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No. 295

April, 1983

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DEADLINE DATES: No. 296 2 May 1983
No. 297 6 June 1983

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. 295

University of Illinois at Urbana-Champaign

Eric Oldfield BSc PhD DSc CChem FRSC
Professor of Physical Chemistry
Telephone 0101 (217) 333-3374

School of Chemical Sciences
505 South Mathews Avenue
Urbana, IL 61801, USA

January 3, 1983

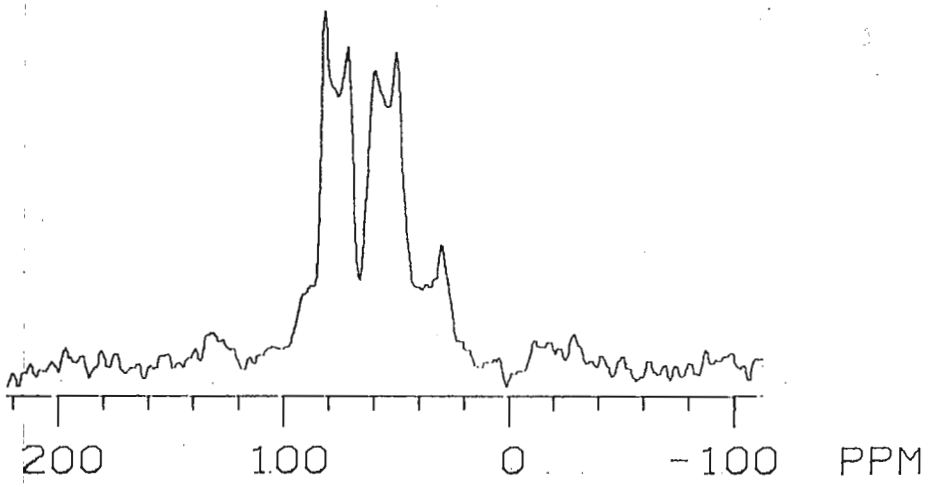
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

Dear Barry,

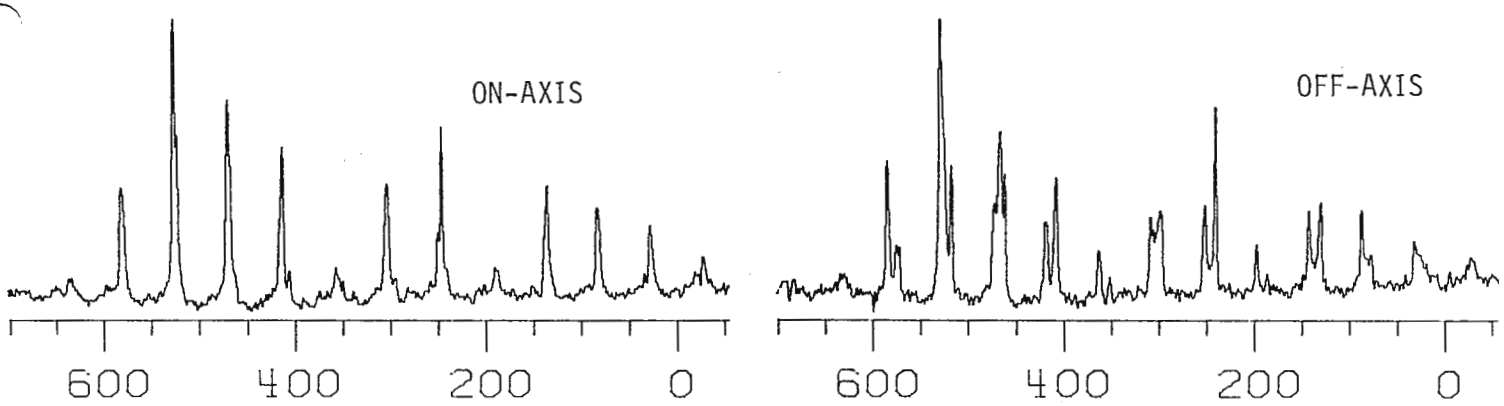
^{17}O in Solids; Slow Off-Axis Spinning

We have recently been turning our attention to ^{17}O in inorganic solids, by means of high-field (11.7 Tesla) MASS and VASS techniques. Somewhat to my surprise, a whole range of systems are amenable to study, including oxides, oxyanions, and even some organometallics. The chemical shift ranges, as expected, are large (>1000 ppm), as are the CSAs (~0→500 ppm) and e^2qQ/hs (~0→6 MHz), and of course the linewidths (<1 ppm→>>50 ppm).

In silicates, for example, it is possible to observe several nonequivalent oxygens where only a single silicon is present, as shown in the following Figure:



In some organometallics, we see large CSAs, as in the following spectra of $Mo(C^{17}O)_6$, and when spinning off-axis, the results are particularly interesting:



This work is being done in collaboration with T.L. Brown, M.A. Keniry, R.J. Kirkpatrick, H.S. Gutowsky, S. Schramm and S. Shinoda.

With best regards.

Yours sincerely,

Eric Oldfield

EO:ch

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DEPARTMENT OF CHEMISTRY
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28 February 1983

SHIFT REAGENT IMPURITIES

Dear Barry:

Although Milt Johnston recently wrote on the subject of possibile impurities of shift reagents, I thought that some additional information on that subject could be valuable to workers in the field. I was first alerted to the problem of sodium or potassium contamination by Joop Peters at Delft. He mentioned in a letter to me last fall that the problem was no longer restricted to ytterbium shift reagents, and that he had found substantial contamination in a commercial sample of EuFOD as well.

We have been using shift reagents purchased from Aldrich Chemical Co. for a number of years, so I discussed the possible problem with their quality control department. They analyzed (using atomic absorption) the material they had on hand and informed me that significant amounts of both sodium and potassium were present. One lot showed 0.19% sodium and 0.74% potassium; the other lot showed 0.21% sodium and 0.11% potassium. The seriousness of the problem can be seen when these numbers are converted to molar ratios. The data for the first of these two samples corresponds to mole percents of EuFOD-NaFOD and EuFOD-KFOD that are approximately 10 and 20%, respectively.

While we cannot improve (or even know) the purity of shift reagents used in the past, it is reassuring that Aldrich has upgraded their purity standards for shift reagents. They informed me that the new upper limits for sodium and potassium will be 0.1% for each. While significant quantities of EuFOD-NaFOD (ca. 5% on a mole basis) might still be present, this probably will not be too important for most experimental uses.

Sincerely,

Douglas J. Raber

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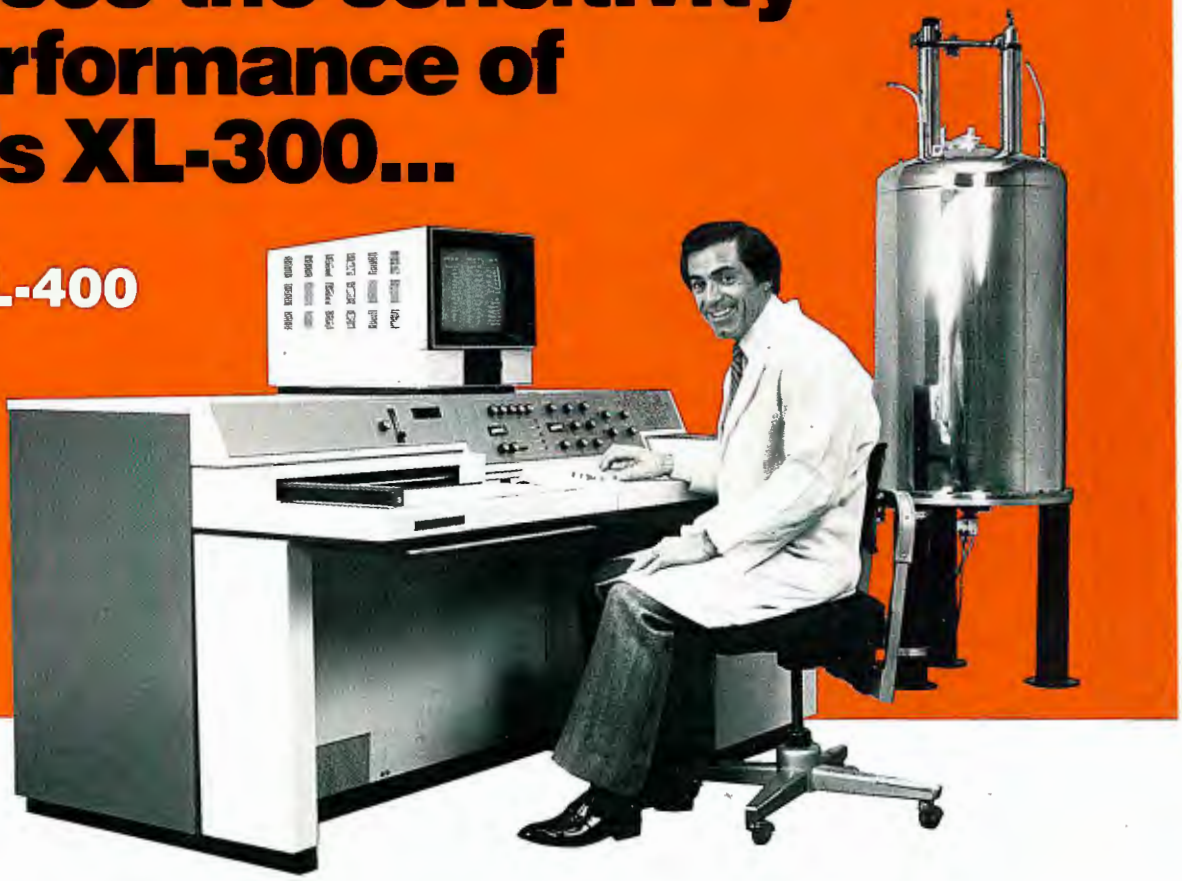

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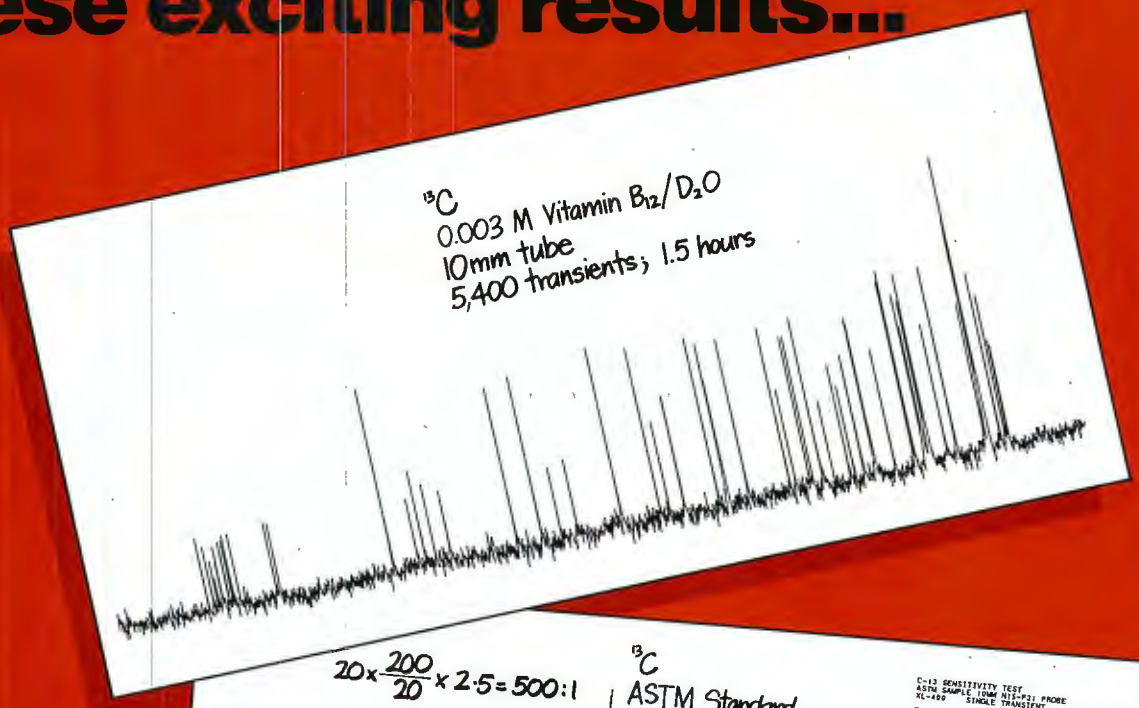

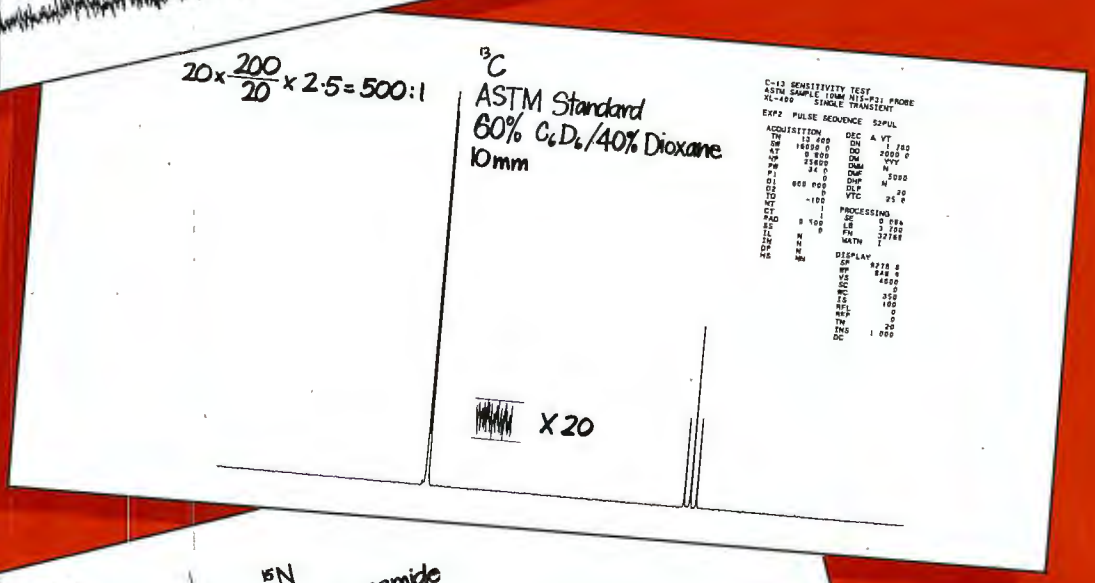

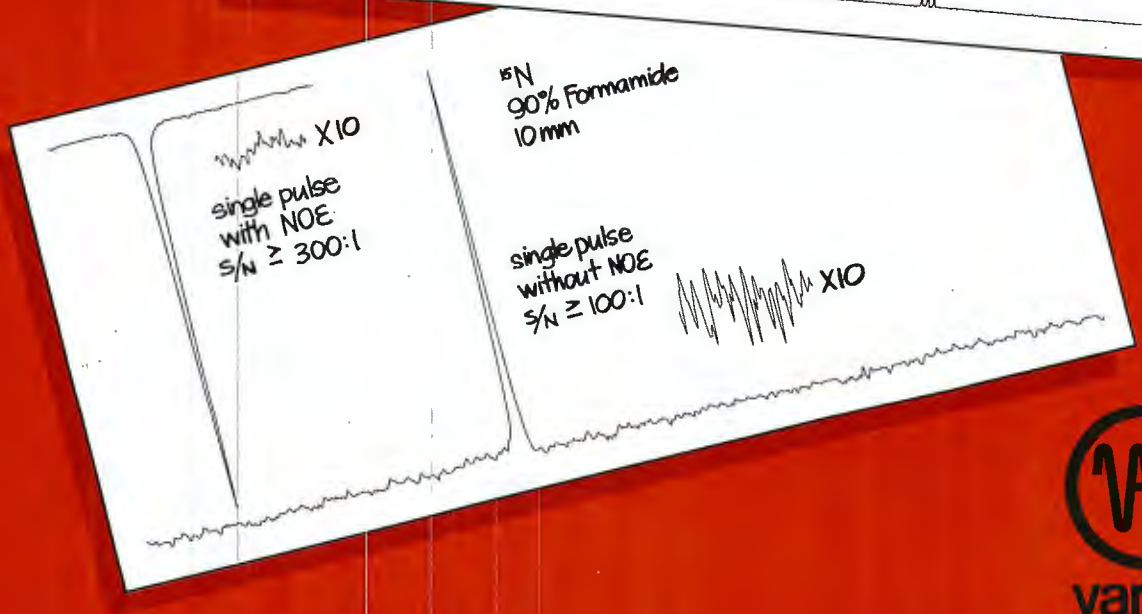

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VARIAN AD No. SER-2847

DOW CORNING

March 4, 1983

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

Dear Dr. Shapiro:

Ref: THE C-13 AND Si-29 NMR CHARACTERIZATION OF A SILALACTONE

As useful intermediates in the preparation of silyl esters and amides, silalactones can be prepared by heating halosilyl carboxylic acid alkyl esters at a temperature of Ca. 150°C.(1) Typically, the silactones are produced at high yield (Ca. 85% or higher) with alkyl chlorides being the principal by-product.

Recently, in our laboratory, we prepared a silalactone in the above manner from compound (I):

$$\begin{matrix} Me_2\text{-}Si\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}C(O)\text{-}OME, \\ \quad Cl \quad\quad Me \end{matrix} \qquad (I)$$

and used C-13 NMR spectroscopy to confirm the presence of the desired product. The C-13 spectrum (Fig. 1) displayed the absence of -OME and so indicated completeness of reaction. Integrated signal intensities were consistent with the formation of the silalactone in high yield (Ca. 95%).

It was noted, however, that there were two Si-Me signals of equal intensity in this spectrum. It was first proposed that this was due to the formation of two distinct silicon compounds. However, the Si-29 NMR spectrum of this material (with the exception of minor amounts of disiloxane and residual starting material) displayed only one signal (Fig. 2).

Later, it was proposed that the formation of diastereomers may account for this. However, no suitable models could be constructed and so this theory was abandoned.

