI=- : Absolute intensity and homo-spoiling.

AI=0 : Neither one.

AI=1 : Only absolute intensity.

The same option is used for the GG-flag:

GG=- : The decoupler is on only during acquisition of the F.I.D.

If SS₁ is set, σD is used for the input of a maximum of 19 little t-values. The accumulated data can be stored as F.I.D. or F.T.-spectrum on tape. An input number between 0 and 99 is used as the number of points on both sides of the peak maximum. The intensities of these points are added and this integral is scaled and printed on the T.T.Y. The plot-procedure became three-dimensional if SS₁ was set, with the same value for vertical- and horizontal off-set, chosen by a command or automatically if SS₂ was set.

Another useful procedure is the calculation of the off-set in those cases where solvent absorptions are used as the reference. After the Zoom-command O, the TTY asks now for the exact place of the reference peak relative to TMS. The peak positions are then calculated relative to TMS. The plot is only moved if $SP \neq 0$.

The RE-function $RE * F.I.D. = F.I.D./SE$ is changed into a convolution function $RE * F.I.D. = (1-SE) * F.I.D.$ This procedure has the advantage that no memory overflow can occur during the calculation. A combination of different RE and SE values can be used in order to obtain narrow lines and to remove the noise.

On request we will transfer the complete program or parts of it to your own cassette-tape.

J. Runsink, W. Mellink.

W. Mellink

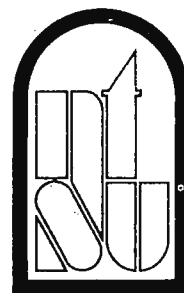
August 24, 1976

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

Dear Barry:

This is to advertise a position for an nmr technician at a salary of \$13,000 for 12 months. This position includes many fringe benefits, including Blue Cross, life insurance, retirement, and credit union. No degrees are stipulated. The duties will include maintaining and running routine spectra with our nmr spectrometers, which include: a brand new JEOL PFT-100, a JEOL PS-100, and a PE-24B. Interested parties can write me or call at 817-788-2031. North Texas State University is an Equal Opportunity Employer.

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Professor B L Shapiro
 Department of Chemistry
 Texas A and M University
 College Station
 TEXAS 77843
 USA

Your reference

Our reference

Date August 27 1976

Dear Professor Shapiro

QUANTITATIVE ^{13}C FTNMR AND TENDER MEAT

As the most highly resolving technique for liquid mixtures, C-13 FTNMR should have considerable direct use in analytical chemistry if one can increase the sensitivity and overcome the inherent non-quantitative aspects. Selective saturation and NOE differences in the sample, and unequal excitation and frequency filtering by the spectrometer are the basic problems. We have been working with internal standards, comparing peak height and/or integration, and point out two small additional factors in choosing a suitable internal standard.

We have had C-13 natural abundances checked for some of our samples and present them with respect to a standard CO_2 (accuracy $\pm 0.03\%$).

SAMPLE	^{13}C δ %
Sucrose (beet sugar)	+0.67
Sucrose (cane sugar)	+1.98
Collagen (bovine)	+1.38
Catechol	+0.90
meso-Erythritol	+0.40
Phenylpropanolamine. HCl	+0.13

In comparing a collagen product (L-hydroxyproline) with our chosen standard, phenylpropanolamine. HCl, we must expect a 1.25% correction if this is significant amongst the other errors. A second factor is the degree of substitution of the carbon of interest. The peak intensity will be reduced by 1.1 n% where n is the number of substituent carbons; probably the easiest way to allow for this is to choose an internal standard with the same substitution pattern.

Small potential errors like these only become significant when the sensitivity is high enough for the noise level to contribute a small standard deviation.

