Texas A & M University N − M − R Newsletter

No. 209

February, 1976

WILMAD® NMR CHART PAPER

WE STOCK ALL THE RECORDING CHARTS YOU NEED ...
- THE WORLD'S FINEST NMR SAMPLE TUBES • EQUIPMENT, GLASSWARE, AND SUPPLIES FOR SPECTROSCOPIC RESEARCH
- EVERYTHING BUT THE SPECTROMETER • SEND FOR OUR NEW FREE 100-PAGE GIANT CATALOG 875. • IF YOU HAVE ANY QUESTIONS, PLEASE CALL.

CHART PAPER

Finest grade NMR Chart Paper made to be used in every model spectrometer. All charts have been updated to coincide with the newest instrument techniques . . . Fourier Transformation, Hetero-Decoupling, and Time Averaging.

NOTE: All charts packaged 500 sheets to a box except roll charts or as otherwise noted.

CATALOG NUMBER	INSTRUMENT	TYPE	PRICE PER BOX			
			1-10 boxes	11-24 boxes	25-49 boxes	50 & over
VARIAN						
WCV-100 (S-100A)	HA-100, HA-100A, and D	Cal.	$35.00	$34.50	$34.00	$33.50
WCV-60 (S-60C)	A-60, A-60A and D	Cal.	35.00	34.50	34.00	33.50
WCV-60EL	HA-60EL and IL	Cal.	37.50	37.00	36.50	36.00
WCV-XL (XL-100)	XL-100 (Standard)	Cal.	35.00	34.50	34.00	33.50
WCV-XL-100FT	XL-100 (Fourier)	Cal.	37.50	37.00	36.50	36.00
WCV-220 (S-220)	HR-220	Cal.	37.50	37.00	36.50	36.00
WCV-56 (S-56A)	A-56/60	Cal.	37.50	37.00	36.50	36.00
WCV-360-K-10	EM-360	Cal.	28.00	27.50	27.00	26.50
WCV-20 (CFT-20)	CFT-20	Cal.	30.00	29.50	29.00	28.50
WCV-EM-300R (3E)	EM-300 (6 rolls/box)	Cal.	14.40	13.80	13.80	13.80
WCV-EM-300F (300X10)	EM-300 (flatbed)	Cal.	28.00	27.50	27.00	26.50
WCV-60T (S-60T)	T-60 (two color)	Cal.	20.00	19.50	19.00	18.50
WCV-60B	T-60 (one color)	Cal.	17.50	17.00	16.50	16.00
WCV-60U (S-60U)	T-60 (multi-nuclei)	Cal.	20.00	19.50	19.00	18.50
WCV-60TS	T-60 (no grid, delta)	Blank	16.00	15.50	15.00	14.50
WCV-BL	11" x 26"	Blank	16.00	15.50	15.00	14.50
WCV-60T-BL	8-½" x 11"	Blank	10.00	9.50	9.00	8.50
WCV-CFT-20K-11	11" x 16"	Blank	13.00	12.50	12.00	11.50
WCV-360BL	11" x 16"	Blank	13.00	12.50	12.00	11.50
JEOL						
WCJ-4HA	C-60H, 4H-100, (9.00 ppm)	Cal.	37.50	37.00	36.50	36.00
WCJ-4HB	C-60HL, MH-100, (9.0 ppm)	Cal.	37.50	37.00	36.50	36.00
WCJ-4HC	MH-100, PS-100 (10.8 ppm)	Cal.	37.50	37.00	36.50	36.00
WCJ-4HD	MH-100, PS-100 (9.0 ppm)	Cal.	37.50	37.00	36.50	36.00
WCJ-4HE	PFT-100 (standard)	Cal.	37.50	37.00	36.50	36.00
WCJ-PFT-100	PFT-100 (Fourier)	Cal.	37.50	37.00	36.50	36.00
WCJ-FX-60(FX-2)	FX-60	Cal.	37.50	37.00	36.50	36.00
WCJ-FX-60-BL	FX-60 (para only)	Blank	19.00	18.50	18.00	17.50
WCJ-PFT-100BL	11" x 17" (para only)	Blank	19.00	18.50	18.00	17.50
WCJ-BL	11" x 17"	Blank	15.00	14.50	14.00	13.50
BRUKER						
WCB-"UC"	HX-90, HFX-10	Cal.	40.00	39.50	39.00	38.50
WCB-BL	12-½" x 29"	Blank	17.00	16.50	16.00	15.50
WCB-WH-90	WH-90	Cal.	35.00	34.50	34.00	33.50
WCB-BX-FT	HX-270	Cal.	40.00	39.50	39.00	38.50
PERKIN-ELMER						
WCPE-2018	R-20, R-20A	Cal.	37.50	37.00	36.50	36.00
WCPE-2021 (WCPE-60)	R-20B	Cal.	37.50	37.00	36.50	36.00
WCPE-462-1075	R-12, R-12A (6 rolls/box)	Cal.	35.00	34.50	34.00	33.50
WCPE-435-0065	R-24 (roll) (6 rolls/box)	Cal.	35.00	34.50	34.00	33.50
WCPE-435-7204	R-24A (rect.) (100 sh./box)	Cal.	7.00	6.50	6.00	5.50
WCPE-441-1580	R-22 (rect.) (100 sh./box)	Cal.	B.00	7.50	7.00	6.50
WCPE-R-32	R-32 (roll) (6 rolls/box)	Cal.	35.00	34.50	34.00	33.50
WCPE-2018BL	11" x 22"	Blank	15.00	14.50	14.00	13.50
WCPE-2021BL	11" x 19"	Blank	15.00	14.50	14.00	13.50
WCPE-526-1102	R-26 (rect.) (100 sh./box)	Cal.	7.00	6.80	6.60	6.40
WCPE-435-9020BL	R-24A (rect.) (100 sh./box)	Blank	4.50	4.25	4.00	3.75
WCPE-441-1580BL	R-22 (rect.) (100 sh./box)	Blank	4.50	4.25	4.00	3.75
NMR SPECIALTIES						
WCN-60/100	A-60, HA-100, A-56/60	Cal.	35.00	34.50	34.00	33.50

WILMAD GLASS COMPANY, INC.

U.S. Route 40 & Oak Road • Buena, N.J. 08310, U.S.A. • (609) 697-3000 • TWX 510-687-8911

DEADLINE DATES: No. 210: 1 March 1976

                 No. 211: 5 April 1976

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.

University of Durham Department of Chemistry

21st November, 1975.

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

Dear Professor Shapiro,

A simple NMR pulse programmer

Pulse programmers seem to become more complicated so this unit, containing only five integrated circuits was designed to produce single pulses from 0.6μs to 106μs spaced by 0.01s to 10s. Up to 10.6μs the pulse length increment is 0.01μs while in the higher range it is 0.1μs. Likewise the delay increments are 0.01s. To do this two sets of decade switches are used. The leading edge of each pulse can be synchronised to an external clock so that successive bursts are phase coherent. Originally the circuit was designed for attachment to a Nicolet computer using PULSE 1 and PULSE 2 to start and stop pulsing, but obviously it could be used on any other suitable system. Apart from gating the transmitter the TTL output is used to trigger the signal averager. Additionally 15V pulses of either polarity are provided.

Though it has not been tried there is the possibility of cascading these units to give multipulse sequences. To do this it is first necessary to start with an interpulse delay rather than a pulse.
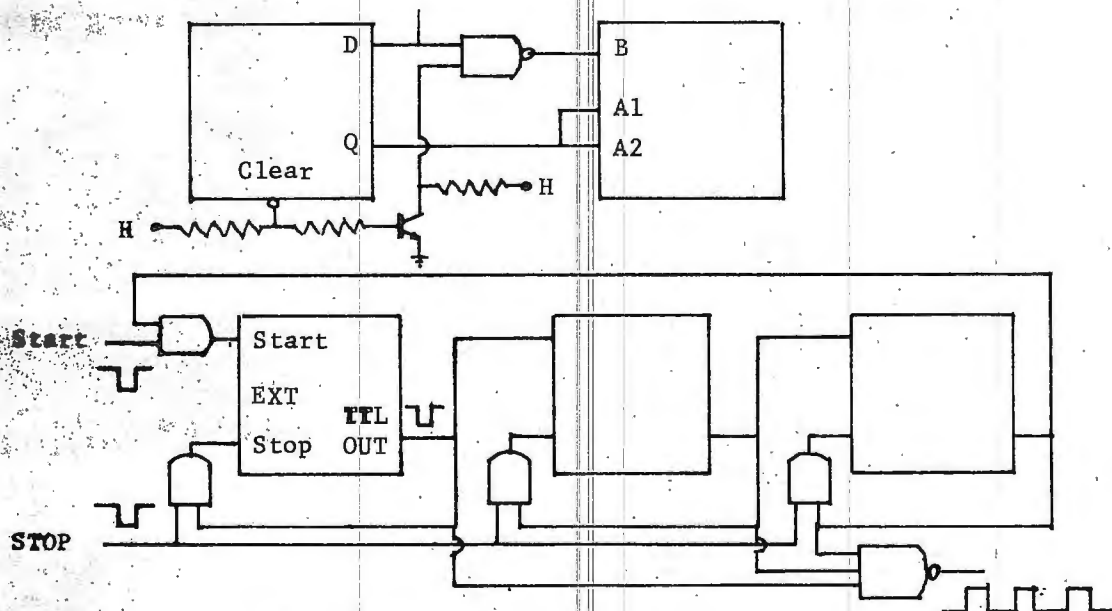
Yours faithfully,

A. Royston

R. Matthews

$R1 = 0$ to $2.1978M$ in $2.2K$ steps

$R2 = 0$ to $32.967K$ in 33Ω steps

UNIVERSIDAD DE BUENOS AIRES

FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, December 12th.1975.

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

Title: Help! It's magnetic!

Dear Dr. Shapiro:

I am glad to announce that next year, or
perhaps even this year, we shall be the happy owners of
a minicomputer of 12 K memory, wired for F.T.S.; the
Nicolet NMR 812.

We have been fighting hard to avoid obso-
lescence with our venerable DP-60 instrument: We built our
own internal lock system; a frequency seep; a solid state
superstabilizer (which, incidentally, works wonderfully!);
a solid state fast sweep, a ^{14}N decoupler and now we took
F.T.S. as our next goal. Since this means an expense of
about 80 K$ and we got only half that amount, we just <u>had</u>
to build something ourselves. We decided on the probe head.
We tried already to build our own "inserts" and we found
that resolution was the main problem. Quite often we got
nice "ghost" spectra, just like in classical grating
spectroscopy: Every line of the main spectrum was accompa-
nied by a small replica, a hertz or two on a side.

After some trials we obtained good
inserts, but please: don't ask me how!
It seems that strained cooper is para-
magnetic (!?).

In building our own probe heads, the first
problem was resolution. We found that almost anything we
used destroys homogeneity, i.e.: We build a new air tur-
bine, in brass. It was a disaster. We build another one in
aluminium: it worked fairly well. We built an aluminium
probe head box: another disaster: Curvature was permanently
"dished".

It seems that (our local) aluminium is
slightly magnetic. Even teflon is magnetic! (Until you
rinse it in hydrochloric acid, to get rid of the fine metal
film(steel) with which it is covered after machining).
If anybody has had experience in building
(successfully) probe heads, we would enormously appreciate
his advice!

