Texas A & M University N-M-R Newsletter

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April, 1978

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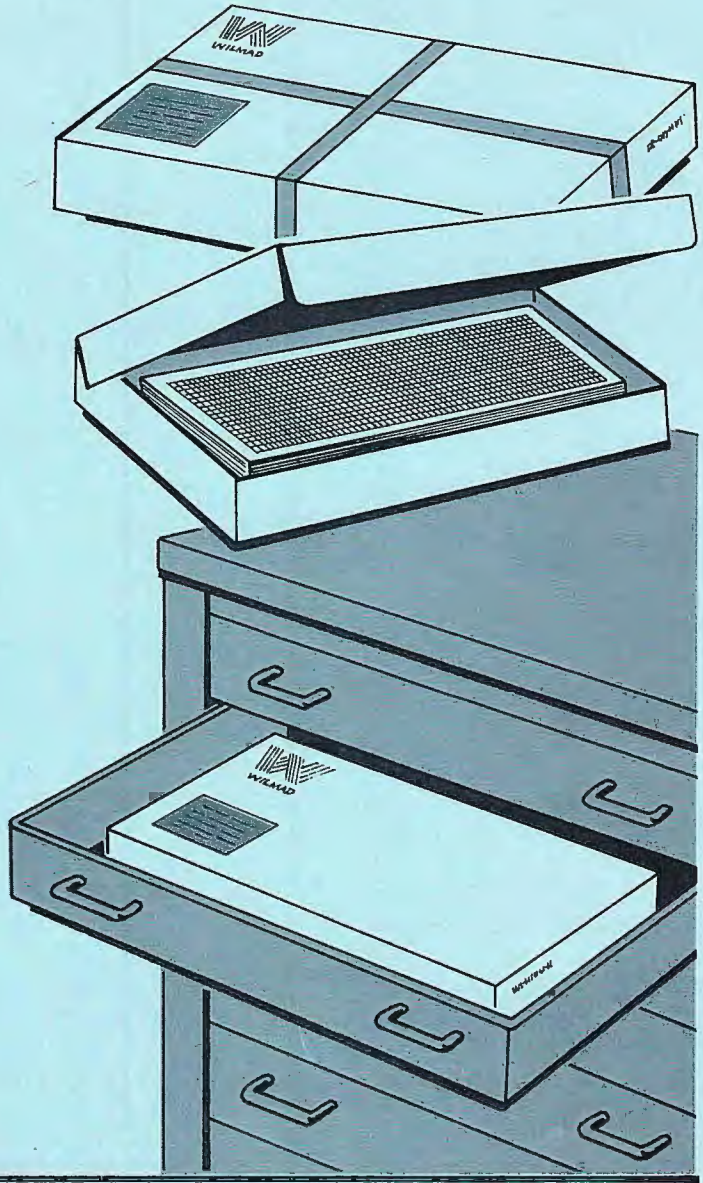

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DEADLINE DATES:	No. 236: 1 May 1978
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All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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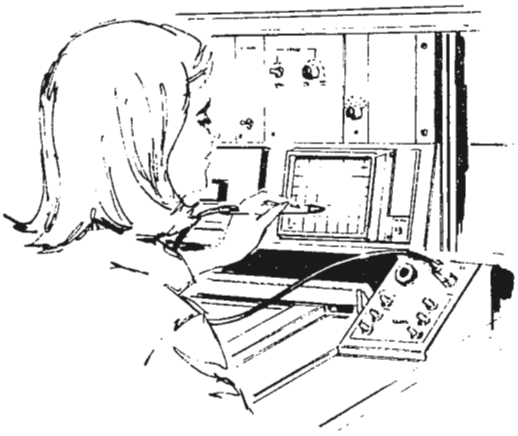

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T. R. Evans Research Center

March 6, 1978

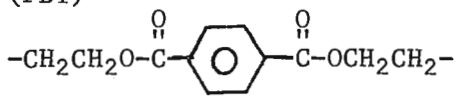
Dr. Bernard L. Shapiro
Texas A&M University
College of Science
Department of Chemistry
College Station, Texas 77843

Dear Barry:

Subject: Chain Mobility of Terephthalic Acid Polyesters

Carbon-13 spin relaxation data are being used increasingly to study chain mobility of synthetic polymers in solution and in bulk. If models of chain dynamics of general applicability are to be developed, it is important that polymers with a wide variety of structural features be studied. Previous investigations have been mainly concerned with vinyl polymers, polysulfones, and diene polymers. An important class of polymers not studied heretofore are the polyesters of terephthalic acid formed by condensation with various aliphatic glycols. One member of this class is polybutylene terephthalate, whose structure and ^{13}C NMR parameters in hexafluoroisopropanol are in the table below.

TABLE 1

Polymer	Carbon	δ(ppm)	T_1(msec)	NOE	Δν(Hz)
Polybutylene terephthalate (PBT) 	CH	131.9	128	2.3	3.8
	C_{np}	136.2	2500	1.9	-
	CO_2	171.1	3200	1.9	-
	C-1	68.4	85	2.0	9
	C-2	27.1	105	2.7	4.5

Dr. Bernard L. Shapira
March 6, 1978

The T_1 data show that the terephthalate units act as centers of restricted motion along the polymer chain, with mobility increasing with distance from these groups. The reduced NOE's suggest that a distribution of correlation times may be used to explain the data. The data for all carbons is reasonably well described by the log χ^2 distribution introduced by Schaefer,[1] with a *p* value of 20 and a variable average correlation time τ that decreases with increasing distance from the terephthalate groups.

Similar polymers (with two and six methylenes between terephthalate groups) gave analogous results. One interesting point is that the motional behavior of the terephthalate units does not depend on the length of the alkyl chains by which these groups are separated. This behavior may be related to the details of polymer-solvent interaction. The terephthalate units are probably highly solvated relative to the aliphatic chains. This solvation would then dominate the motional properties of the terephthalate groups, allowing them to reorient independently.

Sincerely,

Richard A. Komoroski

Richard A. Komoroski

[1] J. Schaefer, *MACROMOLECULES*, 6, 882 (1973).

Prof. M.J. ANTEUNIS
STATE UNIV. of GHENT
ORGANIC CHEM. DEPT.
LAB. for NMR SPECTROSCOPY
Krijgslaan 271 – GENT B-9000
BELGIUM

LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, March 3rd, 1978
KRIJGSLAAN 271 - S 4 Tel. 22 5715
(België-Europa)

How to turn a white crow into a black swan without being a magician; or more[1] about deceptive simplicity and spectral degeneration (at 300 MHz).

Dear Barry,

I recently reported you[1] about a case of isochronism between $\underline{CH}_2$ and $\underline{CH}_3$ in an ethyl fragment. The all-cis derivative 1 (structure and configuration corroborated by chemical derivatization and subsequent ^{1}H-nmr studies), represents a white crow in CCl_4. Here the H-4,5 cis protons have the same shift as the H-4,5 trans, as if 1 had an additional plane of symmetry. Obviously, in CCl_4, the relative shielding[2,3] of H-4(5)cis by the vicinal cis-OH is exactly compensated by the β-deshielding[2,3] of the opposite cis-OH and cis-Me.

In C_6H_6, the spectrum looks normal, although still highly degenerated by the σ plane (through C-1 and the C-4/C-5 bond). Simulation was possible (Table). In contrast to CCl_4 there was a coupling J(1(3),OH) = 5.8 Hz.

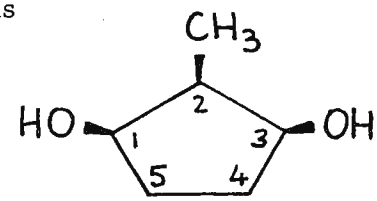
Remarkably, in αBN[4] the white crow turned into a black swan. Now, not only H-1 & H-3 becomes isochronous with $\underline{OH}$, but H-2 is also isochronous with CH_3 resulting into .... <u>two singlets</u> (broadened by averaged <u>apparent</u> small couplings; not resolved) and integrating for four protons each. Don't expect I can picture you a black swan drifting on a pitch-black lake in a moonless night; no, the H-4,5 cis protons resonate at a different position from H-4,5 trans.

One should realize that all spectra were obtained at 300 MHz. As you urgently advised not to overload the newsletters I kept the spectra for me, and gave you the data extracted in a Table.

^{1}H-NMR data of 1 (300 MHz CW, TMS int.)

Shifts in ppm:

Solvent	OH	H-1,3	H-2	CH_3	H-4(5)cis	H-4(5)trans
C_6H_6	2.75	3.81	1.22	1.14	1.58	1.79
CCl_4	3.75	3.97	1.60	1.07	1.85_5	1.85_5
αBN	3.91	3.91	1.14	1.14	1.57	1.83
DMSO-d_6	4.02	3.90	∿1.67	0.91	∿1.62	∿1.72



1

Couplings in Hz

	OH,1(3)	1,2(1,3)	2,Me	4tr,4c(5tr,5c)	4c,5c	4tr,5tr	4c,5tr(4tr,5c)
C_6H_6	5.8	3.9	6.2	-13.8	10.5	9.8	5.9
CCl_4	small	3.9	7.1	—	—	—	—
DMSO-d_6	5.9	4.0	7.1	—	—	—	—

	3,4tr(1,5tr)	3,4c(1,5c)	1,4tr(3,5tr)	1,4c(3,5c)
C_6H_6	2.04	4.7	-1.40	-0.40

The apparent couplings in αBN involving H-4 or H-5 all are identical (from H-1,3 pattern) being four times ∿1.5 Hz. Indeed, $\frac{1}{4}|+2.04+4.7-0.4-1.4| \approx 1.3$

References: [1] TAMU-NMR Newsletters, 224-10 (1977).

[2] Cf. D. Danneels, M. Anteunis, Org.Magn.Res. 7, 345 (1975).

[3] A. De Bruyn, D. Danneels, M. Anteunis, E. Saman; J.Carbohydrates, Nucleos. & Nucleotides 2, 227 (1975).

