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Newsletter

No. 219

December, 1976

- C. K. Tseng, D. H. Marr and D. J. Bowler
Tin-Phosphorus Coupling Constants in
Dithiophosphates 1
- A. D. Sherry
Aqueous Trivalent Lanthanide Ions as NMR
Probes 3
- T. Schaefer
Postdoctoral Position and Equipment For Sale . 4
- J. Kida and M. Imanari
New Multi-Nuclear Capability on the JEOL
FX-100 5
- G. Mavel, F. Mathey and R. Mankowski-Favelier
Bicentennial Contribution - $^{13}\text{C}/^{31}\text{P}$ Ballott
Casting Party 8
- W. Bremser
Philosophy of Collecting Spectroscopic Data . 11
- J. Engel and H. M. Schiebel
Assignments of the Methyl Groups of Open-
Chained Polypyrroles Related to Bile Pigments
by Means of ^1H NMR Spectroscopy 16
- G. Bauer and G. Hägele
Spectral Analysis of a Novel, Stable
Phosphorane. 19
- B. Diter, J. Brondeau and D. Canet
Variable Temperature Problems. 21
- A. G. Marshall
Simple Recipe for pH Meter Reading in D_2O . . 23
- L. F. Johnson
60.72 MHz ^{31}P Spectra of Whole Human Blood . 25
- P. Laszlo
 ^{23}Na Study of the Na^+ -Sugar Interaction in
Non-Aqueous Solvents. 27
- E. A. Sokoloski
Phosphorus-31 Spectra of Lanthanide-Doped
Solutions of Biomolecules 30
- K. D. Berlin
Safety Switch for Power Cut Off from the
Decoupler in ^{13}C MR Analysis with the V-4412
Probe on an XL-100(15). 33
- S. L. Patt
New Varian East Coast Applications Chemist. 34
- G. W. Buchanan
Relative Signs of ^{13}C - ^{15}N Couplings in
Configurational Isomers 35
- H. S. Gutowsky
Lanthanide Shift Reagents; Postdoc Opening. 37
- W. S. Brey
Wide-Line Spectroscopy; Change of Address . 39
- R. B. Johannesen
Prospective Standard Reference Material. . 41
- G. A. Gray
 ^{17}O NMR Determination of $^1\text{J}_{\text{PO}}$ and $^2\text{J}_{\text{FO}}$. . 43
- J. Bus
 ^{13}C NMR of Unsaturated Linear Fatty Acid
Methyl Esters 45

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DEADLINE DATES: No. 220: 3 January 1977
 No. 221: 7 February 1977

All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
 Department of Chemistry
 Texas A&M University
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AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 219

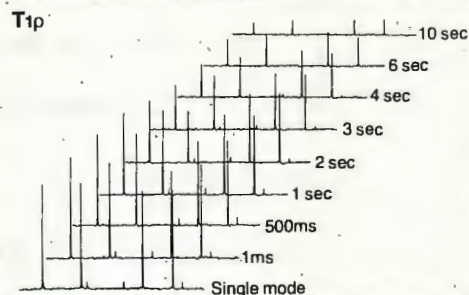
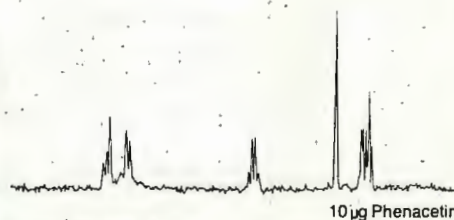
Bauer, G.19	Johannesen, R. B.41
Berlin, K. D.33	Johnson, L. F.25
Bowler, D. J.1	Kida, J.5
Bremser, W.11	Laszlo, P.27
Brey, W. S.39	Mankowski-Favelier, R.8
Brondeau, J.21	Marr, D. H.1
Buchanan, G. W.35	Marshall, A. G.23
Bus, J.45	Mathey, F.8
Canet, D.21	Mavel, G.8
Diter, B.21	Patt, S. L.34
Engel, J.16	Schaefer, T.4
Gray, G. A.43	Schiebel, H. M.16
Gutowsky, H. S.37	Sherry, A. D.3
Hagele, G.19	Sokoloski, E. A.30
Imanari, M.5	Tseng, C. K.1

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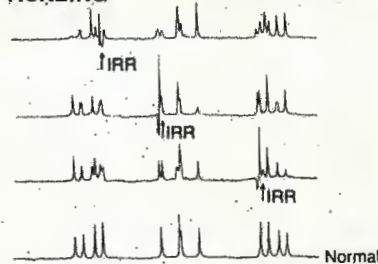
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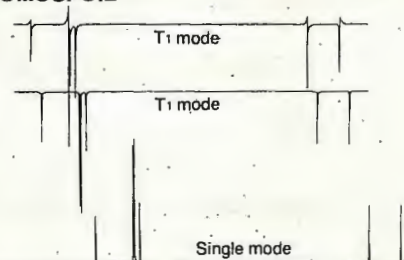
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October 19, 1976

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

SUBJECT: Tin-Phosphorus Coupling Constants in Dithiophosphates

Dear Barry:

We would like to report our data on the Tin-Phosphorus coupling constants for S-(tricyclohexylstannyl)-O,O-diisopropylphosphorodithioate, I, obtained on our CFT-20.

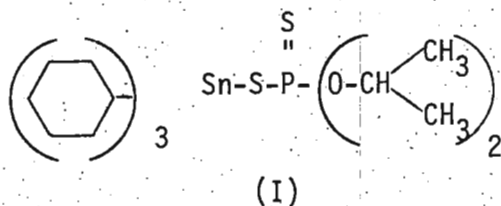
The phosphorus nmr spectrum of I, obtained at 32.1 MHz, consists of the main phosphorus resonance at - 94.6 ppm from 85% H₃PO₄, and the ¹¹⁹Sn and ¹¹⁷Sn satellites, Figure A. The measured coupling constants are:

$$J_{31\text{p} - 119\text{Sn}} = 42.4 \text{ Hz}$$

$$J_{31\text{p} - 117\text{Sn}} = 40.3 \text{ Hz}$$

The value of $J_{31\text{p} - 119\text{Sn}}$ was confirmed by the ¹¹⁹Sn nmr spectrum obtained on a modified Bruker HFX-90 at our Eastern Research Center. The ratio

$J_{31\text{p} - 119\text{Sn}} / J_{31\text{p} - 117\text{Sn}}$ is 1.052. The ratio of the corresponding gyromagnetic ratios of the two tin isotopes is 1.046¹.



Tin-Phosphorus Coupling Constants
in Dithiophosphates

October 19, 1976

Sincerely,

CTg

C. K. Tseng

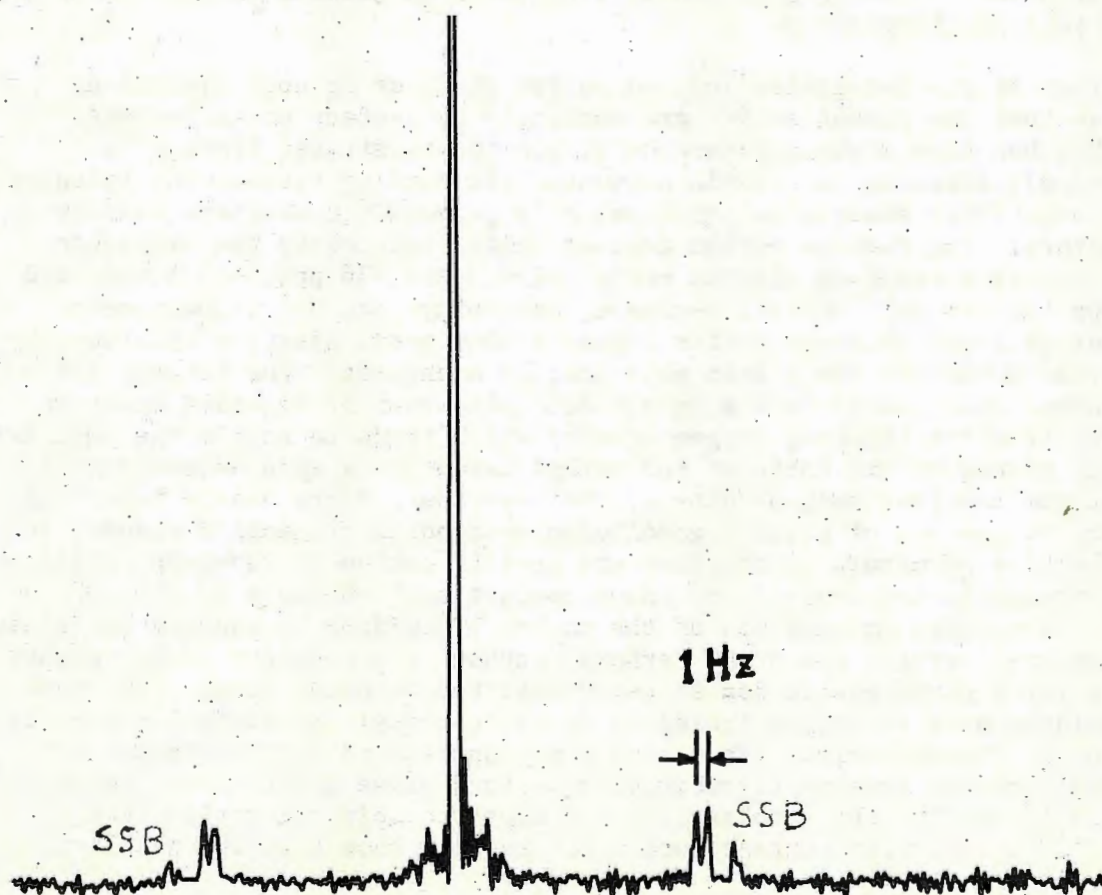
D. H. Marr

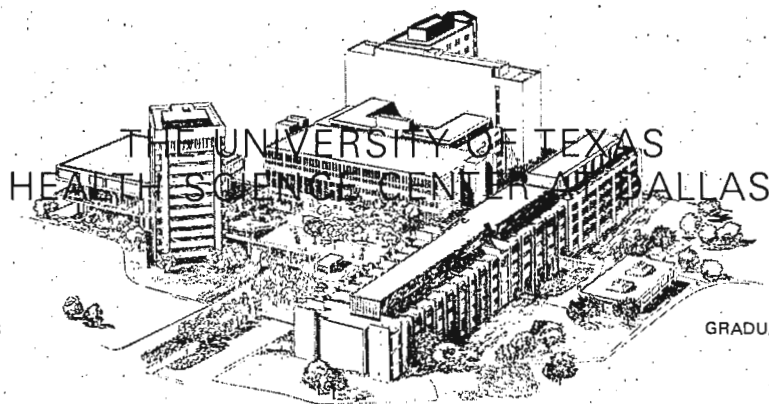
D. H. Marr

D. J. Bowler

D. J. Bowler

¹ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, N. Y. 1965.





GRADUATE PROGRAM IN BIOPHYSICS

GRADUATE SCHOOL OF BIOMEDICAL SCIENCES

15 November 1976

Dr. Bernard Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, Texas 77840

Dear Barry,

As you know, my laboratory has been investigating use of the aqueous trivalent lanthanide ions as NMR probes of metal-amino acid, peptide, and protein structures in solution. Our amino acid structural work has been limited to proton NMR until recently when a Bruker WP-60 NMR spectrometer was installed in the Biophysics Department at the UTHSC in Dallas. I would like to contribute some recent observations concerning carbon-13 linewidths in gadolinium-alanine complexes for your NMR Newsletter.

An examination of the lanthanide induced shifts (LIS) of aqueous alanine at pH 3 reveals that the carbon shifts are dominated by contact contributions. Although this has been shown a common occurrence for substrates binding to neutral $\text{Ln}(\text{dpm})_3$ reagents in organic solvents, the bonding between the hydrated ions and a negatively charged carboxyl group is generally considered largely ionic in nature. The alanine carbon contact shifts induced by the isotropic gadolinium ion at a metal to alanine ratio of 0.5 are -36 ppm, +52.3 ppm, and -3.4 ppm for the carboxyl carbon, α -carbon, and methyl carbon, respectively. The alternating signs in these shifts suggests that metal electron spin density is delocalized primarily via a spin polarization mechanism. The largest shift at the α -carbon must result from a direct delocalization of negative electron spin density from the ligating oxygen atom(s) which tends to negate the positive spin density placed at the carboxyl and methyl carbons via spin delocalization and enhance the negative spin density at the α -carbon. Particularly important with respect to the use of aqueous gadolinium as dipolar relaxation reagent to examine molecular structure in solution and confirm carbon-13 resonance assignments of proteins is the analysis of these contact contributions to the carbon linewidths. A cursory examination of the carbon linewidths in aqueous gadolinium-alanine solutions reveals the order carboxyl carbon > α -carbon > methyl carbon as expected for a paramagnetic ion situated near the carboxyl group. The measured linewidths at half height (relative to the carboxyl linewidths) are 1.00, 0.34, and 0.10, respectively. The scalar contributions to each linewidth may be estimated from the Solomon-Bloembergen equations using a rotational correlation time $\tau_c = 10^{-11}$ sec for the dipolar term and electron spin relaxation time $\tau_e = 1.5 \times 10^{-10}$ sec for the contact term. The results show that the gadolinium

Dr. Bernard Shapiro

11/15/76

contact shift contributes ~20% to the observed carboxyl linewidth, ~75% to the α -carbon linewidth, and only ~2% to the methyl carbon linewidth. Thus, the linewidths may not be used to extract structural information unless the observed carbon resonances are several bonds away from any possible metal coordination positions. Even qualitative use of gadolinium line broadening must be used with caution in view of the fact that the contact shift of the α -carbon is nearly twice as large as that for the much closer carboxyl carbon in the gadolinium-alanine complex.

