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NMR NEWSLETTER

NO. 320

MAY 1985

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NMR NEWSLETTER

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ADVERTISERS

Forthcoming NMR Meetings (Additional listings are solicited)

Seventh International Meeting on NMR Spectroscopy - July 8-12, 1985, University of Cambridge; Chairman: Dr. Derek Shaw; Details from Dr. John F. Gibson, Secretary (Scientific), The Royal Society of Chemistry, Burlington House, London W1V OBN England.

12th FACSS Meeting - Sept. 30-Oct. 4, 1985, Philadelphia, PA; NMR Program Chairman: Rodney D. Farlee, E.I. du Pont de Nemours & Co., Inc., Experimental Station, Building 328, Wilmington, DE 19898; see TAMU NMR Newsletter 319, 9, (April 1985).

27th ENC - April 13-17, 1986, Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, NY 14642.

The Society of Magnetic Resonance in Medicine - August 19-23, 1985, London; Information from either Renee Sauers, Society of Magnetic Resonance in Medicine, 15 Shattuck Square, Suite 204, Berkeley, CA 94704, or Peter Peregrinus Ltd., P.O. Box 26, Hitchin, Hertfordshire, SG5 1SA, United Kingdom.

Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985, Kansas City, Missouri; Dr. Donald Wilk, Symposium Coordinator, University of Missouri-Kansas City, School of Pharmacy, 5100 Rockhill Road, Kansas City, MO 64110-2499.

1985 Eastern Analytical Symposium - November 19-22, 1985, Penta Hotel, New York; NMR Sessions on November 20 and 21: "NMR Spectroscopy in Two Dimensions" (Chairman, R. Freeman); "Applications of Modern NMR Methods" (Chairman, J.A. Ferretti); "Micro and Macro NMR spectroscopy: Polymers to Man" (Chairman, F.A. Bovey); "Advances in NMR Imaging Techniques" (Chairman, D.I. Hoult). Information from G.N. Chmurny, P.O. Box B, Frederick Cancer Research Facility, National Cancer Institute, Frederick, MD 21701, (301) 695-1226. Also tentative short courses on "Inside Your NMR: Introduction to Hardware Aspects of NMR Instrumentation" (R.E. Santini); "Introduction to Interpretation of NMR Spectra" (J.B. Grutzner); and "Introduction to Laboratory Data Systems" (S.N. Deming). For information, contact R.E. Santini, Department of Chemistry, Purdue University, West Lafayette, IN 47907, (317) 494-5230.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed - please make your wishes known.

* *Have you returned the readership survey card which was inserted into issue No. 317 (February)? If not, please let us know promptly how many people routinely read, inspect, or have the opportunity to use your copy of the Newsletter. Your cooperation will be appreciated.*

All Newsletter Correspondence Should be Addressed to:

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

Please note revised dates. →

DEADLINE DATES

No. 322 ------ 25 June 1985

No. 323 ------ 29 July 1985

320-2

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

uw kenmerk	uw brief van	ons kenmerk	datum	bijlage(n)
			25 March 1985	

onderwerp
Is the susceptibility anisotropy of aromatics correlated with the number of rings?

Dear Dr. Shapiro,

Diamagnetic susceptibility anisotropies of molecules are sensitive probes of the electronic structure. For that reason they can be used to investigate the aromaticity of molecules.

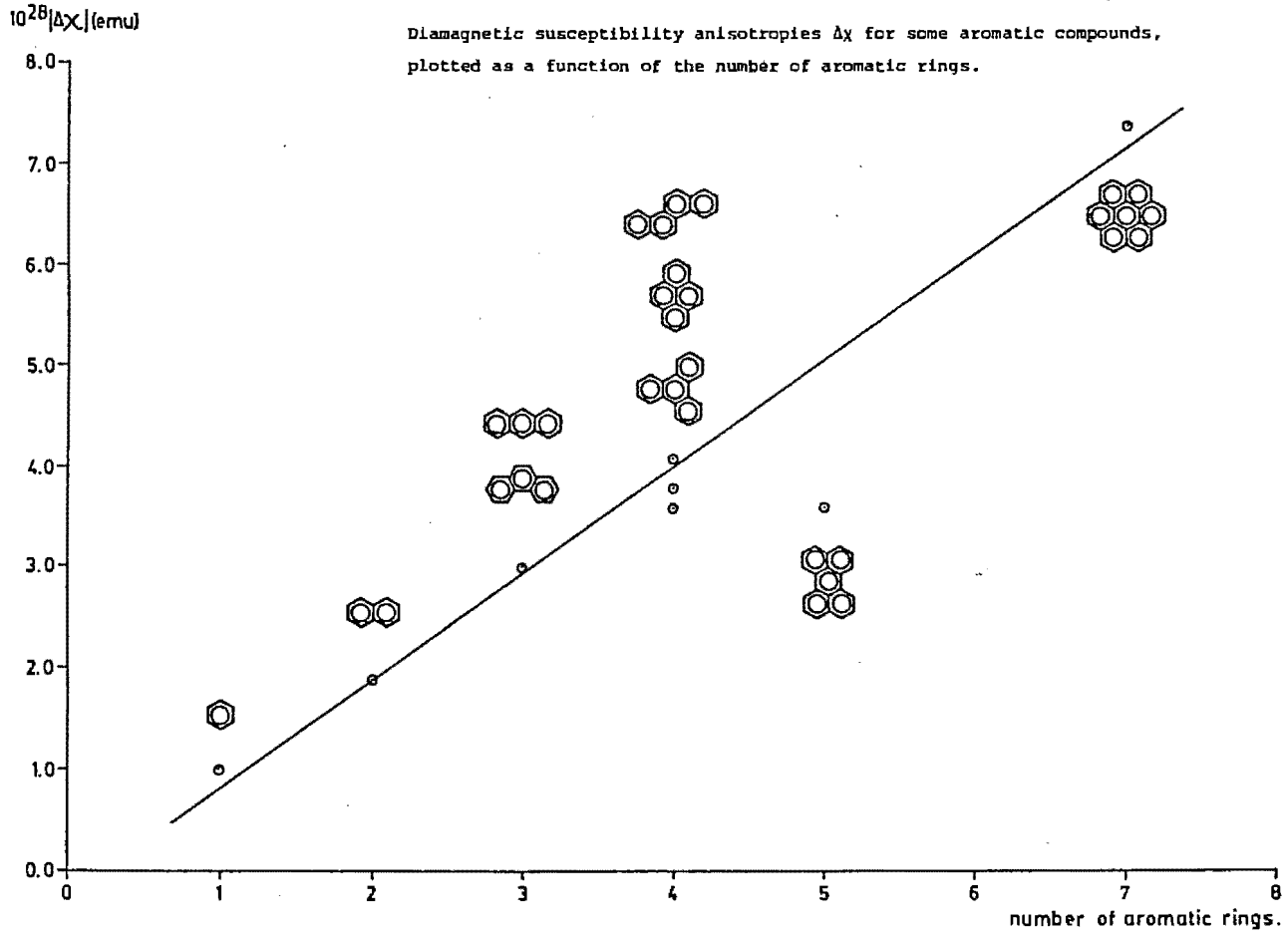
A simple method to determine susceptibility anisotropies of molecules is to measure their high field ^2H NMR spectra (1): Deuteron signals obtained at magnetic fields >10 T (diamagnetic molecules) tend to be split into doublets. These doublets originate from a small alignment of the molecules, caused by the combined action of the anisotropic diamagnetic susceptibility tensor $\bar{\bar{\chi}}$ and the magnetic field $\bar{B}$. The couplings are proportional to the anisotropy in the diamagnetic susceptibility $\Delta\chi$, and can be used to evaluate $\Delta\chi$. This NMR method for obtaining $\Delta\chi$'s has been shown to give reliable results (1,2).

Recently we measured $\Delta\chi$ for perylene and compared the result with previously obtained $\Delta\chi$'s from other aromatic systems. It is well known that susceptibility anisotropies increase almost linearly with the number of aromatic rings. The results obtained for a number of polycyclic aromatics (see table) agree herewith, as demonstrated in the accompanying figure.
All studied compounds, except perylene, show a distinct correlation with the number of rings. Considering perylene as a normal aromatic molecule (all the π-electrons participating in the conjugated system), one would expect perylene to give a $\Delta\chi$-value corresponding to five rings. The above comparison, however, suggests that perylene behaves as a system consisting of four aromatic rings. We conclude that the number of rings is not representative for $\Delta\chi$. Indeed, our $\Delta\chi$-values tally well with M.O.-calculations (3), as shown in the table.

Sincerely,

E.W. Bastiaan P.C.M. van Zijl C. MacLean

compound	10^{28} Δχ (emu) (exp.)	10^{28} Δχ (emu) (theor., ref.3)	no. of rings
coronene	-7.4	-6.74	7
perylene	-3.6	-3.85	5
chrysene	-4.1	-3.71	4
pyrene	-3.82	-3.62	4
triphenylene	-3.61	-3.45	4
anthracene	-2.94	-2.87	3
phenanthrene	-2.94	-2.77	3
naphthalene	-1.9	-1.90	2
benzene	-1.01	-0.98	1



Diamagnetic susceptibility anisotropies Δχ for some aromatic compounds, plotted as a function of the number of aromatic rings.

References

(1) P.C.M. van Zijl, B.H. Ruessink, J. Bulthuis, and C. MacLean, Acc. Chem. Res., 17, 172, (1984).

(2) A.A. Bothner-By, C. Gayathri, P.C.M. van Zijl, and C. MacLean, J. Magn. Res., 56, 456, (1984).

(3) E.R. Long, Jr., and J.D. Memory, J. Chem. Phys., 65, 2918, (1976), and references cited herein.

LABORATOIRES DE CHIMIE

Département de Recherche Fondamentale de Grenoble

Grenoble, le 28 mars 1985

N/référence : DRF/CH/85-110/mjc

Professor Bernard L. SHAPIRO
Department of Chemistry
College Station, Texas 77843-3255
U.S.A.

Reverse DEPT experiments on a WM200 Bruker spectrometer

Dear Dr. Shapiro,

Recently several techniques have been proposed which allow the selective editing of ^{13}C attached proton spectra by using a reverse (or inverse) transfer of polarization from ^{13}C to proton via the $^{1}J(^{13}C-H)$ spin-spin interaction (1)(2)(3). As the first step of these techniques usually consists of a presaturation of the proton magnetization, a very good suppression of the ^{12}C attached proton signals can be achieved resulting in very clean ^{13}C satellite spectra even in natural abundance of ^{13}C.

These techniques can be easily implemented on multinuclear instruments by using the proton decoupler channel and decoupling coil to detect protons while sending the carbon pulses to the ^{13}C observing coil in the usual way.

The only problem is to switch selectively at the RF mixing stage to obtain the proper proton reference frequency while retaining the ^{13}C frequency pulsing capability in the transmitter channel of the spectrometer. With our WM200 Bruker and after a few helpful telephone conversations with M. Yves FRAVAL of Bruker-Wissembourg, it turned out that this problem is easily solved by unpluging the Mixing Unit II in the BSV6-BB panel and replacing it by the L.O. Tripler unit, which is normally used in the generation of the proton observe frequency. In addition, the O_1 offset generation BNC output of the calculator has to be connnected to the decoupler as well as to the transmitter. The figure illustrates a satellite spectrum obtained with a test sample of 1,2-propanediol using this set up and the reverse DEPT technique (2). This technique has been applied to analyse the complex proton NMR spectra of

several heptitols acetates that Ronan LE FUR has been studying in collaboration with Pr. S.J. ANGYAL of the University of New South Wales, Australia.

