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POLICIES AND PRACTICAL CONSIDERATIONS

(Revised 1 September 1983)

1. Policy: The TAMU NMR Newsletter is a means for the rapid exchange of information among active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything." (This is usually followed by the mental reservation, "that won't land us in jail.") Virtually no editorial functions are performed, although I feel the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, still another discovery of non-equivalent methylene protons, etc., should not be considered adequate "for credit" (v.i.). The TAMU NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in. Foreign participants should not feel obliged to render their contributions in English.

2. Finances, Subscriptions, and Advertising: The Newsletter is wholly self-supporting, and depends for its funds on advertising, donations, and individual subscriptions. The subscription rate is \$90.00 for the twelve monthly issues beginning with No. 301 (October 1983). (Back issues are available at reduced rates.) A 50% academic or personal discount is available. Organizations and individuals are also invited to consider becoming a Contributor or Sponsor of the Newsletter and to have their organization's name appear in the appropriate list in each month's Newsletter, as well as gaining the satisfaction of knowing they are helping keep this non-profit Newsletter in a solvent configuration. We will be happy to provide further details to anyone interested.

A major, indeed essential, source of funding for the Newsletter is advertising. We earnestly encourage present and potential participants of the Newsletter to seek advertising from their company or institution. Our rates are modest - please inquire for further details.

3. Participation is the prime requisite for receiving the TAMU NMR Newsletter; in order to receive the Newsletter, you must make at least occasional technical contributions to its contents. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution you will receive a "Reminder" letter. If no contribution is then forthcoming ten months after your last contribution, you will receive the "Ultimatum" letter, and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by submitting a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given. Please note that "Position Available", "Equipment Wanted" (or "For Sale"), etc., notices are very welcome, but only on a not-for-credit basis, i.e., such items do not substitute for a bonafide technical contribution. Similar considerations apply to a few (quasi-) technical items as mentioned above.

Please Note: A subject of concern to several present and potential TAMU NMR Newsletter participants, as well as to ourselves, is whether the Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that a TAMU NMR Newsletter contribution should not duplicate, summarize, or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the Newsletter account. On the other hand, let it be firmly emphasized that if the appearance in a journal is several months away, a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the TAMU NMR Newsletter fulfills one of the very functions which we feel this Newsletter should provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the Newsletter audience before they could read it elsewhere.

4. Public Quotation: Public quotation of Newsletter contents in print or in a formal talk at a meeting, etc., is expressly forbidden (except as follows), and reference to the TAMU NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication."

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with, and abide by, these statements of policy and practical considerations.

5. Practical Considerations:

a) All contributions to the TAMU NMR Newsletter, which should be sent to the undersigned, will always be included in the next issue if received before the deadline dates which appear in each issue.

b) Contributions should be on the minimum (NOTE!!) number of 8 1/2 x 11" (21 x 27.5 cm) pages and printed on one side only. Margins should be between 2 and 3 cm on all sides - Please observe these limits. Black ink for typing, drawings, etc., is essential. We are not equipped to deal with large size pieces of paper, i.e., paper greater than 8 1/2 x 11" (21 x 27.5 cm).

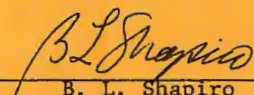
Please conserve space by avoiding double spacing (except where necessary), ultra-wide margins, half-filled pages, etc. In general, please plan and construct your contribution so as to fill the minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility when they are too small. Only in very rare and absolutely necessary circumstances will a contribution in excess of three pages--including drawings, figures and references--be accepted. Economic necessity requires this policy.

Since reproductions of various kinds often do not themselves reproduce too well, contributors are urged to submit their photographic originals to us (if the size does not exceed 8 1/2 x 11"), and we will be happy to return these if requested. Such originals should be mounted in place on the 8 1/2 x 11" pages.

c) Please provide short titles of all topics of your contributions, as they will ensure accuracy in preparing the table of contents.

d) Please do not send in manuscripts, theses, books, etc., and ask us to be your conscience in selecting what should and shouldn't go into the Newsletter.

6. Suggestions: They are always welcome.


B. L. Shapiro
1 September 1983

Address for all Contributions and Inquiries:

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College Station, Texas 77843 U.S.A.

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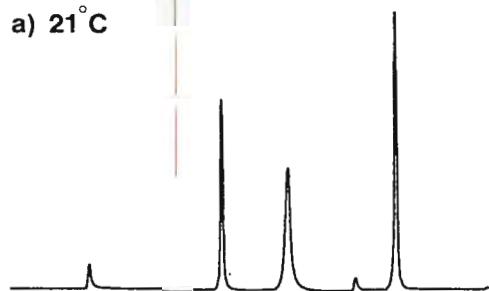
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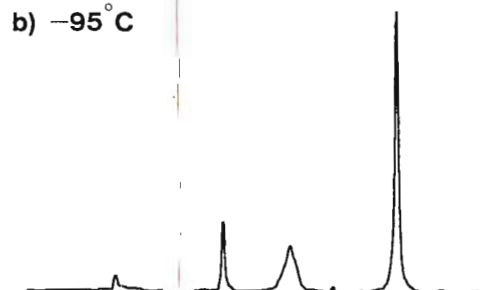
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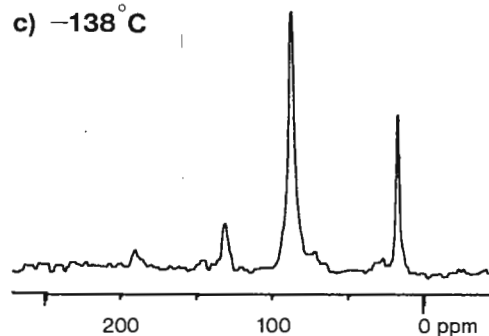
a) 21°C



b) -95°C



c) -138°C



¹³C (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) ¹H-¹³C cross polarization. b) Bloch decay. The peak at ~ 90ppm is due to the Delrin rotor.

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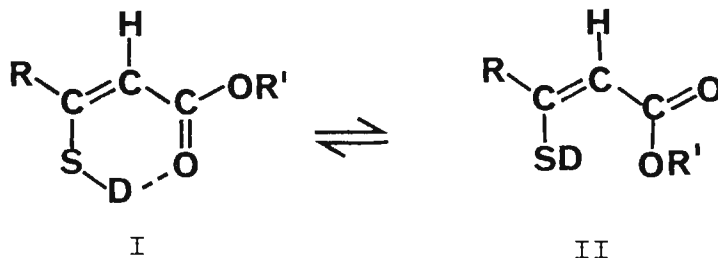
August 11 1983

Deuterium Isotope Effects and non-bonded Interactions.

Dear Prof. Shapiro

Your reminders allways hit me in the middle of my summer-holiday, but I hope my contribution reaches you in time to avoid a black-listing.

I have recently been collaborating with Dr. Fritz Duus of our institute on ^{13}C NMR of β -thioesters. We have shown, that deuterium isotope effects at the nuclear shielding of C-3 may be used to determine the amounts of the two rotamers I and II.



Furthermore, some of these compounds exist also on a non-hydrogenbonded form:

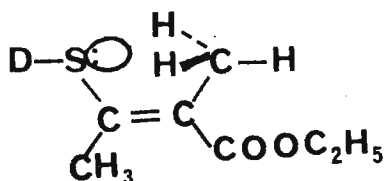


Fig. 2

In this form we could observe not only a deuterium isotope effect of 0.07 ppm at C-2, although the $-\text{SH}(\text{D})$ group is not directly hydrogenbonded, but also a three-bond $^3J(\text{C}-2, \text{SD})$

of 0.83 Hz, corresponding to a $^3J(\text{C-2,SH})$ of 5.4 Hz, was observed. The large magnitude proves, that the coupling pathway is predominantly trans, as shown in Fig. 2. Furthermore, a proton-proton coupling over five bonds, $^5J(\text{CH}_3, \text{SH})$ of 0.6 Hz could be observed. These observations show, that the -SH group exchanges slowly.

The reason is in our opinion, that a non-bonded interaction exists between the sulphur lone pair and the two C-H bonds of the methyl group.

We were also succesful in explaining a number of other trends in other cyclic and acyclic β -thioxo ester by taking into account non-bonded interactions.

These findings will be published in OMR in the near future.

Yours sincerely



Poul Erik Hansen

PS! I am presently preparing a review on: 'NMR of polycyclic Aromatics' to appear in Magnetic Resonance Review. I would be glad to receive recent reprints on this subject as well as preprints. The latter appeal is especially directed towards papers published in american journals as these arrive very late here.



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CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
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1983 August 11

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

Dear Dr. Shapiro,

²⁹Si Spin-Lattice Relaxation in Zeolites

Following Lippmaa's pioneering work (TAMU 264-9), ²⁹Si MAS has become an established method of studying composition and ordering in the framework of zeolites. Si-29 chemical shifts fall into five nearly distinct regions corresponding to the number of Al neighbors attached through oxygen bridges. If Lowenstein's rule (forbidding Al-O-Al linkages) is obeyed, the first moment of the spectrum is equal to 4/(Si/Al) (Melchior, *et al.*, J. Amer. Chem. Soc., 1982, 104, 4859). This framework composition may vary significantly from the bulk composition measured by elemental analyses.

Saturation must be avoided to ensure intensities are quantitative. Si-29 T₁s for a number of synthetic, hydrated zeolites have been measured at 60 MHz. The T₁s are relatively short, 5 to 30 s. in various zeolites. In a given zeolite, T₁s vary little between the Si(nAl) sites or with changes in Si/Al, so the Si-29 relaxation does not seem to be affected by neighboring Al-27 (quadrupolar, typical T₁ ca. 1-2 ms.). Quantitative spectra are obtained most quickly with small flip angle and short recycle delay.

Samples of Na⁺A (Linde 4A, ²⁹Si T₁ = 7 s.) were dehydrated (Si-29 T₁ = 49 s.) and saturated with D₂O (Si-29 T₁ = 33 s.). While the average water hopping rate in Na⁺A is known to be <10³/s. (Basler, Maiwald, J. Phys. Chem., 1979, 83, 2148), this result indicates a significant component of the spectral density of the proton motion at 60 MHz. The Si-29 {H-1} NOE was measured in hydrated Na⁺A and an inversion of the Si-29 resonance is observed; η = -1.10 (see Figure). Smaller NOE enhancements were also found in Na⁺Y (Linde LZ-Y52, η = -0.34) and Na⁺mordenite (Linde M-5, η = -0.15).

In solution, isotropic reorientation can produce Si-29 {H-1} enhancements of η = -2.52 to -0.51 in the fast and slow motion limits, respectively (note that the residual NOE in the slow motion limit is larger for a negative γ than for a positive γ nucleus). While the local proton motions in zeolites do not

follow this simple physical model, it is clear that the dipolar contribution to the Si-29 T_1 in Na⁺A is dominant. The lengthening of the T_1 after D_2O exchange, and the existence of an NOE also suggest that paramagnetic impurities (P. Barron, TAMU 294-15) do not play a significant role in hydrated, synthetic (low Fe) zeolites.

^{29}Si MAS spectra were obtained on a Bruker CXP-300. T_1 s were measured by composite pulse inversion ($90^\circ x, 180^\circ y, 90^\circ x$) T_1 recovery. NOE measurements were made by saturating protons with a train of composite 180° pulses ($\gamma H_2 = 45$ kHz) spaced 5 ms apart for a period of four Si-29 T_1 (e.g. 30 s.), then observing the Si-29 signal following a 90° pulse.

D. R. Corbin and L. Abrams provided samples, and A. J. Vega and J. H. Noggle helpful discussions. Please credit this letter to D. D. Bly's account.

Sincerely,

Rod Farlee

Rodney D. Farlee

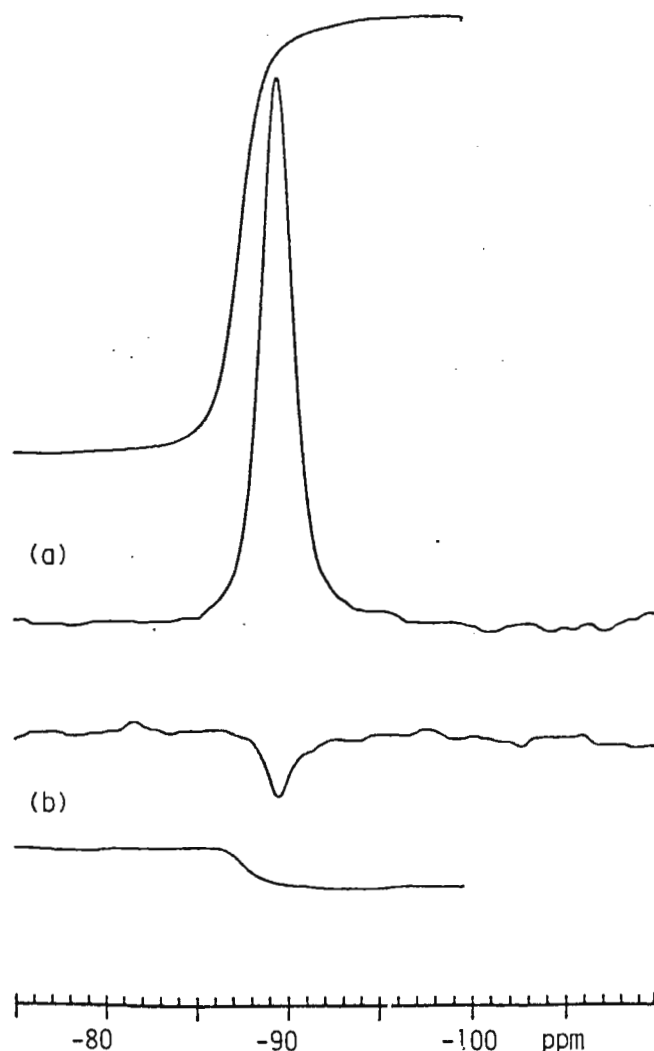


Figure.
Hydrated Linde Zeolite 4A
(a) Normal Si-29 spectrum,
(b) spectrum after 30 s.
proton presaturation
 $\eta = -1.10$

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27 July 1983

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

Dear Barry,

STERIC EFFECTS ON THE CONFORMATION OF Δ -LACTONES

I had drafted a contribution on my recent ab initio studies on the conformation of butyrolactones and INDO calculations of coupling constants in these systems when TAMUNMR Newsletter No. 295 reached me. My attention was drawn to the letter (p.6) by T.M. Carr and D.R. Juen on the C-13 and Si-29 n.m.r. characterisation of a silalactone: it showed a single Si-29 signal but two C-13 signals of equal intensity for the SiMe₂ group.

