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Newsletter

No. 260

May, 1980

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DEADLINE DATES: No. 261 2 June 1980
No. 262 7 July 1980

All Newsletter Correspondence, Etc., Should be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 260

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

Dear Barry:

March 28, 1980

$^{13}C\{^{1}H, ^{11}B\}$ Spectra Using a JEOL PFT-100

The utility of NMR in the study of boron hydrides and the multitude of related compounds is well established. Although ^{11}B and ^{1}H NMR predominate the field, ^{13}C NMR is obviously an inviting structural probe as well. Only a small portion of ^{13}C studies has focused on carboranes, however, since the ^{13}C resonance becomes more difficult to observe when the nucleus is embedded within the carborane cage. Nonetheless, the desirability of ^{13}C chemical shift data led us to investigate the possibility of recording ^{13}C spectra of carboranes and metallacarboranes on our JEOL PFT-100/EC FT NMR.

The major source of the difficulty on observing the ^{13}C cage resonance is undoubtedly unresolved coupling to neighboring ^{11}B (and ^{10}B) nuclei which produces broad singlets. Although the singlet can be narrowed by running the spectrum at a lower temperature (or using a neat sample, when possible) we have attempted to modify our probe to permit broadband ^{11}B irradiation since this would offer easy, routine access to ^{13}C spectral information of cage compounds.

Two major problems needed to be addressed: 1) Would high power 32 MHz r.f. irradiation interfere with the 25 MHz ^{13}C receiver thus degrading S/N? and 2) Would it be possible to transmit ^{11}B irradiation at 32 MHz via the decoupling coils which are wound for 100 MHz ^{1}H irradiation?

We quickly found that the 32 MHz r.f. did indeed increase the noise level substantially in the ^{13}C spectrum. This problem was solved by routing the ^{1}H irradiation (which we deemed necessary) through an external square-wave generator to provide broadband decoupling, and then routing the 32 MHz signal through the JEOL OA-1M homonuclear decoupling channel before amplification so that the ^{11}B decoupling r.f. was gated off during the FID digitization. This improved S/N to an acceptable level.

The second problem was partially solved by constructing an external circuit doubly tuned for 32 and 100 MHz r.f. That this configuration was able to pass both frequencies is shown in Figure 1 where the quartet of the boron-substituted phenyl carbons of $NaB(C_6H_5)_4$ (which proved to be a useful test compound) is seen to collapse upon ^{11}B irradiation. Calculations of the decoupling power gave only 120 Hz, however. Decoupling tests on a metallacarborane (Figure 2) indicate some improvement in the cage carbon resonance.

Obviously, broadband ^{11}B decoupling is highly desirable, but all attempts at this have been fruitless. The problem seems to lie in the inability of the 100 MHz decoupling coils to pass high power 32 MHz r.f.

We communicate this results to inform other PFT-100 owners that triple resonance experiments such as these are possible without major instrumental modifications. Unfortunately (for us), the "third resonance" seems to be restricted to single frequency irradiation (if it is not close to 100 MHz) but this may not be a limitation in other applications.

Sincerely,

Bill

W. C. Hutton

Dave

Dave Finster

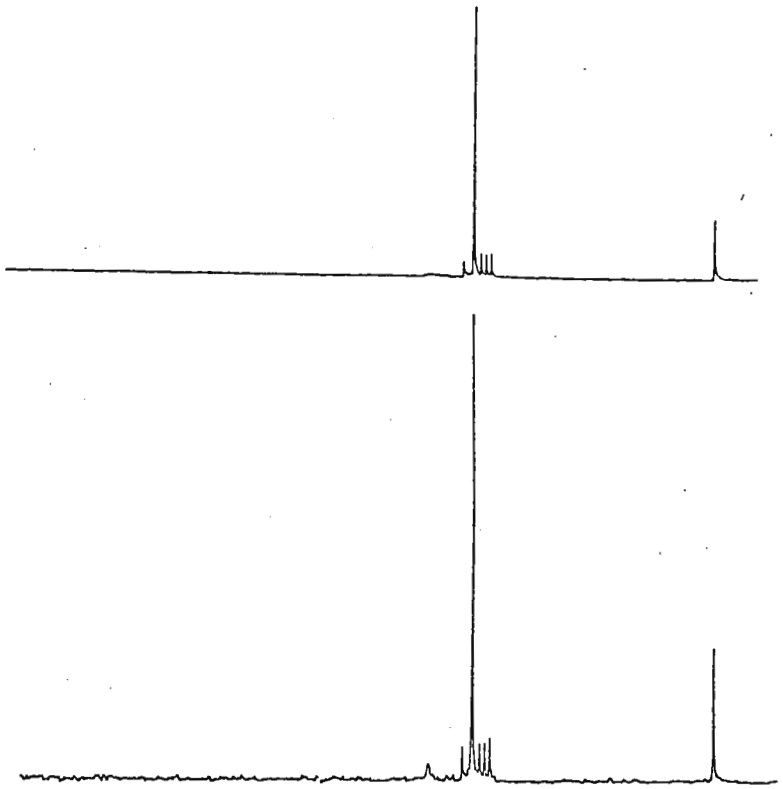

Figure 2. closo-1,2,3-$CpCoMe_2C_2B_4H_4$, broadband proton decoupled. Approximately 1 M.

Top. No ^{11}B irradiation, cage carbon FWHM = 52 Hz.

Bottom. On-resonance ^{11}B irradiation, cage carbon FWHM = 18 Hz.

Shift (vs. TMS)	Assignment
19.3	Me_2
77.1	$CDCl_3$ triplet
80.2	Cp
92	cage carbons

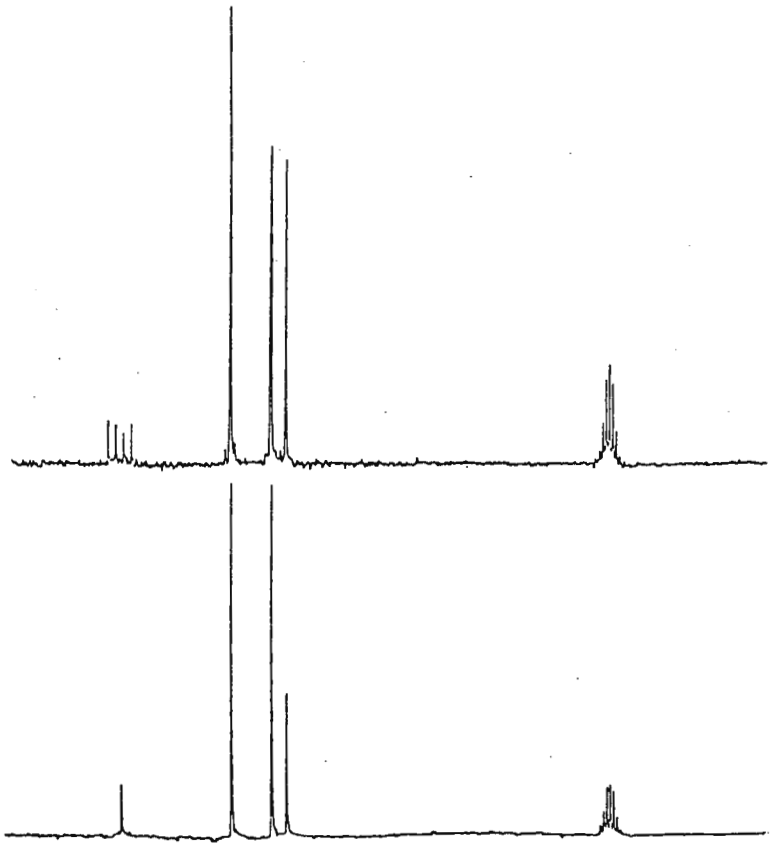

Figure 1. $NaB(C_6H_5)_4$, broadband proton decoupled.

Top. No ^{11}B irradiation.

Bottom. On-resonance ^{11}B irradiation.

Shift (vs. TMS)	Assignment
39.5	DMSO-d_6 multiplet
121.4	C4 (para)
125.5	C2,6 (ortho)
135.7	C3,5 (meta)
163.5	C1

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April 1, 1980

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

Dear Barry:

When doing NMR experiments in which reagent concentrations are varied, but known--hopefully--with accuracy, mixing of the substances directly in the NMR tube is usually the quickest way to do it. Unfortunately, NMR caps are not indestructable and have a tendency to leak at the worst times. Also, shaking the tube vigorously sometimes results in some of the solution sticking to the NMR cap.

To contend with this problem of shaking without leaking, we have developed "Der Walterssplasher." (See attached figure.) It consists of an overhead stirring motor, a ¼" bolt approximately 2" long with a nut, a #8 rubber stopper, and a plastic cap from a one-liter storage bottle. The bolt is placed through the center of the stopper from the botton to the top. The remaining portion of the bolt extends from the top of the stopper. The nut is fastened in place. Next, an off-center cavity, no more than 1/8" from the center is made with a 1/4" drill bit. Care should be taken not to go through the plastic. The cap is placed tightly on the rubber stopper and the bolt is secured in the chuck of the stirring motor.

To use, simply hold the very top of the NMR tube (capped, of course) with your fingers while resting the bottom in the cavity of the plastic cap. Pressing gently but firmly, advance the rheostat until the liquid becomes thoroughly agitated. Even fairly large samples can be thoroughly mixed without contacting the NMR cap. Up to half the volume of a standard 5 mm tube can be used with ease.

