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Newsletter

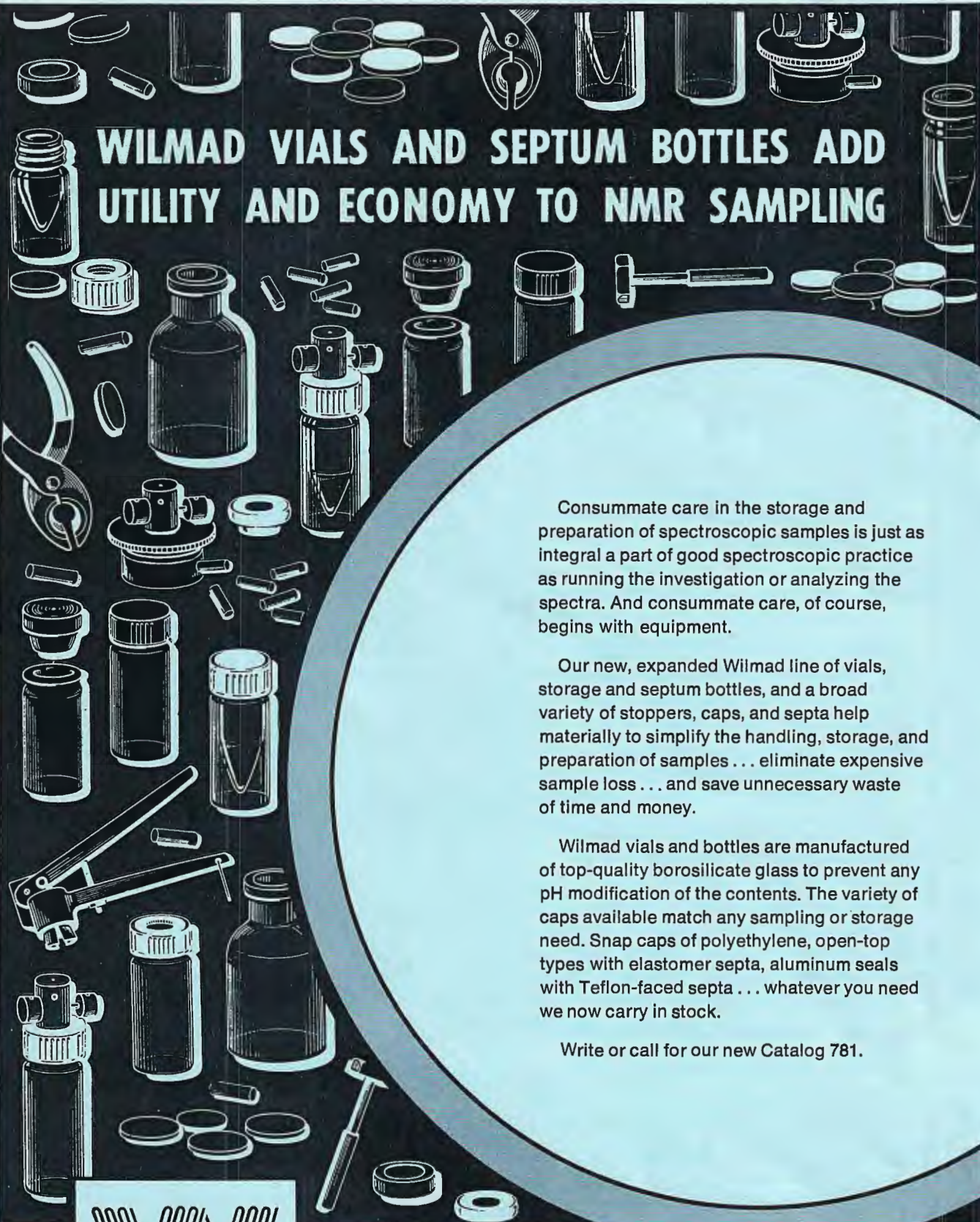
No. 247

April, 1979

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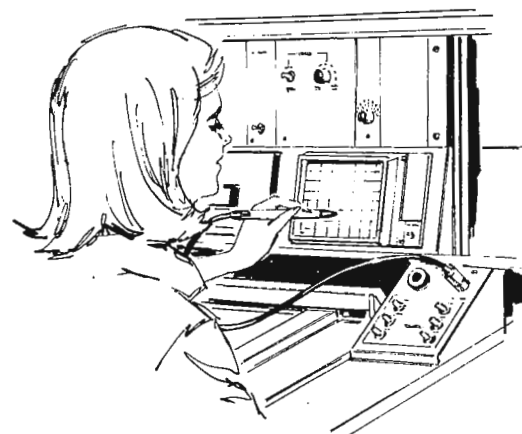
All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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27 February 1979

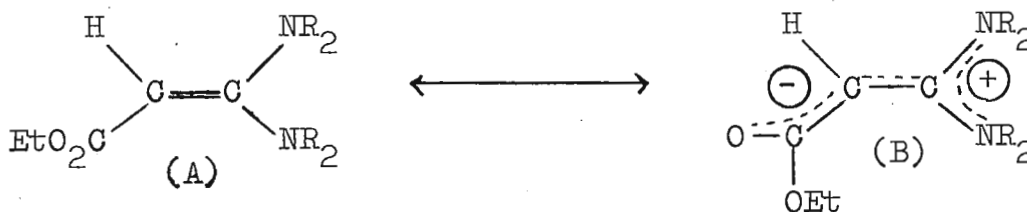
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United States of America.

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Push-Pull Olefins - ^{13}C Effects

Dear Barry

We recently examined the ^1H and ^{13}C spectra of some unusual olefins, where excessive π electron polarisation leads to remarkable differences in chemical shifts, particularly between the two carbon atoms of the double bond. These compounds, available as intermediates in the synthesis of various heterocycles (Dr B P Tong), were run in CDCl_3 or $\text{dmsO}-d_6$. A literature search revealed that considerable work on the n.m.r. spectra of "push-pull" olefins had already been carried out, in which the partial double bond character caused by polarisation of the π electrons led to reduced barriers to rotation about the $\text{C}=\text{C}$ bond (1). This is particularly true for the enamino esters (I,II) where several resonance structures can be drawn, represented by an average structure (B).



(I) R = H
(II) R = Me

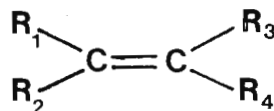
Opinion is somewhat divided as to whether the rate process observed is slow rotation about the $\text{C}=\text{C}$ or the $\text{C}-\text{NR}_2$ bond. We were primarily interested in the enormous chemical shift difference observed between the two carbon atoms of the double bond. In the Table the compounds examined are listed with relevant chemical shift data.

If the extraordinary C_1 , C_2 chemical shifts are caused largely by mesomeric effects then it is clear that NR_2 is far superior to OEt in promoting this, the ethoxy group being almost equivalent to the chloro- substituent in its effect. The fact that the shift difference is even larger for the mixed olefin ($R_3 = NH_2$, $R_4 = OEt$) is at first surprising. This may be due to steric effects, since the sp^2 nitrogens and their substituents (H or Me) cannot exist with all groups coplanar with the double bond so that only one NR_2 group can exert its mesomeric effect at any one time in compounds (I) and (II).

The rate process (ΔG^\ddagger 18.1 Kcal/mole) observed in the compound (II) is probably slow rotation about the $C=NMe_2$ partial double bond. $^1J_{CH}$ for the C-2 carbon is 157.3 Hz, suggesting that the carbon is still sp^2 hybridised.

Finally at the suggestion of Toni Krohn we dug out of our archives the dinitrile (VI) which we predicted should have a new world record value for ΔC_1C_2 . The actual value of 124.5 ppm may well be exceeded by a compound with better electron-donating properties than methyl.

TABLE



	R_1	R_2	R_3	R_4	δC_1	δC_2	$\delta R_1(H)$	$\Delta C_1C_2^e$
(I) ^a	H	COOEt	NH ₂	NH ₂	163.5	63.5	3.77	100.0
(II) ^{ad}	H	COOEt	NMe ₂	NMe ₂	166.6	72.2	3.90	94.4
(III) ^b	H	COOEt	Cl	Cl	137.7	120.5	6.43	17.2
(IV) ^b	H	COOEt	OEt	OEt	137.4	120.4	6.30	17.0
(V) ^{bc}	H	COOEt	NH ₂	OEt	169.2	64.8	3.18	104.4
(VI) ^a	CN	CN	NH ₂	CH ₃	172.3	47.8	-	124.5

(a) in $dmsO-d_6$ (b) in $CDCl_3$ (c) contains 20% of the imine form

(d) in (II) the NMe_2 protons and carbons appear as doublets : in the 1H spectrum coalescence of the two singlets (δ_{AB} 2.5 Hz) occurs at 323K

(e) $\delta C_1 - \delta C_2$.

I hope this contribution fulfils our somewhat delayed subscription.

With best wishes.

Yours sincerely

Tom

Dr W A Thomas

1 See for instance
S Rajappa et al, J.C.S. Perk II,
1978, 912 (and references therein).

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DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

26 February 1979

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

Dear Barry:

Application of the Gutowsky-Holm Equation to Unequally Populated 2-site exchange processes.

Several authors have proposed use of the Gutowsky-Holm equation, $k = \frac{\pi}{\sqrt{2}} \Delta\nu$, for the determination of the rate of exchange between two sites having populations other than 0.5. The simplest of these (1) defines as T_c the temperature (and rate) at which there is a value of zero for the slope of the curve between the maxima. The direct use of the equation does not depend upon the value $K = \frac{\rho_B}{\rho_A}$ (intensity ratio). The accuracy in k

was found to be within 20% of k as determined by CLS. A more laborious mathematical procedure of Shanan-Atidi(2) provides rate constants with an accuracy of 10%.

We propose a different definition of T_c , such that the rate constant can be calculated from the Gutowsky-Holm equation and the value for K ; specifically for

$$A \xrightleftharpoons[k_A]{k_B} B \quad \text{and} \quad K = \frac{\rho_B}{\rho_A}$$

$$k = \frac{\pi}{\sqrt{2}} \Delta\nu = k_A \rho_B \text{ at } T_c$$

and T_c is the temperature at which the spectrum no longer possess four inflection points, i.e. where there is the longest "flat spot" (constant slope) as illustrated in the Figure ($k_{CLS} = 145$ to 149). The Figure shows across calculated by D NMR 3 for the case $k = 2$, $\Delta\nu = 50$ and differencing values for the rate constant k_A . The value for k_A calculated as $\frac{\pi \Delta\nu}{\sqrt{2} \rho_B}$ is 149. Similarly a number

of CLS curves were generated for smaller values of $\Delta\nu$ and a k_{CLS} at T_c was selected for comparison with the k_A (calculated). The table shows the

agreement obtained. It is apparent that the accuracy of k_A obtained by this simple method is equal to or better than that obtained previously.

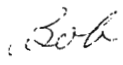
The method is of course limited to obtaining k at one temperature only. Nevertheless, as suggested by Gutowsky (3) and others (4) it would seem preferable to measure k at several T 's either by using different instruments or different nuclei to obtain more reliable values for ΔH^\ddagger and ΔS^\ddagger .

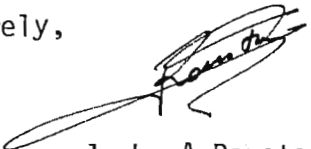
A Comparison of k_A with k^{CLS}

$\Delta\nu(\text{Hz})$	$k_A(\text{sec}^{-1})$	$k^{CLS}(\text{sec}^{-1})$	Precision ^a (%)
50	149	145-150	3
40	119	115-120	4
30	89	86-90	4
20	59	57-60	4
10	29.8	28.5 - 30	5
5	14.9	14.5 - 15	6
4	11.9	10.8 - 12	10
3	8.9	8-9	11

^a The precision is calculated from the range of uncertainty in k^{CLS} as estimated from the average of two independent assessments.