Yours sincerely,

V.J. Kowalewski.

Boston College, Chestnut Hill, Massachusetts 02167   Telephone (617) 969-0100

Department of Chemistry

December 23, 1975

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

Dear Barry:

^{13}C NMR Spectra of 1-Substituted Azulenes

For some time now I have been interested in developing a simple method for describing substituent-induced ^{13}C chemical shifts in π-systems, and a full paper outlining the approach will appear in JACS around March. I also wanted to extend the model to nonalternant π-systems, but there are no data in the literature, other than for parent hydrocarbons. Accordingly, Dr. Tadeusz Holak (currently at the Jagiellonian University in Krakow, Poland) began an experimental study of ^{13}C spectra in 1-substituted azulenes.
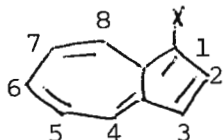
X=H, Cl, NO$_2$, COCF$_3$

Briefly, we find
 a) carbons in the five- and seven-membered rings can easily be distinguished by their one-bond CH couplings ($\sim$170 Hz and $\sim$160-165 Hz, respectively);
 b) in the seven-membered ring, only three-bond couplings can be resolved, whereas two-bond CH couplings are easily seen in the five-membered ring;
 c) C-2 and C-3 are relatively in sensitive to the nature of X, whereas C-5 and C-7 are most sensitive. Thus the perturbation is being transmitted through the five-membered ring into the seven-membered ring.

We are digesting these results (actually, ruminating might be a better term) while proceeding further on both the experimental and theoretical fronts.

Finally, I'd like to acknowledge the hospitality of Dr. Al Redfield (Brandeis University) in whose instrument most of this work was done. George Levy (Florida State University) also permitted Dr. Holak to use his instrument for several experiments.

Sincerely,

Dennis J. Sardella
Associate Professor of Chemistry

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

IN REPLY REFER TO
6052/DWM:dgg
5 January 1976

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

Title: Stereochemistry of Bicylotriazines

Dear Barry,

The work of A. T. Nielsen and R. L. Atkins here on bicyclic tri-
azines (1,3,5-trialkyl-2,4,6-triazabicyclo[3.1.0]hexanes), which form
when chloramine is added to aldehydes, has led to some interesting
^{13}C nmr work. [1,2] Three isomeric products are formed from acetal-
dehyde (R = CH_3) in the amounts shown below with their observed ^{13}C
shifts (rel. to TMS).
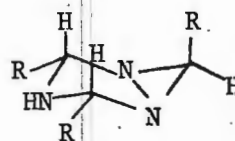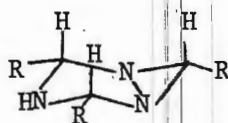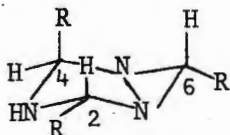
	trans, exo (60%)		cis, exo (30%)		cis, endo (10%)
C-2, ppm	75.31	(-0.38)	74.93	(+ 0.79)	75.72
C-4	72.41	(+2.52)	74.93	(+ 0.79)	75.72
C-6	46.18	(-5.21)	40.97	(+12.24)	53.21
2-CH_3	15.15	(+0.12)	15.27	(+ 9.61)	24.88
4-CH_3	21.35	(-6.08)	15.27	(+ 9.61)	24.88
6-CH_3	16.99	(+0.11)	17.10	(+ 5.94)	23.04

The differences in ^{13}C shifts between isomers (in parentheses) are
generally as would be expected for the two exo-forms where the more
sterically hindered carbons move up-field. In the case of the endo-
form, the large down-field shifts of C-6 and all three methyls suggests
a major change in ring geometry, possibly an increase in dihedral angle
between the 3-ring and the 5-ring.

Sincerely,

D. W. MOORE

(1) A. T. Nielsen, R. L. Atkins, J. DiPol and D. W. Moore, J. ORG. CHEM.,
39, 1349 (1974).

(2) E. Schmitz and R. Ohme, CHEM. BER., 95, 795 (1962).

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT · ISRAEL   רחובות · ישראל

ISOTOPE DEPARTMENT

January 11, 1976

מחלקת איזוטופים

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

Dear Barry:

For quite a few years it has been felt by Israeli "resonators" that they see each other at international conferences more often than at home. Therefore Zeev Luz took the initiative of organizing what is tentatively called The Israeli Club of Magnetic Resonance. It was inaugurated on January 8, 1976, with a formal meeting held at this Institute. The scientific program included presentations (in Hebrew!) by Hadassa Degani (Univ. of Tel Aviv), who presented her work (done at SUNY, Stony Brook) on the Kinetics of Ion-Ionophore Complexation by Proton NMR; by the under-signed, who talked on Aqueous Shift Reagents; by Chaim Levanon (Hebrew Univ., Jerusalem), who described ESR Detection of Paramagnetic Species During Photoexcitation; and by Daniel Kost (Ben Gurion Univ., Beer Sheva), who discussed Energy Barriers of Rotation Around S-N and N-CO Bonds in N-Sulfenyl Uretanes. The meeting was met with great interest and was attended by more than fifty "resonators" from all the academic and research institutions in Israel.

The next meeting is scheduled to take place in Jerusalem on May 20, 1976, and will be organized by Chaim Levanon. Any of the Newsletter readers who happen to be in Israel at that time are invited to attend. I trust that in their honor the talks will be in English.

Sincerely yours,

Jacques

Jacques Reuben

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO   SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY
REVELLE COLLEGE

POST OFFICE BOX 109
LA JOLLA, CALIFORNIA   92037

January 5, 1976

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

Spin Lattice Relaxation in Strongly Coupled Spin Systems

Dear Barry,

Since last summer, when Daniel Canet from Nancy spent a few months with us, we
have been exploring how simple non-selective IRFT relaxation measurements on
homonuclear coupled spin systems can be used in investigations of anisotropic
motion in liquids. Preliminary results (1) show that a detailed analysis of the
complete recovery curves allow the determination of all three components of the
reorientational diffusion tensor.

The following features are characteristic of dipolar spin-lattice relaxation in
strongly coupled spin systems:

a) The rate of recovery of a given line in the spectrum cannot be associated
with a relaxation rate of a particular nucleus since the spin states are not pure.
Observed recovery rates are dependent on the degree of mixing of the spin states
and consequently on the magnetic field strength.

b) Since many coupled transitions are excited, simultaneously decays are strongly
nonexponential and some lines may exhibit "overshoots" reminiscent of transient
Overhauser effects.

c) As first pointed out by Schäublin, et. al. (2), the monitoring pulse introduces
further mixing of the spin states and the observed recovery curves depend on the
flip angle of the monitoring pulse.

d) By properly including cross- as well as auto-correlation functions in the
description of the dipolar relaxation behavior and by using formulas derived
by Hubbard (3), the molecular motion may be described in detail (1). Similar
kinds of information may be obtained from heteronuclear coupled spin systems by
combinations of selective pulses (4).

e) The use of initial slopes for T_1 determinations may not be particularly meaningful
under such circumstances, since the initial slopes are functions of coupling strength
and flip angle α in a $180-\tau-\alpha-$FT experiment.

Professor Bernard L. Shapiro
January 5, 1976

We illustrate this last point here with the following "initial slope T_1 data" on the eight lines of an AB_2 proton spin system. (See Figure for labelling of lines.) The sample is 0.5 M 1,2,3-trichlorobenzene in 100% $CDCl_3$ and the spectrum shown was obtained on our JEOL-PFT-100 + Nicolet 1085 spectruter system.

ν_o(MHz)	J/δ	α	B_1	B_2	B_3	B_4	A_5	A_6	A_7	A_8
100	0.429	90°	51.0	50.5	39.5	38.0	29.0	21.5	19	21
220	0.195	90°	51.0	50.5	45.0	44.0	24.0	21.0	20.0	21.5
220	0.195	5°	49.0	64.0	45.0	53.0	20.5	20.5	20.5	19

As expected, A relaxes more or less twice as fast as B spins. Note, however, that the observed decays are "mixed" in the center of the spectrum, and that this mixing is stronger at the lower field. When a 5° monitoring pulse is used, the decay pattern is different yet, but strong nonexponential character (overshoots, etc.) is still present.

Complete details of the analysis of the recovery curves and the anisotropic motion of 1,2,3-trichlorobenzene and similar systems will hopefully be written up in the near future.
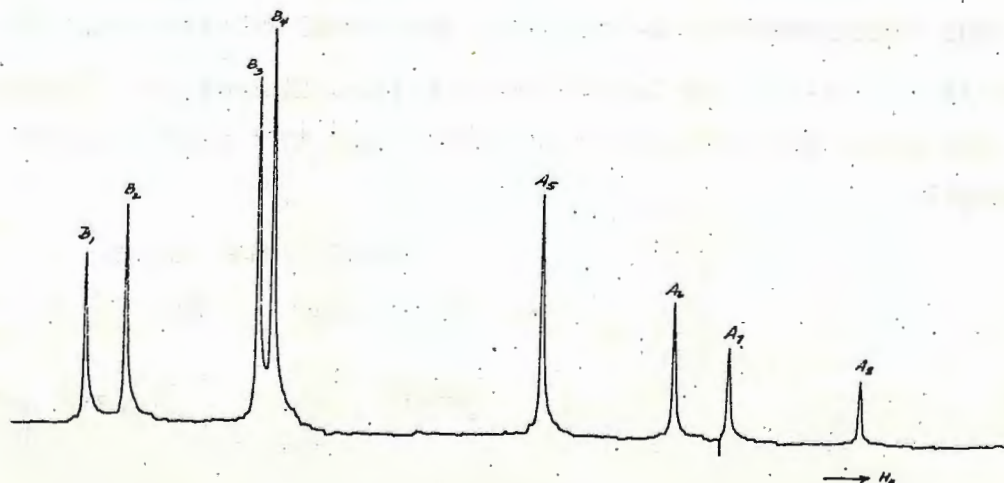
Very best regards,

Bob & Gitte.

Bob & Gitte

mb
References

1. D. Canet, R. L. Vold and R. R. Vold, J. Chem. Phys. 64, XXXX (1976).
2. S. Schäublin, A. Höhener and R. R. Ernst, J. Magn. Resonance 13, 196 (1974).
3. P. S. Hubbard, J. Chem. Phys. 52, 563 (1970).
4. L. G. Werbelow and D. M. Grant, J. Chem. Phys. 63, 544 (1975).

**Laboratorium
für anorganische Chemie**
Eidg. Technische Hochschule
Zürich

8006 Zürich, January 13, 1976
Universitätstrasse 6

Title: Carbon-Platinum Coupling Constants in
Olefin Complexes.

Dear Prof. Shapiro,

We feel you and your readers will find some ^{13}C measurements
of platinum-olefin complexes of interest.

We have recently observed[1] that platinum-195-carbon-13 coupling
constants in platinum-olefin complexes can occasionally be
misleading. Subsequently, we have measured additional ^{13}C spectra
on related complexes and some of these data are shown below.

X	trans-[PtCl$_2$(cis-2-butene)X]		trans-[PtCl$_2$(trans-2-butene)X]	
	^{1}J(Pt,C)	^{2}J(Pt,C)	^{1}J(Pt,C)	^{2}J(Pt,C)
pyridine-N-oxide	206.6	18.4	206.6	36.8
pyridine	150.0	14.7	152.2	33.1
piperidine	142.8	22.0	145.9	33.0

The couplings listed refer to the metal-olefin interactions.

