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Newsletter

No. No. 218

November, 1976

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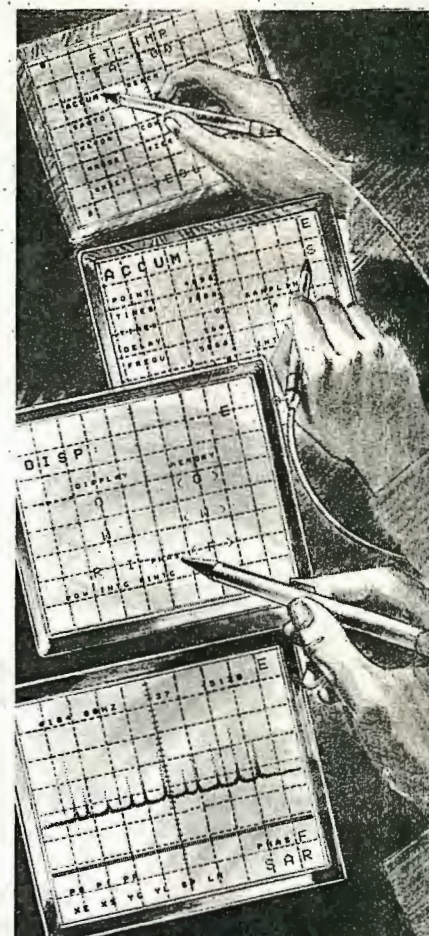
DEADLINE DATES: No. 219: 1 December 1976
 No. 220: 3 January 1977

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

October 4, 1976

Dear Professor Shapiro:

Incipient PARRS

Having spent most of a sabbatical year learning how to relax in George Levy's laboratory, I naturally had paramagnetic reagents in my mind when reading a recent paper on square planar Ni phosphine complexes [Inorg. Chem., 15, 2096 (1976)]. Therein, the absence of observable P-H coupling of a dimethylphenylphosphine ligand on nickel was attributed to "cancellation of coupling".

Seeing no good reason for any such cancelling, it seemed to me that a short lived tetrahedral Ni conformer (an incipient PARR) would effectively remove J_{PH} by relaxing the directly attached phosphorus. It turns out that this has been observed before, although in another earlier paper [Inorg. Chem., 13, 970 (1974)], some surprise was noted at the "as yet unexplained" reappearance of P-H coupling at high temperatures. In fact this is precisely what one would expect from the expression for paramagnetic relaxation which contains a Temp^{-1} term. In fact, several factors will decrease the efficiency of electron-nuclear dipolar relaxation as temperature is increased. If it so happens that the frequency of the coupling and effectiveness of the PARR concerned are just right over an appropriate temperature range then the appearance of AB splitting only at higher temperatures in a PARR...AB situation is easily demonstrated. All that is required is that the PARR affects nucleus A very much more than nucleus B (or you won't see B).

A case in point is $\text{Cr}(\text{acac})_3$ ($1 \times 10^{-2} \text{ M}$) with CHCl_3 (1M) in CCl_4 . It is easy to demonstrate by ^{13}C NMR, (with the H decoupler off of course) that at $+60^\circ\text{C}$ the ^{13}C -H splitting is observed (albeit broadened somewhat - but quite distinct). Down around -10°C the splitting is absent and only a single broad line is observed.

Beyond this point the ^{13}C signal broadens further as electron ^{13}C nucleus dipolar relaxation increases in efficiency. The analogy with the above Ni systems is that a short lived PARR - substrate complex is formed in which the complexing atom (P in Ni case and H in this one) is relaxed a hundred-fold more effectively than the observed nucleus (H in the Ni case and ^{13}C in this one).

Yours relaxfully,

Cline E Holloway

C.E. Holloway
Department of Chemistry

THE JOHNS HOPKINS UNIVERSITY

SCHOOL OF MEDICINE

725 N. WOLFE STREET BALTIMORE, MARYLAND 21205

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

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October 8, 1976

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

Dear Barry:

Some of our current NMR work is directed toward the observation of metal nuclides in metalloproteins. We are especially interested in cadmium (isotope 113, ~ 12.6% natural abundance) which can be substituted into several proteins. The potential for observing still other nuclei which have resonances in the 10 to 30 MHz range at 23KG prompted us to adopt a "wide band" approach in developing circuitry for our spectrometer which comprises a Nicolet TT 23 console (basically a retuned Bruker WH 90) a Varian 15" magnet and V4412 probe.

Figure 1 shows the general scheme for the observation of nuclides in the 10-30 MHz radio-frequency spectrum on our spectrometer. The wideband preamplifier circuit is similar to that of Hawk, et al. One problem on our Nicolet/Bruker/Varian hybrid system has been the amount of harmonic noise present in the reference channel. This has necessitated the use of a tuned circuit on the output of the preamp. stage of that channel. We are presently working on ways to clear up that problem and we would appreciate hearing how others have managed it. The driver stage is a wideband amplifier of our own design and has an approximate output of 12W that is essentially linear over the range of 5-50 MHz. For frequencies falling within $\pm 15\%$ of the ^{13}C resonant frequency (25.16 MHz) of our spectrometer the 50W and 1KW amplifiers may be used without any retuning. The power loss is significant (125 W pulse for 22.22 MHz versus 1KW for 25.16 MHz) if no readjustments are made, but the resultant 90° pulse of 40 μ sec was considered adequate.

Figure 2 shows a T_1 -inversion recovery experiment for a 1M solution of natural abundance Cd Cl_2 (spectropure, Johnson-Mathey) in 90% H_2O /10% D_2O . All spectra were obtained in a 12mm sample tube. The apparent longitudinal relaxation time is 28.86 seconds. Figure 3 shows a single pulse experiment on the same sample for a test of signal-to-noise. All spectra were obtained without benefit of single-sideband filtering or quadrature phase detection.

Sincerely,



Donald P. Hollis - Ray L. Nunnally

1) R.M. Hawk, R.R. Sharp and J.W. Tolon, Rev. Sci. Instrum. 45, 96 (1974).

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Enc.



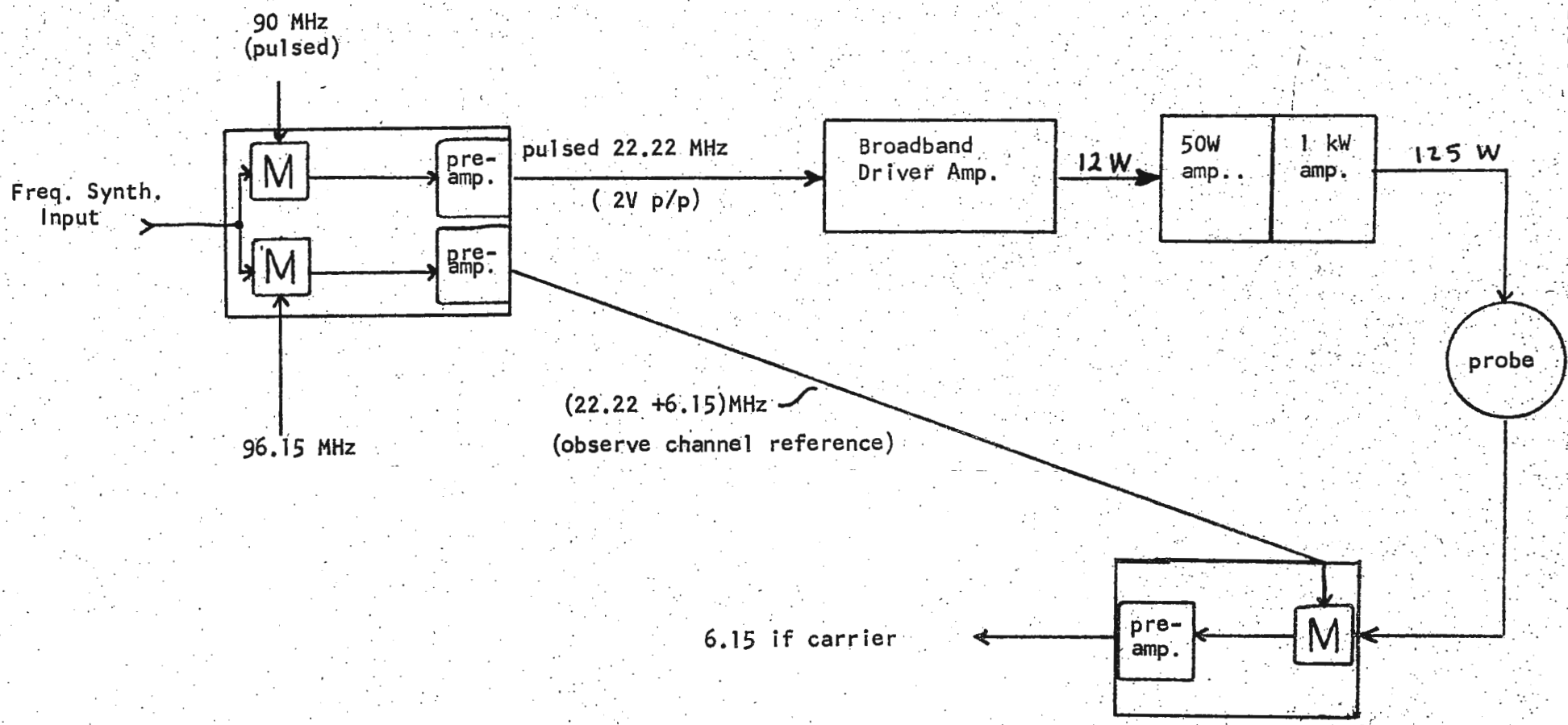


Figure 1.

M = mixer (Relcom M6D or equivalent)

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>LP
RAY 30AUG76
TIIR OF CDCL2
TIIR
P1 = 80.0000 USEC
D1 = 2.00000 SEC
# 2 = 10.0001 SEC
# 3 = 20.0001 SEC
# 4 = 30.0001 SEC
# 5 = 50.0000 SEC
# 6 = 100.001 SEC
# 7 = 120.002 SEC
# 8 = .000000 SEC
P2 = 40.0000 USEC
D5 = 150.000 SEC
ACQ = 1
SIZE = 8192
AT = 2.04594 SEC
ADC = 0
DE = 0
SW = 2002.00
EM = 1.20000
PA = 259.158
PB = -108.830

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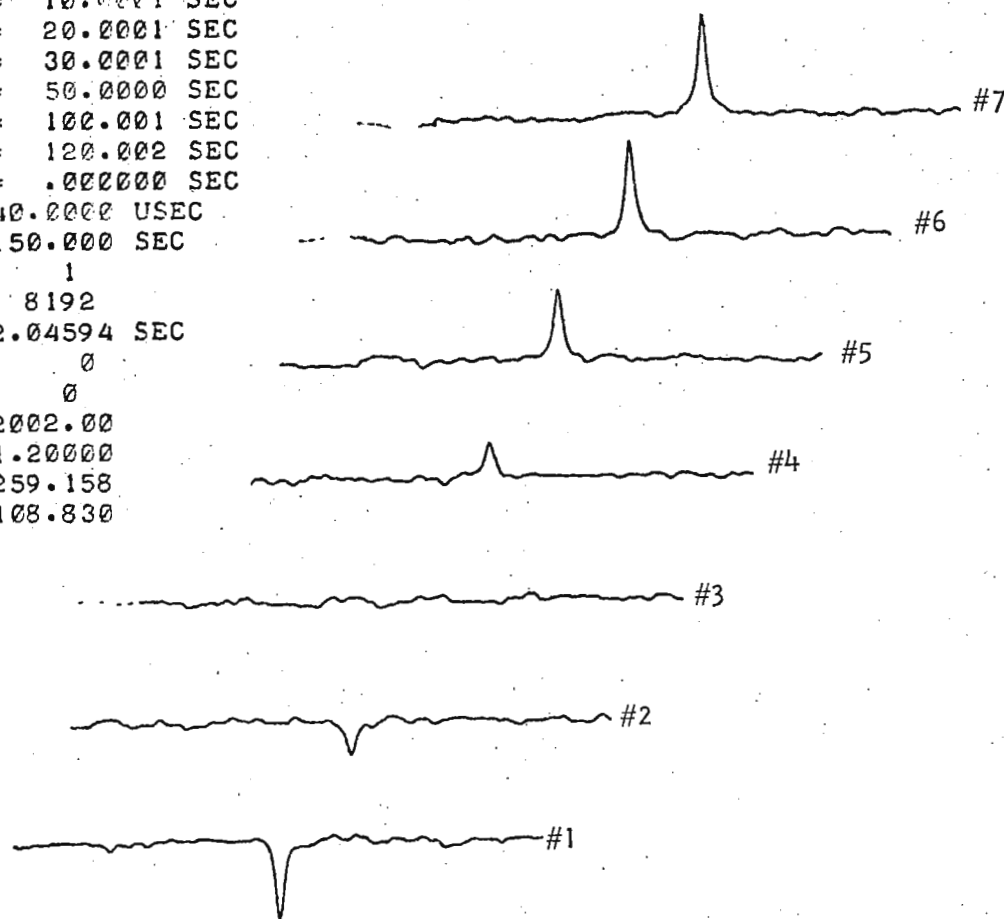


Figure 2.