Sincerely yours,

J. P. Walters

Jayce P. Walters

Milt

Milton D. Johnston, Jr.
Associate Professor

SUGGESTED TITLE: "SAMPLE MIXING MIT DEN WALTERSSPLASHERN"

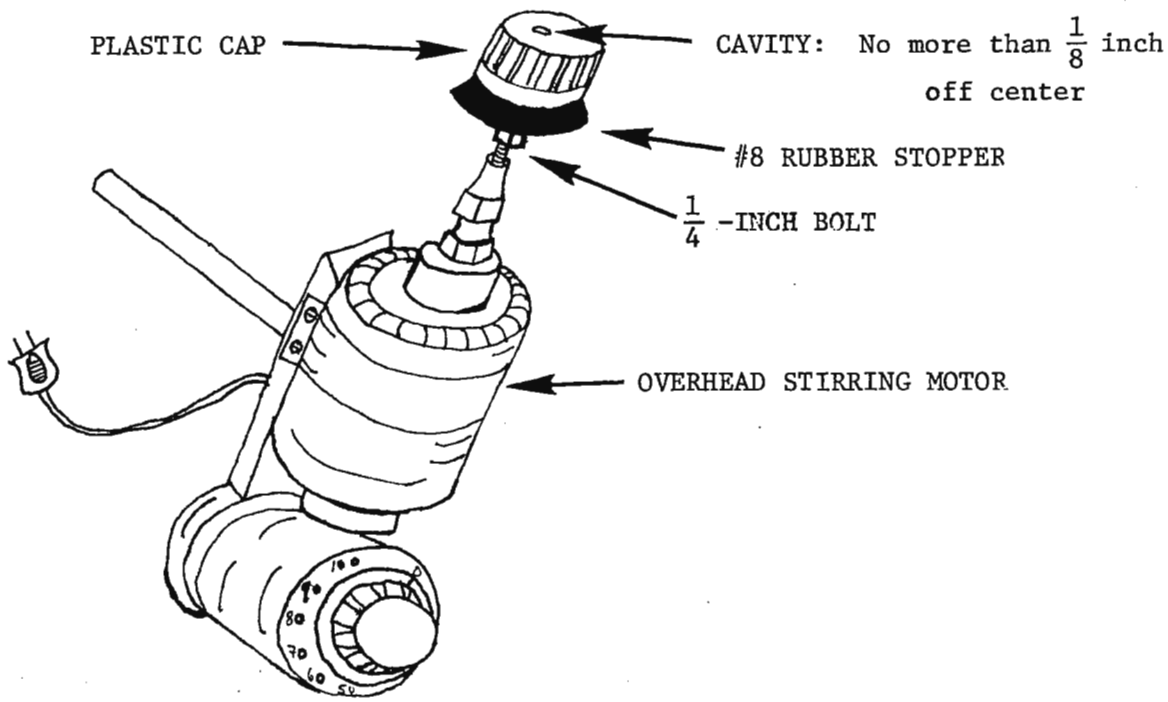


FIGURE: Der Walterssplasher

The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

April 28, 1980

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

Dear Barry:

Having received the complete series of colored reminders, I must now try to reestablish credit with the newsletter. For this purpose I have three topics to raise.

1. A request for reprints and preprints on high resolution ^{2}H mr.
Some months ago I agreed to write a review on applications of high resolution deuterium magnetic resonance and I would welcome any assistance I could have from readers of the TAMU newsletter. To make the review as complete and as current as possible, I would appreciate receiving reprints and preprints dealing with high resolution ^{2}H studies from anyone willing to send them to me. As we all know covering the literature is becoming increasingly difficult and I do not want to miss any pertinent references if I can avoid it. I would be grateful for your help.

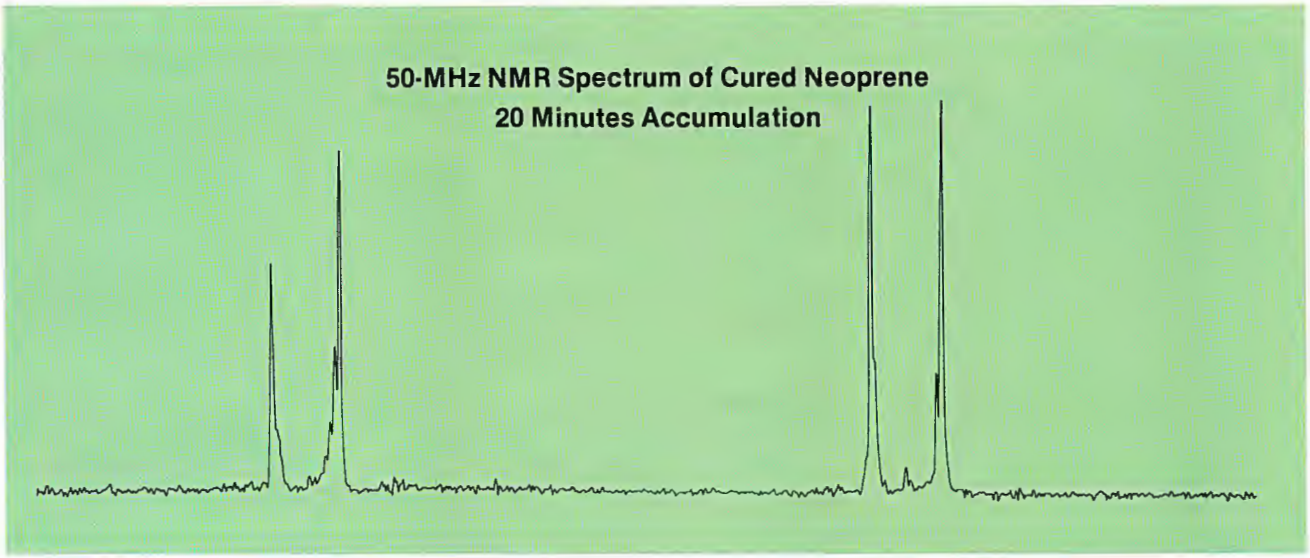
2. A reminder for possible improvement of S/N on old XL-100's.
While it may be common knowledge to many XL-100 owners, there is a feature of the older instruments of which some may be unaware. During a recent visit here Paul Ellis suggested that we examine the level of the transient response at 25.2 MHz with and without the decoupler power on. There was a difference of about 25% indicating that stray 25MHz power from the decoupler was contributing to the noise level. Since we had a filter tuned to 100 MHz which was originally used with a 4415 probe to permit noise decoupling at 100 while locking at 94 MHz, this filter was tuned and placed on the decoupler cable to clean up the signal delivered to the probe. With this filter (described in the Radio Amateur's Handbook) in operation, the S/N results from our sensitivity test sample increased by more than 30%. With such a simple modification, anyone who has been unaware of this can achieve a significant improvement.

3. Notice of availability of XL-100 components.
Toward the end of the year, the XL-100-15 system here will be replaced. Since this instrument depends on a very old 620i it is doubtful that the entire system would be an attractive package. However, components of the system may be of interest to some readers. The instrument operates at 15.4 and 25.2 MHz with ^{2}H or ^{19}F internal lock. There is an old 4415 probe as well as the 4412 probe. There is also a Sykes deck. Any interested buyers for all or parts of the system should write to me indicating their specific needs.

Jake
J.B. STOTHERS

If you can't observe solids as readily as liquids on your superconducting FT NMR...

...you just don't have an XL-200!



^{13}C spectrum of cured neoprene with carbon black in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the fine structure. The width of the plot is 10 KHz. *Sample courtesy of E.I. Du Pont de Nemours and Company*

With the new ^{13}C solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 superconducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; generate your own convenient macro-commands; create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband accessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including ^{13}C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.

varian

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Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Buenos Aires, april 2, 1980.

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

Dear Dr. Schapiro:

A paper on a work made recently in this laboratory, by M.Czekalski,M.E. de Milou and myself, entitlet "A Simple Model of INDOR Spectra", is due to appear shortly in the Journal of Magnetic Resonance.In the meantime it may be of interest to some of TAUMUN readers the following

ABSTRACT.

"A model is made which describes INDOR spectra as the result of "falling into the trough" which is produced when the monitored line is split by tickling,plus the effect of redistribution of populations of the different levels due to the pumping action of the RF fields.This last effect is calculated using an extension of Bloch's "equivalent circuit" model to which,besides the terms representing the spontaneous transition probabilities,terms are added which represent the transition probabilities induced by the RF fields.Calulations made for the AX and AB cases,both homo and heteronuclear,show good agreemant with a specific case studied as well as with data available in the literature, in spite of the simplifying assumpmtions which had to be made in the model."

Yours, sincerily

V. Kowalewski

V.J.Kowalewski.

260-9 FACULTÉ DES SCIENCES
Université de Nantes - U E R DE CHIMIE

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NANTES, le 2.4.80

Professor B.L. SHAPIRO
TEXAS A.M. University
College of Science
COLLEGE STATION

TEXAS 77843

Are solvent effects on chemical shifts and rotational barriers inter_correlated ?

Dear BARRY,

In the course of our investigations of the ^{15}N chemical shifts in relation to rotational barriers, the problem arose of the relative importance of solvent effects on both ^{15}N and $\Delta H^* - \Delta G^*$ values It is well known indeed that intermolecular forces induce significant changes in the values of the structural and dynamic NMR parameters. However chemical shifts and parameters of hindered rotation about C-N bonds for instance, are very different in nature and the study of eventual correlation between their variations as a function of solvent effects, may be expected to produce useful information. Actually a correlation between the induced variations may be anticipated to the extent that they are governed by changes in the HOMO of the planar molecule (assumed to be the ground state of the rotation process). Modifications concerning the LUMO of the planar molecule (which influence $\delta^{15}N$ or $\delta^{13}C$) or the HOMO of the rotational transition state (90° crowded molecule) may be the source of uncorrelated variations.

We have measured the solvent induced shifts of ^{15}N and ^{13}C nuclei in series of amides, thioamides etc... for 16 different solvents. Important effects are observed for ^{15}N: up to 15 ppm, but only 0.5 ppm for ^{13}C, in 0.05 m.f. solutions. Such determinations are very accurate and do not present experimental difficulty... except for the great demand on spectrometer time !

By contrast the problem of precise and accurate measurement of solvent induced changes in activation parameters ΔH^*, ΔS^* is a very critical one. Examination of the literature clearly shows that enthalpy-entropy compensation is effective in most of the published data. From the results of a statistical evaluation of $\Delta H^*/\Delta S^*$ compensation, it appears that for 90 % of the literature data, enthalpy-entropy compensation arises from systematic errors ; In 10 % of the cases only a mechanistic effect may be considered. The "DMF story" is summarized by the correlation

$$Ea\ (\pm\ 0.4)\ kcal.mol^{-1} = -\ 0.9\ (\pm\ 0.9) + 1.73\ (\pm\ 0.06)\ \log A$$

$R^2 = 0.994$ 22 determinations published from 1960 to 1979.

.../...

Indeed if we set log A = 12.5 i.e. $\Delta S^* = 0$ we compute from the above correlation Ea = 20.7 kcal.mol.$^{-1}$ which closely corresponds to the currently adopted value of the free energy of activation ΔG^*_{Tc}.

Thus finding evidence for solvent induced variations of ΔH^* by conventional dynamic NMR is a difficult task. We are presently attempting to solve this problem by using our Varytemp procedure (J. Phys. Chem. 84, 414 (1980) and multicoalescence methods (Tetrahedron Lett. in press). In fact, only small solvent effects are observed (water, glycol, nitromethane, dimethylsulfoxyde, diglyme, dioxane, hexamethylphosphoramide and aqueous LiCl solutions) even in cases where large induced ^{15}N shifts are measured. Moreover, no simple correlation seems to hold between the activation parameters and the ^{15}N or ^{13}C shifts. By contrast the $\delta^{15}N$ values are reasonably correlated with the Dimroth E_T factor, or with the acceptor number A_N of Gutman. Probably the perturbations introduced by the intermolecular forces affect in noticeable and unrelated amounts, energy levels other than the HOMO of the rotational ground state.

G.J. MARTIN M.L. MARTIN

McMASTER UNIVERSITY
Department of Chemistry
1280 Main Street West, Hamilton, Ontario, L8S 4M1
Telephone: 525-9140

April 8, 1980.

