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Newsletter

No. 191

August, 1974

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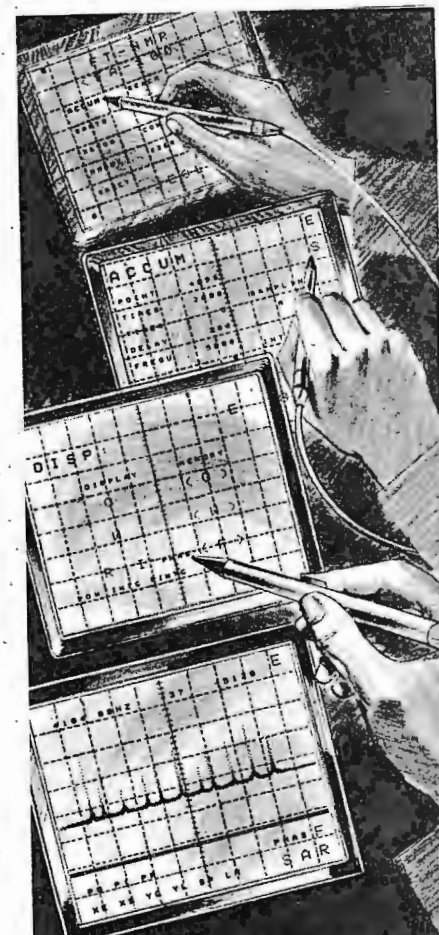
Deadline Dates: No. 192: 2 September 1974
 No. 193: 7 October 1974

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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TEXAS A&M UNIVERSITY

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COLLEGE STATION, TEXAS 77843

5 August 1974

Department of
CHEMISTRYNewsletter Finances and Practical Economies

The Newsletter financial situation continues to be in a most precarious state. Like everything else, our costs are rising markedly and our income is not keeping up with this rise. It is therefore essential that we do everything possible to keep costs down, while at the same time generate the maximum amount of income, if the Newsletter is to survive.

It will be most helpful if all Newsletter subscribers can expedite payment of their annual subscription invoices without delay. Anyone who has not received an invoice by the time they read this notice has the responsibility to let us know immediately. The subscription rates have not increased in the past three years, and only by scrupulous attention to payment matters on the part of all subscribers is it possible for us to try and survive another year at the same rates.

This is certainly the appropriate time and place to say once again what an important and major help with the Newsletter finances has been provided by our Advertisers, Sponsors and Contributors. Please take note of who they are and try to find appropriate ways to let them know directly that their support of the Newsletter is appreciated.

For the coming Newsletter fiscal year, several of our most faithful Advertisers, Sponsors and Contributors have already indicated that they will be renewing their support, some at a substantially higher level than in the past. I am personally not only very grateful for their willingness to do so, but also for the alacrity of their responses to our requests for additional help. Our Newsletter is made possible by a number of individuals who are not only generous but extremely pleasant. The only problem with these very important patrons of the Newsletter is that there are so few of them: all Newsletter subscribers are once again urged to suggest specific contacts in industry or elsewhere where additional advertising and/or sponsorship revenue can be generated. You should also feel free to make appropriate representations to suppliers of hardware, chemicals, etc., with whom you do business to the effect that support of the TAMU NMR Newsletter is worthy of their attention. Only three or four more advertisers per issue would make a major, stabilizing change in the Newsletter finances - conceivably to the point where individual subscription rates could be lowered.

Along the lines of effecting all possible economies, allow me to again make a most strenuous plea for greater care in the preparation of your contributions to the Newsletter contents. Please avoid using half a page for letterhead and inside address, etc., but confine this information to the minimum amount of space. Please avoid the use of wide margins; we *MUST* have 3/4" (2 cm) on both sides and on the top and bottom of each page, but no more please. Single spacing is essential, except where formulas or abundant subscripts, etc., would be a problem. Condense signature space and the spacing of these and references at the end of your letters. Plan your figures carefully, and do not force us to condense your contribution by carving up your figures.

Please adhere to the three-page per contribution maximum. Please do not type or place figures on both sides of a page - one side only!

B. L. Shapiro

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34 0484

TELEGRAMS
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DEPARTMENT OF CHEMISTRY

Parkville, Victoria 3052

25th June, 1974.

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

Dear Dr. Shapiro,

HA-60IL - DIGILAB - PDP-15 Spectrometer

In the past, Drs. Ian Rae and Michael Heffernan at Monash University have kindly allowed us access to the newsletters, which we have found most valuable. Although we have made one contribution previously, on their behalf (TAMU 174-36) we would like to start our own contribution.

In this Department we have a Perkin Elmer R12 for undergraduate and post-graduate use, an HA-100, interfaced to a PDP-15 for C.W. time averaging (^1H and ^{31}P) and an HA-60IL modified for FT operation by DIGILAB and also interfaced to the PDP-15 (^1H and ^{13}C).

Since the third instrument is probably of an unusual configuration other readers may be interested in some of the details. In order to provide for ^1H and ^{13}C pulsed FT operation with deuterium stabilization, DIGILAB supplied a frequency synthesizer (9.2, 15.1 and 60 MHz), 9.2 and 60 MHz transceivers, 400-2 pulser with 15.1 and 60 MHz plug-ins and modifications to our 15.1 MHz V4311 and two probes, V4333 (^1H) and V4336 (^{13}C).

Proton decoupling for ^{13}C operation is achieved by mixing the 60 MHz ("Variable") signal with the digital output of an S.A.I.P. noise generator and amplifying in an E.N.I. 320-L power amplifier. Optimum noise decoupling is achieved with a band width (-3db point) of 450 Hz and 4 watts output to the probe. The S.W.R. is 1.5.

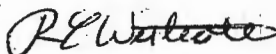
Our home-built interface unit comprises (i) a variable gain (2 to 100) amplifier, (ii) an active filter (4-pole Butterworth) 100-5000 Hz, (iii) a DC offset control (FID baseline must be set at +5 volts above ground for input to the unipolar Raytheon ADC (0 to 10 volts), (iv) an adjustable, 'Lock Gate', and other controls for external frequency sweeping (CW) and for plot-back gain.

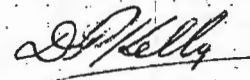
Our 'Mark 1' home-built pulse programmer provides gating pulses for the DIGILAB pulser as well as clock pulses for the ADC. At present we are limited to recycle times of 0.1 to 9.9 seconds and dwell times of 100 to 900 μ sec. Pulse width control is achieved via a DATAPULSE pulse generator. The 90°-pulse time for ^{13}C (ethylene glycol) is 35 μ sec.

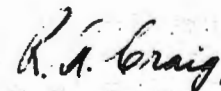
The PDP-15 has 16K core and DECTape. The time domain signal is stored in 4K, the transform in 4K and programs in 4K. These programs, written by R.C.W. with some assistance from R.A.C. provide for all the usual data manipulations. 'Spikes' in the first few locations, resulting from initial transients, are removed prior to transformation of the data. Transformation of 4K data points takes ca. 5 seconds.

Reproduced herewith is a single scan ^{13}C spectrum of 95% ethyl benzene (5% acetone- d_6) in a 12 mm tube showing a S:N of 70:1. Since we have a hybrid system, its performance cannot be predicted. We would therefore welcome comments from interested readers. D.P.K. will be c/- Department of Chemistry, Purdue University, W. Lafayette, Indiana from August 1974 to January 1975.

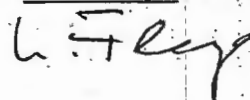
Yours sincerely,


R.C. Westcott.


D. P. Kelly.


R.A. Craig.

U. Flego.



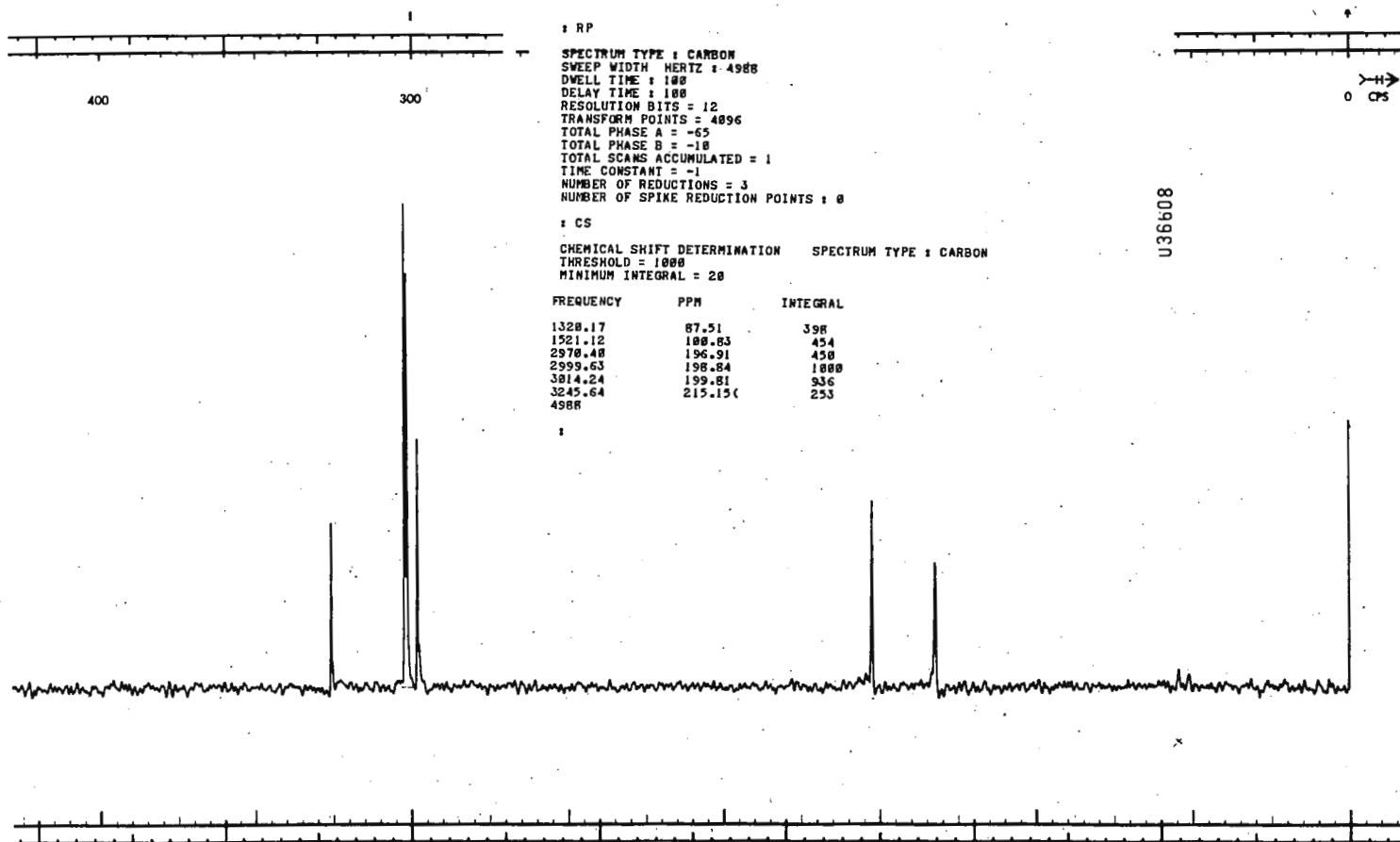
RP

SPECTRUM TYPE : CARBON
SWEEP WIDTH HERTZ : 4988
DWELL TIME : 100
DELAY TIME : 100
RESOLUTION BITS : 12
TRANSFORM POINTS : 4896
TOTAL PHASE A : -65
TOTAL PHASE B : -10
TOTAL SCANS ACCUMULATED : 1
TIME CONSTANT : -1
NUMBER OF REDUCTIONS : 3
NUMBER OF SPIKE REDUCTION POINTS : 0

CS

CHEMICAL SHIFT DETERMINATION SPECTRUM TYPE : CARBON
THRESHOLD : 1000
MINIMUM INTEGRAL : 20

FREQUENCY	PPH	INTEGRAL
1320.17	87.51	398
1521.12	100.63	454
2970.40	196.91	450
2999.63	198.84	1000
3814.24	199.81	936
3245.64	215.15	253
4988		



U36608

HA-60-H/DA-60-H SPECTRUM

15
13C
SPECTRUM NO. 13C
OPERATOR: DPK DATE: 7/4/74
SAMPLE: COTYL. BENTONITE 95%
46 centine

GAIN 20
FILTER 5000

Pulse width 25 μ sec (90°)

4fc 4+

4ft 900

8/width 450 Hz } decoupling
Power 100dB (a width)

2c Re gain 200
5 no

	¹³ C	² H	¹ H
SOLVENT			
TEMPERATURE			°C
FREQ. RESPONSE			cps
R.F. ATTENUATOR	17	0	dB 30
SWEEP TIME			sec
SWEEP WIDTH	4988		cps
SWEEP OFFSET			cps
LOCK SIGNAL			
FIELD MILLIGAUSS (MAN. OSC. FREQ.)		0.7	mG
FIELD MILLIGAUSS (SWEEP FREQ.)			mG
FIELD SWEEP	<input type="checkbox"/>		
SA			
FREQ. SWEEP	<input type="checkbox"/>		

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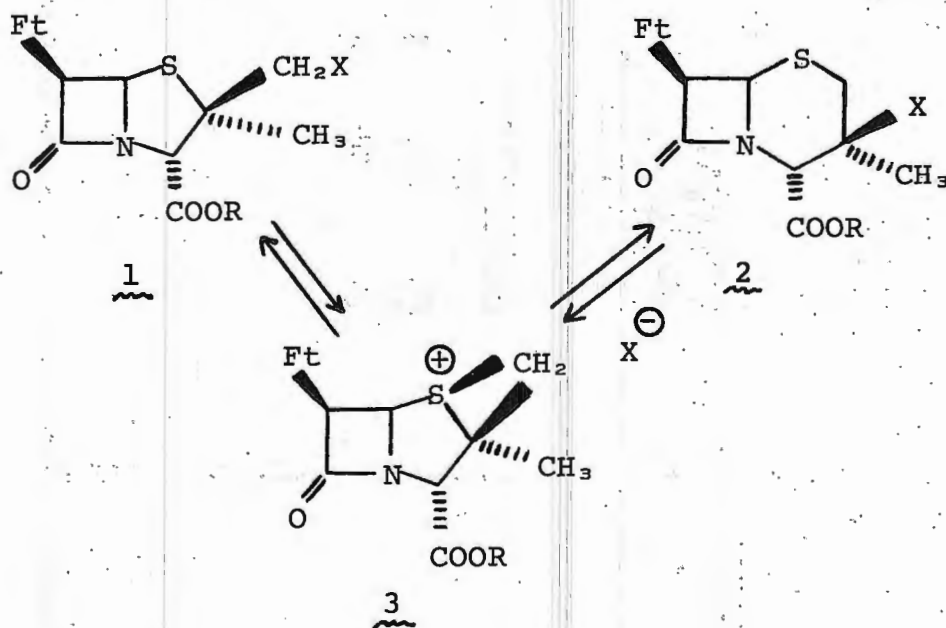
July 2, 1974

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

Dear Professor Shapiro:

^{13}C NMR Spectroscopy of β -Lactam Antibiotics

During studies directed toward the interconversion of penicillin and cephalosporin antibiotics, Stephan Kukolja and co-workers here at Lilly have found that penam derivatives such as 1 can be readily converted to cephams (2) [cf. S. Kukolja and S. R. Lammert, *J. Amer. Chem. Soc.*, 94, 7169 (1972)]. In some cases--for example, when X is Br or ONO_2 --rearrangement of 1 to 2 takes place in the solid state! Such conversions presumably occur through the intermediacy of the episulfonium ion 3.



Professor B. L. Shapiro

July 2, 1974

Because ion 3 can be opened by X^- to either 1 or 2, its generation during chemical reactions leads to mixtures of these two products. Using 1H nmr spectroscopy, it is frequently difficult to distinguish between 1 and 2. Inspection of these two structures shows that the general features of the 1H nmr spectra will be identical: a methyl singlet, an AB pattern due to the methylene, a one-proton singlet, and a second AB (or AX) pattern due to the azetidinone methines. Arguments based on 1H chemical shifts or long-range proton-proton couplings seldom suffice to distinguish between penam and cepham structures.

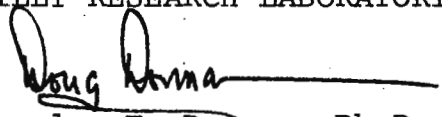
Fortunately, structures 1 and 2 can be easily distinguished by ^{13}C nmr spectroscopy. The easiest method relies on the chemical shift of the methylene carbon, which is easily identified by off-resonance decoupling. In 2, this carbon is substituted by sulfur and carbon, two atoms which are known to exert only moderate α effects. In 1, the methylene is substituted by X, which, by chemical necessity, is electro-negative and therefore leads to substantially larger α effects. As a result, the methylene resonance of basic structure 2 occurs at 35 ± 4 p.p.m., while those of 1 have never, in our experience, occurred above 41 p.p.m.

Of course, the methine carbon resonances can also be easily identified by off-resonance decoupling. This permits a second way of distinguishing between penam and cepham systems. We have found that the sums of the methine carbon chemical shifts of 1 are uniformly about 20 p.p.m. toward lower field than the analogous sum of 2. This parallels the dependence of shielding on ring size noted for furanose and pyranose sugars [cf. A. S. Perlin et al., *Ann. N. Y. Acad. Sci.*, 222, 935 (1973)] and suggests that such a dependence is a widespread and therefore useful phenomenon.

A more complete report of these results is in preparation.

Best regards,

LILLY RESEARCH LABORATORIES


Douglas E. Dorman, Ph.D.
Physical Chemistry Research
Department MC525

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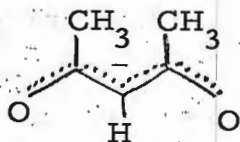
DEPARTMENT OF CHEMISTRY

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

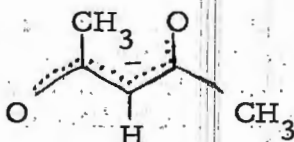
Dear Professor Shapiro:

The Effect of Crown Ether upon the Conformational Equilibrium of Sodium Acetylacetonate

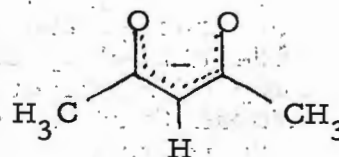
We have examined the low-temperature pmr spectra of sodium acetylacetonate in pyridine- d_5 , and have added different amounts of 18-crown-6 to complex with Na^+ and promote dissociation of the sodium enolate. The Z, Z conformation of the free anion might be expected to suffer considerable



E, E-1



E, Z-1



Z, Z-1

destabilization from coulombic repulsion between the two oxygen atoms, but chelation to Na^+ should stabilize this configuration. In the absence of the cation, the E, Z or E, E conformation could predominate because of a more favorable separation of the carbonyl oxygens in these conformations.