Based on the values ^{2}J(Pt,C) one might consider the metal-olefin
interaction in two types of trans-complexes quite different;
however, the values ^{1}J(Pt,C) suggest a different conclusion. Based
on other nmr measurements we believe the metal olefin bond strength
within these pairs of complex to be similar. Therefore, ^{2}J(Pt,C)
in such complexes may not alway reflect only the olefin-metal
bond strength.

Very truly yours

Dr. S. N. Sze   Dr. P. S. Pregosin

[1] P. S. Pregosin & L. M. Venanzi, Helv. Chim. Acta, 58, 1458 (1975).

ircha

**Institut
national
de recherche
chimique
appliquée**

Centre de Recherche

Boite postale n⁰ 1

91710   Vert le Petit

☎ : 498.24.75

Télex: IRCHA 600820

Pr B.L. SHAPIRO

TEXAS A & M UNIVERSITY

College of Science

College Station

77843 TEXAS

Vert le Petit, le 1.22.76

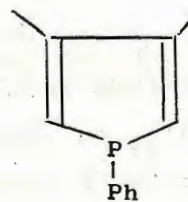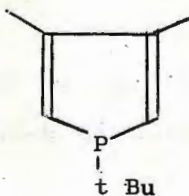Phosphorus-containing organometallic compounds.

Dear Barry,

Mieux vaut tard que jamais, isn't. In a hurry, not to change, I am
giving you a short account of some NMR work on stream dealing with
phosphole organometallics. In addition to an interesting chemistry
(see F. Mathey, J. Organometal. Chem., 93 (1975), 377-388), they pre-
sent NMR peculiarities related to their conjugated system.
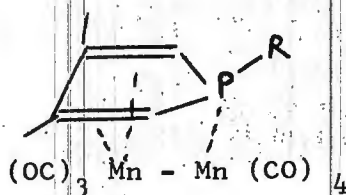
To take two simple ligands in the phosphole family

	t Bu	Ph
δH (1)	6.18	6.36
J_{P-CH}	35.8	38.0
δ CH$_3$ (2)	2.04	1.91
δ ^{31}P (réf. P$_4$O$_6$) high-field	84.8	115.0

Both give σ, π complexes LMn$_2$(CO)$_7$ when heated with Mn$_2$(CO)$_{10}$
under UV irradiation. The following NMR data point to a tridentate
structure, both of the phosphorus lone-pair and the dienic system
being involved

$(OC)_3$ Mn – Mn $(CO)_4$

| L. $Mn_2 (CO)_7$	tBu phosphole	Ph phosphole
δ H (1)	2.38	2.61
J P.C H	29.5	30.3
δ CH_3 (2)	2.28	2.33
δ 31_P	59.2	83.9

The shielding effect on complexing is especially noticeable for the H(1) (nearly 3.8 ppm in both instances), deshielding being sizeable for the rather remote CH_3 (2) (resp. 0.24 and 0.42 ppm)

An important deshielding occurs as well at phosphorus, resp. 25.6 and 20.8 ppm. Similar observations are made on the parent <u>iron</u> complex.
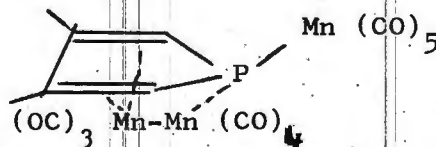

$(OC)_3$ Fe-Fe $(CO)_3$
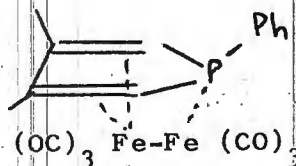
For which δ H (1) : 2.18
JP - CH: 24.3
δ CH_3 (2) : 2.23

A more curious species has been isolated in the case of manganese, $L' Mn_3 (CO)_{12}$ in which a Mn $(CO)_5$ group is σ-bonded to phosphorus replacing the R group.

$(OC)_3$ Mn-Mn $(CO)_4$

δ H (1) : 3.07
JP-CH : 31.3
δ CH_3 (2): 2.48
δ 31 P : 38.5

Last a quite striking complex has been studied

McMASTER UNIVERSITY
Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1
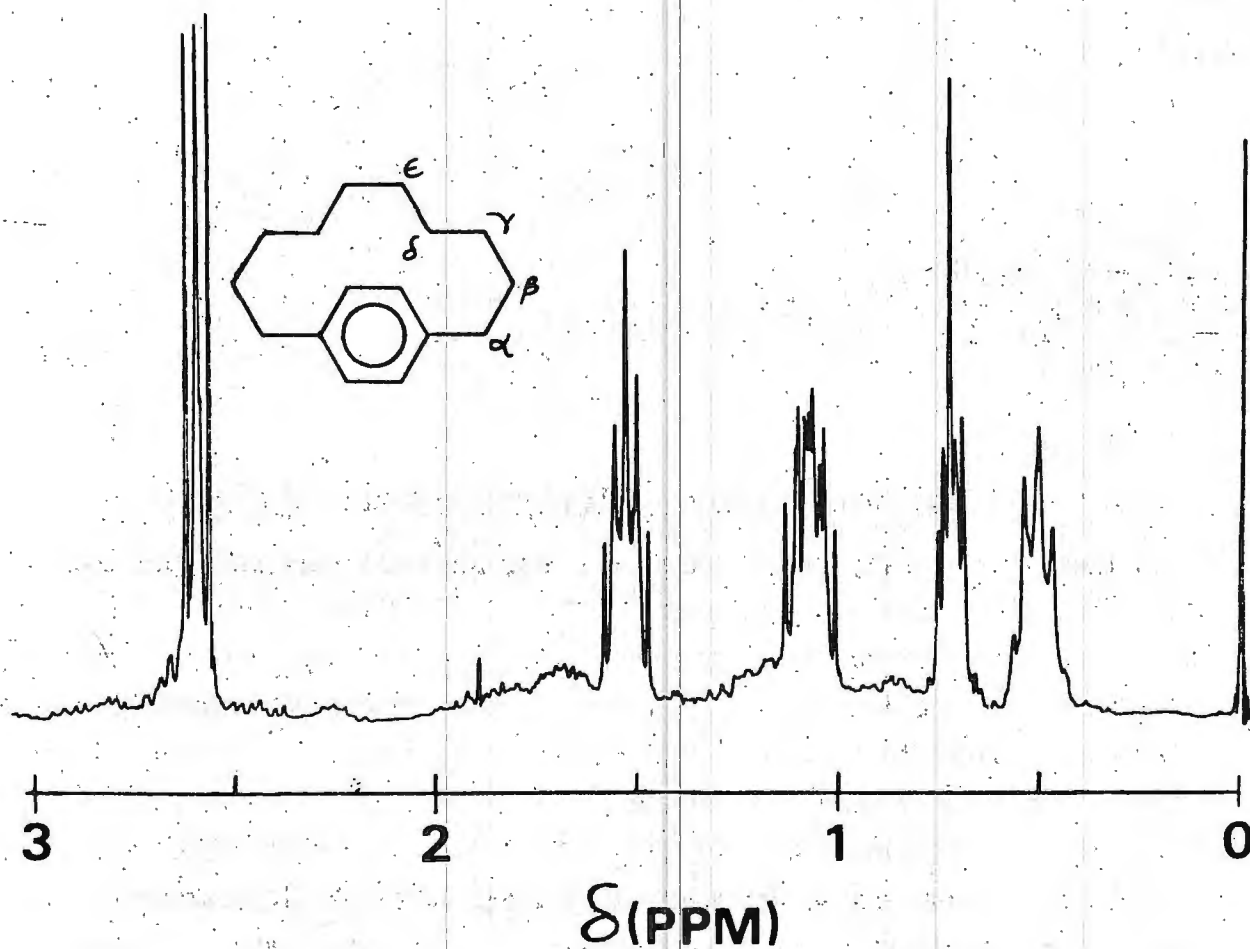Telephone: 525-9140

January 12, 1975

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

Dear Barry:

Evaluation of Ring Current Tables - [10]-paracyclophane at 220 MHz.

In their now classic paper, Waugh and Fessenden (1) developed the idea of
a double loop of circulating π electrons, and presented the spectrum of [10] -
paracyclophane in order to test their theory of ring currents. In particular,
they predicted the chemical shifts of the methylene protons positioned above
the ring and compared these values with the experimental data. Although their
40 MHz spectrum clearly demonstrated the presence of high field protons, the
resolution was insufficient to enable any definitive assignments to be made.
We now present the 220 MHz spectrum in which the five aliphatic proton en-
vironments are clearly resolved and assigned via homonuclear double resonance
experiments and confirmed by selective proton decoupled carbon-13 NMR results;
the order (to increasing field) is α, β, γ, δ, ε and not α, β, δ, γ, ε as
originally postulated.

These accurate proton chemical shifts and coupling constants, together with
a suitably modified Karplus equation (2), allowed the calculation of the most
populated conformation of the molecule; gratifyingly, it matches the conformation
predicted by Allinger's molecular mechanics calculations (3). Using 1.52 δ (the
position at which the β and γ methylene protons of n-phenylbutane absorb) as the
"standard methylene group" appropriate to the environment, one can use the
Johnson-Bovey tables (4) to predict the chemical shifts of the bridging methylene
protons in [10]-paracyclophane. These data are also compared to the predictions
obtained via the quantum mechanical approach used by Haigh and Mallion (5). While
both methods are qualitatively very useful, the semi-classical method shows
excellent agreement for protons held over the centre of the ring but becomes less
reliable as the value of ρ increases (and z decreases). The quantum mechanical
approach gives good agreement in these latter regions but seriously under-estimates

	Exptl 220 MHz	Calc[a] J-B	Calc[b] H-M
Ar	7.04	—	—
α	2.63	—	—
β	1.55	1.75	1.59
γ	1.08	1.45	1.47
δ	0.70	1.15	1.38
ε	0.51	0.56	1.19

a. Johnson-Bovey Tabulations, Ref. 4.

b. Haigh-Mallion Tabulations, Ref. 5.

the upfield shifts of the protons directly above the ring.

A fuller account of this study, including ^1H and ^{13}C spectra of [10]-paracyclophane and of its $Cr(CO)_3$ analogue, will be published eventually.

Yours sincerely,

John L. Fletcher, Michael J. McGlinchey, B.G. Sayer

/rg

Please credit this contribution to the account of Mr. J.I.A. Thompson

References

1. J.S. Waugh and R.W. Fessenden, J. Amer. Chem.Soc., 79 846 (1957); 80, 6697 (1958).

2. A.A. Bothner-By, Advan. Magn. Resonance, 1, 195 (1965).

3. N.L. Allinger, J.T. Sprague and T. Liljefors, J. Amer. Chem. Soc., 96, 5100 (1974).

4. C.E. Johnson, Jr. and F.A. Bovey, J. Chem. Phys. 29, 1012 (1958).

5. C.W. Haigh and R.B. Mallion, Org. Magn. Resonance, 4 203 (1972).

CONTINUED FROM P. 12.
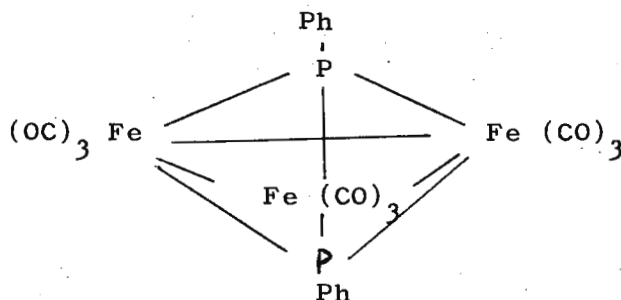
For which a new synthetic way has been found from $Ph\ PCl_2$ (an earlier one starting from $Ph\ PH_2$ is less convenient and general : P. M. Treichel, W.K. Dean and W.M. Douglas, Inorg. Chem., 11 (1972), 1609). Its main particularity is a strongly deshielded phosphorus atom -205 ppm. vs P_4O_6 (-317,5 vs. H_3PO_4) probably the most deshielded phosphorus species reported up to now.