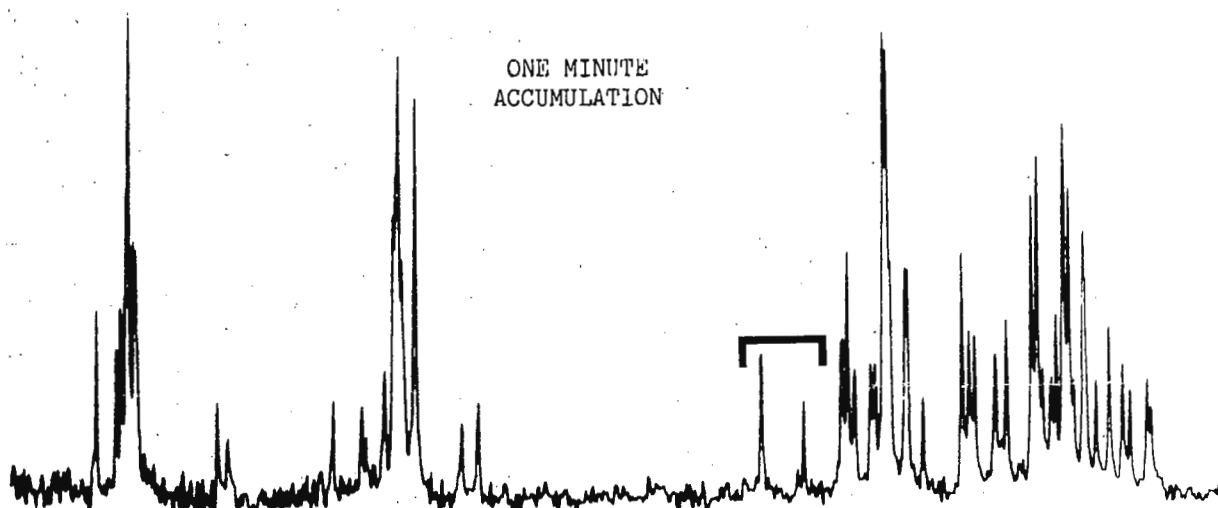
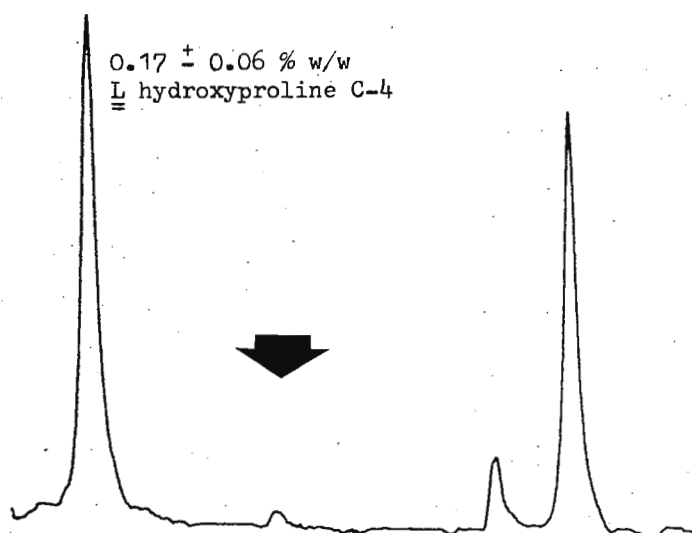


FIG A. 25 MHz ^{13}C spectrum of hydrolysed beef, 10 mm tube.

FIG B. Four hour accumulation, expansion of indicated region in A.



We increased the sensitivity for our protein hydrolysate samples such that we obtain a respectable C-13 spectrum in one minute (Fig A) and can measure L-hydroxyproline at $0.17 \pm 0.06\%$ w/w (13 mmolar) in 4 hours (Fig B). This is the lowest L-hydroxyproline concentration we found and represents very low collagen, i.e. very tender steak. With a normal 1 to 5% w/w level, we use 25 minute accumulations to measure meat quality. This procedure gives assays at least as good quantitatively as obtained by conventional analytical chemistry, plus much superior specificity.

We acknowledge Mr J Casey of M.R.I. for samples of beef muscle.