Spectra were taken under the following conditions: (a) -50° , crown/enolate ratio 1.6; (b) -44° , crown/enolate ratio 1.6; (c) -50° , crown/enolate ratio 3.7.

The observation of two methyl singlets of unequal intensities at δ 2.09 and 2.38, as well as two methine signals at 5.48 and 6.05, indicates the presence of Z, Z-1 and E, E-1 in equilibrium. If E, Z-1 were present, it

should give rise to two equally intense singlets, and its presence in significant amounts can therefore be excluded. A straightforward assignment of configuration can be based upon the changes in peak ratios as a function of the crown ether concentration. Thus, an increase in the crown/enolate ratio from 1.6 to 3.7 (spectra a and c) decreases the intensity of the upfield methyl and methine singlets. These resonances must arise from Z, Z-1, whose concentration is lowered as a result of the decreased concentration of sodium ion available for complexation, and the low field singlet of each set must then be due to uncomplexed E, E-1.

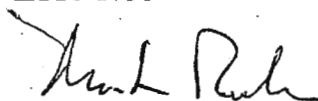
The ratio of E, E to Z, Z conformations decreases at higher temperatures, as shown in spectra a and b. An increase of only 6° lowers the percentage of E, E-1 from 30% to 23%. In another experiment with the same crown/enolate ratio, the percentage decreased from 41% at -65° to 25% at -46°.

Complete line shape analysis at the coalescence temperature, -21° C, afforded a first order rate constant of 30 sec⁻¹ for conversion of E, E-1 to Z, Z-1, which corresponds to a free energy of activation of 12.9 kcal/mol. The barriers for related R COXCOR systems are in the order expected for increased C-X double bond character as the electronegativity of X is decreased: diacetamide, ¹ X = NH, 10.8 kcal/mol, and formic anhydride, ² X = O, 4.4 kcal/mol.

Sincerely,

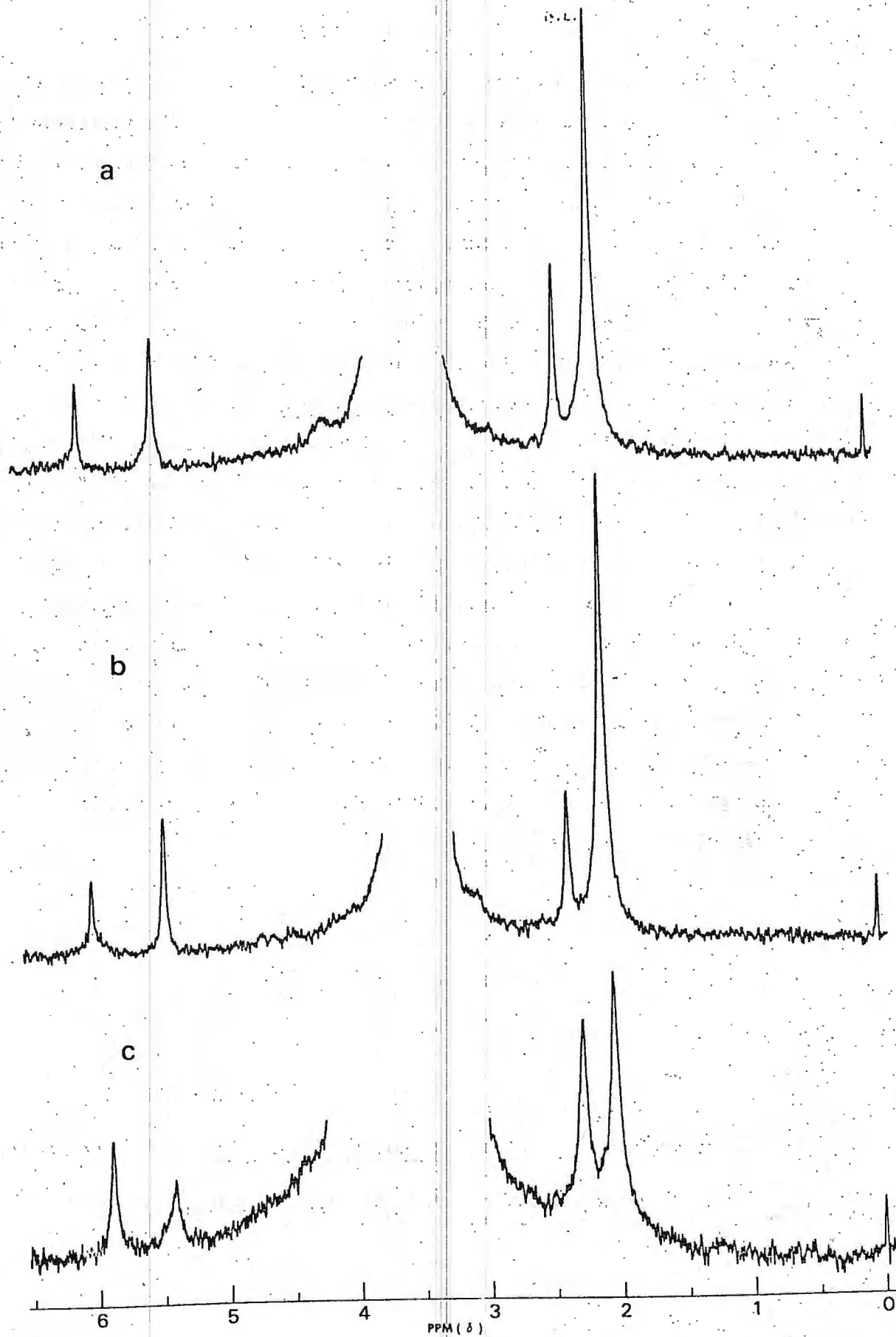


Eric Noe



Morton Raban

1. E. A. Noe and M. Raban, J. Amer. Chem. Soc., 95, 6118 (1973).
2. E. A. Noe and M. Raban, J. C. S. Chem. Comm., 1974, 479.



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PARIS, le 5 juillet 1974

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

Dear Professor Shapiro

A new computer programme called DECHAMIT¹ has been developed in these laboratories for the resolution of 1/2 spin systems. The general procedure is well-known^{2,3} but in order to facilitate data handling for our students it was found advantageous to incorporate certain modifications to the so-called standard programmes.

The 2^n observed energy levels (E_{obs}) and the associated errors (ϵ_i) are calculated from m observed lines and their connection numbers determined by the method of least squares. Next an agreement factor

$$\epsilon_E = \sqrt{\sum (E_{\text{obs}} - E_{\text{calc}})^2}$$
 is iteratively minimized by step by step modification of the trial input parameters δ and j , which are monodimensioned in the same array.

Finally the complete spectrum is calculated and the classical Lorentzian profile realised on a listing and Benson plotter.

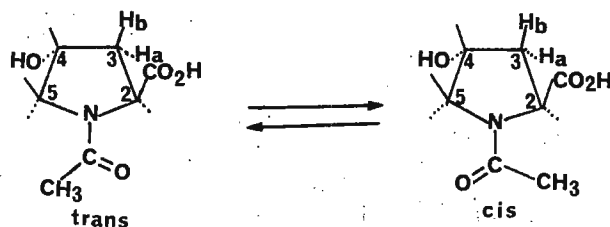
The E_{obs} error (ϵ_i) obtained in the first step is a limit for the final convergence and the line error parameter $\epsilon_v = \sqrt{\sum (v_{\text{obs}} - v_{\text{calc}})^2}$ cannot be less than $\epsilon_i \times (m/2^n)^{1/2}$ where $m > 2^n$.

The initial error ϵ_i is generally due either to imprecise readings of v_{obs} or random fluctuations in the spectrometer recorder - even FT computer data should not be always accepted implicitly !

However a permitted range of 0.2 Hz for each v_{obs} can give a good final convergence provided that the best values be chosen in order to minimize ϵ_i .

As iterative methods are not normally applied to seven spin systems this particular programme is at the moment dimensioned to six spins and it has been useful to use the compressed notation for symmetrical matrices in all the sub-routines. It has also been expedient to make use of the "EQUIVALENCE" FORTRAN IV statement.

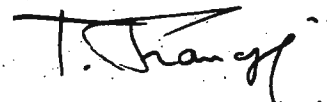
It has proved possible by means of this programme to examine the 2X6 spins pattern of 4-hydroxy-N-Acetyl proline in D₂O and to produce the cis- and trans- conformations superimposed.



You will see that the vicinal J couplings are different in the two conformations on the accompanying Benson curve of the H_{3a}/H_{3b} spectrum run at 300 MHz and thus it is clear that a modification of the averaged cycle geometry occurs by reason of the rotation of the N-acetyl group. More information will be given in a paper which is at present prepared.⁴

Please credit this letter to Bernard ROQUES' account.

Sincerely,


Thierry PRANGÉ

1-Technical data:

a) Average UNIVAC-1108 times:

n=	3	4	5	6 spins
non iterative:	10s	20s	45s	1.5 mn
iterative :	30s	1-2mn	15mn	30mn

b) Size: 8 K octets (6.7 without Benson sub-routines)

18 K in a (REAL*8) off-resonance version (decoupling power and frequency must be added).

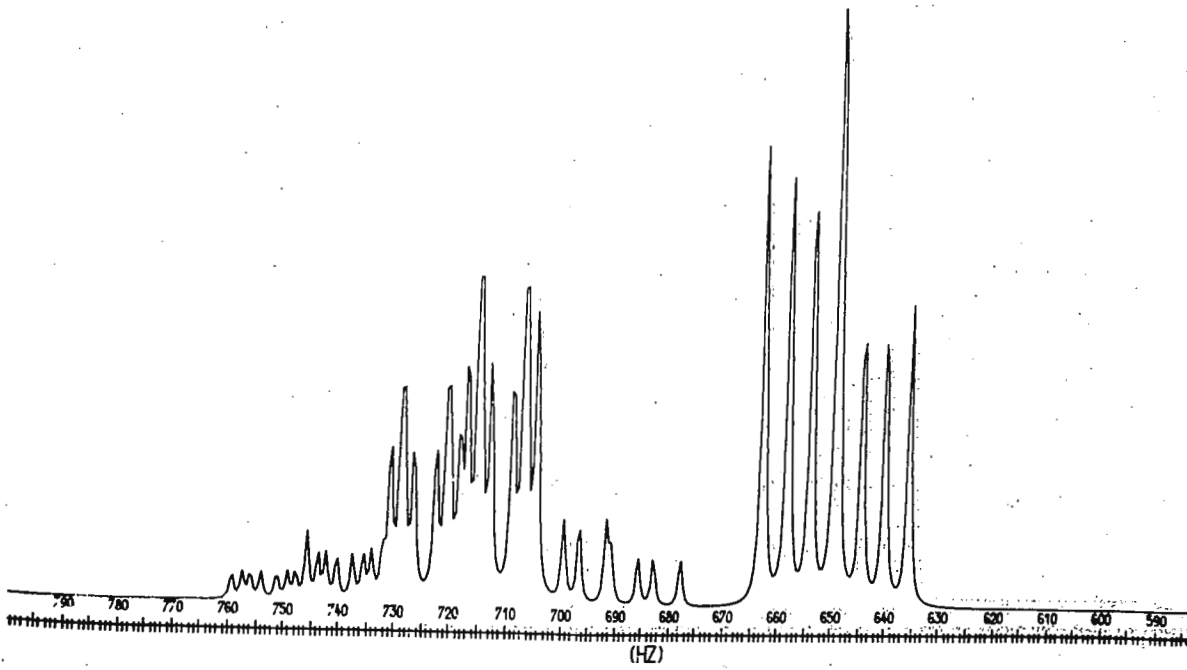
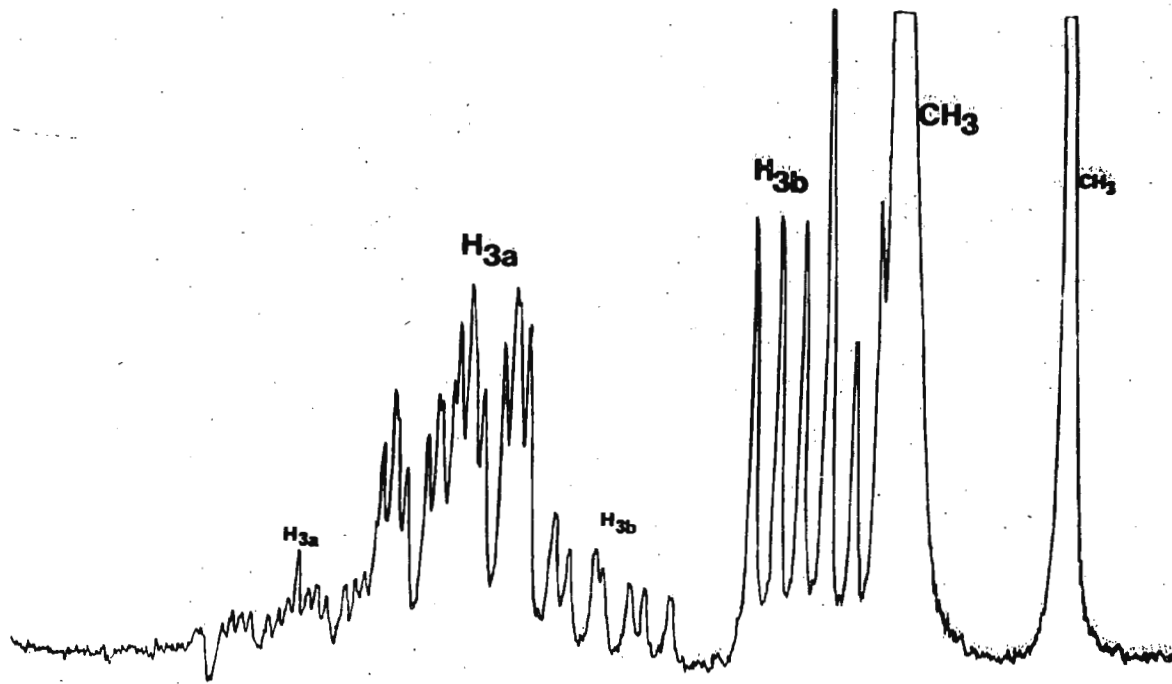
Listings and BCD cards are available upon request.

2- J.D. Swallen and C.A. Reilly, J. chem. phys. 37, 21 (1962);

S. Castellano and A.A. Bothner-By, *ibid.* 41, 3863 (1964).

3-For comparaisons see Y. Kato and A.Saika, *ibid.* 44, 2824 (1966).

4- T. Prangé, C. Garbay-Jaureguiberry, M. Anteunis, B. Roques



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4th July, 1974

RF/EP

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

Dear Barry,

Dipolar Relaxation

My relaxation mechanism is being sorely tried by your barrage of subpoenas. I hope the attached transcript will prove acceptable.

As T_1 gains acceptance as a respectable parameter for high resolution NMR spectra, it is becoming more and more important to discover something about relaxation mechanisms. The key experiment for determining the dipolar contribution to relaxation is of course the well-known internuclear Overhauser effect. Its importance is such that one feels it would have been much more widely employed were it not for the experimental difficulties involved. But the application to homonuclear spin systems, requiring the measurement of small changes in the integral of a signal in coupled and decoupled spectra, is beset by problems of systematic error.

While the Overhauser experiment explores steady-state disturbances of spin populations, the relaxation paths may also be probed in transient experiments. This note describes an alternative method of assessing the dipolar contribution to spin lattice relaxation by preparing the spin populations in various ways and following the rates at which they relax.

The simplest system to think about is a molecule with two spins I and S. We may define the usual relaxation parameters:

$$\rho = 2W_I + W_2 + W_0 \quad (\text{purely dipolar})$$

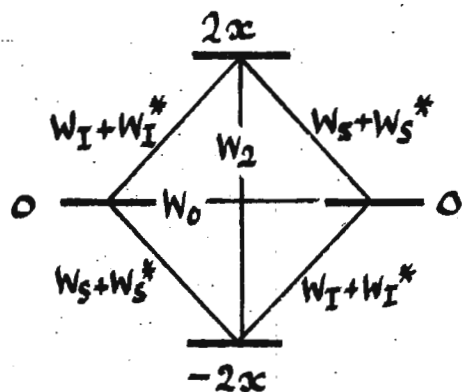
$$\rho^* = 2W_I^* \quad (\text{all other mechanisms})$$

$$\sigma = W_2 - W_0 \quad (\text{cross-relaxation})$$

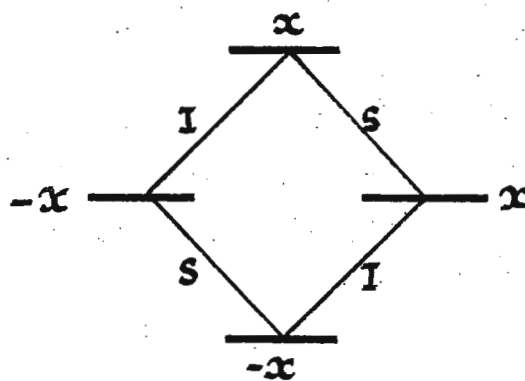
In the limit of high correlation frequencies, $\rho = 2\sigma$ since

$$W_2 : W_I : W_0 :: 12 : 3 : 2$$

We may write the deviations of the spin populations from Boltzmann equilibrium for two different modes of preparation: (a) a non-selective 180° pulse which affects all four lines uniformly, (b) a selective 180° pulse which affects both lines of the I multiplet but leaves the S spin unperturbed.



(a) Non-selective pulse



(b) Selective pulse on I

In case (a) the relaxation is purely exponential and the rate is given by

$$-dx/dt = \rho + \rho^* + \sigma \quad (1)$$

In case (b) the relaxation is only approximately exponential but an initial rate may be defined:

$$-(dx/dt)_0 = \rho + \rho^* \quad (2)$$

We take the ratio of the rate after a non-selective pulse to the rate after a selective pulse on the I spins:

$$R = 1 + \frac{\sigma}{\rho + \rho^*} \quad (3)$$

Now if we consider the relaxation time of the I spins measured under double irradiation conditions where the S spin populations are held saturated, it is readily shown that:

$$1/T_1 = \rho + \rho^* \quad (4)$$

Whereas for exclusively dipolar relaxation,

$$1/T_{1D} = \rho \quad (5)$$

Thus

$$\frac{T_1}{T_{1D}} = \frac{\rho}{\rho + \rho^*} = \frac{2\sigma}{\rho + \rho^*} = 2(R - 1) \quad (6)$$

The determination of R thus gives us the degree to which dipole-dipole interactions control spin-lattice relaxation of the I spins.