Of course it should! It is very likely that the ring assumes a preferred half-chair (not chair) conformation, as was shown (1) several years ago by p.m.r. spectroscopy of (dare I call them) carba-analogues of this silalactone. More recently Dr Devinder Singh and I have recorded and analysed the C-13 n.m.r. spectra of the twelve isomeric gem-dimethylphenylvalerolactones and observed results entirely consistent with the p.m.r. results (1). As I am, at present, on leave at the address on this letter, several hundred miles from my records at the University of New England, I am unable to quote actual chemical shifts, but they would of course be quite different from those in the silalactone.

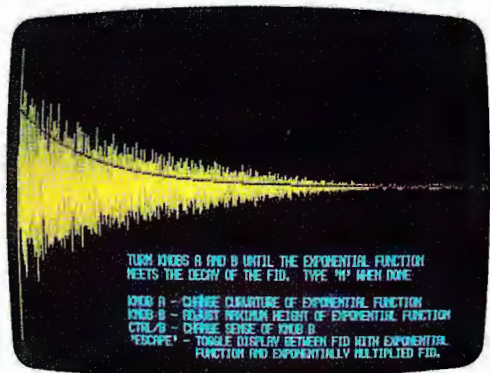
May I, as a member of the Editorial Advisory Committee of the Australian Journal of Chemistry, take this opportunity to point out that this Journal regularly contains a great deal of interesting and often important chemical information.

Yours sincerely,

N.V. Riggs

1. Johnson, R.N., and Riggs, N.V., Tetrahedron Letts., 1967, 5119-22; Aust. J. Chem., 1971, 24, 1643-58, 1659-66.

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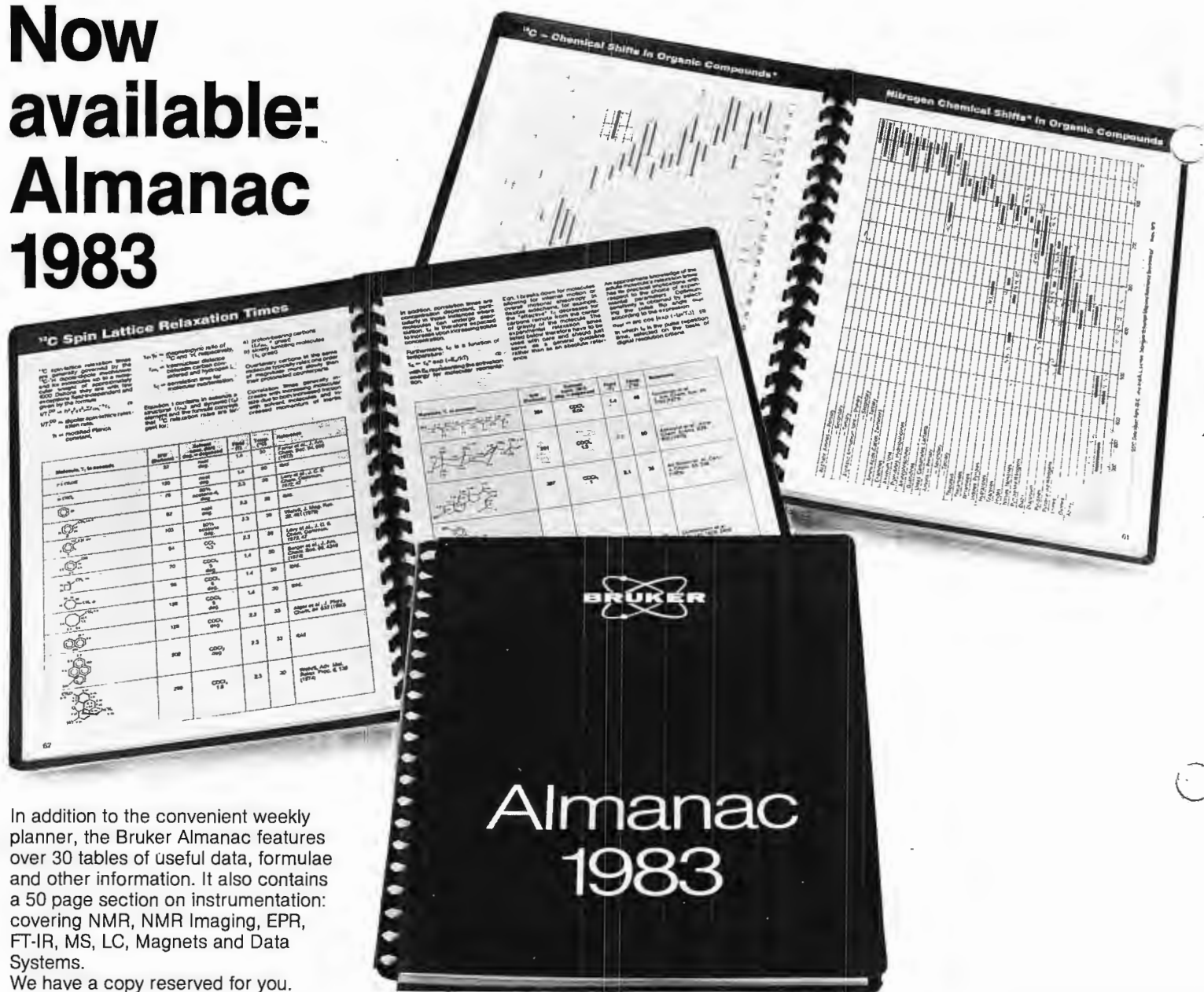
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August 12, 1983

Professor B. L. Shapiro, Editor
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
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Dear Barry:

RE: Long-Range, Carbon-Hydrogen Coupling Constants As An Aid In The Structure Determination of Pyrazines

The substitution pattern in disubstituted pyrazines can often be determined by ^1H NMR using the proton-proton coupling constants. This technique will work in those cases where the chemical shifts are sufficiently separated such that one can observe the coupling constants. Because the above cannot be applied to tri- and tetrasubstituted pyrazines (lack of coupled protons on the pyrazine ring) there exists a need for a definitive method for establishing the relative location of the substituents around the ring in multiple substituted pyrazines.

Previous studies of long-range, carbon-hydrogen coupling constants in pyrazine and methylpyrazines suggested that coupling between ring carbons and protons on substituents might offer a method for structure determination. Thus, we have examined a variety of substituted pyrazines in an effort to develop a method for structure determination of pyrazines. Some of the more interesting findings are given below. For an acetyl and methoxy substituent, we observe coupling between the methyl protons and the substituted ring carbon of 1.1 and 3.9 Hz respectively. There is no evidence for coupling between the remainder of the ring carbons and the protons on the acetyl or methoxy substituent. With a methyl group on C-2, the coupling between the methyl protons and ring carbons is 6.5 Hz for C-2, 4.2 Hz for C-3, 0.9 Hz for C-5 and 0.0 Hz for C-6. In ethylpyrazine we find that only the ring substituted carbon is coupled (4.3 Hz) to the methyl protons.

Provided the substituents on a multiple substituted pyrazine are known, usually from a combination of NMR and mass spec, we have found that the combination of coupling between substituent protons and ring carbons and coupling between ring protons and ring carbons is sufficient to establish the relative location of substituents in most substituted pyrazines. The long-range coupling, $^5\text{J}_{\text{CH}}$, between ring carbons and substituent protons appears to be a general phenomena and we are presently investigating other types of aromatic systems. Please credit this to the Philip Morris account.

Sincerely yours,

Richard H. Cox
Senior Scientist

produits chimiques

UGINE KUHLMANN

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V/réf.

Professor B.L. SHAPIRO
Dpt of Chemistry
Texas A & M University
College Station

TEXAS 77843

U.S.A.

PIERRE-BÉNITE, LE August 16th, 1983

Dear Professor Shapiro,

^{17}O -NMR of peracids

As part of our continuing interest in applications of hydrogen peroxide in organic chemistry, we are currently investigating different kinds of peroxo compounds. The lack of ^{17}O -NMR data in the peracid series prompts us to present some of our results (table).

Table ^{17}O data from "acid + aqueous ^{17}O labeled H_2O_2 "


	$\delta/\text{H}_2\text{O} - (\Delta\nu\ 1/2, \text{Hz})$						
	!!	Acid	!	Peracid	!	Temperature °C	
	!!		!	C=O	-O-O-	!	
Formic	!!	257 (<100)	!		273 (>350)	!	25
Acetic	!!	255.5 (190)	!		273 (~400)	!	50
Propionic	!!	254 (170)	!	332.5 (140)	280-266 (>300)	!	60
Trifluoroacetic	!!	245 (180)	!		280-260 (>400)	!	25

An illustration is given in fig. 1 A for a typical ^{17}O spectrum at natural abundance of an industrial mixture of peracid and acid. We clearly distinguish the oxygen carbonyl ($\delta 332.5 - \Delta\nu 1/2 140 \text{ Hz}$) and overlapping signals ($\delta 260-280$) for the peroxo bridge. The in situ peracid formation, obtained by adding a few drops of ^{17}O -labeled hydrogen peroxide (10 % aqueous, 20 % ^{17}O) to a large amount of propionic acid is shown in fig. 1B : the two non equivalent oxygens for the peroxo bridge are confirmed. Also are noticed some oxygen carbonylenrichment and partial decomposition to ^{17}O labeled CO_2 ($\delta 78$) for which the sharpest line ($\Delta\nu 1/2 < 10 \text{ Hz}$) is observed.

^{17}O NMR spectroscopy appears to be an efficient tool to monitor oxidation reaction, particularly with ^{17}O labeled reagent.


J.C. LECOQ


L. LEGLEUT


J.J. BARIEUX

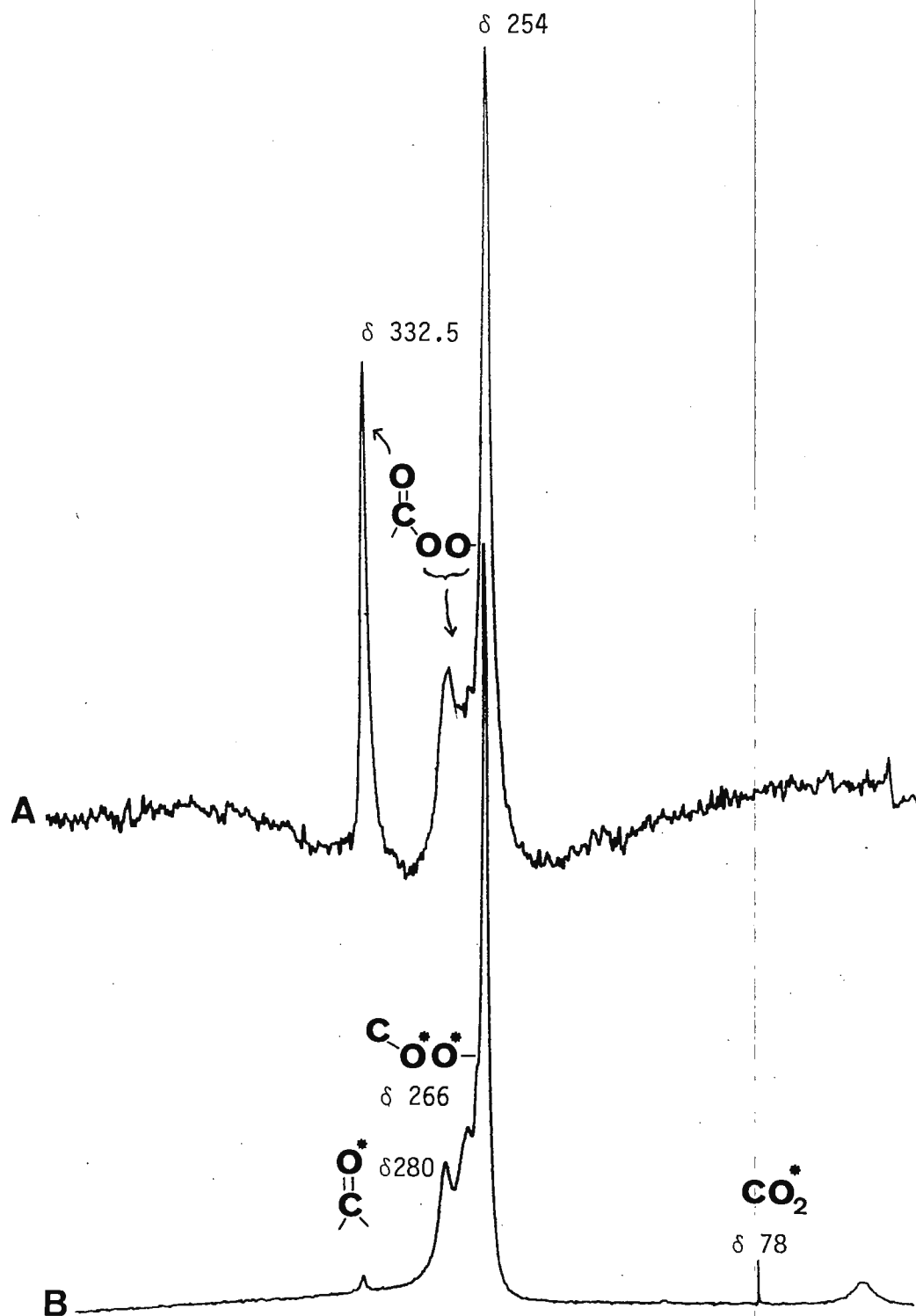


Fig 1 : ^{17}O -NMR (27.02 MHz) spectra of peracid solutions at 50°C

A - industrial solution in 1,2-dichloroethane of equimolar propionic and perpropionic acids (0.3 M) at natural abundance (48 000 scans)

B - propionic acid + ^{17}O labeled hydrogen peroxide (10 % aqueous - 20 % ^{17}O) (6 000 scans)

Prof. Dr. R. Kosfeld
 Universität (GH) Duisburg
 Fachbereich 6 - Chemie
 Fachgebiet Physikalische Chemie
 Bismarckstraße 90
 D-4100 Duisburg 1

Duisburg, 05.07.1983

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

Title: NMR and Neutron Scattering Complementary Experiments

Dear Barry,

from measurements of the frequency and temperature dependence of the proton spin-lattice relaxation time T_1 on a high molecular weight polydimethylsiloxane ($\bar{M}_w = 1,32 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$) we derived a linear plot " $\ln \nu_0$ vs $1/T$ " from the frequency dependent shift of the methyl group rotational T_1 -minimum occurring in the " $\ln T_1$ vs T " representation. Starting from the well known BPP formula

$$R_1 = 1/T_1 = C \left[\tau_c / (1 + \omega_0^2 \tau_c^2) + 4 \tau_c / (1 + 4\omega_0^2 \tau_c^2) \right] \quad (1)$$

one ends up at the relation

$$\ln \omega_0 = -(\Delta E/R)/T_E - \ln [\tau_c(\infty)/0,62] \quad (2)$$

by introducing the minimum condition and, as we are concerned with an activated hindered motional process, an Arrhenius ansatz for the mean correlation time τ_c . As the temperature position of the minimum actually enters into Eq. (2) the temperature variable is subscripted to read T_E .

