Texas A&M University N-M-R Newsletter

No. 190

July, 1974

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Deadline Dates: No. 188: 5 August 1974
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All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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June 5, 1974

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

Dear Barry:

It is with regret and sorrow we report to the readers of the TAMU NMR Newsletter the untimely death of our colleague Ted Lusebrink, who has contributed significantly to the field of NMR. His combination of NMR and computer knowledge led to the important programs DECOMP and ASSIGN. We remember frequently seeing him going from the spectrometer to the terminal, always looking for more direct ways to solve problems in spectral analysis.

His relatives, well-knowing his wishes, have established a T. R. Lusebrink Scholarship Fund. All of his friends who wish to contribute, can do so by sending a contribution to the fund at the:

California Canadian Bank
3902 Middlefield Road
Palo Alto, California 94306

It is truly sad to lose a good friend and colleague.

Sincerely yours,

Jerry
Jerome D. Swalen

Nino
Costantino S. Yannoni

Terry
Terry T. Horikawa

Joachim
Joachim Bargon

John
John I. Crowley

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF GEORGIA ATHENS, GEORGIA 30602

June 6, 1974

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

Dear Barry:

Some Measurements of J_{C-Pb}.

After some initial setup problems, our JEOL PFT 100 system has been in operation for about 8 months. So far, we have obtained spectra on ^{13}C and ^{31}P.

We have examined the ^{13}C spectra of a variety of organolead compounds for information concerning the bonding in these compounds and their solution structures. Chemical shift values found for these compounds are normal for organometallic compounds. However, we find that $^1J_{C-Pb}$ varies by a factor of fifteen in the compounds examined to date. The carbon-lead couplings fall in the following ranges: (a) ^1J, 155-2132 Hz; (b) ^2J, 0-200 Hz; (c) ^3J, 60-350 Hz; and ^4J, 0-33 Hz. The data for compounds of the type R_4Pb appears to support a correlation between $^1J_{C-Pb}$ and the carbon s-character in the bond. When carbon is sp^3 hybridized, $^1J_{C-Pb}$ is in the bond. When carbon is sp^3 hybridized, $^1J_{C-Pb}$ is in the range 190-250 Hz whereas when the carbon is sp^2 hybridized, $^1J_{C-Pb}$ is in the range 454-481 Hz. Although these couplings appear to be dominated by the Fermi term, it is clear that additional terms should be included.

Substituent induced increases in $^1J_{C-Pb}$ can be as large as a factor of three. For example, comparing tetravinyllead with trivinyllead acetate, we find that $^1J_{C-Pb}$ increases from 454 to 1271 Hz. Similar increases are observed with other compounds. We are suggesting that these large increases in $^1J_{C-Pb}$ are a result of a change in the coordination of lead from four to five. Evidence has also been obtained for hexacoordinated lead. It appears that $^1J_{C-Pb}$ may offer a convenient probe into the solution structure of organolead compounds. Preprints of this work are available for those interested.

Sincerely yours,

Dick

Richard H. Cox
Associate Professor

RHC:mjd

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

May 29, 1974

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

Dear Barry:

Elimination of Systematic Noise and the Estimation of Baseline in Signal-Averaged Relaxation Time Determination

Long-term signal averaging is usually necessary for the determination of spin-lattice and transverse relaxation times of nuclei present in samples at low concentrations. In our experience two serious problems arise in experiments of this type. First, low-level, non-random, periodic variations in the output of the spectrometer may tend to accumulate coherently leading to an oscillating baseline in the signal-averaged spectrometer responses. Second, the output voltages that are digitized to provide the representation of the spectrometer responses during the experiment may be offset significantly from zero, so that even when nuclear signal is absent, the digital representation of accumulated responses will numerically increase. Although it is virtually impossible to establish a numerically zero baseline for data collected from an experiment involving a large number of scans by instrumental adjustments, accurate estimation of the baseline position is essential if the data is to be further manipulated by a computer to give the relaxation times (1,2). We have implemented extensions of traditional pulse sequences for the determination of these relaxation times which simultaneously overcome both of these problems.

The philosophy behind our approach is general and has been previously applied to high-resolution FT nmr. In essence a normal signal is generated, digitized and added to the contents of the appropriate locations in the computer memory. This is followed by a second nuclear signal generated in such a way that it is the same as the first signal but opposite in sign. It is subtracted from the corresponding computer memory locations. Periodic noise that is synchronized or can be made synchronous with the appearance of these signals will be subtracted out by this procedure. Moreover, the base line of the data after such a collection cycle will be identically zero.

To implement this regime for the determination of T_1 we have used the pulse sequence

$$(180\text{-}\underline{t}\text{-}90\text{-}5T_1\text{-}90\text{-}5T_1\text{-}180\text{-}\underline{t}\text{-}270\text{-}5T_1\text{-}270\text{-}5T_1)_n$$

The response after the first 90° pulse gives a measure of M_t, the sample magnetization

Professor B. L. Shapiro May 29, 1974

after time t while the second 90° pulse affords M_∞, the equilibrium magnetization. The two 270° pulses give, respectively, the negatives of these quantities which then are subtractively collected. The net result is the accumulation of a series of positive numbers which represent M_t and M_∞ with a baseline identically zero.

Similarly, the sequence

$$90_x\text{-}\tau\text{-}(180_y\text{-}2\tau\text{-})_n\text{-}5T_1\text{-}270_x\text{-}\tau\text{-}(180_y\text{-}2\tau\text{-})_n\text{-}5T_1 \quad ,$$

an extension of the usual Carr-Purcell-Meiboom-Gill sequence, has been used in the same manner to determine T_2. An example of the results using this pulse sequence is shown in the picture (trace B). Trace A, obtained with the usual CPMG sequence, shows evidence of 120 Hz fluctuations on the baseline. The extent of such effects dependsupon the degree of alignment between the repetition time of the experiment and the line frequency and can be made an order of magnitude worse for the experiment shown in Trace A by carefully synchronizing the start of each scan with the line as was done for experiment B. This source of baseline perturbations could potentially be minimized by starting each sequence randomly but an undefined number of scans would be required to average out such effects. Assuming that instrumental drifts are small over the time required to complete the total cycle, the mode of data collection described here will be effective for any number of scans.

References

1. W. S. Moore and T. Yalcin, J. Magn. Resonance, 11, 50(1973).

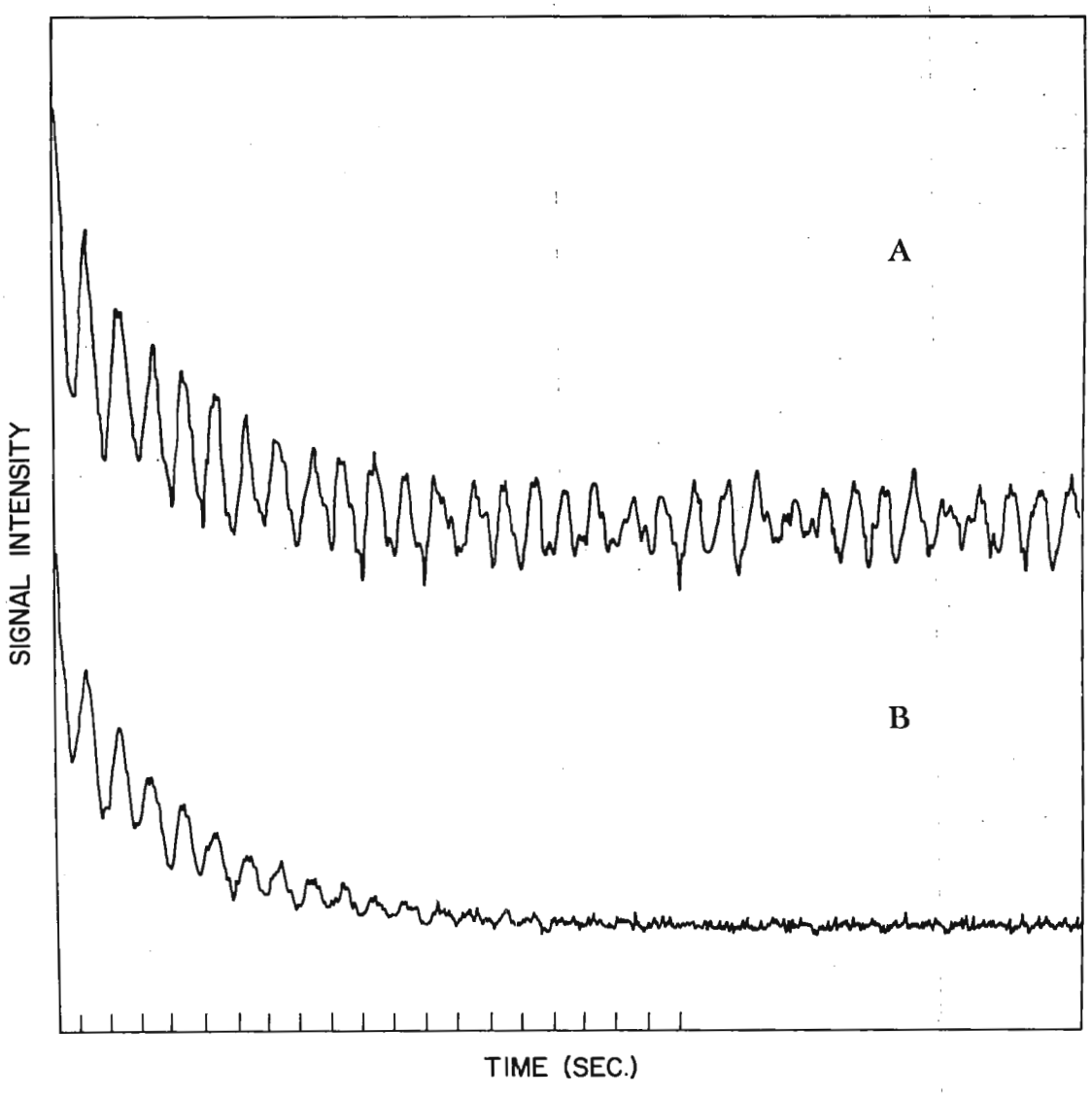
2. J. T. Gerig, G. B. Matson and A. D. Stock, J. Magn. Resonance, 12, 48(1973).

Sincerely yours,

J. T. Gerig

G. B. Matson

A. D. Stock



Carr-Purcell-Meiboom-Gill experiments with 3×10^{-3} M m-trifluoromethylbenzenesulfonic acid doped with Cu^{++}. The fluorine frequency was 51 MHz. Trace A: 1024 collections with all scans added. Trace B: Same sample and pulse settings as for A except that 512 scans were added and 512 scans subtracted alternately. The start of each scan for trace B was synchronized with the line frequency. Collection for trace A was not synchronized with the line although some partial synchronization is evident. Each time mark represents a 180° pulse spaced at 10 msec.

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Professor C.L. KHETRAPAL
Dr. A.C. Kunwar

June 12, 1974

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

Title: Once again 'Oriented' methyl alcohol!

Dear Professor Shapiro,

Thank you very much for the 'blue' reminder.

We have studied the PMR spectrum of methyl alcohol oriented in the nematic phase of EBBA with and without the presence of lanthanide shift reagents . The experiments lead to the following conclusions:

1 The OH exchange in EBBA is considerably slow such that the spectra correspond to AB_3 patterns.

2 The sign of the indirect HH coupling constant (J_{AB}) thus determined is opposite to that of the direct dipolar coupling (D_{BB}) within the methyl protons.

3 Widths of the spectral lines without the lanthanide shift reagents were found to be nearly half compared to those with them.

4 Molecular orientation was found to decrease substantially by complexation with the shift reagents. However, when the shift reagent used was either $Pr(fod)_3$ or $Eu(fod)_3$ (where fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione), the D-values found were about the same.

5 The magnitude of J_{AB} seems to reduce by complexation with the shift reagent .

Details of this work will appear in the August issue of the Journal of Magnetic Resonance.

Yours sincerely,

C.L. Khetrapal. A.C. Kunwar

(C.L.Khetrapal) (A.C. Kunwar)

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

June 14, 1974

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

Dear Barry:

In an effort to provide a basis for the spectroscopic characterization of 5,5-disubstituted barbituric acids and related hypnotic agents for use in binding studies and possible applications to structure-activity relationships we have carried out preliminary CMR investigations of (2,4(6), 5-^{13}C) enriched 5-ethyl-5-phenyl(I) and 5-ethyl-5-(2'-pentyl)(II) barbituric acids as well as (2,4,5-^{13}C) 5,5-diphenyl hydantoin(III). We would like to report some new values of one, two, and three-bond C^{13}-C^{13} couplings (Tables 1 and 2). The effect of ionization of the amide proton on the value of $J_{CC}(4,5)$ and $J_{CNC}(2,4)$ of (I) is 8.0 and 7.6%, respectively.

