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Newsletter

No. 253

October, 1979

- H. L. McPeters
¹³C Chemical Shifts for Alkoxy Substituted
Tricyclo [5.2.1.0^{2,6}]Decenes 1
- H. L. Holland, G. J. Taylor and T. R. B. Jones
Direct Observation of the Microbial
Hydroxylation of Testosterone by CMR 3
- E. T. Samulski
Postdoctoral Position Available 5
- H. N. Cheng
A Chemical "Thermometer" for ¹³C NMR 6
- A. Walker
Fifth Annual Stanford Conference on Molecular
Structural Methods in Biological Research. . 9
- K. Roth
Inexpensive Synthesizer for Audio
Frequencies. 10
- K. Keymel and J. Whitefield
Some Modifications for Selective Excitation
on the FT80A 14
- J. I. Kaplan
Line Shape for Fast Exchange and Slow
Motion 17
- W. S. Veeman and E. deBoer
Postdoctoral Position Available 19
- G. R. Hays, A.D.H. Clague, R. Huis and
D. G. Gillies
High Field (7.05 T) ¹³C NMR Using Cross
Polarization and Magic Angle Spinning . . . 20
- J. P. Heeschen
Position Available Notice 24
- P. Laszlo
Solvent Isotope Effect in ⁵⁹Co NMR 25
- P. Bladon
Slow H/D Exchange in NaBH₄ at High pH . . . 27
- E. Oldfield
High-Field NMR Postdoctoral Positions . . . 28
- T. Schaefer
A Perpendicular Conformer of
2-Hydroxythiophenol 29
- M. W. Baum and D. R. Nordlund
³¹P NMR with ¹³C Preamps 31
- R. Benn and E. G. Hoffmann
Fluxional Behaviour of Tetra-(Allyl)-Hafnium
and Cyclooctatetraen-Bis-(Allyl)-Zirconium . 32
- L. D. Colebrook
NMR Spectroscopist Position Available . . . 35
- R. Kosfeld and E. Schulz
Computer Link Between Cyber 175 and
Nicolet 1080 36
- A. Bax and P. deJong
Remarks about Separating the Various Orders
of MQT Transitions 39
- W. B. Moniz, A. N. Garroway, C. F. Poranski and
H. A. Resing
Positions Available Notice. 41
- J. Mason
¹⁵N NMR Studies on Hydrazido(2-) Complexes
of Molybdenum and Tungsten. 42
- G. Gatti
Conformation of Uronic Acid in GAG 45

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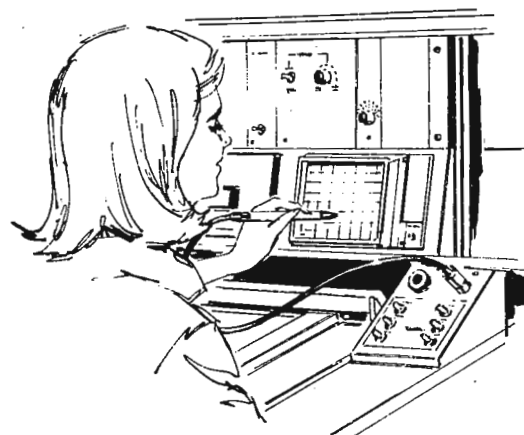
All Newsletter Correspondence, Etc., Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 253

| | | | |
|----------------------|----|---------------------|----|
| Baum, M. W..... | 31 | Keymel, K..... | 14 |
| Bax, A..... | 39 | Kosfeld, R..... | 36 |
| Benn, R..... | 32 | Laszlo, P..... | 25 |
| Bladon, P..... | 27 | Mason, J..... | 42 |
| Cheng, H. N..... | 6 | McPeters, H. L..... | 1 |
| Clague, A.D.H..... | 20 | Moniz, W. B..... | 41 |
| Colebrook, L. D..... | 35 | Nordlund, D. R..... | 31 |
| deBoer, E..... | 19 | Oldfield, E..... | 28 |
| deJong, P..... | 39 | Poranski, C. F..... | 41 |
| Garroway, A. N..... | 41 | Resing, H. A..... | 41 |
| Gatti, G..... | 45 | Roth, K..... | 10 |
| Gillies, D. G..... | 20 | Samulski, E. T..... | 5 |
| Hays, G. R..... | 20 | Schaefer, T..... | 29 |
| Heeschen, J. P..... | 24 | Schulz, E..... | 36 |
| Hoffmann, E. G..... | 32 | Taylor, G. J..... | 3 |
| Holland, H. L..... | 3 | Veeman, W. S..... | 19 |
| Huis, R..... | 20 | Walker, A..... | 9 |
| Jones, T.R.B..... | 3 | Whitefield, J..... | 14 |
| Kaplan, J. I..... | 17 | | |

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August 23, 1979

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

Re: ^{13}C Chemical Shifts for Alkoxy Substituted Tricyclo [5.2.1.0^{2,6}]Decenes

Dear Dr. Shapiro:

Recently we had the opportunity to examine the ^{13}C -NMR spectra of mixtures of alkoxy substituted tricyclo [5.2.1.0^{2,6}]decenes and -decenes in CDCl_3 (See Figure 1). We were able to assign most of the ^{13}C chemical shifts from comparisons of the alkenes and their respective hydrogenated analogues and by calculation using chemical shifts of the parent tricyclo [5.2.1.0^{2,6}] decanes¹ and appropriate substituent effects.² The ^{13}C assignments are given in Table 1. We also make the assumption that the alkoxy substituent is in the exo position.

Compounds like 3 and 4 were made via addition of the appropriate alcohol to the double bond of dicyclopentadiene. Under the conditions of this synthesis, the predominant isomers were 3 and 4 in a ratio of 1:0.37, respectively. Thus, the most favored isomer has the double bond in the three position. Minor components corresponding to the endo ring versions of 3 and 4 were not assigned.

Sincerely,

H. Lee McPeters
 H. Lee McPeters

HLMcP/pgm
 Attach.

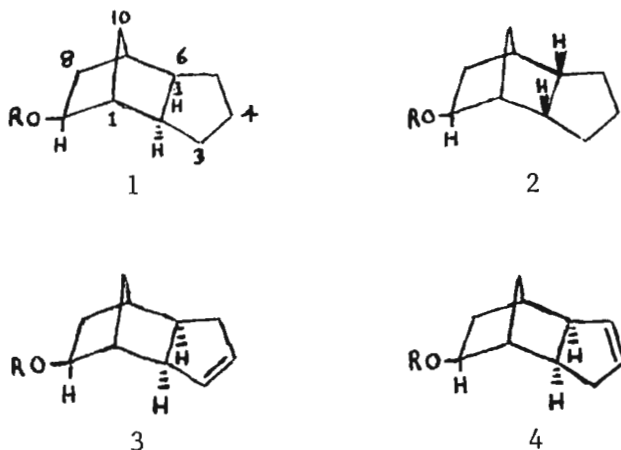


Figure 1 - R = $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_2\text{OH}$

Table I

 ^{13}C Chemical Shifts ^{3,4} of Alkoxytricyclo [5.2.1.0^{2,5}] decanes and -decenesR = -CH₃

| CARBON | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> |
|--------|-----------------------|-----------------------|------------------------|-------------------------|
| C-1 | 44.8 (d) | 45.9 ⁵ | 44.5 (d) | 47.1 (d) |
| C-2 | 43.5 (d) | 44.0 (d) ⁶ | 51.3 (d) | 39.3 (d) |
| C-3 | 31.8 (t) ⁺ | 26.4 (t) ⁺ | 131.0 (d) ⁺ | 39.0 (t) ⁺ |
| C-4 | 27.9 (t) | 28.8 ⁵ | 132.1 (d) ⁺ | 131.9 (d) ⁺⁺ |
| C-5 | 32.1 (t) ⁺ | 27.2 (t) ⁺ | 39.0 (t) ⁺⁺ | 131.8 (d) ⁺⁺ |
| C-6 | 47.8 (d) | 44.4 ^{5,6} | 43.4 (d) | 55.3 (d) ⁶ |
| C-7 | 39.5 (d) | 40.6 ^{5,6} | 41.8 (d) | 39.3 (d) |
| C-8 | 38.9 (t) | 33.3 (t) | 39.3 (t) ⁺⁺ | 39.3 (t) ⁺ |
| C-9 | 83.6 (d) | 79.3 (d) | 84.0 (d) | 83.4 (d) |
| C-10 | 28.9 (t) | 39.9 (t) | 28.3 (t) | 28.3 (t) |
| C-11 | 55.9 (q) | 55.5 (q) | 55.8 (q) | 55.3 (q) |

R = -CH₂CH₂OH

| CARBON | <u>1</u> | <u>2</u> | <u>3</u> | <u>4</u> |
|--------|-----------------------|-----------------------|------------------------|-----------------------|
| C-1 | 45.1 (d) | 46.1 (d) | 44.9 (d) | 47.5 (d) |
| C-2 | 43.4 (d) | 43.9 (d) ⁶ | 51.3 (d) | 39.2 (d) |
| C-3 | 31.7 (t) ⁺ | 26.3 (t) ⁺ | 131.0 (d) ⁺ | 39.1 (t) ⁺ |
| C-4 | 27.8 (t) | 28.5 (t) | 132.1 (d) ⁺ | 131.9 (d) |
| C-5 | 32.0 (t) ⁺ | 27.1 (t) ⁺ | 39.1 (t) ⁺⁺ | 131.9 (d) |
| C-6 | 47.6 (d) | 44.3 (d) ⁶ | 43.3 (d) | 55.2 (d) |
| C-7 | 39.4 (d) | 40.6 (d) ⁶ | 41.7 (d) | 39.2 (d) |
| C-8 | 38.9 (t) | 33.5 (t) | 39.2 (t) ⁺⁺ | 39.2 (t) ⁺ |
| C-9 | 82.4 (d) | 78.1 (d) | 82.8 (d) | 82.1 (d) |
| C-10 | 28.9 (t) | 39.8 (t) | 28.3 (t) | 28.3 (t) |
| C-11 | 61.6 (t) | 61.6 (t) | 61.5 (t) | 61.5 (t) |
| C-12 | 69.7 (t) | 69.3 (t) | 69.7 (t) | 69.3 (t) |

References and Footnotes

1. K. Nakagawa, S. Iwase, Y. Ishii, S. Hamanaka, and M. Ogawa, Bull., Chem. Soc. Japan, 50, 2391 (1977).
2. N. K. Wilson and J. B. Stothers, Top. Stereochem., 8, 1 (1974).
3. δ_{C} in ppm, δ TMS = 0. Signal multiplicities are in parentheses.
4. Chemical shifts marked with + and ++ are interchangeable within the same column.
5. Signal multiplicity was not determined.
6. Tentative assignment.

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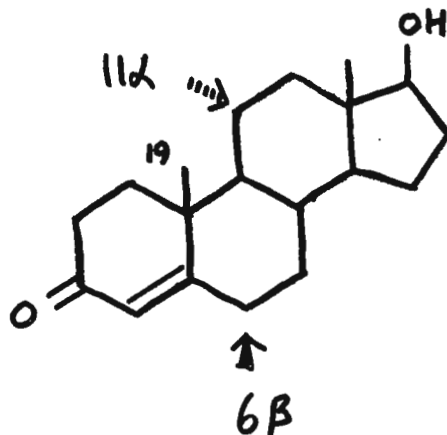
September 5, 1979.

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

Dear Dr. Shapiro:

Direct observation of the microbial hydroxylation
of testosterone by CMR

As part of our programme of investigation of the mechanism of the microbial hydroxylation of steroids, we have considered using CMR to search for transient intermediates. We have been able to monitor the hydroxylation of 19[^{13}C]-testosterone by Rhizopus arrhizus at both the 6 β and 11 α positions in the following way.



Incubation of 3 mg of 19- ^{13}C -testosterone and 40 μL of DMSO with 2 mL of a spore suspension of Rhizopus arrhizus and 150 μL of D_2O in a standard 10 mm tube was carried out over a period of 3 days. Signals were observed which corresponded to C-19 of starting material (δ 17.5 ppm), together with C-6 β -hydroxylated (δ 19.3 ppm) and C-11 α -hydroxylated (δ 18.4 ppm) products. Isolation and tlc analysis at the conclusion of the incubation revealed that both 6 β and 11 α hydroxylated products were present.

We have been unable to observe signals in a similar incubation carried out with mycelia of R. arrhizus, presumably because the steroid becomes rapidly membrane bound, but are currently working on this problem.

Sincerely yours,



H. L. Holland



G. J. Taylor



T. R. B. Jones

P.S. Please credit this contribution to the account of Jack M. Miller of our Department.

P.P.S. The work was done on a Bruker WP-60 at 15 MHz.