Sincerely,

A. Dean Sherry

A. Dean Sherry
Associate Professor of Chemistry
UT-Dallas
Adjunct Professor of Biophysics
UTHSC-Dallas

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2



November 16, 1976.

POST-DOCTORAL POSITION AND EQUIPMENT FOR SALE

This is to advertise a postdoctoral position at a salary of \$850/month (taxable), beginning on or after April 1, 1977. Available machines include an HA100 and a new, multinuclear, WH-90 with an 1180 data system. Applicants should probably have a good background in relaxation measurements, although other abilities will be considered.

For sale is the console from a DP-60, later converted to DA-60I, which includes two thin probes, the lock-box, a tube-type superstabilizer without the coils, two r.f. units, the usual recorder, integrator, and the units concerned with the D of the DP. More details available to interested persons. Any offers?

Yours sincerely,

Ted Schaefer

Ted Schaefer,
Professor of Chemistry.



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November 9, 1976

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

"NEW MULTI-NUCLEAR CAPABILITY ON THE JEOL FX-100"

Dear Professor Shapiro,

As interest in "other-nuclei" NMR rapidly increases, there is a growing need for simplistic multi-nuclear capabilities for NMR spectrometers. However, since most of the non-proton nuclei suffer from low sensitivity and/or low natural abundance, it is extremely important to maintain the efficiency of the system while facilitating observation of different nuclei. In order to meet this need of many NMR spectroscopists, we have developed a multi-nuclear observation system based on the FX-100 which includes a variable frequency probe (TUNABLE PROBE).

With this letter, we include several spectra obtained with the TUNABLE PROBE in our laboratory. The important features are as follows:

1. The electronic circuitry used in the "new" probe does not include any special insert such as a tapped sample coil, since impedance matchings to the receiver and transmitter are made by external capacitors and inductors, respectively.
2. The above enables the use of a "super insert" coil which is wound inside the glass sleeve in order to obtain maximum sensitivity.
3. The $\pi/2$ pulse is between 20 and 50 μ sec over the entire frequency range when using a 20W wide band power amplifier. This is very important in many experiments, such as relaxation times where an even power distribution is required over the observed spectral width frequency range.
4. The probe can be operated at any desired frequency between 5MHz and 41MHz. The frequency range is covered by several frequency channels that are equipped with a vernier. Fixed frequency channels are also available for rapid setting of particular frequencies. Each frequency channel is selected solely by a switch operation.

Since no change of insert or probe head is required over the entire frequency range, operators can quickly select each nucleus without any need for shim re-adjustment. Various experiments can be easily performed on many different nuclei while maintaining excellent sensitivity.

Sincerely yours,

J. Kida

M. Imanari

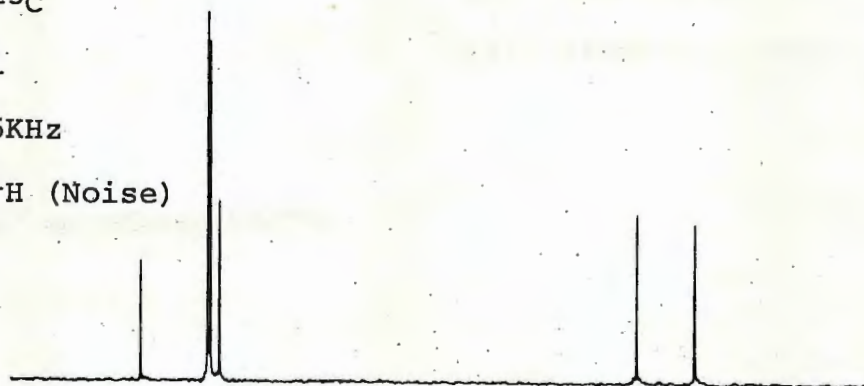
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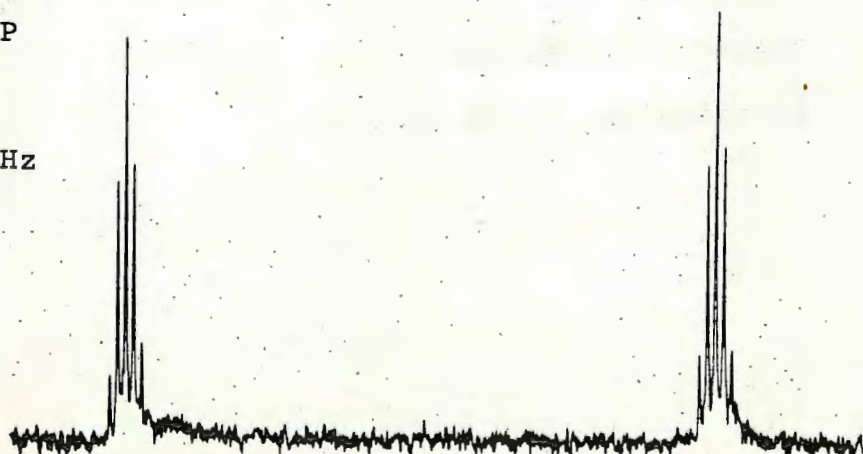
Sample $C_6H_5C_2H_5$ 90%
Nucleus ^{13}C
No. of Pulse 1
Spectral Width 5KHz
Irradiation 1H (Noise)

a)



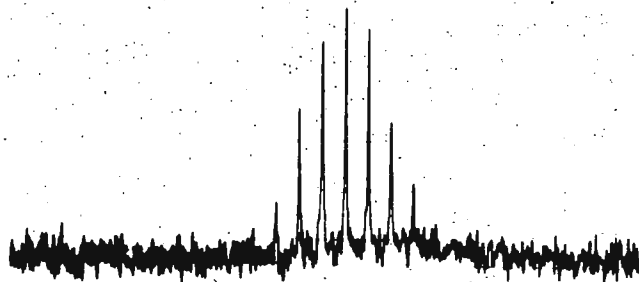
Sample $OP(OC_2H_5)_2H$ 5%
Nucleus ^{31}P
No. of Pulse 1
Spectral Width 1KHz

b)



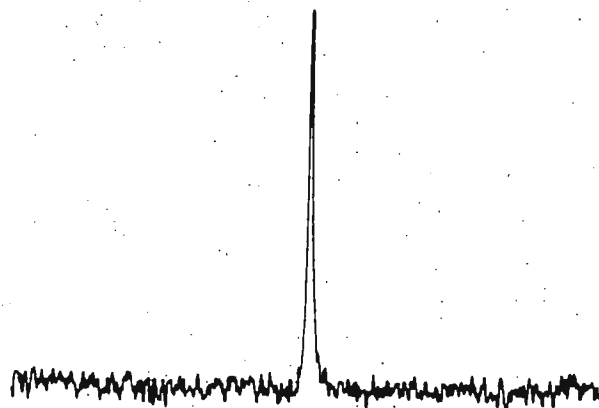
Sample $\text{Si}(\text{CH}_3)_4$ 80%
Nucleus ^{29}Si
No. of Pulse 1
Spectral Width 250Hz

c)



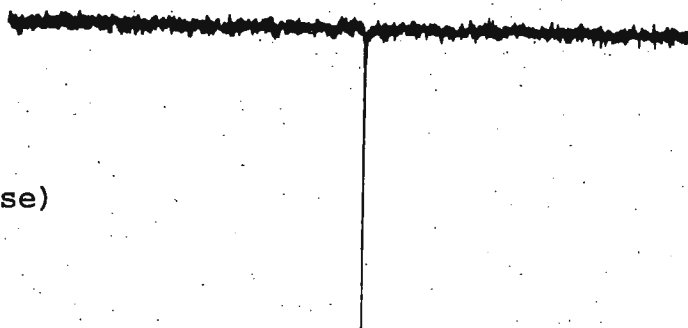
Sample D_2O 100%
Nucleus ^{17}O
No. of Pulses 100
Spectral Width 10KHz

d)




Sample ANILINE 80%
Nucleus ^{15}N
Obs. Time 1 hour
Spectral Width 5KHz
Irradiation ^1H (Noise)

e)



**Siège Social
et Direction générale**

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Professor Bernard L. SHAPIRO
Department of Chemistry
Texas A. M. University
College Station
TEXAS 77843

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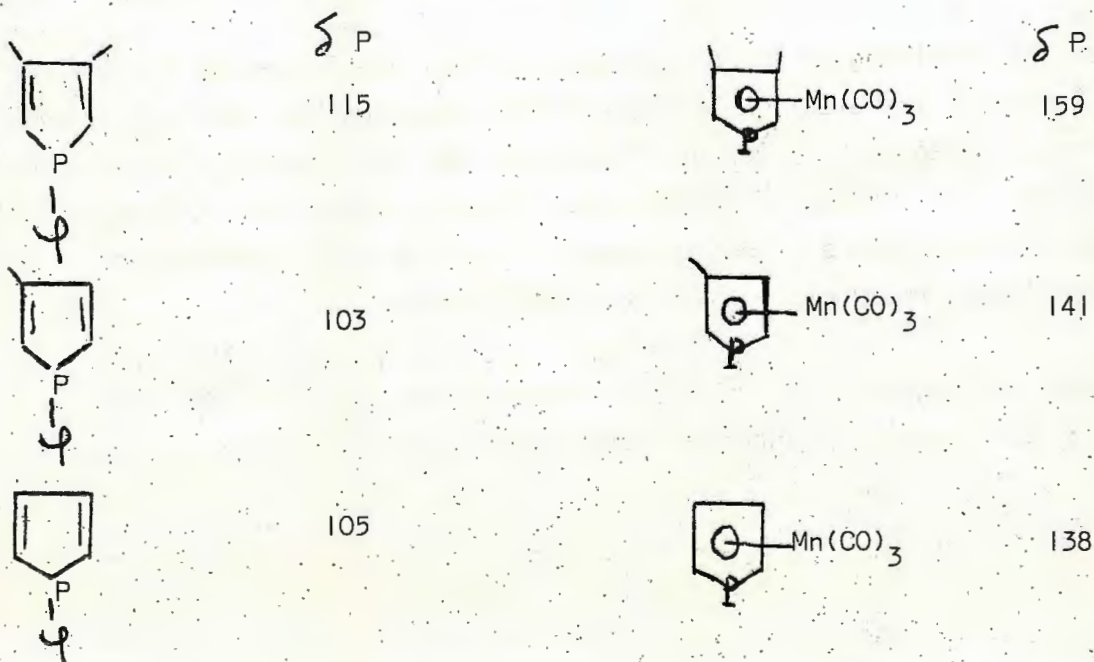
Paris, le November 22, 1976

Bicentennial contribution - $^{13}\text{C}/^{31}\text{P}$ ballott casting party

Dear Barry,


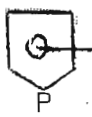
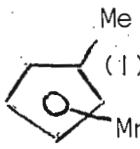
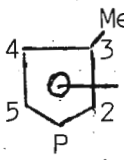
Going on in the study of phosphole-transition metal complexes, we have just discovered a one-step synthesis of phosphacymantrenes (phospholyi-manganese-tricarbonyls) by reaction of $\text{Mn}_2(\text{CO})_{10}$ with P-phenylphospholes at 150°C . We wish to report here after some ^{31}P and ^{13}C N.M.R. data of these new species which are particularly interesting since they are the first phosphorus heterocycles with a truly aromatic chemistry.

The comparison between the ^{31}P chemical shift of P. phenylphospholes and phosphacymantrene ist made below.



The phosphorus shielding in phosphacymantrenes is rather unexpected. Indeed the reactivity of phosphorus is much lower in these compounds than in phospholes (no reduction with I_2 or $\varphi CH_2 Br$) and acylation takes place at α -carbon and not at phosphorus as in phospholes (4). Thus, the electronic density at phosphorus is almost certainly much lower in phosphacymantrenes than in phospholes and, conversely, the lone pair delocalization is probably much higher. So, a deshielded phosphorus would be expected there (see (1) (2) for phospholes), The Letcher-Van Wazer formalism indicating that a delocalization of lone pair produces a shielding (3). However a direct comparison between phospholes and phosphacymantrenes is not fully significant since angular parameters and electronic structures of the exocyclic bonds are quite different ($Mn-P-C \neq \varphi-P-C$).