As far as we can determine, none of these values have been previously reported.

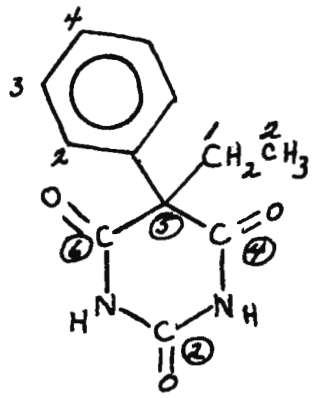
Sincerely,

J. H. Goldstein

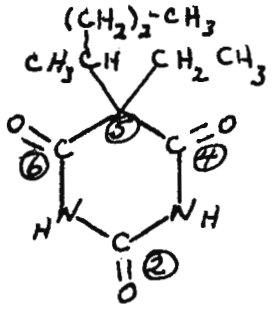
Robert C. Long, Jr.

Table 1. Directly Bonded ^{13}C - ^{13}C Couplings[a]

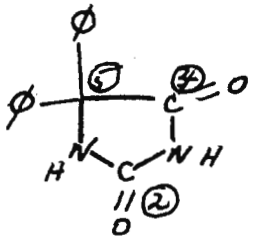
	MeOH	(Buffer,pH = 10.6)
5-ethyl-5-phenyl Barbituric Acid (2,4(6),-^{13}C)		
J_{CC} (4,5) = J_{CC} (6,5)	47.82 ± 0.07	44.26 ± 0.10
J_{CC} (5,1Ø)	40.46 ± 0.10	
J_{CC} (5,1Et)	35.02 ± 0.10	
5-ethyl-5-(2'pentyl) Barbituric Acid (2,4(6),-^{13}C)		
J_{CC} (4,5)	48.21 ± .14	
J_{CC} (6,5)	48.21 ± .14	
5-5-diphenyl Hydantoin (2,4,5-^{13}C)		
J_{CC} (4,5)	46.64 ± 0.05	



(I)



(II)



(III)

[a] The notation 4(6) implies 4 or 6 is enriched. Enrichment is 90.0, 45.25 and 90.5% at positions C_2, C_4, or C_6, and C_5 in I and II and 90.5 at C_2, C_4, and C_5 of III.

Table 2. Two-Bond ^{13}C - ^{13}C Couplings[a]

	MeOH	(Buffer, pH = 10.6)
5-ethyl-5-phenyl Barbituric Acid (2,4(6),5-^{13}C)		
J_{CNC} (2,4) = J_{CNC} (2,6)	3.13 ± .06	2.91 ± 0.10
J_{CCC} (4,1Ø) = J_{CCC} (6,1Ø)	2.22 ± .20	
J_{CCC} (5,2Ø)	2.91 ± .10	
J_{CCC} (5,2Et)	<1.0	
5-ethyl-5-(2'-pentyl) Barbituric Acid (2,4(6),5-^{13}C) (II)		
J_{CNC} (2,4) = J_{CNC} (2,6)	3.16 ± 0.08	
5,5-diphenyl hydantoin (2,4,5-^{13}C) (III)		
J_{CNC} (2,5)	1.43 ± 0.03	
J_{CNC} (2,4)	8.01 ± 0.05	

Three-Bond ^{13}C - ^{13}C Couplings	
5-ethyl-5-phenyl Barbituric Acid (2,4(6),5-^{13}C) (I)	
J_{CNCC} (2,5)	1.10 ± 0.05
J_{CCCC} (5,3(3')Ø)	<1.0
5-ethyl-5-(2'-pentyl) Barbituric Acid (2,4(6)-5-^{13}C) (II)	
J_{CNCC} (2,5)	1.07 ± 0.05

[a] The values in the table reflect only the magnitudes of the couplings, the signs have not been determined.

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P. O. BOX 39175
CINCINNATI, OHIO 45239

June 14, 1974

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

Dear Prof. Shapiro:

About two years ago we converted one of our HA-100 spectrometers to observe phosphorus-31 in the centerband sweep mode, as described in TAMU NMR Newsletter #162. We have been very satisfied with this scanning technique; although, observation of the lock signal was somewhat of a problem. Since the signal from a 1 mm ID (1-1/2 mm OD) P_4O_6 lock reference capillary is too weak to be observed in the usual manner on the instrument oscilloscope, various lock monitoring methods were tested. A recent modification has proven most satisfactory. The only instrument modification requires a sixth position of the function switch on the integrator/decoupler V-3521A. The filtered signal obtained at pin P of connector J-1316 of the internal reference stabilizer V-4354A is connected through the function switch to the microamp meter (accumulated integral meter) on the V3521A integrator. This large meter provides an excellent lock signal monitor, sensitive to the smallest changes in field homogeneity. At present we are in the process of modifying the integrator/decoupler on our fixed RF proton HA-100 spectrometer so that we can monitor the lock on the meter in addition to the oscilloscope lock display.

Yours truly,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

C. D. Sazavsky

C. D. Sazavsky

blk

Suggested Title: "Inexpensive monitor for weak lock signals on internal reference spectrometers"

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2

June 17, 1974

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

Dear Barry,

THE TVIT PULSE SEQUENCE

The new device of Professor Pines (TAMU 188) has led me to develop a new pulse sequence which traces the paths of individual electrons in a molecule. The nature of the pulse sequence can be understood if one considers that three variables are needed to specify position and that one must include the time in a path description: Three variables including time.

A slight acquaintance with quantum mechanics shows that we have here a method worthy of this preliminary communication. My detailed analysis implies that we can now follow the path of one electron as it moves between orbitals[1], so that much of the mystery surrounding molecular events will now be clarified. This discovery will impart fresh meaning to the remarks made in 1955 by Professor Gordy[2] concerning "the highly precise and diverse information" available from r. f. techniques.

The shape of the observed responses[3] indicates that the path is defined by a third-order partial differential equation.[4] One interesting consequence of the boundary conditions is that nuclei do not, in fact, exist, but are simply singularities in unacceptable solutions to this useful equation.

The practical consequences of this result for certain instrument makers (or tenure committees) may be considerable. However, I have taken steps to patent my sequence (spinning of the magnet is an integral part of it) and am open to negotiations.[5]

Yours sincerely,

T. Schaefer
Professor

TS/bm

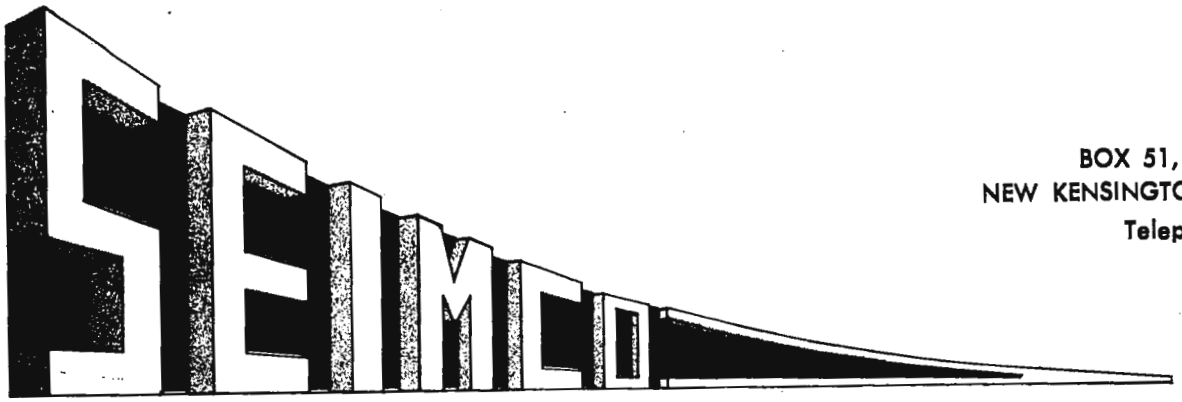
1 Which are now well defined, a subsequence called SPDF being available.

2 Discussions Faraday Society, No. 19, 1955, p. 14

3 One minor difficulty involves the infinite amount of time needed to obtain the transform but a little work should reduce this by a factor of two or more.

4 Suggested name, the Schläfer equation.

5 Various other sequences, such as DAFT and SOFT, will become available and are certifiable.



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SCIENTIFIC ELECTRONIC INSTRUMENT and MANUFACTURING CO. INCORPORATED

June 18, 1974

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M university
College Station, Texas 77843

Dear Barry:

We have received, by postal error, a package of partially mutilated spectra from the postmaster, Detroit, Michigan. The only reference to the sender or the intended recipient is the name of the spectrometer operator, S. BUSMAN.

In that the volume of spectra represent a considerable effort, we wish to return them.

If you can identify S. BUSMAN, please put us in touch with him or vice versa.

Thanks for your help.

Sincerely,

G. D. Vickers
President

cc Postmaster
Detroit, Michigan 48233

We regret that the address of D. N. Lincoln and V. Wray was left off their contribution in the June issue (#189-31). Their address is:

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DEPARTMENT OF CHEMISTRY

May 3, 1974

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

Dear Barry:

SUBSTITUENT DEPENDENCE OF VICINAL ^{13}C-^{13}C COUPLING CONSTANTS

The problems of conformational and substituent effects on vicinal C13-C13 coupling constants are unique and interesting (1,2). The vicinal C13-C13 coupling constant in a sample of 1-fluorobutane [kindly supplied by Dr. J. L. Marshall and Denis Miiller of North Texas State University], which was enriched with C-13 in the 1-position, was found to be 4.1 Hz. The measurements were made on a Bruker Scientific FT spectrometer, operating at a frequency of 22.64 MHz.

Theoretical results for the conformational dependence of the vicinal C13-C13 coupling in fluorobutane were based on the finite perturbation formulation for coupling constants in the INDO approximation of semi-empirical MO theory. The calculated results in the figure exhibit substantial dependence on the dihedral angle ϕ, which is measured about the C2-C3 bond in the figure, but also on the dihedral angle ϕ', which is measured about the C1-C2 bond in the figure. The much larger vicinal coupling in the arrangement for which $\phi = 0°$ and $\phi' = 180°$ is almost certainly attributable to the interaction of the rear lobe of C-F carbon orbital with the orbitals of the C4 carbon and the attached hydrogen atoms.

An average of the nine lower energy conformations, weighted with respect to the Boltzmann factors, yields a calculated value of 3.8 Hz for the vicinal C-C coupling constant. Clearly, there are no other experimental points for comparison with the calculated results in the figure. However, in the cases of acyclic and cyclic acids (1) and alcohols (2) the INDO-FPT results predict the general trends, including cis coupling constants which are larger than trans (2).