The experimental measurement of the two rates is straightforward. Case (a) is the conventional experiment. For case (b) the usual inversion-recovery sequence is modified so as to extend the pulse width of the 180° pulse considerably. For example a width of 50 milliseconds would correspond to a setting of radiofrequency level where $\gamma H_1 / 2\pi = 10$ Hz, which is about the selectivity normally required to perturb one spin multiplet but leave others unaffected. This radiofrequency field would be derived from an auxiliary oscillator that could be tuned into the desired group of lines (the source might be the proton decoupler for example).

The T_{1D} obtained in this way represents the contributions from dipolar interactions of spin I with all other resonant spins S. For proton spectroscopy this would mean interaction with all other protons in the sample. However, it would be possible to examine individual proton-proton interactions if the spin populations were prepared in a slightly different manner - by applying selective 180° pulses to two chemically shifted groups I and S, leaving all other groups S', S'' etc. unperturbed. This experiment would replace the mn-selective preparation to give a rate expressed by Eq (1).

This idea has been used to show that proton relaxation in a pyranose sugar derivative is essentially dipolar; the experiments were carried out in collaboration with Howard Hill at Varian and Laurie Hall at U.B.C. Vancouver.

Happy Thanksgiving,

Ray

Ray Freeman



מכון ויצמן למדע

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ISOTOPE DEPARTMENT

מחלקת איזוטופים

July 5, 1974

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

Dear Barry:

The addition of a lanthanide shift reagent (LSR) to a solution containing an organic molecule (substrate) results in both shifts and line broadenings in the NMR spectrum of the substrate¹. The magnitude of these line broadenings, for a given resonance, varies with the lanthanide used². Under the condition of fast exchange, assuming the exchange is a first order process, the line broadening is given by³:

$$1/T_2 = \sigma/T_{2M} + (1 - \sigma)/T_{2F} + \sigma(1 - \sigma)^2 \tau_M (2\pi\delta_M)^2 \quad (1)$$

where σ is the fractional substrate population in the complexed state; $1/T_{2M}$ and $1/T_{2F}$ are the transverse relaxation rates in the complexed and free states, respectively, δ_M is the chemical shift difference between the two states and τ_M is the mean lifetime in the complex. The last term in equation (1) is referred to as chemical exchange broadening (CEB). For two nuclei within the same molecule, the CEB is generally different (different δ_M 's). Moreover, the CEB term will vary with temperature (via τ_M , δ_M), concentration (via σ) and frequency of measurement (via $2\pi\delta_M$). The ratio of the line broadening of two nuclei within the same molecule can be written as

$$\frac{\Delta W_i}{\Delta W_j} = \frac{\sigma(\frac{1}{T_{2M_i}} - \frac{1}{T_{2F_i}}) + CEB_i}{\sigma(\frac{1}{T_{2M_j}} - \frac{1}{T_{2F_j}}) + CEB_j} \quad (2)$$

Prof. Barry Shapiro

July 5, 1974

If the CEB term is important, the ratio of the line broadening should be dependent on temperature, frequency and concentration of LSR. In addition, different lanthanides may have different relative proportions of the two terms, $(1/T_{2M}, \text{CEB})$. Therefore, the ratio of line broadenings of two nuclei within the same molecule may vary with the lanthanide used. Observations consistent with our interpretation can be found in the literature.^{4,5,6} Additional and conclusive results recently obtained in our laboratory are now being prepared for publication.

Sincerely yours,

*Bob**Jacques*

R.E. Lenkinski J. Reuben

References

1. For review see: J. Reuben, Prog. in NMR Spectrosc., 9, 1 (1973).
2. W. DeW. Horrocks and J.P. Sipe III, J. Amer. Chem. Soc., 93, 6800 (1971).
3. J. Reuben and D. Fiat, J. Chem. Phys., 51, 4918 (1969).
4. G.N. LaMar, TAMU NMR Newsletter, No. 183, p. 6 (1973).
5. M. Okigawa and N. Kawano, Chem. Ind., 850 (1973).
6. J. Reuben and J.S. Leigh, Jr., J. Amer. Chem. Soc., 94, 2789 (1972).

Title: A Comment on Line Broadenings Caused by LSR's



THE UNIVERSITY OF TEXAS AT AUSTIN

AUSTIN, TEXAS 78712

Department of Chemistry

July 8, 1974

Professor Barry Shapiro
 TAMU NMR
 College of Science
 Texas A & M University
 College Station, Texas 77843

Title: Deuteron Relaxation in Liquid Crystals

Dear Barry:

In collaboration with Prof. Bing Fung, University of Oklahoma, and Dr. Richard Orwoll, a former postdoctoral now at Fiber Industries, we have been applying deuteron relaxation to liquid crystals.

The theory of deGennes (1) indicates that in the nematic phase, relaxation is influenced by the orientational fluctuation modes (collective modes). This predicts spin lattice relaxation, $T_1 = f(\omega^{1/2})$ where ω is the Larmor frequency. T_1 can also be influenced by intermolecular diffusion effects which predict $T_1 = f(\omega^{-1/2})$ in the limit of slow diffusion. Both types of frequency dependence have been observed for protons in nematic phases. Various other frequency dependence is predicted (and observed) just above nematic-isotropic phase transition (T_C) depending upon which branch of the collective modes most strongly influences T_1 . Protons have an inherent limitation for use to test relaxation theories: they are subject to intermolecular (diffusion) contributions which are not easily separated from the (intramolecular) collective mode mechanisms except by expensive isotopic dilution studies (2). To avoid this problem we have utilized deuterium relaxation which is almost completely intramolecular. We have studied T_1 of the deuterons in ring deuterated para-azoxyanisole (PAA) and 4,4' diheptyloxyazoxy benzene (HOAB). T_1 increases with temperature across the mesophases. Relaxation is discontinuous at the clearing point with the isotropic phase having the shorter T_1 . In contrast to measurements of deuteron T_1 in other compounds (3), T_1 of the deuterons in PAA is independent of frequency in the range 4.5 to 10.5 MHz (Fig. 1). Deuteron relaxation in oriented samples of HOAB is independent of the angle between the nematic director and the applied field. The apparent lack of sensitivity to collective mode fluctuations is explained on the basis of the molecular geometry of the C-D bond which presumably reduces the relative influence of collective modes and makes other mechanisms, such as molecular tumbling, more effective. 1) P.G. deGennes, *Molec. Cryst. & Liquid Cryst.* **12**, 193 (1971). 2) E.T. Samulski, C.R. Dybowski and C.G. Wade, *Phys. Lett.* **29**, 340 and 1050 (1972). 3) B. deloche and B. Cabane, *Molec. Cryst. & Liquid Cryst.* **19**, 25 (1972).

Yours truly,

Charles G. Wade
 Assoc. Professor

CGW:dj

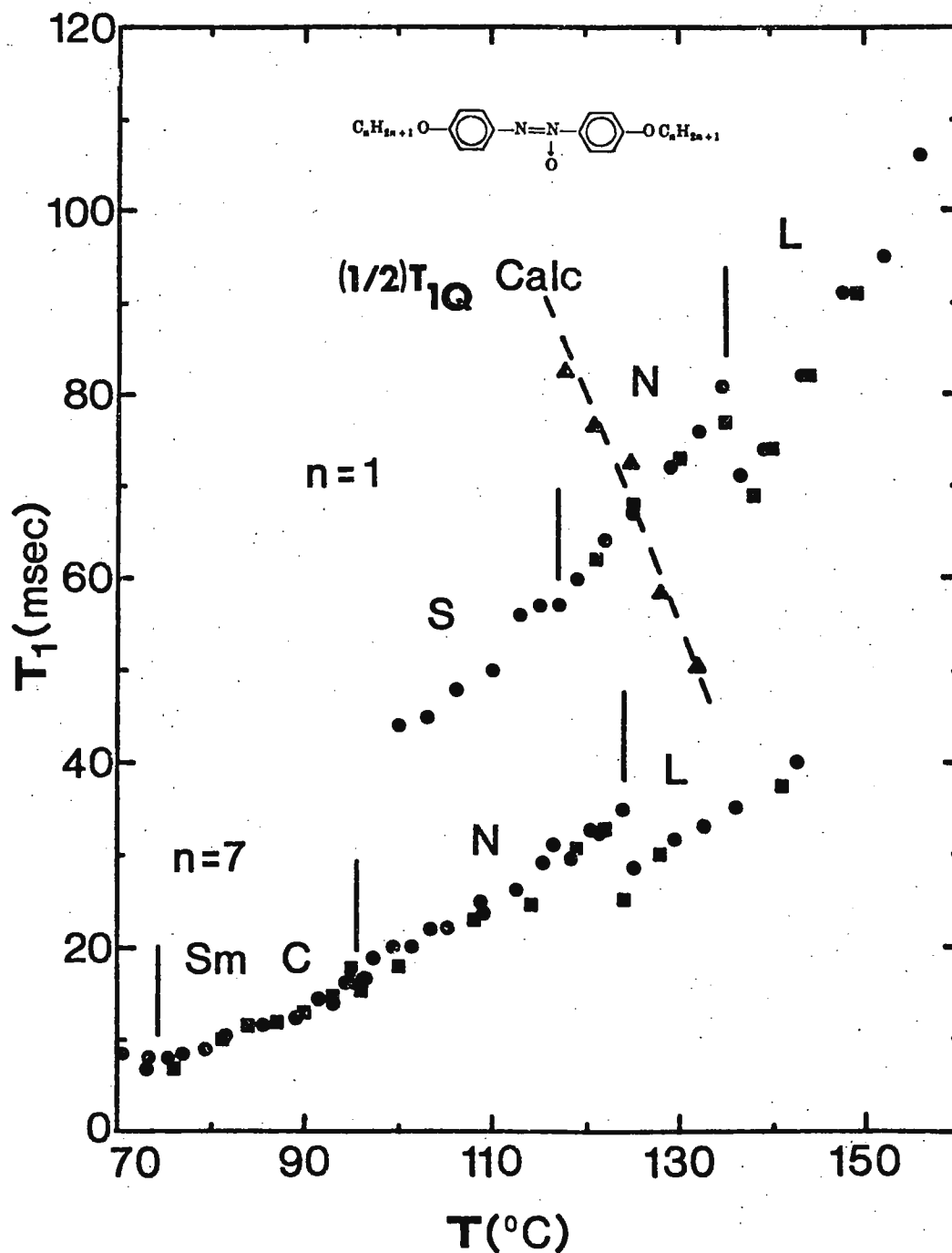


Figure 1. For $n=1$, \bullet -10.5 MHz, cooled; \blacksquare -4.5 MHz heated. For $n=7$, all measurements are at 10.5 MHz: \bullet -cooled, \blacksquare -heated. The line labelled "Calc" is calculated from the theory of Doane and Johnson.


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DEPARTMENT OF CHEMISTRY

CDH/SC

10th July, 1974.

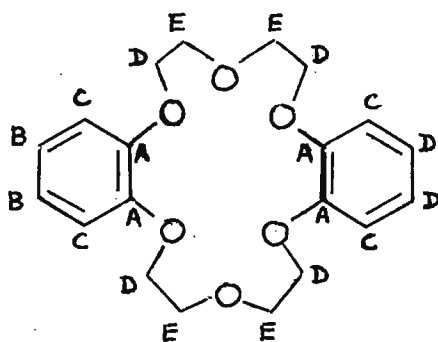
Professor B. L. Shapiro,
Texas A & M University,
College of Science,
College Station,
Texas 77843,
U.S.A.

Dear Professor Shapiro,

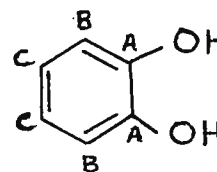
¹³C N.M.R. SPECTRA OF A CROWN ETHER AND ITS POTASSIUM ION COMPLEX

There appears to be little published information concerning the ¹³C spectra of the rapidly developing field of Crown ethers and their cation complexes. Hence, in response to your latest blue note we should like to report our initial findings in this area.

The Table shows the chemical shifts and assignments for (i) dibenzo-18-crown-6 (1), (ii) the 1:1 complex of (1) and potassium iodide and (iii) a 1:1 molar mixture of the complex and (1).



(1)



(2)

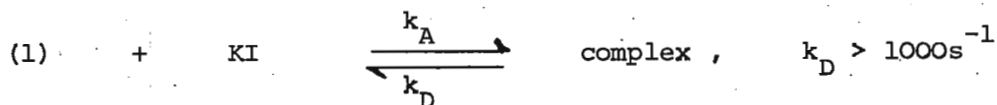
The spectra were run at ambient temperature ($\sim 298^\circ\text{K}$) in 50% MeOH- CDCl_3 as solvent, on a Bruker HFX 90 spectrometer with broad band decoupling and using a Nicolet Fourier Transform system with tetramethylsilane as internal standard. The concentrations of Crown ether (and complex) were maximised at 0.9% ($2.5 \times 10^{-2}\text{M}$) and the quoted chemical shift values are accurate to ± 0.06 ppm. The chemical shift assignments A, B and C are based on a comparison with those for catechol, ¹(2).

^{13}C Chemical shift values, δ (ppm) from TMS in 50% MeOH - CDCl_3

Compound	A	B	δ values (ppm)				MeOH
			C	D	E		
DB-18-C-6 (1)	149.31	121.96	114.41	70.44	69.31		49.95
DB-18-C-6 + 1 : 1 Complex	148.38	122.01	113.11	70.12	68.39		49.95
1 : 1 Complex (1) + KI	147.41	122.11	111.87	69.85	67.53		49.95
(2) *	145.0	122.1	117.3	-	-		-

* In water.

The ^{13}C chemical shift differences between the Crown ether and its complex with KI vary between 0.14 ppm (for $^{\text{C}}\text{B}$) to a maximum of 2.54 ppm (for $^{\text{C}}\text{C}$). These differences are small but two important conclusions may be drawn from the data. First, within experimental error the chemical shifts of the 1 : 1 mol mixture of Crown ether and its complex lie exactly half way between the extremes of Crown ether and complex which confirms the known fact² that the equilibrium constant for complex formation is high ($\log_{10} K \approx 5.0$ with methanol as solvent).^{2,3} Secondly it would appear that since only averaged chemical shifts are observed with the mixtures, the dissociation of the complex is rapid on the ^{13}C nmr time scale. The observation of averaged signals persists down to -60°C (with a little line broadening) and rough calculations reveal that the rate coefficient for the dissociation of the complex at room temperature, k_{D} , is at least 1000s^{-1} .



Thus both association and dissociation in Crown ether complex formation seem to be extremely rapid.

Yours sincerely,

C.D. Hall *Tanner Pomeroy*

1. Varian catalogue, ^{13}C nmr spectra, spectrum number 161 (in water).
2. C. J. Pedersen and H.K. Frensdorff, Angew Chem. Internat. Edit., 11, (1) 16, 1972.
3. J. Smid, Angew Chem. Internat. Edit., 11, (2) 112, 1972.

Université de Nancy I

NANCY, le July 8, 1974

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Tél. 27.00.24 (Poste 2049)

Dr. D. CANET

Professor B.L. SHAPIRO

Department of chemistry

Texas A and M University

College Station TEXAS 77843 USA

Title: "Elimination of solvent background in nematic phase NMR by Fourier transform"

Dear Professor SHAPIRO,

This is my first contribution to TAMU NMR Newsletters. We are mainly interested by nematic phase NMR and ^{13}C longitudinal relaxation times measurements. We are working with a BRUKER HX 90 equipped with a Fourier transform accessory (NICOLET I080 computer-20K memory). The spectrometer is operating for the following nuclei: ^1H , ^{19}F , ^{13}C , ^{17}O , ^{15}N , ^{14}N and ^2H . Furthermore, by lowering the magnetic field we were able to observe easily other nuclei, nuclei such as ^{27}Al or ^7Li .

About NMR in the nematic phase, I wish to report FT procedures which allow the elimination of the solvent hump which is often troublesome mainly in case of dilute solutions. These procedures are based on the fact that the nematics FID vanishes much more rapidly than the FID of the solute molecules. It is then interesting to try and suppress or attenuate the beginning of the interferogram. This is illustrated on the figure. (A) represents the normal FT spectrum of terephthalaldehyde dissolved in MERCK IV Licristal (5mm sample centered in a 10mm tube containing D_2O allowing field-frequency stabilization). The interferogram was stored in 4K-words, Fourier computations were performed with 16K by artificially filling with zeroes the remaining 12K. (B) was obtained in the same manner but in multiplying the interferogram by a trapezoidal window affecting the 150 first addresses. In (C) the first 10 addresses were deleted. Finally (D) is the theoretical spectrum. It is clear that experiments (B) and (C) are of quite better quality than experiment (A). The solvent background has almost been suppressed

in (B). However small lobes appear around each peak in (B) as well as in (C); they are due to the alteration of the interferogram⁽¹⁾. We think that trapezoidal window is a better procedure for two reasons: (i) lobes are less important than in the case of pure truncation (with respect to the number of addresses concerned) (ii) pure truncation implies tedious phase corrections which do not occur with trapezoidal window.

Anyway, care must be taken in altering FID when measuring weak signals such as ^{13}C satellites⁽²⁾. Because of the dynamic range of the analog to digital converter, they may be inobservable, since information to them is mainly stored at the ^{relative} beginning of the interferogram.

Yours sincerely.