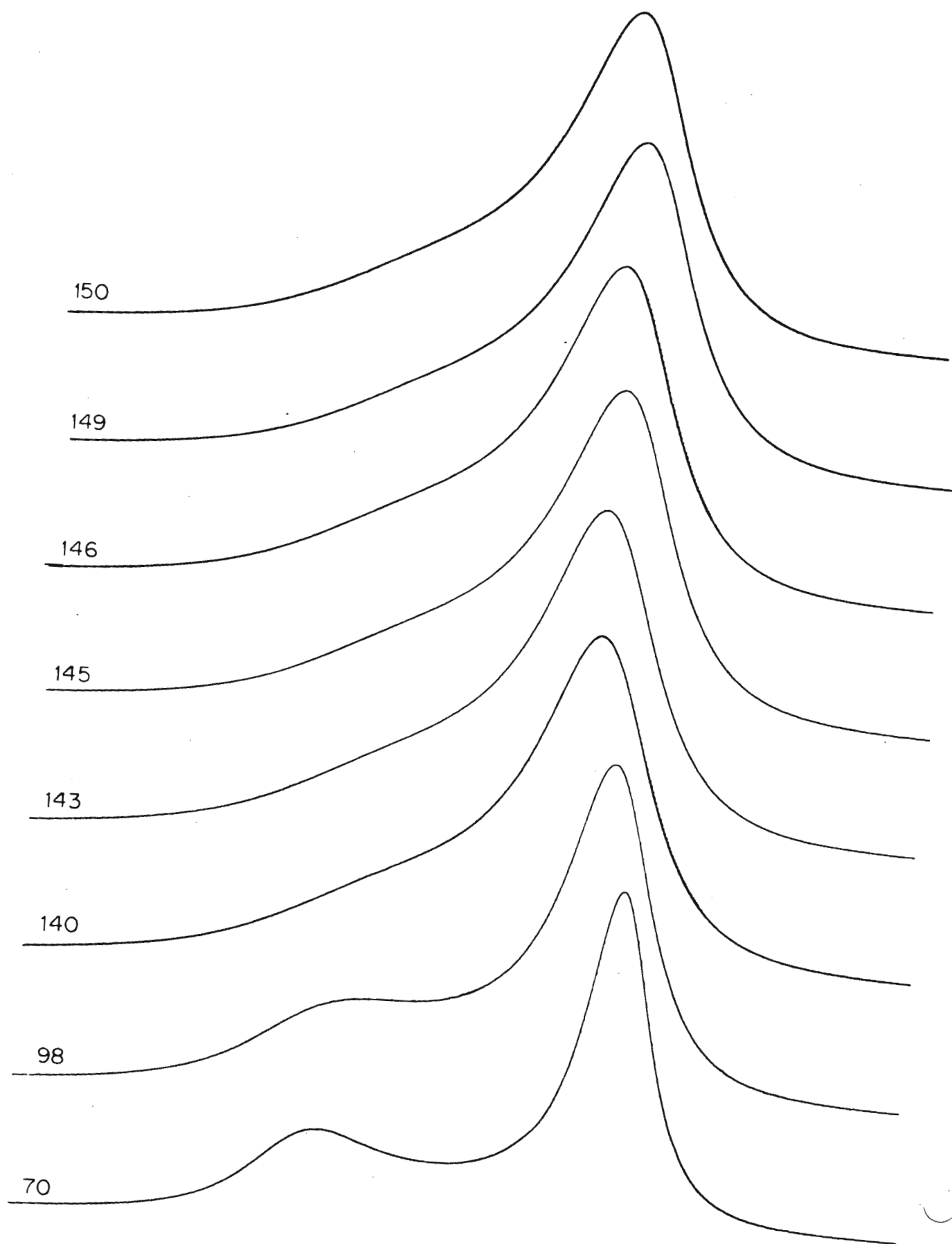
Yours sincerely,


R.R. Fraser


J.-L. A Roustan

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- (1) D. Kost, E.H. Carlson and M. Raban, Chem. Commun, 656 (1971).
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- (3) H.S. Gutowsky TAMU Newsletter, Circum 1974.
- (4) C. Piccinni-Leopardi, O. Fabre and J. Reisse, Org. Mag. Res. 8, 233 (1976).





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March 1, 1979

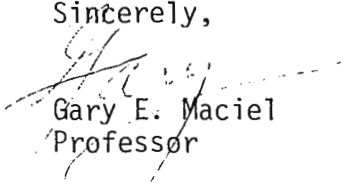
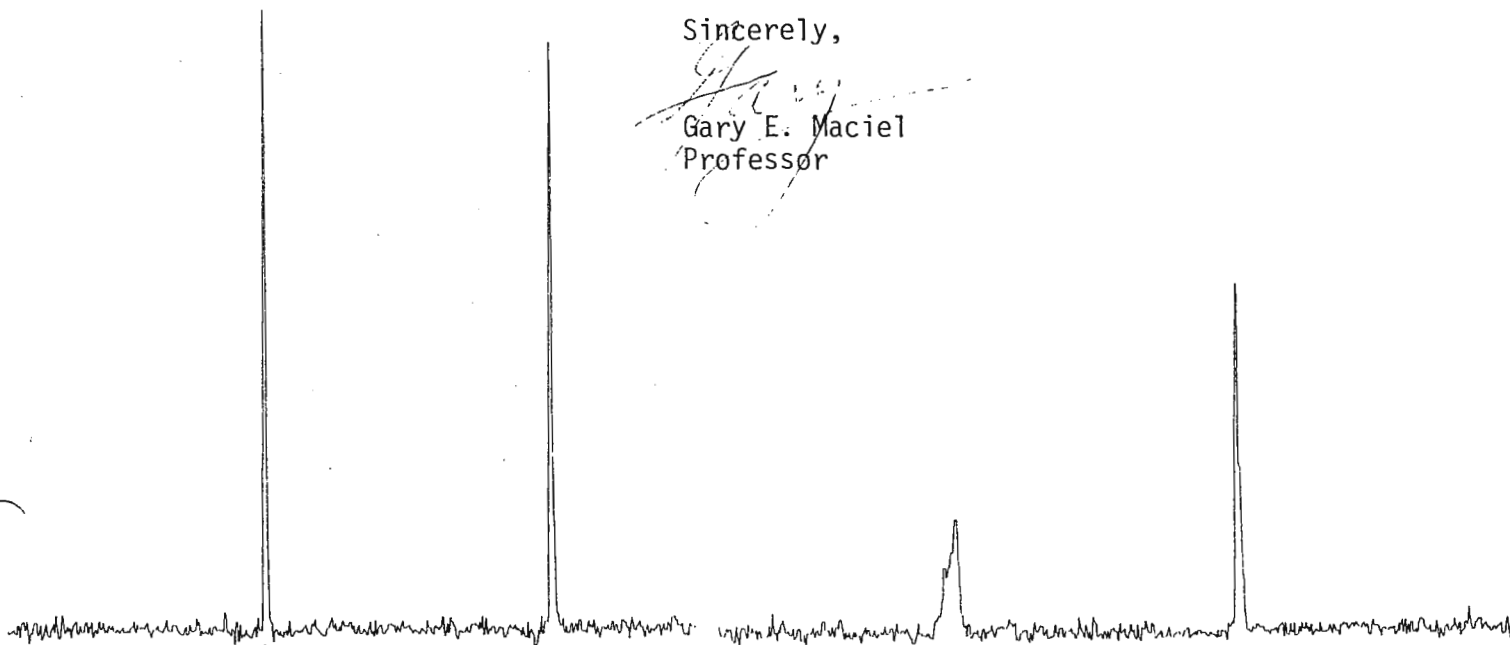
Colorado State University
Fort Collins, Colorado
80523CP/MAS Spectra with ^{13}C and Other NuclidesProf. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

In addition to the many ^{13}C experiments we have been carrying out with cross polarization and magic-angle spinning techniques, we have been employing these techniques to other spin- $\frac{1}{2}$ nuclides. To date we have obtained spectra on ^{29}Si (mainly minerals), ^{31}P (mainly structural models for five coordinate phosphorus), ^{113}Cd (inorganic and organometallic complexes), ^{199}Hg (inorganic and organometallic complexes), and ^{207}Pb (organometallics). In our preliminary ^{13}C work with Grignard reagents and carbonium ions, the need for a reliable low-temperature capability has become acute, and now consumes a considerable effort.

In evaluating the performance of our solid-sample spectrometers, we find hexamethylbenzene to be a good test sample. The spectra below are ten-scan spectra obtained at 14 kgauss with 11 gauss proton H_1 , 44 gauss ^{13}C H_1 and a spinning speed of about 2.4 KHz. The spectrum on the left, obtained at the magic angle, shows a 16 Hz linewidth on the aromatic peak. The spectrum on the right shows the effect of having the spinning axis displaced by 6 degrees from the magic angle. As is well known, the effect is much greater on the aromatic carbon, which has the much larger chemical shift anisotropy. This sample is also useful as a sensitivity standard; the spectra below were obtained on a 0.7 cm^3 sample without apodization.

Sincerely,


Gary E. Maciel
Professor

University of Durham

Department of Chemistry

Science Laboratories, South Road, Durham, DH1 3LE
Telephone: Durham 64971 (STD code 0385)

7th March, 1979.

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

Dear Professor Shapiro,

CONTROL PROGRAMS

For those who are interested in NMR control programs and home-built spectrometers we can offer details of a program which has been developed for a Varian 620/L (20k) computer. It controls a spectrometer based on a PE/R10 magnet which, although ancient, has proved its worth. The program handles FIDs of 2k and 16 bits length or 1k and 32 bits and occupies 7.25 - 9.25k of memory (locations 023660 - 045724) depending on whether the facility of spectrum saving is used. It obeys about 40 commands which can be automatically linked and was intended to deliver upto eight pulses before accumulation of FIDs. It needs the following Varian peripherals (a) analogue to digital converter; (b) buffer interface controller and (c) a 10 bit analogue output drive, and also these home-built units (d) pulse programmer; (e) miscellaneous drivers and timers and (f) an optional controller of a frequency synthesiser. We can supply descriptions of these controllers and a program text (80 pages) together with a binary tape to interested readers.

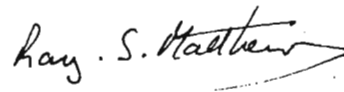
A similar program for a PDP 11/34 is being written and could be supplied on a floppy disk.

If anyone in the U.S. or Canada is interested in an exchange of non-teaching jobs for one year then R.S.M. will answer all enquiries.

Yours sincerely,



A. Royston



R.S. Matthews

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23rd February 1979

Your Reference:

Our Reference: CJT/PME

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

Dear Professor Shapiro

As the new VARIAN NMR Applications Chemist for U.K.,
Holland and Scandinavia I should like to receive TAMUNMR
Newsletter, thus I enclose a contribution.

Sn-119/Sn-117 Primary Isotope effect on Tin Magnetic
Shielding

Primary Isotope effects in NMR are of perennial interest.
An example of such, is the suggestion (1) that in organo-
tin compounds the tin magnetic shielding depends on which
of the isotopes (117 or 119) is studied. It has been
claimed that a significant primary isotope effect exists
which may exceed 2 p.p.m. in certain cases. In itself,
such a large effect would be surprising since the mass
difference is less than 2% and other pairs of isotopes eg
N-14/15 (2) with larger relative mass differences have
been found to have much smaller primary isotope shielding
effects. Furthermore, the species for which the effects
were said to be largest (Tetraethyltin and Triethyltin
Chloride) are those with the most complicated proton-
coupled tin spectra, and this makes it doubtful whether
'H- {Sn} experiments can achieve the necessary precision.

Direct observation of the proton decoupled tin spectrum
is now the best method to determine tin chemical shifts,
since with adequate proton-decoupling power the tin spectrum
can be reduced to single line.

For these experiments we used the Broadband probe on the
FT-80A to determine both Sn-119 and Sn-117 resonance
frequencies for any particular sample without removing the
sample from the probe or disturbing the field-frequency
locking condition.



The results indicate that any Sn-117/119 isotope effect on tin magnetic shielding is less than 0.1 p.p.m. on compounds chosen to give complex proton coupled tin spectra.

Yours sincerely

C J Turner

Dr. C. J. TURNER
NMR Applications Chemist

TABLE

Compound	$\frac{119}{117}$ frequency frequency	$\frac{119}{117}$ ratios
Me ₄ Sn in deuterio acetone	$\frac{29.661915}{28.342806}$	1.0465412
Me ₃ Sn SPh in ³ deuterobenzene	$\frac{29.664546}{28.345321}$	1.0465411
Ph ₂ Sn CL ₂ in ² deuterobenzene	$\frac{29.660904}{28.341840}$	1.0465412
(Bu ₃ Sn) ₂ O in ³ deuterobenzene	$\frac{29.664211}{28.345002}$	1.0465411
(Me ₃ Sn) ₃ P in ³ deuterobenzene	$\frac{29.662854}{28.343704}$	1.0465412

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Mol. Phys (1971), 21, 179
- (2) E.D. Becker, R.B. Bradley and T. Axenrod
J. Magn. Res., (1971), 4, 136

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2nd March, 1979

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

Dear Barry,

Deceptive simplicity in the ^{13}C spectra of 2,6-difluoropyridines

Examination of the proton-decoupled ^{13}C spectra of a series of 2,6-difluoropyridines with a variety of other substituents on the ring has revealed that the resonance of the 3,5 carbons shows a characteristic triplet structure with the unusual feature that the central line is weaker than the two outer ones. This is illustrated for the case of 2,6-difluoropyridine itself.

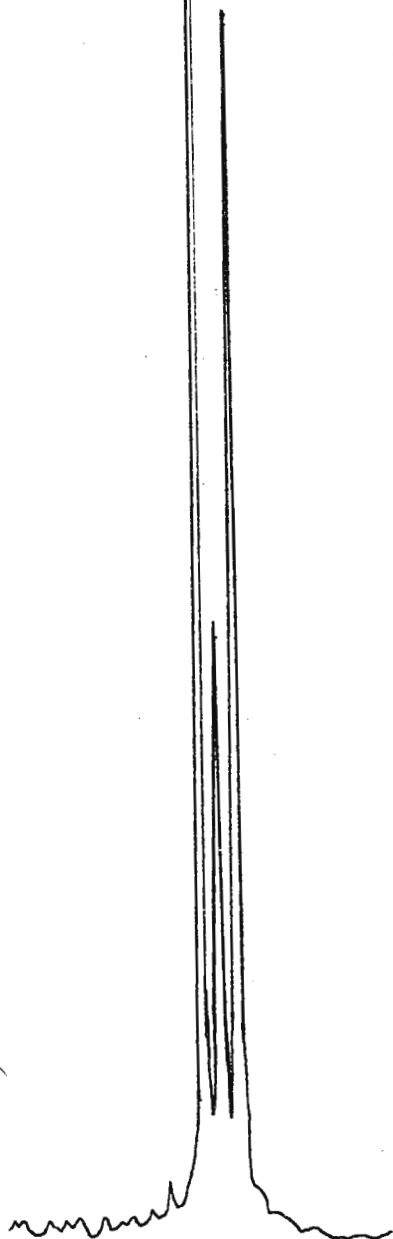
The splitting arises from coupling with the 2,6-fluorines and the spin system is of the $\text{AA}'\text{X}$ type. The transition energies and intensities of the X (^{13}C) spectrum are readily obtained from the ABX case by putting $\delta_{\text{AB}} = 0$. The four transitions then occur at $\nu_{\text{X}} - N$, ν_{X} , ν_{X} and $\nu_{\text{X}} + N$ since $D_+ = D_-$ in the usual nomenclature. The corresponding intensities are 1, $\frac{1}{2}[1 + \cos(\phi_+ - \phi_-)]$, $\frac{1}{2}[1 + \cos(\phi_+ - \phi_-)]$, and 1 but in this case $\cos(\phi_+ - \phi_-)$ must be negative. Only the value of $N = \frac{1}{2}(J_{\text{AX}} + J_{\text{BX}})$ is measurable from the splitting but the correct intensity ratio is obtained with values of $J_{\text{AX}} \sim 35\text{Hz}$ and $J_{\text{BX}} \sim 5\text{Hz}$.