The NMR data points derived from T_1 -measurements at 20, 40 and 60 MHz lie well on a straight line according to Eq. (2) as is demonstrated by Fig. 1.

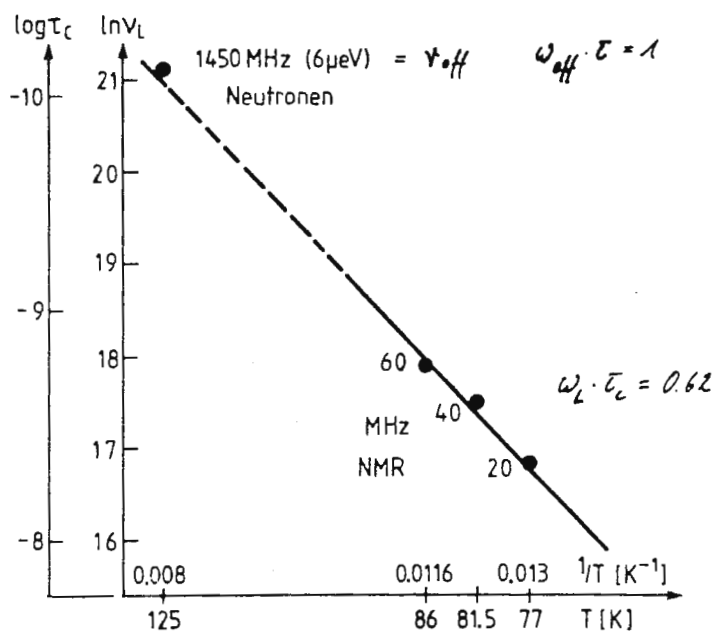


Fig. 1

A relation similar to Eq. (2) can be deduced from concepts of incoherent neutron scattering. Again assuming an Arrhenius ansatz for the mean jump time τ the relation

$$\ln \omega_{\text{off}} = -(\Delta E/R)/T_E - \ln \tau(\infty) \quad (2')$$

follows from the scattering law

$$I \sim S_{\text{inc}}^R(Q, \omega) \sim A_0(Qr_0) \cdot \delta(\omega) + [1 - A_0(Qr_0)] \cdot \tau / (1 + \omega^2 \tau^2) \quad (3)$$

employing the same procedure leading to Eq. (2).

The quasielastic contribution to the scattering intensity I exhibits a single Lorentzian thus showing a frequency and tem-

perature dependence very similar to that of the longitudinal relaxation rate R_1 according to Eq. (1). To have an equivalent to NMR T_1 -measurements a fixed frequency $\nu = \nu_{\text{off}}$ has to be chosen in the scattering experiment. This frequency is related to an offset energy $E_{\text{off}} = \hbar\omega_{\text{off}} = h\nu_{\text{off}}$ the spectrometer is adjusted to, thus ensuring only those scattering events to be registered which are accompanied by a neutron energy change of magnitude E_{off} .


In this experiment the energy transfer was chosen to be $E_{\text{off}} = 6 \mu\text{eV}$ corresponding to a frequency $\nu_{\text{off}} = 1,45 \text{ GHz}$. The methyl group rotational minimum was found to lie at 125 K due to a fit of the data points in the " $\ln(1/I)$ vs T " plot, which is analogous to the " $\ln T_1$ vs T " representation of the NMR relaxation data. As can be seen by inspection of Fig. 1 the corresponding neutron scattering data point lies very well on the extrapolated straight line fitted to the three NMR relaxation data points. The excellent correspondence of the T_1 -measurements to this particular variant of an incoherent neutron scattering experiment thus confirms the validity of an Arrhenius ansatz over a wide frequency range.

More details of the experiment will be given in a forthcoming publication.

The neutron scattering experiment was sponsored by the "Bundesministerium für Forschung und Technologie" (BMFT).

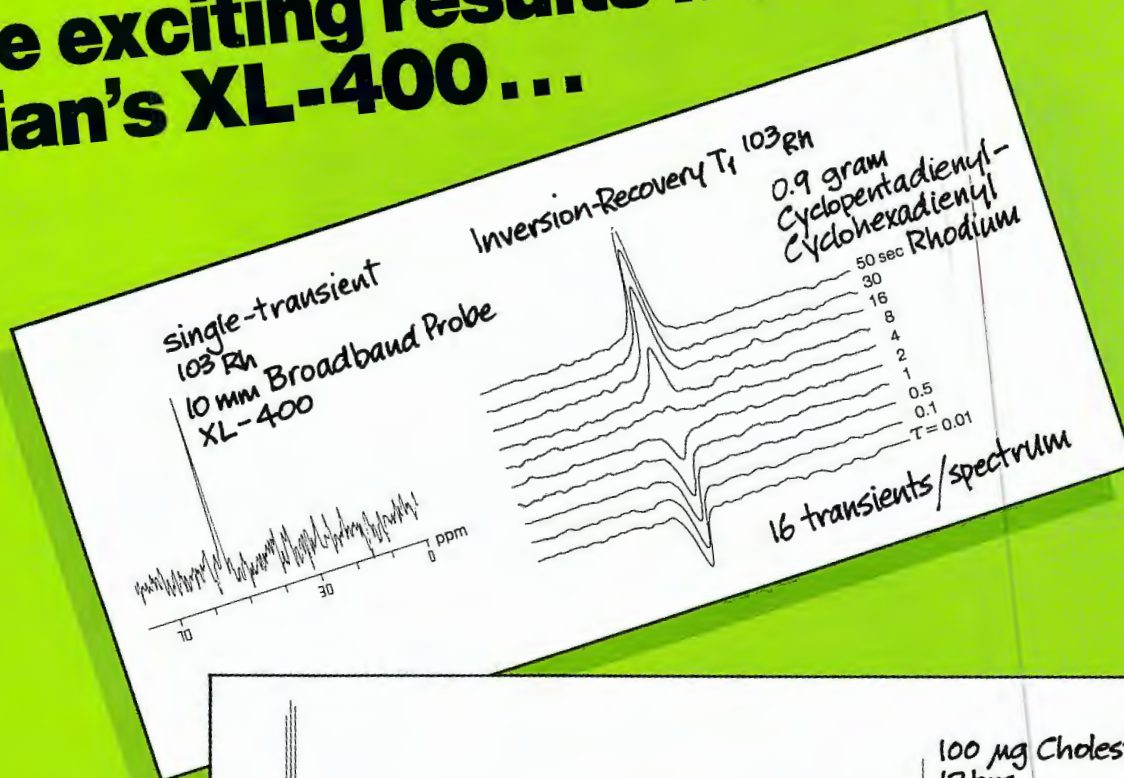
Yours sincerely,


(R. Kosfeld)

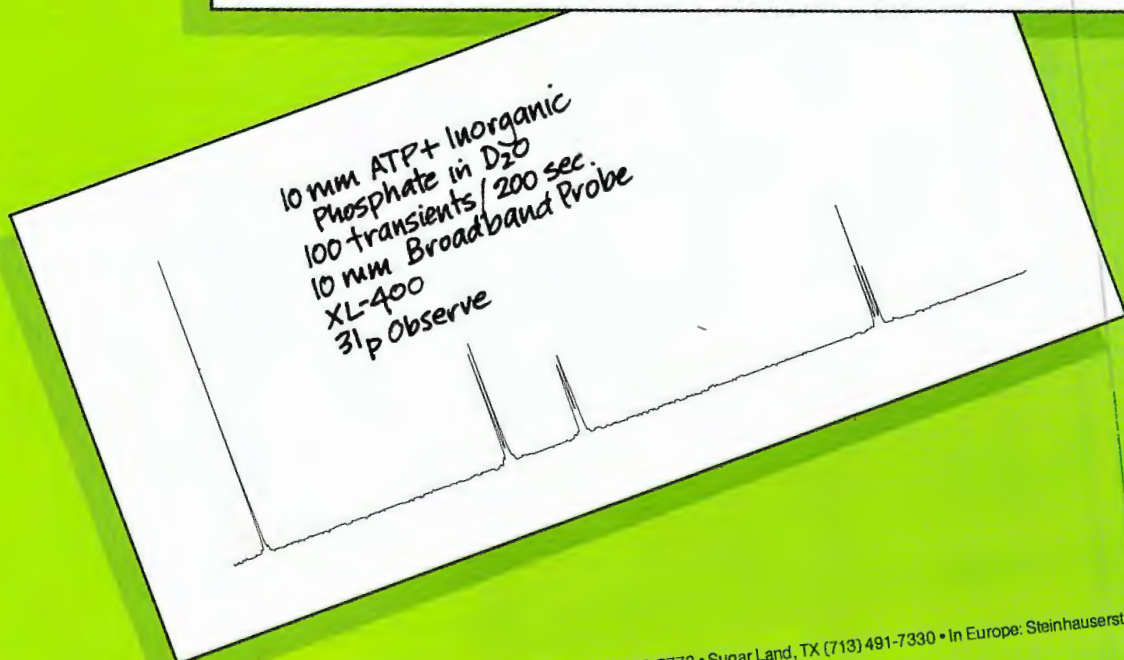
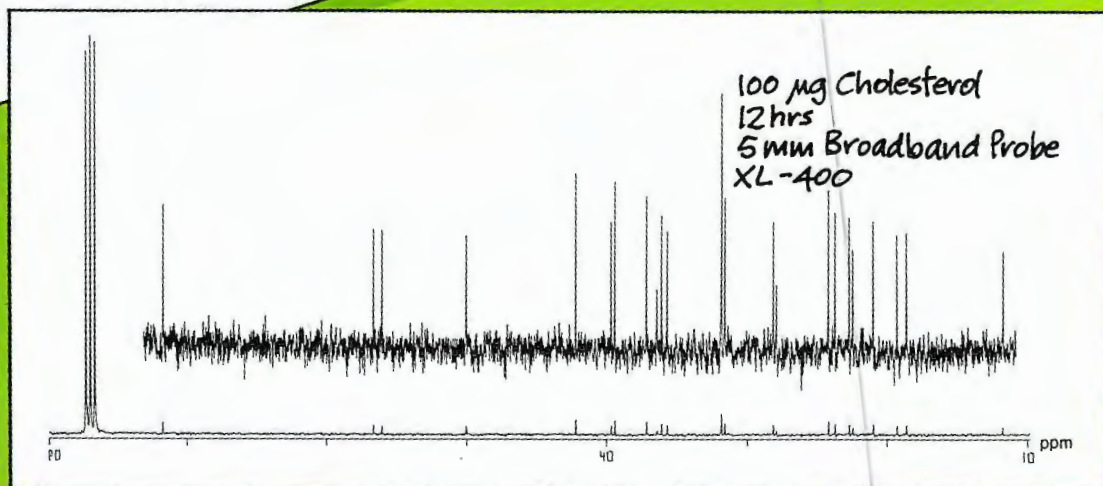

(B. Alefeld)


(H.-H. Grapengeter)

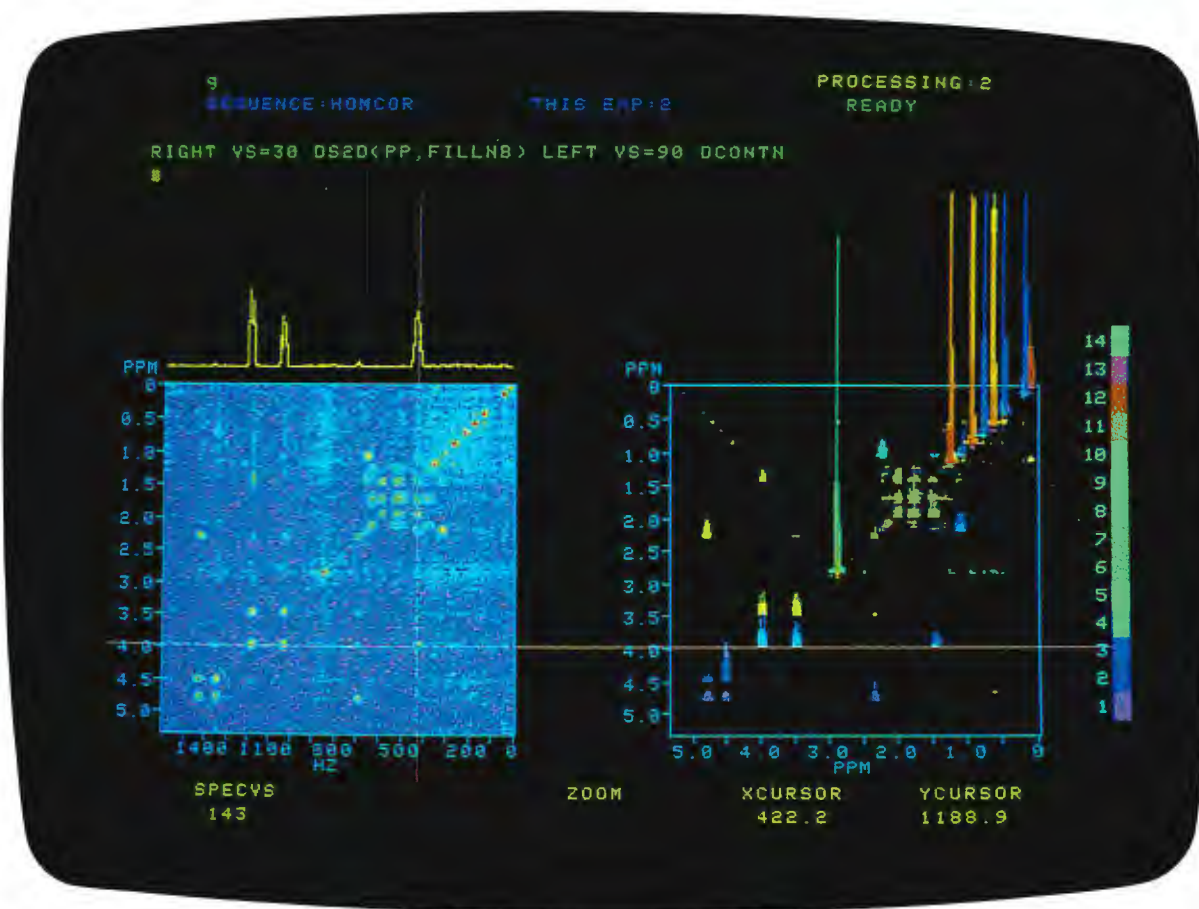
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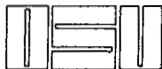
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Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74078

August 8, 1983

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

Title: User Data From the Varian XL-300 NMR Spectrometer

Dear Barry:

It has been about one year since the first XL-300 multinuclear NMR spectrometer was installed in our Department. The specifications have been exceeded better than expectations in our opinion. They are as follows:

^1H (5 mm) - 0.1% ETB: Found: 140:1 (Specs. 75:1 on BBP-5 mm).