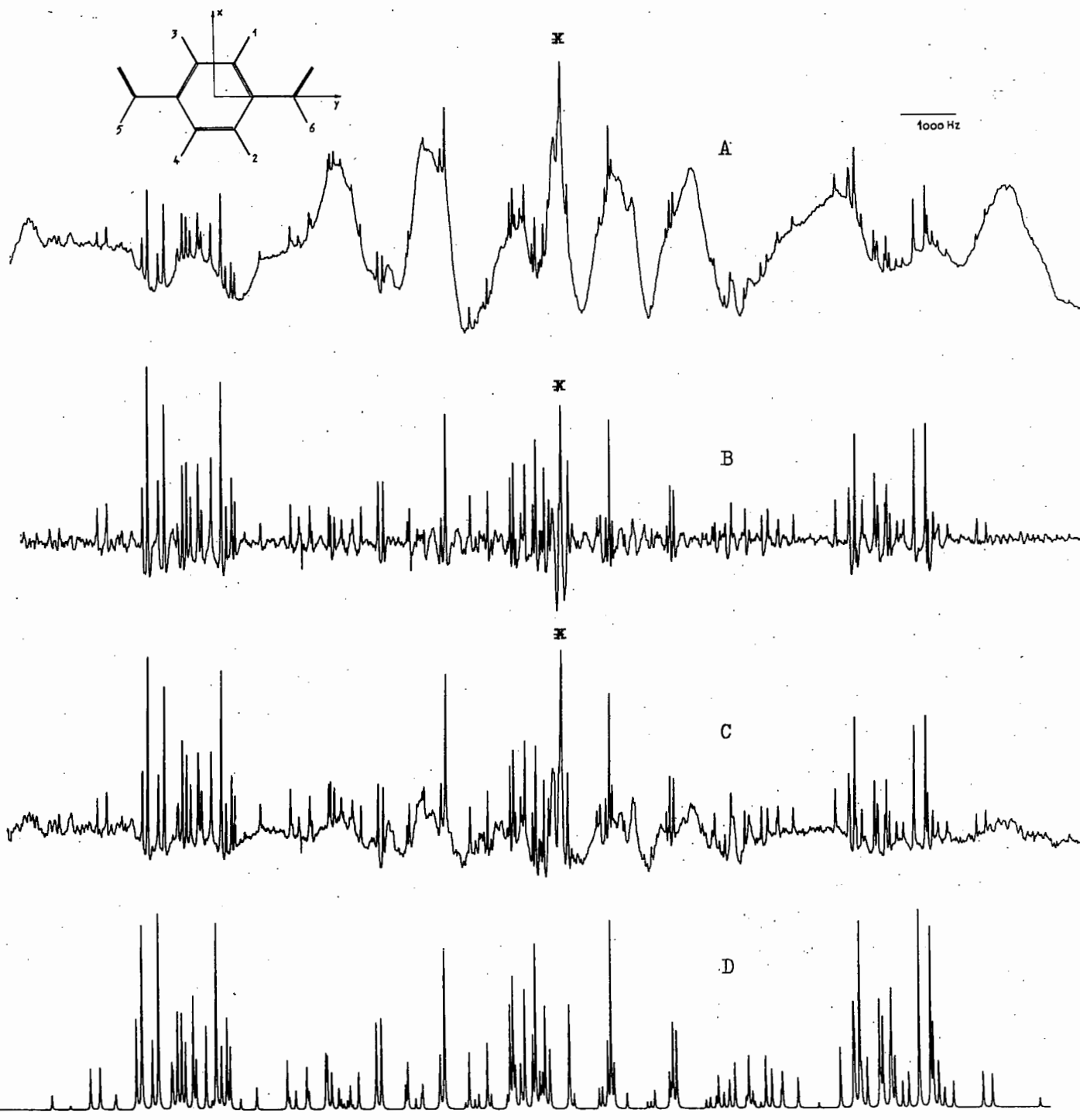


D. CANET

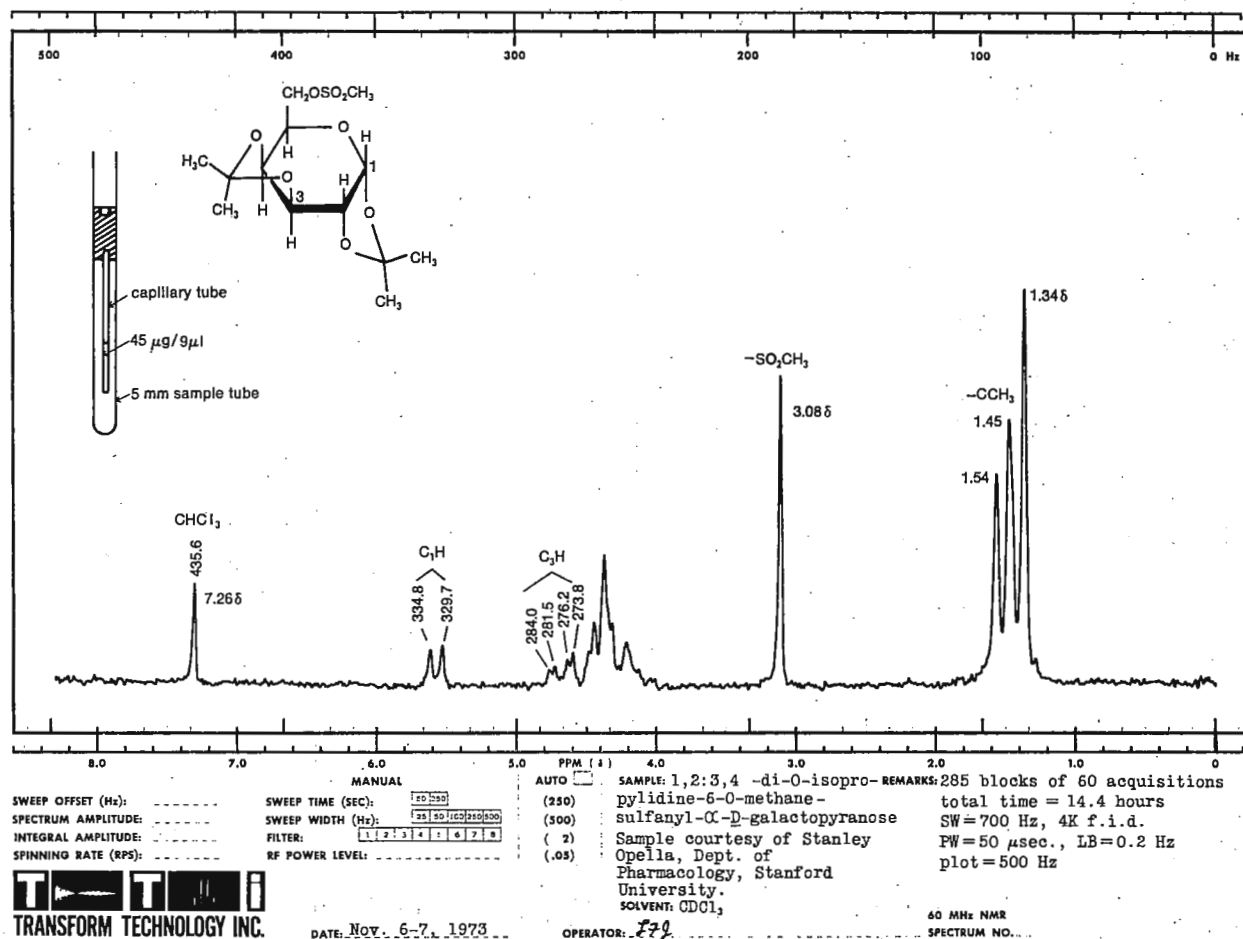
(1) T.C. FARRAR and E.D. BECKER "Pulse and Fourier transform NMR"

Academic Press (1971)

(2) E. HALOUI and D. CANET, Chem. Phys. Lett. 26, 261 (1974)



* Residual H_2O in D_2O serving as lock signal



Analysis of very small samples is best done using a microcell approach. Here, 45 micrograms of a compound with molecular weight 338 was contained in a capillary tube of 1.0 mm I.D. The peak at 3.085, although weak after one block of acquisitions, served adequately for the peak register method, which effectively cancels long-term field drift. Signal frequencies and chemical shifts were copied from an oscilloscope display of peak positions using an assigned value of 435.6 Hz for the chloroform peak. The spectrum is very well defined, and demonstrates that overnight FT operation with a T-60A/TT-7 system is quite feasible and very useful for microsample analysis.

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surements are available using the inversion-recovery technique as well as other multi-pulse experiments. In addition to sensitivity improvement and T₁ measurement applications, the basic TT-7 system will provide computer calculations of theoretical NMR spectra of up to six spins (seven spins with 12K core memory and disk memory system).

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July 25, 1974

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

Dear Barry:

Title: Some Developments in Nitrogen NMR Spectroscopy

Apart from a few annoying birth pains, our JEOL PS/PFT-100 spectrometer is operating reasonably consistently, and we have made some initial forays in our ^{15}N program.

1. In a series of stepwise approximations we are attempting to improve the signal-to-noise ratio of the detected ^{15}N signals. On the assumption that, up to a point, bigger is better, we built a bigger insert by slightly space-winding a coil around a standard JEOL 10-mm bobbin such that the number of turns remained the same while the length was increased by about 50%. Figure 1 shows the result, where we obtain about a 30% improvement in the S/N ratio over the standard insert. We are now building a 12-mm insert.

2. As a prelude to studies of heterocyclic natural products we have been studying substituent effects on the nitrogen shifts of pyridines. Because the relaxation times are long we use $\text{Cr}(\text{acac})_3$ to shorten the T_1 's, and can see signals of neat liquids within an hour. However, as shown in Table I, the resonance positions vary slightly with the concentration of $\text{Cr}(\text{acac})_3$, not enough to cause difficulties for structure elucidation, but enough to suggest caution when subtle changes (e.g., solvent effects) are investigated in the presence of such additives.

3. Additionally, the inverted signal which arises on proton irradiation when N-H dipole-dipole interactions dominate the ^{15}N relaxation can become less negative in the presence of a paramagnetic additive, so that in fact the absolute intensity can diminish. Figure 2 illustrates this for formamide with added $\text{Cr}(\text{acac})_3$.

4. For large molecules T_1 values should be short and spectra within reasonable periods of time can be expected, providing enough material can be crammed into the tube. Figure 3 shows a spectrum obtained after 2 hours (6000 pulses) of penicillin-G methyl ester at a hardly biologically interesting concentration of ca. 2M. We have also determined the spectra of several cephalosporin antibiotics, although with somewhat more difficulty because of limited solubility.

Overall, although we have been on the air with ^{15}N for only a short time, we are very much encouraged by these preliminary results. Let me again point out that to pursue these and related investigations I now have several postdoctoral openings which can begin at anytime.

Sincerely,

Alice J. DiGioia

Alice J. DiGioia

E.H. Cole

Bob

Robert L. Lichter

Assistant Professor

Table I. Dependence of Pyridine ^{15}N Chemical Shift on $\text{Cr}(\text{acac})_3$ Concentration^a

$[\text{Cr}(\text{acac})_3]$	$\delta_{\text{N}, \text{ppm}}^b$
0.0250	293.3
0.0500	292.8
0.1000	292.5
0.1500	292.2
0.2000	291.6

^a Neat liquid ^b with respect to external $^{15}\text{NH}_4\text{Cl}$, estimated error ± 0.15 ppm.

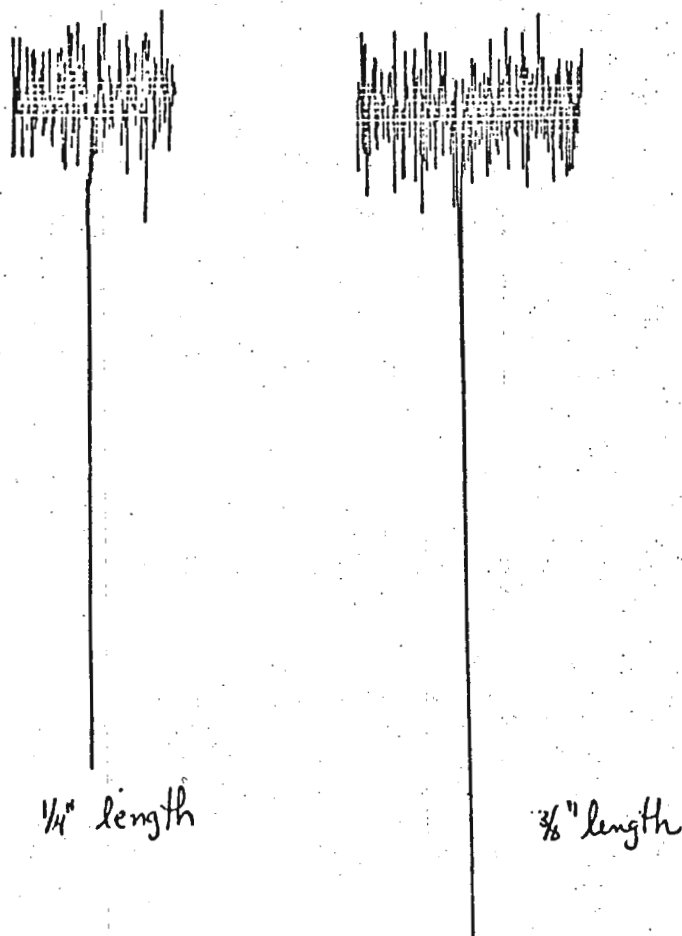
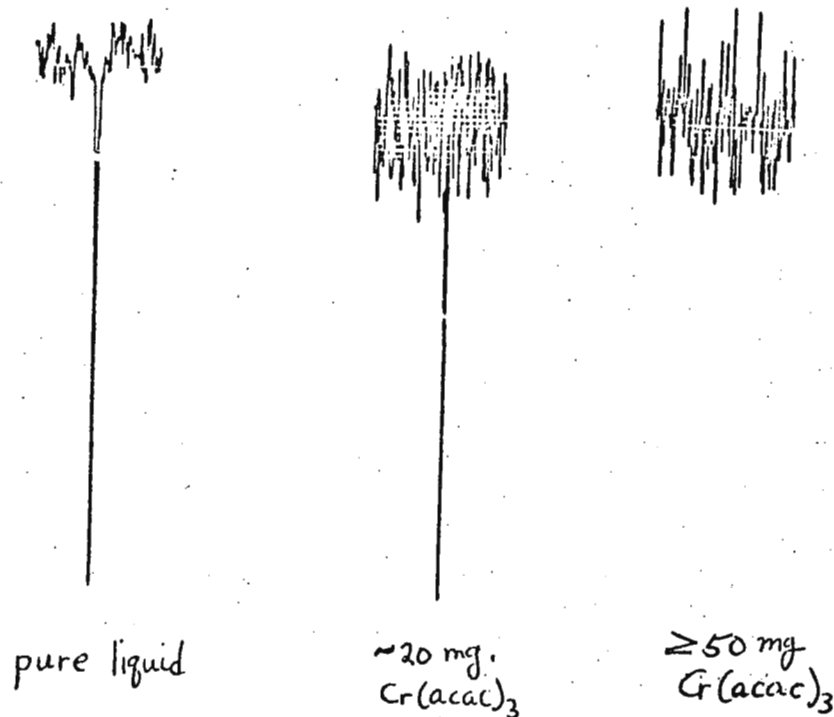


Fig.1. Aniline- ^{15}N resonance, neat liquid, 2000 pulses, 30° pulse width,



$\text{H}_2\text{NCH=O}$
 2 ml + 0.15 ml $(\text{CD}_3)_2\text{C=O}$
 200 pulses, 30°
 2.1 sec rep. rate

Fig. 2. Effect of added Cr(acac)_3 on ^{15}N signal intensity, formamide.

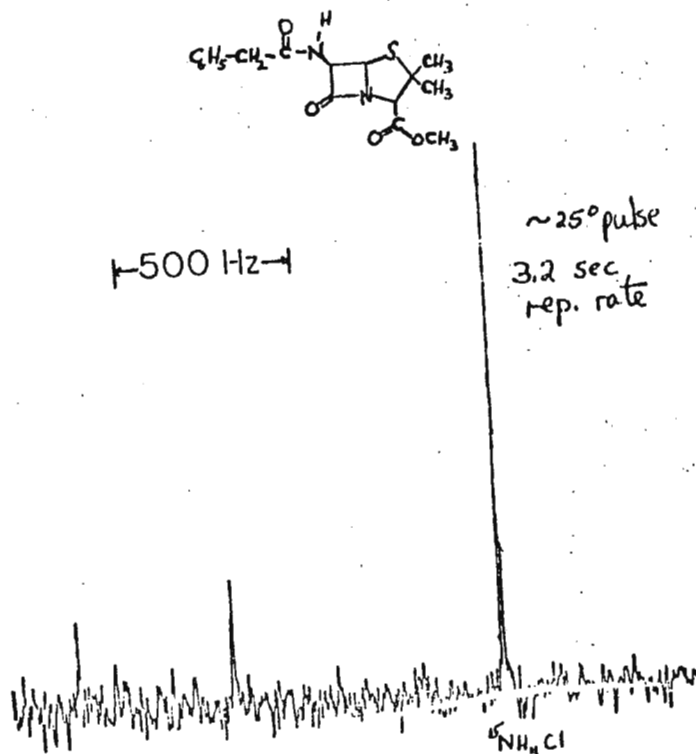


Fig. 3. Natural abundance ^{15}N spectrum of penicillin-G methyl ester.

CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN

Dr. Rudolf Knorr

⑬ MÜNCHEN 2, July 11, 1974
Karlstr. 23 - Tel. 55 79 76

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

Conformational Analysis by Spin Transmission into the Rotating
prim.-Alkyl Group

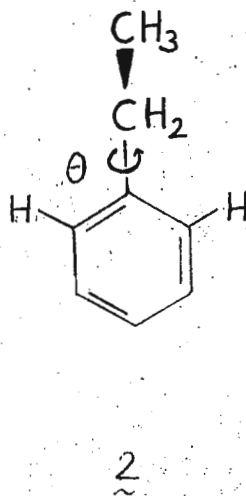
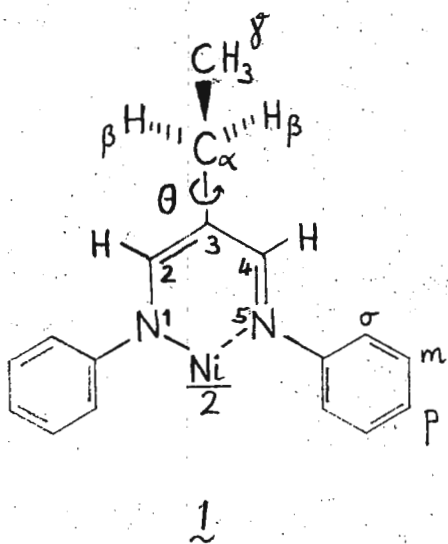
Dear Professor Shapiro:

NMR-shifts $\Delta H_i/H$ of paramagnetic nickel complexes may or may not follow a Curie-type ($1/T$) temperature dependence. A convenient way of checking the Curie law is to define by eq. (I) a new isotropic shift which is reduced from the actual temperature T to 298°K . (δ indicates the difference of

$$\delta = \frac{\Delta H_i}{H} \cdot \frac{T}{298^\circ\text{K}} \quad (\text{I})$$

$$\delta = -60400 \text{ ppm} \cdot g_i^H \quad (\text{II})$$

resonance positions in the complex and the free ligand). Assuming only contact contributions to the shifts of complex 1, we calculate eq. (II) from the fundamental constants and an effective Landé-factor $\bar{g} = 2.20(1)$. Notice from eq. (II) that δ depends only on the spin density g_i^H at a hydrogen atom. Therefore, Curie-type behavior will cause temperature-independent values of δ .