[4] Cf. M. Anteunis, Chr. Becu, F. Anteunis-De Ketelaere; J.Acta Ciencia Indica 1, 1 (1974). Our experience (since 1970) is that αBN seems to work as a "super ASIS" (co)solvent. Spectra run at these laboratories for several small (spiro)ring compounds, especially when polar, have resulted to appreciate the use of αBN for this purpose.

With compliments,

Prof. M. Anteunis.

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De Boelelaan 1083 – Telefoon 548 . . .

AMSTERDAM, March 9, 1978

Uw ref.:

Onze ref.:

Professor Barry Shapiro
Texas A & M University
College of Science
College Station
TEXAS 77843
U.S.A.

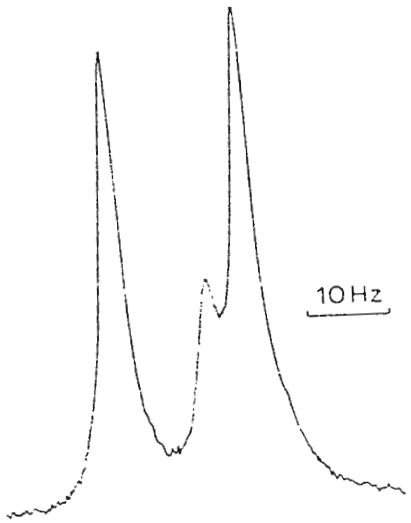
Dear Professor Shapiro,

One of our research interests is the study of a static electric field on NMR spectra of polar molecules. An electric field tends to align polar molecules. Anisotropic interactions, like the quadrupolar- and dipolar couplings, are then not averaged to zero, as in the isotropic liquids. To make these couplings visible, strong electric fields (up to 10^7 V/m) are used to achieve sufficient alignment. Quadrupolar electric field effects have been studied extensively in our laboratory on ^{14}N and ^{2}D.

With the advent of our new WH-180 spectrometer, equipped with a wide bore supercon, new electric field effect cells had to be designed. The requirements are rather severe: a magnetic field homogeneity of a few Hz should be maintained, while the cell is non spinning and contains electrodes for the high tension and membranes for electrodialysis. Cells are machined from teflon because of its excellent insulating properties. In the design great care is taken to avoid electrical breakdown between electrodes and spectrometer probehead.

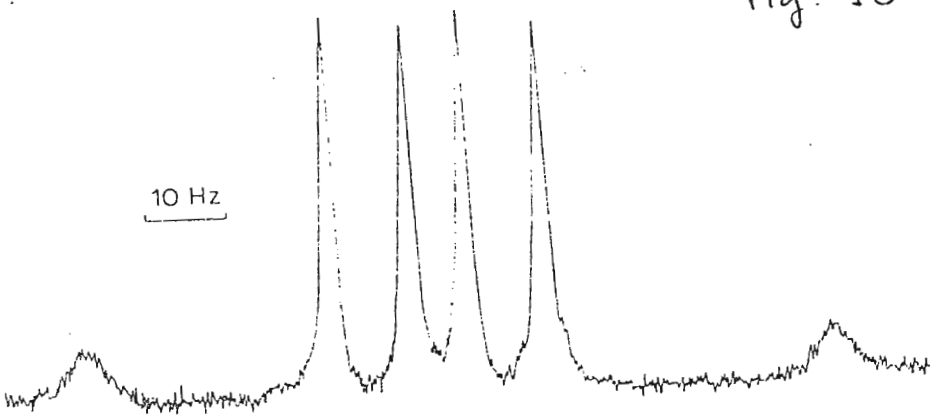
That our new cells operate satisfactorily now is shown in the enclosed ^{2}D-NMR spectra of nitrobenzene-d_5 (figures 1^a, 1^b). The top spectrum was recorded without, the bottom spectrum with an electric field. In the isotropic (= top) spectrum the three peaks correspond to the ortho, para and meta deuterons respectively. The line splittings induced by the applied electric field are proportional to the square of the electric field and to $(\frac{3}{2}\cos^2\gamma_i-\frac{1}{2})$ where γ_i is the angle between the direction of

fig 1a



27.6 MHz ^2D spectrum of
60 mole % Nitrobenzene in
Ethylenecarbonate
E = 0 V/m

fig. 1b



27.6 MHz ^2D spectrum of
60 mole % Nitrobenzene in
Ethylenecarbonate
E = 6.4×10^6 V/m

the electric dipole moment of the molecule and, if the asymmetry parameter can be taken to zero, the C-D bond. The para C-D bond is parallel to the dipole moment, hence the para deuteron shows the largest splitting. The ortho- and meta splittings are about a factor of 8 smaller.

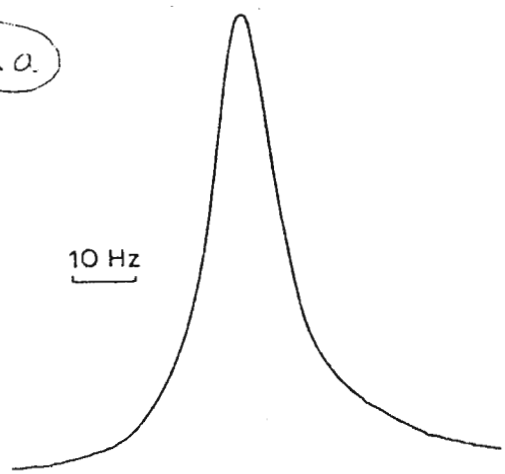
Electric field effects on the ^{1}H spectrum of ethylene carbonate (dipole moment 4.9 debye) due to dipolar interactions between the four protons in this molecule have also been detected (figures 2a, 2b) and interpreted using computer simulation.

In the near future we hope to report on dipolar ^{13}C-H electric field effects. These should be observable since the small magnetic moment of ^{13}C is generally offset by the short C-H distance.

Sincerely,

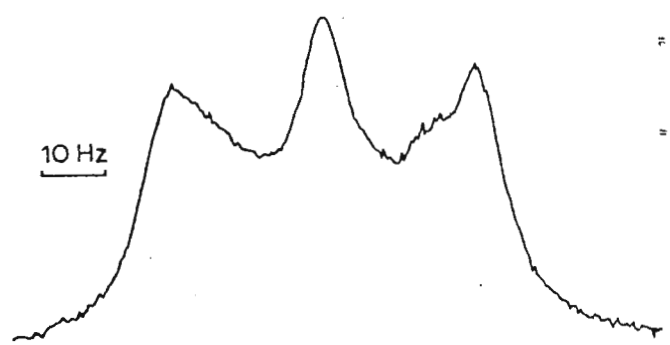
T.M. Plantenga
C.A. de Lange
C. MacLean

2a



180 MHz ^{1}H spectrum of
40 mole % Ethylenecarbonate in
Nitrobenzene
E = 0 V/m

2b



180 MHz ^{1}H spectrum of
40 mole % Ethylenecarbonate in
Nitrobenzene
E = 1.1 x 10^{7} V/m

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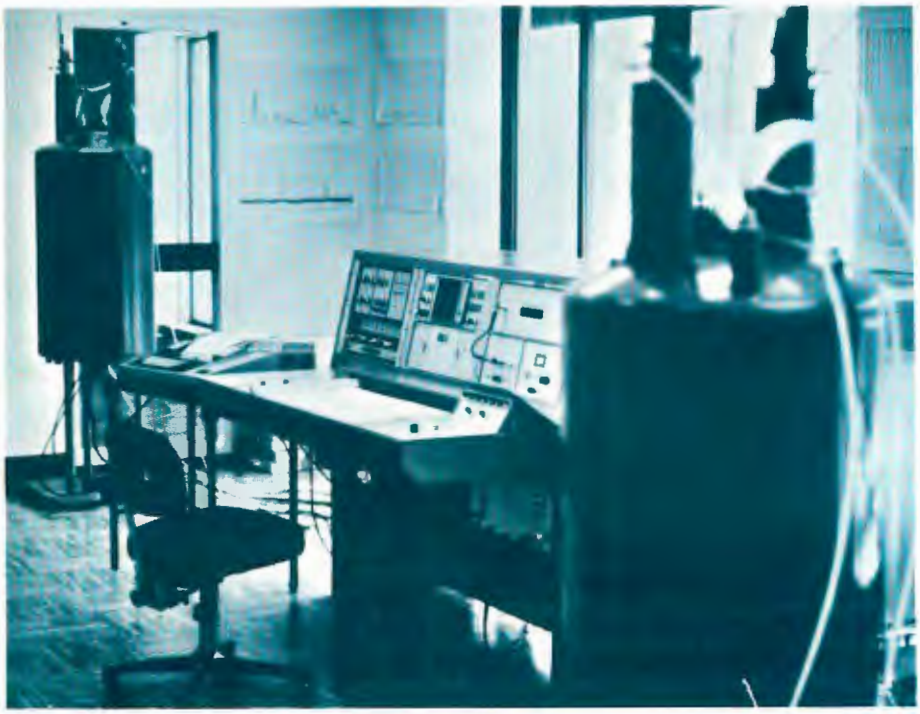

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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

31 March 1978

Dear Dr. Shapiro:

Recent revived interest in the observation of "magnetization transfer" in reversible chemical exchange reactions (1) moved us to construct a simple homonuclear decoupler unit. This capability allows the measurement of unidirectional psuedo-first order rate constants for various types of chemical exchanges. It is of particular interest in the study of enzyme systems of physiological importance.

Figure 1 is a brief schematic of the homodecoupler designed to be used on our Bruker WH-180 spectrometer. With this unit we are able to produce a selective 180° pulse of 5 msec. duration. For saturation a homodecoupler "pulse" of 150 to 250 msec. is nicely selective as can be seen in Figure 2. Spectra A and B of this figure were obtained from a solution of 2mM phosphocreatine (PCr) and 1mM ATP in the presence of 0.14mM phosphotransferase enzyme. Each spectrum is the result of the accumulation of 100 transients obtained from 20 ml. of sample in a 25mm NMR tube. In both cases a (wait-180°-τ-90°) sequence was used with a waiting interval of 12.5 sec. and $\tau \approx 1$ msec. The 180° pulse is the selective pulse of .25 sec. duration and the 90° pulse the nonselective observe. The only difference in acquiring spectra A and B is the frequency of the selective pulse- in B it is applied to the γ-phosphate of ATP, while in A the frequency is offset 10kHz from the γ-phosphate.