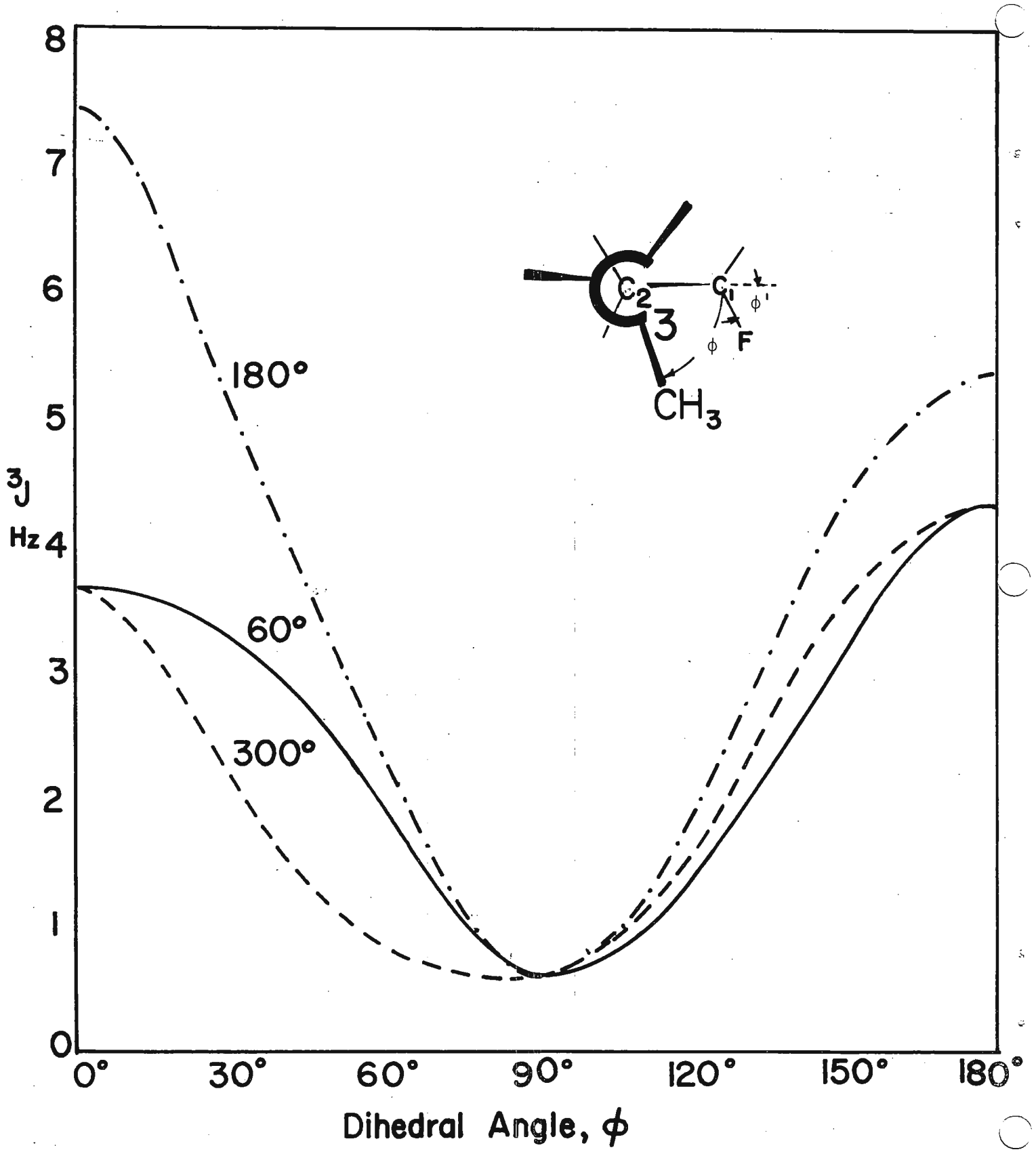
Sincerely yours,

Mike

Mike Barfield

1. J. L. Marshall and D. E. Miiller, J. Amer. Chem. Soc., 95, 8305 (1973).

2. D. Doddrell, I. Burfitt, J. B. Grutzner, and M. Barfield, J. Amer. Chem. Soc., 96, 1241 (1974).


8
7
6
5
4
3
2
1
0
^3J Hz
180°
60°
300°
C_2
C_1
3
ϕ'
ϕ
F
CH_3
0°
30°
60°
90°
120°
150°
180°
Dihedral Angle, ϕ

COLORADO SEMINARY
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UNIVERSITY PARK • DENVER, COLORADO 80210

DEPARTMENT OF CHEMISTRY / 303 • 753-2436

June 18, 1974

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

Dear Barry:

Title: Postdoctoral Position Available

Two postdoctoral positions are available in my laboratory. The project involves synthesis, spectroscopy, and calculations related to the NMR and EPR of interacting spin systems. Since there are two positions available the candidates expertise may be in synthesis, in the theory of magnetic resonance, or in a combination of these.

Please bring these positions, which are available immediately, to the attention of all interested persons. Candidates should send a curriculum vitae and arrange for three letters of recommendation to be sent to me by August 1, 1974.

The University of Denver is an Affirmative Action/Equal Opportunity Employer and encourages applications from women and members of minority groups.

Sincerely,

Gareth

Gareth R. Eaton
Assistant Professor

GRE:pk

ROCHE

30 May 1974

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

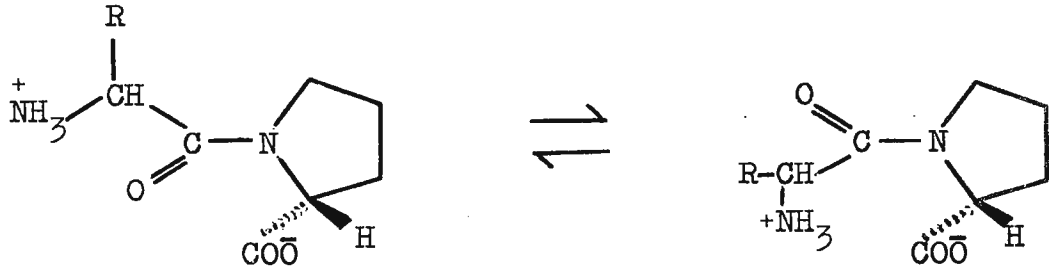
Roche Products Limited Welwyn Garden City Hertfordshire Telephone Welwyn Garden 28128 Telex 262098

Title - Further Perils of Proline - SIMEK programme

Dear Barry

In response to your pink reminder, may I offer some odd facts concerning cis/trans isomerism in proline-containing peptides, plus a plea for help with the SIMEK spectrum calculating/plotting programme.

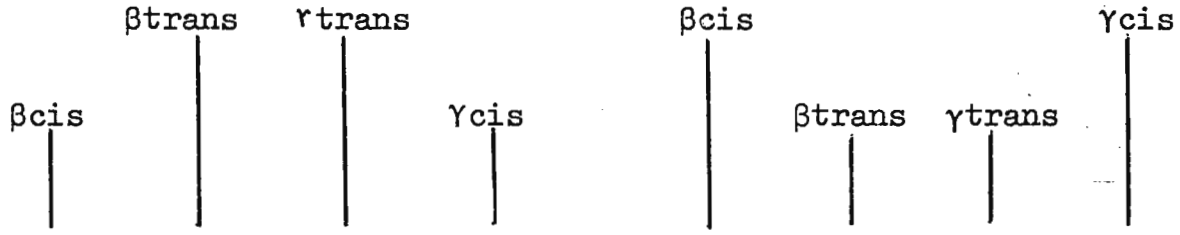
For some time we have been examining the ratios of cis to trans isomers in proline derivatives. In our early studies using ^{1}H and ^{13}C spectroscopy[1], we showed that for Gly-Pro, Ala-Pro and Val-Pro, the cis/trans ratio remained the same (~60% trans) at neutral pH. Voelter and Oster have shown that the ratio is affected by the presence of N-protecting groups[2]. In the ^{13}C spectra, the isomerism is best observed



trans cis

	% trans isomer (D_2O)
Gly-Pro	59
Ala-Pro	57
Val-Pro	61
Phe-Pro	26
Met-Pro	50
Gly-Pro-Ala	22
Ala-Pro-Ala	<10

for the β/γ carbons, which generally appear as a characteristic quartet of lines, with the inner pair (trans isomer) generally predominating (I). In Phe-Pro, however the reverse



(I) (II)

pattern is observed, and since the shift differences βcis - γcis or βtrans - γtrans are consistent with other dipeptides we conclude that the ratio has reversed. This is confirmed in the ^1H spectrum, where a more reliable cis/trans ratio is found. In methionyl proline (Met-Pro) however a 50-50 mixture appears to be present. When proline is no longer the C-terminal amino acid the percentage of cis isomer decreases, but there is still ~20% "cis proline" in Gly-Pro-Ala in D_2O solution.

I was pleased to receive recently, from Jim Feeney and Gordon Roberts at the M.R.C. Unit, Mill Hill a copy of SIMEQ II-16[3], a spin simulation programme written by Dr C W F Kort in (Amsterdam University) and Dr M J A de Bie (Utrecht University), but dismayed to find that the plotting routines in the programme did not work with the Varian 620-L MK II interface. If anyone has found a way around this problem I would be delighted to hear from them as the programme is a very useful addition to the 620L/XL100 library.

Best wishes

Yours sincerely

Dr W A Thomas

References

1. W A Thomas and M K Williams, Chem. Comm. 1972, 994.

2. W Voelter and O Oster, Org. Mag. Res. 1973, 5, 547.

WAT/LS

National Research Council Canada | Conseil national de recherches Canada

Division of Chemistry | Division de chimie

Dr. Alois Steigel

File Référence

20 June, 1974

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

Dear Dr. Shapiro:

Classical and Quantum Mechanical Calculations for AB⇌BA

During my research visit at the NRC I had the opportunity to perform line shape simulations of dynamic NMR spectra (cp. Sydney Brownstein, TAMUNMR 184-33). In my first contribution to your unique Newsletter I wish to draw the attention again to the AB⇌BA case.

An effort to rationalize the effects of exchange on spin systems with simple models has been made recently by Whitesides and coworkers (1). For the most simple second order system, AB⇌BA, Johnson (2) could derive that the exchange modified Bloch equations are adequate to describe the line shapes. I want to illustrate the relation of the quantum mechanical and classical calculations for this case by using the method of Binsch to calculate spectral and shape vectors (see DNMR 3). The nice feature of Binsch's method is that the imaginary part of the spectral and the real part of the shape vector for a special transition correspond to its intensity and frequency respectively; the additional information inherent to these vectors - broadness and deviation from Lorentz shape - will not be used here.

Both the quantum mechanical and the classical calculations have been performed for a representative example (ν_A=20 Hz, ν_B=40 Hz, J=10 Hz, T_2=1) with the same type of matrix equations (1 and 2) using the subroutines ALLMAT, NVRT and CONVEC of DNMR3 to solve them. The values for the line positions, exchange probabilities and populations of the classical equation 2 have been obtained by calculating the spectral and shape vectors for the static AB spectrum (eqn. 1, k=0). They are identical with the values Johnson reported to be adequate for an exact simulation of the line shape ($-\bar{\omega}\pm J/2\pm C$ and $1\pm\sin 2\theta$).

Ottawa, Canada
K1A 0R9

$$G = -iC(1,1,1,1)\begin{Vmatrix} -1-k+(94.248-\omega)i & 0 & k+31.416i & 0 \\ 0 & -1-k+(157.08-\omega)i & 0 & k-31.416i \\ k+31.416i & 0 & -1-k+(219.91-\omega)i & 0 \\ 0 & k-31.416i & 0 & -1-k+(282.74-\omega)i \end{Vmatrix}^{-1}\begin{Vmatrix} 1 \\ 1 \\ 1 \\ 1 \end{Vmatrix} \quad \underline{1}$$

$$G = -iC(1,1,1,1)\begin{Vmatrix} -1-1.4472k+(86.831-\omega)i & 0 & 0.5528k & 0 \\ 0 & -1-0.5528k+(149.663-\omega)i & 0 & 1.4472k \\ 1.4472k & 0 & -1-0.5528k+(227.328-\omega)i & 0 \\ 0 & 0.5528k & 0 & -1-1.4472k+(290.159-\omega)i \end{Vmatrix}^{-1}\begin{Vmatrix} 0.5528 \\ 1.4472 \\ 1.4472 \\ 0.5528 \end{Vmatrix}^{2} \quad \underline{2}$$

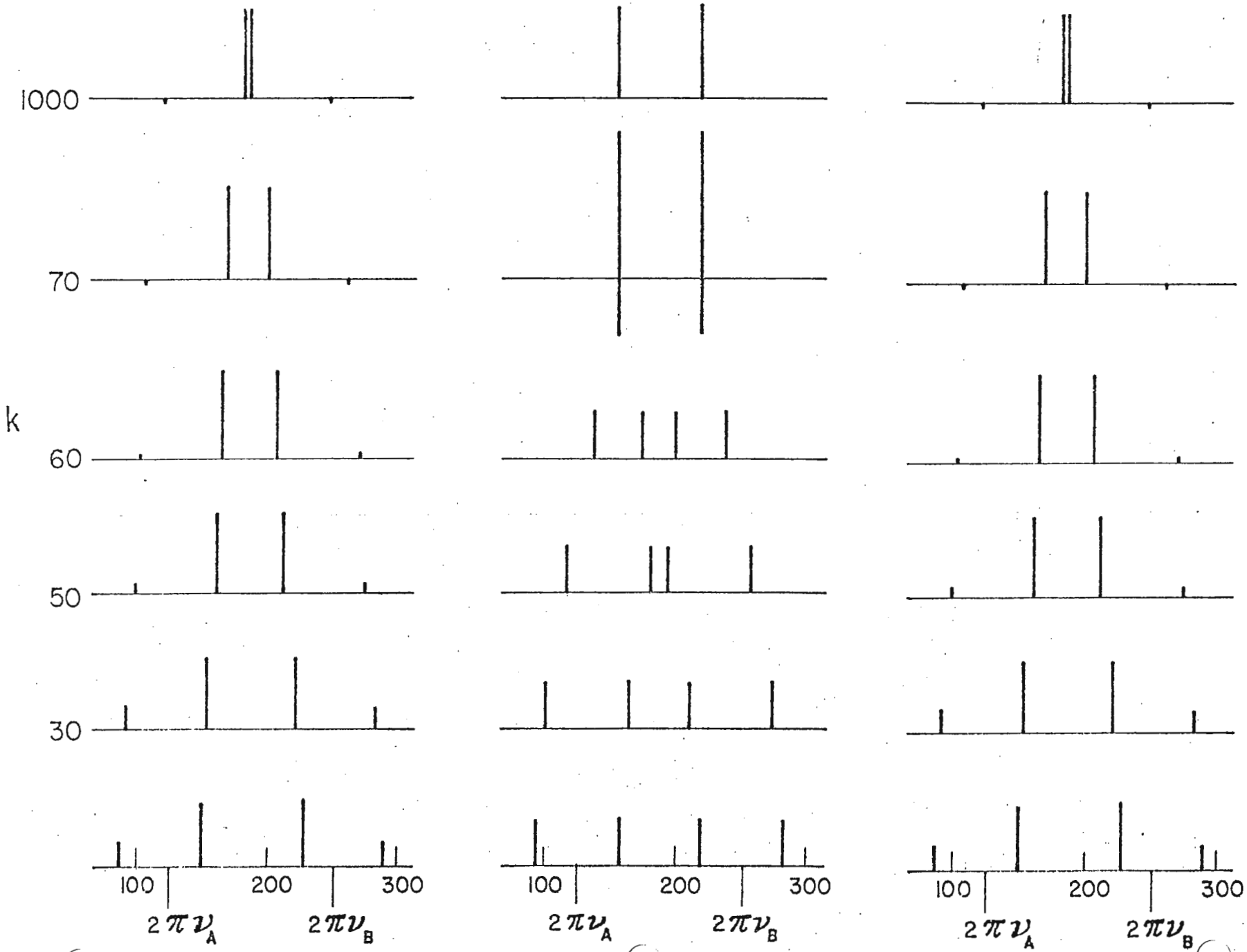
The line positions and intensities calculated from equations 1 and 2 as a function of the exchange rate k are in perfect agreement (left and right side of the figure). For the fast exchange region one sees small "negative intensities"; but the corresponding broadness of these "lines" does not allow for an abnormal line shape. The fact that the outer transitions have been calculated to be negative is thought to be due to the numerical procedure of solving the eigenvalue problem. The results for a first order type calculation are depicted in the middle of the figure. The matrix equation used for these calculations is identical with equation 1 except that the imaginary off-diagonal elements ($\pi \cdot J \cdot i$) have been omitted. Neglecting second order effects evidently does not lead to a collapse of the splitting; the crossover of the two inner lines occurs at k ca. 63.

