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Newsletter

No. 166
June, 1972

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Deadline Dates: No. 167: 7 August 1972 No. 168: 4 September 1972

All Newsletter correspondence, etc. should be addressed to:

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

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TAMU

NMR

Newsletter

Advertising

3 July 1972

Beginning with this issue, the TAMU NMR Newsletter will contain advertisements. It is hoped that income so derived will permit the continued operation of the Newsletter, which is at present - like everything else - suffering from inflationary pressures. We are grateful to those companies which have stepped forward so promptly to provide us with advertisements for this issue, and we look forward to the possibility of additional advertisers. Those companies interested in reaching a relatively small, but highly select audience in the NMR and related areas are invited to contact us for rate information, etc.

It is hoped that advertising revenue will be sufficient such that our present subscription rates can remain in effect for the coming year, and hopefully even be reduced in subsequent years.



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



United States Department of the Interior

BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

June 20, 1972

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

Dear Barry:

In our last letter (Newsletter No. 157, Oct. 1971) we presented ^{33}S NMR spectra of four compounds exhibiting spectral linewidths ≥ 7 gauss. We would now like to report

SOME ADDITIONAL ^{33}S NMR STUDIES

Shown in figure 1 are natural abundance ^{33}S spectra of thiophene in carbon disulfide, powdered sphalerite (ZnS), and 10 N sulfuric acid with an external CS_2 reference. The sulfur resonances of these compounds are the narrowest we have observed to date. Tetrahedral symmetry about $\text{S}^{=}$ ions accounts for the narrowness of the sphalerite spectrum, whereas rapid chemical exchange is the most likely explanation for the narrow sulfuric acid resonance. As indicated in our previous letter, concentrated sulfuric acid gives a quite broad resonance.

^{33}S spectral data for all compounds that we have examined are summarized below:

<u>COMPOUND</u>	<u>No. of Mea.</u>	<u>δ, ppm</u>	<u>ΔH, gauss</u>
Sodium Sulfide (Aqueous)	1	261	5
Sphalerite	3	230 ± 6	< 0.2
Ethyl Disulfide	7	168 ± 88	16
Tetrahydrothiophene	3	89 ± 38	8
Carbon Disulfide		0	0.5
3-Bromothiophene	1	-134	5
2-Methylthiophene	2	-178 ± 9	4
3-Methylthiophene	2	-197 ± 26	5
Thiophene (90% in CS_2)	4	-220 ± 6	1.9
Sulfuric Acid (Conc.)	3	-225 ± 32	7
Dimethylsulfoxide	4	-233 ± 20	8
Sulfuric Acid (10 N)	4	-319 ± 5	≤ 0.5

R. A. Friedel
R. A. Friedel

H. L. Retcofsky
H. L. Retcofsky

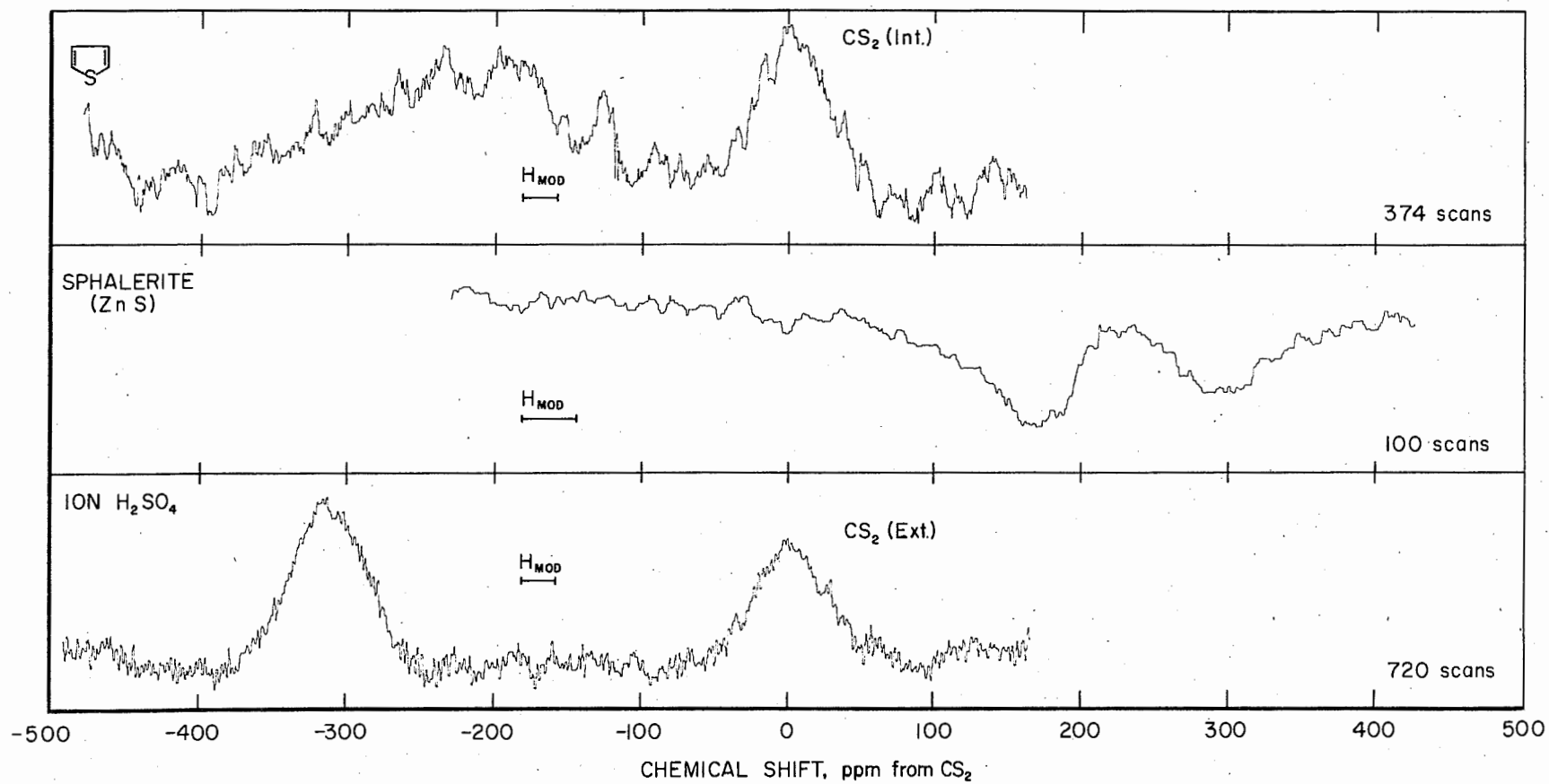


Figure 1 - ^{33}S NMR spectra of selected compounds.

L-12530

DWJ/CMC

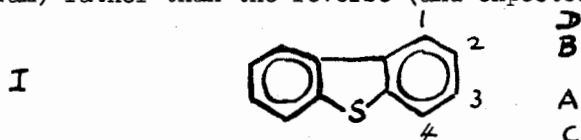
7th June, 1972.

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

Dear Dr. Shapiro,

Indeterminacy and Reaction Fields in Dibenzothiophen Spectra

Following earlier analyses by Faller (Bull. Soc. Chim. Fr., 388 (1967)) and by Clin and Lemanceau (J. Chim. Phys., 66, 1327 (1969)), the ^1H spectrum of dibenzothiophen(I) has been examined in detail as an ABCD system by Balkau, Fuller, and Heffernan (Aust. J. Chem., 24, 2305 (1971)) and by ourselves (Bartle, Jones and Matthews, Tetrahedron, 27, 5177 (1971)). In analyses of spectra of I (5% CCl_4 solution) as ABCD/ABMX or, strictly [ABCD] $_2$ (provided inter-ring coupling is neglected), Heffernan and Balkau noted (TAMUNMR Newsletter No. 145, 31 (1970)) that iteration by LAOCOON III led to $J_{12} > J_{34}$ and $J_{13} > J_{24}$ (in the convention of our diagram) rather than the reverse (and expected) sequence given by the direct ABMX



approach. For 60 and 100 MHz spectra of I at CCl_4 concentrations from 3 to 12% w/w, Dr. K. D. Bartle (Leeds University), D.W.J., and Dr. R. S. Matthews (Durham University) obtained similar results from iterative refinement with LAME (analogous to LAOCOON). Such ABCD systems with small δ_{AB} comparable with J_{AB} exhibit correlations between parameters, which are sensitive to the intensities of some very weak lines; iterative analysis can determine only $J_{12} + J_{13}$ and $J_{24} + J_{34}$, rather than individual coupling constants, and can lead to false solutions.