By consulting the literature, we feel that we have developed a suitable explanation for this behavior. The analogous compound, 1,1,3-trimethylcyclohexane (2) will assume a conformation with the 3-methyl group oriented equatorially. This is because conformations with 1,3-diaxially oriented methyl groups are not favored due to steric crowding. In such an orientation, the equatorially oriented geminal methyl group will give rise to a signal that has a chemical shift which is considerably downfield (34.3 ppm) from that of the axially orientated geminal methyl group (25.5 ppm) (3). This upfield shift of the axial methyl group signal is due to that group's steric proximity to the axially oriented hydrogens at C-3 and C-5 (2). Similar behavior has been observed by other workers (4).

Figure 3 shows the presumably favored conformation of the prepared silalactone. The downfield Si-Me C-13 resonance at 0.1 ppm is assigned to the equatorially oriented methyl group. The upfield resonance signal at -1.0 ppm is assigned to the axially oriented methyl carbon. In our opinion, the smaller upfield shift that is observed is due to two factors:

1. The axially oriented methyl group is in steric proximity to only one axially oriented hydrogen atom at the 3' position. (The 5' position is occupied by a carbonyl carbon.)

2. The silicon atom is larger and the effect is reduced because of the strong distance dependence ($\propto r^{-3}$) (5).

At this writing, it appears that we are the first to report this behavior in such a cyclic silicon compound. We are continuing our work in this area and hope to describe our results in the open literature in the near future.

Sincerely yours,

Thomas M. Carr — Donnie R. Juen

Thomas M. Carr
Analytical Research

Donnie R. Juen
Fluids, Resins and Process
Intermediates Research

1. J.C. Saam, U.S. Patent 3,395,167, Dow Corning Corp. (1968)

2. D.K. Dalling and D.M. Grant, J. AM. Chem. Soc., 89, 6612 (1967).

3. J.B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, P. 64.

4. (A) W.R. Woolfenden and D.M. Grant, J. Am. Chem Soc., 88, 1496 (1966).
   (B) D.M. Grant and B.V. Cheney, ibid., 89, 5315 (1967).
   (C) T.P. Forrest and J. Thiel, Can. J. Chem., 59, 2870 (1981).

5. B.V. Cheney and D.M. Grant, J. Am. Chem. Soc., 89, 5319 (1967).

FIGURE 1

C-13 NMR SPECTRUM OF PREPARED SILALACTONE

A	C=O	169.7 PPM
B	$CDCl_3$	SOLVENT
C	CH_2-C=O	42.4 PPM
D	CH-CH_3	25.6 PPM
E	CH-CH_3	24.5 PPM
F	CH_2-SI	19.8 PPM
G	CH_3-SI	0.1 PPM
H	CH_3-SI	- 1.0 PPM

REF. $CDCl_3$ = 77.0 PPM

* RESIDUAL -OME FROM STARTING MATERIAL

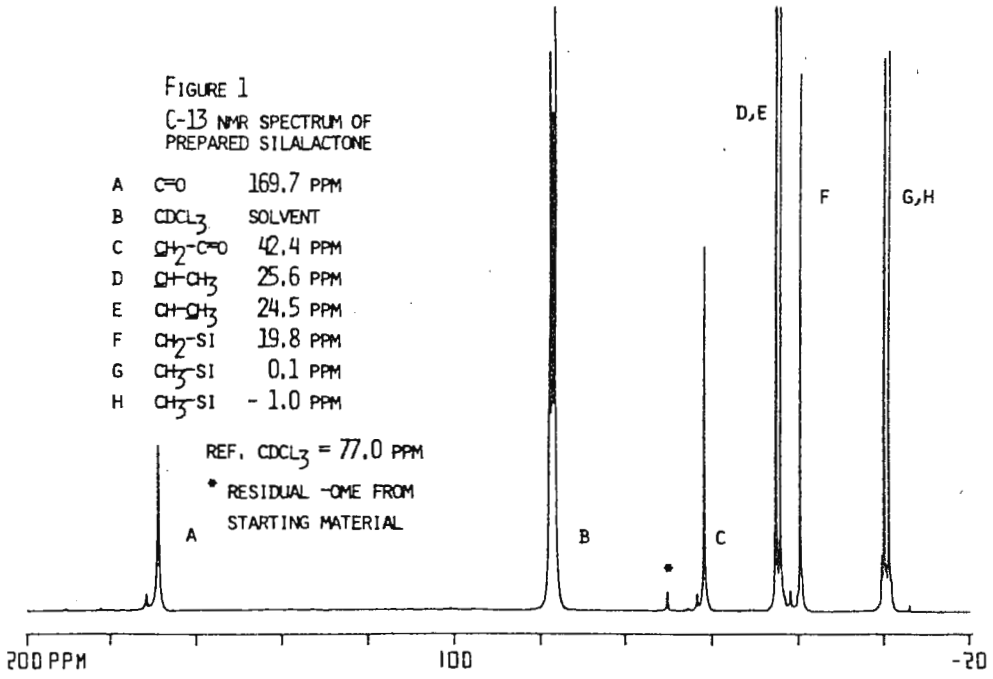


FIGURE 2

SI-29 NMR SPECTRUM OF PREPARED SILALACTONE

A	SILALACTONE	26.0 PPM
B	PRECURSOR	22.0 PPM
C	DISILOXANE	6.8 PPM

REF. TMS = 0.0 PPM (EXT.)

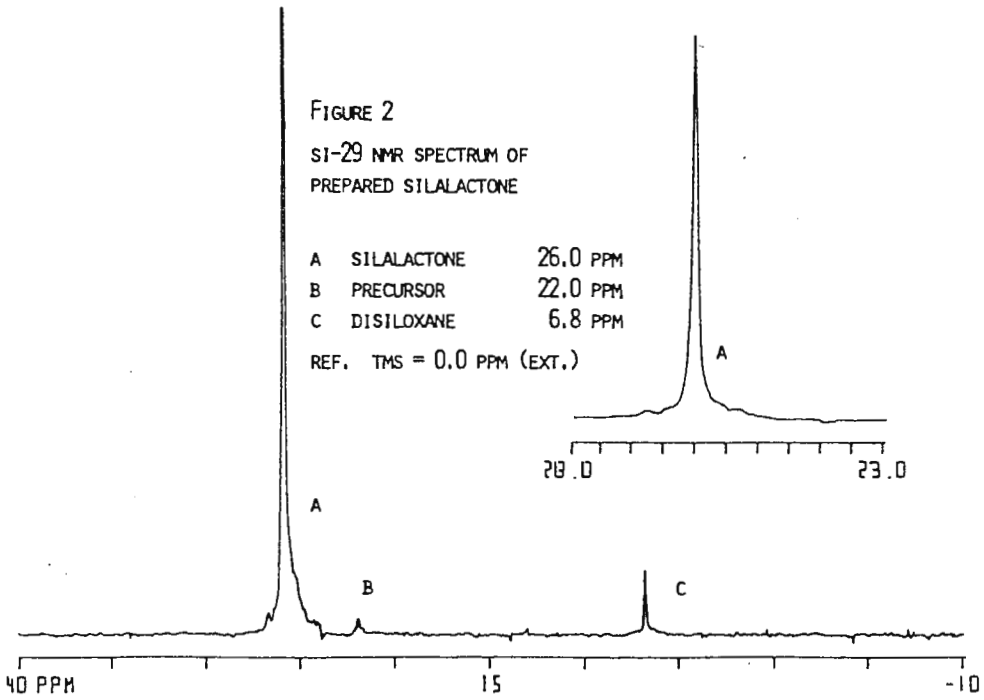
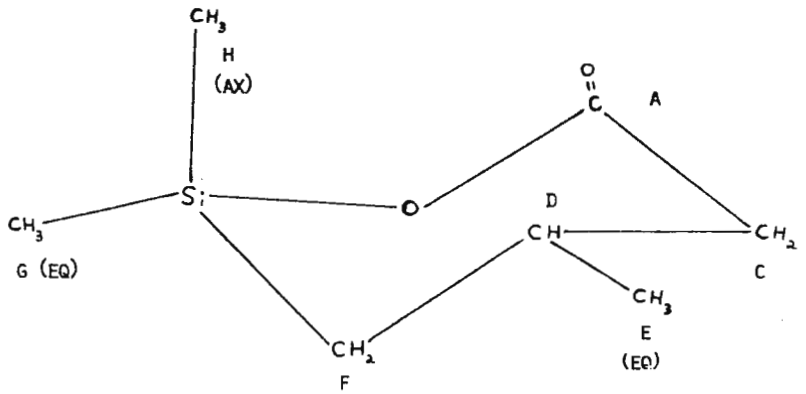


FIGURE 3 ENERGETICALLY FAVORED CONFORMATION OF PREPARED SILALACTONE



The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

March 3, 1983

Dr. Bernard L. Shapiro,
Editor and Publisher,
TAMU NMR Newsletter,
Texas A & M University,
Department of Chemistry,
College Station, Texas 77843, U.S.A.

Dear Barry:

An aid for biosynthetic studies: CCC2D with smaller amounts of labelled products. ^{18}O isotope effects on ^{13}C shieldings in cyclic sultones.

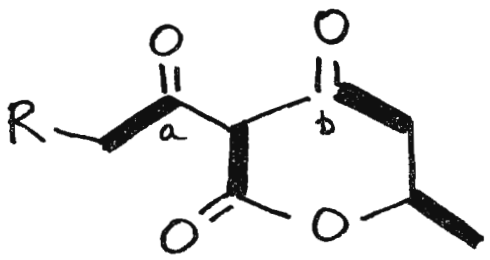
In response to your nagging colored notes, I can mention a couple of current projects, which have been significantly aided by unimaginative, but useful application of straightforward experiments which could have been overlooked.

As you are aware I have been engaged for some years in a variety of biosynthetic studies in collaboration with Albert Stoessl of the Agriculture Canada lab on our campus. Most of these projects have involved the use of doubly labelled sodium acetate-$^{13}C_2$ as the precursor. In general, the intact acetate units incorporated into the resulting labelled metabolites are readily located by pairing the ^{13}C-^{13}C coupling constants observed as satellites with due regard for the shieldings of the appropriate paired carbons. Occasionally, this cannot be done unambiguously and other information must be acquired. For example, some workers have resorted to ^{13}C-^{13}C decoupling to solve the problem. With the advent of 2D techniques, however, this sort of ambiguity is readily eliminated. Of course, this is obvious but I have not seen mention (or application) of it in the literature. The coupled pairs of carbons may be identified by a 2D INADEQUATE experiment and, equally important, such experiments do not require the large samples usually associated with eliciting this information in natural abundance if, as is usually the case, one is primarily interested in identifying the coupled pairs. Even relatively low incorporation levels permit ready detection of the requisite pairs and the nulling of the central signal arising from isolated label is much easier (i.e. one can pulse relatively rapidly compared to the repetition rate necessary for the same sample in natural abundance). As an illustration of the approach, I can mention a recent problem we have been studying, namely, the genesis of alternaric acid. This compound has the part structure shown (for simplicity in the "tri-keto" form); R is a ten-carbon chain bearing a methyl,

...

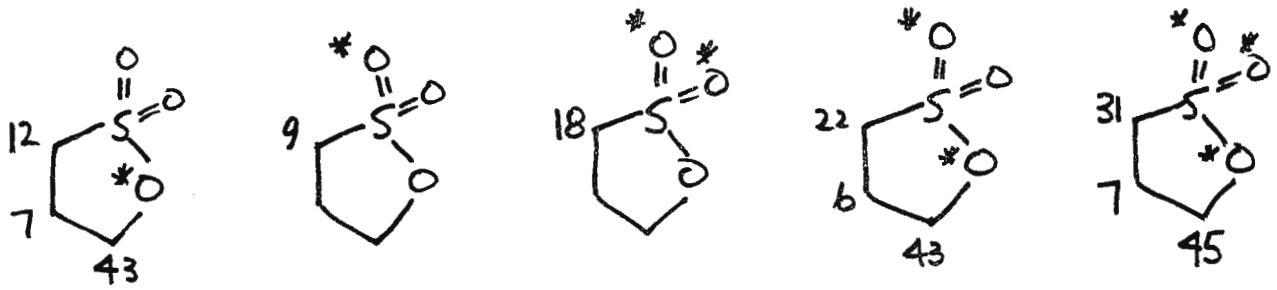
Dr. Bernard L. Shapiro,

March 3, 1983.



a methylene, two-hydroxyls, a carboxyl and containing 3-CH_2's. The five CH_2's in the molecular were unequivocally assigned in the ^1H and ^{13}Cmr spectra by proton-proton and proton-^{13}C correlation experiments in natural abundance. The problem remaining was the unequivocal pairing of the "carbonyl" carbons (a,b) in the part structure with their methylene partners. Since each arises from an intact acetate unit in the labelled product, a 2D INADEQUATE experiment resolved the issue readily.

As part of a collaborative study with J.F. King, ^{18}O isotope effects on ^{13}C shieldings are a prime concern. An examination of some five-membered sultones has revealed the isotope shifts noted below. In these formulae, the location of



the ^{18}O label is indicated with an asterisk; the labelling array was accomplished in various ways using 98% $D_2{}^{18}O$ as the ^{18}O source. As can be seen, the isotope shifts over two bonds strongly depend on the nature of the bonds but the effects are nicely additive. The shifts are given in ppb (1 ppb = 0.001 ppm) with a precision of ± 2 ppb (i.e. ± 0.1 Hz). It may be noted that the enriched water used as the source is also enriched with ^{17}O. Since the ^{17}O level is well above natural abundance (> 12-fold) we can also follow label incorporation using ^{17}O spectra. I want to point this out as a reminder that the dual approach is possible. Although one may tend to overlook the latter feature, it can be helpful for corroboration in more complex cases.

I hope the foregoing will be of interest to some newsletter readers.

With best wishes,

Sincerely,

Jake

J.B. Stothers,
Chairman.

JBS/aadg
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March 11, 1983

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

Minor Modification, Major Convenience

Dear Barry:

We have had need for long term, low temperature control on our FX-90Q. The dewar which JEOL supplies is really inadequate for serious low temperature work so a N_2 delivery system has been fashioned after the JEOL system using a 301 dewar. The heater coil was obtained from JEOL. A serious problem with the NM-VTS controller when used unattended is its lack of shut-off when the liquid nitrogen is depleted. This problem was solved with an Oxford instruments Liquid Nitrogen Level Meter by routing the dewar heater power through one of the level monitor's relays. This relay is set to oper and thus remove power from the heater when the level drops below the heater coil. Nitrogen consumption is quite uniform during the course of a run and varies little with probe temperature (from 30°C to -50°C); consequently, the dewar need only be filled with sufficient nitrogen for the duration of the experiment. The % N_2 meter is very convenient for this as well as giving an indication when refill will be necessary. The extreme limits of the system are about 24 hours with a very comfortable 16 hours, more than enough for overnight runs. On short runs, say about 10 hours, the level meter allows the dewar to be filled with only 12 hours of liquid nitrogen and the experiment left to run during the night without having to return to shut things down.

We will be happy to share the details of this unit upon request.

Very truly yours,

Bob

ROBERT M. RIDDLE

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Université de Nantes - U E R DE CHIMIE

CHIMIE ORGANIQUE PHYSIQUE
E.R.A. nº 315 - C.N.R.S.

Nantes, March 8th, 1983

Wine NMR spectroscopy (WNMR) for vine characterization

Dear Barry,

Thank you for your kind ultimatum ! We have therefore taken a rest from tasting and checking wines in order to write this letter !

When seventeen years ago we received in Nantes our first NMR spectrometer, a Varian A 60 A machine, the first ^{1}H spectrum that we recorded was that of the mixture generally used in France for such a celebration, i.e. a ∿ 12% aqueous solution of ethanol which usually contains some impurities such as acetic, malic, tartric acids, esters anthocyanes etc... However these "impurities" exist in the solution in too small a quantity to be easily detected with this type of spectrometer and a typical ^{1}H spectrum of such a solution is given in figure 1. The signal of the ethyl group of ethanol is clearly recognizable apart from the intense signal of water and exchangeable hydrogen of ethanol. The $^{2}H\{^{1}H\}$ spectrum shown in figure 2 has been recorded at approximately the same frequency as the proton spectrum and thus nearly corresponds to the $^{1}H\{^{1}H\}$ homodecoupled version of figure 1.

Providing that some experimental care is taken the site specific isotope ratios, $(D/H)_i$, can be determined. This new technique offers a way of distinguishing the vine variety and checking the origin of the ethanol which constitutes the wine. Since we can measure the relative deuterium distribution in the ethyl group with a reproducibility of 0.5 % at a 99 % confidence level, the quantity of extra ethanol added to the wine (in the form of sugar for example - a common but often not desirable practice !) can be determined with the same precision. This method presents an obvious interest from the analytical point of view. However as far as the wine consumer is concerned the old French proverb is still popular : "Qu'importe le flacon pourvu qu'on ait l'ivresse".

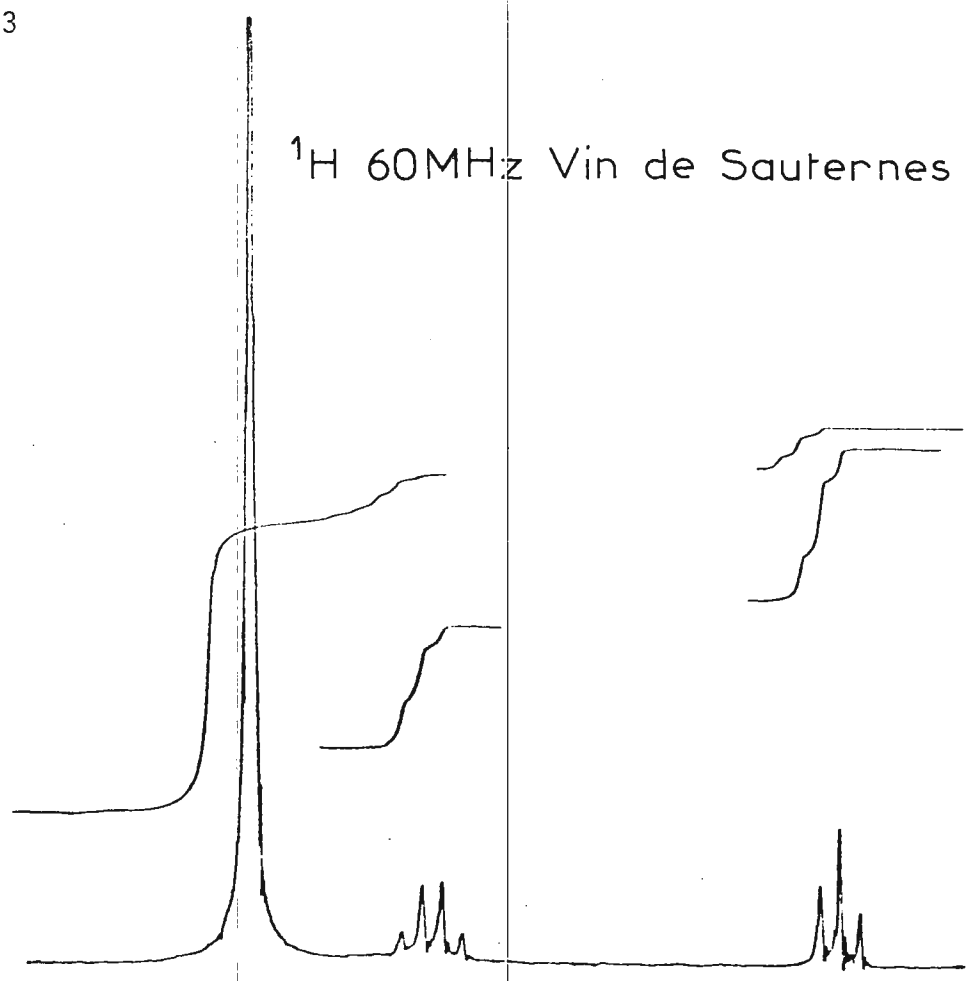
Please credit Gideon Fraenkel with the introduction of the new initials : WNMR.

