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No. 176

May, 1973

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All Newsletter correspondence, etc. should be addressed to:

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

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Department of
CHEMISTRY

4 May 1973

TAMU NMR Newsletter: Advertisers, Advertising, Financial Policies and Readership

As all the Newsletter readers are aware, production and distribution of the TAMU NMR Newsletter is quite costly. Indeed, without the cordial and generous co-operation of our several advertisers, the Newsletter simply could not exist. Our advertisers are like any others in that they like to feel their interest and support is noticed and appreciated. I would therefore suggest that it would be helpful if you could mention the value of the Newsletter and the appearance in it of a particular company's ads when you are in contact with or making purchases from one of our loyal advertisers.

We are, in fact, very anxious to obtain a marked increase of advertising in the Newsletter, and your helpful suggestions along this line will be greatly appreciated. In particular, if any of you at commercial enterprises can induce support from your company, etc., for the Newsletter - either in the form of advertising or via becoming a Contributor or Sponsor - please try to do so. There are two purposes to be served by an increased level of advertising:

(i) Our finances are still slightly unstable and our year-end account balances still dips quite low, although no longer verging on irreversible disaster. Increased revenues would provide some highly desirable stability to the operation.

(ii) I am still highly desirous of being able to lower the subscription rates for all classes of subscribers. One of the founding, and still fundamental principles of the Newsletter, is that its existence and circulation should be self-regulating on a technical need basis. Unfortunately, economic necessity has imposed a financial barrier for many who would otherwise profit by and make useful contributions to the Newsletter. If we are successful in obtaining enough advertising revenue, we will be in a position to make a substantial reduction in the subscription rates, and this will definitely be done at the earliest possible time. Indeed, one can at least hope that we will eventually be able to provide the Newsletter without any individual subscription charges, when a sizeable and stable number of ads are committed each year.

Finally, I would greatly appreciate your helping us improve our service and documenting our circulation by filling out and mailing the enclosed post-card at your earliest convenience. On a trial basis, we now send the Newsletter out to overseas subscribers as "Air Mail-Printed Matter", in the hopes that this will speed up the receipt of the Newsletter. If this experiment proves successful, and the increased cost does not prove to be prohibitive, we may try extending this service to our U.S. and Canada subscribers.

As always, we will be very happy to receive any suggestions or criticisms aimed toward improving the Newsletter.

B. L. Shapiro

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

April 11, 1973

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

Dear Barry,

We have been determining distance ratios of the diazines from their PMR spectra in the lyotropic mesophase first reported by Lawson and Flautt (1). In Table I we show a comparison of our results with values obtained from thermotropic media and, where available, with x-ray and microwave results.

It is interesting to note that the lyotropic and thermotropic results for pyrazine and pyridazine are in considerably closer agreement than is the case with pyrimidine. This may in turn reflect corresponding differences in the effect of the ordered media involved on the diazine structures, a point which will require further investigation.

Sincerely,

Robert C. Long, Jr.

J. H. Goldstein
Professor

(1) Lawson, K. D. and Flautt, T. J., J. Amer. Chem. Soc., 89, 5489 (1967).

(2) Diehl, P. and Khetrapal, C. L., in NMR Basic Principles and Progress, Vol. I, ed. Diehl, P., Fluck, E. and Rosefield, R., Springer-Verlag, Berlin, 1969.

(3) Khetrapal, C. L., Patankar, A. V. and Diehl, P., Org. Mag. Res. 2, 405 (1970).

(4) Schneider, R. F., Dissertations Abstr. 20, 3536 (1960).

(5) Burnell, E. E. and De Lange, C. W., Mol. Phys. 16, 95 (1969).

(6) Wheatley, P. J., Acta Cryst. 10, 182 (1957).

(7) Wheatley, P. J., Acta Cryst. 13, 80 (1960).

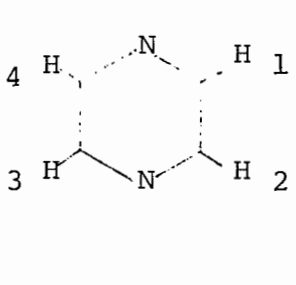
Table I. Distance Ratios for Pyrazine, Pyrimidine and Pyridazine

	NMR Lyotropic	NMR Thermotropic[a]	X-ray[b]	Microwave[c]
Pyrazine				
(r_{14}/r_{12})	1.651 ± 0.004	1.66 ± 0.02	1.703	--
Pyrimidine				
(r_{12}/r_{23})	1.6805± 0.013	1.62 ± 0.01	1.670	1.695
(r_{13}/r_{23})	1.972 ± 0.011	1.90 ± 0.02	1.957	1.979
(r_{24}/r_{23})	1.704 ± 0.004	1.706 ± 0.004	1.720	1.712
Pyridazine				
(r_{12}/r_{23})	0.983 ± 0.015	0.988 ± 0.010	--	1.030
(r_{13}/r_{23})	1.692 ± 0.008	1.693 ± 0.007	--	1.759
(r_{14}/r_{23})	1.897 ± 0.004	1.890 ± 0.004	--	2.033

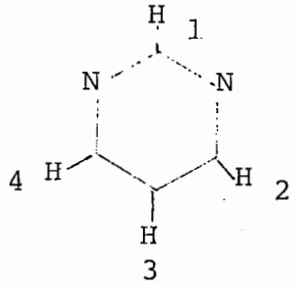
(a) Thermotropic values for pyrazine, pyrimidine, and pyridazine taken from Refs. (2), (3), (4) and (5), respectively.

(b) X-ray data is from Refs. (6), (9).

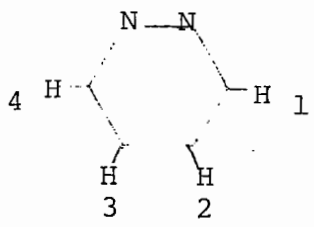
(c) Microwave distance ratios for pyrimidine were reported in Ref. (4). The values for pyridazine were calculated from the model proposed in Ref. (8).



pyrazine



pyrimidine



pyridazine

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Bollate, March 30, 1973

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

ref.: 735 LC/vr

Subject: F.F. coupling of fluorocyclopentenes

Dear Prof. Shapiro,

Thanks for your blue reminder and my apologies for the delay in replying you. My contribution, concerns with the F.F coupling results Dr. Harris (E.A.U) and I have obtained on some fluorocyclopentenes. Four cyclopentenes containing the $-CF_2CF_2CF_2-$ group have been, infact, fully analysed to yield values for the ^{19}F chemical shifts and all the FF coupling constants (except that only relative values of $^2J_{FF}$ are obtained). The Table herebyattached collects the F.F coupling values of the four cyclopentenes analysed. The vicinal coupling constants are found to be in the range $-8.5 \div -4.4$ H_z for the trans orientation and in the range $-1.9 \div +0.7$ H_z for the cis orientation. Details of the methods of analysis and discussion of the results obtained will appear in a forthcoming paper on J.Magn. Res..

Yours sincerely,

L. Cavalli

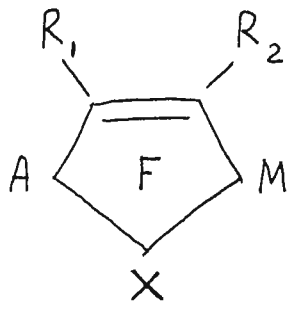
Luciano Cavalli

Coupling Constants of the Fluorinated Cyclopentenes I to IV

Compound	(F,F) Coupling Constant/Hz[a]										
	^2J_A	^2J_M	$^3J_{MX}$		$^3J_{AX}$		$^4J_{AM}$		$^3J_{BA}$	$^4J_{BX}$	$^4J_{BM}$
			trans	cis	trans	cis	trans	cis			
I[b]	+255.30	+255.30	-8.44	-1.37	-8.44	-1.37	+1.24	+4.12	-	-	-
II[b]	+254.3	+254.3	-5.7	-1.0	-5.7	-1.0	+1.3	+3.0	-	-	-
III	+255.7	+254.70	-6.89	-0.7	-6.42	-1.4	+1.28	+3.56	-	-	-
IV	+260.46	+250.88	-5.55	+0.66	-4.45	-1.85	+1.68	+3.07	-15.71	+4.91	+10.64

[a] The value of ^2J_X was kept constant at +240.0 Hz in the iterations.

[b] MeA for I and II.



I $R_1 = R_2 = I$

II $R_1 = R_2 = Cl$

III $R_1 = Cl$; $R_2 = I$

IV $R_1 = F_B$; $R_2 = I$

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JOURNALS DEPARTMENT

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April 3, 1973

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

SUBJECT: ASSIGNMENT OF THE ^{13}C RESONANCES OF THE C-8 SIDE CHAIN IN PROSTAGLANDINS

Dear Barry:

During the past 14 months we have examined the ^{13}C nmr spectra of a number of natural and synthetic prostaglandin (PG) derivatives. Using 5 mm O.D. tubes, quite good spectra can be obtained on samples as small as 8 mg. Since a separate resonance is frequently observed for each carbon of the PG skeleton, far more structural information is available than is found in the ^{1}H spectrum. This technique is proving to be of considerable value for the characterization of this class of biologically important compounds.

However, a completely unambiguous assignment of the observed resonances must be made. Such assignment for carbons 15-20 are possible by comparison with the spectra of 3-octanol[1], 1-octyn-3-ol and the PG intermediate, 3-(3-hydroxy-1-trans-octen-1-yl)-cyclopentanone(I).[2] The olefinic carbons of I can be assigned somewhat tenuously, by considering substituent effects[3] and the ring carbons are assigned by comparison with the spectrum. of 3-methyl-cyclopentanone.[4] As can be seen from the data in Table I, the chemical shifts of carbons 18-20 are essentially unaffected by changes on the 5 membered ring or C-7 side chain. The chemical shifts of C-13 and 14 do change considerable and are not reported here. The chemical shift of C-15 varies between 71.6 and 73.6 ppm and this is influenced somewhat by structural changes in the molecule. The standard deviations in the chemical

shifts of C-16 and C-17 are 3 and 2 times larger than expected and probably reflect some dependence on the structure of the remainder of the molecule.

Sincerely,

Michael L. Maddox

MLM:lo

(1) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz and H. J. Reich, J. Am. Chem. Soc., 92, 1338 (1970).

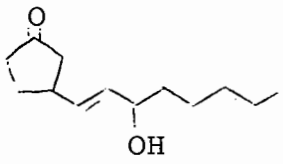
(2) A. F. Kluge, K. G. Untch, J. H. Fried, J. Am. Chem. Soc., 94, 7827 (1972).

(3) D. E. Dorman, M. Jantelat and J. D. Roberts, J. Org. Chem., 36, 2757 (1971).

(4) L. F. Johnson and W. C. Jankowski "Carbon-13 NMR Spectra" Wiley-Interscience, New York, 1972 p. 180.

TABLE I

^{13}C Chemical Shifts [a]

compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	
1-octyn-3-ol	62.06	84.91	72.48	37.53	24.65	31.38	22.52	13.91	
	132.43	132.96	72.32	37.24	24.94	31.59	22.45	13.86	cyclopentanone carbons 44.51-C2, 39.13-C3, 29.56-C4, 37.91-C5
25-15 hydroxy PG derivatives [b]			C-15 72.54 ±0.47	C-16 37.27 ±0.15	C-17 25.07 ±0.10	C-18 31.70 ±0.05	C-19 22.57 ±0.06	C-20 13.98 ±0.02	

a. Chemical shifts are reported with respect to internal TMS

b. Standard deviations

Professeur Pierre Laszlo — Institut de Chimie — Université de Liège — Sart-Tilman par 4000 Liège I — Belgique

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

April 6,1973.

STRAW-MEN ?

Dear Barry,

Rummens (1),in an otherwise useful reiteration of warnings about solvent effects on reference compounds,has somewhat misunderstood, or at least misrepresented the results of our study with Ed Engler of the camphor ASIS (2).It should be clear that our work is entirely based on reference-independent ASIS,obtained by the procedure subsequently labelled "Δ-difference method" by Rummens and Krystynak (1). Such differential information was altogether sufficient for our work,which addressed itself solely to the origin of the ASIS phenomenon,and is thus completely free of internal reference problems.

Your blue and pink reminders came at the same time as the Green letter (3),which I also find a bit hard to take.I must therefore restate the obvious : in principle,site factors should be calculated for each and every polar site in a solute molecule.Camphor is a particularly simple case,because to a very good approximation one may consider the C = O group as the only such polar site.Green (3) looks at the C = O group in crotonaldehyde,a molecule in which it is conjugated to a carbon-carbon double bond.Clearly,in that case, the polar "site" extends from the negatively charged oxygen to the positively charged β carbon;there is considerable ambiguity in locating the radius vector for each proton in the molecule.If we accept that "the solute,bornanone,is rather curious in that the negatively-charged end of the molecular dipole is quite small and readily accessible, whereas the positive charge is more dispersed" (3),what should one say about the unfortunate choice of crotonaldehyde,in which the positive charge is fudged all over ?

We have now completed our study of the T_1 relaxation times for the various carbon-13 nuclei of camphor in benzene solution. We find molecular reorientation to be isotropic and to proceed by small angular steps at 297 °K. At that temperature, the orientational correlation time is 2.1 $\pm$ 0.7 ps. At higher temperatures, there is a substantial spin-rotation component. The mean angle of rotation between collisions, as estimated from the angular momentum correlation time, increases to ca. 25 ° at 329 °K (4).

It was very nice seeing you in Aachen, and hearing about your affair with Lisa. Best regards,

Yours sincerely,

Pierre Laszlo

PL:pl

(1) F.H.A.Rummens, TAMU-NMR, 163-14; F.H.A.Rummens and R.H.Krystynak, J.Am.Chem.Soc., 94, 6914 (1972).
(2) E.M.Engler and P.Laszlo, J.Am.Chem.Soc., 93, 1317 (1971).
(3) R.D.Green, TAMU-NMR, 172-1.
(4) J.Grandjean, P.Laszlo, and R.Price, Mol.Phys. (in press).

DOTT.C.ANDREA BOICELLI
Laboratorio dei composti del carbonio contenenti etero-atomi e loro applicazioni
Consiglio Nazionale delle Ricerche
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li, 23/2/1973

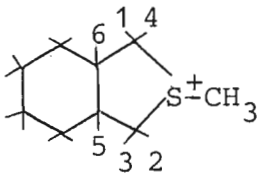
Professor Bernard L.Shapiro
TEXAS A & M UNIVERSITY
College of Science-Department of Chemistry
College Station, TEXAS, 77843 (U.S.A.)

Title: 1H-NMR study on a conformationally rigid thiolanonium cation.

Dear Professor Shapiro,

Thank You for the "blue"reminder. I am sending also my own "reminder": we receive, normally, the TAMUNN issues with two or three months of delay.

We have studied the compound I, where the trans ring fusion constrains the thiolane rigidly in the half-chair conformation. This conformational rigidity ensures for each of the α-ring protons a fixed torsional angle with respect to the "direction" of the lone pair on the sulfur, making this system a very useful model for testing the Wolfe-Czimandia theory.

(I) 

Under conditions of base catalysis sulfonium cations are known to undergo ready H-D exchange at α position. The $\oplus SCH_3$ group exchanges much faster than $-\overset{\oplus}{S}-CH_2-$, however, of the four α ring protons, one of them, H_2, exchanges relatively rapidly with specific rates $9x10^{-5}$ and $5x10^{-4}$ $l.m^{-1}.sec^{-1}$ at 59° and 75° respectively (D_2O/NaOD 1.7 or 1.2 N). Of the remaining protons, two, H_3 and H_4, appear to have approximately the same reactivity; the second or

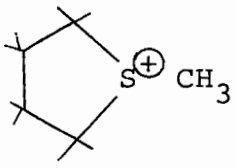
der specific rates are, approximately, 7×10^{-6} and 2×10^{-5} at 75° and 85° respectively. Thus, the rate ratio between H_2 and H_3 (or H_4) is about 75.

The fourth proton, H_1, is less reactive still; its apparent exchange rate is about 2-3 times slower than that of H_3 of H_4, hence some 200 times slower than H_2. It appears, however, that the observed ratio is an upper limit, as pyramidal inversion (wich interchanges H_1 with H_2) becomes competitive.

It is remarkable that exchange of H_2 and, respectively, H_4 is accompanied by a gradual change of the signals for H_3 and H_1, which eventually become doublets, indicating that H_1,H_4 and H_2,H_3 are geminal pairs.

The irradiation of $\oplus S\text{-}CH_3$ in a derivative of (I) with deuterium replacing H_1,H_3 and H_4 gave a n.O.e. of 15±1% for H_2.

In the parent ring cation (II), the n.O.e. were 12±1% for the cis protons and 2±1% for the trans protons (1). As the conformation of the 5-membered ring appears to be the same in (I) and (II), the 15% n.O.e. indicates that, in (I) also, H_2 and $\oplus S\text{-}CH_3$ are cis with respect to each other.

(II) 

1) A.Garbesi, G.Barbarella, A.Fava - Chem.Comm. in press.

Best regards.

Gianfranco Barbarella

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

Your ref | Our ref GJTT/IH | Tel Ext | Date 19 APR 73

Dear Professor Shapiro,

NMR of viscoelastic micellar solutions

In this letter we would like to describe some results we have obtained on the NMR of mixed surfactant solutions. It is well known that surfactant molecules aggregate to form micelles above a certain concentration in water. In these low viscosity micellar solutions the molecular motion is rapid and a high resolution spectrum is observed for the surfactant. We have been investigating the properties of micellar solutions containing mixtures of surfactants which differ from normal micellar solutions in that they exhibit viscoelastic properties.