The significance of reaction-field effects provides a second point of interest in the spectra of I. In collaboration with Dr. K. D. Bartle, T.T.M. has recorded 100 MHz spectra of I in $\text{CCl}_4/(\text{CH}_3)_2\text{CO}$ solvent mixtures of varying permittivity or dielectric constant, ϵ , with correction for bulk diamagnetic susceptibility. When the chemical shifts δ_1 , δ_4 , and $\frac{1}{2}(\delta_2 + \delta_3)$, are plotted against the Onsager expression, $R = (\epsilon - 1)(2\epsilon + n^2)^{-1}$, corresponding to spherical solute molecules (following Balkau, et al., refractive index, n , was taken to be as for the isosteric dibenzofuran), δ_1 and δ_4 tend to increase slightly with R . This is still the case when what might be regarded as a more realistic ellipsoidal model (Diehl and Freeman, Mol. Phys. 4, 39 (1961)) is taken for the solute, to yield $R' = (\epsilon - 1)(\epsilon + 0.18)^{-1}$. Evidently, insofar as the model for I is adequate, these results argue against the dominance of the reaction field.

Yours sincerely,

B. J. Dale

B. J. Dale

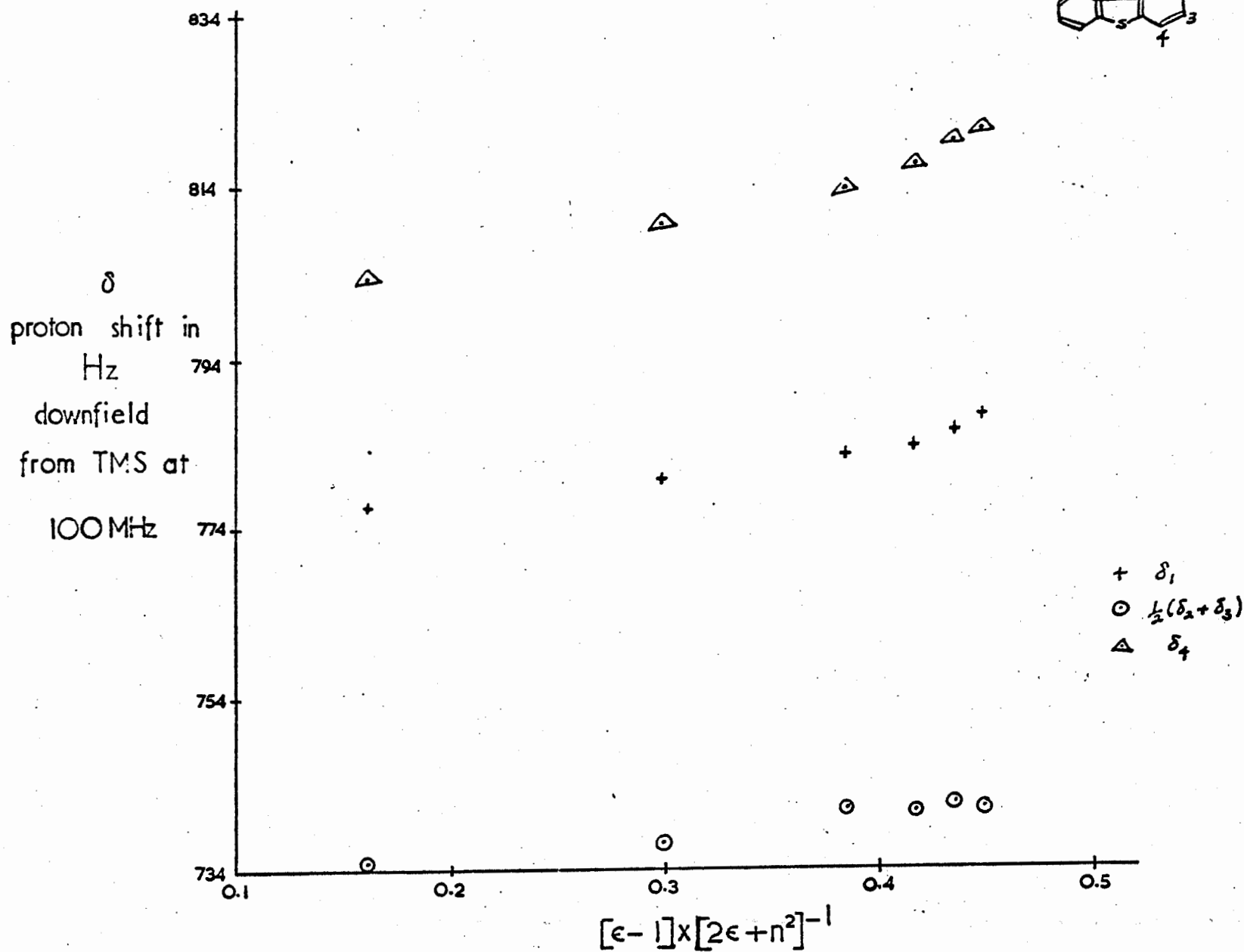
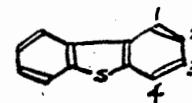
D. W. Jones

D. W. Jones

T. T. Mokoena

T. T. Mokoena

GRAPH OF δ AGAINST $[\epsilon - 1] \times [2\epsilon + n^2]^{-1}$



UNIVERSITY OF WALES



University College of Swansea

Department of Chemistry

J. H. Purnell M.A. Sc.D.
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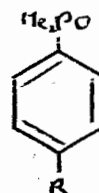
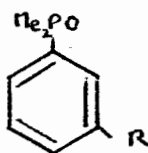
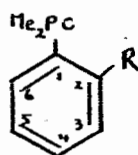
7th June 1972

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

Dear Barry,

N.M.R. Data for Monosubstituted Dimethylphenylphosphine
 Oxides

In order to maintain the Swansea contribution, may I offer some results obtained by Graham Griffin and myself in the analysis of the spectra of a series of 2-, 3- and 4-substituted phosphorus-containing aromatic compounds, with structures as shown.



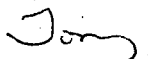
These compounds, kindly provided by Roche Products Ltd. (Welwyn), enabled us to investigate (a) factors controlling the chemical shifts-correlations with Hammett substituent constants, the parameter Q^1 and Diehl's additivity theory²; (b) relative signs and magnitudes of J_{HH} and J_{HP} ; (c) the extent of $d_{\pi} - p_{\pi}$ overlap as reflected in the rotation energy barrier for the aryl-P bond; (d) variations in ^{31}P shifts. Tables 1 and 2 record the results of the analyses, some of the spectra being too complex even at 220 MHz for full analyses to be attempted. With the aid of LAME³ and trial and error methods, most of the compounds were fully analysed with recorded RMS errors.

From the chemical shift data, we find a good linear plot for values of $\delta_{\text{H-3}}$ of the 4-substituted compounds against the Q values for the substituents, and similar linear plots for $\delta_{\text{H-2}}$ and $\delta_{\text{H-4}}$ of the 3-substituted series. The $-\text{P}(\text{O})\text{Me}_2$ group is found to have the Q value 3.96, 4.40 or 4.75 depending on the method used. Less impressive Hammett plots were obtained, values of σ_{m} (+0.6) and σ_{p} (+0.5) being at variance with other determinations. However using the Diehl additivity theory, excellent agreement between observed and calculated shifts was obtained. The ^{31}P shift range for MeOH solutions was disappointingly narrow (-39.1 to -40.3 ppm downfield from external H_3PO_4) and very different from that for TFA solutions (-53.9 to -57.7 ppm) probably due to protonation of the phosphoryl group in the latter case.