I hope that this will suffice to reinstate my name on the mailing list.

Yours sincerely,



John A. Ladd



GENERAL ELECTRIC

CORPORATE
RESEARCH AND
DEVELOPMENT

GENERAL ELECTRIC COMPANY, RESEARCH AND DEVELOPMENT CENTER, P.O. BOX 8
SCHENECTADY, NEW YORK 12301, Phone (518) 385-2211

March 2, 1979

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

Dear Barry:

^{199}Hg NMR Studies of Organomercuriation Reactions

After several attempts to interpret the rather complex ^{13}C spectrum of the product of mercuriation of poly(phenylene oxide) with mercuric trifluoroacetate, we decided to see if ^{199}Hg NMR was useful for studying this type of reaction. The spectra shown in the figure were obtained on a Varian FT-80A with the broadband probe (^{199}Hg at 14.2 MHz). The sample shows the products of reaction of a model compound, 3,5-dimethyl-4-methoxydiphenyl ether, with an equimolar amount of mercuric trifluoroacetate. Field desorption mass spectrometry shows the presence of both mono- and dimercurated species in the reaction mixture. It is interesting to note the change in product distribution from ca. 2 hours after completing the reaction to 3 weeks later. The chemical shifts of peaks B-E relative to A are: B, -4.8; C, -8.8; D, -18.9; E, -23.6ppm.

We think this may be a very useful method for monitoring these reactions. We are currently looking at other model systems and trying to assign A-E.

Sincerely,



E. A. Williams

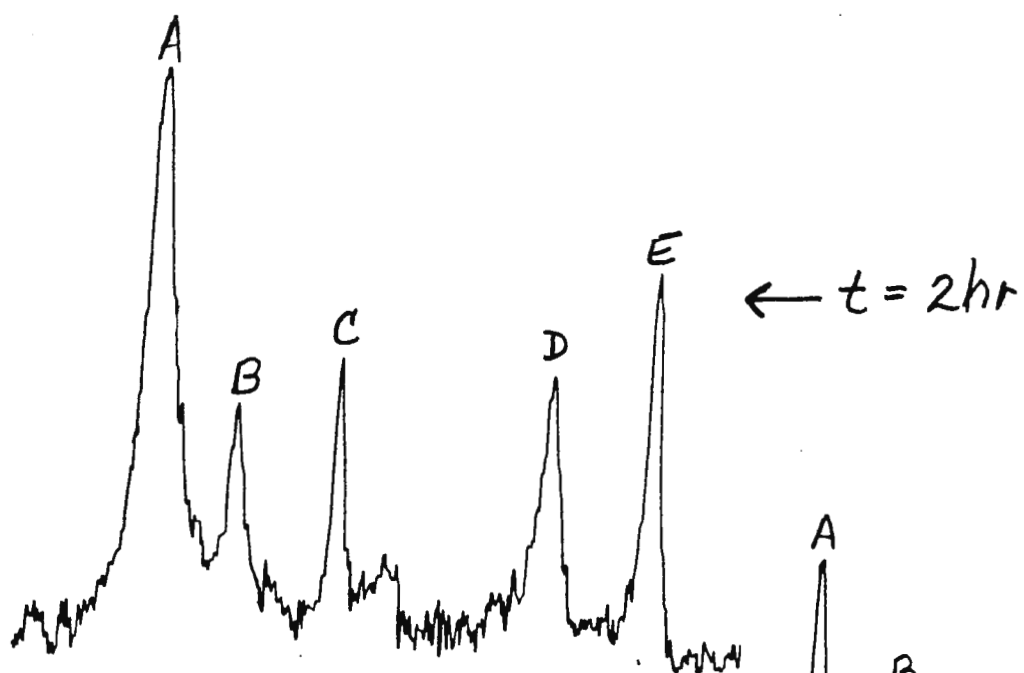


J. D. Cargioli

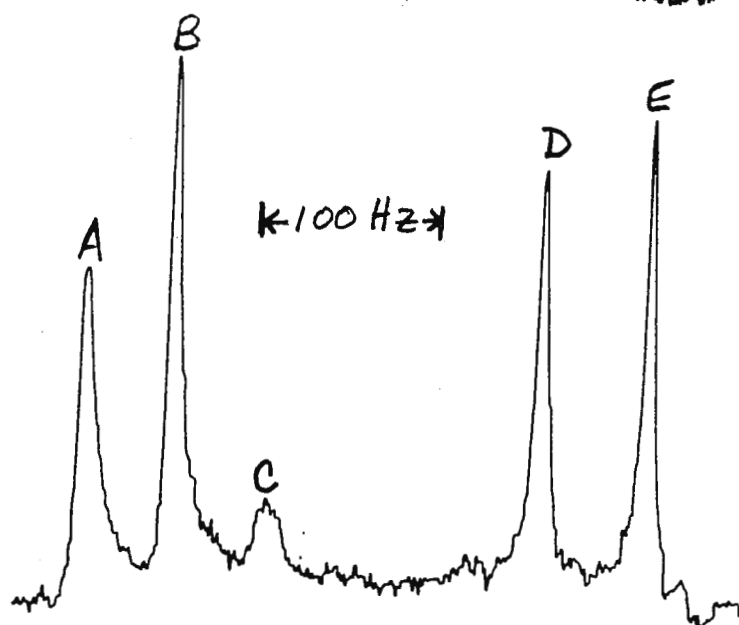
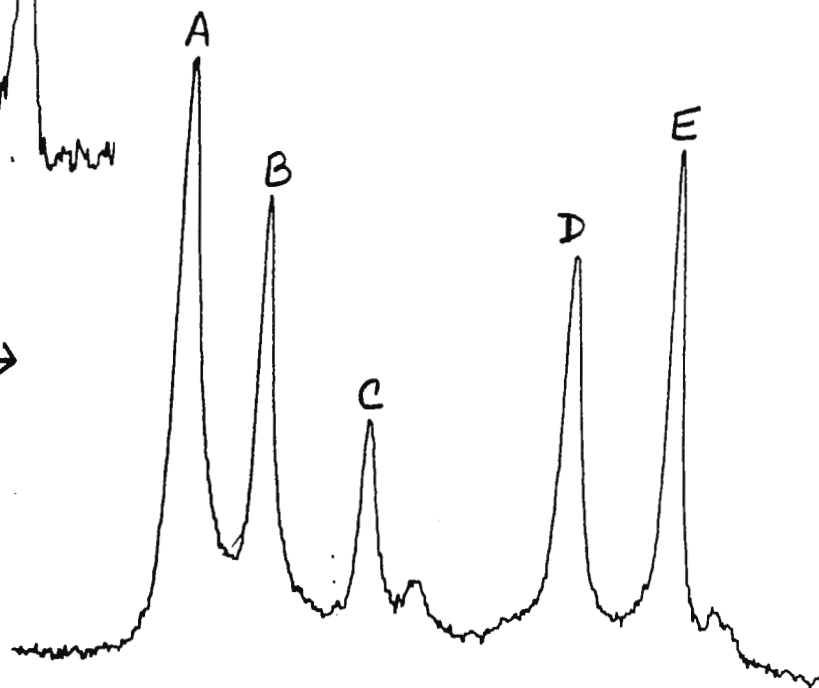


P. E. Donahue
Chemical and Structural Analysis Branch
MATERIALS CHARACTERIZATION LABORATORY

EAW/JDC/PED:ldr



$t = 24 \text{ hr} \rightarrow$



$^{199}\text{Hg} (14.2 \text{ MHz})$

College of Sciences

DEPARTMENT OF CHEMISTRY AND GEOLOGY



February 28, 1979

Professor A. L. Beyerlein
Professor G. B. Savitsky

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

Re: Response to P. Diehl's comments on Quadrupole Coupling Constant Measurements.

Dear Professor Shapiro,

Professor P. Diehl's letter in the January 1979 TAMUNN NMR Newsletter is concerned with the application of vibrational averaging corrections to both NMR relaxation data and nuclear quadrupole coupling constant measurements using NMR methods. We are in general agreement with much of the content of the letter regarding quadrupole coupling constant measurements. However, we believe that the citing of our paper² as an example of "what can go wrong" if vibrational corrections are neglected is unfair and not cognizant of the discussions in our paper. Our paper compares our measurement of the quadrupole coupling constant for the CD bond in benzene with that of P. Diehl and C. L. Khetrapal.³ It is concluded that the two values compare well and pointed out that the discrepancy of 5% could result from the neglect of vibrational corrections which could affect the two measurements differently. Professor Diehl's application of vibrational corrections to our data¹ simply confirms this conclusion⁴ and it is therefore very misleading to use our paper as an example of what can go wrong if vibrational corrections are neglected.

In general, vibrational averaging is only one of several factors (isotope effects⁵⁻⁷; solvent effects⁸, electric field asymmetry about the CD bond, and the amount and accuracy of molecular structure data required to calculate the quadrupole coupling constant from NMR data) affecting the measurement of the

quadrupole coupling constant of the CD bond. Our work^{2,5-7,9} has been concerned with the development of a method which utilizes the ^{13}C -D dipolar splitting in the ^2H spectrum. Many of the above named effects on quadrupole coupling constant measurements are minimized or completely eliminated with this technique because all relevant NMR data are obtained from a single ^2H spectrum, and the application of the method is not affected by molecular symmetry or isotopic substitution and requires only one molecular structure parameter, the CD bond length. When comparing quadrupole coupling constants measured with this method with those obtained by other methods, all factors influencing the measurements, especially vibrational corrections which are known to lower the measured quadrupole coupling constant, were always considered.

The method for making vibrational corrections is well understood. However, its application requires some time and effort and, until recently, the corrections were for the most part only reported for very small molecules. Therefore because the primary purpose of our papers has been to show how one can take advantage of our method to obtain accurate quadrupole coupling constants, we felt justified in neglecting both vibrational and electric field asymmetry corrections to the experimentally obtained values, being fully aware that they will have to be made in the future either by us or other workers. This conforms with the previous practice of Diehl⁸ as well as other investigators.

It is important to have very accurate quadrupole coupling constants, which include vibrational averaging and electric field asymmetry corrections, for interpreting such data in terms of molecular structure and for converting ^2H relaxation times to correlation times. Therefore we are currently applying these corrections to all of our data. A portion of this work⁷, which was performed in collaboration with J. W. Emsley has recently been published. The remainder of this work will be published very soon.

References

1. P. Diehl, TAMUNN NMR Newsletter, 244-11 (1979).
2. J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, J. Magn. Resonance, 31, 347 (1978).
3. P. Diehl and C. L. Khetrapal, Can. J. Chem., 47, 1411 (1969).
4. Professor P. Diehl in Ref. 1 compares our results with data from P. Diehl and M. Reinhold, Mol. Phys., 36, 143 (1978) rather than from Ref. 3. We were not aware of the later work when we submitted our paper (Ref. 2) for publication

March 10, 1978. However since Diehl and Reinhold's work is in agreement with their earlier work (Ref. 3), provided one accounts for the fact that vibrational averaging is included in Diehl and Reinhold's work and not included in Ref. 3, cognizance of the later reference would not have affected our conclusions.

5. J. B. Wooten, G. B. Savitsky, J. Jacobus, and A. L. Beyerlein, J. Chem. Phys., 66, 4226 (1977).
6. J. B. Wooten, G. B. Savitsky, A. L. Beyerlein, and J. Jacobus, J. Magn. Reson., 29, 35 (1978).
7. J. B. Wooten, G. B. Savitsky, J. Jacobus, and A. L. Beyerlein, and J. W. Emsley, J. Chem. Phys., 70, 438 (1979).
8. P. Diehl, M. Reinhold, and A. S. Tracey, J. Magn. Reson., 19, 405 (1975).
9. J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, J. Chem. Phys., 65, 2476 (1976).

Sincerely,



A. L. Beyerlein
Professor of Chemistry



G. B. Savitsky
Professor of Chemistry

University of Illinois at Urbana-Champaign²⁴⁷⁻¹⁸

School of Chemical Sciences
DEPARTMENT OF CHEMISTRY
Roger Adams Laboratory
Urbana, Illinois 61801

March 14, 1979

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

Dear Barry:

I thank you for your reminder of the time passing by too quickly.

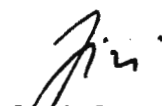
We have recently been involved in designing a new high-pressure, high temperature NMR system using a wide-bore (110 mm with room temperature shim coils) high resolution, superconducting magnet. I hope that within several months we shall be able to report some results.

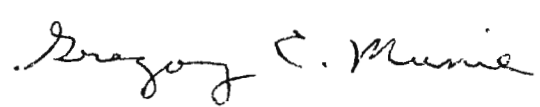
Among other things, we finished an experimental study of the effects of crosslinking on molecular motion in samples of cis-1,4-polybutadiene with well defined crosslink density. We have investigated the temperature dependence of the proton T_1 , T_2 , and $T_{1\rho}$ relaxation times at several frequencies, but, as expected the proton T_2 values are most sensitive to network formation. At high temperatures well above T_1 minimum, T_2 's exhibit "pseudo-solid" behavior reflecting the nonzero averaging of dipolar interactions due to anisotropic motion of chain segments between crosslinks. Also, the magnitude of T_2 , say at 60°C, is proportional to the average mass between crosslinks. We are currently carrying out a more detailed systematic study of the effects of crosslinks and entanglements using well defined monodisperse polymer systems.