In addition to making rheological measurements we have studied the high resolution and pulsed NMR of mixtures of the surfactants sodium dodecyl sulphate (n.$C_{12}H_{25}SO_4Na$, SDS) and octyl trimethyl ammonium bromide (n.$C_8H_{17}NMe_3Br$, C_8TAB) in D_2O. At the 5% surfactant level the phase behaviour is complex since two phase regions can occur; but in aqueous solutions which are viscoelastic we observe differential broadening of surfactant resonances, with line widths of up to 40 Hz. This broadening is independent of measurement frequency over the frequency range 60 - 220 MHz indicating that it is due to proton dipolar relaxation. Spin-lattice and spin-spin relaxation measurements by pulsed NMR show that the system is

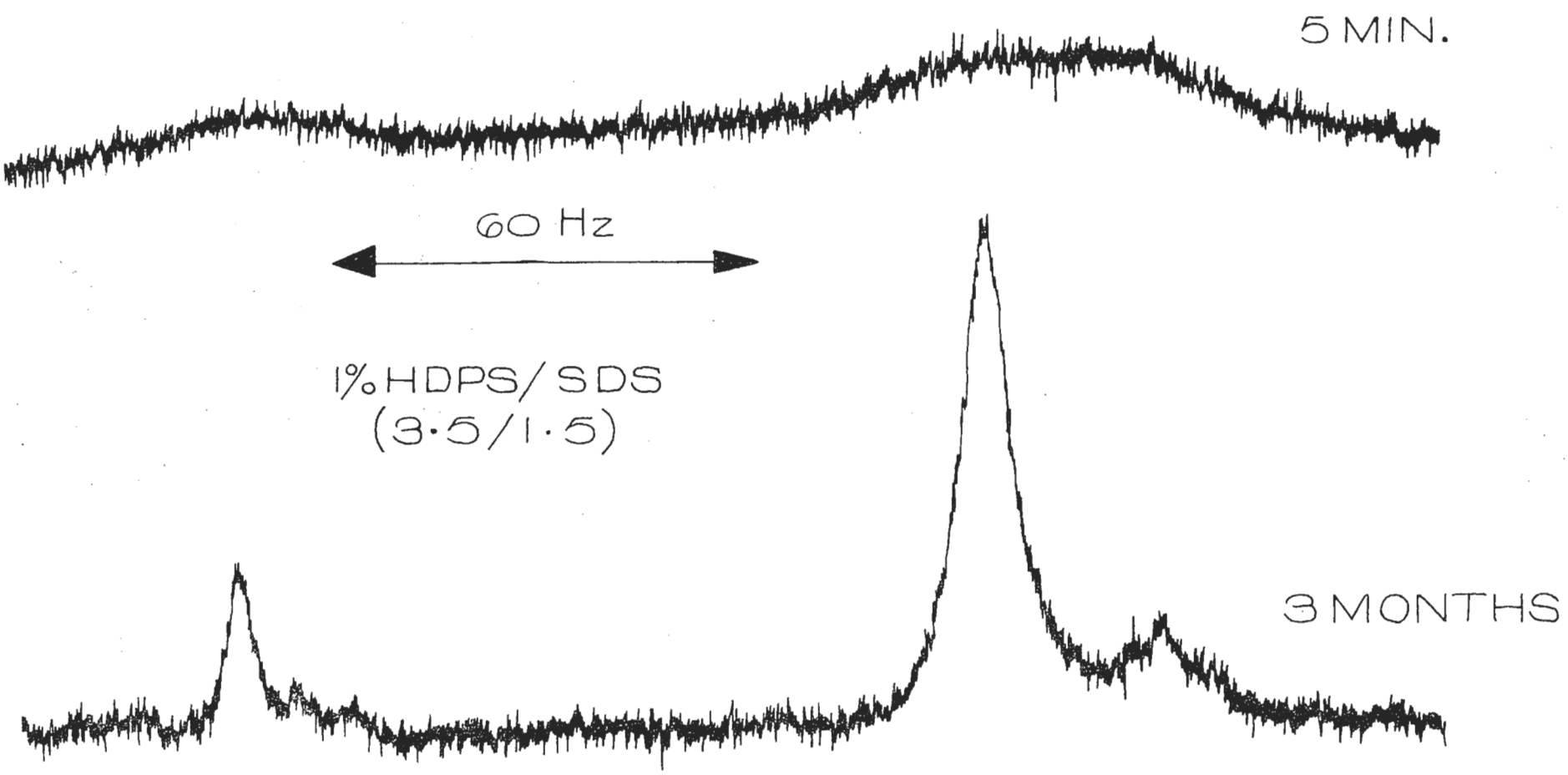
not characterised by a single T_1 or T_2 value (non-exponential recovery/ decay curves) and that the T_1/T_2 ratio is ca 50 with T_1 in the range 0.5 - 1.0 s. We interpret these results as suggesting the presence of a wide distribution of correlation times (τc) for surfactant molecular motions with τc taking values in the range 10^{-8} - 10^{-11}s. It appears to be impossible to account for this behaviour by the presence of only normal spherical micelles in the aqueous solution. We propose that in addition to the normal micelles, restricted cylindrical micelles also occur, in which the surfactant molecules have the long correlation time molecular motions.

Because only a single NMR spectrum is observed rapid exchange ($>10s^{3-1}$) of each surfactant molecule between the two environments must occur.

A more unusual situation occurs with aqueous mixtures of the surfactants SDS and hexadecylammoniopropane sulphonate ($n.C_{16}H_{33}\overset{(+)}{N}(Me)_2\ (CH_2)_3SO_3^{(-)}$, HDPS). Some solutions of these surfactants above 2% total concentration are viscoelastic and show similar rheological and NMR properties to the SDS/C_8TAB solutions. In addition the properties of 1% solutions depend on their method of preparation. Samples prepared from 1% stock solutions of pure surfactants are similar to normal micellar solutions. Samples prepared by dilution of viscoelastic solutions with water initially exhibit viscoelastic properties and broadened NMR spectra, but these 'relax' over a period of hours or days to low viscosity normal micellar samples (see fig 1). We interpret this result as being due to the slow breakdown of the restricted micelles and the kinetics of this process (measured from NMR broadening) is first order in agreement with this. We are in the process of writing up these results for publication.

Yours sincerely,

P A WHEELER B A WHEELER G J T TIDDY



60MHz HIGH RESOLUTION NMR SPECTRA OF A DILUTED VISCO-ELASTIC 5% HDPS/SDS SOLUTION

DEPARTMENT OF CHEMISTRY
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TEL. 0703-59122
TELEX 47661

9th April 1973

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

Dear Barry,

Spinning Liquid Crystal Solutions

The effect of sample rotation on the dipolar coupling constants is well known (1), but there are some misconceptions current about the effect on linewidths, and on ordering parameters. In a recent note (2) we discuss these latter effects under the somewhat obscure title of "Magnetohydrodynamic effects in nematic mesophases", and perhaps a more qualitative description will help those involved in studies of NMR spectra of partially aligned solutes.

Figure 1 shows the ^1H spectrum from CH_3CN dissolved in Phase V at various spinning rates ω. As ω increases the outer lines move towards the centre line, and they also tend to increase in width. This broadening increases very markedly as the critical speed ω_c is approached. Figure 2 shows the result of accurate measurements of the linewidth with rotation speed, and this trend to broader lines is clearly seen. There is in fact a slight decrease on going from $\omega = 0$ to $\omega = 7$, but this is overtaken by a broadening effect as ω increases. The increase with linewidth on rotating is in accord with theory (3), and a qualitative explanation is as follows. In a stationary sample the liquid crystal molecules are on average aligned at an angle θ to the magnetic field. On rotating, the angle θ increases and also acquires an uncertainty $\delta\theta$, giving rise to the line broadening. When $\omega > \omega_c$ the liquid crystal molecules rotate about the spinning axis with a frequency $|\omega_c - \omega|$ and the outer components of the triplet broaden beyond detection. The centre line is unchanged, except for the effects of any chemical shift anisotropy, and remains sharp. Note that the sample is still anisotropic and the order is unchanged.

For solutes with lower symmetry the effects will be more complex since the lines depend on the ordering of the liquid crystal in different ways. For all solutes, however, we can state that in the absence of other effects (temperature or concentration gradients) rotating the sample will lead to broadening of some lines, and rapid rotation does not destroy the ordering.

Best wishes,

Jim

J. W. Emsley

References

1. P. Diehl and C. L. Khetrapal, Mol. Phys., 14, 283 (1967)

2. J. W. Emsley, J. C. Lindon, G. R. Luckhurst and D. Shaw, Chemical Physics Letters, (1973).

3. F. M. Leslie, G. R. Luckhurst and H. J. Smith, Chemical Physics Letters, 13, 368 (1972).

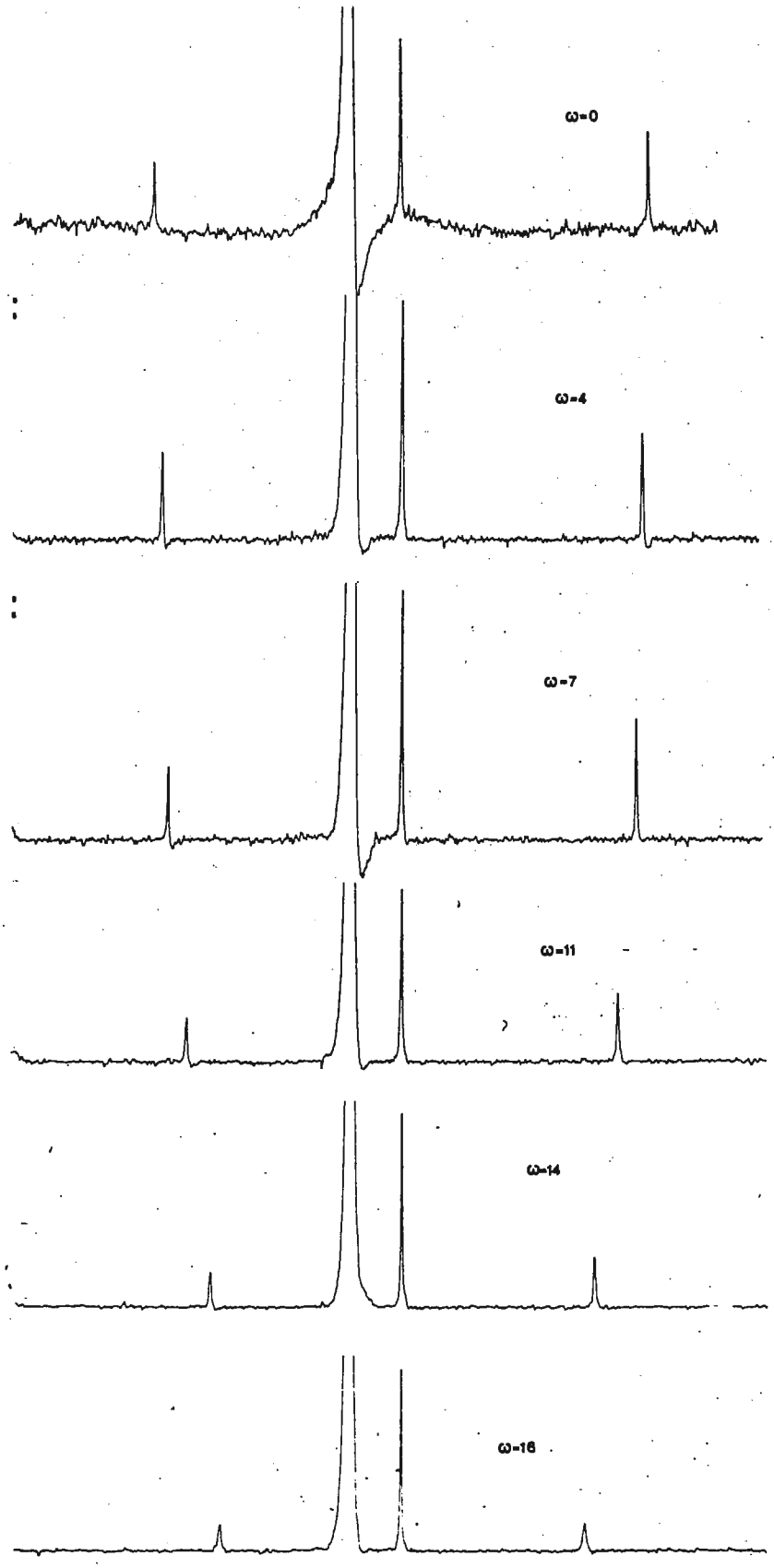

Fig 1. Spectrum of CH_3CN in a nematic phase recorded at different spinning speeds.

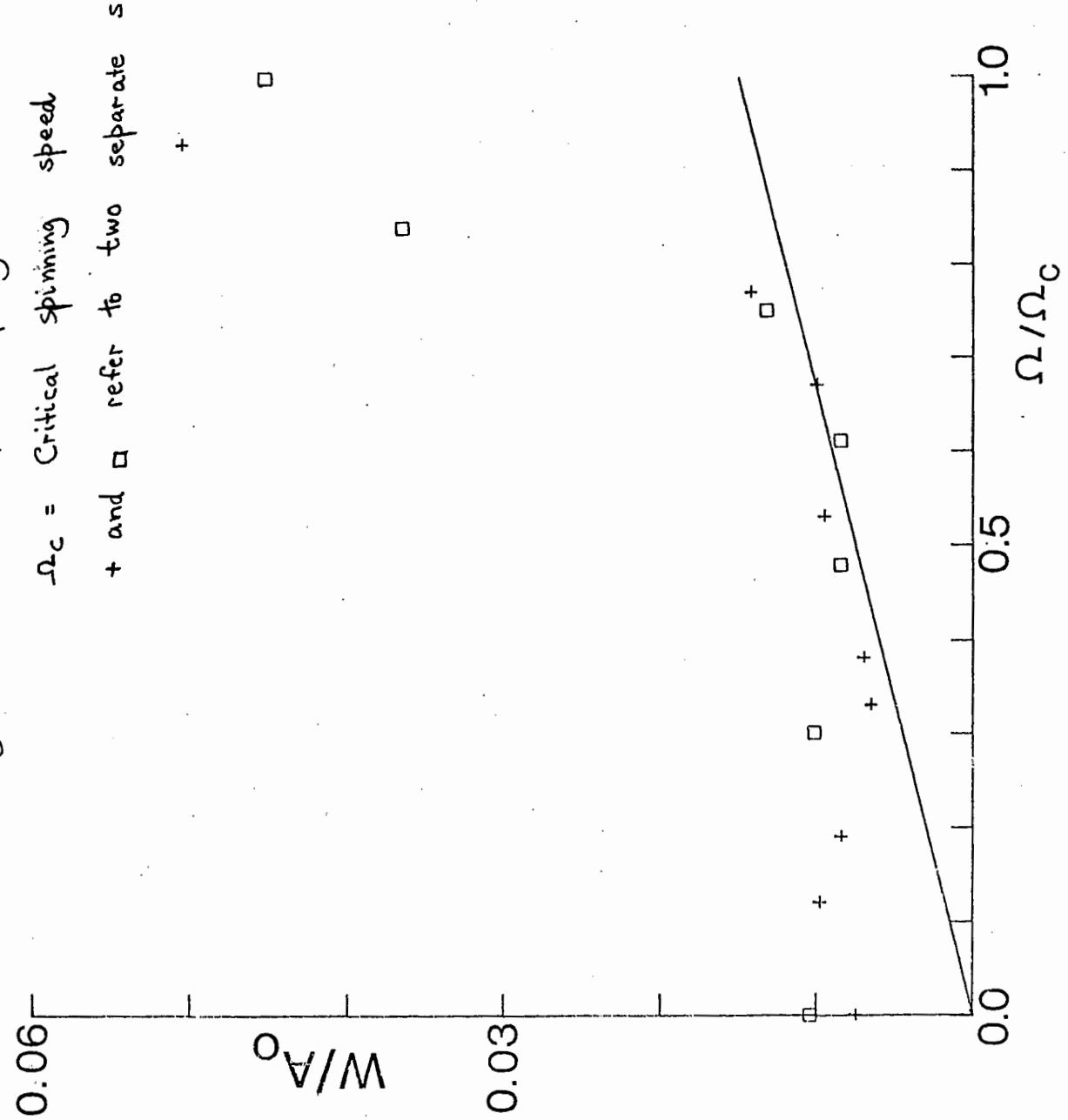

fig 2. W = linewidth at spinning speed Ω
A_o = Dipolar splitting at zero Ω
Ω_c = Critical spinning speed
+ and □ refer to two separate samples