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

Zirconium-91 - The Omega of the Periodic Table

Dear Barry,

Our current research interests have taken us into the area of zirconium chemistry. Apart from the usual methods available, one investigative tool should be zirconium-91 NMR. Much to our surprise very few NMR data on this nucleus are available in the literature,[1,2] hence we anticipated insurmountable problems, e.g., unmanageable linewidths and possible instrumental problems due to the low observation frequency (8.37 MHz).

However, we were able to observe signals from a variety of compounds, e.g. $(C_5H_5)_2ZrBr_2$ (½ width 34 Hz) and $(C_5H_5)_2ZrCl_2$ (½ width 276 Hz), their chemical shifts being 122 ppm apart. Adequate signal to noise was obtained for $(C_5H_5)_2ZrBr_2$ after 5 minutes accumulation.

A fuller account will appear shortly.

Yours sincerely,

Brian Sayer Michael McGlinchey

Brian G. Sayer, Michael J. McGlinchey

Please credit this contribution to the account of Mr. J.I.A. Thompson.

References

1. E. Brun, J. Oeser and H.H. Staub, Phys. Rev., 105, 1929 (1957).
2. S. Büttgenbach, R. Dicke, H. Gebauer, R. Kuhnen and F. Träber, Z. Phys. A, 286, 125 (1978).

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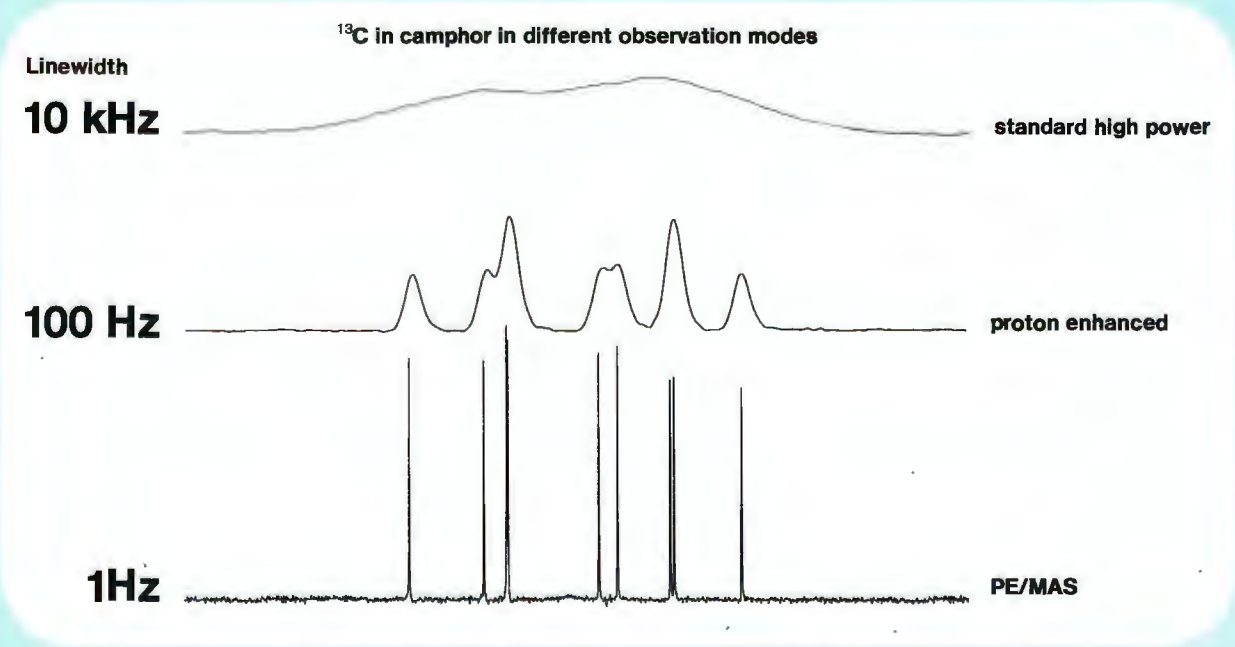


Magic angle spinning with or without cross-polarization is just one of the many applications of the CXP series of pulse spectrometers, the most versatile instruments to date. No other instrument is capable of observing the full range of linewidths (from less than .1 Hz to several hundred kHz).

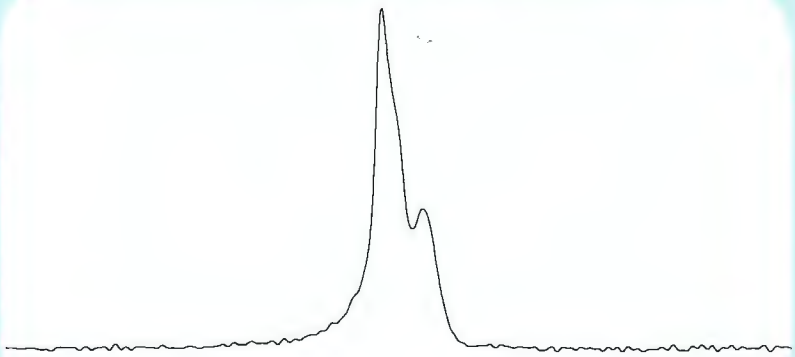
Unique features of the CXP spectrometer line for cross-polarization / magic angle sample spinning experiments comprise:

- **a choice of magnets operating between 2.1 and 7 Tesla;**
- **highest spin-locking fields;**
- **rapid sample spinning;**
- **capability to observe a variety of nuclei (e. g. ^{13}C, ^{15}N, ^{29}Si, ^{31}P, ^{113}Cd);**
- **unmatched sensitivity**
- **a range of rotor sizes (6 to 13 mm o. d.);**
- **a flexible pulse sequence generator for experiments yet to be developed;**
- **ultrafast transmitter/receiver electronics.**

The following spectra exemplify the potential of the BRUKER CXP pulse spectrometers:

Polyethylene

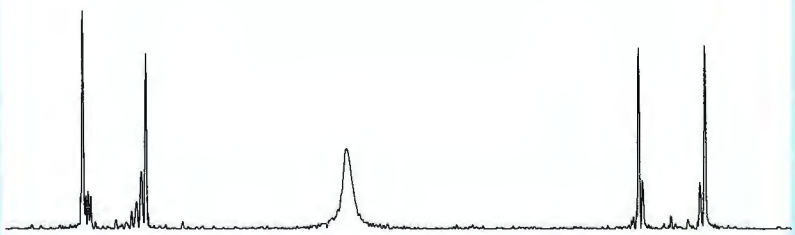
The resolution shown in the spectrum of this highly crystalline polymer required a decoupling field of 20 Gauss.



Cured Neoprene with Carbon Black *)

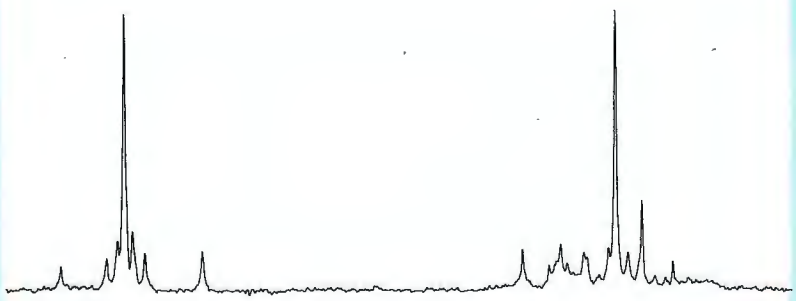
Soft plastics afford excellent S/N and resolution even in the absence of cross polarization and using low decoupling power (35 W, BB-decoupling, 263 transients at 3.5 s recycle time, Gaussian resolution enhancement).

*) sample courtesy of E. I. Du Pont de Nemours and Company.



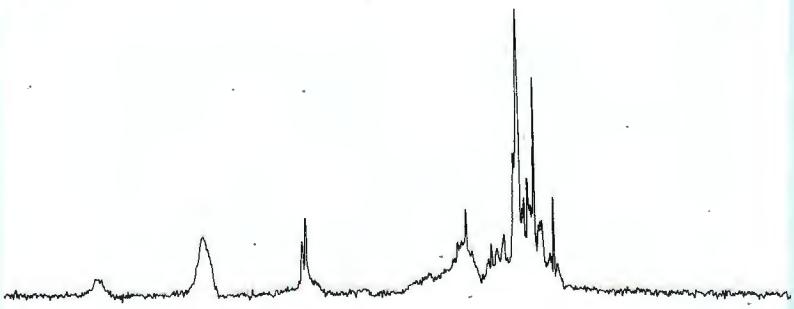
Styrene Butadiene Polymer

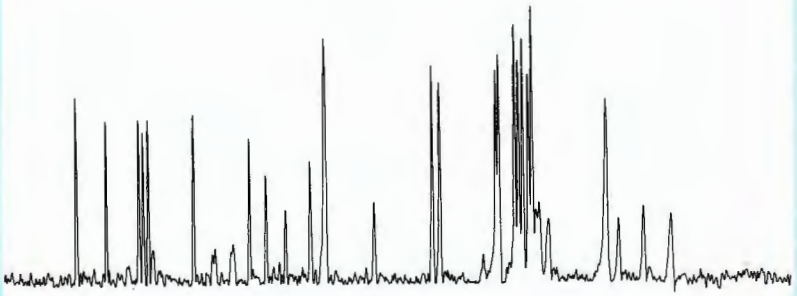
This complex polymer system afforded well separated interpretable lines in 30 minutes experimental time.



Erythrocyte Ghosts

Even this highly complex biological sample gave well resolved resonances.



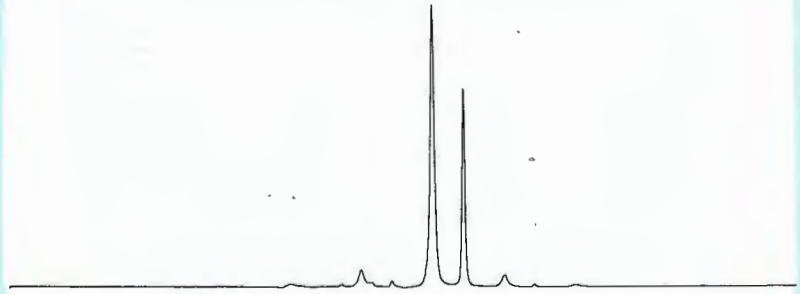


Reserpine

This ^{13}C CP-MAS spectrum demonstrates the feasibility of obtaining high-resolution spectra of complex organic molecules in the solid state. It is to be noted that chiral carbons can give rise to more than one signal, thus providing additional information. In this example, a new technique was applied for removal of rotational sidebands.

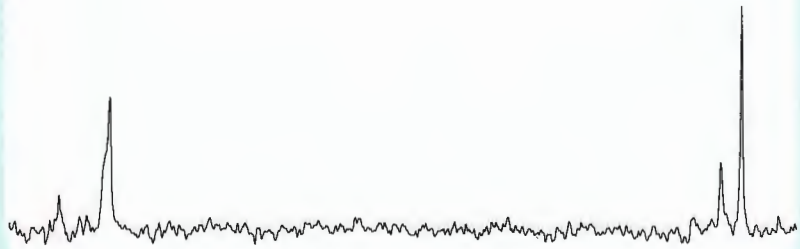
Ammonium Dihydrogen Phosphate

Magic angle spinning reduced the ^{31}P linewidth from 34 to 1.4 ppm.