Similar calculations for more complicated spin systems have been performed (paper in preparation). Just now I am summarizing the recently established methods for studying the mechanisms of exchange processes by line shape analysis in a progress article for the Angew Chemie.

Yours sincerely,

Alois Steigel.

(1) J.K. Krieger, J.M. Deutch, and G.M. Whitesides, Inorg. Chem. 12, 1535 (1973).
(2) C.S. Johnson, Jr., J. Magn. Res. 1, 98 (1969).


1000
70
k
60
50
30
100
200
300
$2\pi\nu_A$
$2\pi\nu_B$

Dr. O. Lutz
PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT TÜBINGEN

7400 TÜBINGEN, den 21.6.1974
Morgenstelle
Telefon (071 22) 71 2423

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

Ihr Zeichen | Unser Zeichen | Ihre Nachricht vom

Dear Professor Shapiro,

Re: NMR of less common nuclei with weak signals.

We are very interested to participate in the TAMMUN Newsletters. Our NMR Fourier-Transform facility is based on an externally ^{7}Li NMR stabilized magnet (18.07 kOe) and a Bruker B-Kr 322s pulse spectrometer with a frequency range of 4 MHz to 62 MHz. In this region the Larmor frequency of about 80 % of the nuclei with non-zero spin is situated. Therefore we are investigating the NMR signals of nuclei other than protons, recently especially less common nuclei with very weak signals.
In the last time investigations of the following nuclei have been done: ^{10}B, ^{25}Mg, ^{43}Ca, ^{67}Zn, ^{85}Rb, ^{111}Cd, ^{115}Sn, ^{117}Sn, ^{119}Sn, ^{207}Pb.
The aimes of our investigations are:

1) Dependence of the NMR frequency of these nuclei in aqueous solution on the concentration and sort of soluted salt.
2) Temperature dependence in aqueous solution.
3) Solvent isotope effect of these nuclei (an unusual effect has been found in the case of ^{67}Zn (1),(Z.Naturforsch. 29a, 660 (1974))
4) Shielding constants of these nuclei and atomic reference scale (2), (Z. Physik 266, 233 (1974) for chemical shifts in the liquid, solid and metallic state.
5) Ratios of Larmor frequencies for the determination of hyperfine structure anomalies and primary isotopic effect.
6) Investigations upon the application of the NMR technique on biological problems using these less common nuclei.

Yours sincerely
O. Lutz
(O. Lutz)

the Nicolet 1020A is a time averaging system for magnetic resonance spectrometers that gives you results like these:

The Nicolet 1020A is an easy-to-use time averaging system combining unique data processing capabilities with extremely useful display and readout routines.

Using a normalized signal averaging method, the 1020A presents a true average on its built-in 5″ CRT display. The complete spectrum (or any expanded portion of it) is continuously displayed throughout the averaging process.

Thumbwheel switches select sweep times from 60 milliseconds to 1,999 seconds for a 2048-word sweep with 4-digit accuracy. The 1020A can provide sweep current to the spectrometer and can compensate for spectrometer field drift when using the Field Stabilization mode. The calibrated sweep widths are front panel selected and can be matched to any spectrometer.

The analog-to-digital converter (ADC) resolution is 12 bits (one part in 4096) for sweep times over 1 second and 9 bits (one part in 512) for sweep times less than 1 second.

Total memory capacity is 2048 words, 24 bits long. The upper 12 bits store the final average while the lower 12 may be used to store the integral. Averaged spectra may be stored in halves of memory and added to or subtracted from one another.

Digital integration is built-in and does not destroy the original spectrum thus allowing simultaneous display of spectrum and integral. Baseline correction can be accomplished during display of the integral to assure optimal results.

Another unique display feature is the ability to expand the displayed spectrum in both the X and Y axes by factors of 2 up to a total expansion of 64 times. (Typical expansion examples are shown to the right). In addition to this analog display a simultaneous numerical display shows the amplitude and address values of any data point selected by a moveable electronic cursor.

Write or call collect for complete details or to arrange a demonstration in your laboratory.

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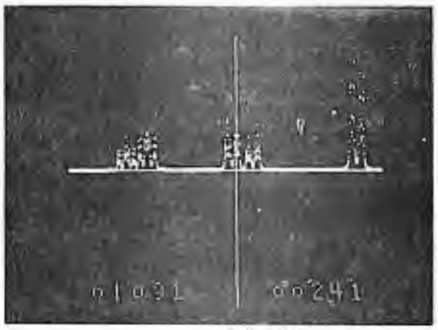
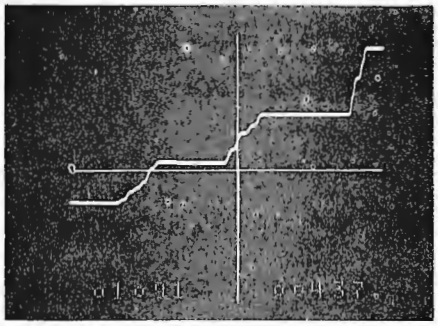
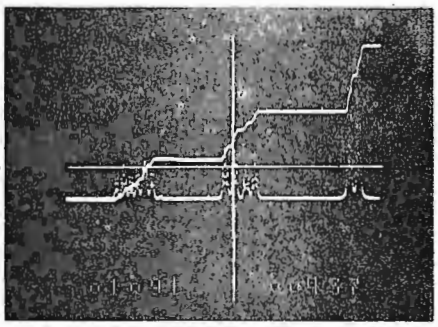


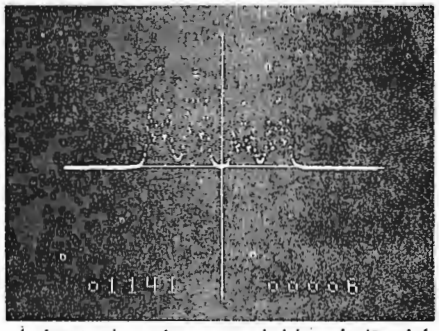
1. Averaged spectrum of 2-butyl-1, 2-dihydropyridene with spectrum expanded on amplitude scale by a factor of 2.



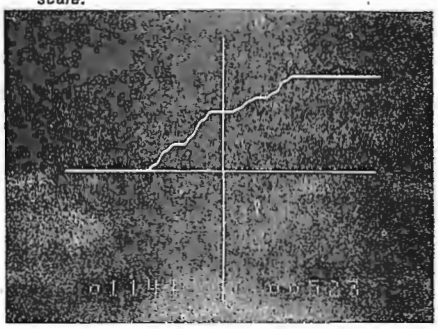
2. Integral of Figure 1 averaged spectrum.



3. Figure 1 spectrum and Figure 2 integral displayed simultaneously.



4. Averaged spectrum expanded by a factor of 4 on both the amplitude scale and the frequency scale.



5. Integral of Figure 4 averaged spectrum.

In Europe: Nicolet Instrument GmbH, Goerdeler Strasse 48, D-605 Offenbach am Main, West Germany, 0611/852028, Telex: 841/4185411

UNIVERSITY OF SOUTH FLORIDA
TAMPA • ST. PETERSBURG

DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813: 974-2571

June 28, 1974

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

Dear Barry:

One of the more annoying problems confronting workers doing *precision* work with lanthanide shift reagents (LSR) is the occasional presence of non-trivial amounts of impurities. Usually, the main impurities encountered are the lanthanide oxide (Ln_2O_3) and excess ligand (in the cases discussed here, the FOD ligand). This list is restricted to reagents stored over P_4O_{10}; it is extended considerably otherwise. The oxide is easily removed--it is simply the residue left behind after vacuum sublimation. However, excess ligand has the annoying property of subliming right along with the LSR and depositing itself on the cold finger.

The excess ligand is probably the source of extra peaks in spectra erroneously attributed by some workers to LSR-dimer formation. If the LSR be pure, one should see only one resonance, namely that of the *t*-butyl group. The presence of extra peaks is almost certainly owing to unwanted ligand.

How to get rid of the excess ligand? I have found one easily-done method which works quite well. When doing the sublimation, use a "hot-finger." That is, use hot water in the sublimer's ex-cold-finger. If one sends through water at ~60°C, the ligand goes on into the cold trap of the vacuum system. This procedure was tested on a bad lot of $Yb(FOD)_3$ and worked quite well. LSR sublimed without the hot-finger gave LSR with two peaks in its spectrum; use of the hot-finger completely removed the impurity resonance. Use of this method is easy and convenient and avoids the necessity for recrystallization.

One final word. $Yb(FOD)_3$ is much more difficult to purify than the Eu and Pr analogs. This is most likely owing to its much lower melting and sublimation temperatures.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Assistant Professor of Chemistry

PURIFICATION OF LSR's

University of East Anglia

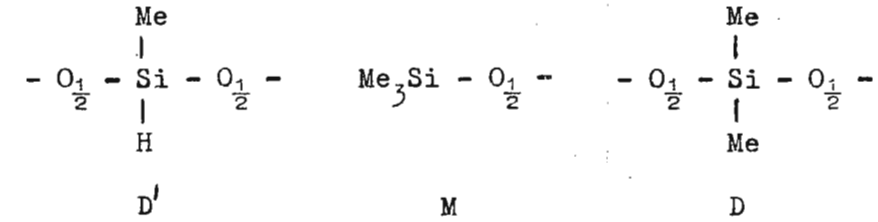
School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH
England

6 June 1974

MICROSTRUCTURE OF SILICONE POLYMERS

Dear Barry,

Our ^{29}Si NMR work is now yielding some very interesting results, in particular for silicone polymers, and we would like to keep our subscription to TAMUNMR alive by mentioning some of the results briefly. The methylsiloxy unit (referred to as D′) has proved to be