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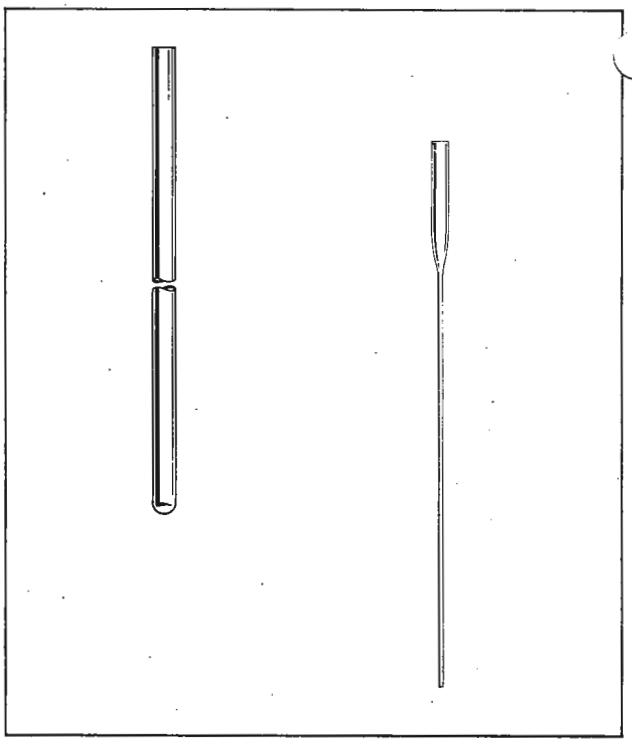

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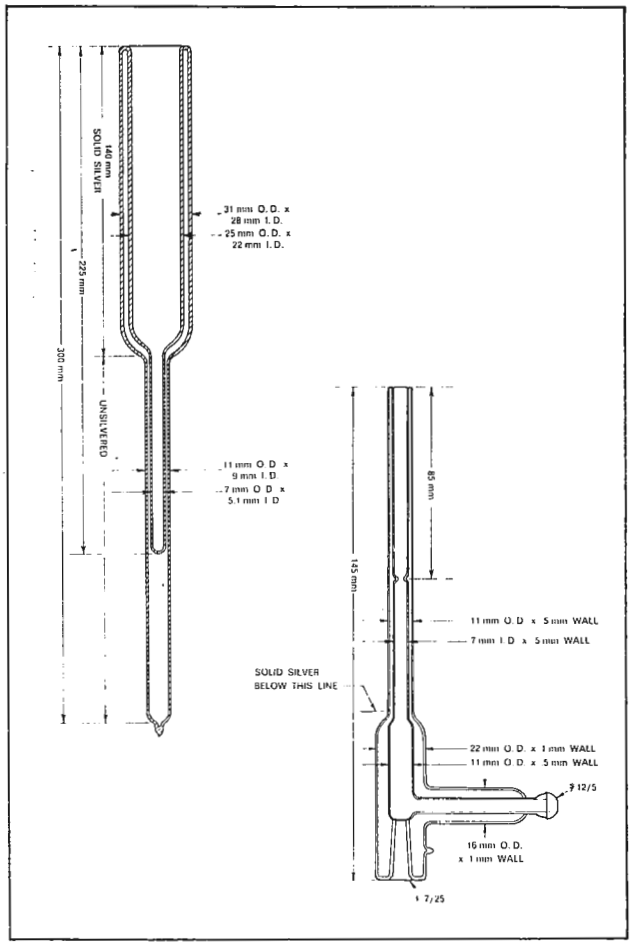

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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April 4, 1973

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

Title: More on Imidazole-N-H, ^{13}C, ^{19}F

Dear Barry:

Imidazole is the only amino acid residue which usually has a pK around neutrality, it is known to be involved in the mechanisms of several enzymes and its unusual chemical properties result in its NMR resonances being well resolved from others within a protein as well as giving rise to NMR titration curves. For these reasons we have been studying imidazole and its derivatives in some detail.

An unusual downfield titrating resonance of ribonuclease A in H_2O was described by Patel, Woodward and Bovey (1) which they attributed to an imidazole NH resonance. We have studied this resonance under several experimental conditions and have correlated it with one of the four imidazole C2-H resonances. For example, the figure shows the titrations of the NH resonance and three of the C2-H resonances carried out on the same sample in H_2O. As one can see the N-H resonance correlates only with resonance H-3. Further details will be described elsewhere (2).

We have recently reported the carbon-13 NMR titration curves of histidine (3) and are extending this to the (1-15) peptide of ribonuclease, as we have done previously using ^{13}C enriched phenylalanine (4). We have also studied the ^{19}F and ^{1}H NMR of 2- and 4- fluoro-imidazole and histidine as a function of pH with some very interesting results (5).

Our Varian 220 FT system has been up and running since installation. With the expected S/N improvement over CW mode — more, as well as better, data for proteins are achieved.

With best regards,

Jack S. Cohen
Physical Sciences Laboratory

References:

1. D. J. Patel, C. K. Woodward and F. A. Bovey, Proc. Nat. Acad. Sci. (USA), 69, 599 (1972).

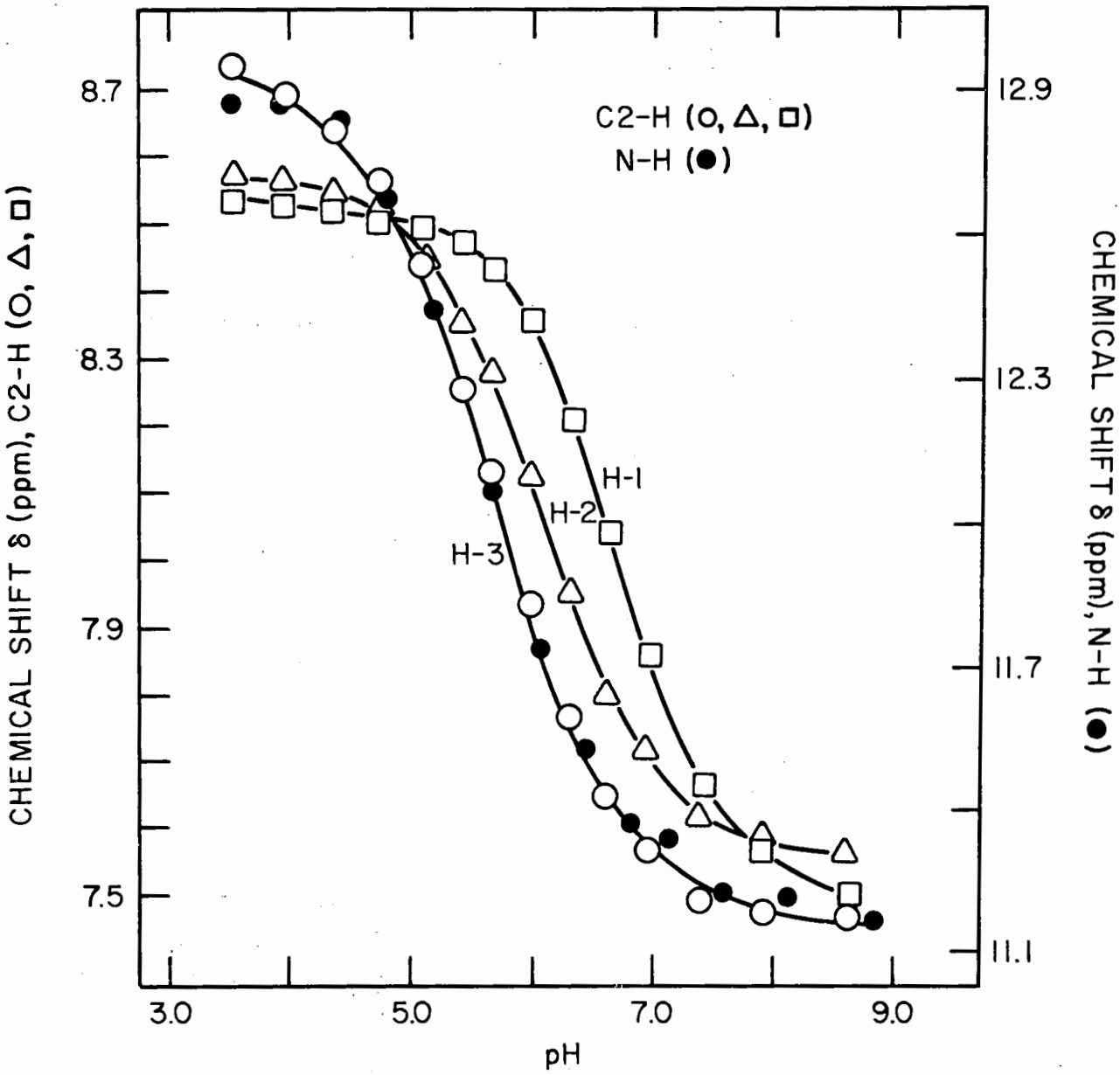
2. J. H. Griffin, J. S. Cohen, and A. N. Schechter, Biochemistry, (in press).

3. M. H. Freedman, J. R. Lyerla, Jr., I. M. Chaiken and J. S. Cohen, Europ. J. Biochem. 32, 215 (1973).

4. I. M. Chaiken, M. H. Freedman, J. R. Lyerla, Jr., and J. S. Cohen, J. Biol. Chem., 248, 884 (1973).

5. H. J. Yeh, J. S. Cohen, K. Kirk and L. A. Cohen, paper in preparation.

Figure Legend: PMR titration of RNase A in 0.1 M NaCl, H_2O at 22°. Chemical shift changes of the NH resonance are normalized with the chemical shift changes of the C2-H resonances to facilitate comparison.


C2-H (O, Δ, □)
N-H (●)
H-1
H-2
H-3
8.7
8.3
7.9
7.5
12.9
12.3
11.7
11.1
3.0
5.0
7.0
9.0
pH
CHEMICAL SHIFT δ (ppm), C2-H (O, Δ, □)
CHEMICAL SHIFT δ (ppm), N-H (●)

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April 10, 1973
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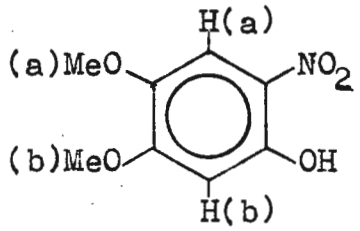
Prof. B. L. S h a p i r o,
Department of Chemistry,
Texas A. & M. University,
COLLEGE STATION,
Texas 77843,
U.S.A.

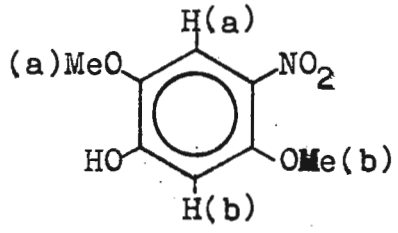
Is there any nuclear Overhauser effect of OH proton in ortho-methoxyphenol?

Dear Professor Shapiro:

Recently we had to choose between the structures A and B for a compound.



A



B

The ^{1}H-NMR spectrum of the compound consists of five lines at: 11.02, 7.45, 6.52, 3.95, and 3.88 δ assigned to OH , H(1), H(2), Me(1), and Me(2) protons, resp.

The NOE results (% of enhancement) are :

Line observed	H(1)	H(2)	OH
irradiated			
Me(1)	0	20%	0
Me(2)	20%	0	0
OH	0	0	X

The twenty percent NOE enhancement allows to assign Me lines (employing the assignment of ring protons based on substituent increments; shifts calculated for H(a) 7.56 and H(b) 6.42 δ): Me(1) and Me(2) lines belong to Me(b) and Me(a), resp. The nil effect observed on OH line would point to the structure A but caution called for additional experiments with model compounds.

NOE on guaiacol (o-methoxyphenol) gave also nil enhancement for the OH line! (Though NOE on ring protons was observed.) Apparently the scalar relaxation or unfavourable geometry reduced the effect.

So, after all, we had to resort to old familiar OH proton chemical shifts which are in o-nitrophenol in the region of 11 δ and in o-methoxyphenol around 6 δ. Therefore the compound has the structure A (in agreement with the nil NOE!).

Sincerely yours,

J. Schraml J. Dědina W.S. El-hamouly

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April 12, 1973

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

TITLE: Post-doctoral and Industrial NMR Openings Plus an Address Change

Dear Barry:

This September I will be leaving General Electric and joining the chemistry department faculty at Florida State University. This move will generate two openings: my present position at GE and also a Post-doctoral appointment at Florida State University.

INDUSTRY - At the General Electric Research and Development Center we will have a staff opening for a Ph.D. chemist with experience in multi-nuclei nmr who is primarily interested in applying spectroscopic techniques to deal with organic and organometallic structure-mechanism problems. The position requires independent support for the research of, as well as consultation with, 30-40 organic chemists. NMR instrumentation includes a Varian XL-100-15 and two T-60 spectrometers.

ACADEMIC - The new nmr facility at FSU consists of two FT spectrometer systems: a Bruker HFX-90 and a Bruker HX-270, each interfaced to Nicolet 1080 series computers. The spectrometers are run by a technical supervisor and technician. This post-doctoral position will thus not require routine running of service samples.

The appointment will involve research in the area of carbon-13 spin-lattice relaxation studies and their applications to physical chemical problems. A physical chemist or physical-organic

GENERAL ELECTRIC

Professor Barry Shapiro April 12, 1973

chemist interested in molecular dynamics should find this experience very rewarding.

HOW TO APPLY: Whether you are interested in the Industrial or Academic position (or both!) send your resume to me at General Electric. Starting dates for the two positions are after July 1 (GE) and after September 15 (FSU).

Yours sincerely,

George C. Levy

Dr. G. C. Levy
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L-Methionine-D or ^{13}C
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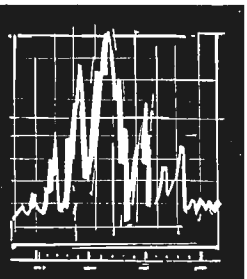
(partial list only)



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DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

April 19, 1973

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

Dear Barry:

PDIGM: A computer program for the simulation of LIS spectra.

After several months of cleaning up the program we developed for the interpretation of LIS data we are ready to distribute it. It is written in Fortran IV. Requests should be addressed to Ray Davis as noted at the bottom of the letter.

The program is essentially the one described in J. Amer. Chem. Soc., 94, 1742 (1972). It accepts as input the coordinates of the atoms in the molecule under investigation, the LIS shifts, and a variety of control characters. The output can be varied from stark (a few lines) to voluminous (reams) by the judicious use of the control parameters. In general we display all fits of reasonable agreement for all acceptable lanthanide positions, and find that the work-up of a single set of data requires a few seconds of computer time, and a thousand or so lines of output.

The approach uses a paradigm, hence the program name PDIGM. Its advantages and disadvantages become evident after one or two trial calculations. To those of you who are interested we say: "Try it. You'll like it."

Sincerely yours,

M.R. Willcott

R.E. Davis
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

RUTGERS UNIVERSITY *The State University of New Jersey*

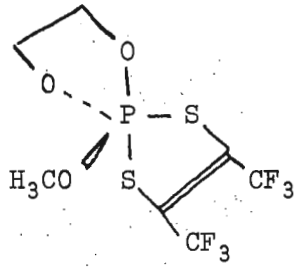
SCHOOL OF CHEMISTRY
Ralph G. Wright Laboratory
New Brunswick, New Jersey 08903

April 25, 1973

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

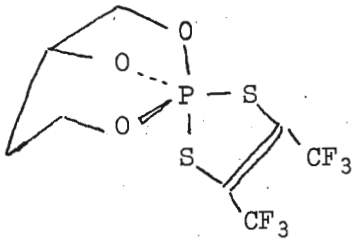
Dear Professor Shapiro:

The phosphoranes, 1-3, were prepared by reaction of the appropriate phosphite with 3,4- bis(trifluoromethyl) 1,2-dithietene. ① The relavent spectral data are tabulated below. ②



1

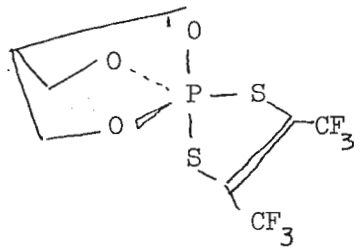
^{31}P -16.5
^{19}F 30° +54.2 doublet
J_{FCCSP} = 5.2 Hz
-80° +52.7 doublet
J_{FCCSP} = 5.2 Hz



2

^{31}P -12.5
^{19}F 30° +54.1 doublet
J_{FCCSP} = 3.6 Hz
25° coalesence temperature
-100° +52.38
+54.15 double quartets
J_{FCCSP} = 3.6 Hz
J_{FCCCCF} = 11.0 Hz

Professor B.L. Shapiro April 25, 1973



3

^{31}P -17.5

^{19}F 30° +53.72 doublet
J_{FCCSP} = 3.4 Hz
-26° coalescence temperature
-80° +52.15
+53.88
double quartets
J_{FCCSP} = 3.4 Hz
J_{FCCCCF} 13 Hz

The results of the variable temperature ^{19}F nmr experiments show that there is an intramolecular exchange process, which can be slowed sufficiently, on the nmr time scale, so that the trifluoromethyl groups in 2 and 3 become magnetically nonequivalent. This could not be demonstrated for 1; which showed no spectral changes on cooling.

These results can be explained in terms of intramolecular permutations, Berry pseudoroations, which allow the 5-membered di-oxygen containing rings to assume di-equatorial positions in the trigonal bipyramid. Alternatively a TR^3 process which bypasses these intermediates can be invoked. It has been reported (3) that $\Delta G\ddagger$ for processes in which 5-membered di-oxygen containing rings go di-equatorial would fall in the range from 15.6 to 18.4 Kcal/mole. Using the method of coalesence temperatures and chemical shift differences at low temperatures (4) one caluclates energies of activation for such processes in 2 and 3 to be 14 and 12 Kcal/mole. However, these numbers are surely subject to large errors since the spectra display fine structure due to spin-spin coupling.