The comparison between the ^{13}C data of cymantrenes and phosphacymantrenes is also interesting :

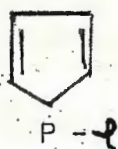
δ					
	C_p	83.1 (5)		C_α	96.2
	CO	224.9 (5)		C_β	93.8
				CO	223.4
	C_1	103 (5)		C_3	113.9
	C_2	83.1 (5)		C_2	97.7
	$C(3)$	82.5 (5)		C_4	94.4
	CO	224.4 (5)		C_5	97.7
				CO	223.8

Since the shielding of the CO groups is rather unaffected by the phospho-substitution, the electron withdrawal from manganese to the ring is quite probably almost the same in both series. Thus, the fact that the ring carbons are strongly shielded (~ 10 ppm) in phosphacymantrenes by comparison with cymantrenes indicates that probably a strong release of the lone pair from phosphorus to the dienic system takes place (strong delocalization).

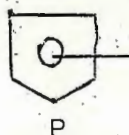
Another indication is given by the comparison of the $^1J_{P-C}$ coupling constants within phospholes, phosphacymantrenes and phosphorins.

IRCHA

N/Réf. Z II GM/mg



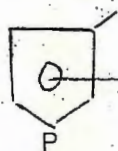
5.18 (6)

 Mn(CO)_3

65.4

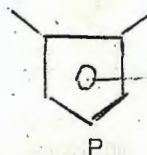


53 (7)

 Mn(CO)_3

P-C (2) : 62.2

P-C (5) : 63.8

 Mn(CO)_3

62.0

The very high coupling constants observed in phosphacymantrenes are very similar to those found in the phosphorin series which are, too, obviously aromatic, whereas phospholes show almost normal and even somewhat low $^1J_{\text{P-C}}$ when compared with ordinary phosphines.

With our very best regards.

G. MAVEL

F. MATHEY

R. MANKOWSKI-FAVELIER

- (1) L.D. QUIN, J.G. BRYSON et C.G. MORELAND - J.A.C.S. 91 (12) 3308 (1969)
- (2) L.D. QUIN, S.G. BORLESKE, J.F. ENGEL - J. Org. Chem., 38 (10) 1858 (1973)
- (3) F. MATHEY and R. MANKOWSKI-FAVELIER - Org. Mag. Res., 4, 171 (1972)
- (4) F. MATHEY - Tetrahedron, 29, 707 (1973)
- (5) P.V. PETROVSKI and al. - Dokl. Akad. Nauk.SSSR, 210 (3) 605 (1973)
- (6) T. BUNDGAARD and H.J. JAKOBSEN - Tetrah. Lett., 32, 3553 (1972)
- (7) A.J. ASHE, R.R. SHARP, J.W. TOLAN - J.A.C.S. 98 (18) 5451 (1976)

Dr. W. Bremser c/o

BASF Aktiengesellschaft

Hauptlaboratorium

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Professor

B. L. Shapiro

Department of Chemistry
 Texas A & M University

College Station
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U S A

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Ihre Nachricht vom

Unsere Zeichen

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Ludwigshafen

01.12.76

Betreff

Philosophy of collecting spectroscopic data

Dear Barry,

Most spectroscopists are interested in fast access to the valuable reference material distributed over various journals. In our group we presently have approximately 9,000 reprints or copies of articles relating to nmr-spectroscopy, and it seems hopeless in many cases to find the desired information, especially when it comes to chemical structures and substructures.

One remedy is computer-aided documentation of spectroscopic features linked to structural information. The latter is best achieved by a topological representation of chemical structures allowing access to almost any structural relationship including many stereochemical questions. The input is sketched on the accompanying figure showing different levels of representing this information. It is essential to find a fast, safe and easy to learn way of entering the data in order to facilitate the input of information and lower the barrier for the spectroscopist unfamiliar to computer language. Plausibility checks help to eliminate many trivial errors, before the computer oriented, but computer independent code of the "exchange format" is generated. At this level the exchange of data between different laboratories should be undertaken to help enlarge the basis for the interpretation of spectra and to generate a large pool of valuable reference material.

The next steps are oriented to specific computers and will necessarily be more difficult to adopt in a new laboratory. However, hard copy printouts of various representations of the data (cf. fig. 2) can be generated and distributed to spectroscopists without easy access to a large computer. For most options a microfiche collection with various inverted files (e.g. chemical shifts, substructures, molecular formulae, molecular weights (for MS)) will be cheaper, faster and more readily available. For example only the hierarchially ordered substructure file of our present ¹³C-nmr-data collection (6000 spectra) would fill with its 60 000 entries a book of nearly 1000 pages, however, it can be well accommodated on 5 microfiches with

Empfänger Prof. Shapiro
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USA

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a reproduction cost of 2 ¢. Also you can easily carry around your complete collection of reference material including registers as a sort of mini-computer in your briefcase to any place you want and access it with the cheap pocket viewers available on the market. Updated (i.e. enlarged and corrected) versions can easily be edited at regular intervals for this low cost.

Interactive use of the computer for library searching is very fancy, however should be restricted to a combination of features as well as the search for similarities. Also here "specfinder"-files as well as computer generated compiche equivalents of perforated cards offer a cheaper, yet certainly less efficient approach.

Yours sincerely,

Wolfgang
W. Bremser

Encl.

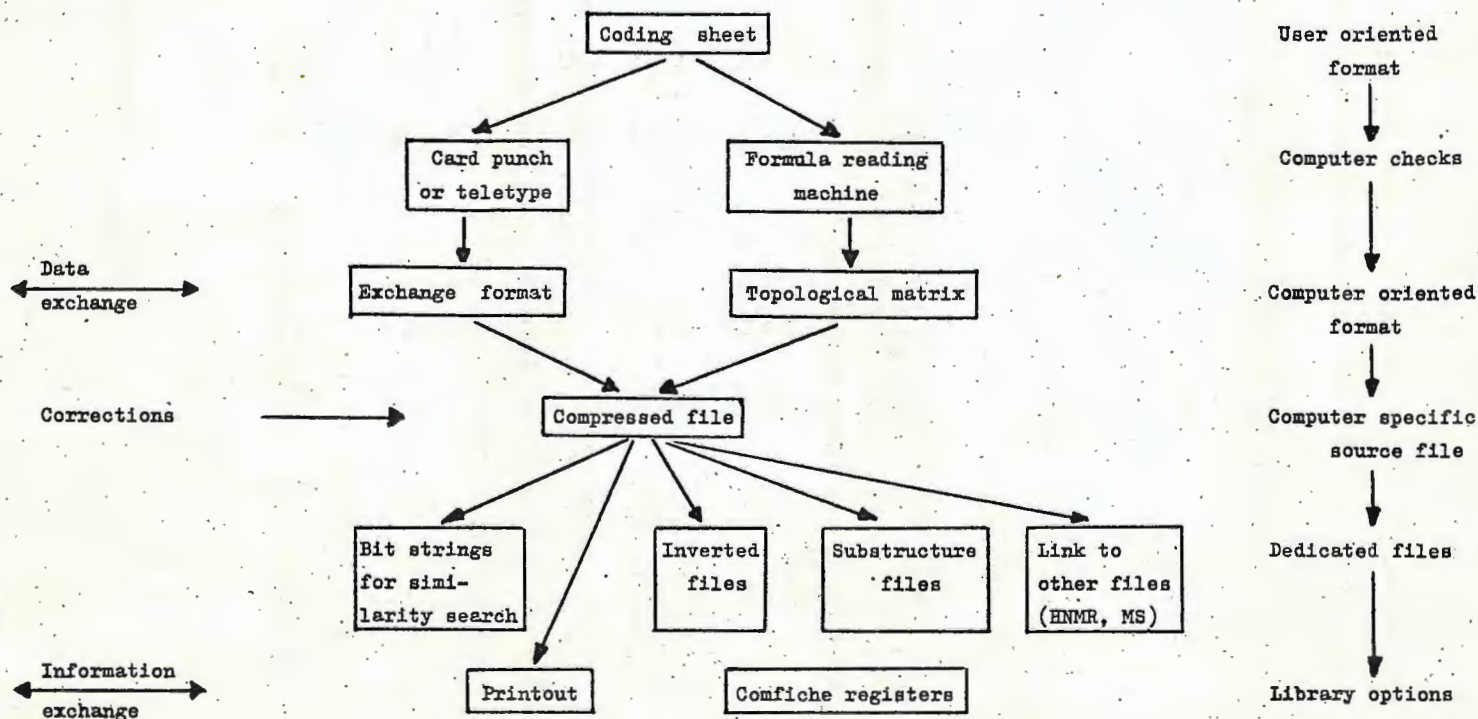


Fig. 1: BASF ¹³C-NMR Data System

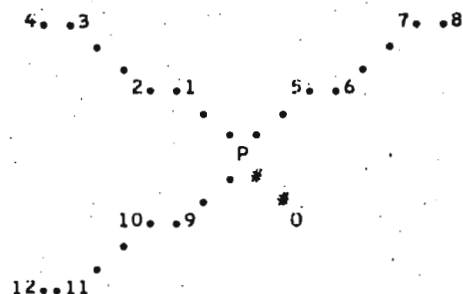
C12 H27 O1 P1

1436

PHOSPHINE OXIDE, TRIBUTYL-

CA: 814-29-9

MW: 218.22



L.D.QUIN,M.D.GORDON,ORG.MAGN.RESONANCE 6,503(1974)
 SO: CDCL3 IN: HFX-90 CO:
 ST: TMS TE: AMBIENT OR: BAS10789

CHEMICAL SHIFTS (PPM), MULTIPLICITY:

1	27.80	-	5	27.80	-	9	27.80	-
2	24.00	-	6	24.00	-	10	24.00	-
3	24.40	-	7	24.40	-	11	24.40	-
4	13.60	-	8	13.60	-	12	13.60	-

COUPLING CONSTANTS (HZ):

J(1,P13)= 66.0	J(2,P13)= 5.0	J(3,P13)= 13.0
J(5,P13)= 66.0	J(6,P13)= 5.0	J(7,P13)= 13.0
J(9,P13)= 66.0	J(10,P13)= 5.0	J(11,P13)= 13.0

T.A.ALBRIGHT,W.J.FREEMAN,J.ORG.CHEM.40,3477(1975)

SO: CDCL3 IN: HFX-90 CO:
 ST: TMS TE: AMBIENT OR: BAS12094

CHEMICAL SHIFTS (PPM), MULTIPLICITY:

1	27.90	-	5	27.90	-	9	27.90	-
2	23.90	-	6	23.90	-	10	23.90	-
3	24.30	-	7	24.30	-	11	24.30	-
4	13.70	-	8	13.70	-	12	13.70	-

COUPLING CONSTANTS (HZ):

J(1,P13)= 65.1	J(2,P13)= 3.9	J(3,P13)= 13.9
J(5,P13)= 65.1	J(6,P13)= 3.9	J(7,P13)= 13.9
J(9,P13)= 65.1	J(10,P13)= 3.9	J(11,P13)= 13.9

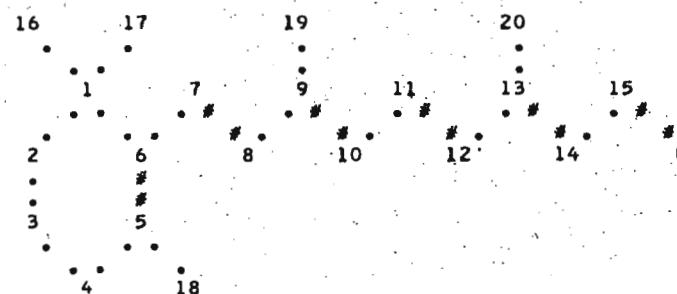
C20 H28 O1

1437

RETINAL

CA: 116-31-4

MW: 284.44



Y.INOUE,A.TAKAHASHI,ORG.MAGN.RESONANCE 6,487(1974)
 SO: CCL4 IN: PS-100 CO: 192.60
 ST: CS2 TE: AMBIENT OR: BAS10749

CHEMICAL SHIFTS (PPM), MULTIPLICITY:

1	33.30	S	8	138.20	D	15	192.40	D
2	38.70	T	9	141.00	S	16	28.00	Q
3	32.10	I	10	129.90	S	17	28.00	Q
4	18.00	T	11	132.40	D	18	20.70	Q
5	130.50	S	12	135.80	D	19	11.60	Q
6	138.50	S	13	153.80	S	20	11.60	Q
7	129.70	D	14	130.50	D			

RELAXATION TIMES:

1	T1 = 4.4 S	8	T1 = 0.6 S	15	T1 = 0.6 S
2	T1 = 0.4 S	9	T1 = 5.0 S	16	T1 = 0.5 S
3	T1 = 0.3 S	10	T1 = 0.6 S	17	T1 = 0.5 S
4	T1 = 0.2 S	11	T1 = 0.6 S	18	T1 = 1.3 S
5	T1 = 4.3 S	12	T1 = 0.6 S	19	T1 = 1.2 S
6	T1 = 5.3 S	13	T1 = 5.3 S	20	T1 = 1.2 S
7	T1 = 0.6 S	14	T1 = 0.6 S		

Fig. 2: Printout of two representative references



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Phone 416-625-2375



2

2



6

7



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assignments of different methyl groups present in the molecule could not be made. With the aid of our empirical rule the signals could be assigned unequivocally (c.f. table 3).