Approximate T_1 for CdCl_3 is 28.86 sec.

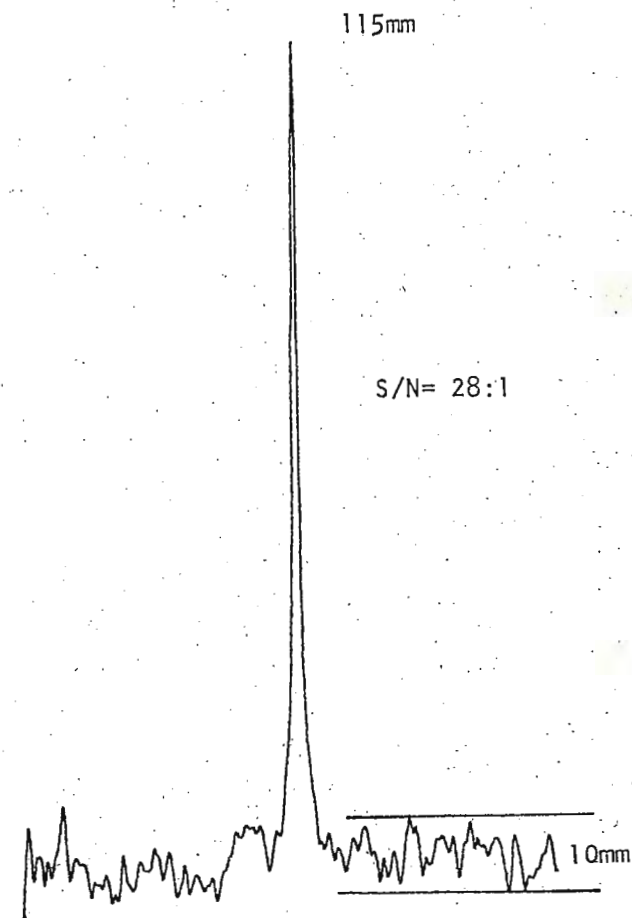


Figure 3.

A 150 Hz plot (20 Hz/cm) of the CdCl_3 spectrum.

Standard Oil Company (Indiana)

Amoco Research Center
P.O. Box 400
Naperville, Illinois 60540
312-420-5111

October 12, 1976

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

Dear Barry:

Quantitative Analysis by ^{13}C Fourier Transform NMR

For the last two years we have been doing quantitative ^{13}C measurements by the Fourier transform technique on petroleum samples. One of the parameters most frequently sought in the petroleum industry is the percent aromatic carbons in a sample or $\%C_A$. In the past these measurements were obtained on a Varian CFT-20 spectrometer. The conditions we are using are: an 80° pulse (we determine a 90° pulse and back off slightly), a delay between pulses of 100 s, an acquisition time of 1.024 s with 8192 data points (spectral width of 4000 Hz), and the decoupler is gated on only during data acquisition. This procedure should suppress any NOE problems. The sensitivity limitations of a CFT-20 require an experimental time of about 10 to 16 hours.

We expect that most carbons having long T_1 's will be aromatic. Consequently, the value of $\%C_A$ should increase with an increase in the pulse delay until a uniform value is reached at a pulse delay greater than $3 T_1$'s. On the CFT-20 we found $\%C_A$ values were equal, within experimental error, for delays of 100 s and 200 s. Consequently, we have selected 100 s as our pulse delay.

Recently we have acquired a Nicolet TT-14 spectrometer. Its higher sensitivity has allowed us to reduce our measurement time to one hour per determination. Since we generally make three determinations of $\%C_A$ per sample this has drastically increased our sample handling capabilities. The superior integration routine has increased our precision from about 1.5% on the CFT-20 to about 0.6% on the TT-14. The higher sensitivity has also enabled us to determine the effect of longer delays on our $\%C_A$ measurements. Values on a single gas oil are shown in the table.

<u>Pulse Delay (s)</u>	<u>Total Time (hr)</u>	<u>No. of Scans</u>	<u>%CA</u>
0	0.01	36	25.3
1	0.02	36	30.7
2	0.06	36	31.4
5	0.06	36	33.5
10	0.11	36	33.4
20	0.21	36	34.6
50	0.5	36	35.2
100	1	36	35.7
200	10.1	180	35.6
300	15.1	180	36.1
400	11.2	100	35.9

We have of course tried to obtain quantitative measurements using $\text{Fe}(\text{acac})_3$ and have found that we consistently got lower values of %CA which we attribute to a nonuniform dispersion of the reagent over the many types of carbons present in gas oils. We feel these reagents must be used with care in quantitative work.



G. J. Ray
Mail Station F-9



R. W. Dunlap
Mail Station F-9

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY


October 5, 1976

Title: Postdoctoral Position: Density Matrix Theory of
Double Resonance

I have immediately available a postdoctoral position for research in Spin-Lock FT NMR and/or related areas. An interest on the part of the candidate in density matrix theory would be helpful but not essential.

Recently, in pondering the effects of strong rf double resonance fields on spin lock experiments (e.g. $\text{C}\{\text{H}\}$) I have reviewed what I used to know about density matrix theory. It seems that most extant theories of double resonance contain limitations on the strength of at least one of the two rf fields or other inhibiting assumptions. I finally realized that the time dependant density matrix equations can, with some rearrangement, be solved directly by a Runge-Kutta iteration to produce an FID directly. The theory is quite general, limited by one's abundance of computer time, although we have had only mixed success in situations where the decoupling field strength is time dependant (as in broad-band decoupling). This could be a mathematical problem in solving the differential equations. Results are too preliminary and unclear to report in any definitive fashion.

Yours very truly,



J. H. Noggle
Professor

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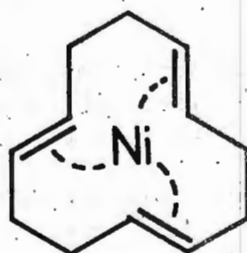
Professor B. L. Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, Texas

Title: ^{13}C NMR Spectra of some Nickel-Olefin Complexes

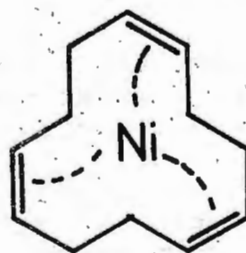
Dear Professor Shapiro,

Our CW XL-100-15 was converted by Varian into an FT-spectrometer just over a year ago, and we are very satisfied with the performance that the instrument has been giving us.

Recently we have measured the ^{13}C NMR spectra of some nickel complexes of 1,5,9-cyclododecatriene (CDT)¹. The data for (all trans-CDT)Ni (I) and (all cis-CDT)Ni (II)



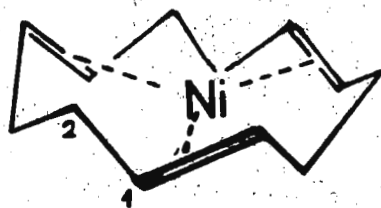
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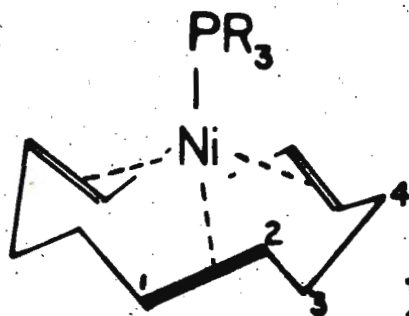
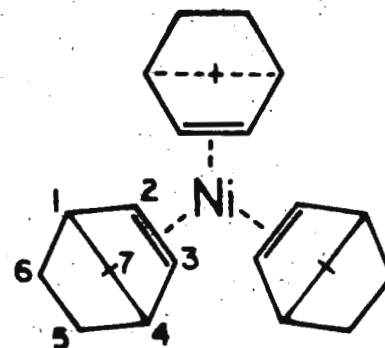
II

are given in the table. All the double bonds in these compounds are complexed and only two signals are found - one for the olefinic carbons and one for the methylenic carbons. The complexation shift ($\Delta\delta$) of the olefinic carbons in I is only -25.0 ppm (i. e., signal is shifted to greater shielding). Extended Hückel calculations indicate that for tris-olefin complexes of nickel(0) a planar arrangement of the double bonds should be the most favourable.² However, the double bonds in (all trans-CDT)Ni are arranged propellor-like around nickel (Ia), so that the optimum metal-olefin interaction is not possible. The complexation shift for the (all cis-CDT) complex in which the double bonds can take up a planar

arrangement about the nickel atom (IIa), is considerably greater (-41.5 ppm).

**Ia****IIa**

We have also examined the ^{13}C NMR spectra of a number of (all trans-CDT)Ni-tertiary-phosphine and -phosphite complexes. The spectra of these compounds are consistent with a pseudotetrahedral structure (III); we find four signals of approximately equal intensities for the CDT residue, two from the complexed olefinic carbons and two from the methylene carbons.

**III****IV**

Another trigonal nickel-olefin complex that we have examined is tris(bicyclo-[2,2,1]-heptene)nickel.¹ The bicycloheptene ligands are free to rotate at room temperature and only four signals are observed in the ^{13}C NMR spectrum. At -60° 9 signals are resolved consistent with the adoption by the complex of the same configuration (IV) as that found by X-ray crystallography to be present in the solid.³ There are no signals found that can be assigned to the isomer with all bicycloheptene ligands having C_7 on the same side of the trigonal plane.

