Texas A & M University
N - M - R
Newsletter

No. 141
JUNE, 1970

READ AND INITIAL

D. E.	
P. F.	
D. H.	
G. S.	
C. T.	

OVER

Deadline Dates: No. 142: 6 July 1970
No. 143: 3 August 1970

All Newsletter correspondence, etc., should be addressed to:

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

International Business Machines Corporation

Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598
914/945-3000

May 7, 1970

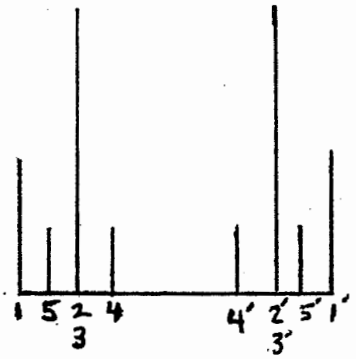
Professor Barry L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

Effects of Spinning on Solute Orientation in Nematic Solutions

I have been interested for some time now in using spinning of nematic liquid crystal solutions to obtain chemical shift anisotropies; the idea is to make a single phase measurement, thereby avoiding the unknown solvent shift change resulting from the phase change. I mentioned some of these results briefly at the 10th ENC and hope to publish in detail along with some results in the smectic phase in the IBM Journal of Research & Development.

One interesting question that arises in the experiment is whether the sample (solute as well as solvent) spins as a whole,[1] or whether the solute orientation changes independently of the solvent ordering. To answer the question, we have used the ^1H spectrum of pyrazine in n-hexyloxyazoxybenzene, already studied by Diel and Khetrapal,[2] and have measured the two independent ordering parameters of pyrazine as a function of spin rate. The spectrum consists of 5 pairs of lines,[3] and is sketched below:



Using the numbering scheme and transition energies of Ref. 3, the following relation holds:

$$\frac{S^i_{11}}{S^i_{22}} = .22\left(\frac{\Delta\nu^i_1 + \Delta\nu^i_4}{\Delta\nu^i_5 - \Delta\nu^i_4}\right)$$

S^i_{11} and S^i_{22} are the ordering factors for the experiment done at the i^{th} spin

rate and $\Delta\nu_j^i = \nu_j^i - \nu_j^i$, is the frequency separation of the j^{th} line pair measured at this rate. The numerical factor results from a geometry for pyrazine assumed to be constant for all spin rates. A plot of S_{11}^i/S_{22}^i for several nominal spin rates (the highest is ~ 3 rev/sec) is shown in Fig. 1. The vertical bars indicate the error limit on each measurement - the lines are very broad (~ 40 Hz full width at half height) perhaps due to unresolved coupling to the ^{14}N, and it appears that the ratio is constant over the spinning range within experimental error. This constancy of solute orientation supports a picture in which the solute turns with the solvent as a whole, consistent with Lippmann's view. Unfortunately, this rules out the possibility (at least by using spinning) of obtaining valuable new information such as both anisotropies in the magnetic shielding ($\sigma_{33} - \sigma_{11}$ and $\sigma_{33} - \sigma_{22}$) for nuclei in molecules with this symmetry.

Regards,

Nino Yannoni

CSY:etc

1. H. Lippmann, Ann. Physik [7] 1, 157 (1958).

2. P. Diehl and C. L. Khetrapal, Mol. Phys. 14, 327 (1968).

3. E. Englert and A. Saupe, Z. Naturforsch. 19a, 172 (1964).

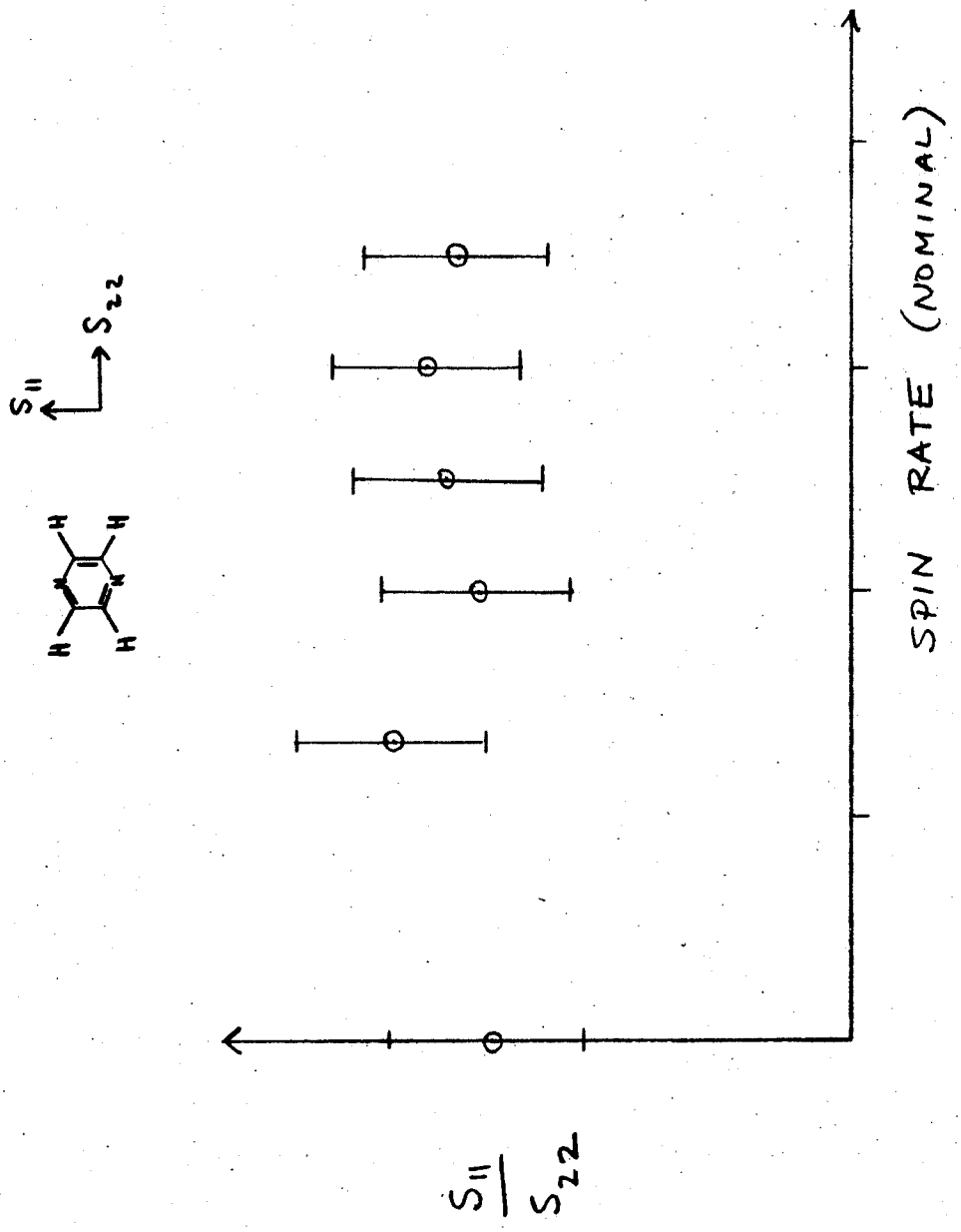


FIG. 1

ANORGANISCH-CHEMISCHES LABORATORIUM
DER
TECHNISCHEN HOCHSCHULE MÜNCHEN

VORSTAND: O. PROF. DR. E. O. FISCHER
O. PROF. DR. H. P. FRITZ

8 MÜNCHEN 2, den Arcisstraße 21
Ruf-Nr. (0811) 2105/330/331/332 / 2105/333 (Prof. Fritz)
Telex Nr. 05/22854

2o. April 197o

Fri/bl

Herrn
Prof.Dr.B.L. S h a p i r o
Department of Chemistry,
Texas A and M - University,
College of Science,
College Station, Texas 77843
U.S.A.

^{7}Li-Quadrupolkopplungskonstanten beim $LiVO_3$

Sehr geehrter Herr Professor Shapiro!

Im Laufe unserer Breitlinien-NMR-Untersuchungen von kleineren Li-Quadrupolkopplungskonstanten wurde das ^{7}Li-Spektrum des Lithiummetavanadats, $LiVO_3$, aufgenommen. Das Spektrum zeigt symmetrisch zum ^{7}Li-Zentralsignal (für $m = \pm 1/2$), je zwei weitere Signale wesentlich geringerer Intensität (für $m = \pm 3/2$), deren Frequenzkanten nach mehrtägigem Speichern (Varian TAC C-1024) bei

$$\nu = \nu_{Li} \pm 21{,}5 \text{ [kHz]} \quad \text{bzw.} \quad \nu = \nu_{Li} \pm 41{,}5 \text{ [kHz]}$$

lokalisiert werden konnten. Wegen der Kleinheit der Kopplungskonstanten für das erste Satellitenpaar und der notwendigen langen Speicherzeit mußten wir die Sendefrequenz (7000,0 kHz) der Variable Frequency RF-UnitV 4210/A stabilisieren. Dies geschah durch Synchronisation mit einer Schomandl-Frequenzdekade ND 30M, die die gewünschten Sendefrequenzen mit 0,1 Hz Genauigkeit und hoher Langzeitstabilität liefert.
Das $LiVO_3$-Gitter ist aus VO_4-Tetraedern mit gemeinsamen O-Atomen aufgebaut, so daß endlose Ketten entstehen [1]), die durch die Li^+-Ionen zusammengehalten werden. Aus der Linienform und den

Intensitätsverhältnissen läßt sich aus den zwei Paaren von Satelliten auf zwei Quadrupolkopplungskonstanten, also auf zwei nicht-äquivalente Arten von Li^+-Plätzen mit verschienen elektrischen Feldgradienten schließen. Die sich aus den inneren Satelliten ergebende ^{7}Li-Quadrupolkopplungskonstante von $(eqQ)_1 = (86 \pm 3)$ [kHz] zeigt, daß eine Gruppe von Li^+-Ionen auf offensichtlich nicht streng oktaedrischen Zwischengitterplätzen liegt, da sonst $(eqQ)_1 = 0$ sein müßte. Wegen der vermuteten, immerhin noch angenähert oktaedrischen Umgebung kann der Assymmetrieparameter $\eta = (V_{xx}-V_{yy})/V_{zz}=0$ angenommen werden. Aus der Linienformfunktion läßt sich die Annahme stützen, daß näherungsweise $0 \leq \eta < 0{,}2$ auch für das zweite Satellitenpaar gilt. Daraus errechnet sich für die zweite Quadrupolkopplungskonstante der Wert von $(eqQ)_2 \approx (166 \pm 3)$ [kHz]. Diese Sorte von Li^+-Ionen ist demnach wesentlich stärker gebunden, wenngleich die geringe Größe der Konstante noch immer auf einen deutlich ionischen Bindungsteil hinweist.
Die bisherige Erfahrung mit ähnlichen Systemen erlaubt den Schluß, daß im Gitter des $LiVO_3$ nur Gitterplätze verzerrt kubischer Symmetrie für die Li^+-Ionen zur Verfügung stehen.

Mit freundlichen Grüßen

Heinz P. Fritz (Heinz P. Fritz)

Paul Burkert (Paul Burkert)

1) D C Wickham, J.Inorg.Nucl.Chem., 27,(1965)1939

AUBURN UNIVERSITY

AUBURN ALABAMA

36830

SCHOOL OF ARTS AND SCIENCES

Department of Chemistry

Telephone 826-4043
Area Code 205

May 6, 1970

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

THE NITROETHANE-ETHANOL HYDROGEN BONDED COMPLEX

Dear Dr. Shapiro:

We have been interested in weak hydrogen bonded complexes for sometime; some observations by Mr. Curt Beeman in our department appear to be of interest in this area.

The influence of hydrogen bonding upon the hydroxyl-proton of alcohols and the dilution technique for studing this bonding are well known. Curt has been investigating some nitroalkanes in hydrocarbon solvents using the ethanol hydroxyl proton resonance as a probe. The observed shift of the hydroxyl proton can be expressed in the following manner in the absence of nitroalkanes,

$$S_{obs} = X_m S_m + 2X_d S_d + pX_p S_p \quad .$$

Where X_m, X_d and X_p are the fractions of the total number of moles of ethanol in the monomer, dimer and polymer form. S_m, S_d and S_p are the repective shifts of the hydroxyl proton in each of the forms. The order of increasing magnitude of these shifts are $S_m < S_d < S_p$. As the system is diluted the shift is in the direction of the monomer. The addition of a second hydrogen bonding species would add another term to the above summation, (i.e. $X_c S_c$, where X_c and S_c have the same meaning as above but refers to the hydrogen bonded complex between ethanol and the added species).

In the attached figure we plot the observed chemical shift of the ethanol hydroxyl proton measured with respect to the center of the ethanol methylene resonance, verses the mole fraction ratio of the ethanol to nitroethane. In this system the ethanol mole fraction was maintained constant, (i.e. 0.32) and cyclohexane was used as a dilutent

to allow the variation of the nitroethane. We note the sharp break at a mole fraction ratio of unity and interpret this to imply a 1:1 H-bonded species between the ethanol and nitroethane. The extrapolation of the mole fraction ratio to zero should give a fair indication of the chemical shift of the complex. This extrapolated shift is approximately the same as the methylene shift of the ethanol. The chemical shift of the ethanol dimer has not been established but Becker and coworkers have estimated it to be 1/4th to 1/2 the shift of the ethanol-nitroethane complex in the same range, it might have been expected to be further down field.

Curt is continuing his investigations of these nitroalkanes and the interactions in hydrocarbon solvents with alcohols.