For the experiment described above the lowering of the integrated intensity of the PCr resonance in spectrum B is ~20% compared with spectrum A. When the same set of spectra were obtained from mixtures of PCr and ATP in solution (no enzyme present), the lowering of the integrated intensity of PCr was less than 3%. The loss of intensity in spectrum B, Figure 2, reflects the transfer of the PCr phosphorus to form ATP in the enzyme mediated reaction.

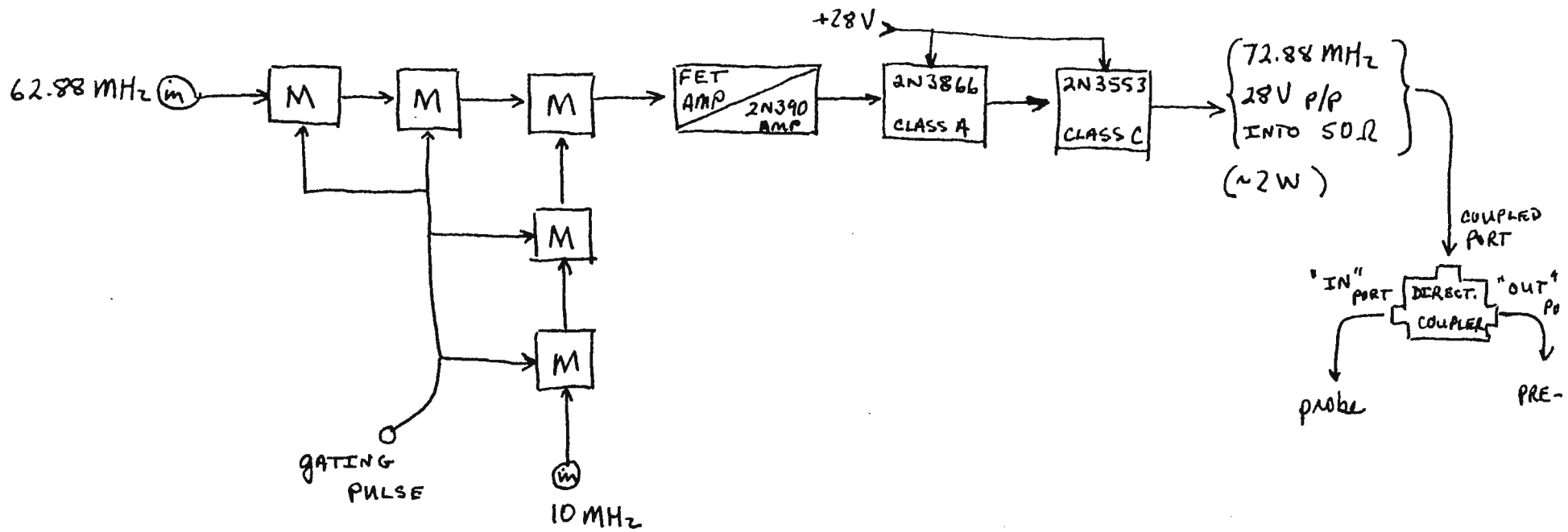
The decoupler required approximately $250.00 in parts and can be assembled in less than a week. Details of the circuit will be supplied upon request (to R.L.N.). Our thanks to Dr. Craig Bradley of Bruker Instruments for many helpful suggestions for the implimentation of the homonuclear decoupler.

Sincerely,

Donald P. Hollis

Ray L. Nunnally

1.) see the following:
H.M. McConnell, J.Chem. Phys. 28,430-431 (1958)
S.Forsen & R.A. Hoffman, J.Chem. Phys. 39, 2892-2901 (1963)
T.R. Brown & S. Ogawa, P.N.A.S.(USA) 74, 3627-3631 (1977)
T.R. Brown, K. Ugurbil & R.G. Shulman, P.N.A.S.(USA) 74, 5551-5553 (1977)



M - MIXER

FIGURE 1

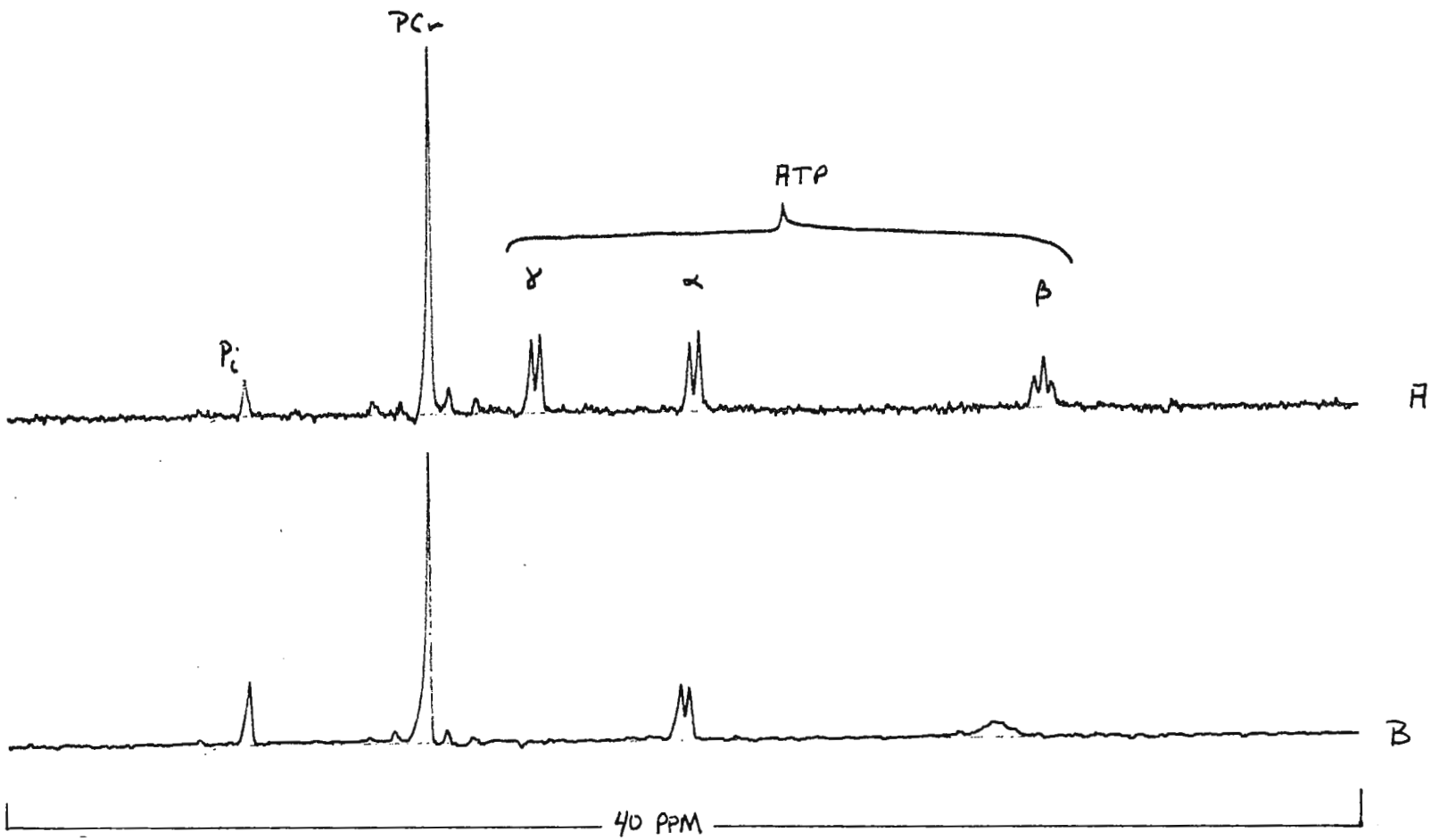


FIGURE 2

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FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN

Geadresseerde
Prof. B.L. Shapiro

Ons kenmerk
U4177/dB/Ek

Datum
March 14, 1978

A pulse sequence and variable temperature assembly for ^{13}C spin lattice relaxation measurements in combination with magic angle proton-enhanced ^{13}C NMR

Dear Professor Shapiro,

The magic angle spinning proton-enhanced ^{13}C NMR technique makes it possible to measure relaxation times of all ^{13}C nuclear spins in a solid powder which yield a resolved peak in the spectrum. For T_1 measurements one can of course adapt the familiar 180°-τ-90° sequence to the proton-enhanced ^{13}C pulse scheme by having immediately after the ^1H-^{13}C mixing pulse with rf phase x a pulse sequence 90^o_y-τ-90^o_y with rf phase y. When τ is varied one finds for each NMR line the usual recovery curve shown in fig. 1. Note that in general, due to the proton-enhancement, $M_o > M_e$ where M_e is the equilibrium ^{13}C magnetization and M_o the magnetization right after the cross-polarization. The disadvantage of this method is that to extract the T_1 value from such a curve by normal graphical means one has to determine M_e and that is very time consuming because for these long τ's the double resonance does not help at all. Of course one can avoid this problem by computer fitting of T_1 to the first part of the recovery curve.

We use another solution to this problem which we think is worthwhile to report here. Consider two consecutive proton spin-locks (fig. 2). Immediately after the mixing pulse in the first proton lock period we give a sequence 90°-τ-270°, 90° out-of-phase with the mixing pulse. In the second lock period this pulse sequence is 270°-τ-90°. By doing this and, as usual, adding all FID's it is a simple matter to derive for the amplitude of the FID (or for the area under each line in the spectrum) that it is proportional to

$$2\, M_o \exp(-\tau/T_1)$$

By varying τ and plotting this amplitude or area on a logarithmic scale one finds T_1, while M_e is not needed.