The H-H couplings fall into the expected ranges, but the H-P couplings are much less dependent on electronegativity than expected ($^3\text{J}_{\text{HP}}$ 11.2 to 13.5 Hz, $^4\text{J}_{\text{HP}}$ 2.0 to 4.3 Hz and $^5\text{J}_{\text{HP}}$ 1.0 to 1.45 Hz). Double resonance experiments on the 3-carboxyl derivative established that $^3\text{J}_{\text{HP}}$, $^4\text{J}_{\text{HP}}$ and $^5\text{J}_{\text{HP}}$ have the same relative sign (probably positive).

Finally, in variance of the ^1H spectra of the 2-methyl and 4-formyl derivatives at -85°C suggest a low barrier to rotation for the aryl-P bond, and hence negligible $p_\pi - d_\pi$ overlap, the aryl group being a poor electron donor.

Best wishes,


W.A. Thomas.

1. T.Schaefer, F.Hruska and H.M.Hutton, Canad.J.Chem., 1967, 45, 3143.
2. P.Diehl, Helv.Chim.Acta, 1961, 49, 829.
3. C.W.Haigh, published programme.

Table 1: Chemical shifts and coupling constants in some 4-substituted dimethylphenylphosphine oxides

Substituent	Solvent	H-2(6) ^(a)	H-3(5)	J _{2P(6P)}	J _{3P(5P)}	J ₂₃₍₅₆₎	J ₂₅₍₃₆₎	J ₂₆	J ₃₅	RMS
CN ^(d)	MEOH	7.991	7.911	11.70	2.00	8.40	-	-	-	-
CH ₂ CN	d ⁴ -MEOH	7.817	7.559	11.74	2.52	8.07	0.31	1.80	2.34	0.064
	CDCl ₃	7.770	7.487	11.45	2.40	8.12	0.30	1.98	2.51	0.075
COCH ₃	MEOH	7.934	8.105	11.53	2.43	8.14	0.27	1.69	2.43	0.078
COOH	MEOH	7.905	8.163	11.73	2.55	8.23	0.33	1.82	2.38	0.056
	TFA ^(b)	9.42 ^(d)	9.79	12.38	2.70	8.52	-	-	-	-
Cl	MEOH	7.777	7.548	11.48	2.20	8.31	0.35	1.77	2.39	0.079
	CDCl ₃	7.683	7.471	11.23	2.21	8.38	0.24	1.71	2.33	0.085
NH ₂	MEOH	7.427	6.749	11.63	2.57	8.29	0.31	1.70	2.49	0.046
OH	MEOH	7.593	6.937	11.76	2.44	8.44	0.34	1.85	2.51	0.067
NHCOCH ₃ ^(c)	MEOH	7.73 [±] 0.02		J _{2P} +J _{3P} =14.50		-	-	-	-	-
Br ^(c)	MEOH	7.71 [±] 0.02		J _{2P} +J _{3P} =13.93		-	-	-	-	-
	CDCl ₃	7.63 [±] 0.02		J _{2P} +J _{3P} =13.83		-	-	-	-	-
CHO ^(c)	MEOH	8.02 [±] 0.02		J _{2P} +J _{3P} =14.41		-	-	-	-	-
	CDCl ₃	7.97 [±] 0.02		J _{2P} +J _{3P} =13.79		-	-	-	-	-

(a) in ppm, downfield from internal tetramethylsilane at 100 MHz

(b) trifluoroacetic acid

(c) deceptively simple spectra, only approximate shifts and the sum of J_{2P}+J_{3P} obtained

(d) broadening of many of the lines precluded accurate measurements of the parameters

(e) all coupling constants (in Hz) positive relative to H-H couplings.

Table 2: Chemical shifts and coupling constants in some 3-substituted dimethylphenylphosphine oxides

Substituent	Solvent	H-2 ^(a)	H-4	H-5	H-6	J _{2P} ^(b)	J _{4P}	J _{5P}	J _{6P}	J ₂₄	J ₂₅	J ₂₆	J ₄₅	J ₄₆	J ₅₆	RMS
COOH	MEOH	8.452	8.217	7.660	8.018	12.23	1.45	2.77	11.52	1.55	0.57	1.56	7.80	1.35	7.66	0.049
	TFA ^(c)	9.645	9.528	8.865	9.189	13.79	1.05	3.05	12.34	1.40	0.4	1.44	8.20	1.26	7.71	0.081
NH ₂	CDCl ₃	7.130	6.784	7.214	6.941	13.20	1.18	3.57	11.48	2.43	0.39	1.36	8.06	1.03	7.44	0.069
	MEOH	7.038	6.849	7.204	6.967	13.48	1.17	3.72	11.73	2.36	0.40	1.44	8.02	0.99	7.46	0.055
Cl	CDCl ₃	7.732	7.489	7.432	7.620	11.88	1.10	3.17	11.44	2.09	0.44	1.42	8.11	0.93	7.7	0.047
OH	CDCl ₃ ^(d)	7.9	7.0	7.3	6.8	13.5	1.2	4.3	11.9	2.5	0.3	1.3	8.1	1.2	7.4	-
	MEOH ^(e)	7.2	7.0	7.3	7.20	-	-	-	-	-	-	-	-	-	-	-

(a) in ppm, downfield from internal tetramethylsilane at 100 MHz

(b) all coupling constants (in Hz) positive relative to H-H couplings

(c) trifluoroacetic acid

(d) sample used was a saturated solution analysed at 250 Hz sweep width

(e) chemical shifts obtained from 220 MHz spectrum.

University of Notre Dame
College of Science
Notre Dame, Indiana 46556

Department of Chemistry

June 1, 1972

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

Swan-Song: Time-Averaged Geminal Anisochronism and Molecular Energetics

Dear Barry:

Here is the swan-song of my stay in the U.S. I have accepted a chair at the University of Munich and shall be moving there in 2 weeks. Please send future TAMU Newsletter issues (and a bill, of course) to

Institute of Organic Chemistry
University of Munich
8000 Munich 2, Germany.

In Newsletter 155 I mentioned that the time-averaged geminal anisochronism $\langle \Delta \rangle$ in asymmetric ethanes of the type RCG_2CXYZ satisfies the transformation properties of a "chirality function" χ , namely: (1) $\chi = 0$ if $X = Y$, etc (2) $\chi \Rightarrow -\chi$ if $X \rightleftharpoons Y$, etc. There is a variety of mathematical forms one could choose for χ , but the simplest looks like follows

$$\chi = (\lambda_X - \lambda_Y)(\lambda_Y - \lambda_Z)(\lambda_Z - \lambda_X),$$

where the λ parameters characterize the ligands at the asymmetric center. To check whether such a relationship holds and to determine the λ 's one needs to minimize the functional

$$f = \sum (\langle \Delta \rangle_i - \chi_i)^2,$$

which was accomplished by a "breathing grid" method. For the complete series of 10 compounds $BrCF_2CXYZ$ with ligands H, F, Cl, Br, Ph one obtains $\lambda_H = 0$ (by definition), $\lambda_F = -0.830$, $\lambda_{Cl} = -2.671$, $\lambda_{Br} = -3.104$, $\lambda_{Ph} = -1.517$. The regression plot (in ppm) of the Figure shows that there is indeed an approximate correlation.