Sincerely yours,

Charles B Colburn

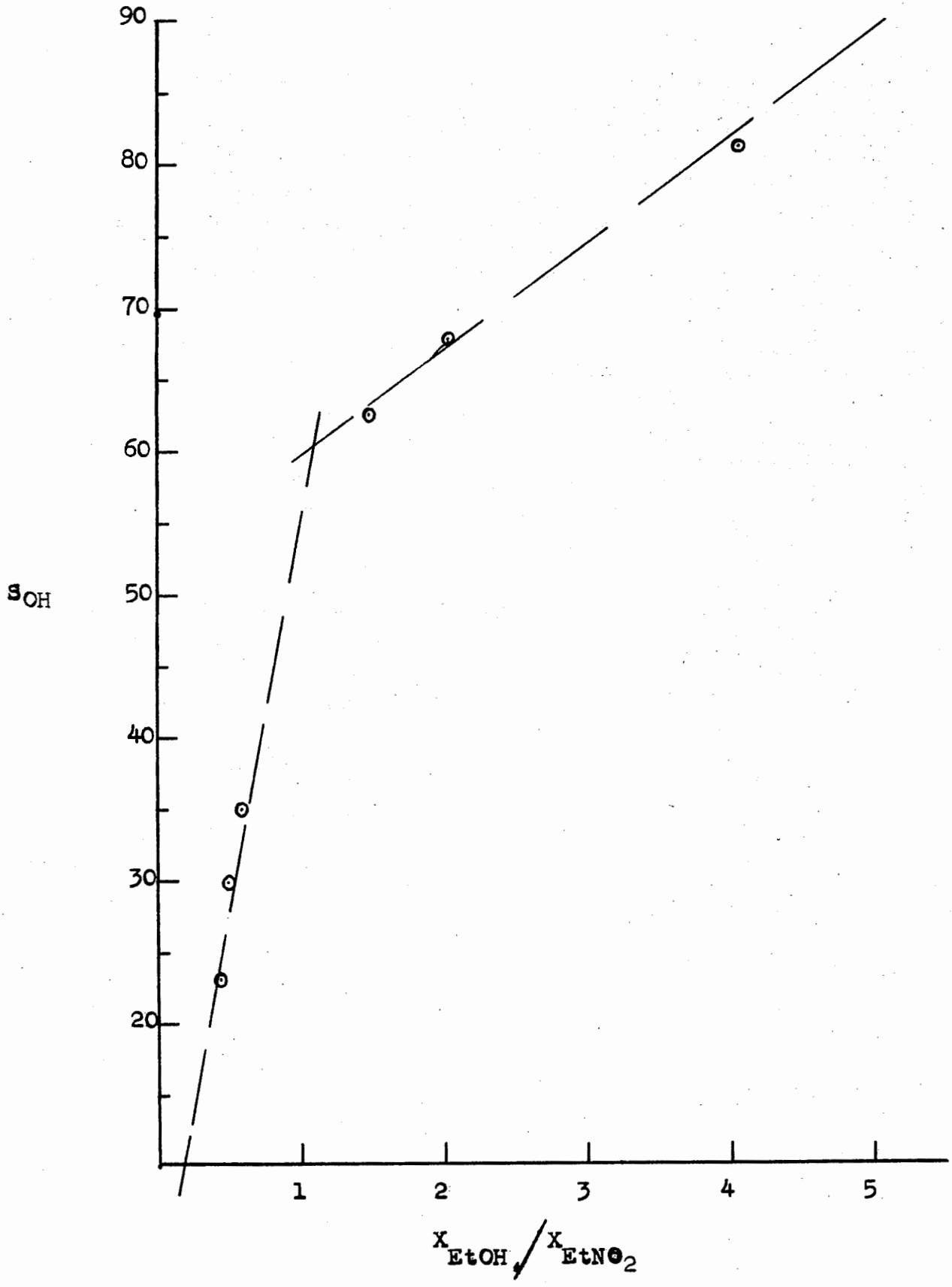
Charles B. Colburn, Head

Dr. Robert Dinius, Professor of Chemistry

R. D Dinius

Mr. Curt Beeman

Curt P. Beeman


90
80
70
60
50
40
30
20
S_{OH}
1
2
3
4
5
X_{EtOH} / X_{EtNO_2}

hooker research center

NIAGARA FALLS, NEW YORK 14302, PHONE (716) 773-2345

May 8, 1970

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

Dear Barry,

Although there has been a large amount of work concerned with quantitative analysis using the ^{1}H and ^{19}F nuclei very little use has been made of the ^{31}P nucleus in this manner. One of the difficulties of course is its low natural abundance. We are presenting here quantitative ^{31}P NMR analyses on three separate systems; sodium tripolyphosphate for which a number of analytical methods including ion exchange and paper chromatography exist; the analysis of Tris-(hydroxymethyl) Phosphine (THP) handled only with difficulty by other methods; and finally the quantitative analysis of mixed sodium thiophosphates for which, to our knowledge, no analytical procedure exists.

Some time ago an example of a phosphate analysis was published in the Varian NMR series (No. 84). An example of a similar analysis run in our laboratory together with an expanded scan showing the areas is given in Fig. 1. The results obtained on two ASTM standard samples using electronic and hand integration of the NMR absorption signals together with those obtained by standard analytical methods are given in Table I. This data was obtained on the saturated H_2O solutions at 40.5 MHz with baseline stabilization.

TABLE I

	ORTHO	PYRO	TRIPOLY	TRIMETA
ASTMF	0.8	7.4	91.1	0.6
NMR Integrator	-	6.5	93.0	0.5
Planimeter	-	6.8	92.5	0.7
ASTMG	1.0	14.8	82.0	2.0
NMR Integrator	1.0	17.0	80.0	2.0
Planimeter	1.0	16.0	81.0	2.0

The above data demonstrates the excellent agreement between the various methods. However, the NMR method is much less time consuming and more convenient to use.

In the THP analysis the major by-products are tris(hydroxymethyl) phosphine oxide (THPO), tetrakis-(hydroxymethyl) phosphonium chloride (THPC) and a thermal rearrangement product dihydroxymethyl methyl phosphine oxide (DMPO). The data obtained on the neat liquids is given in Table II.

TABLE II

Compound	Shift*	%P	Area	Mole%	Wt.%
$THP(HOCH_2)_3P$	+24.4	25.0	81	66.4	61.4
$THPC(HOCH_2)_4P^+Cl^-$	-25.0	16.2	8	10.0	14.4
$THPO(HOCH_2)_3PO$	-47.7	22.1	20	18.6	19.6
$DMPO(HOCH_2)_2CH_3PO$	-50.7	25.0	3	2.5	2.3
?	-45.0	25 ?	3	2.5	2.3

*For the pure components relative to H_3PO_4. Slight shifts with impurity changes are noted.

Finally typical data for duplicate analyses on separate thiophosphate samples is presented in Table III and Fig. 2.

TABLE III

Compound	Chem. Shift	Area Precent Sample A 1	Sample A 2	Sample B 1	Sample B 2
Na_3PS_4	-87	26	25	29	29
Na_3POS_3	-86	28	27	31	32
$Na_3PO_2S_2$	-64	16	15	14	16
Na_3PO_3S	-34	13	14	14	14
$Na_4P_2O_6S$?	-11.5	5.2	4.2	2.1	2.5
Na_3PO_4	- 6.5	8.5	7.9	5.0	4.5
?	+ 3	-			

We believe the above data amply demonstrates the general applicability of the method. A more detailed account of these results will appear elsewhere. We hope this missive will serve to remove the red from your eyes (and ours).

Sincerely,

D H Marr

DHM/mr

TITLE: ^{31}P Quantitative Analysis

FIG. 1

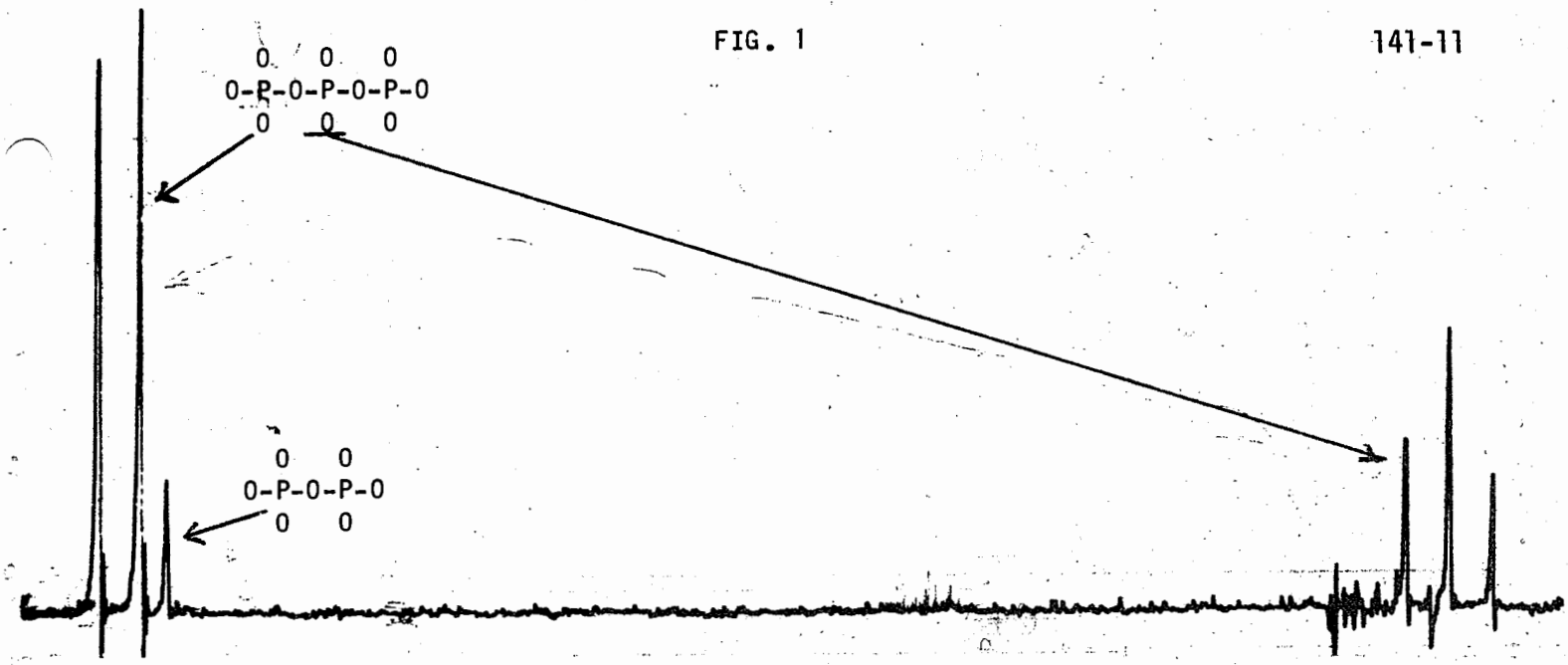


FIG. 1

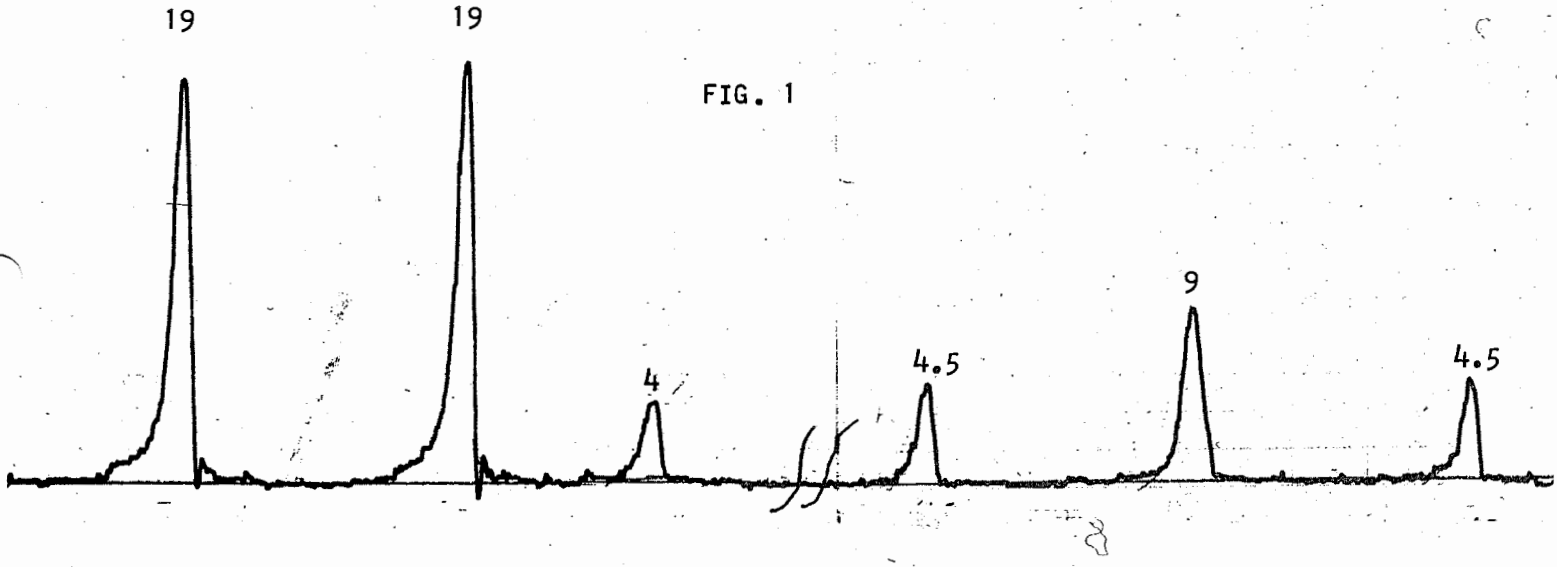
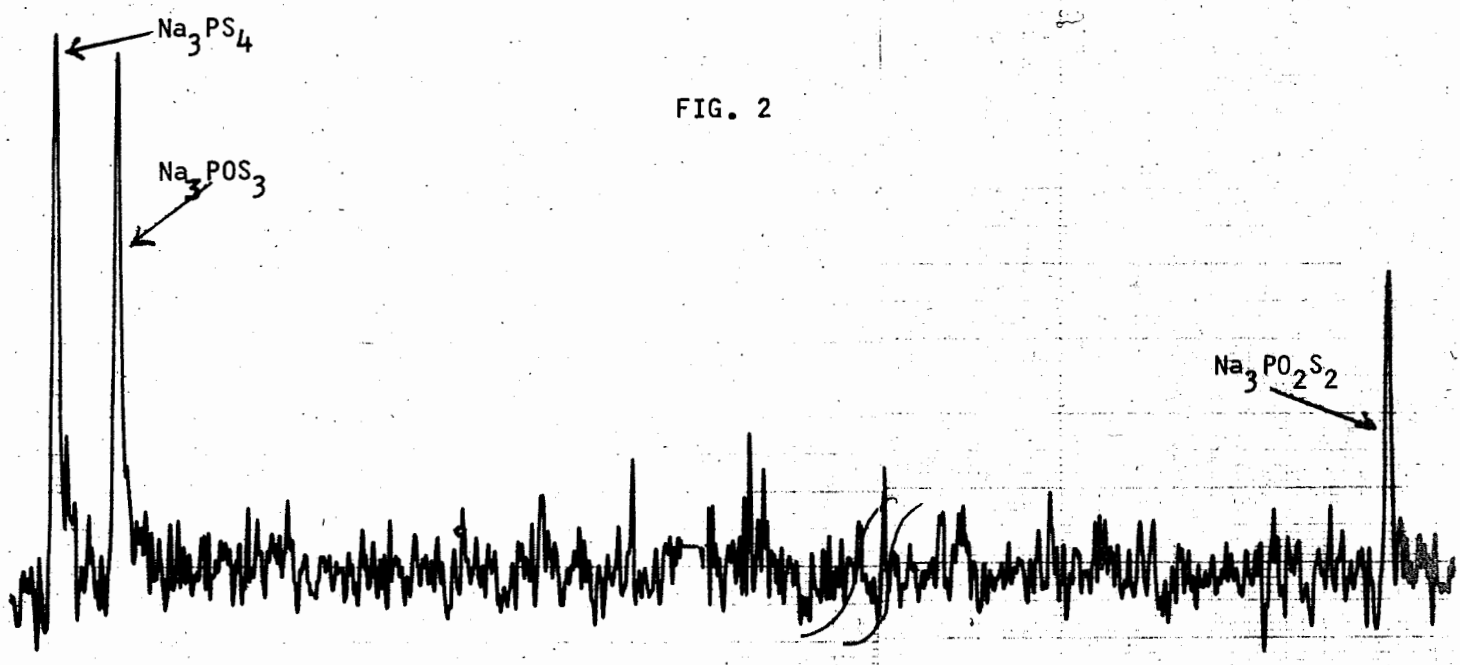