Spin lattice relaxation studies require variable sample temperature. Schaefer reported $T_{1\rho}$ measurements as a function of temperature where the sample temperature was varied by heating or cooling the gas driving the spinner. With our Andrew type of spinner this does not work very well, mainly because of two reasons. First, the shape of the spinner implies a thick layer of insulating spinner material between the sample and the driving gas. Secondly, when this gas leaves the holes in the stator a very noticeable cooling occurs because of the expansion. We found however that when the coil around the sample part of the spinner is glued together to a cilinder, air is sucked into the space between the coil and the spinner when the spinner is in operation (fig. 3). Via a dewar system we bring heated or cooled N_2 gas into this space for heating or cooling the sample. Compared to the volume of driving gas only a small volume is needed for this heating or cooling. The temperature of the sample is not very dependent on the spinning rate and (for -100 to + 100°C) always within 5°C from the temperature of the cooling or heating gas.

Yours sincerely,

(W.S. Veeman) (E.M. Menger) (E. de Boer)

LABORATORIUM VOOR FYSISCHE CHEMIE

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Telefoon (080) 55 88 33

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KATHOLIEKE UNIVERSITEIT
NIJMEGEN

Geadresseerde | Ons kenmerk | Datum | Blad No

Fig. 1

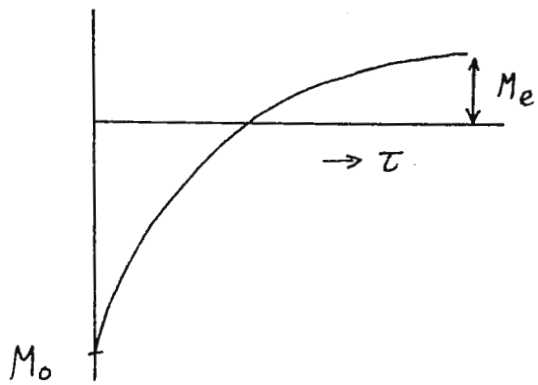


Fig. 3

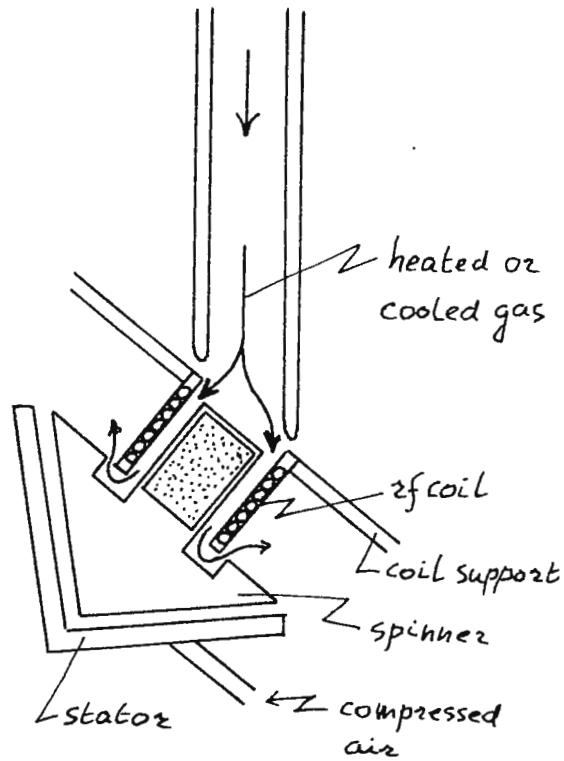
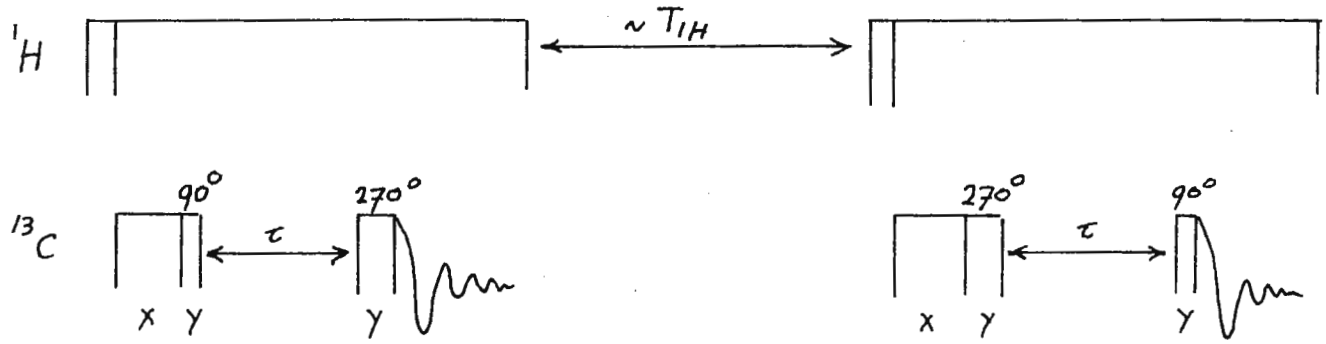


Fig. 2



Hunter College
OF THE CITY UNIVERSITY OF NEW YORK
695 PARK AVENUE, NEW YORK, N.Y. 10021

Department of Chemistry

March 15, 1978

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

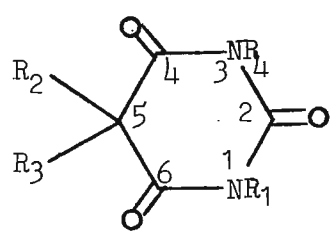
TITLE: Magnetic Nonequivalence in Nitrogen-15 nmr spectroscopy of Barbituric Acids

...

Dear Barry:

Until your pink slip of March 7 arrived we did not realize that our subscription was going to expire soon. We hope this will keep us on the mailing list of the TAMU Newsletter.

We just completed an extensive study of the ^{13}C nmr and ^{15}N nmr characteristics of several barbituric acids that included commercially available ones and several new ones synthesized for the purpose in our laboratories. We observed the first known instance of magnetic non-equivalence in ^{15}N nmr spectroscopy in the case of compounds containing a chiral substituent on C-5; the separation between the two resonances was 0.3 - 0.4 ppm, which is about the same order of magnitude reported[1] earlier for the nonequivalent ^{13}C resonances of C-4 and C-6 C=O groups in these compounds. Data for these compounds are given below.



Natural abundance ^{15}N spectra were obtained for ca. 3 M solutions in DMSO-d_6 on our JEOL PS-PFT/100, each sample requiring accumulation

times of 1.5 - 2 hr; external $CH_3{}^{15}NO_2$ was used as reference and chemical shifts are reported w.r.t. anhydrous liquid ammonia[2].

No.	Substituent			$\delta\,{}^{15}N$ ppm (w.r.t. anhyd. liq. NH_3)
	R_1/R_4	R_2	R_3	
1	H/H	C_2H_5	$CH_3CH_2(CH_3)CH-$	155.11 155.54
2	H/H	allyl	$CH_3CH_2CH_2(CH_3)CH-$	155.15 155.42
3	H/H	C_2H_5	$CH_3CH_2CH_2(CH_3)CH-$	155.57 155.84

Sincerely,

Bob

R. L. Lichter
Associate Professor &
Chairman

P. R. Srinivasan

References:

1. F. I. Carroll and C. G. Mooreland, J. Chem. Soc., Perk. Trans. II, 374 (1974).

2. P. R. Srinivasan and R. L. Lichter, J. Magn. Reson., 28, 227 (1977).

UNIVERSITÉ D'OTTAWA UNIVERSITY OF OTTAWA

OTTAWA ONTARIO
CANADA K1N 9B4

DÉPARTEMENT DE CHIMIE DEPARTMENT OF CHEMISTRY

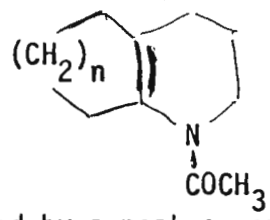
March 15, 1978.

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

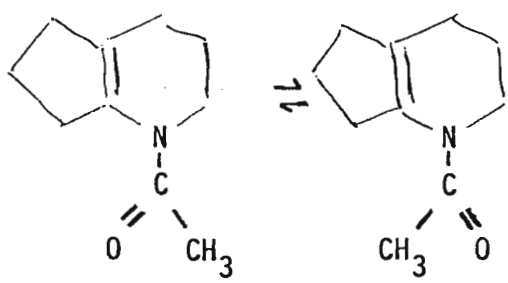
Dear Barry::

Barriers to Rotation about Amide Bonds-Acylenamines

Recently we have been studying a series of acylenamines of general formula I which were prepared by Dr. Rai Mahajan of Brasilia. The problem seemed attractive as there has been only one paper on two acylenamines (J. Org. Chem. 31, 3436 (1966) in which kinetic data for N - vinyl - N - methyl - formamide and - acetamide were obtained by a peak separation method. We have carried out a complete line shape analysis of the A_2B_2 pattern of 1 (n = 1) and obtained the following results for the equilibrium:



I, n = 1,2,3,4,8



$k_{A \rightarrow B} = 34$

The application of the CLS method required the simplified treatment of long range coupling to the alpha protons as an increment to the line width. The normal input parameters were obtained from a LAOCN3 analysis of the α proton absorptions measured at a temperature below the influence of exchange (-40°C)

Interestingly this CLS analysis yielded, after several months of computation, the same $\Delta G^{\ddagger}$ as is calculated by the simple 2 site coalescence equation (This has been noted before by Raban (Chem. Commun 1971, p 656) and by Mislow (JACS, 93,6205).

The barriers for other members of the series were then determined by the 2 site equation: $\Delta G^{\ddagger} = 4.58\, T_c (10.32 + \log \frac{T_c}{k})$ where

$$k_{av} = 2.22\ \Delta V \text{ and } k_A = 2\rho_B\ k_{av}$$

$$k_B = 2\rho_A\ k_{av}.$$

The results in the table show little effect of ring size on the barriers and a generally smaller barrier in all the enamides than in amides due most probably to a stabilizing interaction between the lone pair on nitrogen and the double bond in the transition state.