Mixture of Sodium Chloride and Sodium Nitrite Crystals

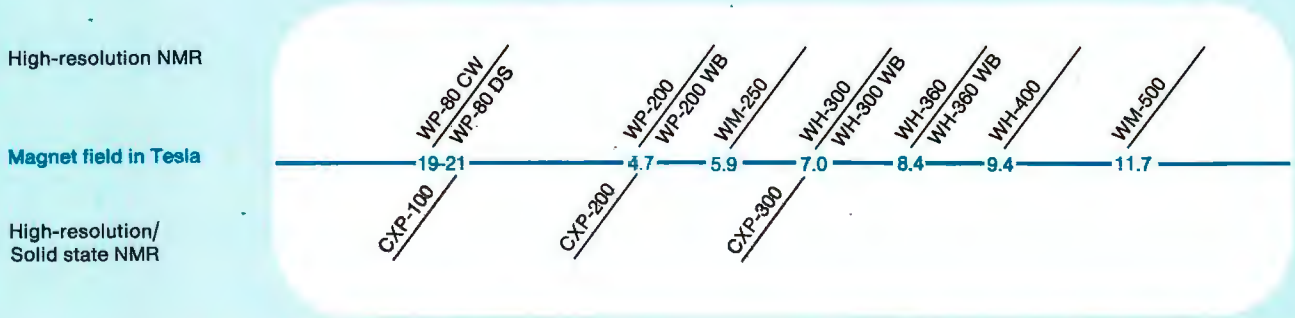
This spectrum shows the chemical shift dispersion of ^{23}Na in the solid state. Magic angle spinning narrowed the lines to 2 ppm.



Ammonium Nitrate

This natural abundance ^{15}N CP-MAS spectrum of solid ammonium nitrate narrows the nitrate resonance from 250 ppm to a few ppm. Interesting is the presence of two further lines probably belonging to a minor constituent.

Whether your NMR needs are governed by scientific demands or budgetary constraints, Bruker is the only real choice. No other manufacturer offers as complete a product line as we do:



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Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77 843

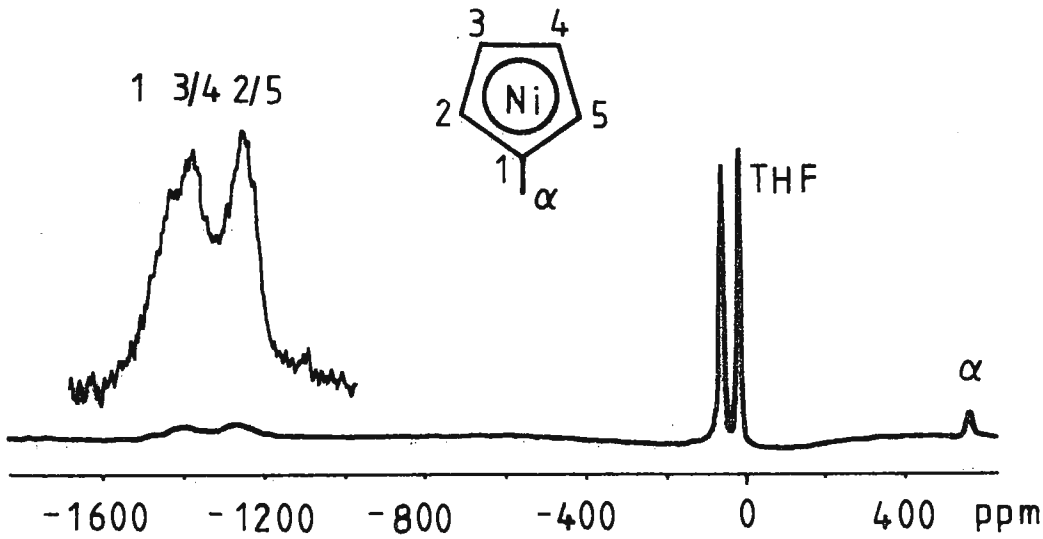
Title: Extreme ^{13}C data

Dear Professor Shapiro!

With our remarkable collection of blue and even pink letters in view I thought that this time it should be possible to contribute to your newsletter without reminder. As usual I do this instead of Prof. H.P. Fritz.

Since quite some time we updated our equipment with a Bruker CXP 200 and a JEOL FX 60 instrument. Especially the latter became an easy to handle and reliable help in high resolution routine work. We now wait for a better (safer) version of the old variable temperature unit. Our CXP 200 is equipped for both high power and high resolution studies. But most of the time we use it to detect broad signals from liquid samples. Due to the nature of our compounds we chose saddle coils with beautiful results whenever all components of the system work satisfactorily (there are some problems with the variable temperature reliability of the high power inserts which Bruker promised to cure soon).

One pleasant improvement the CXP 200 brought about was the high power ^{13}C capability. Informations on metallocene radicals now come from a shift range 2200 ppm and line widths 5000 Hz. As an example the ^{13}C spectrum of methylnickelocene dissolved in THF-h_8 is shown below. It has been obtained at 339 K in less than two hours without lock.



Rather promising is the fact that very broad signals with low signal to noise are easily detected together with narrow and much bigger resonances. Thus $^1J(CH)$ can be obtained in most cases. In the example given here the CH_3-signal of $(CH_3C_5H_4)_2Ni$ remains "decoupled" by the unpaired electrons. Other nickelocenes which we will describe in Angew. Chem. are better examples and allow an easy signal assignment due to $^1J(CH)$ [1]. We currently try to get more insight into the electronic situation of nickelocenes with these data.

Yours very sincerely

Frank H. Köhler

[1] F.H. Köhler, J. Organomet. Chem., 91(1975)57.

UNIVERSITÄT DES SAARLANDES
Fachbereich 14 - Organische Chemie

Professor Dr. H. D ü r r

66 Saarbrücken, den 22.4.8o
Telefon: (0681) 302.3409

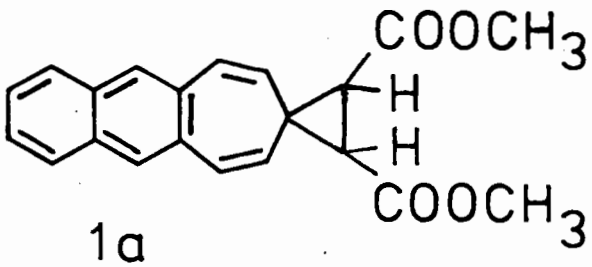
Herrn
Professor Dr. B. L. SHAPIRO
Department of Chemistry
University College Station
Texas 77843 USA

Dear Professor Shapiro,

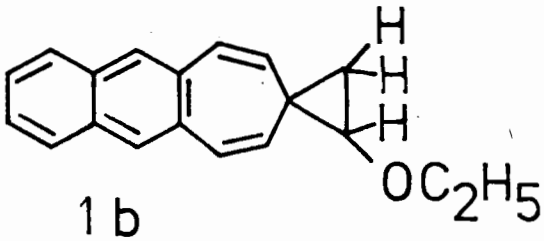
Bestimmung der Aktivierungsparameter der Ringinversion substituierter Cycloheptatriene

Cycloheptatrien ist wie alle nichtaromatischen mittleren Ringe und Elektronenbeugungsmessungen nicht eben und liegt in der Wannenform vor. Bei Raumtemperatur befinden sich die beiden Konformeren in einem schnellen Gleichgewicht, wie bei -15o° durch die Nichtäquivalenz der beiden Protonen nachgewiesen werden kann (Aktivierungsenergie: 6 kcal/Mol.).[1)]

Wir haben eine Reihe neuartiger Spirocycloheptatriene 1 und 2 synthetisiert, bei denen die Cycloheptatrien-Ringinversion in eindeutiger Weise vom Spiro-Rest beeinflusst wird[2)]. Als Beispiel seien die Spirocycloheptatriene 1 a,b und 2 a,b vorgestellt.



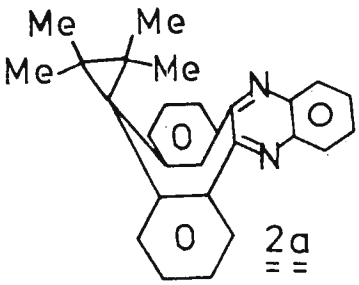
1 a



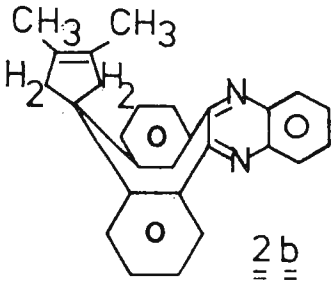
1 b

Die ^{1}H-NMR-Spektren der Naphtocycloheptatrienderivate 1 a, b zeigen, daß diese Derivate sich bei Raumtemperatur ebenfalls in einem schnellen Konformerengleichgewicht befinden.

Bei Raumtemperatur erscheinen die beiden Ester-Methylgruppen von 1 a als ein scharfes Signal. Durch Einfrieren der beiden Konformationen sollten beide als getrennte Singuletts beobachtbar sein. Die Tieftemperaturspektren von 1 a in einem 1:1-Gemisch aus Deuteromethylenchlorid/Perdeuteroaceton bis herunter zu 18o°K zeigen jedoch keine Aufspaltung oder Verbreiterung des Estermethylsignals. Auch die Tieftemperaturspektren ergaben keinen Hinweis von 1 b auf eine Behinderung der Ringinversion bis zu 18o°K. Daraus kann geschlossen werden, daß $\Delta G^{\neq}$ für die Ringinversion der Naphthospirononatetraene 1 a, b kleiner als 8.33 kcal/Mol ist.



2a



2b

Im Gegensatz hierzu folgt aus dem Spektrum der dreifach annellierten Cycloheptatriene 2 a, b daß diese bei Zimmertemperatur in einer starren Wannenform vorliegen müssen. Bei dieser Temperatur beobachtet man deshalb im Spektrum von 2 b je zwei Methylen- bzw. Methylresonanzen im Verhältnis 2:2:3:3. Beim Erwärmen auf über 1oo°C verbreitern sich diese Signale (Spektren b, c). Weiteres Erwärmen führt zur Koaleszenz der Methylprotonen bei 118°C und der Methylenprotonen bei 123°C (Spektrum d). Bei 18o°C erscheinen die beiden Gruppen wieder als zwei scharfe Singuletts. Eine Abschätzung der Energiebarriere für die Ringinversion von 2 b mit Hilfe dieser Werte nach Formel (1) ergab $\Delta G^{\neq}$ = 19.75 kcal/Mol. $\Delta G^{\neq} = 45{,}7 T_c\ (9.97 + \log T_c)$ cal/Mol.