FIG. 2



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

EF/BLM

8th May, 1970.

A simple modification to a Perkin Elmer R10 for T_1 measurements. Relaxation in lecithin.

Dear Professor Shapiro,

In biological research we often have to work with dispersions in D_2O, rather than true solutions. Such samples, although seldom optically clear, do give well defined NMR spectra. However, one of the disadvantages of dealing with samples which may be magnetically anisotropic is that the line width of each resonance does not give a reliable guide to the degree of molecular or segmental motion involved, i.e factors other than the normal motional parameters may determine T_2 as measured by the line width. One solution to this problem is to use T_1 measurements.

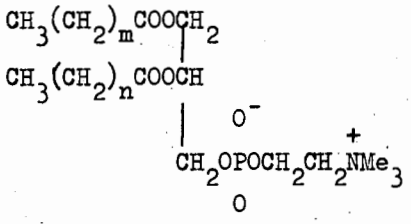
We have applied the direct method of T_1 measurement[1] to several problems, using a Perkin Elmer R10. The conversion in its simplest form requires only a length of wire to connect pin 2 on the front of the phase detector unit to pin 1 on socket 2 on the customers' accessory panel. This gives a 4 KHz modulation on the observation (H_1) and spin decoupling channels simultaneously. The spin decoupling channel is connected up in the usual way except that the frequency sweep generator is not required. The resonance for which T_1 is to be determined is centred on zero on the chart and then the Scale Factor switch is turned off. The resonance should be artificially broadened, either by not spinning or by offsetting the Golays slightly. A suitable monitoring level for H_1 is chosen using the upper attenuator, and then the signal is saturated by using the spin decoupler channel switched to 8×10^4 μV. The saturation is removed by switching the lower attenuator to the "Multiplier" position, the recovery signal is then monitored on the recorder.

Without additional equipment T_1's of the order of a few seconds can be recorded, but if the signal is fed into an oscilloscope then the range may be extended down to 50 m secs.

Using the equipment for a purpose for which it was not intended will require juggling around to get the conditions right for each measurement, but this has not proved unduly time consuming. Although

the method as described has much to recommend it (because of the simplicity and ease of conversion) there is, of course, much scope for improvement by modification of the spectrometer circuits and by use of additional instrumentation. One modification that we have found useful is to feed the signal into a CAT, using the vertical amplifier of an oscilloscope to make the signal output of the R10 compatible with the CAT imput. This allows T_1 measurements of relatively weak signals to be averaged to improve signal to noise. The CAT used is an NS-544 and the internal time bases are used for recording the signal, but the accumulated data is printed out via the interface time base on to the R10 chart recorder. During print-out the Address Identification button is held on in order to give a calibrated time base. The semi-logarithmic plots of the recovery curves obtained by this method are very linear.

We have applied this method to the study of egg yolk lecithin in different physical environments. The results reflect the degree of freedom of motion of the hydrophobic and hydrophilic ends of the molecule.



(the hydrocarbon chains may be unsaturated)

System	Physical State	T_1 of $\overset{+}{N}Me_3$	$T_1(CH_2)_{n+m}$
Egg lecithin in CD_3OD	Monomeric solution	1560 m secs	1390 m secs
Egg lecithin in D_2O	Liquid crystalline bilayer	300 "	300 "
Egg lecithin in $CDCl_3$	Inverted micelles	210 "	1610 "

The similarity of the two relaxation times in D_2O, and possibly in CD_3OD, leads us to believe that spin diffusion is taking place and the relaxation of the whole molecule is governed by T_1 for the $\overset{+}{N}Me_3$. If this is the case, the orientation of the polar head group must be such that the $\overset{+}{N}Me_3$ is near the hydrocarbon chains. When the type of aggregate is changed[3] (e.g. in $CDCl_3$ solution), the orientation of the head group also changes.

Yours sincerely,

Ellick Finer

E.G. FINER (subscription credit)

Alan Flook

A.G. FLOOK

[1] A.L. Van Geet and D.N. Hume, Analytical Chem. 37 983 (1965).

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45239

May 11, 1970

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

Dear Professor Shapiro:

C^{13} on the HA-100--Problems and Solutions

We have recently begun to look at C^{13} NMR using a Varian HA-100 spectrometer, equipped with a 25.1 MHz RF/AF Sweep Unit (V-3530) and an 8 mm. probe (V-4335-1). For H^1 irradiation, we employ a homemade pseudo-random noise generator, Hewlett-Packard 5105A/5110B Frequency Synthesizer/Driver, H-P 10514A Mixer, and Boonton 230A Power Amplifier. A number of technical difficulties were encountered in the beginning which may be worth mentioning for the benefit of those who may have similar problems.

Inability to decouple H^1 was found to be caused by a defective "trap" capacitor in the probe. The latter had to be replaced two times until we decided to try replacing it with a fixed 10 pf ceramic capacitor. To tune the circuit, an 8-turn, 5 mm. diameter coil was substituted for the existing one and with the RF power "on" the coil windings were then separated until maximum power transfer was obtained. The coil shape was secured by application of polystyrene "Q-dope". This has worked satisfactorily to give a decoupling bandwidth of approximately 2 kHz.

Having two HA-100 spectrometers separated only by ten feet, with the other unit used for observing H^1, our noise irradiation caused interference on the proton spectrometer. After trying additional equipment grounding and cable shielding, the C^{13} observing frequency was lowered by ~ 25 kHz. The resulting decrease in the H^1 decoupling frequency eliminated the interference while the linearity of the C^{13} RF sweep remained good.

Predicting the correct analytical channel phase was difficult but this problem had a simple solution. In addition to the "RF Phase" of the Fixed RF unit (V-4311) we utilize an external circuit for controlling the phase of the analytical channel alone. To obtain a stable lock signal in the 2500 to 5012 Hz sweep range the "RF Phase" (V-4311) is adjusted at 2500 Hz in the absence of resonance so that the DC voltage output at

pin P of the AC Amplifier and Phase Detector (J-1316) of the Internal Reference Stabilizer (V-4354A) is zero (the same potential is also obtained for 180° out-of-phase signal but this is immediately obvious once the lock is swept through, and after the initial set up this error is seldom repeated). Consequently, the analytical phase is affected only by frequency offsets. By recording a properly phased spectrum at various offsets, the phase settings thereby obtained will be correct for all subsequent spectra.

The use of C^{13} enriched CS_2 for locking has been abandoned. We found it difficult to homogenize the field and to retain the lock when CS_2 was used. On the other hand, H^1 decoupled methyl iodide was found to be a sharp singlet with a relatively high RF saturation point. We obtain a stable lock at a sweep rate of 25 Hz/sec. on a sweep range of 100 p.p.m. using 50 percent C^{13} enriched 2 mm. diameter methyl iodide capillaries.

Since the elimination of these problems, the overall performance of the system has been very satisfactory.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research and Development Department

C. D. Sazavsky
Research Division

lkb

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY

TEL: (215) LA 5-1000

12 May 1970

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

Dear Barry:

I'd like to report briefly on two items, both of which are based on the recently completed PhD dissertation of Mrs. Agnes Lee.

Liouville-Space Theory: Exchange in Oriented Molecules

A closed-form calculation was performed and programmed in FORTRAN IV-H to calculate, based on Binsch's 'Unified Theory of Exchange Effects,'[1] the NMR spectrum of a two-spin-1/2 system undergoing mutual exchange. A typical calculation is shown in Figure 1. In this calculation, δ = 100 hz, and the direct coupling B = 10 hz. The four traces shown on the typagram[2] represent exchange rates of 1 sec^{-1}(,), 20 sec^{-1}(°), 400 sec^{-1}(*), and 8000 sec^{-1}(.). It is interesting to note that, for direct coupling, the inner two lines of the doublet pair broaden more than the outer two lines. This result, different from indirect coupling, can be used to confirm an assignment of relative signs of J and B throughout the slow exchange region of rates.

At a rapid exchange rate, 8000 sec^{-1}, the spectrum narrows to a doublet, the expected pattern for an oriented A_2 system.

A calculation was performed for dimethylacetamide-d_3, using values (see below) obtained from a low-temperature spectrum. At an intermediate exchange rate, the splitting of the central feature, arising primarily from the 12 hz chemical shift, becomes broadened; at a high exchange rate, a splitting reappears in the central feature, but this splitting measures B_{12}, the inter-methyl direct coupling. (Figure 2).

NMR Spectrum of Oriented Dimethylacetamide-d_3

$CD_3CON(CH_3)_2$ is soluble in the Flautt-Lawson lyotropic nematic solvent (D_2O, *n*-$C_{10}H_{21}OH$, Na[*n*-$C_{10}H_{21}$]SO_4, Na_2SO_4), and affords the spectrum shown in Figure 3. The calculated spectrum (LAOCOON III, modified for direct coupling) appears below it. The parameters are given in the legend to Figure 2.

The temperature range over which the DMA-d_3 solution remained nematic was insufficient for the observation of rate-dependent features suggested by the typagrams of Figure 2.

It is hardly necessary to remark on the impact of the Indochina war on academic life; the political events of the first week of May affect our freedom and ability to carry out our teaching and research effectively. I believe the entrance into Cambodia and the usurpation of Congressional prerogatives by the military and the executive to be improper and perhaps illegal. Whether TAMU NMR readers agree with these sentiments or not, I hope they will exercise their privilege to inform their representatives in government of their views on this critical issue. To those offended, my apology for using these pages for a political message. Peace to all our houses.

Sincerely yours,

Jay Martin Anderson
Associate Professor

Agnes Chung-fung Wu Lee
(at home)

[1] G. Binsch, 1969 J. Am. Chem. Soc. 91, 1304.

[2] A 'typagram' (c Typagraph Corp., 7525 Convoy Ct., San Diego CA 92111) is the output of the Typagraph model 3 plotting teleprinter. See JMA in TAMU NMR Newsletter 135-8.