References

1. For further details, see E. G. Hoffmann, P. W. Jolly, A. Küsters, R. Mynott, and G. Wilke, Z. für Naturforschg. (in press)
2. N. Rösch and R. Hoffmann, Inorg. Chem., **13**, 2656 (1974)
3. C. Krüger and Y.-H. Tsay, quoted in K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, Angw. Chem., **85**, 1002 (1973)

Table. ^{13}C chemical shifts (rel. TMS) of some nickel complexes (ppm)

Compound

	δ_1	$\Delta\delta_1$	δ_2	$\Delta\delta_2$
all <u>trans</u> -CDT	131.6		32.7	
(all <u>trans</u> -CDT)Ni	106.6	-25.0	41.2	+8.5
all <u>cis</u> -CDT	130.5		28.3	
(all <u>cis</u> -CDT)Ni <u>a</u>	89.0	-41.5	28.8	+0.5

Compound

	δ_1, δ_4	δ_2, δ_3	δ_5, δ_6	δ_7
Bicycloheptene	42.1	135.4	24.9	48.8
(Bicycloheptene) $_3$ Ni	43.7	76.0	28.2	40.4
(Bicycloheptene) $_3$ Ni <u>b</u>	43.8	76.5	28.5	40.3
	43.8	76.2	28.2	40.3
	43.8	76.1	27.6	

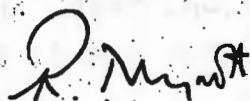
Measurements on Varian XL-100-15 FT Spectrometer at 25.2 MHz in d-toluene at $+32^\circ$, unless otherwise stated.

$\Delta\delta_n = \delta_n(\text{complex}) - \delta_n(\text{CDT})$. a. measured at 0° b. Measured at -60°
The signals for the 11 magnetically different carbon atoms have been assigned to the four types of carbon (olefinic, bridgehead, etc.) and not to individual atoms.

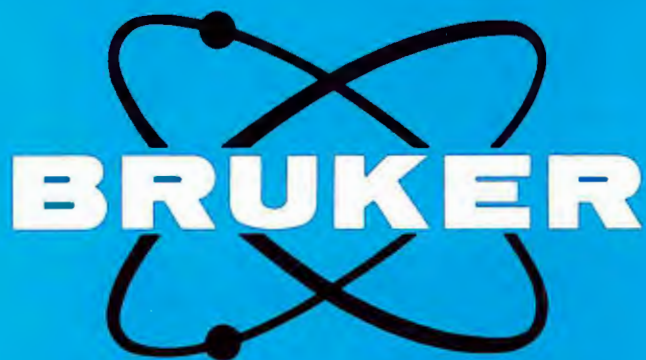
Please credit this contribution to the subscription of

Professor Hoffmann.

Yours sincerely



R. Mynott



New breakthroughs in EPR instrumentation

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A compact EPR system for routine measurements with research performance.

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2

3



4

5



STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062

(415) 497-6153

November 8, 1976

The Stanford Magnetic Resonance Laboratory is currently searching for a spectroscopist. Qualifications for the position include a Ph.D. in one of the exact sciences, experience in Nuclear Magnetic Resonance, and familiarity with NMR theory and instrumentation.

The primary duties consist of providing services as an NMR spectroscopist and scientific consultant to users of the facility, participation in the design, execution and interpretation of experiments involving the 360 MHz instrument and the sharing of responsibility with the Operations Manager for maintenance and development of NMR instrumentation at the facility. Some time for personal and collaborative research will also be available.

The position is currently advertised in accordance with University policy. The Administrative Committee for the Laboratory will be most grateful for your suggestions of suitable individuals. Nominations and applications from women and members of minority groups are especially welcome. It would be greatly appreciated if all applications could be received by December 15, 1976.

Sincerely,



Alice Walker
Administrative Assistant



LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, October 19, 1976

KRIJGSLAAN 271 - S 4
(België - Europa)

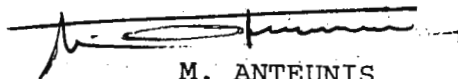
Tel. 22 57 15

Post-doc position available.

A post-doc fellowship for one year or longer in my group in Ghent has become available for people interested in structural chemistry, mainly assisted by NMR Spectroscopy.

Applicants should contact me before January 1977.

Yours sincerely,



M. ANTEUNIS
State University of Ghent
Dept. Organic Chemistry
Krijgslaan 271 (S4-bis)
Ghent - B-9000, Belgium



DEPARTMENT OF THE NAVY
NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:
3852/DWM:lkj
14 October 1976

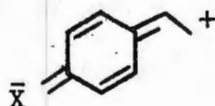
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Title: ^{13}C Shielding in p-Substituted
Alkylbenzenes - the β -Effect

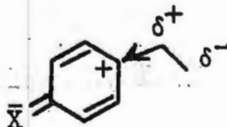
Dear Barry:

Guy Jordan, a National Research Council Postdoctoral Associate here, has just finished an interesting and instructive study of ^{13}C shifts in p-substituted ethyl- and propyl-benzenes in order to compare β -carbon shieldings with corresponding styrenes. The results provide a nice comparison of inductive vs. resonance effects.

In p-substituted styrenes there is a large positive dependence of the β -carbon shift on the electronegativity of the substituent.¹ A plot of the shift against Hammett σ -values has a slope of 6.5 ppm, indicating significant shielding contribution from the quinoid resonance form:



In contrast, the plots of ^{13}C shifts in the substituted alkylbenzenes show an opposite trend. Although the α -carbon shifts (Fig. 1,2) show essentially no correlation with the Hammett σ -value of the substituent, the β -carbon shifts (Fig. 3,4) have a small, but clearly negative, slope, with values of -0.74 and -0.69 ppm for the ethyl and propyl derivatives. The mechanism by which the more strongly electron-donating groups actually reduce the β -carbon shielding must involve an alternant inductive effect:²



The γ -carbon shift for ten propylbenzenes (Fig. 5) shows essentially no variation that can be ascribed to a substituent effect.

Sincerely yours,


D. W. MOORE

1. K. S. Dhami and J. B. Stothers, Can. J. Chem., **43**, 510 (1965)
2. J. A. Pople and M. Gordon, J. Amer. Chem. Soc., **89**, 4253 (1967)

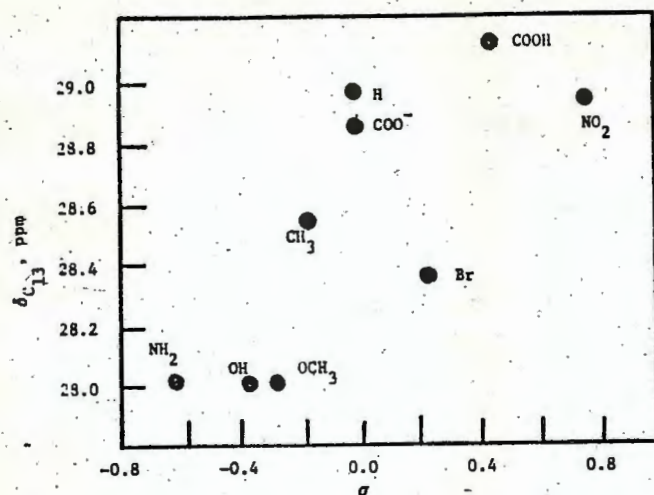


Figure 1. Substituent effect on α carbon chemical shift of para-substituted ethylbenzenes.

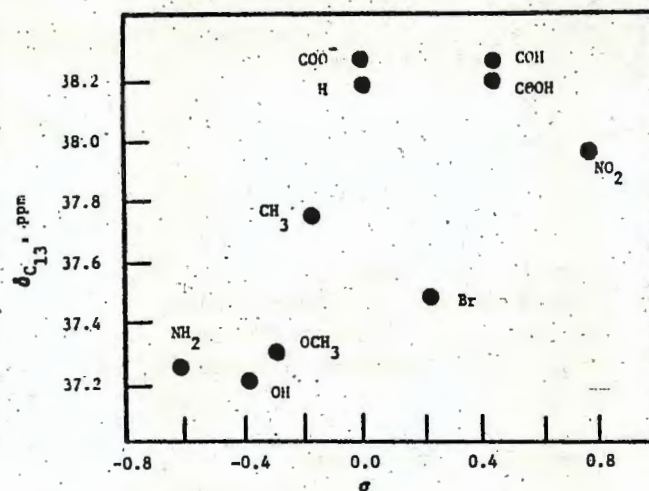


Figure 2. Substituent effect on α carbon chemical shift of para-substituted propylbenzenes.

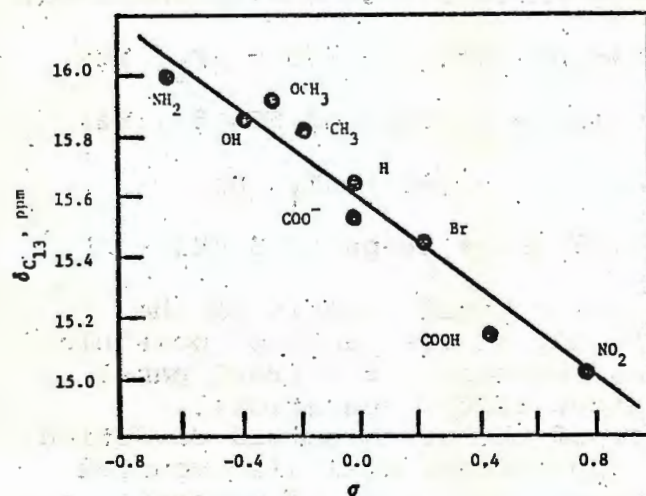


Figure 3. Substituent effect on β carbon chemical shift of para-substituted ethylbenzenes.

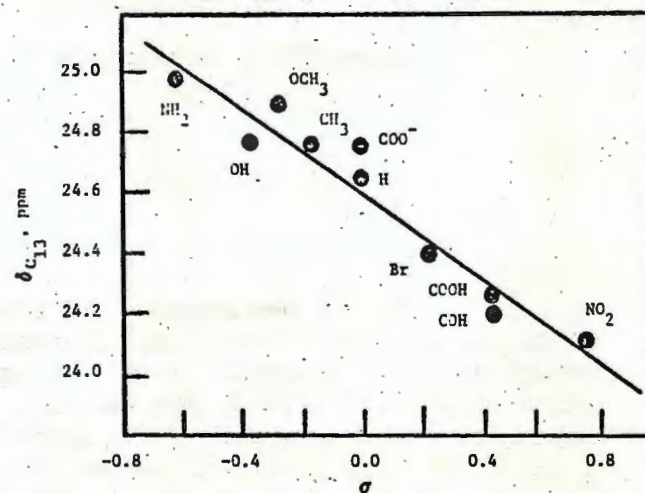


Figure 4. Substituent effect on β carbon chemical shift of para-substituted propylbenzenes.

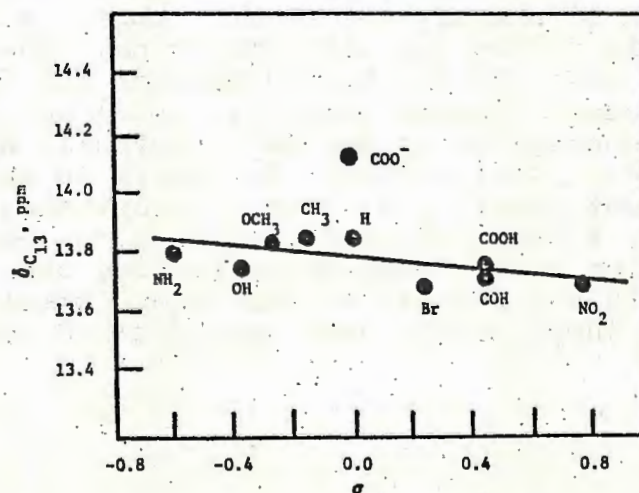


Figure 5. Substituent effect on γ carbon chemical shift of para-substituted propylbenzenes.



McMASTER UNIVERSITY

Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1

Telephone: 525-9140

October 15, 1976.

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

Dear Dr. Shapiro:

Re: Changing ^{19}F Frequency of Bruker WH-90

Fluorine, because of its large chemical shifts, requires a flexibility of observing frequency which is not easily obtained.