TABLE I

Barriers to $N_{-C=O}$ Rotation in 1

Compound 1	Tc	ΔV(at Tc)	ρ_A	k_I	$\Delta G^{\ddagger}_{A \rightarrow B}$
n = 1	291	19	0.56	36	15.0
				34	15.0 (by CLS)
n = 2	269	16.0	0.67	23	14.0
= 3	284	15	0.60	28	14.7
= 4	270	15	0.56	29	13.9
8	279	9	0.55	18	14.7

Best regards,

Bob and Jean-Louis

RRF:JLR:lmb.

R.R. Fraser and J.L. Roustan.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

March 24, 1978

Building 2, Room B2-08

Re: Postdoctoral Fellowship Available; Non-NMR Book

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

Dear Barry:

I have a post-doctoral fellowship available for a Visiting Fellow at NIH. The standard conditions for eligibility are that the applicant must not be a U.S. citizen, and it must not be more than three years since he or she obtained a Ph.D. Applicants with experience in applying NMR spectroscopy (^{13}C, ^{31}P) to biological systems will be preferred. Your readers may be interested in the book I have written with Franklin Portugal, on the history of DNA ("A Century of DNA: A history of the discovery of the structure and function of the genetic substance," published by MIT Press, Feb. 1978). Man does not live by NMR alone.

Sincerely,

Jack S. Cohen
Developmental Pharmacology Branch
National Institute of Child
Health and Human Development

JSC:ell

NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET

For routine NMR and state-of-the-art techniques such as:

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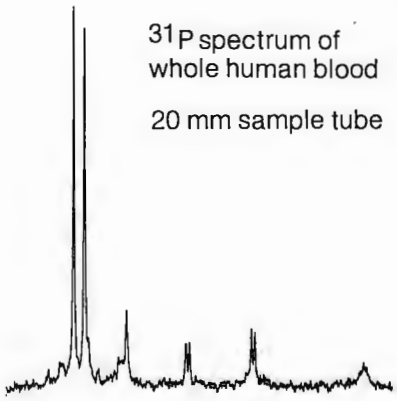


^{31}P spectrum of whole human blood

20 mm sample tube

For more information or to discuss your applications, please telephone or write.

NICOLET TECHNOLOGY CORPORATION
145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076

University of Houston
Central Campus
Houston, Texas 77004

Department of Chemistry
713/749-2612

"Ray Freeman's Velvet Glove Can Be Used on Nicolet Data Systems"
and "A ^{31}P Riddle"

Dear Barry,

We report our successful duplication of Ray Freeman's selective pulse sequence dubbed locally as the Velvet Glove sequence [J. Mag. Res. 23,171 (1976)]. The experiment works by applying many (1-200) short (0.5-1°) pulses separated by the time it takes the magnetization vector to precess once in the rotating frame. The excitation of a single resonance in a given spectrum can be used to sort out complex overlapping coupled spectra.

Our NMR system consists of a Varian XL-100, Nicolet TT-100 data system and MONA multi-nuclear accessory. Execution of the Freeman experiment requires the addition of a 25db attenuator to the power amplifier to increase our normal 90° pulse of 18μsec to 320μsec. This pulse width is calculated using:

db Attenuation = 20 log (Normal 90° pulse width/desired 90° pulse width.)

We modified the NTCFT Carr-Purcell experiment (T2CP) to do the present experiment. This sequence is $P1(D1,P2,D2)_{\#echoes}(acq)$. We set P1 = 0μsec, P2 = 4μsec, (∿a 1° tip angle), and D2 = D1 = 1/2ΔF =/resonance frequence-carrier frequence/.

A jumper on the NIC-293 patch panel can be changed from A/J1-A/C10-B/C8 to A/J1-A/C10-B/C6 and the sequence becomes $P1(D1,P2)_{\#echoes}(acq)$. P1 is set equal to P2 and D1 = 1/ΔF-P1 which causes the 1° tip angle excitation pulse to occur every precession of the resonance of interest. We find it necessary to shorten the calculated D1 by 12μsec for which we can find no explanation. Since D1 has a software limitation of ≥ 250μsec the resonance frequence of interest must be within 4000 Hz of the carrier unless the magnetization vector is allowed to precess two or more times. The resolution of the D1 software timer is 1μsec and the peaks should be close to the carrier since at ΔF of 500 Hz a change of 1μsec results in a 0.25 Hz shift in frequence, whereas at 4000 Hz a 16 Hz difference arises. The accompanying spectra of the ethylbenzene aromatic region show what happens.

We hope to write a $[(P1,D1)_{\#echoes},P2,D5]_{\#acq}$ sequence which will allow a single line to be removed from the spectrum by flipping the peak of interest 180° when data acquisition begins.

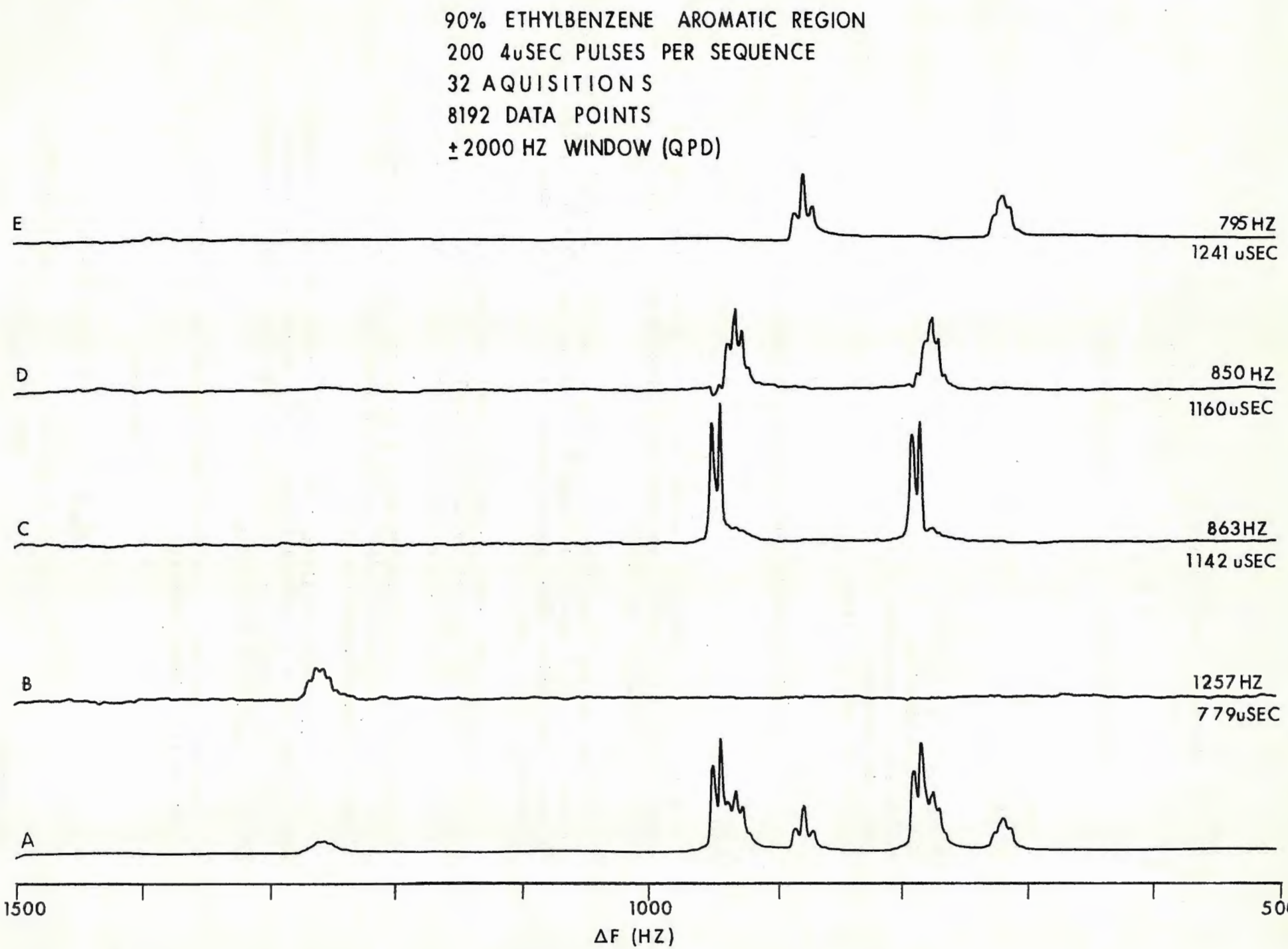
The second subject we would like to discuss is that of T_2* in ^{31}P spectra. We obtain linewidths of 0.25 Hz for ^{31}P in $P(OMe)_3$ proton coupled and linewidths of 0.50 Hz with proton decoupling, although CS_2 shows a carbon linewidth of ∿0.03 Hz. The possibility of incomplete decoupling occurs to us although we are delivering 10 watts to the probe centered at ∿3δ in the ^1H spectra. For T_1 = 5.33 ± 0.07 sec measured by inversion-recovery and T2 = T1 we expect to see ∿0.03 Hz linewidths. We are in need of a phenomenological descriptor of this behavior. Can anyone enlighten us?

Yours sincerely,

Bob

M. Robert Willcott

Steve Silber


90% ETHYLBENZENE AROMATIC REGION
200 4uSEC PULSES PER SEQUENCE
32 AQUISITIONS
8192 DATA POINTS
±2000 HZ WINDOW (QPD)
E
795 HZ
1241 uSEC
D
850 HZ
1160uSEC
C
863HZ
1142 uSEC
B
1257 HZ
779uSEC
A
1500
1000
500
ΔF (HZ)

235-24

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TWIN CITIES

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Minneapolis, Minnesota 55455

NMR Laboratories

612-376-7320

March 3, 1978

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

"NMR Instrumentation Projects at Minnesota"

Dear Barry:

We have been working on a number of small projects to expand the capabilities of our XL-100 spectrometer which we would be happy to share and/or discuss with others.

We have adapted Jake Strothers' "Mickey Mouse Modifications" for the old T-1 program (10616-J) (TAMUNMR 255-55) to the 20309-M version. We have added CAPS to this adaptation such that it will do phase alternating in all modes.

A ^{2}H external lock module compatible with the V-4415 and V-4412 probes has been constructed and works very well. We plan to use this in another probe which we are building for other experiments.