We are planning to do the line shape analyses to derive accurate thermodynamic parameters. These data will be of interest because they will illustrate further the effect of strain on pseudorotational processes.

Sincerely,

Dorothy Z. Denney

Dorothy Z. Denney

Norman J. De'Ath

sm

Subject: Structural Effects on Pseudorotation Rates.

(1) N.J. De'Ath and D.B. Denney, Chem. Comm., 395 (1972).
(2) ^{31}P shifts relative to 85% H_3PO_4, ^{19}F shifts relative to CCl_3F.
(3) D. Houalla, R. Wolf, D. Gagnaire and J.B. Robert, Chem. Comm., 443 (1969).
(4) J.A. Pople, W.G. Schneider and H.J. Bernstein, "High Resolution NMR", M.Graw-Hill, New York, N.Y., 1959, p. 218ff.

UNIVERSITY OF TORONTO
DEPARTMENT OF MEDICAL CELL BIOLOGY
MEDICAL SCIENCES BUILDING
TORONTO, CANADA
M5S 1A8

TELEPHONE: 928-2011
AREA CODE 416

April 18, 1973.

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

Dear Professor Shapiro:

Since this is my first contribution to the TAMU NMR Newsletter I decided to confine myself to a brief description of the research activities and equipment in my laboratory.

We are using a Bruker variable frequency (4-60 MHz) pulsed spectrometer with an 18" Bruker magnet. The equipment was purchased in 1969, including the 18" magnet and a 1062 Fabritek signal averager. I knew we would eventually want to have Fourier Transform capability and felt this was the most versatile route. We have, over the last few years, managed to scrape together the high resolution accessories and are about to take off with variable frequency Fourier transform, having interfaced our signal averager (now a 1072) with a Sigma 5 computer in the Building. Our high resolution work is done at the Canadian 220 MHz NMR Centre which is located at Sheridan Park, just outside Toronto.

There are four problems of major interest to me at the moment.

1. Study of the 220 MHz high resolution proton spectrum of an enzyme from bacteriophage λ (endolysin) and a series of temperature sensitive mutant forms of this enzyme. This is a basic study of primary structure influences on secondary and tertiary structure stability.
2. Proton relaxation enhancement (PRE) studies of a Mn^{2+} requiring allosteric enzyme from Salmonella - phosphoenolpyruvate carboxylase.
3. Structure function relationships of Concanavalin A, a metal requiring plant protein which binds to animal cell surfaces and shows differential effects with normal and malignant cells. We have examined the 220 MHz proton spectrum of the protein and the PRE of the solvent and sugars which bind to Con A.

Professor B. L. Shapiro April 18, 1973.

4. Cell water proton relaxation time measurements of normal tissue, malignant tissues, and cultured cells with a view to understanding the possible role of water structure changes in malignancy and a variety of other abnormal and normal growth and differentiation conditions.

In solvent exchange studies with macromolecules, the ability to measure both T_1 and T_2 as a function of frequency has proved mandatory to adequate analysis. The variable frequency F. T. system will permit us, to some extent, to apply this type of analysis to single lines in the more complex spectra of the low molecular weight compounds which interact with the proteins we are studying.

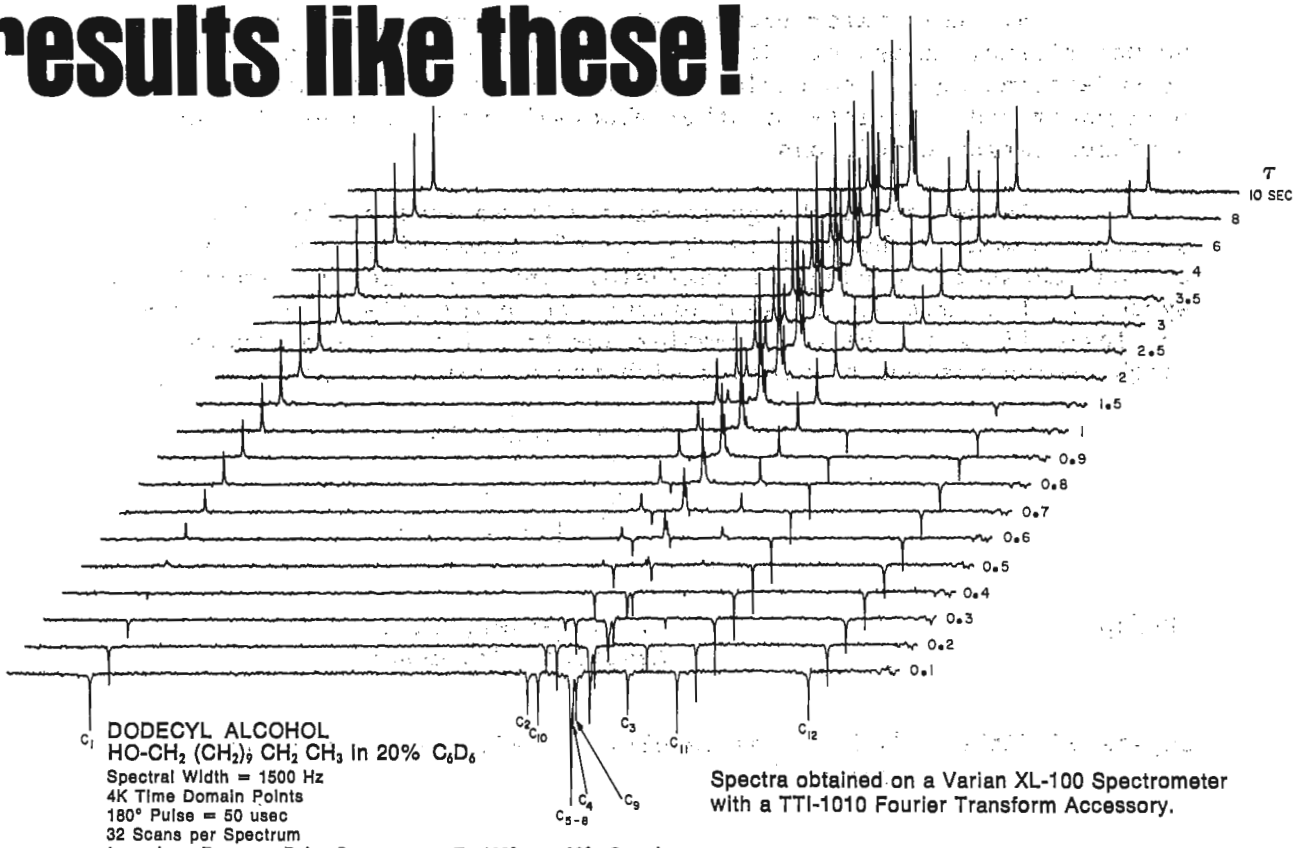
Yours sincerely,

JPC/np

J. P. Carver, Ph.D.,
Assistant Professor.

Suggested Title: "NMR at the Faculty of Medicine, University of Toronto".

Your Ft nmr system can provide results like these!



DODECYL ALCOHOL
$HO\text{-}CH_2\ (CH_2)_9\ CH_2\ CH_3$ in 20% C_6D_6
Spectral Width = 1500 Hz
4K Time Domain Points
180° Pulse = 50 usec
32 Scans per Spectrum
Inversion—Recovery Pulse Sequence . . . T - 180° - τ - 90° - Sample . .

Spectra obtained on a Varian XL-100 Spectrometer with a TTI-1010 Fourier Transform Accessory.

It's easy using the Nicolet 1080 Data System. The 1080 incorporates unique concepts designed specifically for the scientific laboratory. It has two processing units—a wired one for acquiring data and a programmable one for processing data. Thus each unit performs the functions it does best. Signals are digitized and added to memory by the wired processor while it is displaying the entire averaged signal in a continuous, flicker-free display. This unique signal averager approach to data acquisition allows the display to continue regardless of the data acquisition rate (up to 100 kHz) so that the user can examine the input signal or the averaged signal, at any vertical or horizontal expansion, **without interrupting the data acquisition process.** This allows instantaneous inspection of the signal to noise as well as examination of the data for pulse feedthrough, decoupling power, and frequency offset.

The unique 20-bit word 1080 data processor not only allows more single-precision dynamic range than any other, but it also has a much more powerful instruction set. This permits faster and more efficient data reduction and programming simplicity.

The above spectra of dodecyl alcohol were obtained using the Nicolet automatic T_1 program, which utilizes the [180° - τ - 90° - (sample) - T]$_n$ inversion recovery[1] or PRFT[2] pulse sequence. In this experiment, the value of the inter-pulse interval τ is varied from a time much less than the shortest T_1 to a time about 5 times longer than the longest T_1 in the sample. Data are signal averaged at each value of τ and stored on the Nicolet 600,000 word cartridge disk memory.

For $\tau \ll T_1$, nuclear magnetization will still be inverted when the 90° pulse is applied, leading to inverted peaks in the transformed spectrum. For $\tau \approx T_1 \ln 2$, a null will be observed, since at this time the magnetization is just passing through zero when the 90° pulse is applied. Finally, when $\tau \gg T_1$, the nuclei will have returned to their usual precession about the +z axis before the 90° pulse is applied, and the experiment reduces to the usual single pulse Ft nmr experiment.

After all spectra are obtained, they are processed all at once and displayed or plotted as shown. The spin-lattice relaxation times of each line can be estimated from the plots or calculated using a least squares treatment, from the equation $A = A_0\ [1 - 2\ \exp\ (-\tau/T_1)]$. This calculation is performed directly by the program upon command.

This quality of data and ease of operation can be yours with the Nicolet 1080 Data System, including the 600,000, 20-bit word NIC-294 cartridge disk system and the NIC-293 Pulse Controller. This latter unit allows the production of up to eight computer-selectable times corresponding to rf pulses and pulse intervals. This unit is already in use measuring T_1's, T_2's, performing gated decoupling and homonuclear pulsed decoupling and providing the versatility for use in almost any definable experiment.

The Nicolet 1080 Data System has been successfully used with all major spectrometers and is also available with a complete Fourier pulse accessory package for the Varian XL-100 through Nicolet's affiliate, Transform Technology, Incorporated.

Why not investigate the features of the 1080 Data System and find out how it can make your nmr spectrometer perform more efficiently.

1. R. L. Void, J. S. Waugh, M. P. Klein, and D. E. Phelps, **J. Chem. Phys. 48,** 3831 (1968).
2. A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson and F. Gurd, **J. Am. Chem. Soc. 93,** 544 (1971).

NICOLET INSTRUMENT CORPORATION
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THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

20 April, 1973

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

NON-EXPONENTIAL METHYL NUCLEAR RELAXATION FOR MACROMOLECULES

Dear Barry,

We have been interested in the NMR relaxation times of a methyl group on a macromolecule as a probe of flexibility at the site of the methyl group; specifically, we have now collected data on a number of arginine and lysine analogs as inhibitors of the enzyme, trypsin. We knew that non-exponential relaxation had been predicted[1] and observed[2] for solids, but was much less important for small molecules in liquids. Macromolecules might be expected to lie somewhere in between, so to settle the matter, we have extended Hubbard's[3] treatment of intra-molecular dipole-dipole relaxation for a methyl group to the non-extreme-narrowed limit, $4\omega_0\tau_c \geq 1$. The details will appear in J. Mag. Res. (preprints are available on request), and the net outcome is shown in Figure 1.

A number of features deserve comment. First, both longitudinal and transverse relaxation become exponential for a spherical macromolecule (curve "P" in each plot). Second, in the "fast-motion" or "extreme-narrowing" limit, $4\omega_0\tau_c \ll 1$, the longitudinal ("T_1") and transverse ("T_2") relaxation become identical, even though the resultant can still be markedly non-exponential; this result is a generalization of the usual statement that $T_1 = T_2$ under extreme narrowing conditions. (see plot a). Third, relaxation immediately following a 90° or 180° pulse approaches a single exponential--one would have to wait a couple of time constants in order to discover the non-exponentiality of the magnetization time-dependence.

In conclusion, it appears (as expected) that non-exponential methyl relaxation is most pronounced when internal rotation is rapid compared to isotropic tumbling of the molecular frame itself, and that the non-exponentiality for a macromolecule is intermediate between that of a small molecule and a solid. Practically speaking, any non-exponential effect would be difficult to observe experimentally, because both spin-rotation and inter-molecular effects would contribute exponential relaxation which might well mask any non-exponential effect. Finally, CF_3 relaxation may also be non-exponential, but because of cross-correlation between different relaxation mechanisms--this problem is under attention and should be solved shortly.

Alan G Marshall

Sincerely,

Alan G. Marshall and Lawrence G. Werbelow

1. R. L. Hilt and P. S. Hubbard, Phys. Rev. 134, A392 (1964).
2. M. F. Baud and P. S. Hubbard, Phys. Rev. 170, 384 (1968).
3. P. S. Hubbard, J. Chem. Phys. 52, 563 (1970).

FIGURE 1. Plots of log(magnetization) versus time, following a θ-pulse along the y-axis of a rotating frame, for a methyl group attached along the symmetry axis of a symmetric top molecule.

For plots 1b and 1d,

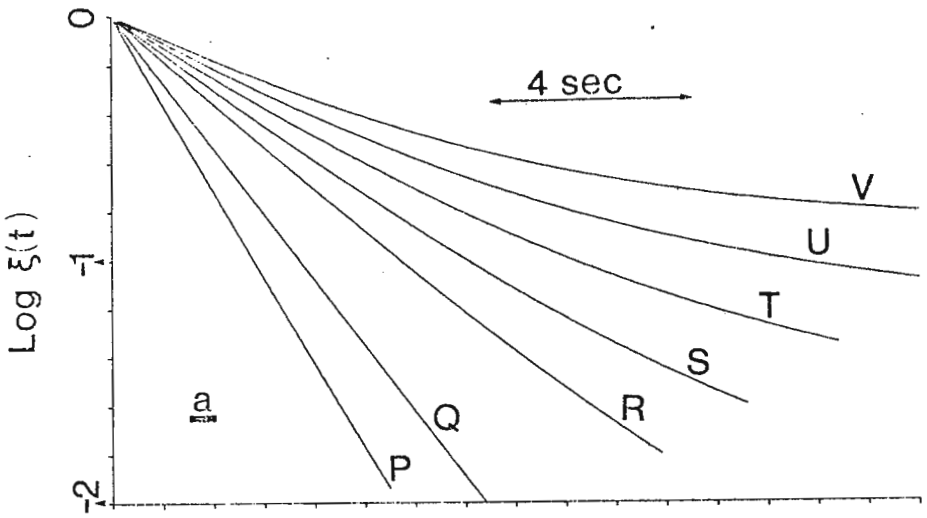
$$\zeta(t) = \frac{\langle I_z \rangle - \langle I_z \rangle_o}{(\cos\theta - 1)\langle I_z \rangle_o} ;$$

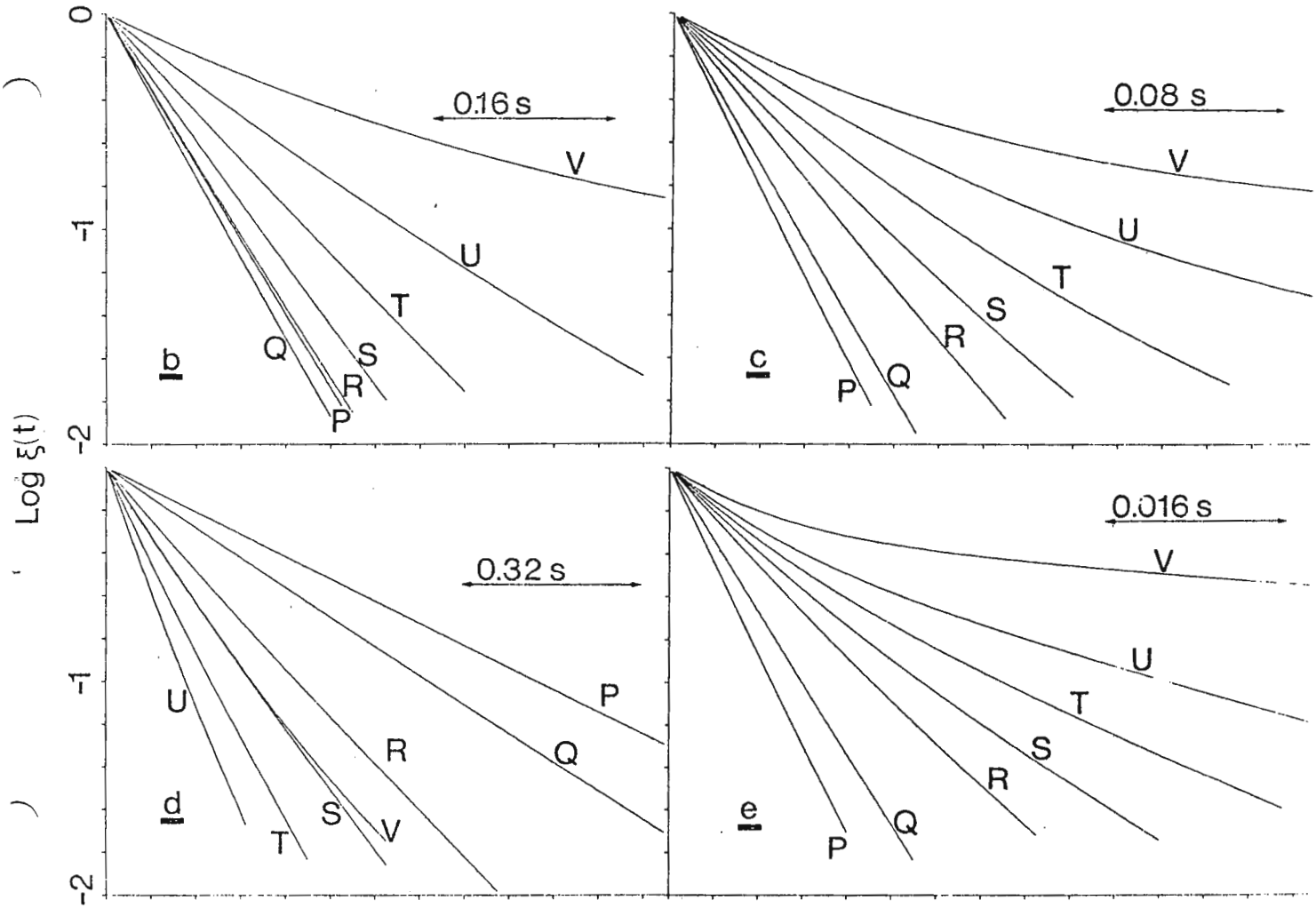
for plots 1c and 1e,

$$\zeta(t) = \frac{\langle I_x \rangle}{\sin\theta \langle I_z \rangle_o} ;$$

for plot 1a, longitudinal = transverse magnetization = $\zeta(t)$.