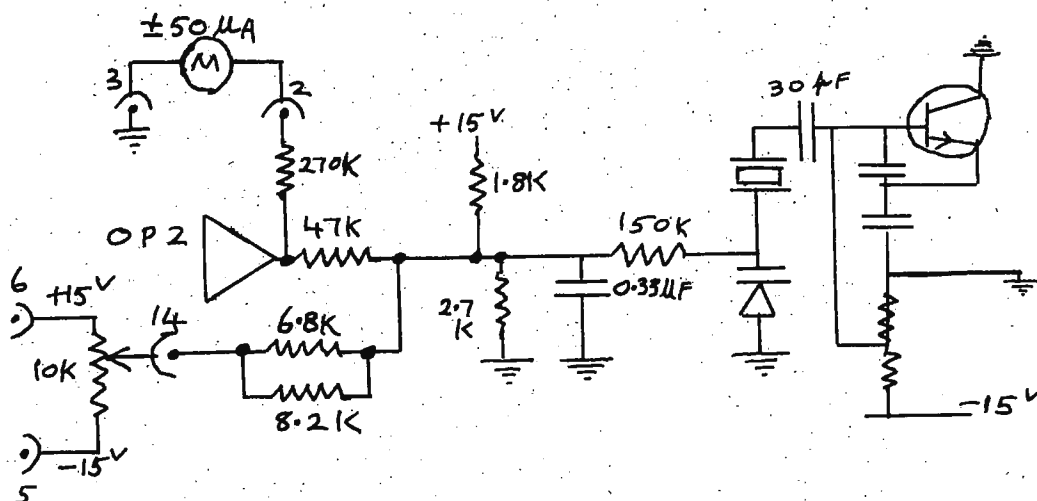
$$\text{Observing frequency} = 9 \text{ (sync. osc.)} - (90 + \Delta F_1) \text{ MHz}$$

$$= 9 (19.41 + \text{steps of } 555.5 \dots \text{Hz})$$

$$- (90 + \Delta F_1) \text{ Hz}$$

$$= 84.69 \text{ MHz} + \text{steps of } 5 \text{ KHz} - \Delta F_1$$

It is desirable to lock the crystal circuit of the sampling synchronised oscillator to any of its range of possible frequencies. A small $\pm 50 \mu\text{A}$ meter mounted on the front panel in series with 270 K ohm at the output of the operational amplifier OP2 is used as a detector of the synchronised condition. A 10 K 10 turn potentiometer with appropriate dial also mounted on the front panel replaces the preset P3 (and P4 if present). With no other changes, the 10 turn pot will give a range of locked frequencies. In our case, the maximum frequency was still not high enough, and so the crystal had an additional 30 pF put in series with it. This was conveniently done by isolating one end of the crystal on its copper island, and bridging the newly formed gap with the 30 pF. The final circuit is as shown, and gave -30 KHz to +40 KHz for the full 10 turns of the potentiometer. Larger capacities will not give such a high maximum frequency; going smaller eventually will not allow oscillations. Dial settings for every 10 KHz are displayed on the front panel. These are approximate, changing with temperature, fitting of oscillator covers, etc. The essential criterion is a steady meter reading near zero, which changes with the setting of the potentiometer until it oscillates or jumps to the next synchronized setting.



MODIFIED SECTION OF SAMPLING OSCILLATOR

HA-100 magnet coil breakdown

This topic is almost on the list of those unacceptable for this newsletter. However, perhaps as a supplement to the previous item, it may pass.

Our HA-100 has a high impedance magnet, V-4014 with V2100B power supply complete with 304TL passing tubes. Tests on the Monday morning after the weekend failure while running unattended indicate that the magnet coils had developed an electrical breakdown to ground and the smell was typical of the disastrous failure which occurs from time to time in transformers, chokes, etc. After 10 years continuous running, a breakdown similar to an earlier failure in the DP-60 magnet seemed to have taken place. The situation was compounded by a loss of recirculating water to the raw water drain, although the flow protection of the V3520A would normally cut off power before a dangerous situation resulted.

However, closer inspection and tests revealed that the electrical breakdown was in the terminal block of the coil sections of the higher voltage half on the magnet and that the overheating and source of smell was confined to the terminal block and its immediate surroundings. Tidying up this area and reorganising the junctions of the ends of the coils put the HA-100 back in operation once again. Checking the exact source of the breakdown had thus "saved" more than \$11,000, and the experience may be useful to others in similar circumstances. It is worthwhile to find the exact point of electrical breakdown of magnets.

Yours sincerely,

J. I. A. Thompson

J. I. A. Thompson
Senior Instrument Technician

COMPAGNIE D'APPLICATIONS MÉCANIQUES

CAMECA103, B^e SAINT-DENIS
92400 COURBEVOIE (France)

AL'ELECTRONIQUE AU CINÉMA ET AL'ATOMISTIQUE

October 18, 1976

Dear Pr Shapiro,

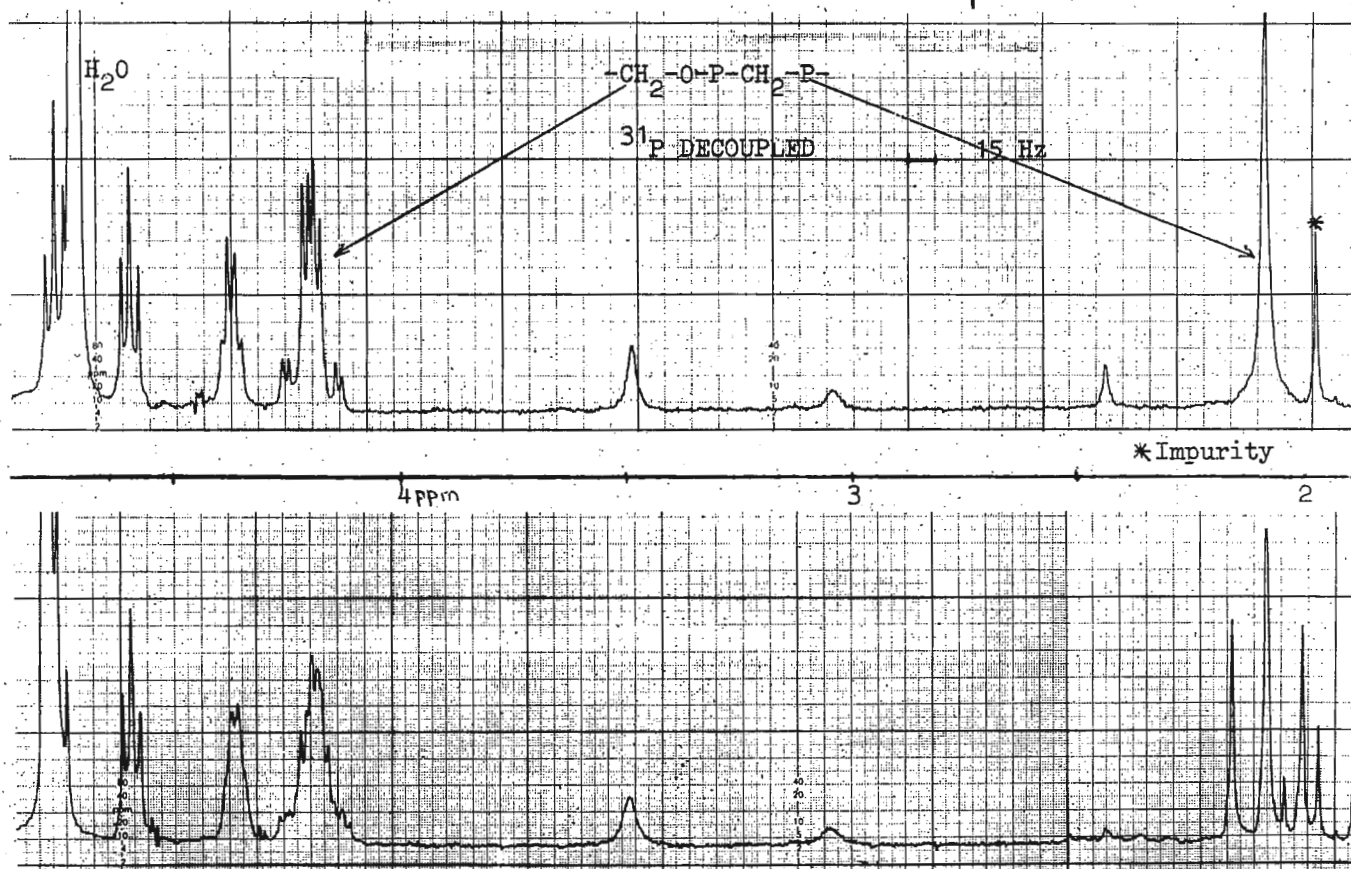
Title : 101 MHz ^{31}P heteronuclear decoupling

In response to your pink letter, here are some preliminary results of ^{31}P heteronuclear decoupling which is now operating in selective or noise modulated mode at 101 MHz, observing proton in Fourier Transform at 250 MHz on our RMN 250 spectrometer.

The figure shows the proton of α , β methylene adenosine 5'-biphosphate (AMP- CH_2 -P) with and without phosphorous decoupling. Sample contains two ^{31}P nuclei which have a chemical shifts difference equal to 10 ppm. Six watts are sufficient to decouple the two ^{31}P nuclei. Stared line is due to the monophosphate as impurity. Shift of H_2O is due to a small change of the temperature of the variable temperature probe to allow the observation of the triplet in the decoupling experiment.

Such heteronuclear plugs are available on requested nucleus and used on the same standard 250 MHz ^1H probe.

J.J. Tassin
J.J. TASSIN



Spectra realized by Mr TRAN DHIN SON - Centre d'Etudes Nucléaires de Saclay (FRANCE)

State University of New York
at Stony Brook
Stony Brook, New York 11794

Department of Chemistry
telephone: (516) 246-5050 / 5051

Stony Brook

October 20, 1976

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

Dear Barry:

I should like to seek your assistance in locating a suitable individual for a postdoctoral position in my laboratory commencing anytime before February 1, 1977. The research would be in utilizing tritium nuclear magnetic resonance spectroscopy to determine the stereochemistry of selected biosynthetic reactions. In addition, the candidate will assist in the instructional program in organic chemistry.

The research requires expertise in three different areas--synthetic organic chemistry (in order to prepare suitable substrates stereo-specifically labeled with tritium), biochemistry (in order to maximize the biosynthetic conversion in either in vitro or in vivo systems),³ and magnetic resonance (in order to optimally obtain and interpret the ¹H NMR spectra). A candidate with accomplished skills in any one of the areas of expertise will be seriously considered.

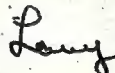
The salary for the period (until 12/31/77) will be at the rate of \$10,000/year and some travel expenditures will be paid for.

Please have suitable candidates contact me directly. In order to be seriously considered, at least two confidential letters of recommendation from people who can adequately assess the candidate's accomplishments and potential must be forwarded.

The State University of New York at Stony Brook is an equal opportunity employer.

Thank you very much for your assistance.

Sincerely,



Larry Altman

LA:dc

Before you order
a Fourier transform accessory
for your nmr spectrometer
you should consult
Transform Technology Inc.
The name is new
but the personnel have
many years experience
in the spectroscopy field.
Write or call collect
to discuss your requirements.

TTI
TRANSFORM TECHNOLOGY INC.
2280 Ross Road, Palo Alto, California 94303
Phone 415/969-2076
(an affiliate of Nicolet Instrument Corporation)

Remember this ad?

We ran this ad in mid-1972 when six of us formed Transform Technology Incorporated with the help of Nicolet Instrument Corporation. Now, less than four years later we have over three dozen employees and are now a Nicolet operating division, known as Nicolet Technology Corporation.