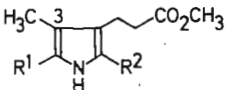
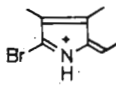
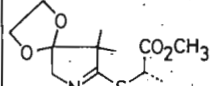
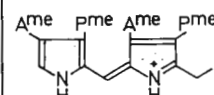
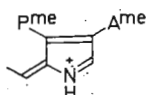
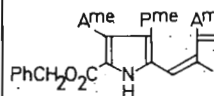
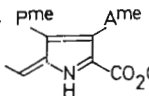
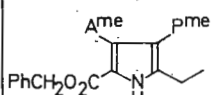
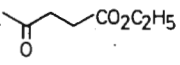
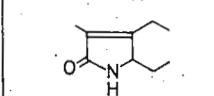
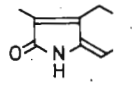
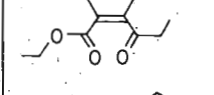
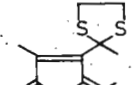
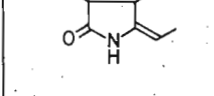
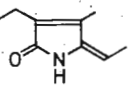
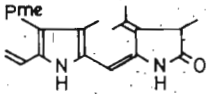
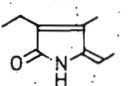
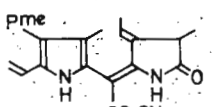
- 1) J. Engel, A. Gossauer, and H.M. Schiebel: TAMU-NMR-Newsletter 210, 1 (1976)
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- 3) A.H. Jackson, G.W. Kenner, and G.S. Sach: J. Chem. Soc. C, 1967, 2045
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- 7) H.H. Inhoffen, H. Maschler, and A. Gossauer: Liebigs Ann. Chem. 1973, 141

J. Engel
(J. Engel)

H.M. Schiebel
(H. M. Schiebel)

Table 1

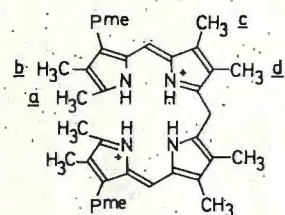
solvent: CDCl₃

					
R ¹	δ(ppm) 3-CH ₃	R ²	R ¹	δ(ppm) 3-CH ₃	R ²
	2.33	CH ₃		2.00	CO ₂ C(CH ₃) ₃
CHO	2.32	CO ₂ CH ₃		2.00	
CO ₂ CH ₂ Ph	2.30	CO ₂ CH ₃		1.99	
CO ₂ H	2.30	CO ₂ C(CH ₃) ₃		1.99	CO ₂ C(CH ₃) ₃
CO ₂ C(CH ₃) ₃	2.24			1.97	CO ₂ C(CH ₃) ₃
	2.13	CO ₂ C(CH ₃) ₃		1.96	CO ₂ C(CH ₃) ₃
	2.12	CO ₂ C(CH ₃) ₃		1.95	CO ₂ C(CH ₃) ₃
	2.11				
	2.09				
H	2.03	CO ₂ C(CH ₃) ₃			

Ph = C₆H₅Ame = CH₃CO₂CH₃Pme = CH₃CH₂CO₂CH₃

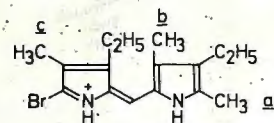
Table 3

 $\delta(\text{ppm})$

 solvent: CDCl_3


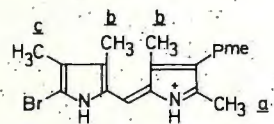
$a = 2.65$
 $b = 2.04$
 $c = 2.27$
 $d = 1.91$

Ref. 3



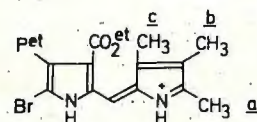
$a = 2.66$
 $b = 2.34$
 $c = 2.03$

Ref. 4



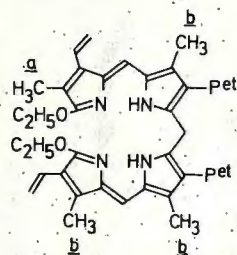
$a = 2.65$
 $b = 2.33 \text{ (6H)}$
 $c = 1.99$

Ref. 5



$a = 2.74$
 $b = 2.02$
 $c = 2.28$

Ref. 5

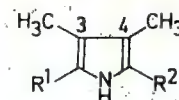


$a = 1.93 \text{ (3H)}$
 $b = 2.15 \text{ (9H)}$

Ref. 6

$\text{et} = \text{C}_2\text{H}_5$ $\text{Pet} = \text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ $\text{Pme} = \text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$

Table 2

 solvent: CDCl_3


R^1	$\delta(\text{ppm})$ 3-CH ₃	R^2	$\delta(\text{ppm})$ 4-CH ₃
Pet			
	2.33	Br	1.99
Ame			
	2.31		1.93
CHO	2.32		2.12
$\text{CO}_2\text{C}_2\text{H}_5$	2.24		1.96
	2.14	CH_3	1.95
$\text{CH}=\text{C}(\text{CN})_2$	2.12	CH_2Cl	2.02
CH_2OCCH_3	2.01	$\text{CH}=\text{C}(\text{CN})_2$	2.13
H	2.00	$\text{CO}_2\text{C}_2\text{H}_5$	2.28
J	1.97	$\text{CO}_2\text{C}_2\text{H}_5$	2.30
$\text{CH}_2\text{OC}_2\text{H}_5$	1.97	$\text{CH}=\text{C}(\text{CN})_2$	2.15
CH_3	1.95	$\text{CH}=\text{C}(\text{CN})_2$	2.12

$\text{Pet} = \text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$

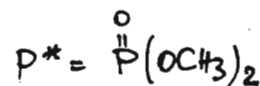
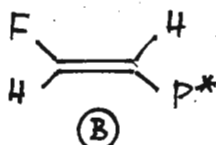
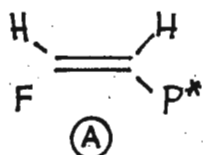
$\text{Ame} = \text{CH}_2\text{CO}_2\text{CH}_3$

Prof. Dr. G. Hägele
 Inst.f.Anorg.u.Strukturchemie
 der Universität Düsseldorf

4000 Düsseldorf, 21.11.76
 Universitätsstrasse 1

Dear Professor Shapiro!

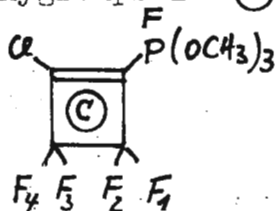
We got our new BRUKER IIX 90 R in July 1976. It is equipped for nuclei ^1H , ^{19}F and ^{31}P in CW and FT mode using a 20 K computer. Double and triple resonance facilities are attached. We are satisfied with resolution and S/N. For testing the spectrometer we used the mixture of stereoisomers of 2-fluorovinylphosphonic acid dimethylester.:



Double resonance experiments $^1\text{H}\{^{19}\text{F}\}$, $^1\text{H}\{^{31}\text{P}\}$, $^{19}\text{F}\{^1\text{H}\}$, $^{19}\text{F}\{^{31}\text{P}\}$, $^{31}\text{P}\{^1\text{H}\}$, $^{31}\text{P}\{^{19}\text{F}\}$, and triple resonances were done successfully for $^1\text{H}\{^{19}\text{F}, ^{31}\text{P}\}$, $^{19}\text{F}\{^1\text{H}, ^{31}\text{P}\}$, $^{31}\text{P}\{^1\text{H}, ^{19}\text{F}\}$.

Parameters for (A) and (B) are given in table 1.

Using the tested equipment we analyzed the novel, stable phosphorane (C). Refined parameters for the $[\text{AB}]_2\text{PF}_6$ -core of the overall $[\text{AB}]_2\text{MPX}_9$ system are listed in table 2. At roomtemperature the phosphorane is subject to a rapid exchange process leading to the equivalence of the three methoxygroups in (C):



Yours sincerely

.....
 Dipl.Chem.G.Bauer

.....
 Prof. Dr. G. Hägele

Table 1: Coupling constants in cis/trans CHF=CHP(O)(OCH₃)₂ given in Hz.

	cis isomer A				trans isomer B			
J-Type	HH	FH	PH	PF	HH	FH	PH	PF
gem	---	83.5	6.2	---	---	83.1	6.7	---
cis	6.1	---	---	13.8	---	21.5	7.4	---
trans	---	49.0	33.8	---	11.9	---	---	73.9

Table 2: NMR data for Phosphorane C

Coupling constants

$$^3J_{FF}^{cis} = -14.59 \text{ Hz}$$

$$^3J_{FF}^{trans} = 25.96 \text{ Hz}$$

$$^4J_{FF} = 0.7 \text{ Hz}$$

$$^5J_{FF} = \sim 0 \text{ Hz}$$

$$^2J_{F_1F_2} = 195.27 \text{ Hz}$$

$$^2J_{F_3F_4} = 190.23 \text{ Hz}$$

$$^1J_{PF} = -845 \text{ Hz}$$

$$^3J_{PF} = -3.88 \text{ Hz}$$

$$^4J_{PF} = +12.59 \text{ Hz}$$

$$^3J_{PH} = +15.13 \text{ Hz}$$

$$^4J_{FH} = 1.81 \text{ Hz}$$

Chemical shifts

$$\delta_{F_{1,2}} = 49.736 \text{ ppm}$$

$$\delta_{F_{3,4}} = 45.539 \text{ ppm}$$

$$\delta_{FP} = 87.500 \text{ ppm}$$

$$\delta_P = -72.820 \text{ ppm}$$

$$\delta_H = 3.730 \text{ ppm}$$

$$\delta_F \text{ vs. } C_6F_6$$

$$\delta_P \text{ vs. } \#3PD_4 \text{ 85\%}$$

$$\delta_H \text{ vs. TMS}$$

NANCY, le november 25, 1976

219-21 LABORATOIRE
DE CHIMIE THÉORIQUE

Case officielle N° 140 - 54037 NANCY Cedex
Tél. 27.00.24 (Poste 2049 et 2051)

Professor B.L. SHAPIRO
TEXAS A & M University
College of Science

COLLEGE STATION, Texas 77843
U.S.A.

Title :
Variable temperature problems

Dear Professor Shapiro

We recently encountered practical problems related to the variable temperature system of our Bruker HX.90

For instance, if one wishes to run overnight unattended experiments at a temperature of ca.4°C, the Bruker system is unsuitable due to the smallness of the liquid nitrogen containers. So, we replaced the small Dewar and its filling unit by a huge Dewar (diameter : 20cm ; height : 50cm) in which a cooling coil of 18cm height is immersed. This quite simple system proved to be useful and yields a very stable temperature.

At high temperatures, if the air (or nitrogen) flow stops, the heating resistor inside the probe is not switched off and there is a risk of causing damage to the probe. This may occur because of the gas source itself or if a tape disconnects somewhere. In order to avoid this sort of damage, we have implemented the small device described below :

- a vertical tube containing a small ball is placed just before the gas input of the probe. A light bulb and a photodiode are installed at the bottom of the tube, controlling the actual pressure inside the probe.

- every time the photodiode is not illuminated a simple circuit integrated in the variable temperature unit (B-ST 100/700) (shown below) switches off the voltage of the probe heating resistor. At the same time, a light on the front panel of the temperature unit is switched on (the light can only be reset by hand) to alert the user that something is wrong. This system however does not work at low temperature since frost appears on the tube containing the ball. Thus, a switch installed on the temperature unit allows disconnection of this safety circuit since it is not necessary at low temperature.

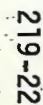
Yours sincerely

B. DITER

J. BRONDEAU

D. CANET

Encl. 1



THE UNIVERSITY OF BRITISH COLUMBIA

2075 WESBROOK PLACE

VANCOUVER, B.C., CANADA

V6T 1W5

DEPARTMENT OF CHEMISTRY

29 November, 1976

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

Simple recipe for pH meter reading in D₂O.

Dear Barry,

Because of the convenience of using a deuterium lock, and to avoid ultra-large water peaks in ¹H NMR spectra, much ¹H NMR work on biological molecules is conducted in D₂O. It is generally appreciated that a typical glass electrode has a different response to D⁺ than to H⁺ ions in D₂O and H₂O, respectively:

$$pD_{\text{in } D_2O} = \log(1/[D^+]) = pH_{\text{meter reading in } D_2O} + 0.41 \quad [1]$$

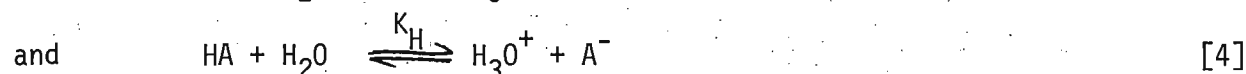
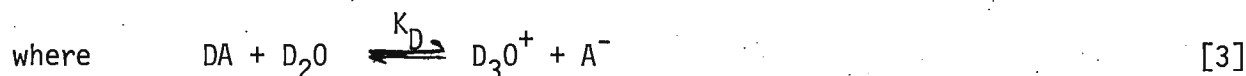
Thus, in order that the concentration of D⁺ in D₂O be the same as the concentration of H⁺ in a corresponding H₂O solution, it would be necessary to titrate the D₂O until the pH meter reading in D₂O is 0.41 pH unit lower than for the corresponding H₂O solution:

$$pH_{\text{in } H_2O} = pD_{\text{in } D_2O} = pH_{\text{meter reading in } D_2O} + 0.41$$

$$\text{or } pH_{\text{meter reading in } D_2O} = pH_{\text{in } H_2O} - 0.41$$

However, this is usually not the desired situation. Typically, we desire that a given buffer or weak acid solute have the same degree of ionization in D₂O as in H₂O, so that (for example) a protein will have the same net charge in either solvent. Fortunately, there is a simple correlation between the pK_a difference in the two solvents and the pK_a-value itself (see Fig. 1):

$$pK_D - pK_H = 0.42 + 0.02 pK_H, \quad [2]$$



serve to define K_D and K_H.