In these compounds the ^{13}C satellite spectra were very useful to remove the accidental degeneracy in the chemical shifts of protons attached to different carbons. Part of the results of this study should appear in a forthcoming issue of Carbohydrate Research (4).

Yours sincerely,

J.P. ALBRAND* M.F. FORAY R. LE FUR

REFERENCES :

(1) R. FREEMAN, T.H. MARECI and G.A. MORRIS, J. Magn. Reson., 42, 341 (1981).

(2) M.R. BENDALL, D.F. PEGG, D.M. DODDRELL and J. FIELD, J. Magn. Reson., 51, 520 (1983).

(3) J.M. BULSING, W.M. BROOKS, J. FIELD and D.M. DODDRELL, Chem. Phys. Lett., 104, 229 (1984).

(4) S.J. ANGYAL, C.T. GRAINGER and R. LE FUR, to be published.

* Departement de Recherche Fondamentale, Service de Physique, Groupe Résonance Magnétique en Biologie et Médecine.

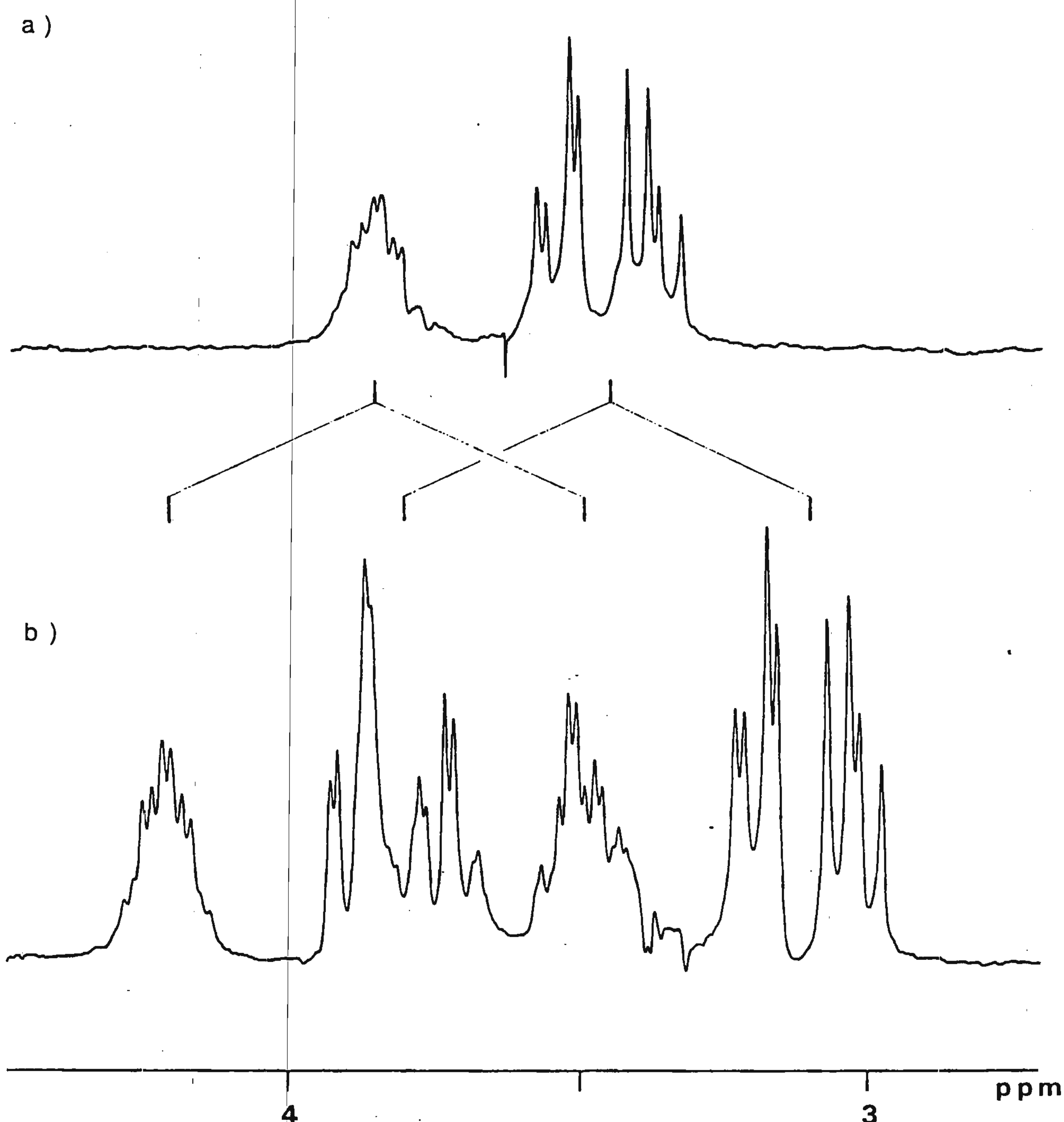


Figure : 200 MHz ^{1}H NMR spectrum of $CH_3-\underline{C}H(OH)-\underline{C}H_2OH$

a) Normal spectrum, 8 scans

b) Reverse DEPT spectrum, 3760 scans, 45° proton pulse to observe all the multiplicities.

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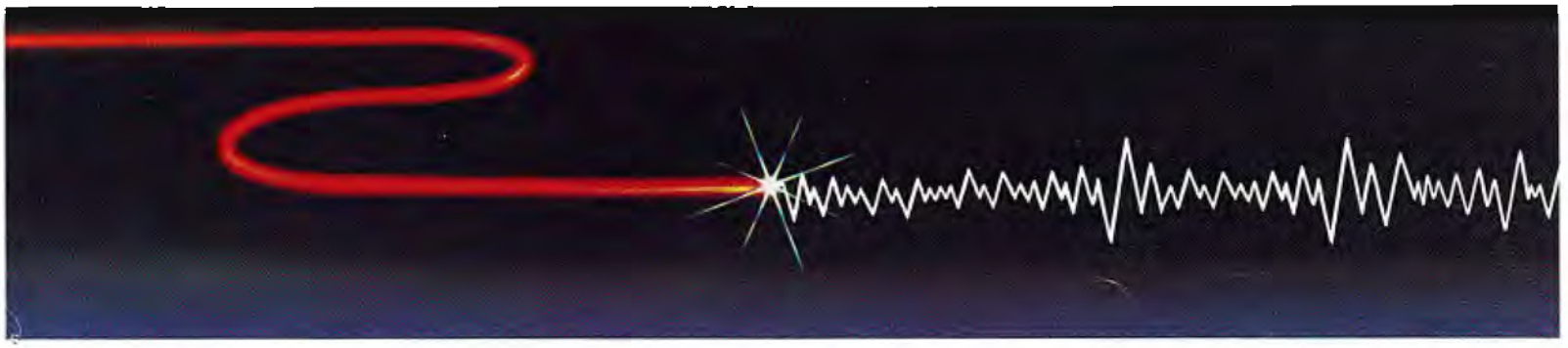

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Professor Bernard L. Shapiro
TAMU NMR Newsletter.
Texas A & M University
Department of Chemistry
College Station, TX 77843, USA

March 26, 1985

Determination of the Efg at Nitrogen in a Pyridine-Borane Complex.

Dear Barry,

We have studied the complex formed between 2,6-dimethyl-pyridine and borane (BH_3). At 298 K, in $CDCl_3$ solution, the T_1 values for carbons-3 and 4 translate into a reorientational correlation time of 6.8 $\pm$ 1.5 ps. Using a pulse sequence designed to reduce acoustic ringing (1), the ^{14}N linewidth is measured on the same sample at the same temperature : $\Delta\nu_{1/2}$ = 130 Hz. Hence, and with the assumption of extreme narrowing, the electrostatic field gradient at nitrogen eq = (5.3 $\pm$ 0.6) x 10^{21}, in SI units (kg s^{-3} A^{-1}).

Otherwise, the Gorbachev appointment in Moscow should not make you unaware of the presence of a new, 26 years old, chef at "Les Vannes", in Liverdun -- which, you assuredly know, is between Nancy and Pont-à-Mousson. I should watch him : his star may be on the rise, given his accomplishments. Be warned, however, that the desserts don't come up to the same very high levels.

Kind regards,

Cordially yours,

Yvette Houbrechts

Pierre Laszlo

PL:nd

(1) C. Brevard in NMR of Newly Accessible Nuclei. Chemical and Biochemical Applications, P. Laszlo, ed., 2 vols. 1983-1984 , New York : Academic Press - vol. 1, p 19.

320-10

United States Department of Agriculture | Agricultural Research Service | North Atlantic Area Eastern Regional Research Center | 600 East Mermaid Lane Philadelphia, Pennsylvania 19118

March 25, 1985

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

Dear Dr. Shapiro:

Title: Hexamethylphosphoramide (1): Reference for IN VIVO ^{31}P NMR

Since the inception of our IN VIVO plant tissue studies, we have had a need for a more reliable and stable ^{31}P reference. Because the ^{31}P chemical shift of phosphoric acid resonates too closely to the vacuole orthophosphate resonance in the spectrum of plant tissue samples, H_3PO_4 is difficult to use in an external capillary as a reference. A convenient alternative reference suggested by Roberts et al. (2) is methylene diphosphonic acid (MDP) which resonates approximately 12 ppm downfield from the lowest field ^{31}P resonance (glucose 6-phosphate) in maize root tissue. Unfortunately, in order to maintain the shift for MDP you must dissolve it in TRIS buffer at pH 8.9 in a sealed capillary. This preparation is stable for a limited time (1 to 2 days), and a fresh sample must be used for each daily experiment. Furthermore, if higher temperature studies (above 28°C.) are to be made, rapid degradation of the MDP signal is immediately apparent, making intracellular pH measurements highly inaccurate.

Hexamethylphosphoramide (HMPA) is an extremely stable compound (B.P. 230°C.), whose chemical shift is independent of its pH environment. Since its chemical shift is at relatively low field (13.84 ppm downfield from MDP) HMPA is convenient as an external reference for most IN VIVO ^{31}P experiments.

Figure 1 shows a typical 161.7 MHz spectrum of corn root tips (~900, 5-7 mm excised tips) whose total concentration of mobile, observable tissue ^{31}P is approximately 12 mM. The signal of the reference is from a capillary containing 120.0 mM HMPA in H_2O. The referencing of a shift position for the ^{31}P compounds in the root tissue are consistent with those already reported in the literature.

Although HMPA contains 9 methyl protons, proton splittings are unresolvable under the experimental conditions of no decoupling and 15 Hz of added computer line broadening (15-20 Hz is the range of line widths observed for this tissue). If a narrower reference line is desired, proton decoupling or perdeutero HMPA could be utilized.

Sincerely,

PHILIP E. PFEFFER
Research Leader

WALTER V. GERASIMOWICZ
Research Chemist

Physical Chemistry and Instrumentation Laboratory

(1) HMPA is a known carcinogen and should be handled with gloves in a well ventilated hood.

(2) J. K. M. Roberts, P. M. Ray, N. W. Jardetsky, and O. Jardetsky. Nature 238, 870-872 (1980.