Yours sincerely

Margh Jozefowicz Ian O'Neill H. J. Prosser
 M L Jozefowicz, I K O'Neill, H J Prosser

**BRUKER SPECTROSPIN (CANADA) LTD.**

September 1, 1976

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

$^{195}\text{Pt} - ^{13}\text{C}$, ^1H Coupling in Platinacyclopentenenedione Complexes

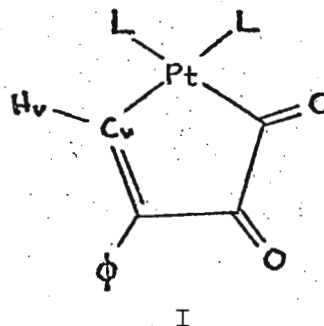
Dear Professor Shapiro:

Having remarked upon a dearth of contributions from this office in the past, I thought that my arrival as the new "chef de mission" in Canada should coincide with the communication of a little information.

I have discovered a rather odd progression of coupling constants in the compound I, as detailed in the table. Based upon normal considerations of the "trans-influence" of the ligands L^1 , one expects a decrease in the values of $^1\text{J}(\text{PtC}_\text{v})$ and $^2\text{J}(\text{PtH}_\text{v})$ as the "trans-influence" of L increases. i.e. As L competes more effectively for S-character in its bond with platinum it denudes the opposite bond of such. If the Fermi contact term describes the couplings accurately, as previous work has shown invariably to be the case¹, one would expect a decrease and not an increase in $^2\text{J}(\text{PtH}_\text{v})$ as aryl groups are replaced by a alkyl - as is in fact observed in the case of $^1\text{J}(\text{PtC}_\text{v})$.

TABLE

L	$^1\text{J}(\text{PtC}_\text{v})$	$^2\text{J}(\text{PtH}_\text{v})$
Py	1158	40.7
AsPh ₃	1056	21.5
PPh ₃	920	21.5
P(OPh) ₃	-	22.0
PPh ₂ Me	892	24.8
PEt ₂ Ph	882	30.0
PMe ₂ Ph	-	31.2
PEt ₃	871	32.0



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page _____ of letter of September 1, 1976 to Professor B. L. Shapiro

The clue to the matter is that pyridine is the only ligand to "behave". In the pyridine complex the coupling constants are the largest observed in their respective series. This is expected from the weak trans-influence of pyridine. Clearly then, the effect is steric in origin.

We have previously observed² that cis and trans-influence have an opposite relationship. Molecular models indicate extreme constraint of H_V especially in the bulky phosphine complexes it is therefore very likely that variation of cis-influence dominates $^2J(P_tH_V)$. An interesting side-product of this argument would be that cis-influence is primarily steric in origin.

A full paper is "in-press" in J.C.S. Dalton.

Please credit this contribution to the account of Bruker Instruments.

Sincerely yours,

BRUKER SPECTROSPIN (CANADA) LTD.

Martin A. R. Smith
Product Manager - Scientific

MARS/df

1. T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 1973, 10, 335.
2. K.R. Dixon, K.C. Moss and M.A.R. Smith, Inorg. Nucl. Chem. Lett., 1974, 10, 373.



August 26, 1976

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

Dear Barry: Raw Water Connections on the CFT-20

Recently, we have been able to clear up problems with the cooling system in our Varian CFT-20 which have been bothering us from the time it arrived over two years ago. We now believe that the directions for the hookup of the inlet and outlet hoses given in Figure 1-4 of the installation instructions are incorrect and that the hoses should be reversed for proper operation, at least for our system.

There were several indications that the figure is in error. One of these is that the connection as shown caused water to flow through the control valve in the opposite direction to that indicated on the valve itself. Furthermore, this mode of connection placed the valve in the water flow following the heat exchanger rather than before as would seem most logical and as is shown in Figure 4-223 of the Principles of Operation. (This latter figure, itself, has other errors, however, in that the heat sensor is located before the reservoir and water flows through the magnet coils in series instead of as shown.) Finally, the suggested mode of connection resulted in concurrent flow of raw and distilled water through the coaxial type heat exchanger. For most heat exchangers, countercurrent flow should be more efficient.¹

The connections as shown resulted both in insufficient cooling and in oscillatory behavior of the proportional controller on the raw water valve. We have routinely monitored the oscillations through measurement of the voltage between ground and the cathode of zener diode CR6. They could be partially removed through careful adjustment of the raw water pressure but have now disappeared entirely since we reversed the water connections. The controller also operates more nearly in the center of its control range now. At one point recently before the changes were made, it had actually gone completely out of control as the temperature of the raw water increased with the warmer weather.