^{13}C (5 mm) - ASTM sample: Found 140:1 (Specs. 100:1 on BBP-5 mm).

^{13}C (16 mm) - ASTM sample: Found 500:1 (Specs. 500:1 on BBP-16 mm)

We have been observing ^{33}S , ^{15}N , ^{77}Se , and ^{17}O regularly and with great sensitivity as well. The boil off rate for N_2 over the year (with refrigerator) has been 0.6 liters/day and 0.3 liters/day for He which is excellent from a cost effective standpoint. The 2-D experiments and contour plots are beginning to become more routine now as research groups become familiar with the potential results available from these types of experiments.

I trust this will serve as our contribution this time and we shall do better the next time. Best regards.

Sincerely yours,

K. D. Berlin
Regents Professor

NATIONAL INSTITUTE OF HEALTH**THE 2ND DEPARTMENT OF BACTERIOLOGY**10-35, KAMIOSAKI, 2-CHOME,
SHINAGAWAKU, TOKYO, JAPAN

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

August 22, 1983

Use of Faraday Shield to Obtain Well-Resolved ^{31}P -NMR
Spectra From a Localized Region in Live Animals

Dear Professor Shapiro:

We wish to report the use of Faraday shield for ^{31}P -NMR spectroscopy of live animals.

Fig. 1 shows ^{31}P -NMR spectra of mouse brain obtained (a) with and (b) without Faraday shield; the signals of phosphorous compounds were better resolved in spectrum (a) than in spectrum (b). The mouse weighing about 20 grams was anesthetized with sodium pentobarbital. The animal was foiled with a sheet of shield material (Faraday shield) except the head and was placed in a 25mm ϕ tube as shown schematically in Fig. 2. The spectra were obtained at 109.14 MHz by a Jeol FX-270 NMR spectrometer from 600 transients of 80 μsec (45°) delivered at 1.00 sec intervals. No convolution technique was used.

To date, several methods have been proposed to obtain ^{31}P -NMR spectra from a localized region in vivo. These include surface coil method, topical NMR method, the projection reconstruction method and sensitive point method. The use of Faraday shield herein reported provides an additional method for obtaining NMR spectra from a localized region in live animals.

Sincerely yours,

Akira Ohsaka
Akira Ohsaka

K. Kato
Kenzo Kato

K. Matsushita
Kazuhiro Matsushita

K. Yoshikawa
Kenichi Yoshikawa

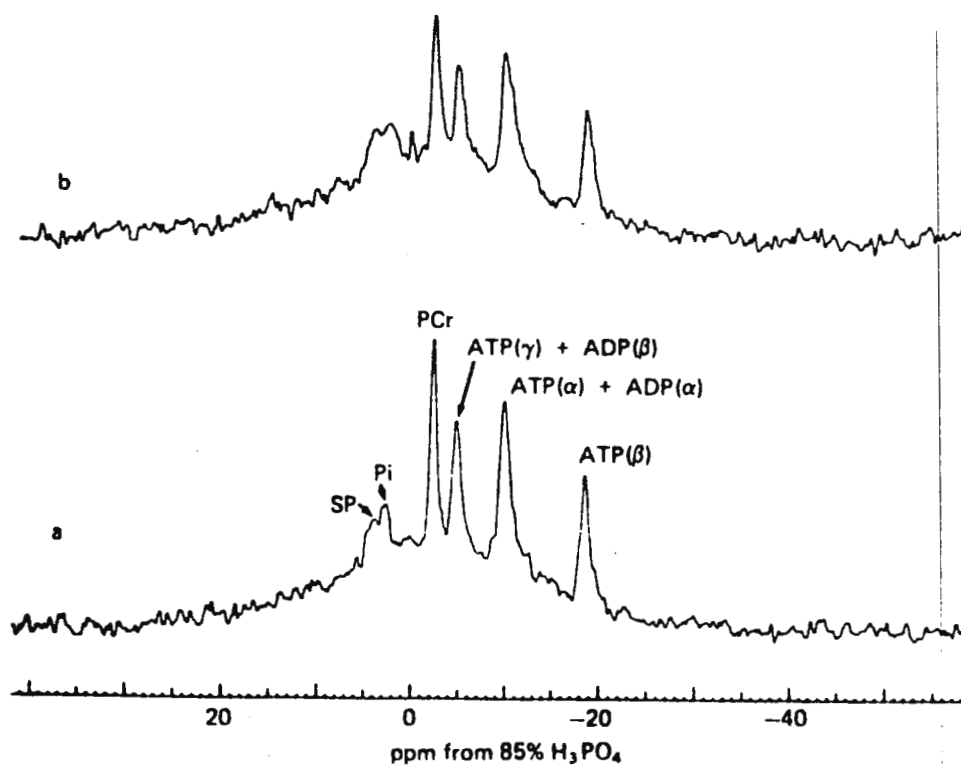


Fig. 1 ^{31}P -NMR (109 MHz) spectra of mouse brain, obtained (a) with and (b) without Faraday shield

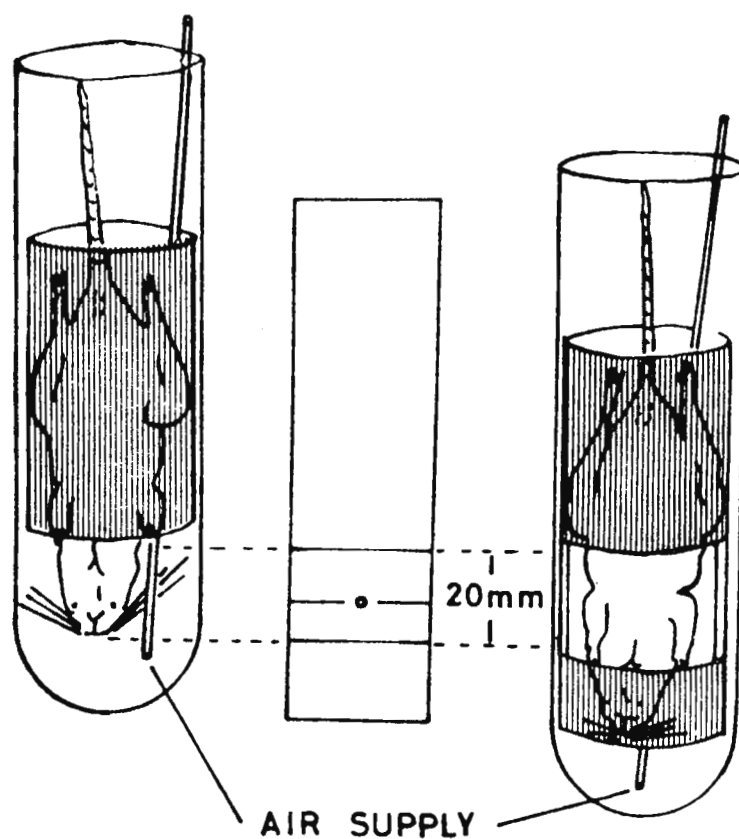


Fig. 2 25mm \varnothing ^{31}P -NMR probe



Professor R. Grigg
Professor of Organic Chemistry

Department of Chemistry, David Keir Building

The Queen's University of Belfast

Belfast BT9 5AG Northern Ireland
Tel. 661111 STD 0232-661111 Ext. 4402 Telex 74487

Our ref.

Your ref.

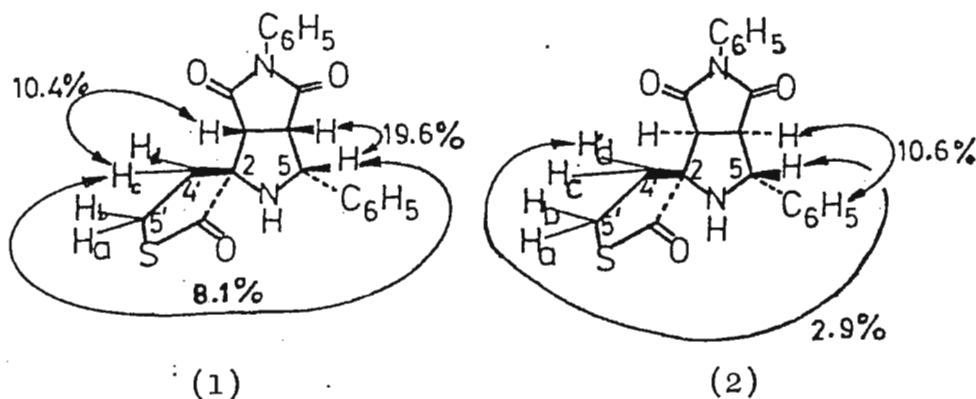
24 August 1983

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

Structural Assignments by NOED Spectroscopy to Stereoisomeric Pyrrolidines

Dear Professor Shapiro:

We have a very productive new 1,3-dipolar cycloaddition reaction¹ that often produces stereoisomeric pyrrolidines arising via endo (usually major isomer)- and exo-transition states. Coupling constants in pyrrolidines are notoriously unreliable for structural assignments² and we now routinely use NOEDs on our Bruker WH250 for stereochemical assignments. Some typical results are appended.



References

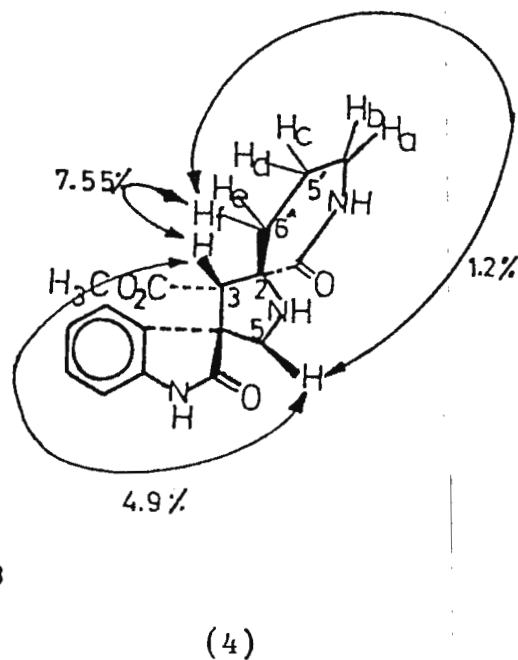
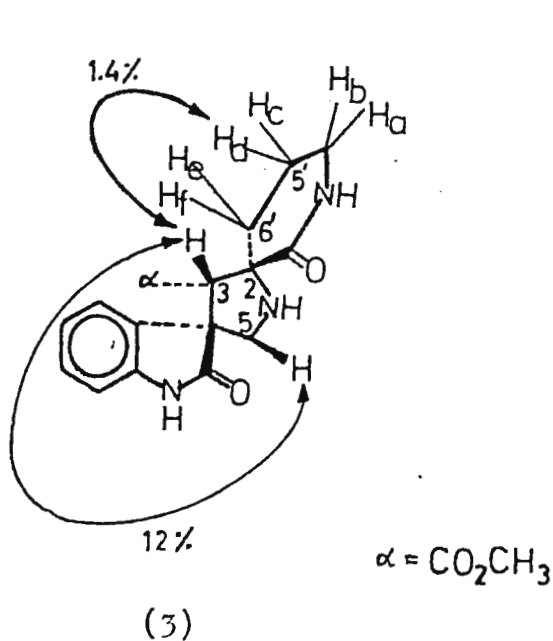
1. R. Grigg, L.D. Basanagoudar, D.A. Kennedy, J.F. Malone and S. Thianpatanagul, Tetrahedron Letters, 1982, 2803.
2. J.H. Hall and R. Huisgen, J. Chem. Soc. Chem. Comm., 1971, 1187.

Yours sincerely,

Ron Grigg

Nuclear Overhauser Difference Spectra of pyrrolidines (3) and (4) (CDCl_3 plus one drop of TFA-d)

Irradiated	Observed	Percentage of Enhancement	
		major isomer (3)	minor isomer (4)
H(5)	H(3)	12	4.9
	ArH	12.2	15.9
	ArH	6	-
H(3)	H(5)	7.6	4.8
	ArH	10.8	-
	H(5'-c)	-	6.1
H(6'-f)	H(5)	-	1.2
	H(3)	-	7.55
H(6'-e)	H(6'-f)	-	3.4
	H(4')	-	1.1
H(6')	H(4')	5	-
	H(5'-c)	2.2	-
	H(5'-d)	-	-
H(5'-c)	H(5'-d)	30	10.6
	H(6')	3.7	1.3
	H(3)	-	13.7
	H(5)	-	5.75
H(5'-d)	H(4')	1.7	-
	H(5')	20	-
	H(3)	1.4	-





UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

SOUTH CAROLINA MAGNETIC
RESONANCE LABORATORY

(803) 777-7341

27 July, 1983

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

Dear Barry,

INADEQUATE: Polarization Transfer to Quarternary Carbons

A DEPT¹ polarization transfer version of INADEQUATE² has been developed and implemented at the South Carolina Magnetic Resonance Facility. Both DEPT-INADEQUATE and INEPT-INADEQUATE³ transfer polarization from protons to carbon and thus benefit from short proton recycle times while INADEQUATE requires longer carbon recycle times. An ostensible drawback of the polarization transfer method is that only protonated carbons may be polarized. We wish to present a way to circumvent the problem of quarternary carbon saturation.

