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University  
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Newsletter

*Bruce Lytle*

No. 248

May, 1979

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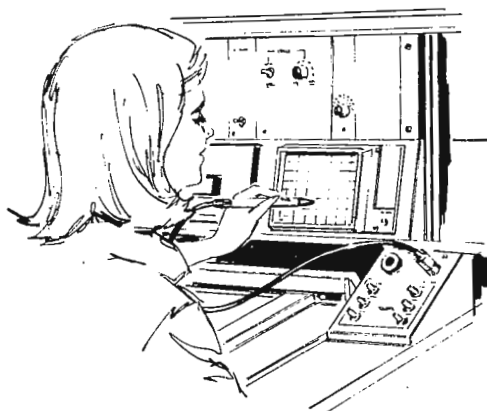
All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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2 March 1979.

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

Dear Professor Shapiro,

New Design for XL-100 5 mm Spinner Turbine

How often have you watched in despair as some wretched compound, perhaps the fruit of many hours of labour and many pounds worth of precious starting materials, died as it warmed above  $-90^{\circ}\text{C}$  because you could neither get the nmr tube right into nor back out of the spinner turbine?

I was plagued by an increasing number of temperature sensitive tubes all, of course, frosty and some oversized too, and lost a good few in transit between their home in a liquid nitrogen dewar and the probe of our XL-100. This is because the standard XL-100 5 mm spinner turbine has barely enough flexibility to be able to cope with the variation in tube sizes between manufacturers, let alone the thickness of a layer of frost on the outside of the tube.

The solution to this problem was quite simple once I had borrowed the idea of the gripping fingers and collar from the 10 mm spinner of our JEOL FX60Q. (see diagram). Our workshop made the design from Delrin some months ago and it has been very successful. It is a rather awkward machining job and the surface finish has to be as smooth as possible. Machining marks and fine surface hairs will at worst prevent it spinning, or floating on the air bearing jets, and at best allow it to spin only slowly.

After removing the collars, a frosty or oversized tube can easily be pushed into the spinner. The fingers bend slightly to allow it through. The collars are then replaced, the depth adjusted and the tube and spinner may then be quickly transferred to the cold probe. The tube need be out of liquid nitrogen for only a second or two between each stage before it goes into the probe.

We now have to find a solution to this same problem for our new WH-360, in which the sample is lowered into the probe on a fountain of warm nitrogen!

Best wishes, and long may your tubes stay frozen!

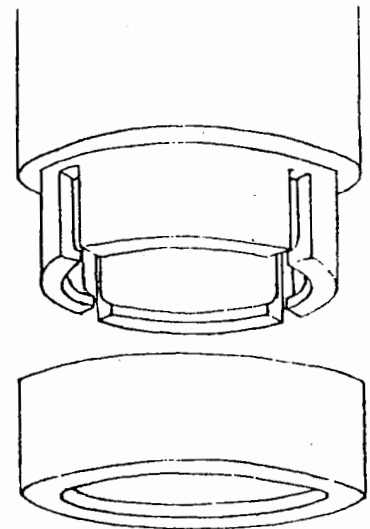
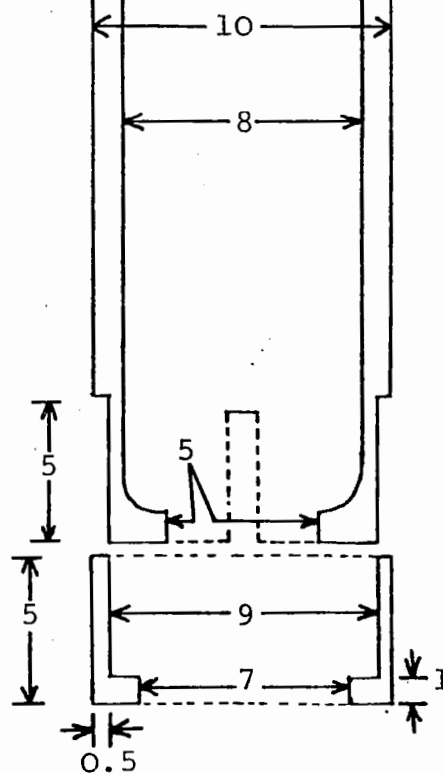
Alan Boyd



Cap →  
is a tight push-  
fit over the  
gripping  
fingers

XL - 100 5 mm  
Spinner Turbine

All dimensions are  
in millimetres.  
Those not shown may  
be obtained from the  
standard spinner  
turbine.



both ends are  
similar.

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NANTES, le 21 Mars 1979

Professor B.L. SHAPIRO  
Department of Chemistry  
Texas A.M. University  
College Station  
TEXAS 77843 (U.S.A.)

Cher Barry,

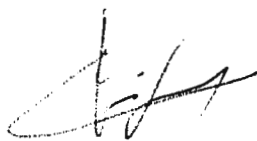
En collaboration avec le Groupe des Interactions Cellulaires dans le cancer de la Faculté de Médecine de Nantes nous développons actuellement une étude par RMN  $^1\text{H}$  (à haut champ) de membranes cellulaires normales et tumorales purifiées.

Nos premiers résultats ont été établis à partir de membranes plasmiques de cellules plasmocytaires MF<sub>2</sub>S du plasmocytome murin MOPC 173 (c.f. figure 1) et de membranes purifiées de cellules spléniques et ganglionnaires normales de la souris (c.f. figure 2).

Les différences relatives de largeur de raies, liées aux mesures des temps de relaxation, nous ont permis de mettre en évidence des mobilités relatives différentes. De même la mesure des temps de relaxation de l'eau dans les deux types de membranes nous a conduit aux mêmes observations que Damadian et ses collaborateurs (1) avaient faites sur des tissus intacts : les valeurs de  $T_1$  sont exaltées de façon très significative par le caractère tumoral. Le rôle de la membrane est donc essentiel dans la compréhension des mécanismes de transfert de l'information du milieu extérieur au sein de la cellule.

Nous avons entrepris une étude de l'interaction de lectines, en particulier la concanavaline A, à diverses concentrations, sur les membranes plasmiques purifiées et pensons suivre la différenciation cellulaire sur des membranes de cellules clonées : un thymome.

Meilleurs sentiments,

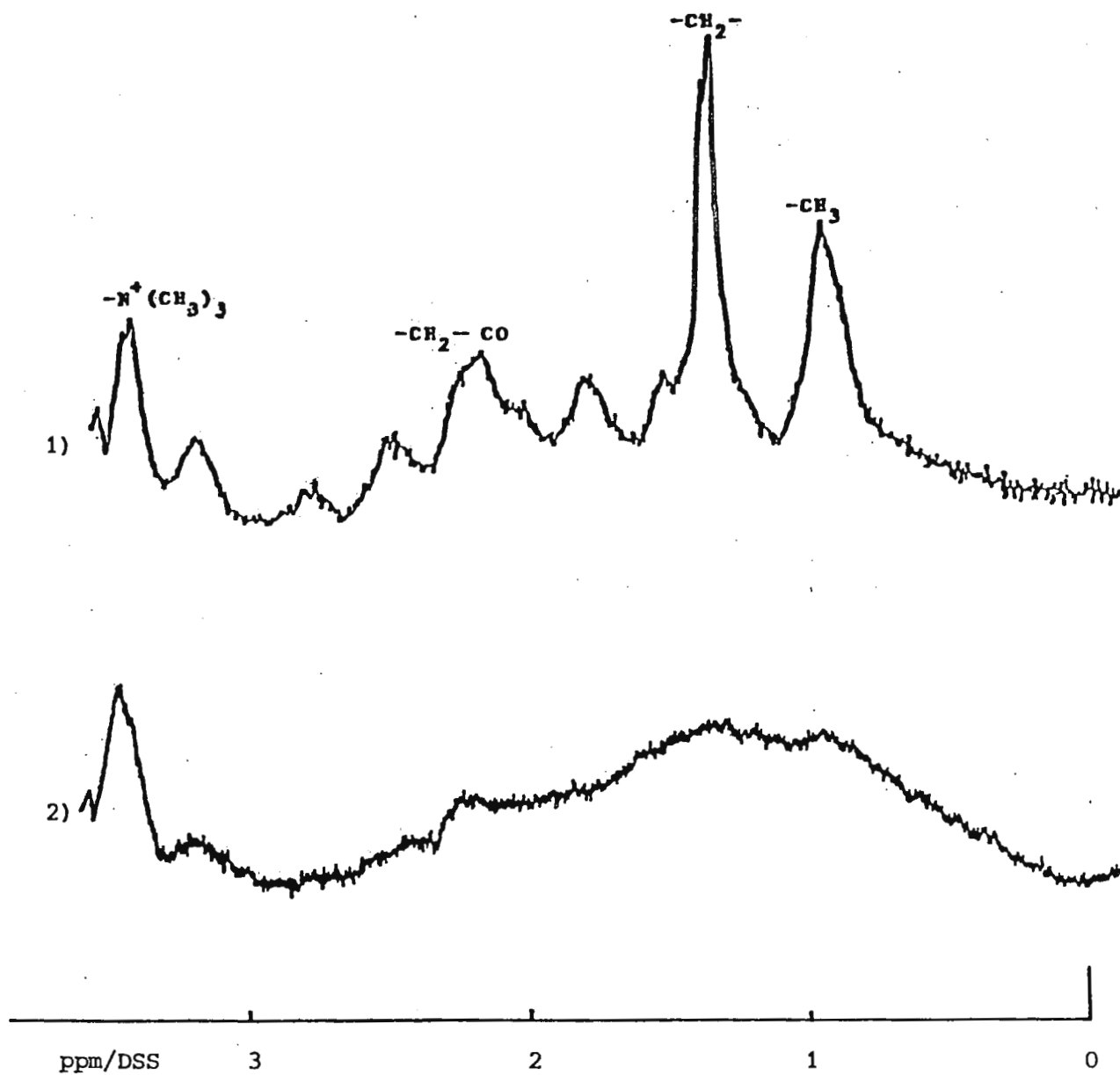


S. POIGNANT.



G.J. MARTIN.

(1) R. DAMADIAN, K. ZANER, D. HOR, T. DI NAIIO, L. MINKOFF, Annals of the N.Y. Acad. of Sciences 1048, 222, 1973.



Spectres RMN  $^1H$  250 MHz dans  $D_2O$ . PD  $\approx 7$ . T  $\approx 23^\circ C$ .

- 1) Membrane du plasmocytome murin
- 2) Membrane de cellules spléniques et ganglionnaires normales.

8000 AARHUS C, DENMARK March 27, 1979  
 HJJ/ATL

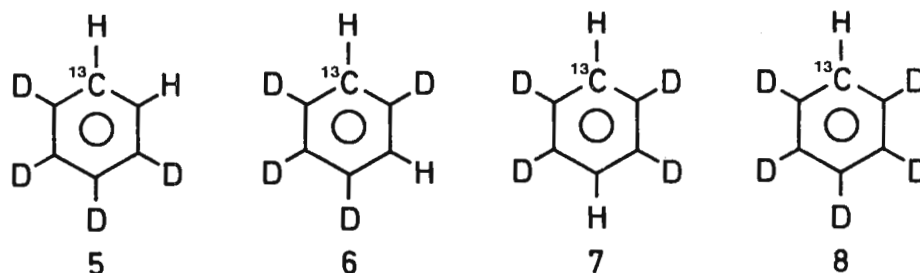
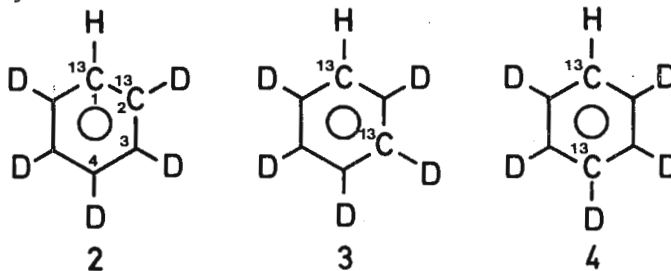
Professor Bernard L. Shapiro  
 Department of Chemistry  
 Texas A & M University  
COLLEGE STATION, Texas 77843  
 USA

Dear Barry,

$^{13}\text{C}$ - $^{13}\text{C}$  SPIN COUPLING CONSTANTS IN BENZENE

Since last year's contribution (TAMU NMR 236-10) on determination of signs of  $^{13}\text{C}$ -X couplings from  $^{13}\text{C}$  satellites in  $^{13}\text{C}$  NMR spectra [1] we have among other experiments determined a number of  $^{13}\text{C}$ - $^{13}\text{C}$  couplings, including long-range, at the  $^{13}\text{C}$  natural abundance level in organic molecules. In some cases, generally for quaternary carbons, we have been able to resolve  $^{13}\text{C}$  satellite splittings as small as 1.8 Hz. In this connection we became fascinated by the challenge of designing experiments which would lift the equivalence of the carbons in benzene, thus allowing a determination of the three  $^{13}\text{C}$ - $^{13}\text{C}$  couplings ( $^1\text{J}_{\text{CC}}$ ,  $^2\text{J}_{\text{CC}}$ , and  $^3\text{J}_{\text{CC}}$ ) for this fundamental molecule. Recently we accomplished this objective by observation of  $^{13}\text{C}$  satellites in the deuterium decoupled natural abundance  $^{13}\text{C}$  spectrum of pentadeuterobenzene, 1. Three  $^{13}\text{C}$  satellite spectra corresponding to the isotopomers 2, 3, and 4 were observed and analyzed. However,  $^1\text{H}$  satellite spectra of about the same abundance were also observed for the isotopomers 5, 6, and 7, which are present in the sample due to only 99% deuterium enrichment of 1. Pentadeuterobenzene, 1, was prepared by electrochemical reduction of pentadeuterobromobenzene (99% deuterium enrichment) and the NMR sample was a mixture of 85% (v/v) 1 and 15% (v/v) TMS in a 12 mm tube.

The  $^{13}\text{C}$  NMR experiments (25.16 MHz) were performed on a Varian XL-100-15 spectrometer using internal  $^1\text{H}$  (TMS, 100.1 MHz) lock and  $^2\text{H}$  decoupling (15.40 MHz) by means of the Gyrocode decoupler. Precautions were taken to eliminate spectral noise introduced into the system by the high-power low-frequency decoupling. This may be achieved by "isolating" the transmitter/receiver system from the decoupling frequency.





The eight  $^{13}\text{C}$  satellite transitions which constitute the AB part of the ABX spin system for 2 were all observed. For the remaining isotopomers (3, 4, and of course 5, 6, and 7) only the satellites surrounding the high- and low-frequency  $^{13}\text{C}$ - $^1\text{H}$  doublet lines ( $^1\text{J}_{\text{C1-H1}}$ ) [2] for the isotopomer 8 were used in the analysis. The spectral detail in figure 1 shows the satellite spectra (3550 transients) observed around the high-frequency line of the  $^1\text{J}_{\text{C1-H1}}$ -doublet. The linewidth at half height for these satellites is 0.10-0.12 Hz. Furthermore, it is noteworthy that the small satellite doublet splitting for the isotopomer 7 (■,  $|^4\text{J}_{\text{C1-H4}}| = 1.28 \text{ Hz}$ ) is clearly observed.

Accurate values for the  $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^1\text{H}$  couplings in benzene were determined using expansions (0.2 Hz/cm) of these spectra; furthermore a wealth of isotope ( $^2\text{H}$  and  $^{13}\text{C}$ ) induced shift data was also obtained. Only the  $^{13}\text{C}$ - $^{13}\text{C}$  couplings are reported here since the  $^{13}\text{C}$ - $^1\text{H}$  couplings fall within the experimental errors of values obtained earlier [2,3]. A value for  $^1\text{J}_{\text{CC}} = 57.0 \text{ Hz}$  in benzene has earlier been quoted as a private communication in reference [4] where some  $^{13}\text{C}$ - $^{13}\text{C}$  couplings in monosubstituted benzenes are reported. Experiments are in progress to determine the sign for  $^2\text{J}_{\text{CC}}$  in benzene and an account of our work will soon appear in the literature.

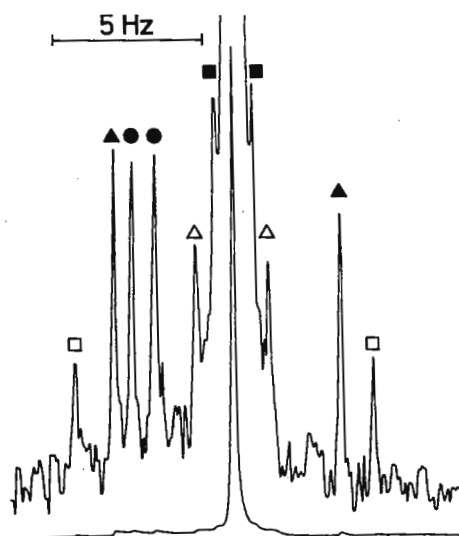


Fig. 1. Satellites observed in the  $^2\text{H}$  decoupled  $^{13}\text{C}$  spectrum of pentadeuterobenzene (see text):

△ 3, □ 4, ● 5, ▲ 6, ■ 7.

#### $^{13}\text{C}$ - $^{13}\text{C}$ Coupling Constants in Benzene:

$$^1\text{J}_{\text{C1-C2}} = +55.95 \pm 0.04 \text{ Hz}$$

$$|^2\text{J}_{\text{C1-C3}}| = 2.46 \pm 0.02 \text{ Hz}$$

$$^3\text{J}_{\text{C1-C4}} = +10.01 \pm 0.02 \text{ Hz}$$

Best regards,

*Hans*

*Torben Lund*

Hans J. Jakobsen

Torben Lund

#### REFERENCES

- [1] H.J.Jakobsen, T.Lund and S.Sørensen, J.Magn.Resonance 33, 000 (1979).
- [2] H.Günther, H.Seel and M.-E.Günther, Org.Magn.Resonance 11, 97 (1978).
- [3] M.Hansen and H.J.Jakobsen, J.Magn.Resonance 20, 520 (1975).
- [4] F.J.Weigert and J.D.Roberts, J.Amer.Chem.Soc. 94, 6021 (1972).

Department of Chemistry

The Florida State University  
Tallahassee, Florida 32306

March 29, 1979

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

Dear Barry:

Recent advances in construction of sideways-spinning tube probes along with continued emphasis in our lab on multi nuclear capability has led to the design and building of a Sideways-spinning Operation Broadband probe, for use in conjunction with our Seminole super-conducting spectrometer system (3.5 T, widebore Bruker magnet).

The broadband capability of this probe covers a frequency range of 36 to 62 MHz ( $^{13}\text{C}$  through  $^{31}\text{P}$ ). Tuning over this range is externally controllable (sample in place) in both the observe and decouple channels; the lock channel is pretuned. Initial sensitivity tests on a number of nuclei indicate that excellent signal-to-noise ratios are obtainable at both extremes of the broadband coverage; using 20 mm diameter tubes holding 7.2 ml of sample.

Initial Single Pulse Sensitivites

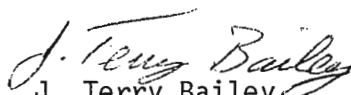
$^{13}\text{C}$ - 90% Dioxane (coupled)	S/N > 500:1 RMS
$^{13}\text{C}$ - 90% Ethyl Benzene	S/N > 1500:1 RMS
$^{31}\text{P}$ - 1% Phosphoric Acid	S/N > 650:1 RMS

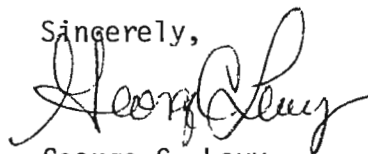
Additionally, we have constructed a microcell design enclosing a spherical cavity with a volume of 3.2 ml for cases of limited sample, or where bulk susceptibility is a problem.

The resolution of the probe is quite acceptable, especially considering the Z-oriented shims available. At  $^{31}\text{P}$  resolution of 0.9 Hz has been obtained for proton decoupled trimethyl phosphate. Over the frequency range of interest, the measured Q factor varies from 180 to 280 which is acceptably high.

Changing nuclei within the same sample requires seconds; when a sample and frequency must be changed, only a few minutes are needed.

Under construction currently is a second S.O.B. probe for the range 10-25 MHz.

  
J. Terry Bailey  
Research Assistant

Sincerely,  
  
George C. Levy  
Professor

GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN  
SUB-FACULTEIT - SCHEIKUNDE

---

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Correspondentie-adres:  
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2300 RA LEIDEN

Telefoon 148333  
toestel:

Afdeling: J. Lugtenburg

Onderwerp:

LEIDEN, 29 maart 1979

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

Dear Professor Shapiro,

The  $^1\text{H}$ .N.M.R. spectrum of triphenyl-isopropyl lead.

Organic lead (IV) compounds have been studied in our laboratory for some time.

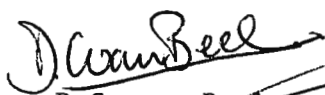
The signals in the aliphatic region due to the  $^{207}\text{Pb}$  isotope containing species show deceptive simplicity, we had not seen before in lead compounds.

With the programme LAME we simulated the 100 Mhz  $^1\text{H}$  NMR spectrum of the isopropyl part of triphenyl isopropyl lead with the following parameters:

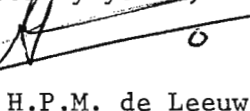
$^{207}\text{Pb}$ abundance: 22%	$J_{\text{CH}_3-\text{CH}}$ 7.4 Hz
$\delta$ CH <sub>3</sub> : 1.739 ppm	$J_{\text{Pb}-\text{CH}}$ -47.7 Hz
$\delta$ CH : 2.833 ppm	$J_{\text{Pb}-\text{C}-\text{CH}_3}$ 172.0 Hz

We hope you will be as excited by these results as we are.