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Professor E. T. Samulski
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June 29, 1979

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

Dear Dr. Shapiro:

A Chemical "Thermometer" for ^{13}C NMR

In contrast to proton NMR where ethylene glycol and methanol have been accepted as thermometric standards, no commonly accepted thermometric material has been used in ^{13}C NMR. Several ^{13}C "thermometers" have been proposed recently, most of which used a mixture of liquids and measured the relative chemical shifts (Ref. 1-4). I wish to report here one additional thermometric material, acetylacetone, which can be used neat, and has a convenient temperature range (-20 to 140°C).

It is well known that acetylacetone (ACAC) undergoes keto-enol tautomerization which is temperature dependent. The relative peak area of enol/keto, therefore, serves as a suitable "thermometer". The appropriate spectral data for this compound are given in Table 1.



Table 1

^{13}C data of ACAC. Data obtained on Varian XL-100 at 40°C
T₁ via progressive saturation

| <u>Carbon No.</u> | <u>C Shift (ppm, TMS)</u> | <u>Assignment</u> | <u>T₁ (sec.)</u> |
|-------------------|---------------------------|-------------------|-----------------------------|
| 1 | 24.3 | enol, methyl | 16 |
| 2 | 30.2 | keto, methyl | 16 |
| 3 | 58.5 | keto, methylene | 17 |
| 4 | 100.4 | enol, methine | 10 |
| 5 | 191.3 | enol, carbonyl | 43 |
| 6 | 201.6 | keto, carbonyl | 33 |

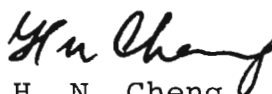
Since the methyl groups have comparable T_1 values, their relative ratio can be used as the temperature indicator. A calibration curve was constructed and given in Fig. 1. The plot is linear, as expected:

$$\log \frac{(\text{enol})}{(\text{keto})} = 797 \times \left(\frac{1}{T} \right) - 1.866$$

The precision in this method is $\pm 1^\circ\text{C}$. This method is relatively easy to use and is particularly suitable for high temperature work where the precise temperature must be known.

Please credit this contribution to Dr. Freeman's "account".

Yours very truly,



H. N. Cheng
Analytical Division

References

1. H. J. Schneider, W. Freitag and M. Schommer, J. Magn. Resonance, 18, 393 (1975)
2. S. Combrisson and T. Prange, *ibid.*, 19, 108 (1975)
3. D. W. Vidrine and P. E. Petersen, Anal. Chem., 48, 1301 (1976)
4. J. J. Led and S. B. Petersen, J. Magn. Resonance, 32, 1 (1978)

HNC:gtg

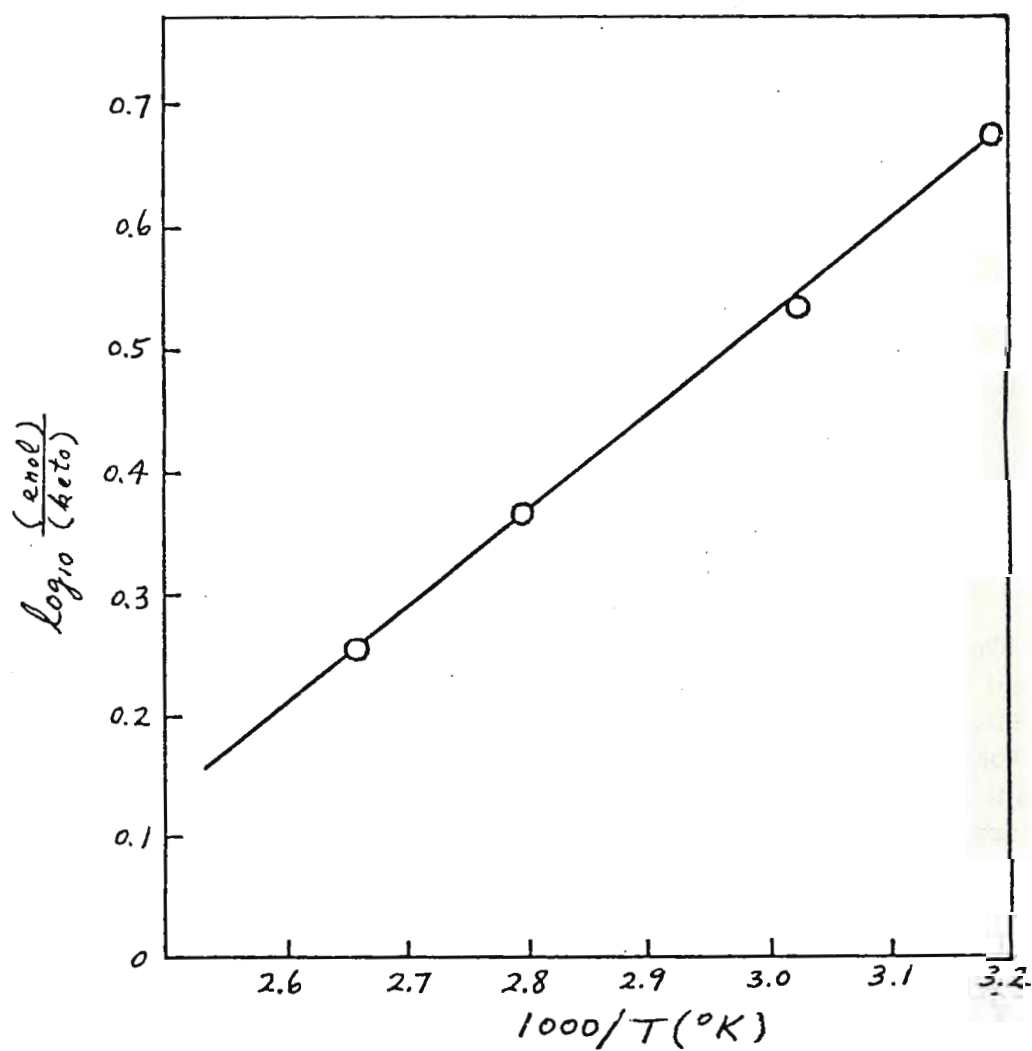


Fig. 1

Plot of \log_{10} enol/keto versus $1/T$. Values obtained from methyl peak height. Instrument = Varian XL-100 at 25.2 MHz, 8 K memory, repetition rate = 25 sec., time constant = -8.

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August 30, 1979

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

RE: Fifth Annual Stanford Conference on Molecular Structural Methods in
Biological Research

Dear Professor Shapiro:

The Stanford Magnetic Resonance Laboratory is announcing the Fifth Annual Stanford Conference on Molecular Structural Methods in Biological Research which will be held November 19 and 20, 1979, at the Fairchild Auditorium at Stanford University. The conference will be devoted to recent advances in the solution of biological structural problems by spectroscopic and crystallographic techniques, with a special emphasis on protein structure and dynamics.

Anyone wishing to register or receive further information should contact me at the letterhead address or call at 415/497-6270. A registration fee of \$30.00 is required and includes the cost of a banquet dinner to be held on November 19. Closing date for registration is October 26, 1979

Sincerely,



Alice Walker
Conference Coordinator

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Fachbereich Chemie (FB 21)
Institut für Organische Chemie (WE 02)

Dr. K. Roth

11-9-79

Freie Universität Berlin,
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Prof. B. L. Shapiro
Department of Chemistry
Texas A&M University
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Dear Prof. Shapiro:

Inexpensive Synthesizer for Audiofrequencies

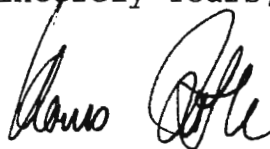
In some spectrometers (VARIAN FT-80) the decoupler frequency can only be varied in a continuous way by modulating the basic decoupler frequency with an audiofrequency. Some double resonance experiments (selective population transfer, tickling) require a highly stable frequency which has to be locked to the master clock of the spectrometer. In these cases VARIAN recommends a commercial frequency synthesizer.

In the German Journal 'Elektor' we have found a very simple circuit for an audiosynthesizer which is a very inexpensive alternative to a commercial product. The principle of operation is illustrated in fig.1.

By substituting the crystal oscillator (fig.2) and the corresponding divider by a simple 1:10,000 divider, the conventional 1 MHz output of the master clock can be used to generate a very stable audiofrequency. For a range from 1 Hz to 9999 Hz suitable for most applications one can omit IC 13, 14 and S1 and connect pin 12 of IC 12 directly with pin 4 of ES1.

A copy of the full article (in German) is available upon request.

Sincerely Yours,



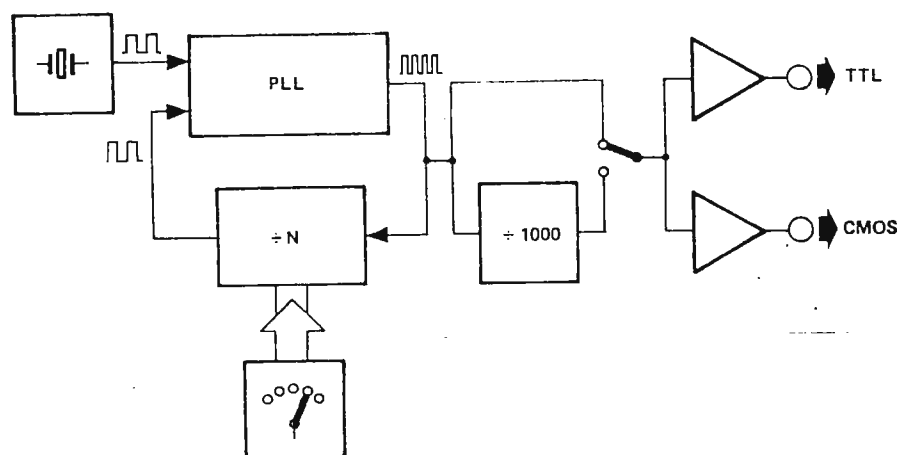


fig.1
(ELEKTOR, 1979, 7-51)