Since I am a chairman of the coming Gordon Research Conference on Magnetic Resonance, I would like to add that its program has just appeared in the March 16 issue of Science. This conference will be held June 18-22, 1979 at the Brewster Academy in Wolfeboro, New Hampshire.

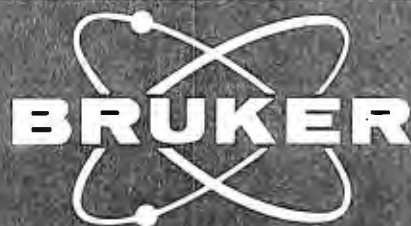
Best wishes.

Sincerely yours,


Jiri Jonas
Professor of Chemistry

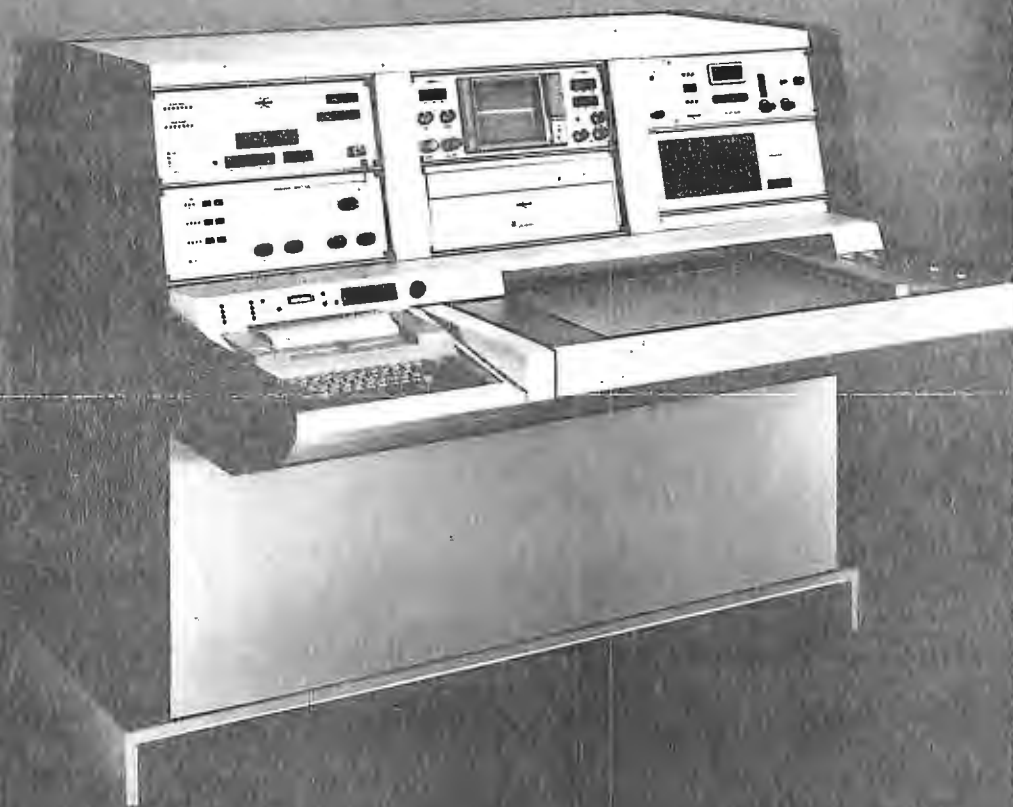

Gregory Munie
Graduate Research Assistant

JJ:kam



BRUKER announces a new landmark
in low-cost high-resolution
superconducting NMR spectrometers with

^1H frequency of 250 MHz



THE JOHNS HOPKINS UNIVERSITY
SCHOOL OF MEDICINE
725 N. WOLFE STREET · BALTIMORE, MARYLAND 21205

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

23 March 1979

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

Dear Dr. Shapiro:

³¹P NMR of Living Mammalian Tissues

There appears to be no end of what we will manage to fit into the NMR probe and obtain useful phosphorous spectra of. The latest experiments involve the use of live mice. These animals are anesthetized and mounted on a plastic rod (Figure 1) head down or hind quarters down to get spectra of the brain or skeletal muscle, respectively. A 25 gm mouse fits into the 25 mm probe of our WH-180 system quite nicely.


The effects of "respiratory acidosis/alkalosis" (changes in the CO₂ concentration of the gas mixture used to ventilate the animal or changes in the rate of ventilation) and "metabolic acidosis" (altering the blood pH by administration of acid) have been studied. Typical results for skeletal muscle are shown in Figure 2. Spectrum A is a typical control and spectrum B shows the effect of mild respiratory alkalosis (following a brief period of acidosis) on pH. There is an approximate 0.15 pH unit change toward more alkaline in B as compared with A. Spectrum A took 7.5 minutes (150 accumulations; 3 sec. cycle time) and B took 10 min. (200 accumulations).

The spectra of mouse brain are not of as good a quality as the muscle. This is probably the result of several problems, including matching the coil impedance, poorer filling factor compared with the hind quarters, the large lipid content of the brain and possible effects of the anesthetic. In general, the brain spectra have much broader lines. T₁ and T₂ measurements should help determine what the differences between brain and muscle tissues are.

Saturation transfer studies of the kinetic effects of these pH changes are being conducted in the living mouse as well. The combination of high resolution spectra (for chemical shift and quantitative data) and saturation transfer (for kinetic data) provides a very useful set of experimental data for physiological studies.

Please credit this letter to the subscription of Dr. Hollis.

Sincerely,


Ray L. Nunnally

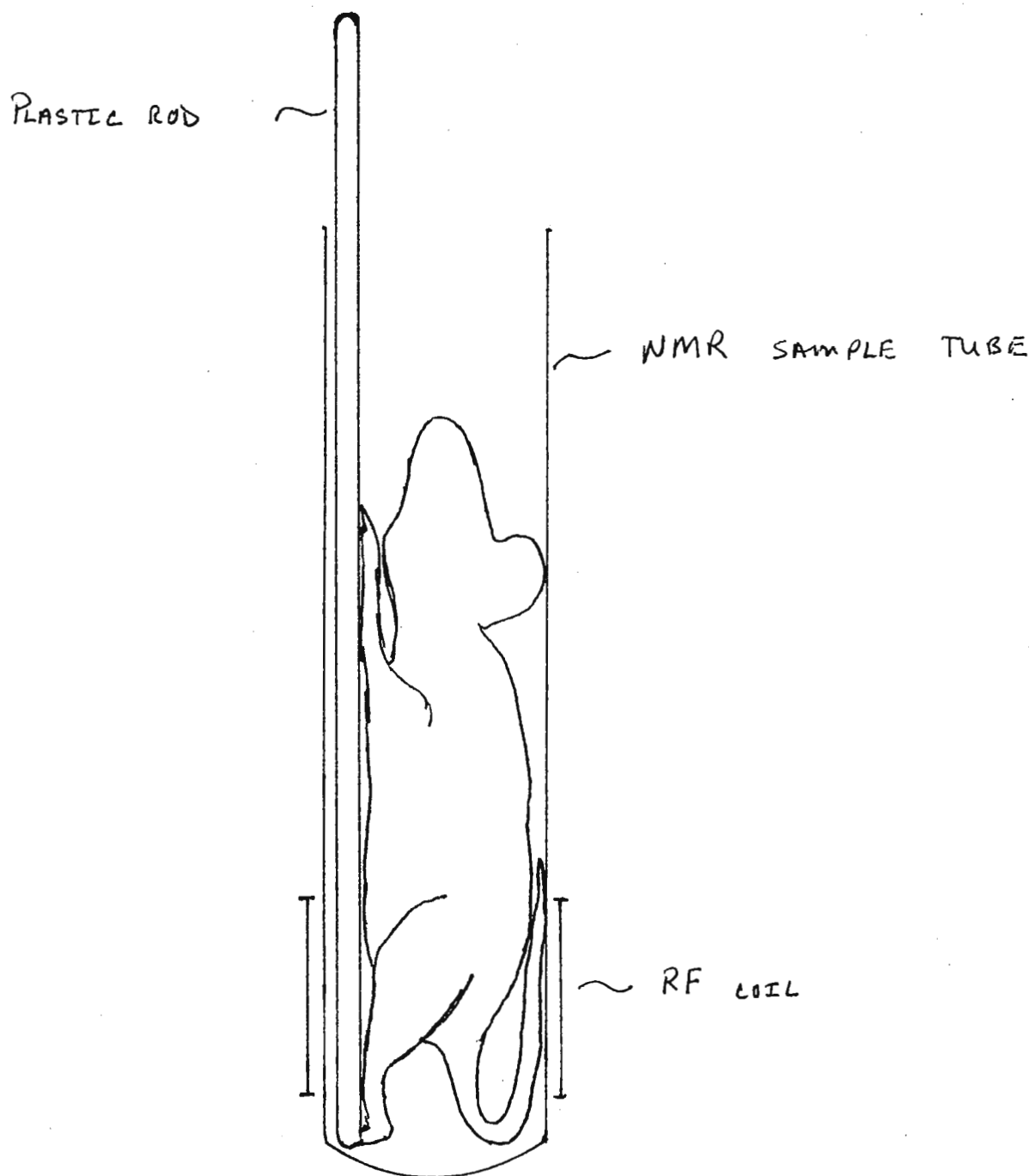


FIGURE 1

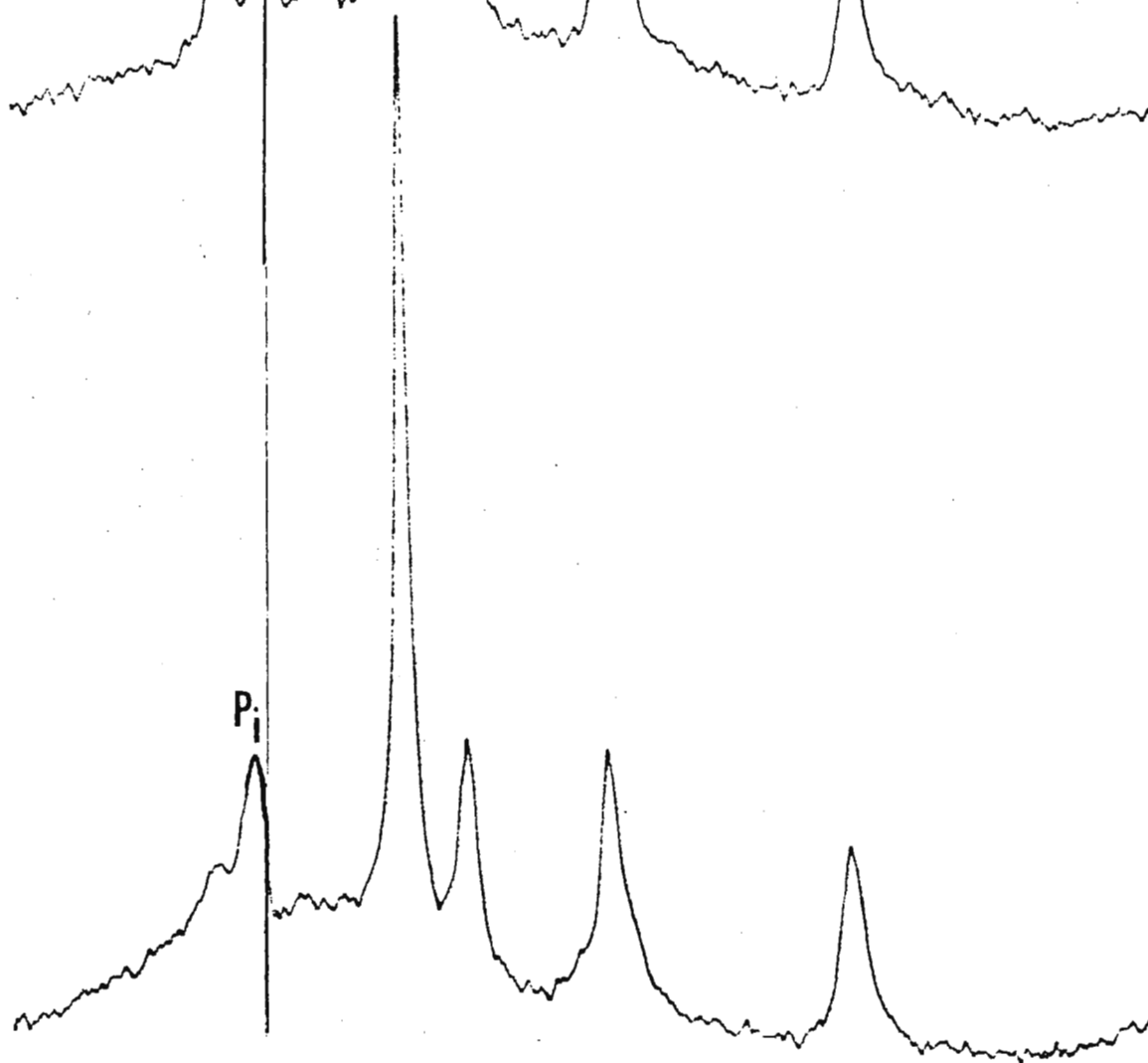
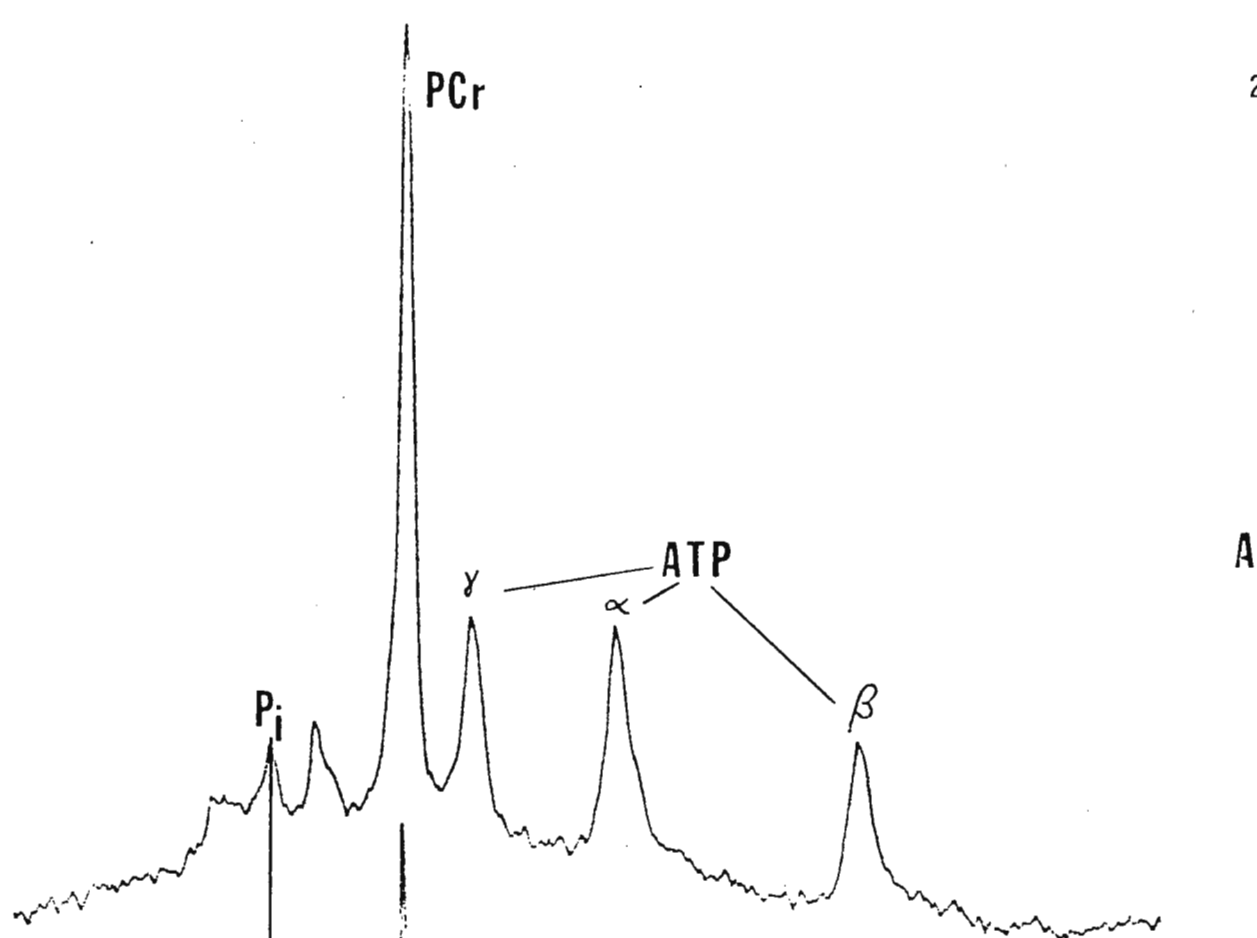