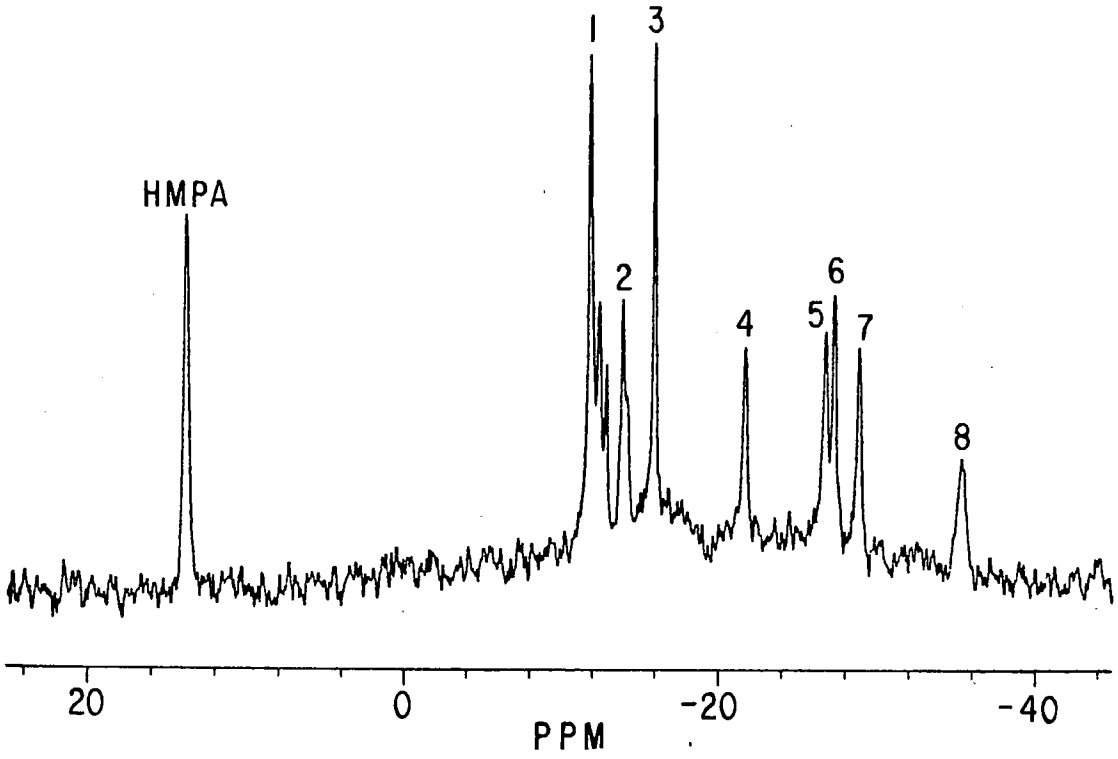

FIGURE LEGEND:

161.7 MHz ^{31}P spectrum of approximately 900 excised maize root tips (5-7 mm long) occupying approximately 3.75 cm of a 10 mm NMR tube (capillary reference of 120.0 mM HMPA placed in the center of this sample). The sample is being continually perfused with an oxygen saturated solution containing 0.1 mM $CaSO_4$ and 50.0 mM glucose. The spectrum was obtained with 10K transients at a 30° pulse angle, 0.162 sec. pulse delay, 16K spectral width and 2K data points zero filled to 16K. Peaks (1) glucose 6-phosphate, (2) cytoplasmic Pi, (3) vacuolar Pi, (4) γ-ATP, (5) α-ATP, (6) and (7) UDPG, (8) β-ATP.

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Priv. Doz. Dr. Stefan Berger

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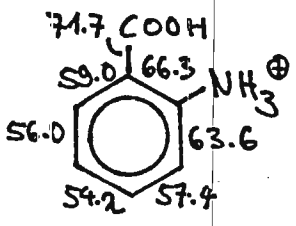
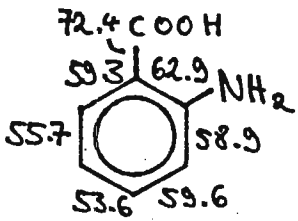
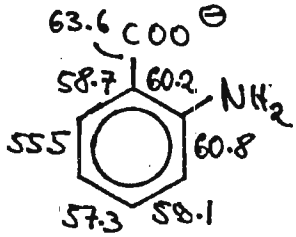
Charge Dependence of $^{13}C^{13}C$-Spin-Spin Coupling Constants

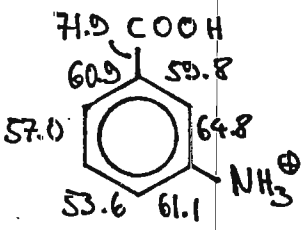
Dear Professor Shapiro,

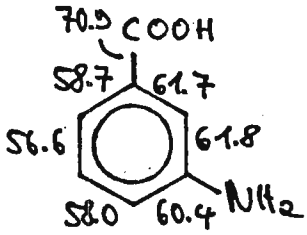
I have recently observed some interesting pH dependent changes of the $^{13}C^{13}C$-spin-spin coupling constants in Vitamin C [1]. As far as I know, no systematic study of the charge dependence of the $^{13}C^{13}C$ coupling constants is published, therefore I subsequently studied the series of ortho-, meta- and para-aminobenzoic acids, where cation, neutral compound and anion are available within the same molecular framework. The values are given in the formula scheme below and I soon hope to be able to write up these results.

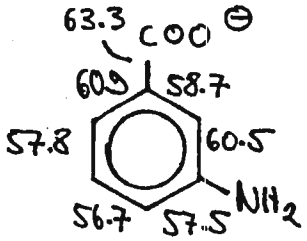


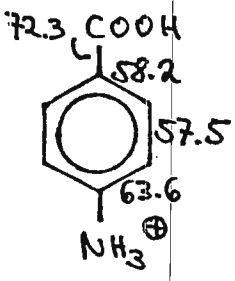


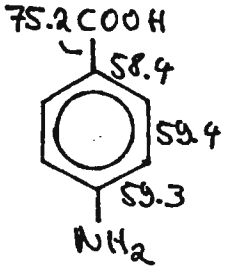


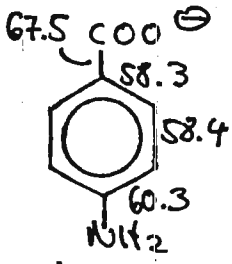












Sincerely yours

Stefan Berger

1) S. Berger, J.C.S.Chem.Comm. 1984, 1252

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Poul Erik Hansen, Institute I, Life Sciences and Chemistry
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Professor Benard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TEXAS 77843
U S A

DATO/REFERENCE 19850325/kt | JOURNALNUMMER | DERES REFERENCE/JOURNALNUMMER

Directional Effects and non-additivity of deuterium isotope effects on nuclear shielding of Acylderivatives.

Dear Professor Shapiro,

In a recent collaboration with K. Schaumburg and F. M. Nicolaisen we have investigated deuterium isotope effects on ^{1}H, ^{19}F and ^{13}C nuclear shielding of deuterium isotopomers of acylderivatives and especially acetylfluoride and acetaldehyde. A total analysis involving also three - bond H - F coupling constants revealed that $^{3}\Delta F(D)$ depends strongly on geometry as $^{3}\Delta F(D)_{\underline{trans}}$ = 0.06 ppm and $^{3}\Delta F(D)_{\underline{gauche}}$ = - 0.06 ppm. Isotope effects, $^{3}\underline{\Delta F(D)}$ of acetylflouride are furthermore non-additive caused primarily by unequal rotamerdistribution of the mono and dideuteroisotopomers. $^{3}\Delta H(D)$ of acetaldehyde is likewise negative indicating that this compound behaves similarly to acetylflouride.

$^{2}\Delta CO(D)$ of a series of carbonylcompounds have also been measured. They range from negative as in acetone * to positive in methylacetate and the order is acetaldehyde > acetone > acetophenone > acetylfluoride > acetic anhydride > acetic acid > methylacetate, a trend that is well known from organic chemistry.

Yours sincerely

Poul Erik Hansen

PS! Reprints and preprints dealing with isotope effects on nuclear shielding are wanted in the preparation of a review in the fall.

* G. E. Maciel, P. D. Ellis and D. C. Hofer, J. Phys. Chem. 71, 2160 (1967).

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

TEXAS 77843 U.S.A.

N/Réf. : AN.179/85
JJB/NF
V/Réf. :

PIERRE-BÉNITE, le March 26th 1985

Dear Professor SHAPIRO,

^{17}O-NMR of tert-butylhydroperoxide

In order to monitor oxidative processes at room temperature, we needed an easy access to ^{17}O spectra of tert-butylhydroperoxide. We were very puzzled about the unique datum published in the pioneering investigations by CHRIST and coworkers (1) in the 1960s. They reported a broad line ($\Delta\nu_{1/2}$ 1000 Hz) at δ 260 for this peroxide.

With a concentrated commercial aqueous solution (7.5 M), we could hardly detect any signal after overnight accumulation at r.t. At 80°C, a spectrum was obtained with difficulty because of extensive decomposition.

Figure 1 illustrates our results with diluted solutions of isotopically enriched $\mathrm{C(CH_3)_3}^{**}\mathrm{OOH}$ ($\sim$ 10 % ^{17}O). As shown by the spectra, two readily assignable oxygen sites are visible (see table). The ^{17}O signals are broader in water, probably due to association and greater viscosity. This may account for the difficulty of getting good spectra at r.t., at natural abundance levels.

(1) H.A. CHRIST, P. DIEHL, H.R. SCHNEIDER, H. DAHN
Helv. Chim. Acta 44, 865 (1961)

Table - ^{17}O data of tert-butyl-hydroperoxide (O^a-O^b-H)

		O^a δ	O^a $\Delta\nu_{1/2}$ (Hz)	O^b δ	O^b $\Delta\nu_{1/2}$ (Hz)
Labeled compound (~ 10 % ^{17}O)	anhydrous in hexane (room temperature)	249	440	206	330
	aqueous solution (room temperature)	246	750	206	650
Natural Abundance (7.5 M)	aqueous solution at 80°C	248	250	205	200

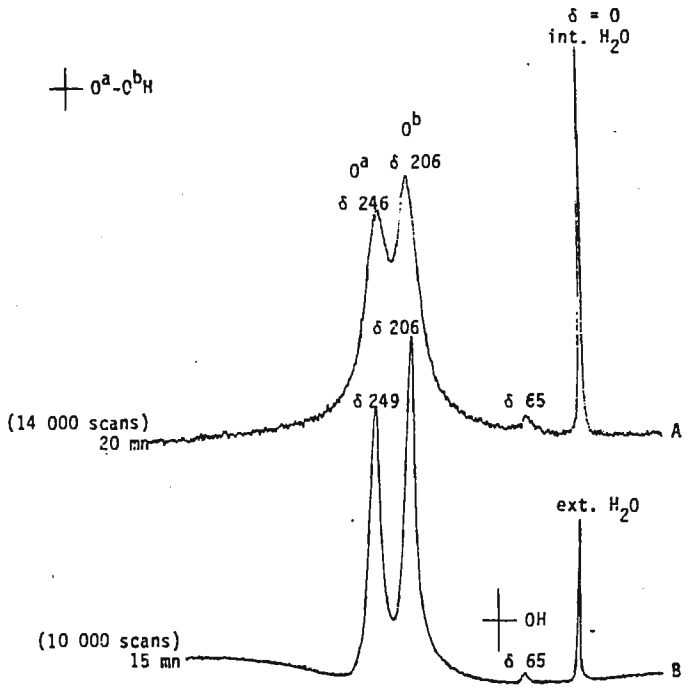

Figure 1 - ^{17}O-NMR (27.02 MHz) of Labeled tert-butyl-hydroperoxide (~ 10 % ^{17}O)

at room temperature

A - aqueous solution (2 M)
B - solution in hexane (1 M)

L. LEGLEUT P. LUBIN J.J. BARIEUX

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DEPARTMENT OF CHEMISTRY
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Professor D.C.Bradley, DSc., FRS
Professor K.W.Sykes, MA.,BSc., DPhil.