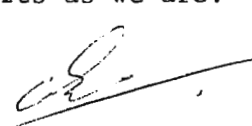
Sincerely yours,



D.C. van Beelen



H.P.M. de Leeuw



C. Erkelens

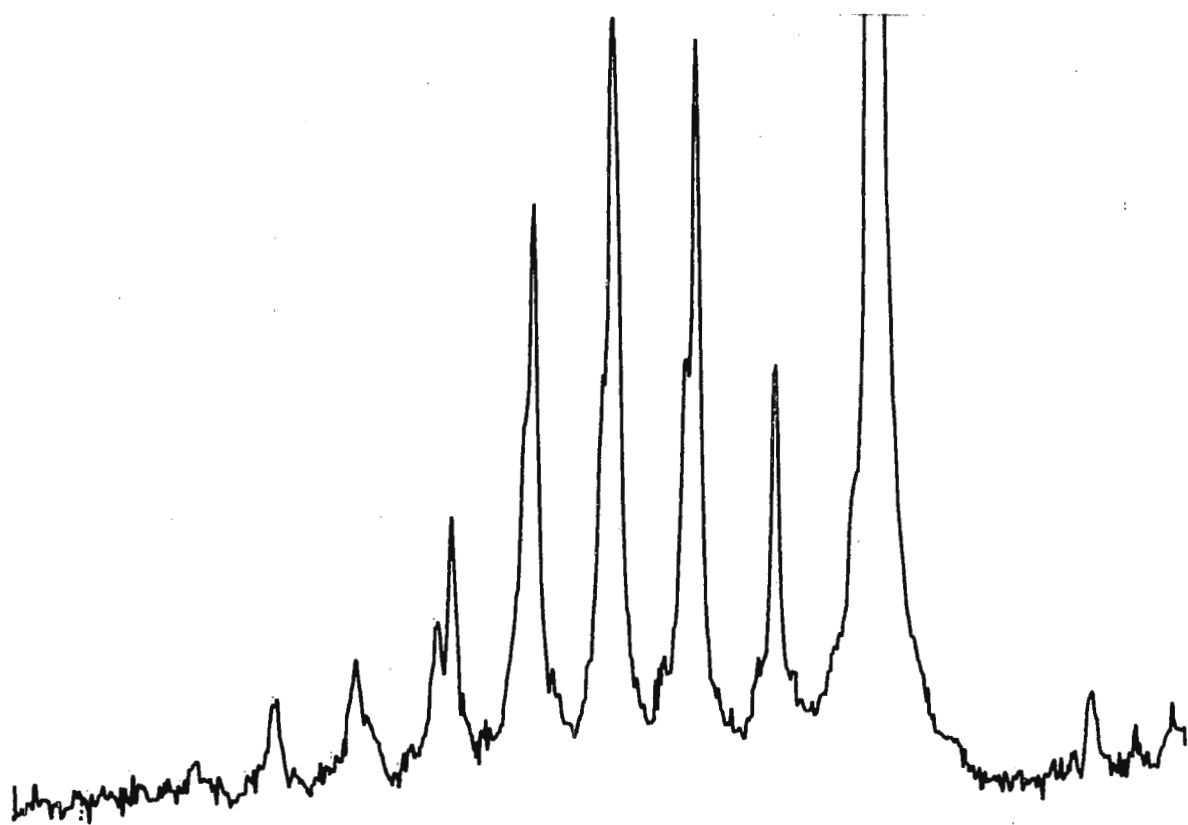
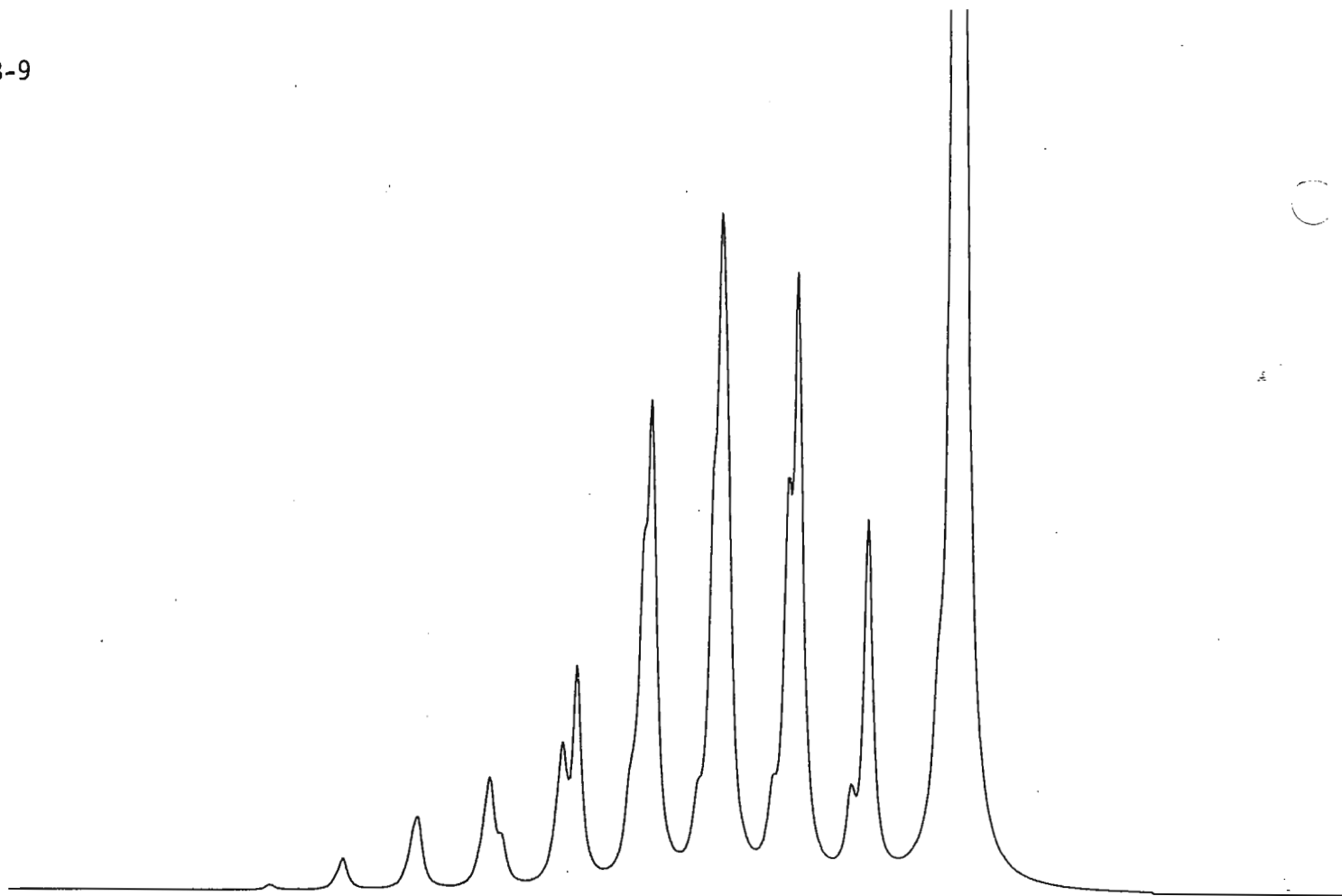


J. Lugtenburg

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97 (1978) 219

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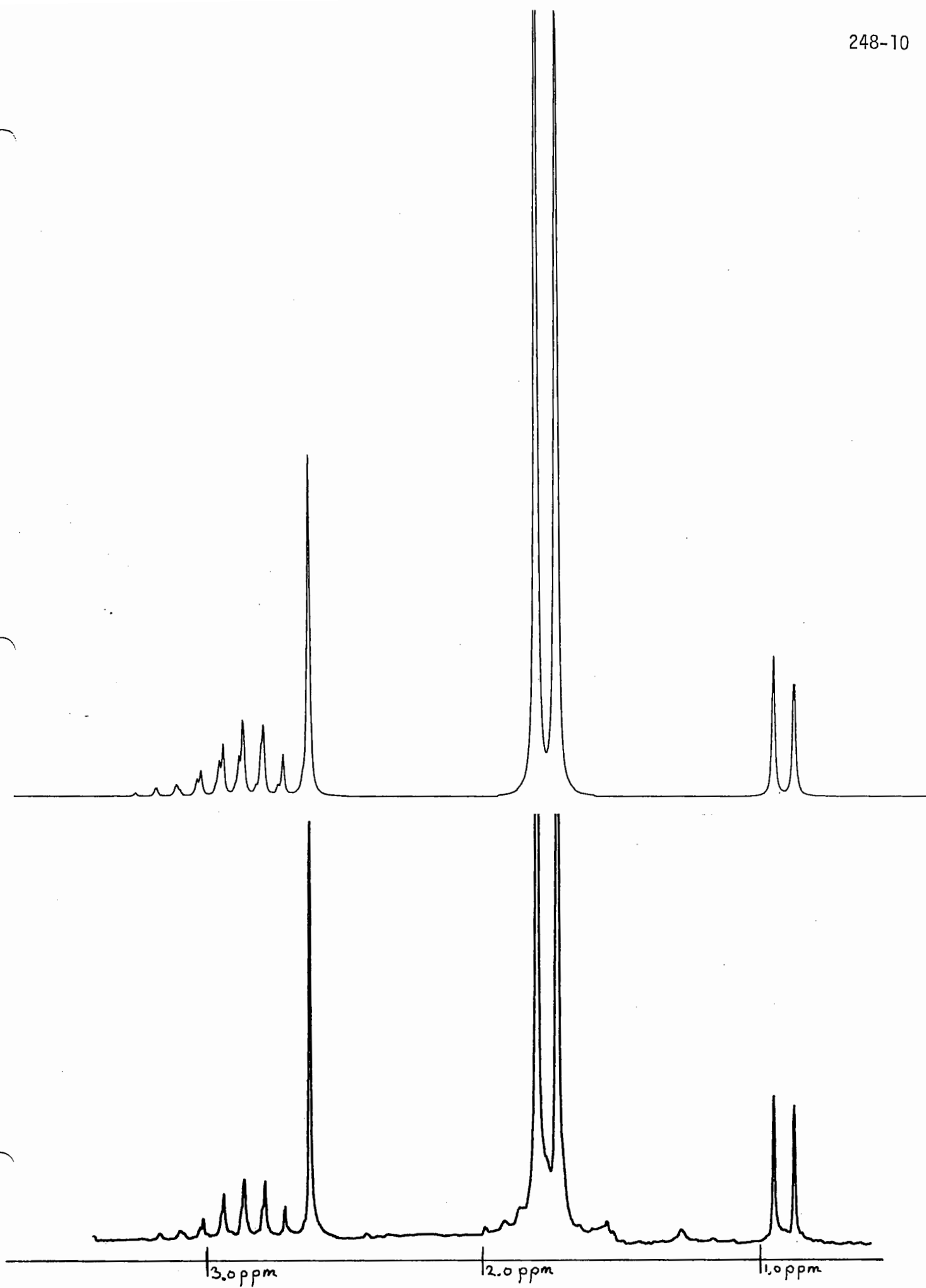


3.5 ppm

3.0 ppm

2.5 ppm







Ref :

Date: March 30, 1979

Professor C.L.Khetrapal  
Dr. Anil Kumar  
Dr. A.C.Kunwar

Participating Institutions

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Professor B.L.Shapiro  
Texas A & M University  
College of Science  
COLLEGE STATION, Texas 77843  
U S A

Title:  $^{13}\text{C}$ -Induced Isotopic Effects in 'Oriented' Molecules

Dear Prof. Shapiro,

For the past few months, we have concentrated efforts on investigations of the  $^{13}\text{C}$ -H satellites in proton NMR spectra of a variety of organic compounds oriented in the nematic phase. In acetone, for example, the spectra due to both types of species containing one  $^{13}\text{C}$  nucleus were observed, interpreted completely and the geometrical information has been derived. A substitution of a  $^{13}\text{C}$ -nucleus has small but significant influence on the proton chemical shift and the H-H dipolar couplings. A  $^{13}\text{C}$  at one of the methyl positions changes the chemical shift of the directly bonded proton upfield by 0.50 Hz (at 270 MHz) whereas the other protons are influenced in the same direction by 0.22 Hz. A  $^{13}\text{C}$  at the carbonyl carbon changes the proton chemical shift upfield by 0.19 Hz. Though such effects for protons directly bonded to a  $^{13}\text{C}$  nucleus may be detected relatively easily from the spectra in the isotropic media, it must be emphasized that it is hard to determine such effects for non-directly bonded carbon-13 and protons in isotropic cases and hence this method is useful. The direct dipolar HH coupling constant (in EBBA) within the methyl protons of the group containing a  $^{13}\text{C}$  is reduced by 0.10 Hz.

Yours sincerely,

*C.L.Khetrapal Anil Kumar A.C.Kunwar*  
C.L.Khetrapal Anil Kumar A.C. Kunwar

# University of Illinois at Urbana-Champaign

248-12

School of Chemical Sciences  
150 Roger Adams Laboratory  
Urbana, Illinois 61801

March 30, 1979

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

POSITION AVAILABLE: NMR SPECTROSCOPIST

Dear Professor Shapiro:

The Molecular Spectroscopy Laboratory in the School of Chemical Sciences has an opening for a spectroscopist. The appointment will be academic/professional. Minimum qualifications include a Ph.D. in a physical science or a graduate degree in engineering. A background in nuclear magnetic resonance is essential, and experience in electronics or chemistry would be helpful.

The duties of the position include design, construction, and testing of electronic equipment related to nuclear magnetic resonance. Some instrument operation may be required. The prospective candidate should be highly motivated and talented; productivity will be an essential consideration.

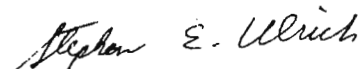
The desired starting date is October 1, 1979. The position is a continuing one and offers one month vacation per year. The starting salary will be \$18,500 or more depending upon qualifications and experience. Persons wishing to apply should send a curriculum vitae to the address below, and arrange for three letters of recommendation to be sent. In order to insure consideration application materials should be received by August 1, 1979.

The University of Illinois is an affirmative action/Equal Opportunity Employer and encourages application from members of minority groups and women.

Inquiries should be sent to:

Dr. Stephen E. Ulrich  
School of Chemical Sciences  
University of Illinois  
Urbana, Illinois 61801 USA

Sincerely yours,



Stephen E. Ulrich



ISTITUTO CHIMICO  
della  
UNIVERSITÀ DI TORINO

TORINO, 31 / 3 / 1979  
CORSO MASSIMO D'AZEGLIO, 48  
Tel. 652.102 - 682.892 - 653.831 - 653.832

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

Title:  $^{17}\text{O}$  NMR OF METAL CARBONYLS AT NATURAL ABUNDANCE

Dear Professor Shapiro,

recently we had the opportunity to record  $^{17}\text{O}$ -n.m.r. spectra of several metal carbonyls on the FX 90 Q machine at Jeol House, London. The results obtained are very promising allowing to foresee that this technique will have a significant impact within this area of chemistry. The time required to obtain a spectrum is comparable with that required to get  $^{13}\text{C}$ -n.m.r. spectra, although the sensitivity of  $^{17}\text{O}$  is  $6.1 \cdot 10^{-2}$  compared to that of  $^{13}\text{C}$ .

The linewidth is very narrow in respect to other  $^{17}\text{O}$ -n.m.r. resonances; for Cr, Mo, W, Fe carbonyls it is below 10 Hz. Of course peaks broaden as the temperature is lowered, but this feature does not seem to make prohibitive DNMR studies, at least when the chemical shift separation between the exchanging sites is sufficiently large. Of relevance, at this stage, is the detection of sharp  $^{17}\text{O}$  resonances for metal carbonyls containing metal nuclei with  $I > \frac{1}{2}$ , such as  $^{55}\text{Mn}$  and  $^{59}\text{Co}$ . The corresponding  $^{13}\text{C}$ -n.m.r. signals are usually very broad and in many cases do not allow a clear assignment. In the figure is reported the spectrum at room temperature of  $\text{Mn}_2(\text{CO})_{10}$  showing two sharp resonances (178.4 and 196.9 ppm

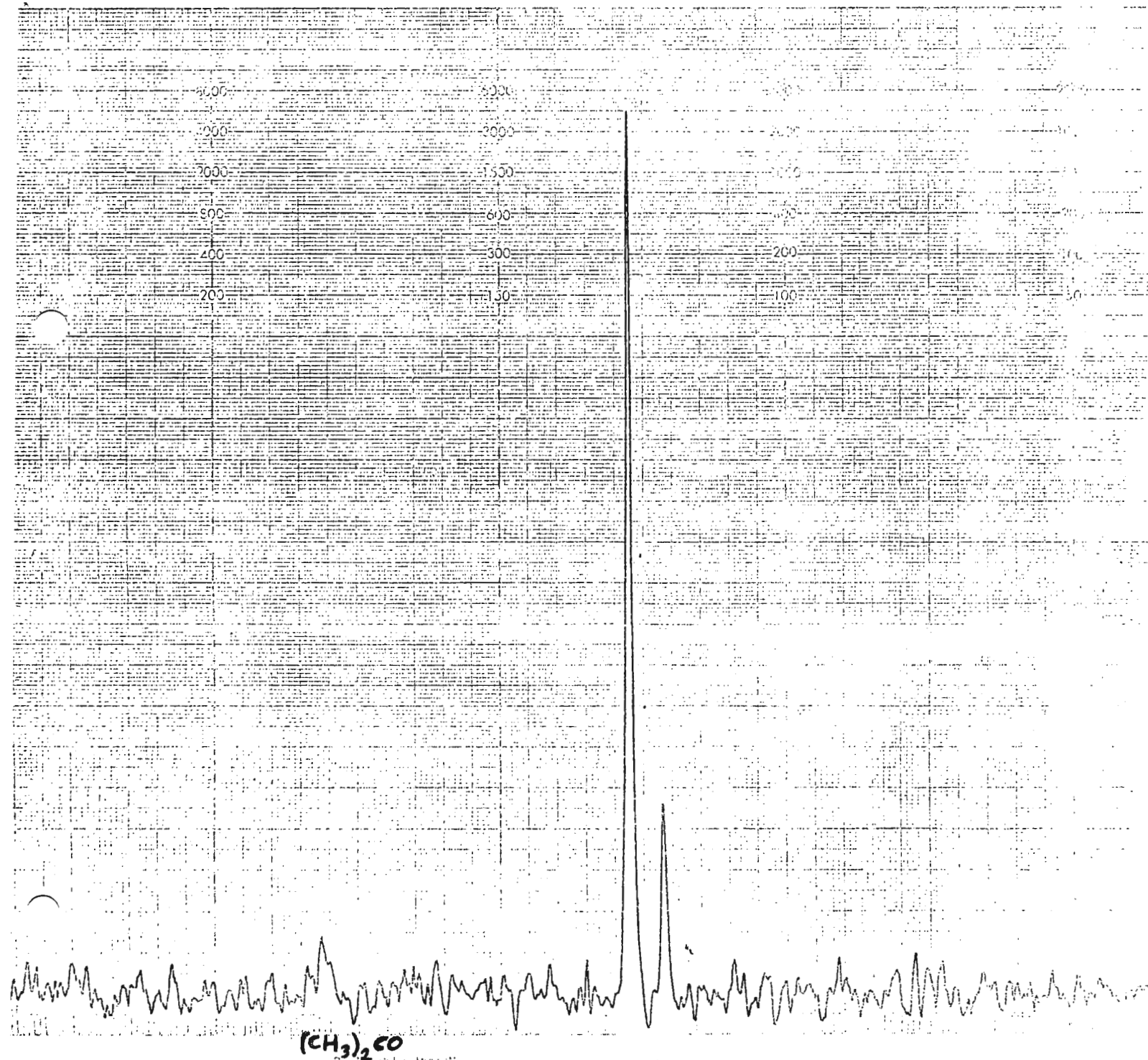


positive upfield from acetone) for the two different types of CO's (equatorial and axial). The spectrum was obtained in 20', using a 90° pulse with a repetition time of 0.15 sec.

*S. Aime*  
S.Aime

*L. Milone*  
L.Milone

*D. Osella*  
D.Osella



$(CH_3)_2CO$

**MERCK  
SHARP  
& DOHME** CANADA LIMITED/LIMITÉE  
ISOTOPE DIVISION

April 1, 1979

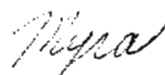
Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, TX 77843

Dear Barry:

In a recent TAMU NMR Newsletter [245, 31 (1979)], Wray and Ernst commented on the lack of availability of consistent  $^{13}\text{C}$  NMR data for deuterated solvents, and included some chemical shifts they had determined. Four years ago, for just this reason, Jake and I ran the  $^{13}\text{C}$  and residual- $^1\text{H}$  spectra of all the solvents then listed in the Merck NMR Solvent catalog. These data were tabulated, along with the useful physical properties, as indicated on the next page.

Merck has been distributing these tables to all who are interested, for both individual and classroom use; apparently they haven't reached as wide an audience as I had thought. Copies of these tables (heavy paper) are available, in reasonable quantities, by writing me at my London address, below.

Sincerely,



Myra Gordon  
606-1209 Richmond St.  
London, Ontario, Canada  
N6A 3L7

P.S. It might be more expedient for your European readers to obtain their copies by writing Dr. Ivar Cooke

IC Chemikalien GmbH  
Sohnckestrasse 17  
8000 München 71

## DEUTERATED NMR SOLVENTS-HANDY REFERENCE DATA

Compound Mol. Wt.	$d_4^{20}$	m.p.*	b.p.*	$d_H(\text{mult})^*$	$J_{HD}$	$d_C(\text{mult})^*$	$J_{CD}(J_{CF})$
Acetic Acid-d <sub>4</sub> 64.078	1.12	17	118	11.53 (1) 2.03 (5)	2	178.4 (br) 20.0 (7)	20
Acetone-d <sub>6</sub> 64.117	0.87	-94	57	2.04 (5)	2.2	208.0 (13) 29.8 (7)	0.9 20
Acetonitrile-d <sub>3</sub> 44.071	0.84	-45	82	1.93 (5)	2.5	118.2 (br) 1.3 (7)	21
Benzene-d <sub>6</sub> 84.152	0.95	5	60	7.15 (br)		128.0 (3)	24
Chloroform-d 120.384	1.50	-64	62	7.24 (1)		77.0 (3)	32
Cyclohexane-d <sub>12</sub> 96.236	0.89	6	81	1.38 (br)		26.4 (5)	19
Deuterium Oxide 20.028	1.11	3.8	101.4	4.63(DSS) 4.67(TSP)			
1,2-Dichloroethane-d <sub>4</sub> 102.985	1.25	-40	84	3.72 (br)		43.6 (5)	23.5
Diethyl-d <sub>10</sub> Ether 84.185	0.82	-116	35	3.34 (m) 1.07 (m)		65.3 (5) 14.5 (7)	21 19
Diglyme-d <sub>10</sub> 146.263	0.95	-68	162	3.49 (br) 3.40 (br) 3.22 (5)	1.5	70.7 (5) 70.0 (5) 57.7 (7)	21 21 21
Dimethylformamide-d <sub>2</sub> 80.138	1.04	-61	153	8.01 (br) 2.91 (5) 2.74 (5)	2 2	162.7 (3) 35.2 (7) 30.1 (7)	30 21 21
Dimethyl-d <sub>6</sub> Sulphoxide 84.170	1.18	18	189	2.49 (5)	1.7	39.5 (7)	21
p-Dioxane-d <sub>8</sub> 96.156	1.13	12	101	3.53 (m)		66.5 (5)	22
Ethyl Alcohol-d <sub>5</sub> (anh) 52.106	0.91	<-130	79	5.19 (1) 3.55 (br) 1.11 (m)		56.8 (5) 17.2 (7)	22 19
Glyme-d <sub>10</sub> 100.184	0.86	-58	83	3.40 (m) 3.22 (5)	1.6	71.7 (5) 57.8 (7)	21 21
Hexafluoroacetone Deuterate <sup>a</sup> 198.067	1.71	21		5.26 (1)		122.5 (4) 92.9 (7)	(287) (34.5)
HMPT-d <sub>10</sub> 197.314	1.14	7	106 (11)	2.53 (2 x 5)	2 (9.5)	35.8 (7)	21
Methyl Alcohol-d <sub>4</sub> 36.067	0.89	-98	65	4.76 (1) 3.30 (5)	1.7	49.0 (7)	21.5
Methylene Chloride-d <sub>2</sub> 86.945	1.35	-95	40	5.32 (3)	1	53.8 (5)	27
Nitrobenzene-d <sub>5</sub> 128.143	1.25	6	211	8.11 (br) 7.67 (br) 7.50 (br)		148.6 (1) 134.8 (3) 129.5 (3) 123.5 (3)	24.5 (p) 25 26
Nitromethane-d <sub>3</sub> 64.059	1.20	-29	101	4.33 (5)	2	62.8 (7)	22
isoPropyl Alcohol-d <sub>8</sub> 68.146	0.90	-86	83	5.12 (1) 3.89 (br) 1.10 (br)		62.9 (3) 24.2 (7)	21.5 19
Pyridine-d <sub>5</sub> 84.133	1.05	-42	116	8.71 (br) 7.55 (br) 7.19 (br)		149.9 (3) 135.5 (3) 123.5 (3)	27.5 24.5 (γ) 25
Tetrahydrofuran-d <sub>8</sub> 80.157	0.99	-109	66	3.58 (br) 1.73 (br)		67.4 (5) 25.3 (br)	22 20.5
Toluene-d <sub>8</sub> 100.191	0.94	-95	111	7.09 (m) 7.00 (br) 6.98 (m) 2.09 (5)	2.3	137.5 (1) 128.9 (3) 128.0 (3) 125.2 (3) 20.4 (7)	23 24 24 (p) 19
Trifluoroacetic Acid-d <sup>a</sup> 115.030	1.50	-15	72	11.50 (1)		164.2 (4) 116.6 (4)	(44) (283)
2,2,2-Trifluoroethyl Alcohol-d <sub>3</sub> <sup>a</sup> 103.059	1.45	-44	75	5.02 (1) 3.88 (4 x 3)	2 (9)	126.3 (4) 61.5 (4 x 5)	(277) 22 (36)

\*Melting and boiling points (in °C) are those of the corresponding light compound (except for D<sub>2</sub>O) and are intended only to indicate the useful liquid range of the materials.