FIGURE 2

DEPARTMENT OF CHEMISTRY
TEL. (403) 432-3254
TELEX 037-2979



THE UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA
T6G 2G2

March 6, 1979

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

Re: ^1H Homodecoupling on the Digilab FTS/NMR-3

Dear Barry,

We have recently incorporated homodecoupling hardware for ^1H on our Digilab FTS/NMR-3-HA-100 system. All it requires is the homodecoupling card (available from Digilab), a synthesizer and several mixers. Shown in the figure are some results. The bottom trace is the normal spectrum covering a 200 Hz window; the top trace is with decoupling of the most deshielded proton. Details are available from Glen Bigam who did all the modifications.

Recently we have made some additions to our NMR facilities. The Bruker WH-200 and WH-400 spectrometers have arrived and seem to be operating very well. The WH-200 is a widebore system (20 mm) and is equipped for multinuclear operation (10-85 MHz). The WH-400 is set up for ^1H , ^{19}F , ^{31}P , ^{13}C and ^2H .

Sincerely,

Tom

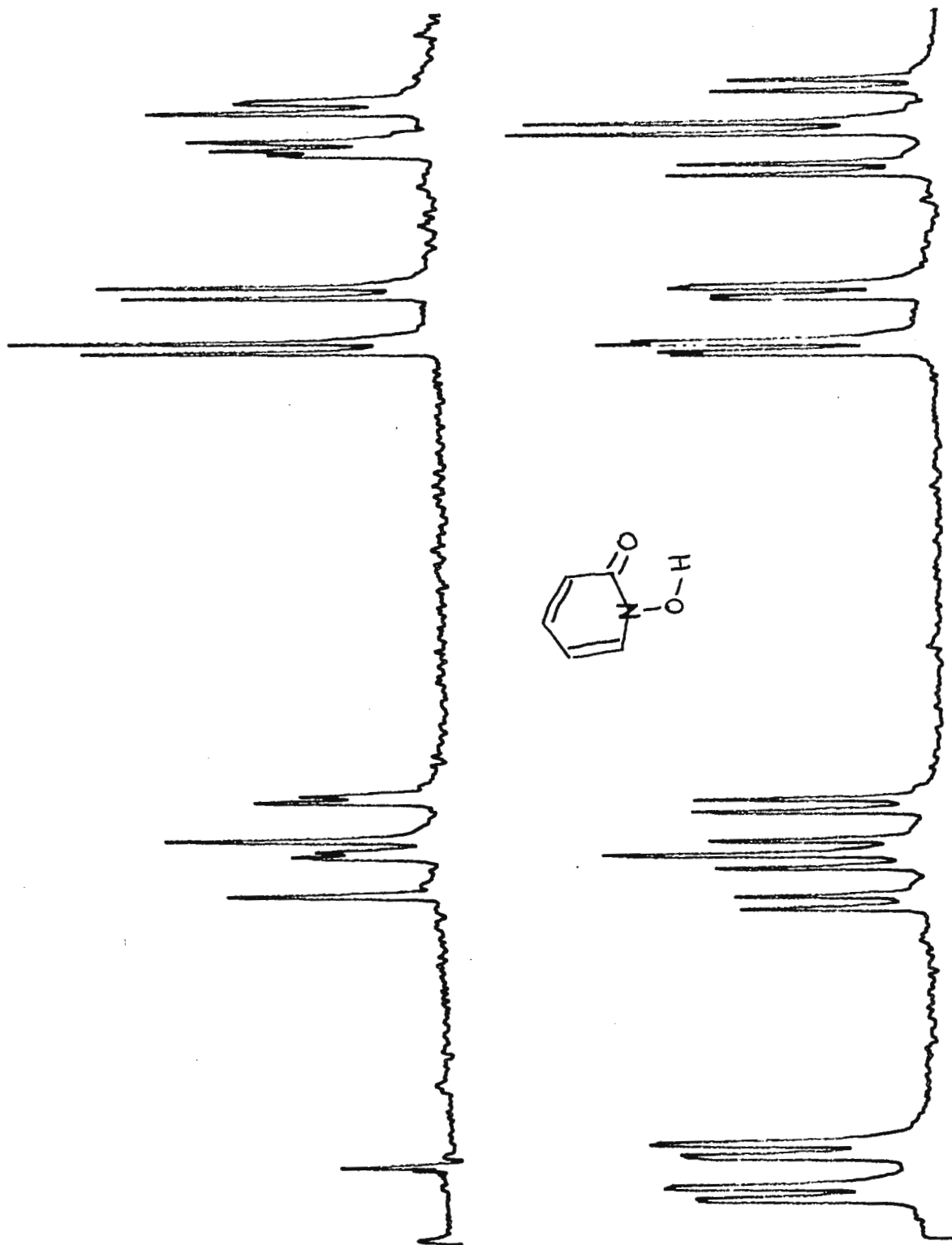
Tom Nakashima

TN/ss

DEPARTMENT OF CHEMISTRY
TEL, (403) 432-3254
TELEX 037-2979



THE UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA
T6G 2G2



CHEMICAL CENTER

PHYSICAL CHEMISTRY 2

Lund, March 15, 1979

Prof. B.L. Shapiro
Dept. of Chemistry
Texas A&M University
College Station
Texas 77843
USA

Dear Barry,

Re: ^{23}Na NMR of DNA, tRNA and DNA-polyamine
interaction

We have been carrying out some ^{23}Na relaxation studies on DNA and tRNA at 2.3T (XL-100) and at 6T on our new home-built wide-bore multinuclear spectrometer. At 2.3 T for the Na^+ -DNA interaction T_1 and T_2 appear very similar, whereas at 6T they differ and we have made a preliminary estimation of τ_c about 1 ns. The relaxation effects for tRNA appear greater per phosphate group than for DNA and we estimate a τ_c of roughly 2 ns for the Na^+ -tRNA interaction.

We have also observed the interaction of Mg^{2+} with DNA and tRNA by the decreasing ^{23}Na linewidth on titration with Mg^{2+} . The titration curves are now under analysis by Håkan Wennerström and Gudmundur Gunnarsson in our lab in terms of polyelectrolyte theories.

In a similar manner as for Mg^{2+} , we have been studying the interaction of polyamines and DNA using ^{23}Na NMR. The di-, tri- and tetra-amines all appear to bind with a stoichiometry of ~1 N per DNA-phosphate group although the different levelling off effects for the three are intriguing (see diagram).

UNIVERSITY OF LUND

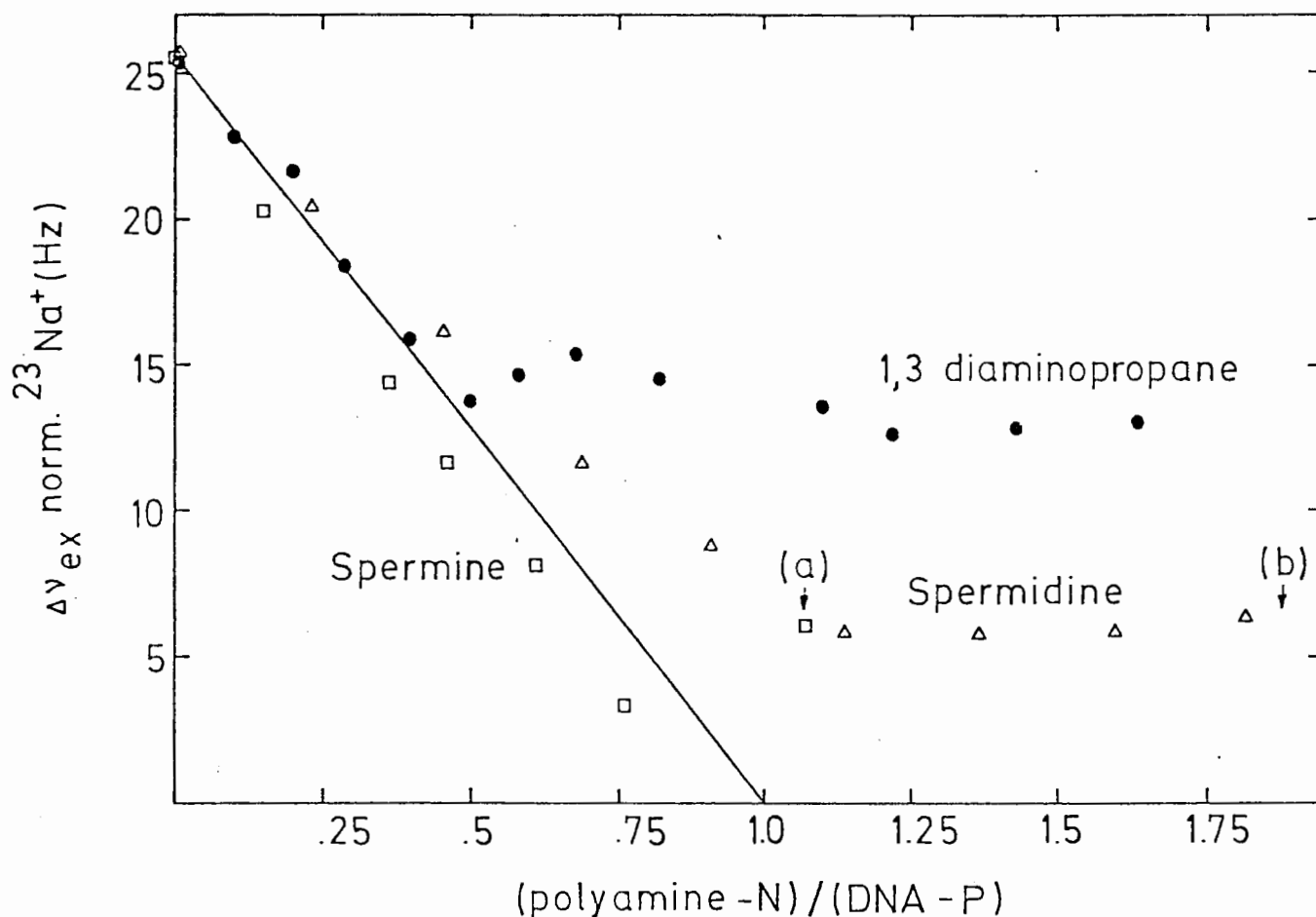
LUND INSTITUTE OF TECHNOLOGY

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GETINGEVÄGEN 60
LUND C

Phone
046-12 46 00
12 46 20




Cable
CHEMCENTER
SWEDEN



Conditions: $\text{Na}^+ \sim 60 \text{ mM}$, DNA-P normalised to 16 mM in each case, pH = 6.8, T = 4°C (a) and (b) indicate the onset of precipitation for spermine and spermidine respectively.

Future plans include the interaction of other positively charged species, such as histones, with DNA by ^{23}Na NMR and even the use of other metal nuclei.