With our very best regards,

F. MATHEY
R. MANKOWSKI
G. MAVEL

NATO ADVANCED STUDY INSTITUTE

ON

ADVANCES IN NMR:

THE LESS RECEPTIVE NUCLEI

LOCATION: Altavilla Milicia (Palermo), Sicily

DATE: 5-18 September, 1976

SPONSORSHIP: The Institute is sponsored and supported by the NATO Scientific Affairs Division.

GENERAL SCOPE: The Institute will deal with the unique kinds of chemical information that can be obtained from high resolution NMR studies. Emphasis will be on recent advances in theory and method as applied to the study of nuclei of low sensitivity, low natural abundance and samples (e.g., biological) constrained to be examined at low concentration.

PROGRAM: The essential principles of NMR will be developed in a coherently structured program of lectures and parallel seminar discussions. Instrumentation and experimental techniques will be covered. Included in the program will be such topics as: Fourier transform methods; relaxation mechanisms; CIDNP; zeugmatography; high field NMR; quadrupolar effects; NMR of oriented samples; as well as the detailed discussion of recent developments in the study of ^{2}H, ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{23}Na, ^{31}P, ^{35}Cl, ^{205}Tl, ^{207}Pb, and other heavy metal nuclides.

LECTURERS: T. Axenrod (CUNY), E.D. Becker (NIH), G. Binsch (Munich), F. Conti (Rome), S. Forsen (Lund), D.I. Hoult (Oxford), R. Kaptein (Groningen), P.C. Lauterbur (SUNY), G.E. Maciel (Colorado), E.W. Randall (Queen Mary College), L. Reeves (Waterloo), D.L. Vanderhart (NBS). A few additional lecturers may be added.

LANGUAGE: All lectures and discussions will be held in English.

PARTICIPATION: Attendance at the Institute will be limited. Applications to attend and contribute to the scientific program are invited from all countries, although preference will be given by the selection committee to applicants from NATO countries.

CONTRIBUTED PAPERS: Short contributed papers can be accepted for inclusion in the program. Participants wishing to present a communication should submit a title and a synopsis along with their application form.

GRANTS: A limited number of grants in partial support of travel and living expenses will be available to chosen participants from NATO countries who cannot obtain adequate support from other sources.

ACCOMMODATION: Participants receiving NATO support will be accommodated in the Hotel Torre Normanna, where all technical sessions will be held.

FURTHER INFORMATION: For further details and application forms, please contact:

Dr. T. Axenrod	or	Dr. E. W. Randall
Department of Chemistry		Department of Chemistry
The City College of CUNY		Queen Mary College
New York, N. Y. 10031		London E1 4NS,
U.S.A.		U.K.

SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY

WESTHOLLOW RESEARCH CENTER

P. O. Box 1380
Houston, TX 77001

January 6, 1976

TSP* as a ^{13}C Internal Reference

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

Dear Barry:

We have recently had occasion to measure some ^{13}C spectra in aqueous solution but were at a loss for an adequate internal chemical shift reference. We tried both p-dioxane and acetone but (not surprisingly) their shifts showed significant dependence upon the nature of the solution and upon the solute concentrations. We did not find any literature data for the ^{13}C shifts of the commonly used proton shift references, TSP and DSS. We finally succeeded in getting both TSP and TMS into the same solution with the aid of p-dioxane as a common solvent. We find a shift of -1.62 ppm for TSP with reference to TMS and a shift of 67.37 ppm for the p-dioxane.

I am interested in what other people are doing about a ^{13}C internal reference in aqueous solution. Tentatively we are using TSP with an assigned shift of -1.62 ppm.

Sincerely,

Charlie

C. A. Reilly

CAR:bls

*Sodium-3-trimethylsilylpropionate-d$_4$.

ADDITIONAL
TMS

20 Hz/CM

ORIGINAL

SOLUTION

TMS

TSP -1.62

TMS
TSP

15   0   -15

PPM

Shell Development Co. Houston, Texas	AR No. CHM 2670

13C NMR 22.63 MHz

SAMPLE DESCRIPTION:

$TSP(d_4)$ 170 mg

TMS ~ 200 μl

DIOXANE 2 ml

D_2O 200 μl

Solvent: _____	Conc.: _____
Temp.: **40°C**	Stab.: **D_2O**
Internal Standard: _____	

Bruker HFX-90 Spectrometer
Digilab FTS/NMR-3S Data System

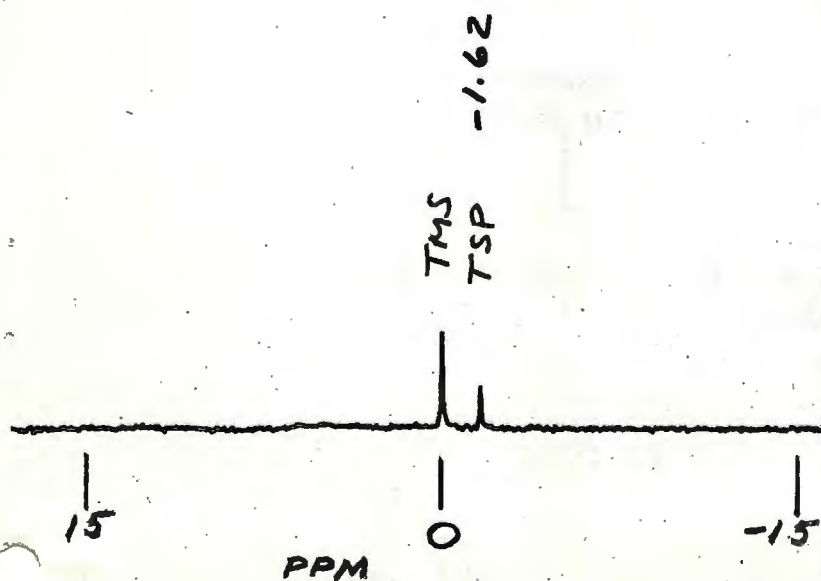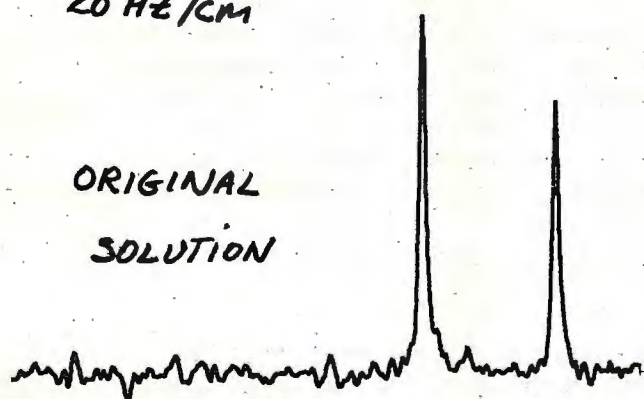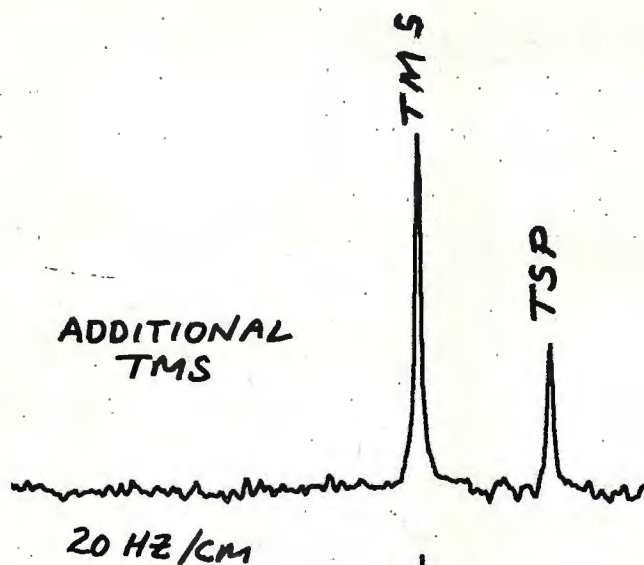|		
Pulse Width ≈ 30°	6	μsec
Delay	1.00	sec
Bandwidth	5	kHz
No. Pts. Collected	8192	
No. of Pulses	1187	
Decoupling Power	~6	Watts
Freq.		Hz
☒ BB Mod	5	
☐ Selective		

REMARKS:

OPERATOR _(signature)_

DATE 8/27/75

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

The School of Medicine

JOHNSON RESEARCH FOUNDATION G4
DEPARTMENT OF
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

7 January 1976

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

Title: <u>Jitter in Field-Lock</u>

Dear Professor Shapiro:

In doing CW spectra on our NV-14 with Deuterium lock we had a problem which I suspect is identical to one seen on the XL100. As one approaches a peak, noise appears on an otherwise quiet baseline and persists until the peak is passed. The cause is that noise from the lock signal detector is unnecessarily emphasized relative to the D.C. component - thanks to the way the signal is applied across the flux pickup coil (a large inductance with 650 ohms D.C. resistance). As a result the magnet field jitters and the recorder in effect registers signal from indefinite locations on the slope of the actual observe peak.

The cure is to open the ground end of the pickup coil and insert a resistor there to serve as a frequency independent load for the lock signal. 220 ohms was chosen more or less arbitrarily. The attenuation of the lock signal applied to the resistor is made variable to allow suppression of a low frequency oscillation (<u>ca.</u> 1 Hz) which appears when we lock on a narrow Deuterium line such as acetone-d_6. When locked on a broader line such as D_2O the D.C. coupling of the lock signal can be increased to maximum. The decrease in the field jitter is dramatic, as may be seen from the traces.