Combining these equations (see example), we obtain a simple recipe for the pH meter reading in D₂O for which a given weak acid has the same degree of dissociation in D₂O as in H₂O: i.e., $([A^-]/[DA])_{\text{in } D_2O} = ([A^-]/[HA])_{\text{in } H_2O}$:

$$pH_{\text{meter reading in } D_2O} = 1.02 pK_H + \log_{10} \frac{[A^-]}{[DA]} + 0.01; \quad 2 < pK_H < 9$$

Simple recipe for pH meter reading in D₂O, continued.

Use of these relations is conveniently illustrated with a numerical example. Suppose we wish to construct a phosphate buffer having 50% degree of ionization in both H₂O and D₂O, where HA = H₂PO₄⁻, so that pK_H = 7.2. The pH in H₂O is simply,

$$\text{pH}_{\text{in H}_2\text{O}} = \text{pK}_H + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_H = \boxed{7.2}$$

In order to obtain the same degree of dissociation in D₂O, we want

$$\text{pD}_{\text{in D}_2\text{O}} = \text{pK}_D + \log \frac{[\text{A}^-]}{[\text{DA}]} \quad , \text{ with } [\text{A}^-] = [\text{DA}]$$

$$\text{and } \text{pK}_D = 7.2 + 0.42 + 0.02(7.2) = 7.76$$

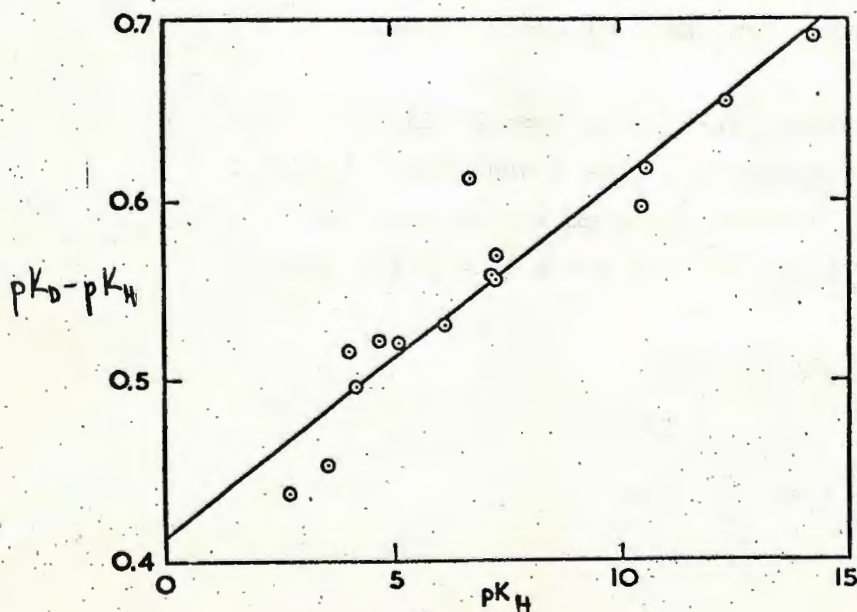
However, we must correct for the fact that the pH meter reading in D₂O is changed:

$$\begin{aligned} \text{pH}_{\text{meter reading in D}_2\text{O}} &= \text{pD}_{\text{in D}_2\text{O}} - 0.41 \quad (\text{from Eq. [1]}), \\ &= 7.76 - 0.41 \\ &= \boxed{7.35}. \end{aligned}$$

Thus, even though the pH meter reading differs by 0.4 pH unit between D₂O and H₂O, we can achieve the same degree of dissociation in either solvent with a much smaller (0.15 pH unit in this case, and even less for lower pK_H-groups) correction to the pH meter reading. In fact, this correction will often be small enough to ignore.

Figure 1 shows that the scatter from Eq. [2] is not excessive, so that this prescription should apply to most pH meter situations in D₂O for 2 < pH_{meter} < 9. Extension to arbitrary degree of ionization should be obvious.

I wish to thank Profs. R. Stewart and A. W. Addison, Dr. D. C. Roe, and Mr. R. Bruce for helpful discussions.



Sincerely,

Alan G. Marshall

Alan G. Marshall
Associate Professor

1. A. K. Covington, M. Paabo, R. A. Robinson and R. G. Bates, *Anal. Chem.* **40**, 700 (1968).
2. Fig. 1 taken from R. P. Bell, "The Proton in Chemistry," Cornell Univ. Press, Ithaca (1959).



145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076

Title: 60.72 MHz ^{31}P Spectra of
Whole Human Blood

November 30, 1976

Dear Barry:

Lately, we have been involved in ^{31}P NMR studies using our NT-150 system which operates at 35.2 kilogauss. The use of 20 mm sample tubes along with quadrature phase detection has provided really good sensitivity and this has been much appreciated in studies of biological samples.

Shown on the next page are spectra of whole human blood {JLH - type AB+ (he'll do anything for the good of the company)} run with broadband proton decoupling. At the suggestion of Dr. James Salhany, of the University of Nebraska Medical School, we bubbled oxygen gas through the blood sample in order to convert the paramagnetic hemoglobin to diamagnetic oxyhemoglobin. The result was a very appreciable reduction in line width for all of the ^{31}P signals. The spectrum of the blood without treatment looked much like that of the nitrogen-bubbled blood, since venous blood is largely deoxygenated. Assignments indicated are in accord with those given by T.O. Henderson et al Proc. Nat. Acad. Sci. USA, 71, 2487 (1974).

Statistical data for the spectra shown are: pulse repetition time = 1.1 sec., pulse excitation = 30° tip, exponential line broadening = 1.0 Hz, and plot width = 30.0 ppm. The O_2 bubbled spectrum was an over lunch run, 4238 pulses, while the N_2 bubbled spectrum was a 1200 pulse run.

Best regards,

A handwritten signature in cursive script that reads "Roy".

LeRoy F. Johnson

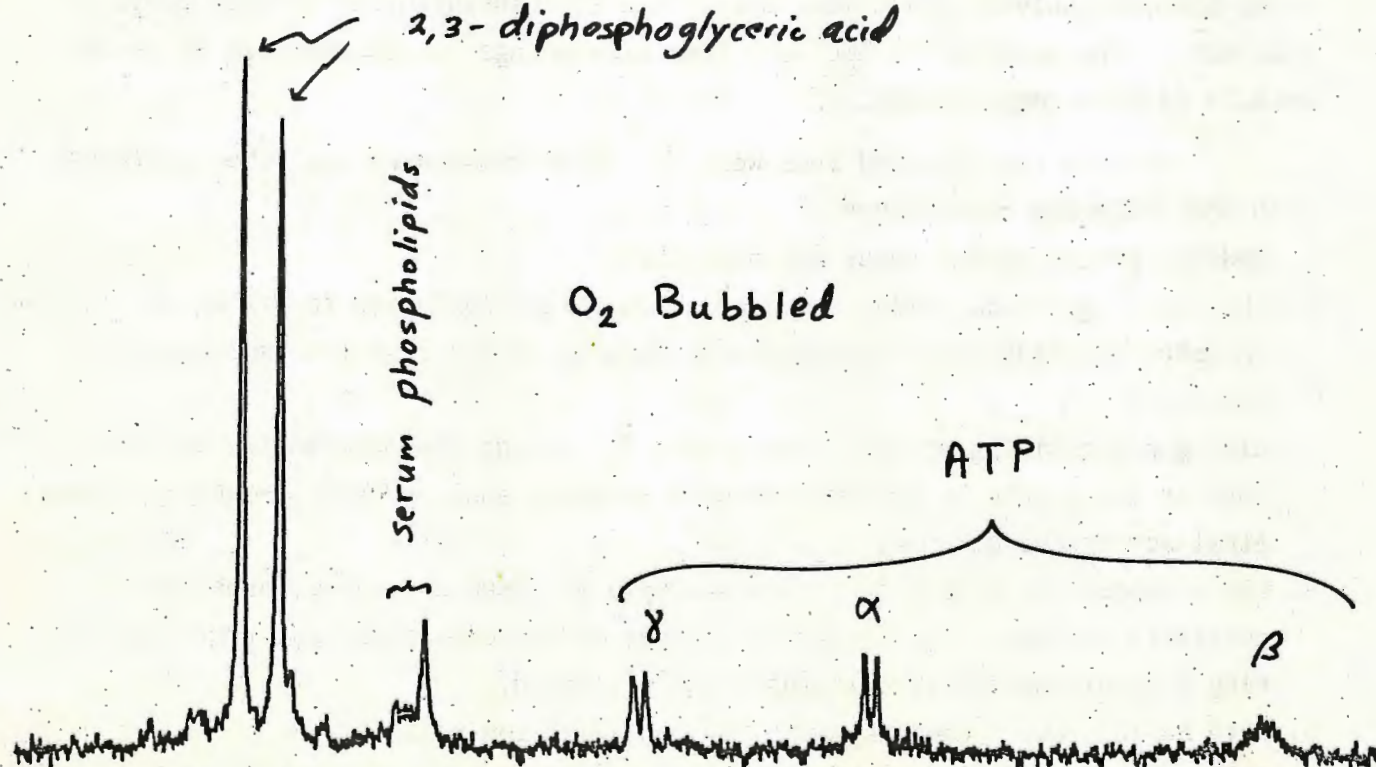
LFJ:nb

^{31}P 60.72 MHz

WHOLE HUMAN BLOOD

 N_2 Bubbled

2,3-diphosphoglyceric acid

 O_2 Bubbled

serum phospholipids

ATP

 γ α β

Professeur PIERRE LASZLO

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

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

December 1, 1976

²³Na study of the Na⁺-sugar interaction in non-aqueous solvents.

Dear Barry,

We have reported¹ on the use of sodium mmr for the study of the sugar-sodium interaction in pyridine solution. Since the sodium cation coordinates on one face to (≥ 3) oxygen atoms from the sugar, and on the other with nitrogen atoms from the solvent molecules, there is a substantial electrostatic field gradient at the quadrupolar nucleus. Line broadenings can be analyzed to reveal details of this complexation.¹

We have now extended this work to other substrates and other solvents, with the following conclusions :

1. hydroxy groups on the sugar are necessary;
2. the *axial-equatorial-axial* sequence of OH groups conducive to strong interaction in water solution is not particularly favored in pyridine (or isopropylamine) solution;
3. nitrogen-containing solvents are useful for making the interaction apparent : none is detectable by this method with solvents such as DMSO, 2-methoxyethanol, ethyl acetate or acetone;
4. *the interaction appears to be non-specific in amine solvents*; formation constants increase roughly as the inverse of the dielectric constant, suggesting a predominantly electrostatic stabilization.
5. with NaClO₄, one is dealing with sugar-bridged ion pairs :
 - (i) the reduced linewidth $\Delta\nu_{1/2} \cdot \eta^{-1}$ (η = measured viscosity) is linear with salt concentration, in pyridine solution, implying proximity of the perchlorate anion;

- (ii) coexistence in pyridine of infrared absorptions at 624 cm^{-1} (T_2 mode of T_d -symmetric species) and at 611 cm^{-1} (A_1 mode of C_{3v} -symmetric or $B_1(B_2)$ mode of C_{2v} -symmetric) for the perchlorate anion; addition of a sodium complexant, such as dibenzo-18-crown-6 or sorbose, increases the former at the expense of the latter;
- (iii) the ^{35}Cl linewidth of ClO_4^- increases from 2 Hz in DMSO (T_d species) to 17 Hz in pyridine ($T_d + C_{3v}$ or C_{2v}); addition of three equivalents of sorbose reduces slightly the chlorine linewidth, from 17 to 13 Hz. These chlorine nmr data were obtained through the kind assistance of Dr. Christian Brevard (Bruker-Wissembourg, France).

Selection of results. (290 K)

	$K\text{ (M}^{-1}\text{)}$	$\Delta\nu_{1/2}\text{ complex (Hz)}$
sorbose/pyridine ^a	7.2 ± 2.2	800 ± 150
sorbose/isopropylamine ^b	19 ± 4	500 ± 150
methyl- β -D-ribosepyranoside/ pyridine	5.5 ± 0.6	730 ± 70
methyl- β -D-ribosepyranoside/ isopropylamine	12.7 ± 1.4	580 ± 60
lactose/pyridine	8.0 ± 1.6	2000 ± 400

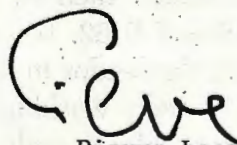
^a $\epsilon = 12.3$

^b $\epsilon = 6.0$

^cdisaccharide : correlation time approximately doubled relative to the other sugars in this table.