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

29th March 1985

Dear Professor Shapiro,

Solid-State ^{13}C Spectra of Metallocarbonyls

If this fails to meet the April 1st deadline, then it must be the fault of the trans-Atlantic postal system. We have one recent result which we find interesting:- while anticipating the arrival of the ULIRS MSL-300 at London University (to be delivered to Duncan Gillies' Lab. at Royal Holloway College) we have been trying to get some first-hand experience of the problems and the rewards of solids n.m.r. in the area of metallocarbonyl chemistry. Professor Silvio Aime (University of Turin) provided a moderately ^{13}C (carbonyl) enriched sample of $Fe_3(CO)_9(EtCCEt)$ and Drs. Chris Dobson and Lu Yun Lian at Oxford ran the ^{13}C spectrum. Our input to the problem of the answer (see Figure) is philosophical:- the low temperature ^{13}C solution spectrum has only 3 peaks (intensity 6:1:2) so why 7 peaks here? This could be (a) more than one crystal modification and/or (b) more than one molecule/unit cell, or (c) we see one molecule but the crystal packing is such that the CO groups are not occupying equivalent sites, and (d) why do the relative intensities of the 7 peaks look so peculiar?

We don't expect that any of the above will excite your average solids n.m.r. buff, but to us it is new, different, and therefore good fun.

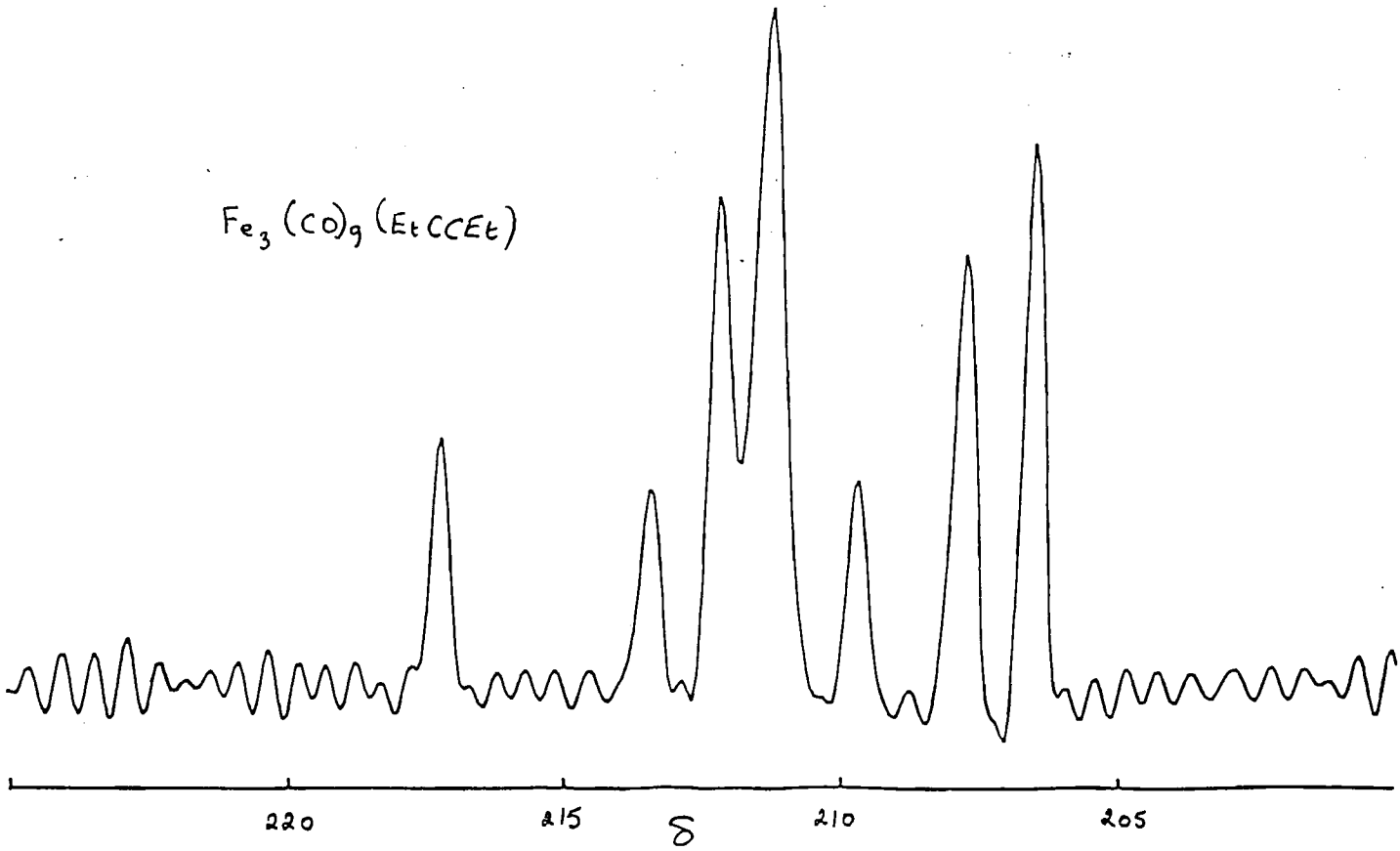
Best wishes

Yours sincerely,

Geoff Hawkes

Dr. G.E. Hawkes

(act. Ed Randall)



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April 2, 1985

Professor Bernard L. Shapiro
c/o TAMU NMR Newsletter
Department of Chemistry
Texas A and M University
College Station, Texas 77843-3255

Subject: Sample Integrity and $Cr(acac)_3$ for Silanol Quantitation by ^{29}Si NMR Spectroscopy

Dear Professor Shapiro:

An area of considerable interest is the quantitation of silanol-bearing species (1). For this, ^{29}Si NMR spectroscopy offers some very real advantages. ^{29}Si NMR is specific for silanol type and the effort required for sample preparation is minimal. In addition, the method is expected to be free of interferences caused by the presence of H_2O and carbinol species.

For dilute solution analysis, the experimental difficulties imposed on the signal averaging process in ^{29}Si NMR by long spin-lattice relaxation times (T_1's) may be reduced by the use of a suitable relaxation agent like $Cr(acac)_3$. As part of our study, we used an acetone-d_6 solution of Me_3SiOH (20% v/v, δ=12.8 ppm) and its condensation product, hexamethyldisiloxane (HMDS) (20% v/v, δ=7.1 ppm). In the absence of $Cr(acac)_3$ the T_1's were found to be 42.5 + 0.6 sec and 45.0 + 0.3 sec respectively. In the presence of $Cr(acac)_3$ at the 0.02 M level, the T_1's were 4.0 $\pm$ 0.1 sec and 5.9 $\pm$ 0.1 sec respectively.

However, organic compounds of metals (2) have been observed to promote silanol condensation and it was of interest to see whether sample integrity would be affected by the presence of $Cr(acac)_3$ at room temperature (ca 20°C). This would be of concern during extensive periods of time averaging. To test this point, six values of the HMDS/Me_3SiOH molar ratio were determined for a freshly prepared solution without $Cr(acac)_3$ and again after 24 hours. In a similar fashion, a freshly prepared solution doped with $Cr(acac)_3$ at the 0.02 M level in acetone-d_6 was studied immediately after preparation and after 24 hours. A comparison of results is shown on the following page.

MEAN FOR 6 VALUES OF THE HMDS/Me_3SiOH MOLAR RATIO

	Without $Cr(acac)_3$	0.02 M $Cr(acac)_3$
Time = 0	mean = 0.753 s = 0.008 s^2 = 7.1×10^{-5}	mean = 0.747 s = 0.012 s_2 = 1.3×10^{-4}
Time = 24 hrs.	mean = 0.745 s = 0.004 s^2 = 1.7×10^{-5}	mean = 0.742 s = 0.008 s^2 = 6.6×10^{-5}

Statistically, the above data is very consistent and it indicates that $Cr(acac)_3$ is chemically inert towards silanols. It would seem that the long term presence of $Cr(acac)_3$ is not a cause for concern about sample integrity.

As an independent confirmation of the method's reliability, the silanol species in question may be reacted with $(HN-(SiMe_2Vi)_2)$ to yield a species with a $O_{1/2}SiMe_2Vi$ endcap. Subsequent analysis by capillary gas chromatography yields quantitative data concerning silanol content. After derivatization, the model system without $Cr(acac)_3$ yields only two species of interest: HMDS and $Me_3Si-O-SiMe_2Vi$. GC analysis provides a value of 0.71 as the HMDS/Me_3SiOH molar ratio. The close agreement of two such different methods is yet another indication of both the chemical inertness of $Cr(acac)_3$ towards silanol species and its utility in timely and accurate silanol quantitation.

Sincerely yours,

Thomas M. Carr Paul J. Garner

Thomas M. Carr
Analytical Research

Paul J. Garner
Analytical Research

1) Griffith, G. W., Ind. Eng. Chem. Prod. Res. Dev., 23 590-593 (1984).

2) Noll, W., Chemistry and Technology of Silicones, Academic Press, New York, 1968, pp. 213-214.

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DEPARTMENT OF CHEMISTRY DAVIS, CALIFORNIA 95616

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

April 9, 1985

Proton-Proton Nuclear Overhauser Effect in High-Spin Metmyoglobin

Dear Professor Shapiro,

One fine day, Gerd entered the lab and said: "In our efforts to apply the nuclear Overhauser effect to the study of paramagnetic proteins at any cost, let's perform the experiment on met-aquo myoglobin to assign some of its heme (Figure 1) resonances."
Rather flabbergasted, we answered: "But it's a high-spin (S = 5/2) ferric form!"
-"Yes, alas, only some of the hyperfine shifted peaks could be identified by isotope labeling, and we must know what the others are."
Now, you see, this sounded impossible and we cried "The proton spectrum of met-aquo myoglobin extends over a range of 100 ppm and exhibits broad lines (Figure 2A)... The spin-lattice relaxation times of the signals appearing downfield from 10 ppm vary between 0.2 and 8 ms, such short times should reduce the observable NOEs dramatically! Besides, we'll never saturate those lines selectively."
-"Keep in mind, we get large NOEs in the low-spin form, we should see something in the high-spin form. Try it ASAP!"
Well, late one night, we did try and in Figure 2B, you can see the results of a regular 1D NOE experiment at 500 MHz: when a 0.05 W r.f. field is applied for 30 ms to the one-proton resonance e, saturating the line to 50%, a negative NOE is observed to the 8-methyl and peak h. The size of the NOE from e to h is 4% whereas that of the reciprocal NOE, from h to e (Figure 2C), is 7%.
Gerd commented: "It's unambiguous. By using the pertinent equation

$$\eta = (\gamma^4 H^2 \tau_c)/(10 r^6 \rho)$$

and the experimental values $\rho^{-1}(e) = 5.1$ ms, $\rho^{-1}(h) = 2.2$ ms and $\tau_c = 10$ ns, we obtain a r_{eh} consistent with the distance expected for a geminal proton pair (1.77 Å). The only pair that would show dipolar connectivity to the 8-methyl is the 7-α-CH_2 propionate. It is also interesting to note that the NOE allows us to distinguish the two protons of the diastereotopic pair: e is close to the CH_3, whereas h is more remote. Doesn't this prove that in spite of the short relaxation times T_1 and T_2, very useful NOEs can be profitably observed in high-spin hemeproteins? Listen, you know what we should try this on..."