Figures:
Original circuit and resulting trace
D_2O lock
H_2O peak
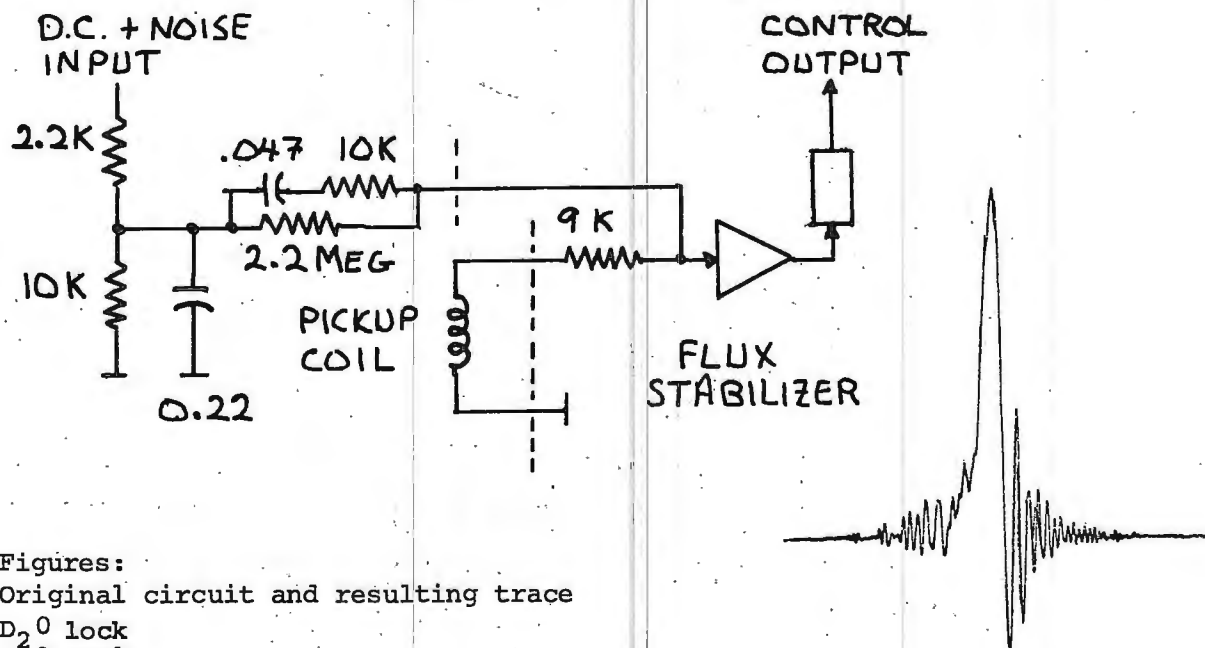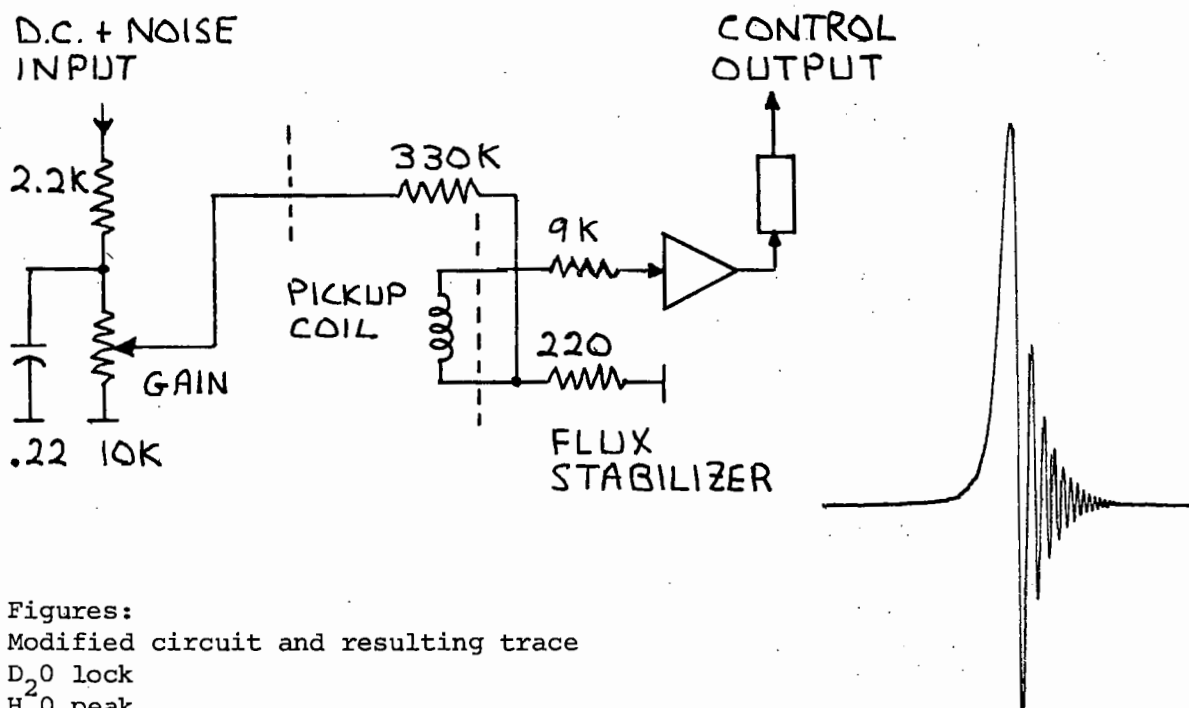
Figures:
Modified circuit and resulting trace
D_2O lock
H_2O peak

Please credit this contribution to the Dr. M. Cohn subscription.

Sincerely,

J. L. Engle

J. L. Engle

JLE:pf

Department of Chemistry   The Florida State University
                                 Tallahassee, Florida 32306

Jan 7th 1976

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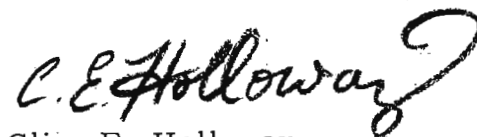College Station,
Texas 77843

Title ^{13}C Studies on Vulcanized Rubber.

Dear Dr. Shapiro,

We have been investigating the use of ^{13}C nmr
for determining component ratios of polymer blends. In the course of this
work we have measured T_1 and NOE parameters for solid raw polymer
blends and the vulcanized products since these factors can affect the
observed peak ratios. Since considerable work has been carried out in
this area elsewhere, we present some of our results for comparison. Except
on high field spectrometers the line widths of undisolved polymers are
normally too broad to permit resolution of components and we have had to
resort to expanding the polymers by soaking in an inert solvent (eg benzene)
in order to obtain linewidths of around 15Hz (the absorbed benzene linewidth
is about 5Hz). Rubber strips so treated and placed in a tube with D_2O as lock
yields spectra comparable to those obtained on untreated samples at 270 MHz.
(We are using a CFT 20). T_1 data obtained on these samples are given in the
table for comparison with other data. Close to full NOE was found for the
protonated carbons, and about 1.4 was the value for the tertiary carbon of
the polyisobutylene component. It appears that the major obstacle in the
use of peak areas to estimate component ratios lies in the reproducibility
of integration methods, and we feel that none are sufficiently accurate at this
stage to give results reliable enough for industry. However, a method using
direct comparisons of the overall spectra of known and unknown samples might
prove a useful fast guestimate for individual operations. The interpretation

of the T_1 and NOE parameters themselves are attendant upon further studies. We also hope to be able to make some comparisons with data obtained at 270 MHz, courtesy of Professor Levy and the FSU Bruker 270.

Yours sincerely

C. E. Holloway

Clive E. Holloway,

Dept. Chem. York University.
on sabbatical at FSU.

^{13}C T_1 Values for Rubber Blends. (major component only)

	$-CH_2-$	$-\overset{\mid}{\underset{\mid}{C}}-$	$-CH_3$
*			
Vulcanized . 100% butyl	0.07 sec.	0.53	0.16
90% "	0.11	0.77	0.20
80% "	0.12	0.60	0.22
65% "	0.10	0.74	0.19

* Other component EPDM . Also contains inorganic filler and C-black.

	$-CH_2-$	$-C-$	$-CH_3$	
Raw polymer 100% butyl	0.15	0.91	0.26	
Crosslinked Butyl rubber	0.16	1.5	0.12	ref 1
24% soln in CCl_4	0.13	1.23	0.19	ref 2

ref 1   R.A.Komoroski & L Mandelkern Private Communication
ref 2   Inoue, Nishioka, & Chujo J.Polymer Sci, 11, 2237 (1973)

ps. Please credit contribution to subscriptipn from York University.

Université de Nancy I

LABORATOIRE

DE CHIMIE THÉORIQUE

Case officielle Nº 140 - 54037 NANCY Cedex
Tél. 27.00.24 (Poste 2049 et 2051)

NANCY, le 8 janvier 1976

D. CANET - J.P. MARCHAL

Professor B.L. SHAPIRO
Texas A and M University
College of Science
College Station Texas 77843
U.S.A.

Title : ^1H – ^{15}N direct couplings observed in natural abundance by proton NMR FT

Dear Professor Shapiro,

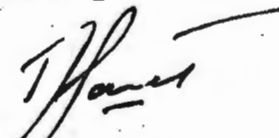Thank you for your blue reminder of december 2, that we received a week ago.

We wish to present further results obtained by our AISEFT (Abundant Isotope Elimination Fourier Transform) method [1]. The figure shows, from top to bottom :

- the normal spectrum of s-triazine partially oriented in Merk Phase IV
- the AISEFT spectrum with ^{13}C irradiation
- the AISEFT spectrum with ^{15}N irradiation.

24 hour accumulations were necessary to get this later spectrum.