Bis zu einer Temperatur von 17o° zeigten die beiden Methylsignale von 2 a dagegen keine Verbreiterung. Deshalb kann für 2 a nur ein unterer Grenzwert für $\Delta G^{\neq}$ angegeben werden. Er beträgt 22.41 kcal/Mol. Die höhere Energiebarriere von 2 a im Verhältnis zu 2 b kann durch die räumliche Behinderung der vier Methylgruppen mit den zwei Wasserstoffen in ortho-Stellung zum Siebenring im pla-

1) F. A. Anet, J. Am. Chem. Soc. 86, 458 (1964).

2) A. Hackenberger und H. Dürr, Tetrahedron Lett., 1979, 1541.

naren Übergangszustand erklärt werden. Die Energiebarriere von 2 b liegt um 13 kcal/Mol höher als beim Cycloheptatrien. Dies dürfte auf eine Fixierung des Siebenrings durch die drei Annelanden zurückzuführen sein. Diese Versteifung ist deutlich größer als in den von Tochtermann untersuchten Dibenzocycloheptatrienderivaten 3 für die Werte um 15 kcal/Mol gefunden wurden[3].

A. Hackenberger

H. Dürr

---

3) W. Tochtermann, U. Walter und A. Mannschreck, Tetrahedron Lett. 4o, 2981 (1964).

Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

(212) 570-5666

11 April 1980

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

Dear Barry:

Title: ^{15}N Chemical Shifts of N-Phenylaziridines; Postdoctoral Position Open

In connection with our work on small-ring nitrogen heterocycles[1] and substituted anilines[2,3] we have determined N-15 chemical shifts of a series of N-arylaziridines (Table I). The range of shifts is smaller than that for the corresponding N,N-dimethylanilines, which implies less extensive interaction between the nitrogen lone pair and the benzene pi system. Steric effects of ortho methyl substitution are also much smaller. Since N-phenylaziridine is sterically more constrained from adopting a twisted conformation than is N,N-dimethylaniline, it is likely that the methyl groups bring about inductive rather than conformational changes.

Using a Taft DSP analysis, the shifts correlate well with σ_I and σ_R^- values. The ratio ρ_R/ρ_I = 11.1/4.41 = 2.52 is unusually high for aniline systems, indicating a higher proportion of resonance interaction with the ring. We are investigating this further.

A postdoctoral position is available in my lab to carry out natural-abundance N-15 studies in organic systems. The salary is $12,000/year. This includes one month's vacation and fringe benefits. Applicants should send me a c.v. and arrange for 2-3 letters of recommendation to be sent.

Regards!

Sincerely yours,

Kenneth Crimaldi

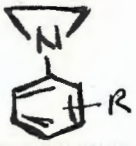
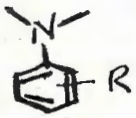
Kenneth Crimaldi

Robert L. Lichter
Professor of Chemistry
Chairman

RLL:hs

1. Crimaldi, K.; Lichter, R.L. J. Org. Chem. 1980, 45, 1277-81.
2. Sibi, M.P.; Lichter, R.L. ibid. 1977, 42, 2999-3004.
3. Sibi, M.P.; Lichter, R.L., unpublished results.

Table I. ^{15}N Chemical Shifts of N-Arylaziridines[a]

R	 δ_N(ppm)	$\Delta\delta_N$[b]	 δ_N[c](ppm)	$\Delta\delta_N$[b]
H	39.8	0.0	44.9	0.0
4-NMe_2	35.0[d]	-4.8	42.6	-2.3
4-OCH_3	36.1	-3.7	40.8	-4.1
4-CH_3	38.0	-1.8	42.8	-2.1
4-F	37.4	-2.4	40.5	-4.4
4-Cl	39.6	-0.2	49.1	4.2
4-NO_2	47.3[e]	7.5	68.6	23.7
2-CH_3	37.9	-1.9	33.8[f]	-11.1
2,6-$(CH_3)_2$	37.8	-2.0	16.8[f]	-28.1

[a]Measured with respect to external $CD_3NO_2/CH_3{}^{15}NO_2$, reported with respect to anhydrous liquid ammonia using relationship $\delta_{NH_3} = \delta_{CH_3NO_2} + 380.2$. Positive values denote shifts to lower shielding. Experimental error ±0.2 ppm. Compounds run as 4M solutions in $CDCl_3$ unless otherwise indicated. [b]$\Delta\delta_{N_R} = \delta_{N_R} - \delta_{N_H}$. [c]Ref. 3. DMSO solutions. [d]δ_{NMe_2} = 41.5 ppm. [e]δ_{NO_2} = 370.1 ppm. [f]Reference 2.

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CHAIRMAN OF DEPARTMENT: PROFESSOR R. D. BROWN
INORGANIC CHEMISTRY: PROFESSOR B. O. WEST
ORGANIC CHEMISTRY: PROFESSOR W. R. JACKSON

11th April, 1980

Professor B.L. Shapiro,
Texas A & M University,
College of Science,
College Station, Texas 77843,
United States of America

Dear Barry,

^{13}C spectra of almost-solids

Faced with the current craze for recording high-resolution NMR spectra of solids, but unable to afford the necessary instrument, we have been exploring what our Bruker WH90 and HX90 spectrometers can do with 'almost solids'. There are some clues in the literature - the ^{13}C spectra of solid natural rubber[1], camphor[2] and adamantane[3].

We had no real trouble obtaining medium-resolution spectra of some solid rubbers, foodstuffs and other commercial materials. A few examples are shown on the next page. The reference is either TMS/$CDCl_3$ capillary or dioxan/D_2O.

'Vegemite' is a protein hydrolysate, like English 'Marmite', which kids eat as a spread: we have yet to find an American who can stand the stuff! 'Pears' is a translucent toilet soap containing glycerol, as you can see. Chocolate shows the typical cocoa (POP) fats, and the auto tire wall is mainly styrene-butadiene rubber. The natural rubber was the finger from a rubber glove wrapped around a lock tube.

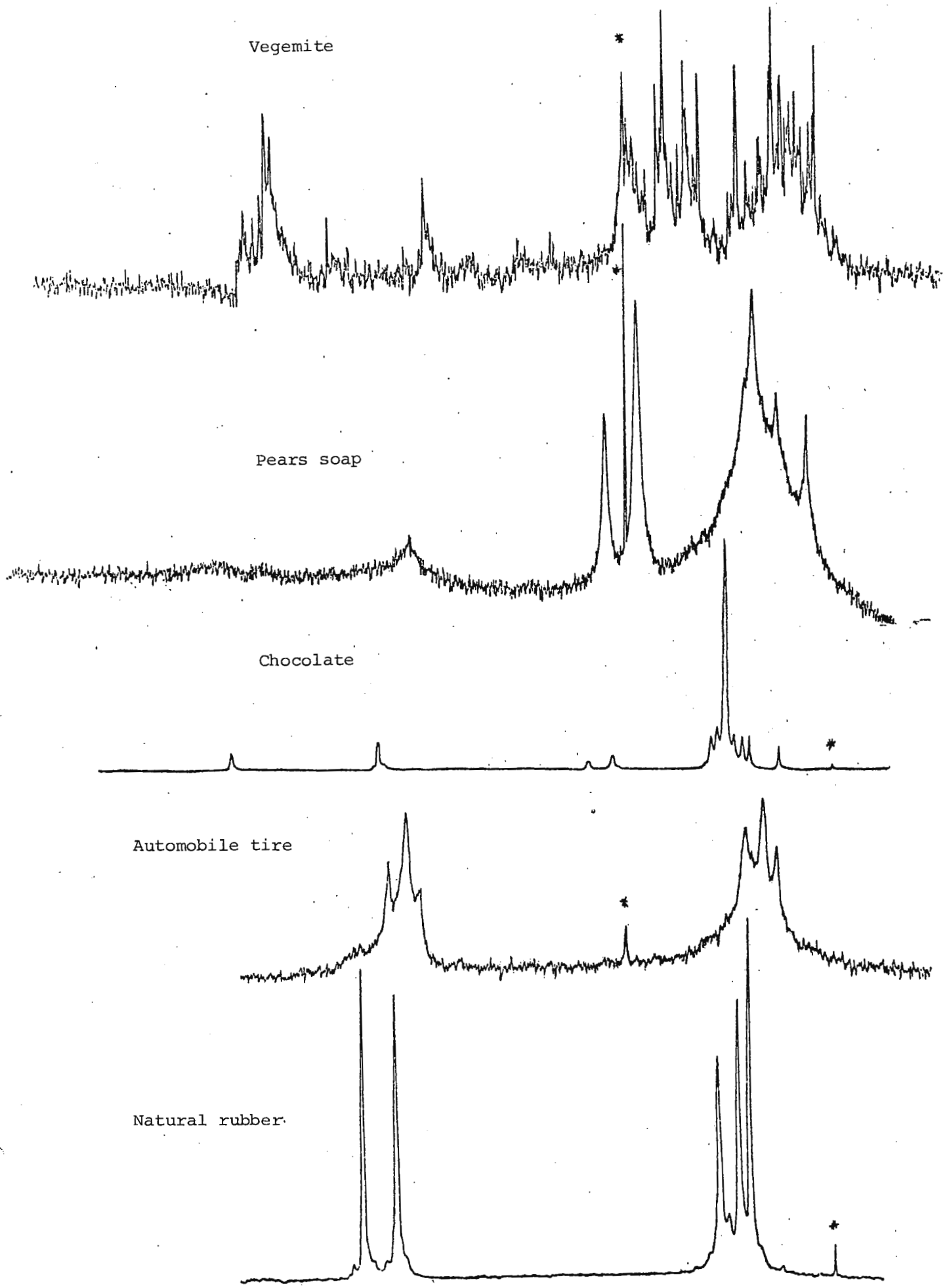
The spectra are useful teaching examples and they also give us an unusual angle on Consumer Chemistry. Please credit this letter to Michael Heffernan's Monash subscription.

Kind regards,

Ian

Ian D. Rae.

1. M.W. Duch and D.M. Grant, Macro mol. 3, 165 (1970).
2. R.E. Wasylishen and M.R. Graham, Mol.Cryst.Liq.Cryst.Letters, 49, 225 (1979).
3. JEOL brochure 'Nano & Micro Resonance', p 31 (1977).


Vegemite
Pears soap
Chocolate
Automobile tire
Natural rubber

NEN New England Nuclear®

April 15, 1980

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

C-13 NMR SPECTRAL STUDIES ON PHTHALALDEHYDIC ACID

Dear Barry:

Phthalaldehydic acid (2-carboxybenzaldehyde) has been found, on the basis of UV, IR and Proton nmr spectral data, to exist in the lactol form IIa in neutral and acidic solutions and as the anion of the free aldehydic form I in alkaline solutions. We investigated the above problem by C-13 nmr in a variety of solvents such as $CDCl_3$, CD_3CN, CD_3COCD_3, CD_3SOCD_3, CD_3OD, CD_3COOD, D_2O, and D_2O-NaOD.