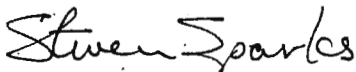
The phase cycling normally employed by each of these three experiments creates and detects coherences $S_{1y}S_{2z}$ or $S_{1z}S_{2x}$ where S_1 and S_2 designate particular carbons in the two carbon spin system. The notation $S_{1y}S_{2z}$ refers to a dispersion mode carbon antiphase doublet with polarization appearing on S_1 ; $S_{1z}S_{2x}$ an absorption mode antiphase doublet on carbon S_2 . Spectra 1a and b illustrate these coherences for ^{13}C enriched acetic acid. The experiment, similar to INEPT-INADEQUATE, consists of presaturation of carbon, polarization transfer from methyl protons to methyl carbon S_1 or carbonyl carbon S_2 , evolution of proton decoupled carbon coherences until $\pi/2$ radians of phase are accumulated, followed by creation and detection of double quantum coherence. Selection of an individual carbon was accomplished by executing only part of the phase cycling usually prescribed; either dispersion or absorption mode. Both protonated and nearest neighbor quarternary carbons will be polarized if full phase cycling is used, as in Spectrum 1c.


To polarize quarternary carbons three bonds removed from the nearest proton, it is sufficient to transfer proton polarization to S_1 via one bond carbon-proton scalar coupling, $^1J_{CH}$, and optimize the remaining delays for detection of two bond carbon-carbon scalar couplings, $^2J_{CC}$. For INEPT-INADEQUATE, this calls for setting $\tau_1 = 1/4 \cdot ^1J_{CH}$ and $\tau_4 = 1/4 \cdot ^2J_{CC}$. Similar methods are used in DEPT-INADEQUATE as will be detailed in a forthcoming paper. Spectra 2a and b demonstrate in pyridine optimization for $^1J_{CC}$ and $^2J_{CC}$, respectively. We recognize the absence of quarternary carbons in pyridine and present these spectra only to show the ease of detecting two bond carbon-carbon couplings. An example more apropos would be 4-cyanopyridine; the cyano carbon being detected through its two bond coupling to C3 of pyridine. This experiment is feasible in principle but has not yet been performed in our lab due to instrument demand.

A word of caution is appropriate. All varieties of INADEQUATE are very sensitive to small errors in spin relabeling. We have found the above methods to be well behaved at low field strengths (e.g. ^{13}C at 20 MHz) but ill or erratically behaved at high fields (100 MHz).

Best regards.

Sincerely,

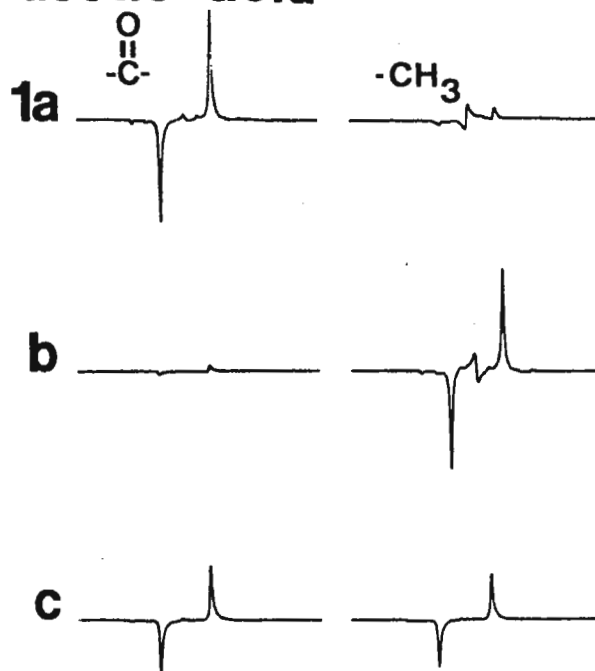

Steven W. Sparks


Paul D. Ellis

Please credit this contribution to Paul Ellis' account.

- 1) D. M. Doddrell, D. T. Pegg, and M. R. Bendall, J. Magn. Reson., 48, 323-27 (1982).
- 2) A. Bax, R. Freeman, T. A. Frenkiel, and M. H. Levitt, J. Magn. Reson., 43, 478-83 (1981).
- 3) a) O. W. Sørensen, R. Freeman, T. Frenkiel, T. H. Marcei, and R. Schuck, J. Magn. Reson., 46, 180-84 (1982); b) G. A. Morris, J. Am. Chem. Soc., 102, 428 (1980); c) G. A. Morris and R. Freeman, J. Am. Chem. Soc., 101, 761 (1979).

acetic acid



pyridine

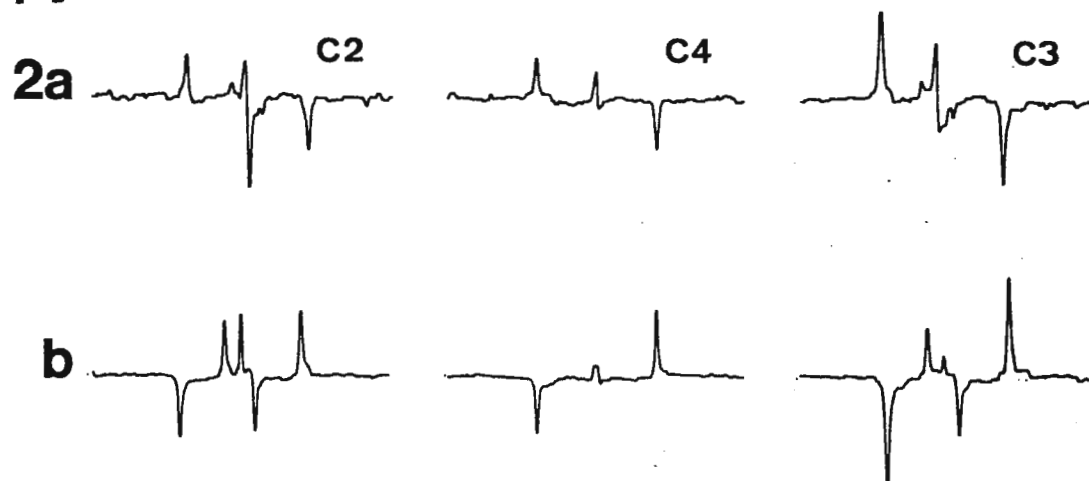


Figure 1. $\text{H}_3^{13}\text{C}-^{13}\text{COOH}$ (80 %) / $\text{H}_3\text{C}-\text{COOH}$ (10 %) / CDCl_3 in 10 mm tube. Signal was acquired at 20 ^{13}C MHz on an IBM NR-80 using DEPT-INADEQUATE.
 a) Eight acquisitions of the absorption mode signal $\text{S}_{1z}\text{S}_{2x}$ using receiver phase x and $-x$.
 b) Eight acquisitions of the dispersion mode signal $\text{S}_{1y}\text{S}_{2z}$ using receiver phase y and $-y$.
 c) Eight acquisitions using full phase cycling.

Figure 2. Pyridine (50 vol %) in CDCl_3 in a 10 mm tube. The natural abundance carbon signal was obtained at 50 MHz on a Bruker WP-200; 512 acquisitions of DEPT-INADEQUATE with 12 second recycle time.
 a) Delays optimized for polarization transfer through one bond carbon-carbon scalar couplings.
 b) Delays optimized for polarization transfer through two bond carbon-carbon scalar couplings. Carbon coherences have acquired approximately $3\pi/2$ radians of phase through one bond couplings and $\pi/2$ radians of phase through two bond couplings. The relative inversion of pairs of antiphase doublets is not due to negative coupling constants.

July 29, 1983

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

Dear Professor Shapiro:

THE AXIAL-EQUATORIAL CONFORMER RATIO OF METHYLCYCLOHEXANE
REVISITED

The noise-decoupled ^{13}C NMR spectra of the equatorial and axial chair conformations of methylcyclohexane have been determined at 188 K and used to estimate the conformational energy both at 188 and 302 K.

The low temperature ^{13}C NMR spectrum of methylcyclohexane has been looked at 1971¹ when the instrumentation had not yet been developed to the present level of sensitivity and resolution. However, the authors¹ were able to observe the axial conformer (Eq. 1) at 163 K and to estimate roughly that its proportion was less than 1 % in relation to the equatorial form.

Recently we had the opportunity to revisit this problem using both Bruker AM-400 (at 173 K) and Jeol GX-400 (at 188 K, Table 1) systems. In this context it should be emphasized that the line shapes and widths are very crucial for a successful analysis at low temperatures. The chemical shifts at 302 K were taken from the report of Vierhapper and Willer² on the long range ^{13}C chemical shift effects in methylcyclohexanes. Practically the same values were obtained on a Jeol FX-60 in Turku.

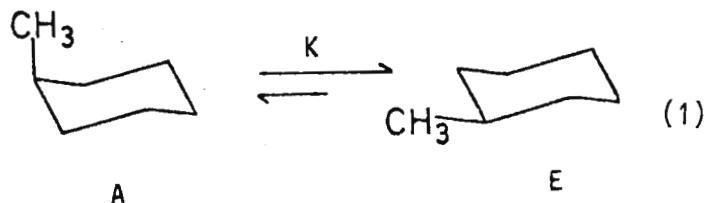


Table 1 shows that despite the temperature variation in the absolute values of the ^{13}C chemical shifts $\delta(\text{E-A})$ remains practically constant at all temperatures. From the values of the chemical shifts at 302 K (E, A and observed) it can be estimated that $K = 21.6 \pm 2.6$ for Eq. 1 (Table 2) which corresponds to $-\Delta G^\circ 7.7 \pm 0.3 \text{ kJ mol}^{-1}$. From the signal intensities at 188 K the equilibrium constant $K = 162 \pm 20$; $-\Delta G^\circ 8.0 \pm 0.2 \text{ kJ mol}^{-1}$ in excellent agreement with the above result. Both of these values are also within the generally accepted range of $-\Delta G^\circ(\text{CH}_3\text{-ax}) 7.1 - 8.0 \text{ kJ mol}^{-1}$ for methylcyclohexane.^{2,3,4}

Table 1. The ^{13}C chemical shifts for methylcyclohexane in p.p.m. from TMS

	C-1	C-2,6	C-3,5	C-4	CH_3	Comments
E	32.57	34.98	26.24	25.88	22.86	CD_2Cl_2 , 188 K, GX-400
A	27.06	31.43	20.22	26.48	16.84	CD_2Cl_2 , 188 K, GX-400
$\delta(\text{E-A})$	5.51	3.55	6.02	-0.60	6.02	CD_2Cl_2 , 188 K, GX-400
$\delta(\text{E-A})$	-a	3.54	6.02	-a	6.03	CD_2Cl_2 , 173 K, AM-400
$\delta(\text{E-A})^b$	5.43	3.40	6.08	-0.78	5.67	See ² Ref. 2, CDCl_3 , 302 K
E^b	33.24	35.80	26.90	26.67	23.20	CDCl_3 , 302 K, Ref. 2
A^c	27.73	32.25	20.88	27.27	17.18	CDCl_3 , 302 K, Ref. 2
Exptl	32.95	35.64	26.64	26.53	22.97	CDCl_3 , 302 K, Ref. 2

^aNot detected. ^b $\alpha_e 6.09$, $\beta_e 8.65$, $\gamma_e -0.25$ and $\delta_e -0.48$ p.p.m. from t-butyl- and trans-1-t-butyl-4-methylcyclohexanes. α_a , β_a , γ_a and δ_a can be obtained correspondingly from cis-1-t-butyl-4-methylcyclohexane. ^c $\delta(\text{E})$ at 302 K - $\delta(\text{E-A})$ at 188 K.

Table 2. Conformer ratios from the ^{13}C chemical shifts at 302 K and from the signal intensities at 188 K.

	C-1	C-2,6	C-3,5	C-4	CH_3	Comments
$K = \text{E/A}^a$	18.0	21.2	22.2	^c	25.2	$K_{av} 21.6 \pm 2.6$, 302 K
$K = \text{E/A}^b$	134	171	175	^c	169	$K_{av} 162 \pm 20$, 188 K

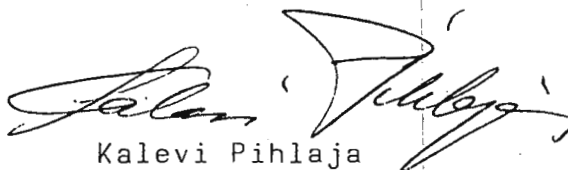
^a $K = (\delta_{\text{obs}} - \delta_a) / (\delta_e - \delta_a)$. ^bIntensity ratios. ^cNot valid.

Accordingly, methylcyclohexane consists of 4.4 % (cf. 4.6 % in Ref. 2) of the axial (A) conformer at 302 K and 0.6 % at 188 K. The above results are also in excellent agreement with that of

Booth and Everett based on the low temperature spectrum of [Me-¹³C] methylcyclohexane at 172 K ($K = 164 \pm 7$, $-\Delta G^\ominus = 7.3 \pm 0.3$ kJ mol⁻¹).⁴

Acknowledgements. The help given by Bruker's and Jeol's demonstration laboratories has been invaluable in preparing this note.

Sincerely yours,


Kalevi Pihlaja

1. Anet, F.A.L., Brandley, C.H. and Buchanan, G.W. J. Am. Chem. Soc. 93 (1971) 258.
2. Vierhapper, F.W. and Willer, R.L. Org. Magn. Reson. 9 (1977) 13.
3. Pihlaja, K. J. Chem. Soc., Perkin Trans 2 (1974) 890.
4. Booth, H. and Everett, J.R. J.C.S. Chem. Comm., 278 (1976).

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

LEIDEN, 25th August, 1983.

Dear professor Shapiro,

Computer simulation of resolution-enhanced spectra.

Pulsed NMR techniques have opened the door for digital data processing of the averaged FID before Fourier transformation. A well-known and widely-used example is resolution enhancement by means of a Lorentzian to Gaussian transformation. This routine is provided by most of the current NMR software packages and extensively used in our lab to obtain coupling constants from well-resolved spectra. However, the traditional computer simulation programs usually produce Lorentzian lineshapes. An intensity distribution is assigned to every calculated transition according to equation 1,

$$I(f) = 1/1 + (2(f-f_0)/L)^2 \quad (1)$$

where f_0 is the transition frequency and L is the desired linewidth. This distribution can be modified into a Gaussian lineshape as given in equation 2,

$$I(f) = \exp\{-2(f-f_0)/L\}^2/1.443\} \quad (2)$$

The factor 1.443 provides an identical linewidth as in the Lorentzian function. Fig. 1 illustrates both lineshapes. If one would like to reproduce also the negative wings which may arise in certain spectra, eqn. 2 can be extended by subtraction of a second Gaussian function with a double linewidth,

$$I(f) = 2 \cdot \exp\{-2(f-f_0)/L\}^2/1.443\} - \exp\{-2(f-f_0)/L\}^2/2.886\} \quad (3)$$

The results are quite satisfactory as can be seen in the example shown in Figure 2. The appropriate modifications can easily be made in the plot or display routines of any simulation program.