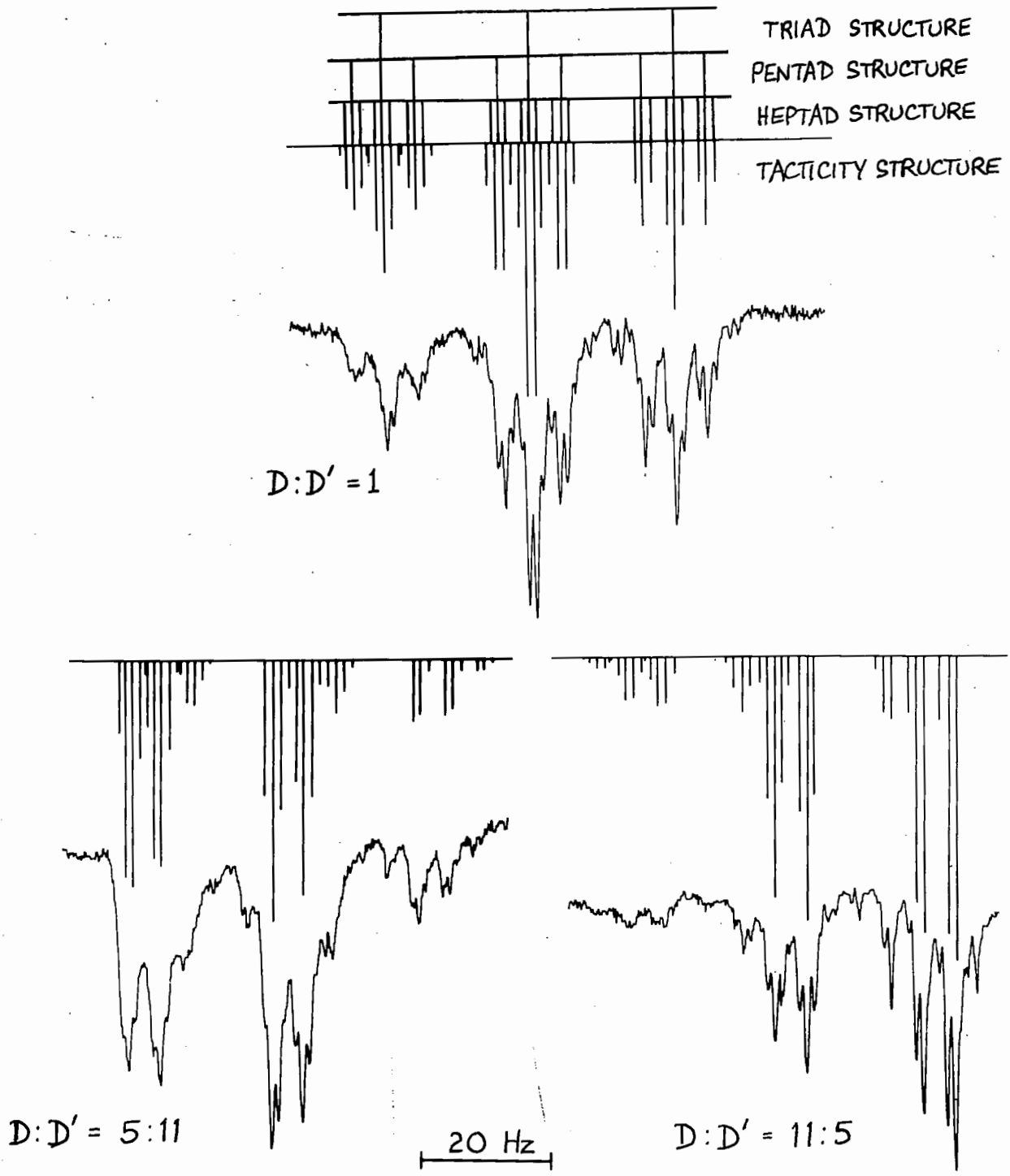
particularly useful, since we can detect tacticity effects - neighbouring units cause a splitting of ca. 1 Hz from this origin. We can also differentiate signals from the end three D units in polymers of the type MD'_nM, where M is the trimethylsiloxy end-stopper group and n is ca. 50. Such results should appear in Chem. Comm. shortly. We have now looked at mixed polymers containing D′ and D units, where D refers to a dimethylsiloxy group, and find a wealth of fine structure for the D′ unit (see the figure). We can, in fact, explain all the features of the observed pattern if we recognize structure at the heptad level, as well as tacticity and end-group effects. The heptad splittings are ca. 1 Hz and differentiate such structures as D′DD<u>D′D</u>′DD from DDD<u>D′D</u>DD. The figure shows how these considerations lead to understanding of the spectra. obviously it is helpful to vary the D:D′ ratio in order to assign the peaks. It should be pointed out that our samples generally have a wide range of polymer chain-length (the average is known from the method of preparation). Oligogomers with chain length <10 have been removed by vacuum stripping. The amount of information about microstructure obtainable from the ^{29}Si spectra far exceeds that which is known from all other techniques. Needless to say we are using FT techniques, with proton noise decoupling. The NOE for $^{29}Si-\{^1H\}$ for the cases illustrated is such that the signal is negative.

We hope this contribution satisfies all your criteria!

Yours sincerely,

Robin Harris Barry Kimber

R.K. Harris, B.J. Kimber



^{29}Si-{^{1}H} NMR SPECTRA FOR THE D′ GROUP OF MIXED SILICONES

The average number of Si atoms in the polymers is 18.

Calculated spectra are shown above the observed spectra

19.9 MHz

Deuterated Solvents
Reference Compounds
Chart Papers Etc:
Shift Reagents

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ORGANISCH CHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT TE UTRECHT
CROESESTRAAT 79
POSTGIRO 65985 - TEL.88 23 11

UTRECHT, June 28, 1974

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

a. Computer control of decoupler offset in the XL100 spectrometer
b. SIMEQ II/16 for MK I and MK II interfaces

Dear Professor Shapiro,

Recently B. Birdsall, N.J.M. Birdsall and J. Feeney described an elegant off resonance CW decoupling technique suited for the assignment of both ^{1}H and ^{13}C chemical shifts in relatively complex molecules (Chem. Commun., (1972) 316). To use this technique partially decoupled ^{13}C NMR spectra have to be obtained at decoupler frequencies that cover the range of proton frequencies of interest at intervals of 10-20 Hz (CW Hetero HI Mode at about 20% of maximum power). For dilute samples this assignment technique is very time consuming and in addition it requires operator attention for the changing of the decoupler frequency.

In order to make use of this technique without operator attention over the weekend we asked H.J. Flick of Varian Benelux BV to bring the decoupler offset under computer control. It turned out that this computer control was already foreseen by the designers of the XL100. The preset logic of the decoupler offset synthesizer (and also of the spectrum offset synthesizer) can be set by 4 x 4 BCD coded lines originating in the offset switches or by a 16 bit word originating in the computer. The mode is selected at the transfer gates. For the decoupler the computer input is wired from J1003 to the console backplane connector J021 and for the spectrum offset from J1417 to J025.

We used the 16 bit inverting register of the ACU tray (MK I interface), that is normally used to bring the filter under computer control, as our source for the computer control word by disconnecting it from the filter logic and wiring it from plug J5 to a mating connector for J021 (or J025). The computer inhibit was taken from J4 - J.

The complete wiring for the decoupler offset is as follows

Switch	J1003	J021	P021	J5	Bit
	T	T	T	r	00
X10	S	S	S	s	01
	R	R	R	t	02
	P	P	P	u	03
	N	N	N	v	04
X100	M	M	M	w	05
	L	L	L	x	06
	K	K	K	y	07
	J	J	J	z	08
X1000	H	H	H	AA	09
	F	F	F	BB	10
	E	E	E	CC	11
	D	D	D	DD	12
X10000	C	C	C	EE	13
	B	B	B	FF	14
	A	A	A	HH	15
INHIBIT	U	U	U	J4 J	EXC 0632
	XL100		Cable	MK I interface	

For the spectrometer offset a similar wiring is possible (see interconnect wiring list 87-126-702 and the book 87-126-400). We did not bring the X1 vernier control under computer control as we did not need it. For a MK II interface the situation is more complex. Here an extra digital I/O board has to be added to the computer.

The instruction sequence to set the offset is as follows:

```
, LDB, OFFS          offset in B register
, TZA,
, DIVI, 10
, TBA,
, CALL, XBTD         integer binary to binary coded decimal
, COMPL, 021
, OAR, 030           output to device 30
, EXC, 0330          output to register
, EXC, 0632          enable computer control
```

This program piece can be patched into the normal program. The representation of the spectra is done similarly as in the T-1 program.
A complete 16 or 24K FT program for MK I interfaces including this possibility and several other new features will be available shortly.

b. A new version of the spin simulation program SIMEQ II/16 (TAMUNMR 150, p20 and TAMUNMR 169, p20)is now available for MK I or MK II XL100 interfaces and SS100 systems.
Those who did already ask for this program and did hitherto not receive this improved version, please contact me and I will send the object tapes.

Yours sincerely,

M.J.A. de Bie

CENTER FOR HEALTH SCIENCES
THE UNIVERSITY OF WISCONSIN-MADISON
MADISON, WISCONSIN 53706

SCHOOL OF PHARMACY
Pharmacy Building
425 North Charter Street

June 6, 1974

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

Title: Fourier Homonuclear Decoupling

Dear Barry:

The July 1973 Newsletter carried a contribution by Jim Cooper and Craig Bradley describing time-shared homonuclear decoupling involving roughly a 30% duty cycle for f_2 unsynchronized with the observing pulse or computer data acquisition. The advantage of their procedure is that the time sharing frequency can be varied independently from the sampling frequency. We wanted better synchronization of data acquisition with the f_2 pulse and those readers using a Nicolet 1080 computer in combination with the Nicolet 293 pulse programmer may wish to know how to accomplish this.

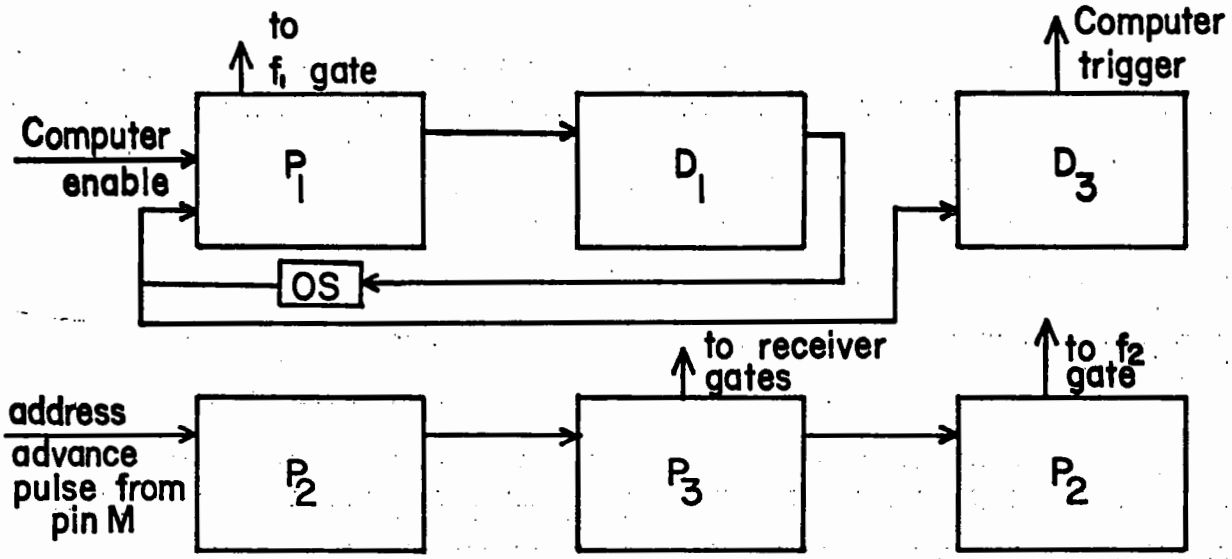
The computer address advance pulse is used to trigger the timing cycle for f_2 and receiver blanking. This pulse can be picked up from pin 2M on the sweep controller outlet of the 1080. The pulse can then be fed to a 293 timer input. The diagrams show the timer arrangement and the corresponding time-sharing sequence.

The parameters shown on the timer diagram give maximum decoupling of the methylene quartet from the methyl triplet of ethylbenzene using 10 db attenuation of the decoupling frequency of our Bruker HX90E spectrometer. The same arrangement works very well for other double resonance experiments and we will shortly report results comparing cw and FT nOe measurements.