These experimental results yield all the H-H, ^{13}C-N and ^{15}N-H direct couplings. Further details and geometrical determinations will be published shortly.
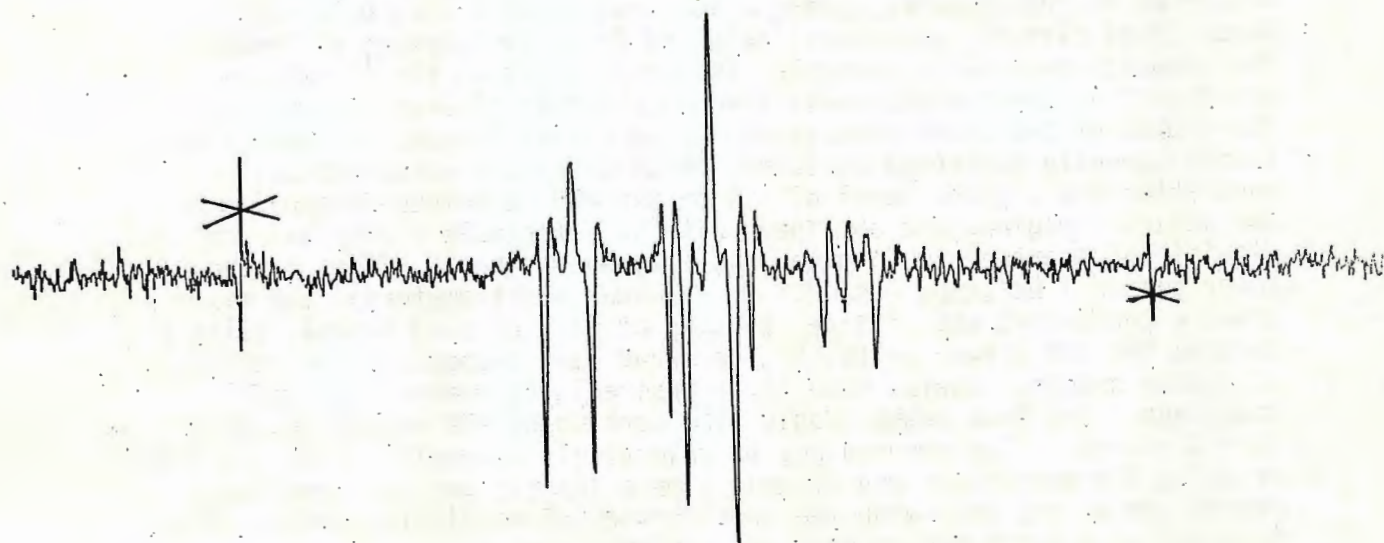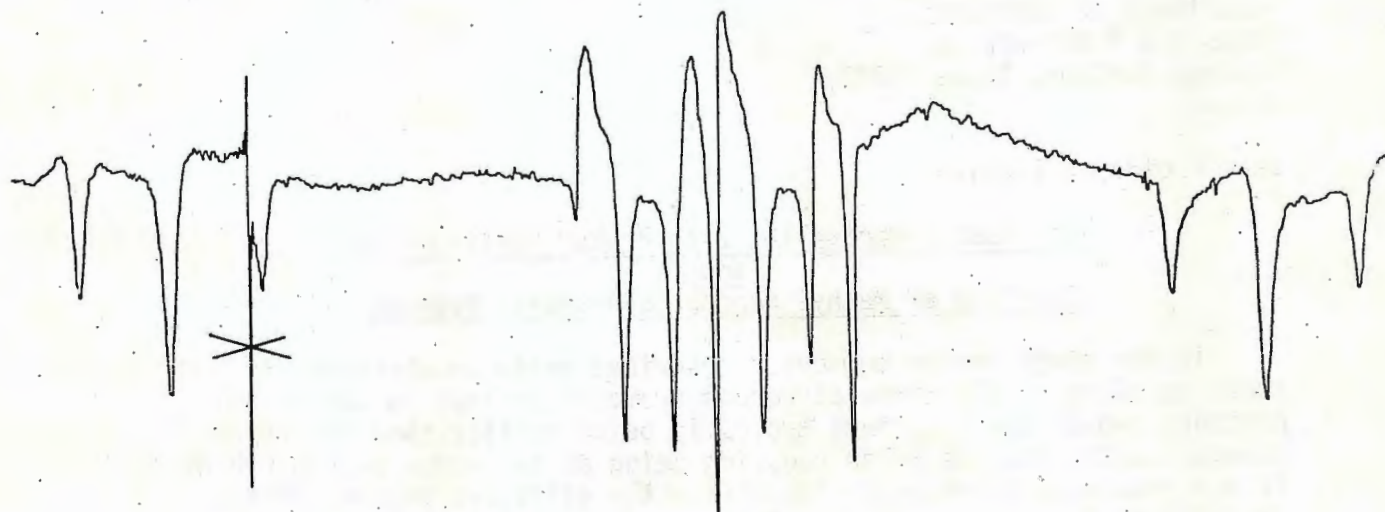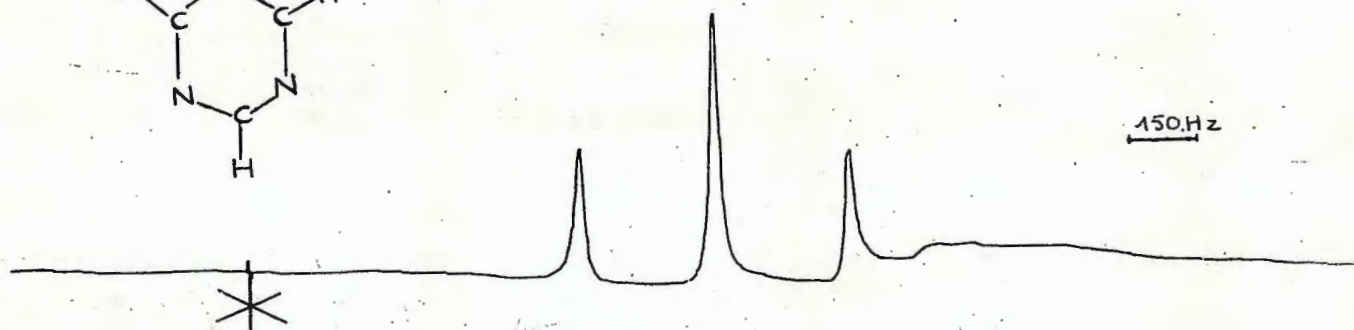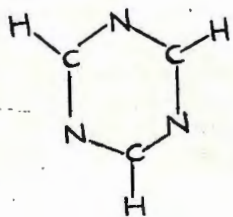
Yours sincerely.

J.P. MARCHAL   D. CANET

[1] D.CANET, J.P.MARCHAL and J.P.SARTEAUX, C.R. Acad. Sc. Paris, _279_, 71, (1974)

J.P.MARCHAL and D.CANET, J. Am. Chem. Soc., _97_, 6581, (1975)

150.Hz

BROCK
UNIVERSITY
REGION NIAGARA

Department of
Chemistry

416/684-7201

January 9, 1976.

Glenridge Campus
St. Catharines,
Ontario L2S 3A1
Canada

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

Dear Professor Shapiro:

Re: Double Decoupling with Bruker Spectrometer
and
### Coupling of Methyl Groups to Aromatic Protons

In our study of the compounds described below we observed for
some, coupling of all three different aromatic protons to the methyl
protons, two of the couplings typically being smaller than the third.
However, with even the large coupling being on the order of 0.5-0.8 Hz
it was necessary to decouple two distinctly different regions of the
aromatic part of the spectrum. This was easily accomplished on our
Bruker WP-60 spectrometer, using a low cost SRA-1 Double Balanced
Mixer (Mini-Circuit Laboratory) obtained from Jim Courtney of Bruker.
The computer controlled decoupler frequency (BU-8 on the ^{1}H LO) was
mixed with an appropriate audio frequency (HP 4204A decade oscillator),
the output of the mixer then going to the Pulsed Homonuclear decoupler
(cable normally connected to BU-8). With a 0.4-0.5 volts RMS audio
modulation and a power level of 8.9 on the PHD complete decoupling of
two separate regions are obtained, with no detectable center band or
significant overtones. On older machines where the O2 offset is com-
puter set in 1 Hz steps (vs. 0.1 Hz on newer spectrometers), the mixer
gives a convenient way of finer setting of O2. We also intend, using a
Wavetek 141 VCG driven by the HP, to broad band decouple whole regions
of proton spectra, useful when it is desirable to remove many small
couplings. The same setup should also work using the hetero-decoupler
in ^{13}C spectra. Two protons may be selectively decoupled in the CW mode,
or using VCG modulation and CW mode a more sharply defined broad band
region can be set than with the uncalibrated BB modulation width. Many
possibilities exist and we have not explored them all.

Dr. B. Shapiro   January 9, 1976.

Coupling of ortho aromatic protons to methyl groups which are meta to an electron-withdrawing group have been reported previously by Spragg (TAMUNMR 179-30). We wish to report an extension of this effect, observed with a series of heterocyclic compounds.

2-methylthioxanthone(I) and 2-methylacridone(II) show a doublet for the methyl group with couplings of 0.77 and 0.82 Hz respectively.
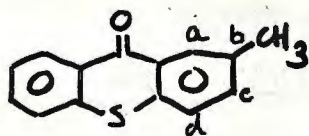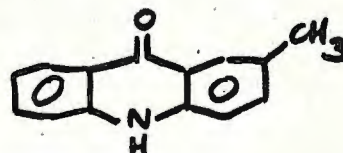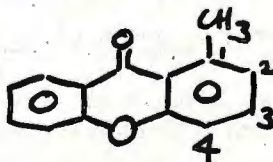
(I)   (II)

Irradiation of the CH_3 produced some decoupling in the low field portion of the aromatic region, which we ascribe to the proton adjacent to the carbonyl, H_a. Irradiation of this proton collapses the doublet. Supportive evidence for the assignment of H_a is the absence of the low field multiplet in 1-methylxanthone(III).

(III)

These observations led us to expect similar behaviour in 2-methylxanthone. However, the methyl group in this compound appeared as a rather broad peak with shoulders. Irradiation of the methyl group gave decoupling in the low field and high field portions of the aromatic region of the spectrum. Irradiation of the high field proton (H_c) produced a doublet (J = 0.55 Hz) in the methyl region.

Coupling of both ortho protons in 3-methylxanthone again complicated the methyl absorption. Decoupling of protons H_b and H_a separately gave an unresolved peak but when a double irradiation of protons H_a and H_b was performed (see above), a doublet was observed in the methyl region (J = 0.55 Hz).

As we expected, the 1-methylxanthone methyl could not be resolved by any single or double irradiation but appeared as a multiplet with couplings ~0.2 Hz.

Yours sincerely,

Ian D. Brindle,   Timothy R. B. Jones,   Jack M. Miller,
Senior Demonstrator. Senior Technician.   Professor, Chairman.

JMM/db

CHIMIE ORGANIQUE PHYSIQUE
—
UNIVERSITÉ DE NANTES
U E.R DE CHIMIE

38, Bd Michelet - 44000 NANTES
B. P. 1044
Tél. (40) 74.50.70

NANTES, le 15.1.76

Professor B.L. SHAPIRO
TEXAS A.M. UNIVERSITY
Department of Chemistry
College Station
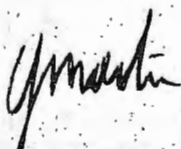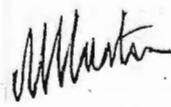
<u>TEXAS 77843</u>   USA

Dear BARRY,

<u>BRUKER-VARIAN comparison for carbon spin-lattice relaxation time measurements</u>

This paper is concerned with the dynamic behaviour of amides
and iminium salts and tries to find a tentative explanation for their reactivity
in electrophilic additions. With this in view, we have measured the carbon rela-
xation times of such compounds in various conditions. The results will soon be
published but we may already present here a comparison of results obtained using
two spectrometers (BRUKER WP 60 DS and VARIAN XL 100-12). In order to extend the
field of comparison, we have taken into consideration two other already published
sets of data concerning dimethylformamide (1)(2). Considering the difficulty of
obtaining accurate relaxation time values, the data collected in the table for
DMF appears quite consistent. Taking into account, however, the difference in
temperature between the spectrometers (a 5 degrees decrease in temperature causes
a five per cent decrease in T_1 for DMF ; Ea $\triangleq$ 3.2 kcal.mole^{-1}) and the difference
in concentration and solvent, results are slightly different.

The T_1 values recorded at 15.1 MHz (WP 60 DS and NV 14) are
very consistent but the values obtained at 25.2 MHz seem to be too low (XL 100-12)
or too high (XL 100-15). The values relative to the iminium salt obtained at
15.1 MHz (WP 60 DS) or 25.2 MHz (XL 100-12) are however, consistent and show
the drastic decrease of T_1 which is due to the reduced motion of the ion-pair
of the salt in solution with respect to the amide.

With best regards.

G.J. MARTIN

M.L. MARTIN

	Our results				G.C. LEVY et al. (1)		H. NAKANISHI (2)	
	WP 60 DS (BRUKER)		XL 100-12 (VARIAN)		XL 100-15 (VARIAN)		NV 14 (VARIAN)	
(A)CH_3 $\;$ O $\quad$ N — C (B)CH_3 $\quad$ H	$T_1(A)$	$T_1(B)$	$T_1(A)$	$T_1(B)$	$T_1(A)$	$T_1(B)$	$T_1(A)$	$T_1(B)$
	16.5	10.5	14.4	9.2	17.8	10.5	17.1	11.4
	(>0.95)	(>0.996)	(>0.98)	(0.98)	(a)	(a)	(a)	(a)
(A)CH_3 $\quad$ S CH_3 $\quad$ N = C (B)CH_3 OSO_2F^- H	$T_1(A)$	$T_1(B)$	$T_1(A)$	$T_1(B)$	/		/	
	4.5	2.2	4.2	2.5				
	(>0.93)	(>0.994)	(>0.96)	(>0.97)				
Conditions	$CD Cl_3$ – 5 M – 10 mm T = 301 K k = −0.997		$CD Cl_3$ $\;$ 5 M – 5 mm T = 305 K k = −0.72		C_6D_6 – 10 M–10 mm T = 298 K k = −0.45		$CD Cl_3$ – 10 M – 8 mm T = 304 K k = (b)	

Carbon spin-lattice relaxation times obtained by the Inversion Recovery, F.T. method. Each reported T_1 value is the average of three measurements (this work). The samples were degassed.

k is the offset parameter defined from the field intensity and the sweep width (3).