All rotational motion is taken as diffusional, with diffusion constants $D_{\parallel}$, $D_{\perp}$, and D_{int} for rotational diffusion of the molecule about its symmetry axis, perpendicular to its symmetry axis, and for internal rotation of the methyl group, respectively. [Note that $D_{\parallel}$ and D_{int} contribute in the same way to the net motion of the methyl group, and thus appear together as $(D_{\parallel} + D_{int})$ in the treatment.] Plot a corresponds to a small molecule, plots b and c to a macromolecule of molecular weight about 15,000, and plots d and e to a macromolecule of molecular weight about 150,000. Curves P, Q, ··· V, correspond to either increasing ellipticity or increasing rate of internal rotation: respective values of $[(D_{\parallel} + D_{int})/D_{\perp}]$ = 1, 7/4, 4, 6, 10, 20, and 100. All calculations were based on a 100MHz resonance ($\omega_o = 2\pi \times 10^8$ sec^{-1}), and a proton-proton distance of 1.8 Å in the methyl group.


Log ξ(t)
0
-1
-2
4 sec
V
U
T
S
R
Q
P
a


Log ξ(t)
0
-1
-2
0.16 s
V
U
T
S
R
Q
P
b
0.08 s
V
U
T
S
R
Q
P
c
0.32 s
P
Q
R
S
V
T
U
d
0.016 s
V
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T
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R
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P
e

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Physics Department
Ciudad Universitaria
Pabellón 1
Buenos Aires
ARGENTINA

Buenos Aires, March 30th, 1973

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

Additivity of Substituent Effects on the Proton-proton Coupling Constants of Disubstituted Pyridines

Dear Professor Shapiro:

We have recently completed a study of the proton-proton coupling constants of several mono- and disubstituted pyridines. From the J constants of pyridine and monosubstituted pyridines we have calculated the effects of several substituents. Assuming an additivity relationship when two of these substituents are present in the same molecule, we have also calculated the spin-spin coupling constants for 11 disubstituted pyridines. The experimental values of these constants are in very good agreement with those calculated using the additivity relationships. These results are shown in Table I.

Sincerely yours,

R.H. Contreras

D. G. de Kowalewski

Observed and Calculated Coupling Constants for Disubstituted Pyridines (Hz)

Substituents	$J^{exp.}_{34}$	$J^{calc.}_{34}$	$J^{exp.}_{35}$	$J^{calc.}_{35}$	$J^{exp.}_{45}$	$J^{calc.}_{45}$	$RMS_{exp.}$	$RMS_{calc.}$
2-CH_3CO-6-CH_3	7.75	7.77	1.09	1.11	7.72	7.68	0.007	0.043
2-NH_2-6-CH_3	8.19	8.19	0.85	0.81	7.29	7.30	0.006	0.036
2,6-diNH_2	7.83	7.81	----	----	7.83	7.81	0.006	0.041
2,6-diCl	7.86	7.83	----	----	7.86	7.83	0.005	0.019
2-CN-6-CH_3	7.65	7.68	1.04	1.01	8.01	8.01	0.005	0.033
	$J^{exp.}_{34}$	$J^{calc.}_{34}$	$J^{exp.}_{36}$	$J^{calc.}_{36}$	$J^{exp.}_{46}$	$J^{calc.}_{46}$		
2-NH_2-5-Cl	8.85	8.93	0.56	0.63	2.69	2.67	0.008	0.035
2-NH_2-5-CH_3	8.45	8.56	0.83	0.71	2,36	2.36	0.013	0.049
	$J^{exp.}_{24}$	$J^{calc.}_{24}$	$J^{exp.}_{26}$	$J^{calc.}_{26}$	$J^{exp.}_{46}$	$J^{calc.}_{46}$		
3,5-diBr	2.00	1.89	-----	-----	2.00	1.89	0.014	0.043
3,5-diCl	2.12	2.11	-----	-----	2.12	2.11	0.020	0.025
	$J^{exp.}_{45}$	$J^{calc.}_{45}$	$J^{exp.}_{46}$	$J^{exp.}_{46}$	$J^{exp.}_{56}$	$J^{calc.}_{56}$		
2,3-diCl	7.96	8.00	1.69	1.62	4.69	4.76	0.005	0.022
2-NH_2-3-CH_3	7.20	7.33	1.80	1.71	5.21	5.32	0.011	0.049

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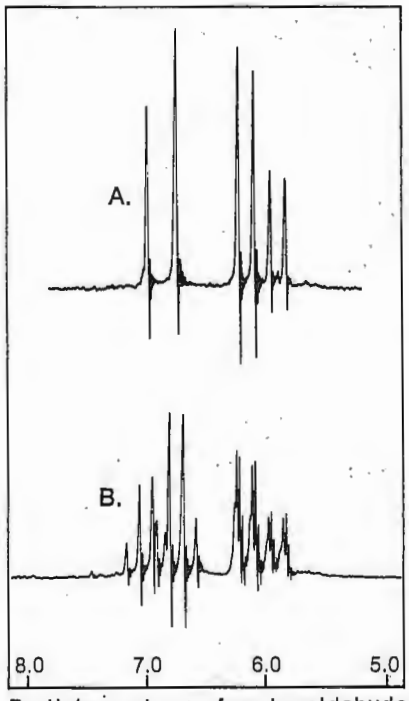


Partial spectrum of crotonaldehyde showing the olefinic region decoupled (A) and undecoupled (B) by irradiation of the sample at the methyl frequency.

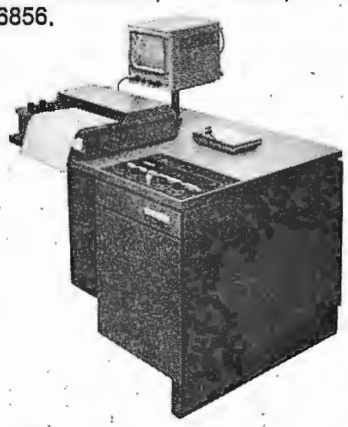
This gives you greater stability in all environments and makes interpretation of complex molecule spectra far easier. Shown in the chart is an example of the superlative performance of the Decoupling and Dynamic Lock feature.

But there's more. The Model R-24 also has the highest integration accuracy of any instrument in its price class. It's been increased from 5% to a guaranteed 2.5% as measured on a 5% ethylbenzene solution. (And the R-24's integral precision is even better than its accuracy!)

The Perkin-Elmer Model R-24 operates at 60 MHz to provide data in a form directly comparable to most published NMR reference spectra. And it has better than 50% improvement in its S/N, making possible precise analyses with only 200 μl of sample solution — about half of that required by most other NMR spectrometers.

And here's good news for present owners of the Model R-24. Your instrument can easily be retro-fitted with the Spin Decoupling and Dynamic Lock accessory. Just ask us.

For details, write the Instrument Division, Perkin-Elmer Corp., XXX Main Avenue, Norwalk, Conn. 06856.



PERKIN-ELMER

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

DEPARTMENT OF CHEMISTRY

May 1, 1973

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

CARBON-FLUORINE COUPLING CONSTANTS

Dear Barry:

Recently we have been looking at ^{13}C chemical shifts and ^{13}C-^{19}F coupling constants in some fluorocarbons and their derivatives. The values obtained for coupling constants include a number of features of particular interest. Our spectra were obtained on an XL-100 instrument in CW mode using time averaging with the Varian C-1024, mostly in 5 mm sample tubes with external lock.

For several typical trifluorovinyl compounds, the one-bond and two-bond couplings to the terminal carbon atom in the vinyl group are as follows, with the shifts for this carbon given in ppm from TMS:

		^1J, Hz	^2J, Hz	Shift
I	CF_2=CF-CF_2Cl	294, 292	41	149
II	CF_2=CF-SCF_3	304, 285	50	157

In line with these compounds are data for a third one, from a paper by Hinton and Jacques to appear in the Journal of Magnetic Resonance:

III	CF_2=CF-CH_2-CH_2Br	286, 272	46	155

When the trifluorovinyl group is conjugated with a carbonyl, the values of ^1J become slightly larger and, surprisingly, become equal, whereas the two-bond couplings remain about the same:

IV	CF_2=CF-C(O)F	304, 304	40	163
V	CF_2=CF-C(O)OCH_3	299, 299	42	158
VI	CF_2=CF-C(O)CF_3	301, 301	39	153

Comparison of the shifts indicates an effect of unshielding when an electronegative atom is attached to the carbonyl carbon.

The most striking aspect of the results is the large value of ^2J observed for certain carbons adjacent to the carbonyl group to a fluorine attached to the carbonyl in the acid fluoride function. Thus in compound IV,

the coupling of the middle carbon to the fluorine in the acid fluoride is 90 Hz. We also have indications (from satellites; the ^{13}C spectrum has not yet been obtained) of a value of 93 Hz for the coupling between the starred atoms in $C(O)F-\overset{*}{C}F_2-O-\overset{*}{C}F_2-C(O)F$. On the other hand, we see no indication of an extraordinarily large coupling in $C(O)F-(CF_2)_4-C(O)F$.

Very large values of two-bond C-F couplings have a few precedents in the literature. Reuben and Demiel reported a value of -102.5 for trans-BrFC=CBrF although the corresponding cis compound was found to have a normal value of -35.8 Hz. Bacon and Gillespie reported values of 103.2 and 97.0 for C(O)F-C(O)F and C(O)Cl-C(O)F, respectively. One is tempted to speculate about some unusual type of overlap of the back end of the -C-F bonding orbital with an orbital of the alpha carbon, the effect of which is emphasized by steric constraints. That the large value in compound IV is not a mere result of modification of the C-C bond by conjugation is indicated by the very reasonable value of 31 Hz for the coupling of the carbonyl carbon to the fluorine alpha to it, a coupling which presumably is transmitted through the same C-C bond. At the same time, the one-bond coupling in the acid fluoride group of IV is unusual in that it is only 333 Hz in magnitude, a value some 30 Hz smaller than that typical of a fluorocarbon acid fluoride such as $C(O)F-(CF_2)_n-C(O)F$.

The behavior of the long range coupling constants also includes some unusual features. In compound VI, the olefinic CF_2 carbon is coupled by about 1 Hz to the trifluoromethyl fluorines, over four bonds. In the same molecule, the trifluoromethyl carbon, in addition to the doubling of 288 Hz from one-bond coupling, shows a tripling of 3.5 Hz, from coupling to two of the three fluorines in the trifluorovinyl group--which two, we do not yet know. In this molecule, as well as in IV, the carbonyl carbon is coupled equally to the two fluorines in the CF_2=unit, whereas the two-bond coupling from the olefinic =CF- carbon to these fluorines is quite stereospecific, values in each molecule (as well as in III) being of the order of 20 and 40 Hz.

Our results thus raise many questions about the mechanism of C-F coupling, and at the same time they indicate that the magnitudes of the coupling constants are often more specific indicators of structural features of fluorocarbon derivatives than are the chemical shifts.

Sincerely yours,

Wallace

Wallace S. Brey
Professor of Chemistry

WSB/ewh

Gesellschaft für Molekularbiologische Forschung mbH
3301 Stöckheim über Braunschweig
Mascheroder Weg 1
Telex 9-52667
Telefon 0531 / 60071

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

Abt. Physikalische Meßtechnik

March 30, 1973

Dear Barry:

Here is another so-so contribution:

Position open

We are looking for a recent Ph.D. with good background in practical and theoretical NMR spectroscopy. NMR activities of the Abt. Physikalische Messtechnik (Division of Spectroscopy) involve analytical studies as well as research in NMR spectroscopy and instrumentation, generated in the NMR Branch of this Division.

Some knowledge of German and an interest in biologically oriented problems are desirable, but by no means a must.

Instruments available are: XL-100/FT, HA-100, A-60 and EM-360.

Best wishes and regards.

Sincerely,

Ernest Lustig

Department of Chemistry

YORK UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

April 6, 1973.

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

Dear Dr. Shapiro:

COMMENTS ON PINK SURPRISES AND $J_{^{14}N-^{13}C}$

We were very much dismayed to receive a shocking pink letter within days of seeing our latest contribution in circulation. However, the primordial guilt complex being what it is - we offer a further communication.

During the recent ^{13}C workshop we ran a series of organic compounds of nitrogen. Normally coupling to ^{14}N is not observed because of quadrupole effects. Some notable exceptions are tetraalkyl ammonium salts and isonitriles, both having a considerable degree of symmetry about the nitrogen. It has been previously illustrated that nitrogen-carbon coupling is affected considerably by the presence of a lone pair of electrons on the N atom (using ^{15}N derivatives). This causes problems in attempts to derive correlations of the Fermi-Contact type which have proved useful in C-C and CH couplings. The one in use[1] does not fit the C-N coupling data for the above mentioned derivatives, the isonitriles being usually dismissed as unusual because of the cylindrical Π-cloud. Yet logically, following the carbon-carbon case and the work of Frei & Bernstein for example[2], these two derivatives should be prime candidates for an s-character relationship, because in neither does the nitrogen carry a lone pair to play havoc with such things as ΔE.

We have found a linear J to s-character correlation between pairs such as tetramethylammonium halide and methylisonitrile which passes almost exactly through zero. Thus N-C(H_3) in these derivatives uses an sp^3 and an sp nitrogen respectively so the correlation has three points, through zero to 25%s to 50%s, and one can derive[1] (correcting for γ)

$$S_N S_C = (-)120 J_{C^{15}N}$$

Using this equation one finds that J_{CN} in acetonitrile is smaller than predicted - which seems to be the general effect of introducing a lone pair. The cyanide ion and the N≡C coupling of the isonitriles are both believed to be of opposite sign to the couplings discussed above - and both contain lone pairs which are essentially delocalized over the entire group.

Substitution of methyl by ethyl & higher homologues makes $^{1}J_{CN}$ smaller in the two series of compounds by the same ratio, so that for each homologue a modified linear correlation is obtained. This type of substituent effect has been predicted for C-C and C-H coupling[3], but is almost never noticed.

Π-bond contributions to the coupling also seem to stand out from the linear correlation (which is derived only from single C-N bonds).

Although we do not wish to profess any lasting faith in s-character pronouncements for nitrogen at this stage, we nonetheless find it intriguing that these two types of nitrogen compound - hitherto outsiders in any s-character correlations - should fit together so well with each other. All the more so because in each case the nitrogen is in a "carbon-like" situation and should therefore be expected to come nearest to exhibiting relationships similar to carbon. Again we thank Varian Associates for use of an NV-14 spectrometer.

Yours sincerely,

D.E. Axelson, Ian M. Walker, C. E. Holloway

D.E. Axelson,
I.M. Walker,
C.E. Holloway.

:CW

1. G. Binsch, J.B. Lambert, B.W. Roberts and J.D. Roberts, J. Amer. Chem. Soc., 86, 5564 (1964).

2. K. Frei and H.J. Bernstein, J. Chem. Phys., 38, 1216 (1963).

3. V.M.S. Gill and J.J.C. Teixeira-Dias, Molec. Phys., 15, 47 (1968).

Comments on Comments on Pink Surprises!

We goofed. Sorry! It is, however, terribly nice to be able to help out with your primordiac guilt complexes. When I grew up in Ontario, we couldn't afford such luxuries!

SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

DEPARTMENT OF CHEMISTRY

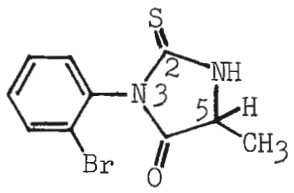
April 4, 1973

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

Dear Barry:

CONFORMATIONAL PREFERENCES IN ARYL SUBSTITUTED HETEROCYCLIC COMPOUNDS

In the course of n.m.r. studies of hindered rotation about aryl C-N bonds in aryl substituted heterocyclic compounds, we have been interested in factors influencing the equilibrium constants between diastereomeric rotational isomers. In particular, we have been looking at some 3-aryl substituted hydantoins and 2-thiohydantoins, such as 3-(o-bromophenyl)-5-methyl-2-thiohydantoin, I.