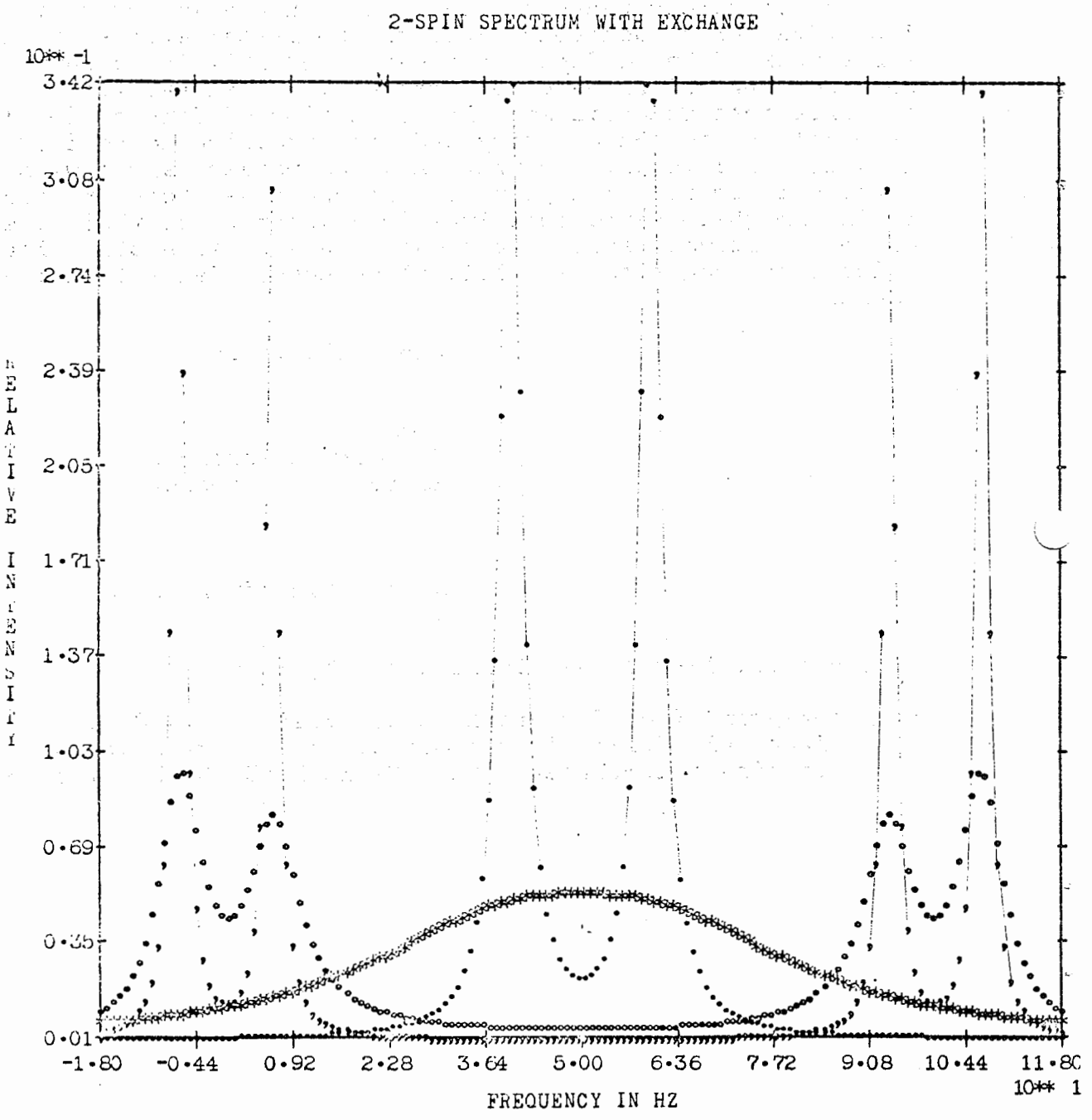


FIGURE 1. Theoretically calculated NMR spectra of an AX $\frac{1}{2}$ system exchanging between two environments in an anisotropic solution. Cases B(1-4) on Table 2-1.

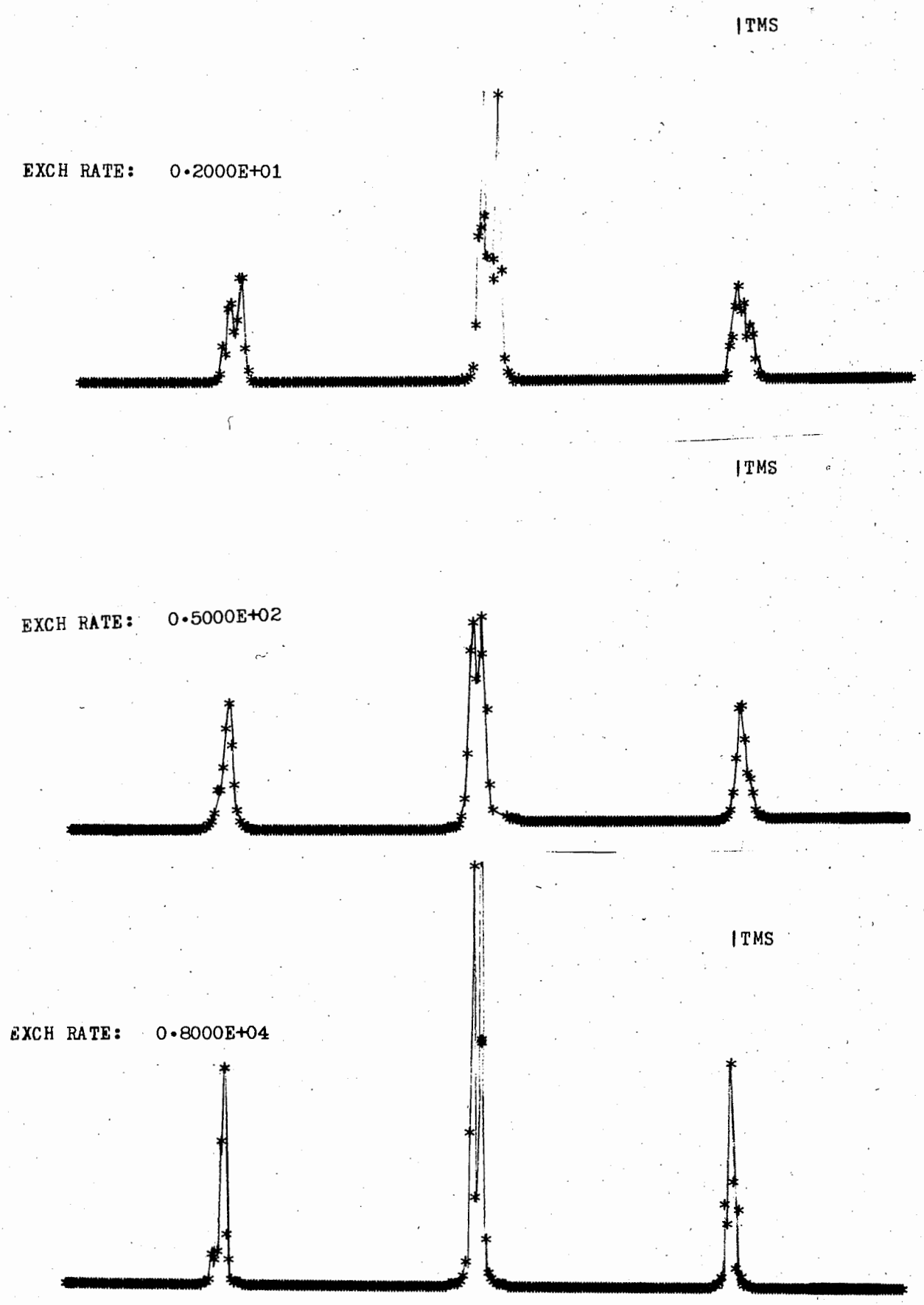


FIG. 2. Calculated spectra of DMA-d_3 at different exchange rates. Chemical shifts are -301.16, -313.96 hz; $B_{11} = B_{22} = 151.86$ hz, $B_{12} = 3.35$ hz.

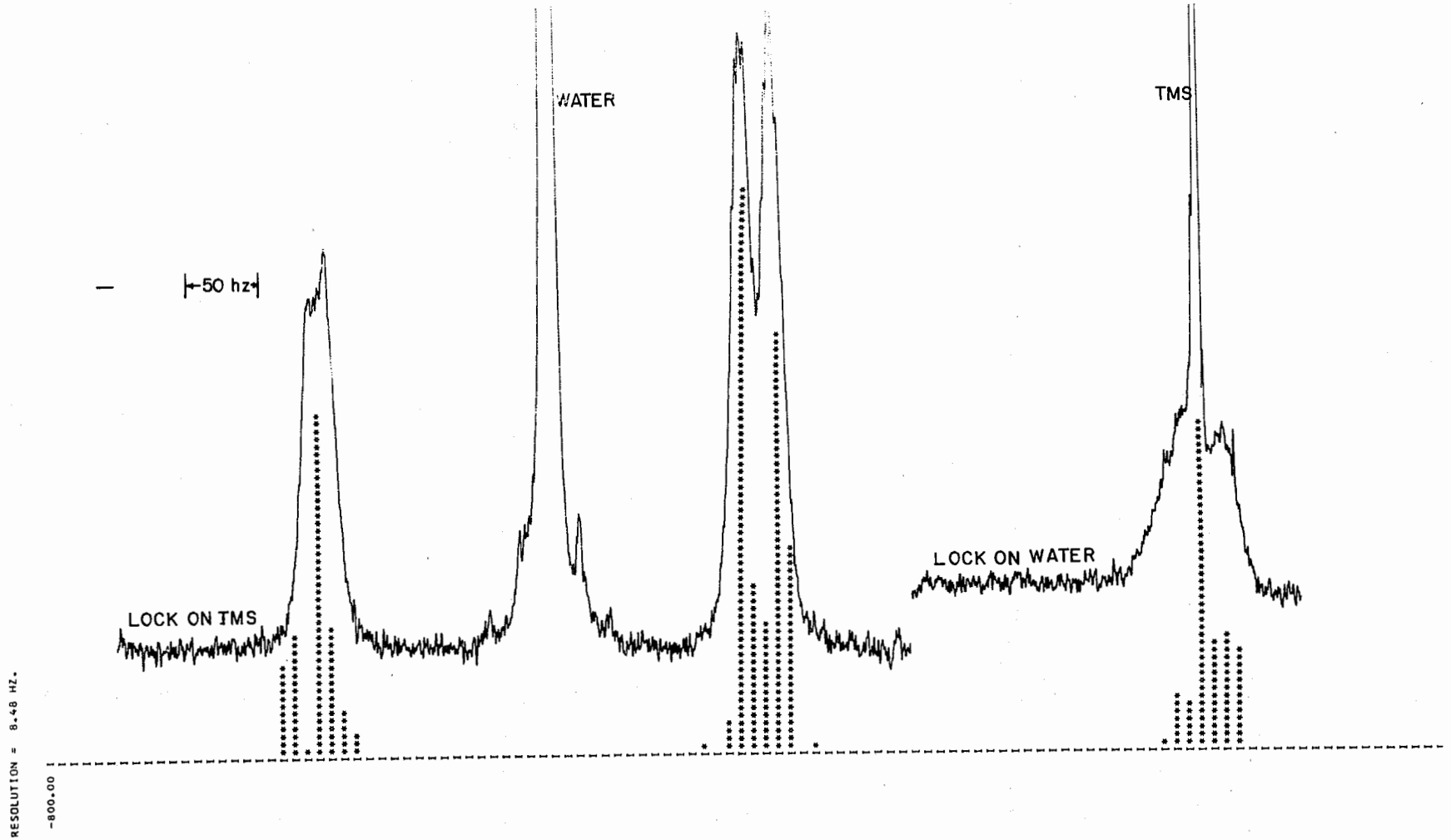


FIGURE 3. Observed and calculated NMR spectra of DMA-d_3 in a lyotropic nematic solvent at 25°c. Assigned parameters are shown with Figure 2. Spectrum taken at 100 MHz on a Varian HA-100.

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

DEPARTMENT OF CHEMISTRY

19 May 1970

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

Dear Barry: Ailuroperusal

Before we developed CHEETAH (TAMUNMRN #130, p. 40), we put together two systems for extracting digital spectra from the Varian C-1024 with our IBM 1800 computer and storing them for further processing. Several expressions of interest in those systems prompt us to announce their availability to those members of the NMR community still prosperous enough to afford this Newsletter.

The more advanced of the two programs, RDCTA, is called into the 1800 by pressing a button on an interface next to the spectrometer. The operator then selects the read-out time and switches the C-1024 to the read-out mode. Several spectra can be stored successively on a magnetic disk file before they must be transferred to cards or magnetic tape. The actual operation involves reading of the data points from the binary output of the C-1024, through a voltage amplifier, into the 1800. There are 26 bits of output, 10 for the channel numbers and 16 for the data points, and each is connected to a digital input bit of the 1800. We also use two process interrupts, one of relatively low priority to call the program and one of high priority, triggered by the channel advance of the C-1024, to initiate the reading of each data point. One ECO bit is also needed to turn on a recognition light on the interface. The configuration of the 1800 used for this program includes 16K of core with two disk drives and one magnetic tape drive, and operates under the IBM TSX system Version 3 Mod 6.

We also have an early version of the program (RDCTD) that was used before the 1800 time-sharing system was operational. RDCTD treats the data transfer as a nonprocess job, which means that the program has to be called into core by the card reader and monopolizes the computer while the operator leaves the second-floor computer room, walks down the hall, waits for an elevator, takes it to the basement, strolls down a couple of hallways to the NMR room, and turns the switch on the cat. Although this is an inefficient use of computer time, RDCTD can be useful in the early system debugging stages since it does not have to be stored as a process core load.

Listings for both programs, as well as circuit diagrams and a parts list for the interface, are available from one of us (P.C.L.) at the address below.

Yours truly,

Paul

Paul C. Lauterbur

R. S. Hutton

R. S. Hutton

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11790 U.S.A.

LABORATORIUM VOOR ORGANISCHE
SCHEIKUNDE DER UNIVERSITEIT VAN
AMSTERDAM
NIEUWE ACHTERGRACHT 129
TELEFOON 947174 (5 LIJNEN)

AMSTERDAM, May 14, 1970. 19

vdH/LR

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

"Time dependent" rotational barriers in N,N-dimethylamides.

Dear Professor Shapiro,

While investigating the substituent effect on the rotational barriers of a series of N,N-dimethylbenzamides and cinnamamides (1) we could not reproduce some of our measurements. The discrepancies could not be attributed to the usual sources of error (2, 3, 4) since:

- high quality spectra were digitized and punched automatically
- temperatures were measured with a thermocouple inside the spinning sample tube (technical details of HA100 probe cap modification viz (1)). The temperature did not vary more than .1°C over periods of at least half an hour
- an iterative total line-shape analysis was used.

The source of our trouble turned out to be the solvent, chloroform - d. We found coalescence temperatures to differ more than 20°C, depending upon the chloroform used. In some cases we even observed a time dependent line-shape at constant temperature. These spectra were completely analogous to those normally observed when one varies the temperature. (The spectra changed rather drastically: from the slow exchange - to the fast exchange limiting case within half an hour).