<sup>1</sup>H (of the residual protons) and <sup>13</sup>C spectra were determined on HA-100 and XL-100-15 spectrometers, respectively, for the same sample of each solvent containing 5% TMS (v/v). The chemical shifts are in ppm relative to TMS; the coupling constants are in Hz. (Since deuterium has a spin of 1, triplets arising from coupling to deuterium have the intensity ratio of 1:1:1, etc.) The multiplicity br indicates a broad peak without resolvable fine structure, while m denotes one with fine structure. It should be noted that the chemical shifts, in particular, can be dependent on solute, concentration and temperature.

<sup>a</sup> $d_r(\text{CFCl}_3)$  82.6 (1)

<sup>a</sup> $d_r(\text{CFCl}_3)$  76.2 (1)

<sup>a</sup> $d_r(\text{CFCl}_3)$  77.8 (5),  $J_{FD}$  1.2

all determined on an HA-100 spectrometer.

DEPARTMENT OF ORGANIC CHEMISTRY  
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX

TEL: 051 - 709 - 6022

The University of Liverpool

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

2nd April, 1979.

Dear Barry,

Conformer Energies in 2-Chlorocyclohexanone.

In reply to your reminders, Lee Griffiths and I have just completed a solvent study on the conformational equilibrium in 2-chlorocyclohexanone<sup>1</sup>, essentially similar to that of Pan and Stothers<sup>2</sup>, but in a much wider range of solvents to better test our reaction field theory.

The results are shown tabulated, and the agreement with our reaction field model is sufficiently good to allow the prediction of the vapour state conformer energy differences. These are for the 2-fluoro, 2-chloro and 2-bromo cyclohexanone ca. 0.8, 1.7 and 1.9 kcals/mole respectively, which may be compared with the values for the corresponding cyclohexyl halides of -0.2, -0.4 and -0.5 kcals/mole.

The reaction field model has also been applied to a variety of 2- and 4-substituted halo-cyclohexanones with generally good agreement.

Interestingly the main problem in the application of the model was in the determination of the precise geometry of the halo-ketone ring.

With best wishes,

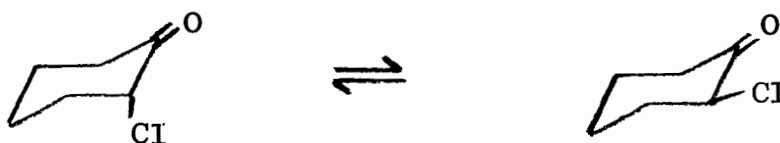
Yours sincerely,

Dr. R.J. Abraham.

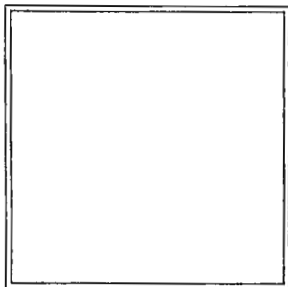


1. R.J. Abraham and L. Griffiths (manuscript in preparation).
2. Y. Pan and J.B. Stothers, Can. J. Chem., 45, 2943 (1967).

Table 4. Observed and Calculated Conformational Free Energies  
( $\Delta G$ , kcal/mole) of 2-chlorocyclohexanone.



Solvent	$\epsilon$	$\Delta G$	
		Obsd	Calc
Vapour	1.0		1.75
n.Pentane	1.96	1.04	1.00
n.Hexane	2.00	0.91	0.98
c.Pentane	2.05	0.99	0.95
C <sub>2</sub> Cl <sub>4</sub>	2.37	0.84	0.80
C <sub>2</sub> HCl <sub>3</sub>	3.61	0.46	0.42
CDCl <sub>3</sub>	5.05	0.08	0.17
CD <sub>2</sub> Cl <sub>2</sub>	9.40	-0.06	-0.18
d <sub>6</sub> Acetone	21.60	-0.31	-0.48
CD <sub>3</sub> NO <sub>2</sub>	35.90	-0.42	-0.61
d <sub>7</sub> D M F	36.70	-0.50	-0.61
CD <sub>3</sub> CN	37.10	-0.39	-0.61
d <sub>6</sub> D M S O	47.50	-0.59	-0.67



April 3, 1979

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

RE:  $^{13}\text{C}$  NMR Probe of Lysine Function in Proteins

Dear Professor Shapiro:

We have recently developed a mild procedure for reductively methylating proteins with [ $^{13}\text{C}$ ]formaldehyde and sodium cyanoborohydride (J. Biol. Chem., July-August). It has been determined that this method is specific for the  $\epsilon$ -amino groups of lysine and the N-terminal  $\alpha$ -amino group of proteins, yielding N,N-dimethyl derivatives. Since methyl groups are small and the pKa of the amino group is not significantly perturbed, we feel reductive methylation is an ideal method to label protein amino groups for  $^{13}\text{C}$  NMR studies.


Our initial studies with  $^{13}\text{C}$ -methylated ribonuclease-A (which contains an active site lysine) will also be published in J. Biol. Chem. (July-August). We have since expanded our studies to several other proteins including the work shown here on  $^{13}\text{C}$ -methylated HEW lysozyme.

The cmr of methylated lysozyme at pH 8.5 (Figure 1) shows that all 6 of the dimethyl  $\epsilon$ -amino lysyl residues as well as the  $\alpha$ -amino terminus have different chemical shifts. We have found for methylated lysozyme, that most lysyl residues are unique with respect to chemical shift, pKa, and  $T_1$ . This is in contrast to  $^{13}\text{C}$ -methylated ribonuclease-A where only two signals are observed for the methylated lysyl groups - one from lysine 41, the active site residue, and the other from the 9 bulk lysyl residues. At pH's below 6, the cmr of  $^{13}\text{C}$ -methylated lysozyme show increasing line broadening (figure 2). Some of the signals appear to split into broad "doublets" (e.g. the  $\alpha$ -amino signal) which sharpen as the pH is further decreased below 4. It is interesting that the pH optimum for lysozyme activity is within this pH range.

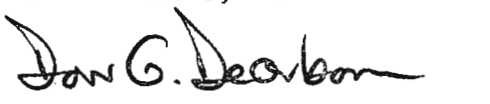
Please credit this contribution to Bill Ritchey's Account.

Sincerely yours,

  
Tom Gerken, Ph.D.

  
Neil Jentoft, Ph.D.

  
Joyce Jentoft, Ph.D.

  
Dorr G. Dearborn, Ph.D., M.D.

/bp

Department of Pediatrics  
School of Medicine  
Rainbow Babies and Childrens Hospital

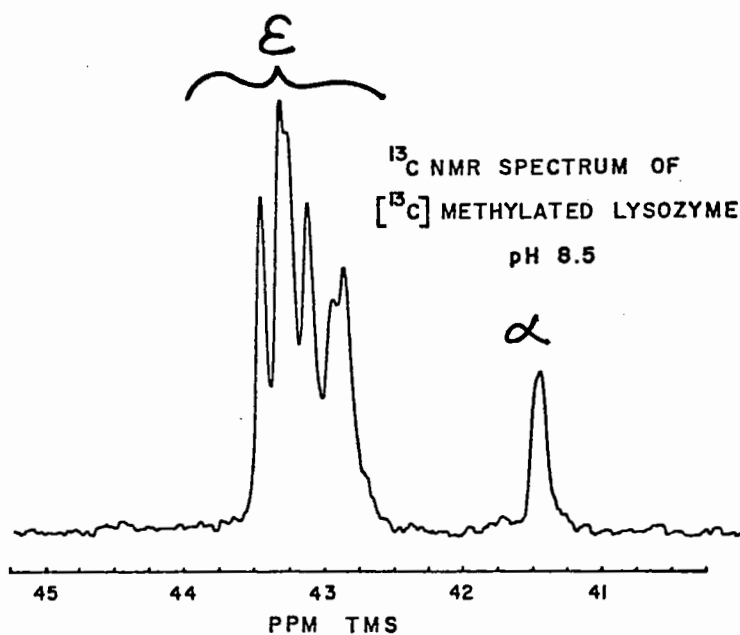


Figure 1

(Spectra obtained at ambient temperature using a Bruker WH 180 at 45 MHz with a 20 mm tube. Protein concentration  $\sim 10$  mg per ml requiring  $\sim 200$  scans.)

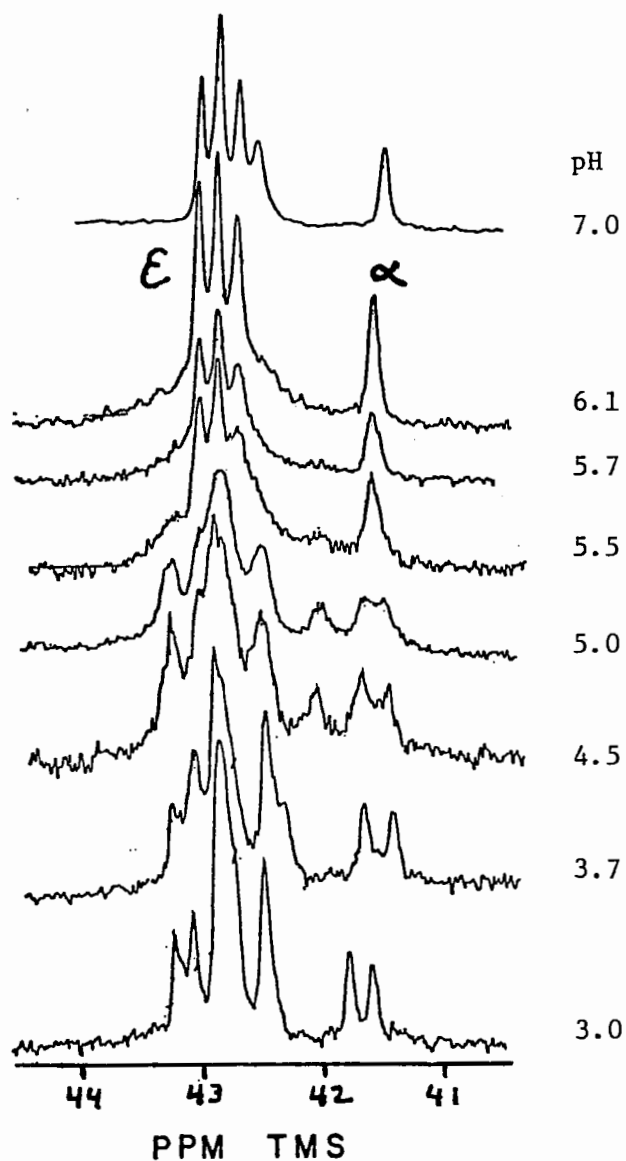


Figure 2

pH Dependence of  
 $^{13}\text{C}$  Methylated Lysozyme  
(Same NMR parameters as above)



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
PUBLIC HEALTH SERVICE  
NATIONAL INSTITUTES OF HEALTH  
BETHESDA, MARYLAND 20014

April 5, 1979

Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, TX 99843

Modification on JEOL FX-series NMR Spectrometers  
for Large Offsets

Dear Professor Shapiro:

We have recently made a simple modification on our JEOL FX-100 system so that we can observe  $^{13}\text{C}$  signals which resonate outside the offset frequencies ( $\pm 50$  KHz) provided by the manufactory. We feel that this modification may be of interest to FX-series owners.

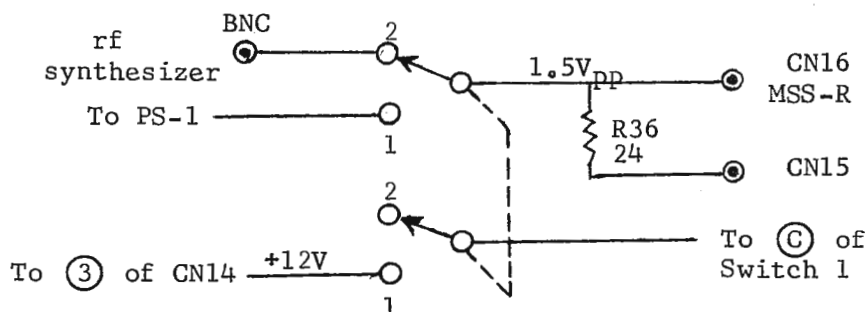
The modification basically was to replace the  $^{13}\text{C}$  local oscillator with a rf synthesizer. The variable frequency from the synthesizer, which was phase locked to the spectrometer, was fed to point CN16 ( $1.5\text{ V}_{\text{pp}}/50\Omega$ ) of the  $^1\text{H}/^{13}\text{C}$  local oscillator unit (see figure below). To avoid interference from original circuitry, the  $^{13}\text{C}$  local oscillator section was disabled by cutting off its +12V supply during the variable frequency operation. It is very convenient to make changes between the normal  $^{13}\text{C}$  and the modified variable frequency operations by using a double-pole, double throw switch as shown in the figure.

A bonus from this modification is that one can take advantage of the variable frequency of synthesizer to observe other nuclei which have resonance frequencies near that of  $^{13}\text{C}$ . With this modification, we are able to observe  $^{23}\text{Na}$  ( $90^\circ$  pulse  $\sim 150\text{ }\mu\text{sec}$ ),  $^{27}\text{Al}$  ( $\sim 90\text{ }\mu\text{sec}$ ),  $^{53}\text{Mn}$  ( $\sim 8\text{ }\mu\text{sec}$ ),  $^{79}\text{Br}$  ( $\sim 14\text{ }\mu\text{sec}$ ) and  $^{81}\text{Br}$  ( $\sim 250\text{ }\mu\text{sec}$ ) without retuning the  $^{13}\text{C}$  matching networks.

Sincerely yours,

*Herman J. C. Yeh*

Herman J. C. Yeh



(See page 10 of  
FX-100 circuit  
diagram)

(See page 9 of  
FX-100 circuit  
diagram)

Switch	
1. normal	2. modified



## CENTRO DE INVESTIGACION DEL IPN

APARTADO POSTAL 14-740

MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

April 5, 1979

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

Dear Professor Shapiro:

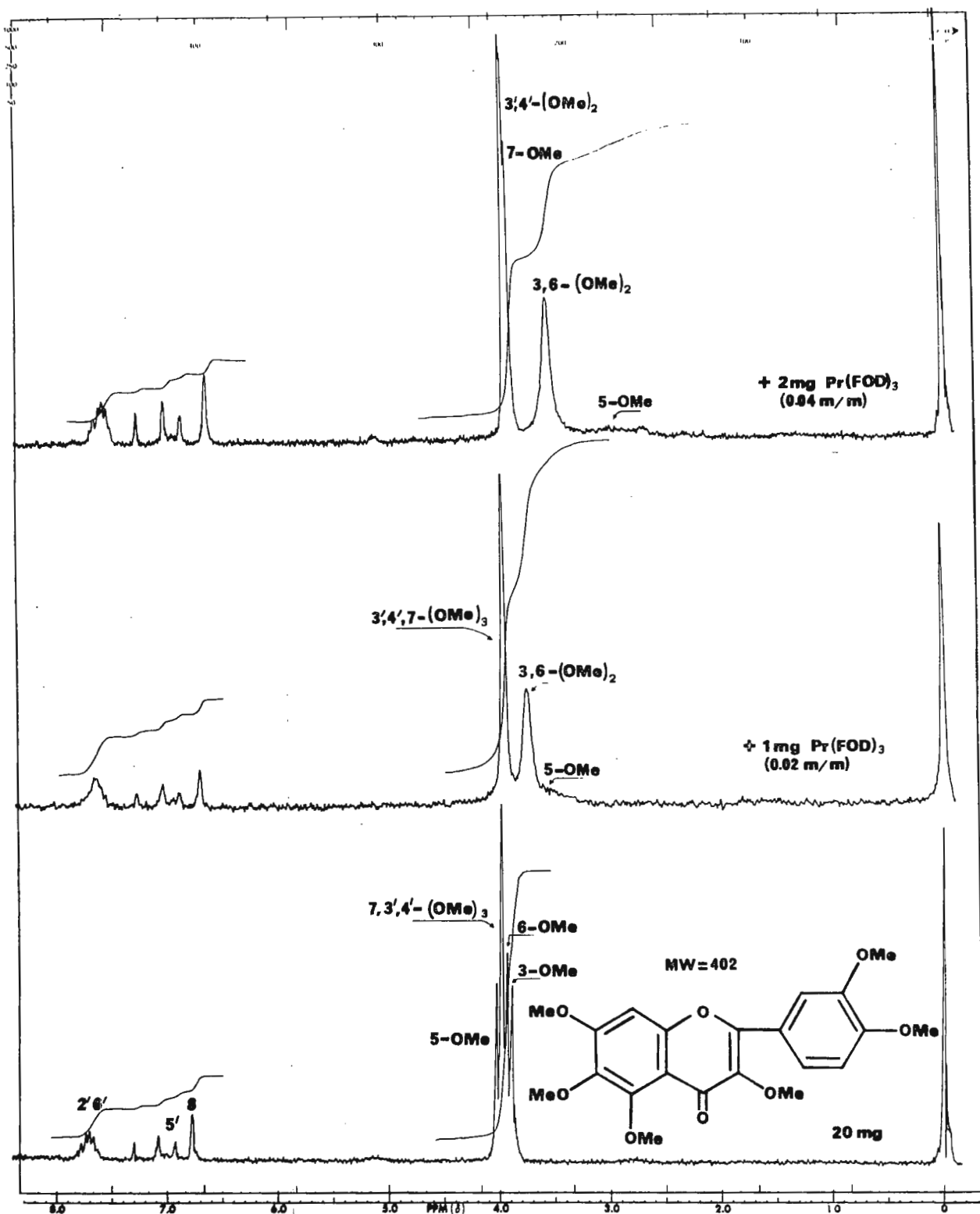
Severe Broadening of proton methoxyl signals by use of  
 small amounts of a shift reagent

In one of our earliest contributions to the newsletter (1) we described the shift reagent behavior of the four flavones having one methoxyl group at the A-ring. The work with all possible monomethoxylflavones has been completed, the lanthanide position during interaction have been assessed by computer calculations and the data will appear soon (2) together with those of 3,5-dimethoxyflavone.

In that study it was concluded that four types of compounds have to be considered for the elucidation of substitution patterns of flavones using  $\text{Pr}(\text{fod})_3$  shift reagent, as follows:

- 1.- Unsubstituted flavones at both 3 and 5, in which the lanthanide induced shifts (LIS) are:  $\text{H-5} > \text{H-3} > \text{H-8} > \text{H-6} > \text{H-7} > \text{H-2'}$  and  $\text{H-6'} > \text{H-3'}$  and  $\text{H-5'} > \text{H-4'}$ . The methoxyl groups of these substances remain as sharp singlets.
- 2.- Flavones with methoxyl group at C-3 and hydrogen at C-5 for which the LIS are:  $\text{H-5} > \text{H-2'}$  and  $\text{H-6'} > \text{H-3'}$  and  $\text{H-5'} > \text{H-8} > \text{H-4'} > \text{H-6} > \text{H-7}$ . The 3-OMe signal broadness to  $W(1/2) \approx 4$  Hz after addition of 0.1 mole of  $\text{Pr}(\text{fod})_3$  per mole substrate.
- 3.- Flavones with methoxyl at C-5 and hydrogen at C-3 for which the LIS are:  $\text{H-6} > \text{H-3} > \text{H-7} > \text{H-8} > \text{H-2'}$  and  $\text{H-6'} > \text{H-3'}$  and  $\text{H-5'} > \text{H-4'}$ . The 5-OMe signal broadness to  $W(1/2) \approx 8$  Hz after addition of 0.1 mole of  $\text{Pr}(\text{fod})_3$ .
- 4.- Disubstituted flavones with methoxyl at both 3 and 5 positions for which the LIS are:  $\text{H-6} > \text{H-7} > \text{H-8} > \text{H-2'}$  and  $\text{H-6'} > \text{H-3'}$  and  $\text{H-5'} > \text{H-4'}$ . The 3-OMe signal broadness to  $W(1/2) \approx 3.5$  Hz and that of 5-OMe to  $W(1/2) \approx 20$  Hz after addition of only 0.04 mole of  $\text{Pr}(\text{fod})_3$  per mole substrate.

We are now using this information to study polymethoxyflavones and until now the following compounds have been measured: 5,7-dimethoxy-; 5,7,4'-trimethoxy-; 5,7,3',4'-tetramethoxy-; 3,



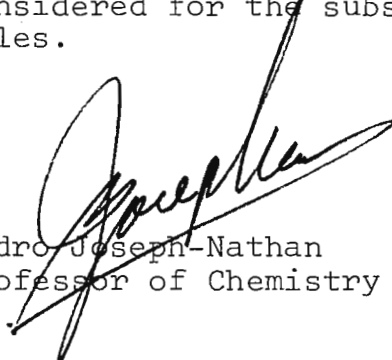
Proton nmr spectra of 3,3',4',5,6,7-hexamethoxyflavone.  
 Lower: Pure substrate; Center: in the presence of 1 mg  $\text{Pr}(\text{fod})_3$ ;  
 Upper: in the presence of 2 mg  $\text{Pr}(\text{fod})_3$ .

5,7-trimethoxy-; 3,5,7,4'-tetramethoxy-; 3,5,7,3',4'-pentamethoxy-; 3,5,7,2',4'-pentamethoxy-; 3,5,7,3',4',5'-hexamethoxy-; 3,3',4',7-tetramethoxy-; 3,5,6,7,4'-pentamethoxy- and 3,5,6,7,3',4'-hexamethoxyflavone.

With the exception of the last two molecules, the flavones behave in accordance with the classification into the four groups.

