Texas A&M University N-M-R Newsletter

No. 223

April, 1977

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DEADLINE DATES: No. 224: 2 May 1977
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All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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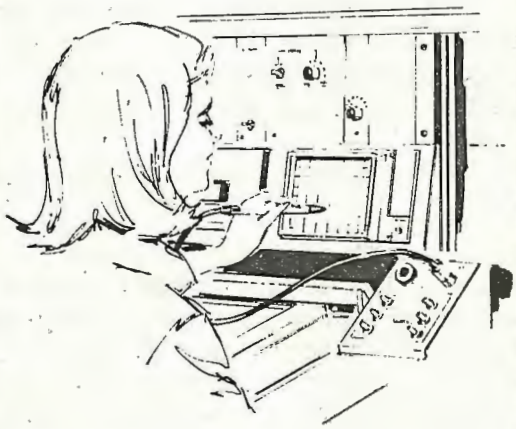

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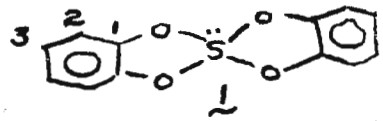
February 28, 1977

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

Dear Barry:

Sorry I'm late-aber we have been installing our new ^{1}H probe and homonuclear decoupler in the CFT-20. For years we have only seen a five line pattern for the methylene hydrogens of trimethyl phosphate. Please note that with the new probe we see the expected double quartet.

More recently Dr. Grace Hsu has prepared the sulfurane (1): 

Our interest in this compound stems from the fact that the analogous phosphorus compounds exist as tetragonal pyramids. This is a marked deviation from other phosphoranes which prefer trigonal bipyramidal structures. The ^{13}C nmr spectrum of 1 shows only three absorptions at 144.2, 123.4 and 111.8 ppm relative to TMS. Clearly, this spectrum could arise from a static tetragonal pyramid, a freely pseudorotating trigonal bipyramid or from a compound where there is rapid S-O bond cleavage and recombination. At -90° the ^{13}C nmr spectrum clearly demonstrates that the one and two carbons are found as separate resonances (See attached spectra). Quite obviously, the low temperature spectrum demonstrates that the preferred structure, at these temperatures, is the trigonal bipyramid. The process that leads to the equivalency of these carbons at room temperature is probably an intramolecular permutational isomerization. We believe this to be the case because Professor J. C. Martin (Illinois) has shown that ionization has an activation energy of about 20 Kcal/mole whereas we find that the activation energy required to achieve equivalence of carbons one and two is about 9-10 Kcal/mole. We have not been able to pin point this energy more accurately because of problems associated with determination of the exact coalescence temperature.

In the realm of hypervalent molecule chemistry David Bowman has prepared $\phi P[OCH_2C(CH_3)_3]_4$. We noted what appeared to be a very large coupling constant between the phosphorus and the aromatic ipso carbon of 227 Hz. In order to determine whether this was in fact a true coupling, we investigated the FT ^{31}P nmr spectrum of this compound. Happily we found that the ^{13}C - ^{31}P coupling constant agreed perfectly with that found in the ^{13}C spectrum.

We are extremely pleased with the multi-nuclear capability of our CFT-20 and fully hope to report to your readers in the future of our ongoing investigations.

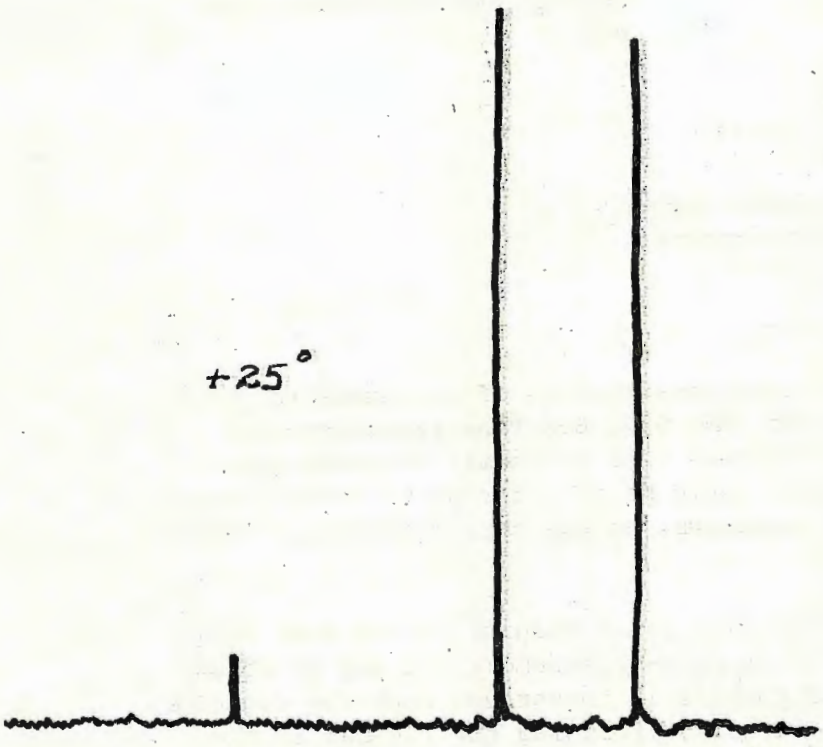
Be of good cheer!

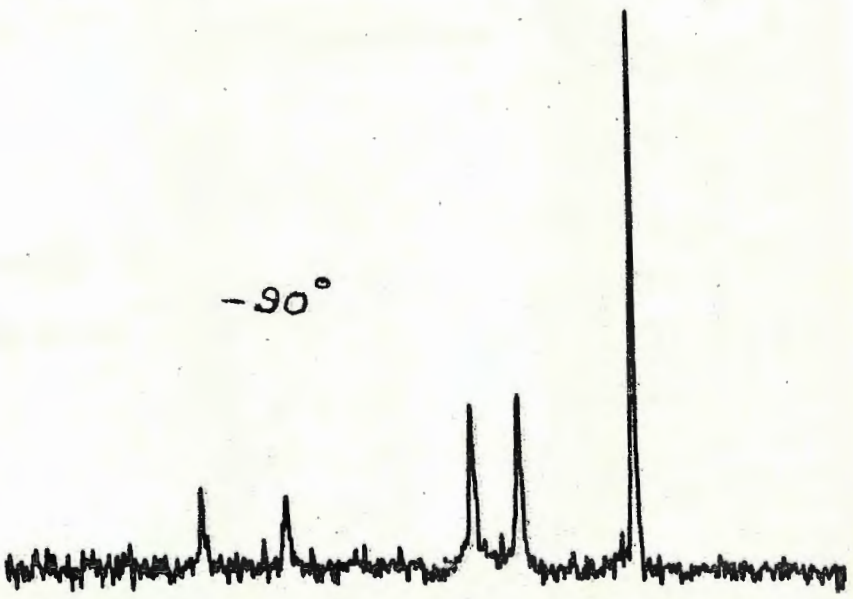
Sincerely yours,

Dorothy

DZD:mhs

Dorothy Z. Denney





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CH-8049 Zürich
Prof. Dr. K. Wüthrich
Tel. (01) 57 57 70

8049 Zürich, March 7, 1977 KW/as

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

Interface VDM 620i - Remex HSRP

Dear Barry:

We have recently completed construction of an interface for the use of the Remex Mod. RAF 6375 BDX Tape reader/puncher with the Varian Data Machines 620i computer. Since we could imagine that this gadget could be of interest to other owners of Varian 620 series computers, we use this material to answer your blue reminder.

The figure shows a simplified block diagram of the home built interface, which should be self-explanatory. It may be added that our interface was physically integrated into the computer mainframe. Additional details, including the lay-out of the print, are available on request.

Best wishes,

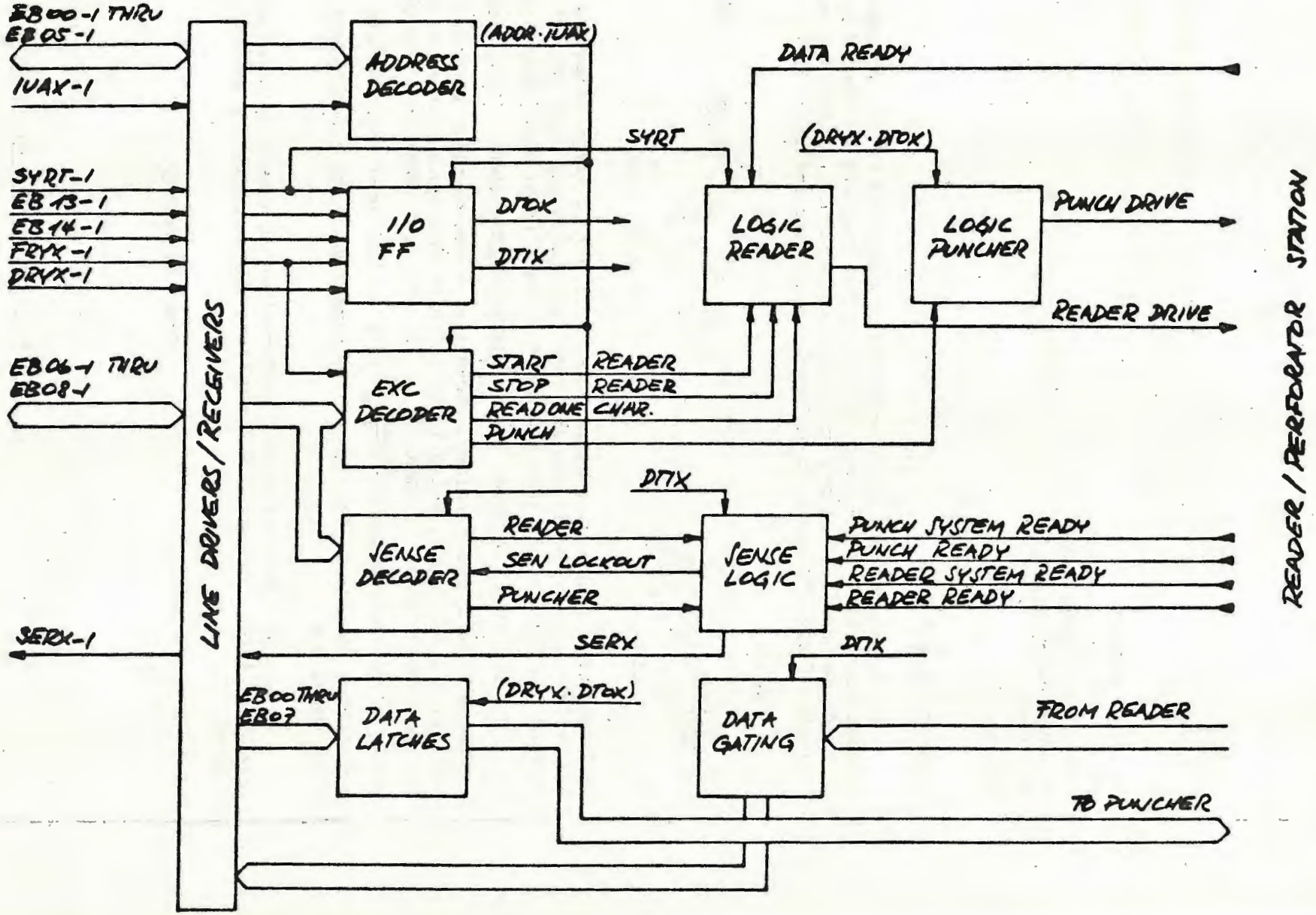
Sincerely yours,

R. Baumann K. Gabler Kurt

Rudolf Baumann Kurt Gabler Kurt Wüthrich

INTERFACE

VDM 620i – REMEX MOD. RAF 6375 BDX TAPE READER/PERFORATOR



223-5

University of Durham Department of Chemistry

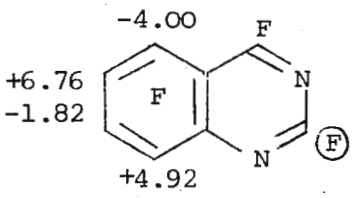
Science Laboratories, South Road, Durham, DH1 3LE
Telephone: Durham 64971 (STD code 0385)

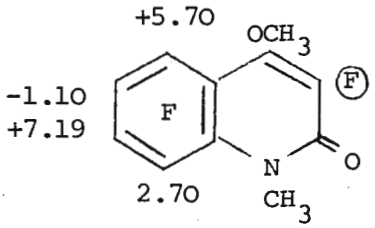
3rd March, 1977.