Sincerely yours

Phillip A. Hart

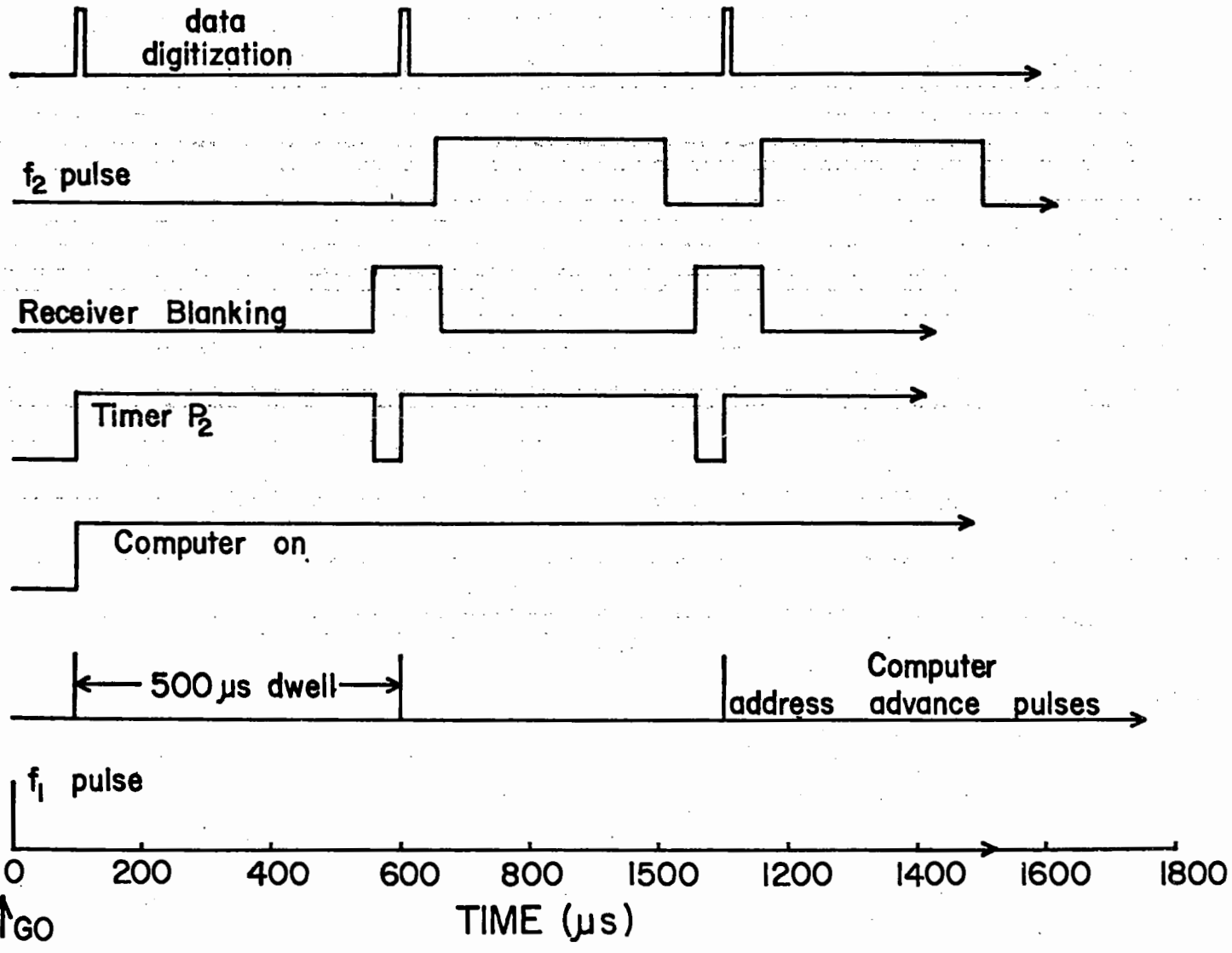
James Blackbourn



$P_1 = 2\ \mu s$ $P_2 = 460\ \mu s$

$D_1 = 4.25$ sec for 8K $P_3 = 100\ \mu s$

$D_3 = 100\ \mu s$ $D_2 = 350\ \mu s$



UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

June 10, 1974

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

Dear Dr. Shapiro:

Programming WEFT Computations

The WEFT method[1] for eliminating unwanted solvent resonances is exceedingly useful in proton FT NMR studies of necessarily dilute biological samples. Benz, Feeny and Roberts[2] derived the following null condition in the steady state of the pulse sequence $(\pi\text{-}t\text{-}\pi/2\text{-}T)_N$:

$$e^{-\left(\frac{T_1 \ln 2 + T}{T_1}\right)} + e^{-\left(\frac{T_1 \ln 2 - t}{T_1}\right)} = 1$$

where T_1 refers to the unwanted resonance, e.g. HOD. Each choice of T leads to a unique value of t for each sample, so that a more useful rearranged form of the above equation is:

$$t = T_1 \ln(2 - e^{-T/T_1})$$

In attempting to incorporate this handy calculation into the FT NMR software for routine use, one needs subroutines for calculating negative exponentials and natural logarithms that may not exist in a minicomputer FT software. Wishing to avoid pre-empting large amounts of program core for such a simple matter, I have derived an easily programmable approximation to the above equation for generating t values as follows:

$$t = TT_1/(T + T_1)$$

The basis for this is that the function $\ln(2 - e^{-x})$ can be approximated by $x/(1 + x)$ with an accuracy of 2% at $x = 1$ and <u>greatly</u> improving for smaller values of x. (The accurate range is less extended for negative x.) In the above context, $x = T/T_1$, and most applications would be in

the range $T < T_1$. Since maximum "WEFT'ing" requires adjusting delay times to $\pm$ 1 or 2 msec by trial and error, i.e. to far better accuracy than T_1 can be measured, the approximation is more than adequate to quickly generate trial values of t.

Please credit this contribution to our Department's account initiated by Bruce Martin.

Sincerely yours,

Raja Khalifah

Raja G. Khalifah
Assistant Professor of Chemistry

RGK/dhw

1. Patt, S. L., and Sykes, B. D., J. Chem. Phys., 56, 3182 (1972).
2. Benz, F. W., Feeny, J., and Roberts, G. C. K., J. Mag. Res. 8, 114 (1972).

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375

IN REPLY REFER TO:
6120-165:WBM:mjt

6 June 1974

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

Laser-induced CIDNP

Dear Barry:

Using the Chromatix tunable UV-visible laser system which the Chemistry Division recently acquired, we have observed proton CIDNP from a solution of di-t-butyl ketone in CCl_4. The signal levels were comparable to those we obtained with arc source excitation (600 W Hg-Xe).

Average laser power at the sample was approximately 0.7 milliwatt, and CIDNP was observed over the tuning range of 285-305 nm. We have not as yet experimented with more difficult molecules than di-t-butyl ketone, so the generality of laser-induced CIDNP at these power levels is not established.

Sincerely,

W. B. MONIZ C. F. PORANSKI, Jr. S. A. SOJKA

Organic Chemistry Branch
Chemistry Division
Code 6120

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

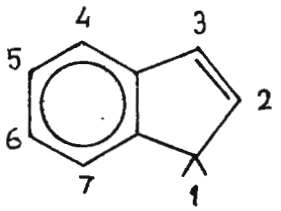
AMSTERDAM, June 10th. 1974.

Uw ref.:

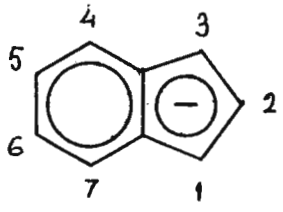
Onze ref.:

Dear Professor Shapiro,

The proton exchange between methylene-group containing aromatic hydrocarbons and their conjugate bases is an almost unexplored topic in carbanion chemistry. Brauman et al.[1] observed this process for fluorene/fluorenyl anion with proton magnetic double resonance. We have studied the exchange between indene (InH_2) and indenyl anion (InH^-) in various solvents, using NMR line-broadening, in the same way as has been done for carbonium ions[2].



InH_2



InH^-

In 1,2-dimethoxyethane and diglyme line-broadening occurred noticeably above 180° and 150° C, respectively. In the more polar solvent hexamethylphosphortriamide (HMPT), however, the exchange can be observed by NMR already at room temperature.

The line shapes of the 1,3-proton doublet in the spectrum of the carbanion InH^- in HMPT have been measured as a function of temperature. The line widths of the components of this doublet were

determined by computer simulation. After correction for the line width without exchange (measured from a TMS side-band placed near the doublet), the second-order rate constant was calculated from the following formula

$$k = \frac{\tau^{-1}_{InH^-}}{[InH_2]} = \frac{\pi \Delta \upsilon_{InH^-}}{[InH_2]}$$

in which $\tau^{-1}_{InH^-}$ is the mean life time of InH^- and $\Delta\upsilon_{InH^-}$ is the line broadening. As an example, k = 35 M^{-1} sec^{-1} at 52°C. From the temperature dependence of k the following quantities have been calculated: frequency factor f = 1.1 x 10^7 M^{-1} sec^{-1}; activation enthalpy $\Delta H^{\ddagger}$ = 8.5 ± 1.5 kcal/mole and activation entropy $\Delta S^{\ddagger}$ = -27±4 cal/mole °K.

The low values of f and $\Delta S^{\ddagger}$ classify this exchange as a "slow reaction". A discussion of the rate and its dependence on the polarity of the solvent will be presented separately.

Rapid exchange sharpening is observed at higher temperatures for all protons, except 1 and 3 (even at 180°C). This is caused by the large difference in chemical shift between a proton in the CH_2-group and the other ones (see table).

Table: chemical shifts in ppm from TMS

proton:	1	2	3	4,7	5,6
InH_2/HMPT	3.38	6.57	6.93	7.1-7.5	
InH^-/HMPT	5.73	6.37	5.73	7.05	6.07

References: 1. J.I. Brauman, D.F. McMillen and Y. Kanazawa, J. Am. Chem. Soc. 89 1728 (1967)

2. D. Brouwer, E.L. Mackor and C. MacLean, in G.A. Olah and P. von R. Schleyer (eds.) Carbonium Ions, Vol. 2, Wiley Interscience, New York, 1970, p.837.

Sincerely,

H.W. Vos

Y.W. Bakker

N.H. Velthorst

C. MacLean

SCIENTIA
WNNR·CSIR

NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

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AIR MAIL

OUR FILE 60/21/4221/1

YOUR FILE

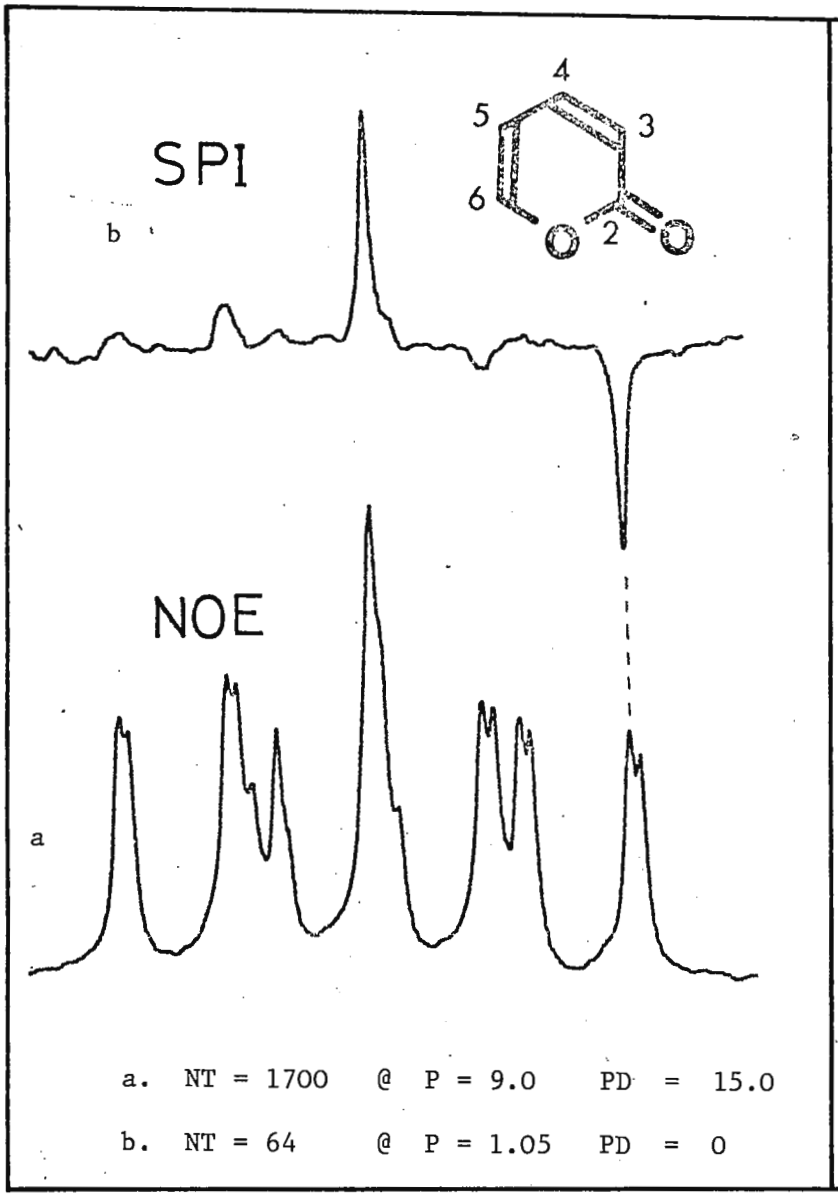
Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station
TEXAS 77843
U.S.A.