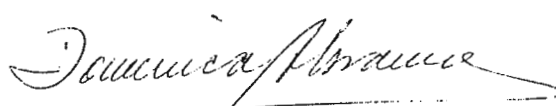
However in the case of flavones having methoxyl groups at 3,5 and 6 a new situation arises: The 60 MHz spectrum (A-60) of a solution containing 20 mg of 3,3',4',5,6,7-hexamethoxyflavone in 0.3 ml  $\text{CDCl}_3$  is shown in the low trace of the figure. Addition of only 1 mg  $\text{Pr}(\text{fod})_3$  (central trace) broadens the 5-OMe signal so severely that it is almost lost in the base line. The signals of the OMe groups at 3 and 6 are also quite broad while the remaining three methoxyl groups give a single sharp peak at  $\sim 4$  ppm. The effect of adding a second mg of the shift reagent is shown on the top trace, where the 5-OMe group has virtually disappeared, the signals of 3 and 6 shift again and the singlet due to the substituents at 3', 4' and 7 start to resolve into three peaks. Further additions of shift reagent cause the complete loss of the 5-OMe signal. When the spectrum is measured in the presence of 20 mg of  $\text{Pr}(\text{fod})_3$ , which correspond to a ratio of approximately 0.4 mole of shift reagent per mole of substrate, the broad signal due to the 3 and 6 methoxyl groups, which is found around 1 ppm, also starts to resolve into two peaks. Furthermore, the signal owing to the  $\text{Pr}(\text{fod})_3$  is found always in the 0.5 ppm region except in these two molecules where it is found upfield from TMS.

This data suggest that a fifth group of flavones has to be considered for the substitution pattern elucidation of these molecules.



Pedro Joseph-Nathan  
Professor of Chemistry

Sincerely yours,



D. Abramo Bruno  
Graduate Student

- (1) P. Joseph-Nathan and J. Mares, TAMU NMR Newslett., 194, 17 (1974).
- (2) P. Joseph-Nathan, J. Mares and D.J. Ramírez, J. Magn. Resonance, (in press).

Gerhard Hägele  
Winfried Boenigk

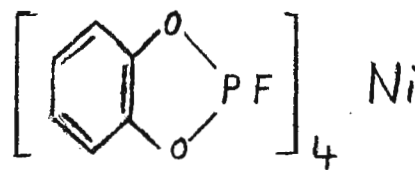
Düsseldorf, 6.4.79  
Universitätsstraße 1

Prof. B. L. Shapiro  
Dept. of Chemistry  
TEXAS A&M University  
College Station  
TX 77843 U. S. A.

Dear Professor Shapiro!

In J. Magn. Res. 26, 505 (1977) Volker Lueg and G. H. reported on a new computer program SYMTRY for the calculation of NMR spectra of spinsystems with general symmetry. SYMTRY was designed for the CYBER-computer at Cologne using FORTRAN and CDC-ASSEMBLER-language. The program was tested with spinsystems familiar to our chemistry. Continuing these studies we developed a FORTRAN-only version of SYMTRY, expanded a number of arrays and changed the handling of symmetry-operators. The new version is running on the Düsseldorf TELEFUNKEN-computer and should be adaptable to other computing facilities more easily now. SYMTRY will handle greater spin systems like the  $[[A]_2X]_3$  of  $[NPF_2]_3$  or the five hypothetical  $[AX]_4$  systems in cyclobutanes  $C_4H_4F_4$ . To check the program we choose that fine piece of research given by Linden-Bell in Mol. Phys. 15, 523 (1968) concerning a nickel-O-complex with tetrahedral symmetry.:

Subsequent spectra show the proton-decoupled phosphorus- and fluorine-spectra in  $[RPF]_4Ni [AX]_4 (T_d)$ .

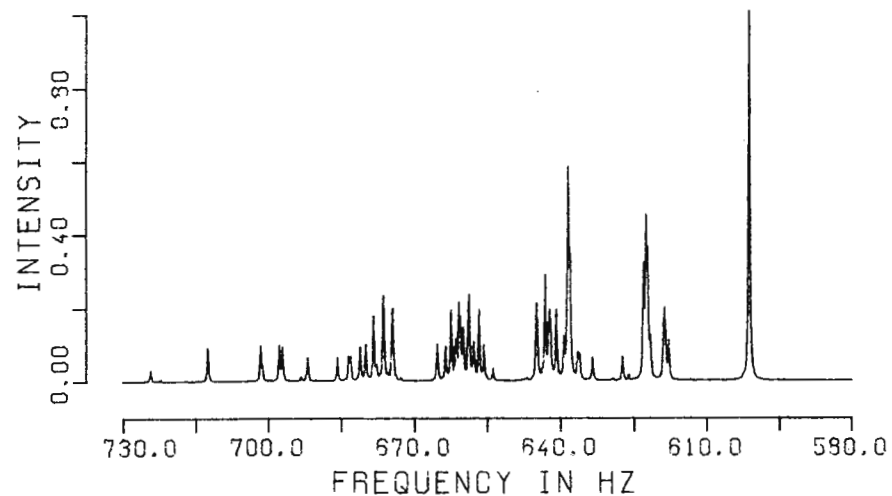


Yours sincerely

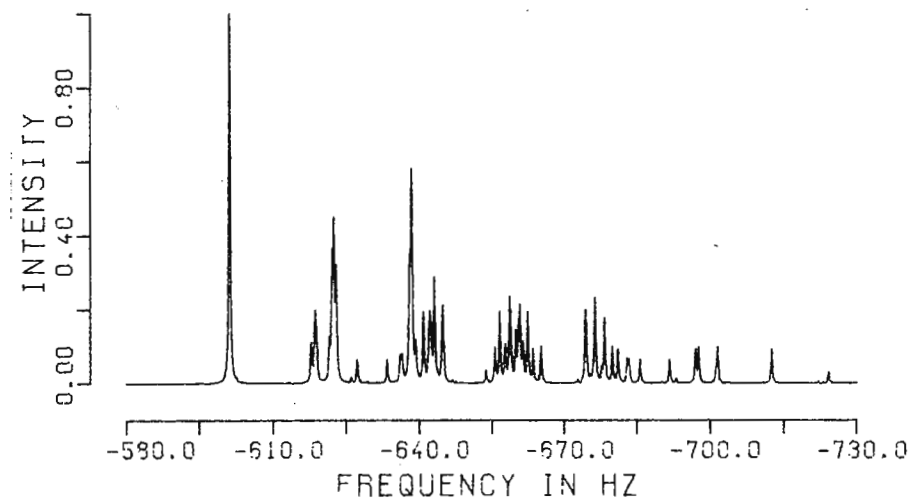
*Gerhard Hägele Winfried Boenigk*

Gerhard Hägele and Winfried Boenigk  
Institut für Anorganische und Struktur-  
chemie der Universität Düsseldorf

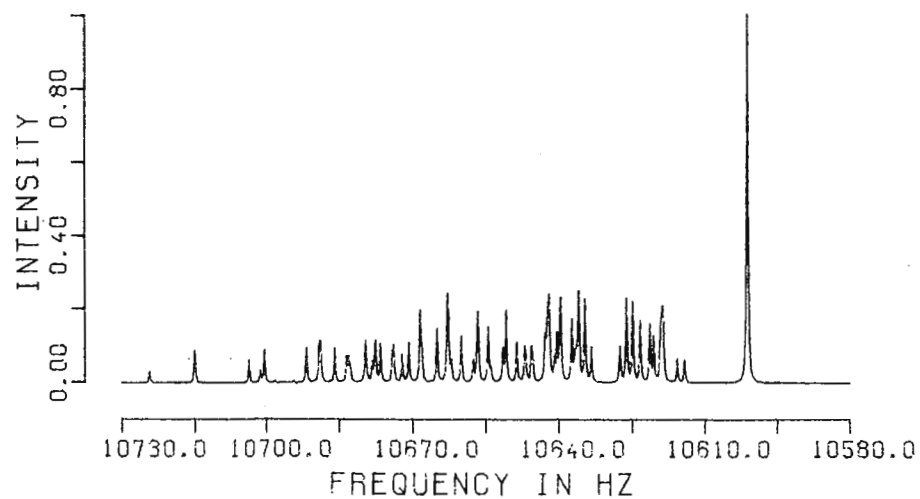
CASE 791 PLOT 4 NI (PFR2) 4 P-TEIL



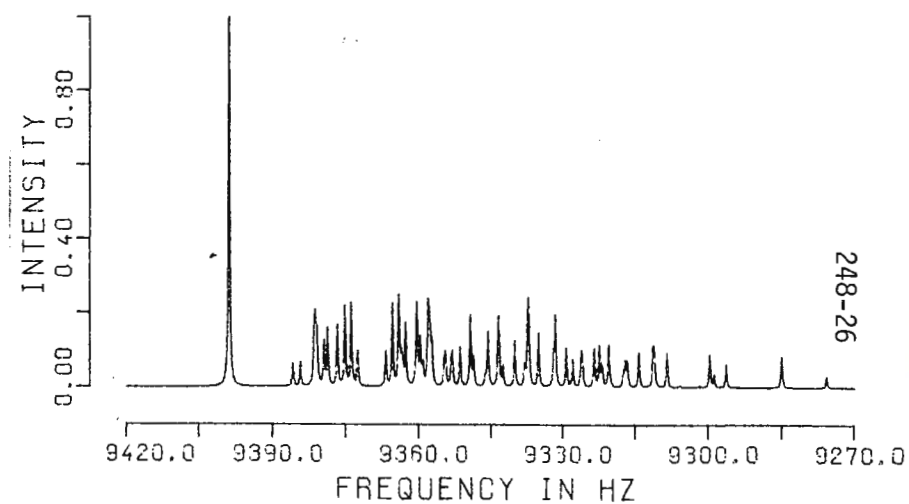
CASE 791 PLOT 2 NI (PFR2) 4 P-TEIL



CASE 791 PLOT 8 NI (PFR2) 4 F-TEIL



CASE 791 PLOT 6 NI (PFR2) 4 F-TEIL





## TEXAS A&amp;M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of  
CHEMISTRY

3 April 1979


Dr. Ray Ettinger  
Varian Instrument Division  
611 Hansen Way  
Palo Alto, CA 94303

Dear Ray:

I hope you will not mind if we remind you that it has been quite some time since you have sent in a technical contribution to the TAMU NMR Newsletter.

As you know, we have made it a rule that recipients of the Newsletter must contribute technically at least once every nine or ten months. Please supply us with a short title(s) of all the topics you discuss in your contribution. Thanks!

Yours sincerely,

  
Bernard L. Shapiro  
Professor



THE ABOVE, OUR STANDARD "REMINDER" LETTER, WAS ERRONEOUSLY SENT TO RAY ETTINGER OF VARIAN. "ERRONEOUSLY" BECAUSE AS HIS FRIENDS KNOW, ALL OF RAY'S TECHNICAL CONTRIBUTIONS IN RECENT YEARS HAVE BEEN OF A CLASSIFIED OR OTHERWISE UNPRINTABLE VARIETY. AND THEY SAY THAT CAPTAINS OF INDUSTRY HAVE NO SENSE OF HUMOR!

B. L. SHAPIRO

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000



April 11, 1979

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

Dear Barry:

I hope you will not mind if we remind you that it has been quite some time since you have sent in a purchase order to the Varian Instrument Division.

As you know, we have made it a rule that recipients of our NMR T-shirts must contribute financially at least once every nine or ten months. Please supply us with a short listing of all the instruments you will acquire in your next order. Thanks!

Yours sincerely,

  
Ray Ettinger  
Product Marketing Manager,

# If your superconducting FT NMR can't achieve a dynamic range of 6,000,000:1 or better...

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# University of Illinois at Urbana-Champaign

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DEPARTMENT OF CHEMISTRY

April 9, 1979

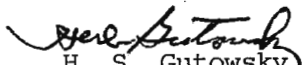
Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Postdoc opening

Dear Barry:

This is a quick note to let you know that I have a couple of openings for postdocs starting this summer and/or fall. Work in progress includes: i) The use of proton relaxation measurements to study the effects of various chemical treatments and of light upon the oxidation state and structural environment of manganese in chloroplasts. ii) Phosphorus -31 and deuterium FT studies of the dynamic state of phospholipids in artificial and natural membranes, with and without proteins. iii) Setting up pulsed ESR facilities for studies similar to those outlined in i).

Sincerely yours,

  
H. S. Gutowsky  
Professor

HSG:sc

## CARLETON UNIVERSITY

OTTAWA, CANADA

K1S 5B6



DEPARTMENT OF CHEMISTRY

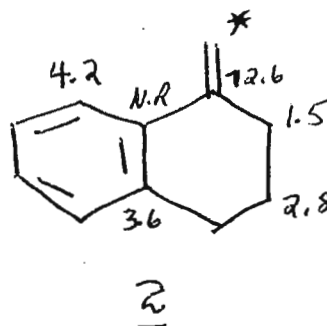
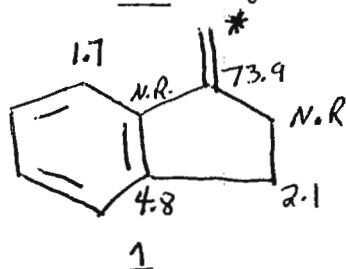
April 6, 1979.

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

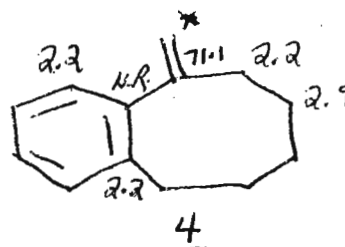
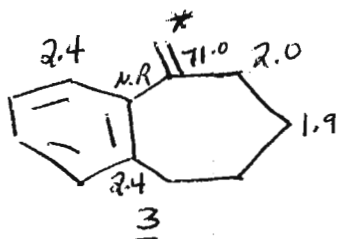
Title: " $^{13}\text{C}$ - $^{13}\text{C}$  Couplings in exo-methylenebenzocycloalkanes"

Dear Barry,

For her honors B.Sc. project, Jocelyn Selwyn has prepared the 4 compounds shown below, enriched with  $^{13}\text{C}$  at the exo-methylene carbon.



$N.R. \equiv < 0.6 \text{ Hz}$



The  $^{13}\text{C}$ - $^{13}\text{C}$  couplings to individual positions are indicated in the diagram. A force field program, "GEMO" (1), has been used to calculate preferred geometries. The calculated torsional angles between the plane of the benzene ring and the exo-methylene carbon for compounds 2-4 are in good agreement with the only available experimental data, those from photoelectron

spectroscopy (2). Using these geometries as input, the Fermi-contact contributions to the couplings were then calculated via the INDO MO program (3). Agreement for  $J$ 's is excellent, but poor for  $^2J$ 's and  $^3J$ 's.

For the vicinal couplings, an approximate Karplus relation was found, with a  $^3J$  minimum in the range of dihedral angles from  $80$ - $100^\circ$ , and maxima near  $0$  and  $180^\circ$ . Deviations from "Karplus-like" behavior were found for bonding situations involving unusually large or small C-C-C valence angles. These results are reminiscent of results for  $^3J_{HH}$  for the alkene protons of 3-7 membered cycloalkenes (4), in which an increase in the valence angle (C-C-H), causes a marked reduction in  $^3J_{HH}$  for constant dihedral angle. We are presently exploring, in more detail, the influence of valence angle changes on  $^3J_{CC}$ , for fixed dihedral angles in dimethylated cycloalkenes.

Spectral assignments for the non-protonated aromatic carbons of 1-4 were confirmed via deuteration of the exomethylene group. From our results, it appears that the previous assignments for these carbons of 1, (5) should be reversed. Best personal regards.

Sincerely,



G.W. Buchanan,  
Associate Professor.

#### References

1. N.C. Cohen, Tetrahedron 27, 789 (1971).
2. J.P. Moier and D.W. Turner, J.C.S. Far. Trans. 2, 69, 196 (1973).
3. Obtained from QCPE #224
4. "Organic Structural Analysis", J.B. Lambert et al P. 68 (1976).
5. D.W. Hughes, B.C. Nalliah, H.L. Holland and D.B. MacLean, Can. J. Chem. 55, 2252 (1977).



Gesamthochschule Siegen  
 Fachbereich 8, Organische Chemie II  
 Prof. Dr. H. Günther

5900 Siegen 21, den April 7, 1979  
 Adolf-Reichwein-Straße  
 Fernruf 0271/740 - 1  
 Nebenstelle 4390, 4400

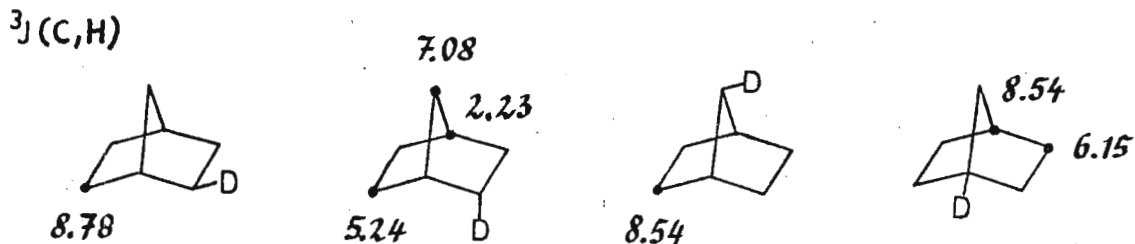
Gesamthochschule Siegen, Postfach 21 02 09, 5900 Siegen 21

Prof. Dr. B. L. Shapiro  
 Texas A and M University  
 College of Science  
 College Station, Texas 77843  
 U S A

### Karplus-Curve for $^3J(C,H)$ in Norbornane

Dear Barry,

continuing our studies of  $^{13}C, ^1H$  coupling constants we have extended earlier measurements on deuterated adamantane (TAMU Newsletter 238/28; R. Aydin and H. Günther, Z. Naturf. 34b, March issue 1979) to the following set of monodeuterated norbornanes:



The values for the  $^3J(^{13}C, ^1H)$  couplings (in Hz) given were calculated from the observed  $^3J(^{13}C, ^2H)$  data using the conversion factor 6.5144.

The Karplus-like treatment of the data using the experimental geometry for norbornane [1] is shown in Fig. 1. The best fit was obtained using a least squares procedure. The result (equ. given in Fig. 1) agrees well with that derived theoretically for propane by Wasylishen and Schaefer [2] (values in the 2nd line).

Two aspects remain for clarification:

- (1) Can vicinal C,H couplings indeed be negative?
- (2) Do isotope and/or relaxation effects [3] spoil the picture?

With respect to (1), further data for  $\phi = 40^\circ$ - $110^\circ$  seem desirable to close the experimental gap. Point (2) is presently investigated.

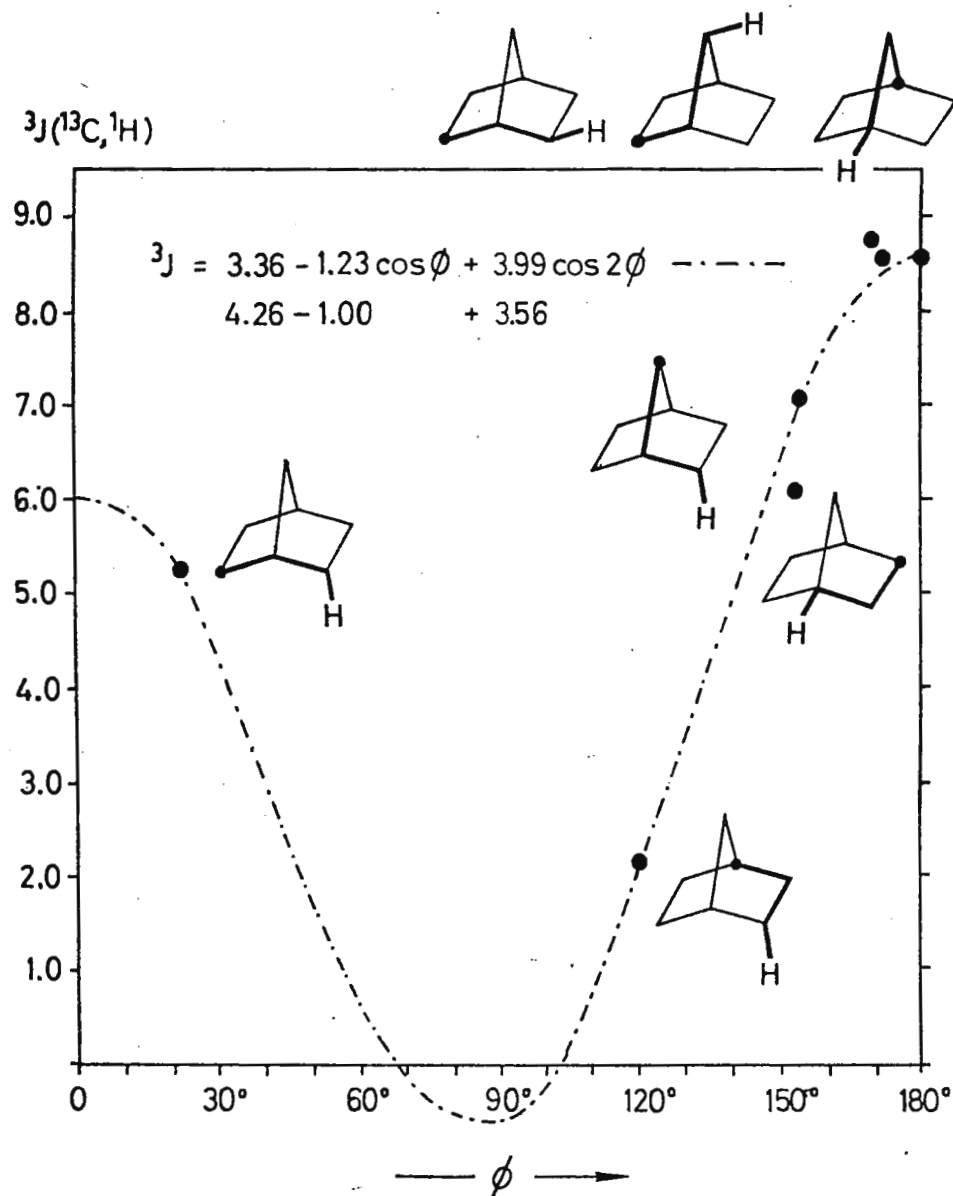


Fig. 1. Dihedral angle dependence of  $^3J(^{13}\text{C}, ^1\text{H})$  in norbornane

In acknowledgement of your green reminder,

Sincerely yours,

*R. Aydin*  
R. Aydin

*H. Günther*  
H. Günther

- [1] J. F. Chiang, C. F. Wilcox, and S.H. Bauer, J. Am. Chem. Soc. 90, 3149 (1968).
- [2] R. Wasylishen and T. Schaefer, Can. J. Chem. 51, 961 (1973).
- [3] J. M. A. Al-Rawi, J. A. Elvidge, J. R. Jones, and E. A. Evans, J. C. S. Perkin II, 1975, 449.