It is known that the exchange is subject to acid catalysis (5). Indeed, adding a trace of HCl (which is a very good proton donor in $CDCl_3$) caused the collapsing of the N-methyl signals, which could be reversed by the addition of a trace of pyridine. The time dependent phenomena could be reproduced

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AMSTERDAM, May 14, 1970. 19

Professor Bernard L. Shapiro, College Station, Texas 77843.

by adding a solution of fosgene to an otherwise "normally" behaving sample.

All chloroform we use is obtained commercially, stored over silver in dark bottles as supplied by the manufacturer, and is kept in a refrigerator.

We wonder if some of the discrepancies in literature might be due to similar contaminations with catalytic amounts of acid.

K. Spaargaren

P.J. van der Haak

C. Kruk

J.C. van Velzen

1. K.Spaargaren, Thesis, to be published fall 1970.
2. G.Binsch, in "Topics in Stereochemistry", vol. 3. E.L.Eliel and N.L.Allinger, ed., Interscience Publ., New York 1968.
3. C.W.Fryer, F.Conti and C.Franconi, Ric.Sci. 35, (2A), 788 (1965).
4. A.Allerhand, H.S.Gutowsky, J.Jonas, R.A.Meinzer, J.Am.Chem.Soc. 88, 3285 (1966).
5. A.Berger, A.Lowenstein and S.Meiboom, J.Am.Chem.Soc. 81, 62 (1959).

PERKIN-ELMER

THE PERKIN-ELMER CORPORATION
NORWALK, CONNECTICUT 06852
TELEPHONE: (203) 847-0411
CABLE: PECO-NORWALK

May 14, 1970

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

Dear Dr. Shapiro:

While waiting for the installation of the new R20B in our laboratory, we have spent recent weeks working with the R12A installed here, especially with its spin decoupler. While our main purpose is to solve real problems sent to us, we find that we have now found a solution to a problem that is, as yet, still academic.

Spin decoupling can be performed in either field sweep or frequency sweep mode. The former method has fallen into disrepute since the advent of the latter for well known reasons. Two advantages of field sweep have been (a) the phase consistency of the spectrum and (b) the relative ease of decoupling resonances close together. Frequency sweep experiments were unsatisfactory because of the occurrence of beats at the irradiation point and other parts of the spectrum (typically, side beats were thrown up on either side at the spinning frequency and line frequency positions).

However, as a result of improvements in spectrometer design, it is possible to perform these "close" spin decoupling experiments using a frequency sweep -- See Spectrum 1. Also the modern technique of sweeping the decoupling frequency rather than the observing frequency produces phase-consistent frequency-swept spectra. Therefore, it seems that field-sweep really is out of fashion!

However, one application of the field sweep method would be to spin decouple weak samples while using a time averaging computer to enhance the single to noise. This is what we have tried and with some success. A result is shown in Spectrum 2. Abscissa stability during the experiment is ensured by using an NMR trigger signal to start the computer scan. The field sweep spin decoupling is necessary because in this mode the decoupling condition is independent of absolute field strength. A frequency sweep condition would demand field stability of less than 1 Hz over the whole averaging time -- which would be difficult considering the heating effect of the H_2 irradiation.

What we need now is a sample that is sparingly soluble and whose spectrum needs decoupling for interpretation. But with your circulation we are not inviting any!

Please credit this to P. A. Strauss' account.

Sincerely yours,

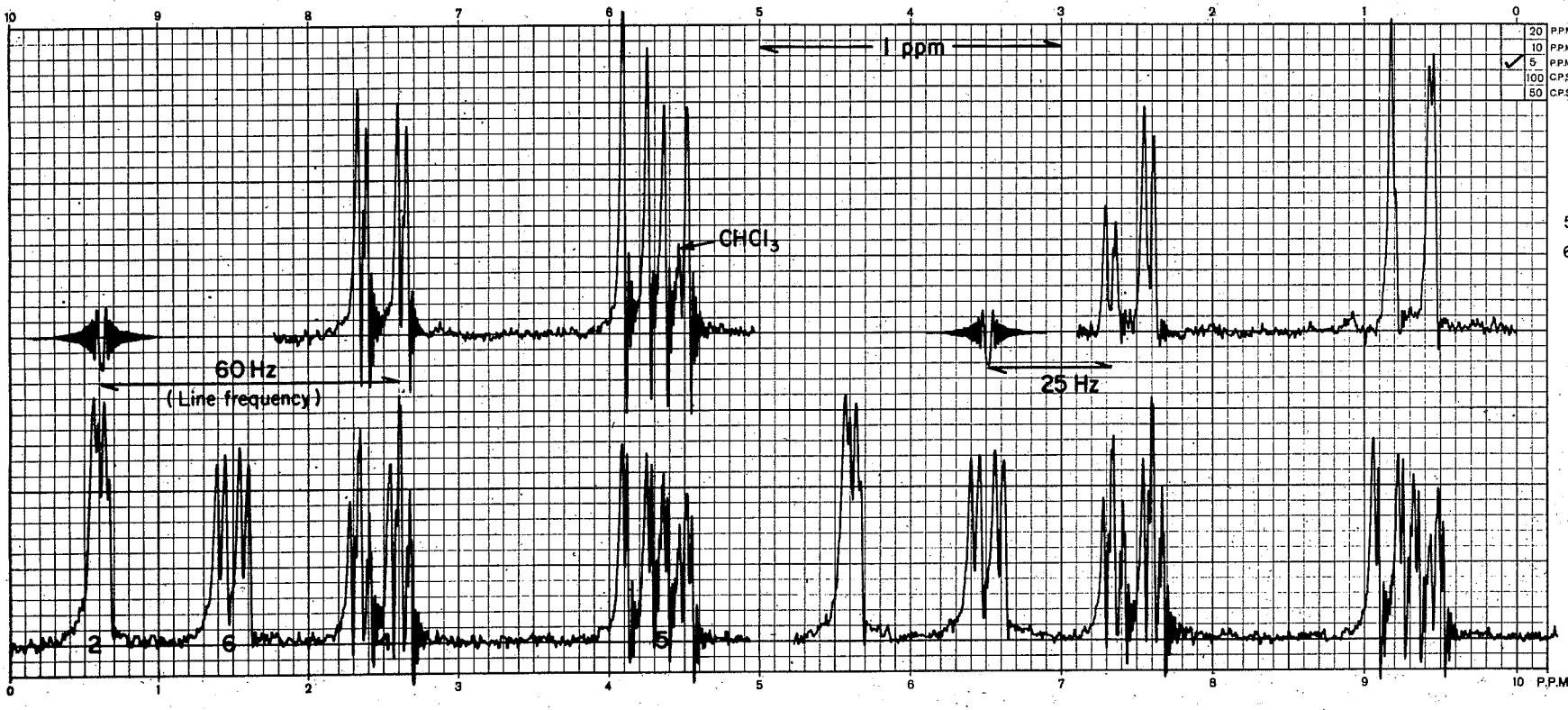
THE PERKIN-ELMER CORPORATION

A. R. J. Arthur
Sr. Product Specialist, NMR

S. M. Coles
Applications Chemist

ARJA:djs

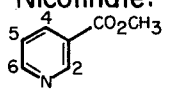
Title: A CURE WITHOUT A DISEASE



SPECTRUM No.	
DATE	6TH May 1970
SOLVENT	$CDCl_3$
CONC.	10%
REF STD.	—
SUBMITTED BY	—

COMPOUND

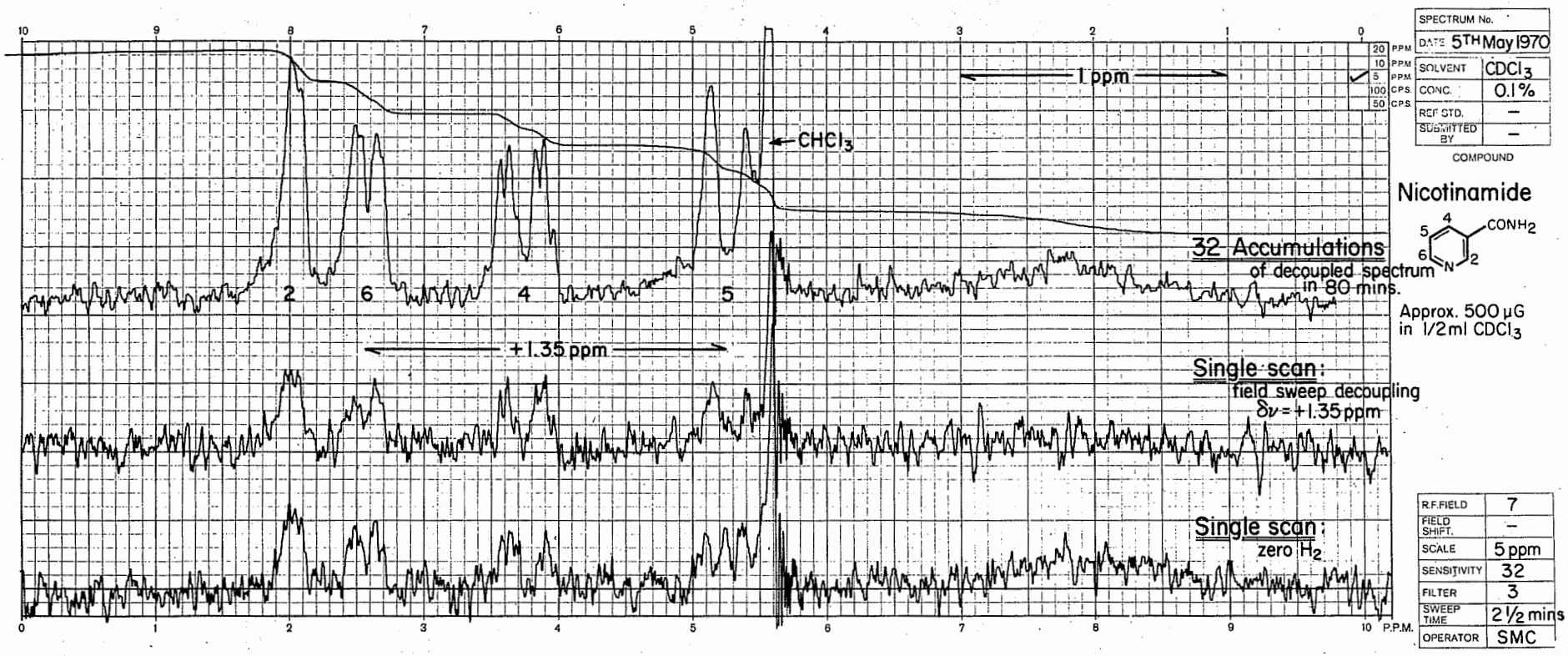
Methyl Nicotinate:



Frequency sweep decoupling of aromatic resonances

R.F.FIELD	5
FIELD SHIFT.	—
SCALE	5ppm
SENSITIVITY	4
FILTER	3
SWEEP TIME	5mins.
OPERATOR	SMC.

Spectrum 1



SPECTRUM No.	
DATE	5TH May 1970
SOLVENT	$CDCl_3$
CONC.	0.1%
REF STD.	–
SUBMITTED BY	–

COMPOUND

Nicotinamide

R.F.FIELD	7
FIELD SHIFT.	–
SCALE	5 ppm
SENSITIVITY	32
FILTER	3
SWEEP TIME	2½ mins
OPERATOR	SMC

Spectrum 2

University of East Anglia

From Professor N. Sheppard F.R.S.

School of Chemical Sciences
University Plain
Norwich NOR 88C
Telephone Norwich (0603) 56161

15th May 1970

Dear Barry,

I am sorry to be a little behind with our contribution to the Newsletter. This is as follows :-

The N.M.R. Spectra of Ethylene Oxide and Ethylene Sulphide dissolved in the nematic phase.

The spectra of these molecules were recorded in a nematic phase of a 60:40 molar mixture of butyl (p-ethoxyphenoxycarbonyl) phenyl carbonate and 4 butoxy 4'heptoxy asoxybenzene in approximately 10 mole.% concentration. The spectra were recorded on a Varian HA100 using the HR mode.

The spectrum of ethylene oxide consisted of 5 pairs of lines and was analysed as an A_{1x4} using the expressions of C.M. Woodman.[1] The resulting dipolar coupling constants obtained after an iterative fitting procedure using a modified LAOCOON 1968[2] program were:-

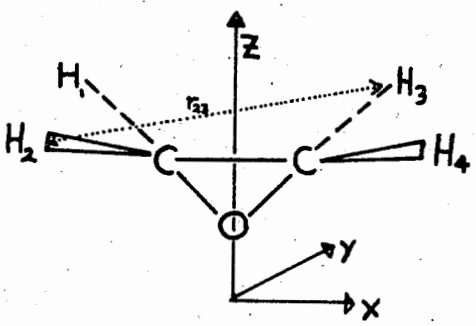
$$D_{12} = D_{34} \text{ (geminal)} = 1642.8 \text{ Hz}$$
$$D_{13} = D_{24} \text{(cis)} = -1054.2 \text{ Hz}$$
$$D_{14} = D_{23} \text{ (trans)} = -236.1 \text{ Hz}$$

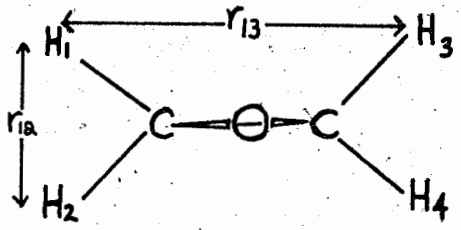
The overall R.M.S. error on these results was 1.4 Hz.

From the following equation

$$D_{ij} = -2/\sqrt{5}\ K_{ij}\ \{C_{3z^2-r^2}\ (\langle \Delta z_{ij} \rangle^2 / r_{ij}^5 - \tfrac{1}{2} \langle \Delta x_{ij} \rangle^2 / r_{ij}^5 - \tfrac{1}{2} \langle \Delta y_{ij} \rangle^2 / r_{ij}^5)$$
$$+ C_{x^2-y^2}\ (\tfrac{1}{2} \langle \Delta x_{ij} \rangle^2 / r_{ij}^5 - \tfrac{1}{2} \langle \Delta y_{ij} \rangle^2 / r_{ij}^5)\}$$

three equations can be set up containing D_{12}, D_{13}, D_{14}, r_{12}, r_{13} and r_{23} and the ratio $X = r_{12}/r_{13}$. These three equations can be solved to give $C_{3z^2-r^2}$, $C_{x^2-y^2}$ and X. The coordinate system used in the above equations is shown below.