Yours sincerely.

G.J. MARTIN M.L. MARTIN F. MABON

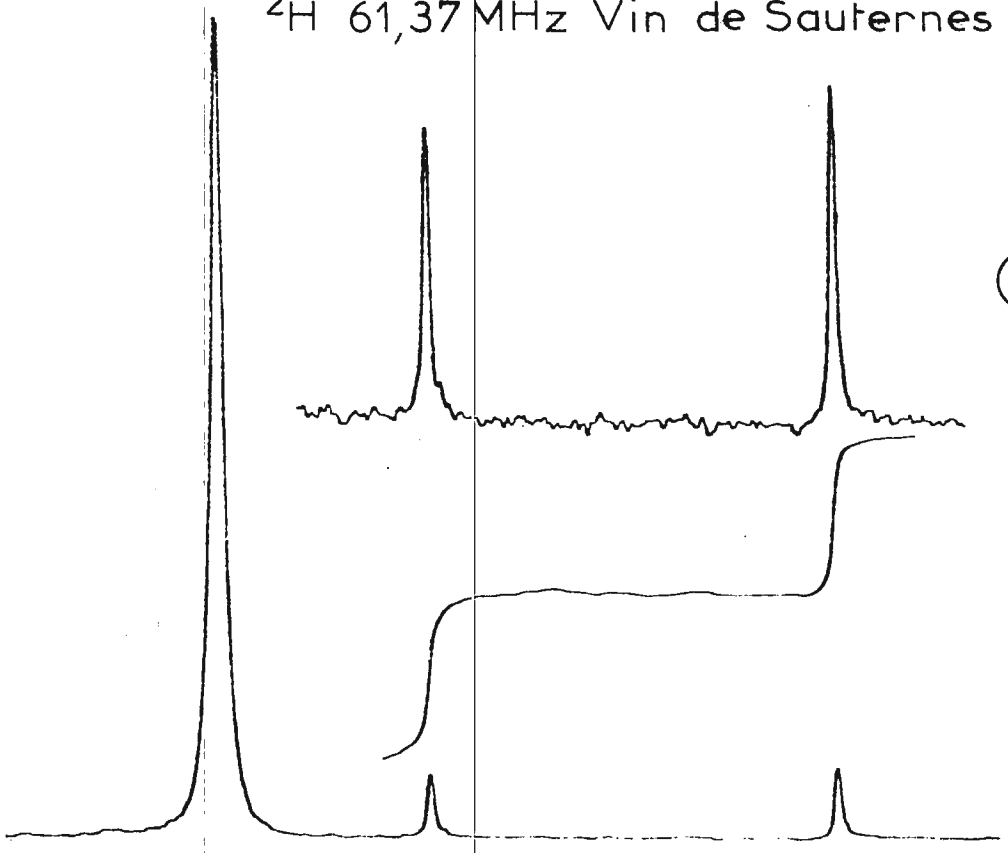
Téléphone (40) 74.50.70 - 2, rue de la Houssinière - 44072 NANTES-CEDEX (FRANCE)

^{1}H 60MHz Vin de Sauternes 1981



①

^{2}H 61,37 MHz Vin de Sauternes 1981



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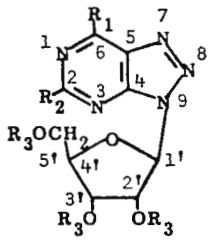
March 29, 1983

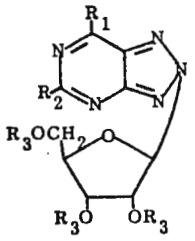
Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Title: ^{13}C-NMR Spectra of Some Nucleosides of 8-Azapurines

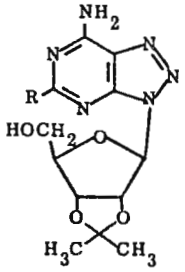
Dear Barry:

The threatening yellow letter inspires me to write about some nucleosides of 8-azapurines for which we have obtained the ^{13}C NMR spectra. The glycosidic bond in these compounds can be at either N-9 or N-8, and we have the spectra of corresponding pairs.

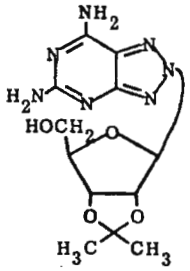




a) $R_1 = R_2 = SCH_3$, $R_3 = Ac$
b) $R_1 = NH_2$, $R_2 = SCH_3$, $R_3 = H$
c) $R_1 = NH_2$, $R_2 = SO_2CH_3$, $R_3 = H$
d) $R_1 = R_2 = NH_2$, $R_3 = H$
e) $R_1 = NH_2$, $R_2 = F$, $R_3 = H$
f) $R_1 = NH_2$, $R_2 = OH$, $R_3 = H$
g) $R_1 = NH_2$, $R_2 = OCH_2CH_3$, $R_3 = H$



a) β; R = H
b) β; R = NH_2
c) β; R = SCH_3
d) α; R = SCH_3



The chemical shifts are given in the accompanying table. Of special note are the large differences for C-4 and C-1' in the corresponding pairs. This appears large enough, and consistent enough, to be of diagnostic value as to the point of glycosidation. Our assignments, however, were not made on this basis, but from the ^{1}H-coupled spectra and UV data.

The preparation and biologic evaluation of these compounds has been submitted for publication, and the paper will include ^{1}H-NMR data as well as the ^{13}C-NMR data given here.

Hope to see you at ENC this year.

Sincerely,

Martha Thorpe
Senior Chemist

MT/cpm

25.16MHz ^{13}C-NMR Chemical Shifts[a]

Compd.	$C_{1'}$	$C_{2'}$[b]	$C_{3'}$[b]	$C_{4'}$	$C_{5'}$	C_2	C_4	C_5	C_6	Other
6a	87.46	72.55	70.02	79.73	62.32	170.74	147.61	131.81	164.71	11.60, 14.23 (2 SCH_3), 20.26 ($COCH_3$), 169.27, 169.45, 169.83 ($COCH_3$)
6b	89.37	72.58	70.67	85.85	61.91	170.42	149.70	122.65	154.97	13.63 (SCH_3)
6c	89.66	72.97	70.52	86.17	61.62	163.55	148.69	124.42	156.70	39.06 (SO_2CH_3)
6d	88.66	72.58	70.81	85.74	62.12	162.63	151.66	120.40	156.13	
6e	89.53	72.87	70.58	86.11	61.78	161.34	151.11	123.64	157.90	
7a	95.10	73.83	70.30	80.60	c	169.64	156.11	131.94	165.74	$COCH_3$(c), 11.77, 14.13 (2 SCH_3)
7b	97.36	74.72	70.68	86.35	61.99	169.94	158.23	124.50	155.41	13.50 (SCH_3)
7c	98.06	74.98	70.61	86.66	61.86	164.04	156.67	126.08	157.84	38.86 (SO_2CH_3)
7d	96.74	74.46	70.72	86.04	62.14	162.61	160.09	122.96	156.63	
7e	97.64	74.76	70.65	86.53	61.94	161.58	157.92	125.08	159.17	
7f	96.49	74.23	70.54	86.13	61.92	156.99[d]	156.50[d]	121.86 (br)	150.83[a]	
9a	90.56	81.85[b]	83.01[b]	88.05	61.27	157.13	148.84	123.98	156.30	25.08, 26.83 (2CH_3), 112.97 (C-$(CH_3)_2$)
9b	89.54	81.89[b]	82.88[b]	87.78	61.35	151.59[d]	156.19[d]	120.24	162.92[d]	25.11, 26.84 (2CH_3), 112.75 (C-$(CH_3)_2$)
9c	90.25	81.85[b]	82.96[b]	88.23	61.22	170.75	149.47	122.50	155.02	25.02, 26.78 (2CH_3), 112.88 (C-$(CH_3)_2$), 13.67 (SCH_3)
9d	87.83	80.16[b]	81.58[b]	84.65	62.07	169.83	149.78	121.98	154.92	24.48, 24.95 (2CH_3), 114.17 (C-$(CH_3)_2$), 13.63 (SCH_3)
10	97.15	81.91[b]	83.81[b]	88.63	61.37	156.66[d]	160.28[d]	123.26	162.80[d]	24.95, 26.67 (2CH_3), 112.58 (C-(CH_3)($_2$

[a] In DMSO-d_6. Chemical shifts are in ppm downfield from internal tetramethylsilane.
[b] Assignments of $C_{2'}$ and $C_{3'}$ may be reversed.
[c] Hidden under the corresponding signal for 6a.
[d] In this compound, the assignments of these carbons may be revised.

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9 March, 1983

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

Dear Professor Shapiro,

One of our ongoing projects is the elucidation of structure and mechanism of the HPr protein of S. aureus. HPr is a soluble component at the bacterial phosphoenolpyruvate dependent phosphotransferase system (PTS). It transports a phosphate group via a phosphohistidine intermediate.

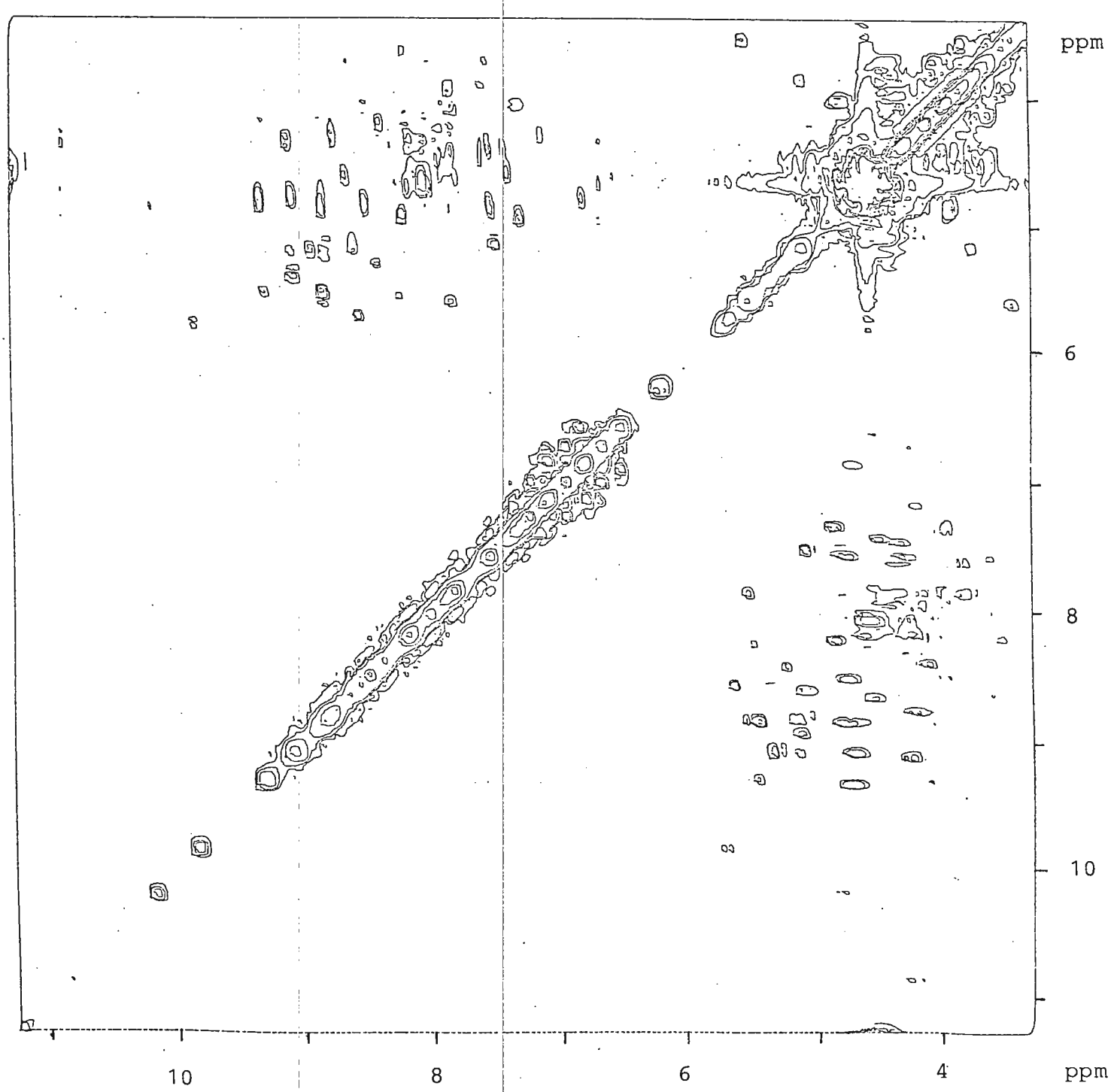
Recently, we started out with 2-D spectroscopic studies in order to obtain more information about the 3-D structure of this so far non-crystallizable protein. HPr should be especially suited for this kind of work because of its low molecular weight and its high stability.

As an example of the quality of the spectra a 2-D COSY spectrum measured in H_2O is shown in the figure. The signals of 95 exchangeable protons are to be observed separately, which could not be resolved in the 1-D spectrum. Vice versa, the chemical shifts of the corresponding J-coupled protons (mostly C_α protons) could be determined.

Yours sincerely,

H.-P. Neidig Kalbitzer Rösch

P. Neidig H.R. Kalbitzer P. Rösch



2-D COSY spectrum of HPr in H_2O.
Acquisition time about 60 hours. Frequency 360 MHz.

IBM Instruments Inc.

Orchard Park
PO Box 332 Danbury CT 06810

Telephone: 203 796 2500

March 10, 1983

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

HETERONUCLEAR COSY

Dear Barry:

Heteronuclear shift correlated 2D spectroscopy is limited by the requirement that the proton-X nucleus coupling constant be fairly well known and it will reveal only transitions which involve this coupling. For example, quaternary and carbonyl resonances do not show up in proton-carbon shift correlated spectra. We want to introduce a simple extension of the proton COSY experiment to proton-X nucleus 2-D spectroscopy, which does not have these limitations.

The spectra generated by this technique contain the following information:

- All proton/X nucleus chemical shift correlations, including those of non-protonated nuclei.
- All proton/X nucleus couplings, including long range couplings.
- Solvent resonances are suppressed in most cases.
- Data acquisition time is determined by the T_1's of the protons.

Two proton 90° pulses P_1 and P_2 separated by the interval $D\phi$ produce a selective proton 180° pulse. The X-nucleus transitions are sampled at time $D\phi$ by a 90° pulse P_3. No proton decoupling is used. Incrementing $D\phi$ generates the frequency F_1. The phase programs which suppress direct signals in the F_2 dimensions and which allow quadrature detection in the F_1 dimension are similar to the phase cycles used in proton-carbon shift correlation.

The technique is illustrated by the carbon-proton spectrum of camphor in deuteroacetone. The two quaternary carbons and their long range coupling to protons can be recognized. The extension to other nuclei is evident. The technique should allow the identification of carbonyl resonances in peptides, a prerequisite to the mapping of long-range couplings and their use in conformational studies.