Inserts for 8 mm ^{13}C and ^{1}H and a 2 mm insert for ^{13}C have been wound. We are especially pleased with the performance of the 2 mm insert and make frequent use of it.

We are currently installing a frequency synthesizer based observe modification which we believe represents the best of all the various approaches to multinuclear capability. We can direct those interested to the developers of this scheme.

Hopefully our next contribution will illustrate some chemistry resulting from these projects.

Sincerely,

Bob Lenus

Robert M. Riddle Lenus J. Hedlund

NMR Laboratories

RMR,LJH:deb

University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

Yr. ref.:
Our ref.:

Tel. 031 - 667 1081
Extn. 3416

Professor B.L. Shapiro,
Department of Chemistry,
Texas A.&.M. University,
College Station,
Texas USA
TX77843.

8.3.78

Dear Professor Shapiro,

Lock Interference on the XL-100

XL-100 users may be interested in this unusual problem we encountered with our instrument.

Not long after our XL-100 was installed (November 1972) we noticed a sinusoidal oscillation of the deuterium lock signal level. This was at a variable low frequency, usually less than 10 Hz, and of variable amplitude, from zero to ± 3v peak to peak. When it was bad we could not hold lock, but it came and went as it pleased, and was dubbed the lock wobble.

Various service engineers looked at it, said they'd seen it in other XL's but did nothing except mutter about the mysteries of RF earth loops.

The lock wobble came and went over several months and was once absent for over a year. Then it reappeared and during one six-week period it was so bad that we could run no spectra at all. Thus, eventually was a service engineer constrained to investigate the problem systematically. After two days we decided that RF interference was entering the system from outside at a frequency very close to that of the ^{2}H lock receiver, thus giving a low frequency beat - or wobble.

After eliminating a number of likely local sources we called in the Post Office radio engineers who quickly found a broadcast transmission on 15.36 MHz with a varied programme of folk music and interviews in a language we guessed to be Portuguese or Romanian. We didn't listen long enough to get a station identification.

We still see our lock wobble from time to time but after tying down some earths here and there, especially around the lock receiver, it's not so bad as it was. The reason for its long absence appears to have been due to the effect of sunspots on RF propagation. We would like to screen it out of the lab. altogether but our electronics workshop claim they can't find a big enough biscuit tin!

I'd be interested to know if other XL-100 users have experienced this problem and if effective screening is possible. If anyone has successfully identified the offending station perhaps we could try a deluge of requests for QSL cards!

Yours sincerely,

Alan. S. Boyd

Dr. A.S. F. Boyd

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

March 14, 1978

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

An Economical Instrument-Computer Interface
Based on the SDK-80 Microcomputer

Dear Barry:

We have developed an interface package based on the SDK-80 microcomputer which links a DECsystem-10 computer to NMR spectrometers (HFX-90 and CPS-2) through the Fabritek 1074, the latter equipped with a "T" option card for transfer of data to magnetic tape. This linkage provides a reliable, economical and reasonably fast method of data transfer for subsequent computer processing, eliminating inefficient manual transfer methods previously used.

Features of the system include: minimal hardware design; ease of operation; the use of LED program state indicators; and the use of structured programming techniques. Several months of use have been logged with no problems. More complete details will be reported in the near future.

Sincerely yours,

Mark Abramson

M. J. Abramson

J. H. Goldstein

J. H. Goldstein
Professor of Chemistry

JHG/jd

GBF Mascheroder Weg 1 D-3300 Braunschweig-Stöckheim

GBF

Gesellschaft für
Biotechnologische
Forschung mbH

Abteilung
Physikalische Meßtechnik
Leiter
Dr. Ernst Lustig

Professor B.L. Shapiro,

Department of Chemistry
Texas A& M University,
College Station,
Texas 77843,
USA

Ihre Nachricht vom	Telefon 05 31/70 08-1	Telefondurchwahl	Datum
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Disk maintenance and patches for CFT-20

Dear Barry,

1. Recent correspondence in these columns concerning Diablo disk systems (J.M. Williams, TAMUNN-226, and W.P. Niemczura, TAMUNN-233) indicates that the following simple maintenance steps, that we have suggested elsewhere (Varian Interface Vol. 4), are also worth mentioning here.

1.1. Disk heads should be cleaned regularly with isopropanol by the use of a lintless tissue attached to a wooden spatula. Extreme care is necessary, as replacement heads are costly. The heads of removeable-disk systems should be cleaned every 2-3 months; those of fixed-disk systems should only require cleaning every six months.

1.2. Disk cartridges must be stored in plastic bags to exclude dust; the disk surfaces should be professionally cleaned and tested every 6-12 months. A computer maufacturer should be able to offer this rather inexpensive service.

1.3. The filter system should be replaced regularly. It is particularly important after head crashes to have the disks cleaned and tested. After a series of such incidents we found that 50 % of our disks did not give error-free tests!

2. We possess a magnetic tape unit hooked into our CFT-20 spectrometer. Therefore we have modified the latest version of the program (P/N 94130-07F), in order to be able to store temporary and permanent copies of spectra on magnetic tape. Thus, at the end of an experiment a temporary copy of the FID is written as the first file on the tape. After appropriate data manipulation, permanent copies are stored as consecutive files on tape, each of which is preceded by a filename.

A further patch incorporated into this program makes the intervention of the operator unnecessary between experiments on the same sample. Thus, service work samples, that often require normal noise-modulated ^{1}H-decoupled and single-frequency off-resonance ^{1}H-decoupled ^{13}C spectra, can be run by one series of computer instructions. This saves time, as overnight and over-weekend runs can be optimally arranged without the necessity of attending the spectrometer at unreasonable hours. Similarly multiple experiments at different decoupler offsets may be performed.

Both the above patches are available on request.

We hope the above quenches the inter-continental flow of multicoloured stationery.

Yours sincerely,

Victor Wray

Victor Wray

David N. Lincoln

235-29

ROCHE

21 March 1978

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

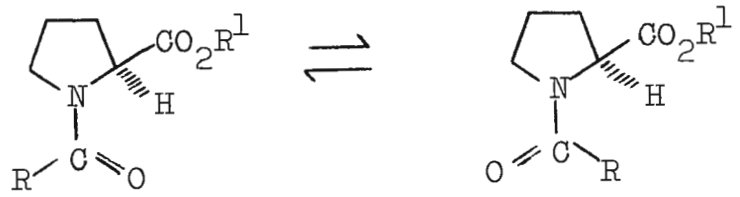
Title: Further Contortions of Acyl Cyclic Imino Acids

Roche Products Limited PO Box 8 Welwyn Garden City Hertfordshire AL7 3AY Telephone Welwyn Garden 28128

Dear Barry

To offset my pending removal from the Newsletter list, may I present some data from Kevin William's PhD thesis concerning a variety of interesting effects emerging from n.m.r. studies of acyl prolines and other ring systems. The cis/trans amide bond in X-proline compounds has been exhaustively covered in the literature since the first ^{13}C results in 1972.[1] We have measured the cis/trans effect in a large number of proline compounds, and also the corresponding 3,4 and 6 membered rings; in addition the energy barriers to rotation and the conformation of the rings have been investigated. The following results were obtained:

(a) In N-acyl prolines, the percentage trans increases with the size of the acyl group and is not dramatically changed in the methyl esters, ruling out any stabilising effect of an intramolecular H-bond (O-H...O=C)

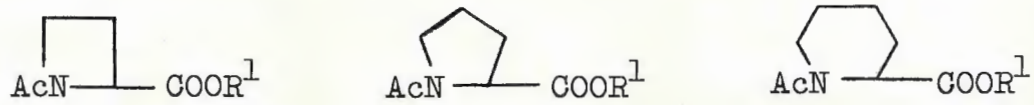


trans cis

% trans isomer

R	H	CH_3	CF_3	CH_3CH_2	$(CH_3)_2CH$	
R^1=H	54	73	74	78	80	$CDCl_3$
R^1=CH_3	56	83	73	79	80	
R^1=H	54	66	70	69	81	d_5-pyr.
R^1=CH_3	42	75	-	75	79	

(b) The effect of ring size on cis/trans isomerism in the N-acetyl series is more dramatic.



R^1	H	Me	H	Me	H	Me
$CDCl_3$	92	58	73	83	60	77
pyr.	47	65	66	75	58	75
CD_3OD	59	59	67	73	68	72

(c) The energy barriers about the amide bond were measured in the ^1H spectrum by the relatively crude coalescence temperature method. In the N-acyl prolines, $\Delta G^{\ddagger}$ varies from 77 to 83 KJ/mole. The barrier increases in N-acetyl proline from 78(dioxan) 81(dmso) to 84(formamide) KJ/mole. In d_5-pyridine N-acetyl azetidine (72 KJ/mole) and N-acetyl pipecolic acid (72) have smaller barriers than the proline (78). This was expected for the four but not for the six-membered ring. We have also examined the 3-membered ring, 1-acetyl-2-carbethoxy aziridine, in which the rate process observed is thought to be nitrogen inversion rather than amide bond rotation due to the inability of the nitrogen lone pair to delocalise into the C-N bond.[2] In toluene/CS_2 at -101°C two forms are observed in the ^1H spectrum indicating a barrier of ca 41 KJ/mole.

(d) The conformations of the 4,5 and 6 membered rings were examined, together with those of corresponding hydroxylated derivatives in the proline and pipecolic acid series. The main feature is the clear desirability of the α-carboxyl function to move out of the amide plane, which is not possible in the planar azetidine ring, partially found in the prolines; and in the pipecolic acids, the coupling constants of the α-proton in cis and trans forms indicate a chair conformation with the α-carboxy group axial favoured by >90%. This phenomenon, previously noted in piperidines[3] and N-nitroso pipecolic acid[4], has interesting implications for the conformation of poly-L-pipecolic acid.

I hope this will restore our subscription for a while.

Yours sincerely

Dr W A Thomas

1. See for instance the review by V.J. Hruby, Chemistry and Biochemistry of Aminoacids, Peptides and Proteins, ed. B. Weinstein, Marcel Dekker, New York, 1974, vol.3, p.1.