U.S. Department of Energy  
Laramie Energy Technology Center  
P.O. Box 3395, University Station  
Laramie, Wyoming 82071

April 13, 1979

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

Re: NMR Symposia

Dear Barry:

Enclosed is the preliminary program for the NMR Symposium on Macromolecules to be held in conjunction with the 21st Annual Rocky Mountain Conference on Analytical Chemistry at the Denver Convention Complex, Denver, Colorado from July 30 to August 1, 1979.

Both Gareth and I are pleased with the response we have received to our invitations. There are over 100 papers dealing with the applications of magnetic resonances to chemistry and biology and we extend an invitation to all readers of the Newsletter to attend the Conference. Additional information about the Conference can be obtained from either Dr. Gareth Eaton or me.

Dr. Gareth R. Eaton  
EPR Symposium Chairman  
Department of Chemistry  
University of Denver  
Denver, Colorado 80208  
(303) 753-2507

Dr. Daniel A. Netzel  
NMR Symposium Chairman  
Laramie Energy Technology Center  
P. O. Box 3395, University Station  
Laramie, Wyoming 82071  
(307) 721-2370

Sincerely,

A handwritten signature in cursive script, which appears to read "Daniel A. Netzel", is written over the typed name.

Daniel A. Netzel  
NMR Symposium Chairman

# SYMPOSIUM ON THE NMR OF MACROMOLECULES

D. A. Netzel, Chairman

## SESSION I - SOLID STATE NMR

Monday Morning, July 30 - Gary E. Maciel, Presiding

- 8:30 Introductory Remarks - Daniel A. Netzel
- 8:35 EXPECTATIONS FOR RESOLUTION IN HIGH RESOLUTION  $^{13}\text{C}$  NMR OF SOLIDS--PARTICULARLY POLYMERS, D. L. VanderHart, W. L. Earl, National Bureau of Standards, Washington, D.C., and A. N. Garroway, Naval Research Laboratory, Washington, D.C.
- 9:00  $^{23}\text{Na}$  SOLID-STATE NMR OF BETA-ALUMINAS, R. W. Vaughan, M. Polak, and A. Highe, California Institute of Technology, Pasadena CA.
- 9:30 HIGH RESOLUTION SOLID STATE NMR OF HYDROGEN ON CATALYTICALLY ACTIVE SURFACES, B. C. Gerstein, P. Dubois Murphy, L. M. Ryan and R. E. Taylor, Iowa State University, Ames IA.
- 10:00 Coffee Break
- 10:30 LOW TEMPERATURE NMR OF SMALL MOLECULES BY MATRIX ISOLATION, K. Zilm and D. M. Grant, University of Utah, Salt Lake City UT.
- 11:00 RECENT DEVELOPMENTS IN HIGH RESOLUTION DEUTERIUM NMR IN SOLIDS--DOUBLE QUANTUM NMR AND MAGIC ANGLE SPINNING, M. Alla, Estonian Academy of Sciences, Tallinn, Estonian SSR, D. Eckman and A. Pines, University of California, Berkeley CA.
- 11:30 DYNAMIC FREQUENCY SHIFTS IN SPECTRALLY DEGENERATE SPIN SYSTEMS, L. G. Werhelow, Montana State University, Bozeman MT.
- 12:00 Lunch

Monday Afternoon, July 30 - Vic Bartuska, Presiding

- 1:30 RELAXATION STUDIES OF POLYMERIC BLENDS, M. D. Sescik, J. Schaefer, E. O. Stejskal, and R. A. McKay, Monsanto Company, St. Louis MO.
- 2:00 HIGH RESOLUTION  $^{13}\text{C}$  NMR INVESTIGATION OF SOLID PHENOLIC RESINS AND RELATED COMPOUNDS, C. A. Fyfe, A. Rudin and W. J. Tchir, University of Guelph, Guelph, Ontario, Canada.
- 2:30  $^{13}\text{C}$  NMR SOLIDS TECHNIQUES FOR CHARACTERIZING BLENDS OF ELASTOMERS AND POLYOLEFINS, C. J. Carmen, J. B. Pausch, BF Goodrich Company, Brecksville OH, and A. N. Garroway, Naval Research Laboratory, Washington, D.C.
- 3:00 Coffee Break
- 3:30 C-F DOUBLE RESONANCE STUDIES OF BULK FLUOROPOLYMERS, J. Lyerla and C. S. Yannoni, IBM, San Jose CA.
- 4:00 SOLID STATE NMR OF ELASTOMER: LOW AND HIGH RESOLUTION, J. Ackerman and J. E. Mark, University of Cincinnati, Cincinnati OH.
- 4:30 MACROMOLECULAR DYNAMICS OF FLUOROCARBON POLYMERS STUDIED BY MULTIPLE PULSE NMR, A. J. Vega, DuPont, Wilmington DE.

## SESSION I - Continued

Tuesday Morning, July 31 - Daniel A. Netzel, Presiding

- 9:00  $^{13}\text{C}$  NMR STUDIES OF COALS, V. J. Bartuska, G. E. Maciel, Colorado State University, Fort Collins CO, and F. P. Miknis, Laramie Energy Technology Center, Laramie WY.
- 9:30  $^{13}\text{C}$  NMR STUDIES OF OIL SHALES, F. P. Miknis, Laramie Energy Technology Center, Laramie WY, V. J. Bartuska and G. E. Maciel, Colorado State University, Fort Collins CO.
- 10:00 Coffee Break
- 10:30 FURTHER  $^{13}\text{C}$  NMR STUDIES ON SOLID FOSSIL FUELS, R. J. Pugmire, K. W. Zilm and D. M. Grant, University of Utah, Salt Lake City UT.
- 11:00  $^{13}\text{C}$  NMR STUDIES OF SOLID PLANT MATERIALS, G. E. Maciel and V. J. Bartuska, Colorado State University, Fort Collins CO.
- 11:30 SOLID STATE HIGH RESOLUTION  $^{13}\text{C}$  NMR STUDIES OF CELLULOSE, W. L. Earl and D. L. VanderHart, National Bureau of Standards, Washington, D.C.
- 12:00 Lunch

## SESSION II - FUELS

Tuesday Afternoon, July 31 - Francis P. Miknis, Presiding

- 1:30 CARBON-13 SPECTRA-STRUCTURE CORRELATIONS FOR HYDROCARBONS, N. F. Chamberlain, Exxon Research & Engineering Co., Baytown TX.
- 2:00 APPLICATION OF RELAXATION RESOLUTION TO CARBON-13 FT NMR OF FOSSIL FUEL FRACTIONS, M. Melchoir, Exxon Research & Engineering Co., Linden NJ.
- 2:30 HIGH TEMPERATURE CARBON-13 NMR STUDIES OF POLYCYCLIC AROMATIC COMPOUNDS AND COAL PRODUCTS, H. C. Dorn, I. T. Taylor and T. Glass, Virginia Polytechnic Institute, Blacksburg VA.
- 3:00 Coffee Break
- 3:30 CHARACTERIZATION OF HETEROATOM CONTENT IN COAL PRODUCT FRACTIONS BY  $^{19}\text{F}$  NMR, L. T. Taylor, H. C. Dorn, P. Slervi and T. Glass, Virginia Polytechnic Institute, Blacksburg VA.
- 4:00 NMR EXAMINATION OF FUELS AND FRACTIONS FROM SHALE OIL, R. N. Hazlett and J. Solash, Naval Research Laboratory, Washington, D.C.
- 4:30 AVERAGE MOLECULAR STRUCTURE ANALYSIS OF COAL DERIVED LIQUID BY NMR SPECTROMETRY, D. M. Cantor, Phillips Petroleum Co., Bartlesville OK.

## SESSION III - BIOPOLYMERS

Tuesday Morning, July 31 - Martin P. Schweizer, Presiding

- 9:00 HIGH FIELD NMR STUDIES OF BIOLOGICAL SYSTEMS, E. Oldfield, University of Illinois, Urbana IL.
- 9:30 MOBILITY IN BIOPOLYMERS INVESTIGATED BY NMR RELAXATION, T. L. James, University of California, San Francisco CA.
- 10:00 Coffee Break
- 10:30 OLIGONUCLEOTIDE CONFORMATION. PHOSPHORUS-PROTON AND PROTON-PROTON NUCLEAR OVERHAUSER EFFECTS, P. A. Hart, University of Wisconsin, Madison WI.
- 11:00  $^{113}\text{Cd}$  NMR INVESTIGATIONS OF CADMIUM COMPLEXES WITH MODEL METAL BINDING SITES IN MACROMOLECULES, J. R. Alger, T. Freedman, J. D. Otvos and I. M. Armitage, Yale University, New Haven CT.
- 11:30 NMR STUDIES OF MODEL BIOMEMBRANES: STRUCTURE AND METAL ION BINDING, C. S. Springer, Jr., State University of New York, Stony Brook NY.
- 12:00 Lunch

Tuesday Afternoon, July 31 - Nicholas Matwiyoff, Presiding

- 1:30 PROTON NMR STUDIES OF METAL BLEOMYCIN A<sub>2</sub> COMPLEXES, E. Mooberry, J. Greene and R. Lenkinski, North Carolina A & T State University, Greensboro NC.
- 2:00 NMR STUDIES OF BLEOMYCIN BINDING TO NUCLEIC ACIDS, J. D. Glickson, T. T. Sakai, J. M. Riordan, J. M. Geckle, University of Alabama, Birmingham AL, and D. J. Patel, Bell Telephone Labs, Murray Hill NJ.
- 2:30  $^{23}\text{Na}$  AND  $^{31}\text{P}$  NMR STUDIES OF METAL ION BINDING TO PHOSPHATIDYL-SERINE VESICLES, R. J. Kurland, State University of New York, Buffalo NY, D. Papahadjopoulos, M. Hammoudah, J. Benz and S. Nir, Roswell Park Memorial Institute, Buffalo NY.
- 3:00 Coffee Break
- 3:30 SOLVENT PROTON MAGNETIC RELAXATION STUDIES OF CONCANAVALIN A: RELATION OF CONFORMATION TO METAL AND SACCHARIDE BINDING, R. D. Brown, III, S. H. Koenig, IBM, Yorktown Heights NY, and C. F. Brewer, Albert Einstein College of Medicine, Bronx NY.
- 4:00 2,5-DICHLORO-4-NITROANISOLE, STUDIES OF SOLUTE CONCENTRATION UPON OBSERVED NUCLEAR OVERHAUSER EFFECT, E. Mazzola and S. W. Page, Food & Drug Administration, Washington, D.C.
- 4:30 THE NITROGEN-15 NMR SPECTRA OF NO COMPLEXES, J. V. Dubrawski, R. D. Feltham, University of Arizona, Tucson AZ, and J. D. Gust, Arizona State University, Tempe AZ.

## SESSION III - Continued

Wednesday Morning, August 1 - Jerry D. Glickson, Presiding

- 9:00 CARBON-13 NMR STUDIES OF DIHYDROFOLATE REDUCTASE ENRICHED WITH  $^{13}\text{C}$  LABELED AMINO ACIDS, N. Matwiyoff, Los Alamos Scientific Laboratories, Los Alamos NM.
- 9:30 CARBON-13 NMR STUDIES OF  $^{13}\text{C}$  LABELED TRANSFER RNA, M. P. Schweizer and W. D. Hamill, Jr., University of Utah, Salt Lake City UT.
- 10:00 Coffee Break
- 10:30 THE STRUCTURE AND CONFORMATION OF DIDEOXYRIBONUCLEOSIDE METHYL PHOSPHONATES, A NMR STUDY, L. S. Kan, D. Cheng, K. Jayaraman, P. S. Miller, E. Yano, J. Yano and P.O.P. Ts'o, John Hopkins University, Baltimore MD.
- 11:00 NMR STUDIES OF PEPTIDE CONFORMATIONS THROUGH AMIDE HYDROGEN EXCHANGE MEASUREMENTS, H. R. Krishna, J. D. Glickson, D. H. Huang and G. Goldstein, University of Alabama, Birmingham AL.
- 11:30  $^{13}\text{C}$  AND  $^2\text{H}$  NMR STUDIES OF LABELED COLLAGEN IN SOLUTION AND THE SOLID STATE, D. A. Torchia, L. W. Jelinski, and C. E. Sullivan, National Institutes of Health, Bethesda MD.
- 12:00 Lunch

Wednesday Afternoon, August 1 - Winslow Caughey, Presiding

- 1:30  $^1\text{H}$  NMR INVESTIGATION OF PHOSHOPEPTIDES, D. Ziessow, Iwan N. Stranski-Institut, University of Berlin, Berlin, Germany.
- 2:00 HIGH RESOLUTION PMR STUDIES OF PHOSPHOLIPID STEROL INTERACTIONS, G. G. McDonald, University of Pennsylvania, Philadelphia PA.
- 2:30  $^1\text{H}$ ,  $^2\text{H}$  AND  $^{17}\text{O}$  RELAXATION STUDY OF MUSCLE WATER, B. M. Fung and T. W. McGaughy, University of Oklahoma, Norman OK.
- 3:00 Coffee Break
- 3:30  $^1\text{H}$  NMR STUDIES OF ANTIBIOTICS IN PERDEUTERATED LIPID BILAYERS, G. W. Feigensohn and P. R. Heers, Cornell University, Ithaca NY.
- 4:00 STRUCTURE OF SATRATOXINS F AND G, METABOLITES OF STACHYBOTRYS ATRA: APPLICATION OF PROTON AND CARBON-13 NMR, E. Mazzola, M. E. Stack, and R. M. Eppey, Food & Drug Administration, Washington, D.C.

SESSION IV - POLYMERS

Wednesday Morning, August 1 - Samuel Kaplan, Presiding

- 9:00 OXYGEN-17 NMR STUDIES OF MACROMOLECULES, D. Fiat, University of Illinois, Chicago IL.
- 9:30 NMR RELAXATION MEASUREMENTS ON MACROMOLECULES, N. Wade-Jardetzky and O. Jardetzky, Stanford University, Stanford CA.
- 10:00 Coffee Break
- 10:30 INTERNAL MOTIONS IN COPOLYESTERS CONTAINING TEREPHTHALIC ACID, BUTANEDIOL, AZELAIC ACID, AND ETHYLENE GLYCOL AS STUDIED BY  $^{13}\text{C}$  RELAXATION TIMES, J. M. Hewitt, P. M. Henrichs, G. A. Russell and M. A. Sandhu, Eastman Kodak Co., Rochester NY.
- 11:00 QUANTITATIVE DETERMINATION OF RESIDUAL POLYVINYL ACETATE AND SODIUM ACETATE IN PVA:PMR INTEGRATION, J. R. DeMember, Polaroid Corp., Cambridge MA.
- 11:30 QUANTITATIVE ANALYSIS OF THE MICROSTRUCTURE AND TACTICITY OF POLYBUTADIENE BY 300 MHz PROTON NMR AND 20 MHz CARBON-13 NMR, D. H. Beebe and R. C. Hirst, Goodyear Tire & Rubber, Akron OH.
- 12:00 Lunch

Wednesday Afternoon, August 1 - Daniel Fiat, Presiding

- 1:30 APPLICATION OF  $^{13}\text{C}$  NMR TO UREA FORMALDEHYDE POLYMERS AND TO ACETAMIDE FORMALDEHYDE MODEL COMPOUNDS OF UF POLYMERS, L. K. Woods and S. F. Lange, Owens-Corning Fiberglass, Granville OH.
- 2:00 PULSE NMR RELAXATION OF A POLYSTYRENE-POLYETHYLENE OXIDE DIBLOCK COPOLYMER, S. Kaplan and J. J. O'Malley, Xerox Corp., Webster Research Center, Webster NY.
- 2:30 AN NMR STUDY OF THE POLYMERIZATION OF NORBORNENE ENDCAPPED POLYIMIDES, A. C. Wong and W. M. Ritchey, Case Western Reserve University, Cleveland OH.
- 3:00 Coffee Break
- 3:30 INTERNAL MOTION IN PERDEUTERATED POLYMERS BY  $^2\text{H}$  NMR, K. Seidman, J. McKenna, G. B. Savitsky and A. L. Beyerlein, Clemson University, Clemson SC.
- 4:00 INVESTIGATION OF THE ASSIGNMENT OF THE  $2190\text{cm}^{-1}$  BAND IN POLY-FUMARONITRILE: A MULTIPLE TECHNICAL APPROACH, K. L. Gallaher, J. G. Grasselli and D. Barięc, Sohio, Cleveland OH.

POLITECNICO DI MILANO  
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20133 MILANO - Piazza Leonardo da Vinci, 32  
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April 17, 1979

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

NH<sub>2</sub> GROUP STRUCTURES IN SUBSTITUTED ANILINES BY LXNMR

Dear Barry,

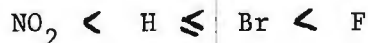
Many thanks for your bleu remainder. We would like to report on a study of the NH<sub>2</sub> group by NMR in nematic solvents carried out in collaboration with Prof. E. W. Randall (Queen Mary College, London) and Drs. F. Lelj and C.A. Veracini (University of Calabria and of Pisa respectively).

The main purpose of the investigation was to study the conformation and the internal motion of the NH<sub>2</sub> group of p-NO<sub>2</sub>- and p-Br-aniline [1-<sup>15</sup>N] (I and II resp.). The use of the enriched samples, as well as producing narrower lines, provides us with a larger number of dipolar couplings for the determinations of the molecular shapes. The early difficulties experienced with this kind of molecules, namely broad <sup>1</sup>H lines, were attributed to the quadrupole effect of the N-14 nucleus (1). We have found that although the quadrupole effect of the N-14 nucleus is not negligible, the main reason for line broadening is the effect of water catalyzed exchange of the NH<sub>2</sub> hydrogens. In order to prevent proton exchange a small quantity of basic alumina or anhydrous Na<sub>2</sub>CO<sub>3</sub> was added to the solutions. The spectrum of the unenriched p-NO<sub>2</sub>-aniline exhibited no <sup>14</sup>N-<sup>1</sup>H interactions and only some small additional line broadening (10-20 Hz line-width) compared with the enriched sample case (10 Hz).

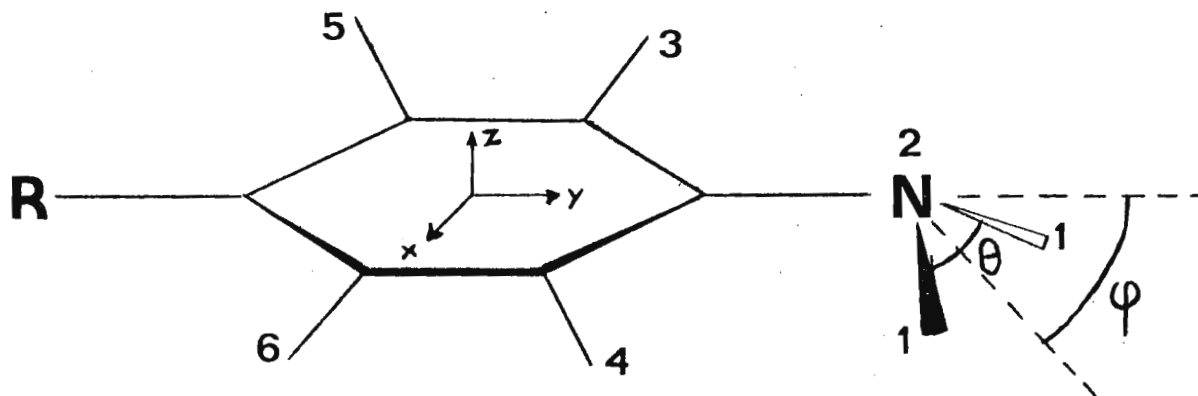
The internal motions, rotation and N-inversion of the NH<sub>2</sub> group, together with the reorientational motion of the whole molecule are fast enough to cause the rigid part of the molecule to possess an effective C<sub>2v</sub> symmetry. The geometry of these fixed parts differs little from other similar phenyl derivatives studied so far.

For the internal motion of the NH<sub>2</sub> group we have assumed a model already used for I.R. and microwave studies, which excludes all twisted conformations and which has only four equivalent conformers (one of which is shown in the figure). The NH<sub>2</sub> internal motion was found to be correlated with the reorientation motion; in fact this gave a better fit to the D<sub>ij</sub> values.

The results for the geometrical analysis are reported in the Table for the best fit N-H distance. Since the number of unknowns and of D<sub>ij</sub> values is the same an "exact solution" with zero r.m.s. error has been obtained. Assuming slightly different values for the N-H bond length all structural parameters change. Despite this interdependence of the structural parameters, we have applied vibrational corrections to our data in order to assess their effect on the derived geometries and motional constants. It is clear that both I and II are non planar in solution just as I is non planar in the solid state, and p-F-aniline and aniline are non planar in the gas phase. Moreover it appears that the order for  $\varphi$  with respect to the substituent R is:







GEOMETRICAL PARAMETERS FOR THE  $\text{NH}_2$  GROUP IN  $\text{p-NO}_2$ -(I) AND  $\text{p-Br-ANILINE}$  [ $1\text{-}^{15}\text{N}$ ](II).<sup>a,b</sup>

WITHOUT VIBRATIONAL CORRECTIONS

	$r_{\text{N-H}}^{\circ}(\text{\AA})$	$\theta$	$\varphi$	$S_{yz}$	r.m.s.	Method
I	0.985	118.6	20.4	-0.1445	0.0	LXNMR
II	0.970	118.2	28.8	-0.0745	0.0	LXNMR
p-F-aniline	$1.00^c$	111.86	46.36			MW
Aniline	$1.00^c$	113.26	37.65			MW

WITH VIBRATIONAL CORRECTIONS

	$1.051 \pm 0.027$	$101.4 \pm 0.1$	$33.4 \pm 0.1$	-0.0603	0.03	LXNMR
II	$1.038 \pm 0.056$	$102.3 \pm 0.1$	$40.2 \pm 0.1$	-0.0146	0.02	LXNMR

<sup>a</sup> The microwave values for p-F-aniline and aniline are also reported for comparison

<sup>b</sup> The LXNMR parameters are scaled to the reference distance  $r_{56}^{\circ} = 4.30 \text{ \AA}$ .