Values in brackets are those of R^2, the coefficient of confidence of the exponential adjustment.

(a) not indicated ; (b) data not available for computation.

(1) G.C. LEVY and G.L. NELSON - J. amer. Chem. Soc. 1972, 94, 4897 -

(2) H. NAKANISHI and O. YAMAMOTO - Chem. Phys. Letters 1975, 35, 407 -

(3) G.C. LEVY and I.R. PEAT - J. Magn. Res. 1975, 18, 500.

LILLY RESEARCH LABORATORIES

January 5, 1976

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

Dear Professor Shapiro:

^{15}N Spectra of Aminoglycosides

During recent months, we have had very good luck measuring the
^{15}N nmr spectra of some of the factors of the nebramycin complex
of antibiotics. The spectra are surprisingly easy to measure.
On our JEOL spectrometer, we have measured the spectra of
solutions as dilute as 0.2 M, though this admittedly required
overnight scanning. The spectra show well-resolved nitrogen
resonances at the acidic and basic extremes of pH, while
occasional peak overlaps occur at intermediate pH. We have
been able to assign most of the resonances simply by comparison
of the spectra of the various factors.

tobramycin   apramycin
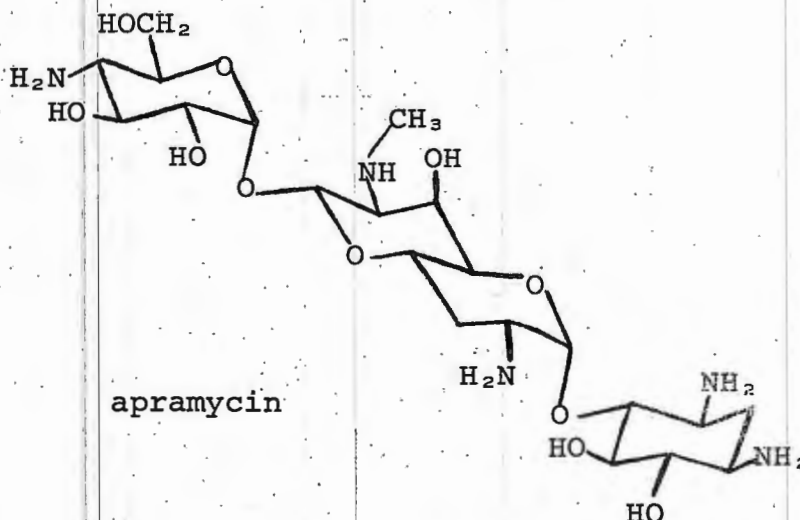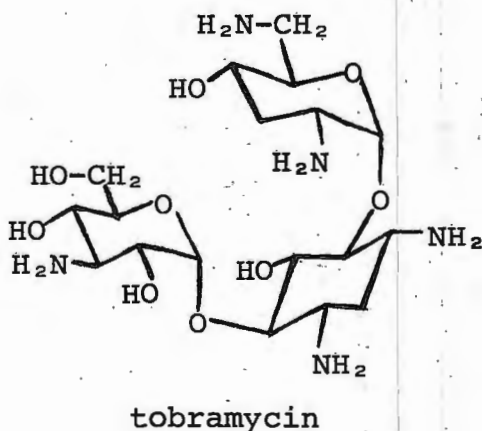
We have also measured the pH dependences of the nitrogens of two
of the major factors, tobramycin and apramycin. The pK_a values
of the various amine nitrogens all seem to fall into a narrow range
centered at about 7, except for the $-CH_2NH_2$ group which is sig-
nificantly more basic.

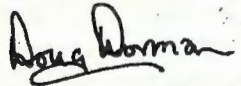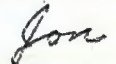Professor B. L. Shapiro   January 5, 1976

At high pH, we find no splitting of the ^{15}N resonances when the decoupler is turned off. Under conditions of proton decoupling, the resonances all have the same phase as the NH_4Cl standard and are therefore presumably "inverted." The T_1 values must be rather short, as we pulse with a 45° pulse every 2 seconds. As yet, we have taken no precautions to preclude paramagnetic impurities. However, some recent samples, which give ^{13}C spectra with relatively broad lines, give no ^{15}N spectra at all. We hope to investigate the cause of this problem as time permits.

We hope to be able to submit a manuscript based on this work in January, 1976.

Sincerely,

LILLY RESEARCH LABORATORIES

Douglas E. Dorman, Ph.D., Jonathan W. Paschal
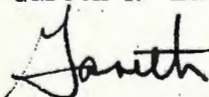Physical Chemistry Research

DED/JWP:vr

CONTINUED FROM P. 32.

The closest analogy we can find is to racemization of para-substituted biphenyls where the rate enhancement by electron donating substituents is attributed to resonance stabilization of the intermediate and/or facilitation of bending at the C_1 carbon of the phenyl ring.
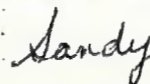We are also in the process of looking at other metals to clarify the influence of the metal ion on the rate of rotation and sensitivity to para-substituent.

Sincerely,

Gareth R. Eaton   Sandra S. Eaton

COLORADO SEMINARY

UNIVERSITY OF DENVER

UNIVERSITY PARK • DENVER, COLORADO 80210

DEPARTMENT OF CHEMISTRY/303·753·2436

January 19, 1976

Effect of Para-substituent on Rate of Phenyl Ring Rotation in Ruthenium(II)
and Titanium(IV) Complexes of Tetrakis(p-R-phenyl)porphyrin.

Dear Barry,

We have recently shown that rotation of phenyl rings in metal complexes
of tetraphenyl porphyrins with protons in the ortho positions of the phenyl
rings can be observed by dynamic nmr. Currently we are finding that the rate
for the process depends on the electron-donating or withdrawing properties
of the para-substituent as well as on the metal ion.

We are using DNMR3A, a faster version of DNMR3, kindly provided by Hack
Bushweller and Jacques Brunelle of Worcester Polytechnic Institute to obtain
rates of exchange for the 4-spin phenyl proton systems in a series of
complexes of tetrakis(p-R-phenyl)porphyrin, M(p-R-TPP)(X)(Y). We have looked
at M=Ru, X=CO, Y= 4-t-butyl-pyridine (t-Bupy), R = Et_2N, OMe, Me, iPr, CF_3
and M=Ti, X=O, R = OMe, Me, iPr, CF_3. The difference in axial ligands on
the two sides of the porphyrin plane results in nonequivalence of the ortho
protons and of the meta protons. The slow exchange chemical shift differences
for the ortho protons are ca. 20 Hz and 30 Hz for M=Ru and M=Ti, respectively.

The rates of phenyl ring rotation for M=Ti are about 20 times faster
than for M=Ru and are considerably more sensitive to the electronic effects
of the para-substituent. On going from R=CF_3 to OMe the rate of ring
rotation increases by about 50 % for M=Ru, but about a factor of 4 increase
occurs for M=Ti. We attempted to use Hammett σ values to correlate the
rates with the electronic effects of the substituents. A plot of log(rate
constant) vs. Hammett σ_p values for the Ruthenium complexes has a slope (ρ)
of ∼-.25 (ignoring R=Et_2N) but the point for R=Et_2N is way off the line.
An analogous plot for the Titanyl complexes gives a slope of ∼-.70, but
we do not yet have the point for R=Et_2N. The use σ^+ or σ^- values does
not give an improved correlation. However, for M=Ru, we get a good correlation
between the rate of phenyl ring rotation and either λ_{max} or intensity ratios
in the electronic spectra. Further investigation of other para-substituents
and possible correlations are in process. Comments regarding correlations
that have fit other systems would be welcome.

Typical thermodynamic parameters obtained from the total lineshape
analysis as a function of temperature are given below. Uncertainties are +3SD.

| Complex	$\Delta G^{\neq}_{298}(\frac{kcal}{mole})$	$\Delta H^{\neq} (\frac{kcal}{mole})$	$\Delta S^{\neq}$ (e.u.)
Ru(CO)(p-CF_3-TPP)(t-Bupy)	18.4±1.3	16.5±1.0	-6.6±2.8
Ru(CO)(p-OMe-TPP)(t-Bupy)	18.3±1.4	16.5±1.1	-6.1±3.0
Ru(CO)(p-Et_2N-TPP)(t-Bupy)	17.3±0.9	15.8±0.7	-5.2±1.8
TiO(p-CF_3-TPP)	16.2±1.4	13.6±0.8	-8.7±2.6
TiO(p-OMe-TPP)	15.5±0.8	12.0±0.6	-11.7±1.7

January 26, 1976

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

Dear Barry:

Carbon-Phosphorus Coupling Constants in Phosphonic Acids

Recently we have studied the ^{13}C NMR spectra of various phosphonic acids with the following general structure:

$$ClCH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-X$$
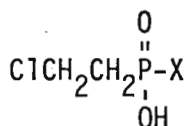
The one bond phosphorus-carbon coupling constants are in the range of 131.5-139.1 Hz, which are close to the values observed by Gray on phosphonates (G.A. Gray, J. Am. Chem. Soc., **93**, 2132 (1972). However, it is interesting that the coupling between phosphorus and the carbon adjacent to chlorine was not observed. Table 1 presents the coupling parameters of three phosphonic acids in DMSO-d_6 solution.

Table 1.   Carbon-Phosphorus Couplings

X	Jcp	Jccp	Jcop	Jccop	Jcpop
OH	131.5	~ 0			
OCH_2CH_2Cl	133.6	~ 0	5.3	7.1	
$O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-CH_2HC_2Cl$	139.1	~ 0			4.3

Sincerely yours,

C. K. Tseng

CKT:mar

Department of Chemistry   The Florida State University
                                  Tallahassee, Florida 32306

NMR SPECTROSCOPY POST DOCTORAL FELLOWSHIPS AVAILABLE

Dr. Leo Mandelkern and I have several postdoctoral fellowships
available with starting dates as early as January or as late as
September, 1976. These positions are based on 68 MHz ^{13}C and
270 MHz ^1H nmr studies of synthetic and biopolymer systems; also ^{13}C,
^{15}N and other nuclei T_1 studies of small molecules. The table
below summarizes our planned research effort.

Project	Earliest Starting Date	Required Specialty	Research Advisor(s)
(a) peptide structure and conformation	1/76	physical, organic or biochemistry	LM or joint (LM and GCL)
(b) synthetic polymer structure in the bulk phase	3/76	physical or organic	joint
(c) multi-nuclei NMR (^{15}N, metals) on small molecules	7/76	physical	GCL
(d) building and exploiting a new ultra-high-sensitivity ^{13}C and ^{15}N spectrometer (half time can also be spent on project (c) or other research)	6/76	physical (or organic with electronics experience)	GCL and RR (Richard Rosanske)

Leo Mandelkern and I are particularly anxious to fill positions
a,b, and d. All interested persons should write directly to me
(or to Dr. Mandelkern) indicating their interest. They should
include a curriculum vitae and arrange for two letters of recom-
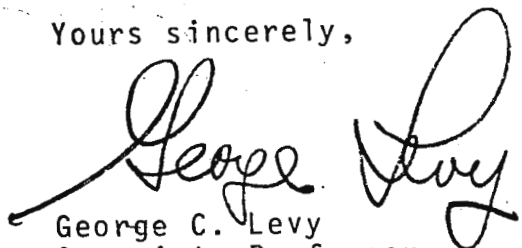mendation to be sent directly to us.