Sincerely,

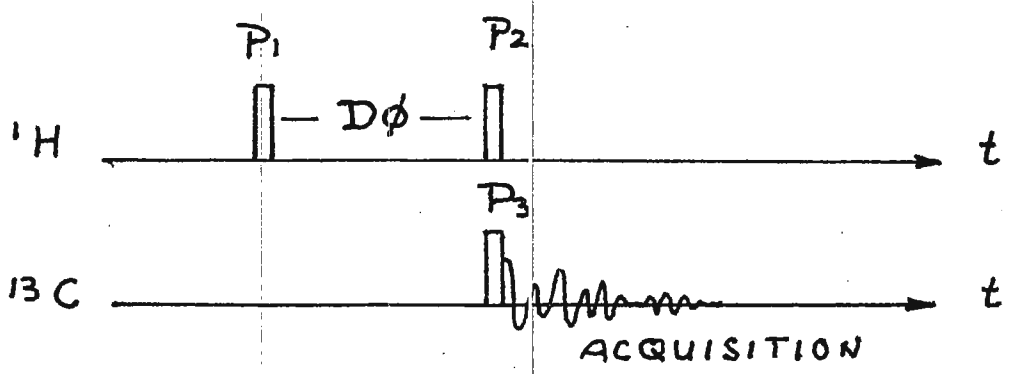
Hermann Bleich Richard E Schwe

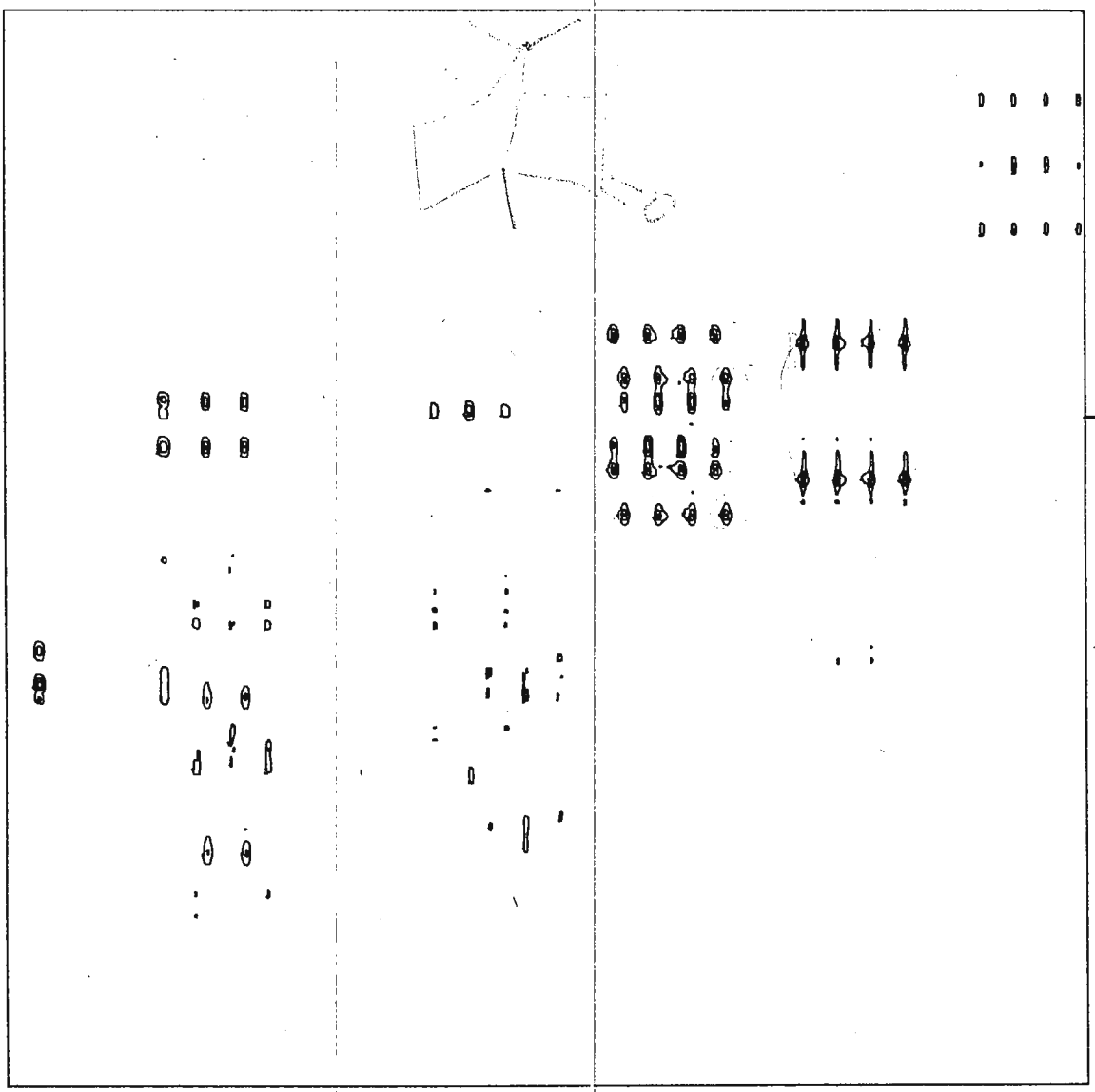
Hermann E. Bleich Richard E. Schwemm

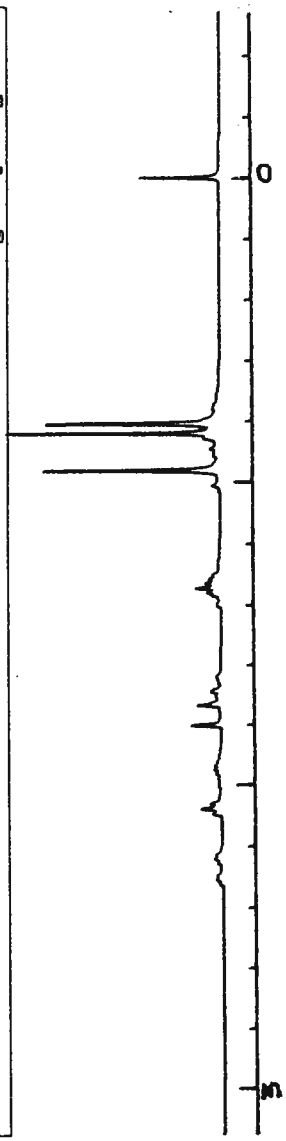
P.S. In the enclosed example the proton irradiation was set accidentally on the resonance near 1.35 PPM. This should always be avoided. A similar experiment, but with a different purpose, has been reported by Bodenhausen and Freeman (J. Magn. Resonance 28, 471 (1977)).

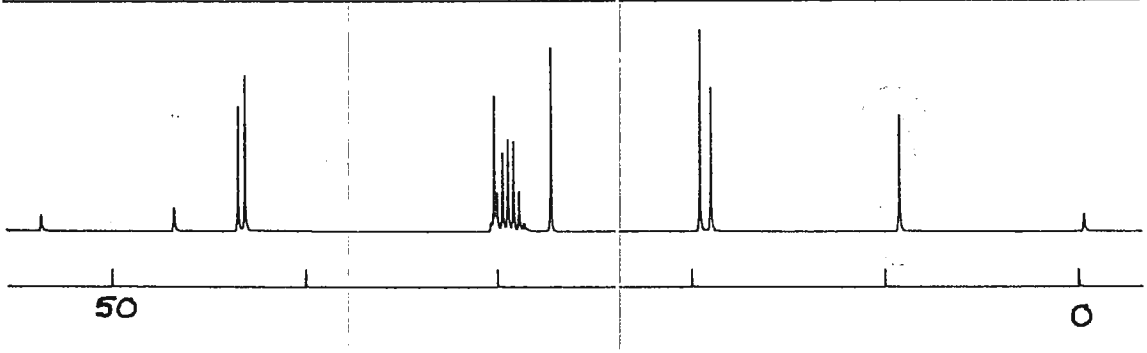
/lw
Enc.

HETERONUCLEAR COSY









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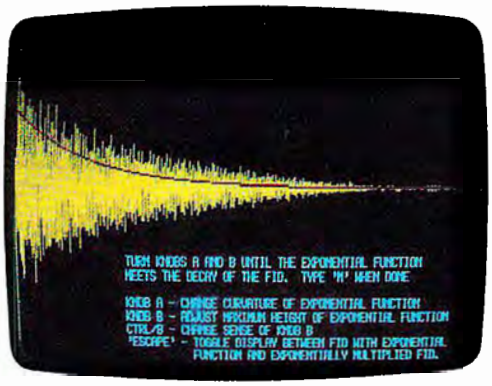

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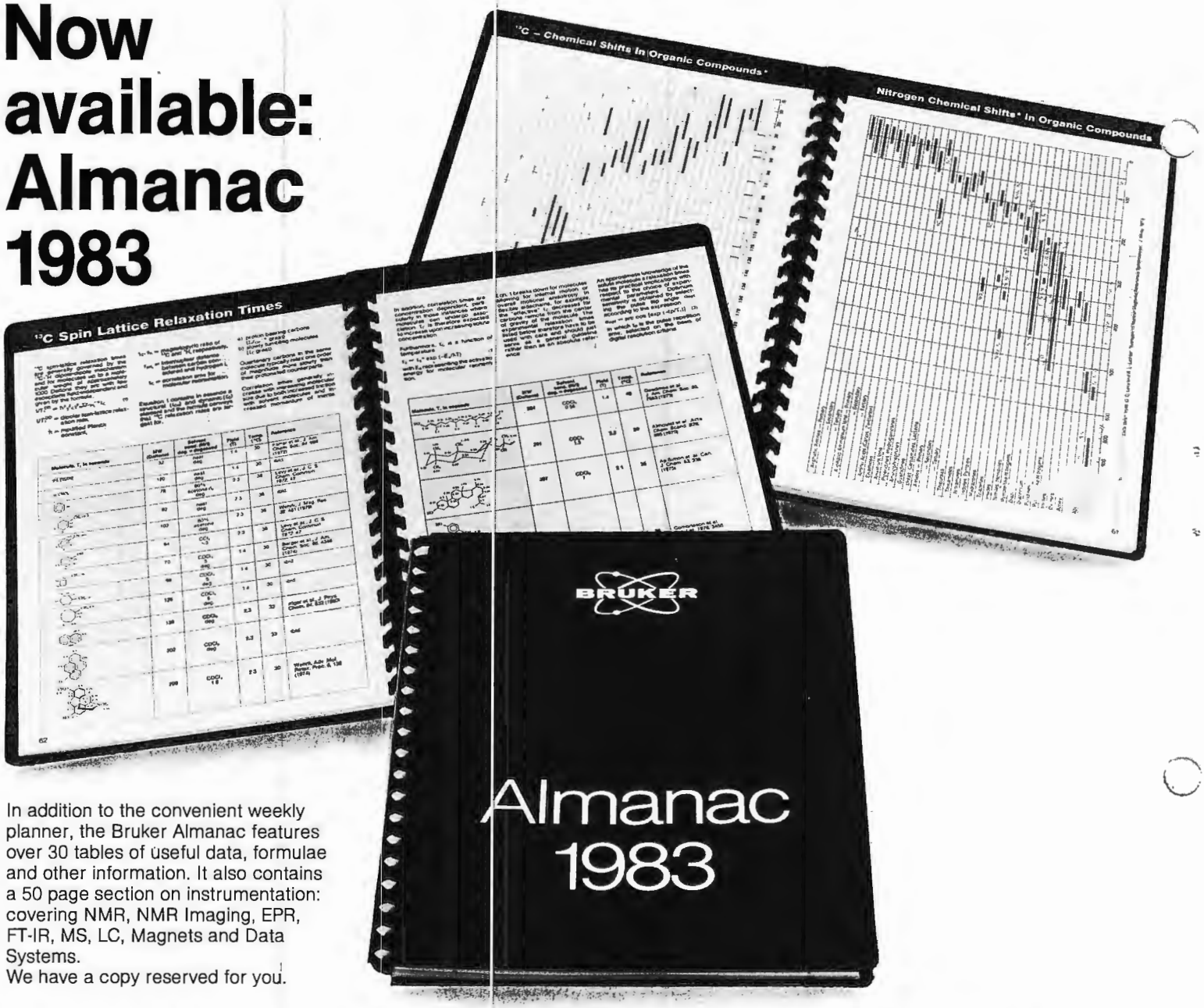

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Your Ref:

25th February, 1983

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

Dear Barry,

Re: GASPE for $^{13}CH_n$ Multiplicity - It's Really Very Easy

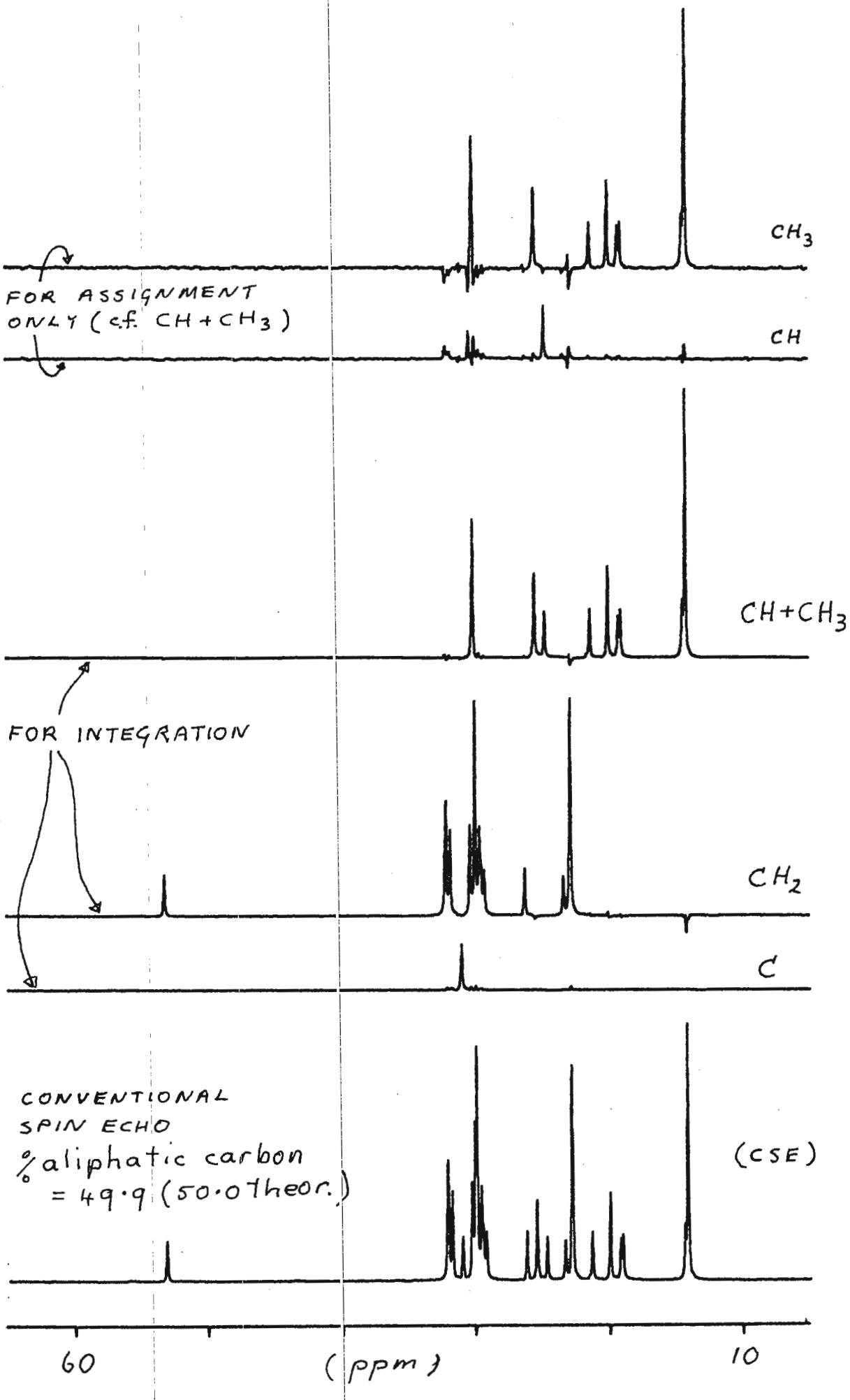
We have been reading your Newsletters now for some time (sharing with Ian Rae of Monash University) with much pleasure. In the following we contribute a little controversy to your pages.

In 1981 we published a method for determining ^{13}C multiplicity (1) using a gated spin echo (GASPE) methodology at about the same time as two other groups (2,3). An alternative route was taken by some other groups using population transfer as a component of their methods. This lead to an extended INEPT sequence, which appears to have been abandoned in favour of DEPT (4). Despite some bad press, the GASPE sequence has much to offer, including experimental simplicity, NOE enhancement if required, quantitation if required, the ability to handle various J values (see Reference 1), and a direct means of observing quaternary carbons. Polarization transfer sequences differentiate between CH and CH_3 groups more cleanly.

We have been prompted to write by a recent letter (TAMU NMR Newsletter 289-17) claiming GASPE to be non quantitative for a test mixture of hydrocarbons. This seemed very surprising since we developed the technique explicitly to be quantitative for hydrocarbons - and demonstrated (1) that it was so. So, we repeated the experiment of Netzel and Clennan using an equimolar mixture of toluene, 2, 2, 4 - trimethylpentane, o-ethyltoluene, acenaphthene, 2, 3-dimethylnaphthalene, 1-methylnaphthalene, tetralin, n-hexane, n-heptane and n-tetradecane, in $CDCl_3$ solvent in the presence of 0.44 wt% Cr $(AcAc)_3$. As expected, the results are excellent. For the high field region:

	Observed	Calculated
CH_3	37.3	35.4
CH_2	57.6	60.4
CH	2.2	2.1
C	2.9	2.1

Note that the C value is our worst possible number since there is clearly a weak contribution from abundant CH_2 intensity (2% relative) to the quaternary C spectrum. The spectra are shown in the figure. CSE, C, CH_2 and CH + CH_3 spectra are used for integration whereas individual CH and CH_3 subspectra are used only for assignment. A relaxation delay (between end of decoupling and start of new cycle) of 5.5 T_1 is necessary (to be published) and the exact nature of the calculation of subspectra has been slightly modified from Reference 1 (submitted to Fuel, 1983).


CH3
FOR ASSIGNMENT ONLY (c.f. CH+CH3)
CH
CH+CH3
FOR INTEGRATION
CH2
C
CONVENTIONAL SPIN ECHO
% aliphatic carbon = 49·9 (50·0 theor.)
(CSE)
60
(ppm)
10

Professor B.L. Shapiro

25th February, 1983

We continue GASPEing happily, and without problems (on a Bruker WP-200).

Yours sincerely,

David Cookson

Brian Smith

DAVID J. COOKSON

BRIAN E. SMITH

1. D.J. Cookson and B.E. Smith, Org. Magn. Reson., 16, 111 (1981).
2. D.W. Brown, T.T. Nakashima and D.L. Rabenstein, J. Magn. Reson., 45, 302 (1981).
3. C. Le-Cocq and J-Y. Lallemand, Chem. Communs., 150 (1981).
4. D.M. Doddrell, D.T. Pegg and M.R. Bendall, J. Magn. Reson., 48, 323 (1982).

295-27

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

March 11, 1983

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

Ref.: Two-Dimensional, Homonuclear, J-Correlated ^{11}B NMR

Dear Barry:

One of the more pleasant surprises in our investigations of two-dimensional spectroscopy has been the application of COSY to ^{11}B nmr spectra (J. Amer. Chem. Soc., 1982, 104, 4716). The enclosed Figure demonstrates the utility of this technique for structural analysis in polyhedral metallaboranes.

A 2 mg sample of 5-$C_5(CH_3)_5CoB_9H_{13}$ was dissolved in THF (6.5×10^{-3} mmoles, 1.6 mM) and the data collected as a 128 x 256 (reals + complex) matrix. Accumulation of 2016 requisitions for each of the 128 blocks using the COSY 16 pulse sequence required ~2.6 hrs. Low level (~2 watts) broadband proton decoupling was maintained throughout the collection. The data was zero-filled once in each dimension and then processed with cosine bell apodization before contour plotting. All data manipulation involved standard Nicolet software.