Dear Professor Shapiro,

SELECTIVE POPULATION INVERSION TECHNIQUE (SPI)

The GASP technique described by Runsink[1] is similar to the method developed in this laboratory[2] which we call SPI and which, of course, we believe to be somewhat superior. In the use of SPI for ^{13}C-H studies a π pulse is applied, ($\gamma H_2 . T_p = \pi$ using XL decoupler and gate), to a single ^1H line in the carbon-13 satellite spectrum and then the usual non-selective $\pi/2$ pulse is applied to sample the ^{13}C spectrum. The π pulse inverts the populations of the upper and lower energy levels of the selected transition and this shows up in the ^{13}C spectrum as positive and negative contributions to the connected transitions in the same way as for INDOR or GASP. The advantage of SPI is that (a) like GASP it is applicable to FT operation and (b) the population inversion leads to the maximum possible contributions $\pm$ ($\gamma H/\gamma c$) I_o; whereas the other methods must give less. We have successfully used $^{13}C-\{^1H\}$ SPI to give signs and magnitudes of the long-range ^{13}C-H couplings in AMX systems due to 2,3-dibromothiophene[3], and a 1,2,2-trisubstituted ethane[4]. Fired with enthusiasm we have tackled the 5-spin systems of 2-pyrone and obtained all sixteen long-range couplings with their signs. (Table). The figure shows the single resonance spectrum of $^{13}C_2$ and above it the SPI spectrum from irradiation at the lowest field line of the $^{13}C_2$-isotopomer H_4 multiplet. Thus the experiment gives the magnitude of $J(C_2,H_4)$ and sign information on the other couplings to C_2.

Further experiments give the other couplings.



a. NT = 1700 @ P = 9.0 PD = 15.0

b. NT = 64 @ P = 1.05 PD = 0

TABLE

JH,C	Hz
3,2	4.7
3,4	< 0.4
3,5	7.9
3,6	-0.8
4,2	11.2
4,3	0.9
4,5	1.5
4,6	7.6
5,2	-0.4
5,3	6.8
5,4	1.3
5,6	7.6
6,2	6.7
6,3	-1.4
6,4	7.8
6,5	7.6

[1]J. Runsink TAMUNN 185-18.

[2]K.G.R. Pachler and P.L. Wessels, J. Magn. Res., 12, 337 (1973).

[3]A.A. Chalmers, K.G.R. Pachler and P.L. Wessels, J. Magn. Res. in press.

[4]A.A. Chalmers, K.G.R. Pachler and P.L. Wessels, Org. Mag. Res. in press.

w
Yours sincerely,

A.A. Chalmers

K.G.R. Pachler

P.L. Wessels

SFU

June 20, 1974

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

Post-Doctoral - Biophysical Chemistry

Dear Barry:

I have immediate openings for one or two post-doctoral fellows of exceptional quality. There will also be a number of openings for high calibre students at the graduate level.

My research interests are in the area of biological applications of nuclear magnetic resonance, with particular emphasis on carbon-13 spectroscopy. Included in these areas are the following topics:

Visualization of Enzyme-Substrate Transition States by Carbon-13

Carbon-13 Conformational Studies of Membranes and their Constituents

Vitamin E and Cell Function

Elucidation of Biosynthetic Pathways by Carbon-13 Fourier Transform Techniques

Backgrounds in enzyme chemistry, ^{13}C FT techniques and physical biochemistry or a predilection for these areas of research would be the requisites.

Our equipment comprises the latest Transform Technology Fourier Transform Accessory to the Varian XL-100-15. The FT package includes a 20K, 20 bit computer, a 600K disk and multiple pulse capability. There is also a good selection of other instrumentation in the Department. There is also free access to the National High Field NMR spectrometer located in Ontario.

Funds available to me provide a salary at the NRC rate of $8700 per year (up to three years). Removal expenses to the value of return air fare are also provided. Candidates are asked to submit a curriculum vitae and have two or three letters of reference sent to me as soon as possible.

Simon Fraser University sits atop Burnaby mountain in Vancouver, on Canada's west coast. With a population of ~ 1 million, Vancouver has excellent cultural, recreational and entertainment facilities. The weather is moderate (one can play golf on Christmas day).

Sincerely,

Bob

Robert J. Cushley
Associate Professor

RJC/md

THE UNIVERSITY OF BRITISH COLUMBIA

2075 WESBROOK PLACE
VANCOUVER, CANADA V6T 1W5

DEPARTMENT OF CHEMISTRY

June 20, 1974

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

SODIUM - 23 N.M.R.

Dear Barry,

We are continuing to extend the number of nuclei which we can detect using our modified XL-100 spectrometer (Newsletter (185) 40 (1974)).

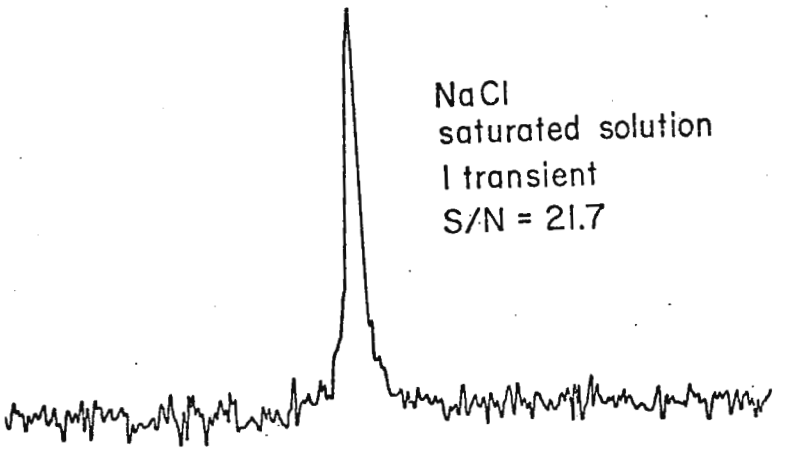
Attached is a copy of the sodium-23 resonance of sodium chloride... a saturated solution in D_2O in a 5 mm O.D. n.m.r. tube. There is nothing particularly significant about this measurement except that it cost us less than $200 over and above our previous investment.

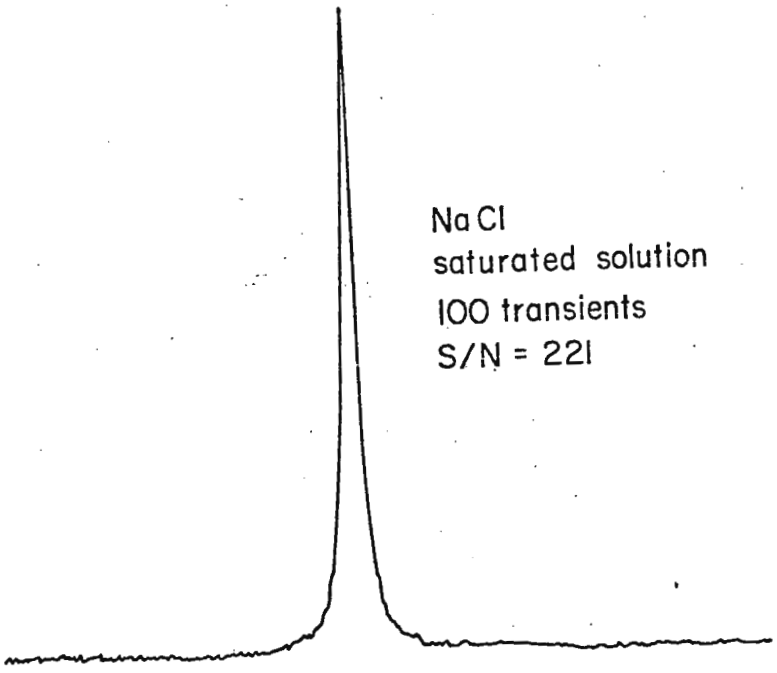
With all best regards.

Victoria Gibb L. D. Hall

LDH:dm

Enclosure


NaCl
saturated solution
1 transient
S/N = 21.7


NaCl
saturated solution
100 transients
S/N = 221

190-43

ת.ד. 2053, טל. 71241
באר־שבע
P.O.B. 2053, TEL. 71241
BEER-SHEVA
ISRAEL

UNIVERSITY OF THE NEGEV

הפקולטה למדעי הטבע
המחלקה לכימיה
FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

מספרנו: / OUR REF.

תאריך: / DATE

אוניברסיטת הנגב

June 20, 1974.

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

Title: Effects of Rotation on NMR Linewidths in Nematic Solvents.

Dear Professor Shapiro,

We were intrigued by the study of Emsley et al (TAMU 176, p18, Chem.Phys.Letters, 345, 19, (1973)) on the behavior of linewidths of samples dissolved in nematic solvents. In particular, the rapid broadening of the linewidths as the spinning speed ω approaches a critical value ω_c intrigued us. Accordingly, we performed the experiment using 1,2,3,4-tetrachlorobenzene dissolved in ethoxybenzylidene butylaniline and observed the same overall behavior. Emsley at al have shown that the line broadening is due to the spread in the angle between the director and the external magnetic field and thus have predicted a linear dependence of the linewidths on spinning speed. However, this does not explain the dramatic broadening of the lines as ω approaches ω_c . We have shown that if in addition the uncertainty in the spinning speed is taken into account then the observed line broadening can be calculated. The figure shows both our data and Emsley's data where the y axis is a normalized linewidth and the x axis is a normalized spinning speed. The solid line is a calculated "best fit" where the parameter used in the fitting is the uncertainty in the spinning speed. A value of 0.08 Hz fits both sets of data and this agrees well with the estimated experimental uncertainty of 0.1 Hz in the spinning speed. Too much significance should not be attached to this since the linewidths are only an indication of the spread of the director.

Credit for this work also goes to Dr's Shaul Goren and Ruth Potashnik.

Sincerely,

Stephen Marks

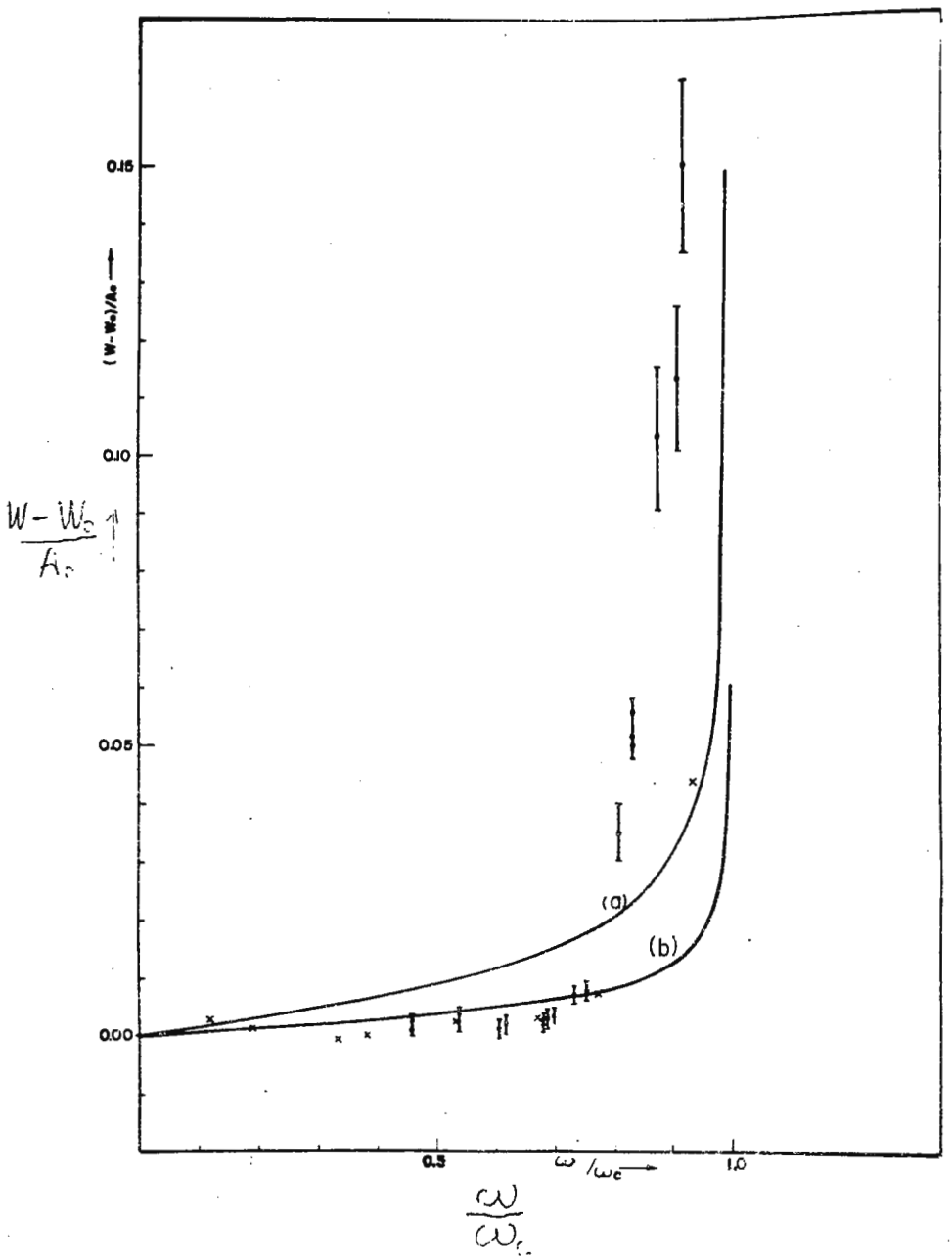


FIGURE TITLE

Variation of $(W-W_o)/A_o$ vs ω/ω_c . The bars (I) are data reported here, the crosses (x) are data taken from reference 3. Solid line (a) is the theoretical fit to the bars. Line (b) is the theoretical fit to the crosses.