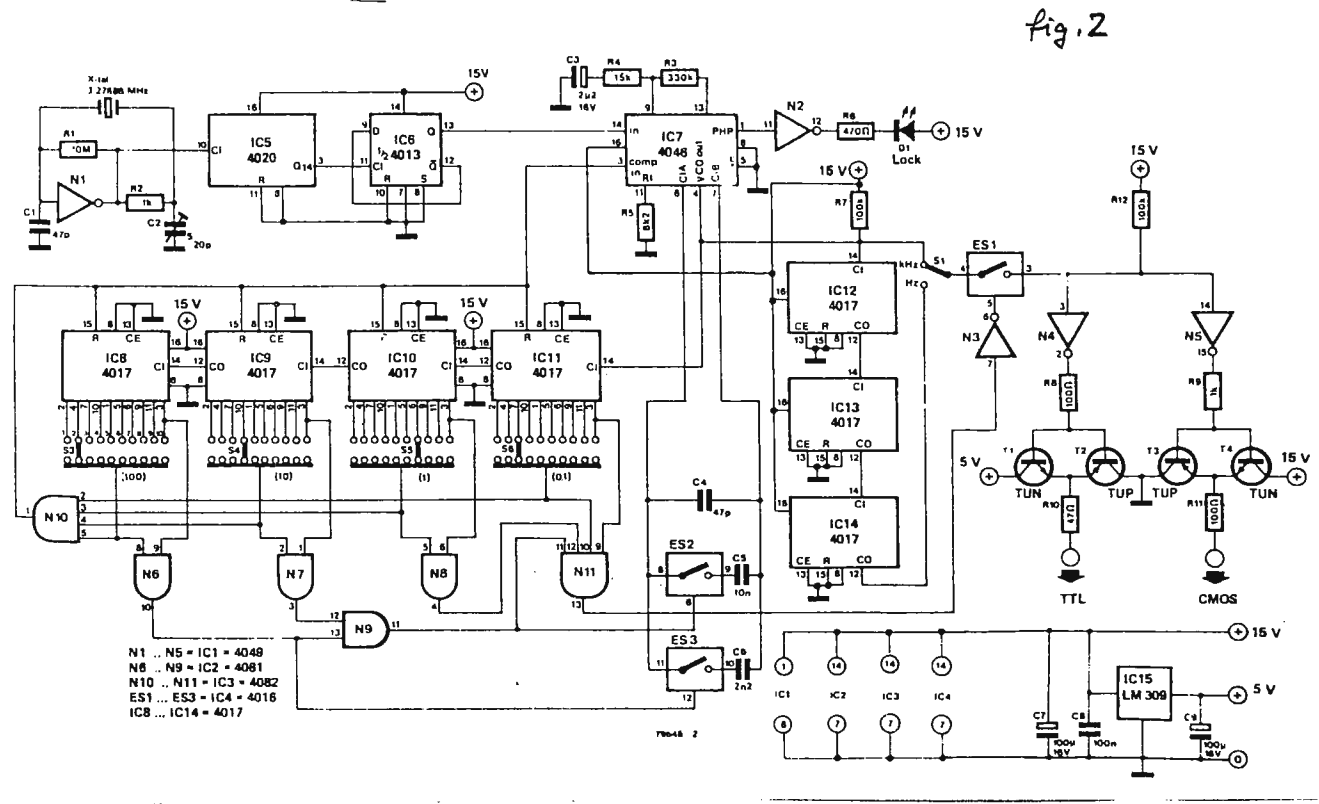
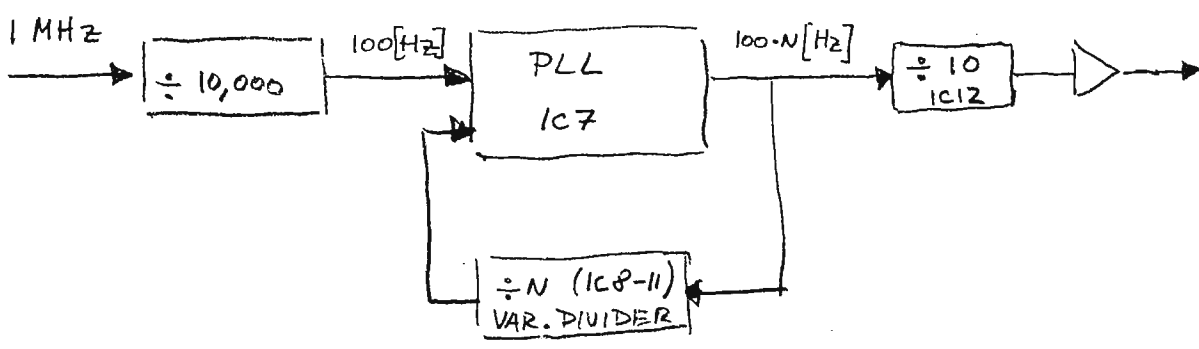
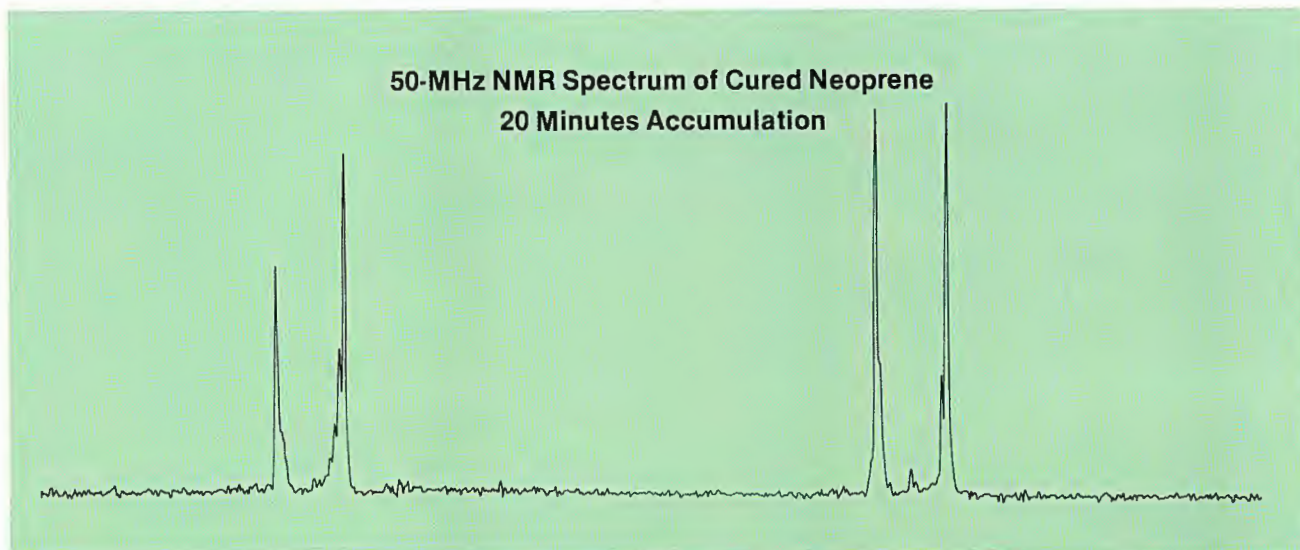


fig.2



If you can't observe solids as readily as liquids on your superconducting FT NMR...

...you just don't have an XL-200!



¹³C spectrum of cured neoprene with carbon black* in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the line structure. The width of the plot is 10 KHz. *Sample courtesy of E. I. Du Pont de Nemours and Company

With the new ¹³C solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 superconducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; generate your own convenient macro-commands;

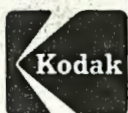
create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband accessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including ¹³C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

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9 August 1979

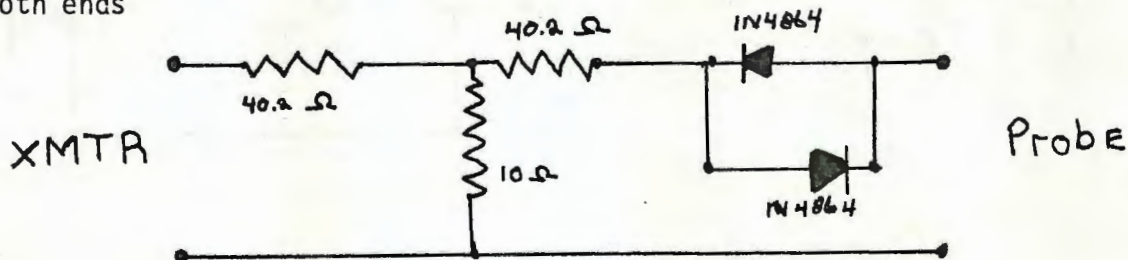
Professor B L Shapiro
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Some Modifications for Selective Excitation on the FT80A

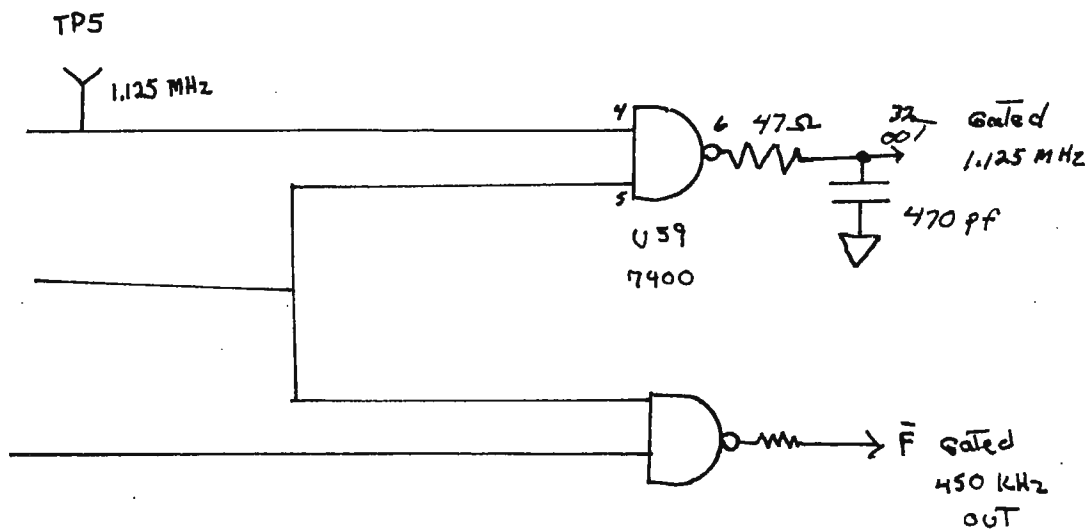
Dear Barry

The combination of selective excitation and gated decoupling can be very useful for structure elucidation in aromatic systems. During the course of an ongoing investigation of some Naphthalene derivatives, we found it necessary to employ some selective excitation techniques. Our initial results were not satisfactory in that the selectivity achieved was only about 10-15 Hz.

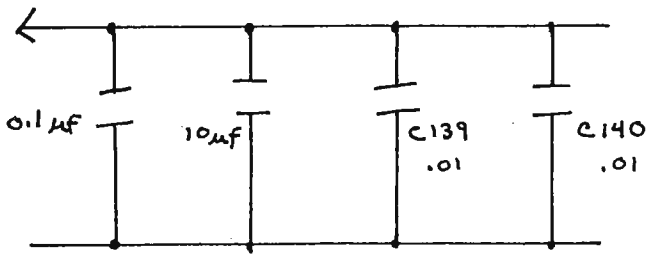
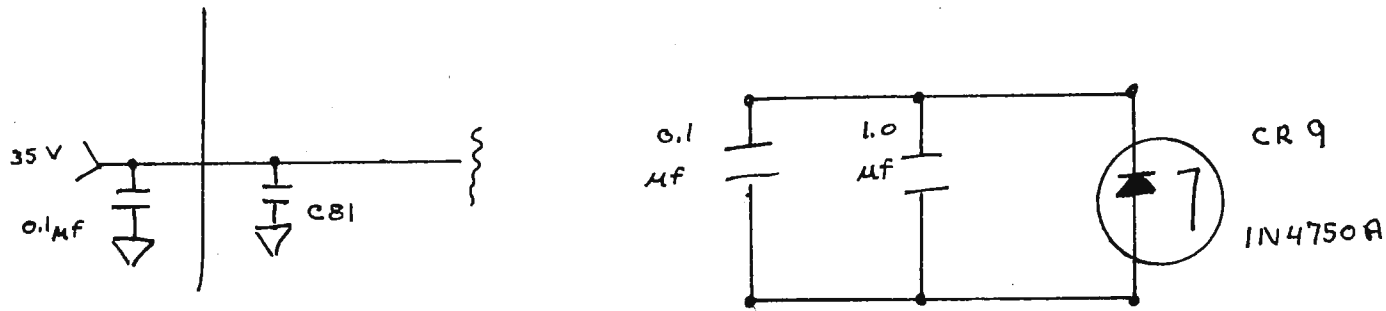
Our first modification was to lengthen the 90° pulse width to about 200 μ s. This was done by building our own version of the resistive attenuator recommended by Varian. Our unit is a 20 db T-network matched to a 50Ω load using low noise 1% resistors. After the attenuator, a pair of crossed diodes were added to help gate the transmitter reducing noise and pulse distortion. The unit is in a 5.5 cm x 2.5 cm x 2.5 cm R_f shielded box with BNC connectors at both ends



Observing the transmitter pulse with an oscilloscope, we noticed an envelope of harmonics superimposed on the pulse, at the short pulse widths needed for a selective pulse train, e.g. 2 μ s - these harmonics caused a great deal of distortion. The source of the harmonics was traced back to the 1.125 MHz square wave coming from logic gate U59 on the Master clock board (schematic No. 87-144-755). The harmonics were substantially reduced by adding a low pass filter consisting of a 47 ohm 5% 1/4 watt resistor and 470 pf 5% silvered mica capacitor to the gate U59.




We also noticed that at the high pulse repetition rate of a selective train, the 26.3 volt power supply for the transmitter output stage became unstable. To stabilize the supply, it was necessary to add more filtering. This filtering consisted of 10 μ f, 0.1 μ f capacitors across the 26.3 volt supply and further filtering of the reference diode CR9 (schematic No. 87-144-718) by 1 μ f and 0.1 μ f capacitors. A 0.1 μ f capacitor was also added to the 35 volt supply to reduce noise generated at the higher repetition rate. The capacitors used for filtering were 50 volt ceramic or 35 volt tantalum because of their stability and frequency response.



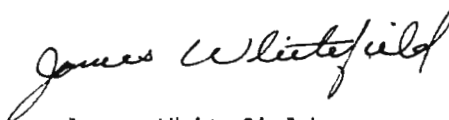
These modifications resulted in a improved pulse shape even at pulse widths of 2 μ s. This improved pulse combined with third sideband excitation and appropriate placement of the transmitter has allowed us to achieve selectivity of at least 5 Hz. The software used was the "Selectex" program supplied by Varian. We hope this is of interest to other FT80A users.

Also, our thanks to Mr. Art Backer of Varian for helpful conversations.