What has happened since our first ad? Well, we don't mind tooting our horn by pointing out that NTC has become established as a leader in the development of FT NMR equipment. We have developed, produced and installed scores of FT accessories for use on instruments such as the XL-100, HR-220, T-60, R-12 and R-32. In fact, for over a year we have been the leader in U.S. sales of FT data systems. Now we're working on becoming the leader in overseas sales as well.

Why the success story? We feel it's because we're responsive to customers' needs. Being a relatively small group of dedicated souls we can move quickly in the development of equipment which utilizes the latest techniques.

Consider some of our "firsts" in commercial equipment:

FIRST to employ a single sideband crystal filter for improved signal-to-noise ratio,

FIRST to provide phase shifted rf pulses for high resolution T_2 studies,

FIRST to use Quadrature Phase Detection,

FIRST to provide plots of relaxation recovery curves with data points, and

FIRST to develop a complete software package which includes provision for five methods of measuring T_1 values and three methods for T_2 values.

You can be sure that we are actively working on new "firsts." For example, we'll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another "first."

NTC NICOLET
TECHNOLOGY
CORPORATION

145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076
(formerly Transform Technology Inc.)

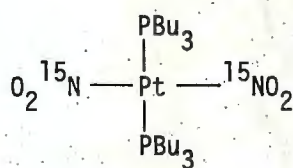


One Bond Platinum-Nitrogen & Platinum-Phosphorus Couplings
in cis & trans $\text{Pt}(\text{}^{15}\text{NO}_2)_2(\text{PBu}_3)_2$

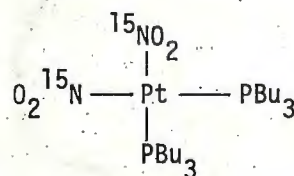
Dear Prof. Shapiro,

Although there is a strong tendency towards the study of ^{15}N in natural abundance, we still find it useful to study enriched substrates, especially when solubility is a problem. This is often the case for transition metal complexes containing nitrogen ligands. We have already suggested¹ that the coupling of ^{15}N to ^{195}Pt ($I = 1/2$, natural abundance = 34 %) can be of interest and as a follow-up we have been looking at some systems where all the ligands and the metal are readily measured by nmr techniques.

Given below are some values for $^1\text{J}(\text{Pt}, \text{N})$ and $^1\text{J}(\text{Pt}, \text{P})$ in the complexes cis & trans $\text{Pt}(\text{}^{15}\text{NO}_2)_2(\text{PBu}_3)_2$.² Worthy of note is the good correlation between the increase in $^1\text{J}(\text{Pt}, \text{P})$ on going from trans to cis and the increase in



trans



cis

$$^1\text{J}(\text{Pt}, \text{N}) = 453 \text{ Hz}$$

$$^1\text{J}(\text{Pt}, \text{P}) = 2,728 \text{ Hz}$$

$$= 390 \text{ Hz}$$

$$= 2,996 \text{ Hz}$$

$^1\text{J}(\text{Pt}, \text{N})$ on going from cis to trans. We haven't changed our opinions on how one should explain these observations.¹ Not surprisingly $^2\text{J}(\text{N}, \text{P})$ in the cis isomer is, about one order of magnitude larger than in the trans analog.

We should like to announce that a post-doctoral position involving nmr (^{195}Pt , ^{31}P & ^{15}N) studies of metal complexes may be available some time around June 1977. Salary in the range \$14,000/year.

Interested parties should write to me directly.

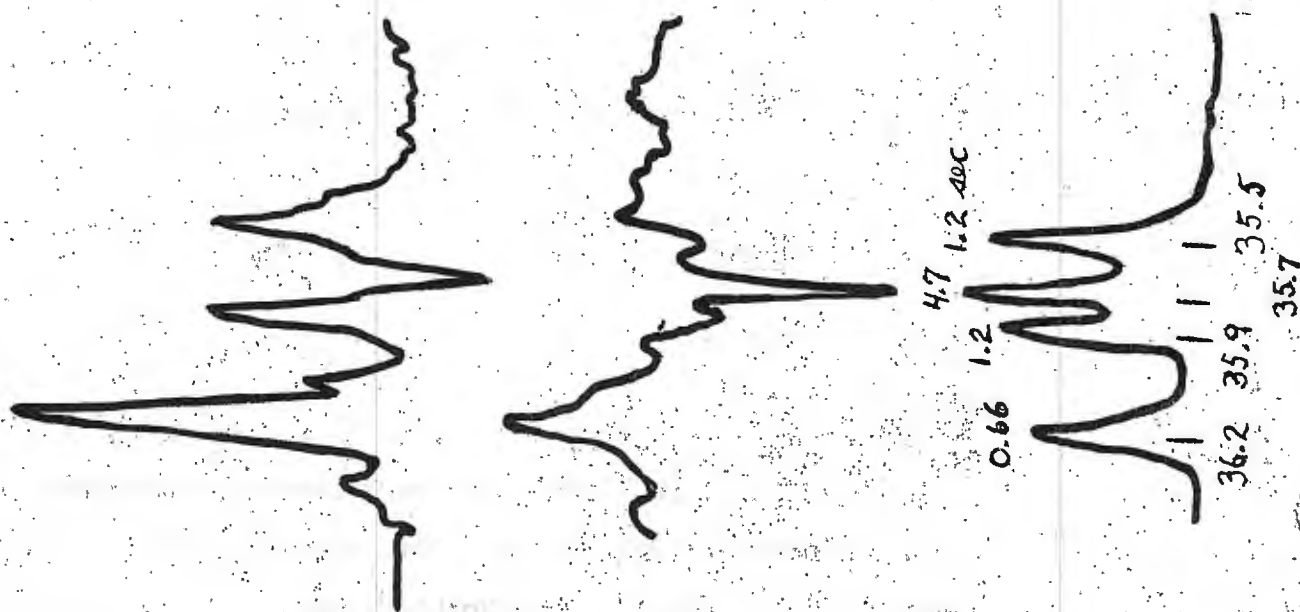
Please credit this contribution to the account of Prof. L. M. Venanzi.

Best wishes

Paul Pregosin
Dr. P. S. Pregosin

- ¹ P. S. Pregosin, H. Omura and L. M. Venanzi, J. Amer. Chem. Soc. 95, 2047 (1973).
- ² R. W. Kunz and P. S. Pregosin, unpublished results.

(CONT'D. FROM P. 22)





TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129
817-926-2461

Department of Chemistry

October 25, 1976

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

Dear Barry:

Recently we have taken to playing the game of measuring steroid carbon T_1 's in an effort to see just how far one can push such numbers to conclusions about molecular structure as well as chemical shift assignments. Being new to the game we started by doing some systems which have already been reported in the literature. Because of the strong concentration dependence, T_1 's in different molecules can only be compared by carefully maintaining the same concentrations and temperature for all determinations. Upon examining our data, we've become rather sassy about our abilities to get good numbers using the FIRT technique.

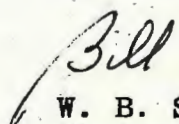
One rather trivial result will be reported here with more significant stuff to follow (hopefully). In their original work Roberts et al., JACS, 91 7445 (1969) assigned the four lines in 3-cholestanone clustered around 36 ppm to carbons 10, 8, 20 and 22 in progressive order downfield. Subsequently, Wehrli, Adv. Mol. Relax. Proc., 6, 139 (1974) altered the downfield sequence to 20, 10, 22, 8 based upon relaxation measurements. Since not all of the experimental details could be given in his article, it is a little hard to reconstruct the argument. However, his solution was quite concentrated (1.8M) and resolution for steroid C-13 NMR suffers under these conditions plus the fact that T_1 's are shortened and badly compressed. Thus, Wehrli's reported values 0.19, 0.14 and 0.16 sec for carbons 20, 22, and 8 respectively--not likely a significant difference.

*

Shown below is an expanded version of the region in question with two partially relaxed spectra above. The frequencies and T_1 's are given (the latter from a far more detailed study than shown). The line at 35.7 is clearly the slowly relaxing carbon 10; while that at 36.2 belongs to the C-22 methylene. Relaxation rates cannot differentiate between C-8 and 20. However, earlier chemical shift reagent studies on 3 β -cholestanol are consistent with the assignment shown, and it seems unlikely that the alteration at the 3-position would change this.

Yours sincerely,

* see p. 21.


W. B. Smith,
Chairman

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

*School of Medicine G3*DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

October 21, 1976

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

Multinuclear FT on the NV14

Dear Professor Shapiro:

Quite a while ago, we acquired an NV14 (CW, 60MHz protons, homo lock) with the idea of mating it with a computer and converting it to FT, multinuclear, deuterium lock. The labor involved was, as ever, a lot more than the block diagram would lead one to think. In fact, at one point, we re-named the NV14 the DH60, since Bruker has a Work Horse 60 while we were beating a Dead Horse. But now, we are pleased to report that the horse lives and is running nicely.

The system uses no I.F. but lets the frequency synthesizer provide the transmitter frequency directly, and mixes the broadband preamplifier output to give the baseband (low frequency) output directly. Lots of care must be taken against R.F. leakage, such as locating the mixer and FT gates and first A.F. amplifier very close to the frequency synthesizer, i.e. mounted on its back.

What we particularly wanted to report on is what we think is a useful improvement on D. Traficante's multinuclear probe using a tapped coil (Journal of Magnetic Resonance 15, 484-497 (1974)).

The goal in these multinuclear probes is to tune easily over a wide frequency range without radically changing the output impedance of the probe and thus degrading the signal to noise ratio (S/N). The circuit losses should be low and all located in the NMR coil proper.

The conventional matching circuit using two capacitors shows good S/N but is only useful over a very narrow frequency range.

Traficante and Simms used a tapped coil (a) with great success. There are some difficulties with this approach, however. The tap occurs very near to the end of the coil. In fact, for the coil we made (16 turns, maximum frequency 40 MHz), the tap had to be placed $\frac{1}{2}$ turn from the end to provide 50 ohms at 25 MHz. At higher frequencies, the construction becomes even more peculiar. It is also inconvenient to change the matching adjustment

once the coil is built into the probe.

The matching can also be accomplished (b) by in effect moving the last piece of the coil out into the probe where there is no mutual inductive coupling. It is then found that more turns may be used e.g. about 2 turns in the above case. The NMR coil is then a conventional coil, and could perhaps even be one from a single-frequency probe. The plot of impedance vs. frequency is about the same for both methods. We decided to use two probes to cover the frequency range of 5.5 to 38 MHz rather than compromise too much on matching using one probe only. We cover each frequency range (ca. 2.6:1) with a single tuning capacitor C1 whose capacitance ratio is increased by a factor of 3 through application of silicone grease to the plates. Time will tell if this is a good idea.

The sensitivity was compared between the three methods on the bench at a single frequency (25 MHz, 50 ohm match) by insertion into the NMR coil of a tickler coil emitting a standard level CW signal. All three methods gave the same result.

The circuit is shown (c) double tuned for internal lock. To prevent too much interaction with the observe circuitry L3 must be made with perhaps 5 times as much inductance as the NMR coil L1. C2 and L3 resonate at the lock frequency. There is a compromise on the sensitivity in the lock channel.