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Department of Chemistry
The Mile High PENIS Laboratory

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80523
(303) 491-6480

March 23, 1978

Titles: ^{13}C Spectra of Solids Using ^{1}H Decoupling with Cross Polarization and Magic-Angle Spinning; NMR Service Position Available

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

Dear Barry:

As there appears to be a great deal of interest of late in ^{13}C spectra of solids, we thought the newsletter readers might be interested in some of our recent results obtained with a homebuilt system using the above-mentioned techniques. Vic Bartuska has built the system about an old 14-kgauss Varian magnet. With a cross-coil configuration, the Hartmann-Hahn condition is achieved with a 10 gauss ^{1}H rf field at 60 MHz and a 40 gauss ^{13}C rf field at 15 MHz. Using "house" compressed-air pressure of 14 psi, our Kel-F spinner (Andrew type) operates at about 2.2 KHz.

On the accompanying page are shown four representative spectra of solids obtained with our system. Each spectrum has a width of 8KHz (530 ppm) and was obtained with 4-sec intervals between repetitions, 1 msec cross polarization contact time and 26 msec of ^{1}H decoupling. From the chemically homogeneous polymethylmethacrylate and d-catechin (a plant material), rather well defined peaks are obtained. For the more complex oil shale kerogen and coal samples, only aromatic/olefinic and aliphatic regions are distinctly separated. However, even such broad peaks often have reproducible shoulders that may be resolvable in static magnetic fields of higher strength. Studies on these types of samples are underway in our laboratory.

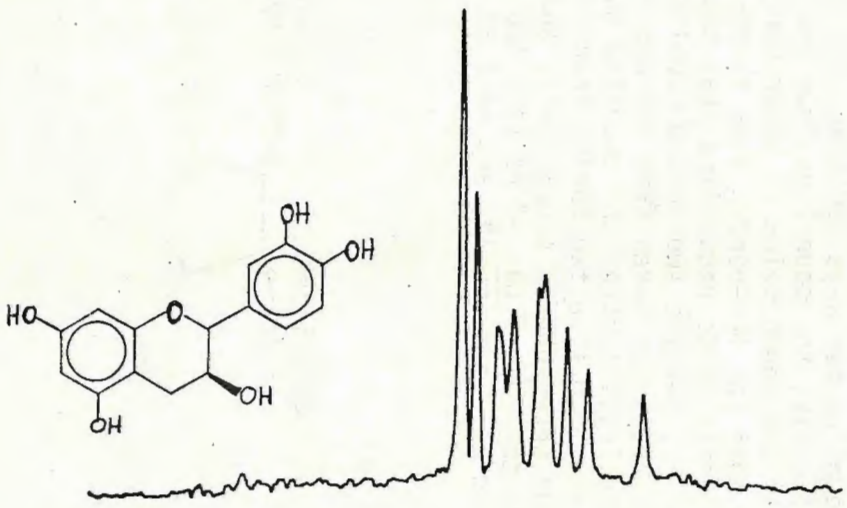
The Department of Chemistry has an opening for a full-time research associate to operate a nmr service facility, based mainly on a JEOL FX-100 spectrometer. Details available upon request. Colorado State University is an equal opportunity employer.

Sincerely,

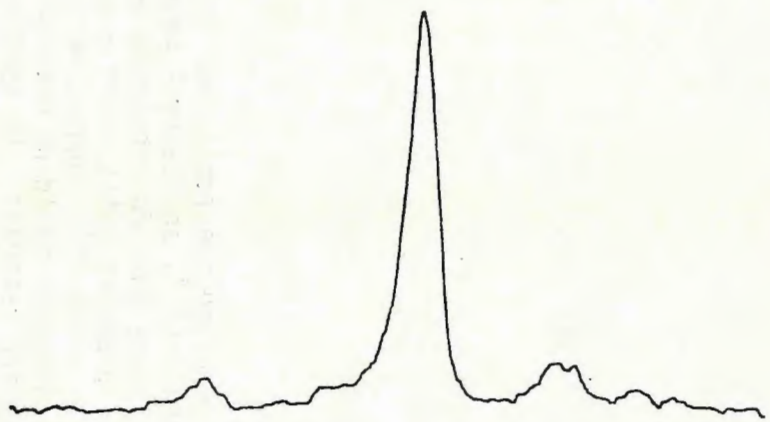
Gary

Gary E. Maciel
Professor

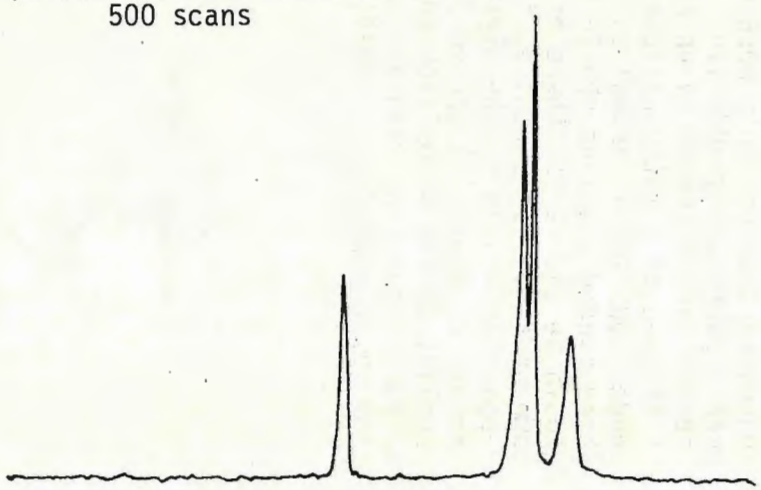
d-catechin
500 scans



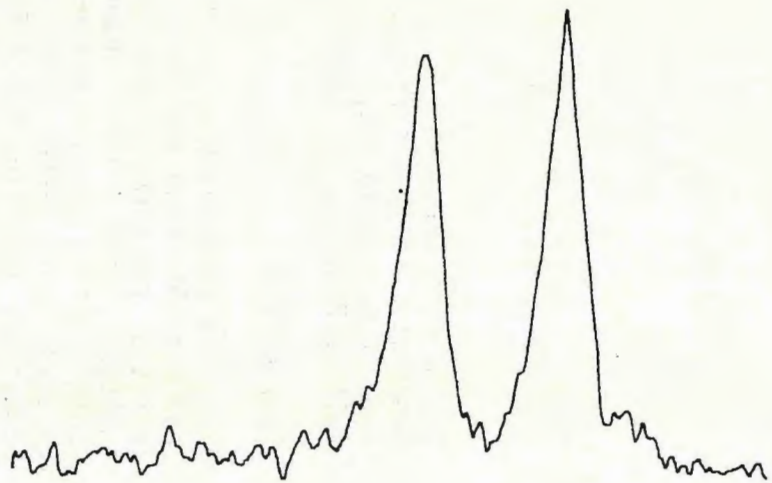
Pocahontas No. 4 Coal
1000 scans



poly(methylmethacrylate)
500 scans



Kentucky oil shale kerogen
1000 scans



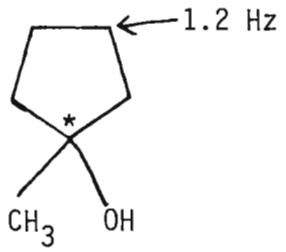
North Texas State University
Denton, Texas 76203
Department of Chemistry

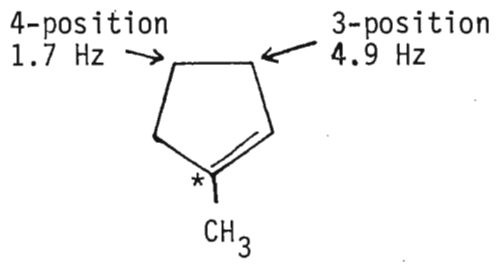
March 24, 1978

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

Dear Barry:

The additivity of nmr spin-spin coupling constants over more than one path has been implied in the literature[1-7], and several examples exist of two simultaneous coupling pathways that do appear to be anomalously large.[3,5,6,8] However, other examples exist where a dual-path coupling appears reasonably low in value.[9-11] Hence, we initiated a study where carbon-carbon coupling constants could be determined in compounds involving two different coupling pathways. We synthesized several such compounds with specific ^{13}C-labeling (fluorene, fluorenone, acenaphthenone, 1-methylcyclopentanol, 1-methylcyclopentene), and the two last compounds of this series particularly exhibited behavior that suggested that not only were dual-coupling pathways additive, but they were algebraically additive. Specifically, the couplings from the labeled carbon (shown by an asterisk) are shown below to other carbons. It is seen in 1-methylcyclopentanol that the two-bonded plus three-bonded coupling is anomalously low, until it is recognized that the three-bonded coupling should be +4-5 Hz, and the two-bonded coupling should be ca. -2 Hz (these expected values are taken from various model compounds[12,13]). Likewise, in 1-methylcyclopentene the coupling to the 3-position should be the algebraic sum of 0 (the two-bonded coupling through an olefin[14]) and +4-5 Hz (the three-bonded coupling[15]); and the coupling to the 4-position should be the sum of ca. -2 Hz (the two-bonded aliphatic coupling with an sp^2 carbon at a terminus[14]) and +4-5 Hz (the three-bonded coupling[15]).





Dr. B. L. Shapiro March 24, 1978

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15. For $^3J_{CC}$ the olefin functionality has little effect, whether it is internal (C=C-C-C), external (C=C-C-C-C), or absent (ref. 14). For a cisoid butane linkage, $^3J_{CC}$ should be 4-5 Hz (ref. 12).

Sincerely,

James L. Marshall
Professor of Chemistry

lgw

GENERAL ELECTRIC

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GENERAL ELECTRIC COMPANY, RESEARCH AND DEVELOPMENT CENTER, P.O. BOX 8
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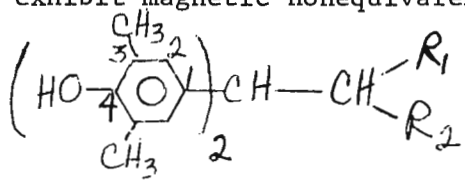
Building K-1, Room 2A18
March 7, 1978

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

Dear Barry:

SUBJECT: ^{13}C Chemical Shift Nonequivalence of Diphenylmethyl Groups.