Yours sincerely



Kenneth Keymel
Industrial Laboratory



James Whitefield
Industrial Laboratory



PHYSICS DEPARTMENT (38th Street Campus • Downtown Campus)
1201 East 38th Street • 46205 • (317) 923-1321

September 6, 1979

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

TITLE: Line Shape for Fast Exchange and Slow Motion

Dear Professor Shapiro:

The problem of how to treat NMR line shapes when the assumption ($\tau_{\text{correlation}} \ll \tau_{\text{exchange}}$) is no longer valid has been previously treated⁽¹⁾ from the point of view of a single line (collapsed doublet?) with a line width derived from a correlation function compounded of a molecular correlation time τ_c and a chemical exchange time τ_e . A general theory which is valid when $\tau_c < \tau_e$ but does not require a totally collapsed line and includes effects arising from the entire system is simply formulated. The essential point in the derivation is to note at what point in the general theory of NMR line shapes in the presence of exchange⁽²⁾ is the condition ($\tau_c \ll \tau_e$) used. It is seen to be in the assumption that between exchange collisions the spin density matrix equation has the form

$$\dot{\rho}_A = -i[H_{Ag}, \rho_A] + R_{\text{rel}, A} \rho_A \quad (1)$$

where R is the relaxation operator first obtained by Wangness and Bloch⁽³⁾ and for extreme narrowing

$$R \approx A_0 \int_0^\infty e^{-t'/\tau_c} dt' = A_0 \tau_c = R_0 \quad (2)$$

If the condition $\tau_c \ll \tau_e$ is removed the defining equation for R must include the finite time " t " elapsed between exchange collisions and so now

$$R \approx A_0 \int_0^t e^{-t'/\tau_c} dt' = R_0 (1 - e^{-t/\tau_c}) \quad (3)$$

Solving Eq (1) in the form $\rho_A(t, t_0)$ where t_0 is the time of the last exchange event one has the usual exchange averaged result

$$\bar{\rho}_A(t) = \int_{-\infty}^t \frac{e^{-(t-t_0)/\tau_e}}{\tau_e} \rho(t, t_0) dt_0 \quad (4)$$

and then taking the time derivative of Eq (4) using R as defined in Ref (3) one obtains exactly

$$\dot{\bar{\rho}}_A = -i[H_A, \bar{\rho}_A] + R \bar{\rho}_A - \frac{1}{\tau_e} (\bar{\rho}_A - \rho_{\text{col}}) \quad (5)$$

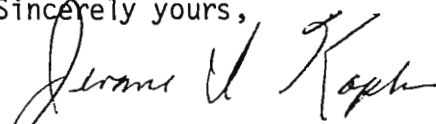
where ρ_{col} is evaluated in Ref (2) for a variety of exchange processes. Replacing Eq (2) by Eq (3) in Eq (1) and then carrying out Eq (4) and the time derivative leads to the modification of Eq (5) which is

$$\dot{\bar{\rho}} = -i[H_A, \bar{\rho}_A] + R\bar{\rho}_A - \frac{1}{\tau_e}(\bar{\rho}_A - \rho_{\text{col}}) + \frac{\tau_c}{\tau_e} R\rho_{\text{col}} + \text{higher order terms in } \tau_c/\tau_e \quad (6)$$

Eq (6) is our final result. The assumption of extreme narrowing can of course be dropped and the more general R used. Space does not permit a discussion of the added effects on the line shape arising from the new term in Eq (6).

-
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 - 2) J. I. Kaplan and G. Fraenkel, J. Chem. Phys. 94, 2907 (1972).
 - 3) R. K. Wangness and F. Bloch, Phys. Rev. 89, 728 (1953).

Sincerely yours,



Jerome I. Kaplan

P.S. Please credit this contribution to the account of Durgu Rao (B.D. Nageswara Rao).



LABORATORIUM VOOR FYSISCHE CHEMIE

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

Toernooiveld
Nijmegen
Telefoon (080) 55 88 33

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

Uw kenmerk

Uw brief van

Ons kenmerk
U4565/dB/dw

Datum September 3, 1979

Onderwerp

Postdoctoral position available

Dear Dr. Shapiro,

From January 1st we have a postdoctoral position available in our high resolution solid state NMR group. We are focussing our attention to organic polymers and are interested, among others, in structural effects, influence of composition and internal movements of the polymer on relaxation times (T_1 , $T_{1\rho}$, T_2 , T_D). Two instruments stand to our disposal, operating for proton resonance at 60 and 180 MHz. High resolution ^{13}C spectra are obtained by using proton enhanced NMR, combined with magic angle spinning.

Familiarity with NMR and/or polymer chemistry is desirable. The salary is F 3400 - F 4400 per month depending on level of experience. Those interested should send a curriculum vitae, publication list and addresses of two persons, willing to give a letter of recommendation.

Sincerely Yours,

(W.S. Veeman)

(E. de Boer)

Shell Research B.V.

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

Uw ref.:

Onze ref.: AG-79.053

Amsterdam, 31st August 1979
Postadres: Postbus 3003
Tel. via telefoniste (020) 20 91 11
Tel. rechtstreeks (020)
Hr/Mw

Dear Professor Shapiro,

High field (7.05 T) ^{13}C NMR using cross polarization and magic angle spinning

Please accept our apologies for this very tardy contribution; we will not waste valuable newsletter space with extended excuses!

We are in the process of installing a Bruker CXP-300 spectrometer with cross polarization and magic angle spinning capability for ^{13}C NMR of solids. The two attached examples of spectra illustrate both the advantages and disadvantages of a 300 MHz spectrometer for such experiments.

Figure 1 shows a spectrum of camphor, where owing to the high field, resonances F and G are separated. In previous CP-MAS spectra by investigators using lower fields, these two peaks have never been resolved.

Figure 2 shows a spectrum of hexamethylbenzene. Magic angle spinning is, of course, employed in these experiments to spin out any chemical shift anisotropy broadening the lines. The higher the magnetic field, however, the greater the broadening, and hence the faster the spinning speed must be to completely average out the interaction. At 300 MHz it may be that we cannot always spin fast enough, and the HMB spectrum (with 2.4 kHz MAS) displays spinning sidebands. (It is of interest to note that the sidebands are of varying intensity owing to the inherent anisotropy of the incompletely averaged aromatic peak.)

Trusting this missive renews our lapsed subscription,

Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

Gary Hays

G.R. Hays

Derek Clague

A.D.H. Clague

R. Huis

R. Huis

D. G. Gillies

D.G. Gillies*

*On sabbatical leave from the Royal Holloway College, London.

Shell Research B.V.
Gevestigd te 's-Gravenhage

Badhuisweg 3, Amsterdam-N.
Telex: 11224 ksla nl
Telegram: Konshellab
H.reg. Amsterdam 111841

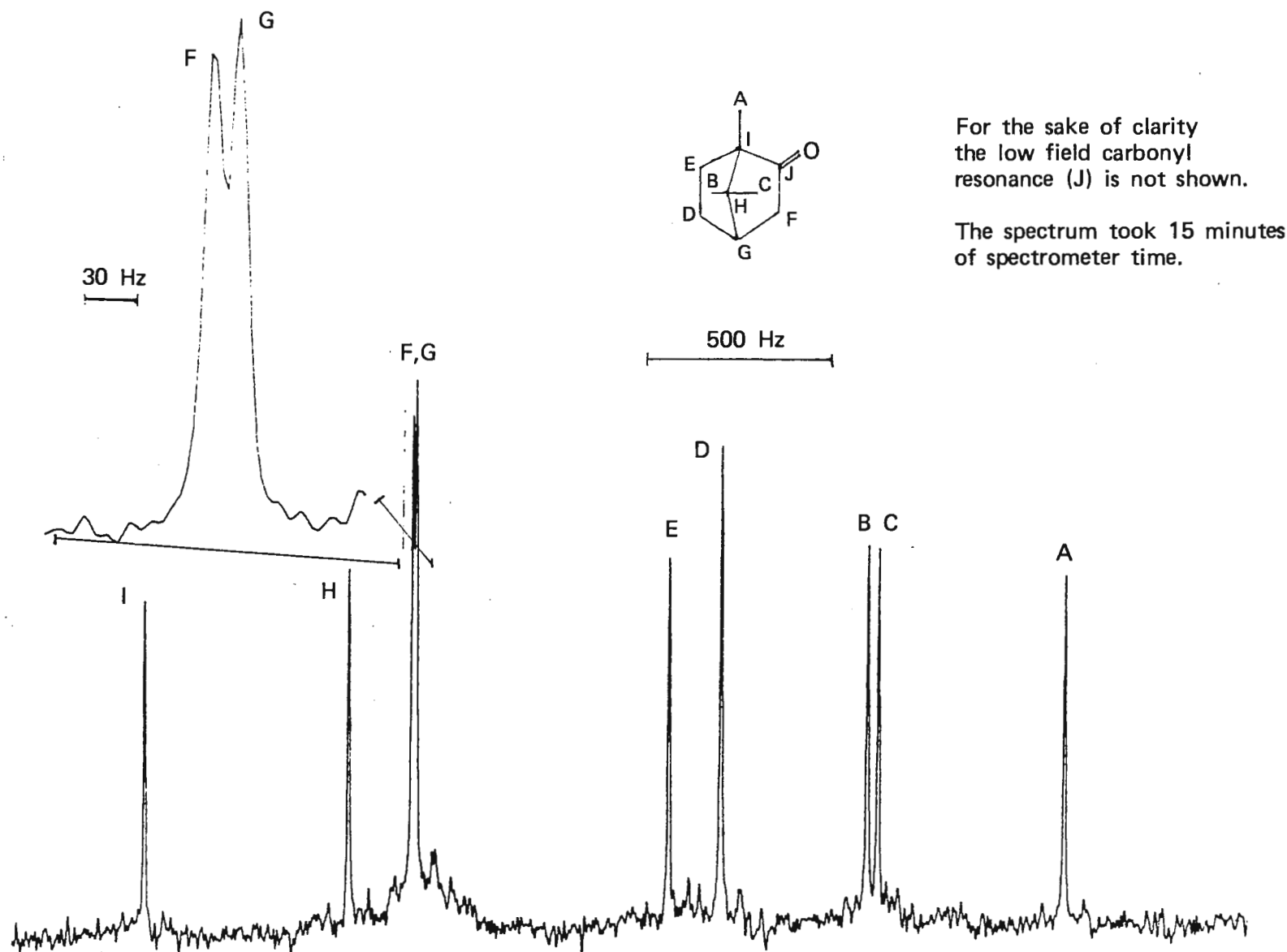
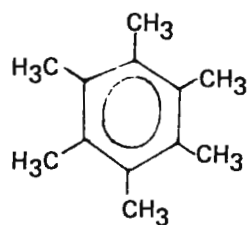


FIGURE 1: CAMPHOR



Spinning (as judged from position of sidebands) is 2.4 kHz.

The spectrum is the result of 1000 transients.

ssb: spinning sidebands

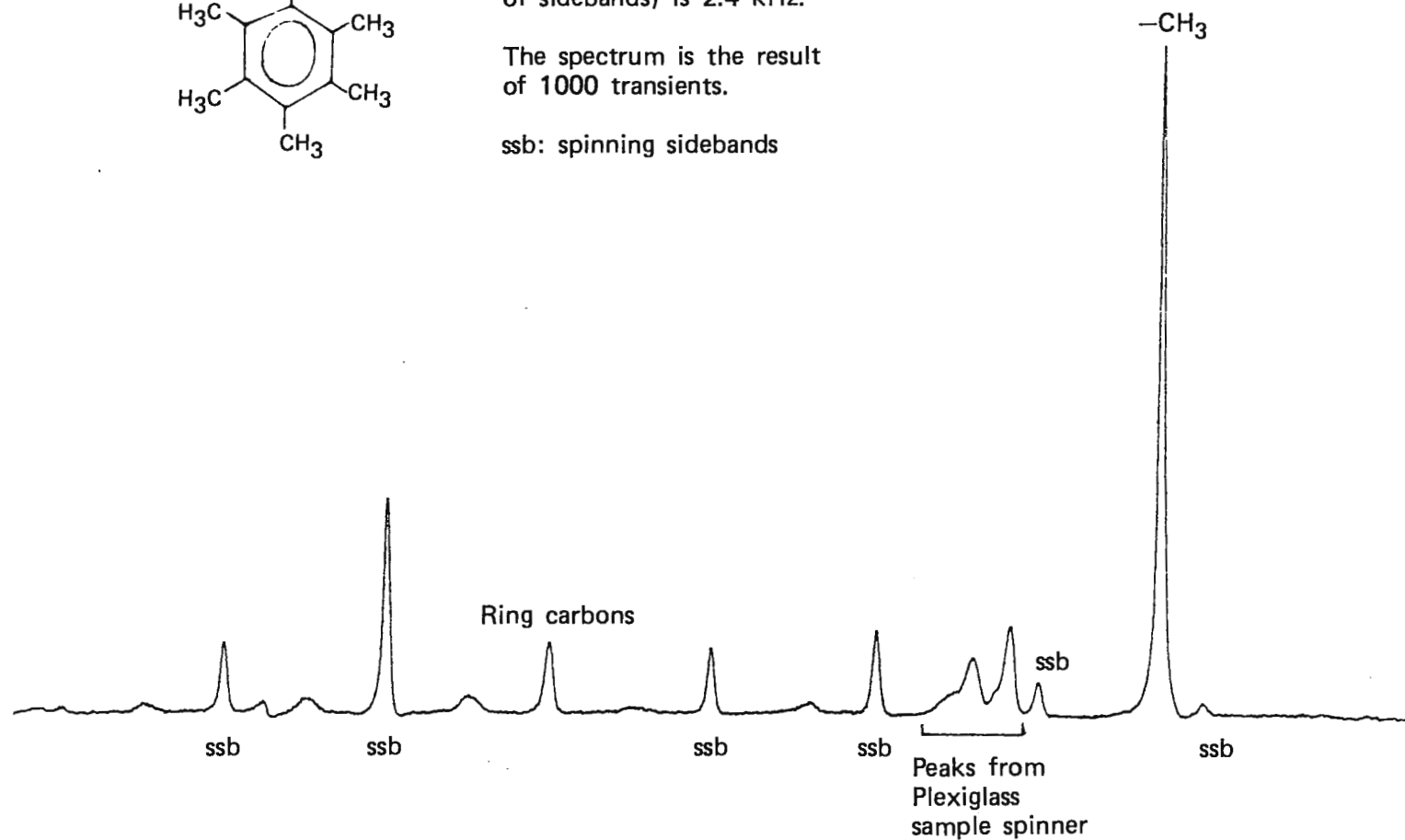
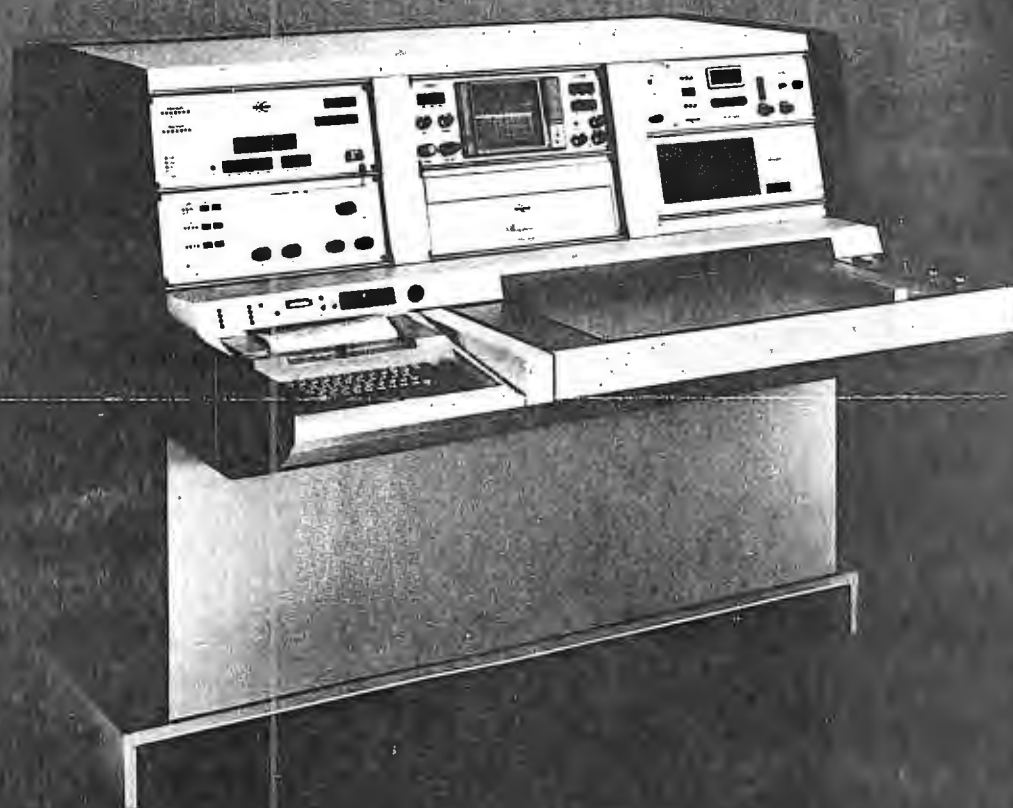