THE OHIO STATE UNIVERSITY

June 21, 1974

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

Re: Book on Nmr Line-Shape Analysis

Dear Barry:

Jerry Kaplan and I are writing a book on nmr line-shape analysis of chemically exchanging systems which will describe the density matrix formalism for spectra obtained under different sets of conditions. Although we do not intend to review all line-shape research we do plan to describe selected examples of interesting systems where kinetic data have been extricated from nmr line-shapes. In particular, we seek examples of systems undergoing intermolecular exchange, for instance,

$$AB + CD \rightleftarrows AC + BD$$

including quadrupolar nuclei. Readers willing to divulge interesting examples of analysed exchanging systems should write to me at Ohio State.

Sincerely yours,

Gideon

Gideon Fraenkel
Professor of Chemistry

GF:es

Department of Chemistry / 140 West 18th Avenue / Columbus, Ohio 43210 / Phone (614) 422-2251

THE OHIO STATE UNIVERSITY

June 21, 1974

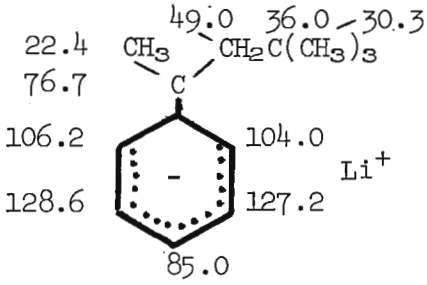
Dr. B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station 77843

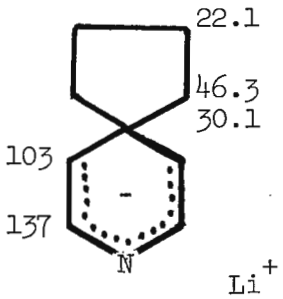
Re: Organolithium compounds - Postdoctoral appointment

Dear Barry:

2-Methylbutyllithium (RLi) is a hexamer at 25° in pentane. At -25° the CH_2Li proton resonance of d-RLi, 100 MHz, looks like a badly smudged and overlapping AB part of an ABX spectrum indicating slow inversion at the C-Li carbon. At 300 MHz the spectrum is unambiguous and we have utilized the CH_2Li line-shapes to calculate rates of inversion. When the experiment is repeated with dl-RLi the low temperature spectrum shows two different ABX systems. That means we have resolved diastereomers of the RLi aggregate. Above -30° the shifts between the diastereomers average. Thus we are seeing two kinds of exchange behavior, inversion and intermolecular exchange between aggregates, We are analysing these line-shapes and it seems now that inter-aggregate exchange is 4000 times as fast as inversion.

In other work we have lately been looking at ^{13}C shifts in π-conjugated anions. Some recent results are diagrammed below, without comment.





^{13}C shifts from TMS

T_1 sec

4.7 2.8
$CH_3CH_2CH_2CH_2Li$
2.7 0.72

I have funds for one post-doctoral to work in the organometallic field 50:50 synthesis and nmr on a variety of problems concerning structure and dynamic behavior of carbanionic substances. For this we have the latest in Bruker (A.G.) HX-90 equipment, cw, ft, disk, etc. Interested persons should write to me.

Sincerely yours, Gideon

Gideon Fraenkel, Professor of Chemistry

GF:es

Department of Chemistry / 140 West 18th Avenue / Columbus, Ohio 43210 / Phone (614) 422-2251

June 25, 1974

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

Dear Dr. Shapiro:

Title: Selective C^{13}-Proton Decoupling on a Varian CFT-20 Spectrometer

We have developed a simple, inexpensive accessory for doing precise selective decoupling experiments on our CFT-20. Such experiments require a continuously variable -- yet highly stable -- proton decoupling oscillator. Varian recommends using a frequency synthesizer; this is certainly the most straightforward, though expensive, approach.

Our alternative method is to disconnect the 100 KHz translating signal at pins T and 16 on the spin decoupler card and to substitute the output of a 100 KHz ± 10 Hz variable crystal oscillator (see diagram next page). If the above connections are unsoldered on the extender board, no modifications to the card itself are necessary.

The actual decoupler frequency is then:

$$f_{dec} = 5(100{,}000 - f_{osc}) + (100)DO + 79{,}537{,}500$$

f_{dec} = decoupling frequency output in Hz

f_{osc} = frequency of the variable crystal oscillator

DO = decoupler offset $35 \leq DO \leq 65$

Because of the factor of 5 it is only necessary that the range of the variable crystal oscillator be 20 Hz in order that a 100 Hz range be obtained. The crystal-oscillator frequency should be measured to ± 0.1 Hz, with the 1 MHz master clock output of the CFT 20 at J532 as a time base for the counter.

Professor Bernard L. Shapiro
Texas A and M University
June 25, 1974

We observed a stability in the decoupling frequency of better than ± 1 Hz over a period of eight hours.

Very truly yours,

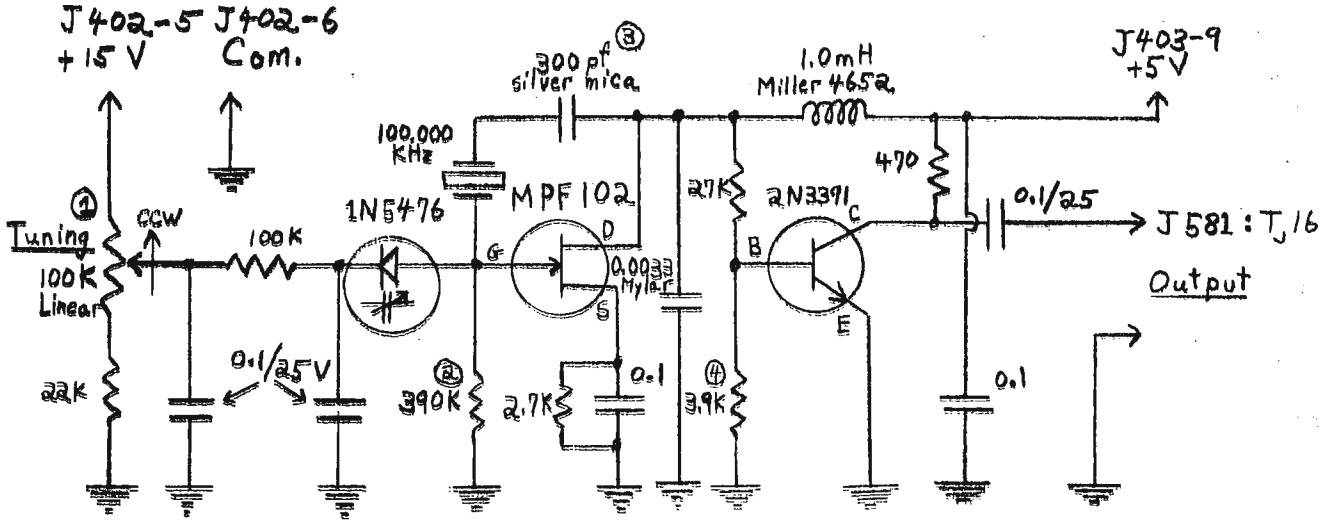
Paul Mark Henrichs

PMH/SC/nc

P. M. Henrichs
Chemistry Division
Research Laboratories

Stanley Gross

S. Gross
Chemistry Division
Research Laboratories



Notes	
1.	All resistors 1/4 watt, 5% tolerance.
2.	Pot may be remotely located.
3.	Select for 22-24 Hz tuning range.
4.	Select to center tuning range at 100,000 KHz.
	Trim for best symmetry of output waveform.

Now the XL-100A NMR Spectrometer lets you think small.

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

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

The two spectra of Δ^9-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 μg of sample in a 1-mm tube) and Spectrum C (20 μg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

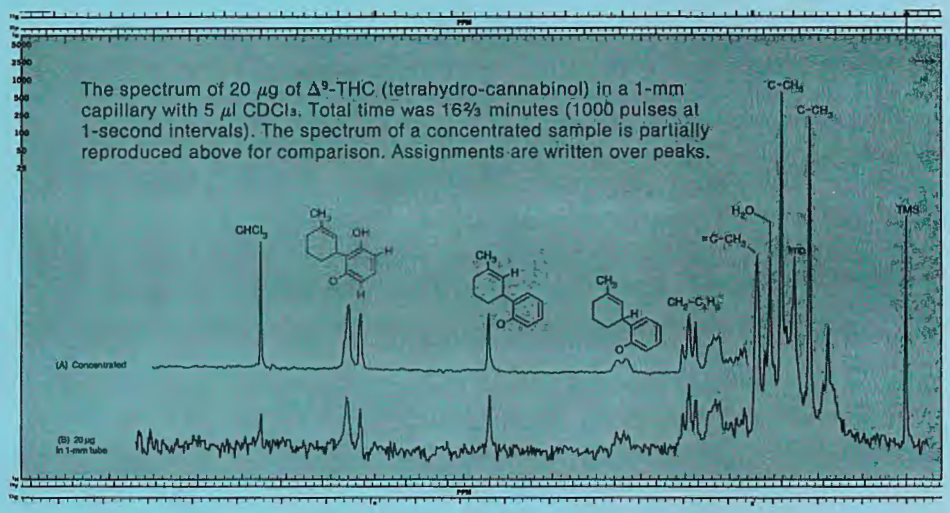
This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

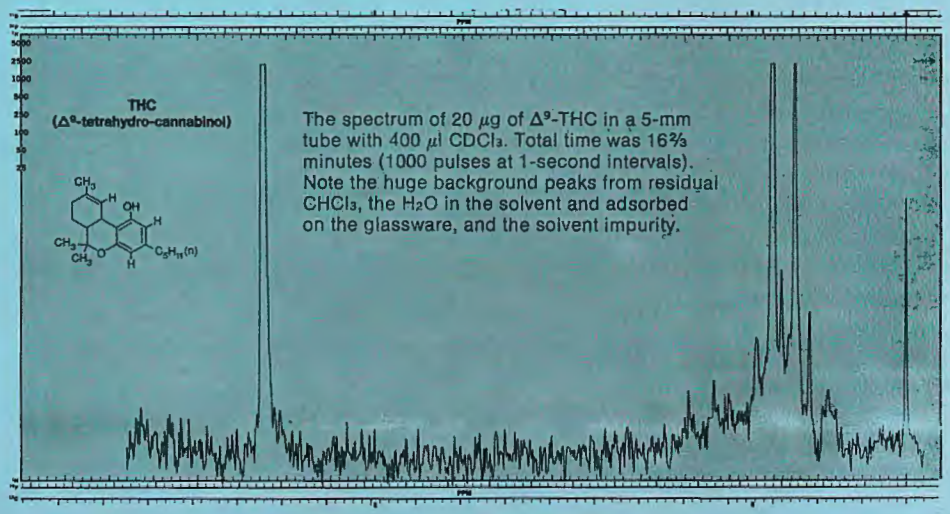
To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5 μl of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

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

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

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





Varian Associates
611 Hansen Way, Box D-070
Palo Alto, California 94303

varian

Your light touch to FT NMR Spectroscopy

The new JEOL **FX60**, a low-cost, routine FT NMR Instrument, adds a new dimension in simplicity of operation by replacing the standard keyboard with the **Light Pen Control System** (LPCS). The **FX60** provides routine high performance and reliable data for both ^{13}C and ^{1}H studies. Sample tubes up to 10mm OD are standard. For complete information write to . . .

JEOL

Analytical Instruments, Inc.

235 Birchwood Ave., Cranford, NJ 07016
201—272-8820

The FX60 was recently previewed at the ENC Conference, Raleigh, North Carolina, April 28, 1974.

INSTRUMENTATION: NMR Spectrometers/Mass Spectrometers/ESR Spectrometers/Laboratory Computers/Scanning Electron Microscopes/Electron Microscopes/ X-ray Microprobes/X-ray Diffractometers/Electron Beam Apparatus/Amino Acid Analyzers/Sequence Analyzers.