The salaries for positions (a) - (c) range from $8000. - $9,500 depending on experience; for position (d) the maximum salary can be significantly higher for especially qualified candidates. Tallahassee is an inviting community of 100,000 with a significantly lower cost of living than typical for larger cities.

Our laboratory currently includes a Bruker HX-270 equipped for ^{13}C, ^{15}N, and 270 MHz ^1H nmr and a Bruker HFX-90 set up for most magnetic nuclei. Both instruments have dedicated disc-augmented computers and have been modified for improved quadrature detection. In house construction of 13mm (and soon hopefully 15mm) sample capability gives added ^{13}C and ^{15}N sensitivity.

Please bring these positions to the attention of anyone who has potential interest.

With appreciation from Leo Mandelkern and from me.

Yours sincerely,

George C. Levy
Associate Professor

Opening for a Postdoctoral Fellow at the ETH in Zürich

We will have an opening in fall 1976 for a postdoctoral fellow with a strong interest in the development and application of new techniques in NMR. A good theoretical background and experimental skill are required at the same time. Possible areas of research are: High resolution solid state resonance, two-dimensional spectroscopy, zeugmatography, optical polarization, relaxation in coupled spin systems.

Please contact   Prof. Dr. Richard R. Ernst
Laboratorium für physikalische Chemie
Eidgenössische Technische Hochschule
Universitätstrasse 22
8006 Zürich, Switzerland

⊓⊏U

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

Department of Chemistry

January 26, 1976

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

Dear Barry,

First, our FX-60 has arrived and is up and running. In fact,
we were obtaining spectra 24 hours after the service man arrived
for the installation. We have been in operation for almost a
month and we have had no serious problems. All in all I think we
will be very happy with the system.

Second, in response to your blue reminder, let me tell you
a story whose ending has yet to be written. In connection with
some other work, we became interested in the bromination (in
acetic acid) of diphenylcyclopropyl carbinol. The reaction was
simple enough to run and the product was a nice crystalline solid
and it was easily purified.

A 100 MHz proton spectrum showed, in addition to a signal for
the acetate methyl (δ=2.04) and the aromatic protons, four addi-
tional multiplets at δ=6.26 (1H), 3.59 (2H) 2.58 (1H) and 1.71 (1H).
The one proton signal at δ=6.27 bothered us quite a bit since it is
difficult to write a structure for this product which would have
a proton this far downfield without including a double bond.

We obtained a ^{13}C spectrum and this seemed to raise further
questions. The chemical shifts (relative to TMS, of course) and
multiplicities (from off-resonance decoupling) were; δ=169.0(s)
139.6(s), 129.1(d), 128.1(d), 127.5(d), 127.0(d), <u>86.3</u> (s) 56.6 (d)
37.7(t), 31.2(t) and 22.1(q).

From these spectra we have tentatively assigned the following
structure to the product;

$$\phi_2 \underset{1}{\overset{OAc}{\underset{|}{C}}} - \underset{2}{\overset{Br}{\underset{|}{CH}}} - \underset{3}{CH_2} - \underset{4}{CH_2} Br$$
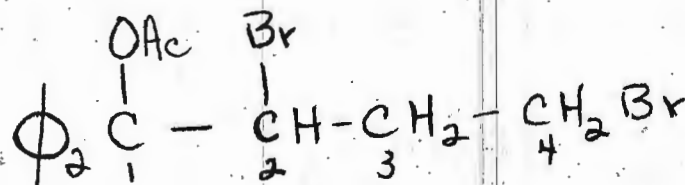
the ^{13}C chemical shift of C-1, we feel is consistent with the proposed structure rather than the, perhaps, more reasonable structure where the acetate at C-1 and bromine at C-4 are interchanged. In addition, the following reaction is known to occur readily.

$$\underset{\phi_2 C}{\overset{Br}{|}} - \underset{\underset{H}{|}}{\overset{Br}{|}} CR \xrightarrow{-HBr} \phi_2 C = C \overset{R}{\underset{Br}{\diagdown}}$$
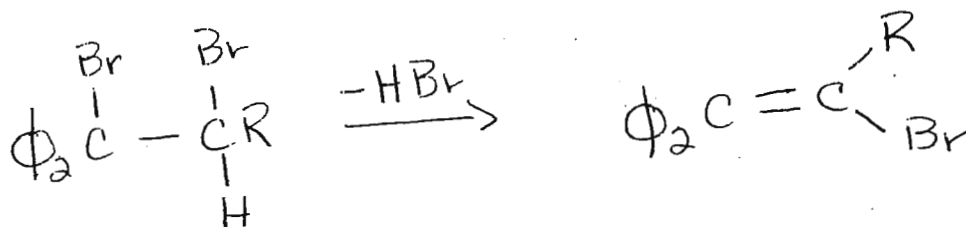
It therefore seems that the proposed structure is the more reasonable one. It is not easy, however, to write a mechanism for the reaction and we are, at present, working toward this end. We hope to have all of the details completed and a manuscript prepared in a short while.

In the meantime, we have given some crystals of the product to Bill Watson and we hope that he will soon have the structure for us. If our propsed structure is correct, the chemical shift of the proton at C-2 of $\delta=6.27$ must be some sort of a record.

Our best regards to everyone.

W. B. Smith   T. W. Proulx   G. Barnard

IBM

International Business Machines Corporation

Monterey & Cottle Roads
San Jose, California 95193
408/227-7100

January 23, 1976

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

Dear Barry:

Dr. Hans-Martin Vieth from the Max-Planck Institute of Heidelberg has
been visiting my laboratory and has been helping to build a steady-state
double resonance spectrometer. One of the difficult parts of this experi-
ment is to create sufficiently strong, yet homogeneous, rf fields.
Hans-Martin has succeeded in putting together a coil system which is
capable of producing 20 gauss H_1 at 25 MHz. The coil is saddle shaped,
1.5" in diameter by 3" long, and specifically designed to meet the
Helmholtz condition over a large volume--it is a single-turn gold-plated
copper ribbon. In order to dissipate the power required to generate the
field, the coil is cooled by a liquid nitrogen flow. At 77K, 600 watts
are required to produce the field, and the duty cycle is 33%, so the
system runs at 200 watts average power, with minimal effect on the
ambient temperature of the probe. The coil has a Q of ~200, so several
kilovolts appear across the coil and series capacitor, which is home-
made from copper and teflon. The parallel capacitors, which have more
capacitance, must handle several hundred volts, and we use commercial
capacitors (Vitramon porcelain capacitors) for this.

After this exercise, we would be very interested to know if anyone has
had systematic success in shimming an rf coil.

Best regards,

C. S. Yannoni
Research Laboratory

/jmv

New XL-100A Feature:

Single-Sideband Filter Cuts Data Acquisition Time in Half

Each time we introduced a new performance refinement for the XL-100A NMR Spectrometer, it's been a technological milestone in its own right. But when we added the latest — a single-sideband filter which eliminates negative frequency noise — something else happened. It combined with the unshakeable magnet stability and sophisticated interlocking electronics of the XL-100A to create a quantum jump in performance: the ability to obtain outstanding spectra from microgram samples.

We ran a 5-μg sample of gelsemine ($C_{20}H_{22}O_2N_2$) with the result you see here. We think the spectral quality speaks for itself.

Microgram sample capability, of course, is good news if you are involved in metabolite studies, biosynthetic research, flavors and fragrances — any field in which samples come from GLC or TLC, or are scarce for any other reason.

The features that form the backbone of the XL-100A's microsample capability include:

1-mm Microinsert
Ensures best possible signal from small samples by optimizing the rf coupling between the sample and the system's receiver coil.

Single-Sideband Filter
Cuts data acquisition time in half by eliminating the noise which normally folds into an FT spectrum.

FT Disk Accessory
Permits acquisition of high-resolution FT spectra by expanding the maximum data table capacity of the system to 32K words.

For further information write to:
Varian Instruments, 611 Hansen Way, Box D-070, Palo Alto, CA 94303.

varian
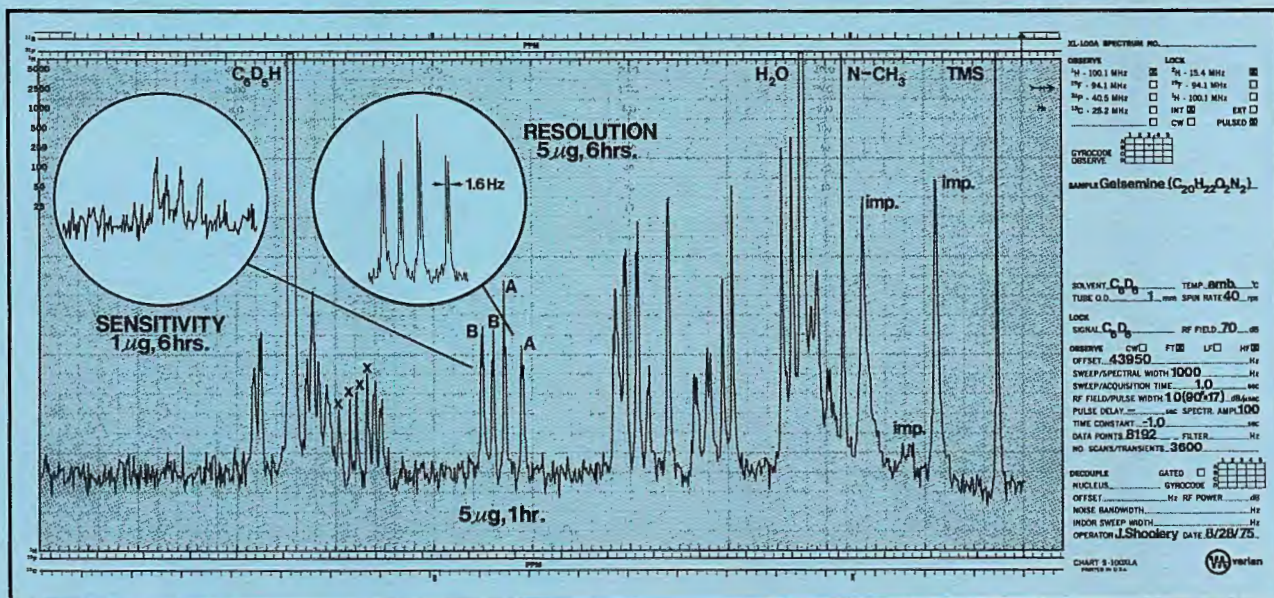
We dissolved 5 μg of gelsemine in 5 μl of C_6D_6 and pulsed it at one-second intervals for one hour, using a tip angle of 53° (10 μsec pulse) and a 2,500-Hz spectral width. Note the clear ABX pattern from the three vinyl protons and the excellent resolution of the 1.6-Hz geminal coupling! The spectral excerpts show two six-hour runs of 5-μg and 1-μg samples to demonstrate how resolution or sensitivity can be further enhanced at the expense of time.