FIGURE 2: HEXAMETHYLBENZENE



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

^1H frequency of 250 MHz





DOW CHEMICAL U.S.A.

MICHIGAN DIVISION
September 10, 1979

MICHIGAN DIVISION
MIDLAND, MICHIGAN 48640

JOB OPPORTUNITY

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

Dear Barry:

There is a good opening here in the Analytical Laboratories for an NMR spectroscopist. Emphasis is on technique development and interpretation of spectral data to solve problems in research and production. Time is allotted to the development of new technology.

Current instrumentation is XL-100, FX-60, and EM-390. We are searching now for high field/high sensitivity and high resolution solids instruments to be acquired soon.

The Analytical Laboratories is a department of about 200 technical people and NMR is located in the Instrumental Analysis Group. We deal with all aspects of industrial chemistry, and with Dow locations throughout the world.

Preferred applicants will have Ph.D. or equivalent background in nuclear magnetic resonance. Genuine interest in problem solving, innovation, and development of new technology are essential.

Please send a resume and letter to:

Dr. G. L. Kochanny, Jr.
Dow Chemical U.S.A.
Analytical Laboratories, 574 Bldg.
Midland, MI

or give me a call at (517) 636-5330.

Dow Chemical U.S.A. is an equal opportunity employer.

Jerry
Jerry P. Heeschen
Analytical Laboratories
574 Bldg.
Midland, MI 48640

JPH/bjh



Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000 Liège 1, Belgique

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

September 10, 1979

Solvent Isotope Effect in ^{59}Co nmr.

Dear Barry,

With a ca. 15,000 ppm range for chemical shifts¹, ^{59}Co nmr is a sensitive means for studying solute-solvent interactions²⁻³. One has to be careful however to minimize temperature gradients in the sample tube, because of the large temperature dependence of the chemical shifts^{4,5}.

We have measured the variation of the chemical shift for $\text{K}_3\text{Co}(\text{CN})_6$ (0.1 M) in H_2O - D_2O mixtures. There is a linear dependence of the shift upon mole fraction of D_2O , pointing to the absence of preferential solvation. The magnitude of the solvent isotope effect is 1.10 ± 0.05 ppm, with a high-field shift in D_2O as compared to H_2O . This observation is consistent with weaker hydrogen-bonding of D_2O ⁶ to the nitrogens in the CN ligands.

We have made sure that the measured chemical shift difference does not originate in a significant difference in magnetic susceptibility between light and heavy water. The temperature coefficient for our samples is ca. 1.6 ppm per degree : spectra were recorded at 310 K, each sample was allowed to equilibrate to this temperature for 30 mn.

This work, which was done in collaboration with Dr. Arnel Stockis, will proceed now to examine deuterium solvent isotope effects for a series of organic solvents.

With best personal regards,
Cordially yours,



Pierre Laszlo

1. W. Hackbusch, H.H. Rupp, and K. Wieghardt, J. Chem. Soc. Dalton, 1015 (1975).
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3. G. Gonzalez, U. Mayer, and V. Gutmann, Inorg. Nucl. Chem. Letters, 15, 155 (1979).
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6. P. Laszlo and Z. Welvart, Bull. Soc. Chim. France, 2412 (1966).



University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

7th September, 1979.

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

Slow H/D exchange in NaBH_4 at high pH.

Dear Barry,

For sometime now we have been using a D_2O solution of sodium borohydride containing NaOH as a tune-up sample for ^{11}B work on our PFT 100 machine, as the FID is quite characteristic. The solution is best if freshly made, but out of laziness I have successfully used the same sample for several weeks now. To my surprise on running the sample recently I found that the spectrum contained, besides the expected 1:4:6:4:1 quintet due to BH_4^- , a series of satellite peaks forming a 1:3:3:1 quartet of 1:1:1 triplets.

This pattern is due to BH_3D^- . Now as far as I know, exchange of deuterium for protium in borohydrides in alkaline solution has not hitherto been reported, although the more stable cyanoborohydrides $[\text{BH}_3(\text{CN})]^-$ does undergo exchange at low pH.

The reaction is so slow as to be useless for making NaBD_4 for example, (on the other hand by reporting it I can satisfy the prompting of your recent green! reminder and maybe I can report on BH_2D_2^- for my next contribution!). For the record the coupling constants for BH_3D^- are $J_{\text{BH}} 80.7\text{Hz}$ (same as in BH_4^-), $J_{\text{BD}} 12.4\text{Hz}$. The chemical shift of BH_3D^- is 0.14 p.p.m. upfield of BH_4^- .

Kind regards,

Yours sincerely,

Peter.

Dr. P. Bladon.

School of Chemical Sciences
Urbana, Illinois 61801

September 11, 1979

(217) 333-3374

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77840

Dear Barry:

High-Field NMR Postdoctoral Positions.

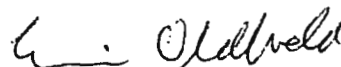
There will be several postdoctoral openings in my group beginning next Spring. We currently have "home-built" widebore supercon FT spectrometers operating at 360, 220 and 150 MHz (^1H) frequencies, with SST and "magic-angle" capabilities for multinuclear studies of solids and liquids. Projects are available in the following areas:

1. NMR of membranes, using ^2H , ^{13}C and ^{31}P NMR. Emphasis is on protein-lipid interaction and the study of glycolipids.
2. NMR of proteins and protein crystals, using ^2H , ^{13}C and ^{57}Fe NMR. Work involves "magic-angle" and magneto-orientation experiments, and is aimed at solving the problems of the ^{13}C chemical shift nonequivalences seen in native proteins, crystal vs. solution structures, and the dynamic structures of protein crystals.
3. Laser-NMR, involving ^1H CIDNP experiments with an Ar^+ ion laser. Systems of interest include soluble proteins and membrane-associated polypeptides.
4. Metal-ion NMR, especially of photochemical solar-energy conversion systems. Work will involve synthesis of a variety of organometallic compounds and multinuclear NMR studies.

Applicants should submit a curriculum vitae and list of publications, and must arrange for three letters of recommendation to be sent to:

Professor Eric Oldfield
School of Chemical Sciences
University of Illinois at Urbana
Urbana, IL 61801 USA

Yours sincerely,



Eric Oldfield
Assistant Professor
of Chemistry

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2



September 12, 1979.

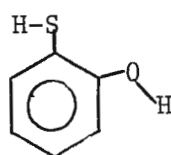
Professor B. L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, Texas,
U.S.A. 77843.

Dear Barry:

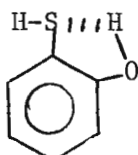
A Perpendicular Conformer of 2-Hydroxythiophenol

As an old hand at the coupling constant game, the following may amuse you.

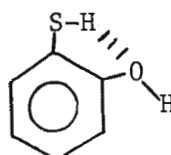
The title compound has been discussed before in terms of planar forms, 1 to 3. Intuitively, one would pick 2 as the most stable. Now, if you "stop" the intermolecular proton exchange of a 3 mol % solution in



1

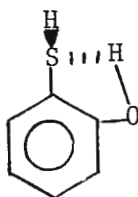


2

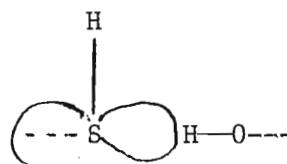


3

CCl_4 , you find that "everything is coupled to everything" in the ^1H nmr spectrum at 305 K. The magnitudes of the couplings and the chemical shifts are consistent only with form 4, in which the S-H bond lies in a



4



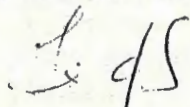
plane approximately perpendicular to the benzene plane. Extensive STO-3G MO calculations can be used to support the conclusion that greater than 95% is in form 4. Of course, if the polar O-H bond is tied up in this way, the absence of extensive self-association is understandable.

A simple interpretation of the stability of 4 notes that a C-S-H angle of 95° (from STO-3G optimization) means that the 3s orbital is only weakly involved. In turn, a good description of the lone-pairs on the sulfur in planar thio-phenol places one pair into the mainly 3s orbital and locates the other pair in the 3p orbital perpendicular to the benzene plane. The lone-pair in the mainly 3s orbital is diffuse but the directional lone-pair in the mainly 3p orbital is twisted into the benzene plane by electrostatic forces from the polar O-H bond. Consequently, the S-H bond now occupies the plane previously preferred by the 3p electron pair. In addition, 4 is favored by an entropy of $R \ln 2$ over any one of 1 to 3.

I have the impression that Can. J. Chem. is overburdened by my perambulations, so that a full discussion will be found in JACS at the turn of the year.

Some Canada geese were flying south last week. I hope they don't know something I don't know.

Cheers and best wishes from,


Ted Schaefer,
Professor.

TS/dm

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08544

September 12, 1979

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

Dear Professor Shapiro:

^{31}P NMR with ^{13}C Preamps

As many of our instruments become older and more finicky, we find ourselves frequently in a position of being unable to convince the purse-strings-that-be to spend money on replacement parts, and so must often improvise with what we have. Our XL100 consumed its ^{31}P observing preamplifier in a display of smoke that would chill the heart of any NMR spectroscopist. The cost/benefit factor for replacing it was a subject of debate until we discovered that one can observe ^{31}P signals (CW and FT) using the ^{13}C observing and locking preamp, retuned to match the ^{31}P transmitter matching network and insert, with no loss of S/N or resolution, surprisingly. We have been doing this now for about 2 years, with no problems at all, and hope this arrangement proves useful to others who find themselves in a similar predicament.

I hope this contribution will serve to reinstate our subscription to the TAMU NMR Newsletter after a long hiatus.