Work done with Dr. J. Grandjean.

Warmest regards,


Pierre Laszlo

(1) C. Detellier, J. Grandjean, and P. Laszlo, J. Am. Chem. Soc., 98, 3375 (1976).

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.

T T
TRANSFORM TECHNOLOGY INC.
3380 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.)



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

NATIONAL HEART, LUNG, AND BLOOD INSTITUTE

December 8, 1976

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

Dear Barry:

Lanthanide shift reagents have found limited use in aqueous solutions. Dr. Bystrov's¹ application to sonicated phospholipids demonstrating the bilayer nature of sonicated sphingomyelin by ³¹P NMR was a particularly vivid example of a system where a reagent functions to give valuable information.

Plasma lipoproteins have as major components the phospholipids, sphingomyelins and lecithins which should show much the same binding characteristics as the sonicated lipids. Differential scanning calorimetry² and neutron diffraction studies³ of low density lipoprotein (LDL) have been interpreted to propose a micelle rather than the earlier bilayer theory from small angle x-ray scattering data. We felt that examination of this system by lanthanide addition and ³¹P NMR would contribute to the question of micelle or bilayer in the LDL particle.

The ³¹P spectra with increasing increments of praeosodium nitrate added are shown in the accompanying spectra. The sharp resonance at low field is a sealed capillary of Dimethyl methylphosphonate which we use as a reference. The broad high field resonances are lecithins ($\delta=+0.9$) and sphingomyelins ($\delta=+0.4$ from 85% H₃PO₄.)

Both resonances shift and broaden, leaving no resonance at the original chemical shift. Since a bilayer should have only a portion of the polar head groups exposed to the reagent, this result confirms the micellar nature of the particle. Addition of EDTA to the solution returns the resonances to their original chemical shift and intensity (top scan) and circular dichroism studies showed the helical content of the protein to be unperturbed. The results of NMR agree nicely with the data from other methods for this important biomolecule.

Prof. Bernard L. Shapiro

December 8, 1976

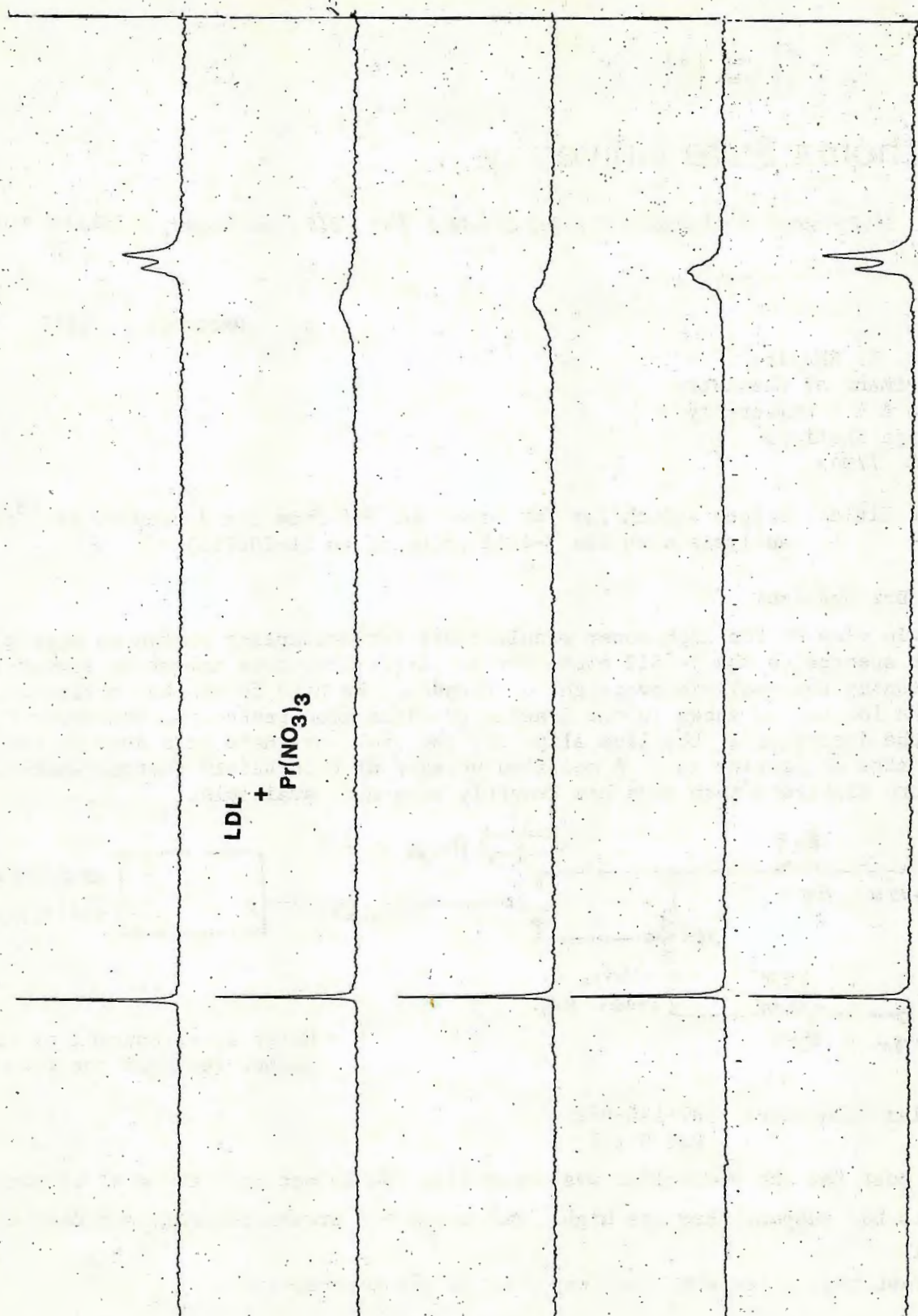
Best wishes for a happy holiday season to you and your family. Please credit this contribution to Dr. Highet's subscription.

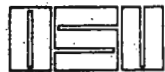
Best regards,



E. A. Sokoloski
Laboratory of Chemistry

1. Bystrov, V. F.; Dubrovina, N.I.; Borsukov, L.I. and Bergelson, V. F.; Chem. Phys. Lipids 6, 343 (1971)
2. Deckelbaum, R. J., Shipley, G. G.; Small, D. M.; Lees, R. S.; and George, P. K.; Science 190, 392 (1975)
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Oklahoma State University

Department of Chemistry / (405) 372-6211, Ext. 7215 / Stillwater, Oklahoma 74074

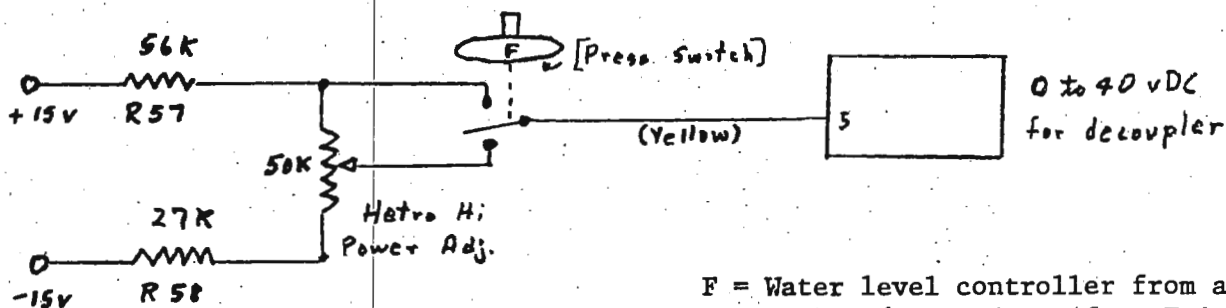
December 1, 1976

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

Short Title: Safety switch for for power cut off from the decoupler in ¹³CMR analysis with the V-4412 probe on an XL-100(15)

Dear Dr. Shapiro:

¹³In view of the high power requirements for decoupling proton to obtain ¹³CMR spectra on the V-4412 probe for an XL-100(15), some danger is involved in running the analysis overnight unattended. We have found that a simple switch located as shown in the drawing provides good protection and shuts off the decoupler if the line slips off the probe or there is a drop in the flow rate of carrier gas. A modified version of this safety feature which is more elaborate than ours has recently been made available.



F = Water level controller from a washer (we used one from Frigidaire)

Varian Schematic: 87-126-852
Rev B 171

The cost for the controller was under \$13. We do not know the cost of commercial units but suspect they are high. Our setup has proven reliable and easy to install.

We trust this meets with your approval as our contribution.

Sincerely yours,

K. D. Berlin
K. D. Berlin
Regents Professor



December 6, 1976

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

NEW VARIAN EAST COAST APPLICATIONS CHEMIST

Dear Barry:

I would like very much to announce to TAMU-NMR readers that I have joined the Varian NMR group. I will be located in the brand new Varian regional office in Florham Park, New Jersey, where I will be serving as the NMR Applications Chemist for the Eastern U.S.

The new office is equipped with fully loaded XL-100, CFT-20, and EM-390 spectrometers, so it's all ready to go. The new address is 25 Hanover Road, Florham Park, New Jersey 07932, and the new phone number is 201-822-3700. The new office is considerably more attractive than the old Springfield office and visitors are most welcome. I'm looking forward to being of service to as many of you as is possible.

Sincerely,

Steve Patt

Steven L. Patt
Varian Instrument Division

SLP:c

OTTAWA, CANADA

K1S5B6



DEPARTMENT OF CHEMISTRY

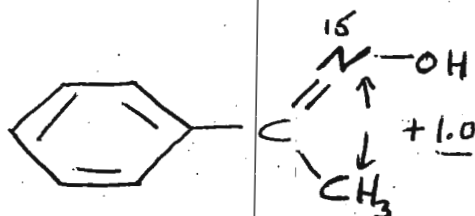
December 2nd, 1976.

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

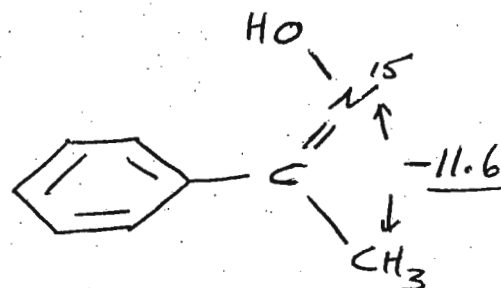
Relative Signs of ^{13}C - ^{15}N Couplings in Configurational Isomers

Dear Barry,

Recently (1) it has been predicted, although not experimentally verified, that ^{13}C - ^{15}N J's in configurational isomers should have opposite signs. Ph.D. student Brian Dawson, in connection with his studies of ^{13}C - ^{15}N interactions (2) has now determined the relative signs of such couplings in Z and E acetophenone oximes using an off-resonance ^1H decoupling procedure (3). In the E-isomer, where the N lone pair is trans to the CH_3 , the coupling is small (1.0 Hz) and positive, whereas in the Z case the geminal J is large (11.6 Hz) and negative. These signs are relative to the ^{15}N -C-C-H J's which are known to be negative (4).



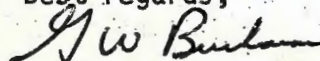
E



Z

Presently, we are using the GEMO program to generate optimum geometries for these oximes. Subsequently, the INDO MO approach will be employed to calculate the Fermi contact contributions to all the observed ^{13}C - ^{15}N couplings.

Best regards,



G.W. Buchanan
Associate Professor.

GWB:mcs

REFERENCES

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Tet. Letters 1621 (1976).
2. G.W. Buchanan and B.A. Dawson
Can. J. Chem. 54, 790 (1976).
3. H.J. Jakobsen, T. Bundgaard and R.S. Hansen
Mol. Phys. 23, 197 (1972)
4. R.L. Lichter and J.D. Roberts. JACS 93, 5218 (1971).

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *Urbana, Illinois 61801**School of Chemical Sciences*
DEPARTMENT OF CHEMISTRY*Administrative Offices*

December 3, 1976

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

Lanthanide Shift Reagents
Postdoc Opening

Dear Barry:

A review of work done here at Illinois on lanthanide shift reagents (LSR) may be of interest to high-resolution types among the avid readers of the Newsletter. The theory for the lanthanide-induced (LIS) shift has generated some controversy about the temperature dependence, with Bleaney's elegantly simple approach [J. Magn. Res. 8, 91 (1972)] predicting a T^{-2} dependence and Horrocks et al favoring T^{-1} . (NMR Shift Reagents, R. E. Sievers, Ed., Academic Press, 1973, p. 53).