COSY spectra of other quadrupolar nuclei, where $\nu_{\frac{1}{2}} > J$, should reveal spin coupling which has not been documented before. We think homonuclear, J-correlated, two dimensional spectra will be of general use to chemists interested in the structure of molecular clusters.

Sincerely yours,

William C. Hutton
Analytical Chemist

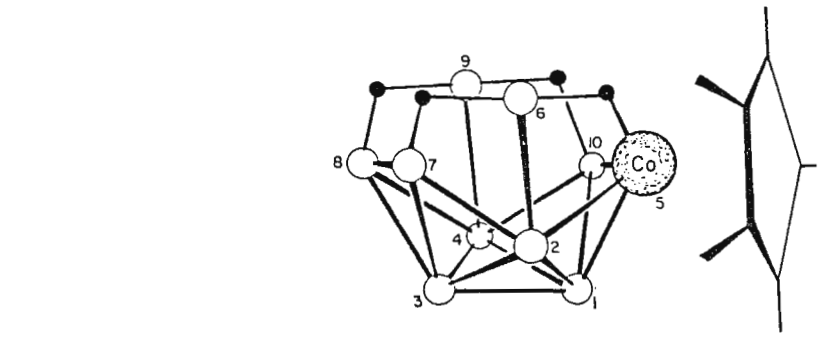
T. Leon Venable

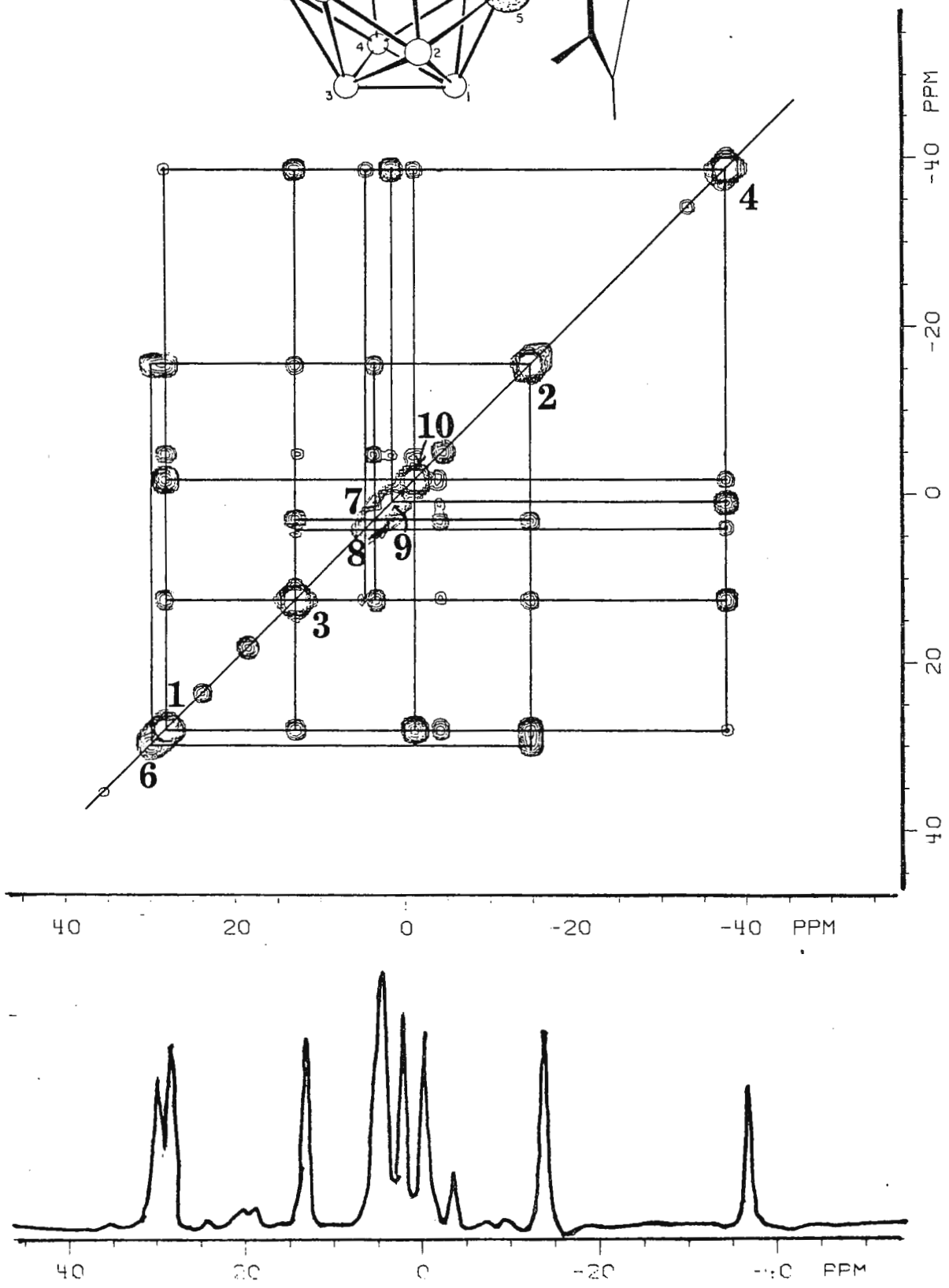
T. Leon Venable

R.N. Grimes
Professor and Chairman

WCH:ttn

5-PCPCCB3H13
HEXANE





THE UNIVERSITY OF ARIZONA
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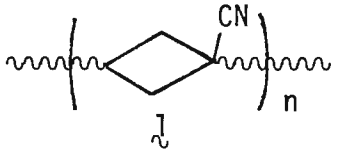
March 12, 1983

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

Dear Barry:

The ^{13}C Nitrile Resonance as a Probe of Cis/Trans Stereochemistry in 3-Substituted Cyclobutane-1-Carbonitriles. For several years we (especially Jeff Kao, Glen Snow, and H. K. Hall, Jr. of this Department) have been trying to infer something about the stereochemistry of PBBC 1 from the ^{13}C NMR spectra. In the course of interpreting the spectra of a large number of 3-substituted cyclobutane-1-carbonitriles, it was concluded that any cis substituent at C3 shifted the ^{13}C nitrile resonance 1 - 1.5 ppm to higher field than the trans-3-substituted cyclobutane-1-carbonitrile. At a later stage in these studies, it was indeed rewarding to obtain the four trimers 17cc - 17tt as this prediction for the nitrile resonances was elegantly reproduced in the spectra of these compounds (Figure 1). Moreover, the



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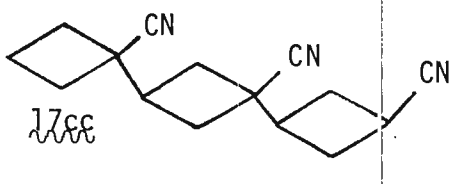
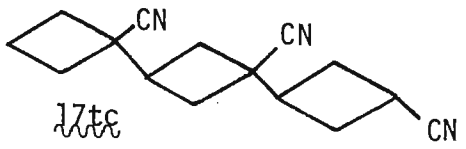
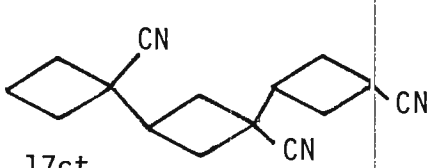


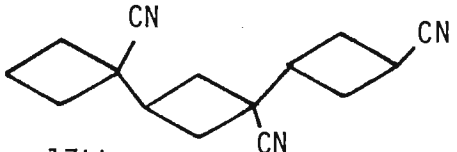
17cc



17tc



17ct



17tt

^{13}C resonances of central cyclobutanecarbonitrile moieties of these trimers are consistent with the spectrum of PBBC; four nitrile resonances are observed for the polymer, and the ratios of their areas suggest that the fusions of the rings are approximately 75% trans, such as in 17cc and 17tc.

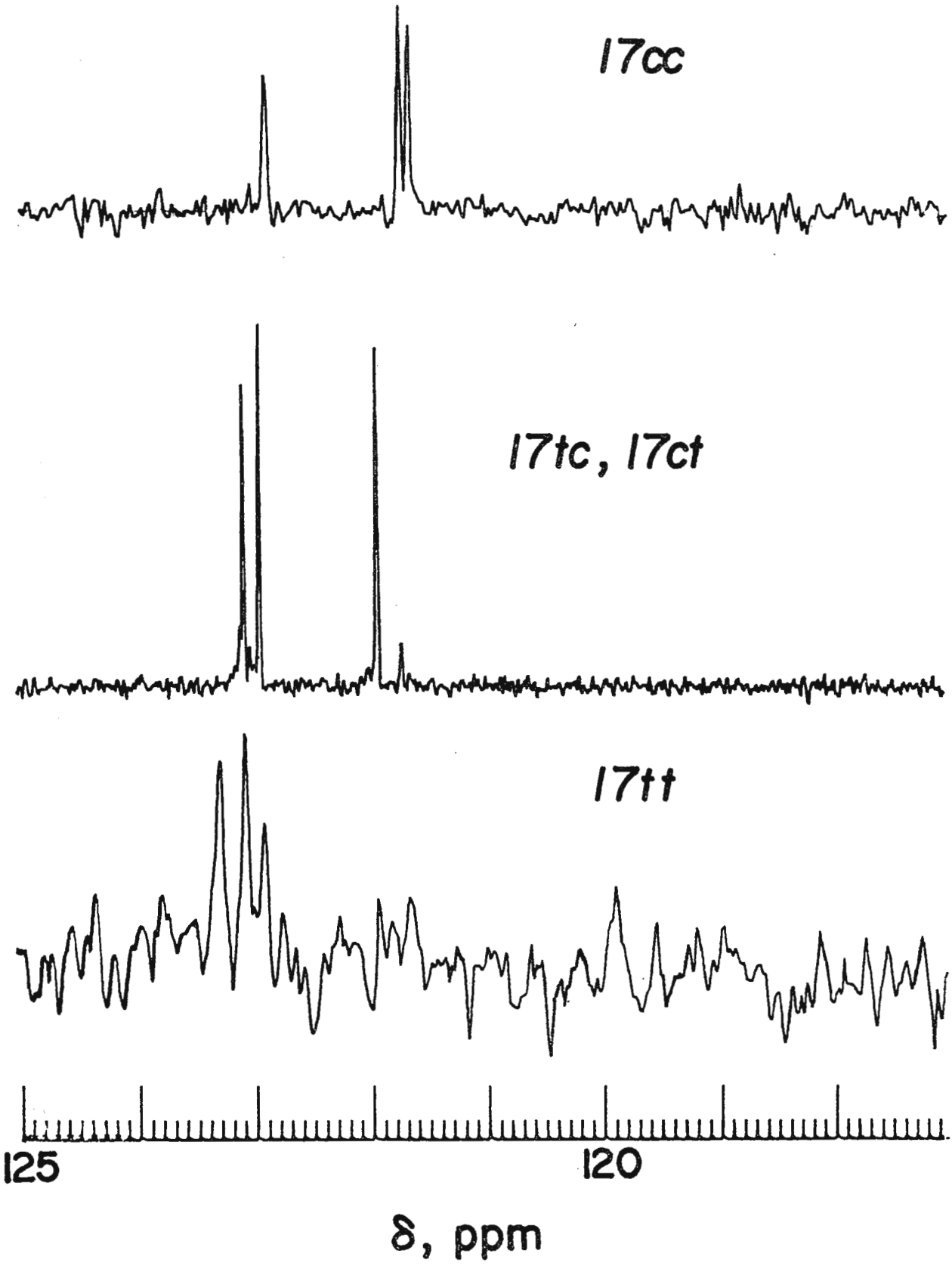
We will see you in Asilomar next month.

Sincerely yours,

Mike

Mike Barfield

Figure 1



295-31

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March 24, 1983

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

Dear Barry:

We have an opening in the Spectroscopy Group for a research chemist/physicist with a background in high-resolution and solid-state NMR spectrometry. High-resolution work will encompass compound-catalyst interactions and investigations of proprietary products and oligomers. Solid-state research will involve CP-MAS ^{13}C and ^{29}Si NMR on bioproducts and catalysts, respectively. An immediate assignment would be the selection of a solid state system; subsequently, the acquisition of a high-field instrument is contemplated.

Interested applicants should send their inquiries and resumes to:

D. J. Clancy
Spectroscopy Section
Analytical Research Department
W. R. GRACE & CO.
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Columbia, MD 21044

Sincerely,

Friso Willeboordse.

FGW:al
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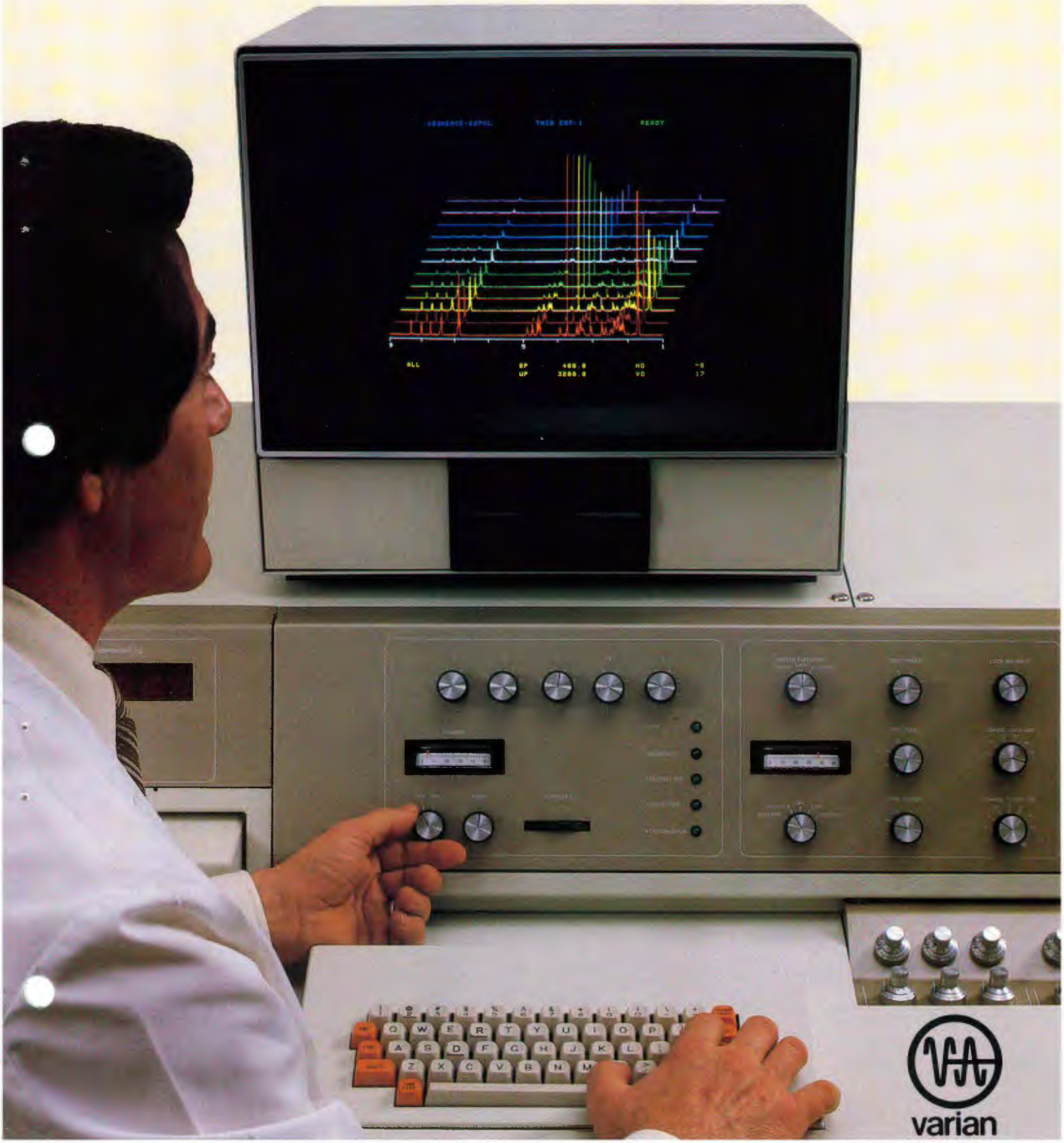

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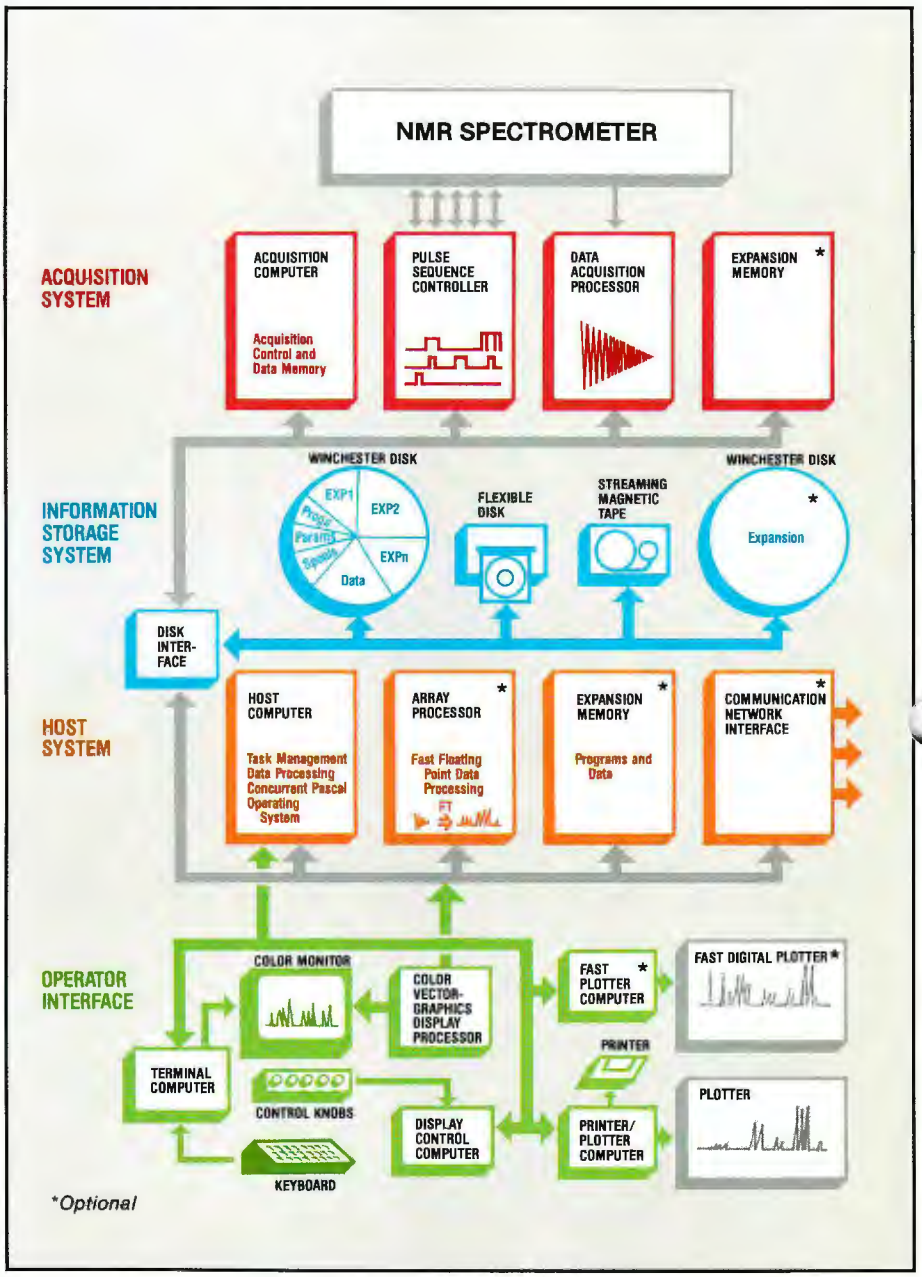
- Pulse Sequence Controller automatically calculates phase tables, pulse widths and pulse delays.
- Experiment capabilities include INEPT, DEPT, cross-polarization and various coherence transfer 2D sequences.
- Information Storage System provides both flexible disk and Winchester disk as standard.
- Optional storage devices include streaming magnetic tape, 9-track tape, additional flexible and hard disks, and computer networking capability.
- VERSAbus structure lets you simply add peripherals as you need them.
- Pascal software sets the industry standard for throughput, ease of operation, and user programming.
- New diagnostics system monitors system status and operation via the keyboard or a modem.
- Double your processing productivity: ADVANCE is also available as a stand-alone unit, with all the speed, power and storage of the parent system.