Moral: the boss is always right but should never leave on sabbatical.

With our best regards,

Juliette

Gerd La Mar Juliette Lecomte Steve Unger

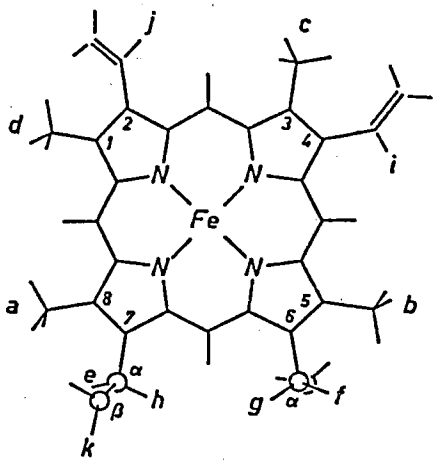

Figure 1: the heme structure in met-aquo myoglobin (CO_2 groups omitted)

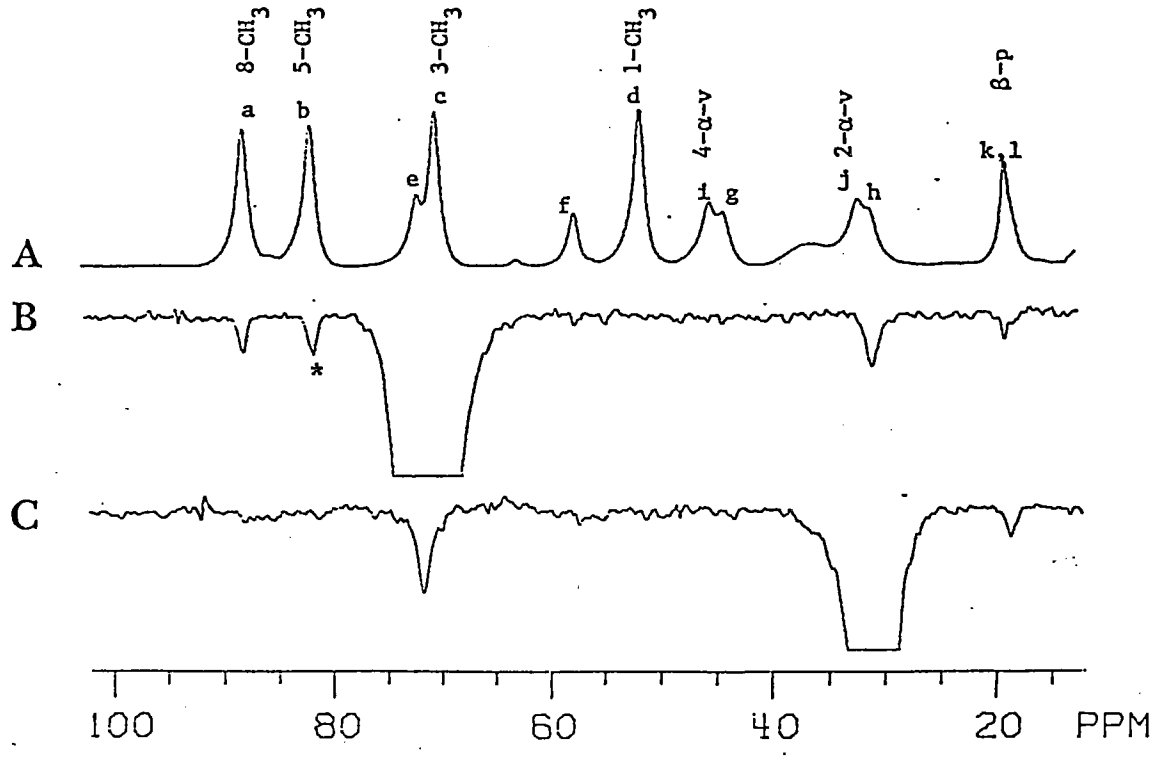

Figure 2: A, 500 MHz spectrum of met-aquo myoglobin (40°C, pH 6.4).
B, NOEs obtained by irradiation of e, the * indicates intensity solely due to off-resonance effect.
C, NOEs obtained by irradiation of h.

OPERATIONS DIRECTOR
Purdue Biochemical Magnetic Resonance Laboratory
and
POSTDOCTORAL RESEARCH ASSOCIATES IN BIOLOGICAL NMR SPECTROSCOPY AND PROTEIN DESIGN
Chemistry Department, Purdue University

Operations Director: NMR Spectroscopist (Ph.D.) to manage, collaborate, and interact with the user community of the Purdue University Biochemical Magnetic Resonance Laboratory (an NIH Regional Resources Facility). The facility has the latest state-of-the-art Nicolet 470 MHz and Varian XL-200 instruments (the later has a wide-bore magnet and an array processor for very fast 2-D processing). In addition a wide-bore Nicolet 200 MHz spectrometer is available in an adjacent laboratory. This position will be available Fall, 1985. Salary is commensurate with skills for an NIH supported staff-level position.

Post-Doctoral Associates: Several postdoctoral positions are available for Fall, 1985. These studies are directed towards the development of new applications of NMR spectroscopy to probe the detailed molecular structure and dynamics of biological molecules. Multinuclear (^{1}H,^{2}H,^{13}C,^{17}O,^{19}F,^{31}P, etc.) NMR of enzyme complexes, nucleic acids, nucleic acid-drug and carcinogen complexes and nucleic acid-protein complexes is being pursued. The laboratory is involved in new instrumentation and computer soft-ware development, and will include state-of-the-art 470 MHz and two 200 MHz NMR spectrometers. Two-dimensional NMR studies will be used to describe the three-dimensional structure of proteins, nucleic acids, and their complexes.

Site-specific mutagenesis, recombinant DNA methodologies will be used to design new proteins for NMR study. One project will involve the site-specific mutagenesis of the lac repressor.

Other projects will involve ab initio molecular orbital and molecular mechanics computer calculations to probe the reactivity of bio-organic model systems and their enzymatic counterparts. The model system studies center on the stereoelectronic effect in phosphoryl and acyl transfer reactions. Additional calculations on the Purdue University Cyber 205 "super" computer will involve modeling of protein reaction pathways and DNA repressor protein complexes.

A background in enzyme isolation, enzymology, recombinant DNA molecular biology, NMR spectroscopy or computational chemistry would be appropriate.

The salary is comparable to the NIH postdoctoral scale and commensurate with experience. The positions are available for one year and are renewable for a second year if desired. Interested candidates should send a copy of their curriculum vitae and have two or three letters of reference forwarded directly to

Dr. David Gorenstein

After August 15, 1985
Department of Chemistry
Purdue University
West Lafayette, Indiana 47909

Prior to August 15, 1985
Department of Chemistry
University of Illinois at Chicago
P. O. Box 4348
Chicago, Illinois 60680

D. G. Gorenstein (Editor), ^{31}P NMR: Principles and Applications, Academic Press, 1984.

D. G. Gorenstein, K. Lai, and D. O. Shah, "P-31 and Two-Dimensional $^{31}P/^{1}H$ correlated NMR Spectra of Duplex d(Ap(O-17)Gp(O-18)Cp(O-17)T) and Assignment of P-31 Signals in $d(ApGpCpT)_2$·Actinomycin D Complex, Biochemistry, 23, 6717 (1984).

D. O. Shah, K. Lai, and D. G. Gorenstein, "^{13}C NMR Spectroscopy of 'Transition-State Analogue' Complexes of N-Acetyl-L-Phenylalaninal and α-Chymotrypsin, J. Am. Chem. Soc., 106, 4272 (1984).

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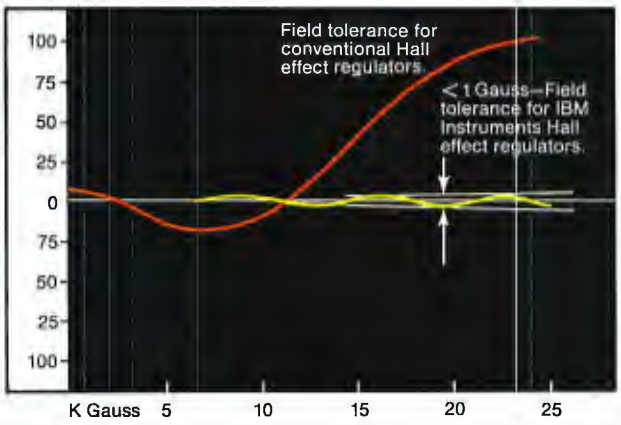

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April 3, 1985

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

RE: A Simple Relationship to Check the Validity of NMR Data of Fossil Fuels

Dear Barry:

Both ^{1}H and ^{13}C NMR have been used extensively in qualitative and quantitative characterization of fossil fuels. Data from ^{1}H NMR are generally quite good because there are essentially no instrumental or physiochemical difficulties in acquiring good quantitative data. However, with ^{13}C NMR, obtaining quantitative data are more difficult. The problems associated with obtaining quantitative ^{13}C data have been addressed by many investigators. Even though the methods described in the literature do provide quantitative ^{13}C data, it would be more assuring if the NMR data of fossil fuels could be internally evaluated in conjunction with data obtained for another technique without the addition of a standard calibrant which for most fossil fuel studies would be most difficult.

A relationship (equation 1) is given which compares the fraction of Tertiary aromatic carbon resonances in the ^{13}C spectrum with the aromatic atomic hydrogen to carbon ratio, $(H/C)_a$, obtained from ^{1}H and ^{13}C aromaticity values, and elemental analysis.

$$f_t^c = (12H_w/C_w)_T \times (f_a^h/f_a^c) = (H/C)_a \qquad (1)$$

where:

f_t^c = Fraction of aromatic tertiary carbons (C_t/C_A)

H_w = Weight percent of hydrogen

C_w = Weight percent of carbon

f_a^h = Hydrogen aromaticity value

f_a^c = Carbon aromaticity value

C_t = Integrated area of tertiary aromatic carbons

C_a = Integrated area of total aromatic carbons

Table I gives the results for four fuel samples investigated.

Table I
Fuel Samples

	A	B	C	D
f_t^c	0.62	0.51	0.65	0.57
$(H/C)_a$	0.58	0.53	0.59	0.61

The close agreement between the values gives some assurance that the integrated values obtained from the NMR spectra represent the hydrogen and carbon types within sample.

Sincerely,

Daniel A. Netzel

Lila F. Thompson

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

April 22, 1985

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

Dear Dr. Shapiro

Re: A WP-80/90 Spectrometer

The pending arrival of two new Bruker NMR spectrometers has created a pressure on space in the NMR area. Our venerable (but still working) multi-nuclear WH-90 has been offered for sale in the NMR newsletter, but before disposing of it, we thought we might update the system by "hooking it up" to a WP-80 restricted to observing protons and carbon-13 only.