Sincerely,

Mary W. Baum
Daniel R. Nordlund
Mary W. Baum*
Daniel R. Nordlund

MWB/bwc

Phys. Opt. Laboratorien

4330 MÜLHEIM A. D. RUHR I. POSTFACH 0113 25

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

Title:
Fluxional Behaviour of Tetra-(Allyl)-
Hafnium and Cyclooctatetraen-Bis-
(Allyl)-Zirconium

Dear Professor Shapiro,

The structure and fluxional nature of the allyl groups in metal-allyl-compounds has been widely investigated. From a ^1H -NMR point view one can distinguish between allyl systems with AM_2X_2 spectral patterns (η^3 -allyl systems or ionic species $\text{M}^+(\text{C}_3\text{H}_5^-)$ and ABCX_2 spectral patterns (η^1 -allyl systems). Some of these compounds showed simple AX_4 spectra at room temperature, however, the type of allyl bonding could be assigned to one of these three types at low temperatures (down to -120°C). For $\text{Hf}(\text{C}_3\text{H}_5)_4$ (I) and $\text{COT-Zr}(\text{C}_3\text{H}_5)_2$ (II) this had not been possible up to now by NMR methods because the rates of rearrangement are too fast for observing frequencies smaller than

100 MHz [1]. IR- and Raman spectra give some indications that in these cases observable amounts of the η^1 -(propyliden)-forms are involved in the equilibrium [1]. The activation barriers are expected to be remarkable low. Measurements at 400 and 270 MHz show clearly that the ground states of the allyl groups in I and II are η^3 -structures.

I (dissolved in d_{10} -pentane) shows in the 400 MHz spectra at -70°C the well known AX_4 pattern ($\delta_{\text{A}} = 5.39$, $\delta_{\text{X}} = 2.74$, $J_{\text{AX}} = 12.6$ Hz). At lower temperatures the resonances of the doublet broaden and at -123°C two broad resonances at $\delta = 3.25$ ($W_{1/2} = 52$ Hz) and $\delta = 2.01$ ($W_{1/2} = 80$ Hz) and an imperfectly resolved multiplett at $\delta = 4.9$ appear. Coalescence is observed at -110°C (400 MHz). The broader (smaller) resonances at $\delta = 2.01$ ($\delta = 3.25$) are assigned to the anti (syn) protons due to the larger (smaller) vicinal coupling of the anti (syn) protons with the meso proton. The low temperature spectrum indicates four equivalent symmetrically bonded η^3 -allyl groups. The activation parameters resulting from a preliminary line shape analysis are listed in Tab. 1. In this analysis spin couplings were neglected and the permutational scheme (mutual exchange of the terminal protons) corresponding to the well known π -G- π -exchange mechanism was applied [1]. This process has been shown to account for the fluxional behaviour of tetra-(η^3 -allyl) zirconium (III),

whose activation parameters are also listed in Tab. 1. The latter result from a reinvestigation of the temperature dependend spectra of III dissolved in toluene- d_8 . A complete line shape analysis including the vicinal coupling constants was performed: The activation parameters (c. f. Tab. 1) agree with earlier results [1] and in addition the activation entropies were calculated with Binsch's program DNMR3 in a modified version [2]. Furthermore COT-bis(allyl)-zirconium (II) (dissolved in toluene- d_8) was studied between -60°C and -105°C at 270 MHz (c. f. Fig. 1). At temperatures below -100°C two broadened signals are observed at $\delta = 2.94$ ($W_{1/2} = 54$ Hz) and $\delta = 2.14$ ($W_{1/2} = 35$ Hz); these resonances are assigned to the anti- and syn-protons of II. Again the assignment is based on the larger (smaller) vicinal coupling of the anti- (syn)-protons with the meso-proton. The procedure for the line shape analysis was the same as for I and the exchange rates are listed in Fig. 1 and the activation parameters in Tab. 1. The thermodynamic data reveal different properties for I, II and III. Significant differences in behaviour have also been found in the CIDNP experiments for I and II on the one hand and for III on the other hand [3]. The large differences in ΔS^\ddagger are of special interest.

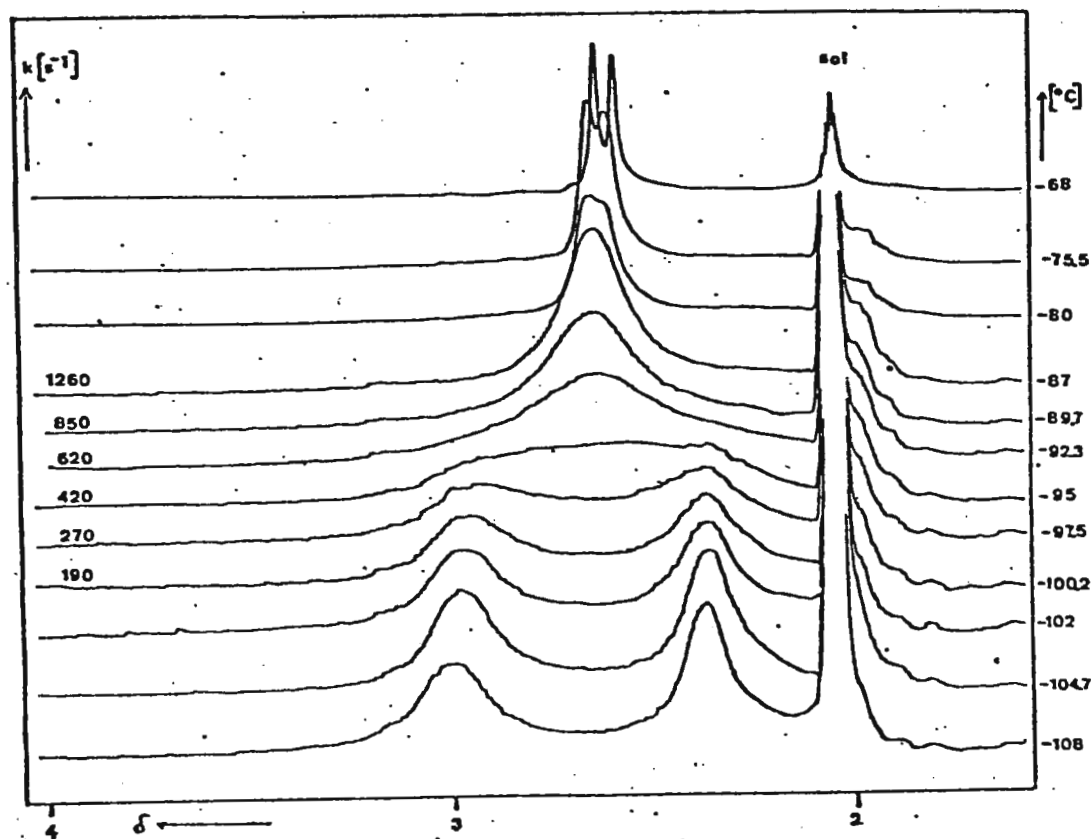


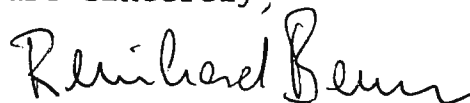
Figure 1

| | Hf(all) ₄ (I) PENTAN | Zr(all) ₄ (III) Tol | COT-Zr(all) ₂ (II) Tol |
|------------------------|------------------------------------|-----------------------------------|--------------------------------------|
| $\Delta H^\#$ Kcal/mol | 6.1 ± 0.5 | 14.7 ± 0.5 | 8.7 ± 0.3 |
| $\Delta S^\#$ e. u. | -5.6 ± 3.1 | $+19.0 \pm 2.3$ | $+3.3 \pm 1.5$ |

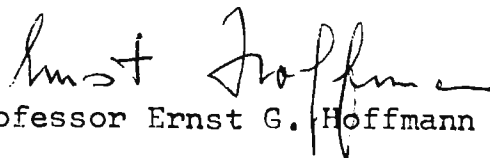
Table 1References

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W. Stempfle and G. Wilke, J. Organomet. Chem., 97(1975)183
- [2] TAMUNMR, 208(1976)22
- [3] R. Benn unpublished results
R. Benn and G. Wilke, J. Organomet. Chem., 174(1979)C38

Yours sincerely,



Dr. Reinhard Benn



Professor Ernst G. Hoffmann

CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY



September 14, 1979

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

Dear Barry:

NMR SPECTROSCOPIST POSITION

A regional NMR Centre is being established in Montreal. It will be equipped with a Bruker WH-400 multinuclear superconducting magnet spectrometer, and will be located at the University of Montreal. The institutions involved in setting up and operating the Centre are the University of Montreal, McGill University, the University of Sherbrooke, and Concordia University. Service will be provided to universities and industries in Eastern Canada.

Highly qualified applicants are invited to apply for the position of laboratory manager for the Centre. A strong background in FTNMR is essential and candidates must have a Ph.D. in chemistry. Familiarity with electronics and small computers would be an asset. Furthermore, the candidates should be dynamic and have demonstrated a capacity for personal initiative.

Responsibilities will include: nmr service, user operator training, consultation, collaboration, spectrometer maintenance and coordination of repairs as well as day-to-day administration of the laboratory. The position will be at the professional level and will command a starting salary between \$21,000 and \$25,000 depending on qualifications. The anticipated starting date is February 1, 1980.

A knowledge of French is an asset but is not a condition of employment; the selected candidate will be expected to learn enough basic French to communicate with users in about one year.

Applicants should send a resume and three letters of reference to: Dr.M. St-Jacques, Department of Chemistry, University of Montreal, Montreal, Quebec, H3C 3V1.

Best regards,

Yours sincerely,

L.D. Colebrook
Professor of Chemistry

LDC/ac

Prof. Dr. R. Kosfeld
Physikalische Chemie
Universität Duisburg

D-4100 Duisburg, 06.09.1979
Bismarckstraße 90
Telefon: 0203/392319/320

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

TX 77843 USA

Computer Link Between Cyber 175 and Nicolet 1080

Dear Barry,

Most FT-NMR-Computers are not suited for complicated spectra manipulations as both their size and number of available peripherals is too small.

Furthermore, the required programs are written in languages which can be used only in connection with larger computers. In order to perform an analysis of high-resolution NMR-Spectra it is therefore necessary to transfer the spectral data to a larger computer, using punched cards or punched tapes as intermediate storage.

This time-consuming procedure can be avoided by linking a FT-NMR-Computer to an accessible larger computer (mainframe). Such an alternative is illustrated by I. D. Gay in TAMU NMR Newsletter No. 244; the author describes the coupling between a Nicolet 1080 and an IBM 370 computer.

Some time ago we have coupled our Nicolet 1080 with a Cyber 175, using an entire computer network as link. This kind of connection which proved to have additional advantages, was suggested by spatial arguments.

The coupling between the Dietz Computer and Nicolet 1080 has been accomplished by using an RS 232 interface in the usual manner in which this kind of interface is applied to terminals.

Viewed from the Dietz Computer this interface represents a terminal in a time-sharing operation system. The advantage of such a procedure is that no special software has to be written for the operating system. Therefore, the Nicolet 1080 offers all the possibilities which are usually given to the user of such a terminal:

- access to the whole periphery of the computer system
- storage and loading of programs and spectra
- edition of programs in various languages
- starting the programs in the Dietz Computer with spectral data
- measurements at the spectrometer with Nicolet 1080 while the program is running
- blocking and admission of answer from the programs
- starting of programs in the CYBER from the spectrometer board by using the RJE-connection (Remote Job Entry)
- automatic transfer of spectral data or output of results to the CYBER, to the poolcomputer, to the terminal computer or to the spectrometer board.

The hardware used is a standard RS 232 interface at the Dietz Computer; the second interface, placed on the I/O board of Nicolet 1080 (RS 232) had to be further developed.

This was done in such a way that the information flow between Nicolet 1080 and the Dietz computer is partially controlled by the hardware and no information can therefore be lost. A data transfer with 9600 Baud is possible.

A Small program had to be written for the Nicolet. It consists of two parts:

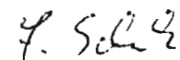
1. Communication with the computer-network (command KO)
2. Data transfer (command TA)

Both commands can be found in the list of commands of the FT program. About 600 Byte/sec can be transferred.

We conclude with the remark, that this kind of coupling which uses an RS 232 interface and links the Nicolet to a computer instead of a terminal can be accomplished with any kind of computers.