With best regards,

Jan-Rens Mellema
J.R. Mellema

Marjan Pieters
M. Pieters

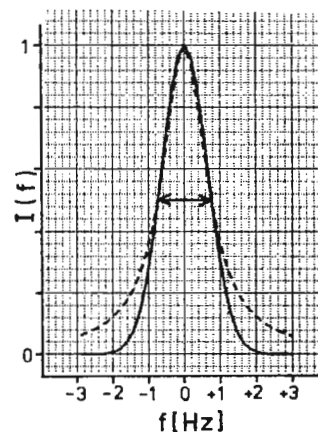


Fig.1. Lorentzian (dashed line) and Gaussian (solid line) lineshape function for $L = 1.5$ Hz.

N.B. The Bruker PANIC eight-spin simulation program (version 820601) already provides a Gaussian lineshape, but not the negative wing feature.

Please credit this contribution to the account of Dr. J. Lugtenburg.

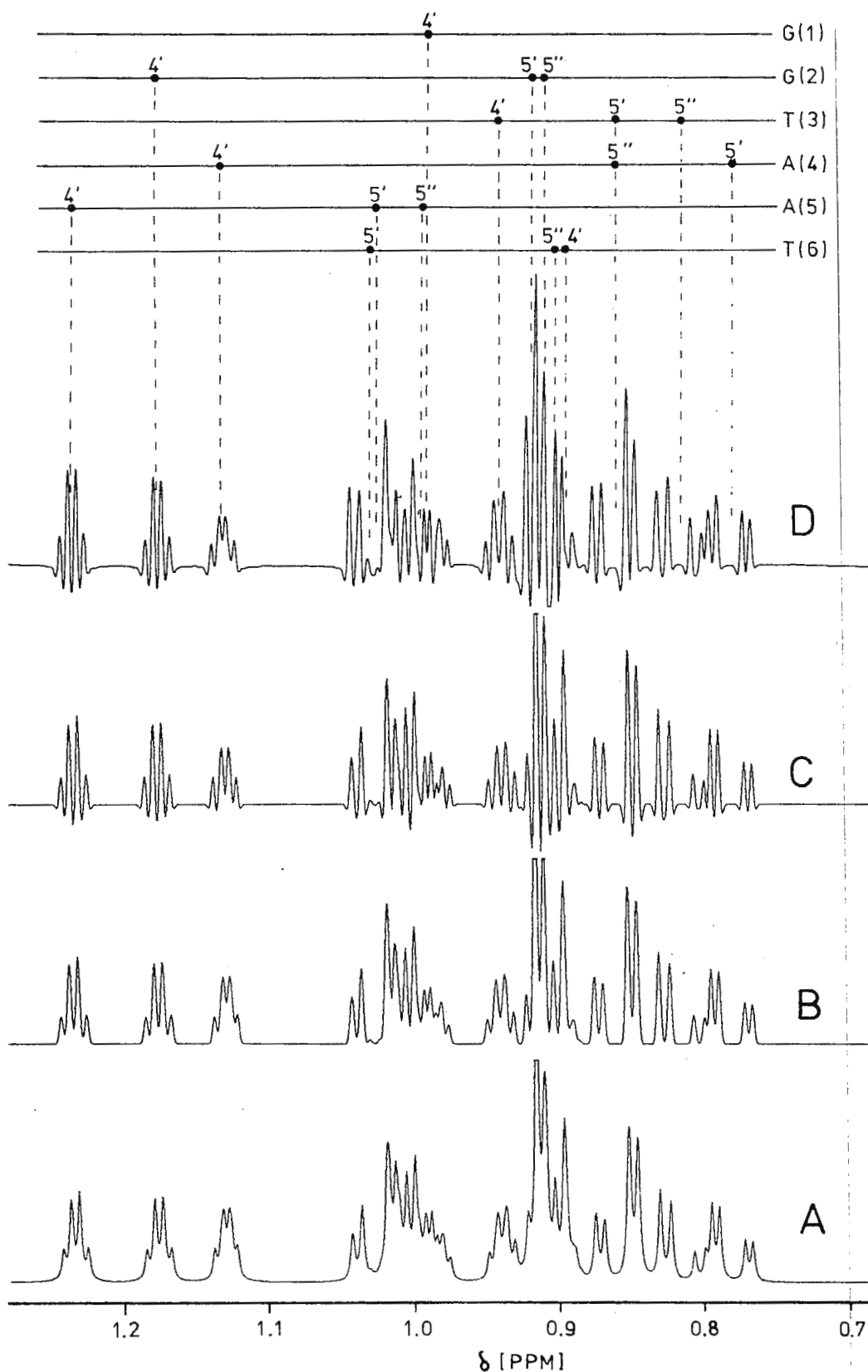


Fig. 2 Part of the 500 MHz spectrum of the DNA hexamer d(GGTAAT) at 37° C. Assignment followed from Spin-Echo-Correlated-Spectroscopy (SECSY) and comparison with the tetramer constituent compound d(TAAT). The experimental phosphorous-31 decoupled spectrum is shown at the top (trace D). Traces A, B and C are computer simulations with lineshapes according to eqn. 1 (trace A), eqn. 2 (trace B) and eqn. 3 (trace C). A linewidth of 1.5 Hz was used in all cases. Chemical shifts are referenced relative to TMA (about 3.18 ppm from DSS). Spectrum was recorded at the Dutch National 500-200 MHz HF NMR Facility at Nijmegen.

University of Wyoming Research Corporation

P.O. Box 3395, University Station
Laramie, Wyoming 82071

August 11, 1983

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

BINUCLEAR SHIFT REAGENTS IN COMPLEX MIXTURES

Dear Barry:

In 1980, Robert Sievers¹ introduced binuclear shift reagents that are effective in inducing shifts in the proton spectrum of a number of weak Lewis bases such as olefins and aromatics. The reagent consists of silver (to bond to the pi system) and a traditional paramagnetic lanthanide ion.

We have been interested in using lanthanide shift reagents in complex mixtures such as those associated with liquid fossil fuel samples, and are currently investigating the nature of the olefins formed during the retorting of oil shale. Through a series of chromatographic separations, the olefin fraction from the oil obtained from oil shale via the Fischer assay process was isolated (12.7%). The olefinic portion of the proton spectrum obtained on a JEOL FT-270 NMR is shown in Figure 1a. Note that the cis and trans protons overlap.

In 1981, Sievers² reported that binuclear shift reagents resolved the signals of cis and trans isomers in mixtures of both cis and trans 2-hexene and 2-octene. To attempt to resolve the cis and trans signals in our olefin fraction, the following method was used.

The amounts of Ag(fod) and Pr(fod)₃ needed to prepare a solution that was 0.1 M of each, were mixed with the appropriate amount of CDCl₃ containing 1% TMS. One-half milliliter (0.5) of the resulting solution was placed in an NMR tube. The olefin fraction was dissolved in 0.5 ml of CDCl₃ and was added in increments to the shift reagent with a microliter syringe until the desired resolution in the olefinic region was obtained.

The resulting spectrum is shown in Figure 1b. The cis and trans protons are now resolved. Although the cis protons now overlap those due to trisubstituted olefins, their contribution to the area under the peak can be easily calculated. The identifiable olefin resonances were integrated and the following preliminary results were obtained:

Olefin type	Unshifted spectrum		Shifted spectrum	
	Chemical shift (ppm)	Mole %	Chemical shift (ppm)	Mole %
Monosubstituted	5.8, 4.9	41.2	4.3, 3.8	41.0
Disubstituted RHC=CHR (cis + trans)	5.4	33.8	-	37.2
cis	-	-	5.1	10.5
trans	-	-	5.3	26.7
CH ₂ =CR ₂	4.7	9.1	4.4	8.0
Trisubstituted	5.1	15.6	5.1	13.7

In these studies and in mixtures of model olefins and aromatics, it was found that the shift reagent preferentially complexes with the olefin.

Sincerely,

Elena J. Colicelli

Elena J. Colicelli

Dan

Daniel A. Netzel

References:

- ¹ Wenzel, Bettes, Sadlowski, Sievers, *J. Amer. Chem. Soc.*, 1980, 102, 5904
- ² Wenzel, Sievers; *Anal. Chem.*, 1981, 53, 393

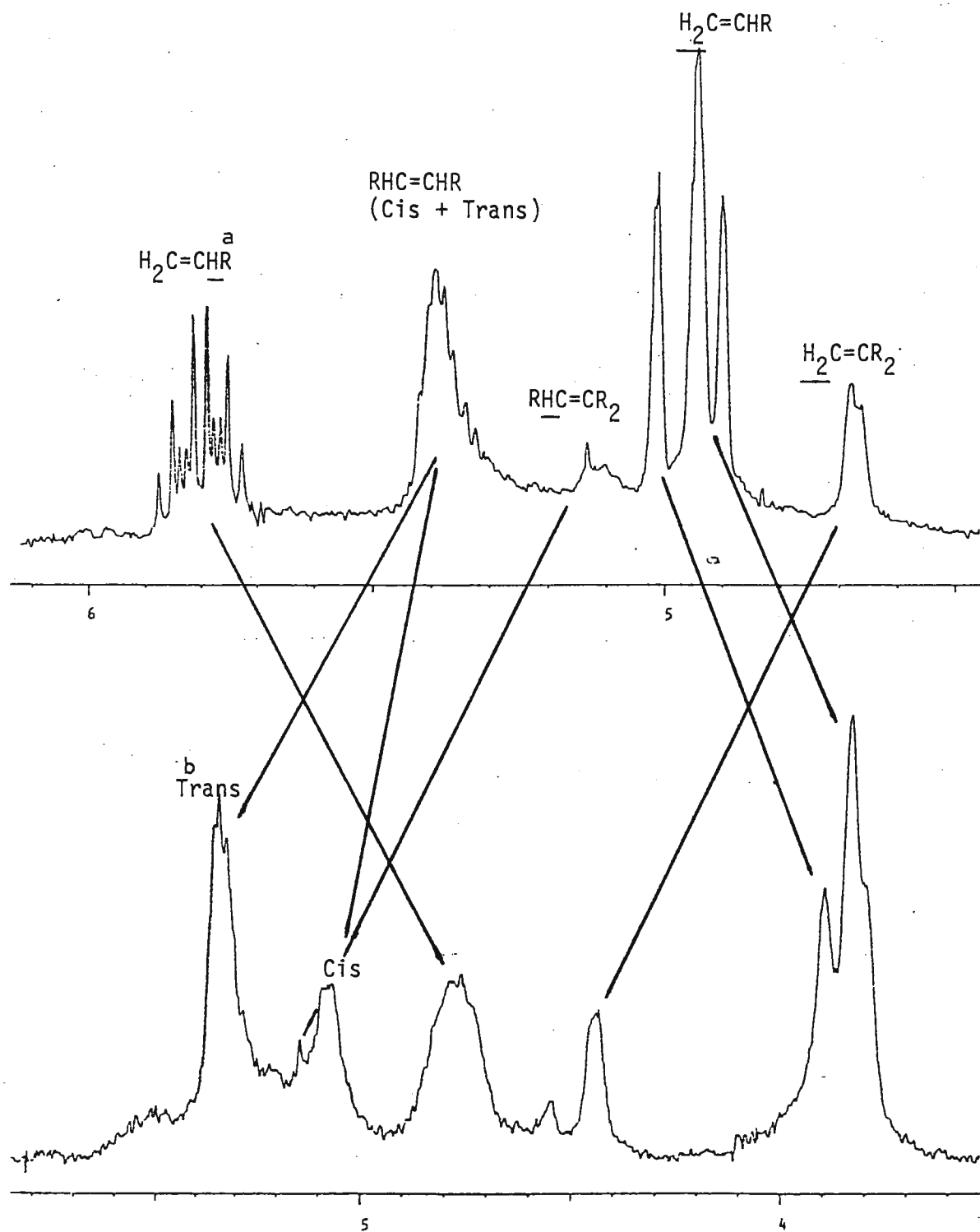


Figure 1. 270 MHz ^1H NMR of olefinic protons from shale oil, a) no shift reagent present, b) shift reagent present.

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29th August, 1983

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

ZEPT: A pulse sequence of limited utility?

Dear Dr. Shapiro,

We wish to report a new pulse sequence "useful" in editing proton H_2O spectra. It is shown that by using ZEPT (following the popular trend to derive Zero Enhancement by Polarization Transfer), one line proton spectra can be reduced to nothing. As an example we show water can be reduced by a factor of about 3×10^4 thus giving clean editing of water spectra. The pulse sequence is

decouple 1H $\left| \begin{array}{c} \tau - \theta[H,x] - \tau - \pi[H,y] - \tau - \theta[H,x] \end{array} \right|$ acq. $\left| \begin{array}{c} \text{decouple } ^1H \end{array} \right|$

A minor modification to this sequence will possibly improve its applicability. If for example ^{13}C pulses are added as follows,

dec. 1H $\left| \begin{array}{c} \frac{\pi}{2}[C,\pm x] - \frac{1}{2J} - \pi[C]\theta[H,x] - \frac{1}{2J} - \frac{\pi}{2}[C,y]\pi[H,y] - \frac{1}{2J} - \theta[H,x] \end{array} \right|$ acq. 1H $\left| \begin{array}{c} \text{dec. } ^1H \\ \text{rec. } \pm \end{array} \right|$

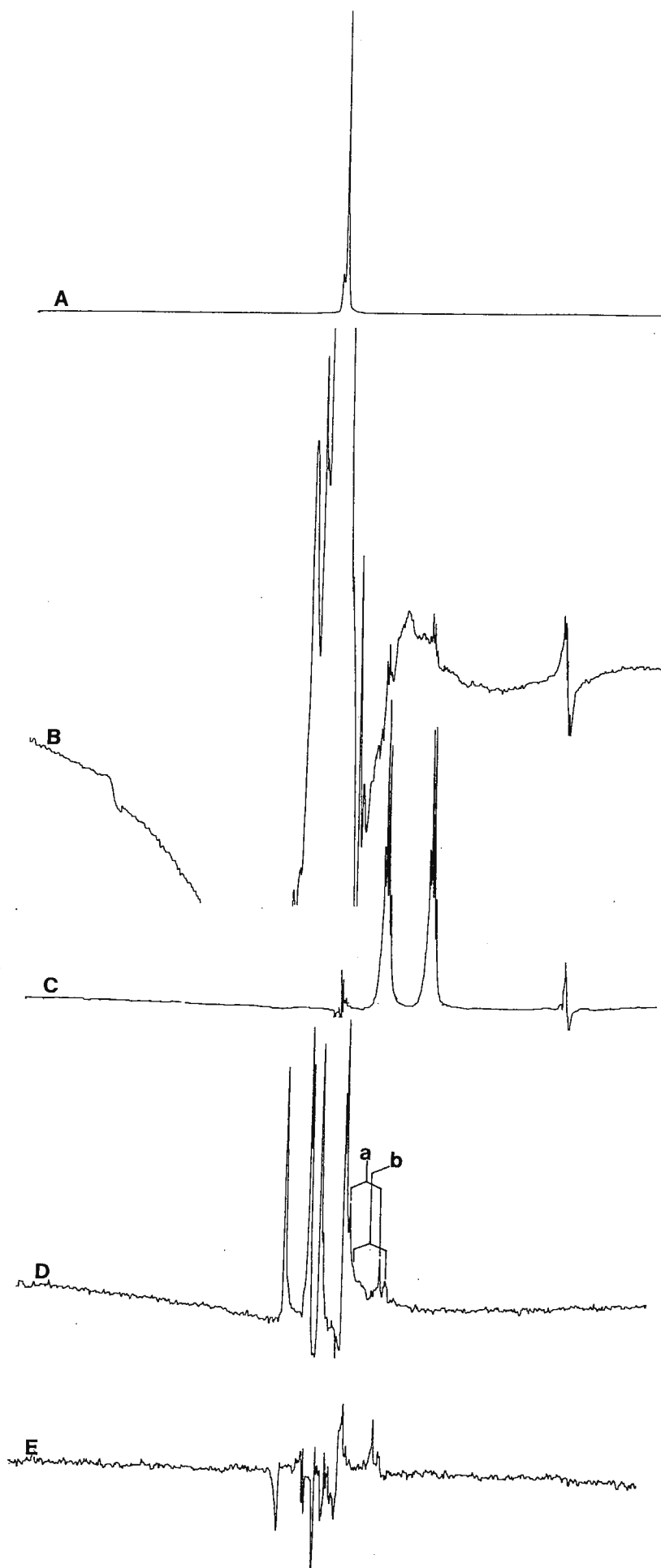
We have Inverse DEPT from which signals of only protons bound to ^{13}C nuclei are observed in H_2O . This has been used to follow metabolites in cells.