Cui bono? This question is partially answered by noting that the product of the free energy differences

$$\Gamma = (\Delta G_{\alpha\beta}^O)(\Delta G_{\beta\gamma}^O)(\Delta G_{\gamma\alpha}^O)$$

between the conformers α, β, γ also satisfies the transformation properties of a chirality function. By a series of heuristic arguments one is finally led to the formula

$$\Delta G_{\xi\eta}^0 = (\Gamma/\chi)^{1/3} (\lambda_U - \lambda_V),$$

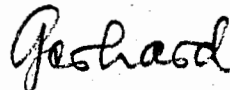
in which the index pairs $[\xi\eta, UV]$ correspond to the combinations $[\mu\nu, XY]$ $[\nu\sigma, YZ]$ and $[\sigma\mu, ZX]$ or $[\mu\nu, XY]$, $[\nu\sigma, ZX]$ and $[\sigma\mu, YZ]$ and where $\mu\nu\sigma$ is any cyclic permutation of $\alpha\beta\gamma$. This heuristic equation has the form of a linear free energy relationship and might hence be dubbed the "Hammett equation of conformational analysis". The results are shown in the Table.

Calculated and Observed Ambient-Temperature Populations

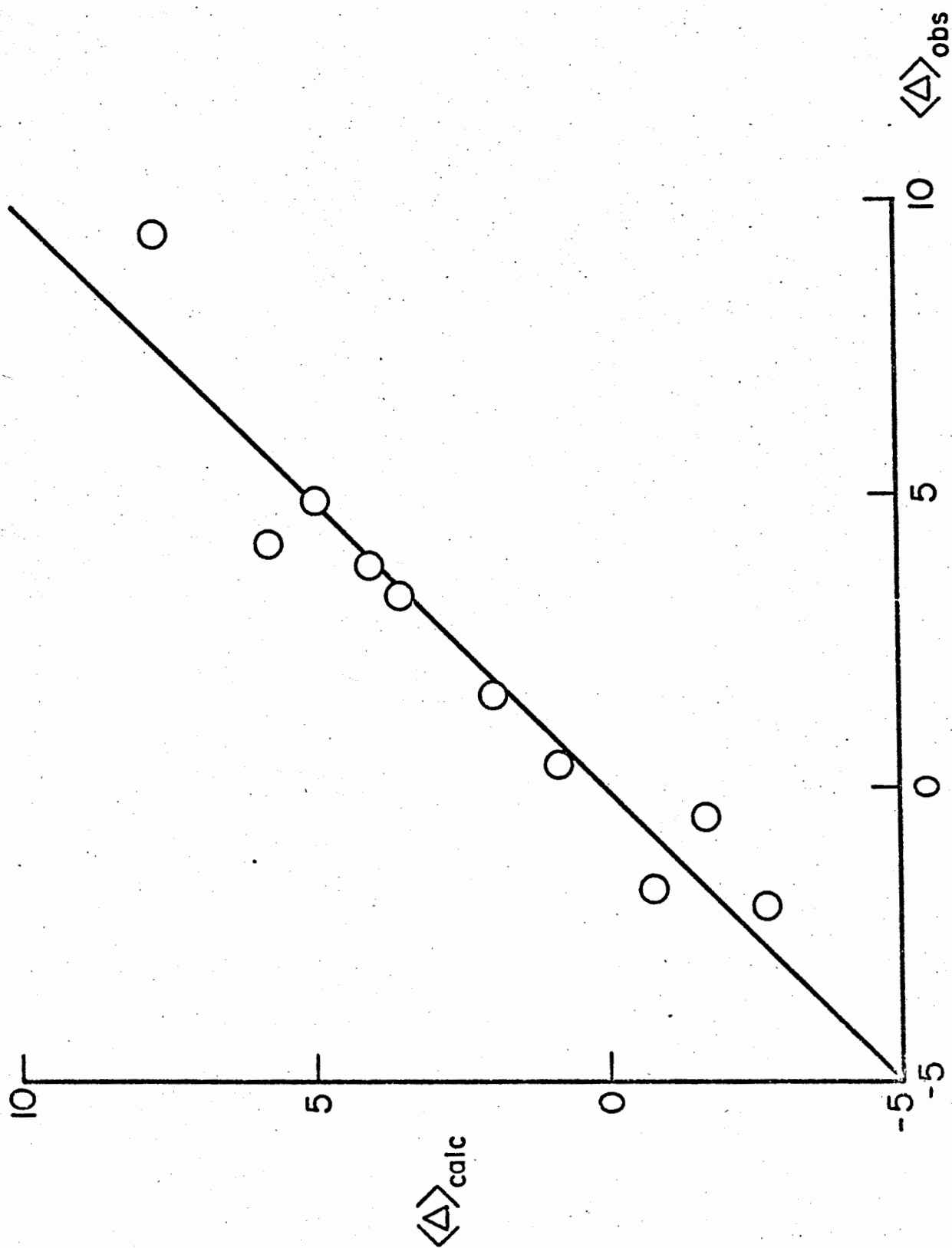
X	Y	Z	P_α		P_β		P_γ	
			calcd	obs	calcd	obs	calcd	obs
Cl	F	H	0.41	0.41	0.24	0.21	0.35	0.38
Br	F	H	0.47	0.50	0.17	0.19	0.36	0.31
Br	Cl	H	0.41	0.43	0.29	0.28	0.30	0.29
Br	Ph	H	0.78	0.81	0.04	-	0.18	0.19
Cl	Ph	H	0.46	0.52	0.23	0.22	0.31	0.26
F	Ph	H	0.29	0.29	0.33	0.33	0.38	0.38
Br	Cl	Ph	0.46	0.58	0.25	0.20	0.29	0.22
Br	F	Ph	0.66	0.70	0.05	-	0.29	0.30
Cl	F	Ph	0.49	0.47	0.18	0.13	0.33	0.40
Br	Cl	F	0.51	0.53	0.38	0.32	0.11	0.15

If this formalism manages to survive the test of further experimental scrutiny, we would have a method for the conformational analysis of asymmetric ethanes. Since most amino acids are represented by the general formula RCH_2CHNH_2COOH , the implications are obvious.

Sincerely yours,



Gerhard Binsch



**are you
playing
hide
and seek
with
your
Ft nmr
data**



?

Are you losing as much data as you're getting . . . or aren't you sure? Can you monitor your f.i.d. signal when time averaging . . . or do you just assume everything's going well?

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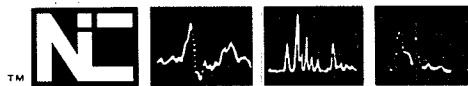
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June 8, 1972

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

Dear Barry:

Re: Analysis of A_3B_2 and $AA'BB'$ Multiplets of AFM-137.

We participated in the interlaboratory analysis of the AFM sample which you conducted for the National Research Council. Our spectra were obtained on a Varion A-60A which had been upgraded to an A-60D.

The A_3B_2 multiplet of the 3,3-diethylpentane component revived an old interest in the ethyl group¹ so we analyzed this multiplet in more detail. Readers of the newsletter may be interested in the results.

The A_3B_2 multiplet was first analyzed arithmetically. The chemical shift of A was obtained from the frequency of line A6 and that of B from the mean of lines B₄ and B₅, Figure 1 (lines are numbered according to Corio). J was calculated from the equation:

$$\delta - 5/2J = 2\nu_{A6} - \nu_{A3} - \nu_{B3}$$
 which was derived from the calculated transition frequencies. Several other equations are possible. The parameters were refined using the computer program² LAOCN-3 on an IBM 370/145. One iteration yielded a best fit with an RMS error of 0.068 in the line positions. The computed spectrum is shown in Figure 1 and the parameters are recorded in Table 1. Although the AFM sample was a mixture of seven components in carbon tetrachloride the parameters differ only slightly from those reported by Ebersole, Castellano and Bothner-By³. They were obtained on a 10 per cent solution of 3,3-diethylpentane in carbon tetrachloride.