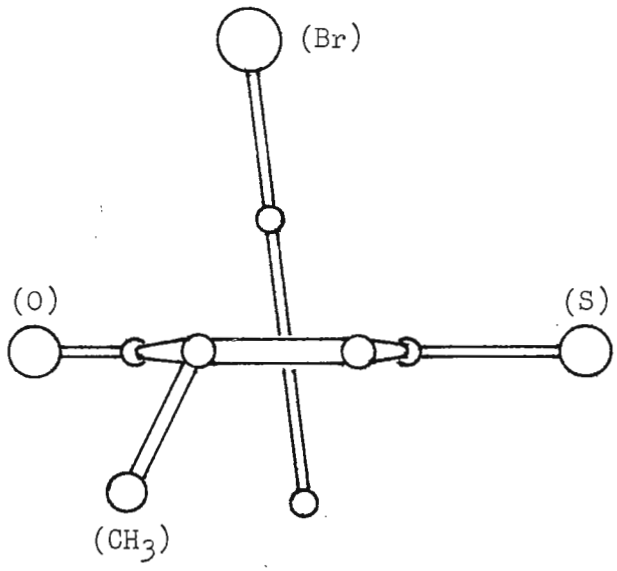


(I)

Compound I has an equilibrium constant of 1.9 ± 0.1[1] in pyridine solution. In addition to having non-unity equilibrium constants, the compounds unsymmetrically substituted on C-5 show "abnormal" activation parameters.

Slow crystallization from methanol of the mixture of diastereomers of I produced on synthesis yielded only the thermodynamically less stable isomer (> 99%). Equilibration of this isomer over a range of temperatures was followed by the method previously described,[2,3] except that the composition of the mixture was determined from the n.m.r. spectrum using a DuPont curve resolver. The following activation parameters were obtained (25°C): $\Delta G^{\ddagger}$ = 25.2 ± 0.1 kcal/mol, $\Delta H^{\ddagger}$ = 17.6 ± 1.7 kcal/mol, $\Delta S^{\ddagger}$ = -25.5 ± 5.2 e.u.[1]

Since it was not clear how the stereochemical information was being transmitted from the asymmetric centre at C-5 to the unsymmetrically substituted aryl group, and also since the steric relationships between the bromine atom and the C-5 methyl group in the two rotational isomers were unknown, an X-ray crystallographic study of the less stable isomer was carried out.



View along the aryl C-N bond from a position midway between N(1) and C(5)

The crystal structure shows that, in the thermodynamically less stable rotamer, the bromine atom is transoid to the C-5 methyl group (see figure) and the heterocyclic ring is planar. This eliminates one of the possibilities suggested earlier, namely a puckered hetero ring.[3]

We may infer that, in the thermodynamically more stable rotamer, the bromine atom is cisoid to the methyl group. In order to explain this behaviour, we conclude that the more stable rotamer must be strongly solvated on the less hindered side of the molecule in pyridine solution. Examination of models indicates that the transoid (less stable) isomer is appreciably more hindered to close approach of solvent molecules on both sides of the solute molecule than is the cisoid (more stable) on the favoured side. Hence it appears that the thermodynamic preference results from differences in the energies of the solute-solvent interactions of the two rotamers in their ground states, and that the stereochemical information is, in effect, transmitted between the methyl and the aryl group by means of an unsymmetric solvent shell. We have observed that, in general, the thermodynamically less stable isomer is the less soluble isomer.

It would appear that the unexpectedly large negative entropies of activation that we have measured for this and related compounds result from differences in the extent of solvation in the ground and transition states for rotation about the aryl C-N bond. Steric hindrance to approach of solvent molecules should be much reduced in the nearly planar transition state for rotation of the solute molecule.

Yours sincerely,

L.D. Colebrook H.G. Giles P.H. Bird A.R. Fraser

1. 90% confidence limits
2. TAMU NMR Newsletters, 143, 16 (1970).
3. Chem. Commun., 974 (1970).

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Dear Professor Shapiro,

^{13}C NMR of hydrogenated polybutadienes

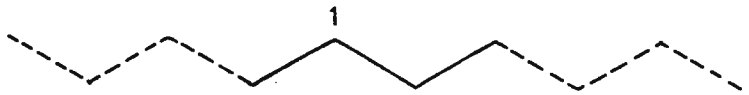
As part of an investigation into the microstructure of polybutadienes we measured the ^{13}C spectra of the corresponding hydrogenated products.

An empirical chemical shift formula derived for saturated hydrocarbons[1] was applied to predict the resonance positions of the various carbon atoms in the polymer chain.

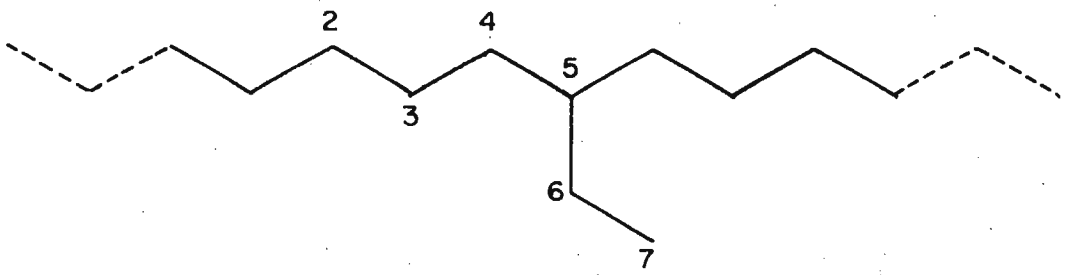
Fig. 2 depicts the ^{13}C spectra of three hydrogenated polybutadienes, III, IV and V, having 43 %, 64 % and 75 % of 1,2 structure (hanging ethyl groups), respectively. The CH_3 groups at 11 ppm relative to TMS are not indicated. The spectra were recorded on a Varian XL-100-15 (500 scans each spectrum).

The stick spectra show calculated chemical shifts[1] and line intensities. In calculating the intensities we assumed a random distribution of 1,4 and 1,2 elements in the polymer chain.

The numbering of the ^{13}C lines refers to the following polyad sequences:



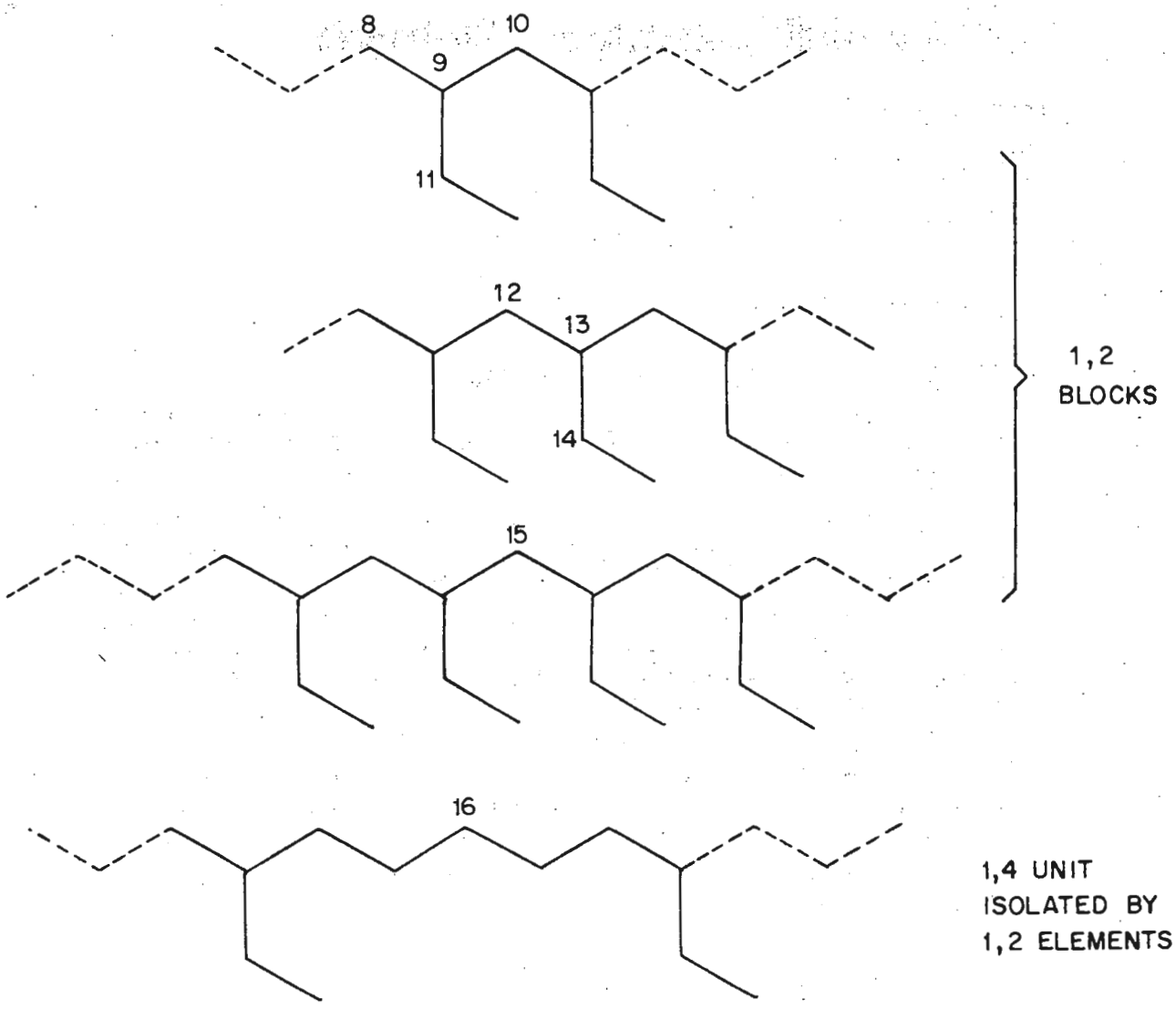
1,4 BLOCK



1,2 UNIT
ISOLATED BY 1,4
UNITS

73.04.1115

1. L.P. Lindeman and J.Q. Adams, Anal. Chem. 43 (1971) 1250.



The broadness of lines 9 to 15 is due to tacticity effects within the 1,2 blocks.

Please credit this contribution to Dr. R. Prins.

Yours sincerely,

J.A.M. van Broekhoven A.D.H. Clague

Amsterdam, 11 April 1973

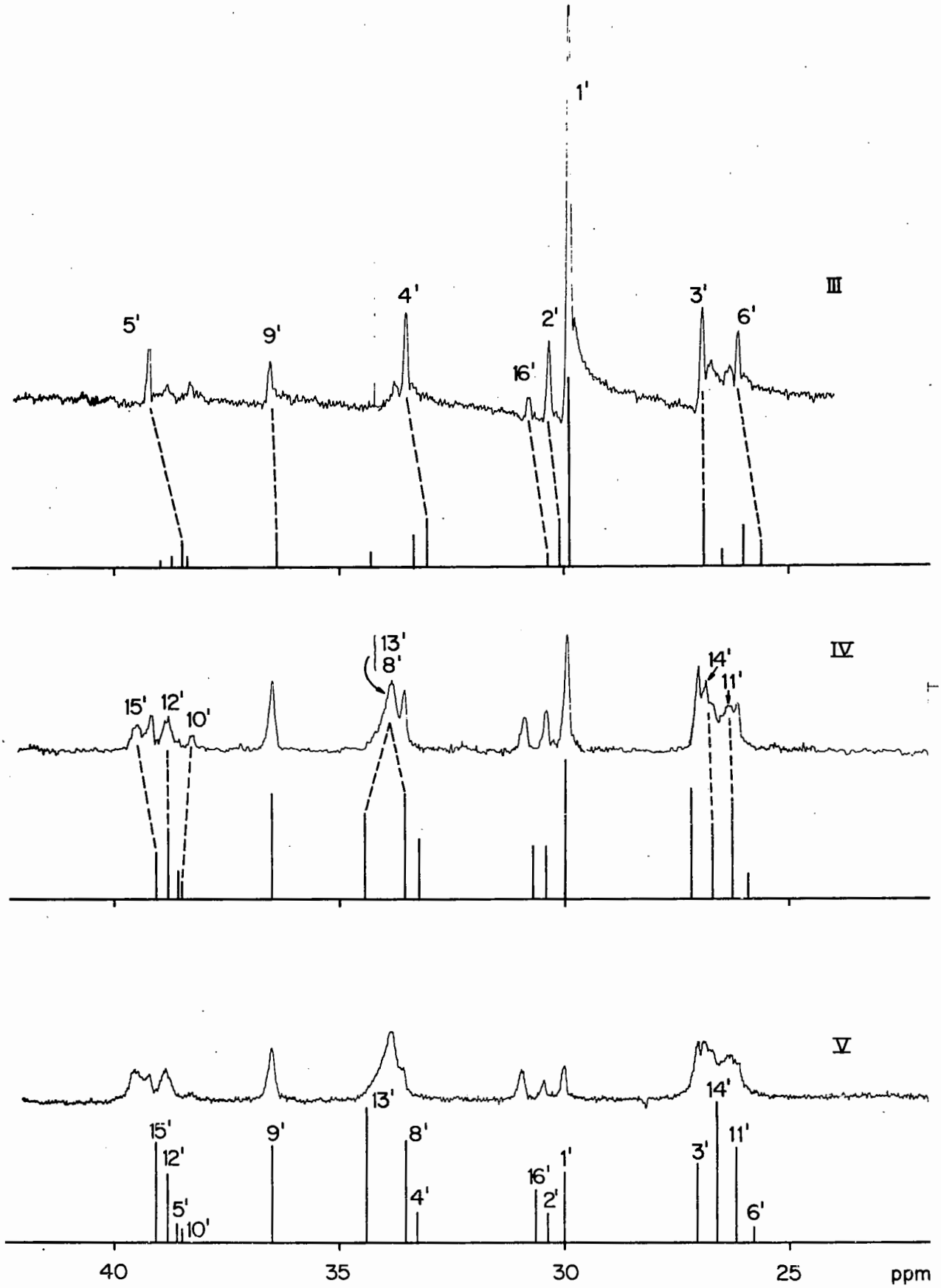


FIGURE 2

^{13}C NMR SPECTRA OF THREE HYDROGENATED POLYBUTADIENES IN CCl_4
SHIFTS ARE IN ppm RELATIVE TO TMS

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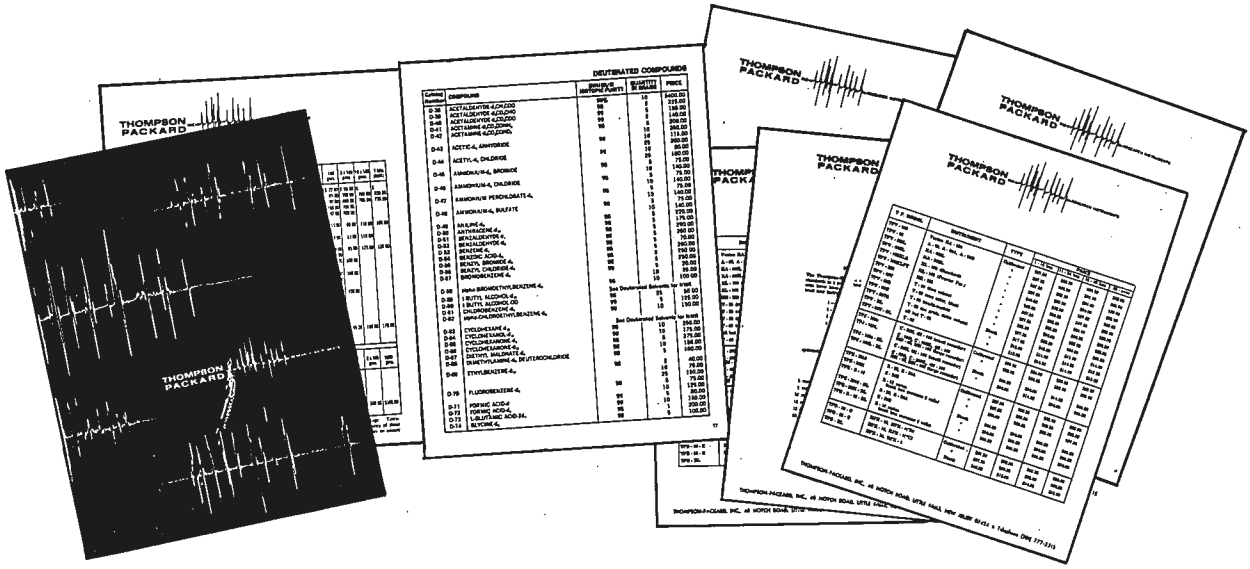
wrote the book on
single-source
buying of
NMR supplies and accessories

. . . and we're still adding chapters.



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DEPARTMENT OF CHEMISTRY

April 26, 1973.

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

Dear Barry:

Varian HA-100 owners have recently been circularised with a Tech Note on maintenance of the water cooling system. This is intended to supplement the maintenance procedures contained in the system instruction manual, and suggests the installation of a deionizer resin bed in the recirculating water where some of the water will flow through it continuously. The suggested installation is in series with the existing loop but we have set up an alternative parallel system which has the following advantages:-

(1) Installation of system and renewing resin can be carried out without interruption of secondary water flow which would necessitate turning off magnet power.