Best wishes




 Sture Forsén Dennis Burton Pétur Reimarsson



247-27

Rijksuniversiteit Utrecht

Organisch chemisch laboratorium

Croesestraat 79
Utrecht 2503
Telefoon 030-882311

Prof. B.L. Shapiro
Texas A & M University
College Station, Texas 77843
U.S.A.

Datum March 19, 1979

Uw kenmerk

Ons kenmerk

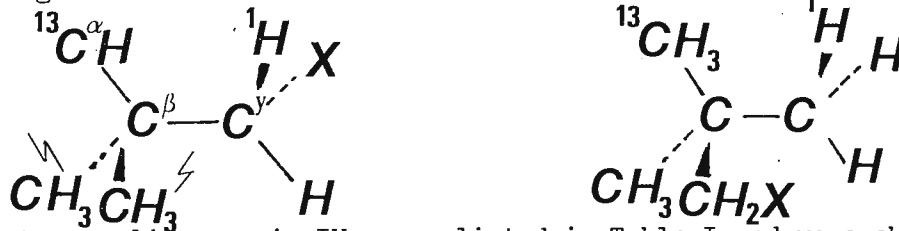
Onderwerp

TITLE: γ -Substituent Effects on $^3J(C-H)$ in Aliphatics.

Dear Prof. Shapiro,

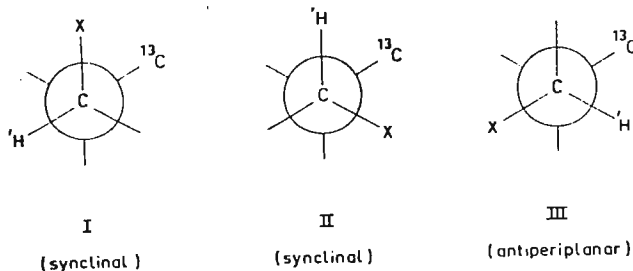
The following is our "Renewal" for subscription to the TAMU NMR Newsletter.

In the scope of conformation studies by means of $^{13}C-^1H$ coupling constants we have calculated the γ -substituent effects on $^3J(C-H)$, Δ^{γ} , in the coupling pathway $^{13}C^{\alpha}-C^{\beta}-C^{\gamma}-H$ with respect to $^3J(C-H)$ in propane (5.86 Hz)(Ref. 1). Neopentyl compounds have the advantage that all three $C^{\beta}-C^{\gamma}$ rotamers (I, II and III) occur in equal populations ($p_I=p_{II}=p_{III}$). Two different types of vicinal $^{13}C-^1H$ coupling constants can be measured (IV a and b):



Only the couplings as in IV a are listed in Table I and were obtained through selective 1H -decoupling of the indicated Me-resonances. These couplings were corrected twice for the known β -Me-effect, $\Delta^{\beta}_{CH_3} = -0.57$ Hz (Ref. 2). The values thus obtained are the $^3J(C-H)$'s in the corresponding n-propyl compounds for equal rotamer populations. A plot of these values against the Pauling electronegativity, E_x , yields a straight line:
 $^3J(C-H)(p_I=p_{II}=p_{III}) = -0.4 E_x + 5.9$ ($r = 0.95$).

The observed $^3J(C-H)$ values in n-propyl compounds deviate from this line. The observed values are weighted averages of the coupling constants in the three rotamers:



Ref. 1: T. Spoormaker and M.J.A. de Bie, Rec. Trav. Chim. Pays-Bas, **98**, 59, (1979).

Ref. 2: J.E. Anderson, C.W. Doecke and H. Pearson, J. Chem. Soc. Trans 2, **1976**, 336.

If the observed values of the coupling constants in the case of the first row elements of the periodic table are plotted against E_x one obtains the line: $^3J(C-H)_{obs.} = 0.4 E_x + 3.0$ ($r = 0.98$).

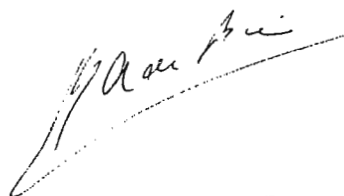
Going from the element C to N, O and F one observes a decrease in $\Delta(^3J_{C-H}^{calc.} - ^3J_{C-H}^{obs.})$ with increasing substituent electronegativity, which can only be explained by a decrease of p_{III} with respect to p_{II} , which is equal to p_I .

This observation is completely in line with the hypothesis that the attracting interaction between $CH_3CH_2^-$ and XCH_2^- dipoles counteracts their sterical repulsion.

Finally, the pure γ -increments to $^3J(C-H)$, Δ_x^γ , with respect to $^3J(C-H)$ in propane are listed in the last column of Table I.

X	E_x	Table I.				
		neopentyl	n-propyl comp.		Δ	Δ_x^γ
		$^3J(C-H)$ observed	$^3J(C-H)$ calc. for $p_I = p_{II} = p_{III}$	$^3J(C-H)$ observed		
CH_3	2.55	3.87	5.0	4.0	1.0	-0.9
NH_2	3.04	3.59	4.73	4.3	0.4	-1.1
OH	3.44	3.50	4.64	4.4	0.2	-1.2
F	3.98	-	-	4.6	-0.2*	-1.5
Cl	3.16	3.54	4.68	4.5	0.2	-1.2
Br	2.96	3.62	4.76	4.5	0.3	-1.1
I	2.66	3.72	4.86	4.7	0.2	-1.0

*est.


M. J. A. DE BIE


T. SPOORMAKER

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

March 23, 1979

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

Dear Barry:

Return of magnetization after an inversion-recovery pulse sequence follows a time dependence of the form

$$M_z(t) = M_0 - 2 M_0 e^{-t/T_1}$$

In an exchanging system (two sites, A and B), in which magnetization flows from one site to the other, the time dependence assumes a double exponential form (c_1 , c_2 , λ_1 , and λ_2 depend on T_1^A , T_1^B , and τ).

$$M_z^A(t) = M_0^A + c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t}$$

We have exploited this behavior to extract rates from coalescing relaxation times.

We examined dimethylformamide in order to compare our kinetic results with those from lineshape studies. All our measurements were made at temperatures below the onset of any lineshape perturbations. The first figure shows the apparent temperature dependence of the $T_1(\text{eff})$ for the methyl resonances, as calculated from the usual single exponential expression. The effective A and B relaxation times coalesce by about 70 °C. Least-squares regression analysis of the data according to the double exponential expression gives quite a different picture (second figure). The true methyl T_1 's have the usual dipole-dipole dependency on temperature and do not coalesce. The single exponential $T_1(\text{eff})$'s correspond to the actual T_1 's only in the slow exchange limit below 35 °C. Above 70 °C they coalesce to a value that corresponds to the mean of the true T_1 's.

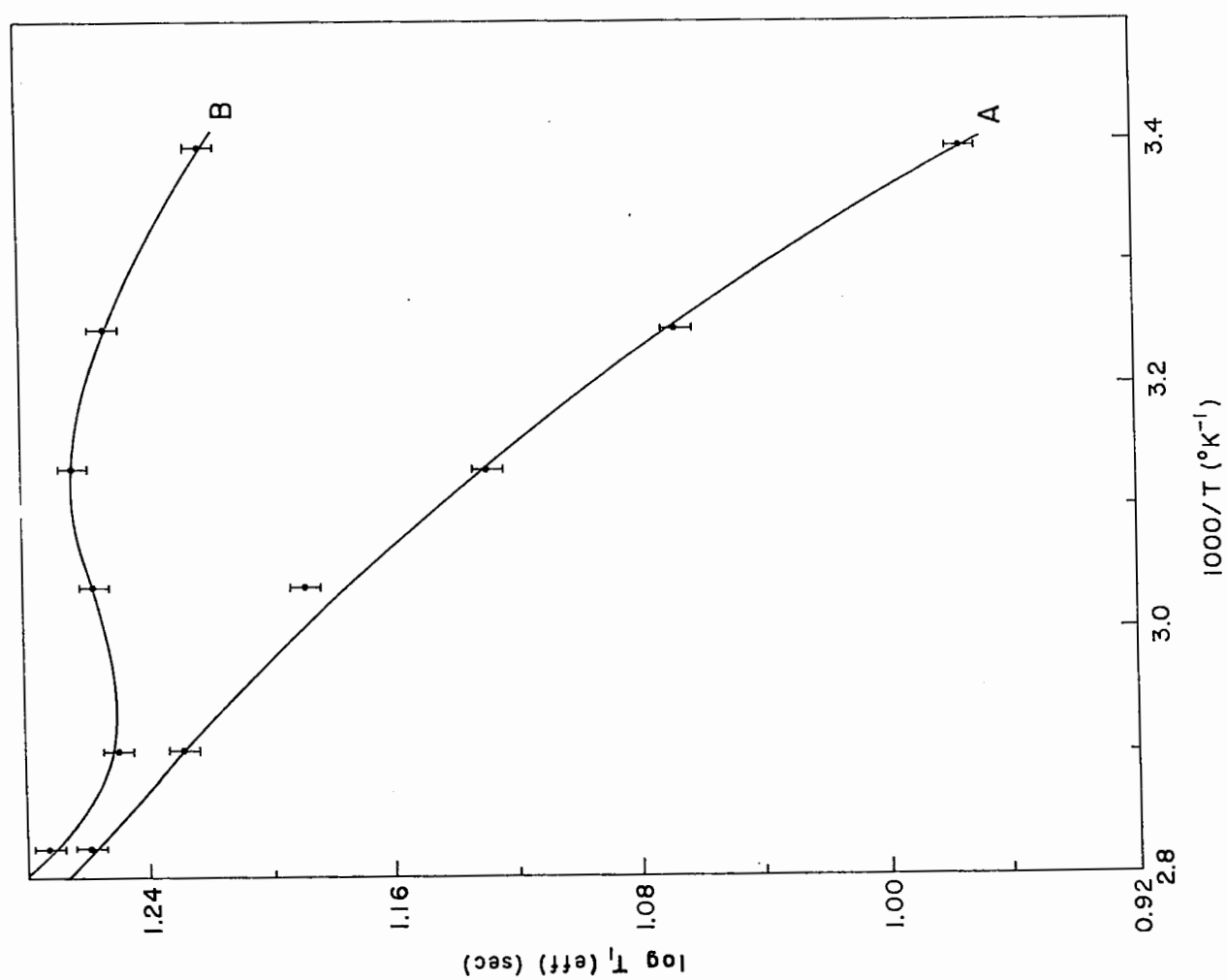
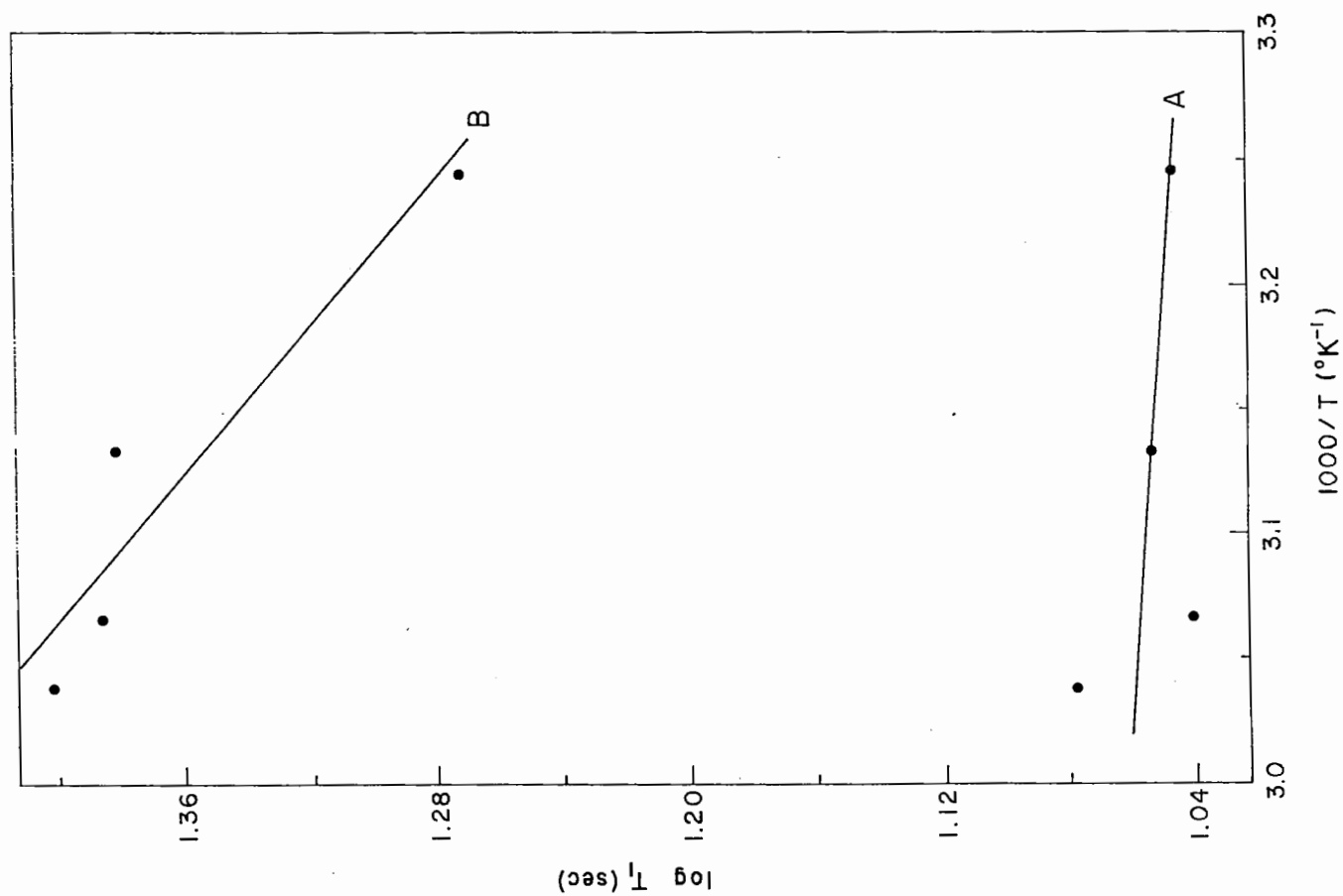
This approach not only gives the correct T_1 's in the entire temperature range but also gives τ (the reciprocal of the exchange rate constant). The method is independent of the relative values of T_1^A and T_1^B . The resulting rate constants are very close to those calculated from the lineshape approach at much higher temperatures. Thus we can measure barriers by relaxation time coalescence that are out of range of the lineshape coalescence method.