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

Dear Dr. Shapiro,

In experiments on perfluorobicyclic compounds of the azanaphthalene type, we have found that long-range inter-ring F,F coupling constants alternate in sign and magnitude in accord with simple theoretical predictions e.g. a direct analysis of the ^{19}F spectrum of hexafluoroquinazoline gave





Ⓕ = coupled nucleus

Seven bond F,F coupling constants are, in general, larger than the other inter-ring coupling constants and some prior evidence does support our results in that Doddrell et al. (J.C.S. Perkin II 402, 1976, small print, p. 404) found $^{7}J_{F,F}$ = 7 Hz. in a ^{13}C study of 2,6-difluoronaphthalene. In planar styrene-type molecules (hexafluoroquinolone, above right) the coupling constants are surprisingly similar, the magnitudes being in accord with analogous values in indans (I.D. Rae and co-workers, Aust. J. Chem. 29, 1435, 1976 and subsequent papers). We are now in a position to use $J^{\text{inter-ring}}_{F,F}$ as a structural tool in more heavily substituted polyfluorobicyclic and to investigate the substitution-sensitivity of these couplings.

Following the experimental difficulties of measuring cross-ring H,H or C,H couplings, large cross-ring F,F couplings are analytically valuable and reassuringly visible.

Yours sincerely,

R S Matthews A Royston

R.S. Matthews & A. Royston.

DOWELL DIVISION OF THE DOW CHEMICAL COMPANY

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March 8, 1977

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

Dear Dr. Shapiro:

Re: PLACING REFERENCE SOLVENTS IN MICROSAMPLE TUBES

We recently received a carbon microsample probe for our CFT-20 and are extremely pleased with the performance (S/N > 30:1). We have identified several GC and LC effluent samples collected in microsample tubes.

One problem we encountered initially was placing an appropriately small volume of reference solvent (TMS, dioxane, etc.) in the tube. Initial attempts to place the reference solvent in the lock solvent before adding the lock solvent to the tube were unsuccessful because of variations in sample size. We have found, however, that the tip of a conventional long tip disposable pipet can be drawn to an even longer and smaller-diameter tip with a Bunsen burner and used very conveniently to place a reference solvent in the capillary tube. As long as the glass is removed from the flame before being drawn out, the tip will not seal; extending the pipet tip in this manner requires even less skill than sealing the sample tube properly.

Sincerely,

David R. Bell

David R. Bell

an

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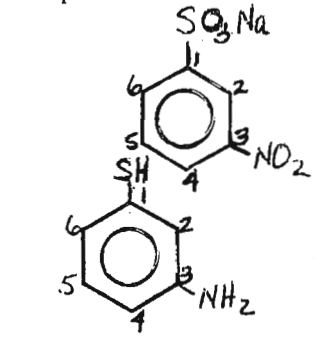
March 7, 1977

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

Dear Barry:

Our increasing use of ^{13}C nmr to identify a variety of sulfur-containing aromatics prompted us to evaluate the substituent effects for a series of sulfur derivatives of benzene[1]. Although a large body of data has been collected for many other substituents, very few sulfur derivatives have been examined[2,3]. Values were tentatively assigned from the ^{13}C spectra of the monosubstituted benzene derivatives. Confirmation of the assignments was obtained by comparing calculated experimental chemical shifts for several disubstituted benzenes. The data are collected in Table 1.

Examination of the para carbon shieldings suggests the following order of electron donating ability: $-SCH_3$ > -SH > -SPh > -SSPh. Several examples of calculated and experimental chemical shifts are shown below:



	C-1	C-2	C-3	C-4	C-5	C-6
Calc.	145.4	121.3	149.5	127.2	131.3	133.1
Exp.	145.3	121.5	148.3	126.6	131.3	132.7
Calc.	131.7	116.3	147.6	112.1	130.5	119.8
Exp.	131.5	115.2	147.1	112.3	129.8	118.9
Calc.	127.9	132.9	117.1	156.3		
Exp.	126.9	133.7	117.0	157.7		

Taft et. al have recently pointed out that di- and polysubstituted benzenes can deviate markedly from additive behavior[4]. Nonetheless, in all the meta and para disubstituted benzenes we examined, reasonably good agreement between calculated and experimental values was obtained. We have found this data to be very useful in structure identification.

Regards,

E. A. Williams
Chemical & Structural Analysis Branch
Materials Characterization Laboratory

J. D. Cargioli
Chemical & Structural Analysis Branch
Materials Characterization Laboratory

REFERENCES

1. This work was carried out in conjunction with J.L. Webb, M. Cipullo and J.H. Ligon, also of General Electric Research and Development

2. G.W. Buchanan, C. Reyes-Zamora and D.E. Clarke, Can. J. Chem., 52, 3895 (1974).

3. M.S. Chauhan and I.W.J. Still, Can. J. Chem., 53, 2880 (1975).

4. J. Bromilow, R.T.C. Brownlee, R.D. Topsom and R.W. Taft, J. Amer. Chem. Soc., 98, 2020 (1976).

Table. ^{13}C Shielding Parameters for Sulfur Derivatives of Benzene[a]

Substituent	C-1	ortho	meta	para
$-OSO_2Ph$[c]	+20.9	-6.3	+1.5	-1.1
$-SH$	+2.3	+1.1	+1.1	-3.1
$-SCH_3$	+10.2	-1.8	+0.4	-3.6
$-SPh$	+7.3	+2.4	+0.5	-1.7
$-SOCH_3$[b]	+17.6	-5.1	+0.7	+2.3
$-SOPh$	+17.1	-3.8	+0.8	+2.5
$-SO_2CH_3$[b]	+12.3	-1.5	+0.6	+4.8
$-SO_2Ph$[c]	+13.5	-0.8	+1.1	+4.9
$-SO_2Cl$	+15.9	-1.6	+1.3	+7.0
$-SO_2F$	+4.7	+0.1	+1.6	+7.6
$-SO_2NH_2$	+15.3	-2.9	+0.4	+3.3
$-SO_2OCH_3$[c]	+6.4	-0.6	+1.5	+5.9
$-SO_2OPh$	+6.3	-0.2	+1.2	+6.4
$-SO_3H$[c]	+18.7	-0.7	+2.3	+4.1
$-SO_3Na$[c]	+19.0	-2.9	-0.8	+0.3
$-SO_3Na$[d]	+15.4	-2.2	+1.3	+3.7
$-SO_2Na$[d]	+26.3	-4.0	+1.4	+2.8
$-SSPh$	+ 8.4	-1.2	+0.4	-1.6

a Chemical shifts in ppm relative to benzene. Positive values are downfield. Samples were run as 10-20% solutions in $CDCl_3$ using TMS as an internal standard unless otherwise noted.

b Values from ref. 2.

c In DMSO-d_6.

d In D_2O. Dioxane (δ67.4) used as an internal reference.

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

March 3, 1977

Sodium-23 Q : Quid ?

Dear Barry,

I would appreciate it very much if one of your readers could help me to pinpoint the correct value of the quadrupole moment Q for the ^{23}Na nucleus. Conflicting values ranging between 0.10 and 0.15 barns can be found in the literature [1-5], with sometimes the same author using different values in quasi-contemporary papers !

Obviously, a 50 % difference (error) in Q will lead to a 100 % difference (error) in the correlation time inferred from an experimental linewidth.

I shall be very grateful to anyone who can help me to resolve these discrepancies.

With best regards,
Sincerely,

Pierre Laszlo

1. P.W. Langhoff and R.P. Hurst, Phys. Rev., 139A, 1415 (1965).
2. Varian NMR Table, 1968 (Wallet format).
3. C.A. Melendres and H.G. Hertz, J. Chem. Phys., 61, 4156 (1974).
4. G. Lindblom, H. Wennerström, and B. Lindman, in Magnetic Resonance in Colloid and Interface Science, ACS Symposium Series No.34, H.A. Resing and C.G. Wade, Eds., American Chemical Society, Washington, D.C., 1976, p. 372-396.
5. S. Forsén and B. Lindman, Chemistry in Britain, in press.

הטכניון — מכון טכנולוגי לישראל

TECHNION — ISRAEL INSTITUTE OF TECHNOLOGY

הפקולטה לכימיה

DEPARTMENT OF CHEMISTRY

14 March 1977

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

Dear Barry,

I shall be grateful to you if this letter appears in the TAMU NMR Newsletter.

A postdoctoral position is available immediately for a Physical Chemist to work on nmr of solutes in liquid crystals (thermotropic and lyotropic systems). The applicant should write to me adding a brief curriculum vitae and names of referees.

I haven't subscribed to the TAMU NMR for some time! Would you please advise me on the renewal of my subscription.

Yours sincerely,

A. Loewenstein.

A. Loewenstein

AL/ajs

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.

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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

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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."

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SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

March 14, 1977

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

Translational Motion in Phospholipid Bilayers Studied With Rotating Frame Spin-Lattice Relaxation

Dear Barry:

Our interest in the "fluidity" of membrames has led us to measurements of the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) as a possible means of investigating the translational motion of phospholipids in the membrame. The $T_{1\rho}$ experiment allows direct determination of the lateral self-diffusion coefficient within phospholipid bilayers. If translational diffusion contributes to the fluctuating dipolar fields responsible for the proton relaxation, i.e., intermolecular relaxation, the $T_{1\rho}$ relaxation rate exhibits a radiofrequency dependence from which the diffusion coefficient may be calculated (1,2). We have examined the radiofrequency dependence of the proton $T_{1\rho}$ relaxation rates, using the "spin-locking" technique, for dipalmitoyl phosphatidylcholine (DPPC) in the homogeneous bilayer above the Chapman phase transition temperature, i.e., the smectic liquid crystalline phase. The temperature and frequency dependence of the proton $T_{1\rho}$ values for DPPC suggest that intermolecular dipole-dipole contributions to relaxation are important. Dilution of the samples with perdeuterated DPPC (kindly loaned to us by Sunney Chan) exhibits a decrease in $T_{1\rho}$ relaxation rates confirming the significance of intermolecular contributions to $T_{1\rho}$ relaxation. The radiofrequency field dependence of the proton $T_{1\rho}$ values of DPPC (80.3% DPPC/19.7% D_2O) at 55°C yields a diffusion coefficient of 0.4×10^{-8} cm^2/sec. The dependence of the diffusion coefficient on DPPC concentration has also been examined.

1. J.F. Harmon and B.H Muller, Phys. Rev., 182, 400 (1969).
2. L.J. Burnett and J.F. Harmon, J. Chem. Phys., 57, 1293 (1972).

Best regards,

Tom

Thomas L. James
Assistant Professor of Chemistry
and Pharmaceutical Chemistry

Ross W. Fisher

Ross W. Fisher

TLJ/RWF:bw

223-13

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RESEARCH TRIANGLE PARK, N.C. 27709

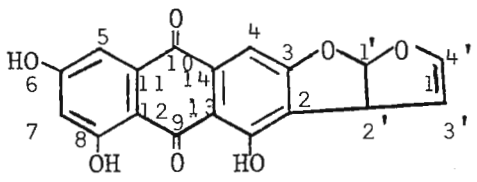
March 8, 1977

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

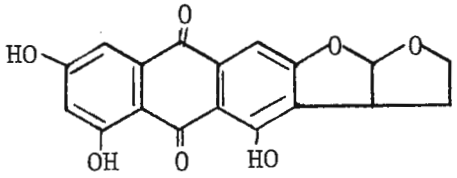
Dear Barry:

^{13}C NMR of anthraquinones; change of address

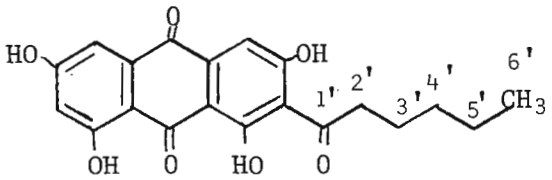
During some labelling experiments with aflatoxin B_1 biosynthesis (to appear shortly in J.A.C.S.), we had the opportunity to examine the spectra of several of the anthraquinone intermediates found in the biosynthetic pathway. Since the spectra of a few of these and similar compounds have already appeared in the literature,[1,2] I thought the readers might be interested in the additional compounds we have examined that will not be in the above paper. The ^{13}C chemical shifts for versicolorin A (I) and C (II) and norsolarinic acid (III) are given below. One of the more interesting trends in these and related compounds[1] is the effect of H-bonding on the carbonyl chemical shift (~5 ppm downfield shift for each H-bond).



I



II



III

Carbon	I	II	III	Carbon	I	II	III
1	158.9	158.6	161.0	11	135.8	134.8	134.7
2	121.1	119.7	121.1	12	109.0	107.9	108.9
3	165.8	165.1	163.0	13	109.4	110.4	108.0
4	101.9	100.9	107.8	14	135.3	134.2	134.5
5	109.4	108.6	108.7	1'	113.6	112.9	202.6
6	165.8	164.8	165.0	2'	47.9	43.3	43.5
7	108.5	107.6	108.0	3'	102.4	30.0	22.6
8	164.7	163.8	164.1	4'	146.3	66.9	30.6
9	189.5	188.4	188.0	5'	-	-	21.8
10	181.2	180.1	181.1	6'	-	-	13.7

In addition, I would like to inform the readers that I will be on leave from the University of Georgia at NIEHS until December 31, 1977.