Plotting δ against the temperature we find from Figure 1 that the m-, p-, and γ -shifts of 1 are indeed reasonably constant. Therefore, the Curie law is valid and the magnetic properties of the complex as a whole do not change over the broad range of working temperatures (spectra were taken in 1,1-dideuterio-1,1,2,2-tetrachloroethane). In marked contrast, the reduced shifts of the two equivalent β -hydrogens drift strongly downfield with increasing temperature. We postulate that this "abnormal" temperature dependence is due to a modulation of the spin density, eq. (II), by torsion and/or rotation about the $C^\alpha C^\beta$ bond in 1. The geometrical situation is shown in the Newman projection in Table 1, looking from C^α toward C^β and the nickel atom.

$$\delta_\beta = \delta_0 + \delta_2 \cdot \langle \cos^2 \theta \rangle \quad (\text{III})$$

$$\langle \cos^2 \theta \rangle = \int \cos^2 \theta \cdot e^{-V(\theta)/RT} d\theta / \int e^{-V(\theta)/RT} d\theta \quad (\text{IV})$$

$$V(\theta) = V_2 \cdot \sin^2(\theta - 60^\circ) \quad (\text{V})$$

Spin transmission from a 2p-Orbital into a $C^\alpha H^\beta$ bond depends on the dihedral angle θ of the respective axes; eq. (III) is well established by theory as well as esr spectroscopy. The expectation value $\langle \cos^2 \theta \rangle$ may be computed classically according to eq. (IV) if the potential energy function $V(\theta)$ for the rotation is known. Assuming a \sin^2 potential, eq. (V), with a rotational barrier V_2 and an equilibrium angle of 60° , a theoretical temperature dependence may be calculated. The heavy trace through the β -shifts of Figure 1 results with $V_2 = 2.5$ kcal/mole; the parameters of eq. (III) are $\delta_0 = +17$ ppm and $\delta_2 = -200 (\pm 20)$ ppm. Data on a whole series of related complexes are collected in Table 1, taking always the same equilibrium conformation and the same δ_2 . The picture is quite consistent, including free rotation of the β -methyl group. The δ_0/δ_2 ratio of -0.08 is in line with theoretical estimates which have been positive or negative. Spin polarisation and hyperconjugation of positive spin density from C^β account for the low-field β -shifts.

Ethylbenzene 2 should be a good model for the electronic and steric requirements of the ethyl rotation in 1. A previous ab-initio calculation by Pople *et al.* (2) provided a barrier to rotation of 2.2 kcal/mole which compares very well with our estimate. Furthermore, the theoretical equilibrium angle θ_0 is identical with ours. The theoretical curves can be fitted to the experimental shifts only with $\theta_0 = 60 \pm 2^\circ$. Apparently our method is in the right ball park and constitutes a very sensitive tool of conformational analysis.

Please credit this contribution to the account of Prof. Gerhard Binsch over whose shoulder we are reading these Newsletters. Sincerely yours,

R. Knorr

Rudolf Knorr

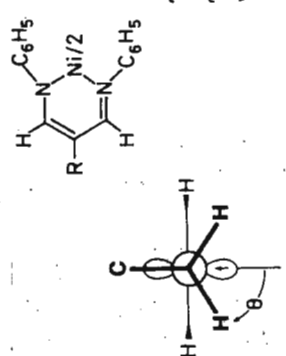
H. Polzer

Heinz Polzer

References:

- 1) We find this same \bar{g} value for more than 50 nickel complexes of 1,3-dianils, independent of the temperature, in accord with some earlier observations of:
 - a) J.E.Parks and R.H.Holm, *Inorg.Chem.*, **7**, 1408 (1968)
 - b) C.L.Honeybourne and G.A.Webb, *Chem.Phys.Letters*, **2**, 426 (1968); also *Mol.Phys.*, **17**, 17 (1969).
 - c) C.P.Richards and G.A.Webb, *J.Inorgan.Nucl.Chem.*, **31**, 3459 (1969).
- 2) W.J.Hehre, L.Radom, and J.A.Pople, *J.Amer.Chem.Soc.*, **94**, 1496 (1972).

TABLE 1



$\bar{g} = \bar{g}_0 + \bar{g}_2 \cdot \cos^2 \theta$
 $\bar{g}_2 = -200 (\pm 20) \text{ ppm}$
 $V = V_2 \cdot \sin^2 (\theta - 60^\circ)$

R-	\bar{g}_0 [ppm]	V_2 [kcal/Mol]
CH ₃	16	0
CH ₃ -CH ₂ -	17 ± 3	2.5 ± 0.3
CH ₃ -CH ₂ -CH ₂ -	14 ± 4	3.9 ± 0.5
CH ₃ -CH ₂ -CH ₂ -CH ₂ -	14.5 ± 2	3.5 ± 0.3
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	14.5 ± 2	3.5 ± 0.3
Ph-CH ₂ -	13.5 ± 2	3.2 ± 0.3
H ₃ C-CH ₂ -	12 ± 3	3.2 ± 0.3
H ₃ C-CH ₂ -	13 ± 2	3.5 ± 0.4
H ₃ C-CH ₂ -CH ₂ -	20 ± 2	3.2 ± 0.3
H ₃ C-CH ₂ -CH ₂ -CH ₂ -	18 ± 3	4.0 ± 0.3

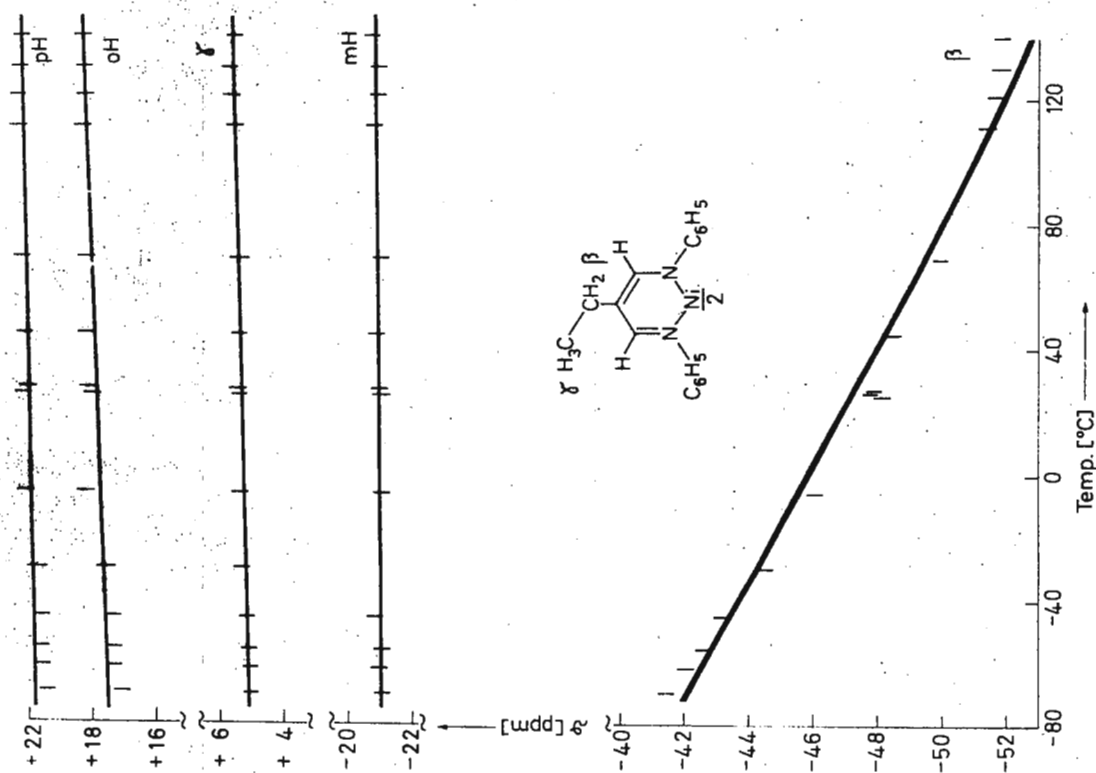


FIGURE 1



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July, 13, 1974

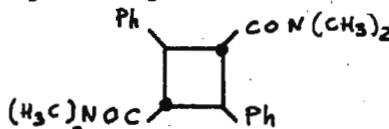
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Title: AN AUTHENTIC A_2B_2 SYSTEM.

Dear Prof. Shapiro,

please, excuse us for being slow in submitting this to you. We are now reporting¹ LAOCOON III simulation of 1H nmr spectra of some photodimers of cinnamic acid and related compounds, containing the cyclobutane ring.

Among the compounds we studied, an interesting example is the methine pattern of the cyclobutyl ring in the N,N-dimethyl- ϵ -truxilloylamide (trans,trans,trans)



This provides a theoretical A_2B_2 spin system with a very good half-spectrum of seven lines. $J_{AB} = J_{AB}' = 9.21$; $J_{AA}' = J_{BB}' = 0$.

In a recent review² and in the book of Bovey(3) , it was remarked the lack of examples of such symmetrical systems. However, in a literature survey, some A_2B_2 systems for cis,cis,cis substituent relationship between the ring protons are reported.¹

sincerely yours

Salvatore Caccamese *Giorgio Montaudo*
Salvatore Caccamese Giorgio Montaudo

1. G. Montaudo, S. Caccamese and V. Librando, Org. Magn. Resonance, in press.
2. H. Günther, Angew. Chem. int. ed. Eng., 11, 871 (1972).
3. F. A. Bovey "NMR spectroscopy" Academic Press 1969, p. 121.



THE UNIVERSITY OF ARIZONA

TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS

DEPARTMENT OF CHEMISTRY

July 15, 1974

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

Dear Barry:

POSTDOCTORAL POSITION AVAILABLE; BRUKER WH-90; TICK MARKS

A postdoctoral position is available starting September 1, 1974. The general area of interest is experimental and theoretical studies of magnetic resonance parameters. Recent work has been concerned with conformational and substituent effects on various types of nuclear spin-spin coupling constants, especially those involving C-13. I would appreciate receiving a resume and two letters of recommendation. The University of Arizona is an equal opportunity employer.

Experimental NMR data is obtained on a Bruker Scientific WH-90 FT Spectrometer, equipped for C-13 and proton NMR. We have now had about eighteen months experience with this spectrometer system, which was the first one installed in the U.S. We are quite pleased with the instrument. Except for some early minor difficulties with the deuterium lock system, there have been no problems with the electronics. Most of the down-time has been due to a bad batch of recorder pots and problems with the cooling water.

In my extreme haste to meet your final deadline on my previous contribution, I forgot to put the tick marks on the figure. So here they are: - - - - - , | | | | |.

Sincerely yours,

Mike

Michael Barfield
Professor of Chemistry

MB/re



EIDGENÖSSISCHE
TECHNISCHE HOCHSCHULE ZÜRICH

Laboratorium
für Physikalische Chemie

8006 ZÜRICH, 15 July 1974
Universitätstrasse 22
Telefon (01) 32 62 11

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

NMR - FOURIER - ZEUGMATOGRAPHY

Dear Barry,

P.C. Lauterbur (TAMU NMR Newsletter 175, 34; Nature 242, 190 (1973)) has recently described an ingenious technique to determine two- or three-dimensional images of the nuclear spin density in a macroscopic sample. In a set of experiments, linear magnetic field gradients are applied in different directions and the resulting spectra are recorded. From a sufficient number of such traces, it is possible to partially reconstruct the two- or three-dimensional spin density function by means of well known image reconstruction techniques.

We propose here another technique which is remarkable by its simplicity and by its inherent high sensitivity. It is based on the application of a sequence of pulsed linear field gradients to the sample during a free induction decay. The spin density function can then be reconstructed by means of a straightforward two- or three-dimensional Fourier transformation. No interpolation procedure is required to obtain equally spaced data in the Fourier space.

The principle of the technique for the two-dimensional case is shown in Fig. 1. After the application of a 90° pulse to the sample, a linear gradient, e.g. along the z-axis, is applied. At time t_z , the gradient is removed and a linear gradient is applied along an orthogonal direction, e.g. along the x-axis. N equally spaced samples of the FID are recorded during the second time interval as a function of t_x . These values are functions of t_x and t_z and are denoted by $s(t_x, t_z)$. A set of N experiments is performed for

equally spaced values of t_z . The $N \times N$ samples of $s(t_x, t_z)$ are submitted to a two-dimensional Fourier transformation to obtain the two-dimensional spectrum $S(\omega_x, \omega_z)$. It can be shown that this function represents a filtered image of the spin density function $c(x, z)$:

$$S(\omega_x, \omega_z) = \bar{c}(x, z) = \iint c(x', z') G(\eta_x(x' - x)) G(\eta_z(z' - z)) dx' dz'$$

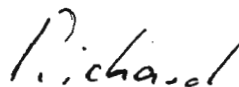
where $G(\omega) = M_0 / (1/T_2 - i\omega)$ is the complex line shape function and η_x and η_z are the linear field gradients expressed in frequency units. $\bar{c}(x, z)$ is thus related by a two-dimensional convolution to the undistorted spin density $c(x, z)$. For a sufficiently narrow line shape or for sufficiently strong gradients, it is a good measure for $c(x, z)$. In a Fourier zeugmatogram, the absolute value $|\bar{c}(x, z)|$ is plotted as a function of x and z .

An example of a Fourier zeugmatogram is shown in Fig. 2. The sample consisted of two parallel sample tubes with an inner diameter of 1.0 mm and a separation of the centers of 2.2 mm filled with H_2O and surrounded by D_2O . 64 x 64 samples have been Fourier transformed to obtain a 64 x 64 zeugmatogram printed directly on the teletype. The method is completely automatic, requires a small on-line computer only and produces without any intervention by the operator in about 15 minutes a two-dimensional zeugmatogram. A full paper with an analysis of this technique is in the process of being submitted for publication.

Sincerely yours,



Anil Kumar



Richard R. Ernst

FIG.1

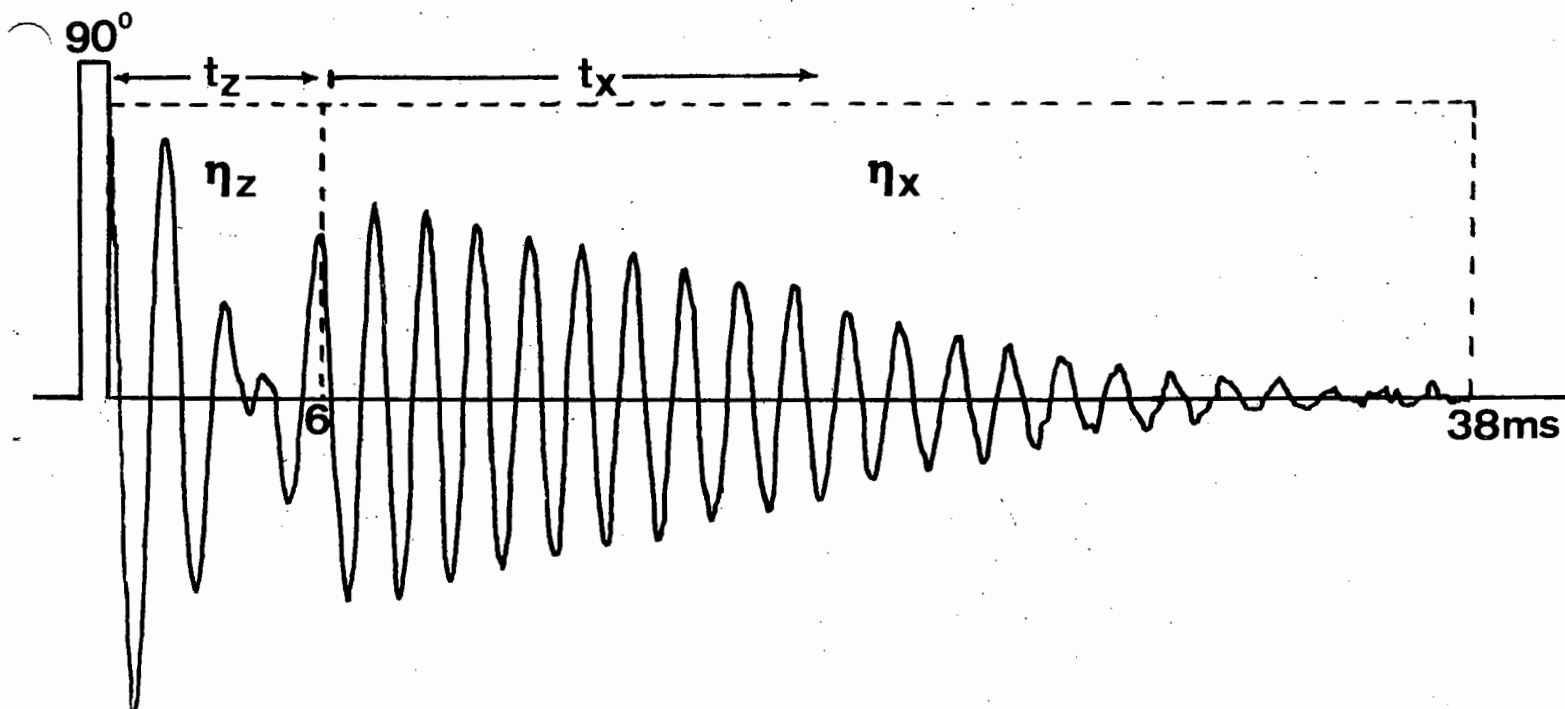
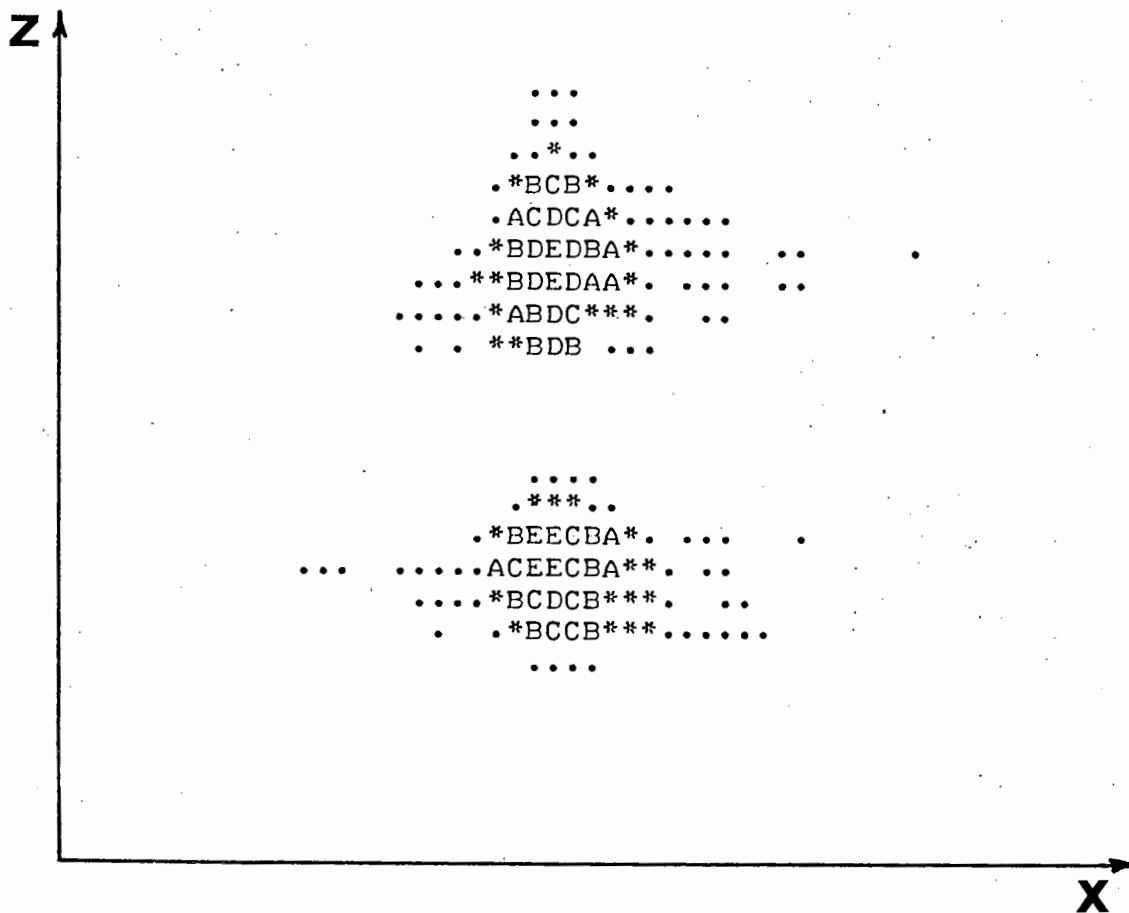