An identical method was followed for ethylene sulphide to give the following dipolar coupling constants

$$D_{12} = D_{34} \text{ (geminal)} = 2346.2 \text{ Hz}$$
$$D_{13} = D_{24} \text{ (cis)} = -508.4 \text{ Hz}$$
$$D_{14} = D_{23} \text{ (trans)} = -9.0 \text{ Hz}$$

with a computed R.M.S. error of 3.6 Hz.

The parameters for the two compounds are recorded below

	$C_{3z^2-r^2}$	$C_{x^2-y^2}$	X (N.M.R.)	$X(^{\text{electron}}_{\text{diffraction}})^3$
Ethylene oxide	∓ 0.05814	± 0.1439	1.358 ± 0.005	1.37 (4)
Ethylene sulphide	± 0.05875	± 0.1203	1.372 ± 0.005	1.36 (3)

References.

(1) C.M. Woodman, Ph.D. thesis, University of East Anglia, 1967.

(2) S.R.C. Atlas Computer Laboratory, Bulletin No. 4.

(3) Cunningham, G.L., Boyd, A.W., Myers, R.J., Gwinn, W.D., Le Van, W.I., J.C.P., 4 (1951) 676.

Yours sincerely,

M. Livock.

p.p. I.J. Gazzard and N. Sheppard.

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

Oregon Graduate Center / for Study and Research

May 19, 1970

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

^{13}C NMR of Organophosphonates

Dear Barry:

We've had our ^{13}C set-up going for almost a year now, apart from the usual down-time. The apparatus consists of an HA-100, 25.1 MHz ^{13}C rf unit, spinning 8-mm tubes - double tuned (^{1}H and ^{13}C) probe, noise decoupler, 8K 620-i computer and HP 500 MHz synthesizer. We are deriving our 25.1 MHz centerband from 251 MHz divided down by exactly 10, giving selectable centerband to 0.01 Hz. We are in the process of going to heteronuclear lock (either ^{19}F or ^{2}H) which will enable us to use a digital sweep of the synthesizer from the computer under soft-ware command. Judicious surgery on one of Varian's programs has permitted us to use up to 5 K of the 8 K for data storage along with data acquisition and instrument control. To achieve ultimate accuracy all frequencies will be generated by the synthesizer or its driver.

Until the above is finished we are using the 620-i-VCO option. This provides us with variable sweep widths. We've found this very useful for ^{13}C spectra - especially for eliminating the variable base-line (or potato) found at modulation frequencies lower than 3000 Hz. The enclosed spectrum is that of a cyclic phosphonate provided by Dr. S. E. Cremer at Marquette University. It is a result of 18 scans at 2 Hz/sec locked on the lower sideband of 60%-enriched methyl iodide enclosed in a 2 mm capillary tube surrounded by a solution of 0.9 gm of the phosphonate in $CHCl_3$. Had a modulation frequency of -4259 Hz (instead of -6659 Hz) been used the baseline would have wandered from top to bottom. The VCO software can use some alteration. The minimum width that can be entered is 25 Hz and the maximum 1575 Hz. More seriously is the problem with the programmed scan. This allows up to four slow scan portions within a large scan. The remaining portions of the scan are slewed at a high rate. If one wants to get accurate peak positions for a scan that runs over 2500 Hz he's in a bind. The computer gives the same attention to the slew points as the slow-scanned points. The program we are currently using has 2500 data points so that's 1 data point/Hz or poor resolution. For a spectrum with two or three peaks that's a lot of data points sacrificed. The alternative - which we must use for accurate peak

position - is separate scanning for each multiplet over (usually) 25 Hz regions. In time we will adjust the program for more flexibility. Another annoying factor is one facet of the field shim option of the 620-i. It works well but doesn't know how to handle lower sideband locks! It earnestly makes the lock signal more positive until lock is lost. Undoubtedly this is an easy one to fix, we just haven't gotten around to it.

Since we are locking on capillaries our resolution in the sample hasn't been as good as we'd like but has been running around 1 Hz. The couplings are good to $\pm$0.1 Hz and the shifts to $\pm$0.01 ppm.

Dr. Cremer and I are working together on a series of these phosphonates, examining the ^{13}C-^{31}P couplings and ^{13}C shifts as a function of substituent (in this case methyl) on the phosphous, and degree of methyl substitution on the ring. There is a dramatic stereochemical effect on C_2 of +4.4 ppm in going from the molecule shown to the isomer in which the methyl and oxygen have exchanged position. The $C_{1,7}$-P coupling is unchanged, while the C_3-P coupling increases to 23.0 Hz and the C_3-P coupling decreases to 6.3 Hz. This is exactly the same behavior as in the case where phenyl replaces methyl as the phosphorous substituent. These patterns are proving helpful in assigning the conformation of other phosphonates.

Sincerely yours,

George

George A. Gray
Assistant Professor of
Chemistry

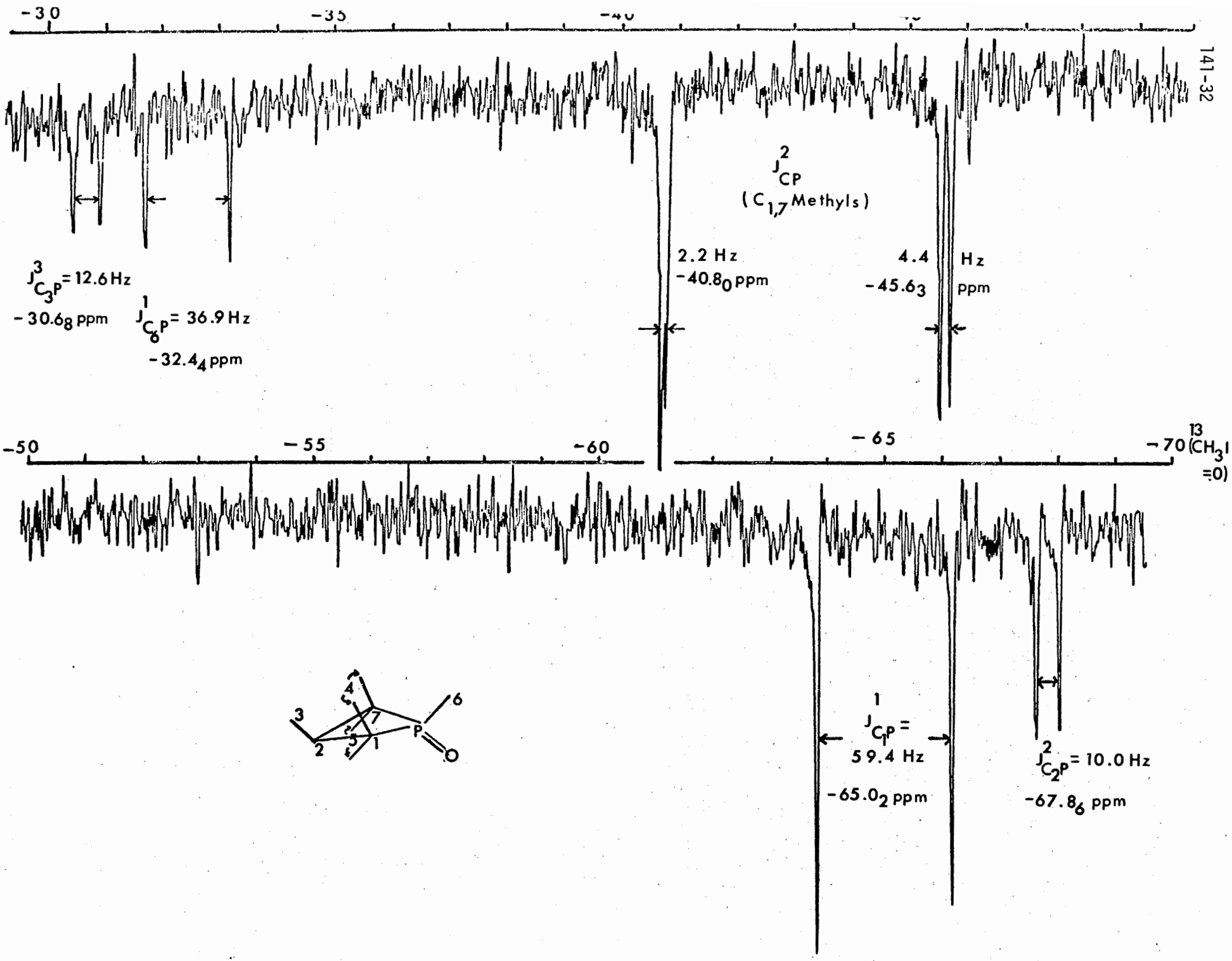
GAG:nw

P.S. Barry - Our normal summer daily high temperature is in the mid seventies. How's it doing down there?

George:

Our normal <u>winter</u> daily high temperature is in the mid 60's!

BLS


-30
-35
-40
141-32
J^{2}_{CP}
($C_{1,7}$ Methyls)
2.2 Hz
-40.8$_0$ ppm
4.4 Hz
-45.6$_3$ ppm
$J^{3}_{C_3P}$= 12.6 Hz
-30.6$_8$ ppm
$J^{1}_{C_6P}$= 36.9 Hz
-32.4$_4$ ppm
-50
-55
-60
-65
-70
^{13}(CH_3I =0)
$J^{1}_{C_1P}$ = 59.4 Hz
-65.0$_2$ ppm
$J^{2}_{C_2P}$= 10.0 Hz
-67.8$_6$ ppm
1
2
3
4
5
6
7
P
O

MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075

May 22, 1970

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

Alternation of Substituent Effects in Some Difluorocyclopropanes

Dear Barry:

We have synthesized a number of 1-chloro-1-fluoro and 1,1-difluorocyclopropanes substituted at C-2 and analyzed their spectra. The principal results are summarized graphically in the accompanying figure. J_{F_1X} and J_{F_2X} which are part of the fragment F H C-C-R decrease as the electronegativity of R($Si(OEt)_3$, C_6H_5, OAc) increases. But J_{F_1A}, J_{F_1B}, J_{F_2A} and J_{F_2B} which are part of the fragment F H C-C-C-R all increase as the electronegativity of R increases. This is a dramatic example of an effect noted by Schaefer[1] and Castellano[2] for proton-proton coupling. An angular dependence of the substituent effect on coupling constants is also evident since F_2 coupling with protons A, B and X shows a greater dependence on the electronegativity of R than does F_1 coupling with protons A, B and X. The electron withdrawing ability of R must have a greater effect on F than H and it must also be more efficient when the dihedral angle is 0° (as it is for F_2) than when it is 144° (as it is for F_1). This alternation in substituent effects with the number of intervening bonds is obviously related to the alternation in charge densities calculated by Pople and Gordon.[3]

Sincerely yours,

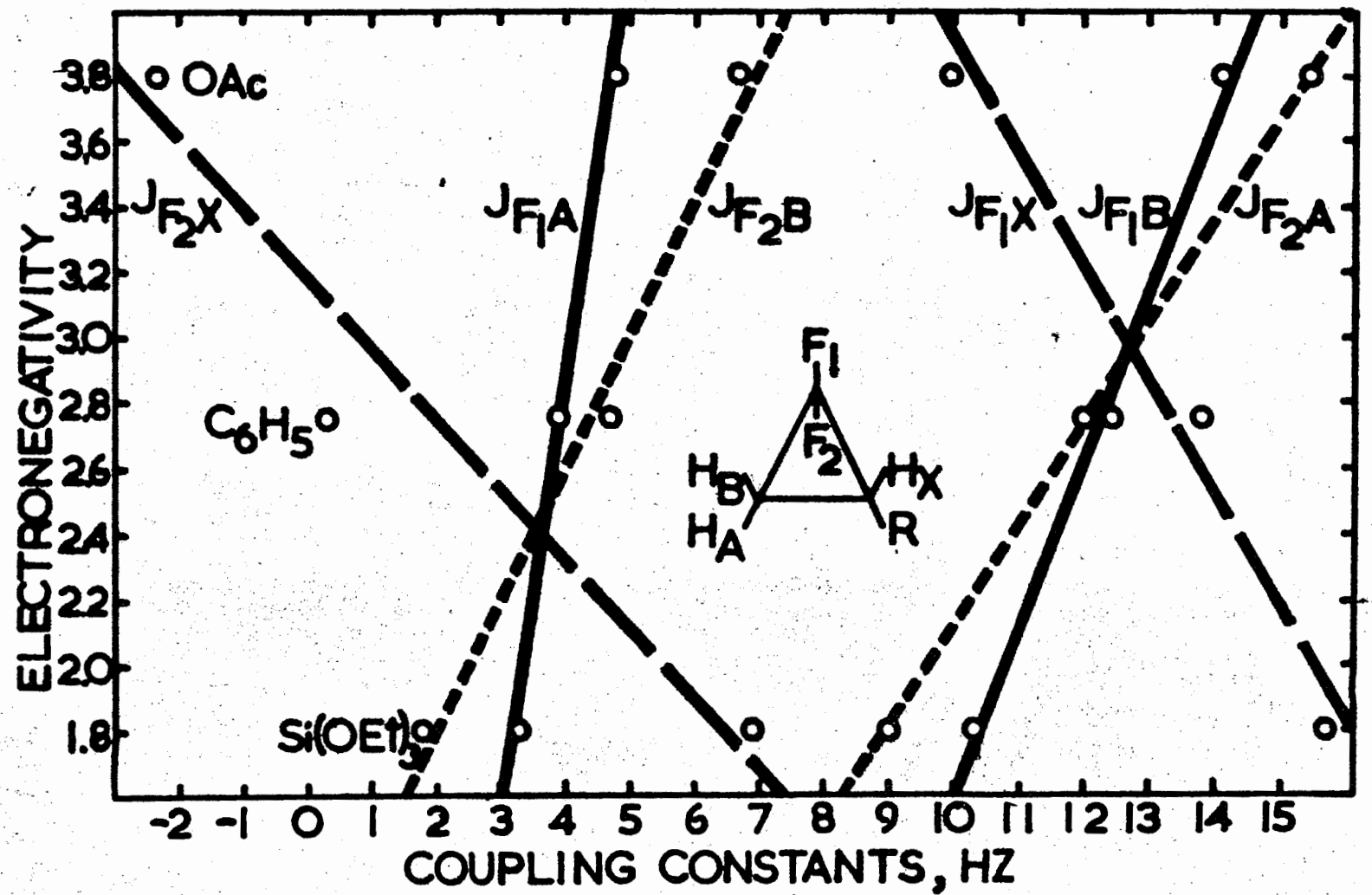
Elaine Stedman

D. Elaine Stedman
Northwestern University

Ken Williamson

Kenneth L. Williamson
Professor of Chemistry

1) Schaefer, et al., Can. J. Chem., 43, 75 (1965); Mol. Phys., 10, 209 (1966).
2) Castellano and Kostelnik, JACS, 90, 141 (1968).
3) Pople and Gordon, JACS, 89, 4253 (1968).