We don't know if this problem has been general with the CFT-20. We suspect that the error is in the figure; however, it is possible that our CFT-20 was merely connected incorrectly internally. For other spectrometers, the connections may also have been made properly in spite of the misleading installation instructions. Nevertheless, it might be worthwhile for those having problems of insufficient cooling to check for countercurrent operation of the heat exchanger and proper flow direction through the water valves.

Sincerely yours,

Mark Henrichs

P. M. Henrichs
Chemistry Division
Research Laboratories

Stan Gross

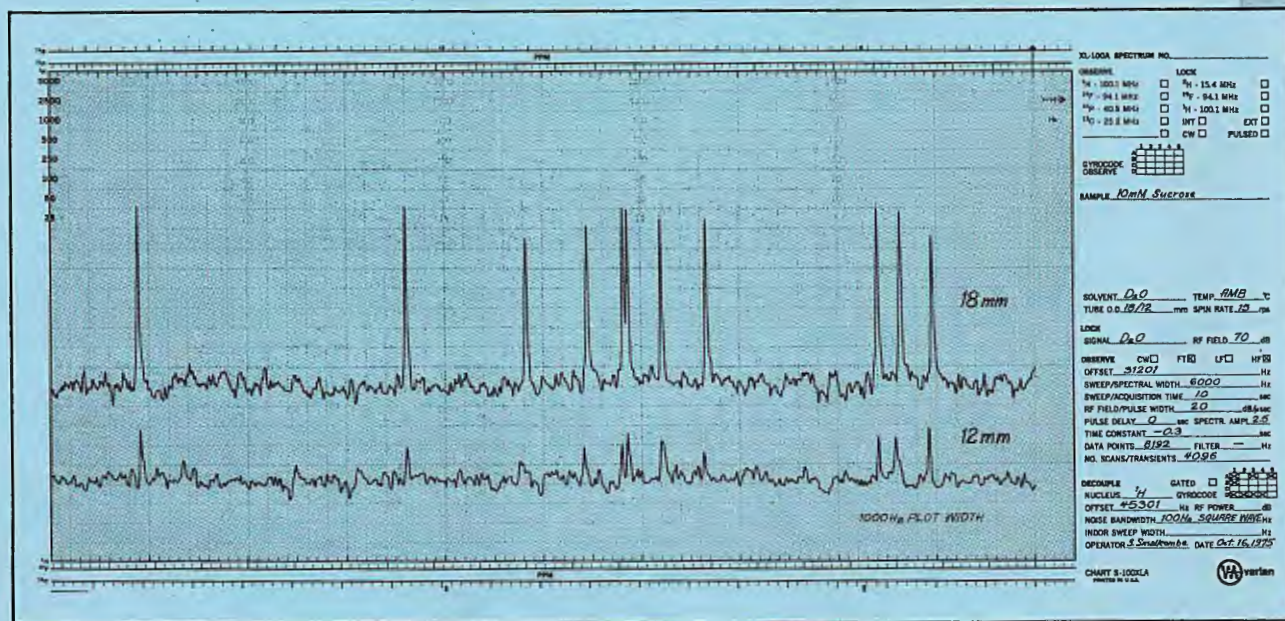
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¹A. S. Faust, "Principles of Unit Operations," Wiley, New York, pp. 229-230.

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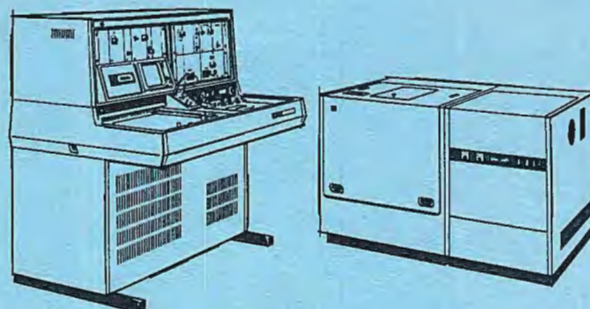


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