In his work here on the theory, Ed Stout concluded that shifts arising from a pseudocontact mechanism should in general show a T^{-2} behavior as predicted by Bleaney. In some instances a fortuitous combination of crystal field parameters can lead to additional T^{-n} components ($n > 3$) which cause the overall shift to appear to be a linear function of T^{-1} with a large intercept at $T^{-1} = 0$. Extension of Bleaney's method to the (positive) T^{-3} term shows it to be negligible compared to that in T^{-2} for systems with $J = 3/2$ and relatively small ($\sim 10\%$) for larger J . It seems likely that for the majority of lanthanide adduct systems the most realistic description of the proton shifts is in terms of the well-established T^{-2} dependence.

The observed temperature dependence of the LIS is often complicated by the effect of temperature upon the LSR-substrate equilibrium, the theory applying of course only to the "intrinsic" part of the observed LIS. This requires that the experimental data be corrected for any changes in the equilibrium concentrations of the associated species. H. N. Cheng has completed an experimental study of the proton shifts in N,N-dimethylacetamide (DMA) for the $\text{Pr}(\text{fod})_3$ -DMA complex in tetrachloroethylene solutions. A detailed analysis of the temperature dependences observed for the three different methyl groups as a function of the $\text{Pr}(\text{fod})_3/\text{DMA}$ ratio has enabled him to separate the contributions to the LIS from the change in equilibrium and from the intrinsic temperature dependence, and obtain approximate values of the equilibrium constants. The intrinsic shifts are found to be linear in T^{-1} over the temperature interval from 30 to 72 °C. However, the intercepts at $T^{-1} = 0$ are large indicating, in combination with the shortness of the range studied, that the linearity may be more apparent than real. The results of fitting the data to a T^{-2} dependence are similar.

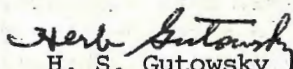
Dr. Shapiro

December 3, 1976

Another aspect of the $\text{Pr}(\text{fod})_3$ -DMA complex formation explored by Cheng is its effect upon the internal rotation of the dimethylacetamide. The shift reagent is found to participate in the chemical exchange by the formation of complexes with different barriers to internal rotation of DMA than the parent compound. A kinetic analysis indicates that whereas the LSR increases the barrier to rotation in DMA, it has little effect on the activation entropy. The question of analyzing dynamic NMR data in the presence of LSR has been carefully treated and several practical approaches developed for the use of LSR in studying rate processes.

Finally, I will have a couple of postdoctoral positions available starting about the middle of 1977 for persons interested in NMR research. Facilities are available for a broad range of work on solids or liquids, relaxation or high resolution.

Sincerely yours,


H. S. Gutowsky
Professor

HSG:sc

UNIVERSITY OF FLORIDA
GAINESVILLE, 32611

DEPARTMENT OF CHEMISTRY

December 8, 1976

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

Subject: Wide-line spectroscopy; change of address

Dear Barry:

During the past summer, we had the opportunity to use the Nicolet-Varian Fourier XL-100 system to look at hydrogen and fluorine spectra of some organic adsorbates on metal oxides. There were still in the lab some samples of $\text{CF}_3\text{CF}=\text{CF}_2$ on aluminum oxide which had been examined some years ago, using line widths and saturation to estimate T_1 values. The FT results, using the standard inversion recovery method gave unexpectedly short T_1 values, about 15 milliseconds for a fully covered surface at room temperature. The difference may be a result of the different method, or it may result from changes in the sample with the passage of time; however, the line widths for each of the four well-separated peaks had not changed substantially from the previous values.

The FT method takes more instrument time to make the observations than did the CW saturation method, but obviously much less operator time. The precision is quite a bit better, and leads us to conclude that the T_1 values of all the fluorines in adsorbed perfluoropropylene are identical.

We have also looked at some new samples of $\text{CF}_3\text{CH}_2\text{OH}$ on alumina. The hydrogen inversion recovery spectra show structure for intermediate recovery times, indicating either that the two kinds of hydrogen in the molecule are relaxing at different rates or that molecules are adsorbed in different environments, alternatives which can be evaluated by further experiments. An example is shown in the accompanying figure. The value of the relaxation time depends upon how one interprets the structured spectra, but it is about one second. For the same samples, the fluorine relaxation time is shorter, a few tenths of a second, and the logarithmic plot seems to be composed of two sections, lending some support to the theory of multiple adsorption sites.

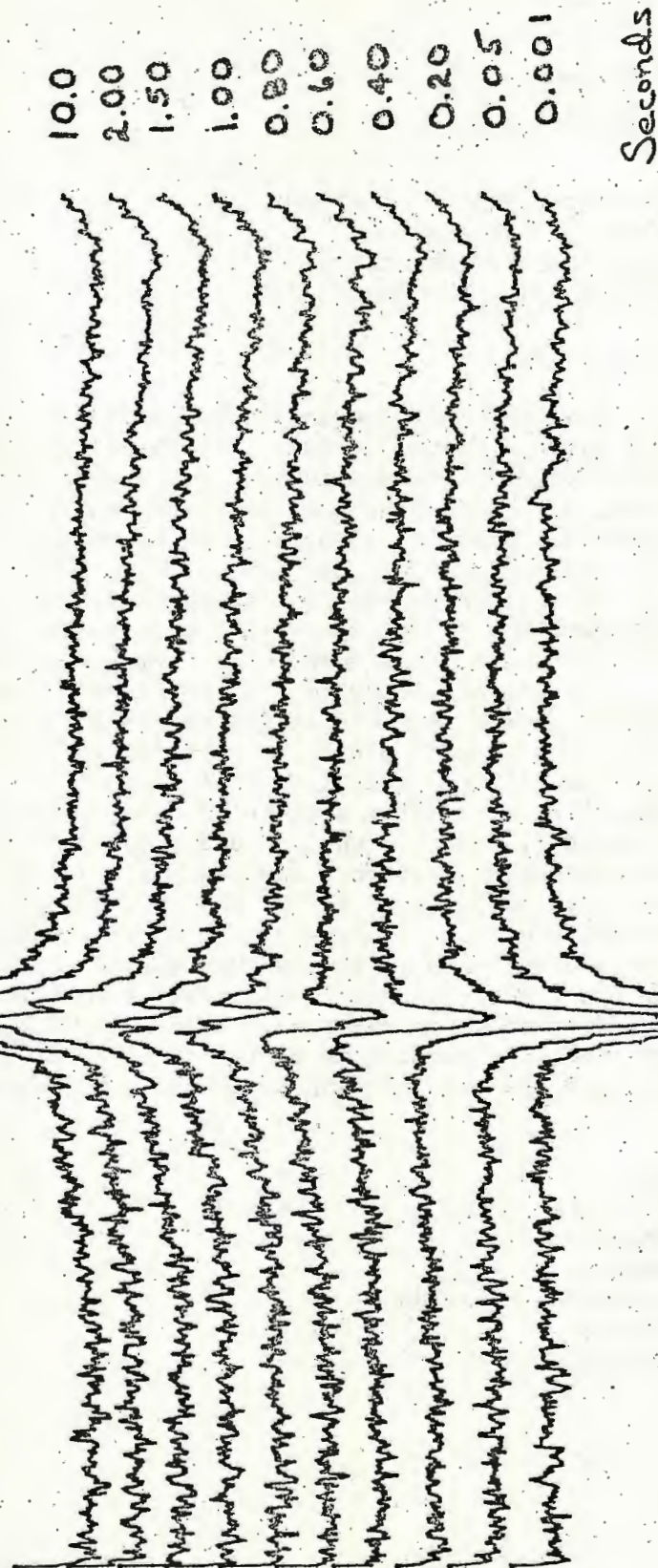
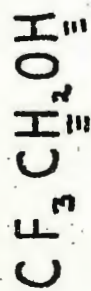
As a second item, by the time your readers receive this, I shall be on leave from the University of Florida, working in the Chemistry Division of the NSF in Washington. The Editorial Offices of the Journal of Magnetic Resonance will continue to be in Gainesville, and manuscripts will continue to be received there, but anyone wishing to talk to me personally about NMR or Journal matters can reach me in Washington at 202-632-7418. Also, I hope to receive this valuable publication at the NSF Chemistry Division, Washington, D.C., 20550.

Cordially yours,

Wallace

Wallace S. Brey
Professor of Chemistry

WSB/js
encl.





UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
 Washington, D.C. 20234

December 6, 1976

313.01

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

Dear Barry:

We have been pursuing the question of a standard reference material for line positions in NMR. A test mixture has been prepared and circulated in the Washington, D. C. area for a small round robin. Several results have come in by now and I feel that I know the ^1H chemical shifts as a function of temperature between 0° and 40°C with a precision of .001 ppm or better. The ^{13}C chemical shifts are not as well known--for one thing the digital resolution is in the neighborhood of .01 ppm--and I have fewer results to work with. The purpose of this note is to invite interested parties to make up mixtures according to the recipe used here and measure proton and/or carbon chemical shifts and send the results to me. This will allow the round robin to be extended far outside our local area and provide better statistics. The composition of the mixture follows: TMS, 1.5 cc; t-butyl acetate, 2.0 cc; perdeuteroacetone, 2.0 cc; p-dioxane, 1.5cc; methylene chloride, 3.0 cc; benzene, 1.5 cc; carbon tetrachloride, 8.5 cc. Dioxane was freshly distilled from LiAlH_4 to avoid peroxides. All of the liquids except TMS were measured and combined at room temperature. TMS was kept in a refrigerator about 5°C and measured in a cold syringe; it was introduced below the surface of the liquid mixture to minimize evaporation. The mixture was transferred to an NMR tube by syringe and degassed on a vacuum line by a single freeze-thaw cycle, then sealed off. Chemical shifts to 0.1 ppm are tabulated below for identification purposes:

	^1H	^{13}C
TMS	0.0	0.0
t-butylacetate	1.4, 1.9	22.1, 28.1, 79.5*, 169.4*
deuteroacetone	----	29.6* (multiplet), 204.3*
dioxane	3.6	67.1
methylene chloride	5.3	53.7
benzene	7.3	128.4
carbon tetrachloride	----	96.3*

The * signals arise from C with no directly bonded H. Under usual F_T conditions of rapid pulsing and proton decoupling, these signals are very weak.

It is known that variations in composition of this mixture have an effect on the chemical shifts which is large compared to the random errors. So far, we have not been troubled by excessive loss of TMS in the degassing step. Detailed results of the round-robin will be made available to all participants. The results received to date give reasonably good temperature-dependence data for protons, but very little for carbon.

The Bureau is also considering the preparation of T_1 standards. This project is still in the thinking stage but I hope to begin preparing candidate SRM's early in 1977. Thoughts of others will be welcome.

Yours very truly,

Rolf B. Johannesen/rjl
Rolf B. Johannesen
Inorganic Chemistry Section



December 8, 1976

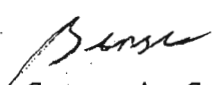
Professor Barry L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

^{17}O nmr determination of $^1\text{J}_{\text{PO}}$ and $^2\text{J}_{\text{FO}}$

Dear Barry,

In exploring the nature of spin coupling to phosphorus we have looked at ^{13}C and ^{15}N nmr extensively and have recently used the XL-100A GyroObserve accessory to do the same for ^{17}O . Although the quadrupolar broadening of the ^{17}O resonance is considerable in some cases (particularly P-O-R) we have been pleasantly surprised by the sharp (10-30 Hz linewidth) resonances observed in some cases. Enclosed is a spectrum of trifluorophosphine oxide showing the doublet expected for $^1\text{J}_{\text{PO}}$ but also the long-range coupling to the fluorines. I am not aware of any previously reported two bond ^{17}O couplings and would appreciate hearing from anyone who is aware of such. POCl_3 and POBr_3 also give completely resolved doublets. Tom Albright has done some CNDO/2 Finite Perturbation calculations and it appears that the Fermi contact mechanism dominates these couplings. We have submitted a full account of work for publication.