Operational schematic of the XL Series ADVANCE NMR data system.

The ADVANCE concept

The new ADVANCE NMR Data System is an integral part of all XL Series NMR spectrometers. ADVANCE is the result of a team of Varian chemists, spectroscopists and digital systems specialists working together to bring state-of-the-art data system technology into the NMR laboratory.

Distributed intelligence puts power where you need it to get the job done faster. Multiple independent computers are distributed throughout the ADVANCE system. Two major computers independently control data acquisition and data processing. Four other dedicated computers handle individual input and output functions. Working together, these provide the ultimate in true multi-tasking capability and increased spectrometer productivity.

A high-speed, 32-bit bus structure links these computers into a single, powerful system controlled by Varian's high-level concurrent Pascal operating system.

ADVANCE system computer power totals over 464K bytes of memory. This can be expanded to over 16 megabytes.

The schematic diagram on the facing page illustrates the ADVANCE system architecture.

The **Keyboard** and **Control Knobs** serve as the **Operator Interface,** transmitting commands to the **Host Computer** that oversees task management on the spectrometer. The **Acquisition Computer** independently runs the NMR experiment and acquires data. The **Host System** processes the data, displays it for the operator and stores it within the **Information Storage System.**

Each of these computer systems is described in further detail below.

■ **Host System performs data processing and task management for the entire spectrometer.** Based on the powerful Motorola 68000 microprocessor, the 144K-byte Host Computer features 32-bit math operations and memory addressing capabilities up to 6 megabytes.

With an interactive, disk-based concurrent Pascal operating system, and a large, expandable memory base, the Host System allows several programs to be resident simultaneously. This minimizes disk access requirements and speeds all computer operations.

An optional **Array Processor,** capable of performing simultaneous operations on data arrays, reduces calculation times for complex operations by several orders of magnitude. It speeds Fourier transforms, phasing, and exponential weighting operations.

The Host Computer and Array Processor work together to make ADVANCE the *fastest* NMR processing system today. It performs 8K floating point transforms in less than 500 milliseconds. This exceptional speed removes the historical time limitations on 2D calculations.

The overall result is a more productive system with floating point math accuracy faster than most systems can perform integer math calculations.

Multi-experiment, multitasking and queueing capabilities increase your productivity. ADVANCE's Host Computer simultaneously manages up to nine independent experiments, each with separate parameter tables, FIDs, and spectral storage.

Each of these nine experiments also can include a series of spectra related by the variation of one or more parameters. For example, ADVANCE can automatically perform T_1 as a function of temperature, or a selective NOE experiment as a function of both frequency and temperature.

Furthermore, an operator can command the system to plot spectral data from a previous experiment, list parameters of an ongoing experiment on the line printer, and set up a future experiment through the keyboard – all at the same time.

ADVANCE's sophisticated queueing system handles any task "overruns," automatically arranging and executing all remaining tasks as soon as the appropriate resource (printer, plotter, etc.) becomes available.

■ **ADVANCE Acquisition System gives you total, full-time control of every experiment.** The Acquisition Computer System, also incorporating a separate Motorola 68000 microprocessor, independently manages the NMR experiment. Its Pulse Sequence Controller controls the timing of pulse sequence events. The Data Acquisition Processor time averages the NMR data from a 12-bit (or optional 15-bit) ADC.

The Acquisition Computer accepts data tables with either 16-bit or 32-bit precision for large dynamic range experiments. Its data table memory, expandable from 128K bytes to over 3 megabytes, gives good digital resolution at even the largest spectral widths.

ADVANCE's Pulse Sequence Controller combines the accuracy of hardware timing with the flexibility of a software-defined sequence. It automatically calculates and sets pulse delays, widths, phases, frequencies and offsets for both observe and decoupler channels. It also establishes modulation modes, receiver gatings, and homospoil pulses.

Because this controller calculates pulse sequence events from NMR parameters (such as coupling constants and frequencies), it eliminates tedious precalculations of phase tables, pulse widths and pulse delays.

User-created pulse sequences can have an unlimited number of steps, and the availability of both hardware and software looping capabilities allows repetitive fast events to be accomplished accurately. FIDs can be sampled *during* a pulse sequence. INEPT, DEPT, cross-polarization, all modern 2D sequences and various connectivity experiments are all easily performed.

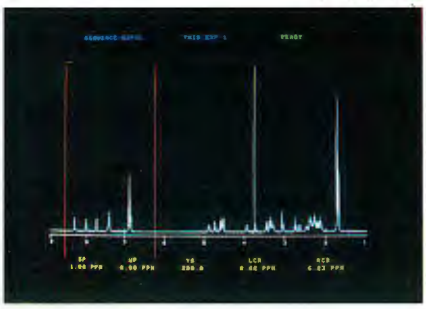
For the less experienced NMR operator, ADVANCE's Pulse Sequence Controller allows immediate use of the most sophisticated experiments, while experienced NMR operators have the power available to design their own pulse sequences.

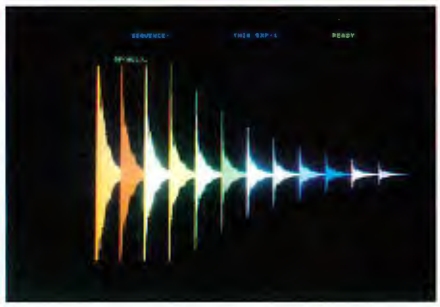
■ **Expandable Information Storage System solves data archiving problems.** Both the Host and Acquisition Computers have direct bus linkage to a 30-megabyte Winchester disk, which contains the modular Pascal operating system program. This disk also serves as the storage center for collected data and user-created programs. It can hold large 2D data tables of over 10M words. An additional 30-megabyte Winchester disk can be added for even larger storage capacity.

The standard system also includes a 1-megabyte flexible disk, which provides a convenient medium for software updates and individual user files.

You can also add more storage devices to meet your particular needs: streaming mag tapes with up to 30 megabytes of data for user libraries; 9-track magnetic tapes; extra hard disks and/or flexible disks; or combinations of these devices.

For maximum central storage/information access capabilities, the ADVANCE system is designed to communicate with other computer systems via state-of-the-art, high-speed networking protocol, as well as RS-232C Interfaces.





■ Responsive Operator Interface with large, 16-color display makes data interpretation easier.

ADVANCE's 13-inch display screen features a fast, high-level graphics controller providing 16-color presentations. The intelligent use of color graphics allows you to make faster and more accurate decisions based on visual displays.

Operators communicate with the system via a standard keyboard and five user-assignable control knobs. Used to manipulate a variety of display parameters, these shaft-encoded knobs provide rapid responses to operator commands.

Industry-standard bus structure + modular software = unlimited peripherals. ADVANCE lets you add a variety of commercially available printers, plotters and other devices for special needs. Since a dedicated computer and accompanying software are assigned to each input/output device, tasks are initiated, run and completed without interruption.

Automatic self-monitoring diagnosis of hardware and system functions improves reliability. ADVANCE circuit boards are equipped with status registers and LED indicators that allow you to interrogate the board's condition from either the operator keyboard or from a remote station via a modem.

Special diagnostic software is available to help you determine whether instrument operations are functioning in the proper manner. Other design features, such as the interchangeability of the Host and Acquisition CPU boards, also improve system reliability and aid in servicing.

Varian's Pascal-based software is the industry standard for NMR. ADVANCE's comprehensive and flexible software package is based on six years of Varian development and customer use on XL Series Spectrometers. It is the recognized standard in the industry. ADVANCE software gives users all the benefits of true modularization: the ability to add new programs to system files, to reallocate disk files... even to write your own programs quickly and easily.

Several disk-resident libraries contain pre-set parameters for system operations. The result is faster and simpler access to the XL Systems's capabilities.

User-programming functions are completely independent from spectrometer functions. You can write, display, print or plot without interrupting other spectrometer functions.

The user can customize instrument operation by combining several spectrometer and peripheral system functions into single-word MACRO commands. These are stored in the command library and recalled through the keyboard as needed. This simplifies and speeds complicated, yet repetitive, operations.

ADVANCE software is both easily accessible and highly sophisticated. Concurrent-Pascal provides the power necessary for even the most complex experiments, including user-created ones. Yet the software will also provide step-by-step guidance through experiments for new users.

Add more productivity and power when you need it. ADVANCE is also available as a stand-alone data station, which provides a second, yet separate, data processing system. All capabilities, except data acquisition, of the standard XL Series ADVANCE Data System are identical.

You command two, totally independent work centers, which create a "double production" system for handling acquired data. Throughput is *easily* doubled, and at a fractional cost compared to purchasing a second spectrometer.

For immediate assistance: In the United States call—**Northeast** Florham Park, New Jersey (201) 822-3700
Midwest Park Ridge, Illinois (312) 825-7772 • **South & West** Sugar Land, Texas (713) 491-7330
Or write: Varian, 611 Hansen Way, Palo Alto, California 94303 • **In Europe** Steinhauserstrasse, CH-6300, Zug, Switzerland • **In Canada** 45 River Drive, Georgetown, Ontario L7G 2J4 • **In Latin America North** FCO Petrarca 326, Mexico 5, D.F. • **In Latin America South** Av. Dr. Cardoso de Melo, 1644, CEP 04548, Sao Paulo, Brazil
In Australia 679 Springvale Road, Mulgrave, Victoria 3170 • **In the Far East** Eastern Commercial Center, Room 1103, 393-407 Hennessy Road, Wanchai, Hong Kong

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2628 BL DELFT
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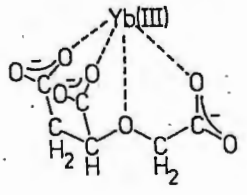
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Delft, March 21, 1983
JAP/MK/114

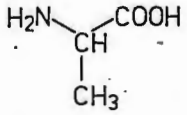
Dear Professor Shapiro,

Yb(S)-carboxymethyloxysuccinate: a chiral lanthanide shift reagent for the NMR resolution of enantiomeric amino acids in aqueous solution

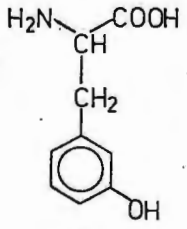
The NMR resolution of enantiomers of amino acids is a longstanding problem. In a previous contribution to the TAMU NMR Newsletter (284, 41 (1982)), we mentioned the chiral shift reagent Eu(S)-carboxymethyloxysuccinate (Eu(S)-CMOS), which could be employed for the spectral resolution of (oxy)carboxylic acids in aqueous solution. We have investigated the applicability of other lanthanide (S)-CMOS salts as shift reagents. It was found that Yb(S)-CMOS (1) is able to bring about NMR resolution of enantiomers of amino acids. Upon stepwise addition of the solid Yb-salt to an aqueous solution of an (R)/(S)-mixture of alanine (2) at pH 3.3, resolution of the enantiomers was obtained. At



1



2



3

a molar ratio of Yb(S)-CMOS/alanine of 0.63 separations of 0.06 and 0.04 ppm were obtained for the CH and CH_3 signals, respectively (Figure 1). It may be noted that the signals for the CMOS ligand did

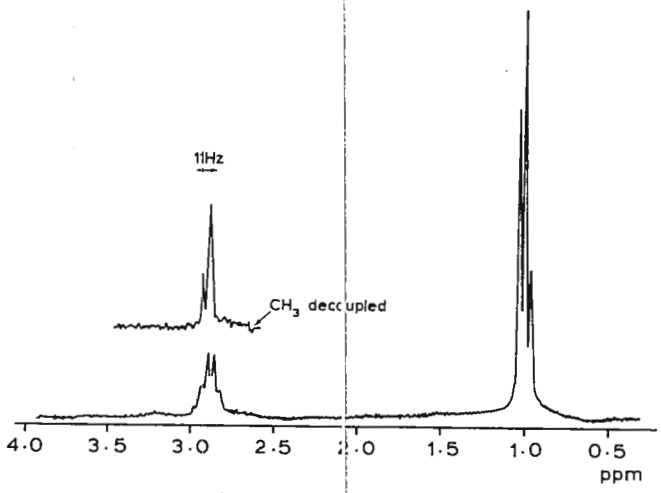


Figure 1. 200 MHz ^1H NMR spectrum of 13.2 mg alanine (R:S = 1:2) in D_2O in the presence of 35.2 mg Yb(S)-CMOS at pH 3.3 (20 ^oC).

not appear due to strong broadening as a result of slow CMOS-ligand exchange with respect to the ^1H NMR time scale. We assume mixed complexes of Yb(S)-CMOS/alanine to be responsible for the resolution. (S)-CMOS coordinates predominantly tetradentately (via the 3 COO^- groups and the ether oxygen), whereas under the conditions used alanine coordinates bidentately (via the COO^- group).

The Yb(S)-CMOS shift reagent could be successfully employed for the solution of a practical problem. In connection with a study of structure-activity relationships of pharmacological compounds both enantiomers of the unnatural amino acid m-hydroxyphenylalanine were required. These compounds were synthesized via stereospecific enzymatic hydrolysis of the corresponding racemic ethyl esters. The optical purity of the amino acids obtained cannot easily be determined with reasonable accuracy with other methods. With the use of Yb(S)-CMOS the optical purity of both enantiomers was determined to be more than 98%. Moreover, a comparison of the relative Yb-induced shifts of the enantiomers with those of alanine, supported the assignments of the absolute configurations.

Sincerely yours,

J.A. Peters

A.M. van Leersum

A.P.G. Kieboom

H. van Bekkum

UNIVERSITÉ CLAUDE BERNARD LYON I
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SENSITIVE LINE IN NMR IMAGING

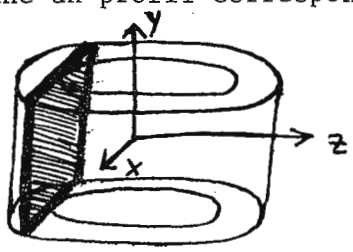
Villeurbanne, le 23 Mars 1983

Cher Docteur Shapiro,

Nous développons actuellement au laboratoire des méthodes de mini-imageries sur un spectromètre conventionnel XL100. C'est ainsi que nous avons mis au point une méthode de ligne sensible : nous appliquons un gradient périodique (fréquence 1000 Hz) selon la direction z du champ directeur et un gradient constant selon x. On sélectionne ainsi une tranche de l'échantillon $z = z_o$ qui donne un profil correspondant à la direction x.

La résolution spatiale dans la direction z va dépendre |1|

- de l'intensité g_z du gradient périodique $g_z(z-z_o)f(\omega_1 t)$
- de la forme de ce gradient en fonction du temps $f(\omega_1 t)$



Nous expérimentons différentes formes de gradients. Pour vérifier la sélectivité de la réponse nous plaçons la ligne sensible tangentiellement à un tube d'eau annulaire (voir figure 1).