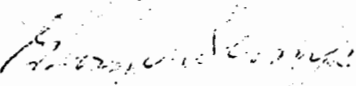
The internal spacing relationships were tabulated by the computer and are also shown in Figure 1. These space relationships help locate and identify lines and also give a check on the linearity of the spectrometer sweep. The AB_2 subspectrum also falls out of this line sort, Figure 1, and could have been used in the original analysis to find J. Here the equation would have been $J = (\nu_{A5} + \nu_{B6} - \nu_{A2} - \nu_{B2})/3$.

Professor B.L. Shapiro
Texas A. and M. University
June 8, 1972

The AA'BB' subspectrum of the O-dichlorobenzene component is more familiar⁵ and need not be described here. One iteration yielded a best fit with RMS error of 0.021. The parameters which we found are shown in Table II. The input line frequencies were average values measured on four successive spectra from our A-60D.

We now have an XL-100. In order to perform ¹³CFT measurements we plan to interface it to our IBM-1800 laboratory computer through an 8K, 16 bit NOVA. I would be pleased to learn of others' experiences along these lines.

Sincerely,


George Slomp
Physical and Analytical Chemistry
Research

GS/smm

Enclosures

References

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G. Slomp, J. Am. Chem. Soc. 84, 673 (1962).
2. S. Castellano and A. A. Bothner-By, J. Chem. Phys. 41, 3863 (1964)
plus a plot program which drapes a Lorentzian curve over the lines.
3. S. Ebersole, S. Castellano, and A. A. Bothner-By, J. Phys. Chem.
68, 3430 (1964).
4. D. M. Grant, R. C. Hirst and H. S. Gutowsky, J. Chem. Phys.
38, 470 (1963).
5. G. Slomp, These newsletters 154, 8 (1971) and references cited therein.

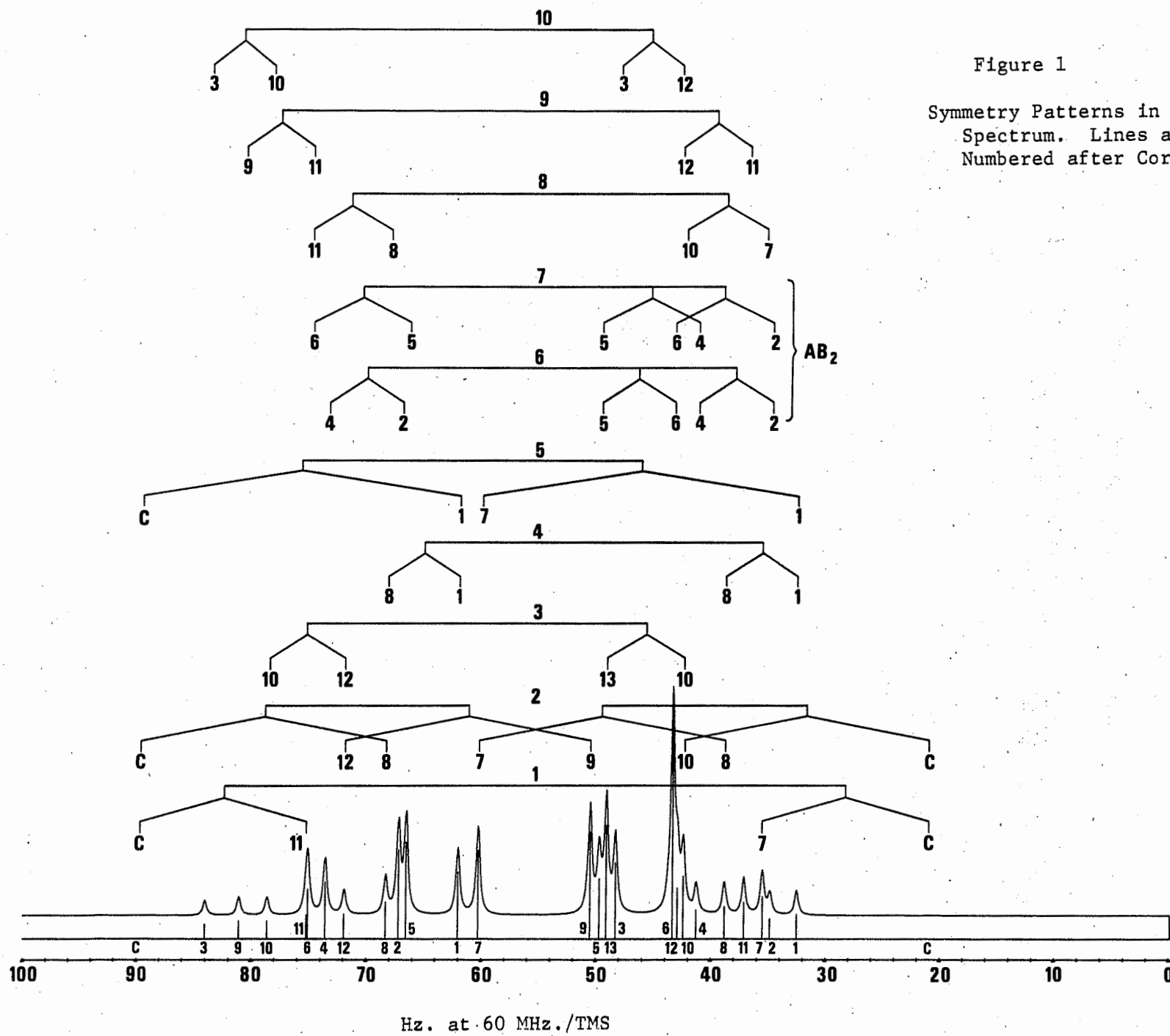


Figure 1
Symmetry Patterns in the A_3B_2
Spectrum. Lines are
Numbered after Corio.

TABLE IAnalysis of the A_3B_2 Multiplet at 60 MHz.

Parameter	RESULTS		
	By Factoring, Hz.	After Iteration, Hz.	Bothner-By ³
δ_A	43.4	43.379 ± 0.008	43.6560 ± 0.0005
δ_B	70.2	70.121 ± 0.010	70.254 ± 0.0006
J_{AB}	7.48	7.555 ± 0.009	7.528 ± 0.026

TABLE IIAnalysis of the $AA'BB'$ Multiplet at 60 MHz.

Parameter	By Factoring	Results	Grant ⁴
		After Iteration	
δ_A	430.8	430.742 ± 0.006	
$\delta_{A'}$	430.8	430.742 ± 0.006	
δ_B	445.2	445.222 ± 0.006	
$\delta_{B'}$	445.2	445.222 ± 0.006	
$J_{AA'}$	7.54	7.547 ± 0.008	7.5
J_{AB}	8.10	8.142 ± 0.010	8.1
$J_{AB'}$	1.56	1.538 ± 0.008	1.5
$J_{BB'}$	0.32	0.354 ± 0.008	0.3

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Prof. H. Günther

5 KÖLN, June 15, 1972
ZOLPICHER STRASSE 47
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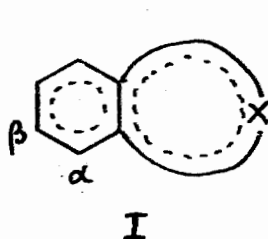
Prof. B. L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77843
USA

Assignment of Resonance Frequencies in
AA'BB'-type NMR-Spectra

Dear Barry,

Please excuse the delay of our contribution that forced you to send already two reminders. We have been busy in recent weeks to install our new BRUKER HF-90 spectrometer and I hope to have some ^{13}C -results for our next letter.

This time I merely want to draw the attention of your readers to a convenient method for the assignment of ^1H -resonance frequencies in certain AA'BB'-type spectra that we used recently for a number of compounds of type I, where a benzene ring is fused symmetrically to a carbocyclic or heterocyclic annulene. The method is based on



X = CH
O
SiR₂
S
C=O

the observation of the ^{13}C -satellites, whose overall width must be larger for the β -protons than for the α -protons, since $(2 \times J_o + J_m) > (J_o + J_m + J_p)$. Fig. 1 demonstrates this for naphthalene, where the α -protons resonate at lower field. We have also verified

that for biphenylene $\delta_\alpha < \delta_\beta$. This will be reported shortly, since several authors disagree in this respect.