Sincerely,

Dick

Richard H. Cox, Ph.D.

1. F. Toma, et al., Org. Magnet Res., 7, 496 (1975).

2. K. G. R. Pachler, et al., Chem. Commun., 916 (1976).

БЪЛГАРСКА
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BULGARIAN
ACADEMY OF SCIENCES
INSTITUTE OF ORGANIC CHEMISTRY
1113, Sofia, Bulgaria

Sofia, 10th March, 1977

Professor Bernard L.Shapiro,

TAMU NMR Newsletter,
Department of Chemistry,College of Science
Texas A.& M.University,
College Station,
TEXAS 77843. U.S.A.

Dear Professor Shapiro,

An Approach to Lanthanide Induced Shift Simulation Based on the General Dipolar Shift Equation

Most of the lanthanide induced shift (LIS) quantitative approaches are based on the McConnell-Robertson equation/1-3/. It is known that this equation is a special axial symmetry case of a more complicated dipolar shift equation:

$$\Delta_i = K_1 G_{1i} + K_2 G_{2i} = K_1 \frac{(3\cos^2\Theta_i - 1)}{r_i^3} + K_2 \frac{\sin^2\Theta_i \cos 2\phi_i}{r_i^3}$$

where G_{1i} and G_{2i} are the geometric factors and Θ_i, ϕ_i, r_i are the i-th proton spherical coordinates. Hence, the use of the McConnell-Robertson equation to systems lacking axial symmetry is without any physical justification. On the other hand the LIS simulation is usualy carried out by means of the least squares technique. Application of this technique to the general dipolar shift equation implies variation of five independent parameters: $K_1, K_2, \omega, \varphi$ and d, the latter three defining the lanthanide ion position. The large number of free parameters however increases the incertainty, particularly in cases when the number of the experimental LIS data is relatively small.

In order to exclude the parameters K_1 and K_2 from the direct variation scheme we suggest the following approach. Applying the conditions of minimum of the least squares function against K_1 and K_2

$$\frac{\partial \sum_i (\Delta_i^{obs.} - \Delta_i^{calc.})^2}{\partial K_1} = 0$$

$$\frac{\partial \sum_i (\Delta_i^{obs.} - \Delta_i^{calc.})^2}{\partial K_2} = 0$$

we obtain two equations against two unknowns (K_1 and K_2). Solving these equations we find the following formulas:

$$K_1 = \frac{(\sum_i \Delta_i^{obs.} G_{1i})(\sum_i G_{2i}^2) - (\sum_i \Delta_i^{obs.} G_{2i})(\sum_i G_{1i} G_{2i})}{(\sum_i G_{1i}^2)(\sum_i G_{2i}^2) - (\sum_i G_{1i} G_{2i})^2}$$

$$K_2 = \frac{(\sum_i \Delta_i^{obs.} G_{2i})(\sum_i G_{1i}^2) - (\sum_i \Delta_i^{obs.} G_{1i})(\sum_i G_{1i} G_{2i})}{(\sum_i G_{2i}^2)(\sum_i G_{1i}^2) - (\sum_i G_{1i} G_{2i})^2}$$

In this way the only variable parameters remain ω, φ and d - the same as in the McConnell-Robertson equation (K_1 in the latter can be determined in a similar way). On the basis of this approach a NONAX programme in BASIC language is developed. Its application to some conformationaly mobile systems is in progress.

Sincerely yours,

S.L.Spassov I.P.Bangov

1. A.F.Cockerill, G.L.O.Davies, R.C.Harden, and D.M.Rackham, Chem.Rev., 73(6), 553(1973).
2. O.Hofer, Top.Steriochem., 9, 111(1975).
3. G.R.Sullivan, JACS, 98(23)7162(1976).

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Professor B L Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION
Texas 77843
United States of America

11. MAR. 1977

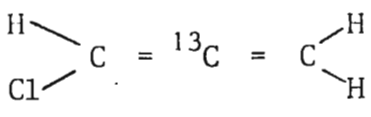
Dear Professor Shapiro

SPI VERSUS SPT

The terms SPI (selective population inversion)[1] and SPT (selective population transfer)[2] are both used in the literature to describe the same FT experiment in which a π-pulse is applied selectively to one or more transitions of a spin-coupled system prior to observation of the spectrum.

It has recently been suggested[3] that SPT would be the better term because the experiment does not lead to a complete inversion of energy-level populations. The reason for this is the necessary compromise between rf power and duration of the π-pulse dictated by the condition $\gamma H_2 \tau = 0{,}5$. Intensity losses are due to either relaxation during relatively long pulses or to effects on neighbouring transitions when the rf power level is too high for the peak separations. We have in the past always been able to observe effects reasonably close to the theoretical maximum. Koole and de Bie[3], however, reported enhancement factors of +4 and -2 (theory: +9, -7) for lines X6 and X3, respectively, of the C-2 resonances of chloroallene, after "inverting" proton transition B4 (Figure 1, $\gamma H_2 \approx 0{,}15$ Hz, $\tau = 3$s).

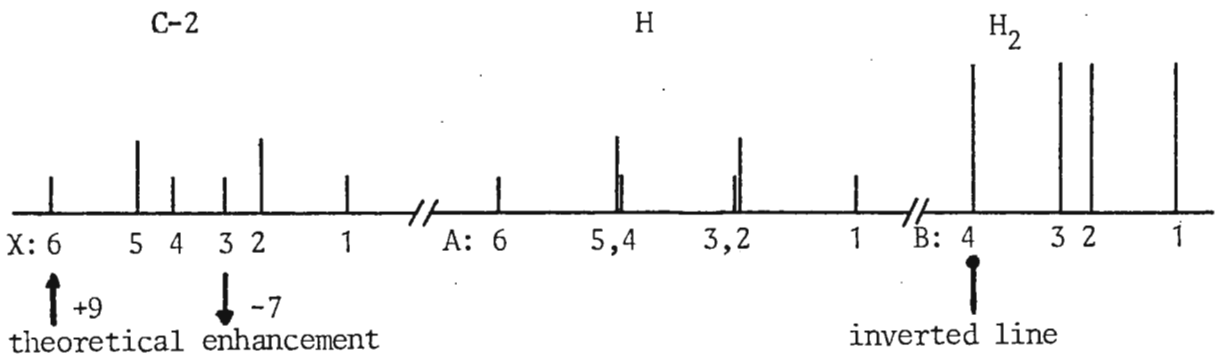
FIGURE 1



$^2J(C\text{-}2,H_2) = -4.5$ Hz

$^2J(C\text{-}2,H) = +6.3$Hz

$^2J(H_2,H) = -6.05$ Hz



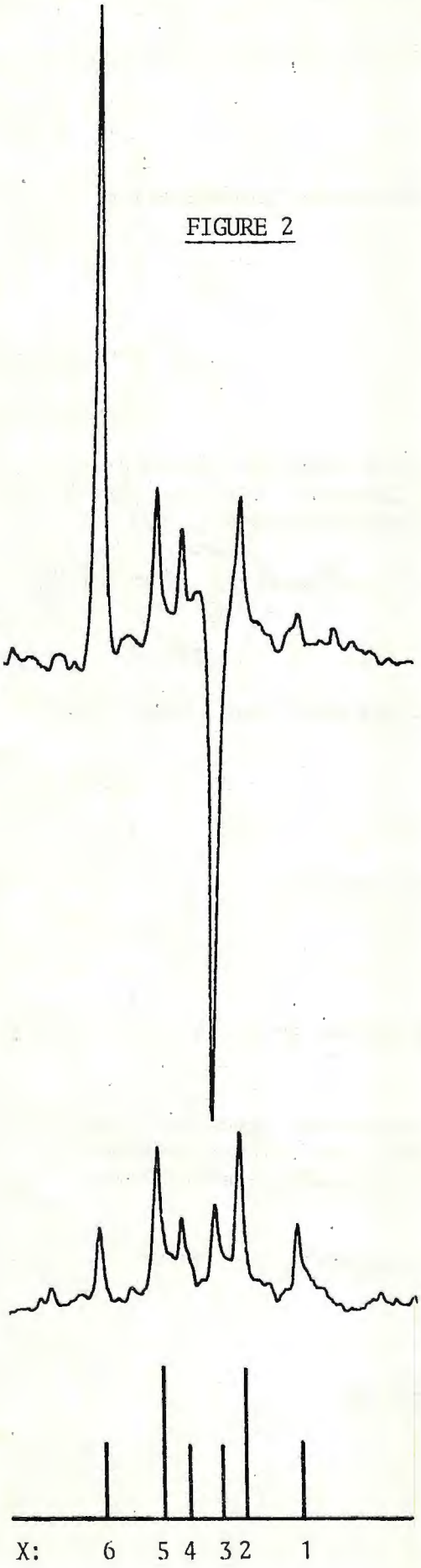


FIGURE 2

These factors were only slightly larger than those observed by them in a continuous irradiation experiment. We repeated their experiment and determined enhancement factors of +8 and -6, which are as close to the theoretical values as can be expected (Figure 2, γH_2 = 2,5 Hz, τ = 0,2s). The observed intensity changes though critically dependent on the choice of experimental parameters, do not seem to provide a convincing argument in favour of "SPT".

The term "SPT" is furthermore rather non-specific and can be applied to any type of generalized Overhauser effect, whether of steady-state nature as in INDOR spectroscopy or of the non-equilibrium kind as encountered during Torrey oscillations, and has also been used by Koole and de Bie[3] for the continuous irradiation experiment. Its use could be ambiguous or misleading.

We should therefore like to suggest that "SPI" should be used instead for the non-equilibrium GOE-type experiment as described at the beginning of this letter.

Critical comments from readers of this Newsletter will be very much appreciated.

Yours sincerely

K Pachler
SENIOR CHIEF RESEARCH OFFICER

P L Wessels
CHIEF RESEARCH OFFICER

1. K.G.R. Pachler and P.L. Wessels, J. Magn. Resonance, 12, 337 (1973).

2. S. Sørensen, R.S. Hansen and H.J. Jakobsen, J. Magn. Resonance, 14, 243 (1974).

3. N.J. Koole and M.J.A. de Bie, J. Magn. Resonance, 23, 9 (1976).

SHELL DEVELOPMENT COMPANY
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WESTHOLLOW RESEARCH CENTER
P. O. Box 1380
Houston, TX 77001

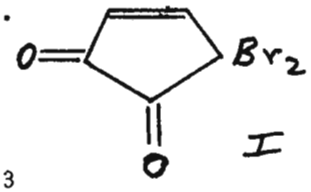
March 15, 1977

Subject: A "Tricky" Structural Determination

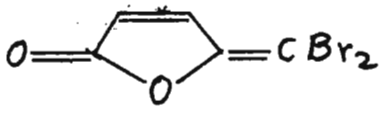
Dr. B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Tx. 77893

Dear Barry:

Recently, a compound with a m.p. of 136°C and an empirical formula of $C_5H_5O_2Br_2$ was prepared at the Shell Laboratories in Modesto. The Structure I below was initially proposed on the basis of chemical and spectroscopic (UV, IR, and proton NMR) evidence.



I



II

However, the ^{13}C NMR data suggest that Structure II is much more likely. The NMR data are:

^{1}H 2 doublets of equal intensity
(δ= 6.41 & 7.67 ppm; J = 5.5HZ)

^{13}C (See enclosed Figure)
5 resonances of equal intensity ($CDCl_3$ + FeAcAc)

δ (ppm)	J (HZ)	
81.6	<1	
122.5 (DD)	186.5, 2.3	
140.7 (DD)	183.1, 3.6	In $CDCl_3$ Solution
150.8 (DD)	11.0, 7.8	
167.6 (DD)	13.8, 8.7	

The observed shift of 81.6 for $=CBr_2$ is in reasonable agreement with the value of 78 predicted for Structure II from observed shifts in $Br_2C=CHCOOH$ and $Br_2C=C(CH_3)COOH$. For Structure I the predicted shift would be much closer to zero.