Best regards,
Yours sincerely

(R. Kosfeld)



(E. Schulz)

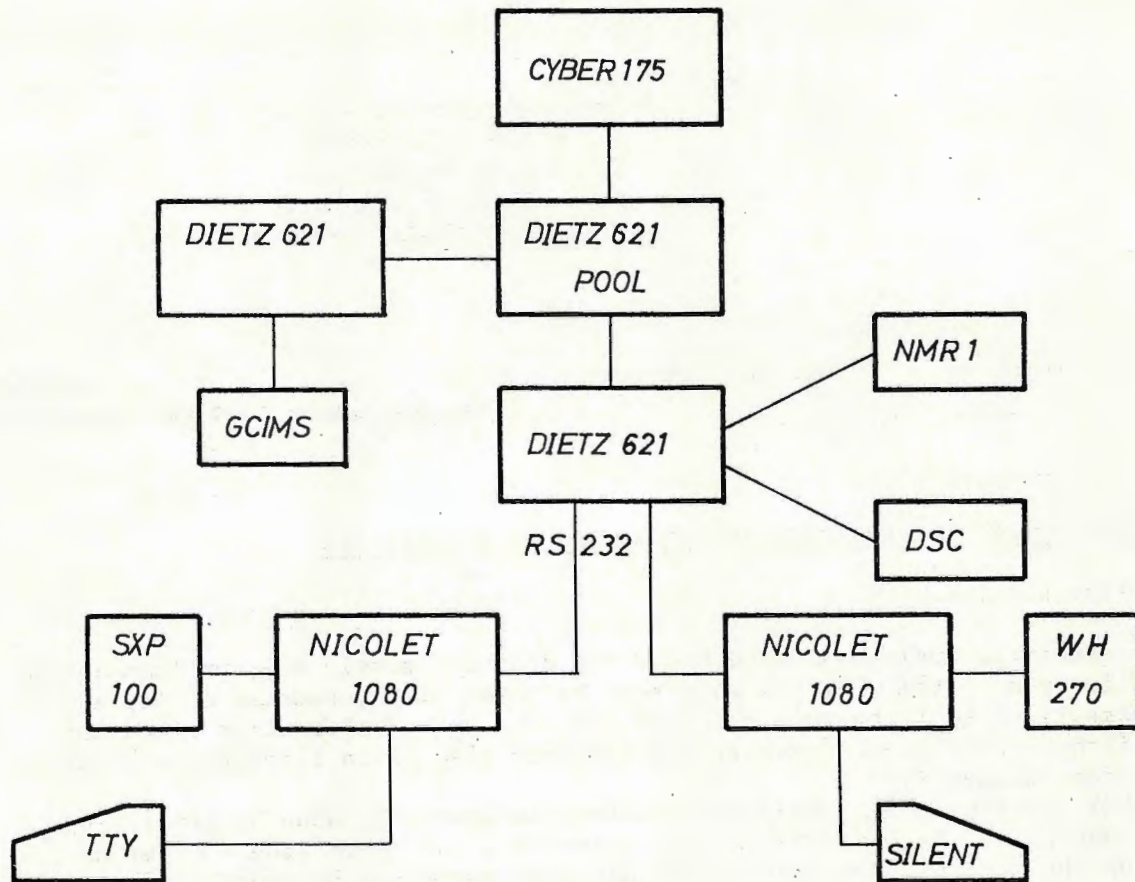


Fig. 1: Computer coupling of CYBER 175 with NICOLET 1080



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

Uw kenmerk

Uw brief van

Ons kenmerk

Datum

Delft, Lorentzweg 1

13th September 1979 Doorkiesnummer (015) 78 4058

Onderwerp

Remarks about separating the various orders of MQT transitions

Dear Professor Shapiro,

The time a chemist is only concerned about the ordinary single quantum transitions in a magnetic spin system will probably soon be gone. This, because multiple quantum transitions (MQT) contain a lot of rich and extra information about the topology of the energy level diagram, and also can give extra information about the relaxation process (1).

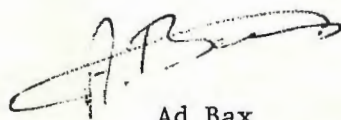
Recording MQT spectra on a modern spectrometer can easily be done by generating the pulse sequence of Fig.1a for a set of values t_1 , and performing 2D Fourier transform on the obtained data matrix, as has been described by Ernst and co-workers (2). A projection of such an absolute value 2D spectrum gives a 1D MQT spectrum which contains lines corresponding with all transitions in the spin system. Therefore such a MQT spectrum will be more complicated than the corresponding 1 QT spectrum. In practice it can even be hard to detect which line belongs to which order of transitions. However, there are several methods to solve this problem:

1. One can make two MQT spectra with slightly different irradiation frequency $\Delta\omega$. Knowing that the MQT lines of order p then will be shifted $p \times \Delta\omega$ in the MQT spectrum (2), one can in principle detect which resonance line corresponds to which order. In practice this method will be time consuming and difficult because also intensities of the resonance lines will change if the r.f. offset is varied.
2. One can make the offset frequency so large that different orders do not overlap. In this case a high sampling rate along the t_1 -axis is needed which gives an unnecessarily large data matrix or a poor resolution. Also H_1 -amplitude can be a problem if the offset frequency is large.
3. Combination of several sequences shown in Fig.1a but with phase-shifted pulses can give each order of transitions separately (3). This method gives excellent results, but a complicated phase-shifter is needed and much data space on disc is required if the results of the phase-shifted experiments have to be combined afterwards. A minimum of N experiments is necessary to separate N orders of MQT's.
4. MQT's of order p can also be selected by applying a pulsed field gradient along the spinning axis of the sample during a time T in the evolution period and a time pT at the beginning of the detection period (Fig.1b) (4). This method can be performed quite easily, does not require extra disc storage space, but gives a S/N loss because magnetization components of order not equal to p are simply destroyed.

Because the acquired signals are parts of coherence transfer spin echoes (5) they are unsensitive to static magnetic field homogeneity, i.e. natural line widths can be obtained with this method for any order p .

As is clear from the above, each method to separate the different orders of quantum transitions has its own advantages and disadvantages. Probably time will learn which method is the best in practical circumstances.

Yours sincerely,



Ad Bax



Paul de Jong

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Please credit this contribution to Prof. J. Smidt.

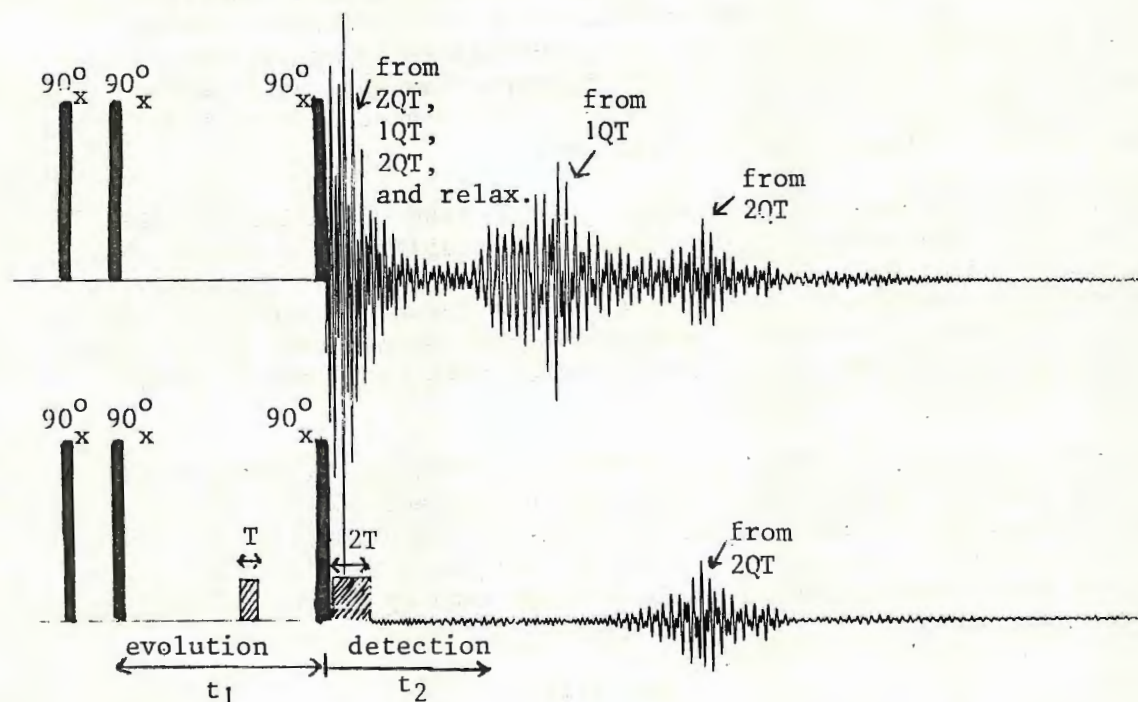


Fig. 1 (a) General pulse scheme of a 2D MQT experiment. Coherence transfer echoes originating from 1 QT and 2 QT transitions during t_1 arise for $t_2 = t_1$ and $t_2 = 2 t_1$ respectively, in the case of an AX spin system.
 (b) The 2 QT coherence transfer echo can be "filtered" out by applying pulsed gradients.



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:
6110-705:CFP:djs
18 September 1979

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

Dear Dr. Shapiro:

Postdoctoral fellowships tenable at the Naval Research Laboratory are awarded annually through a competition under the auspices of the National Research Council. There are 15-20 of these throughout NRL awarded annually at a stipend of about \$19 K; renewal for a second year is often made. Applicants must be citizens of the United States. As the complete application must be in the hands of NRC by January 15th, and as the competition is great, prospective applicants are advised to begin preparation of proposals, etc. as soon as possible. Materials may be obtained from the NRL, NRC, or from the undersigned.

The Laboratory also has a program for visiting faculty members on sabbatical or leave, under the provisions of the Intergovernmental Personnel Act (IPA). Depending on the circumstances, supplemental or full support may be available. An IPA agreement may cover any period from a few months to two years. Allowances are provided for moving expenses, travel to scientific meetings, etc.

Three spectrometers are available: a JEOL FX60 Q, a liquid state double resonance spectrometer which uses the J coupling to polarize the nuclei, and a solid state ^{13}C spectrometer with magic angle spinning. Limited multinuclear capabilities are available for high resolution and solid state relaxation studies. There is an EPR spectrometer and purchase of an ENDOR machine is planned. Developmental work on an NMR imaging spectrometer will begin this coming year.

Current interests include: a) analysis, mechanical properties and other basic studies of structural polymers; b) characteristics of energetic materials; c) NMR imaging in solids; d) electroactive materials, e.g. $(\text{SN})_x$, polyacetylene and graphites; and e) the analysis of molecules chemisorbed on surfaces. We invite letters of inquiry which outline the applicants interests.

Sincerely,

Bill *AI* *CF*
W.B. Moniz, A.N. Garroway and C.F. Poranski
Code 6110 (202-767-2323)
(polymers, energetic materials, imaging)

Henry
H.A. Resing
Code 6170 (202-767-2025)
(electroactive polymers, graphites, and surfaces)



THE OPEN UNIVERSITY

September 10, 1979

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

Dear Professor Shapiro

^{15}N nmr studies on Hydrazido(2-) Complexes of Molybdenum and Tungsten

Following our work on dinitrogen-15 complexes of Mo and W,¹ we have been studying the hydrazido(2-) complexes which represent an intermediate stage in the reduction of M-N_2 to ammonia. The Table gives the ^{15}N chemical shifts and coupling constants together with some values for related compounds. The assignment of the terminal nitrogen ($^{15}\text{N}_\beta$) resonance at relatively high field is established by measurement of $^1\text{J}_{\text{NH}}$. The β -nitrogen resembles amide nitrogen² in being deshielded as compared with nitrogen in hydrazines,³ and this can be attributed to the near planarity of the NH_2 group in M=NNH_2 and in amides, which allows deshielding of the nitrogen (as of carbon in amides⁴) by $\pi \rightarrow \sigma$ circulations which are of lower energy than the $\sigma \rightarrow \sigma^*$ circulations in pyramidal hydrazine groups.

Like the chemical shift of the β -nitrogen, the coupling constants in the M=NNH_2 groups resemble those for comparable planar groups (such as amides) rather than those for hydrazines (Table). Similarly, our NN coupling constants of about 10 Hz agree with the values predicted by Schulman and his co-workers⁵ for N_2H_4 with both nitrogens planar, as opposed to values of -2 or -3 Hz predicted for pyramidal nitrogen. These relationships are in accord with the Schulman theory, whereby a lone pair on (pyramidal) nitrogen gives a positive contribution to the Fermi contact term which tends to cancel the negative contribution from the bonding electrons. It seems likely then that $^1\text{J}(\text{NH})$ in the hydrazido(2-) group is negative as for formamide; on the Schulman theory, $^1\text{J}(\text{NN})$ is positive.