(2) The improvement is resistivity and pH which is given by the resin can readily be monitored by before and after measurements. Reduction in resin activity will be easily observed.

(3) It follows from (2) that the use of a less expensive resin instead of the variety which changes colour is possible. Our local "Culligan Man" provided the first batch free of charge. The strong base anion and cation resin costs $120 per cu. ft. for the first loading but is renewed at the rate of $7 per cu. ft.

(4) For those without a transparent filter bowl it is less expensive to install.

The system depends on the use of an aquarium power filter Cat. #3 SF-520 made by the Biozonics Corporation, 15 Tech Circle, Natick, Massachusetts 01760 obtained by us for about $15 in a local pet store. The diagram shows the installation which depends on siphoning water out of the V-3520 reservoir and pumping it back in. Minor flooding

may take place during the setting up but once installed it is self regulating and should be "fail safe" for most foreseeable possibilities. The junction at the entrance to the reservoir may be spliced together with silicon rubber and tape, although others may consider glass or metal more suitable. Our arbitrary resistance measurement showed the following:-

tap water (town mains)	=	20 K ohm
distilled water	=	80 K
water in magnet before installation of "polisher"	=	40 K
after several days "polishing":-		
before resin	=	600K
after resin	=	700K

pH measurement by pH indicator paper was unreliable. With a poor instrument and/or poor technique it was not much better. However, with an experienced operator on a good pH meter the value was 7.3.

It is appreciated that the topic of this letter verges on a forbidden zone - the suggested title is

Polishing Water for Spectrometer Cooling Systems.

Yours sincerely,

R.A. Bell

R.A. Bell,
Associate Professor of Chemistry.

RAB/ph
Encl.

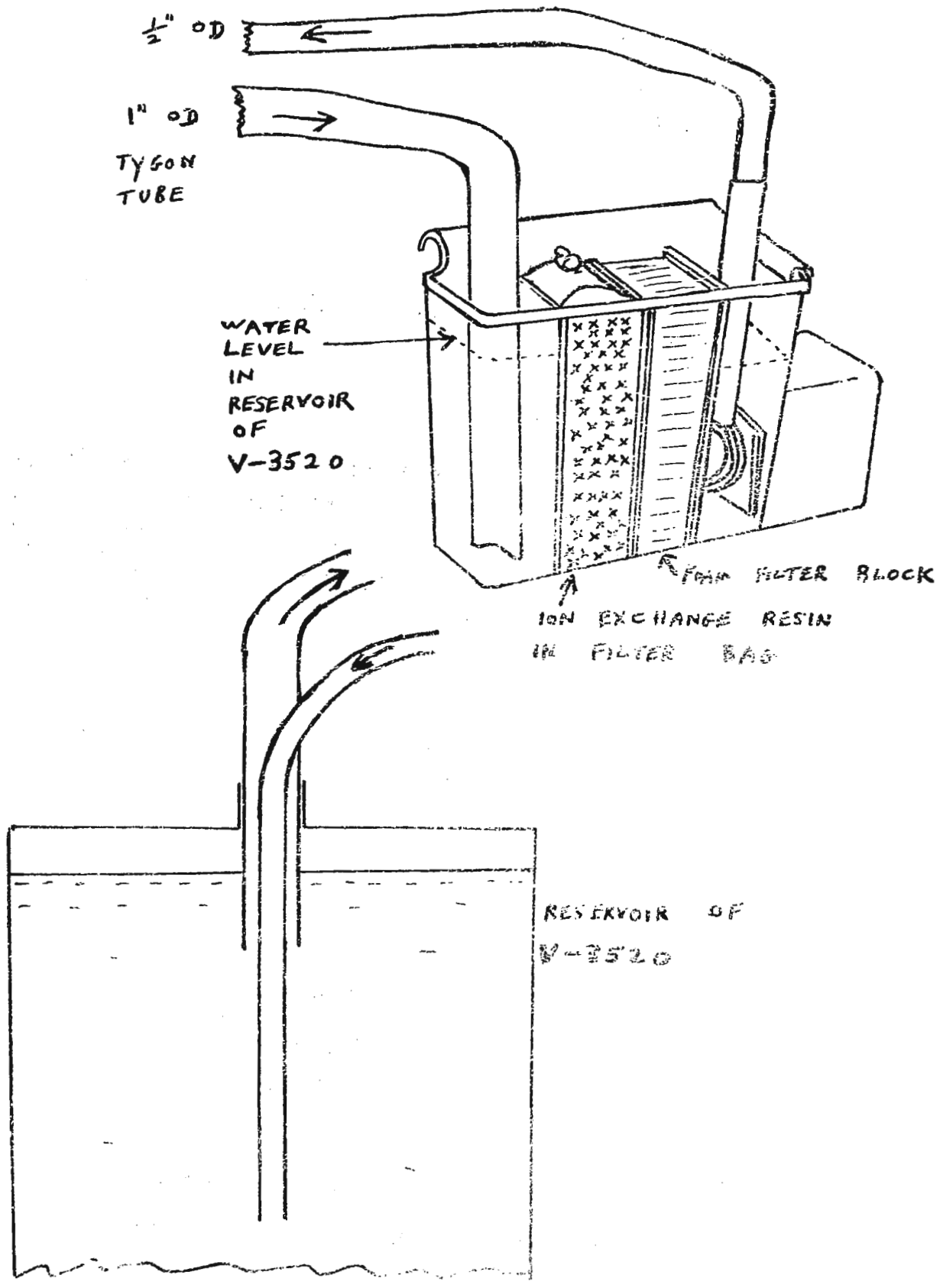
P.S. Please consider this a contribution from McMaster in the name of R.J. Gillespie.

Professors Bell and Gillespie:

While I am happy to include this contribution in the TAMU NMR Newsletter, I am afraid it must be on a "No Credit" basis. As you will note in our most recent Statement of Policies and Practical Considerations, the time has come when I feel that water cooling system considerations are no longer appropriate for credit as a technical part of ones subscription - as you so kindly suspected. I hope you can see this matter from our point of view.

All best regards,

B. L. Shapiro


½" OD
1" OD
TYGON TUBE
WATER LEVEL IN RESERVOIR OF V-3520
FOAM FILTER BLOCK
ION EXCHANGE RESIN IN FILTER BAG
RESERVOIR OF V-3520

176-58
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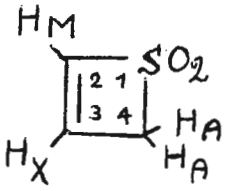
Milano, March 15th, 1973

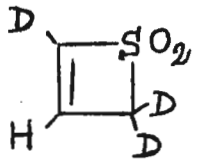
Prof. B.L. Shapiro
Dept. of Chemistry
Texas A & M University
College Station, Texas 77843

"Sign determination of all C-H coupling constants (^2J and ^3J) in thiete-sulphone."

Dear Professor Shapiro,

I would like to report here another result of our investigation on four-membered rings. All C-H and H-H coupling constants of thiete-sulphone have been measured from ^{13}C, ^1H and ^{13}C satellites spectra, and sign determinations performed by tickling and triple resonance experiments. The results are listed below:





J_{AX} + 1.60
J_{AM} - 0.52
J_{MX} + 4.10

$^1J_{C_4,H_A}$ + 150.5
$^1J_{C_3,H_X}$ + 186.5
$^1J_{C_2,H_M}$ + 198.5

$^2J_{C_4,H_X}$ + 9.0
$^2J_{C_2,H_X}$ + 6.5
$^2J_{C_3,H_A}$ - 6.5
$^2J_{C_3,H_M}$ + 1.8
$^3J_{C_2,H_A}$ + 6.5
$^3J_{C_4,H_M}$ +14.5

$^1J_{C_2,D}$ 30.2

In the triple resonance experiments, the decoupling frequency (ν_2) was provided by the Gyrocode of the XL-100-15 Spectrometer, and the ti-

ckling frequency (ν_3) by a Hewlett-Packard 4204 oscillator, which was connected to the Spectrometer through a directional coupler module[1] placed between the output of the 94-100 MHz Power Amplifier and the Low Power Attenuator (figure 1). Thus the audiooscillator provided two modulation sidebands by $2(\nu_3-\nu_2)$ Hz; one of them (the low field one) was used for tickling, whereas the central band of the Gyrocode, still remaining, was used for the decoupling.

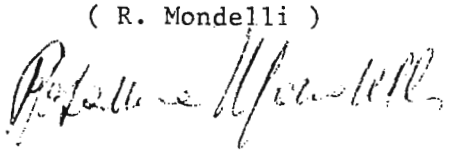
The sign determination of $^2J_{C_3,H_M}$ relative to $^1J_{C_3,H_X}$ is given in figure 2, as an example. All the spectra were obtained in a single scan. Through the decoupling of the methylene A protons (a), the five--spin system, $A_2MX^{13}C$, is simplified to a three-spin $MX^{13}C$. Only the low field satellite of H_X can be observed. H_M inner satellites are then tickled, while H_X outer satellites are observed, by exploring with the ν_3 frequency a range of 10 Hz around ν_M by 0.1 Hz (b).

X_1 and X_2 lines are split, when $\nu_3 - \nu_2$ = 235.8 (irrad. M_1) and 232.0 Hz (irrad. M_3). Considering that $^2J_{C_3,H_M}$ = 1.8 Hz, the expected tickling frequencies are 235.8 and 231.7 Hz. The pairs M_1, X_1 M_3, X_2 result regressive, while the pairs M_1, X_2 and M_3 ,X_1 progressive. According to the energy level diagram, the one-bond and the two--bond couplings have the same signs.

[1] We thank L. Hlavka, Varian (Palo Alto), who drew and made for us this module.

sincerely yours

(R. Mondelli)



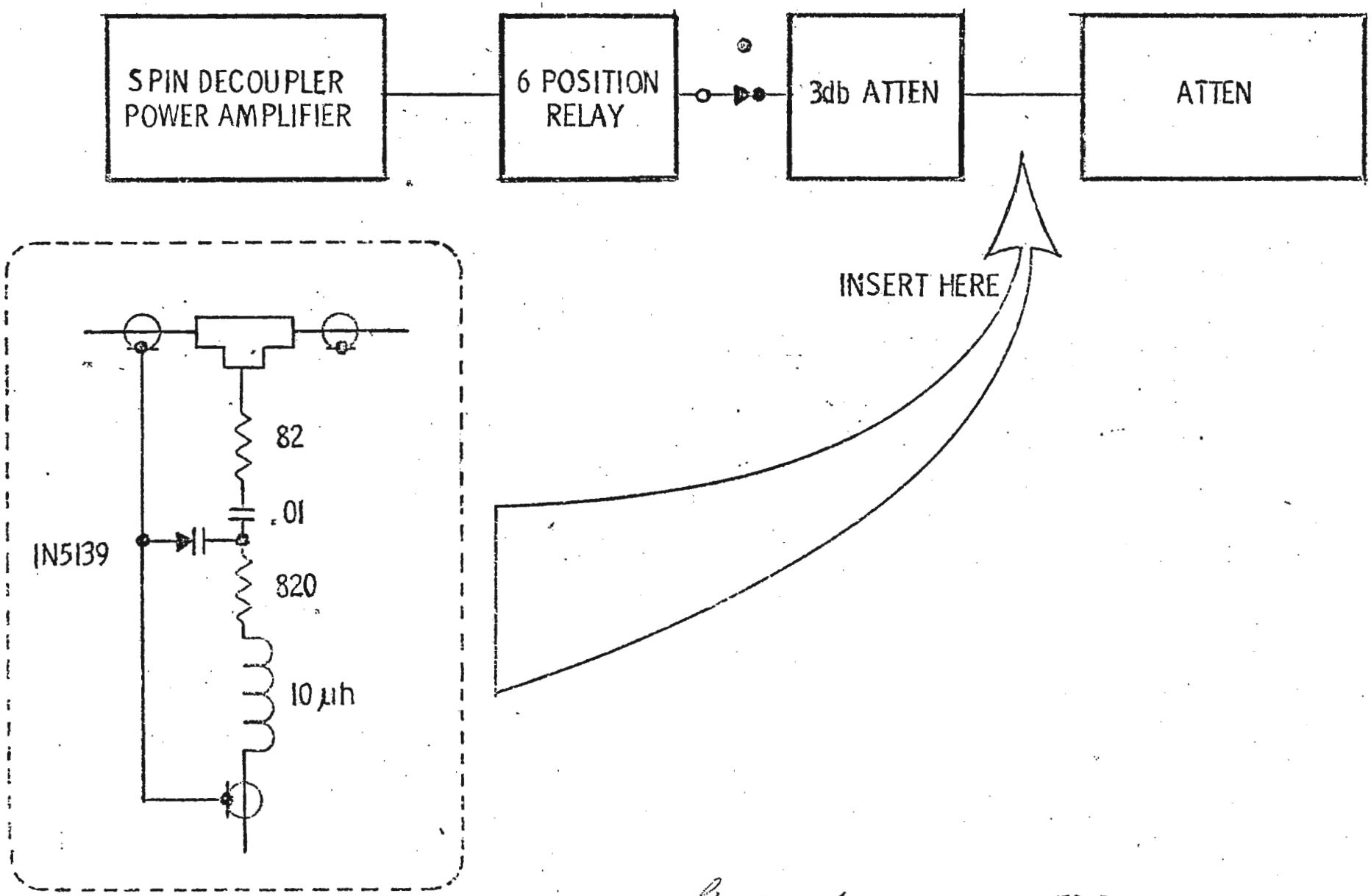


Figure 1

TRIPLE RESONANCE NETWORK

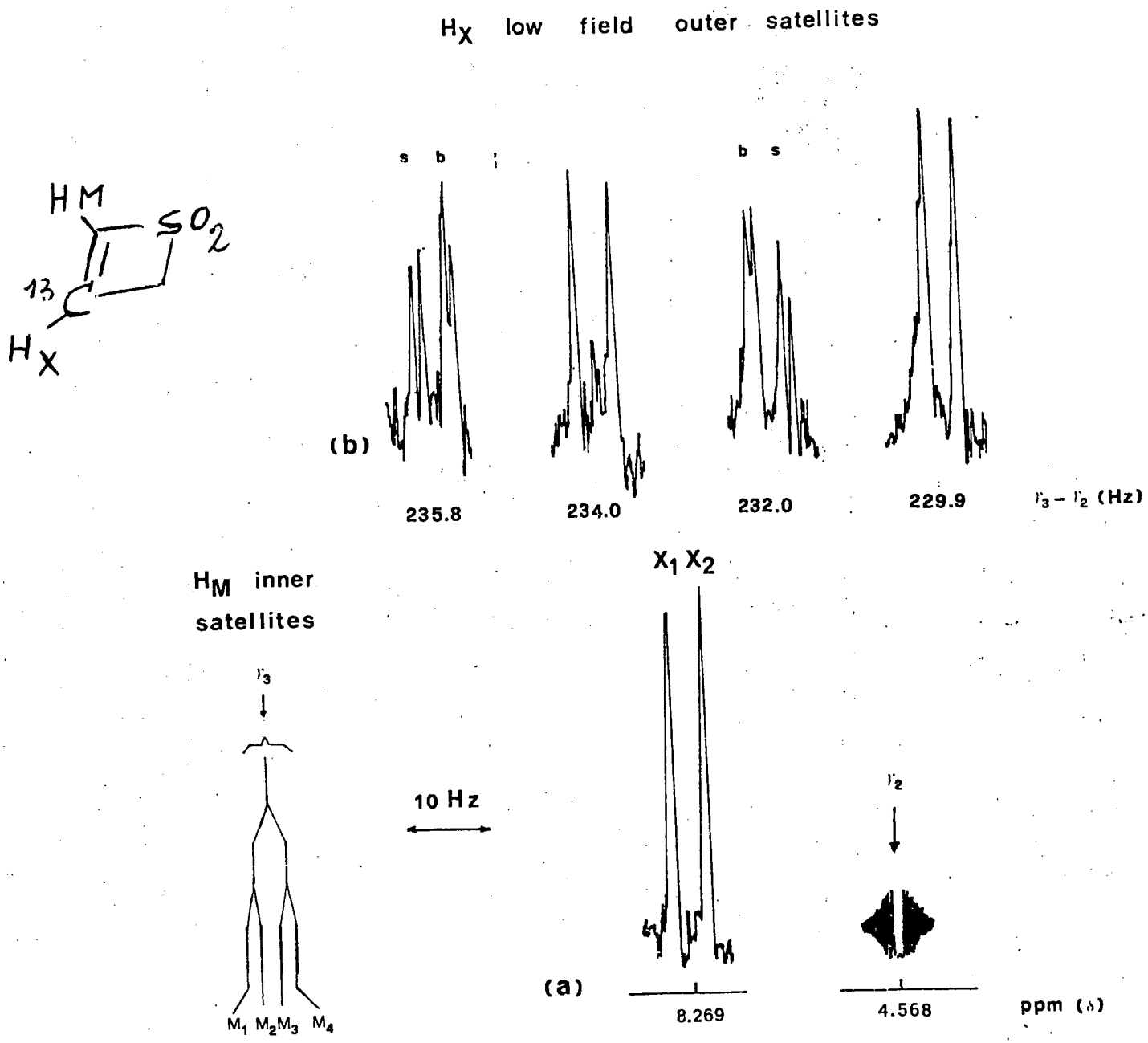

H_X low field outer satellites
HM
SO_2
13
C
H_X
s b
b s
(b)
235.8
234.0
232.0
229.9
$\nu_3 - \nu_2$ (Hz)
H_M inner satellites
ν_3
M_1 M_2M_3 M_4
10 Hz
X_1 X_2
(a)
8.269
ν_2
4.568
ppm (δ)

figure 2

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May 2, 1973

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

A Convenient T_1 Sequence

Dear Barry:

We have recently examined the various sequences available for measuring spin-lattice relaxation times, (T_1's). Although the $(180^\circ,\tau,90^\circ,T)_n$ sequence appears to be the one most commonly employed, the novel "intensity ratio" method for the $(90^\circ,\tau,90^\circ,\tau)_n$ sequence recently reported by Freeman, Hill and Kaptein[1] appears to have certain advantages over the $(180^\circ,\tau,90^\circ,T)_n$. This is especially true for nuclei with inherently low sensitivity (i.e., C^{13}) where (S/N) per unit time is of the utmost concern.