Sincerely,


 Joseph B. Lambert

Joe W. Keepers

Rates from the Coalescence of Relaxation Times



UNIVERSITY OF MUNICH

8000 MUNICH 2

INSTITUTE OF ORGANIC CHEMISTRY
KARLSTRASSE 23GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

March 23, 1979

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



Dear Barry:

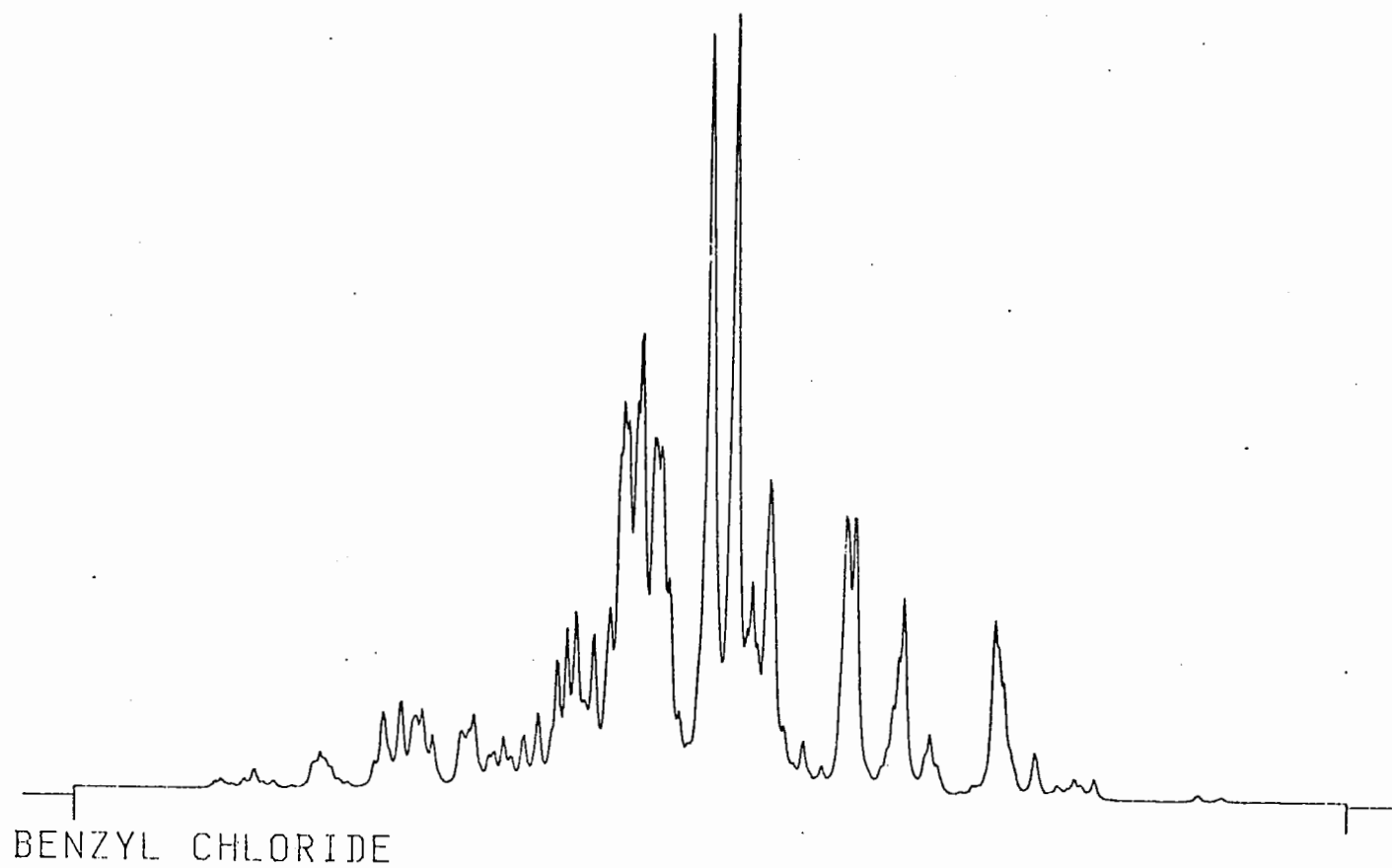
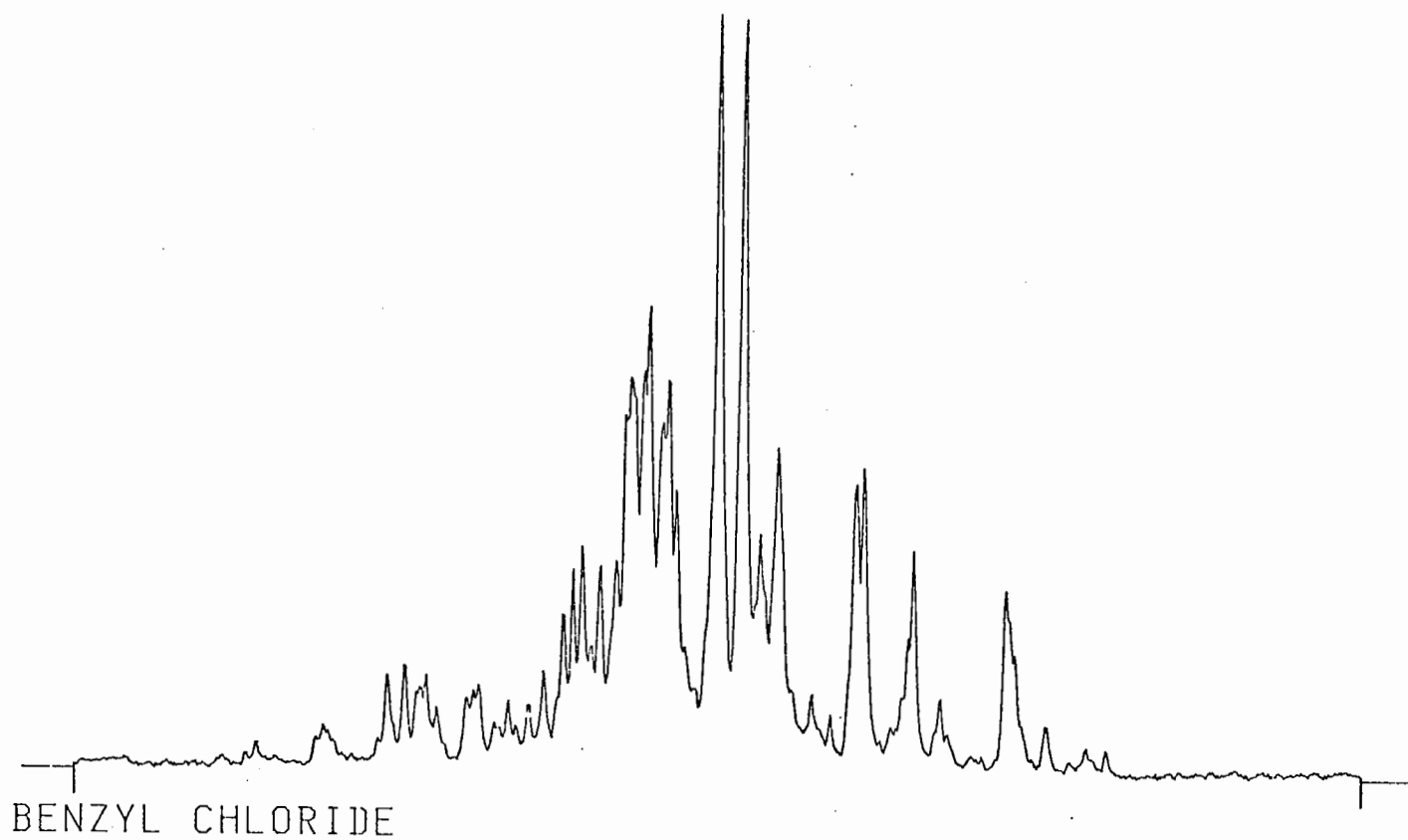
We wish to announce that DAVINS, known to your readers under his adolescent name of DAVIN1 (TAMU NMR Newsletter 231, 33 (1977)), is now fully grown up and has surpassed the fondest expectations. You may now start to throw away all your other NMR analysis computer programs. Two papers describing the computational principles embodied in DAVINS and his performance in practical applications have been submitted to *JMR* in February 1979. The program itself is presently being tested by QCPE and will shortly be made available by them (on a tape), together with a 55-page document.

On the Figure we illustrate a typical application of DAVINS to the aromatic region of the $[AB]_2CD_2$ proton spin system of benzyl chloride. The preprocessed experimental spectrum is shown on top. Preprocessing includes data format conversion (from the 16-bit words of a VDM computer to the 60-bit words of a CDC), pretruncation, baseline flattening, smoothing and posttruncation, all performed automatically. The computed spectrum shown on the bottom was calculated without assigning a single line. The results are (in Hz)

ν_A	=	739.722 \pm 0.002	$^4J_{AC}$	=	1.242 \pm 0.004
ν_B	=	733.191 \pm 0.002	$^5J_{AB'}$	=	0.605 \pm 0.003
ν_C	=	728.937 \pm 0.004	$^4J_{AD}$	=	-0.491 \pm 0.003
$^3J_{AB}$	=	7.752 \pm 0.005	$^5J_{BD}$	=	0.295 \pm 0.004
$^3J_{BC}$	=	7.497 \pm 0.005	$^6J_{CD}$	=	-0.331 \pm 0.006
$^4J_{AA'}$	=	1.978 \pm 0.006	$W_{1/2}$	=	0.148 \pm 0.002
$^4J_{BB'}$	=	1.406 \pm 0.006			

The cited errors are honest-to-God errors, completely free of human bias since they are based on the total information content of the spectrum and not just on the frequencies. The global R factor was 0.8 % .


David S. Stephenson
Gerhard Binsch



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March 26, 1979

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

Dear Barry,

The methodology described below may be obvious to the more sophisticated nmr researchers, but a sufficient number may benefit from it to warrant exposure of this generally applicable approach in the Newsletter.

A System Which Allows Rational Evaluation and Choice of Instruments

Basically:

1. Analyze your needs for the intended time span of use of the instrument.
2. Merge this with the capabilities offered by instruments on the market.
3. Finalize your scale of values.
4. Rank each choice, including costs, support.

It is important to do a good job on 1. before the others. It is the last time you have a clear head, before the manufacturers open the flood gates of their information on you. On the other hand precisely through the latter, one may wish (in 2.) to add to one's list capabilities that one didn't know of before.

A good set of sealed, stable (unchanging) test samples must be made up after 1., possibly enlarged during 2.

Practical details:

Feature listing. Write down on individual slips of paper all capabilities, features, properties, assets, possible faults and danger points, parameters of the instruments, you can think of. It is advantageous for the later evaluation to have these broken down to as elementary components as possible.

Examples would be "Resolution, ^1H , 5-mm" and "Resolution, ^1H , 10-mm", "Spectrum subtraction" and not " ^1H performance", "Software features".

The list would include all features which would enter the decision, including details of warranties, (time) response to service requests, details of service contracts, probability of honoring obligations based on track record in house and with other owners.

Order the features into your preferred logical sequence along one (e.g. left vertical) axis. Paste or write them down, leaving plenty of space for additions. (Ideally, computer storage, updating and manipulation of the

resulting large matrix can be done, but the end calculation is very simple:). One may then, on the left edge list in a hierarchical fashion the titles, composite names for groups and families of the elementary features, e.g. "¹³C capabilities", "Decoupling" "Software" "Support". Such hierarchies are often multidimensional; the best projection into one dimension determines the sequence of elementary features. It is useful to leave spaces so that summary grades can be entered for these composite features. A large space at the end of the list will make it "open ended" until final showdown.

Choice of Values. One assigns the elementary features each a range of value or score around 0., usually a range of -n to +n, sometimes -k to +l ($k \neq 1$). Thus the dynamic range is 2n or (k+1) and resolution is unity. Very important features have n=large. Features whose presence is "understood", "natural", but which if not provided would mean great hardship, can have a large k. Conversely, non-essential but "come in handy", "a bonus", "extra" features can have low k but higher l.

[(Kepner-Tregoe Decision Analysis employs weight x score (score only positive) and a "must" list. We rejected this system because:

A "must"-list may leave one without an instrument.

There can be degrees to which a "must" is realized.

Hardly anything in this life is not subject to tradeoff.

Missing information is not easily accommodated, since a blank, taken as 0 (zero) in the summation equals the worst possible grade. It is unrealistic to assume that in evaluations all features for each alternative will be known. We take missing information as 0 = mean or slightly negative (since it is a reasonable assumption that if it were that good, the manufacturer would have prided himself by making it available).

Our system takes weighting into account automatically by the choice of $\pm n$].

Sum the $\pm n$ and -k +l's for the elementary features to arrive at the corresponding -K to +L range for groups, families, classes of features. This is not essential for the evaluation but provides a global look.

Note of caution: In feature classes where many items can be named one should check by summing that they will not unduly outweigh classes where only a single or few can be named.