This work was done in collaboration with Joseph Chatt, Martin Fakley, and Ray Richards of the ARC Unit of Nitrogen Fixation, University of Sussex, and with Ian Stenhouse of PCMU Harwell, Oxfordshire: an account will appear in the Journal of Chemical Research.

| Compound ^a | δppm^b | | | J/Hz^c | | | | | | |
|--|----------------------|-----------------|-----------------|-------------------|---|-------------------|-------------------|-------------------|---------------------|-------------------|
| | ^{15}N | ^{19}F | ^{31}P | $^1J_{\text{NN}}$ | $^1J_{\text{NH}}^d$ | $^1J_{\text{NW}}$ | $^2J_{\text{NP}}$ | $^1J_{\text{PW}}$ | $^2J_{\text{FN}}^e$ | $^2J_{\text{FP}}$ |
| | α | β | (trans) | | | | (cis) | | (trans) | (cis) |
| <u>trans</u> -[MoF(NNH ₂)(dppe) ₂]BF ₄ | -83.3 | -243.9 | -160.14 | -94.7 | $ ^1J_{\text{NN}} + ^3J_{\text{FN}} $ 24 (3) | 86 (3) | - | 6 (3) | 77 (3) | 32 |
| <u>trans</u> -[WF(NNH ₂)(dppe) ₂]BF ₄ | -101.4 | -255.1 | -172.21 | -105.2 | $ ^1J_{\text{NN}} + ^2J_{\text{FN}} $ 62 (3) | - | - | 11 (3) | 288 | 58 |
| [Mo(NNH ₂)(8-quin)(PMe ₂ Ph) ₃]Cl ^f | -64.3 | -220.8 | | | ~ 10 (2) | | | | | |
| [W(NNH ₂)(8-quin)(PMe ₂ Ph) ₃]Cl ^f | -82.1 | -241.6 | - | -146.0 -150.7 | 8.8 (1) | - | 114.0 (1) | 361 300 | - | - |
| [MoCl(NNH ₂)(C ₅ H ₅ N)(PMe ₂ Ph) ₃]Cl ^g | -72.8 | -227.0 | - | | 9.8 (1) | 83 (1) | - | - | - | - |
| [WCl(NNH ₂)(C ₅ H ₅ N)(PMe ₂ Ph) ₃]Cl ^g | -90.6 | -240.6 | - | -153.3 -153.4 | 10.5 (1) | 83 (3) | 124.5 (1) | 5 (1) | 347 298 | - |
| PhNHNH ₂ (1) ^h | -294.8 | -320.0 | | | 6.7 ^j | 68 | | | | |
| PhCH=N-NHC ₆ H ₄ (p-)Cl ⁱ | -52.0 | -234.2 | | | | - | | | | |
| p-NO ₂ C ₆ H ₄ CH=NNHPh ^j | | | | | 10.7 | | | | | |
| [WF ₅ (NME)] ^{-k} | -7.2 | -101.5 | - | - | - | 98 | - | - | 56 | |
| <u>trans</u> -[WF ₄ (NMe){(MeO) ₂ SO}] ^k | 10.1 | - | - | - | - | 140 | - | - | | |
| PhN=N-NMe (CDCl ₃) ^l | -21, 71, -225.7 | | | | N=N 12.8 (0.7) N=N 14.0 (0.7) | | | | | |
| N ₂ H ₆ SO ₄ (aq) ^m | -335.6 | | | | | -86.9 | | | | |
| HCONH ₂ (aq) ⁿ | -265.6 | | | | | -91.3 | | | | |

TABLE continued

a ^{15}N spectra measured in CH_2Cl_2 solution at 18.24 MHz unless otherwise described. dppe is $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

b Positive downfield. ^{15}N shifts measured relative to external CD_3NO_2 liquid containing $[\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3]$ (30 mg dm^{-3}); ^{19}F shifts relative to CFCl_3 ; ^{31}P shifts relative to $\text{P}(\text{OMe})_3$. c No signs have been determined, except as indicated.

In parentheses, spectral resolution in Hz. d Proton spectrum. e Confirmed in ^{19}F spectrum. f 8-quin=quinolin-8-olate, O is trans to N-NH_2 . g Cl is trans to N-NH_2 . h Ref.3b; $^1\text{J}(\text{NH}_2)$ estimated from the given spectrum. i Ref. 6; ^{15}N shifts measured relative to saturated $\text{NH}_4\text{Cl}(\text{aq})$, for which we assume δ -353. j S. Bulusu, J.R. Autera and T. Axenrod, J.C.S. Chem. Comm., 1973, 602. k Ref. 10. ^{14}N double resonance measurements, originally referred to NO_3^- for which we assume δ -6. ^{14}N coupling constants converted to ^{15}N values by $|\text{J}(^{15}\text{NX})/\text{J}(^{14}\text{NX})| = 1.40$. l Ref. 8. Shifts reported relative to saturated $\text{NH}_4\text{Cl}(\text{aq})$ for which we assume δ -353. m ^{15}N in natural abundance: resonant species is $[\text{}^{14,15}\text{N}_2\text{H}_5]^+$, exchanging. n Ref. 2. ^{15}N shifts referred to "8 mole per cent" acidified $\text{NH}_4^+(\text{aq})$ for which we assume δ -358.

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Yours sincerely,

Joan Mason

Dr. Joan Mason



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20133 MILANO, 17.9.79

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TEL. 29.28.93 - 29.30.97 - 29.36.04 - 29.37.81

29.52.78 - 29.54.82 - 29.60.71 - 29.53.10

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

No. Riv. Prot. N.

Dear Doctor Shapiro,

many thanks for your blue reminders.

CONFORMATION OF URONIC ACID IN GAG

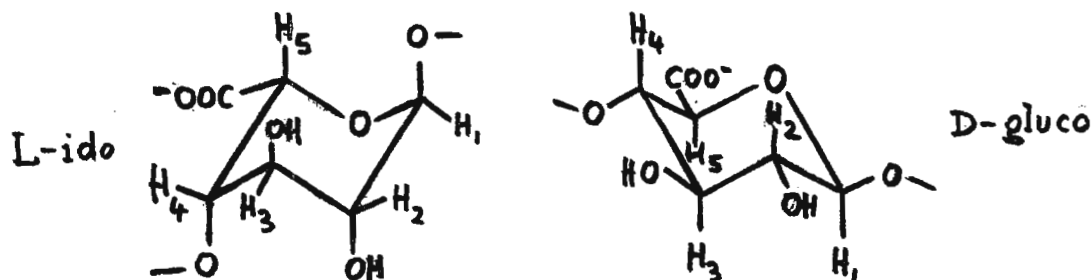
Recently I have been concerned with spectra of glycosaminoglycanes (GAG) such as heparin (1,3) dermatane sulfate (2) and chondroitine sulfate (2).

Proton spectra at 270 MHz with digital resolution enhancement can afford for these biopolymers interproton coupling constants which indicate the ring conformation of the uronic acid residues.

The relevant numbers are the following:

| | J_{12} | J_{23} | J_{34} | J_{45} |
|-----------------------|----------|----------|----------|----------|
| Heparin | 2.6 | 5.9 | 3.4 | 3.1 |
| Dermatan sulfate | 3.0 | 6.0 | 3.5 | 3.3 |
| Chondroitin-4-sulfate | 8.0 | 8.5 | 9.0 | 9.0 |

The data for heparin and dermatan sulfate show that the L-iduronic acid residue is in the 4C_4 conformation whereas the glucuronic acid of chondroitin sulfate is in the 4C_1 form.



Sincerely yours

G. Gatti

G. Gatti

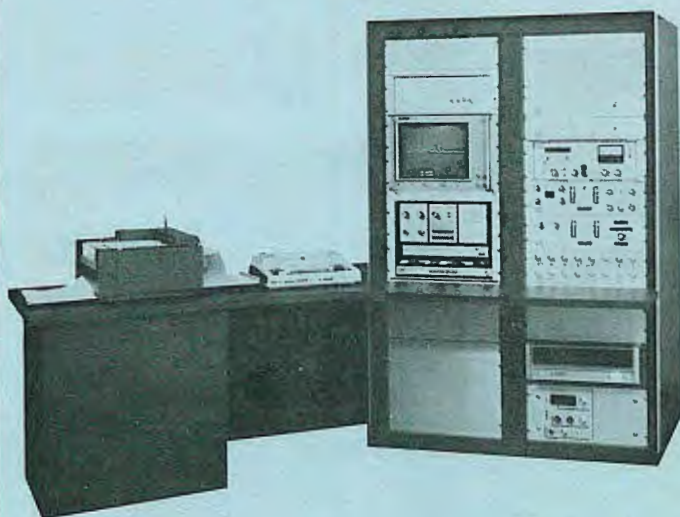
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(3) G.Gatti, B.Casu, G.K.Hamer, A.S.Perlin, Macromolecules (in press)

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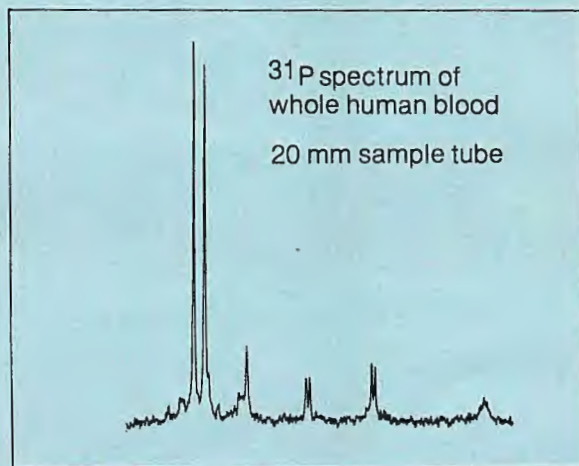
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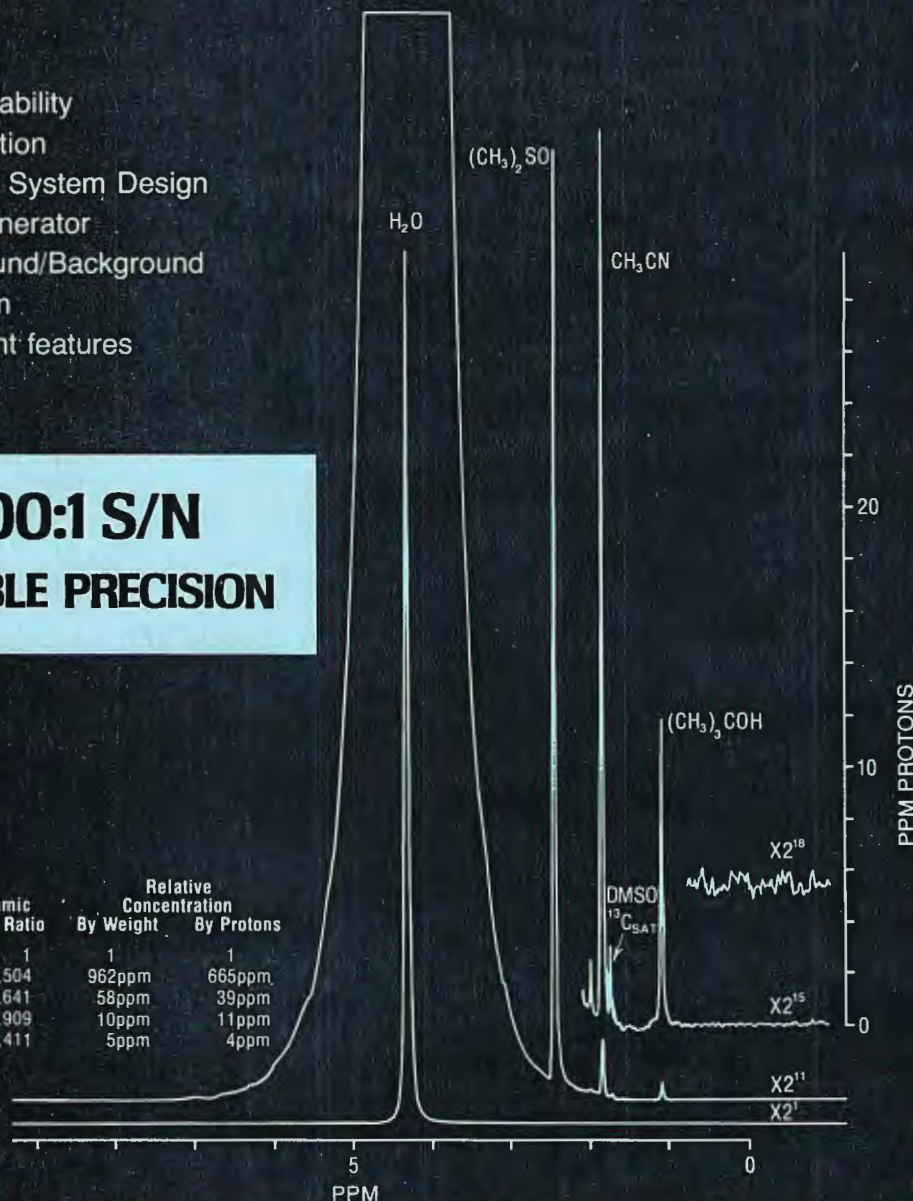
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5mm sample
8192 data points (32 bit words)
Transform time 30 sec
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1.224 sec repetition
2000Hz plot

| Compounds | ml | %Protons | Dynamic Range Ratio | Relative Concentration | |
|-----------------------|------|----------|------------------------|---------------------------|------------|
| | | | | By Weight | By Protons |
| Water | 800 | 100% | 1 | 1 | 1 |
| DMSO | 0.70 | 0.0665% | 1,504 | 962ppm | 665ppm |
| Acetonitrile | 0.06 | 0.0039% | 25,641 | 58ppm | 39ppm |
| t-butanol | 0.01 | 0.0011% | 90,909 | 10ppm | 11ppm |
| DMSO- ¹³ C | — | 0.00037% | 273,411 | 5ppm | 4ppm |
| Satellite | | | | | |



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