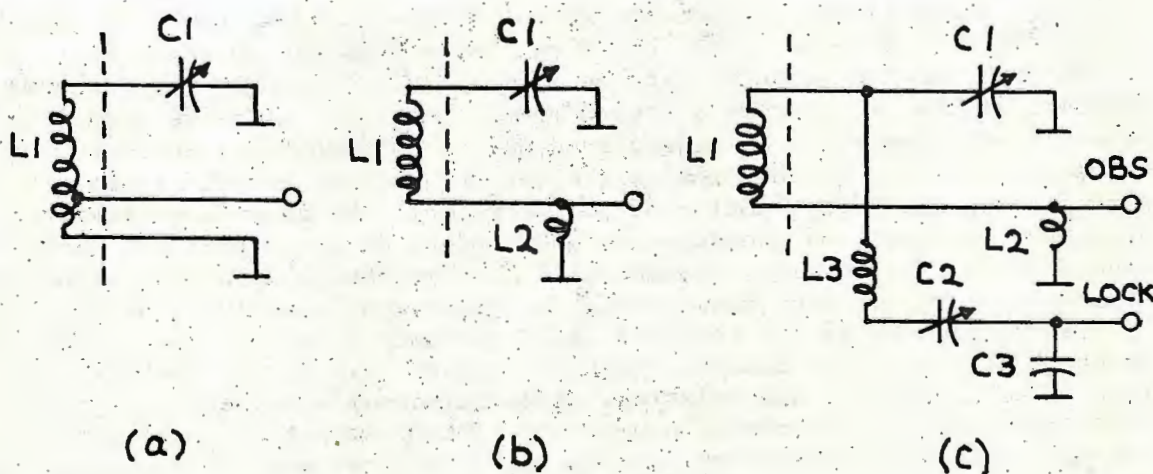
The actual sensitivity in the observe channel was as good (when measuring ^{31}P at 24 MHz) as with a probe designed especially for phosphorus and better than the sensitivity of the XL100 with the conditions (frequency, sample volume, etc.) converted to those of our machine.

Please credit this contribution to M. Cohn's account.

Yours Sincerely,

James L. Engle

James L. Engle



- (a) Multinuclear probe using Traficante tapped coil
- (b) Impedance matching using a discrete coil
- (c) Double tuning for internal lock

UNIVERSITY OF DENVER

UNIVERSITY PARK • DENVER, COLORADO 80210



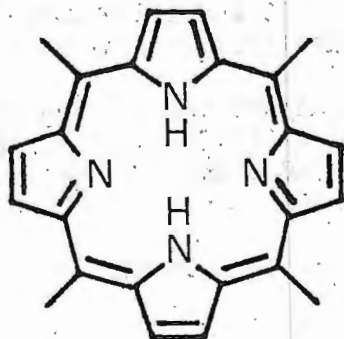
DEPARTMENT OF CHEMISTRY / 303.753-2436

October 22, 1976

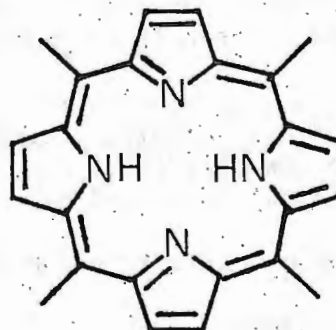
Prof. B.L. Shapiro
 Department of Chemistry
 Texas A&M University
 College Station, TX 77483

Kinetic Isotope Effect on Proton Tautomerism in Tetra-aryl-porphyrins

Dear Barry,

Proton tautomerism ($I \rightleftharpoons II$) in tetra-aryl-porphyrins exhibits an enhanced

I

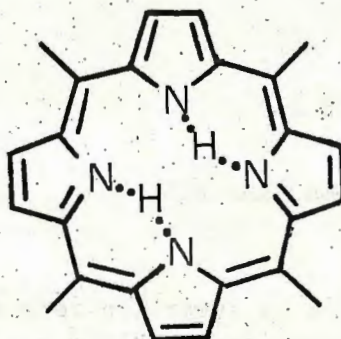


II

kinetic isotope effect. Storm and Teklu¹ estimated k_H/k_D to be 67 and Abraham et al.² obtained a value of 12, based on single temperature estimates. Storm's suggestion that the enhanced isotope effect could be due to simultaneous movement of the two hydrogens seemed worth checking. Since we have been investigating the range of molecular dynamics in porphyrins and metalloporphyrins we were interested in determining whether the isotope effect relates to the simultaneous equivalent motion of two hydrogens. We have found that the rates of proton and deuterium exchange are independent of concentration, phenyl ring substituents, and solvent, consistent with a mechanism involving simultaneous movement of the two hydrogens through a symmetrical transition state, III.

At slow exchange the chemical shift difference between the pyrrole protons in protonated and unprotonated rings is 18.5 to 22.0 Hz (at 100 MHz) for 1,1,2,2-tetrachloroethane solutions of tetra(pentafluorophenyl)porphyrin, tetra(p-trifluoromethylphenyl)porphyrin, tetra(p-isopropylphenyl)porphyrin, and tetra(p-diethylaminophenyl)porphyrin. A typical two site exchange pattern is observed between -50° and +10° C for the N-H form of the porphyrin. However, when MeOD is added to the sample, forming the N-D porphyrin, exchange is observed between -10° and +50° C. By total lineshape analysis we have determined the rates of tautomerism for these porphyrins in both the N-H and N-D forms throughout the exchange region. We find that the ratio of the rates

for proton and deuterium tautomerism, k_H/k_D , at 298°, 263°, and 243° is 19±5, 32±7, and 48±14, respectively.



III

The isotope effect on tautomerism is consistently greater than the semi-classical values for breaking an N-H bond. If two N-H vibrations are largely eliminated in the transition state, the isotope effect at 298°K could be 70 - 80. We thus believe that the porphyrins are the only class of compounds in which the simultaneous and exactly equivalent motion of two hydrogens has been observed and the kinetic isotope effect determined.

We submitted the details for publication in J. Amer. Chem. Soc. in late July and the manuscript was finally disgorged, without criticism, by the referees this week.

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2. R.J. Abraham, G.E. Hawkes, and K.M. Smith, Tet. Lett. (16) 1483 (1974).

Sincerely,

Sandy
Sandra S. Eaton

Gareth
Gareth R. Eaton

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

3, place du Château 1005 Lausanne (Suisse)

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

October, 21, 1976

FRUSTRATING PROBLEMS IN T_1 MEASUREMENTS.

Dear Dr. Shapiro,

Our studies of ^{17}O and ^2H T_1 's by inversion recovery Fourier transform techniques have led to several experimental difficulties each of which has been discussed in the literature. However the sum of all of them took us several months to correct and we thought it worth reviewing the problems in order that others new to the field might not repeat our errors. These problems are particularly important in quadrupolar relaxed systems where $T_1/T_2^* \approx 1$ and in single coil spectrometers where H_1 homogeneity is liable to be poor.

The first problem resulted from non-ideal pulses (H_1 inhomogeneity) which are virtually inherent in single coil spectrometers. An inhomogeneous H_1 leaves a net component of magnetization in the x-y plane after the 180° pulse. This component, after the 90° pulse, results in an echo which is added to the normal FID causing non exponential behaviour of the inversion-recovery. Demco, et al.¹ discuss this problem and a solution, Cutnell, et al.² present a solution which is formally the same but somewhat faster and more elegant. Their technique is to apply the pulse sequence $\{180_x^\circ - \tau - 90_x^\circ - (+AT) - PD - 180_x^\circ - \tau - 90_x^\circ - (-AT) - PD\}_n$. The phase inversion of alternate 90° pulses accompanied by complementing the FID acquired, results in the elimination of the echo while coherently adding the FID. They describe a circuit applicable to their Jeol spectrometer. Varian provides CAPS and Bruker PAPS which in principle do the same thing³. For quadrupolar relaxed nuclei, with short relaxation times, homospoil techniques are impractical, saturation recovery takes a great deal of H_1 power and progressive saturation has proven to be inaccurate so we think that the above phase inversion sequences are the only accurate ways to measure T_1 .

For reasons discussed in the literature⁴ we have determined our T_1 's by a non-linear least squares curve fit using the integral area of the power spectrum and the delay time, τ , as variables. We have found that in very wide lines (> 100 hz halfwidth) it is often difficult to decide what the frequency dependent phase should be, so the power spectrum is somewhat easier to use. But one has to be careful with the power spectrum because all noise becomes positive thus introducing a constant in the integral⁵.

The H_1 inhomogeneity causes a loss of magnetization after the 90° pulse in the phase inversion sequence above. This is equivalent to having the 180° pulse adjusted to something other than 180° . So the equation which is fit by the non-linear least squares computer program must be a three parameter fit (see Levy and Peat's equation 6)⁶. For our Bruker HX-90 spectrometer we have

found that the formal result for the flip angle is between 140° and 160° depending upon the position and shape of the sample, even when the 180° pulse has been properly set by the operator.

The final problem which we encountered was the fact that the values of τ are set by a do-loop in the BNC-12 computer and our original program set values (in the 1 to 50 millisecond range) which were not those entered by the operator at the teletype. We have found it necessary to time our delays with a counter or oscilloscope.

Since correcting these problems we estimate that our T_1 measurements are good to 10% or so.

Bill

William L. Earl

Sincerely yours

Rosalind Southwood-Jones

Rosalind V. Southwood-Jones

References.

1. D.E. Demco, P. Van Hecke and J.S. Waugh, J. Magn. Res., 16, 367 (1974).
2. J.D. Cutnell, H.E. Bleich and J.A. Glasel, J. Magn. Res., 21, 43 (1976).
3. There exist PAPS circuit boards for which the 180° pulse is inverted as well as the 90° pulse, these do not correct the echoes. We had such a problem which took us a long time to find and which was finally corrected by Spectrospin, A.G., Zurich (Bruker).
4. R. Gerhards and W. Dietrich, J. Magn. Res., 23, 21 (1976).
5. Our program for calculating the power spectrum and its integral (for use with a BNC-12 computer) should shortly be available from the Nicolet users society or we can provide details on request.
6. G.C. Levy and I.R. Peat, J. Magn. Res., 18, 500 (1975).

International Business Machines Corporation

5600 Cottle Road
San Jose, California 95193

October 27, 1976

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

Dear Barry:

I have been interested for several years in the fascinating optical "photon dressing" experiments of Cohen-Tannoudji¹ and the analogous rotating frame NMR work by Hashi.² Recently, in collaboration with Hans-Martin Vieth from Heidelberg, this interest has stimulated some experiments which led to a new type of line-narrowing technique in solids.

We use the Fourier transform of a transient nutation³ to get the rotating frame spectrum. This nutation is modulated with audio fields comparable in amplitude and frequency to H_1 and ω_1 , respectively. The top spectrum in the figure is the proton FID of adamantane at -40°C ; the bottom spectrum is the Fourier transform of the transient nutation of the same sample taken on resonance with $\omega_1 = 31$ kHz. During the nutation an audio modulation of ~ 9 gauss peak at 39 kHz is applied to a set of Helmholtz coils parallel to H_0 . The result is a line shifted downward in rotating frame frequency (from ω_1) by 15%, and narrowed by 2 orders of magnitude. This is the same width as that of a liquid under these experimental conditions. The experiment also works with the rf off resonance, so that chemical shift information is retained. Hans-Martin solved this problem both numerically and in approximate analytical form, both solutions agreeing very well with experiment.

I hope that the concept of using field (or frequency) modulation to reduce dipolar broadening appeals to those who are interested in gaining higher resolution in the NMR spectra of solids with relatively simple instrumentation.