In all solvents except D_2O-NaOD (see also below for its behaviour in $CDCl_3$ and CD_3OD), the observed C-13 chemical shifts pointed out to its existence solely in the lactol form IIa; in D_2O-NaOD, the resonance due to C-7 observed in other solvents at ca. 99 ppm was absent and a broad C=O resonance due to the free aldehyde appeared at about 196 ppm showing it to be the anion of I.

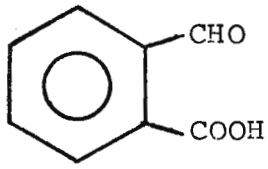
In $CDCl_3$ that was used straight from the container from the supplier (wherein the solubility of phthalaldehydic acid was not great), moisture present in it appeared adequate to hydrate the free aldehyde form I to IIIa leading to a rapid equilibrium between the lactol IIa and IIIa as evidenced by the abnormally broad C-7 resonance and comparatively broad signals for C-1, C-4 and C-6. Upon pre-drying the $CDCl_3$ over Drierite for 1 hr prior to dissolution of the substrate, all the above resonances became sharp indicating that only the lactol IIa was present.

In CD_3OD, there were two sets of resonances with intensity ratio of 3:1, the major lines corresponding to the pseudo-ester IIb (or the acetal IIIb) and the minor ones corresponding to the lactol IIa. Nearly same chemical shifts observed for all the carbons except C-1 and C-7 in the two species are indicative that the major one is the pseudo-ester IIb rather than the acetal IIIb. Further evidence for the presence of the $-OCD_3$ group on C-7 was provided by the downfield shift of C-7 by nearly 5 ppm compared to the lactol IIa and the appearance of a weak multiplet due to $-O\underline{C}D_3$ about 7.5 ppm downfield of the main $\underline{C}D_3OD$ multiplet.

Additional evidence for the free aldehyde group in D_2O-NaOD was provided by the $^2J_{CCH}$ of 26.54 Hz observed due to the coupling of C-1 with the C-7 proton in the ^1H-gated decoupled spectrum.

A full report is being submitted to an appropriate journal.

549 Albany Street, Boston, Massachusetts 02118 Telephone 617-482-9595 Telex 94-0996



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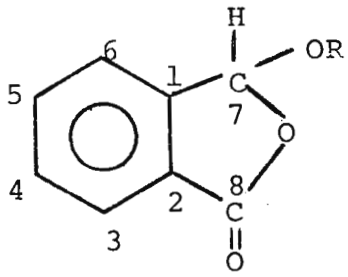
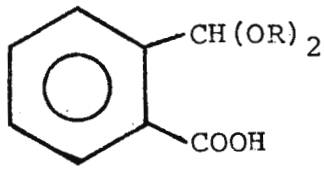


II a, R=H
b, R=CD_3



III a, R=H
b, R=CD_3

TABLE: Carbon-13 Chemical shifts of phthalaldehydic acid

Solvent	Chemical shift (ppm)							
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
$CDCl_3$	146.15	127.12	131.06	123.84	134.64	125.80	97.86	169.35
" dry	146.40	126.71	130.79	123.42	134.67	125.34	97.94	169.58
CD_3CN	147.87	127.77	131.58	124.52	135.50	125.62	98.74	169.80
CD_3COCD_3	148.02	127.72	131.29	124.36	135.17	125.36	98.75	169.30
CD_3SOCD_3	147.44	126.61	130.63	123.74	134.58	124.64	98.41	168.78
CD_3OD* (i)	146.29	127.89	131.95	124.77	135.72	125.92	104.96	170.44
(ii)	148.60	127.69	131.60	124.53	135.72	125.78	99.72	170.94
CD_3COOD	147.92	127.82	131.67	124.50	135.62	126.06	99.41	171.07
D_2O	146.75	126.76	131.99	124.50	136.22	126.13	101.00	172.49
D_2O-NaOD	134.43	142.73	130.15	134.92	129.27	128.61	196.06	176.47

* (i) represents signals due to the pseudo-ester IIb
(ii) represents signals due to the lactol form IIa

(All spectra were run on a Bruker WP-200 NMR Spectrometer equipped with ASPECT 2000 Computer in 10 mm o.d. tubes at room temp.)

Sincerely,

Lawrence P. Thomas

Lawrence Thomas

Puliyur R. Srinivasan

Yale University *New Haven, Connecticut 06510*

DEPARTMENT OF MOLECULAR BIOPHYSICS
AND BIOCHEMISTRY
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Sterling Hall of Medicine, 333 Cedar Street
(203) 432-3722

April 16, 1980

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

Dear Barry:

Spectral Simplification by the Simultaneous Application of the Carr-Purcell Pulse Sequence and Homonuclear Decoupling.

In the October, 1979 issue of TAMU, Drs. Mildvan and Gupta, using homonuclear phosphorus decoupling, showed unequivocally that the origin of the splitting in the ^{31}P spectrum of ATP was due to ^{31}P-^{31}P spin coupling. Just in case any doubt remains, we present here additional experimental verification of the fact. The ^{31}P spectra shown here in Figure 1 were acquired using the Carr-Purcell pulse sequence ($90°-\tau-180°-\tau$) for two values of 2τ ($\frac{1}{2J}$; $\frac{1}{J}$) and show the expected scalar modulation of the spin echo due to the $\frac{1}{J}$ homonuclear coupling (Figure 1A and D). In spectra (B and E; C and F) we demonstrate the effect of the simultaneous application of a homonuclear decoupling pulse (↓) during acquisition on the γ and β resonance respectively. The spectra in the right hand column show the 'expected' collapse of the multiplets for a value of $2\tau = \frac{1}{J}$ which leaves the doublets 180° out of phase with respect to the triplet. Interesting, and perhaps useful in situations where there is extensive resonance overlap, is the effect of the saturating pulse in the spectra in the left hand column where $2\tau = \frac{1}{2J}$. With the decoupling pulse centered on the γ phosphate resonance, the resonance intensity for the β phosphate is almost totally absent. Similarly in spectrum C, resonance intensity for both the α and γ phosphate is abolished with the β phosphate decoupled. If care is taken to set the delays accurately in both these cases, the decoupled resonances would have zero intensity.

Sincerely,

Ian

Ian M. Armitage

Jim

James H. Prestegard

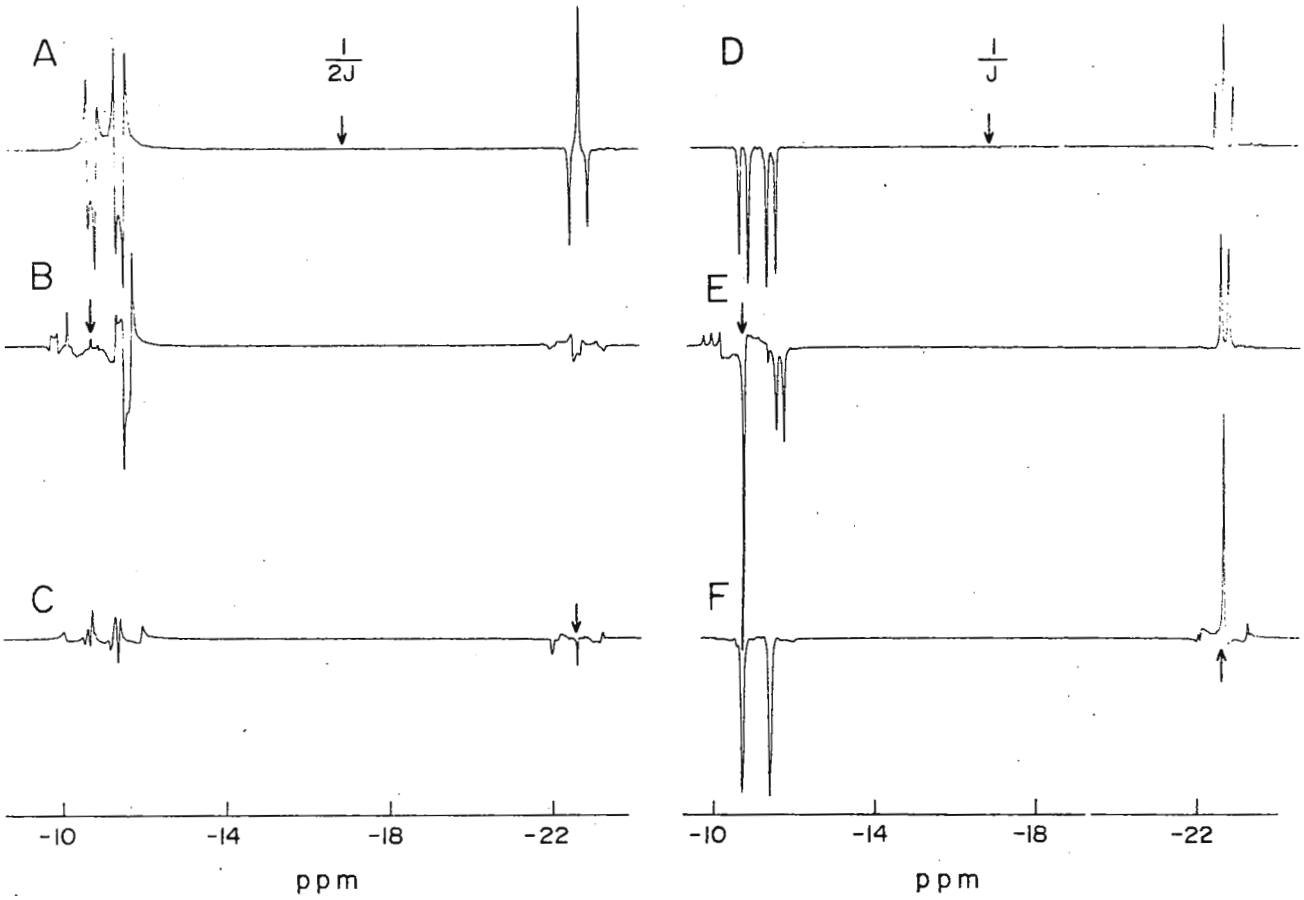


Figure 1. Proton decoupled ^{31}P NMR spectra at 80.9 MHz (Bruker CXP 200) of ATP. Spectra were acquired using the pulse sequence 90°τ 180°τ with the homonuclear decoupling pulse set at the frequency indicated by (↓). A value of $2\tau = \frac{1}{2J}$ was used for spectra A,B and C; $2\tau = \frac{1}{J}$ for spectra D,E and F.