Sincerely yours,


George A. Gray, Manager
NMR Applications Laboratory
Instrument Division

$$^1\text{J}_{\text{PO}} = 184 \pm 3 \text{ Hz (F}_3\text{P=O)}$$

$$^1\text{J}_{\text{PO}} = 205 \pm 3 \text{ Hz (Cl}_3\text{P=O)}$$

$$^1\text{J}_{\text{PO}} = 201 \pm 5 \text{ Hz (Br}_3\text{PO)}$$

$$^2\text{J}_{\text{FO}} = 31 \pm 3 \text{ Hz}$$

Natural Abundance ^{17}O nmr

$F_3P=0$ at -40°C

25,130 transients 12 mm tube

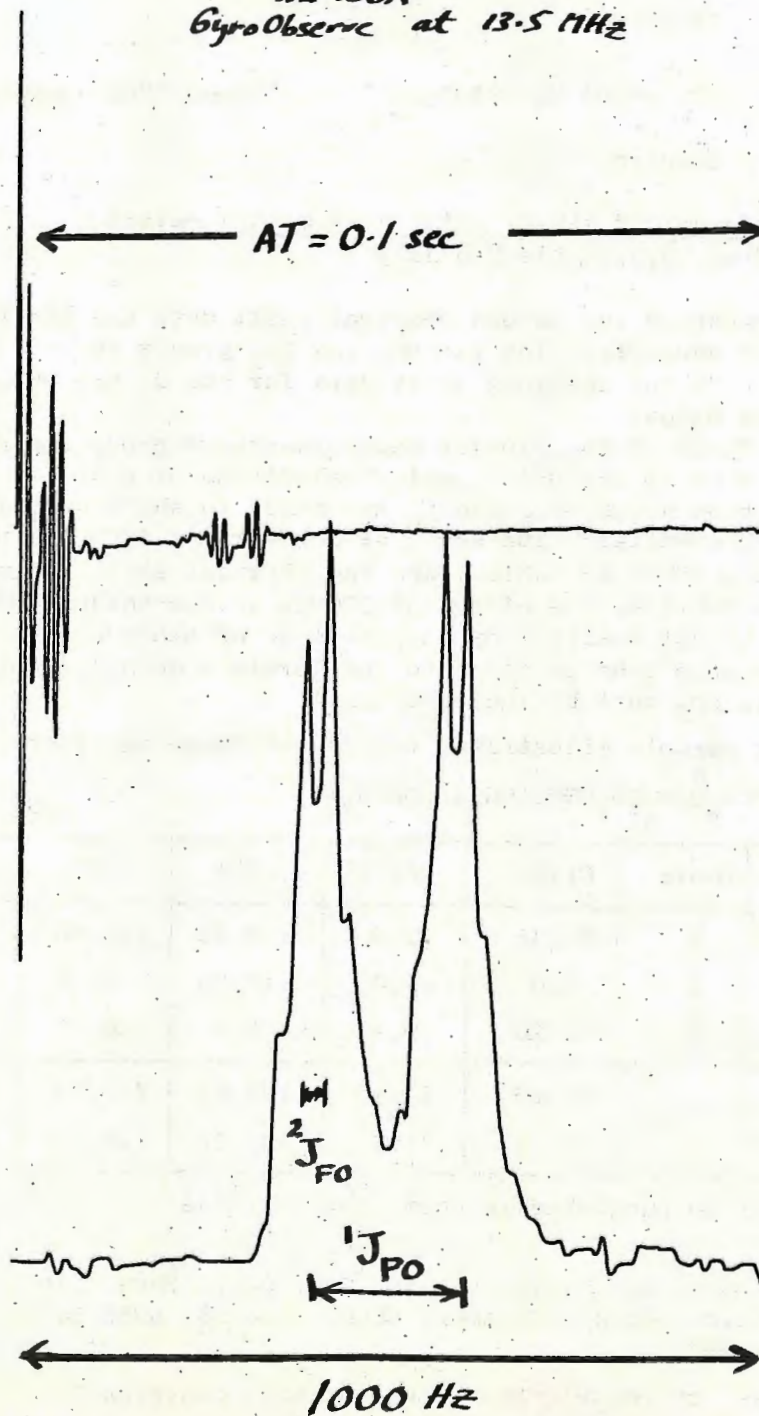
ext ^{19}F lock 90° pulses

2500 Hz Spectral Width

no exponential weighting

XL-100A

GyroObserve at 13.5 MHz





Vlaardingen/Duiven
Olivier van Noortlaan 120
Vlaardingen
postbus 114

telefoon 010-353000
telex 23261

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

uw ref.

onze ref. MA/6650/eds

toestel 2762

datum 8th December 1976

Dear Professor Shapiro,

¹³C-NMR of unsaturated linear fatty acid methyl esters
(J. Bus, I. Sies, M.S.F. Lie Ken Jie)

Recently we reported the carbon chemical shift data and the empirical chemical shift parameters for the CH₃ and CH₂ groups in unsaturated esters. A part of the chemical shift data for the double and triple bonds is given below.

The electric field of the dipolar methoxycarbonyl group induces a charge separation in the polarisable π -electrons of a double or triple bond² at position n, causing the C_n resonance to shift upfield and the C_{n+1} resonance downfield. The basic values derived from 102 unsaturated fatty acids are given in table 1 and the chemical shift increments are reproduced in table 2. The effect of COOCH₃ on non-conjugated double or triple bonds is not modified by the presence of other double or triple bonds. If a double bond is close to the terminal methyl group then the effect of this CH₃ must be included (table 3).

The following example illustrates the use of these empirical parameters.

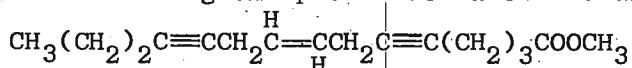


	Table	C(12)	C(11)	C(9)	C(8)	C(6)	C(5)
Basic	1	82.45	77.00	126.45	126.45	77.00	82.45
COOCH ₃	2	0.0	-0.05	+0.20	-0.30	+1.20	-1.45
CH ₃	3	-0.20	+0.20	0.0	0.0	0.0	0.0
Calculated		82.25	77.15	126.65	126.15	78.20	81.00
Experimental		82.30	77.15	126.55	126.20	78.20	80.95

This work will be published in Chem. Phys. Lipids.

References:

1. J. Bus, I. Sies and M.F.S. Lie Ken Jie, Chem. Phys. Lipids, 17(4) 501(1976).
2. J.G. Batchelor, et al. J. Amer. Chem. Soc. 95, 6358(1973) and J.Org.Chem. 39, 1698(1974).

With apologies for the delay in sending you this contribution.

Yours sincerely,

Dr J. Bus

Table 1

219-46

Basic carbon chemical shifts (δ /ppm) of the carbon atoms of double and triple bonds in various unsaturated fatty acid methyl esters.

Solvent: CDCl_3 . Internal reference: TMS. Bruker WH90.

$\begin{array}{c} \text{H} \quad \text{H} \\ \text{C}=\text{C} \end{array}$			$\begin{array}{c} \text{H} \\ \text{C}=\text{C} \\ \text{H} \end{array}$			$\text{C}\equiv\text{C}$		
130.00			130.45			80.20		
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}=\text{C} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}=\text{C} \\ \text{H} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{C} \\ \text{H} \end{array}$		
a b			a b c d			a b c d		
n	a	b	n	a	b	c	d	
1	130.20	128.05	0	130.05	125.80	128.80	134.70	
2	130.50	129.05	1	130.55	127.85	128.45	130.95	
			2	130.35	129.25	129.80	130.95	
$\begin{array}{c} \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}=\text{C} \\ \text{H} \quad \text{H} \end{array}$			$\begin{array}{c} \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{C} \\ \text{H} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{C} \\ \text{H} \quad \text{H} \end{array}$		
a b			a b c d			a b c d		
n	a	b	n	a	b	c	d	
0	132.35	130.55	1	131.95	124.80	77.65	82.10	
1	131.15	128.70	2	131.75	128.65	79.75	80.60	
$\text{C}\equiv\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{C}$			$\begin{array}{c} \text{H} \quad \text{H} \\ \text{C}=\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{C} \\ \text{H} \quad \text{H} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-\text{CH}_2-\text{C}\equiv\text{C} \\ \text{H} \end{array}$		
a b			a b c d			a b c		
n	a	b	n	a	b	c	d	
1	80.50	74.60	1	131.40	125.10	78.40	80.05	
2	81.20	78.80						
$\begin{array}{c} \text{H} \\ \text{C}\equiv\text{C}-\text{CH}_2-\text{C}=\text{C}-\text{CH}_2-\text{C}\equiv\text{C} \\ \text{H} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-\text{CH}_2-\text{C}\equiv\text{C} \\ \text{H} \end{array}$			$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-\text{CH}_2-\text{C}\equiv\text{C} \\ \text{H} \end{array}$		
a b c			a b c			a b c		
a	b	c	a	b	c	a	b	c
82.45	77.00	126.45	130.50	127.80	128.30			

Table 2

Effects ($\Delta\delta$) of methoxycarbonyl group on carbon chemical shifts of C(n) and C(n+1) of double and triple bonds (locant n) in fatty acid esters. Values for cis and trans are the same, except for n=2 and n=3 (trans between brackets).

n	C=C		C \equiv C	
	$\Delta\delta$ C(n)	$\Delta\delta$ C(n+1)	$\Delta\delta$ C(n)	$\Delta\delta$ C(n+1)
2	-10.75(-9.40)	+21.05(+19.45)	- 7.25 ^a	+ 9.80 ^a
3	- 9.20(-8.90)	+ 3.70(+ 4.60)	- 8.90	+ 3.70
4	- 2.55	+ 1.75	- 2.15	+ 1.00
5	- 1.55	+ 1.30	- 1.45	+ 1.20
6	- 0.85	+ 0.65	- 0.80 ^a	+ 0.60 ^a
7	- 0.50	+ 0.40	- 0.40	+ 0.30
8	- 0.30	+ 0.20	- 0.20	+ 0.25
9	- 0.20	+ 0.15	- 0.15	+ 0.15
10	- 0.10	+ 0.10	- 0.05	+ 0.05
11	- 0.05	+ 0.05	- 0.05	0
12	0	0	0	0

^a) Deviating values were found for methyl 2,6-octadecadiynoate (- 7.75; + 9.15; - 1.50; + 1.10). The values in this table may, therefore, not be valid for 2-alkynoates of a second unsaturated bond is present.

Table 3

Carbon chemical shift parameters describing the effects of a methyl group on double or triple bond C-atoms in linear esters.

α , β , for the effect on the nearer C-atom, α' , β' , for the remote one.

The effect on trans has not been measured.

H H
CH₃ on C=C

$\alpha = - 6.40$	$\alpha' = + 1.00$
$\beta = + 1.60$	$\beta' = - 0.55$
$\gamma = - 0.35$	$\gamma' = + 0.15$
$\delta = - 0.15$	$\delta' = - 0.05$

CH₃ on C \equiv C

$\alpha = - 4.85$	$\alpha' = - 0.80$
$\beta = + 1.30$	$\beta' = - 0.65$
$\gamma = - 0.20$	$\gamma' = + 0.20$
$\delta = - 0.05$	$\delta' = + 0.05$

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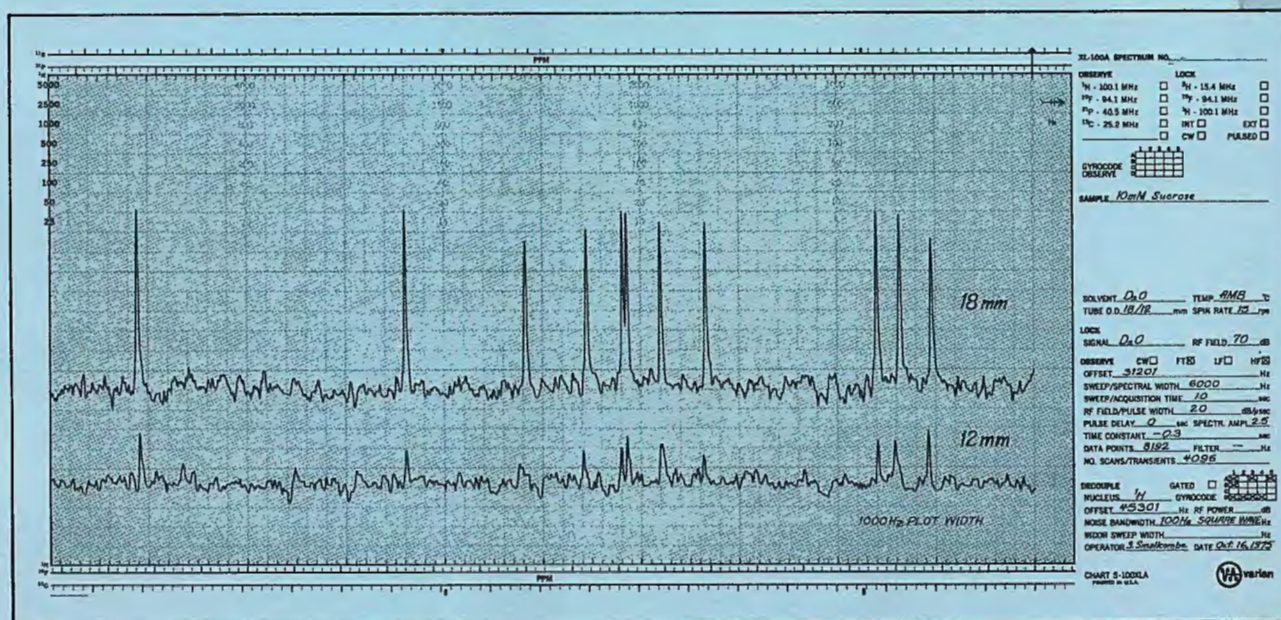
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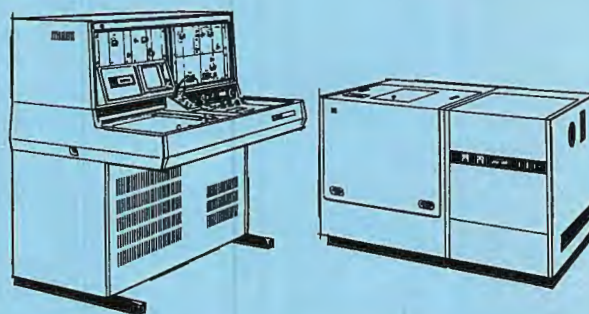


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