<sup>c</sup> Assumed.

which is precisely the order expected from the mesomeric effects of the substituents as assumed by the Taft  $\sigma_R$  values which are (in the same substituent order):

+0.46      0.0      -0.19      -0.45

Sincerely yours

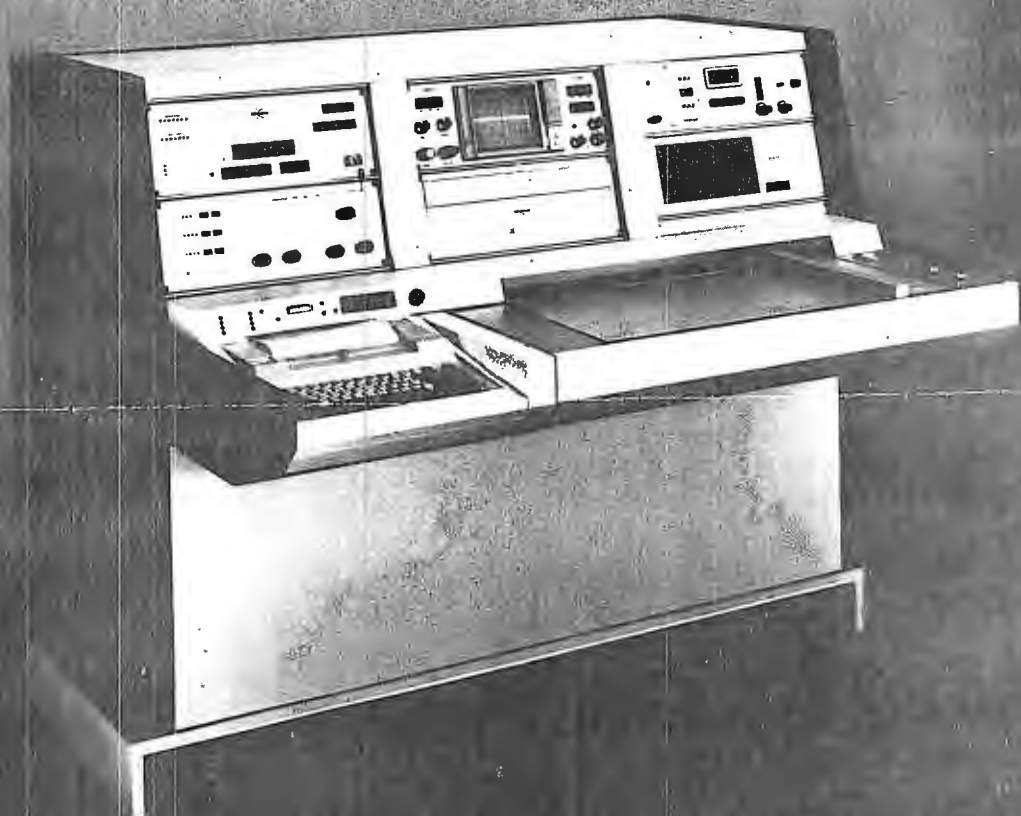
*Rosanna Mondelli*  
Rosanna Mondelli

*Giovanni Fronza*  
Giovanni Fronza



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

$^1\text{H}$  frequency of 250 MHz





National Research Council  
Canada

Conseil national de recherches  
Canada

Division of Chemistry

Division de chimie

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

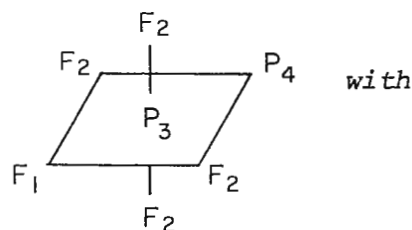
April 17, 1979

Dear Barry:

HELP

$\text{PF}_3$  reacts with some anions  $\text{A}^-$  to give, eventually,  $\text{PF}_5\text{A}^-$  among other products. Fluorine and phosphorus resonance spectra for one intermediate are shown in Figures 1 and 2. The theoretical

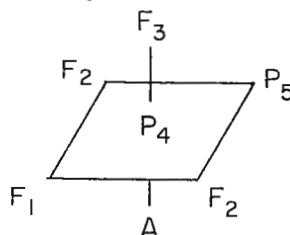
spectra are calculated<sup>(1)</sup> for the skeleton parameters



$\delta_1 = -66.8$	$J_{1\ 2} = 44.2$	$J_{2\ 4} = 122.9$
$\delta_2 = -56.4$	$J_{1\ 3} = 736.9$	$J_{3\ 4} = 946.9$
$\delta_3 = -132$	$J_{2\ 3} = 825.9$	

The fit is excellent except that I cannot find any signal from  $\text{P}_4$ ! Can any of your readers suggest a way of fitting the observed spectra without invoking unobserved resonances? A second, similar, case is an intermediate observed earlier in the reaction sequence. Figures 3 and 4 show its fluorine and phosphorus spectra. Theoretical spectra

are calculated<sup>(1)</sup> for the skeleton



with parameters

$\delta_1 = -64.2$	$J_{1\ 2} = 50.1$	$J_{2\ 3} = 32.7$	$J_{4\ 5} = 831.5$
$\delta_2 = -55.6$	$J_{1\ 3} = 67.0$	$J_{2\ 4} = 739.0$	
$\delta_3 = -44.3$	$J_{1\ 4} = 846.8$	$J_{2\ 5} = 91.1$	
$\delta_4 = -157$	$J_{1\ 5} = 114.0$	$J_{3\ 4} = 694.9$	

Again no resonance of  $\text{P}_5$  is found.

Sincerely yours,

S. Brownstein

(1) Calculations were done with the program NUMARIT kindly supplied by Prof. J. Martin, U. of Alberta, in advance of its publication.

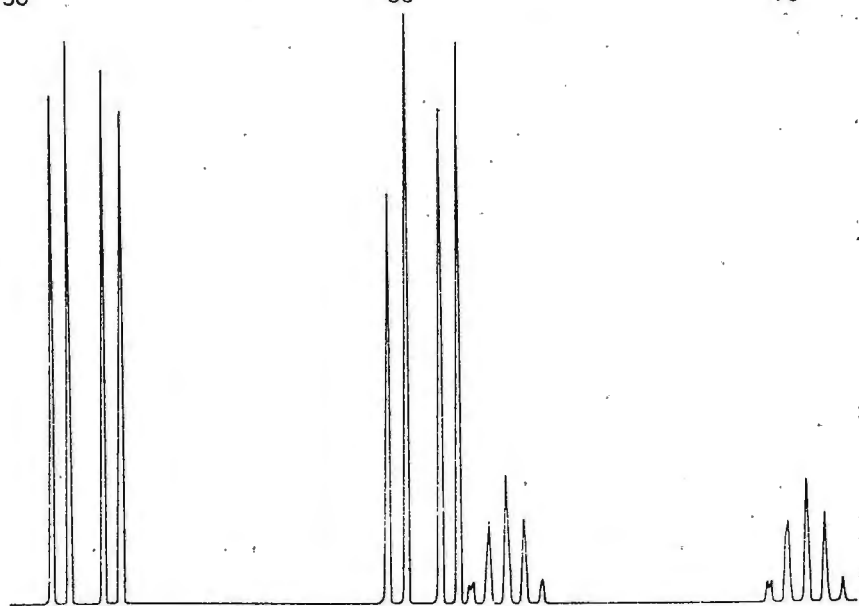
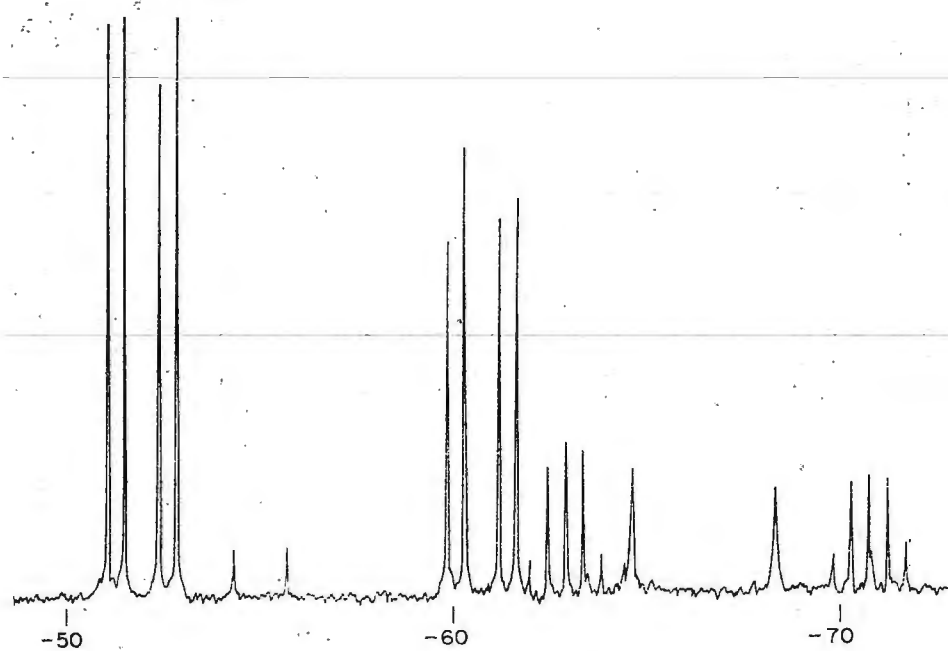


Figure 1

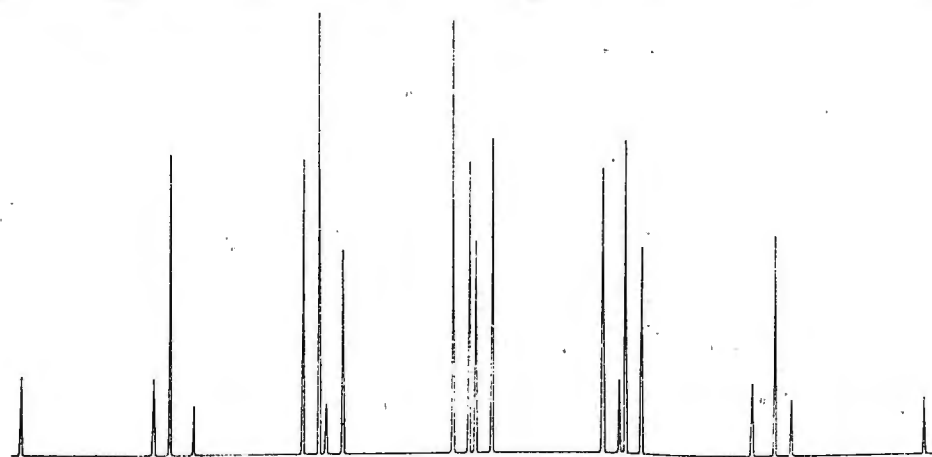
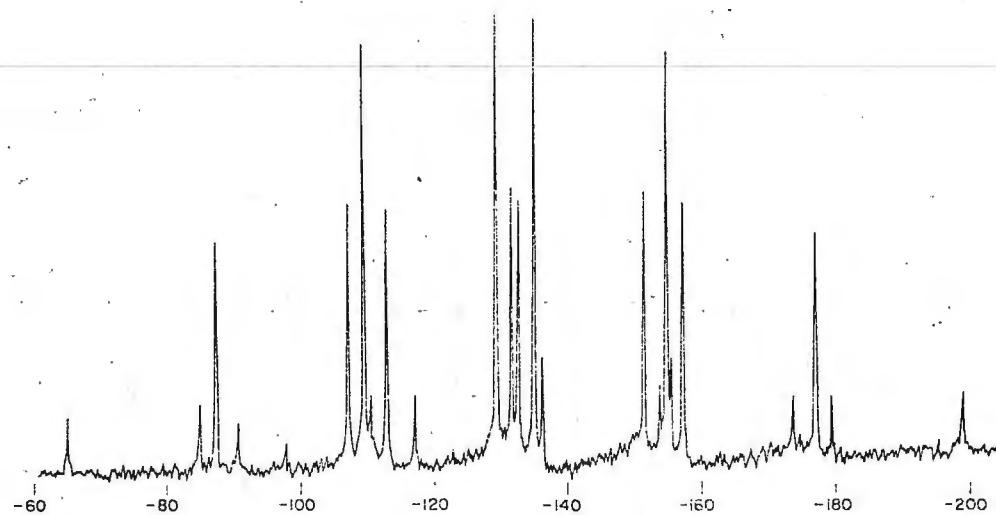


Figure 2

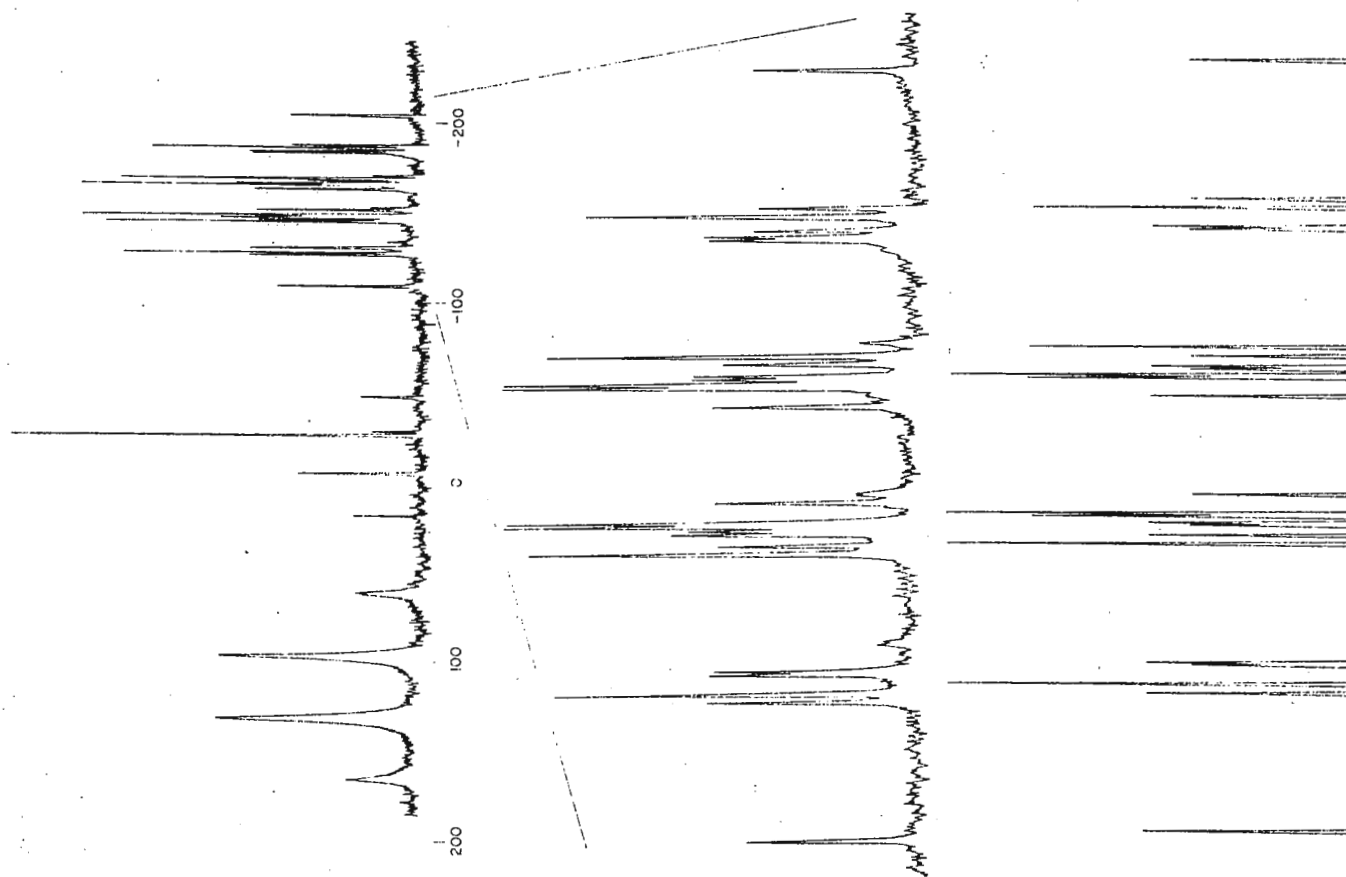


Figure 4

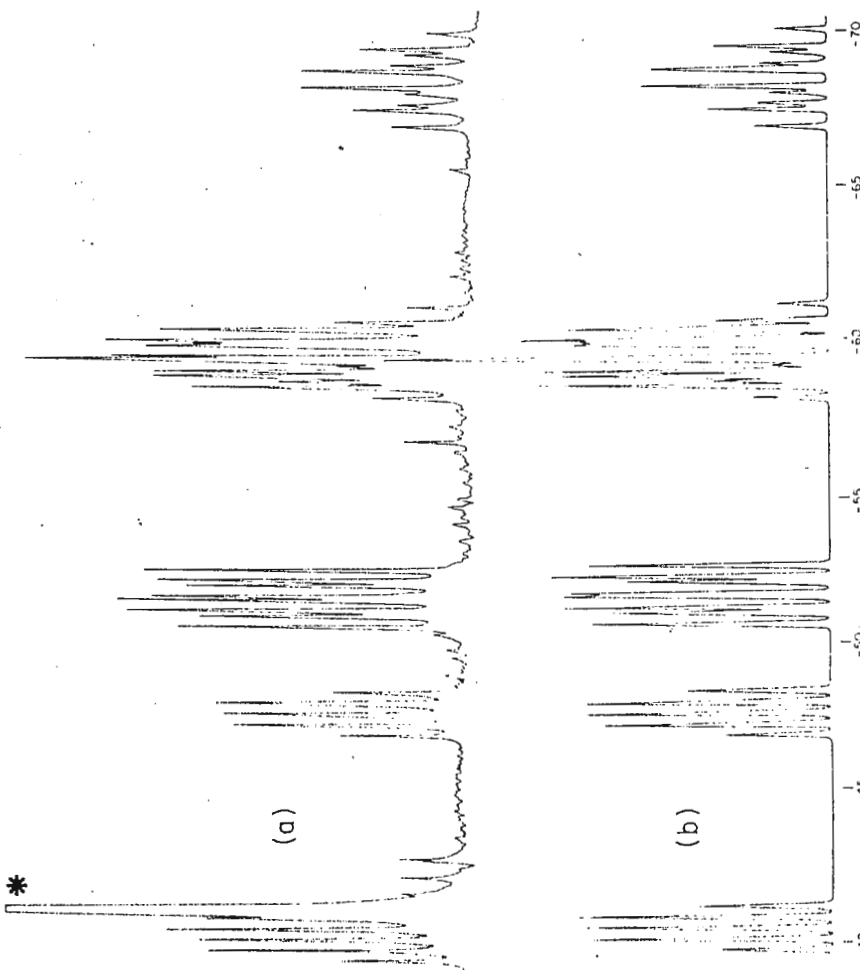


Figure 3



# GRIFFITH UNIVERSITY

Nathan, Brisbane, Queensland, 4111. Telephone (07) 275 7111. Telegrams Unigriff Brisbane

248-45

School of Science  
Chairman: Dr. D. M. Doddrell

Ref: DMD:KW

18th April, 1979.

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

Dear Prof. Shapiro,

## Field Dependence of Chemical Shifts - Experimental Measurements

Thank you for your reminder. It is not appreciated<sup>1,2</sup> by most workers in nmr spectroscopy that the assumed linearity of nuclear screening with applied field is an approximation - the total magnetic shielding should be written :

$$\sigma^T = \sigma + H_0 \cdot \tau \cdot H_0 + \dots$$

Recently,<sup>2</sup> we gave a theoretical expression for  $\tau$  based on fourth-order perturbation theory and paramagnetic currents.

We have recently<sup>3</sup> measured what we believe to be the first field dependent chemical shift of the <sup>59</sup>Co resonances in Co(AcAc)<sub>3</sub> and Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> between field strengths of 2.1T and 0.34T. We have also checked the linearity of the resonance frequency versus applied field for <sup>23</sup>N in NaCl, <sup>7</sup>Li in LiCl, <sup>27</sup>Al in AlCl<sub>3</sub>, and <sup>55</sup>Mn in KMnO<sub>4</sub>. The attached table sets out the results of our frequency measurements with field.

Yours sincerely,

D.M. Doddrell

1. N.F. Ramsey, *Phys. Rev. A*, 1, 1320 (1970).
2. D.M. Doddrell, D.T. Pegg & M.R. Bendall, *Aust. J. Chem.*, 32, 1 (1979)

Table 1  
Results

Compound <sup>a</sup>	Frequency at 2.1T, Hz	Temperature, K	Temperature dependence of chemical shift, HzK <sup>-1</sup>	Width of resonance at half height, Hz	Field dependence of chemical shift		
					No. of measurements	Difference <sup>b</sup> , Hz	Standard deviation Hz
*NaCl	23,805,750	300	0.1	7	4	0.9	0.6
*LiCl	34,975,992	300	0.3	0.3	4	-1.0	1.1
*AlCl <sub>3</sub>	23,450,228	300	0.3	16	3	0.4	2.6
K*MnO <sub>4</sub>	22,309,469	313	2.6	5	4	0.1	0.6
K <sub>3</sub> *Co(CN) <sub>6</sub>	21,353,907	313	29.4	3	4	0.6	0.7
*Co( <sup>15</sup> NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>	21,528,438	313	32.0	29 <sup>c</sup>	4	6.7	2.2
*Co(AcAc) <sub>3</sub> <sup>d</sup>	21,621,896	313	61.4	96	6	7.3	3.9

\*Nucleus studied.

<sup>a</sup> A half-saturated solution of AlCl<sub>3</sub> in H<sub>2</sub>O and a saturated solution of \*Co(AcAc)<sub>3</sub> in CHCl<sub>3</sub> was used. All others were saturated solutions in H<sub>2</sub>O.

<sup>b</sup> Difference = (frequency at high field) -  $\frac{(\text{frequency at low field}) \times ({}^1\text{H frequency at high field})}{({}^1\text{H frequency at low field})}$

<sup>c</sup> Line-broadening due to <sup>1</sup>H-<sup>59</sup>Co coupling occurs. Line-width of proton decoupled spectrum is 10Hz.

<sup>d</sup> Cobalt acetylacetonate.



Herrn

Professor Dr. B. L. Shapiro

Department of Chemistry

Texas A and M University

College Station

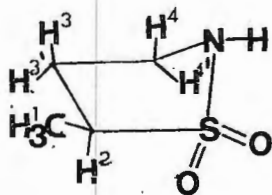
Texas 77843

USA

Dear Professor Shapiro!

## Conformational analysis by the R method

Five-membered rings e.g. cyclopentanone possess several half-chair conformations which interconvert rapidly. <sup>1)</sup> We have been interested in the 250 MHz <sup>1</sup>H-NMR spectrum of the butanesultam-(24) 1 and determined the coupling constants by first order analysis. The data are given in table 1.

Table 1: Chemical shifts  $\delta$  and coupling constants [Hz]1

	$\delta$	$^2J$		$^3J$	
		position of H		position of H	
H <sup>1</sup> :	1.40				
H <sup>2</sup> :	3.14			12	6.8
H <sup>3</sup> :	2.57	33'	-13.0	23	7.5
H <sup>3'</sup> :	2.13	44'	-11.0	23'	8.8
H <sup>4</sup> :	3.35			34	5.2
H <sup>4'</sup> :	3.34			34'	6.9
N-H :	4.2			3'4	8.4
				3'4'	7.3

Assuming that 1 exists also as mixture of rapidly interconverting half-chair enantiomers having a trigonal symmetry, we can also use Lipnick's equation (1) for determining the torsional angles  $\varnothing$  from the coupling  $J$  <sup>1)</sup>.

$$(1) \quad R = \frac{J_{\text{trans}}}{J_{\text{cis}}} = \frac{\cos^2 (120^\circ + \varnothing) + \cos^2 (120^\circ - \varnothing)}{2 \cos^2 \varnothing}$$

The R-values and the torsional angles between several bonds and the corresponding planes are listed in table 2.