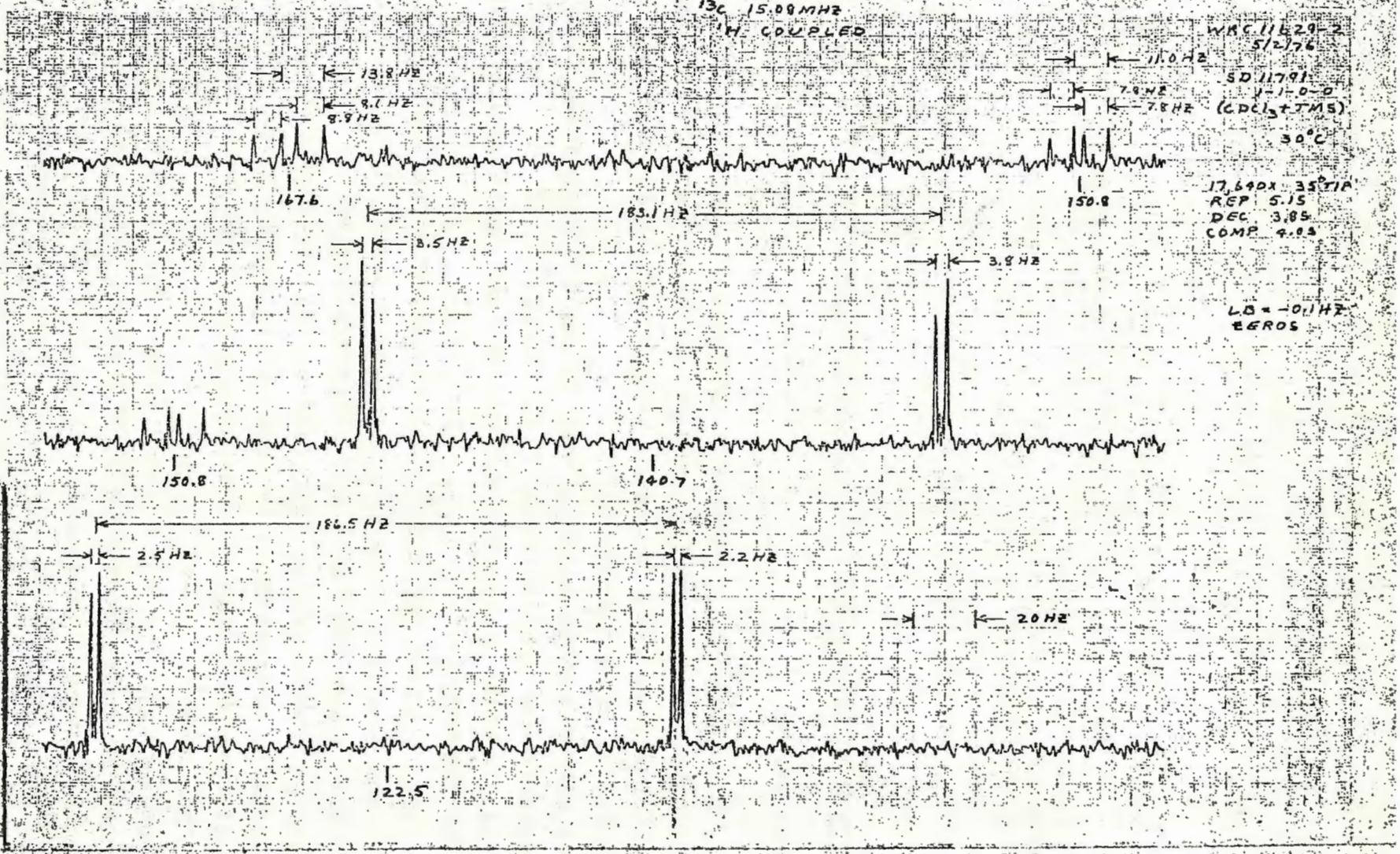
The lack of any resolvable long range H----C coupling also seems to be more consistent with II than with I.

Sincerely,

Charlie

C. A. Reilly

Attachment


13C 15.08 MHz
1H COUPLED
WRC 11629-2
5/27/76
SD 11791
V-1-0-0
(CDCl3+TMS)
30°C
17,640x 35°TP
REP 5.15
DEC 3.85
COMP 4.93
LB = -0.1 HZ
EGROS
13.8 HZ
9.7 HZ
8.9 HZ
167.6
11.0 HZ
7.9 HZ
7.8 HZ
150.8
183.1 HZ
8.5 HZ
3.8 HZ
150.8
140.7
186.5 HZ
2.5 HZ
2.2 HZ
20 HZ
122.5

PROFESSOR DR. R. KOSFELD
Abteilung für Physikalische Chemie der Kunststoffe

5100 Aachen, den 9.3.1977
Templergraben 59
Postfach der RWTH
Tel. 0241/[redacted] 42-4754

Professor B.L. Shapiro
Department of Chemistry
Texas A+M University

College Station, Texas 77843

Automated Relaxation and Diffusion Measurements

Dear Barry,

We have connected a real time computer of type Mincal 621/8 (Dietz, Mülheim/Ruhr) to a pulse spectrometer (Bruker Physics, Karlsruhe) in order to measure relaxation times (T_1, T_2) and diffusion coefficients (D_s).
The aim of our development was to achieve automation of the spectrometer control as well as automation of the complete detection and evaluation process through onset of the real time computer.
To this purpose essential control-construction parts such as HF- and gradient pulse units had to be built by us or modified in such a way that they can be controlled by the computer through corresponding interface units. The programs used for executing measurements are written in BASEX (basex = basic + real time function) in overlay structure and consist of about 25 segments.
The sequence (T_1, T_2, D_s) and extent temperature range of the experiment are determined in a dialogue with the computer and the measurement is started. After this no more manipulations will be necessary at the computer and spectrometer as well.
The optimal spectrometer settings such as HF- and gradient pulse length, amplifier setting etc. are determined by computer controlled premeasurements and are set on the spectrometer by the computer. The variation of the experimental parameters, signal recording and spectrometer control are regulated by the computer and evaluation is started.

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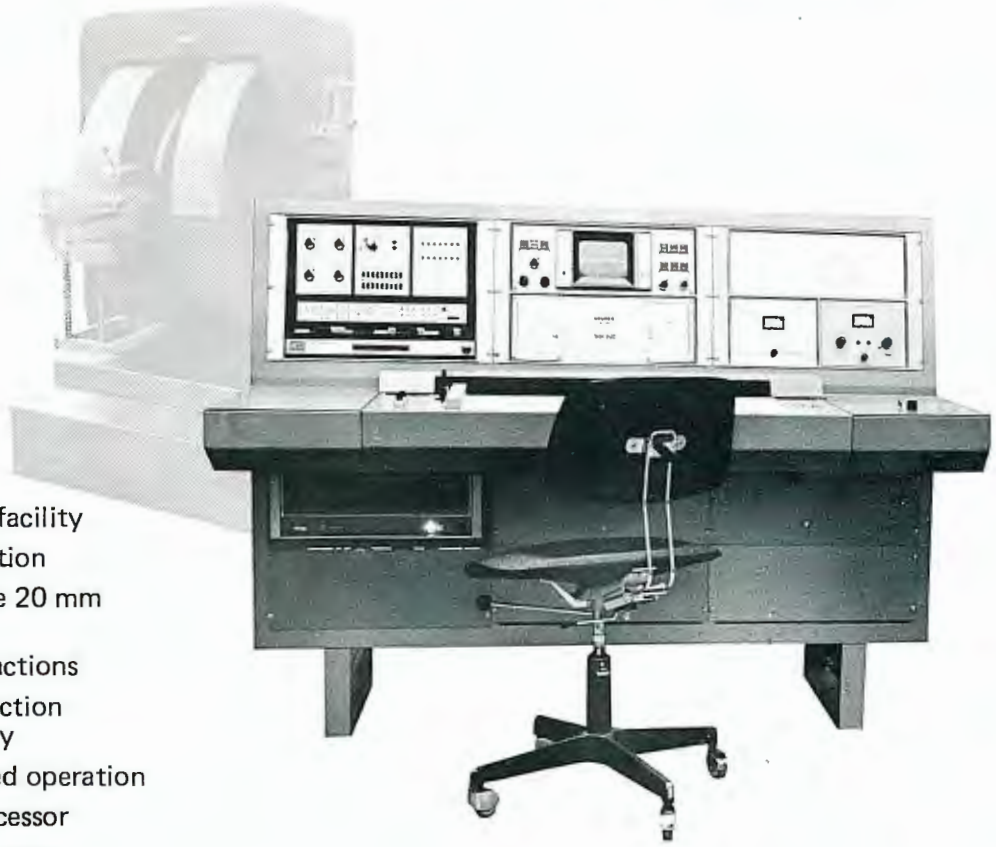

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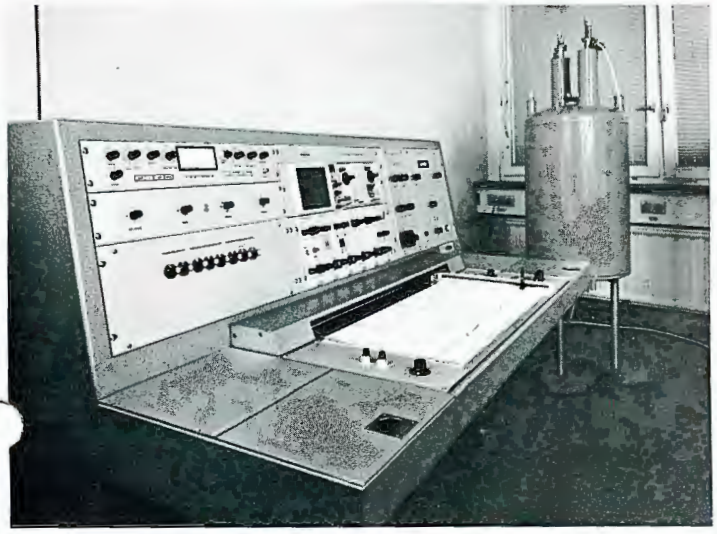

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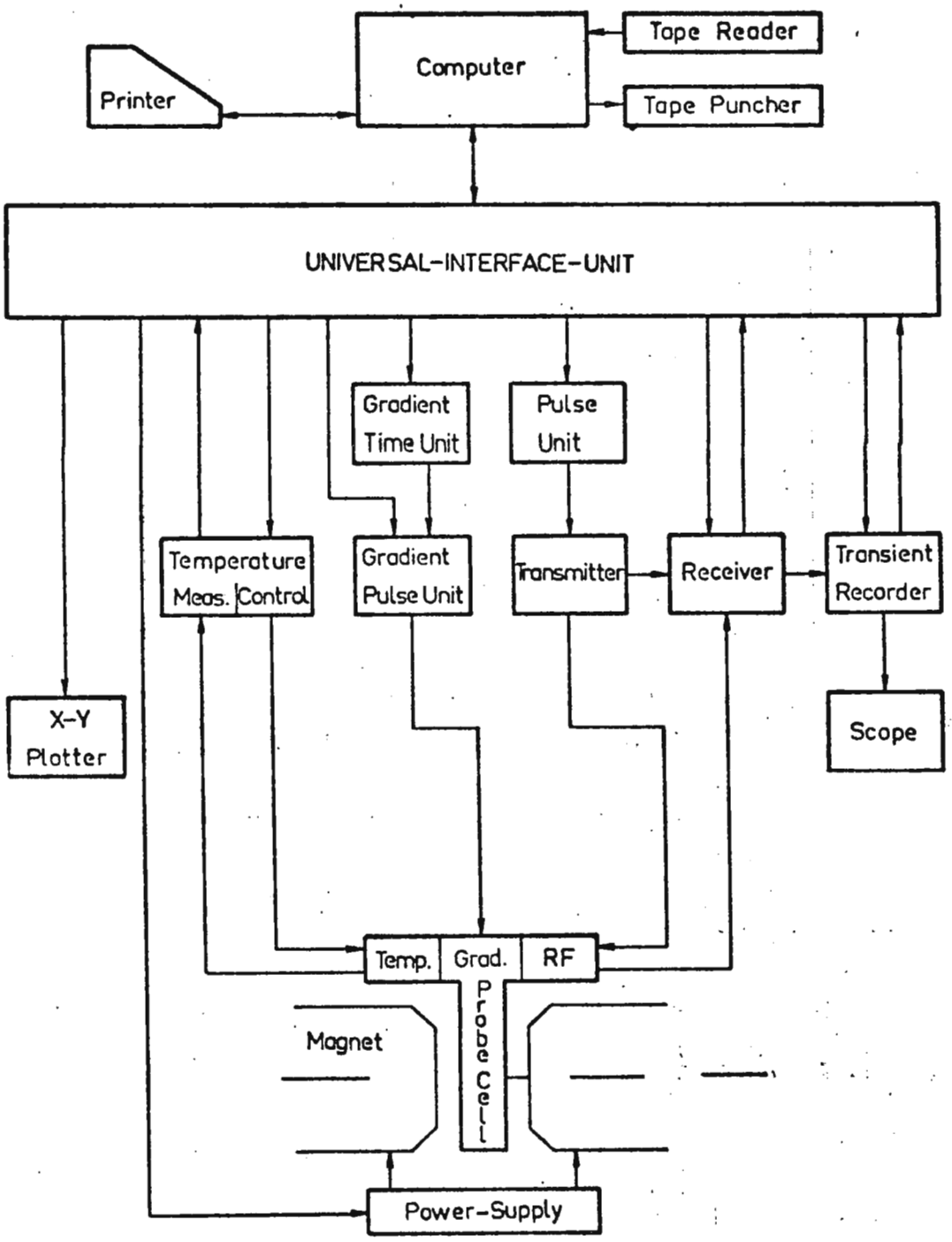
5200 Dixie Road, Ste. 116
Mississauga, Ontario, Canada L4W1E4
Phone 416-625-2375