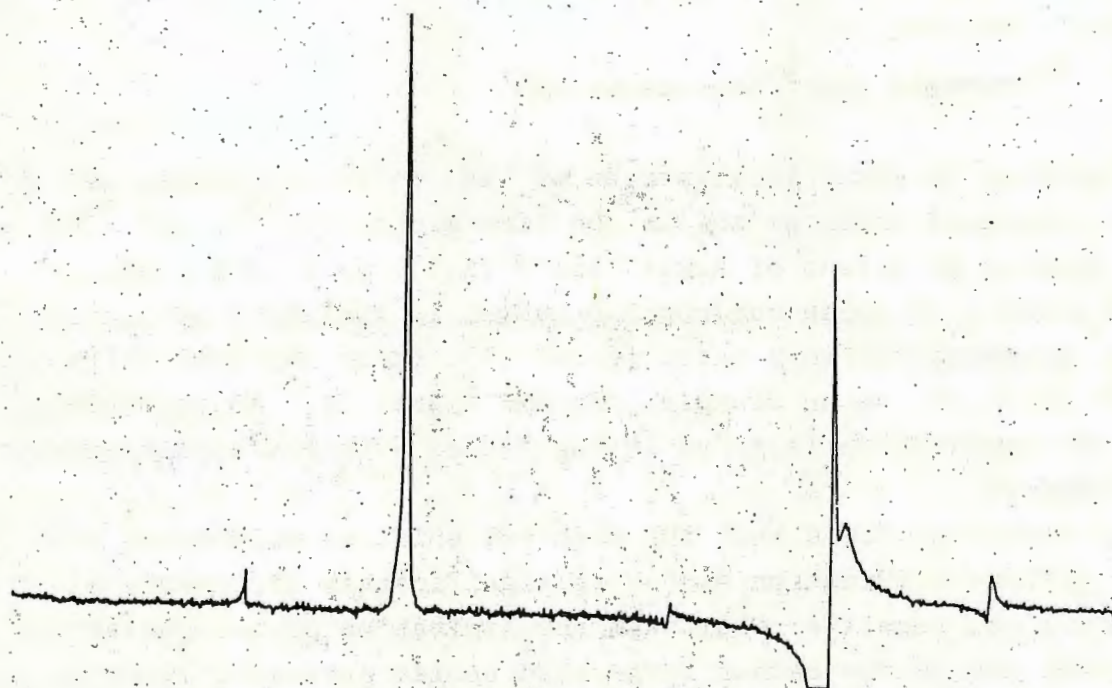
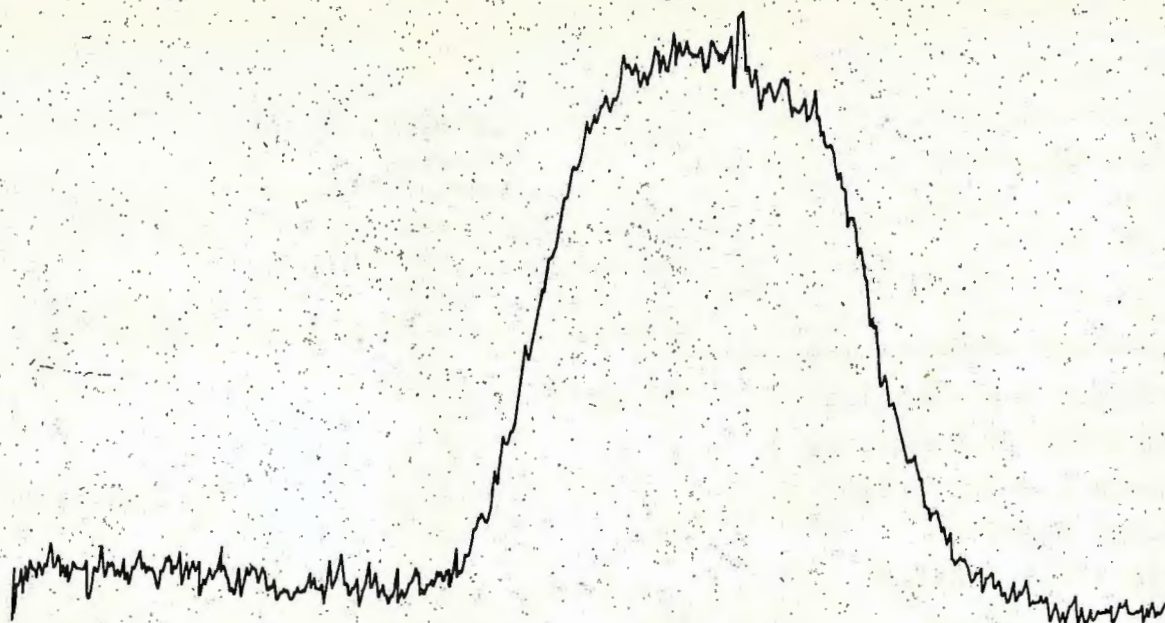
Best regards,

C. S. Yannoni

C. S. Yannoni
Research Laboratory

/to

1. C. Cohen-Tannoudji and S. Haroche, *Compt. Rend.* 262, 268 (1966).
2. M. Kunitomo and T. Hashi, *Phyr. Lett.* 40A, 75 (1972).
3. H. C. Torrey, *Phys. Rev.* 76, 1059 (1949).



Proton spectra of polycrystalline adamantane at -40°C

Top: FID: linewidth ~ 13 kHz.

Bottom: Fourier transform of modulated transient nutation: linewidth ~ 130 Hz. The sharp resonance on the right is the modulation peak.

UNIVERSITÄT TUBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz
Dr. A. Nolle

D-7400 TUBINGEN 1, den 27.10. 1976
Morgenstelle
Telefon (0 70 71) 29 67 14

Physikalisches Institut, D-7400 Tübingen 1, Morgenstelle

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

Ihr Zeichen

Unser Zeichen
Lu/Ru

Ihre Nachricht vom

Dear Prof. Shapiro,

⁵³Chromium and ⁹⁵Molybdenum NMR

Proceeding in our investigations of less receptive nuclei we have measured chemical shifts and line widths of ⁵³Cr and ⁹⁵Mo in aqueous solutions of alkali salts (1,2). As a next step, NMR signals of these quadrupolar nuclei in further compounds e.g. in carbonyls were investigated (3). Large chemical shifts were observed. As an example, the NMR signal of ⁹⁵Mo in Mo(CO)₆ in tetrahydrofuran is given in the figure with the experimental parameters.

As a result we found that the chemical shift of molybdenum in the different oxidation states is significantly different. A further but negative result was the limitation of such investigations due to the rather large quadrupolar broadened lines in asymmetrical compounds.

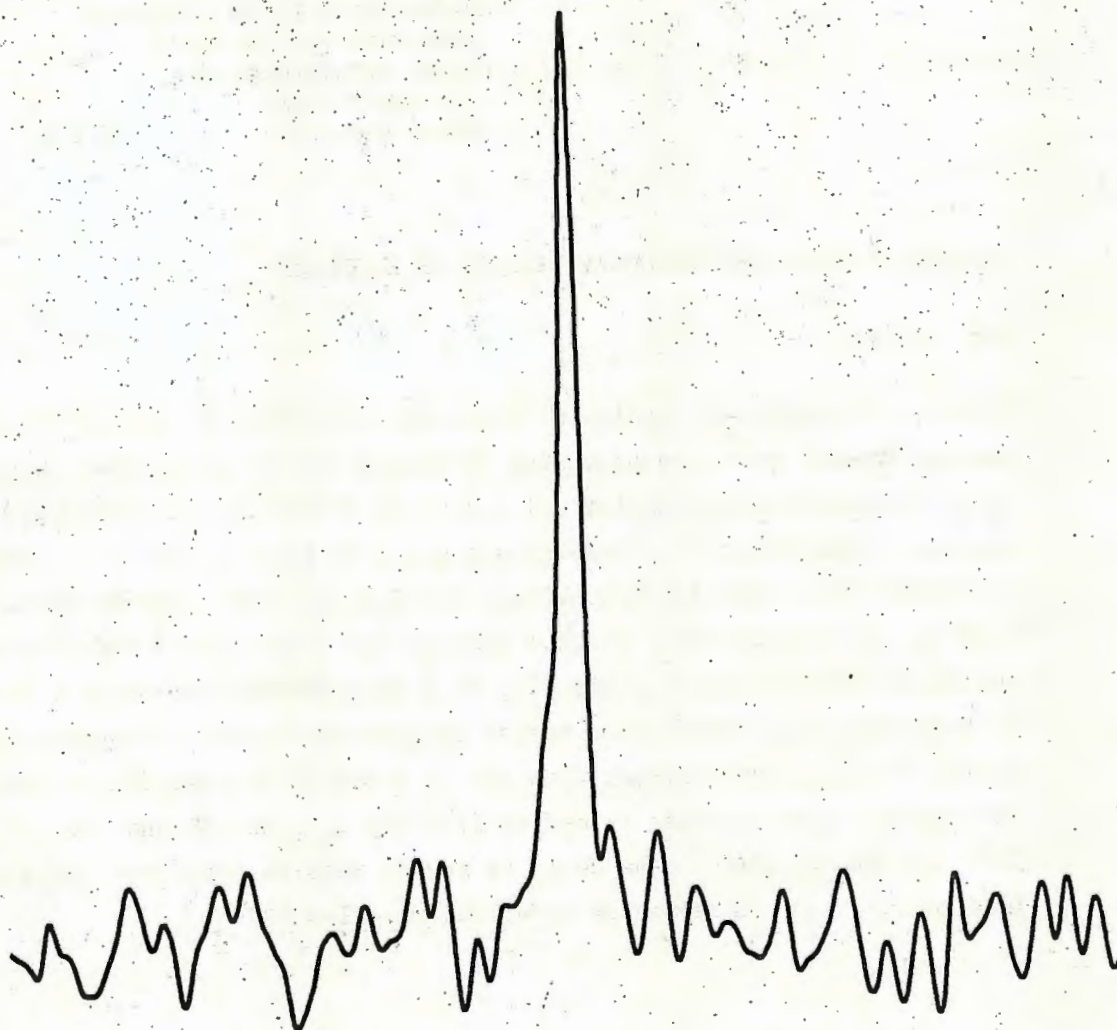
Further work in this field is running.

Sincerely

O. Lutz
(O. Lutz)

A. Nolle
(A. Nolle)

- (1) B.W. Epperlein, H. Krüger, O. Lutz, A. Nolle, and W. Mayr
Z. Naturforsch. 30a, 1237 (1975)
- (2) W.D. Kautt, H. Krüger, O. Lutz, H. Maier, and A. Nolle
Z. Naturforsch. 31a, 351 (1976)
- (3) O. Lutz, A. Nolle and P. Kroneck
Z. Naturforsch. 31a, 454 (1976)



^{95}Mo pulse FT-NMR signal of a 0.08 molal solution of $\text{Mo}(\text{CO})_6$ in THF in a 10 mm rotating cylindrical sample at 5.854 5704 MHz. The chemical shift relative to the MoO_4^{2-} signal at infinite dilution in H_2O is 1856.1(0.2) ppm to lower frequency.

Experimental parameters:

Excitation frequency: 5.854 471 MHz; magnetic field 2.114 T;
 experimental spectrum width: 200 Hz; plotted spectrum width: 50 Hz;
 linewidth: 1 Hz; pulse repetition frequency: 0.3 Hz;
 pulse duration: 15 μsec (90° pulse); number of pulses: 200;
 temperature: (300 ± 2) K.