Nous avons comparé les profils obtenus à partir de gradients alternatifs de même amplitude, de même période mais dont l'un est de forme sinusoïdale (1), l'autre carrée (2). La forme de la réponse peut se calculer. On trouve |2| :

pour (1) $\quad R_1(z-z_o) = J_o\alpha(z-z_o) \qquad \alpha = \dfrac{g_z}{\omega_1}$

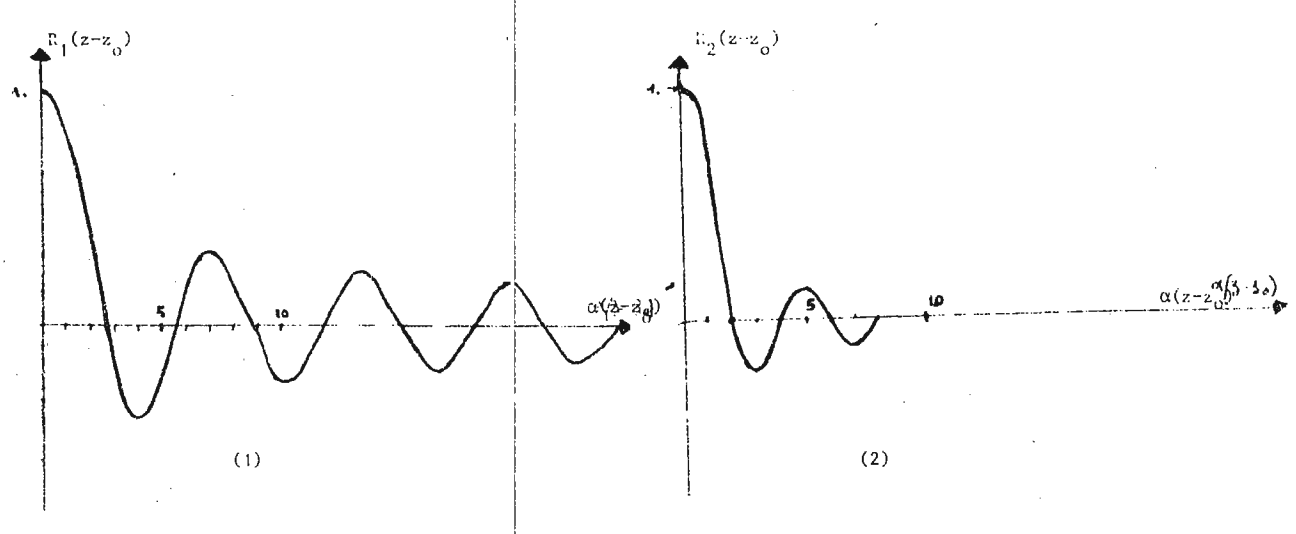
pour (2) $\quad R_2(z-z_o) = \dfrac{\sin(z-z_o)g_z T_1/4}{(z-z_o)g_z T_1/4} \qquad \omega_1 = \dfrac{2\pi}{T_1}$

La réponse R_2 est plus sélective que R_1. C'est bien ce que l'on vérifie sur le profil (2) dans lequel la tranche observée (z_o) ne déborde pas sur le tube de D_2O (un débordement sur le tube de D_2O a pour effet de diminuer le centre du profil et donc de privilégier les bords où D_2O est remplacé par H_2O : le profil présente alors deux maxima (profil 1)).

La recherche de forme de gradient conduisant à une sélectivité encore plus grande est possible. Elle impose néanmoins de travailler à des fréquences élevées (supérieures à 1000 Hz) pour éviter que les bandes latérales créées par le gradient alternatif ne se mélangent au profil obtenu. De ce fait il faut une intensité du gradient alternatif très élevée pour conserver à la tranche observée une finesse compataible avec la résolution recherchée (inférieure à 0,1 mm).

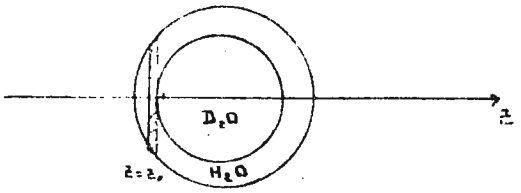
|1| M.M. TROPPER Journal of Magnetic Resonance 42 193-202 (1981)
|2| J.C. DUPLAN, B. FENET Résultats non pibliés

A. BRIGUET J. DELMAU J.C. DUPLAN B. FENET



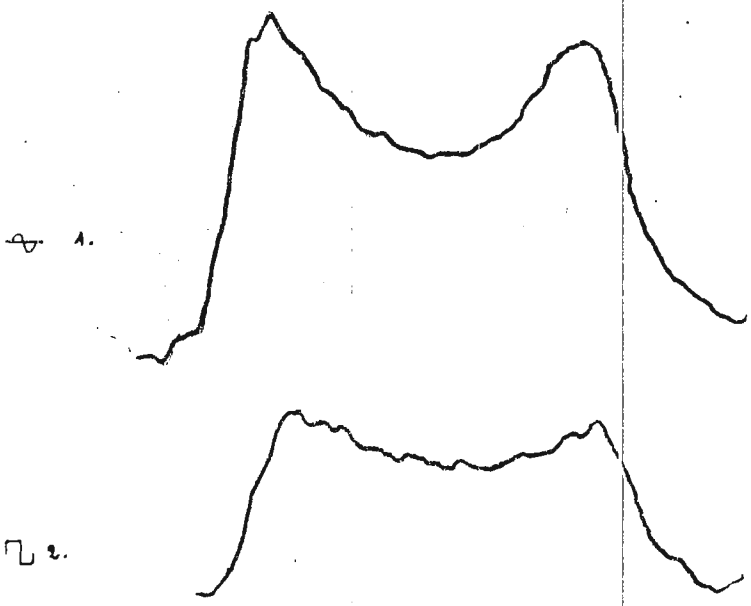
Courbes de réponse spatiale pour un gradient alternatif sinusoïdal (1)
pour un gradient alternatif carré (2)

LIGNE SENSIBLE POUR UN ECHANTILLON D'EAU COMPRISE ENTRE DEUX TUBES CONCENTRIQUES POUR UN POINT $Z = Z_0$ SENSIBLEMENT TANGENTE AU TUBE INTERIEUR

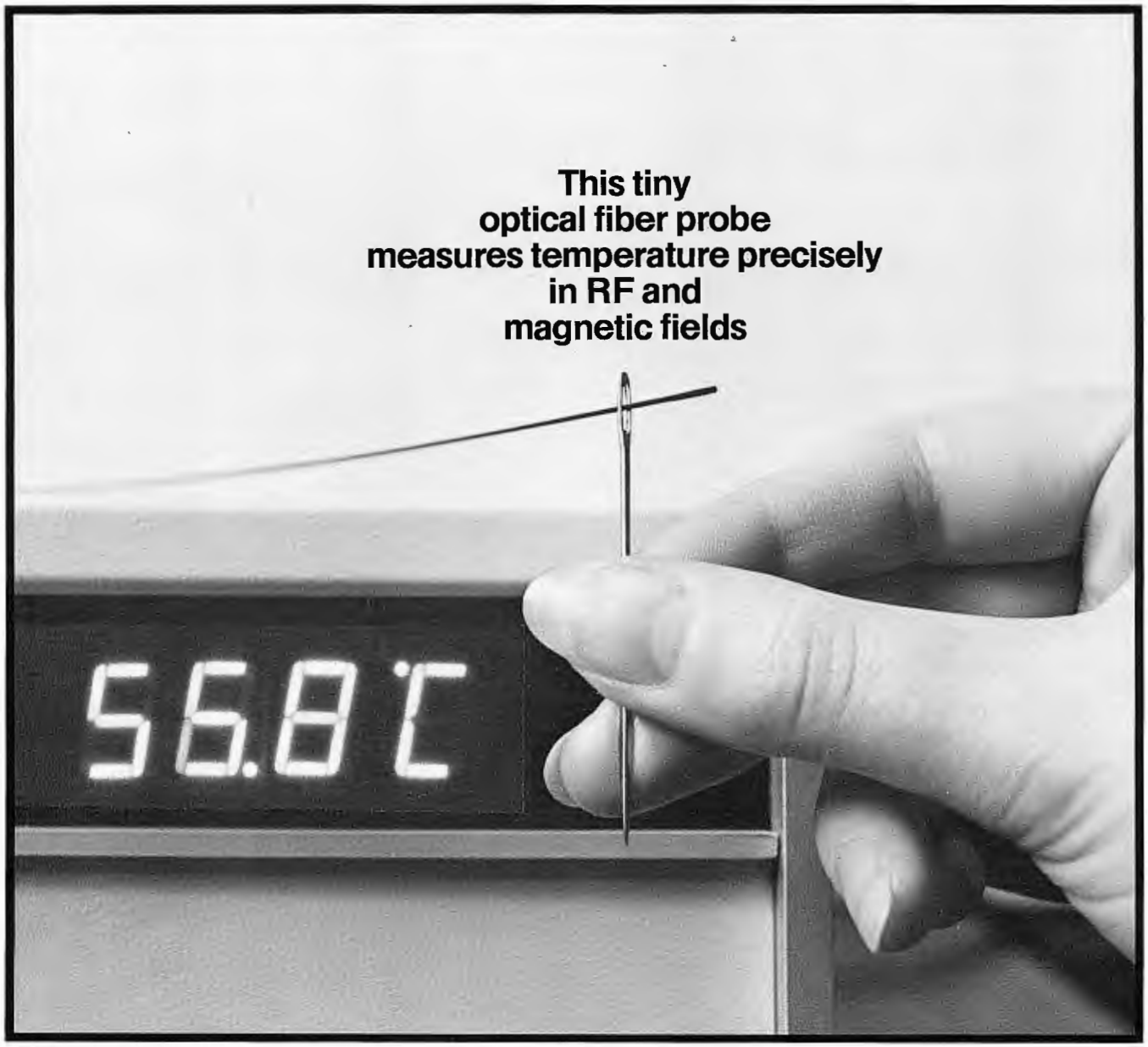


1 - AVEC UN GRADIENT ALTERNATIF
2 - AVEC UN GRADIENT EN CRENEAUX CARRES

La sélectivité est meilleure dans le deuxième cas. La participation des autres points $z \neq z_o$ à la réponse est plus faible.



BREAKTHROUGH



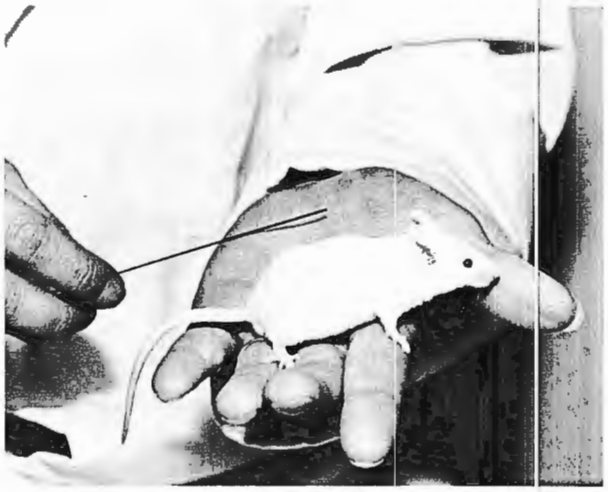
Did you ever wonder how you could measure temperatures during NMR studies? Whether you are doing bioeffects studies, investigating patient heating effects during NMR imaging or making fundamental measurements on temperature-sensitive materials of biomedical interest, Fluoroptic™ Thermometry by Luxtron provides an important new investigational tool. Autoclavable probes are nonconducting, minimally perturbing and small enough to be inserted through an 18 gauge catheter. With our new automatically calibrated Model 1000B, accuracies of 0.1°C are readily achievable. Call or write for the complete story.

LUXTRON

Fluoroptic™ Temperature Sensing
1060 Terra Bella Avenue, Mountain View, California 94043
Telephone (415) 962-8110

Model 1000B Applications

Several characteristics of Luxtron's fiber optic probe distinguish it from conventional temperature sensors and permit creative biomedical researchers to tap new realms of temperature data. These distinctive characteristics include: autoclavability for direct insertion into tissue; local sensing for pin-point readings; slender size for insertion via 18 guage catheter needles; versatile lengths for routing through apparatus or into screen rooms; total safety for isolated, non-electrical sensing; small thermal mass for rapid readings; RF/microwave immunity for non-perturbance in or by electromagnetic fields.



Benefits of Fluoroptic™ probe for small animal research include: small size, autoclavable, fast response, localized sensing, non-contaminating.

Model 1000B Specifications

SYSTEM PERFORMANCE

Temperature Range:
0° to 80°C (32° to 176°F)

Precision (Repeatability):
±0.1°C with 1 second measurement time

Resolution of Display:
0.1°C or °F

Resolution of Outputs (Analog and digital):
0.01°C; 0.02°F

Method of Calibration:
Automatic using 2 reference points within hyperthermia range (37° to 50°C)

Accuracy:
Using Floating Internal Temperature References:
1. 37-50°C: ±0.25°C
2. 0° to 20°C: ±1.2°C
3. Remainder of Range: ±0.6°C

Using Optional Precision External Temperature References:
1. 37-50°C: ±0.1°C
2. 0° to 20°C: ±1.0°C
3. Remainder of Range: ±0.5°C

Stability:
Less than 0.2°C change per degree change in ambient from 15° to 35°C

Measurement Times:
⅓, 1 or 4 seconds, operator selectable

PROBE

Materials:
Single strand plastic clad optical fiber with black PFA Teflon® external jacket.

Lengths:
2 meter lengths standard; longer probes and extensions available with some reduction of performance.

Diameter:
Less than 0.7mm throughout, excluding connector. Sensor can easily pass through the sheath of an 18 gauge I.V. catheter placement unit.

Flexibility:
While the fiber is quite flexible, the sensor end is sufficiently stiff to be self-guiding during insertion into catheter or placement unit.

Sterilization:
Because of the unusually hardy materials and construction techniques used, probes can be sterilized by autoclaving.

INSTRUMENT

Front Panel Indicators:
LED display for temperature in °C or °F plus overrange, underrange, probe fault and lamp out indicators, warm-up and calibration status indicators.

Internal Selectors:
°C or °F; measurement time; calibration mode and settings; output parameters.

Rear Panel Analog Output;
10mV per degree C or F with adjustable zero offset; BNC connector.

Rear Panel Digital Output (Optional):
RS 232C Serial with switch-selectable BAUD rates. An optional conversion to IEEE standard 488 output also available.

Temperature References:
Two floating temperature reference wells, accurate to 0.25°C, are provided within the instrument for routine calibration. A high precision temperature reference, with two fixed point wells, is also available as an option.

Packaging:
RF-shielded and filtered, bench-style instrument with tilt-up bail. With standard shielding, displayed temperature will not change by more than ±1.0°C with a radiation flux density of 10mW/cm² at frequencies up to 2.45 GHz. Optional heavy-duty shielding also available to reduce this RF field susceptibility to ±0.1°C.

ENVIRONMENTAL SPECIFICATIONS

Temperature:
Operating 10°C to 40°C; storage −55°C to 75°C

Humidity:
10° to 25°C, 95% RH; 25° to 40°C, 75% RH

Vibration:
Meets requirements of MIL-T-28800 for Style E Class 6 equipment

Size and Weight:
16¾" wide by 13" deep by 4" high;
18 pounds (8.2 Kg)

Power:
100, 120, 220, 240 VAC ±10%; 50-60 Hz; 60 Watts

LUXTRON

Fluoroptic™ Temperature Sensing
1060 Terra Bella Avenue, Mountain View, California 94043
Telephone (415) 962-8110, Telex 348-399 KARMIGA

Printed in U.S.A. 4/82

NATIONAL CANCER INSTITUTE
FREDERICK CANCER RESEARCH FACILITY
P.O. Box B, Frederick, Maryland 21701

March 24, 1983

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

Dear Dr. Shapiro:

The Chemical Synthesis and Analysis Laboratory is a technical resource for the Frederick Cancer Research Facility and the National Cancer Institute (Bethesda, MD). The NMR area relies on a Nicolet NT-300 WB (1280, 293C) as its principal research tool, and is in the process of replacing its smaller, outdated NMRs with a workhorse narrow bore supercon (any helpful comments, horror stories, etc. from readers would be appreciated).

We have just completed construction of a live animal surface coil probe, designed for us by R. Balaban (NIH) and have begun ^{31}P studies on rats in collaboration with him and Dr. Craig Reynolds. This technique should produce interesting research at the cancer facility.

One brief technical comment which may save the reader a few minutes. We discovered that the Nicolet 1280 pulse sequence implementing Patt and Shoolery's[1] "APT" experiment is improperly phase cycled so that non-90° observe pulses cannot be used. (At least for their pulse sequence library as of 3/21/83.) With L. Johnson's assistance we provide a corrected version:

```
APT
APT- PHASE CYCLED
#   1: D5.NØ
#   2: P3/Ø.NØ
#   3: D1
#   4: P2/@A+Ø.NØ
#   5: P1/@C+Ø.NØ
#   6: P2/@A+Ø.NØ
#   7: D1.NØ
#   8: D6,NØ
#   9: P2/@B+Ø.NØ
#  1Ø: P1/@D+Ø.NØ
#  11: P2/@B+Ø,NØ
#  12: D6,NØ
#  13: A,NØ,T
#  14: D2,NØ,T  JUMP TO #    1

PHASE A=2*(S/2)+1
PHASE B=(2*S)+1
PHASE C=2*(S/2)+2
PHASE D=(2*S)+2
```

We have noticed an occasional difficulty with APT resulting from non-standard coupling constants. Recently, we observed no signal intensity for the two expoxide methine carbons of a small antibiotic using APT with

a 8 msec D1. The large $^{1}J_{CH}$ of about 180 Hz for these carbons resulted in near zero intensity at 8 msec as was predicted from the equations given in Patt and Shoolery's paper[1]. We thus caution users who routinely run a simple APT experiment as the only carbon spectrum.

[1] S.L. Patt and J.. Shoolery, J. Magn. Res., 46, 535-539 (1982)

Regards,

Bruce D. Hilton

Bruce D. Hilton, Ph.D.

Gwendolyn N. Chmurny

Gwendolyn N. Chmurny, Ph.D.

CHEMICAL SYNTHESIS AND
ANALYSIS LABORATORY

Universiteit van Amsterdam
ANORGANISCH CHEMISCH LABORATORIUM
J. H. van 't Hoff Instituut
Nieuwe Achtergracht 166, 1018 WV Amsterdam, Tel. (020) 522 9111

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

AMSTERDAM, March 28th, 1983

Dear Professor Shapiro,

TITLE: Second order Pt-195 spectra in dinuclear Pt(+3) systems.