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

Department of Chemistry

April 24, 1980

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

AMPLIFIER NOISE SUPPRESSION

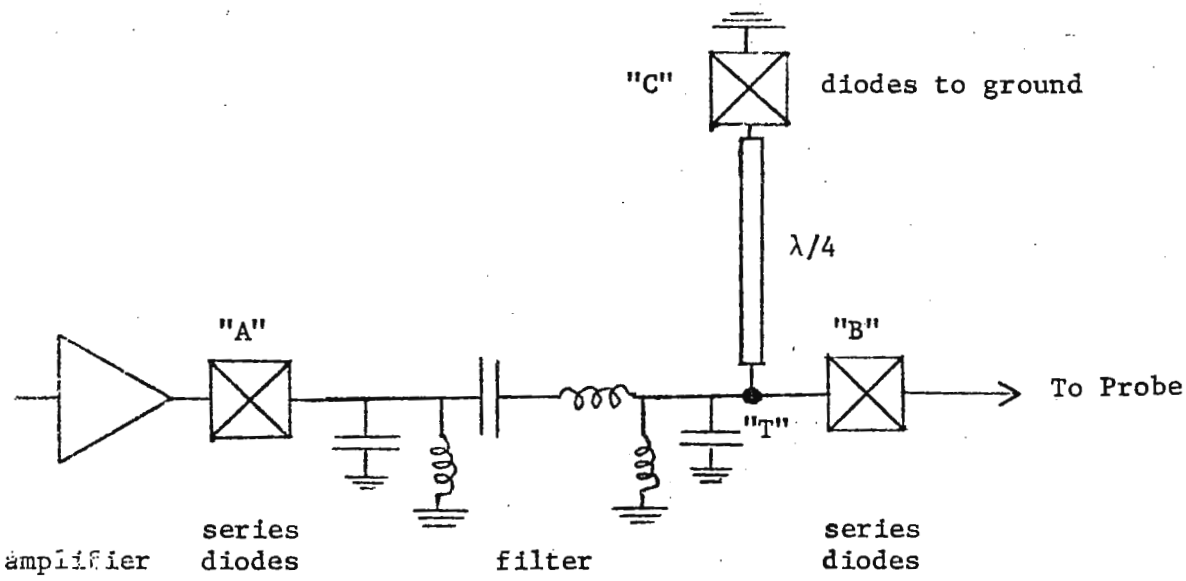
Dear Dr. Shapiro:

Broadband radiofrequency amplifiers are used in many NMR spectrometers. When these amplifiers provide the pulsed rf power to the probe there are often difficulties associated with their relatively high levels of residual noise even when they are not being driven. This noise interferes with observing weak nuclear resonance signals, since series diodes are usually not adequate for suppressing the noise. This problem is present in both solid state and tube amplifiers. At least one manufacturer provides blanking circuitry for turning off the final stage of the amplifier to reduce residual noise. This works well for those experiments that can tolerate a 10-20 μsec delay after the rf pulse before the start of data acquisition.

In order to perform multiple pulse line narrowing experiments and to observe the initial part of free induction decays from very broad lines, we have developed a circuit for noise suppression that is passive, rapid, and effective. It has the disadvantage of being tuned for a particular frequency. We use it on an Amplifier Research Model 200L, but it is probably compatible with any amplifier.

The device is basically a voltage variable "T" attenuator where a band pass filter limits the range of rf frequencies from the amplifier under both high and low power conditions, and a $\lambda/4$ line removes residual rf under low but not high power conditions. The schematic diagram is shown below. It consists of two sets of series diodes, a butterworth band pass filter and a diode terminated $\lambda/4$ line.

During the high power rf pulse all three sets of diodes are turned on. Diodes "A" and "B" present a low impedance to the rf which passes through the filter to the probe; since diodes "C" are also turned on the λ/4 line is shorted to ground and presents a high impedance at point "T" effectively removing the influence of the λ/4 line. When the amplifier is not driven the diodes are not turned on. While the diode sets "A" and "B" are not sufficient to prevent the amplifier noise from getting to the probe, with diodes "C" off the λ/4 line presents a short to ground at "T" for rf not removed by the filter. Noise suppression with the circuit is greater than 60db which is fully adequate for limiting noise to below detection levels of the receiver. The insertion loss is about 0.2db.



SCHEMATIC DIAGRAM

Sincerely,

Stanley J. Opella
Assistant Professor of Chemistry

Joseph A. DiVerdi

UNIVERSITY OF DENVER
An Independent University
University Park, Denver, Colorado 80208

Department of Chemistry / 303·753-2436

April 24, 1980

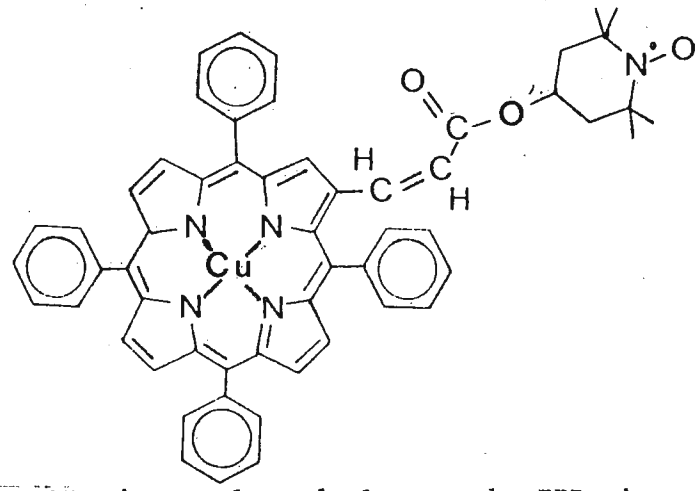
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Title: NMR and EPR Evidence for Donor-Acceptor Interactions between nitroxyl radicals and halocarbons.

Dear Barry:

We have recently observed that the nitroxyl group in 1 forms a complex with CHX_3 (X = Cl, Br, I). The rate of exchange between free and coordinated

1



CHX_3 is fast on the NMR time scale and slow on the EPR time scale. The differences between the EPR spectra of 1 and 1·CHX_3 help to interpret the factors influencing the magnitude of the nmr contact shifts observed for CHX_3.

The nitroxyl region of the EPR spectrum of 1.0 x 10^{-3}M 1 in $CHBr_3$ is shown in the figure. The two components differ in g-value, in the value of the nitrogen hyperfine coupling constant, A_N, and in the value of the electron-electron coupling constant, J. Two components are also observed in the presence of $CHCl_3$ and CHI_3 but not in solvents which contain no halogens. To minimize general solvent effects while comparing

Professor Shapiro
April 24, 1980,

interactions with CHX_3, NMR and EPR spectra were taken in the presence of 1.2M CHX_3 in CS_2. The EPR parameters for the component with the larger values of A_N and J were similar to those obtained for 1 in CS_2. Therefore the component with the smaller values of J and A_N is assigned to $1 \cdot CHX_3$. The decreased values of A_N and J are consistent with donation of some of the unpaired spin density from the nitroxyl to CHX_3. Based on computer simulation of the EPR lineshape the equilibrium constants for formation of $1 \cdot CHX_3$ are all about 1 and fall in the order $CHCl_3 < CHBr_3 > CHI_3$. The difference between J for 1 and $1 \cdot CHX_3$ fall in the same order.

The ^1H NMR contact shifts were determined using concentric tubes with CHX_3 in CS_2 containing 4% TMS in one tube and CHX_3 plus 1 in CS_2 containing 4% TMS in the second tube. The ratio of $\Delta\nu$ CHX_3 to $\Delta\nu$ TMS is then a measure of the contact shift due to formation of $1 \cdot CHX_3$. The contact shifts fall in the order $CHCl_3 < CHBr_3 > CHI_3$ which is the same as was observed for the equilibrium constants and for perturbation of the EPR parameters, J and A_N. Thus the trends in the NMR shifts are due both to changes in the equilibrium constants and in the extent of spin transfer.

In closely related compounds we do not see two species in the EPR spectra in the presence of CHX_3 so this may be a fortunate case of slow exchange.

Morishima et al[1] have found that the ^1H and ^{13}C contact shifts induced in the NMR spectra of CHX_3 by di-t-butyl nitroxide increase in the order $CHCl_3 < CHBr_3 < CHI_3$. For 1 plus CHX_3 the effects are larger for $CHBr_3$ than for CHI_3. This may indicate that steric hindrance is greater when CHI_3 interacts with tetramethylpiperidine nitroxyl than with di-t-butyl nitroxide. Morishima et al[1] attributed the trend in the contact shifts for CHX_3 to formation of a donor-acceptor complex between the π-orbital containing the nitroxyl unpaired electron and a halogen atom of CHX_3. The differences between the EPR spectra of 1 and $1 \cdot CHX_3$ are consistent with this interpretation.

Sincerely,

Gareth

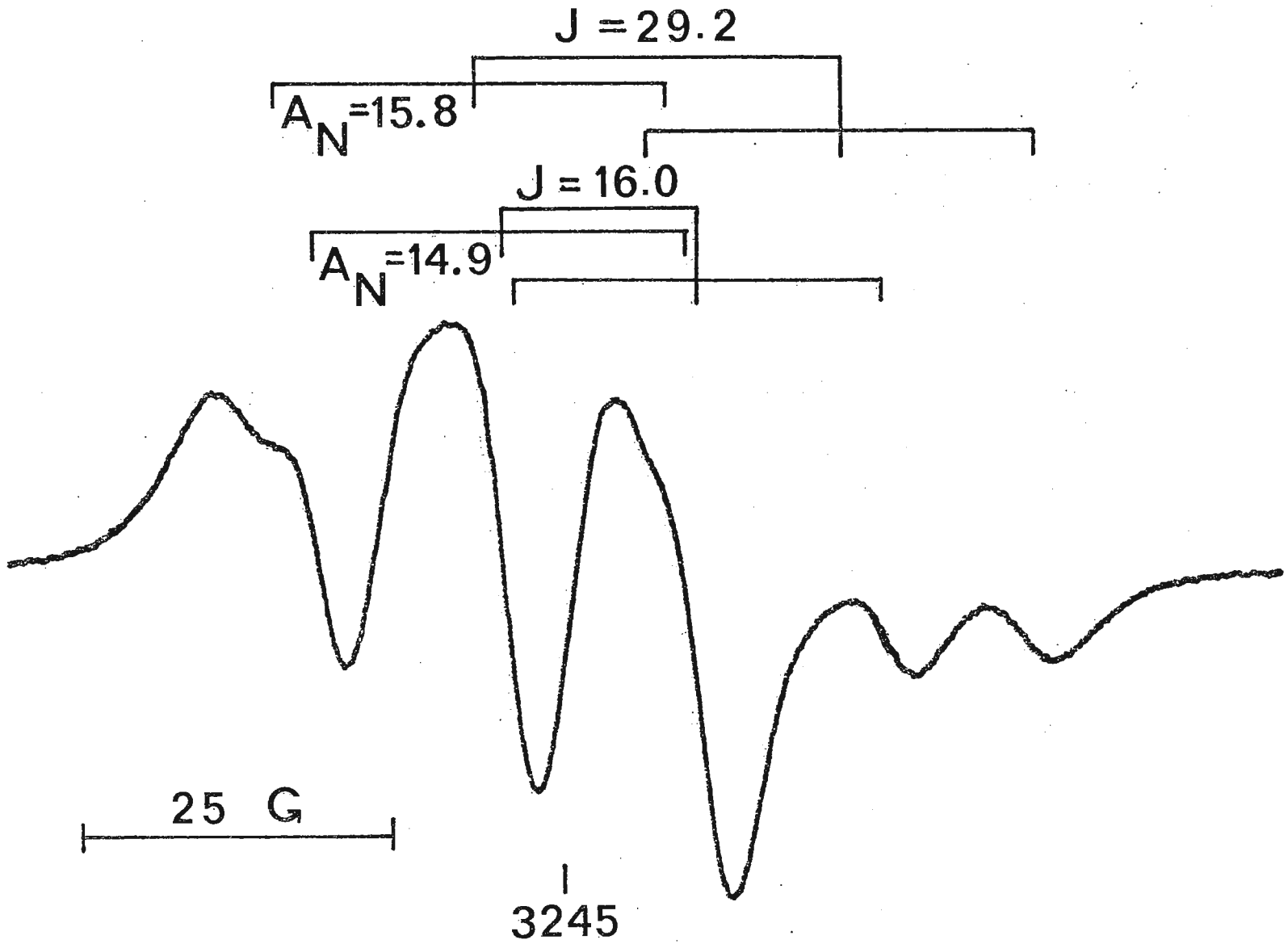
Gareth R. Eaton

Sandy

Sandra S. Eaton

[1] I. Morishima, T. Inubushi, T. Yonezawa, J. Am. Chem. Soc. 98, 3808 (1976) and references therein.