ELECTRONEGATIVITY
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
OAc
J_{F_2X}
J_{F_1A}
J_{F_2B}
J_{F_1X}
J_{F_1B}
J_{F_2A}
C_6H_5O
$Si(OEt)_3$
F_1
F_2
H_B
H_X
H_A
R
-2 -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
COUPLING CONSTANTS, HZ

הטכניון - מכון טכנולוגי לישראל
TECHNION — ISRAEL INSTITUTE OF TECHNOLOGY

הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

25 May 1970

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

A.f.p.: attachment to DP-60

Dear Professor Shapiro,

We have constructed a trapezoidal sweep unit for T_1 measurements by the adiabatic fast passage (a.f.p.) technique. The details of the unit are given in the attached figures. The sweep width is $\pm$ 10 Gauss in 10 msec<t'<10sec. The hold times between sweeps are 1 msec<t''<10sec. These time limits can be changed. Sweep times are independent of hold times. The up-and down-field sweeps can be made unequal in time by disconnecting RV1a from RV1b.

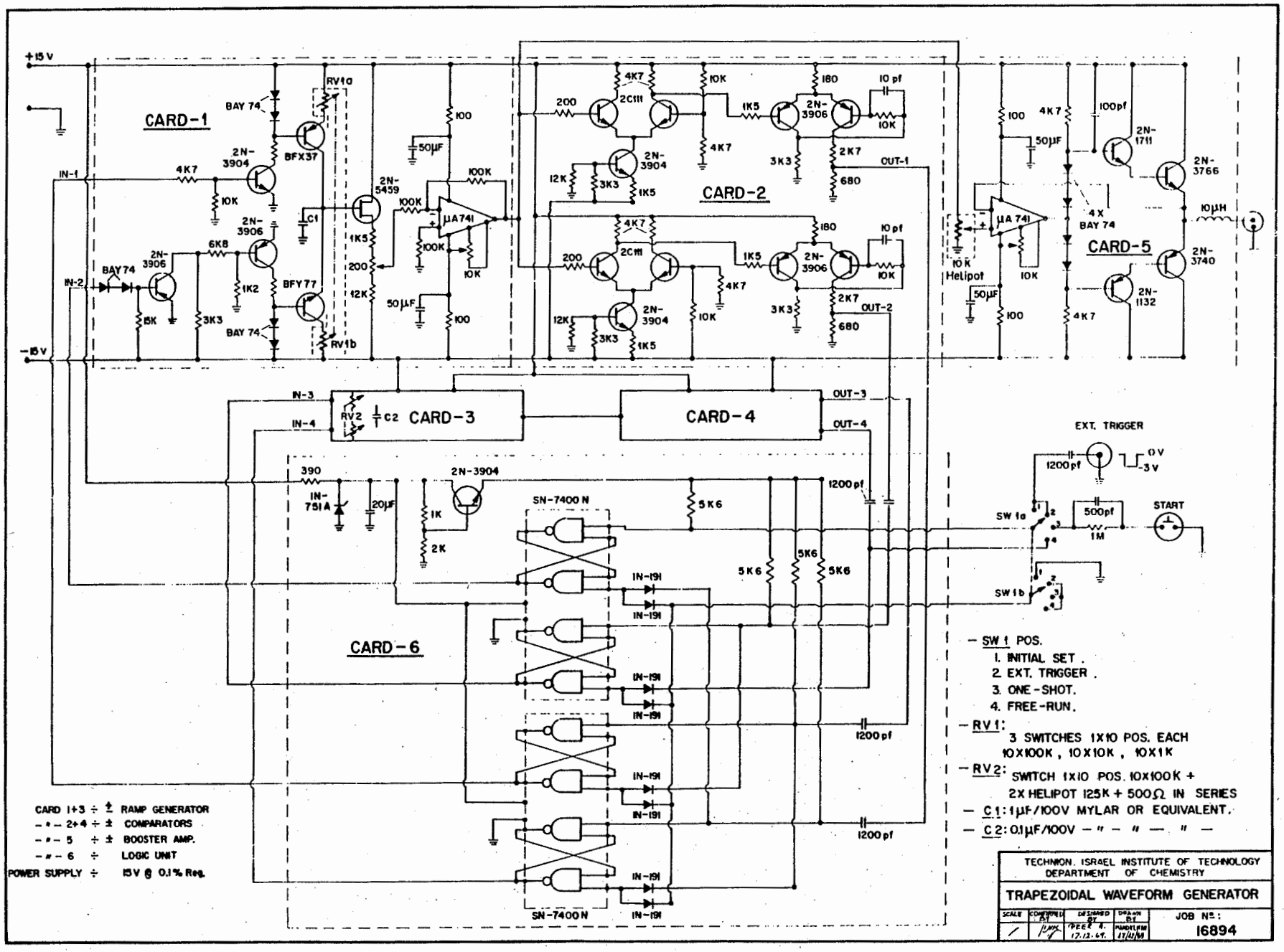
We are busy measuring ^{59}Co T_1's in various complexes and hope to report the results soon. We use a C-1024 to improve the S/N.

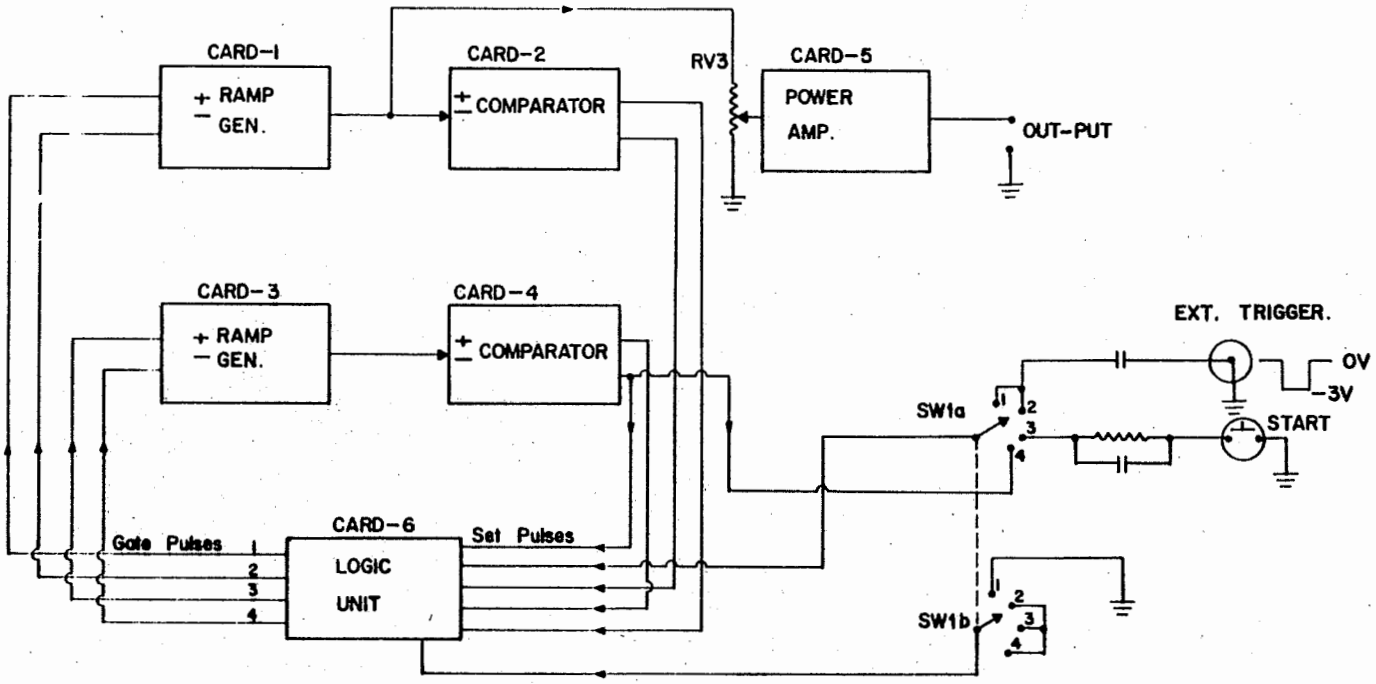
Yours sincerely,

A. Peer

A. Peer

P.S. Please credit this contribution to Prof. A. Loewenstein.


+15 V
-15 V
CARD-1
CARD-2
CARD-3
CARD-4
CARD-5
CARD-6
IN-1
IN-2
IN-3
IN-4
OUT-1
OUT-2
OUT-3
OUT-4
BAY 74
BFX37
BFY77
2N-3904
2N-3906
2N-5459
2C111
2N-1711
2N-3766
2N-3740
2N-1132
μA 741
IN-751A
IN-191
SN-7400 N
RV1a
RV1b
RV2
C1
C2
4K7
10K
6K8
1K2
15K
3K3
100K
1K5
200
12K
680
2K7
180
10 pf
100
50μF
20μF
390
1K
2K
5K6
1200 pf
100pf
10μH
10K Helipot
4 X BAY 74
EXT. TRIGGER
0 V
-3 V
1200 pf
500pf
1M
START
SW 1a
SW 1b
CARD 1+3 ÷ ± RAMP GENERATOR
-*- 2+4 ÷ ± COMPARATORS
-*- 5 ÷ ± BOOSTER AMP.
-*- 6 ÷ LOGIC UNIT
POWER SUPPLY ÷ 15V @ 0.1% Reg.
- SW 1 POS.
1. INITIAL SET.
2. EXT. TRIGGER.
3. ONE-SHOT.
4. FREE-RUN.
- RV 1: 3 SWITCHES 1X10 POS. EACH 10X100K, 10X10K, 10X1K
- RV 2: SWITCH 1X10 POS. 10X100K + 2X HELIPOT 125K + 500Ω IN SERIES
- C 1: 1μF/100V MYLAR OR EQUIVALENT.
- C 2: 0.1μF/100V - " - " - " -
TECHNION. ISRAEL INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
TRAPEZOIDAL WAVEFORM GENERATOR
SCALE
CHECKED BY
DESIGNED BY PEER A. 17.12.69.
DRAWN BY HANDLEIM 17/12/69
JOB Nº: 16894



CARD-1 ÷ (upward + downward) SWEEPS TIME. SET BY (RV1 x C1)
CARD-2 ÷ (up + down) LEVEL COMPARATORS.
CARD-3 ÷ (upper + lower) HOLD TIME. SET BY (RV2 x C2)
CARD-4 ÷ (upper + lower) LEVEL COMPARATORS.
CARD-5 ÷ POWER AMPLIFIER TO PROBE MOD. COIL.
CARD-6 ÷ LOGIC UNIT CONTROLS RAMP CARDS.
RV3 ÷ OUT-PUT VOLTAGE CONTROL.

— SW1 POS.

1. INITAL SET.
2. EXT. TRIGGER.
3. ONE - SHOT.
4. FREE - RUN.

TECHNION. ISRAEL INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY

TRAPEZOIDAL WAVEFORM GENERATOR

SCALE	CONFIRMED BY	DESIGNED BY	DRAWN BY	JOB N° :
			Haezrahi Sima.	16894

BROWN UNIVERSITY *Providence, Rhode Island • 02912*

DEPARTMENT OF CHEMISTRY

26 May 1970

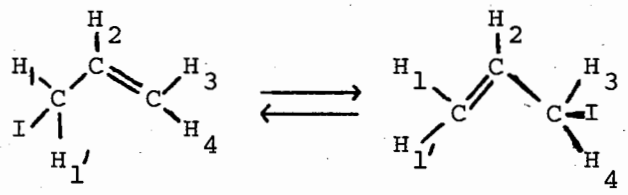
Professor Bernhard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Evidence for Iodine Atom Transfer During Reactions Exhibiting CIDNP.

Dear Professor Shapiro:

During our studies of chemically induced dynamic nuclear polarization (CIDNP), we have obtained nmr spectra which seem to indicate the presence of a rapid iodine atom exchange reaction catalyzed by reactive alkyl and aryl free radicals.

The reaction under investigation was between allyl iodide and free radicals produced by thermal decomposition of acyl peroxides[1]. The iodide exhibits selectively broadened nmr lines (Fig. 1b, c) during the peroxide decomposition which is complete in a few minutes at 100°C. The appearance of sharp outside lines in the multiplet at 5.7 ppm, arising from the proton at the 2-position, is characteristic of a correlated chemical exchange process such as (1)

(1) 

This is accomplished via the reaction sequence (2) - (4).