Table 2: R-values and torsional angles in 1

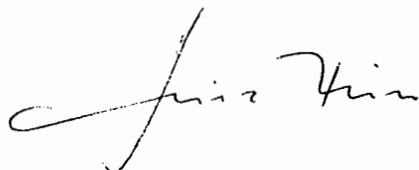
plane	bond	R	$\varnothing$
S C-2 C-3	C-3-C-4	0.852	41.85°
C-2 C-3 C-4	C-4 - N	1.327	50.15°
N C-4 C-3	C-2-C-3	1.058	46.06°

The angles are in agreement with the theoretical value for the half-chair (48.2° found by Pitzer and Donath <sup>2)</sup>) and the experimental value (46.3° reported by Altona et al. <sup>3)</sup>) from a study of a ring D geometry in a series of steroids) and agree with the results obtained for cyclopentanone <sup>1)</sup>. Lambert et al. <sup>4)</sup> observed similar torsional angles for tetrahydrothiophene, cyclopentanone and pyrrolidine by the same method. Our conclusions for the angles therefore seem to be of the right order.

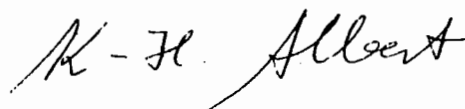
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- 1) R.L. Lipnick, J. Mol. Struct. 21, 411 (1974).
- 2) K.S. Pitzer and W.E. Donath, J. Am. Chem. Soc. 81, 3213 (1959).
- 3) C. Altona, H.J. Geise and C. Romers, Tetrahedron 24, 13 (1968).
- 4) J.B. Lambert, J.J. Papay, S.A. Khan, K.A. Kappauf and S. Magyar, J. Am. Chem. Soc. 96, 6112 (1974).

Yours sincerely



Prof. Dr. H. Dürr



Dipl.-Chem. K.-H. Albert



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
PUBLIC HEALTH SERVICE  
NATIONAL INSTITUTES OF HEALTH  
BETHESDA, MARYLAND 20014

April 23, 1979

Building 2, Room B2-08

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

Title: Mobility & Self-Association of Proteins by Deuterium NMR.

Dear Barry:

Although deuterium NMR has been extensively used as a probe for mobility in membrane systems (1), and to a lesser extent in peptides (2), there are no reports of observation of deuterium NMR of labelled proteins (except for heme group methyls, 3). We have prepared hen egg white lysozyme in which the single histidine residue at position 15 in the amino acid sequence is deuterium labelled. The presence of a single deuterium atom avoids the problems usually associated with broad overlapping lines.

The deuterium NMR spectrum contained a broad signal due to the [ $\epsilon$ - $^2\text{H}$ ] His 15 lysozyme, which varied in line width from ca. 500-1500 Hz depending on concentration and pH (Fig.). This histidine residue is known to be involved in the self-association process of lysozyme in solution (4). Correlation times calculated from the  $^2\text{H}$  line widths indicate that the His 15 residue is restricted in motion and that the lysozyme is predominantly dimerized at pH >7.

Such studies cannot generally be observed by  $^1\text{H}$  NMR because of paramagnetic relaxation due to trace metal ion impurities (5). Imidazole itself shows a titration curve of deuterium  $T_1$  (as well as chemical shift) which probably results from a change in the quadrupole coupling constant between the two ionized species. A poster was presented on this work at the recent ENC Conference and a paper is in preparation for publication.

Yours sincerely,

Jan

Jan B. Wooten & Jack S. Cohen  
Developmental Pharmacology Branch  
National Institute of Child  
Health and Human Development

JBW:ell

Refs.

- (1) H. H. Mantsch, H. Saito and J. C. P. Smith, Prog. Nucl. Mag. Res. Spec. 11, 211 (1977).
- (2) J. A. Glasel, V. J. Hruby, J. F. McKelvy and A. F. Spatola, J. Mol. Biol. 79, 555 (1973).
- (3) O. Oster, G. W. Neireiter, A. O. Clouse and F. R. N. Gurd, J. Biol. Chem. 250, 7990 (1975).

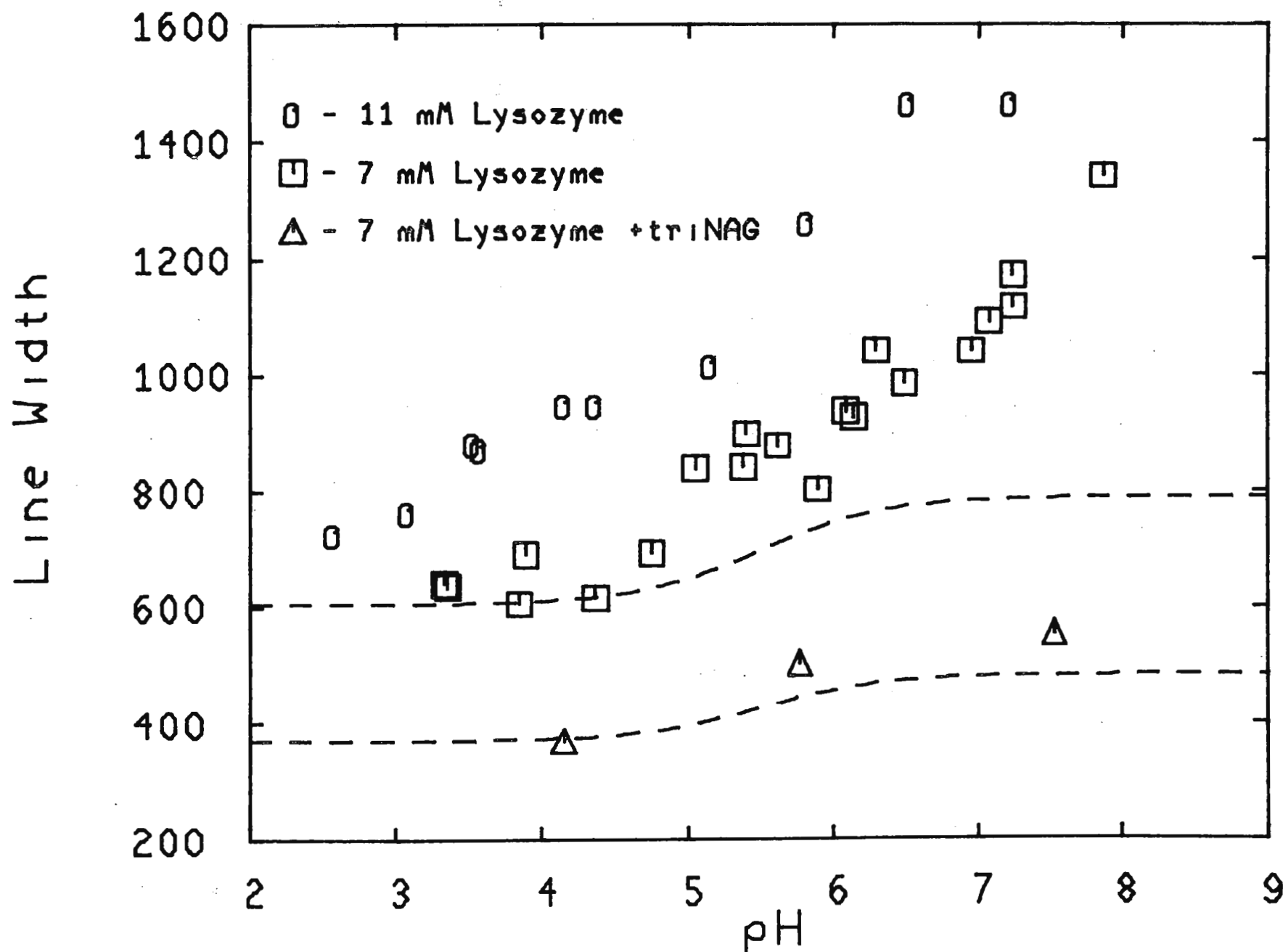


Fig. legend:  $^2\text{H}$  line width of  $[\epsilon\text{-}^2\text{H}]$  His 15 lysozyme vs. pH. ○, 11mM lysozyme; □, 7mM Lysozyme; △, 7mM Lysozyme + triNAG. - - - - Line width of constant  $\tau_c$  with a change of  $(e^2Qq/h)$  from 168 to 192 KHz from low to high pH.

- (4) H. Shindo, J. S. Cohen and J. A. Rupley, Biochemistry 16, 3879 (1977).
- (5) R. E. Wasylishen and J. S. Cohen, J. Amer. Chem. Soc. 99, 2480 (1977).

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CONTINUED FROM P. 248-52

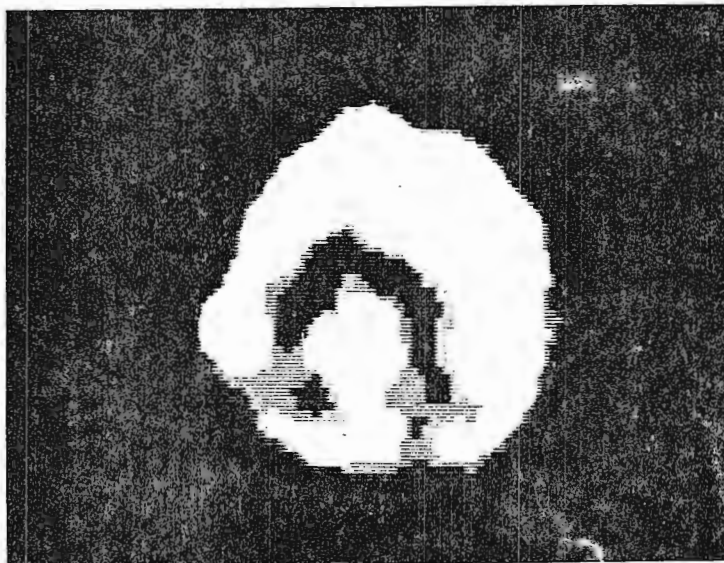
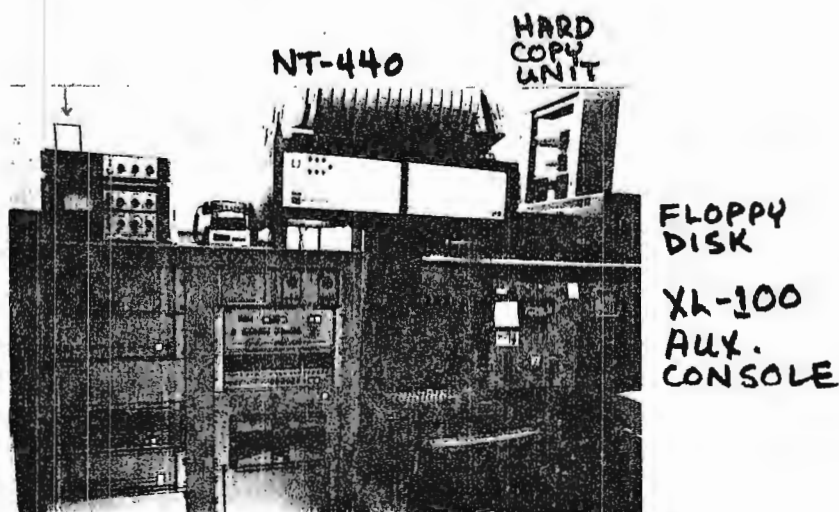


Image transversale d'une queue de rat (Diamètre de l'ordre de 5 mm). La densité en protons est d'autant plus faible que le noircissement de l'image est plus élevé. On distingue une région sombre qui doit correspondre aux vertèbres caudales.

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CONTINUED FROM P. 248-53



TT-100 4014

FIGURE 1.

UNIVERSITÉ CLAUDE BERNARD, LYON I

## LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918

69621 VILLEURBANNE - FRANCE

TÉL. (78) 52.07.04

"Spin-mapping", utilisation de la méthode de rétroprojection de profils.

Cher Monsieur Shapiro,

Tout le monde connaît actuellement l'intérêt porté aux méthodes d'imagerie de spin par R.M.N. et notre vénérable HA 100 n'a pas échappé à ce genre de tâche.

Les premières expériences que nous avons effectuées l'ont été en mode C.W. Des images d'objets allongés (distribution des spins indépendante de la coordonnée  $y$ ) ont pu être obtenues par rétroprojection des profils de raie enregistrées pour différentes orientations de l'échantillon dans le champ directeur  $\vec{B}_0$ . Ces profils sont digitalisés, en 64 ou 128 points, traités à l'aide d'un ordinateur Philips M 850 et les images présentées sur un moniteur T.V. couleur.

Les méthodes numériques de reconstruction employées sont l'A.R.T. (algebraic reconstruction technique) et la B.P.F.P. (Back projections of filtered projection) cette seconde technique donnant des résultats à notre avis plus probants.

Les expériences préliminaires portent sur des échantillons fabriqués à l'aide de tubes à microhématocrites (1 mm de diamètre) contenant de l'eau. Nous avons étudié l'influence du temps de relaxation (par adjonction de substances paramagnétiques), de la puissance R.F. appliquée, ou du débit de liquide à travers ces tubes.

Enfin un rat coopératif a accepté de bien vouloir introduire sa queue dans l'insert. Nous en avons profité pour faire une tomographie de l'appendice naturel de cet animal. Veuillez trouver cette image jointe à notre contribution un peu tardive - nous nous en excusons - au TAMU NMR News Letters.

Recevez, Cher Monsieur Shapiro, l'expression de nos sentiments les meilleurs.

J. DELMAU, A. BONMARTIN\*, A. BRIGUET, J.C. DUPLAN, C. LAPRAY, J.J. MALLET\*,  
M. MEHIER\*.

\* Laboratoire de Biophysique, Faculté de Médecine, 69008, LYON



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
HEALTH EFFECTS RESEARCH LABORATORY  
RESEARCH TRIANGLE PARK  
NORTH CAROLINA 27711

April 27, 1979

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

Dear Barry:

FAST TALKING WITH THE NIC-80:  
Tektronix 4014/NIC-80 Interface for the TT-100/XL-100 NMR System

For a long time, we have been thinking of ways to use our high speed Tektronix 4014 graphics terminal rather than the slower silent 700 terminal to talk with the NIC-80 minicomputer. Both the NIC-80 Nicolet computer system and the Tektronix 4014 use an ASCII character set for code transmission, but they are incompatible in standard form. A little experimentation showed that the 4014 uses a standard 7 bit code with the eight bit used as a parity check. The NIC-80 communicates with the eight bit always on.

On the 4014, bit 8 can be sent by connecting the SEND 8 (pin 27 on the minibus extender board to the terminal ground. To allow the terminal to be used intermittently with parity-checking systems, the connection was made through one of the auxiliary switches on the front panel. Activating the switch and grounding the SEND 8 pin makes the 4014 compatible with the NIC-80.

To eliminate the strange abstract patterns and unusual character deformations produced on the Tektronix scope by the fringe field of the XL-100 magnet, we rearranged the furniture as shown in Figure 1. The 4014 terminal was placed between the TT-100 and the XL-100 auxiliary console so that the main axis of the scope was on the x-axis and perpendicular to the y and z axes of the magnet. The 4014 operates perfectly in this orientation.

We now enjoy communications at 2400 baud compared to our old I/O speed of 300 baud. Currently no graphics routines are available for NIC-80/Tektronix 4014, but they could prove very useful for data processing. We would be very interested in knowing if anyone has done this.

Sincerely yours,

*Steve Maher Nancy*

Steven Maher/Nancy K. Wilson  
Methods Development Section (MD-69)  
Analytical Chemistry Branch



Prof. Dr. R. Kosfeld  
Physikalische Chemie  
Universität Duisburg

D-4100 Duisburg, 24.04.1979  
Bismarckstraße 90  
Telefon: 0203/392319/320

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

TX 77843 USA

Magnetic Resonance Meeting at Steinhagen / Germany

Dear Barry,

the first meeting of the "Fachgruppe Magnetische Resonanzspektroskopie" former "German NMR discussion group" see TAMU-NMR-NEWSLETTERS 238, 16 (1978) and 245, 16 (1979) of the Gesellschaft Deutscher Chemiker (GDCh), will be held from October 2 - 4 at Steinhagen (Germany).

Steinhagen is a sleepy village which is situated near the Teutoburger Wald where the Roman legions of Varus have been destroyed by those furious old Germans. This, however, should not be the fate of the NMR group. Steinhagen is known for the famous "Steinhäger" and the very delicious "Westfälischer Schinken".

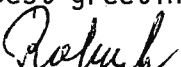
The main topics of the meeting (including NMR as well as ESR) will be:

1. Structure and dynamics of molecular systems
2. Conformation and configuration (including polymers)
3. Relaxation
4. NOE
5. Spin-labelling

The program will contain 30 contributions which will be followed by round-table discussions.

Anyone who intends to participate should contact the organizing committee at the above address for further information.

Best greetings

  
(R. Kosfeld)

Yale University *New Haven, Connecticut 06520*

## DEPARTMENT OF CHEMISTRY

*Sterling Chemistry Laboratory  
225 Prospect Street  
203-432-4520  
Box 1901A-Yale Station*

April 23, 1979

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

SUBJECT: "Simulation of Exchange Broadened Spectra"

Dear Barry:

Computer simulation of second order nmr spectra and nmr spectra broadened by chemical exchange is a well established practice in cases where quantitative results must be extracted from data on complex spin systems. Most programs for simulation date back to the time when virtually all nmr spectra were run in frequency or field sweep modes and are constructed with frequency domain simulation as their only objective.

Most data are now accumulated in the time domain and Fourier transformed to the frequency domain. It would seem that there may be advantages in simulating spectra in the time domain. For example, at the recent ENC, A. Wokaun et al., described some novel kinetic experiments which have no direct frequency domain analogs and have to be simulated in this fashion.

A density matrix treatment provides directly time derivative expressions for the behavior of contribution to transverse magnetization which may be numerically integrated to give an FID. The FID may be transformed to give the simulated frequency domain spectrum. We have recently written a simulation program (for use on our PDP 11/03) which operates in this fashion. Although it currently runs slowly and is in need of some polish, it is already proving to be a useful tool.

As an illustration, we include experimental and simulated spectra of 6,6 difluoromyristoyl acyl carrier protein. The  $^{19}\text{F}$  spectrum shows the two fluorines to be non equivalent giving rise to an AB quartet. We also believe the asymmetry in the quartet to result from chemical exchange. The spectrum at 85 MHz was fit assuming an

exchange mechanism and the spectrum at 188 MHz predicted on the basis of the field dependence of the chemical shift difference. Agreement with experiment is reasonable.

Sincerely,

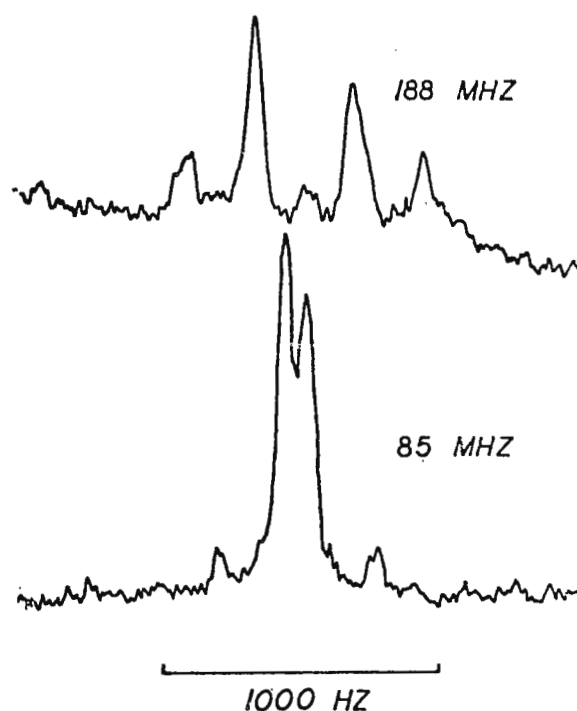
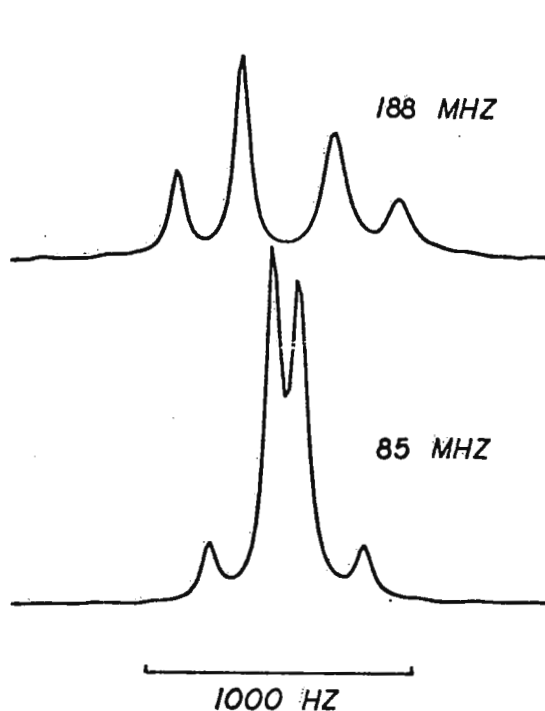
*J.H. Prestegard*  
J.H. Prestegard

*A.K. Spencer*

A.K. Spencer

*I.M. Armitage*

I.M. Armitage  
Southern New England High  
Field NMR Facility





**COMMITTEE E-13  
ON  
MOLECULAR  
SPECTROSCOPY**

ASTM, 1916 Race St., Philadelphia, PA 19103 (215) 299-5400

*Chairman:* CLARA D. CRAVER, Chemir Labs., 761 West Kirkham Rd., Glendale, Mo. 63122 (314-962-6704)

*Vice-Chairman:* H. L. HOOVER, Corning Glass Works, Research Lab. SP-FR-4, Corning, N.Y. 14830 (607-974-3168)

*Secretary:* CONCETTA PARALUSZ, Johnson & Johnson, Permacel Div., Route 1, North Brunswick, N.J. 08902 (201-524-5633)

*Staff Manager:* JANET SCHROEDER (215-299-5529)

Dr. Rolf B. Johannesen  
National Bureau of Standards  
A329 Materials Building  
Washington, D. C. 20234

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

Dear Barry:

I enclose a copy of the new part 7 (only) of ASTM Standard E386 (NMR). The enclosure is taken from a manuscript copy, but the version to be published by ASTM later this year should be identical. Copies of the complete E386-78, including part 7 as given here, may be obtained after publication from ASTM, 1916 Race Street, Philadelphia, PA 19103.

Yours very truly,

A handwritten signature in cursive script, appearing to read "Rolf", is written above the typed name.

Rolf B. Johannesen, Chairman  
ASTM Committee E 13.07

Revision of ASTM E 386-76

MAY 8, 1978

Edited FEB 8, 1979

The following material is to be inserted as a new section 7. Existing section 7 and all paragraph members therein are to be renumbered as section 8.

7. Recommended Practice for Signal-to-Noise Determination in Fourier Transform NMR

7.1 General - This section gives the recommended practice for signal-to-noise ratio (S/N) determination in three specific situations: (a) proton single pulse mode; (b) carbon-13 single pulse mode; (c) carbon-13 multiple pulse mode. (Note 1.)

7.2 Proton Single Pulse Mode

7.2.1 Sample - Dilute ethylbenzene in  $\text{CDCl}_3$

7.2.2 Measurement - Proton signal-to-noise ratio is measured using a single pulse of RF power applied to a dilute solution of ethylbenzene in  $\text{CDCl}_3$ , with the spectrometer locked to the deuterium signal of the solvent. Choose the concentration of ethylbenzene appropriate to the sensitivity of the instrument under test, such that the S/N as measured on the methylene quartet is  $\leq 25:1$ . State the determined S/N as "equivalent one percent ethylbenzene sensitivity".