Sincerely yours,

Handwritten signature

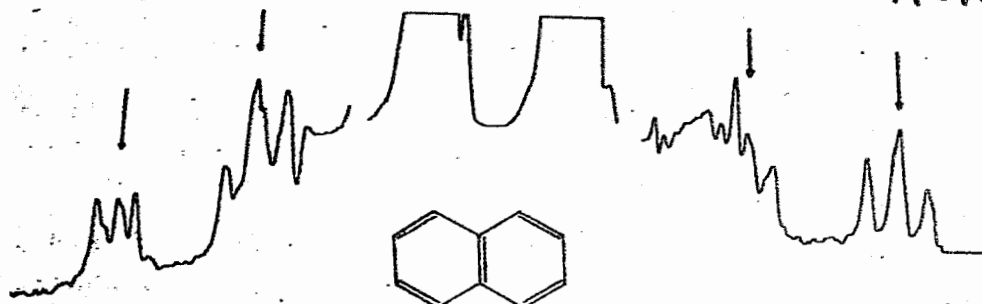


Fig 1: ^{13}C -satellites of naphthalene (A. Shyoukh, thesis, university of Cologne 1972).

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DIRI
CENTRO RICERCHE DI BOLLATEProf. B.L. Shapiro
Dept. of Chemistry
Texas A & M University
College Station,
Texas 77843

Bollate, June 9, 1972

Si prega indirizzare la risposta a:
MONTECATINI EDISON S.p.A.
DIRI Centro Ricerche di Bollate
Via S. Pietro, 50
20021 Bollate (Milano)

ref.: 7116 LC/vr

Subject: NMR data of 1,3,3¹-trichloro,4-chloromethylcyclohexane

Dear Professor Shapiro,

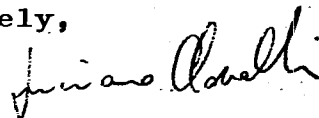
my apologies for being so late in maintaining my subscription to your Newsletter.

The two isomers of 1,3,3¹-trichloro,4-chloromethylcyclohexane(I) were separated by GLC and identified by NMR. The NMR parameters of interest, obtained at room temperature for CCl₄ solutions using a Varian HA 100 spectrometer, are collected in the table hereby attached. The spectrum of the cis isomer is temperature dependent in agreement with the existence of a rapid equilibrium between the two possible chair conformations. The spectrum of the trans isomer, on the contrary, is consistent with the presence of only one conformer, which is likely to be that with the 1- and 4- substituent in equatorial positions. The chemical shifts of the $\text{>CH}-\text{CH}_2\text{Cl}$ protons, being overlapped by other resonances, in particular by those of the methylene group in C-6, were measured by INDOR experiments. The ν_2 frequency was swept through the spectrum, maintaining the ν_1 frequency on resonance for some lines of the $-\text{CH}_2\text{Cl}$ absorption. The low field proton absorption of the methylene group at C-2 shows an additional coupling in both isomers. This coupling (doublet, $J = 2.0 \text{ Hz}$, for the trans isomer and triplet, $J = 1.0 \text{ Hz}$, for the cis isomer) can be assigned to a four-bond interaction of the equatorial proton in C-2 with the protons in C-6.

I am indebted to Dr. Piccardi for the compounds.

Yours sincerely,

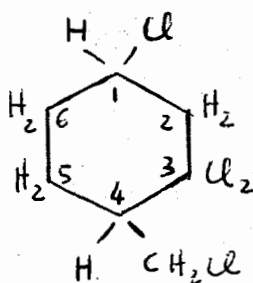
L. Cavalli



Table

NMR parameters of the two isomers of

1,3,3'-trichloro,4-chloromethylcyclohexane, (I)



I

	Cis Isomer				Trans Isomer			
	δ	J_{AB}	J_{AX}	J_{BX}	δ	J_{AB}	J_{AX}	J_{BX}
>CHCl	4.21				4.04			
$\text{>CHCH}_2\text{Cl}$	2.52				2.18			
$\text{-CH}_2\text{Cl}$ $\left\{ \begin{array}{l} \text{A} \\ \text{B} \end{array} \right.$	4.12	-11.4	3.5	10.6	4.17	-11.0	2.5	10.0
	3.50				3.34			
$\text{-CH}_2\text{-(2)}$ $\left\{ \begin{array}{l} \text{A} \\ \text{B} \end{array} \right.$	2.87	-14.6	4.5	8.6	3.10	-14.0	4.0	11.7
	2.52				2.43			

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

June 15, 1972

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

Title: A Remarkable Correlation and Some Stimulating Simulations

Dear Barry:

I would like to describe a quite remarkable correlation between an nmr parameter and a reaction of biochemical interest.

It was reported some time ago that polyhistidine produces a greatly enhanced rate for the oxidation of p-hydroquinone and ascorbic acid in the presence of cupric ion in the pH range 3.5-5.5¹. This enhancement was two orders of magnitude greater than the rates for such liquids as imidazole, histidine and polylysine. I have studied the line widths and chemical shifts of the imidazole proton resonances of polyhistidine at several cupric ion concentrations as a function of pH. The line width of the C2 proton resonance shows a maximum at pH 3.4 (in D₂O). There is no comparable effect on the chemical shift value, and zinc at the same concentration gives no line broadening effect. These results indicate the formation of a specific copper (II)-polyhistidine complex in which the cupric ion competes with protons for the imidazole nitrogen atoms in the pH range 2.5-4.5. This complex is most likely responsible for the enhanced catalytic activity observed in the oxidation reactions, and may be relevant to the mechanism of action of copper (II) oxygenases.

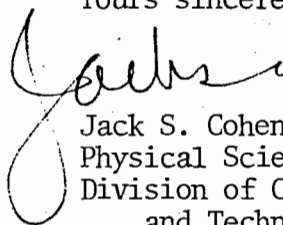
Now that carbon-13 FTNMR is all the rage some of your readers may be interested in the simulation of CMR spectra of peptides. This is particularly easy for noise-decoupled spectra since each resonance is a singlet. I use the MLAB program with the interactive graphics system on the DEC PDP10 computer to sum a set of Lorentzian lines. The chemical shifts are derived from a master set for all the amino acids^{2,3} given the composition of the peptide and the region of the spectrum of interest. This form of comparison to actual CMR spectra is much more informative and versatile than stick diagrams. For example, we have found that

Dr. B. Shapiro

June 15, 1972

an internal peptide shift of ca. 1.2 ppm for the C α atom⁴ is indeed indicated for our spectra of the amino-terminal peptides of ribonuclease⁵.