FIG.2



K-897265 NMR TUBE, QUARTZ, 5 mm., GRADE I

K-897266 NMR TUBE, QUARTZ, 5 mm., GRADE II

Fabricated from thin wall, precision bore, clear fused quartz tubing, and highly polished for maximum spectral resolution, and optimum sensitivity. These tubes are especially useful in all-quartz optical systems for ^{13}C Fourier Transform studies of CIDNP in Photochemical reactions.

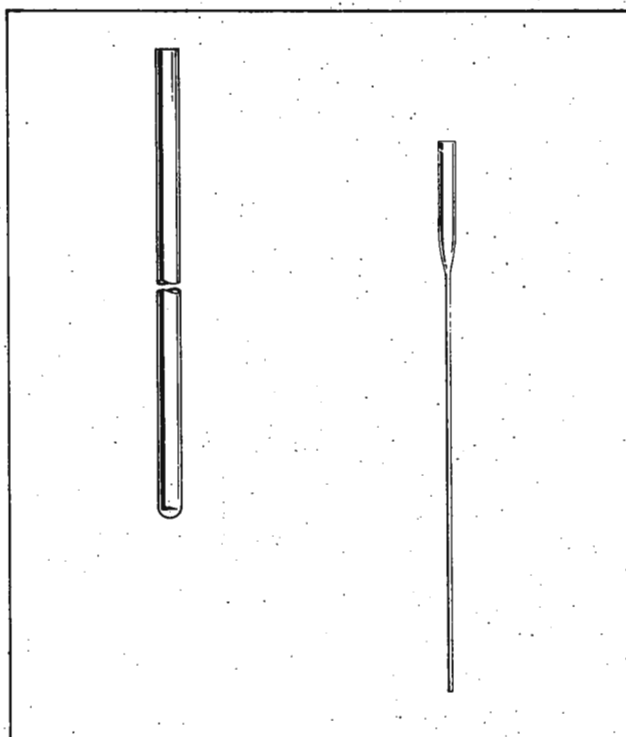
Cat. No.	Grade	Length	I.D.	O.D.
K-897265	I	7"	0.1665"	0.1955"
			± 0.0005 "	± 0.0005 "
K-897266	II	7"	0.1665"	0.1955"
			± 0.0005 "	± 0.0005 "

Cat No.	Wall Variation	Maximum Camber	Wall Thickness	Each
K-897265	± 0.002 "	± 0.002 "	0.015"	6.59
K-897266	± 0.001 "	± 0.001 "	0.015"	8.75

K-897085 PIPET, LONG TIP, NMR

Special, long tip pipet for transferring solutions in NMR studies. Overall length is 9", with $1\frac{1}{2}$ " body, and $7\frac{1}{2}$ " tip. Body O.D. is 7.0 to 7.5 mm; tip O.D. is 1.5 to 2.0 mm. Manufactured from standard flint glass. Packed 100 pipets per package.

Per Package 15.75



K-611680 EPR COLD FINGER DEWAR, QUARTZ

A high performance Liquid Nitrogen dewar. Designed to minimize conduction through the walls while assuring wall parallelism in the sample zone. Reservoir is solid silvered. Please specify size when ordering.

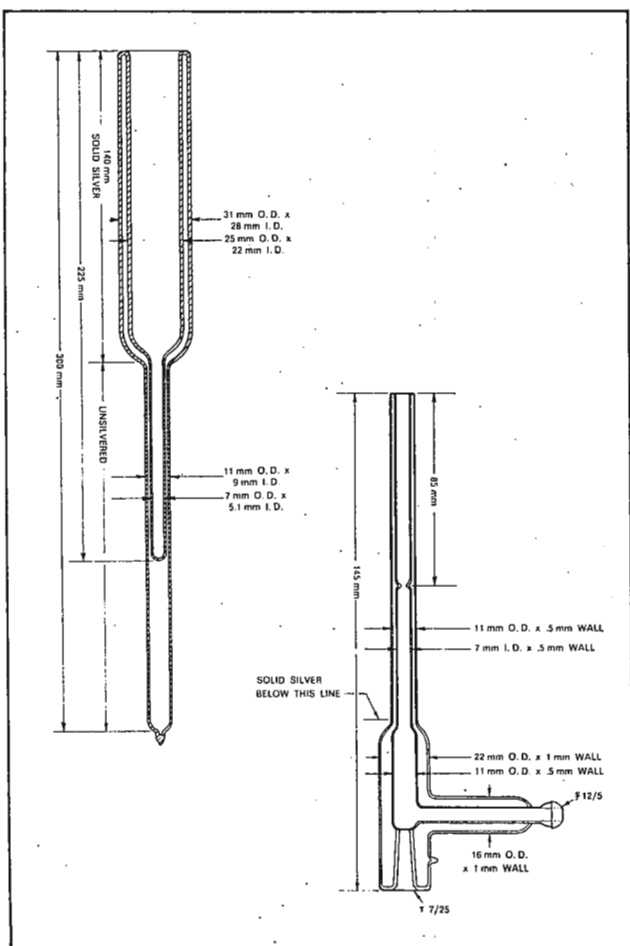
Specifications, mm	Size 0001	Size 0002
Overall Length	300	355
Reservoir Length	140	195
Reservoir O.D.	31	50
Reservoir I.D.	22	40
Inner Tail I.D.	5.1	5.1
Inner Tail Length	85	85
	Size 0001	Each 125.00*
	Size 0002	Each 145.00*

K-611690 ESR-EPR DEWAR, FLOW THROUGH, QUARTZ

Fabricated from high grade Amersil quartz for use in variable low temperature applications. Base of dewar body is solid silvered for more efficient operation. Size 0001 Dewar fits Varian E-Line and Bruker spectrometers. Size 0002 fits the Varian V-Line Spectrometer. Please specify size when ordering.

Specifications, mm	Size 0001	Size 0002
Overall Length	220	288
Body I.D.	7.0	14.5
Body O.D.	11	16.5
Joint $\frac{1}{8}$ "	12/5	12/5
Joint $\frac{1}{4}$ "	7/25	—
	Size 0001	Each 185.00*
	Size 0002	Each 200.00*

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SANTA BARBARA • SANTA CRUZ

SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

July 23, 1974

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

Title: Water in Red Cells; Position Open

Dear Barry:

Your recent reminder catches us between experiments.

We have completed the first stage of a study on the properties of water in sickle and normal red cells. The general findings are quite similar to most water/cell experiments: T_2 's are considerably shorter than T_1 's; line widths are somewhat broader than would be calculated from T_2 's. These effects are much more marked for sickled (deoxygenated) red cells than for normal or unsickled cells.

There is no single correlation time that is consistent with our data or that of others (G.L. Cottam, S.H. Koenig), and we are led (naturally enough) to the three state model for water in biological preparations that I spoke of last time. Our preliminary experiments suggest that there is no dramatic change in hemoglobin hydration on sickling. Presumably the water motion is being influenced by a slow tumbling of the (aggregated) sickled hemoglobin. This work has been in collaboration with Drs. Adam Zipp and Tom James of our department and Drs. Jerry Rehfeld and Steve Shohet of Hematology.

We expect to have a position open for this fall for an operator/maintainer/spectroscopist for the departmental NMR equipment. Salary will depend on qualifications. Anyone interested should contact me for more details.

Regards,

*Taek*I.D. Kuntz
Associate Professor of Chemistry
and Pharmaceutical Chemistry

IDK:ftf

Prof. Dr. Hanns Fischer

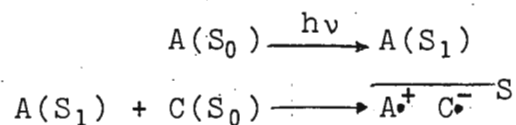
Physikalisch-Chemisches Institut
der Universität ZürichCH-8001 Zürich 16. Juli 1974
Rämistrasse 76
Telefon 01 / 32 26 20Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College StationTexas 77843

U . S . A .

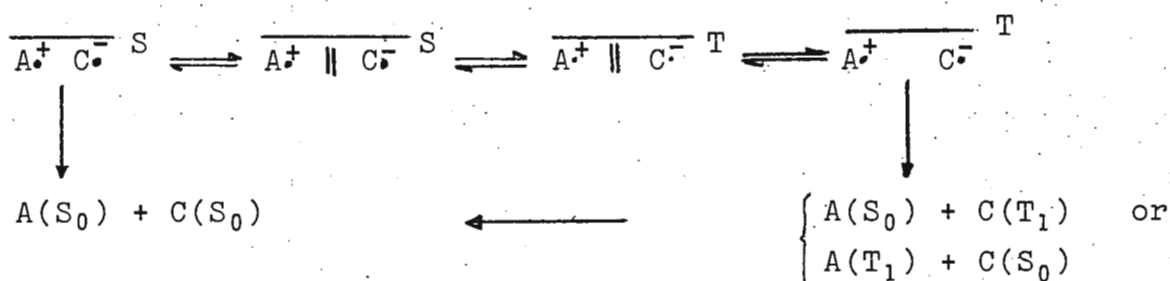
CIDNP in Photochemical Charge Transfer Processes

Dear Dr. Shapiro:

UV-irradiation of a solution containing an aromatic hydrocarbon (A) and a cyano compound (C) leads to electron transfer via [1]



and possibly to the following secondary reactions



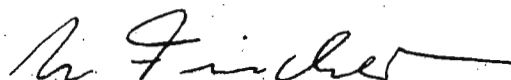
In such reversible processes CIDNP caused by nuclear spin dependent intersystem crossing of the radical ion pairs can be expected for the products $A(S_0)$ and $C(S_0)$ only if nuclear relaxation in the free ions or in the T-state molecules effectively competes with product formation. Since this is seldom the case only small effects should appear. In accord with expectation NMR.-spectra taken during irradiation of solutions of several hydrocarbons (A) with 1,2-dicyanocyclobutene, tetracyanoethylene and p-dicyanobenzene in acetonitrile exhibit only minor CIDNP for A and C. However, for benzene,

naphthalene and chrysene with t-dicyanoethylene (t-DCNE) large effects for t-DCNE (enhanced absorption) and c-DCNE (emission) are found. Also, large effects are observed for t-stilbene (emission) and c-stilbene (enhanced absorption) during the photoreaction of t-stilbene with p-dicyanobenzene and t-dicyanoethylene in acetonitrile. Following Roth [2] this is explained in terms of the above reactions and the additional trans-cis-isomerization of t-dicyanoethylene or t-stilbene in the triplet states ($C(T_1)$, $A(T_1)$). For t-dicyanoethylene with anthracene and pyrene no isomerization and CIDNP is found, in agreement with their low triplet energies ($E^T(A) < E^T(C)$). Since radical ions are formed also with these compounds isomerization in the anions can be ruled out.

Sincerely yours



B.M.P. Hendriks



H. Fischer

[1] A. Weller, Pure Appl.Chem. 16, 115 (1968)

[2] H.D. Roth, Mol.Photochem. 5, 91 (1973)

DEPARTMENT OF ORGANIC CHEMISTRY
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX

TEL: 051 - 709 - 6022

The University of Liverpool

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

19th July, 1974.

Dear Barry,

^1H [^2D] Study ; ^{13}C shift of TMS in TFA; position available.

We were interested in the TAMUNMR letters of Professor De Puy (186-38) and Drs. Tseng and Mihailovski (188-28) as we have some related results.

For the former Jose Monasterios has been utilising the reverse technique of Professor De Puy i.e. ^1H [^2D] spectroscopy to determine the stereochemical course of the addition of DBr to cis and trans-2-t-butylstyrene and also thus to assign the diastereotopic methylene hydrogens of $\text{Ph.CHBr.CH}_2.\text{tBu}$. (see figure) . It would appear that the method offers a general route to the assignment of such protons, which formerly could only be made by assumptions about the most stable rotamer.

We can extend the cautionary tale of TFA as solvent to the question of ^{13}C chemical shifts in this solvent. Geoff Hawkes has just finished an investigation on the effect of protonation on the ^{13}C shifts of porphyrins both in CDCl_3 with TFA added and neat TFA. The shifts were always further downfield in neat TFA, and we decided to run some reference compounds in CDCl_3 and TFA from an external reference. It turns out that it is the TMS signal which moves upfield in TFA by 1.5 ppm compared to CDCl_3 . The origin of this shift may be related to the silicon polarisability, in the same manner as the large upfield shifts found for fluorine attached to C.Cl and C.Br groups, but whatever the reason this must be taken into account when determining protonation shifts from measurements in CDCl_3 and neat TFA.

Finally, if all the available P.D.F. talent has not already been tapped, we have a possible opening for someone interested in a ^{13}C study of metal-porphyrin interactions. Anyone interested contact me.

With best wishes,

Yours sincerely,



Dr. R.J. Abraham.

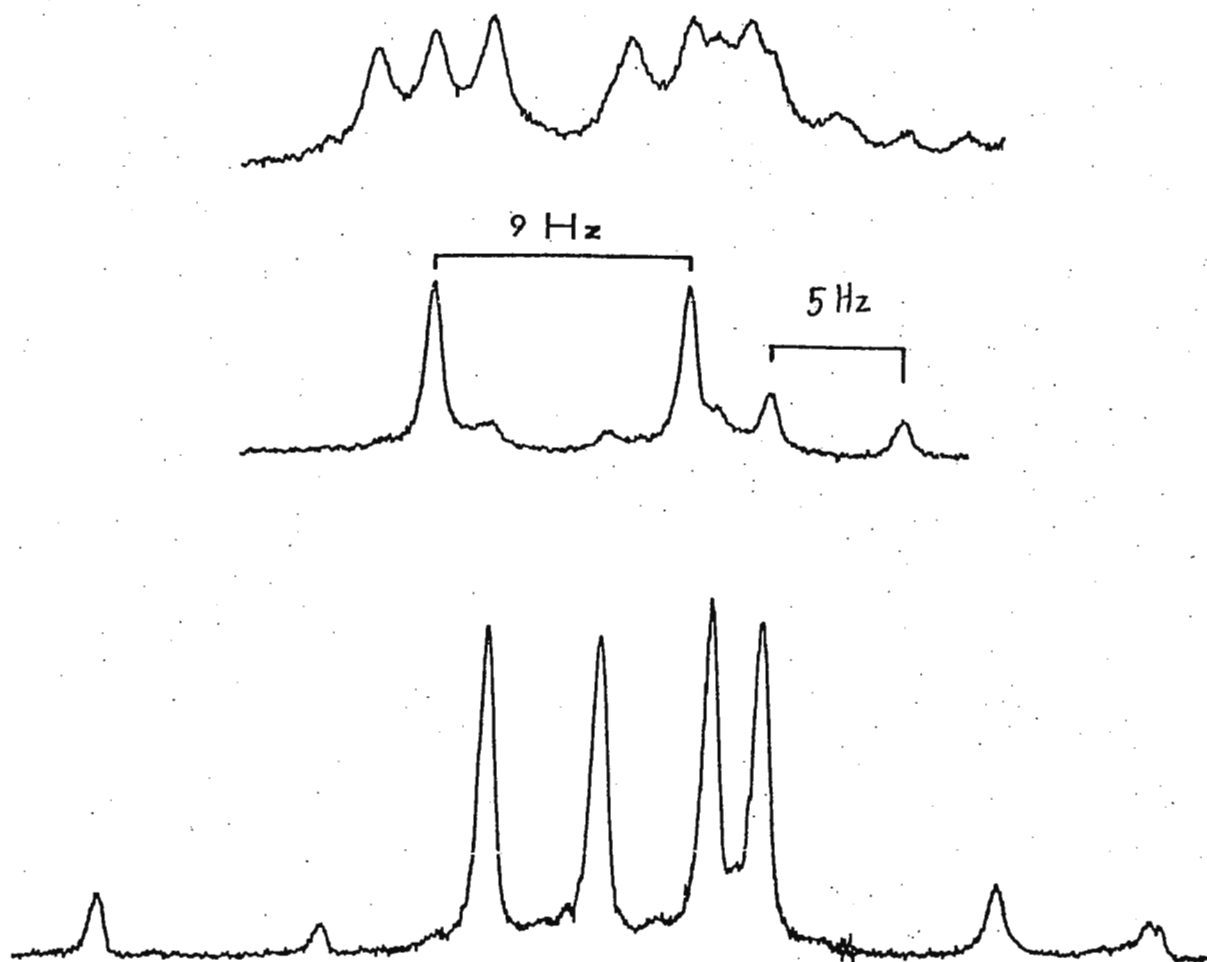


Figure 1.