This turned out to be surprisingly simple. The RF interconnect cable giving transmitter and receiver connections from console to magnet is identical for the two systems. This cable is really 4 RF cables and 5 DC connections, and depending on layout the cable is either extended from the WP-80 magnet to the WH-90, or else the WH-90 cable plugs direct into the WP-80 console, taking the place of the usual connection. The manually set frequency synthesizer (from the WH-90) now provides the mixing frequency for the WP-80 pulse transmitter, which then supplies either system. The lock and decoupler frequencies for the WH-90 are still obtained from the WH-90 electronics and hence the 10 MHz source is extended from the WP-80 and substituted for that in the WH-90 console. Spf2 pulse signals for control of decoupling are taken from the WP-80's ASPECT 2000 computer to an appropriate BNC connector which was part of an already existing modification to the decoupler unit. The auto stop signal is also easily taken from the back of the D2 lock unit to be put in parallel at the back of ASPECT 2000 with the auto stop signal of the WP-80.

The advantages of this set up are numerous. Besides costing very little, we continue to use the low field multinuclear system but now with a more modern computer and software. Pressure on space is relieved by removal of the recorder and supporting wings from the WH-90 console, and a general packing together of items. Moreover, we still have a BNC-12 computer and other assorted electronic goodies available to any interested buyer!

Yours sincerely

J.I.A. Thompson

B.G. Sayer

J.I.A. Thompson

320-30

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215/728-6900

April 24, 1985

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843-3255

Re: A standard for ^{103}Rh?

Dear Professor Shapiro:

Here is a copy of the 103-rhodium NMR (9,469,263 Hz) spectrum of a sample of dicarbonyl (5-hapto-cyclopentadienyl)rhodium (2 grams) in 2 cc benzene-d_6 in a 10 mm sample tube. The material was purchased from Strem Chemicals, Inc., Newburyport, MA 01950. The spectrum was obtained on a NT-300 NMR spectrometer. Our low-band probe is specified from ^{14}N-^{17}O (21.6-40.7 MHz). We found the actual tuning range to cover ^{103}Rh-^{187}Re (9.4-68.3 MHz). We used the INEPT pulse sequence, with a 25 second cycle time, to get a sufficiently strong signal (FID) so that the magnetic field homogeneity could be maximized on the ^{103}Rh signal. That shimming resulted in a linewidth of 0.062 Hz for the ^{103}Rh spectrum shown here. (The $^{2}J_{Rh-H}$ coupling is 0.70 Hz.)

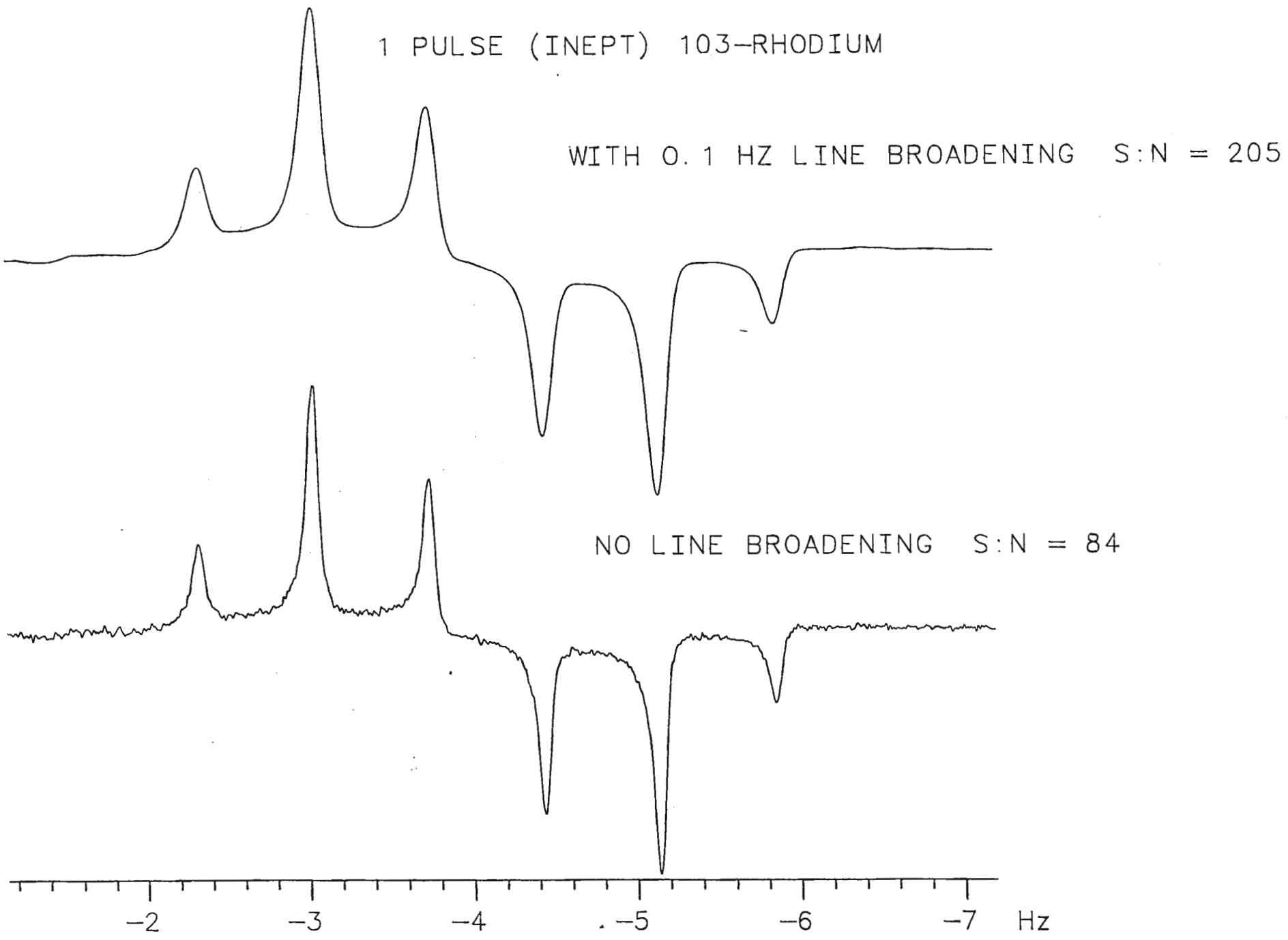
In the absence of a standard sample for ^{103}Rh performance, it is suggested that this material and this method (INEPT) be used for establishing resolution and sensitivity specifications. While the results given here are, we feel, impressive, they are not necessarily optimum as only a moderate effort was given to obtain this spectrum.

Please credit this contribution to the subscription of Dr. Mildred Cohn.

Sincerely yours,

Robert W. Dykstra

RWD/msw
Enclosure


1 PULSE (INEPT) 103-RHODIUM
WITH 0.1 HZ LINE BROADENING S:N = 205
NO LINE BROADENING S:N = 84
-2
-3
-4
-5
-6
-7
Hz

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

your ref.	your letter dated	our ref.	date
		JB/JABL/IS	April 11, 1985

subject

ALTERNATE SCAN ^{1}H and ^{31}P SPECTRA OF RAT MUSCLE

Dear Professor Shapiro,

A well known application of in vivo NMR is the study of the kinetics of phosphorus containing metabolites from ^{31}P spectra of muscle tissue. From the resonance position of the inorganic phosphate signal the intramuscular pH may be inferred. It is tempting to relate this quantity to the lactate concentration but this is not a straightforward matter [1].

In a recent experiment we have applied J-modulated echo difference spectroscopy [2] to measure lactate concentrations from in vivo proton spectra. In timesharing with these we recorded the ^{31}P spectra thus showing the feasibility of applying alternate scan multinuclear NMR to in vivo problems. The samples studied where the excised m.gastrocnemius medialis from the hind legs of a Wistar rat. Phosphorus spectra at 101 MHz were taken at 8.4 seconds intervals during which four 250 MHz proton difference spectra were recorded.

In the figure the time course of the spectra is shown for a period of 7 hours, one pair of spectra every 30 minutes. Each pair of spectra took 14 minutes to acquire. Presently we are developing a double tuned $^{31}P/^{1}H$ probehead for a 4.2 Tesla 89 mm bore magnet. This is expected to be large enough to accomodate an anaesthetized rat along with provisions to keep the temperature constant, to stimulate the hind leg muscle and to measure its force.

(Continued on page 35.)

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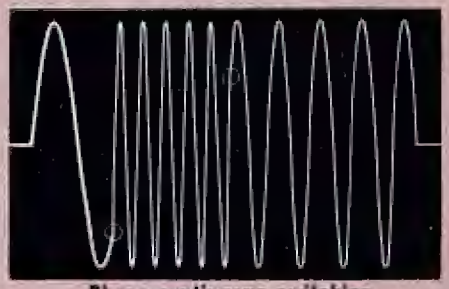

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FREQUENCY RANGE	DC - 3,000,000,000Hz (3MHz)
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SWITCHING SPEED	**<500 NANOseconds to .1 radians of new phase, between any two frequencies in band.**
CHARACTERISTICS	Phase-continuous at switch point
SPECTRAL PURITY	Spurious: <—55dB, Harmonics: <—50dB
PHASE NOISE	**@1Hz <—85dBc/Hz** **@1kHz <—110dBc/Hz**
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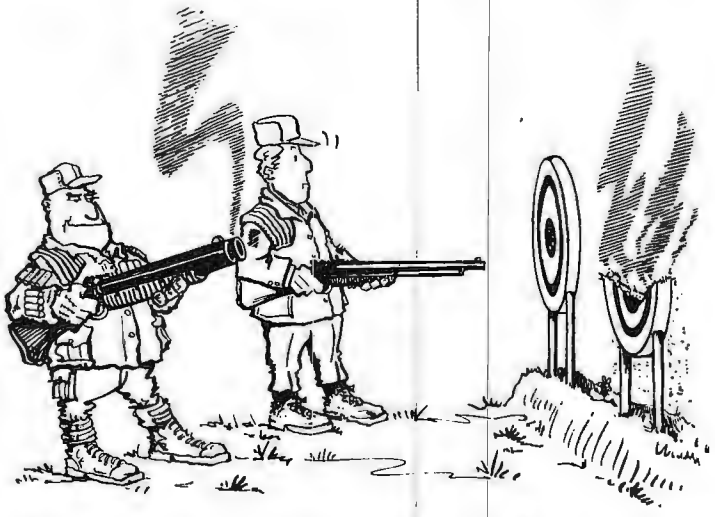
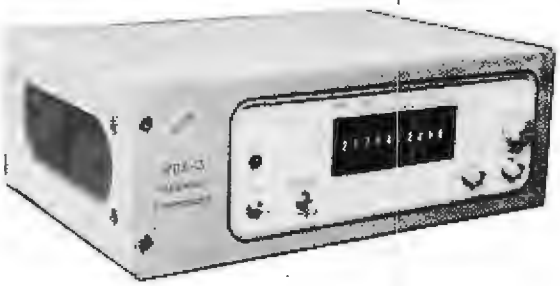


Why use a shotgun instead of a rifle?



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(Continued from page 32.)

We are confident that alternate scan NMR in combination with J-modulated echo difference spectroscopy will prove applicable to living samples.