Course of measurement:
First the temperature value at which measurements should be done is adjusted by the computer at the temperature regulator. Depending on the temper medium the probe cell can be tempered in the range from 13 K up to 613 K. Then the Larmor condition is set. To this purpose the FID signal is analyzed by phase sensitive detection. The signal beats resulting from the difference between spectrometer and Larmor frequency serve to control the sweep unit of the magnet power supply by the computer.
Through variations of the HF-pulse lengths and spacings the pulse times for $\pi/2$- and π-pulses are determined and the pulse programs for the respective measurements are set. To this purpose a pulse unit is used.
The computer is able to set pulse lengths from 50 ns to 650 s in steps of 50 ns and pulse spacings from 100 ns to 6500 s in steps of 100 ns at this unit.
It has 5 independent channels all known pulse programs can be realized with. Furthermore the trigger starting, the signal recording system and the gradient unit are generated.
The selfdiffusion measurements are performed with pulse field gradients of alternating sign. The timing of the pulse gradients to each other and the HF-pulse sequence as well can be determined by the computer in multiples of 1, 10, 100 µs up to 1, 10, 100 ms. The signal is recorded as a function of the field gradients $E(g)=f(g,T)$. The gradients can be varied from $2 \cdot 10^{-3}$ T/m to 2 T/m in units of $2 \cdot 10^{-3}$ T/m and the variation is done by the computer.
Signal recording is achieved by a system consisting of a transient recorder with 4k-byte memory and a resolution of 8 bit as well as an analogue digital converter with 12 bit resolution . The computer can modify both the sweep width of the transient recorder and the input sensitivity.
The digital values are transmitted to the computer after each signal recording. Having done the measurement the computer evaluates and gives out the result. The data can be saved in a data bank for further handling.

Sincerely yours

Prof.Dr.R.Kosfeld E.Schulz

Computer Controlled NMR-Spectrometer



Dr. W. Bremser c/o
BASF Aktiengesellschaft
Hauptlaboratorium

BASF

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

College Station
Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Telex	Ludwigshafen
		WHE-WBr/Dg	(0621) 60- 8401	464-	15.03.77

Betreff

Dear Barry,

Dr. O'Neill inquired in his letter (TAMU NMR 216-8) about the existence of larger ^{13}C-data collections. As this might be of general intrest to some of your readers, here are the three groups with the largest collections:

1. NIH/EPA (Dr. W. Milne, Washington), presently 4400 spectra
2. CNIC (Prof. J. Dubois, Paris), presently over 5000 spectra
3. BASF/GBF (Dr. W. Bremser, Ludwigshafen), presently 8500 spectra

The names in brackets indicate the person responsible. All three collections contain structural information and can be made available to the scientific community in one way or other. We still hope that the efforts will be united and the data merged into a common base.

Yours sincerely,

Wolfgang

W. Bremser

3 Lg.-Nr. 9030210

TELEPHONE: 031-667 1081

DEPARTMENT OF CHEMISTRY
WEST MAINS ROAD
EDINBURGH.
EH9 3JJ

17th March, 1976

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

Dear Professor Shapiro,

Some ^{15}N Double Resonance Experiments

Off-resonance and partial decoupling experiments are familiar to all users of ^{13}C nmr as means of unravelling complex ^{13}C and ^{1}H spectra. Their use for other combinations of nuclei is not often reported, so I hope this piece of work will show how useful they can be.

$^{31}P-\{^{15}N\}$ and $^{19}F-\{^{15}N\}$ off resonance partial decoupling experiments were carried out to obtain nmr spectral data from the compounds $PF_2{}^{15}NCS$, $PF_2{}^{15}N{}^{13}CS$, $PF_2{}^{15}NCO$ and $PF_2{}^{13}C{}^{15}N$. All observation was done on our XL-100 by FT, and double resonance experiments made use of the built-in heteronuclear decoupler. To analyse the data extensive use was made of the graphical method.[1] (Fig.1) This provided ^{15}N chemical shifts and the relative signs of coupling constants. As the compounds could be considered A_2MX systems, the A-{X} off resonance spectra gave the relative signs of J_{A-M} and J_{M-X}, determined by the order in which the A-X multiplets collapsed as the decoupler frequency moved through the X spectrum.[2] From this information, and the assumption that $^{1}J_{F-P}$ was always negative, many signs were obtained. (Table 1)

There is a clear parallel with INDOR in these experiments and this method of analysis does provide much of the information available from that technique. However, the relative intensities of the {X}-multiplets are lost, as are the A-X multiplets themselves, for the 'spectrum' obtained from the crossing points of the graphs is equivalent to the X-{A} spectrum. Nevertheless, the technique is very much faster than INDOR and instrument settings are far less critical.[3] We have also used it for $^{1}H-\{^{11}B\}$ and $^{31}P-\{^{13}C\}$ experiments.

Finally, a possibility which we have recently investigated is the automatic collection and storage of a series of off-resonance spectra to provide the data for a plot such as Fig. 1. This would require the addition of some wire to connect the decoupler offset to the computer and some software to perform the experiments. Both are relatively straightforward.

References

1. B. Birdsall, N. Birdsall, J. Feeney, J.C.S. Chem.Comm., 1972, 316
2. H. Jakobsen, T. Bundgaard, R. Hansen, Mol. Phys., (1972), 23, 197

The compounds studied in this work were made by Stephen Reid while he was a final year undergraduate here.

Yours sincerely,

Alan. S. Boyd

Dr. A.S.F. Boyd

P.S. We would like to claim a 'world record' ^{31}P chemical shift: the $-PF_2$ group of $PF_2P(SnBu^n)_3$ has been found to have a shift of +322 ppm from ext.H_3PO_4.

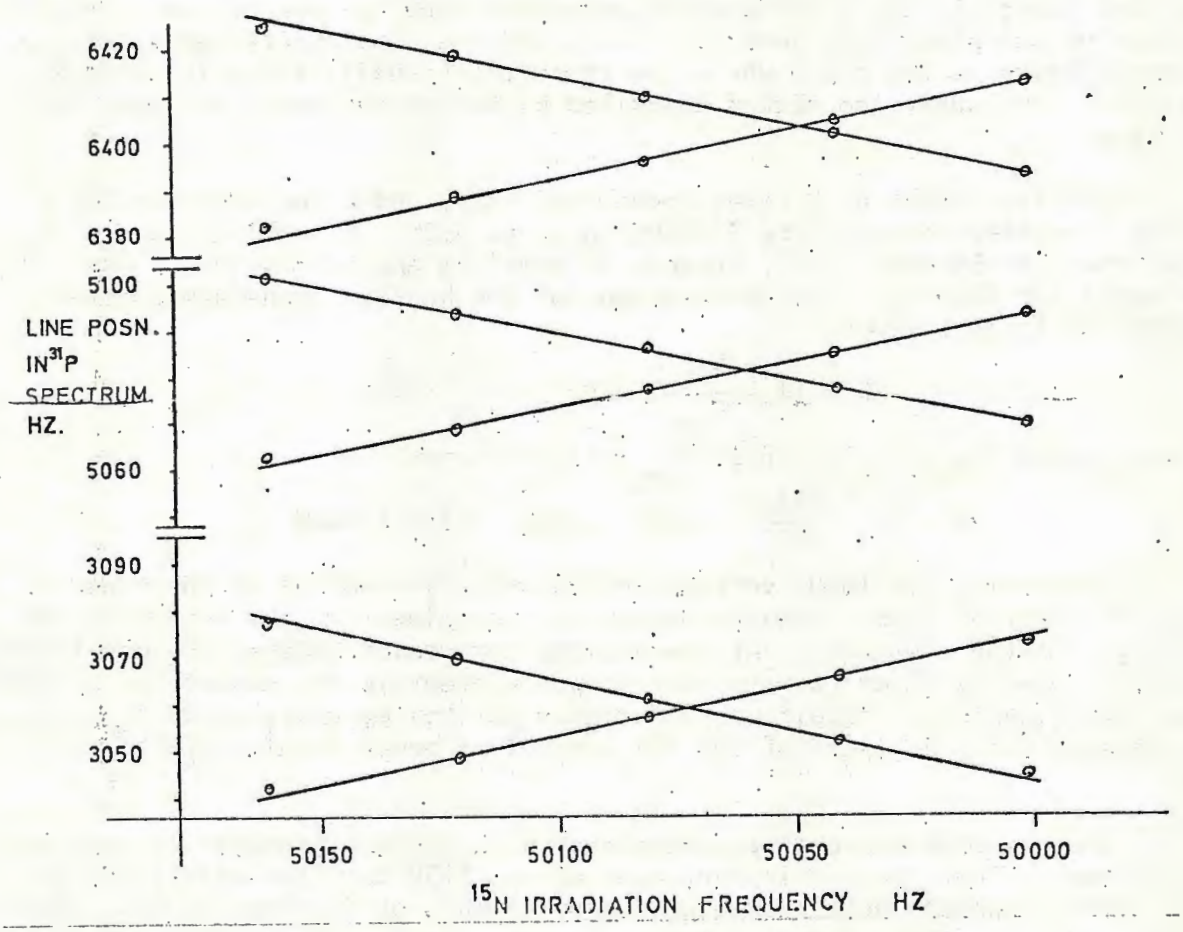

Fig. 1 Plot obtained from $^{31}P-\{^{15}N\}$ experiments on $PF_2{}^{15}NCS$.

Table 1

	δ_P	δ_F	$\delta^{15}N$	δ_C	J_{PF}	$J_P{}^{15}N$	J_{P-C}	$J_F{}^{15}N$	J_{FC}	$J_C{}^{15}N$
PF_2NCS	+125.5	-54.6	+87	+150.1	-1322	+93.8		-12	+5.1	-31
PF_2NCO	+130.5	-52.3	+24		-1310	+89		-13.7		
PF_2CN	+142.3	-86.2	+250	+120.3	-1266	+10.1	-133	<+1	+22	-9.7

Chemical shifts are positive to high frequency and are measured in ppm from ext.H_3PO_4(δ_P), ext.$CFCl_3$(δ_F), ext.Me_4NI($\delta^{15}N$) and int.TMS(δ_C)

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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

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

March 17, 1977

V2708 POWER SUPPLY-REVISITED

We would like to report yet another way to salvage (or resalvage) a V2708 power supply. After working flawlessly for twenty months following the initial disaster,[1] the power supply once again tried to self-destruct. The resultant damage to the transformer's secondary windings was severe. Three windings on one phase were severely pitted and one winding cracked - leaving an open winding at the place where the commutator usually rides for 23.48kG operation. Obviously the method described by Nakashima[2] would not work for this case.

Charlie Peters at Nicolet Technology Corp. and a few other reliable sources suggested boosting the 3ø/480V input to 550V. A small booster transformer for 3ø/480V input, capable of handling approximately 3kW was fabricated for $260.00. The calculation for the booster transformer power dissipation is as follows:

$$kW = (1 - \frac{E_{in}}{E_{out}}) \cdot E_{out} \cdot I_{in} \cdot \sqrt{3}$$

For our system the calculation of KV_a (Kilovolt-amps) is:

$$kW - (1 - \frac{480}{550}) \cdot (550) \cdot (20) \cdot \sqrt{3} = 2.42\,kW$$

Increasing the input voltage to the primary windings of the power supply transformer causes the commutators to ride closer to the bottom of the secondary winding armatures. At present the commutator brushes are positioned 5 winding segments lower for the same output current to the magnet for a 550V input. This temporary repair was undertaken to provide utilization of our spectrometer until delivery of the SCR controlled power supply (V7808) was made.

Another problem we have encountered with our spectrometer is that of voltage regulation. In particular, many of the ±15V supplies consist of an IC (Silicon General 3501) regulated output capable of dissipating only 100mW for each output. The simplest solution to date has been to discard the SG3501's and replace them with LM320MP's (National Semiconductor, -15V regulator) and LM341's (N.S., +15V). These are three pin, flat transistor packages with an input (±30V max. input) lead, ground lead and regulated output. These devices will handle approximately 5-10W when properly heat sinked. This has cured overheating and failure problems in every case. The size and mounting requirements makes this a very quick and easy conversion.

Sincerely,

Ray Nunnally, Donald P. Hollis, Joseph W. Schaffer

1) R. Nunnally and D.P. Hollis, TAMU NMR Newsletter, 206, 16 (1975).

2) T. Nakashima, TAMU NMR Newsletter, 215, 11 (1976).