Yours sincerely,



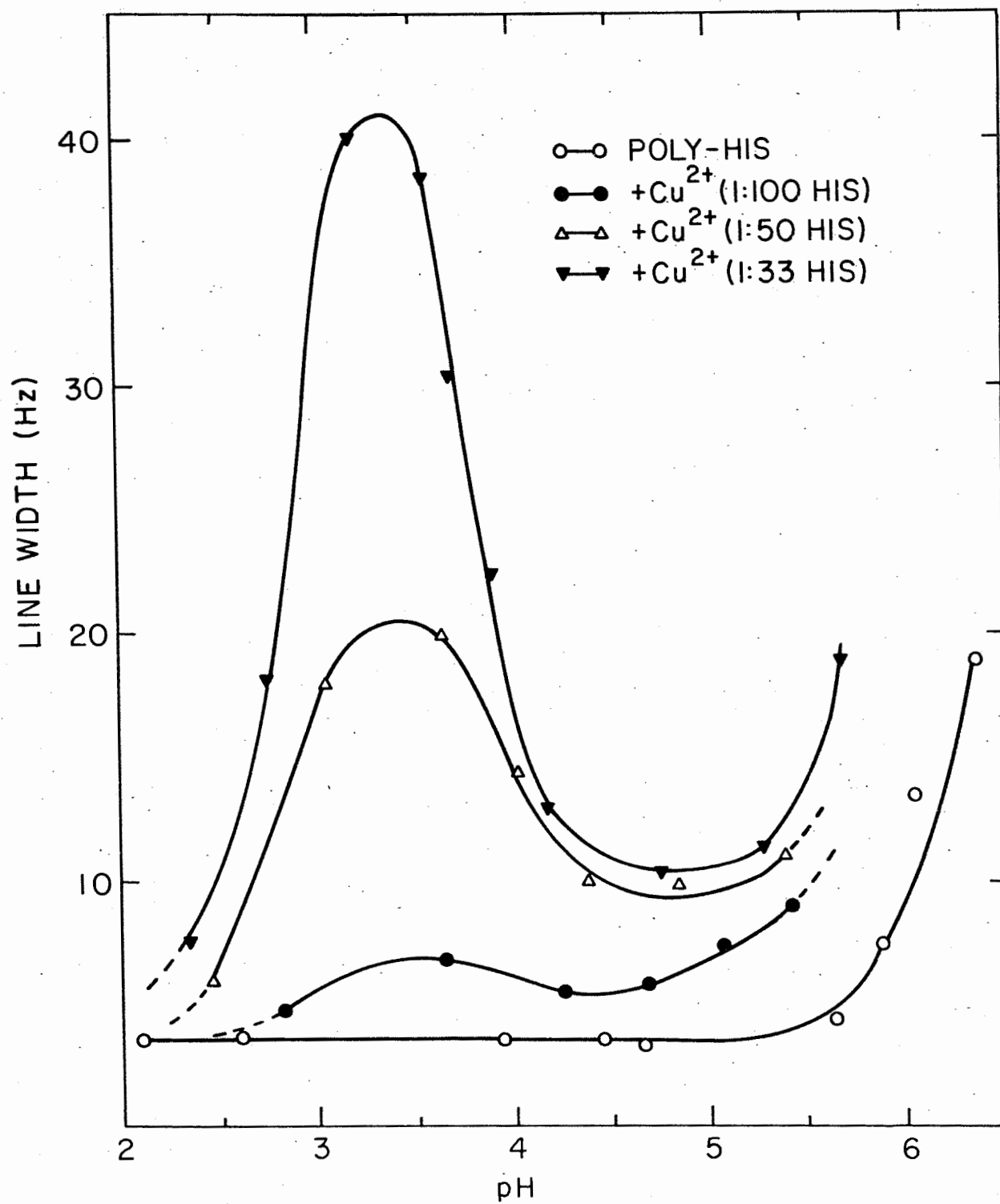
Jack S. Cohen
Physical Sciences Laboratory
Division of Computer Research
and Technology

References

1. A. Levitzki, I. Pecht and M. Anbar, Nature, 207, 1386 (1971).
2. W. Horsley, H. Sternlicht and J.S. Cohen, J. Am. Chem.Soc., 92, 680 (1970).
3. M. H. Freedman, J. S. Cohen and I. Chaiken, Biochem. Biophys. Res. Comm., 42, 1148 (1971).
4. F.R.N. Gurd, P. J. Lawson, D. W. Cochran and E. Wenkert, J. Biol. Chem., 246, 3725 (1971).
5. M.H. Freedman, J.R. Lyerla, Jr., I.M. Chaiken and J.S. Cohen, paper in preparation.

Figure Legend

The line width at half-height of the imidazole C2 protons of poly-L-histidine (Miles-Yeda, M.W. \approx 10,000) at a concentration of 20 mg/ml in 0.1 M NaCl/D₂O, as a function of pH (direct meter readings) and at various cupric ion (Cu SO₄) concentrations. (The material precipitates above pH 6).



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Ul. Vavilova, 32
Moscow V-312
USSR

June 16, 1972

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

Title: ^{31}P Signals from Inner
and Outer Surfaces of "Soap
Bubbles".

Dear Barry,

It was shown that PMR in the presence of paramagnetic ions is able to distinguish between the inner and outer surfaces of a phospholipid membrane (versicules) [TAMU NMR Newsletters 156-17]. As there is grounds to believe that paramagnetic cations will interact with the negatively charged lecithin phosphate groups, one would expect larger effect in using ^{31}P -NMR spectroscopy.

The ^{31}P spectra were obtained for three versions of 20% sonicated lecithin dispersion in D_2O :

- A - before treatment with additives;
- B - on treatment with 0.01 M $\text{Pr}(\text{NO}_3)_3$;
- C - on subsequent treatment with 0.1 M KNO_3 .

The ^{31}P spectrum of A sample is a singlet (Fig. A). Subsequent addition of Pr^{3+} ions results in two signals (Fig. B), the signal in the higher field having practically the same shift as the A sample singlet (Table). Clearly this upfield signal is due to the phosphate groups located on the inner surface which do not come into contact with the Pr^{3+} ions, whereas the signal moving downfield belongs to the phosphate groups situated on the outer layer of the membrane.

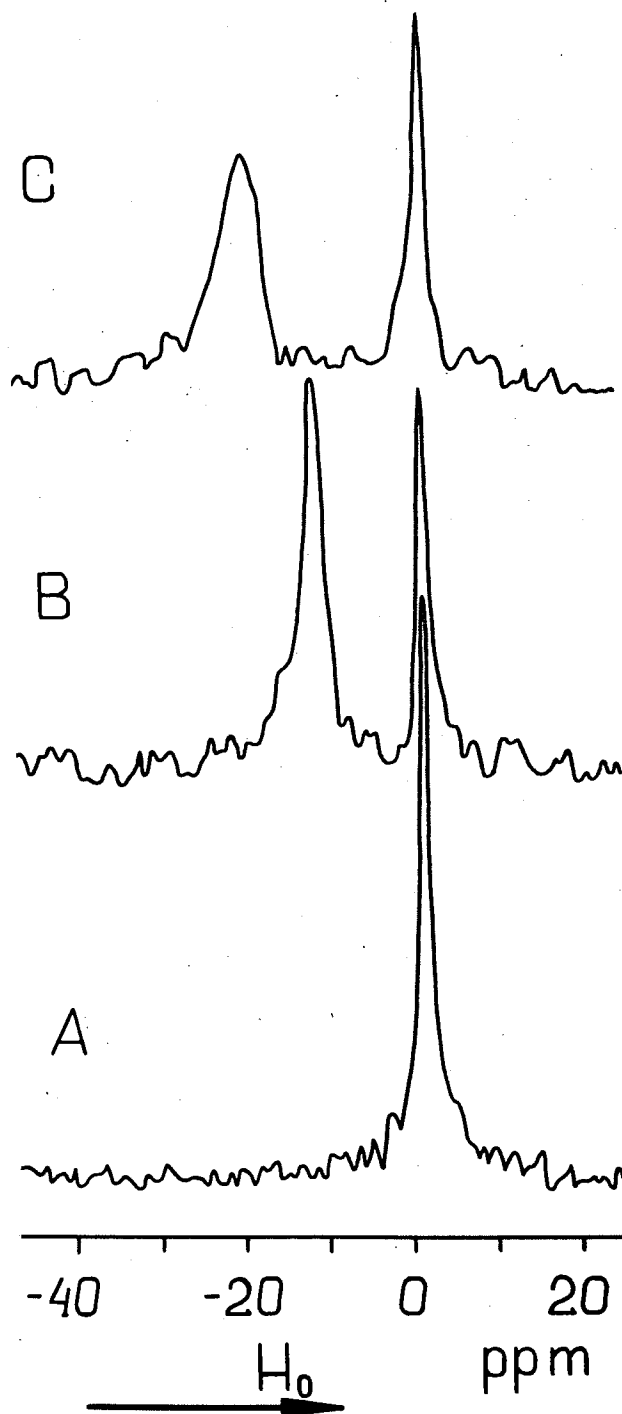


Fig. ^{31}P FT NMR spectra of lecithin dispersions, 6000 scans. External 85% H_3PO_4

The integral intensity ratio of ^{31}P signals attributed to the inner and outer surfaces (Table) is in accord with the PMR data and satisfies the surface ratio for bilayer vesicles.