GRE:SSE:ms


J = 29.2
A_N=15.8
J = 16.0
A_N=14.9
25 G
3245

The University of Alabama in Birmingham
Comprehensive Cancer Center
205/934-5696

25 April 1980

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

Sub: Underwater Decoupling in FT NMR

Dear Barry,

I would like to report the results of pulsed FT NMR underwater decoupling (UWD) experiments that we have performed some time back. As you know, underwater decoupling is the method of choice to assign peptide NH hydrogens of biomolecules (rather than the tedious solvent titration method). The original UWD experiments were performed by Dadok (1) in the correlation NMR mode. The accompanying figure shows the results we obtained on our WH-400 in pulsed FT NMR mode. The sample, a solution of a peptide fragment (36 mM in H_2O, with 5% D_2O, pH = 3.1), was contained in a 5 mm o.d. NMR sample tube. The spectra were gathered, not with a proton probe (as it was sent out for repair) but with a 10 mm ^{13}C probe adapted for ^{1}H observation (using the ^{1}H decoupler coils). The dynamic range problem was avoided by presaturation of water (2-4). At the end of presaturation, the frequency of the time-shared decoupler (HD) was set on the $C^{\alpha}H$ proton that is to be decoupled. The strength of irradiation used for water saturation and spin decoupling was the same ($\gamma H_2/2\pi \simeq 35$ Hz). The strong interfering signal resulting from the excitation of water is considerably minimized by multiple point saturation of the water resonance. This is accomplished by defining a frequency list containing 6 or 7 frequencies spanning the water resonance. The $C^{\alpha}H$ proton frequency is entered as the last entry in the list. A microprogram is written in which the decoupler is looped to jump from one frequency to another in the list, spending about 10 ms at each. This process is repeated several times until the signal from water is minimized. The spectra shown were gathered under less than ideal conditions (5 mm sample tube with a 10 mm ^{13}C probe, 20° flip angle for observation, 200 scans). With a normal proton probe, we are certain that these experiments can be performed easily on more dilute samples. Since most peptides have their exchange minimum in the range pH = 2-3.5, adjustment of sample pH to this range assures that the reduction in NH proton intensity due to a transfer of solvent saturation is minimal. In addition to the underwater decoupling experiments, we have also been performing peptide NH exchange rate measurements on our WH-400 using the transfer of solvent saturation method. These details will appear elsewhere (5).

Comprehensive Cancer Center

Please credit this letter to the account of Bob Lenkinski.

Yours sincerely,

Ramu

N.R. Krishna
Assistant Professor
of Biochemistry and Physics

References

1. J. Dadok, P.H. Von Dreele and H.A. Scheraga, J. Chem. Soc., 1055 (1972).

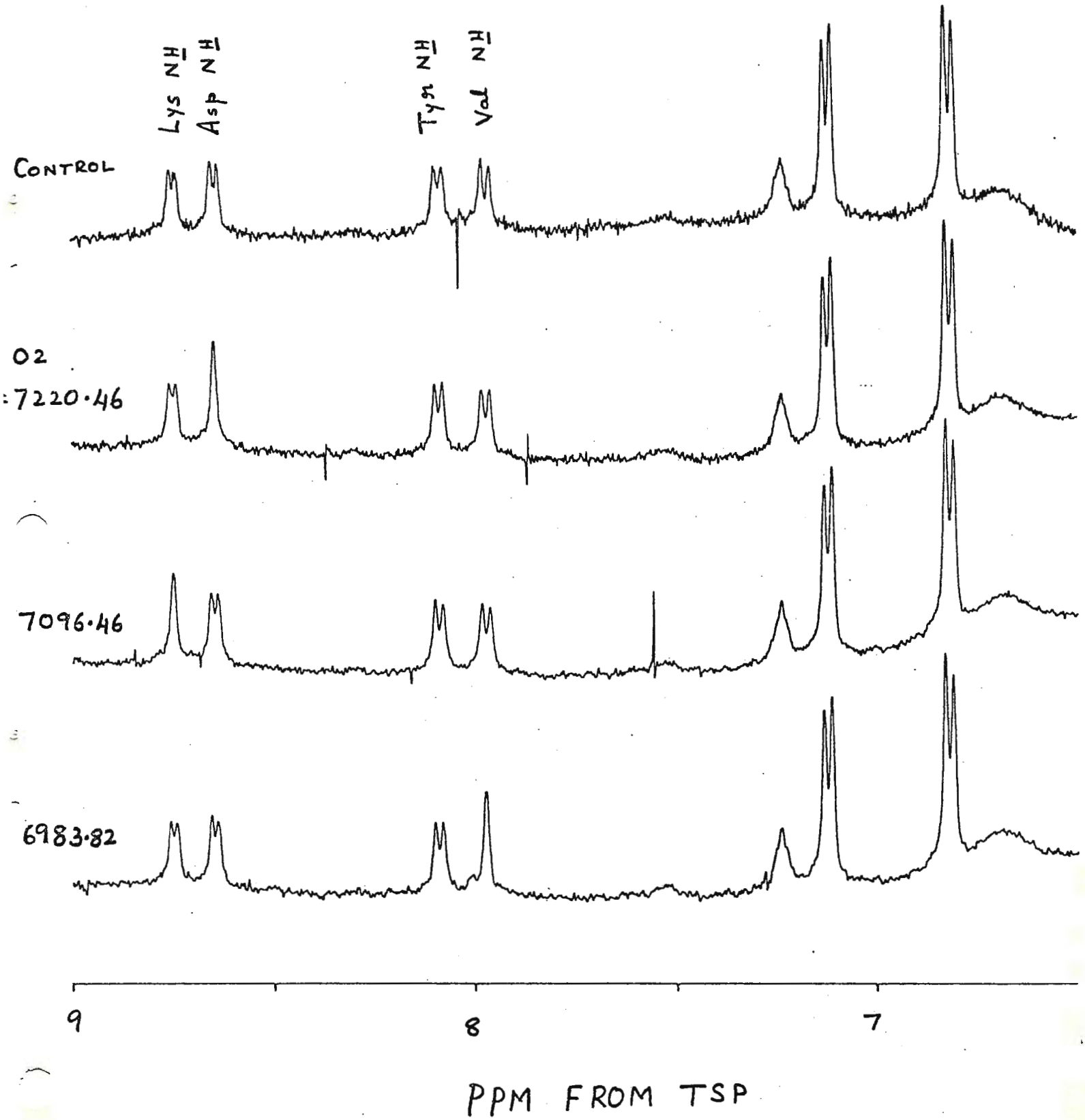
2. A.G. Redfield, Methods in Enzymology, XLIX 253 (1978).

3. H.E. Bleich and J.A. Glasel, J. Mag. Res., 18, 401 (1975).

4. N.R. Krishna, J. Mag. Res., 22, 555 (1976).

5. R.E. Lenkinski, R.L. Stephens and N.R. Krishna, submitted for publication, (1980).

Underwater Decoupling in FTNMR



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April 10, 1980

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77483

"XL-100 Or Modified XL-100 Wanted"

Dear Barry:

We are currently interested in updating our ancient Varian HA-100, which is equipped with a wide gap 15" magnet, into a pulse FT spectrometer. Our current thought about this process is to purchase an existing XL-100 or modified XL-100 console with the original data system as the first step. The second step would involve updating the data system adding multinuclear capability.

As a result, we are interested in purchasing an XL-100 or modified XL-100 console. A magnet and magnet power supply would not be essential since we already have both.

Anyone interested in selling an XL-100 or modified XL-100 system should contact Ed Hsi at (201) 356-8000, Ext. 3537. Any suggestions and advice on alternative methods of updating our HA-100 from readers would be greatly appreciated.

Yours sincerely,

Edward Hsi

Edward Hsi

EH/tr

JOB DESCRIPTION

A Senior Research Associate position will become available in September/October, 1980, at the University of Edinburgh to work with Professor A. I. Scott on NMR in biological systems. The project involves complete responsibility for the operation and design of experiments in 10 and 20 mm tubes of a dedicated Brüker WB-300 MHz instrument. The experiments involve pure enzymes, living cells and whole organisms using ^{13}C, ^{15}N, ^{2}H, ^{1}H and ^{31}P. ^{13}C and ^{15}N experiments are concerned with intracellular metabolism of substrates, while the enzyme experiments are cryobiochemical (~-60°C). Programming, flow-cell design, state-of-the-art upgrading of probes, spin-echo ^{13}C-NMR and decoupling problems in 20 mm tubes are the main responsibilities. The position will be filled by advertised competition (salary, $18,000-$22,000), but interested specialists are invited to correspond at this stage with Professor Scott, Department of Chemistry, Texas A&M University, College Station, Texas 77843 (Telephone: 713-845-3243) until June 1. After that date, to Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland (Telephone: 031-667-1081, Ext. 3403).

TEXAS A&M UNIVERSITY
DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843

5 May 1980

POSITION AVAILABLE

NMR specialist to supervise Texas A&M University's NMR laboratory and staff. Instruments include multinuclear Varian XL-200, FT-80 and JEOL PFT-100 spectrometers as well as routine CW instruments. Present staff includes an operator, graduate assistants, and maintenance personnel. The successful applicant should have a degree in chemistry and experience in NMR spectroscopy and/or maintenance of spectrometers. Interactive participation with faculty on NMR problems is encouraged. Application, curriculum vita, and two letters of recommendation should be sent to Dr. A. E. Martell, Head, Department of Chemistry, Texas A&M University, College Station, Texas, 77843, U.S.A. Texas A&M University is an equal opportunity, affirmative action employer.

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