UNIVERSITY OF WISCONSIN-MADISON
CENTER FOR HEALTH SCIENCES

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Telephone: 608/262-1415

March 21, 1977

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

Nucleotide Conformation via $P^{31}\{H^1\}$ NOE's

Dear Professor Shapiro:

I hope this belated contribution will return me to the Newsletter family. I have found that careful single frequency proton irradiation of 0.1 M AMP (pH 8) yields a spectrum of phosphorus enhancements that allows a rather detailed conformational analysis of the 5'-phosphate side-chain. Irradiation at low power so as to minimize multiple-proton irradiation, gives the results tabulated below. By assuming that the data indicate more than one side-chain

Proton Irradiated	% Enh. P
5',5''	23
4'	12
3'	5
2'+HOD	13
8	0
2	0

conformation and by using slight modifications of equations developed previously by Noggle and Schirmer it is possible to arrive at an approximate distribution of 50% gg, g'g', 25% tg, t'g' and 25% gt, g't' about C4', C5' and C5', O5' respectively.

Values gotten by this method represent joint distributions about the two bonds of the side-chain, thus should be compared with values of $^4J_{H4',P}$ that also express the joint distribution when they can be observed.

Sincerely yours,

Phillip A. Hart

Phillip A. Hart
Associate Professor

PAH:ig

CHEMICAL INSTITUTE
UNIVERSITY OF AARHUS

DEPARTMENT OF ORGANIC CHEMISTRY
HANS JØRGEN JAKOBSEN

8000 Århus C, Denmark
Telephone (06) 12 46 33

March 25, 1977
HJJ/EL

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

SPT VERSUS SPI - DEPENDENCE ON COUPLING CONSTANT (J_{C-H})/SPIN-LATTICE RELAXATION TIMES (T_{1C} and T_{1H})

Dear Barry,

In a private letter we have been informed by Dr. Pachler, Pretoria, South Africa, about a recent contribution from his lab to your Newsletters [1] on "SPI versus SPT". Dr. Pachler has asked for our opinion concerning the most appropriate name, SPI (selective population inversion) [2] or SPT (selective population transfer) [3], for the selective ^1H π-pulse ^{13}C FT experiment (or similar A-{X} selective X π-pulse FT experiment) performed independently in the two labs some years ago and applied widely in recent years. Indeed, we faced this question at the time of introducing the term SPT for the π-pulse experiment.*

In our opinion the most appropriate name for the experiment would be SPT, or better and more specific, the "π-pulse SPT" experiment. The reason is that this term would also include those experiments for which a complete inversion of energy level populations cannot be obtained due to the inherent spectral parameters of the ^{13}C-^1H spin system, i.e. J_{C-H}, T_{1H}, and T_{1C}. Although Pachler and Wessels in the past always have been able to

---

*It should be mentioned that the performance of the experiment in our lab was inspired by the some ten years older ^1H-{^1H} TSI (transitory selective irradiation) CW NMR experiment introduced for the determination of relative signs of coupling constants by Hoffman and Forsén [4]. Actually, in their review on NMR double resonance these authors also suggested the π-pulse version of the TSI experiment [4]; i.e. the CW analogue of the "SPI/SPT" π-pulse experiment, today carried out routinely on FT spectrometers. However, a name related to "TSI" would be inappropriate for the π-pulse FT experiment.

observe intensity changes close to the theoretical maximum values [5], spin systems are often encountered where this is not true (*e.g.* for "small" values of J_{C-H} and/or T_{1H}, T_{1C}).

These effects are probably best illustrated in Fig.1 which shows calculated ^{13}C intensity enhancements for a ^{13}C-^{1}H two-spin system (J_{C-H} = 3.0 Hz) using (a) the ^{13}C-{^{1}H} π-pulse SPT experiment, and (b) ^{13}C-{^{1}H} continuous irradiation SPT [6]. A series of different computer simulated ^{13}C-{^{1}H} SPT experiments have been performed [7] by means of the program DYNAMARCA which is based on the density matrix formalism developed elsewhere [8]. The curves in Fig.1 show plots of the peak heights for the positively enhanced ^{13}C transition as a function of the irradiation amplitude, $\gamma H_2/2\pi$, applied to the progressively connected ^{1}H transition. Both π-pulse perturbation, $\gamma H_2 \tau = \pi$ (Fig.1a) and continuous irradiation (Fig.1b) SPT experiments were simulated. Peak heights are in units of the 1:1 intensity for the unperturbed ^{13}C doublet. The individual curves represent the results for a certain combination of the relaxation times, T_{1C} and T_{1H}, which for the calculations in Fig.1 were taken to be due to both ^{13}C-^{1}H dipole-dipole (DD) and exter-

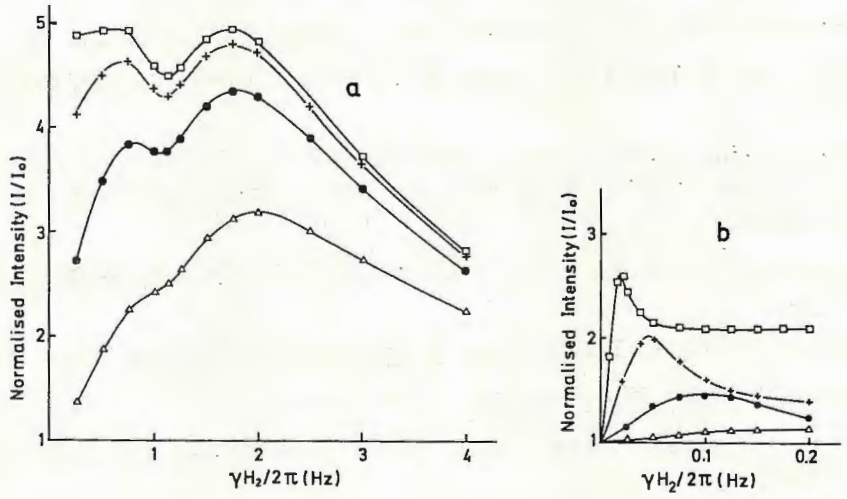

Fig.1. Calculated ^{13}C intensity enhancements for a $^{13}C^{1}H$ two-spin system (J_{C-H} = 3.0 Hz) using SPT techniques. The normalized intensity of the ^{13}C transition connected progressively to the perturbed ^{1}H transition is plotted against the amplitude of the perturbing rf field. (a) π-pulse method (max value: +5) and (b) continuous irradiation. For all calculations $T_{1H} = T_{1H}(DD)$ = 9 sec. The contribution from the ERF mechanism to T_{1C} was varied so as to give the following cases: □ $T_{1C} = T_{1C}(DD)$ = 9 sec, + T_{1C} = 3 sec, ● T_{1C} = 1 sec, Δ T_{1C} = 0.3 sec. Interchange of the values for T_{1H} and T_{1C} has almost no effect on the curves in (a).

nal random field (ERF) relaxation. The contribution from the DD mechanism is fixed to yield $T_{1H}(DD) = T_{1C}(DD) = 9$ sec. All simulations performed so far, indicate that the sensitivity of the π-pulse method is clearly superior to that for continuous irradiation SPT in contrast to the reports by Koole and de Bie [9]. Obviously, these findings are due to an improper choice of experimental parameters [1, 6] (the inverted line in Fig.1 of Ref.[1], should be B1 and not B4). It is noteworthy that the π-pulse SPT curves (Fig.1a) show maximum enhancements for $\gamma H_2/2\pi \approx 0.6 \times J_{C-H}$ and a decrease for larger H_2 amplitudes due to perturbation of the regressively connected ^1H transition.

Finally, we should like to point out that the term "π-pulse SPT" also would be the appropriate name when performing a repetitive $^{13}C-\{^1H\}$ selective π-pulse FT experiment in which the spin system is not allowed to relax fully between each pulse sequence, and which consequently leads to reduced enhancement factors.

REFERENCES

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2. K.G.R.Pachler and P.L.Wessels, J.Magn.Resonance 12, 337 (1973).
3. S.Sørensen, R.S.Hansen, and H.J.Jakobsen, J.Magn.Resonance 14, 243 (1974).
4. R.A.Hoffman and S.Forsén, "Progress in Nuclear Magnetic Resonance Spectroscopy" (Emsley, Feeney, Sutcliffe) Vol.1, pp.34, 88, Pergamon Press, 1966.
5. H.J.Jakobsen, S.Aa.Linde, and S.Sørensen, J.Magn.Resonance 15, 385 (1974).
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Sincerely yours,

Hans J. Jakobsen H. Bildsøe

Hans Jørgen Jakobsen Henrik Bildsøe

SFU
SIMON FRASER UNIVERSITY, BURNABY 2, B.C., CANADA
DEPARTMENT OF CHEMISTRY; 291-3345

March 22, 1977

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

Dear Barry and colleagues,

I am soliciting your aid in obtaining a high calibre candidate for an upcoming post-doctoral position in biophysical chemistry. Experience should include NMR and/or biochemistry. Research topics fall in the broad areas of:

Visualization of Enzyme-Substrate Transition States by Carbon-13 NMR

Carbon-13 NMR Conformational Studies of Membranes and their Constituents

Our equipment comprises the latest Transform Technology Fourier Transform Accessory to the Varian XL-100-15. The FT package includes a 20K, 20 bit computer, a 600K disk and multiple pulse capability. As well, we have just installed the TT14, a 20 mm probe, FT-NMR machine ideally suited to biological studies.

Salary will depend on qualifications but will be a minimum of $9600 per year.

The SFU campus is situated atop Burnaby mountain, 7 miles east of Vancouver, Canada's fourth largest city.

Thank you for your co-operation and please notify interested parties that two letters of recommendation should be sent to me directly.

Sincerely yours,

R. J. Cushley

R.J. Cushley
Associate Professor

RJC:SB

223-35
SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-1011

De Boelelaan 1083 – Telefoon 548 . . .

AMSTERDAM, March 24, 1977

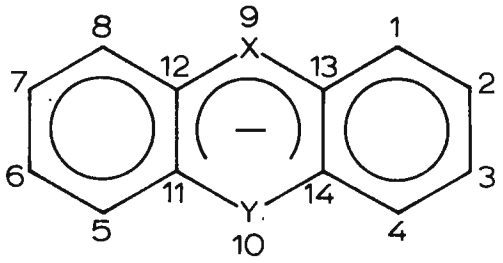
Uw ref.:

Onze ref.:

Dear Professor Shapiro

Calculations of paramagnetic ring-current effects.

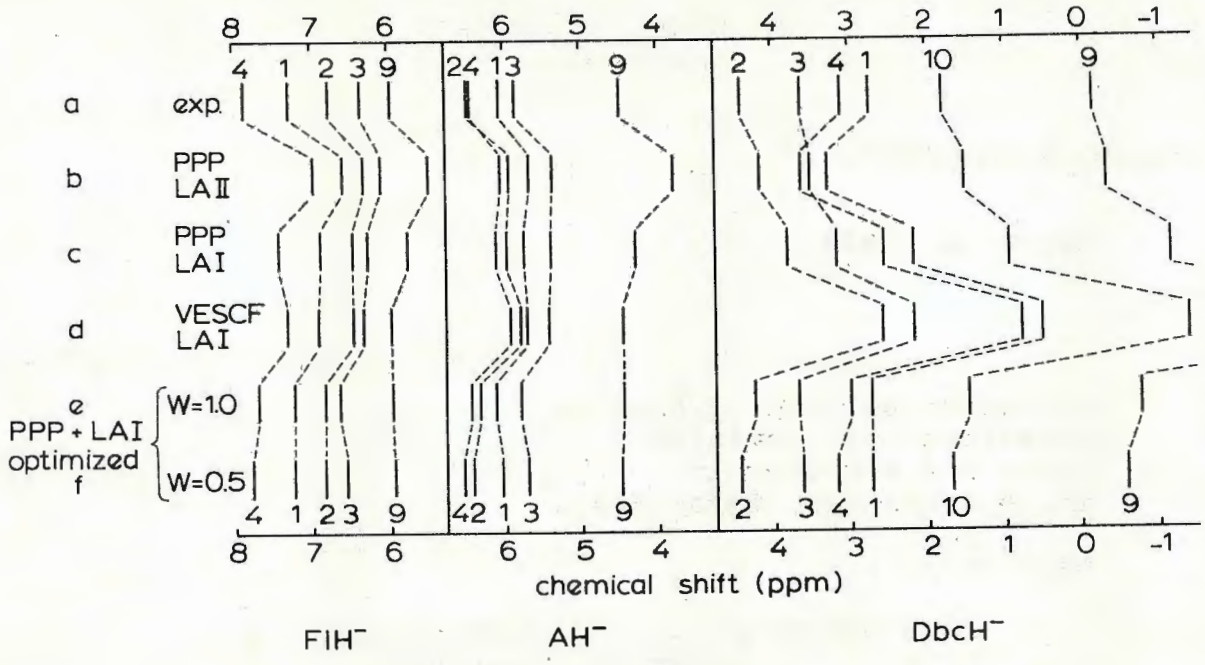
Some years ago we have published the proton NMR spectra of a series of bicyclic conjugated anions (fig. 1) [1]. These anions display a large range of chemical shifts (fig. 2.a), despite



	X	Y
FlH^-	-CH-	-
XH^-	-CH-	-O-
TxH^-	-CH-	-S-
AH^-	-CH-	$-CH_2-$
$DbcH^-$	-CH-	-CH=CH-
Dba^-	-N-	-CH=CH-

their analogous structures. The reason was supposed to be a variation of the ring current in the central ring from positive (diamagnetic) in fluorenyl anion (FlH^-), via zero in dihydroanthracenyl anion (AH^-), to strongly negative (paramagnetic) in dibenzocycloheptenyl anion ($DbcH^-$). The remaining anions show weaker paramagnetic shifts. The effect is related to the presence of a 16π-electron perimeter.