Methylene (lower-trace) protons (AB part of an ABX spin system) of $\text{PhCHBr}.\text{CH}_2\text{tBu}$. The same region (upper-trace) for the mixture of products obtained (erythro and threo $\text{PhCHBr}.\text{CHD}^*\text{tBu}$) when DBr was added to the trans-olefin. The middle-trace is the corresponding deuterium decoupled spectrum.



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

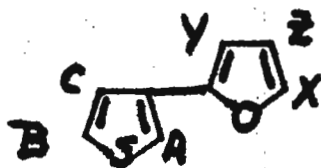
Department of Chemistry

July 22, 1974

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

Dear Barry:

One of Manny Reinecke's students made the rather unusual heterocyclic below, and we thought it appropriate to record the proton NMR parameters here. The molecule was treated as two three spin systems though there is clearly a small long range interring coupling as noted.



2-(3-thienyl)furan

H_A 7.32; H_B 7.18; H_C 7.12;

H_X 7.24; H_Y 6.30; H_Z 6.26

J_{AB} 3.02; J_{AC} 1.21; J_{BC} 5.22;

J_{XY} 0.73; J_{XZ} 1.82; J_{YZ} 3.40;

$J_{AX} \approx J_{AY} \approx 0.25$

Also I have a postdoctoral position available in September for someone to do synthesis and NMR on steroids related to the moulting hormones. Interested parties may consult me for details.

Sincerely,

W. B. Smith

WBS/dc



Laboratoire des Organométalliques

J. C. MAIRE, Professeur.

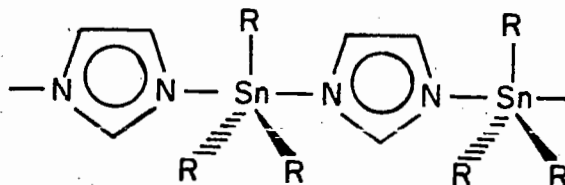
July 24, 1974

Prof. B. SHAPIRO
Dept. of Chemistry
College of Science
Texas A&M University
College Station
TEXAS 77843 (USA)

Dear Barry,

^1H , ^{13}C and low temperature measurement on tin derivatives
of nitrogen heterocycles

The structure of tin derivatives of aromatic heterocycles such as imidazole including a tin nitrogen bond is well known. It is a polymer, with five coordinated tin atoms, compatible with the 1,3 position of the two nitrogens.

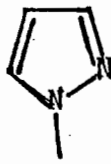


These compounds are not soluble in usual organic solvents but methanol, where tin-nitrogen bonds are broken, and the ^1H NMR spectra in CD_3OD gives the same chemical shift for protons 4 and 5.

The structure is quite different when the two nitrogens are in 1,2 position such as pyrazole derivatives.



$\text{Sn}(\text{CH}_3)_3$

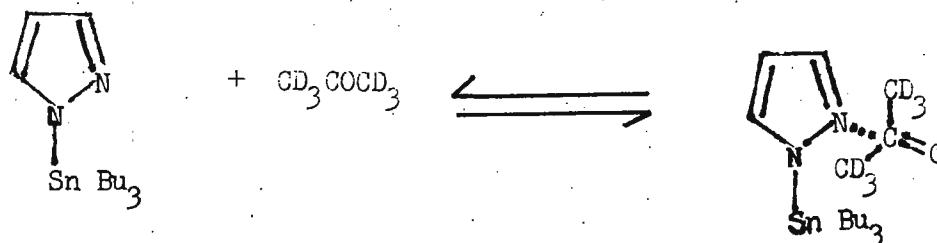


SnEt_3



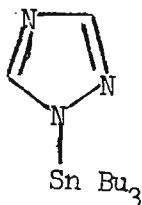
Sn Bu_3

Polymeric association is sterically impossible. The N-tributylstannylpyrazole is a liquid. The ^1H NMR spectra in different solvents, even in pure liquid, still give the same chemical shift for protons 3 and 5. Same results have been obtained with N-triethylstannylpyrazole. We also recorded the ^{13}C spectra in the same conditions but we found the same chemical shift for carbons 3 and 5. The reason can be a fast exchange of the tin atom between the two nitrogens. So, we did some low temperature measurement on N-tributylstannylpyrazole. Using pentane like solvent, even at -80°C , we still have the same spectrum. If we replace pentane by acetone one can see a change. The exchange of $\text{Bu}_3\text{Sn}-$ is slowed enough to allow a complexation of the second nitrogen to give the equilibrium:



As we decrease the temperature the quantity of complexed form increased. At -70°C we just have the complexed form.

Room temperature spectra of N-tributylstannyl 1,2,4 triazole have also been recorded.



N-tributylstannyl 1,2,4 triazole is a solid soluble in different organic solvents. There is a change in solubility and in chemical shift with the solvent, but protons 3 and 5 still give one peak.

Solvent.	CS_2	CCl_4	pentane	CDCl_3	dioxan	THF	CD_3OD	CD_3COCD_3	DMSO.
Chemical shift of protons 3 and 5 in ppm	7.75	7.84	7.87	8	8	8	8.14	8.15	8.16

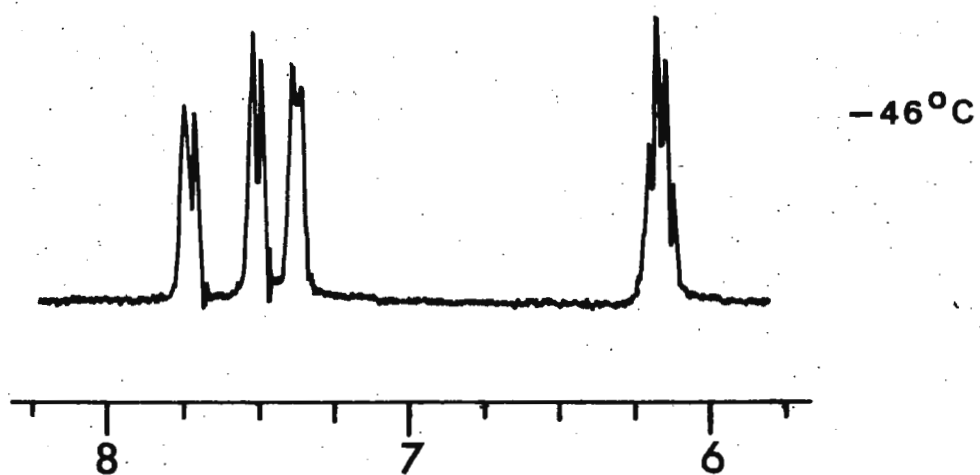
Low temperature measurements and protons spectra have been recorded on a Jeol C 60 H and ^{13}C spectra on a Varian NV 14 with FT.

Yours Sincerely,

J.C. MAIRE

R. GASSEND

Temperature study on N-tributylstannylpyrazole



29th July, 1974

Dear Professor Shapiro,

Inter- and Intra-molecular Exchange in
the System 1,3,5-Trioxan/1,3,5,7-Tetroxan

University of Salford

Salford M5 4WT

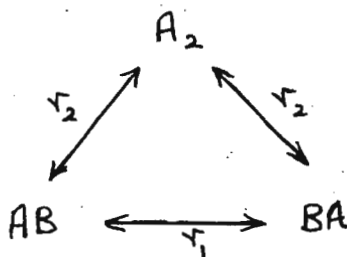
Department of Chemistry
and Applied ChemistryTelephone 061-736 5843
Telex 668680 (Univ Salford)

Few studies of ring inversion in 8-membered rings have been reported in the literature¹ and the simplicity of the proton spectrum of 1,3,5,7-tetroxan provides an ideal system for examination. Bearing in mind that the barrier to ring inversion in cyclo-octane is relatively high², one expects decoalescence into an AB-spectrum to occur readily on lowering the temperature.

We were surprised to find that the proton spectrum of a 5% solution of this material in a 1:1 mixture of chloroform-d and m-fluorotoluene, which was a singlet at ambient temperatures, decoalesced below -17°C into the expected AB-spectrum but with an additional peak (approx. 33% contaminant) near the centre.

After four sublimations of the solid tetroxan this singlet still persisted in the low-temperature proton spectrum and it was identified as trioxan by addition of some of this material to the sample. Evidently a dynamic equilibrium between tetroxan and trioxan existed in solution and this was further confirmed by the observation of a symmetric, sharp singlet resonance (at 100 MHz) for the sample at ambient temperature.

We therefore investigated the exchange in this system as being $\text{AB} \rightleftharpoons \text{BA} \rightleftharpoons \text{A}_2$ using Binsch's program DNMR3. In this way we were able to identify the inter- and intra-molecular exchange processes in the following scheme



Here rate r_1 gives directly the rate of ring inversion k_1 while rate r_2 is related to the inter-molecular exchange rate by $k_2 = 2r_2$ since the populations of all the sites are equal.

Temperature dependence studies therefore yielded a value of $\Delta G^\ddagger = 57.7 \text{ kJ mole}^{-1}$ for the inversion barrier in tetroxan (assuming crown \rightleftharpoons crown) compared with $38.8 \text{ kJ mole}^{-1}$ for cyclo-octane². The activation energy for the inter-molecular exchange was comparable at $58.9 \text{ kJ mole}^{-1}$.

Yours sincerely,

J. A. Ladd.

1. Anderson, Quart. Reviews 19 (1965) 426.
2. Anet and Hartman, J. Am. Chem. Soc. 85 (1963) 1204.

International Business Machines Corporation

Monterey & Cottle Roads
San Jose, California 95114
408/227-7100

July 30, 1974

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

Quest for a ^{13}C Knight Shift in TTF/TCNQ

Dear Barry:

Some time ago, Wiebren Veeman (now at Nijmegen) and I looked for a Knight shift for ^{13}C in TTF/TCNQ and failed to detect one, at least in the signals we observed. We were able to see ^{13}C signals from -110°C to -180°C using the Bleich-Redfield double resonance technique. The material acts like a metal down to 60K. We recorded a strong, rather broad (600 Hz) but symmetrical resonance centered in the same frequency region where one observes ^{13}C in solid benzene (5.783 - 5.784 MHz at 5400 gauss). We looked over a very large frequency range, but found no additional signals. We therefore conclude that the Knight shift (if there is one) for the detected carbons is no larger than 100 ppm. From the simplest double resonance ideas, one would guess that these are the carbons to which protons are bonded, and may not be the ones for which a Knight shift would be predicted. Still, we do not understand the symmetry of the signal (no chemical shift anisotropy ?) and we welcome suggestions from interested readers. We have been able to observe both a narrow methyl carbon resonance and not-so-narrow signals from other carbons in the pure tetramethyl derivative of TTF.

Sincerely yours,

Nino Yannoni
C. S. Yannoni
bat

1 August 1974

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

Dear Professor Shapiro:

¹³C=O Spectral Assignments in Peptides
 by Double Resonance Techniques

Allerhand and coworkers¹ have shown that nonprotonated aromatic carbons of proteins give resolved ¹³C resonances which are sensitive to conformational and redox state effects. Since backbone carbonyl resonances are similarly narrow, they too should be of use as probes of solution structure, providing they may be assigned to individual amino acid sites, and ¹³C shift models are found which reproduce the observed spectral effects.

The ferrichromes offer an excellent prototype system for such an approach. This class of ferric cyclohexapeptides has been well characterized by x-ray crystal analysis² and ¹H NMR³. The parent compound, ferrichrome, has the primary structure



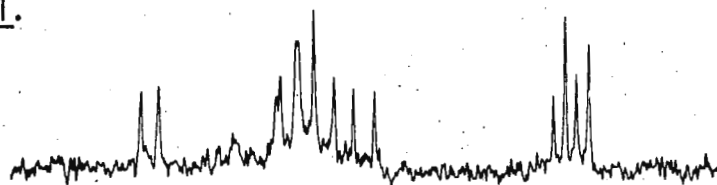
where the Orn residue denotes δ -N-acyl- δ -N-hydroxy-L-ornithine, and the iron atom is octahedrally coordinated to the three Orn hydroxamate groups.

Selective enrichment techniques have been reported for carbonyl assignments of other peptides⁴. We have made these assignments for ferrichrome (where, for NMR spectra, aluminum replaces iron to eliminate paramagnetic line broadening) by isolating approximately 95% ¹⁵N-enriched ferrichrome and taking advantage of the known peptide N-¹H assignments³. By selectively decoupling ¹⁵N and observing the ¹H spectra⁵, then selectively decoupling the ¹⁵N and observing the ¹³C spectra, individual ¹³C=O resonances can be connected to these N-¹H assignments, in a manner similar to that reported by Birdsall et al⁶. This technique avoids the complications of selective enrichment (metabolic branching, availability of aa- mutants, etc.).

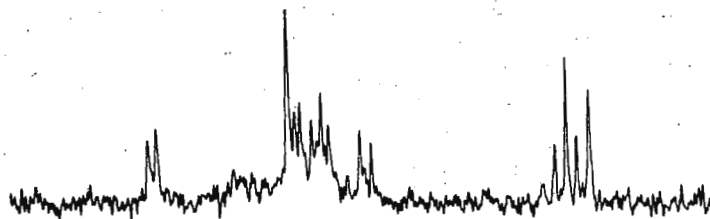
¹⁵N Figure 1A shows the ¹H-noise decoupled spectrum of approximately 100 mg ¹⁵N-enriched ferrichrome, at 50°C in DMSO. Figure 1B shows ¹H-noise decoupled, ¹⁵N-coherently decoupled ¹³C spectra of the same sample at various ¹⁵N-decoupling

Figure 1.

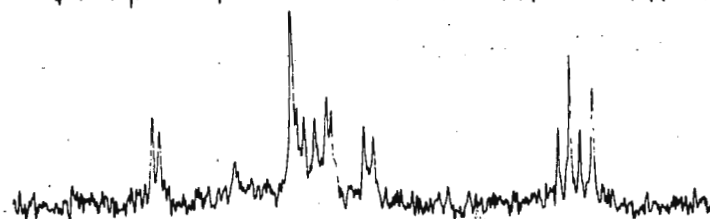
A



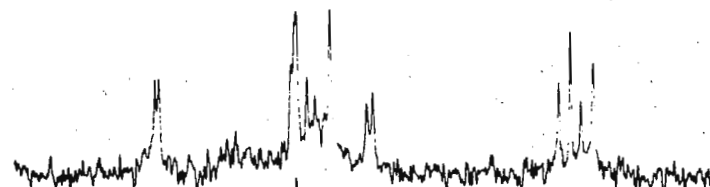
B



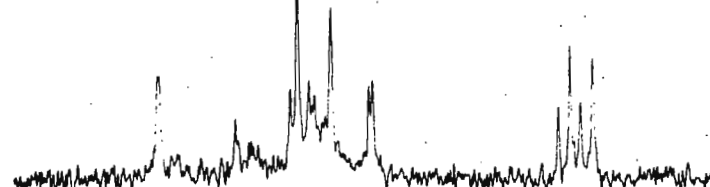
10.140101 MHz



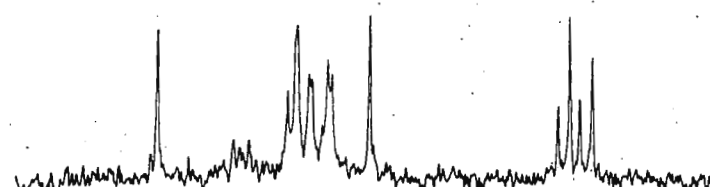
10.140128 MHz



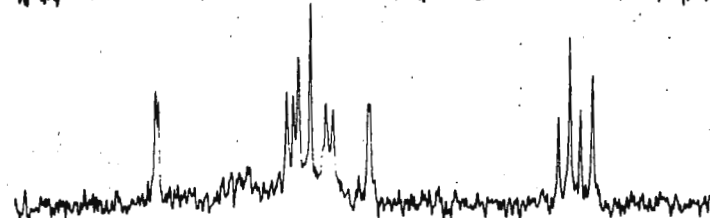
10.140163 MHz



10.140190 MHz



10.140218 MHz



10.140251 MHz

-130

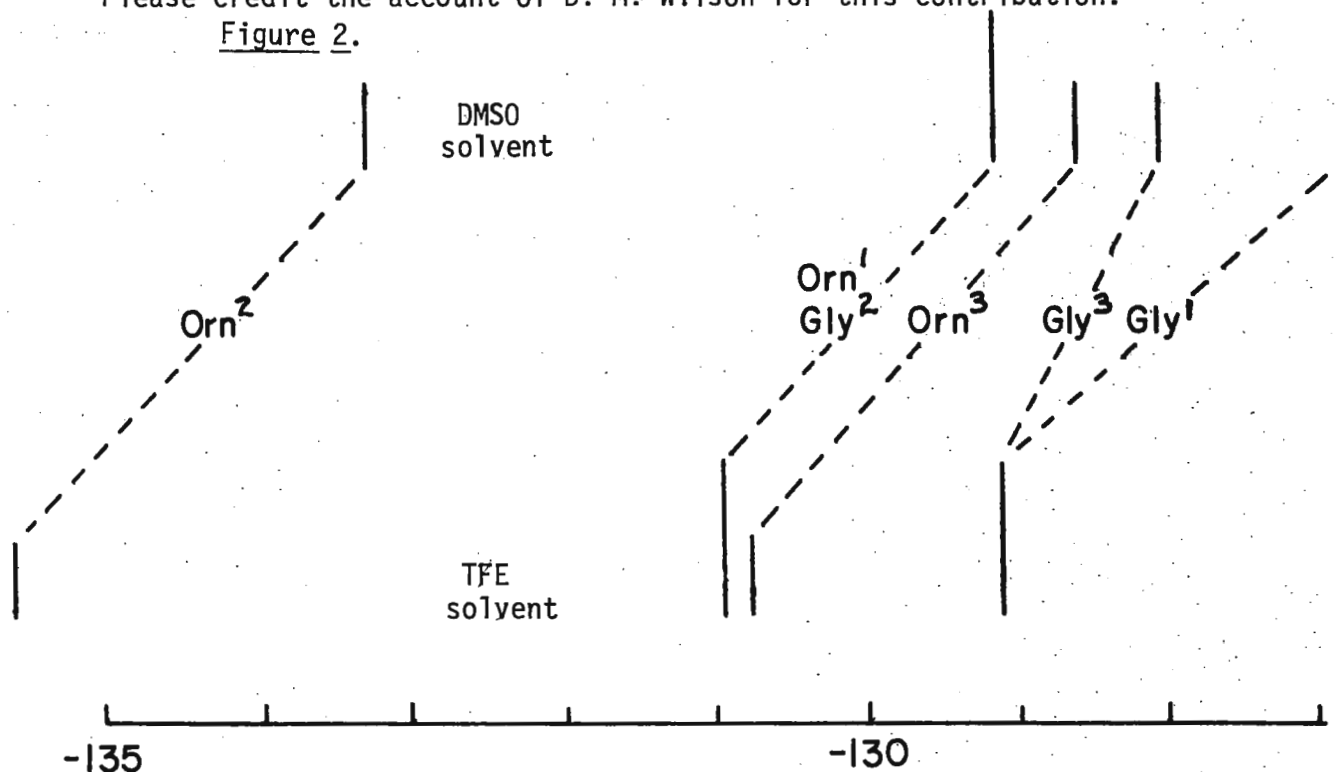
-120

frequencies. The abscissa is in ppm from the C_{α} resonance of free glycine at neutral pH⁷, which is taken to be 25.4 ppm upfield from an internal dioxane reference. These results were obtained on a Varian XL-100 instrument set up for double-decoupling⁸ and dual phase detection⁹, each spectrum representing 5-hour accumulation time. The four upfield resonances arise from the hydroxamate carbonyls of the Orn sidechains, and are not affected by ^{15}N decoupling since their ^{15}N resonances are distant from the amide decoupling frequencies.