The figure shows (A) low gain spectrum of ^{13}C -1 labelled ethanol [100 mM] in 1H_2O . (B) spectrum (A) at high gain showing ethanol CH_2 protons (C) Inverse DEPT spectrum of the same sample. (D) Inverse DEPT spectrum of ^{13}C -1 labelled glucose in a mouse liver-cell extract after $1\frac{1}{2}$ hours metabolism showing (a) and (b) two new CH_2 resonances (E) Editing by subtracting spectra with $\theta = \frac{3\pi}{4}$ from $\frac{\pi}{4}$ to show CH_2 fragments.

We have subsequently developed a sequence termed Inverse POMME which gives a further significant improvement in suppression. Please credit this contribution to David Doddrell's account.

Yours sincerely,

William Brooks Mark Bulsing
W.M. Brooks J.M. Bulsing



PHILIPPS-UNIVERSITÄT MARBURG

FACHBEREICH CHEMIE

PD Dr. Stefan Berger



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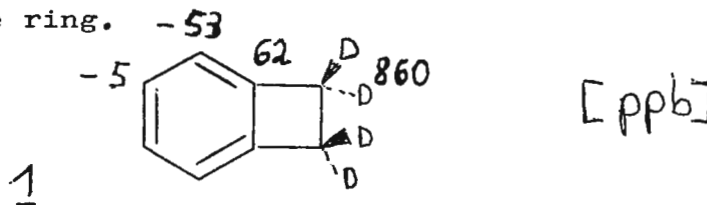
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Department of Chemistry
Texas A M University
College Station, TX 77842
USA

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Hyperconjugation and Deuterium Isotope effects ?

Dear Professor Shapiro,

In TAMU 297/15 L. Ernst postulates a hyperconjugative mechanism for the "wrong way" isotope effect of deuterium on ^{13}C -chemical shifts. For the ortho carbon atoms of tri-deuteriomethylated aromatic compounds a superposition of normal (upfield) and hyperconjugative (downfield) isotope effects is formulated. To test this intriguing idea we have recently synthesized benzocyclobutene 1, perdeuterated in the cyclobutene ring.



In 1 we find a very strong γ -downfield deuterium isotope effect. Following Ernst's reasoning, there should be a large degree of hyperconjugation in 1 compared with his examples, e.g. toluene¹⁾. However, this may be unlikely, since no CH-bond of the cyclobutene ring is coplanar with the π -orbitals and the CH-bonds have a higher s-character²⁾. A comparison of the PE-spectra³⁾ of o-xylene and 1 is inconclusive. Whether the rigidity of 1 contributes to the large isotope effect is just one more open question.

Sincerely yours

Stefan Berger

1) J.R. Wesener, H. Günther, Tetrahedron Letters 1982, 2845

2) H. Günther, W. Herrig, J. Am. chem. Soc. 1975, 97, 5594

3) F. Brogli, E. Giovanni, E. Heilbronner, R. Schurter, Chem. Ber. 1973, 961

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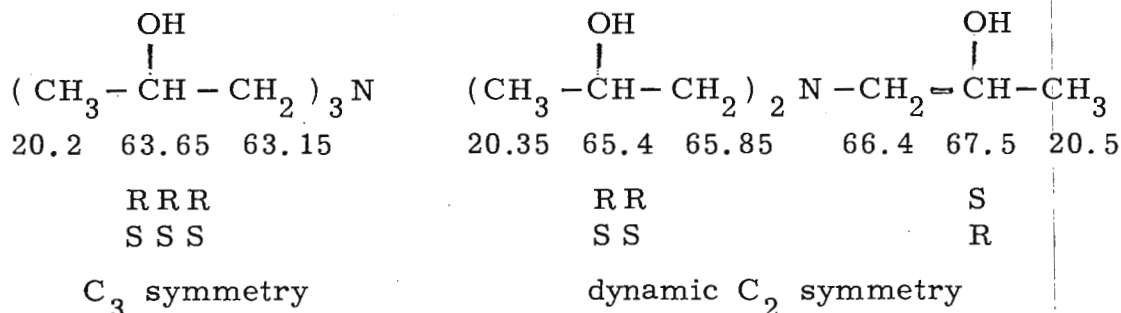
Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

^{13}C NMR of Triisopropanolamine

Dear Professor Shapiro:

Triisopropanolamine is a commercially available low melting solid known to consist of two diastereomers. An indirect kinetic analysis by Steinberg and Hunter (JACS 82, 853 (1960)) indicated the presence of the diastereomers in a ratio of 38 : 62.

Being an interesting case of three identical asymmetric centers, we considered it worthwhile to have a look on its ^{13}C NMR spectrum. The assignment of the 3 large and the 6 approximately half as large signals was achieved by determining the multiplicity of the resonances and by measurement of samples of different diastereomeric composition obtained by repeated fractional distillation.

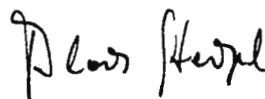


Statistically, the isomer in which the 3 asymmetry centers do not have the same configuration is favored by a factor of 3, thus explaining the similar intensity of 3 of its signals to those of the minor isomer, while the other 3 signals are twice as large.

The symmetry property of the two isomers requires some comment. While the C_3 symmetry of the minor isomer is not surprising, molecular models of the major isomer show the absence of symmetrical conformations. However, it can easily be demonstrated that fast $\text{N}-\text{CH}_2$ rotation and fast N inversion lead to a time-averaged C_2 symmetry.

It is also remarkable that all resonances of the major isomer are downfield to the corresponding resonances of the C_3 symmetrical isomer.

Sincerely yours,



Alois Steigel

Book Reviews

Editor: W. B. Smith
Texas Christian University
Fort Worth, Texas

Nuclear Magnetic Resonance Spectroscopy (A Physicochemical View)
by Robin K. Harris (School of Chemical Sciences, University
of East Anglia, England)

Pitman Publishing Co.
1020 Plain Street
Marshfield, Mass., 02050

Pitman Books Limited
128 Long Acre
London WC2E 9AN, U.K.

1983, 250 pages, \$34.95

In 1969, Robin Harris and Ruth Lynden-Bell coauthored a text with this same title, which presented the subject matter using a physical chemistry approach. Since the first version appeared just before the rapid developments in the field occasioned by FT techniques, there is plenty of new material in this new text. The presentation is aimed at upper level undergraduate students and graduate students. Those of us who simply cannot keep up with the latest developments in this exciting field will also welcome the arrival of this volume.

Chapter titles, which give us some idea of the book's content, are:
1. The Fundamentals; 2. Analysis of NMR Spectra for isotropic solutions;
3. Relaxation and Fourier transform NMR; 4. Dipolar interactions and double resonance; 5A. Chemical exchange, and B. Quadrupolar effects;
6. NMR of the solid state; 7. Special pulse sequences and two-dimensional NMR; and 8A. Chemical shifts and B. Coupling constants. There are four helpful appendixes, suggestions for further reading, and answers to selected problems appearing at the end of the chapters. Also given at the end of each chapter are a modest number of literature references and a few explanatory notes. At the end of the book there is a subject index of perhaps marginal extent, but no author index.

Not unexpectedly, the text opens with the usual introduction to the NMR phenomenon, chemical shifts, coupling constants, CW instruments, and first-order spectra. Harris does not assume a familiarity with quantum mechanics but rather gives a brief introduction to operators and wave functions in Chapter 2 and proceeds to apply these to spin functions for the AX and AB systems. Perhaps the text is open to criticism at this point for not going into more detail on spectral fitting, but there are lots of other things to be covered if the author wanted to keep the text within 250 pages. Chemical shifts and coupling constants are treated in more depth in Chapter 8.

As indicated in the Preface, Harris has elected (for reasons of space) to omit completely any discussions of NMR involving liquid crystal species and media, imaging theory and techniques, and CIDNP. He has also chosen to omit ("largely") biochemical applications.

There are now several books providing detailed accounts of FT-NMR, but to my knowledge this is one of the few general NMR texts presenting the subject in this detail and clarity. A nice discussion of relaxation is given, and with the information on dipolar interactions and double resonance in Chapter 4, the scene is set for introduction to recent developments of CPMAS in solids and the various forms of 2D-NMR in Chapters 6 and 7.

If, like myself, you are a chemist who likes to use NMR to solve problems, then chapters 6 and 7 will be particularly valuable in bringing you up to the state of the art. I intend to read them each a couple of more times in the hope that I may yet understand what the Ray Freemans, Richard Ernsts, and John Waughs of the world are trying to tell us.

W.B.S.

POSITION AVAILABLE

NMR Laboratory Director - University of Virginia

The Department of Chemistry at the University of Virginia is seeking qualified applicants for a permanent, state-supported staff position. The successful applicant will be expected to (i) assume responsibility for management of the Departmental NMR spectroscopy laboratory (presently includes Nicolet superconducting NT-360 and Varian EM-390 instruments), (ii) perform routine maintenance and repair, and (iii) supervise assistant spectroscopists. Faculty research interests presently include organic, inorganic, and biophysical chemistry, and collaboration is supported and encouraged. Background in modern NMR theory and practice is essential, and an advanced degree in chemistry is desirable. In addition, experience with electronics and computer systems would be advantageous.

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

25th August, 1983.

Dear Dr. Shapiro,

One regularly sees advertisements in TAMU Newsletter for positions available but none that I can recall for positions wanted. Assuming that this is just coincidence and not a matter of policy, I should be most grateful if you would publish this request.

I have been working towards a Ph.D. at Griffith University under the guidance of David Doddrell for three years largely in the fields of multipulsed NMR, but have also worked in the application of NMR to study biological (whole organ) systems. My initial work was with INEPT and more recently we have developed selective versions of both INEPT and DEPT using soft pulses to generate ^1H - ^{13}C correlations in a 1D experiment.

My latest work developed an inverse version of DEPT which transfers magnetization from ^{13}C to ^1H and hence allows observation of proton NMR signals in H_2O while suppressing the normally dominant water signal to negligible levels. This technique has been applied to cell suspension to observe the metabolism of glucose through glycolysis.

With the installation of a wide-bore 130mm 200 MHz magnet, I have also worked on perfused organ and whole animal projects and hope to apply multipulse approaches to these more complex and demanding systems.

In summary, I am keen to apply modern NMR techniques to the solving of biological problems. In particular, I should like to become involved in Imaging or TMR research. I expect to complete my Ph.D. early in 1984 and would like to be considered for any suitable position after that.

Please pass this information on to any person who may be interested.

Yours sincerely,

William Brooks

William Brooks



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Department of Chemistry / 303-753-2436

August 4, 1983

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

Dear Barry:

MAGNACHEM A200

We are purchasing the new Magnachem A200 NMR spectrometer. We expect delivery in about two months.

Many people are wondering whether this spectrometer will have as revolutionary an impact on magnetic resonance as the A60 did. Having operated the prototype, and examined its innards, we think it will do what it is advertised to do. When it is installed we will report on its performance to readers of the Newsletter. We will also welcome visitors to our lab to get hands-on experience with the A200.

To make room for this modernization of our lab, we would like to sell our cw XL-100. We are willing to sell either the whole spectrometer or parts, in accordance with the best offers we get by the time we have to move it. Make us an offer we can't refuse.

Sincerely,


Gareth R. Eaton


Sandra S. Eaton



TOWSON STATE UNIVERSITY
TOWSON, MARYLAND, 21204

Department of Chemistry

(301) 321-3058

August 6, 1983

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

Dear Barry:

We have recently purchased a multinuclear JEOL FX-90Q for the use of the department and local industry. This instrument has a TI-980B computer. We would like to populate the memory to its maximum but balked at the list price of \$2300 for 8K (I just installed 196K in my IBM for \$361). In particular, one board with at least 16K would suffice. We would appreciate any advice or hints from subscribers to the Newsletter regarding cheap sources for memory boards for this computer, new or used. Please write or call if you have any suggestions.

Yours sincerely,

Linda M. Sweeting
301-321-3113

varian / instrument group
25 hanover road / florham park / new jersey 07932
telephone (201) 822-3700



August 16, 1983

Dear Barry,

VARIAN NMR APPLICATIONS CHEMIST

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Relevant experience reflects the diverse nature of the job, and includes liquid-state nmr of all types (organic, inorganic, biological, polymers), solid-state nmr, 2D nmr, hardware development, software, teaching. "Technique"-oriented research, public speaking ability, and the ability to interact well with others are all characteristics which will be sought. Strength in as many areas as possible is desirable. Experience with Varian XL-series instrumentation is an asset but in no way a requirement.