We have studied this subject theoretically, and found that semiempirical calculations on the PPP level, using coupled Hartree-Fock pertubation theory, can well account for the observed shifts. Besides, it appeared feasible to discriminate between various ring-current models: the Johnson-Bovey model and the so-called London Approximation I are superior to others, e.g. the LA II model [2] and the bond-current model of Salem [3]. The VESCF method over-estimates the paramagnetic shift (fig. 2d). Figs. 2e and f show the



results of a least-squares optimization of the adjustable parameters i.e. the reference chemical shift σ_o (for a hypothetical aromatic ring without ring current), the benzene ring current σ_{bz}^{RC} and the parameters A and B which determine the electric charge effect [1]. The description of the latter effect is improved by lowering the relative influence of the non-neighbour atom field (indicated by w). The optimal values are: σ_o= 6.12 ppm, σ_{bz}^{RC}= 1.39 ppm, A= 2.71 x 10^{-12} esu^{-1}, B= 0.66 x 10^{-18} esu^{-2}, w= 0.5. The r.m.s. error of 31 chemical shifts (including benzene) is 0.088.

1. H.W. Vos, Y.W. Bakker, C. MacLean and N.H. Velthorst, Org. Magn. Res. 6, 245 (1974); Chem. Phys. Lett. 25, 80 (1974).
2. H.G.F.J. Roberts and A.T. Amos, Mol. Phys. 6, 1089 (1971)
3. L. Salem, "the MO theory of conjugated systems" (Benjamin, New York, 1966) CH. IV.

Sincerely,

H.W. Vos
C. MacLean
N.H. Velthorst

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

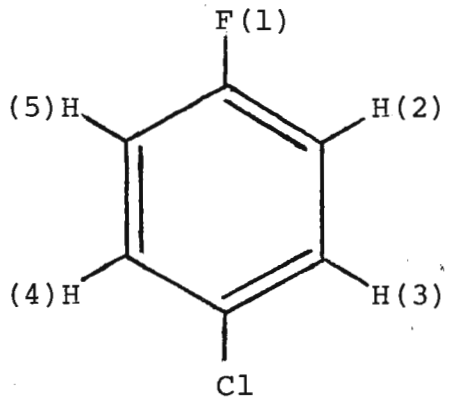
March 25, 1977

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

Dear Barry:

NMR of p-Chlorofluorobenzene in a
Lyotropic Mesophase

We have carried out preliminary NMR investigations of p-chlorofluorobenzene partially oriented in the lyotropic mesophase based on potassium laurate. A previous investigation of this molecule was limited by the deceptive simplicity of the spectral pattern in a thermotropic medium[1]. Under this condition, only D_{23}, D_{24}, and $(D_{12} + D_{13})$ could be determined with any precision from which a complete spectral analysis could not be obtained (see Figure below for numbering scheme).



In the lyotropic system used here we observed an increase in the number of distinct, recorded spectral lines (35) compared to the number predicted in the earlier work (24). Moreover, the spectral analysis provided not only D_{HH} coupling parameters but also J_{HH}, D_{HF}, and chemical shift information (see table below).

Spectral Parameters

$\omega_2-\omega_3 = 28.31\pm0.16$

J_{12}	= (8.08)	D_{12}	= 450.39±0.85
J_{13}	= (4.66)	D_{13}	= 103.38±0.65
J_{23}	= 9.13±0.34	D_{23}	= 689.90±0.50
J_{24}	= 0.32±0.12	D_{24}	= 66.11±0.08
J_{25}	= 2.98±0.15	D_{25}	= 90.14±0.08
J_{34}	= 2.65±0.11	D_{34}	= 89.58±0.11

Using these parameters, the 35 lines of the spectrum were reproduced with an rms error of approximately 0.2 Hz.

We have also carried out structural calculations by (1) using only proton-proton dipolar coupling data, and (2) using D_{HH} and D_{HF} information. No significant structural differences were observed when the results of the two treatments were compared. Structural results are as follows:

$(r_{13}/r_{25}) = 1.070$, $(r_{23}/r_{25}) = 0.597$, $(r_{24}/r_{25}) = 1.166$, and $(r_{34}/r_{25}) = 1.003$.

Yours truly,

Stephen A. Spearman

J. H. Goldstein
Professor of Chemistry

[1] Diehl, P., Khetrapal, C. L., and Lienhard, U., Org. Magn. Res. 1, 93 (1969).

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215 FIDELITY 2-1000 · CABLE ADDRESS: CANSEARCH

March 29, 1977

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

Dear Barry:

Use of ^{31}P Coupling Constants and Chemical Shifts to Detect Mg^{2+}-Complexation by Enzyme-Bound ATP.

The magnesium ion is an essential co-factor for all enzyme-catalyzed phosphoryl transfer reactions involving ATP and ADP. Under suitable conditions, ^{31}P spin-spin coupling constants as well as chemical shifts may be used to determine the state of complexation of Mg^{2+} by enzyme-bound ATP and ADP. Since the dipolar contributions to the transverse relaxation are small, and since the anisotropy of the chemical shift does not appreciably broaden the lines at 40.5 MHz, this technique has been used on pyruvate kinase, an enzyme of molecular weight 237,000 (1). Under conditions in which >80% of the ATP is enzyme-bound, and in the presence of a small amount of EDTA to remove paramagnetic contaminants, Mg^{2+} causes a 5 ± 1 Hz decrease in the $^{31}P - {}^{31}P$ coupling constants and large downfield shifts of the ^{31}P resonances of ATP indistinguishable from those found in the binary MgATP complex (Fig. 1).

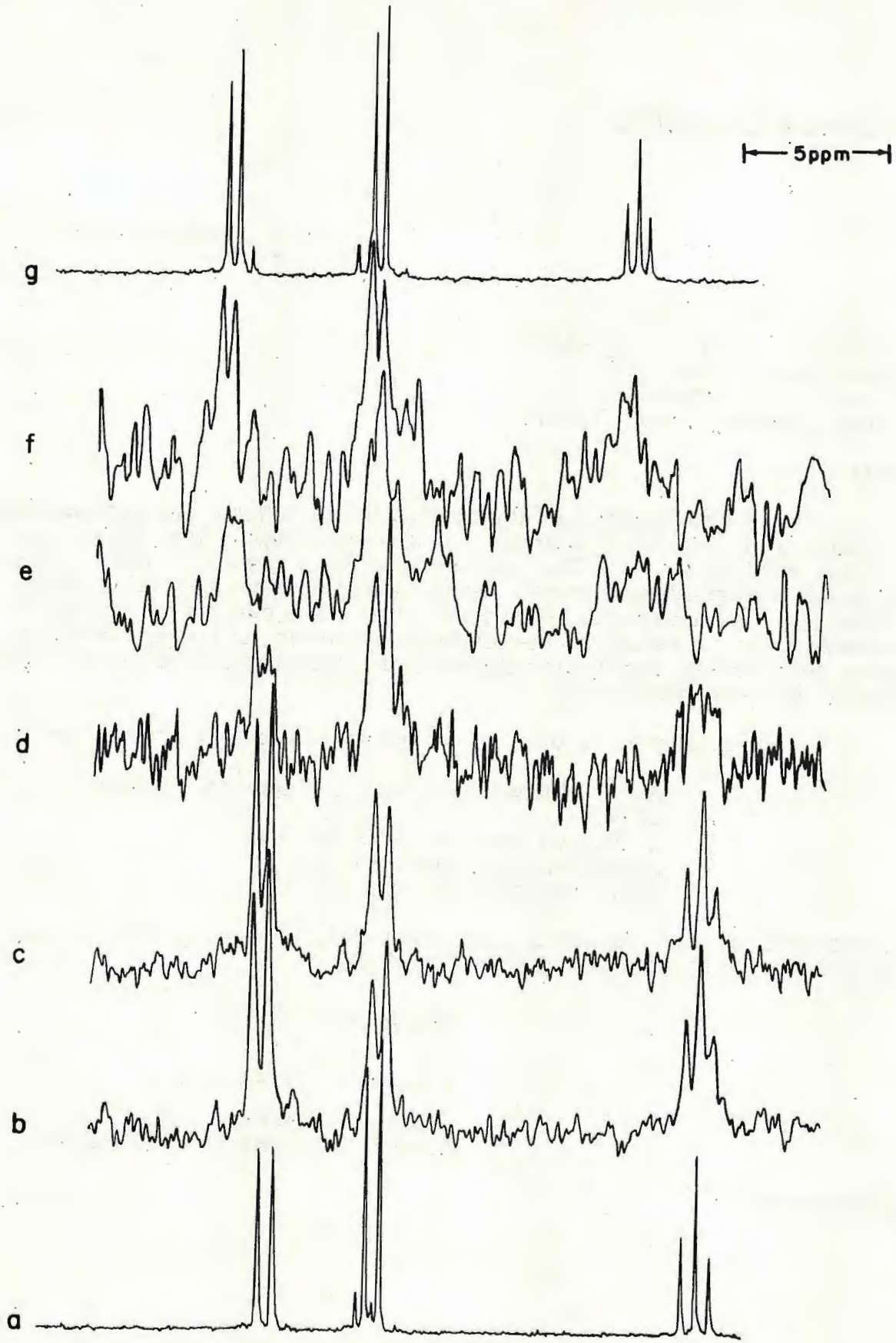
These results with the diamagnetic Mg^{2+} confirm our earlier findings of a functional (enzyme-Mg)-(ATP-Mg) complex which were based on studies with the paramagnetic probes Mn^{2+}, Co^{2+} and Cr^{3+} (2, 3).

Sincerely yours,

Raj K. Gupta Albert S. Mildvan

(1) Abs. Biophysical Society Mtg. 17, 112a (1977). (2) J. Biol. Chem. 250, 8193 (1975); 251, 2412, 2421, 2431 (1976). (3) Biochemistry 15, 2881 (1976).

Fig. 1: Titration of the ^{31}P resonances of pyruvate kinase-bound ATP with $MgCl_2$ in the presence of oxalate. The spectra of free ATP (a), and free MgATP (g) are shown under the same conditions for comparison. Components present in all cases were KCl (0.15 M), K-PIPES pH 6.9 (50 mM), D_2O (15%), potassium EDTA (0.75 mM). In addition, the following were present: a, ATP (33 mM); b, ATP (2.3 mM), pyruvate kinase sites (2.3 mM); c = b + potassium oxalate (5.5 mM); d = c + $MgCl_2$ (3.0 mM); e = c + $MgCl_2$ (5.3 mM); f = c + $MgCl_2$ (10.1 mM); g = a + $MgCl_2$ (77 mM). The number of transients was 15,000 (b-f) and 500 (a, g). T = 15°. For spectra a and g, the flip angle was 90°, the recycle time was 2 sec., and the exponential filtering time constant was 1 sec. For spectra b-f, the flip angle was 30°, recycle time 0.2 sec., and the exponential filtering constant was 50 msec (b-d) and 10 msec (e, f).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223-41

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

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

StonyBrook

23 March, 1977

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

Dear Barry:

I would like to announce the availability of at least one postdoctoral position in my laboratory starting anytime after September, 1977, when I return to Stony Brook. The work involves high resolution NMR studies of model biological membranes, usually employing the hyperfine shifts produced by paramagnetic metal ions. There are currently two major aspects of the research: a) the intrinsic properties of highly curved bilayer membranes, and b) the detailed mechanisms of mediated ion transport across phospholipid bilayers.

Anyone interested in this (these) position(s) should write to me at:

A. A. Noyes Laboratory of Chemical Physics
127-72
California Institute of Technology
Pasadena, California 91125
(213) 795-6811, ext. 2524

where I will be until the end of July. The State University of New York is an equal opportunity affirmative action employer.