Figure 2 shows the assignments of the ferrichrome carbonyls in DMSO and trifluoroethanol which were made using our technique. The resonance least shifted between these two solvents is seen to be the Gly³ carbonyl, which is not exposed to solvent, taking part in a transannular hydrogen bond to the peptide N-H of Orn³. We are presently trying to rationalize the nonequivalence of the three Orn and three Gly residues in terms of specific chemical shift models. At this time we can eliminate electric field effects caused by the ligand field, and peptide group magnetic susceptibility anisotropy, as dominant determinants of the backbone carbonyl shifts.

Please credit the account of D. M. Wilson for this contribution.

Figure 2.



M. Llinás
M. Llinás⁺

D.M. Wilson
D. M. Wilson^{*}

M. P. Klein
M. P. Klein⁺

Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory⁺
and Space Sciences Laboratory^{*}, University of California, Berkeley,
California 94720

- ¹A. Allerhand, R. F. Childers and E. Oldfield, Biochemistry **12**, 1335 (1973); E. Oldfield and A. Allerhand, Proc. Nat. Acad. Sci. USA **70**, 3531 (1973).
- ²A. Zalkin, J. D. Forrester and D. H. Templeton, J. Amer. Chem. Soc. **88**, 1810 (1966).
- ³M. Llinás, M. P. Klein and J. B. Neilands, J. Mol. Biol. **52**, 399 (1970); Int. J. Peptide Protein Res. **4**, 157 (1972); J. Mol. Biol. **68**, 265 (1972); J. Biol. Chem. **248**, 915 (1973); ibid., 924; J. B. Neilands, Inorganic Biochemistry, Vol. 1, G. L. Eichhorn, Ed., Elsevier, Amsterdam (1973), pp. 167-202.
- ⁴C. Grathwohl, R. Schwyzer, A. Tun-kyi and K. Wuthrich, FEBS Lett. **29**, 271 (1973); J. A. Sogn, L. C. Craig and W. A. Gibbons, J. Amer. Chem. Soc. **96**, 3306 (1974).
- ⁵M. Llinás and M. P. Klein (manuscript in preparation).
- ⁶B. Birdsall, N. J. M. Birdsall and J. Feeney, J. C. S. Chem. Comm. **1972**, 316.
- ⁷W. Horsley, H. Sternlicht and J. S. Cohen, J. Amer. Chem. Soc. **92**, 680 (1970).
- ⁸D. M. Wilson, R. W. Olsen and A. L. Burlingame, TAMU NMR 180-51.
- ⁹D. M. Wilson, R. W. Olsen and J. J. Chang, TAMU NMR 171-48.

10 July 1974
1217 Birch
Richland, Wa. 99352

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

Dear Barry,

I would very much appreciate your inserting my letter in the NMR newsletter.

I am interested in a postdoctoral position for research in NMR. The Ph.D. was a study of keto-enol tautomerism in β -dicarbonyls. Other research was performed in NMR for two years.

Sincerely,

Jane L. Burdett
Jane L. Burdett



August 1, 1974

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

Dear Barry:

Selective Relaxation in Proton NMR

We have recently been using a modification of the Fourier synthesized excitation technique (1), in which a spin system is excited by a sequence of modulated pulses, to perform selective relaxation measurements in proton NMR.

Consider a sequence of rf pulses (carrier frequency ν_o , amplitude H_1) with a repetition frequency ν_r and pulse widths given by $\tau = \tau_o \cos 2\pi\nu_m$, i.e. the widths are modulated by a frequency ν_m . If the pulse widths are small compared with the pulse spacing, then to a good approximation the frequency spectrum of the sequence consists of components with amplitudes $H_1\nu_r\tau_o$ at frequencies $\nu_o \pm n\nu_r \pm \nu_m$ for $n = 0, 1, 2, \dots$. When these sidebands are well separated compared with their intensities, their effects may be considered independently and only nuclear resonances close to a sideband will be significantly affected. By applying the pulse sequence for a time T_s , short compared with the relaxation times, a resonance close to a sideband will experience a "selective α^o pulse", where

$$\alpha = \gamma H_1 \nu_r \tau_o T_s \quad (1)$$

As in other selective pulse methods (2), the selectivity depends on the effective rf field intensity ($H_1\nu_r\tau_o$). A number of selective pulses may be applied simultaneously by superimposing modulation frequencies onto the pulse sequence. Following the method of reference (1), the modulation function is synthesized in a computer from the selected components and the length of the pulse sequence is chosen according to Eq. (1) to give the required flip angle.

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

August 1, 1974

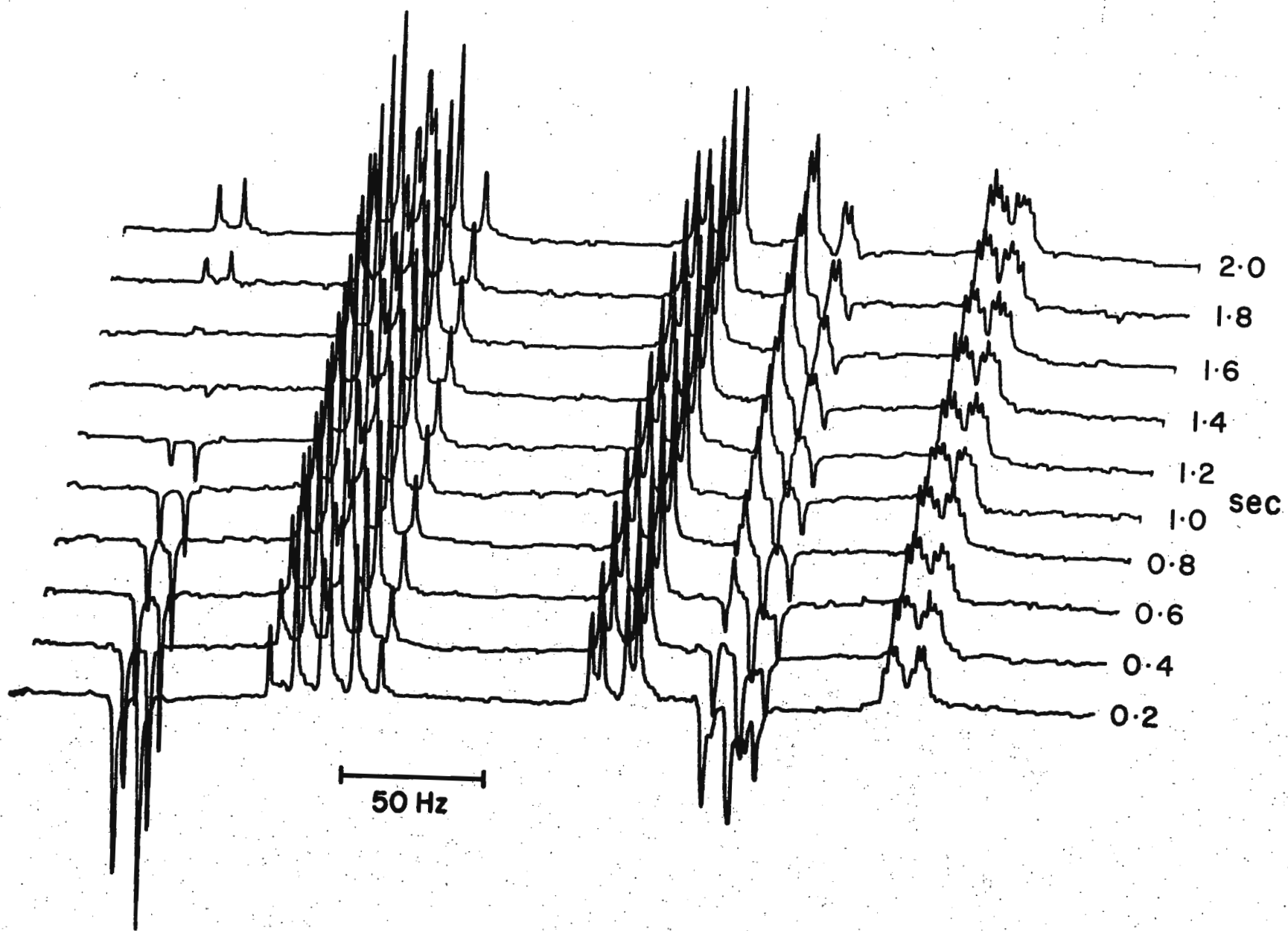
The figure shows a set of inversion-recovery spectra for the ring protons of 3,4,6-tri-O-acetyl-1-O-benzoyl-2-chloro-2-deoxy-D-glucopyranose (3) in which the "180° pulse" was a sequence of pulses (at 250 μ s intervals and total duration about 15 ms) which was selective for two of the resonance groups while the 90° pulse was non-selective. The initial rate of relaxation of a signal from a particular proton depends upon the perturbation of other protons to which it is coupled via a dipolar interaction. Measurement of this rate as other protons in turn are simultaneously inverted allows the evaluation of the relative dipolar interaction between the selected proton and each of the others. Results using this technique are in good agreement with results from nuclear Overhauser measurements on the same molecule.

Yours sincerely,

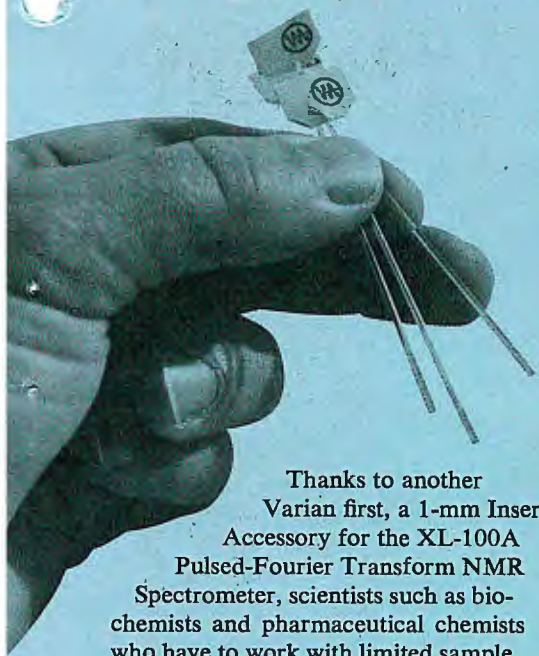
Howard.

H.D.W. Hill

- (1) B.L. Tomlinson and H.D.W. Hill, J.Chem. Phys. 59, 1775 (1973)
- (2) R.Freeman and S.Wittekoek, J.Mag. Res. 1, 238 (1969)
- (3) from L.D. Hall, U.B.C. Vancouver



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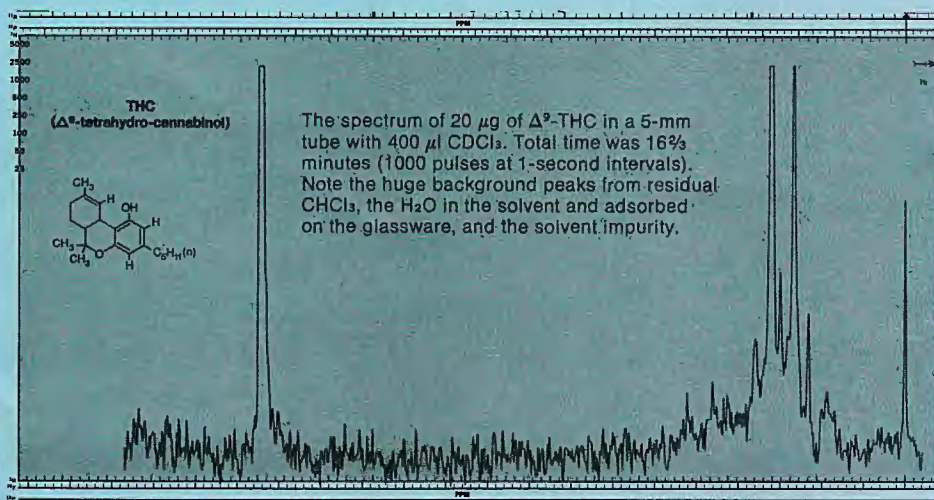
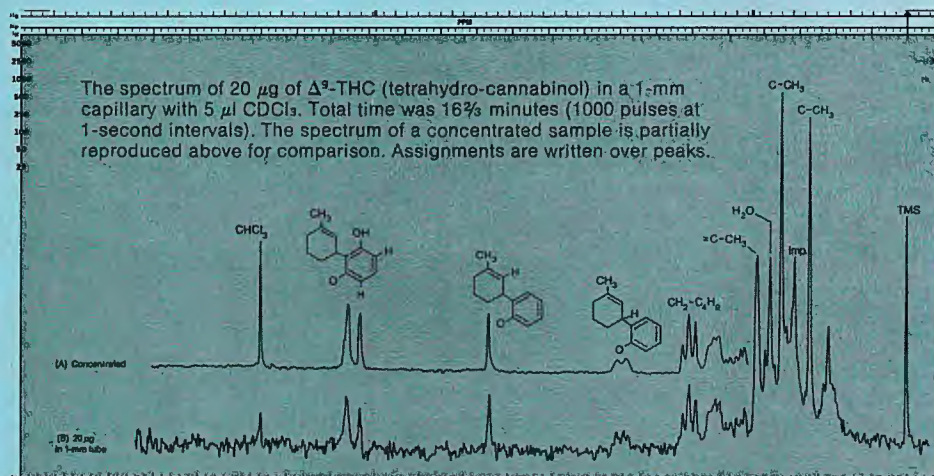
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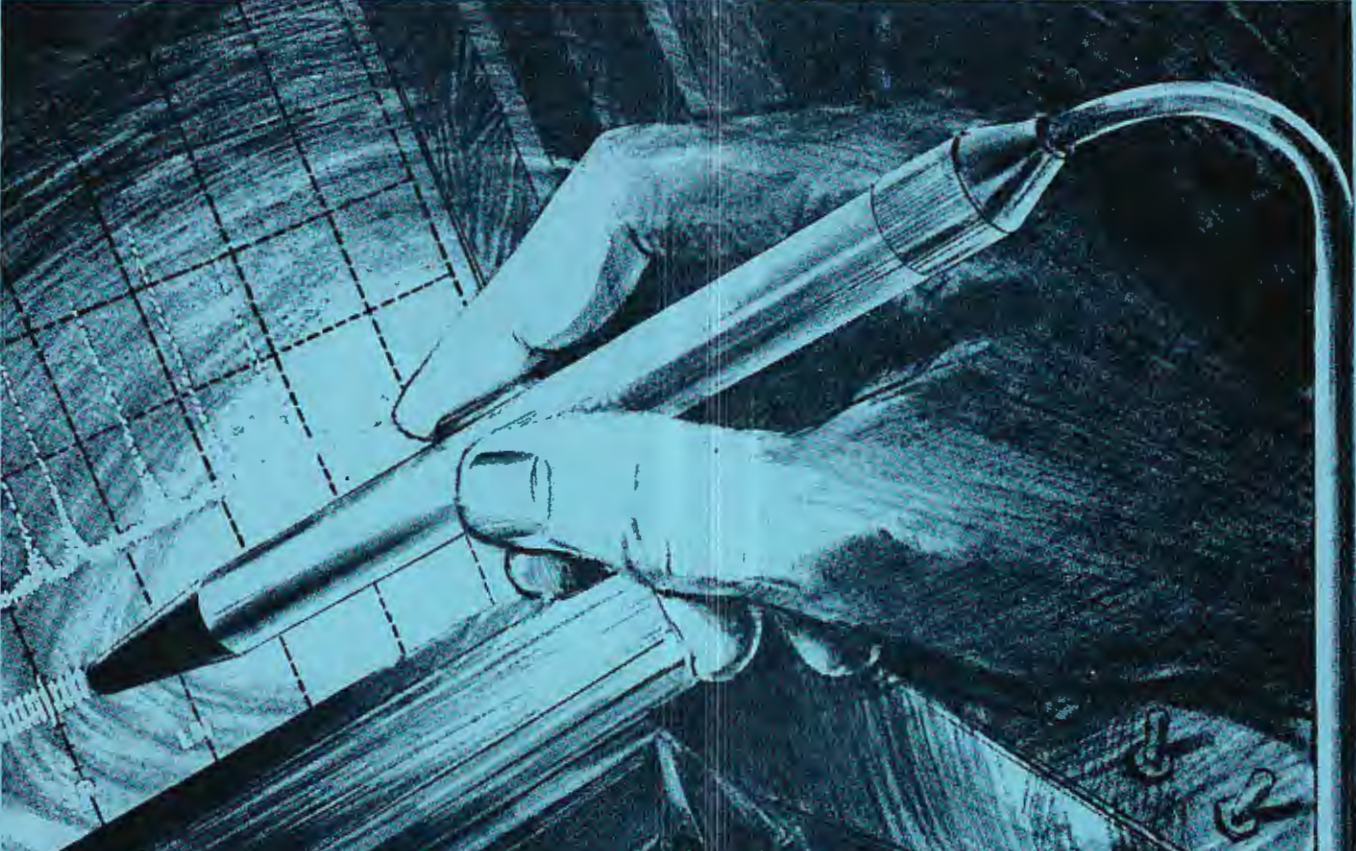
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Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.



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