Please send resumes and salary requirements to Dr. Steven L. Patt, Varian Instrument Group, 25 Hanover Rd., Florham Park, N.J. 07932. For more information call 201-822-3700 ext. 34. Varian is an equal opportunity employer.

Sincerely,

Steve Patt
NMR Applications Chemist

P.S. - Access to a \$250,000 word processor is an ancillary benefit of the job, as evidenced by this letter.



August 25, 1983

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

Dear Barry,

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August 31, 1983

Dr. Barry Shapiro
TAMUNMR Newsletter
Texas A & M University
Department of Chemistry
College Station, TX 77843

"Position Available"

Dear Barry:

We have an immediate opening for a scientific software specialist with a chemical background. Familiarity with minicomputers, Pascal and some assembly language is assumed. Please send resumes to my attention.

Best Regards.

James W. Cooper, Ph.D.
Vice President
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1 August 1983

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

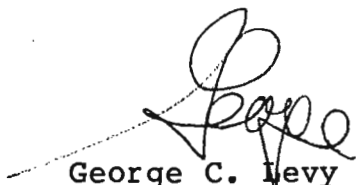
Dear Barry:

We anticipate one or two postdoctoral openings at the Resource Facility beginning April 1984, possibly sooner. Research will involve synthesis of oligonucleotides and high-resolution ^1H , ^{31}P , and ^{13}C -nmr studies directed toward determining structure and dynamics in double-helical DNA and RNA. Other projects can involve various 2D-nmr methods, transfer NOE studies of enzyme/substrate complexes, and metabolic ^{31}P -nmr studies. Applicants should have experience in high-resolution nmr or biophysical chemistry.


The Resource has multinuclear 360 wide-bore, 250, and 150 MHz nmr spectrometers. Most of the data is processed on Data General MV-8000 and MV-4000 computers with powerful software systems written here. Our laboratories have uv/vis and cd spectrometers, and the assorted equipment and expertise necessary for chemical and enzymatic synthesis of oligonucleotides.

We encourage suitable candidates to write or call us at the phone number below.

Sincerely,



George C. Levy
Professor and Director



Philip N. Borer
Research Associate Professor

GCL/PNB:cma

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

August 10, 1983

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

Dear Barry:

POSTDOCTORAL POSITIONS AVAILABLE

I shall have several postdoc positions available for the coming year, in the following areas:

- 1) High resolution NMR of inorganic solids, such as minerals and heterogeneous catalysts (in collaboration with geochemists and industrial laboratories).
- 2) High resolution NMR of proteins and biological membranes, with emphasis on surface dynamics, protein-lipid interactions and metalloprotein systems.

Our group is well equipped, and several 500 MHz, 360 MHz, and other lower field instruments will be available to the successful applicants.

Interested candidates should submit a letter of application including a curriculum vitae and list of publications, and arrange to have three letters of recommendation forwarded to:

Professor Eric Oldfield
School of Chemical Sciences
University of Illinois
505 South Mathews Avenue
Urbana, IL 61801 USA

Sincerely yours,



Eric Oldfield
Professor of Chemistry

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

Department of Chemistry

August 10, 1983

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

Dear Dr. Shapiro:

NMR TECHNICAL STAFF POSITION AVAILABLE


A permanent position is available in the Department of Chemistry at the University of Pennsylvania. The job is for an electronics technician whose main responsibility is to carry out the maintenance and modification of nuclear magnetic resonance spectrometers. While most of the work involves radio-frequency and digital electronics, there are some general duties associated with the position such as the filling of dewars with cryogenics.

The person will report to one faculty member, but will interact on a day-to-day basis with students and faculty in several research groups. Some informal teaching and assistance with electronics in this environment would be desirable.

There will be opportunities for learning additional skills and advancement in this position.

Interested candidates should write directly to me.

Sincerely,


Stanley J. Opella
Professor of Chemistry

SJO/bk



UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

August 25, 1983

Professor Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

POSTDOCTORAL RESEARCH ASSOCIATESHIPS AT NBS

I would like to publicize the availability of National Research Council-National Bureau of Standards Postdoctoral Research Associateships at the National Bureau of Standards. These associateships are competitive, depending on evaluation of qualifications and a research proposal submitted by the applicant. A booklet that describes application procedures, research opportunities, and research advisers may be obtained by writing or calling Dr. Robb Thomson, National Bureau of Standards, Washington, DC 20234, telephone 301/921-2103.

Final applications must be postmarked not later than January 15, 1984, and received in the Associateship Office not later than January 25, 1984. The Associateship Office will notify applicants of the disposition of their applications in March 1984. Appointments usually begin after October 1, but may begin during the period April 1, 1984 to February 1, 1985. The NRC-NBS Associateships are for U.S. citizens only; the current annual salary, subject to taxes, is \$24,508, and costs of travel and transportation of household effects within the U.S. are paid on appointment.

The NMR instrumentation available at NBS includes a Bruker WM-400 with new pulse programmer, magnetic tape drive, color graphics display, and a multi-color digital plotter, and also a Bruker CXP-200 with a variety of capabilities.

Early contact of interested applicants with a potential research adviser is advisable so that the adviser may assist with the writing of the research proposal.

Yours sincerely,

Bruce

Bruce Coxon
Organic Analytical Research Division
Center for Analytical Chemistry
Room A361, Bldg. 222
Telephone: 301/921-2867



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

August 30, 1983

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

Re: Postdoctoral Position

Dear Barry:

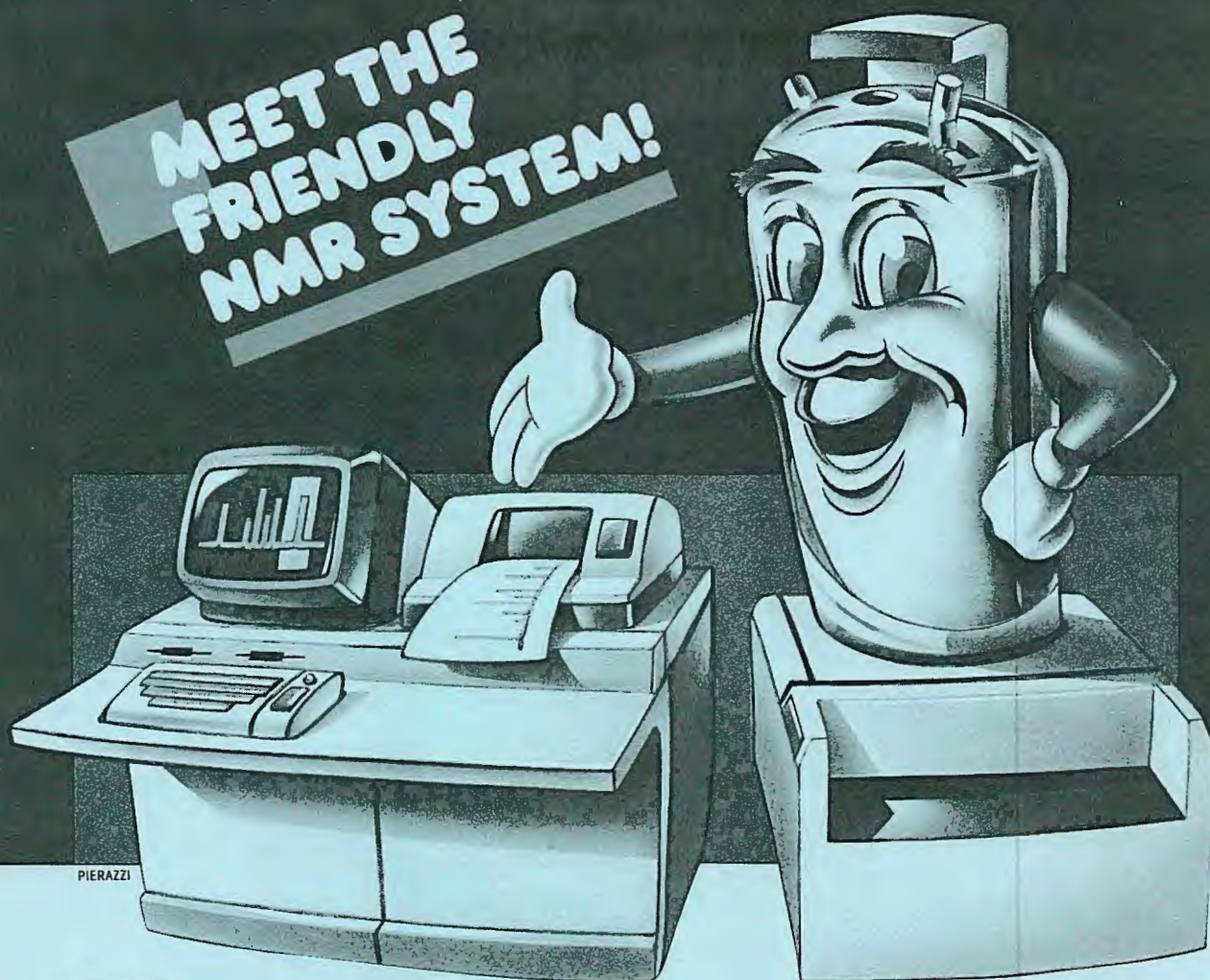
I would like to announce a postdoctoral opening in my laboratory at the Cancer Center. The work will involve the structural investigations of peptides and small proteins using various NMR techniques including 2D-NMR methods. Prior experience in this area and/or computer programming (Fortran and Basic) would be a definite advantage. The facilities at the Cancer Center include two high-field superconducting NMR spectrometers (Bruker WH-400 and CXP-300/200). Interested candidates may send a resume and arrange for three letters of recommendation to reach me at the Cancer Center.

Yours sincerely,

A handwritten signature in cursive script, which appears to read 'Ramu'.

N. Rama Krishna, Ph.D.
Assistant Professor of
Biochemistry and Physics

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That's why Nicolet developed the QE-300—a low cost, high performance NMR system for routine analysis of organic materials.

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The QE-300 has all the power you need for high sample throughput, high production laboratory use. A 300 MHz superconducting magnet combined with optimized RF electronics and a specially designed single carbon/hydrogen probe provide you with greater chemical shift dispersion and sensitivity. So you can run more samples faster and interpret results with less ambiguity.

Complete computer control

The QE-300 makes it possible for virtually anyone to get high quality NMR spectra—quickly and easily—without previous training or NMR experience.

A powerful NMR software package lets you set up and automate sample runs to your own criteria. And since the software is completely menu-driven, it's almost impossible to make a mistake.

All an operator has to do is slip a sample in and type a single key on the control console. The computer controls the spin rate, magnet shimming, lock frequency, and spectral phasing, acquires data to preset default parameters, and prints out the results, complete with full annotation of system settings.

You don't even have to change probes to get carbon and hydrogen spectra on the same sample. Just enter a single command, and the QE-300 makes the ^1H to ^{13}C conversion automatically.

Attractive features The QE-300 has features that make it a pleasure to use, too. Like a color display, an eight-pen color plotter, and a dual floppy disc system for interactive spectral analysis and unlimited external data storage.

And just as importantly, the QE-300 won't lead you down an alley of obsolescence. Its open-ended design leaves plenty of room for adding even more high performance capability in the future.

The Nicolet QE-300. It's the ideal NMR system for routine analysis, QC, and troubleshooting.

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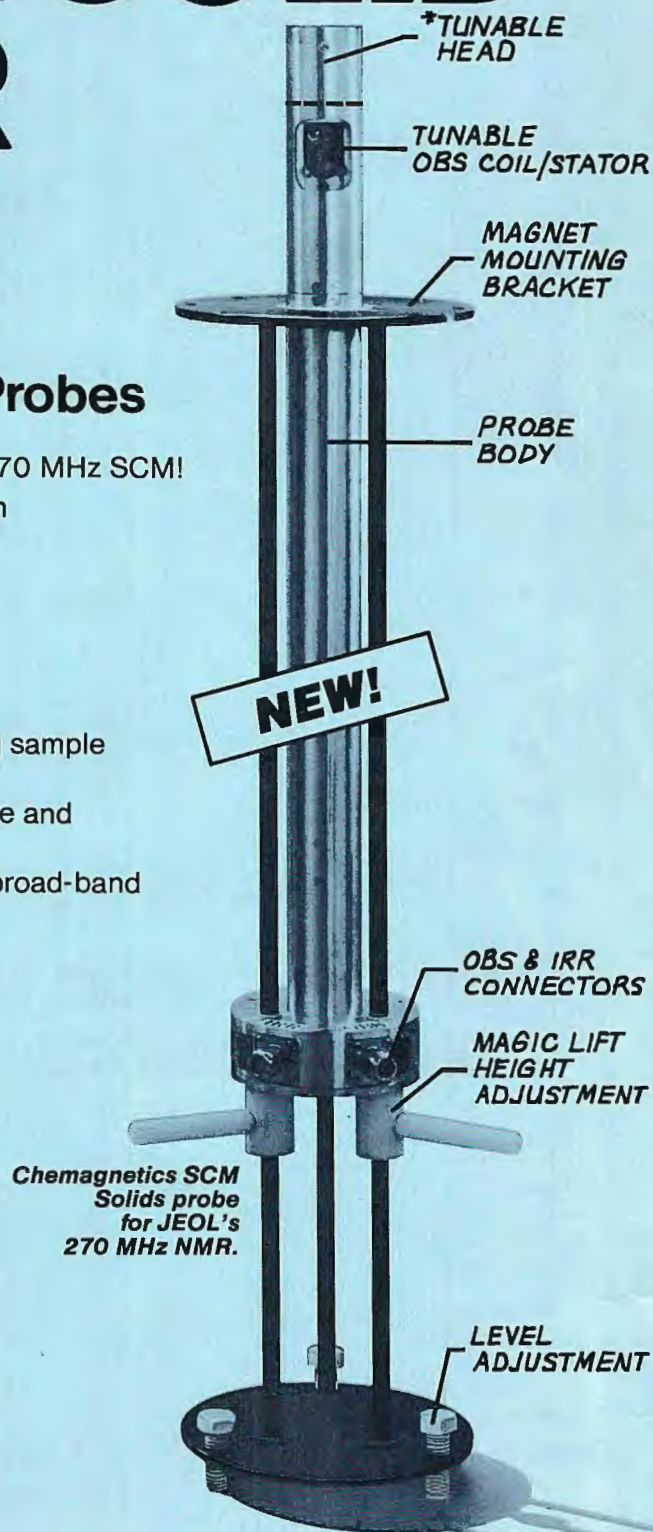
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with one probe!

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