Consistency in proper relative emphasis of features can be arrived at by two approaches: 1. Since the whole is made up of its parts, if one gives the elementary features the score range they deserve, the summary scores should come out correct. 2. One can decide on the summary score ranges and allocate (subdivide) them over the elementary features. The latter creates problems with adding features, may need decimal fractions, etc. Approach 1. seems better but should be checked via the summary score ranges for consistency.

Score ranges should be entered into a column adjacent to the features.

It is possible, but may not be necessary or desirable to assign a \$ value to a unit of score.

Feature 1	Score range	Instrument 1		Instrument 2
		Obs, data, comm.	Score	Score
	-20+20	-----	--	
2	-50+ 5	-----	--	
3	- 2+10	-----	--	
-	-	-----	--	
-	-	-----	-	
Group 1			xxx	xxx
Feature -	-			
-	-			
Group 2				
GRAND TOTAL				

Instruments and Observations, data on them. The perpendicular, e.g. top horizontal axis should list instruments to be compared. (These can include some obviously too simple or fancy beyond reach, for the sake of providing a framework.)

The matrix elements of the table accommodate comments (with a number of specification or observed result) and the score for each feature, each instrument.

Major alternative and mutually exclusive options, packages would have to be treated as distinct choices.

Add-on options could just be accommodated towards the end of the feature list.

In arriving at the score for each feature on an instrument, the following are considered: is it a numerical specification or feature which is guaranteed or just advertised or just promised for the future, was it observed in testing or did the instrument "have a headache", etc. The less concrete these are, the more the past reliability of the manufacturer has to be an indicator.

Evaluation: At a point when one has sufficient observations from testing, data from other users and from the manufacturers and one has reached agreement on support, service, etc., one simply adds the scores and titrates them against the costs, initial and on-going. Alternatively costs can be part of the feature list.

Without disclosing specific details, it should be stated that a spectrometer has been operating in our laboratory since 1973 without major disappointments in face of the rational evaluation of the kind described here, which lead to choosing it.

Sincerely,



Sandor Barcza

**CENTRAL RESEARCH**

PFIZER, INC., EASTERN POINT ROAD, GROTON, CONNECTICUT 06340
203 445 5611

March 8, 1979

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

SUBJECT: Undeemphasis on Proper Grammar

Dear Barry:

At the risk of undepolarizing the NMR community, I would like to undemobilize what opinion remains against the undecontamination of our language by such undemystifying jargon as the use of "undecoupled" to describe an NMR spectrum in its natural (i.e., spin coupled) state without a second perturbing experiment. While not being sure of the best method to undemount a challenge to those who act as if such terminology is deungrammatical, and tending to agree that such matters are hard to underegulate, perhaps by this forum I can begin to undepopulate the ranks of us who object before the usage becomes too unde-institutionalized to stop.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "E. B. Whipple".
E. B. Whipple

mjh

Dr. W. Bremser c/o

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Hauptlaboratorium

BASF

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Telex 464811 basf d (Zentrale)

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6700 Ludwigshafen, Girokonto 545 07300

Luftpost

BASF · 6700 Ludwigshafen

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

College Station, Texas 77843

U S A

Ihre Zeichen

Ihre Nachricht vom

Unsere Zeichen

Telefon-Durchwahl

Telex

Ludwigshafen

WHE-WBr/Dg

(0621) 60-

8401

464-

26.03.1979

Betreff

And again: substructure search

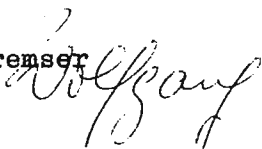
Dear Barry,

a week ago I received a copy of Bill Milne's contribution /1/ and with the ambition of a sportsman we tried our CNMR information system at the same problem. Here is the printout of our computer program, thus the readers may compare the slightly different philosophies behind these two approaches and enjoy a fair sportive competition across the ocean.

A few comments will help to understand the details despite the German text. The cnmr data collection /2/ presently contains 19,000 spectra of 15,000 different compounds with 72,000 different substructures characterized by HOSE-codes /3/. After constructing the desired fragment /4/ (here with '?' for undefined environment) the spectroscopist generates the HOSE-code of node 2 (command 'T2') and cuts it down to the desired length (here description of only two spheres). The substructure search ('J') generates 23 references. Their individual chemical shifts ('C') together with both mean and standard deviation can be listed in decreasing order together with solvent, reference number, daughter index and node and, if necessary, ambiguity mark (*). The first three entries result from delocalized positive charges, as can be seen from the list of the compound's names ('D'). In the same fashion structures and/or spectra can be edited, however, the printout is too spacious for TAMU. Obviously the description of the desired carbon atom with only α - and β -substituents is not precise enough, especially when a large data bank is at hand. Therefore the substructure search was repeated including a third sphere resulting in 5 references with a much smaller standard deviation of 0.6 ppm.

Despite the low cost of 2.41 DM (duration of the session 4 minutes) we favour the approach of direct estimation of complete spectra or individual lines via shift range registers /5/, because this technique is definitely faster and cheaper. Best regards,

W. Bremser



References:

- 1) C.L. Fisk, G.W. Milne, TAMU-NMR 245, 22 (1979)
- 2) W. Bremser, L. Ernst, B. Franke, Carbon-13 NMR Spectral Data, Verlag Chemie, Weinheim (1979)
- 3) W. Bremser, Anal. Chim. Acta 103, 355 (1978)
- 4) W. Bremser, E. Frank, B. Franke, W. Wagner, J. Chem. Res. in press
- 5) W. Bremser, TAMU-NMR 243, 9 (1978)

SYSTEM ?/C13NMR

B A S F 13 C NMR DATENSYSYEM

VERSION NOVEMBER 1977

GUTEN TAG, WIE GEHT ES IHNEN?

IHNEN NAMEN, BITTE
=BREMSE

WELCHES SYSTEM WOLLEN SIE BENUTZEN?

1. DATENSAMMLUNG
2. TEILSTRUKTURSUCHE
3. STRUKTUREINGABE
4. SPEKTRENBERECHNUNG
5. LINIENSUCHE
6. AEHNLICHKEITSSUCHE
7. NAMENSUCHE
8. HOSE/HORD REGISTER
9. FILEAUSDRUCK
10. BRUTTOFORMELSUCHE
11. MOLMASSEN-BERECHN.
12. ENDE
13. ?

ANFANGSBUCHSTABEN DES GEWUENSCHTEN SYSTEMS?
=TE

SUCHE NACH STRUKTUREN UND STRUKTURTEILEN

HOSE/HORD -- TEILSTRUKTUR-DATEI MIT
71884 KODES VON 14956 STRUKTUREN

WOLLEN SIE VOLLSTAENDIG NUMERIERTE STRUKTUREN?
=J

UND WEITER?
=>K4

1C 3C
 . .
 . .
 2C 4C

UND WEITER?
=2/3,4.?

1C 3C 5?
 . . .
 . . .
 2C 4C

UND WEITER?
=T2

STRUKTURKODE: %CC(C,/'?'/)

SUCHEN ?

=)

SCHREIBEN SIE EIN ')' UNTER DAS ERSTE GEKUEERZTE SYMBOL

%CC(C,/'?'/)
=)

STRUKTURKODE: %CC(C,/'

SUCHEN ?

=J

23 REFERENZEN GEFUNDEN

SUCHEN ?

=C

MITTELWERT 88.60 PPM ± 32.17 PPM

219.10 PPM (FS) 14463-0-02
 165.10 PPM (FS) 14465-0-03
 130.80 PPM (SF) 14560-0-03
 94.40 PPM (O2) 14474-0-03
 91.60 PPM (CD) 8434-0-12
 88.80 PPM (NR) 11657-0-02
 83.40 PPM (CD) 14464-0-03
 80.90 PPM (BD) 11655-0-09
 80.70 PPM (NR) 11660-0-02
 80.60 PPM (NR) 11656-0-02
 80.50 PPM (NR) 11661-0-02
 80.20 PPM (AD) 4831-1-03
 79.40 PPM (NR) 12071-0-02
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 75.20 PPM (CD) 4014-0-02
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 74.30 PPM (NT) 2586-1-02
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 73.70 PPM (NT) 2585-0-02
 73.60 PPM (NT) 4831-0-03
 72.00 PPM (CD) 10339-0-05

SUCHEN?

=D

BUTYNOYL CATION
 1-BUTYNOYL-FLUORIDE
 1,1-DIPHENYL-2-BUTYN-1-YL-CARBENIUM CATION
 1,1-DIPHENYL-2-BUTYN-1-OL
 4-METHYL-2-PENTYN-4-YL-CARBENIUM CATION
 4-METHYL-2-PENTYN-4-OL
 TRANS-1,2,3,4-TETRAMETHYL-3,4-DI(1-PROPYNYL)-CYCLOBUTENE
 CIS-4,6-DIOXA-3-(HEXA-2',4'-DIYN-1'-YLIDENE)-SPIRO(4.4)NON-1-E
 4,6-DIOXA-1,2-EPOXY-3-(HEXA-2',4'-DIYN-1'-YLIDENE)-9-HYDROXY-S
 TRANS-4,6-DIOXA-3-(HEXA-2',4'-DIYN-1'-YLIDENE)-SPIRO(4.4)NON-1
 1-METHOXY-PENT-1-ENE-3-YNE
 4,6-DIOXA-3-(HEXA-2',4'-DIYN-1'-YLIDENE)-9-HYDROXY-SPIRO(4.4)N
 DEC-2-ENE-4,6,8-TRIYNOIC ACID METHYL ESTER
 2,4,6-OCTATRIYNE
 2,4-HEXADIYNE
 1-(5'-PROPYNYL-2'-THIENYL)-2-(2'-THIENYL)ACETYLENE
 2-BUTYNE
 2-TRIDECYNE
 2-DODECYNE
 2-OCTYNE
 2-HEPTYNE
 2-HEXYNE
 2-BUTYNE-1-OL

CNM14560
 CNM14474
 CNM14465
 CNM14464
 CNM14463
 CNM14462
 CNM14125
 CNM12071
 CNM11661
 CNM11660
 CNM11657
 CNM11656
 CNM11655
 CNM11650
 CNM10339
 CNMR8434
 CNMR4831
 CNMR4014
 CNMR2588
 CNMR2587
 CNMR2586
 CNMR2585
 CNMR0483

SUCHEN?

=F

1C 3C 5?
 2C 4C

UND WEITER?

=5#C,5.?

1C 3C 5C
 2C 4C 6?

UND WEITER?

=T2

STRUKTURKODE: %CC(C,/C/'?')

SUCHEN ?

=)

SCHREIBEN SIE EIN ')' UNTER DAS ERSTE GEKUEERZTE SYMBOL

%CC(C,/C/'?')

=

STRUKTURKODE: %CC(C,/C/

SUCHEN ?

=J

5 REFERENZEN GEFUNDEN

SUCHEN ?

=C

MITTELWERT 74.41 PPM ± 0.59 PPM

75.40 PPM (TC) 2585-2-02
 75.20 PPM (CD) 4014-0-02
 74.80 PPM (NT) 2587-0-02
 74.30 PPM (NT) 2586-1-02
 74.20 PPM (NT) 2588-0-02 (NT) 2586-0-02
 74.10 PPM (NT) 2587-1-02
 73.80 PPM (NT) 2585-1-02
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SUCHEN?

=E

WIEDERSEHN, HERR BREMSER
 AUF BALD

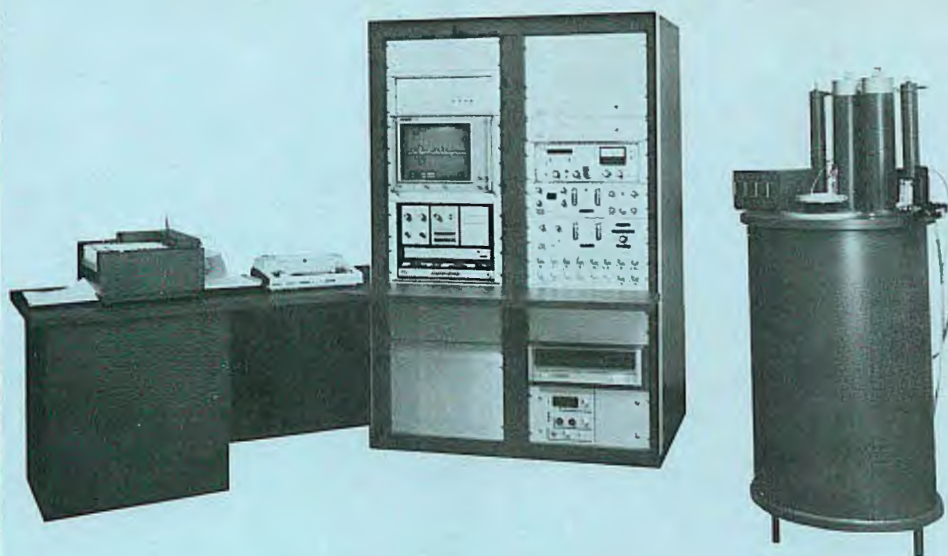
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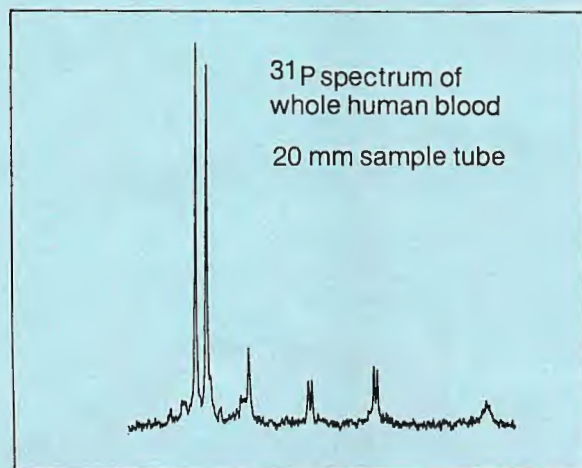
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