Yours sincerely,

J. Bulthuis
Dept. of Physical Chemistry

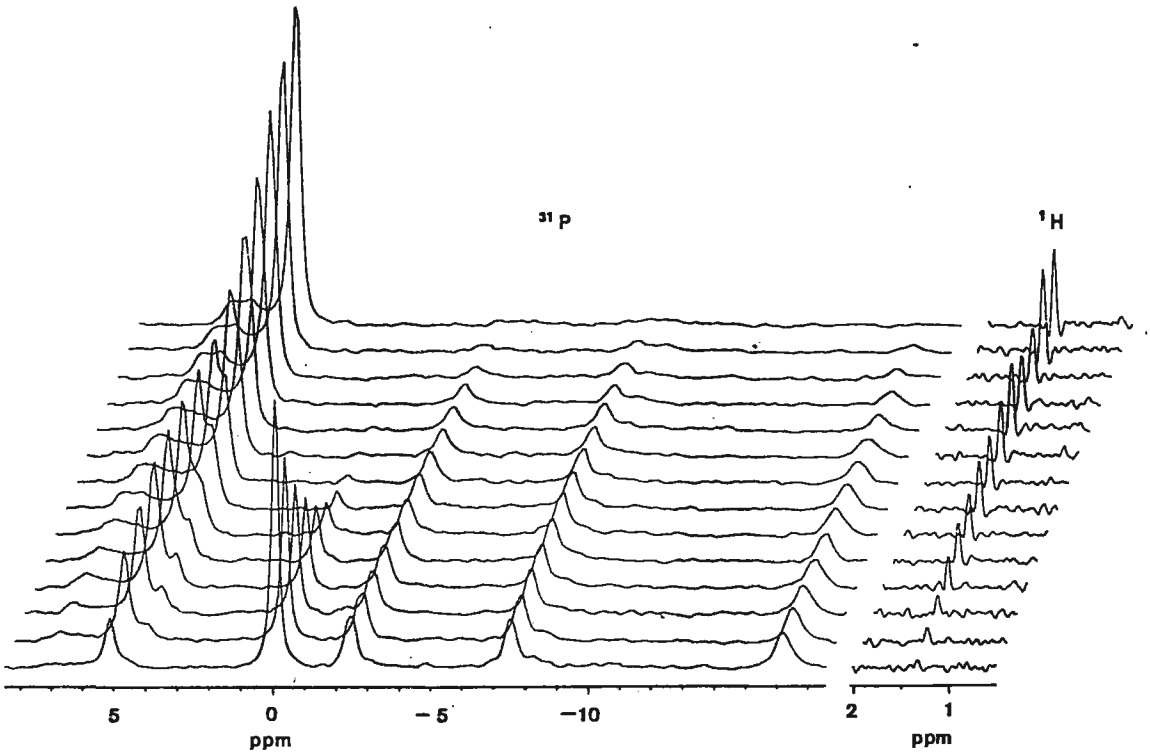
P.A. Huijing
Interfaculty of Physical Education

J.A.B. Lohman
Oxford Research Systems
Abingdon, Oxon
U.K.

[1] R.J. Newman, J. Bone Joint Surg., 66-B, 434 (1984)

[2] D.L. Rothman, F. Arias Mendoza, G.I. Shulman and R.G. Shulman, J. Magn. Res., 60, 930 (1984).

We wish to thank Bruker Spectrospin N.V. in Wormer, The Netherlands, for the use of their 250 MHz NMR spectrometer.



TCU
TEXAS CHRISTIAN UNIVERSITY
Box 32908
Fort Worth, Texas 76129
817-921-7195

Department of Chemistry

April 29,1985

From the Despairs of DEPT

Dear Barry:

At the Varian users' meeting before the ENC several people indicated they were having troubles using the standard DEPT sequence on their XL-instruments. We have had difficulties also with this experiment on our XL-300 5.1 version software; so I made a nuisance of myself raising questions with the applications chemists. Slowly a picture of what was going on emerged, and on my return yesterday from Alisomar I tried out a simple fix which worked very well indeed.

Since we did not anticipate needing a solids probe for our XL-300, we received the usual configuration of the high and low-powered decouplers. The 5.1 version software calls for the continuous mode use of the high-powered decoupler during the first two cycles and Waltz-16 with the low-powered decoupler during the third cycle. The assumption of the programmer was that everybody would have the bilevel decoupler system required as a solids accessory. This system has a very fast switch which allows for the employment of both decouplers during the DEPT sequence. With the routine decoupler setup, the switching is much slower(ca. 10 ms). The effect is to produce spectra that appear to have a small amount of residual coupling intact, i.e. the lines are flanked by small broad peaks. Furthermore, one cannot find a value of PP, the 90^{0} pulse on the proton decoupler, which will produce the correct DEPT spectra.

The problem could be solved by using the high-powered decoupler throughout(DHP=YYY), but a safer way is to use the decoupler low-power mode(DHP=NNN, DLP=1 leaving DMM as CCS). Our parameter set comes up with the decoupler offset at 350 Hz which is way downfield from our aliphatic region. I used DO=-100 which puts the decoupler in the middle of the aliphatic region. The value of PP was determined by setting MULT = 1.0 and arraying PP over a range of values while using a menthol sample. The correct spectrum is shown in the Advanced manual. On the adjoining page are the ADEPT5 spectra of a sample of 4-androstene-3,17-dione. Only the saturated carbon region is shown. The printout with this program not only gives the totals of each type of carbon but also specifies each carbon by type.

The heteronuclear correlation software(HETCOR) also suffers from the decoupler switching problem. Again it is best to go with decoupler low power all the way using the value of PP determined above.

Best regards,

Bill

William B. Smith

(Continued on page 39.)

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(Continued from page 36.)

ACQUISITION	
SFRQ	75.429
TN	13.750
SW	5920.7
AT	0.970
NP	11486
FB	3300
BS	64
SS	0
PW	23.5
P1	0
D1	2.000
D2	5.00E-2
TO	-3800
NT	8
CT	8

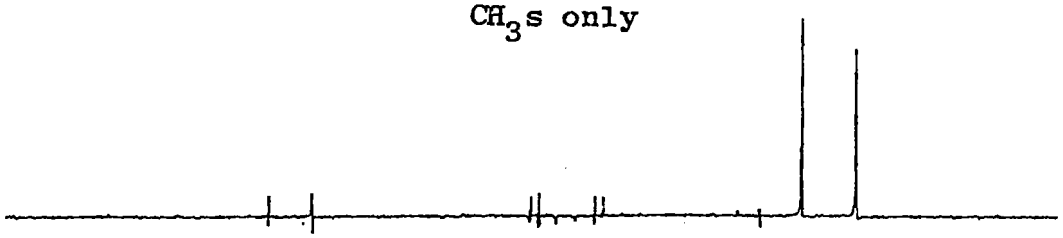
DECOUPLING	
DN	1.750
DO	-100.0
DM	NNY
DMM	CCS
DMF	9900
DHP	NNN
DLP	1
PP	90.0

FLAGS	
IL	N
IN	N
DP	N

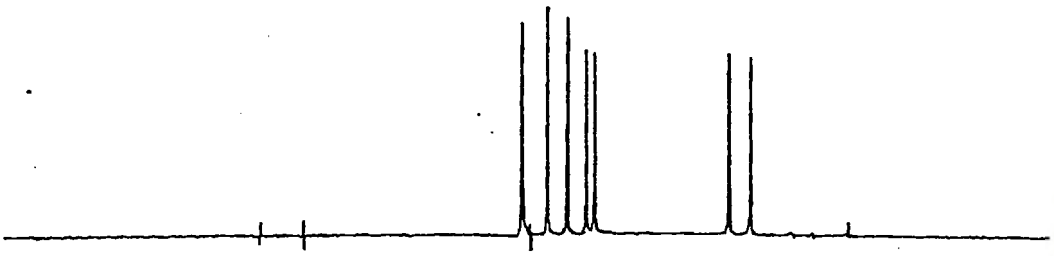
PROCESSING	
SE	0.318
LB	1.000
RE	NOT USED
CD	NOT USED
CCD	NOT USED
AF	NOT USED
FN	NOT USED
MATH	F

SPECIAL	
TEMP	NOT USED
VTC	25.0
PW90	23.5
MULT	ARRAY1
J	140.0
D3	0

CH_3s only

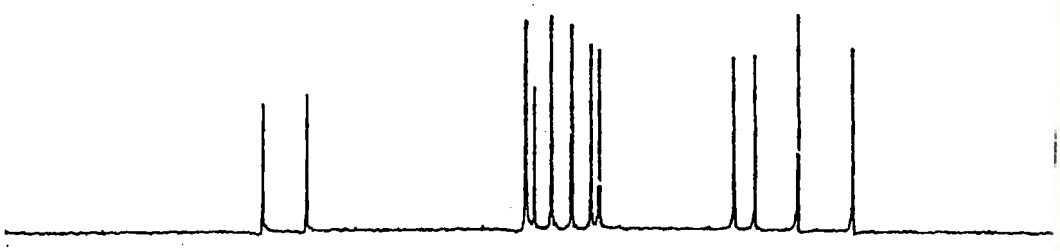


CH_2 only



CH only

All protonated carbons



320-40

Lilly

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307 East McCarty Street
Indianapolis, Indiana 46285
(317) 261-2000

18 April, 1985

Professor B. L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, TX 77843-3255

Dear Barry:

NMR and Information Management

One of the functions of our laboratory is to provide spectroscopic services for the organic and biological chemists throughout the corporation. Perhaps unlike other industrial spectroscopy laboratories, we also have the responsibility of archiving all the data we generate. At present we do this using the good old-fashioned method of printing our spectra on paper and then sorting these, collating them with the spectra of other spectroscopic laboratories, copying all spectra, and finally microfilming all the data. If this sounds like a system that was invented over 30 years ago and which badly needs replacing using more recent technology, then my description has been accurate. We too have recognized the obvious, and we are actively investigating the possibilities of a LIMS (Laboratory Information Management System). My purpose in this letter is share what little we have learned and to solicit the experiences of others who routinely generate more data than their present filing systems can accommodate.

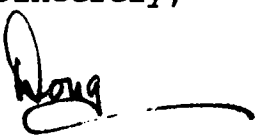
So far we have identified a rather short list of commercial LIMS which we feel will satisfy both our requirements and management's wish list. In all cases the major problem we have identified is that of interfacing: if we are really constrained to include in this system all the spectroscopic and analytical services we provide---as indeed we are---we face the problem of interfacing <u>all sorts</u> of computers to one LIMS computer. We have an Apple II+ on the

UV machine, Nicolet 1280's in the IR and NMR labs, an H-P A700 in the microanalytical lab, and down in MS...would you believe...we have a Varian 620 (remember them?). While we have not yet decided on what computer the LIMS will reside, the fact is that the corporation has four VAX computers, and that it is considered desirable to get the data on one of these machines eventually. Hence, we would be interested in hearing what other folks have learned about interfacing lab computers such as those I listed above to VAX 11/780 systems.

Another problem we have worked on is that of mass storage. Of course, we have limited mass storage in each of the laboratories, but this is not sufficient to take care of our long-term archival needs. We would prefer to delegate the problem of mass storage to our corporate data processing group, who have had to establish routine facilities for archiving to satisfy the needs of our business people and the government regulators. One of the reasons I suppose I was chosen to look into this problem is that it is well known that NMR eats up mass storage faster than other spectroscopic methods. In our department---which provides support in NMR, IR, UV, MS, elemental analysis, optical rotation, and titration---a simple calculation based on the system manuals for the various instruments showed that NMR accounts for 90% of the mass storage needs!

I hope that we are not alone in facing such difficulties, and I would be very pleased to hear from anyone who can suggest solutions to any of the problems I described above.