Along similar lines we have been employing a $(90^\circ\text{-}X^\circ,\tau,90^\circ\text{-}X^\circ,\tau)_n$ sequence ($X^\circ<90^\circ$), with a fixed τ value and where X° is varied from one spectrum to the next to characterize the T_1 dependence. Using the same notations as Freeman, et.al.[1], the expression for the ratio of signal intensities of a given line for two different spectra "a and b" obtained with two different "flip angles" is given below:

$$\frac{Sa}{Sb} = \frac{(1-k_bE_1)\ \beta_a}{(1-k_aE_1)\ \beta_b} \qquad E_1 = e^{-\tau/T_1}$$

where the β's and k's are as previously defined by Freeman. The expression above when rearranged allows computer calculation of all pairwise data with different flip angles.

The ^{13}C spectra for the aromatic region of toluene shown in Fig. 1 were obtained with a τ value of 0.5 sec. and a mean random delay of 50 msec. with 1500 transients collected for each spectrum. The total experimental time for the ten spectra was two hours. The T_1 measurements were repeated using the $(180^\circ,\tau,90^\circ,T)_n$ sequence with T = 220 sec. and 16 transients collected requiring a total time of 11.5 hours for the ten spectra!

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Professor Barry Shapiro May 2, 1973

Spectra a and b of Fig. 2 give a comparison of the (S/N) for the C_1 carbon atom, ($T_1 \approx 50$ sec.) obtained for the equilibrium magnetization (M_∞), ($\tau = 220$ sec.) for the $(180^\circ,\tau,90^\circ,T)_n$ experiment and the $(90^\circ\text{-}X^\circ,\tau,90^\circ\text{-}X^\circ,\tau)_n$ experiment with $X^\circ \cong 80^\circ$, respectively. The derived T_1's were in generally good agreement for the two sequences.

An apparent advantage of the $(90^\circ\text{-}X^\circ,\tau,90^\circ\text{-}X^\circ)_n$ sequence in comparison with the $(90^\circ,\tau,90^\circ,\tau)_n$ sequence is the ability to correct for the problem of the finite rf field (H_1) in comparison with the spectral width, (ΔH). This correction enters into the above expression in terms of the β's and k's and is also implemented in the computer program. Another slight advantage could be one of (S/N) per unit time depending upon the τ values necessary to characterize the T_1's in the $(90^\circ,\tau,90^\circ,\tau)_n$ experiment. A more detailed report of this sequence is being submitted for publication.

Sincerely,

Harry

Harry C. Dorn
NMR Application Chemist

[1] R. Freeman, H. D. W. Hill and R. Kaptein, J. Magn. Resonance, 7, 82 (1972).

Figure 1

Sample: 95% Toluene (Aromatic Region)
5% C_6F_6
Sequence: $(90°\text{-}x, \tau, 90°\text{-}x, \ldots)_n$, $\tau = 0.55$ sec.
1500 Pulses Per Sequence
Sampling Frequency: 4000 Hz
Transform Size: 4K
Total Time: ≈ 2 hr.

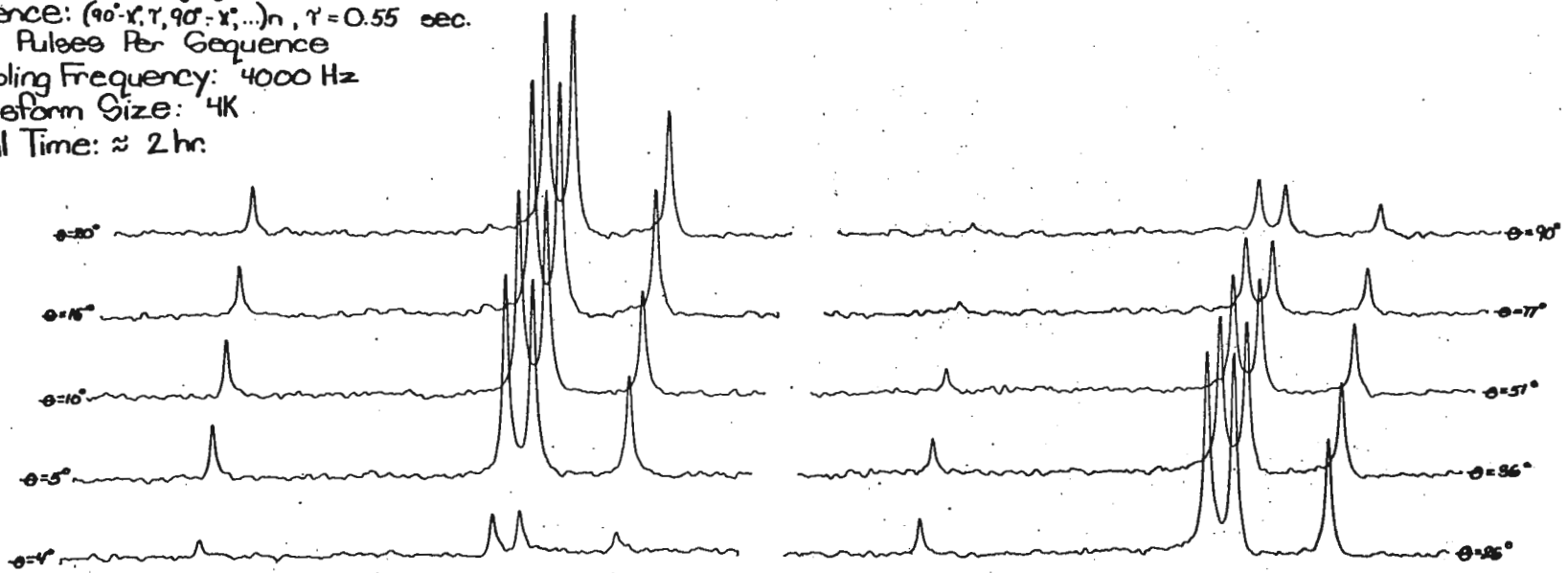
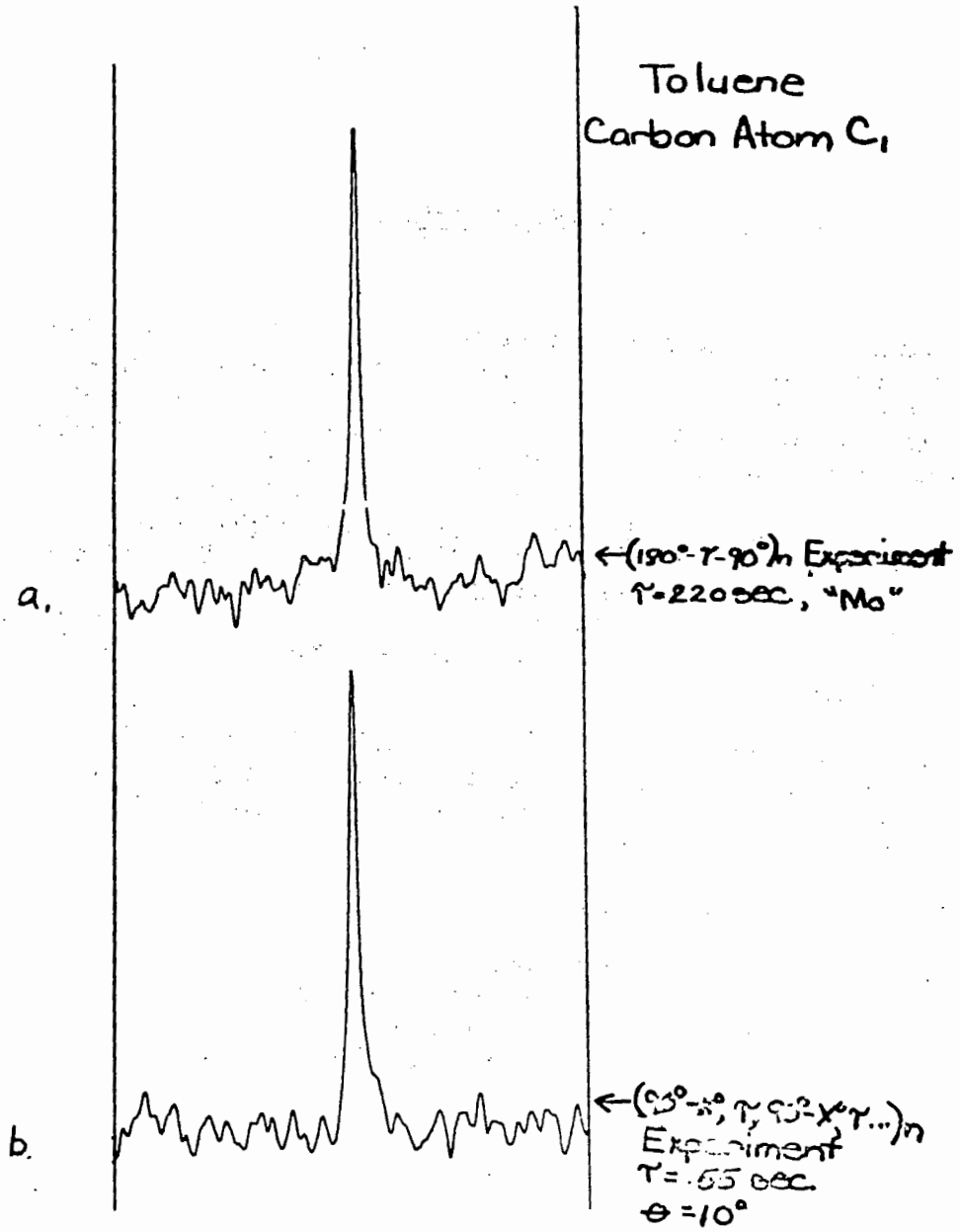


Figure 2


Toluene
Carbon Atom C_1
a.
$\leftarrow(180°-\tau-90°)_n$ Experiment
τ=220 sec, "Mo"
b.
$\leftarrow(90°-x°, \tau, 90°-x°\tau\ldots)_n$
Experiment
τ=.55 sec.
θ=10°

176-66

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

Department of
CHEMISTRY

3 May 1973

Postdoctoral Position Available

I will have a position available for a postdoctoral fellow in my research group effective approximately 1 September 1973, and interested persons are invited to contact me. The position available should be filled by either: (a) someone with extensive NMR experience, preferably with FT hardware, or (b) someone who might have less (but still significant) NMR experience but with a very strong background in organic synthesis, or preferably (c) someone with both types of qualifications. We are an equal opportunity employer, and applications from women and members of minority groups are particularly welcomed. Only in an exceptional case will it be possible to consider someone who is not a U.S. citizen.

All inquiries will be promptly acknowleged and held in complete confidence. Initial inquiries should include a complete vita and at least two names of people who will provide letters of reference, if such become appropriate.

Address all inquiries to:

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

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This is the turning point in FT NMR research.

Introducing the JEOL EC-100. It's the first commercial real-time NMR data reduction system.

Now, simply by touching a button and turning the single parameter vernier control, accurate and reliable analysis can be accomplished in real-time.

Such functions as vertical expansion or shift, horizontal expansion or shift and real-time phase correction have been simplified as never before. Not only has data manipulation been advanced, data display is more complete. Results are provided in real-time CRT display, on direct frequency shift display, by digital printout, and through traditional plotting methods.

The EC-100 is a joint development of our computer engineers and analytical research staff. They set about designing a system that would be fast, accurate and reliable. They also sought to create a computer system that virtually anyone in the lab can utilize. The result is the EC-100, a system for truly practical research. Practical in capability, operation and price.

Currently, the EC-100 is being utilized with all models of JEOL FT NMR systems. In the near future it will encompass applications on all appropriate JEOL systems and will offer retrofitting packages for many non-JEOL products.

You should learn more about it. Simply write JEOL, Analytical Instruments Division, 235 Birchwood Ave., Cranford, N.J. 07016. Tel. (201) 272-8820.

JEOL

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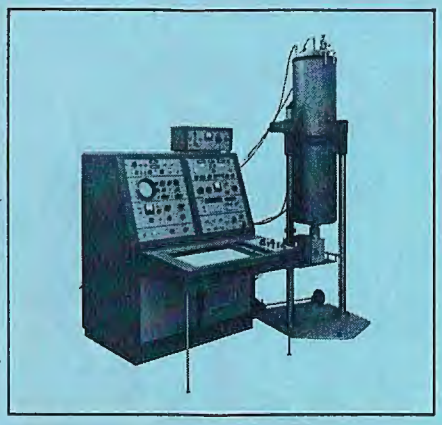
When You Need an NMR System, See Varian First.

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometer systems; from low cost systems designed to solve the typical problems of industrial and academic laboratories to the ultimate in research NMR systems.

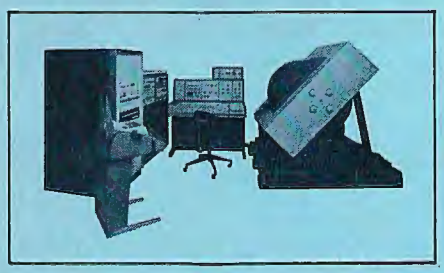
Our basic systems are briefly described here. Ask us what's new for any one, since we're continually expanding the flexibility and research capability of NMR instrumentation.

HR-220 and HR-300



These offer the highest performance in commercially available high resolution NMR spectrometers. The HR-220 (220 MHz) and HR-300 (300 MHz) spectrometers are engineered for use in those applications requiring the highest magnetic field strengths such as liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{11}B, and ^{2}H in both the continuous wave and Fourier transform modes.

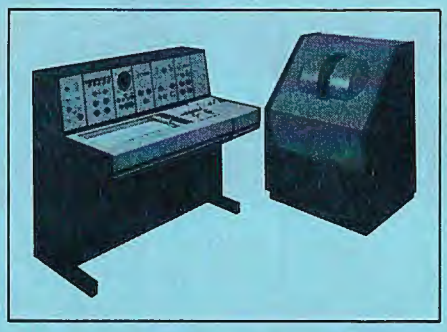
XL-100



A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz, and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments.

Locking flexibility for homo- or heteronuclear internal lock on ^{1}H, ^{19}F, and ^{2}H, and external lock on ^{1}H and ^{19}F are provided. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

NV-14



A moderately priced 14-kG, ^{13}C research spectrometer offering the highest performance per dollar of any NMR system now available. Accessories include Fourier transform for ^{13}C, and other nuclei such as ^{1}H, ^{19}F and ^{31}P. It is a solid state, frequency swept spectrometer ideal for either high performance routine tasks, or for those research requirements demanding state-of-the-art capabilities along with versatile lock, spin decoupling, and variable temperature capability using 8mm sample tubes.

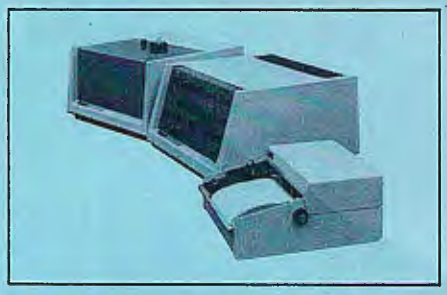
New System T-60A

The T-60A is the newest Varian NMR system, a new system with a heritage, a solid tradition of fine workmanship and reliability inherited from its predecessor, the renowned System T-60. T-60A sensitivity is in excess of 30:1, and resolution is better than 0.3 Hz. Modular accessories include internal lock, variable temperature, wide sweep, and spin decoupling.

EM-360

A 60-MHz instrument which embodies Varian Anaspect's expertise in producing low cost spectrometers and Varian technical leadership in resonance spectroscopy. The result is an instrument which is far ahead of the field in combining economy and performance, flexibility and simplicity. The newest Varian NMR system, it's the low cost leader in the 60-MHz field, yet it delivers high priced performance. Guaranteed sensitivity of 18:1 signal-to-noise and 0.6-Hz resolution are performance features which suit this instrument to a wide variety of routine and research applications.

EM-300



A rugged, low priced 30-MHz spectrometer giving excellent results with minimum effort. The EM-300 can easily handle routine proton applications. The instrument's ability to offset, expand or integrate have made it the preferred system in hundreds of teaching laboratories. Other owners have found the EM-300 to be just as useful in simple, routine control applications.

Write: 611 Hansen Way, Palo Alto.
California 94303

varian instruments

Brand names: ANASPECT™ • CARY® • MAT • VARIAN®
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