(2) $(RCO_2)_2 \xrightarrow{k_2} 2CO_2 + 2\,R^{\cdot}$

(3) $R^{\cdot} + ICH_2CH{=}CH_2 \xrightarrow{k_3} RI + {\cdot}CH_2CH = CH_2$

(4) $CH_2{=}CHCH_2I + {\cdot}CH_2CH{=}CH_2 \underset{k_4}{\rightleftharpoons} CH_2{=}CHCH_2{\cdot} + ICH_2CH{=}CH_2$

Unfortunately, we have so far been unable to increase the broadening effects to the point where the lines from H-1, H-1' (3.4 ppm) and H-3, H-4 (4.5-5.0 ppm) coalesce, as they should. This will require some type of steady state measurement, e.g. by using a flow system, since the reaction would be over before even a partial scan could be completed. Furthermore, when the rate of reaction is increased, CIDNP in the products of the reaction (1,5-hexadiene, allyl benzene, undecene, etc.) ensues and makes the spectrum much more difficult to interpret. CIDNP can, in fact, be seen in Figure 1c at 2.8 ppm for protons in undecyl iodide formed from undecyl radicals by reaction (3).

If we optimistically assume that the broadening arises from the simple scheme (2)-(4), we can use the absence of broadening of the lines at 5.3 and 6.0 ppm and the known proton hyperfine splittings in the allyl radical to place a lower limit on the length of time the nuclei in allyl iodide are subjected to the field of the unpaired electron. This yields a lower limite of about 10^7 M^{-1} sec^{-1} for k_4 and confirms our previous hypothesis [1] that iodine transfer reactions can compete successfully with radical recombination.

(1) H.R. Ward, R.G. Lawler and R.A. Cooper, Tetrahedron Letters, 1969, 527.

Sincerely yours,

Ronald G. Lawler

Ronald G. Lawler
Harold R. Ward
Richard Allen

rgl:er

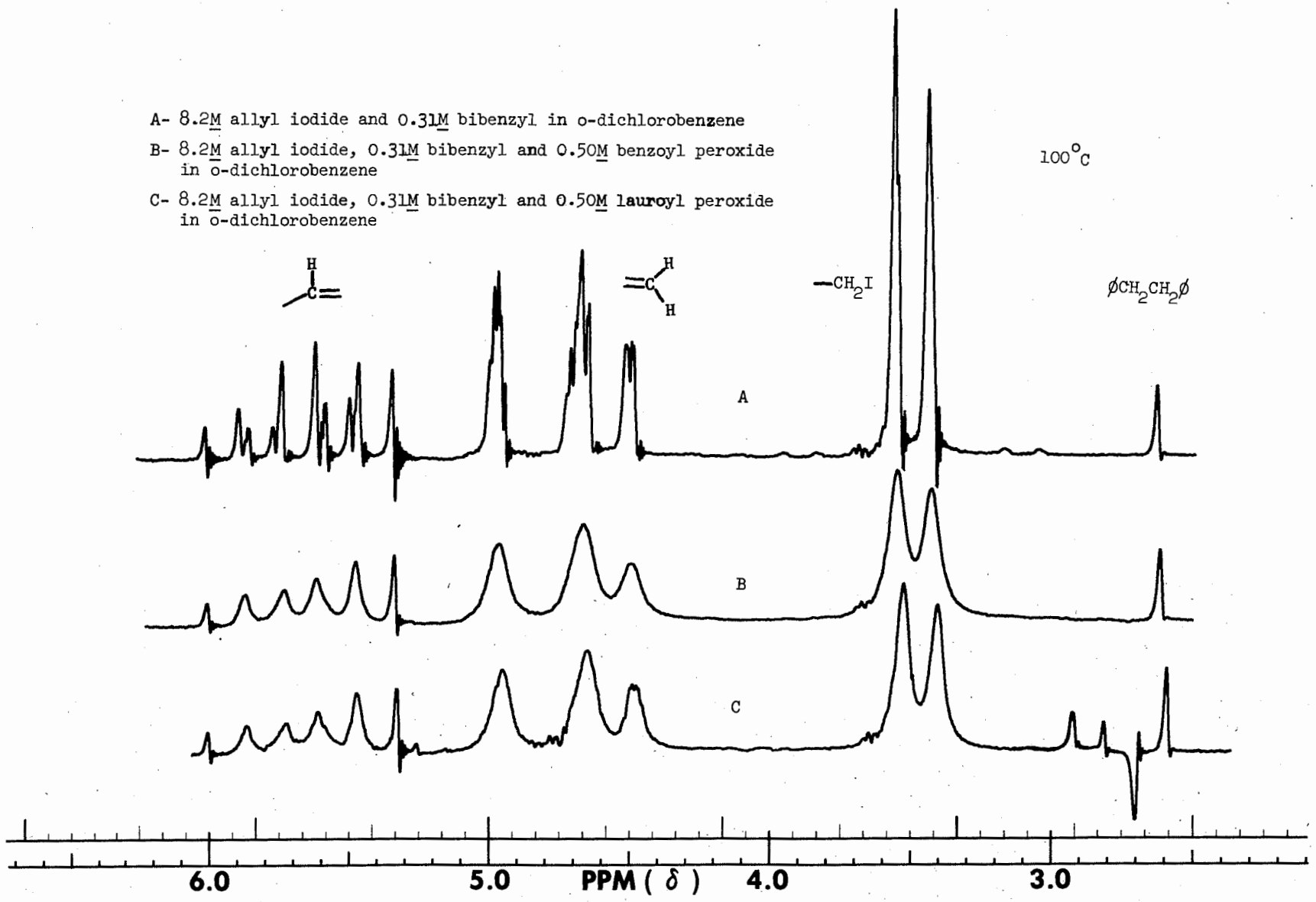

A- 8.2M allyl iodide and 0.31M bibenzyl in o-dichlorobenzene
B- 8.2M allyl iodide, 0.31M bibenzyl and 0.50M benzoyl peroxide in o-dichlorobenzene
C- 8.2M allyl iodide, 0.31M bibenzyl and 0.50M lauroyl peroxide in o-dichlorobenzene
100°C
—CH2I
ØCH2CH2Ø
A
B
C
6.0
5.0
PPM (δ)
4.0
3.0

FIGURE 1

DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

May 27, 1970

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

^{13}C Contact Shift Studies

Dear Professor Shapiro:

We make apology for the delay in sending our contribution.

Recently nmr contact shifts have been extensively studied for various paramagnetic systems including transition metal complexes and organic free radicals.[1] However, studies of contact shifts for nucleus other than proton have been quite limited. The study on the ^{13}C contact shifts possibly provides fruitful informations about the mode of electron spin distribution on the carbon skeleton.

In collaboration with K. Goto (JEOL Co. Ltd.) we have observed ^{13}C shifts for pyridine and aniline derivatives in the absence or presence of nikel(II) acetylacetonate ($Ni(AA)_2$), using proton decoupled ^{13}C nmr technique. Large, concentration-dependent chemical shifts arom the value in the diamagnetic ligand were observed for ^{13}C resonances of various ligand molecules when these are placed in liquid or in chloroform solution containing the paramagnetic metal chelate.
The relative values of the shifts from the diamagnetic value (relative contact shifts) are listed in the Table. The plus and the minus sign mean upfield and downfield contact shifts, respectively.

It is of interst to compare these contact shifts with the relative values of ^{13}C hyperfine coupling constants, a^{13}_{C}, for the free radicals with isoelectronic structure. The pyridine type bases complexed with $Ni(AA)_2$ may correspond to phenyl radical (typical σ radical) and aniline to benzyl radical. Because of lack of the observed a^{13}_{C} data for these radicals, MO theorefical values obtained by Pople et al. using unrestricted Hartree-Fock method (INDO calculation)[2] are listed in the Table. In the Table are also given relative proton contact shifts together with calculated (INDO method) a_H for the corresponding radical.[2] The correspondence between observed contact shifts and theoretical hyperfine coupling constants is fairly satisfactory for aniline and pyridine. For pyridine and piperidine, all the protons experience downfield contact shifts and this has been interpreted in term of electron spin delocarization through the lone pair orbital.[1] While in the ^{13}C resonance showing alternating contact shifts, it is revealed that spin polarization is of importance in the mechanism of electron spin transfer through the carbon skeleton.

The similar studies for other nigrogen-containing molecules will be published shortly.

Yours sincerely,

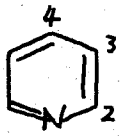
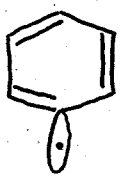
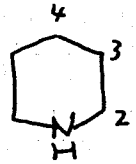
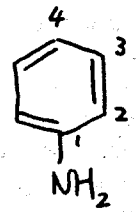
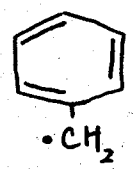
I. Morishima

T. Yonezawa

References

1. D. R. Eaton and W. D. Phillips, Advances in Magnetic Resonance, Vol. 1, p103, Academic Press, New York, 1965; T. Yonezawa, I. Morishima and Y. Ohmori, J. Am. Chem. Soc., 92, 1267(1970); T. Yonezawa, I. Morishima, Y. Akana and K. Fukuta, Bull. Chem. Soc. Japan, 43, 379(1970).
2. J. A. Pople, D. L. Beveridge and P. A. Dobosh, J. Am. Chem. Soc., 90, 4201(1968).

Table Relative ^{13}C and ^{1}H Contact Shifts

Ligand	Position	^{13}C-C.S.	^{1}H-C.S[a]	Radical	Calcd[b] a^{13}_C	a^{1}_H
	2	10.0	-10.0		-10.0	10.0
	3	-16.7	-2.9		22.3	3.3
	4	4.5	-0.8		-5.4	2.1
	2	10.0	-10.0			
	3	-16.0	-4.7			
	4	—	-1.1			
	1	10.0	—		10.0	
	2	-8.9	10.0		9.5	-10.0
	3	3.4	-4.2		-6.9	5.6
	4	-5.6	10.0		8.3	-8.7

a) Ref. 1.

b) Ref. 2.

141-44

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FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

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

Uw kenmerk | Uw brief van | Ons kenmerk

Datum 28-5-1970.

Onderwerp Fermi Contact NMR Shifts in Solvation Complexes of Ionpairs of Aromatic Radical Anions.

Dear Professor Shapiro,

The proton NMR solvent shift for ethereal solutions of aromatic hydrocarbon radical anions is often considerably less than the value theoretically predicted for solutions of paramagnetic species. The upfield paramagnetic bulk susceptibility shift appears to be partially balanced by a downfield shift, probably because a fraction of solvent molecules is specifically coordinated to the radical anion pair, and therefore in close contact with the unpaired electron.

We observed a striking example of this effect for glyme complexes of the sodium salt of coronene in THF. Fig. 1 shows the NMR spectrum (taken with a Varian DP 60) of a mixture of aequivalent amounts of coronene$^-$, Na^+ and triglyme (triethyleneglycoldimethylether) in THF at 33°C. The triglyme, all of which is coordinated to the Na^+ ion is forced on top of the aromatic ring and its protons are therefore in close proximity to the unpaired electron. This induces spindensity on the glyme protons, and the resulting Fermi contact shift is evident from fig. 1. The terminal CH_3 protons are shifted 380 cps downfield with respect to the α-THF peaks, while the CH_2 protons are represented by three peaks of equal intensity at 532, 620 and 682 cps downfield from α THF. The detail shown in the NMR spectrum of the glyme is surprising, and we hope that further exploration may yield more information regarding the actual structure of these ionpair complexes. Other glymes (e.g., tetraglyme) show a similar behavior, although the NMR shifts may vary somewhat).

Solvation of the Na^+ by the glyme also results in a change in the solvent shift. While in the absence of glyme a 0.1 M sodium coronene solution in THF at 33° shows a solvent shift of only 3 cps, addition of an aequivalent amount of glyme brings the solvent shift to its theoretical value of 15 cps.

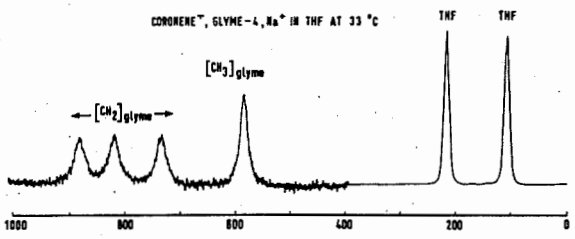

Fig. 1.

The magnitude of the Fermi contact shifts depends on the type of radical anions. Glyme complexes of sodium naphthalene, triphenylbenzene and anthracene show only very small shifts. With triphenylene, shifts up to 200 cps were observed. Apparently, the spindistribution and the size of the aromatic ring play an important role.

Sincerely yours,

(E. de Boer) (A.M. Grotens) (J. Smid)

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DEPARTMENT OF CHEMISTRY

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PROFESSOR B. C. L. WEEDON, D.Sc., Ph.D., F.R.I.C.
PROFESSOR D. C. BRADLEY, D.Sc.

26th May, 1970.

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

Dear Barry,

^{13}C Fourier; Senior Research Assistant Wanted

I would like to advertise in T.A.M.U.N-M-R, a senior position here for work in ^{13}C Fourier n.m.r.

We expect delivery at the end of August, 1970, of a Bruker HFX-90 spectrometer for observation of ^{1}H, ^{2}D, ^{19}F, ^{13}C, ^{14}N or ^{15}N resonances. Heteronuclear locking and broad band, noise, decoupling will also be available. Additionally we shall have a Fourier Transform Accessory employing the Fabritek FT 1074 and the Digital PDP-8/I computor with fast arithmetic unit for ^{13}C (and the other) nuclei.

We require a senior man, on a pay scale to be invented, to take charge of the instrumentation and its service commitments. He will be aided by a technician for routine operation, and also by a research assistant from my group. He should have a good working knowledge of n.m.r. with experience of electronics and instrumentation development as well as an ability to speak to computors. The post is for 3 years in the first instance and we hope that in kudos and salary, it will be at Lecturer level (area £1,600).

Applicants are asked to write to me directly and to ask their referees to do likewise.

Yours expectantly,

Ed

EDWARD W. RANDALL

EWR/TG

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