Sincerely,

Charlie Springer

Charles S. Springer, Jr.
Associate Professor of Chemistry

CSS, Jr. :tw

University of East Anglia

From Dr. R. K. Harris

School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ, ENGLAND
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR NORWICH

24th March, 1977

Dear Barry,

PERKIN-ELMER R10 60 MHz SPECTROMETER AVAILABLE

No doubt the trade in second-hand NMR spectrometers is not a brisk one, but there's always a chance that someone may benefit from equipment that is no longer needed elsewhere. Consequently I felt it worth while to announce to Newsletter readers that we have a Perkin-Elmer R10 spectrometer for which we no longer have space since it has been replaced by FT equipment. It was in good working order immediately prior to the arrival of the FT spectrometer last September. It operates at 60 MHz for protons. It is equipped with variable temperature, homonuclear double resonance and ^{31}P accessories, though the double resonance has never been much of a success. We would be happy to make the instrument available to anyone prepared to pay the removal costs plus a small (negotiable) contribution to our funds. Anyone interested should write to me.

Best wishes,

Yours sincerely,

Robin

R. K. Harris

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

RKH/KJS

3389-43

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

27 April 1977

TAMU NMR Newsletter Practical Matters

1. We regret greatly that the February and March 1977 issues of the Newsletter were considerably delayed in being mailed to you. These delays were occasioned by production problems, including those resulting in the change-over to a new printer. We hope that the First-Class mailing of the February and March issues helped at least a little in making up for the delay. Production matters should be back on our normal schedule in another month. Thanks for bearing with us.

2. Financial matters - the eternal problem. Again, we are requesting our readers aid in soliciting additional income for the Newsletter. In particular, we are most anxious to get a few more ads, for a substantial amount of our operating income derives from advertising revenues. Production and mailing costs have increased to the point where we will have to increase the subscription rates unless additional advertising or contribution revenues can be generated. Your help is earnestly solicited.

B. L. Shapiro

Varian introduces: the FT-80

A powerful new Fourier transform NMR spectrometer with an experimental array of over 40 nuclei

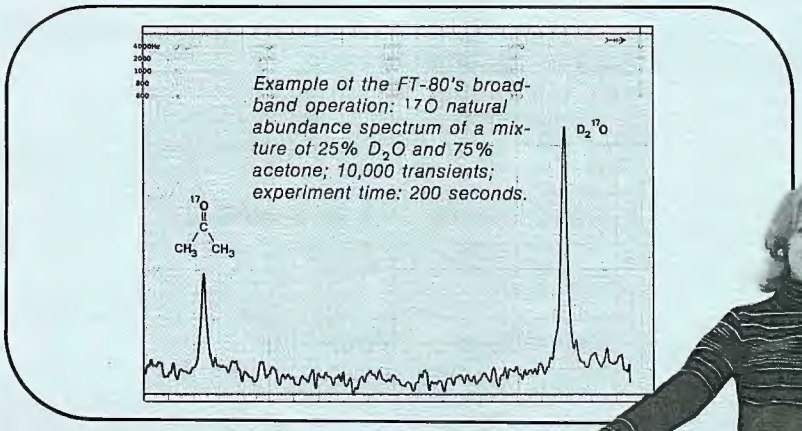
With the FT-80, new ground will be broken. Its broadband synthesizer and its tunable probe place an immense frequency range at the operator's fingertips, a range that covers over 40 nuclei currently of interest. Many of these nuclei are scarcely explored and may yield as yet undetermined problem-solving potentials.

Above all, its simplicity of operation lets the FT-80 handle complex research projects with the same ease as straightforward routine work.

It's the combination of experimental sophistication, exceptional flexibility, and operating convenience that makes the FT-80 a unique NMR spectrometer.

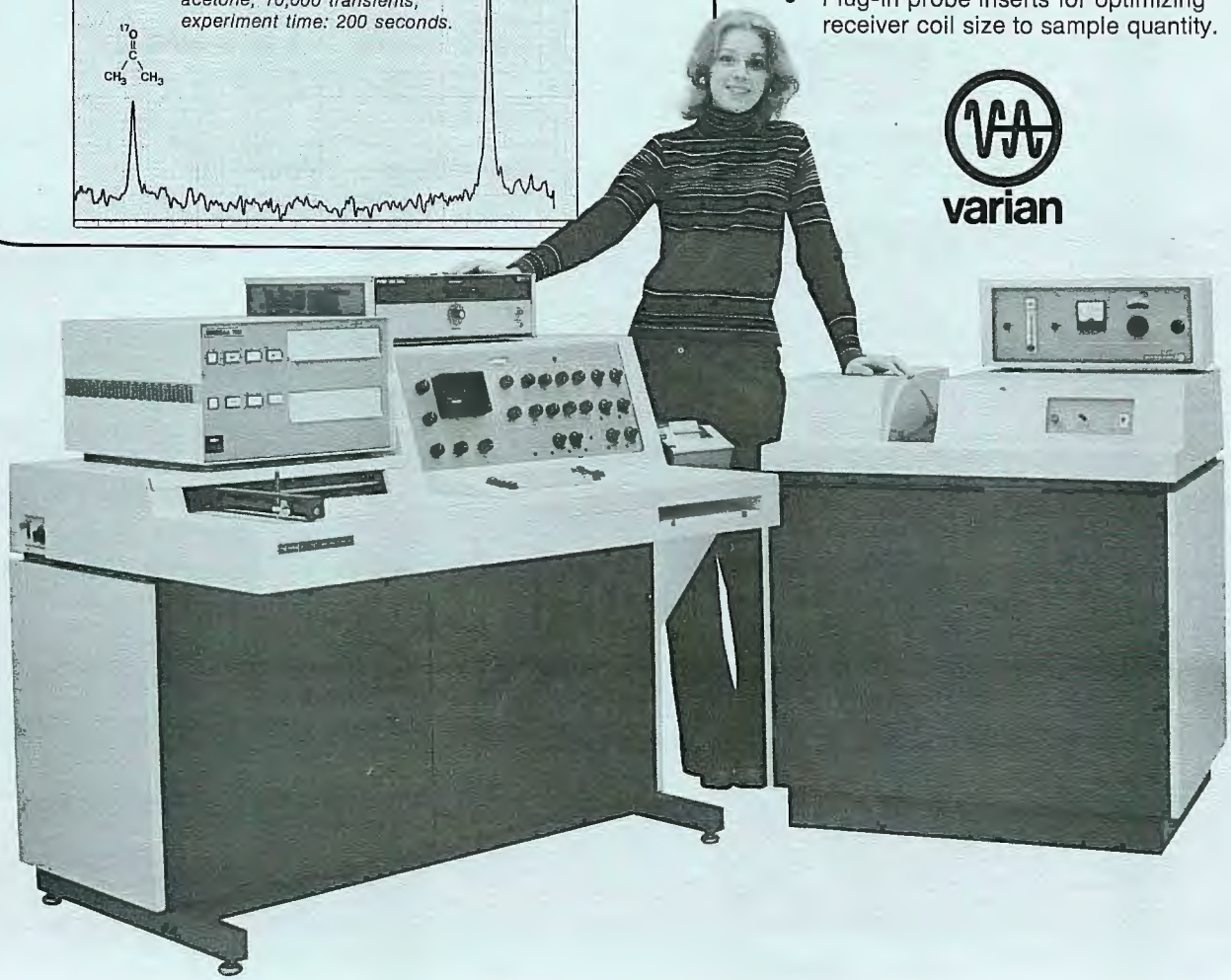
If you would like more information on the FT-80, write to: Varian Associates, Inc., 611 Hansen Way, Box D-070, Palo Alto, Calif. 94303.

- Broadband tunable probe—for variable-temperature observation of nuclei from ^{14}N to ^{31}P.
- Broadband frequency source—delivers 5 to 80 MHz at the turn of a dial.
- $^{1}H/^{13}C$ switchable probe—permits instant switchover.
- 24K-word computer—allows acquisition of 16K-word data table.
- 4-Pole phase shifter — 0°, 90°, 180° and 270° precisely selectable.
- Flexible-disk data system—with capacity of up to 4 million bits.
- 13-Bit analog-to-digital converter—offers extended dynamic range.
- Built-in computer alternating pulse sequence (CAPS).
- Software packages for 2-D spectra, relaxation experiments, spin simulation, etc.
- Plug-in probe inserts for optimizing receiver coil size to sample quantity.



Example of the FT-80's broadband operation: ^{17}O natural abundance spectrum of a mixture of 25% D_2O and 75% acetone; 10,000 transients; experiment time: 200 seconds.

varian



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- RF crystal filter detection system
- 12 bit AD/DA for increased dynamic range
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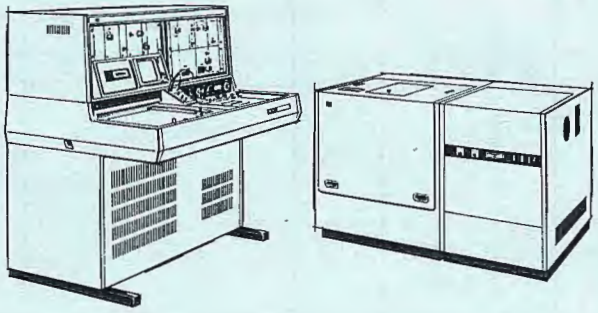
- 8, 16 and 32K word data collection
- Built-in Read/Write Cassette System
- ^{19}F, ^{31}P, ^{15}N extensions are available



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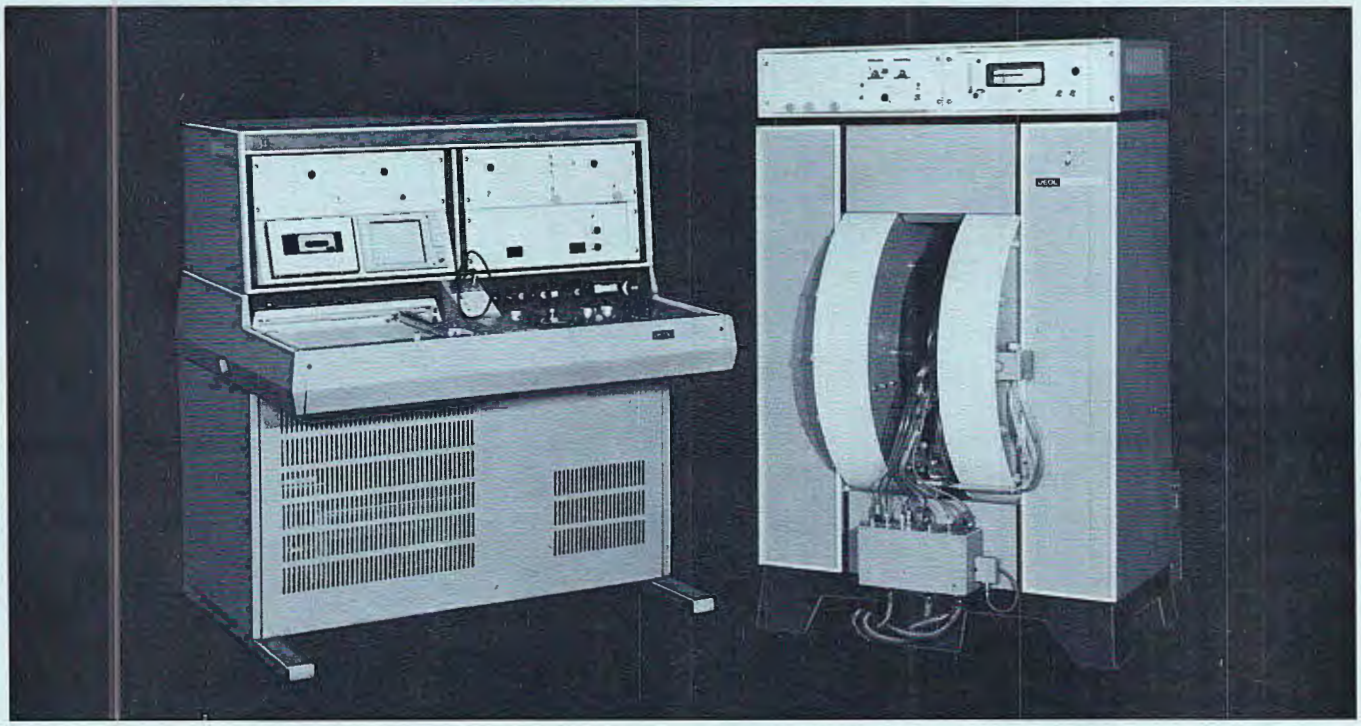
- Computer based pulse programmer
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- $T_1\rho$/spin locking system
- Disc storage systems
- Multi-Frequency HOMO/HETERO decoupling capabilities
- Multi-Frequency observation

For detailed brochure, demonstration or information, phone or write . . .

JEOL

Analytical Instruments, Inc.

235 Birchwood Ave., Cranford, NJ 07016

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