1 K data points were accumulated;
 this 1 K + 3 K of zeros were Fourier transformed.

THE ROYAL INSTITUTE OF TECHNOLOGY
DIVISION OF PHYSICAL CHEMISTRY
S-100 44 STOCKHOLM 70
SWEDEN

Cable address: Technology

Stockholm, October 28, 1976

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station
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DEUTERIUM RELAXATION OF SOLUBILIZATES IN MICELLES

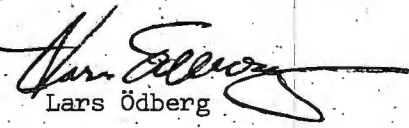
Dear Barry:

We are continuing our studies of magnetic relaxation in aqueous micellar system. Presently we are measuring ^2H relaxation of solubilized C_6D_6 and C_6D_{12} in hexadecyltrimethylammonium bromide (CTAB) and sodiumdodecylsulphate (SDS) solutions. Results are given in Figs. 1 and 2. T_2 was determined from the line width. Only for C_6D_6 in CTAB could we observe $T_1 \neq T_2$. It is known that benzene induces the formation of rod like micelles in CTAB (1) which gives rise to a slow anisotropic motion. As can be seen from Fig. 2 this slow motion contributes to the transverse relaxation of C_6D_6 , which agrees with the proposed solubilization of benzene at the micelle/water interface (1). For C_6D_6 in SDS and for C_6D_{12} in CTAB and SDS no slow motion could be found. This is consistent with solubilization in the interior of spherical micelles (2).

Sincerely yours


Ulf Henriksson


Tomas Klason


Lars Odberg

References

1. J.C. Eriksson and G. Gillberg, Acta Chem. Scand. 20 (1966) 2019.
2. F.J. Fendler, C.L. Day and J.H. Fendler, J. Phys. Chem. 76 (1972) 1460.

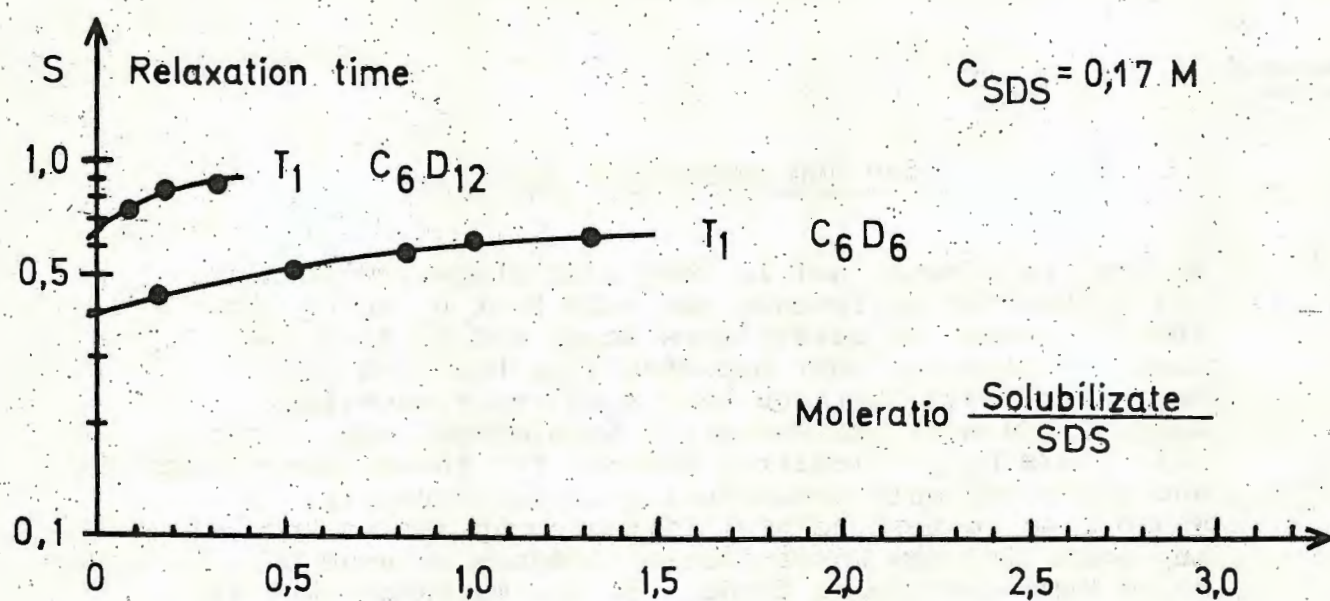


Fig. 1

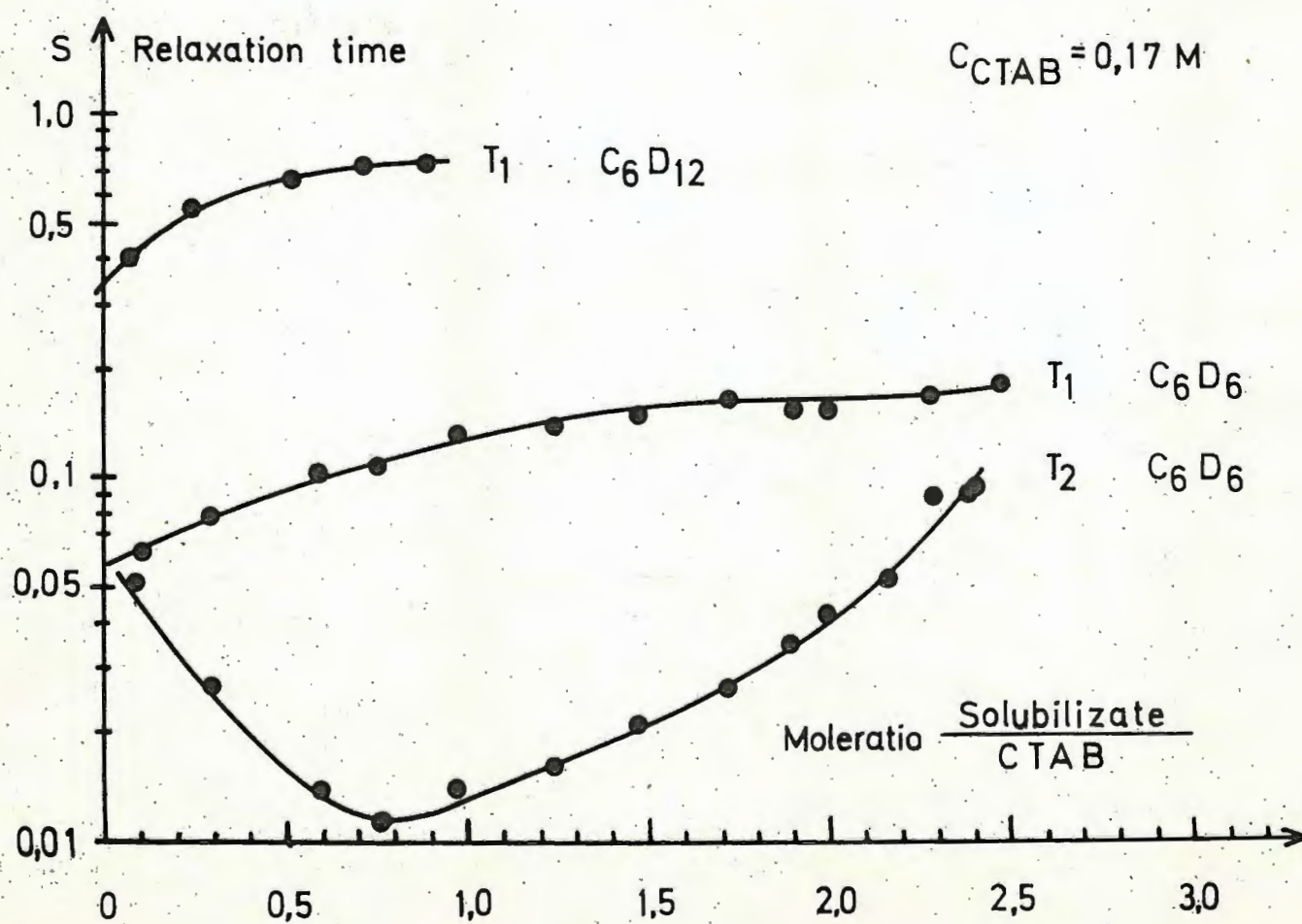


Fig. 2

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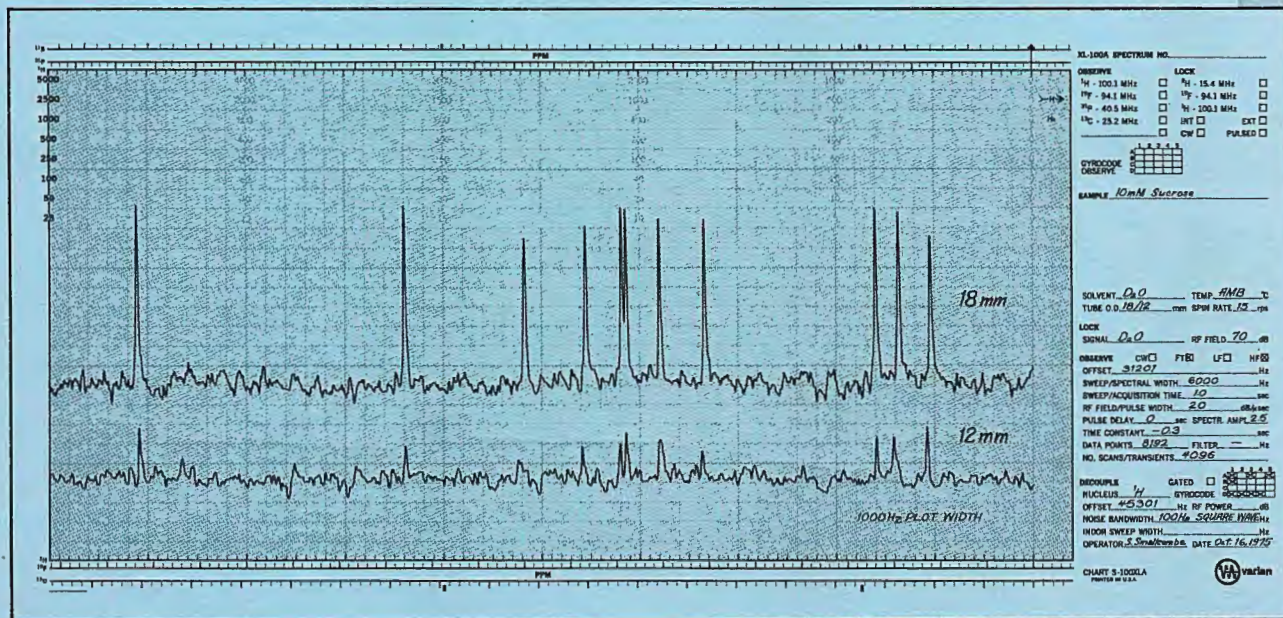
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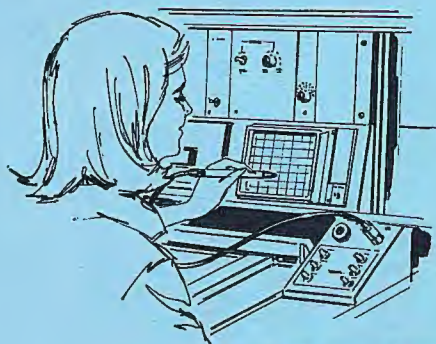
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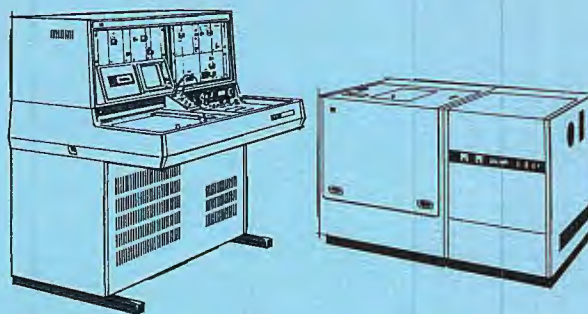


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