Sincerely,



Doug Dorman,
Mc525,
The Lilly Research Labs,
Indianapolis, IN 46285

320-42

ARIZONA STATE
UNIVERSITY TEMPE, ARIZONA 85287
DEPARTMENT OF CHEMISTRY

March 26, 1985

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

VARIAN XL-100 FOR SALE

Dear Professor Shapiro:

We are currently awaiting delivery of a Bruker AM400 spectrometer, but in order to make room for the new equipment, we need to dispose of our old XL-100 CW spectrometer. The system is fully operational, and comes equipped with a 12 in magnet, magnet power supply, recently refurbished heat exchanger, console, and variable temperature controller. We are willing to part with the complete system or individual components. Interested parties should contact Dr. Devens Gust or me at the above address or call (602) 965-3613.

Sincerely,

Ronald A. Nieman

Ronald A. Nieman
Research Specialist

STANFORD UNIVERSITY

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April 10, 1985

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Nicolet Disc Memory Coupler	Model	294
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Diablo Disc Drive with:	Model	31
Terminator	Model	30
Cables and Manual		

If you should have any questions please feel free to call me at (415) 497-3001.

Sincerely Yours,

John B. Pipkin,
Manager

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

March 27, 1985

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

Problems/Opportunities from a Peripatetic NMR Facility

Dear Barry:

You really should charge for colored paper. Once again we have the dubious excuse that we are having to relocate our NMR facility. From the relocation in August, 1983 we learned at least one lesson which the bio NMR people may find of interest. After moving our NT300 wide-bore spectrometer we began to experience difficulty in keeping our 200g rats happy, and in two instances, alive. The source of the problem was discovered with the use of a Luxtron fiber optic temperature probe* and proved to be a heating of the magnet gap by the room temperature shim coils. The shim settings on several of our coils were toward the extremes of the pot. These changes resulted because of changes in setting of the super-con shims after it was brought back to field following the move. Our animal work has ground to a halt while we wait for a Luxtron probe to be modified for use in a high field magnet. The outer coating on the standard Luxtron probe (LMC-6) is paramagnetic; this gives erroneous temperature readings. [This discovery was made by Dr. Paul Fagerness of Texas A & M University]. We took our experiment down to Jim Ferretti and Bob Balaban at NIH and found their NT360 wide-bore to have a "cold" bore. They in fact have very small room temperature shim correctiions and need to heat the probe air to prevent hypothermia in their 200g rat studies which involve long acquisitions.

On the high resolution side of our research, we are happily cranking along on routine 2D NMR applications to organic structure analysis using both our new Varian XL200 and the NT300 spectrometers. We thank the physicists once again for the beautifully useful techniques of 2D NMR. The streaming mag tape on our new XL is a real godsend with the 2D data piling up.

We would also like to recommend to our collegues that they build or purchase a hardware Waltz decoupler: Varian sells one for their new systems and we purchased one for our GE NT300 from Bob Santini through Bio-Magnetic Instruments, Inc. This update is money well spent.

A quick note of an error in the Nicolet (GE) 1280 NMC Manual (p. 236): The "U1 COMMAND" example has the definitions for BLKSTA and BLKSIZ switched; i.e., BLKSTA = 422 and BLKSIZ = 421. We hope this saves other beginners sometime.

Hopefully, next year we will have results which are of a less routine nature. Please credit this to Dr. Chmurny's account.

Sincerely,

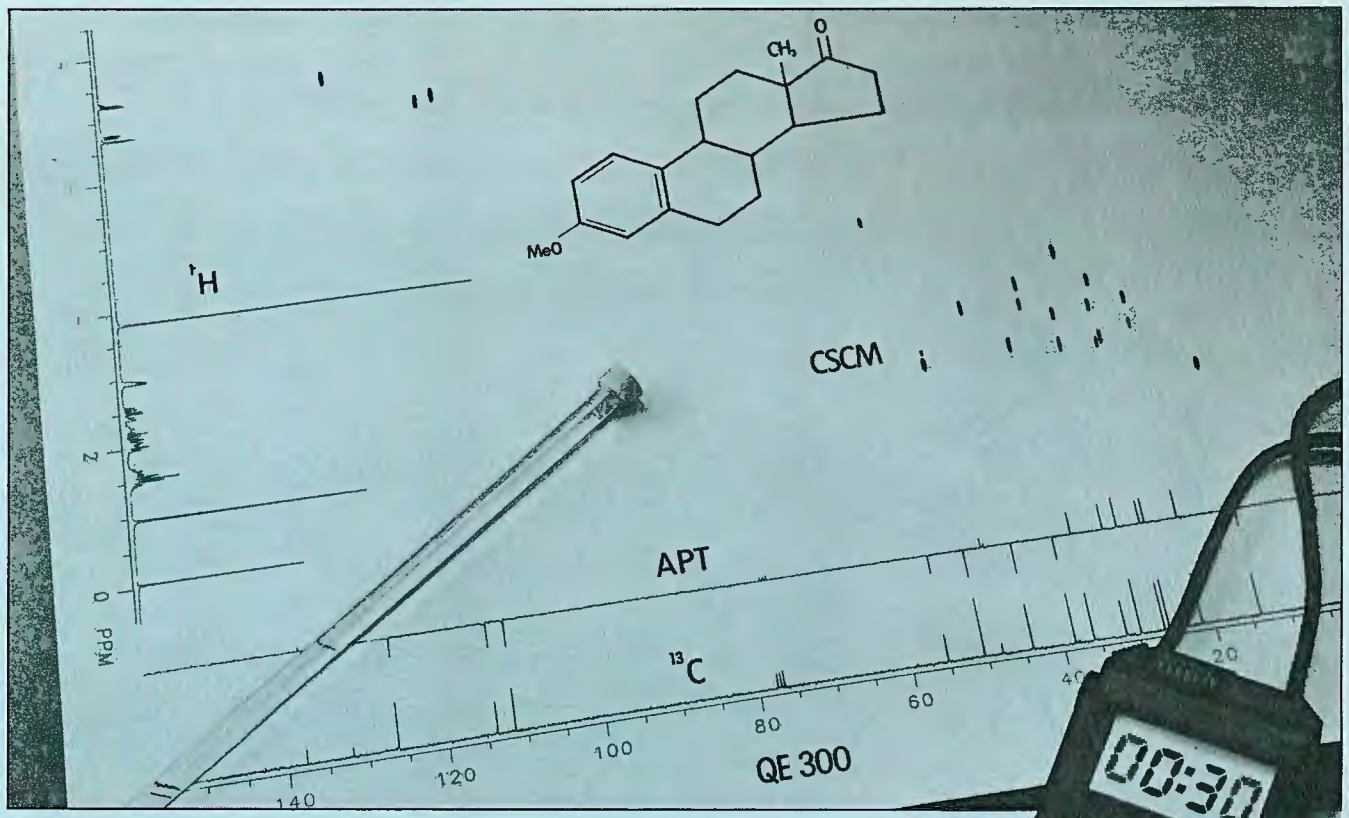
Gwendolyn N. Chmurny, Ph.D.

Bruce D. Hilton

Bruce D. Hilton, Ph.D.
Chemical Synthesis
and Analysis Laboratory

L.T. Martensen*
Martensen Company, Inc.
P.O.Box 261
Williamsburg, VA 23187

* Marty Martensen very kindly helped us with the Luxtron probe experiments during a very lengthy demonstration of the probe.



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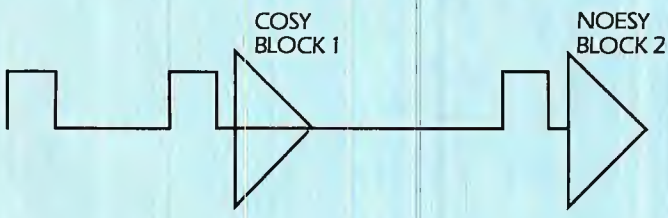
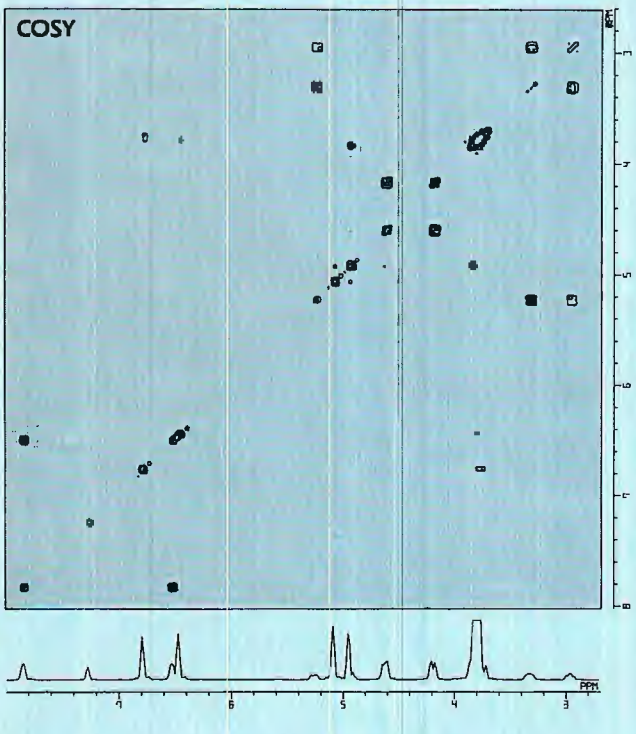
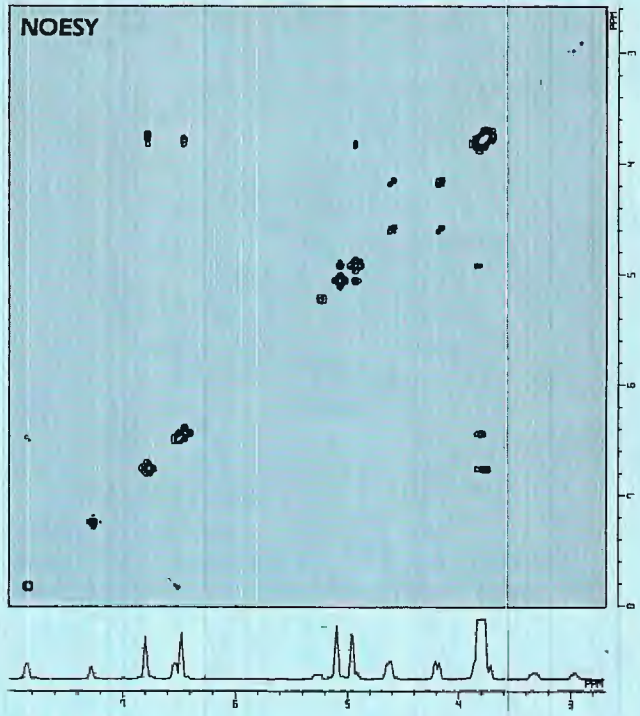


- Simultaneous acquisition of COSY and NOESY





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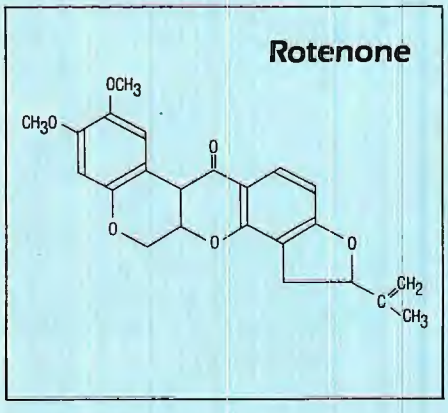
*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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