We are currently reinvestigating some dinuclear complexes of the type $Pt_2(OAc)_2R_4L$ (L=donor ligand) in which two different,formally +3, Pt centres lie in close proximity[1].Naturally there is good reason to believe that a direct metal-metal bond is present.In particular,when L is a phosphorus donor P-31 spectra reveal that $^1J(Pt,P)$ and $^2J(Pt,P)$ are of similar magnitude.The best way to look for a stong Pt-Pt interaction, we reasoned, was to directly observe Pt-195 and hence J(Pt,Pt). Two sets of NMR data,so obtained,are given below for L=$POMe_3$(1a) and PEt_3(1b). Despite the absence of a ligand at one centre the two Pt-195 chemical shifts are similar and for 1a (see Spectrum) remarkably so. Note also that the 4- and 5-coordinate metal centres give rise to resonances with different linewidths.In this spectrum the value of $^1J(Pt,Pt)$ results in a subspectrum for the molecules containing two Pt-195 centres that is severely second order. This is the AB part of an ABX spectrum in which X=P-31 and for 1b is a more readily recognizable pattern of eight lines with each set of four,for the individual metals, showing the usual roofing effect. For 1a computer simulation/iteration has been used to extract $^1J(Pt,Pt)$ and to confirm that the outer lines of the pattern are of low intensity (i.e. below the noise level).Although this data is limited (we hope to overcome some synthetic problems) the $^1J(Pt,Pt)$ values are,as far as we know , the largest seen for a Pt(+3)-Pt(+3) system.

With Best Regards,

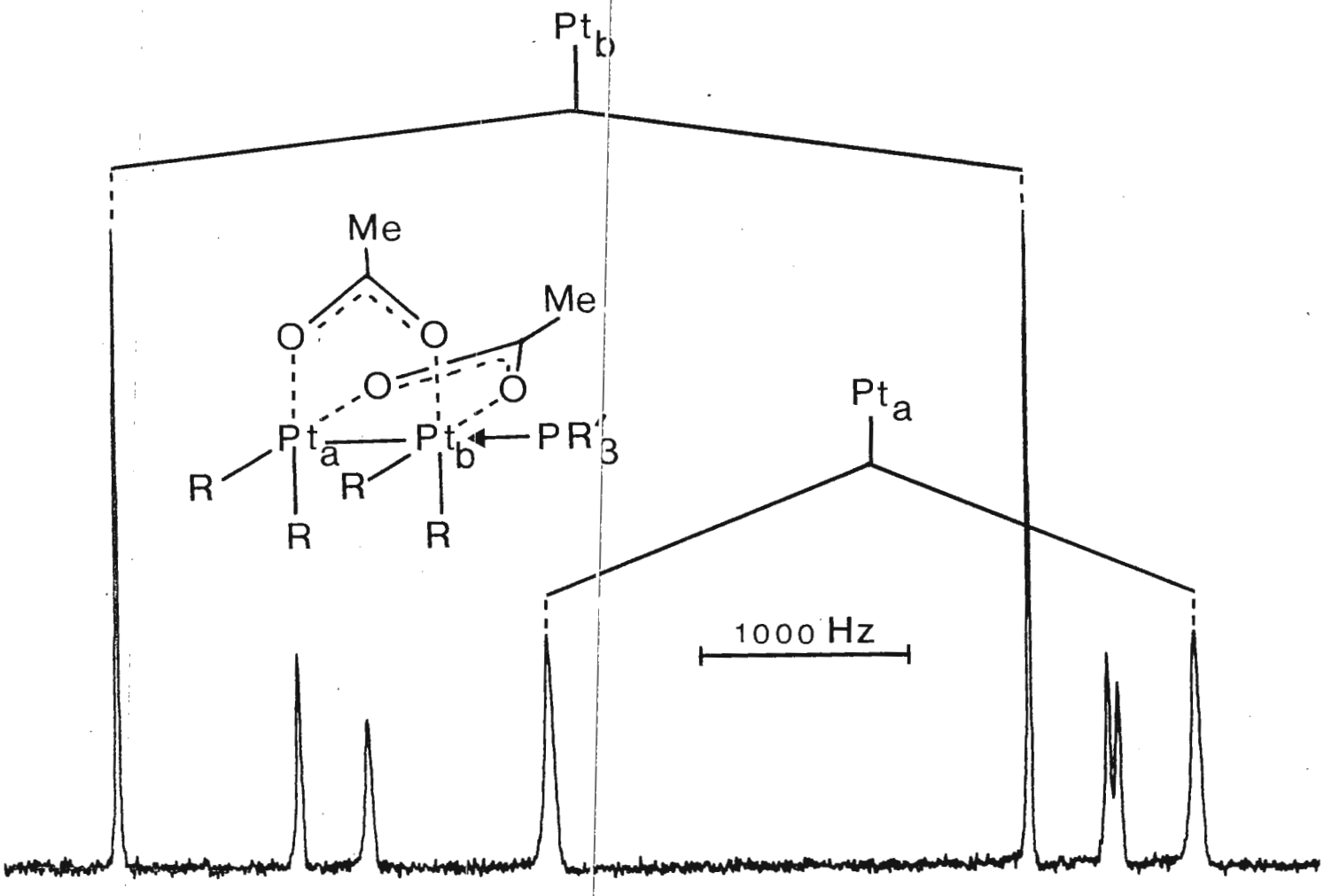
David M. Grove.

D.M.Grove.

Reference.

1) B.R. Steele and K. Vrieze, Transition Metal Chem., 2,169-174(1977).

The 98.2 MHz 195-Pt Spectrum of 1a (R = Ph, R´= OMe)



Extracted Nmr Data

R´	R	$^2J(Pt_a,P)$	$^1J(Pt_b,P)$	$^1J(Pt,Pt)$	δ Pt_a	δ Pt_b
OMe	Ph	3150	4337	6044	+2487	+2514
Et	Ph	1933	2347	6541	+2584	+2403

Coupling constants are in Herz and 195-Pt chemical shifts are referenced to 21.4 MHz. The solvent was $CDCl_3$.

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JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

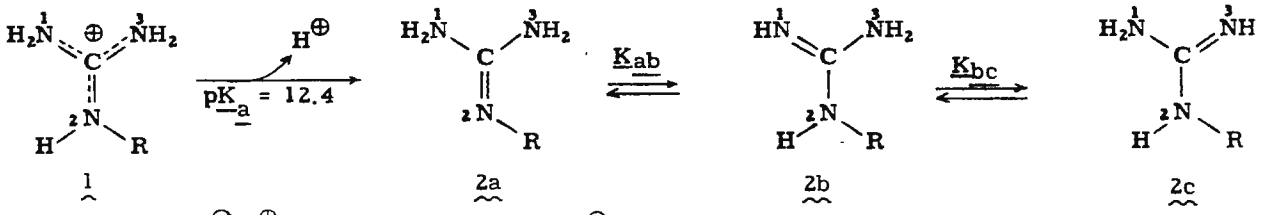
March 18, 1983

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

An N-15 NMR Study of the Barriers to Isomerization about Guanidinium and Guanidino Carbon-Nitrogen Bonds in L-Arginine

Dear Barry,

While barriers to rotation about the carbon-nitrogen bonds in amides have been extensively studied by NMR spectroscopy, corresponding studies on guanidines have been mostly limited to ^{1}H NMR studies of tetramethylguanidine derivatives and their salts.(1) Guanidinium ions and guanidines substituted on N2 (1 & 2) occur in a number of biologically important molecules such as L-arginine and streptomycin, and it is important to understand their isomerization behavior. We have used N-15 NMR spectroscopy to determine the barriers to isomerization about the C-N2 bond of L-arginine as 1 & 2 through line-shape analyses of N1 and N3 resonances at a series of temperatures.



1 2a 2b 2c

R = $-(CH_2)_3CH(\overset{\ominus}{C}O_2)\overset{\oplus}{N}H_3$ (pH<9) = $-(CH_2)_3CH(\overset{\ominus}{C}O)_2NH_2$ (pH>9)

Figs. 1 and 2 show the temperature dependence of broadband proton-decoupled ^{15}N spectra obtained at 50.65 MHz of the N1 and N3 resonances in 50% (v/v) dimethyl sulfoxide/water at pH 7.0 and 14.1, respectively. In both the guanidinium and guanidino forms of L-arginine, rotation about the C-N2 bond is rapid at room temperature so that a single averaged peak for N1 and N3 is observed (Figs. 1a and 2a). At lowered temperatures, isomerization is slowed and separate N1 and N3 resonances appear (Figs. 1h and 2g).

The rates obtained by matching theoretical (right) and observed spectra (left) in Figs. 1 and 2 gave free energies of activation, $\Delta G^{\ddagger}$, for isomerization about the C-N2 bond of 10.4 kcal/mol for the guanidine species (pH 14.1), which is considerably lower than the $\Delta G^{\ddagger}$ of 12.9 kcal/mol for the guanidinium species (pH 7.0).

The ^{15}N chemical shifts of these nitrogens in the regions of fast and slow isomerization are also shown in the figures. It is interesting that the chemical-shift differences between the two nonequivalent nitrogens, N1 and N3, is only 2.4 ppm for the guanidinium group of L-arginine but is 42.3 ppm for the corresponding guanidino group. The latter is the largest N1-N3 difference so far reported for guanidine derivatives.

The value of $\Delta G^{\ddagger}$ of 10.4 kcal/mol for rotation of the guanidino group of L-arginine, 2, is very much smaller than the 18.8 kcal/mol reported for pentamethylguanidine. (2) If isomerization occurs by rotation, the lower barrier in 2 can most simply be explained by a lesser double-bond character of C-N2 in 2, compared to pentamethylguanidine, as the result of tautomeric equilibrium between 2a-2c.

The $\Delta G^{\ddagger}$ of 12.9 kcal/mol obtained for isomerization of the guanidinium form of L-arginine, 1, is very close to the upper bound of $\Delta G^{\ddagger}$ = 13.0 kcal/mol deduced for unsubstituted guanidinium ion.(3)

...../

Most ^{15}N NMR spectra of free arginine in aqueous solution, or arginyl residues in protein proteins, or of intracellular arginine in microorganisms have been taken at or above room temperature and at N-15 resonance frequencies of less than 18 MHz. Under such conditions, the resonances of N1 and N3 will be observed as a single peak, because $k_{ex} \gg \pi\Delta\nu$, where k_{ex} is the rate of isomerization and $\Delta\nu$ is the chemical-shift difference in Hz between the nitrogens in the absence of isomerization. However, at 50 MHz (^1H resonance frequency of 500 MHz), the N1-N3 peak is considerably broadened and has a $\nu_{\frac{1}{2}}$ of 30 Hz at 4°C in neutral aqueous solution. Such line broadening resulting from slow isomerization should be taken into account in N-15 NMR studies or arginine and arginyl residues in enzymes at high magnetic fields.

The guanidinium group of arginine clearly plays an important role in binding anionic substrates and cofactors at the active sites of a number of enzymes. Valuable information on enzyme-substrate complexes and transient intermediates can be obtained by "trapping" them at subzero temperatures in mixed aqueous organic solvents.(4) The use of NMR for "low-temperature" enzymology is just emerging (5) and the nonequivalence of N1 and N3 resonances of arginine at subzero temperatures may be useful in this connection.

Best wishes,

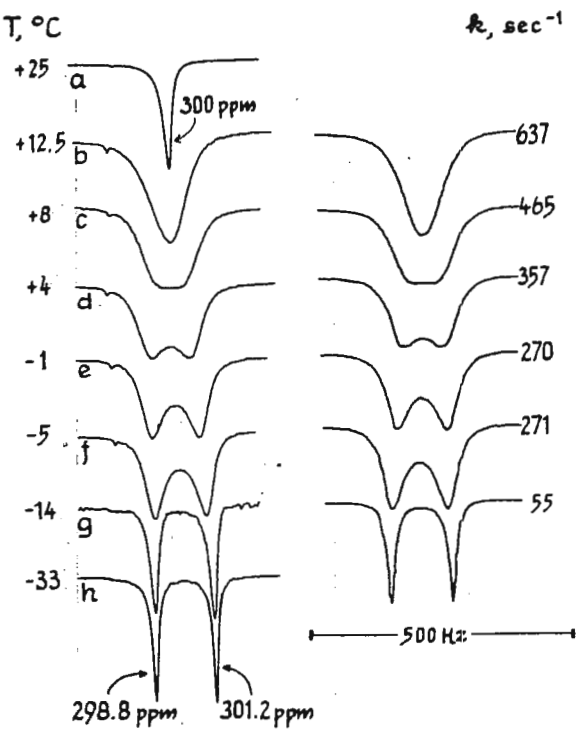
Very truly yours,

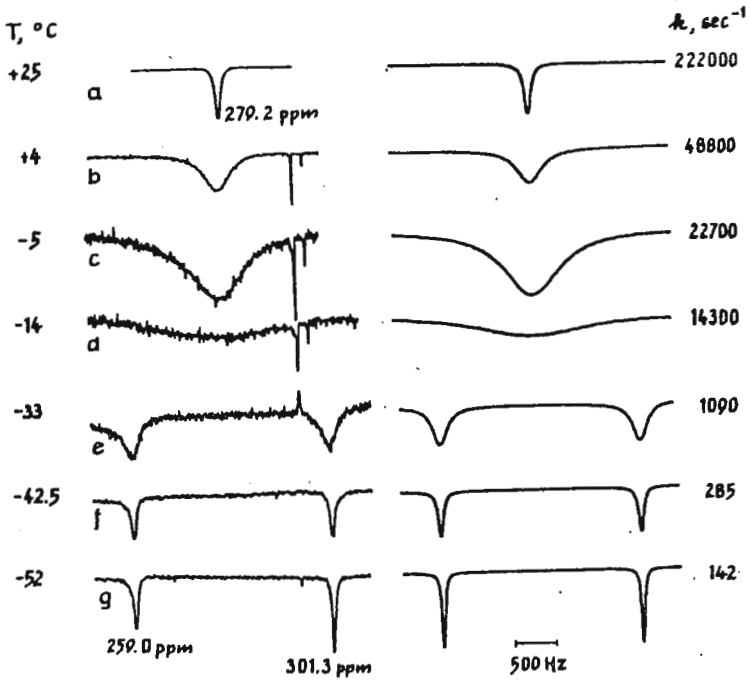
Keiko Kanamori

Jack

Keiko Kanamori John D. Roberts

1. H. Kessler, Angew. Chem., Int. Ed. Engl. 9, 219 (1970), and references therein.
2. H. Kessler and D. Leibfritz, Tetrahedron 26, 1805 (1970).
3. T. Bally, P. Diehl, E. Haselbach and A.S. Tracey, Helv. Chim. Acta 58, 257 (1975).
4. J.L. Markley, D.E. Neves, W.M. Westler, I.B. Ibanez, M.A. Porubcan and M.A. Baillargeon Baillargeon in "Frontiers in Protein Chemistry", T.Y. Liu, G. Manuya and K.T. Yasunobu, eds., Elsevier/North-Holland, New York, 1980, pp 31-61.





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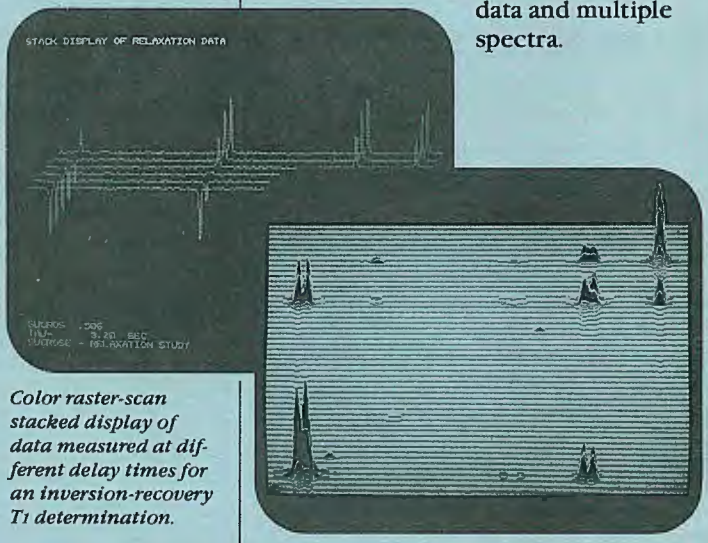

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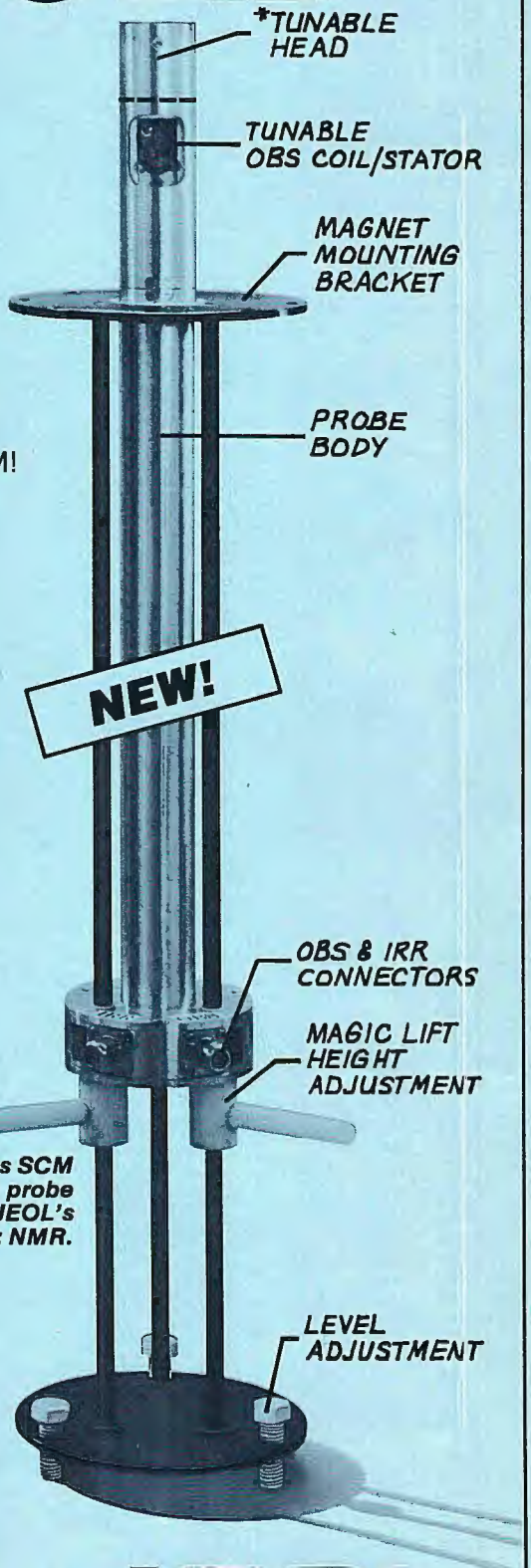

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