A few examples of magnetic nonequivalence of prochiral diphenylmethyl[1] and diphenylsilyl[2] groups as observed in the ^{13}C nmr spectra have been reported in the last few years. Recently, we've been examining some bisphenols of general structure I by ^{13}C nmr. When $R_1 \neq R_2$, the geminal phenyl groups are diastereotopic and exhibit magnetic nonequivalence. In Ia, both nonequivalent phenyl



I

a. $R_1=CH_3$, $R_2=\underline{i}Pr$

b. $R_1=CH_3$, $R_2=\underline{i}Bu$

groups and methyl groups are observed in the same molecule. In this example the phenyl rings are split only at the C-1 and C-2 (ortho) carbons, and the magnitude of the splitting at C-1 is <1ppm. The spectrum of this compound is shown in the Figure. When the isopropyl group at R_2 is replaced by an isobutyl group (Ib), two adjacent centers of asymmetry are present, and four distinct chemical shifts are observed for C-1. In Ib, the C-2 carbon resonance is broadened but the splitting is too small to be observed on our XL-100.

We apologize for the delay in sending this contribution.

Regards,

Victor Mark

V. Mark
Plastics Division
Mt. Vernon, Indiana

E. A. Williams/J. D. Cargioli
Chemical and Structural Analysis Branch
Materials Characterization Laboratory

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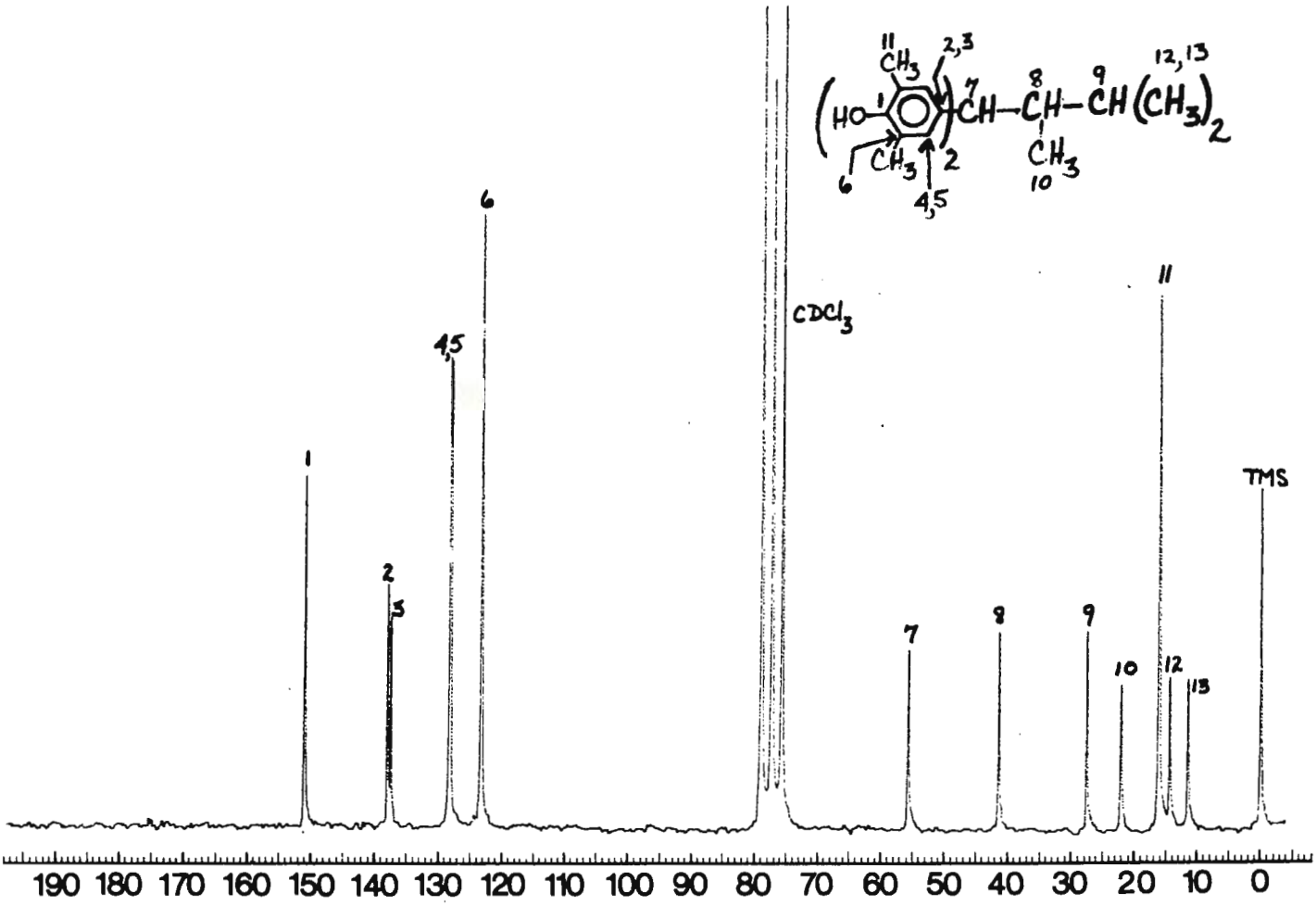
CDCl3
TMS
1
2
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4,5
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190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

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March 20, 1978

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

Position Available: Software Development Engineer

Dear Barry:

We are currently recruiting for a position in our new product development group in Palo Alto, California. The successful candidate will have experience in the design and implementation of real time operating system software. He should be familiar with the hardware interface to a pulsed NMR spectrometer as well as the requisite algorithms for the acquisition and management of data from a high resolution in solids NMR experiment.

Advanced degree requirements as well as salary are negotiable. We are primarily interested in an individual with the appropriate experience who is motivated and feels he can contribute as a member of our development team.

Please have interested candidates write to me. Thank you for your cooperation.

Yours sincerely,

Michael Gross

Michael H. Gross
Manager, Digital Systems
Instrument Division

MHG:jr

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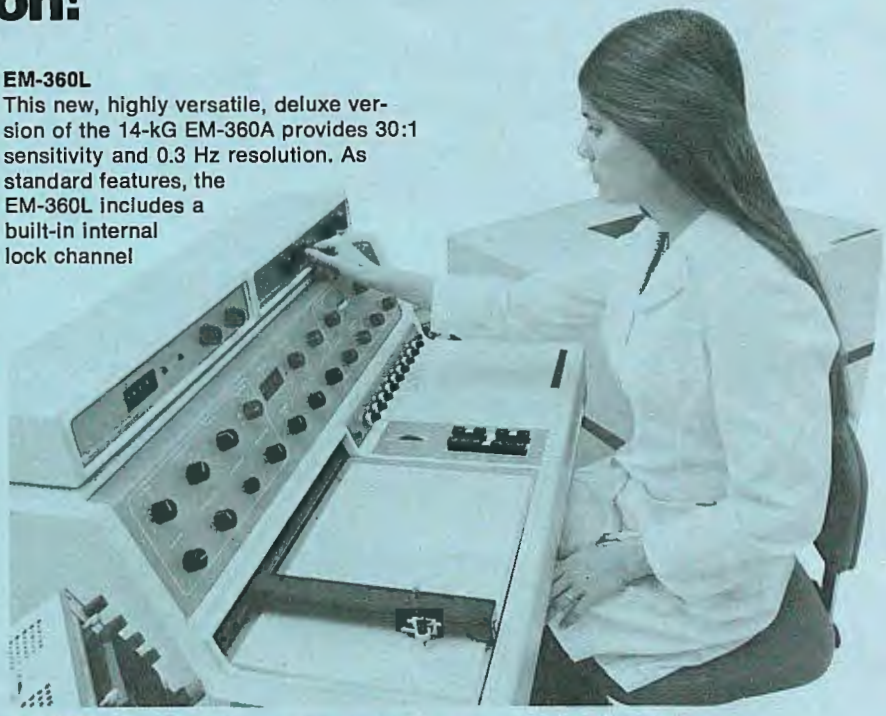

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EM-390

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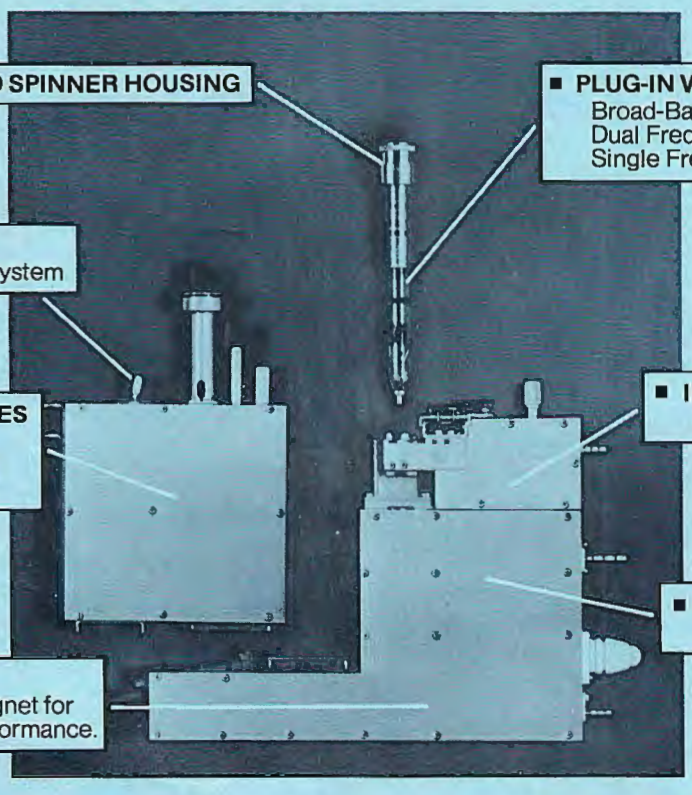

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