Carry out the measurement using the following conditions:

Spectral Width	0-10 ppm ( $\delta_{\text{TMS}}^1\text{H} \approx 0$ ppm)
Data Acquisition Time	$\geq 0.4$ sec
Flip Angle	$90^\circ$
Analog Filter	Appropriate for method of detection
Detection Method	Specify (e.g., single phase, SSB, QPD)
Equilibration Delay	60 sec

Following the data acquisition multiply the data by a decaying exponential function of the form  $e^{-t/A}$ , where A is equivalent to a  $T_2$  contribution. A may be expressed as a time constant in units of seconds, or, alternatively, the line broadening (LB) resulting from the exponential multiplication may be expressed in units of Hz. For the measurement,  $A = 0.3$  or  $\text{LB} = 1$  Hz. Perform no data smoothing after

transformation. Plot the resulting absorption mode spectrum over the full 0-10 ppm. Measure S/N on a plot expansion covering the range 2-6 ppm, in which the methylene quartet is plotted to fill the chart paper as closely as practical. Use sufficient vertical amplitude to obtain a peak-to-peak noise measurement greater than 2 cm. Measure peak-to-peak noise over the 4-6 ppm region on the same trace or calculate rms noise by computer (see Note 2). The S/N is then calculated on the strongest line in the quartet as

$$[(\text{Signal Intensity})/(\text{Peak-to-Peak Noise})] \times 2.5 = \text{S/N}$$

See Figure 1.

7.2.3 Discussion - The one percent ethylbenzene S/N measurement is a widely-used method for  $^1\text{H}$  S/N both in CW and FT NMR. Although presenting few difficulties in CW work, the typical samples used in FT NMR do present some problems which we hope to avoid using the above procedure.

1. The one percent concentration traditionally employed generates a very high S/N on modern FT spectrometers, particularly at very high magnetic field strengths.

2. TMS is usually present in standard samples at the one percent level. This causes a very strong signal which can lead to an erroneous S/N measurement.

3. The variety of sample tube sizes and S/N values has made it inconvenient to use a uniform concentration. The solution(s) should be made up by volume composition at  $25^\circ\text{C}$  using good volumetric practice. Suggested solutions:

#	Ethylbenzene (%)	TMS (%)
1	3.0	0.3
2	1.0	0.1
3	1.0	1.0 (also valuable for CW TMS-locked spectrometers)
4	0.33	0.03
5	0.10	0.01
6	0.033	0.003
7	0.010	0.001

The TMS is added for a reference material.

- 3 -

## 7.3 Carbon-13 Single Pulse Mode

7.3.1 Sample - 60% C<sub>6</sub>D<sub>6</sub> (>98 atom% D), 40% p-dioxane

7.3.2 Measurement - Measure carbon-13 signal-to-noise ratio on the benzene carbon signal in a solution of 60% perdeuterobenzene--40% p-dioxane, with the spectrometer locked to the deuterium in the sample, using the following conditions:

Spectral Width	0-200 ppm ( $\delta_{\text{TMS}}^{\text{C}13} \approx 0$ ppm)
Data Acquisition Time	$\geq 0.4$ sec.
Flip Angle	90°
Analog Filter	Appropriate for method of detection
Detection Method	Specify (e.g., single phase, SSB, QPD)
Equilibration Delay	300 sec.
Decoupler	Off

Following the data acquisition, multiply the data by a decaying exponential function of the form  $e^{-t/A}$ , where A is equivalent to  $\frac{e}{A} T_2$  contribution. A may be expressed as a time constant in units of seconds, or, alternatively, the line broadening (LB) resulting from exponential multiplication may be expressed in units of Hz. For the measurement, A = 0.3 or LB = 1 Hz. Perform no data smoothing after transformation. Plot the resulting absorption mode spectrum over the full 0-200 ppm chemical shift range. Plot the C<sub>6</sub>D<sub>6</sub> triplet to fill the vertical range of the chart paper as closely as practical. Use sufficient vertical amplitude to obtain a peak-to-peak noise measurement greater than 2 cm. Signal-to-noise is to be measured as

$$[(\text{Average Triplet Intensity})/(\text{Peak-to-Peak Noise})] \times 2.5 = S/N$$

Measure the peak-to-peak noise between the C<sub>6</sub>D<sub>6</sub> and dioxane triplets, specifically between and inclusive of 80 and 120 ppm on the <sup>13</sup>C chemical shift scale, or calculate rms noise by computer (see Note 2). See Figure 2.

## 7.3.3 Characteristics of the Proposed Standard

1. The S/N of the C<sub>6</sub>D<sub>6</sub> triplet is low enough to permit a plot from which both signal and noise may be measured. For a full scale vertical display of the C<sub>6</sub>D<sub>6</sub> triplet the peak-to-peak noise amplitude should be adequately measured and have two significant figures.

- 4 -

(For those spectrometers with very high sensitivity, noise would still have to be blown up to at least 2 cm peak-to-peak in a separate trace of the same transformed data.)

2. The C<sub>6</sub>D<sub>6</sub> triplet has linewidth of  $\sim 4$  Hz under these conditions, reasonably independent of magnet resolution, permitting easy tune up and small  $\sim 4$  K data table for the measurement.

3. The C<sub>6</sub>D<sub>6</sub> S/N can be measured in the presence of or absence of high power proton decoupling facilitating servicing diagnostic procedures. It is particularly valuable in diagnosing decoupler-caused noise contributions.

4. The broad lines of the C<sub>6</sub>D<sub>6</sub> result from long-range <sup>13</sup>C-<sup>2</sup>H coupling and thus the linewidth is not field-dependent.

5. C<sub>6</sub>D<sub>6</sub> has no nuclear Overhauser enhancement (NOE).

6. The reference material is widely available and can serve as an internal <sup>2</sup>H lock.

7. The C<sub>6</sub>D<sub>6</sub> S/N is independent of applied lock power in normal locking power range up to and beyond saturation of the deuterium signal.

8. The C<sub>6</sub>D<sub>6</sub> S/N is temperature independent over normal working temperatures.

9. The dioxane serves several purposes: ready reference to prior data; a conveniently short T<sub>1</sub> (< 10 sec); under decoupled conditions it possesses a strong signal serving for  $\gamma H_1/2\pi$  measurement via a 90° pulse determination; under off-resonance conditions its residual <sup>13</sup>C-<sup>1</sup>H coupling can serve to measure  $\gamma H_2/2\pi$ ; the decoupled singlet can be used to measure resolution in terms of full linewidth at half-height, also line shape and spinning sidebands; under coupled conditions and longer acquisition times it can provide a coupled spectrum with long-range couplings. The strong signal available from decoupled dioxane permits facile tests of decoupler gating through measurement of the NOE via "Suppressed Overhauser" gating schemes vs use of coupled dioxane as the base point for calculating the NOE. The short T<sub>1</sub> of dioxane allows routine check of automatic T<sub>1</sub> programs and calculations.

7.3.4 Discussion - The proposed measurement is possible and convenient on any modern FT instrument. The method insures that the maximum available S/N is obtained, thus preventing confusion in parameter choice, particularly in the case of the exponential weighting. A new standard is necessary in view of the difficulty in widespread reliable use of the 90 percent ethylbenzene sample previously used. The natural linewidths of the ethylbenzene lines are less than 0.1 Hz requiring exacting field homogeneity to obtain maximum resolution. The narrow lines also demand long data acquisition times in each FID to adequately define the lines. Since ethylbenzene S/N is measured on a decoupled protonated carbon signal, decoupler power, modulation efficiency and offset are all factors in determining S/N. The S/N for most spectrometers is  $> 100:1$  for 90 percent ethylbenzene making noise measurements the primary factor in the derived S/N.

Dioxane has been proposed for the S/N sample but it has some serious drawbacks in addition to several advantages shared with deuterobenzene. Its  $T_1$  is dipole-dipole dominated and has full NOE in the decoupled experiment. It is easily possible to have residual NOE in a coupled spectrum by not waiting long enough for the NOE to decay away prior to the sampling pulse. Although deuterobenzene has the common requirement of sufficient equilibration delay the error is always on the side of lower S/N, whereas dioxane's apparent S/N can be up to a factor of three greater than that assumed by simple inspection of the spectrum. This makes comparison of intrinsic S/N susceptible to error. The addition of dioxane to the 40 percent level provides all the advantages listed above for routine tuning up and quick S/N checking, while the  $C_6D_6$  permits an absolute measurement. The other major disadvantage of dioxane is the dependence of the character of the spectrum on acquisition time and weighting function. If more than 0.5 sec acquisition is used with a less severe weighting function than above, the fine structure from the long-range coupling becomes visible. While no problem for the experienced spectroscopist, this can be and has been confusing to inexperienced users.

In summary, the above sample for S/N measurement is recommended particularly when comparing instruments in different laboratories. For use within a laboratory by knowledgeable operators, ethylbenzene still offers a practical sample for simultaneous checking of S/N, resolution and decoupling efficiency. The adoption of an intrinsic S/N sample such as that described above also identifies the need for separate measurement of resolution and  $\gamma H_2/2\pi$  to more completely characterize the performance of an FT spectrometer on  $^{13}C$ . In addition, this measurement is understood to measure only intrinsic sensitivity and not the sensitivity of a time-averaged spectrum on a "routine" sample.

#### 7.4 Carbon-13 Multiple Pulse Mode

7.4.1 Sample - 0.1 M Sucrose in  $D_2O$  equilibrated with toluene. Dissolve 3.423 g of sucrose (stored at a relative humidity of 50 percent or less; NBS SRM sucrose is satisfactory) in about 90 cc of  $D_2O$  in a 100 cc volumetric flask, then dilute to the mark at 25 °C with  $D_2O$  after all the sucrose is dissolved. Add 0.05 ml toluene as a preservative.

7.4.2 Measurement - Carry out the measurement in the multiple-pulsed mode locked to the internal  $D_2O$  using the following conditions:

Spectral Width	0-200 ppm ( $\delta C_{TMS}^{13} \equiv 0$ ppm)
Data Acquisition Time	$\geq 0.4$ sec
Flip Angle	90°
Analog Filter	Appropriate for method of detection
Detection Method	Specify (e.g., single phase, SSB, QPD)
Pulse Repetition Rate	1 pulse per second
$^1H$ Decoupler	Broadband
$^1H$ Decoupler Frequency	Centered at $5 \pm 1$ ppm in the $^1H$ spectrum ( $\delta_{TMS}^{1H} \equiv 0$ )
$^1H$ Decoupler Modulation Mode	Specify (e.g., noise, square wave, etc.)
$^1H$ Decoupler Modulation Frequency	Specify
Number of Transients	4000 for 5 mm sample size 1000 for 10-12 mm sample size 100 for $> 12$ mm sample size
Operating Temperature	Specify

- 7 -

Following the data acquisition multiply the data by a decaying exponential function of the form  $e^{-t/A}$ , where A is equivalent to  $\frac{1}{\lambda} T_2$  contribution. A may be expressed as a time constant in units of seconds, or, alternatively, the line broadening (LB) resulting from the exponential multiplication may be expressed in units of Hz. For the measurement  $A = 0.3$  or  $LB = 1.0$  Hz. Perform no data smoothing after transformation. Plot the resulting absorption mode spectrum over the full 200 ppm chemical shift range. Plot the spectrum to fill the vertical range of the chart paper as closely as practical. Measure the peak-to-peak noise between 120 and 140 ppm of the spectral window or calculate rms noise by computer (see Note 2). For those spectrometers with very high sensitivity, noise may have to be blown up at least 2 cm peak-to-peak in a separate trace of the same transformed data. Measure signals  $\#1$ ,  $\#2$ ,  $\#3$ ,  $\#4$ ,  $\#10$ , and  $\#12$  (identified on Figure 3) and calculate  $S/N$  as shown below

$$[(\#1 + \#2 + \#3 + \#4 + \#10 + \#12) / (\text{Peak-to-Peak Noise})] \times 0.625 = S/N$$

See Figure 3.

**7.4.3 Discussion** - This measurement permits evaluation of sensitivity under "typical" conditions; that is, the decoupler is on and many transients are obtained. In addition to a knowledge of the basic, or intrinsic,  $^{13}\text{C}$  sensitivity as measured in the  $\text{C}_6\text{D}_6$  test, it is extremely important to evaluate the long term sensitivity as reflected in a proton-decoupled, time-averaged spectrum. The type and quality of the decoupling, as well as long term and short term instabilities in any instrument element, can profoundly affect sensitivity. This test is designed to monitor this performance.

**7.4.3.1** Sucrose is chosen because of its widespread availability, purity, low cost, stability (in toluene equilibrated water) and spectral characteristics. Among these are the reasonable (1 Hz) linewidths, short  $T_1$ 's, and full NOE. The number of transients is chosen to provide a reasonable total experimental time, typically 20 minutes, while still running long enough to simulate normal experiments adequately.

- 8 -

**7.4.3.2** Decoupling efficiency is another highly variable element in "routine sensitivity". It certainly determines the ultimate sensitivity in the 90 percent ethylbenzene sensitivity test (magnet homogeneity permitting). For this reason ethylbenzene is unsuitable for an absolute sensitivity determination. Yet, it is necessary to include the decoupler in sensitivity considerations since a poorly operating decoupler can be the main determinant in apparent sensitivity. Thus, proper consideration must be given not only to intrinsic sensitivity but also to "routine" sensitivity in characterizing spectrometer performance.



Note 1: Some of the materials recommended for use in this Section are known to present health hazards if used improperly. Anyone making up solutions containing benzene, dioxane or chloroform should consult and abide by OSHA regulations 29CFR 1910.1000 (solvents) and 29CFR 1910.1028 (benzene).

Note 2: The true rms noise can be calculated by computer and used in the S/N determination. Since peak-to-peak noise is approximately five times rms noise, rather than 2.5 times, the rms noise must be doubled to obtain a comparable S/N. When this is done, it is felt that the S/N determined by computer should be more reliable and less subject to human error than the alternate method of estimating peak-to-peak noise from a chart recording. The computer program should do the following:

- (a) Select the region in which noise is to be measured as specified in the above test.
- (b) Obtain the algebraic mean of all the observed points in this region, and subtract the mean from each point (zero-order correction).
- (c) If the base line slopes, a first order correction may be made by using a standard least-squares method to obtain the slope and intercept of the baseline, then subtracting each calculated point from the corresponding observed point.
- (d) Corrections calculated on the noise in the specified region of the spectrum should be applied to that region and also to the spectral region containing the signal.
- (e) Form the sum of the squares of each amplitude (point), corrected as described above, divide by one less than the number of points in the region, and take the square root. This is the rms noise.

$$\text{rms noise} = [(\sum[\text{amplitude}]^2)/(N - 1)]^{1/2}$$

No other processing should be done; in particular, points that appear to be extreme should not be deleted. S/N becomes simply

$$(\text{Signal Intensity}) / (\text{Rms Noise}).$$

Figure Captions:

1. Typical S/N measurement on the proton signal in dilute ethylbenzene.
2. Typical S/N measurement on single pulse  $^{13}\text{C}$  spectrum of  $\text{C}_6\text{D}_6$ -dioxane mixture.
3. Typical S/N measurement on accumulated  $^{13}\text{C}$  spectrum of 0.1 M sucrose in  $\text{D}_2\text{O}$ .

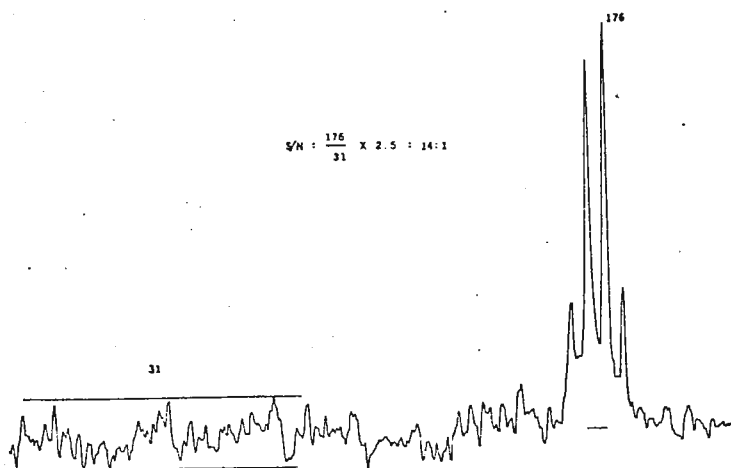
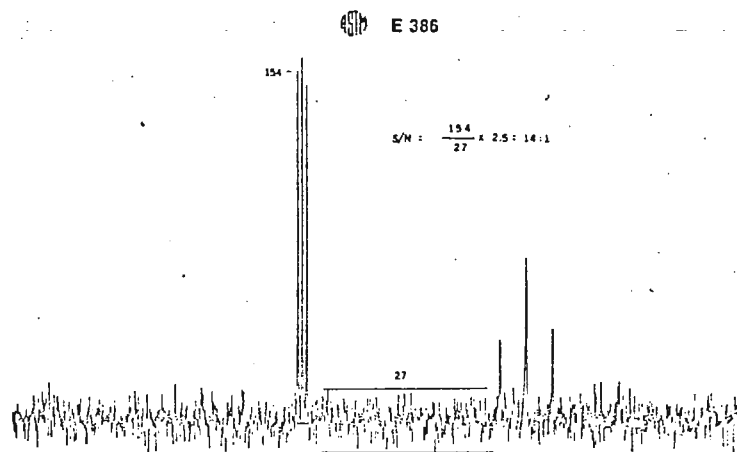
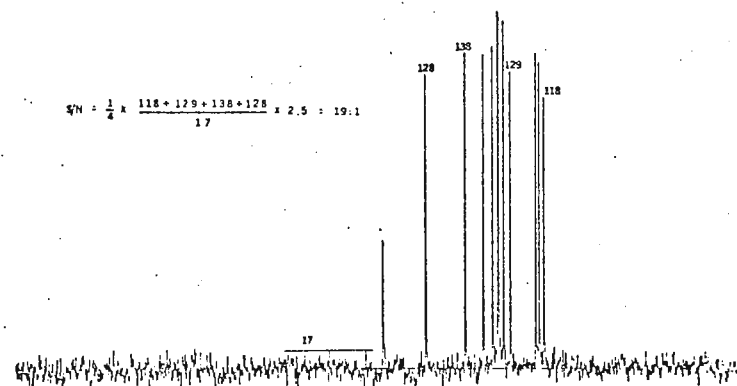


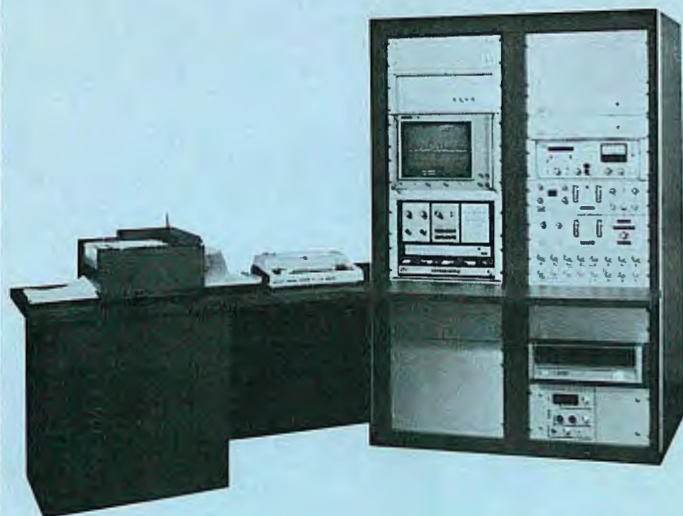
FIG. 1 Typical S/N Measurement on the Proton Signal in Dilute Ethylbenzene.

FIG. 2 Typical S/N Measurement on Single Pulse  $^{13}\text{C}$  Spectrum of  $\text{C}_6\text{D}_6$ -Dioxane Mixture.FIG. 3 Typical S/N Measurement on Accumulated  $^{13}\text{C}$  Spectrum of 0.1 M Sucrose in  $\text{D}_2\text{O}$ .

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# NT-150

## A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



**For routine NMR and state-of-the-art techniques such as:**

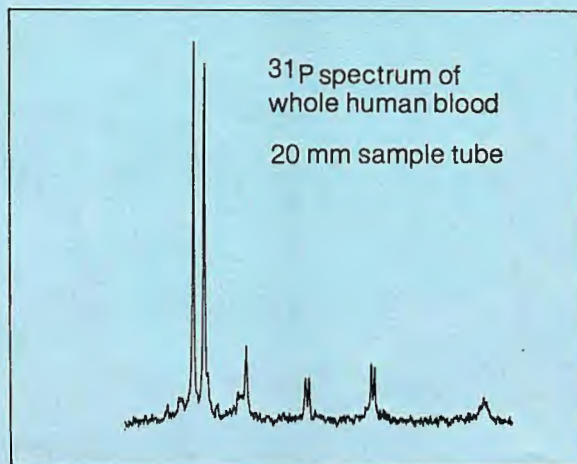
- $^{31}\text{P}$  experiments on living organs.
- Cross-polarization studies on solids.
- $^{13}\text{C}$  studies of high molecular weight polymers.
- Two-dimensional FT-NMR.

### FEATURES INCLUDE:

- 3.5T superconducting magnet with 10 cm room-temperature bore.
- Straight-through access to sample area.
- Quick-disconnect probes for rapid changeover.
- 5, 12 and 20 mm sample tubes as standard, 30 mm optional.
- Quadrature phase detection as standard.
- Computer-controlled audio filter from 100 Hz to 51,100 Hz in 100 Hz steps.
- Nicolet 1180 data system with simultaneous acquisition, processing and plotting.
- Digital plotter with plot lengths selectable from 1 cm to 900 cm.

### OPTIONS INCLUDE:

- NT-150 MF: broad-band multi-nuclei observe for 4 to 60 MHz.
- NT-150 CP: optimized system for Waugh-Pines cross-polarization studies.



*For more information or to discuss your applications, please telephone or write.*

**NTC** NICOLET  
TECHNOLOGY  
CORPORATION

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# **FX SERIES OF FT NMR SYSTEMS**

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## **FX-90Q** OMNI Probe™ System 10mm, 5mm, micro inserts



**FX-60Q**  
Solids Probe ( $^{13}\text{C}$ ) with  
Magic Angle Spinning  
High Resolution Probe ( $^{13}\text{C}/^1\text{H}$ )

**FX-200**  
Dual Probe ( $^{13}\text{C}/^1\text{H}$ )  
Broad Band ( $^{15}\text{N}$  to  $^{31}\text{P}$ )  
50 KHz Spectral Width

## **System Features**

- Light Pen Control System
- Foreground/Background
- Digital Quadrature Detection
- Multi Frequency Observation
- Programmable Multi Pulser
- Module Performance Indicator Lights
- Comprehensive Auto Stacking
- $T_1$ -rho
- Double Precision (32 bit word length)
- Floppy; MH Disc Storage
- 50KHz Spectral Width
- CPU Expansion to 65K

# **JEOL**

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