Treatment of the B sample with KNO_3 leads to additional shifting of the low field ^{31}P signal. One could attribute this to stronger binding of Pr^{3+} to the membrane when NO_3^- anions have been incorporated in the membrane surface.

Comparison of ^{31}P and ^1H signals shifting of the lecithin molecules located on the outer surface makes it clear that ^{31}P spectroscopy is ~ 130 times more sensitive to the influence of Pr^{3+} ions. It is also remarkable that this ratio does not change in the presence of diamagnetic KNO_3 .

The intense shift and the simplicity of the spectrum makes possible to assay by ^{31}P /NMR all phospholipids under the action of paramagnetic probes - in contrary to PMR which needs choline residues to be contained in phospholipid molecule.

³¹P signals from inner and outer phosphate moieties
of lecithin vesicles

Sample	Inner surface		Outer surface		Intensity ratio I_{out}/I_{inn}
	δ , ppm	Line width, cps	δ , ppm	Line width, cps	
<u>A</u>	1.10	50 \pm 5	1.10	50 \pm 5	-
<u>B</u>	1.37	67 \pm 5	-11.52	116 \pm 5	1.85
<u>C</u>	1.65	70 \pm 5	-19.49	229 \pm 5	1.98

This investigation has been done in collaboration with
Yuri Shapiro, A. Viktorov, Dr. L. Barsukov and Prof. L. Bergelson.

Truly yours,

Vladimir

Vladimir Bystrov

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

June 22, 1972

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

Subject: Appeal for help in obtaining some Fluorine spectra
 at 52 kgauss.

Dear Barry:

Recently I have had occasion to review the procedures for studying the kinetics of micelle dissociation in aqueous detergent solutions, i.e.



where S is a detergent molecule or ion. Past nmr studies of these systems have shown only that the reaction is "fast on the nmr timescale." Other kinetic measurements, such as T-jump or ultrasonics, give some quantitative results, e.g. relaxation times, but it is not really clear how these are related to the rate constants for (1).

It does appear probable that in favorable cases the rate constants would be such as to produce an "intermediate" rate of exchange if the materials used were fluorine-labelled, and the F-19 spectra were obtained at 52 kgauss, where the chemical shift difference between monomeric and micellar species is about 240 Hz. We have an assortment of detergents with $CF_3(CH_2)_n$ - chains, but no facility for looking at the spectra at 52 kgauss (or more).

I would very much appreciate hearing from any reader of the newsletter who has apparatus capable of producing such spectra and would be willing to collaborate with us in an attempt to pin down these exchange rates.

I hope you've fully recovered from the damage sustained at Asilomar.

With best wishes,

Sincerely,

Norbert Muller
 Norbert Muller
 Professor of Chemistry

NM:JHB

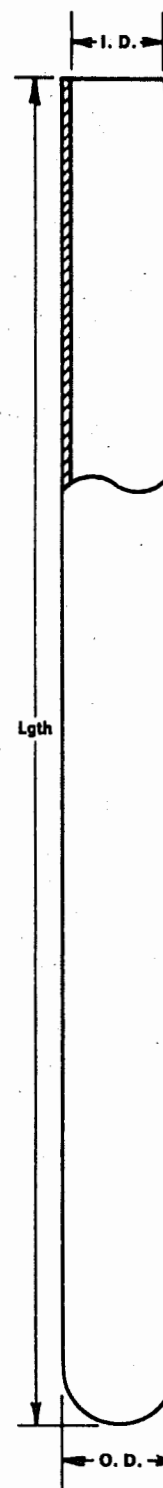
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K-897290	7.5mm Sample Tube, Grade III	7	.2550 ±.0005	.2950 ±.0005	±.001	±.0005	7.00
K-897295	7.5mm Sample Tube, Grade IV	7	.2550 ±.0005	.2950 ±.0005	±.00075	±.00025	8.50
K-897300	8mm Sample Tube, Grade I	7	.2750 ±.0005	.3150 ±.0005	±.005	±.001	4.00
K-897305	8mm Sample Tube, Grade II	7	.2750 ±.0005	.3150 ±.0005	±.0015	±.00075	6.00
K-897310	8mm Sample Tube, Grade III	7	.2750 ±.0005	.3150 ±.0005	±.001	±.0005	7.00
K-897315	8mm Sample Tube, Grade IV	7	.2750 ±.0005	.3150 ±.0005	±.00075	±.00025	8.50
K-897320	10mm Sample Tube, Grade I	7	.3569 ±.0005	.3937 ±.0005	±.005	±.001	4.00
K-897325	10mm Sample Tube, Grade II	7	.3569 ±.0005	.3937 ±.0005	±.0015	±.00075	6.00
K-897330	10mm Sample Tube, Grade III	7	.3569 ±.0005	.3937 ±.0005	±.001	±.0005	7.00
K-897335	10mm Sample Tube, Grade IV	7	.3569 ±.0005	.3937 ±.0005	±.00075	±.00025	8.50
K-897340	12mm Sample Tube, Grade I	7	.4350 ±.0005	.4750 ±.0005	±.005	±.001	4.00
K-897345	12mm Sample Tube, Grade II	7	.4350 ±.0005	.4750 ±.0005	±.0015	±.00075	6.00
K-897350	12mm Sample Tube, Grade III	7	.4350 ±.0005	.4750 ±.0005	±.001	±.0005	7.00
K-897355	12mm Sample Tube, Grade IV	7	.4350 ±.0005	.4750 ±.0005	±.00075	±.00025	8.50
K-897360	13mm Sample Tube, Grade I	7	.4610 ±.0005	.5110 ±.0005	±.005	±.001	4.25
K-897365	13mm Sample Tube, Grade II	7	.4610 ±.0005	.5110 ±.0005	±.0015	±.00075	6.50
K-897370	13mm Sample Tube, Grade III	7	.4610 ±.0005	.5110 ±.0005	±.001	±.0005	7.50
K-897375	13mm Sample Tube, Grade IV	7	.4610 ±.0005	.5110 ±.0005	±.00075	±.00025	9.00
K-897380	15mm Sample Tube, Grade I	7	.5305 ±.0005	.5905 ±.0005	±.005	±.001	4.25
K-897385	15mm Sample Tube, Grade II	7	.5305 ±.0005	.5905 ±.0005	±.0015	±.00075	6.50
K-897390	15mm Sample Tube, Grade III	7	.5305 ±.0005	.5905 ±.0005	±.001	±.0005	7.50
K-897395	15mm Sample Tube, Grade IV	7	.5305 ±.0005	.5905 ±.0005	±.00075	±.00025	9.00



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3737 BELLAIRE BOULEVARD
HOUSTON, TEXAS

MAILING ADDRESS
P. O. BOX 481
HOUSTON, TEXAS 77001

June 23, 1972

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

Dear Barry:

We are slowly getting settled in our new location in the Houston area.

We will not have either of our spectrometers running until the installation of a chiller to supply cooling water for the magnets has been completed.

Several months ago we replaced the 304TL tubes in our Varian V2100A power supply with transistors according to the description given by Pearson (Rev. Sci. Inst., 42, 713 (1971)). Our experience has indicated that several modifications to Pearson's circuit were necessary before the power supply could be considered satisfactory. The unit has now been operating for several months with no difficulty.

Initially, we had several failures in which all five IN3340 Zener diodes (see enclosed schematic) were destroyed. It was thought that voltage transients were responsible. No further breakdowns occurred after we added an RC bypass circuit consisting of a 100 ohm resistor and a 0.25 μ F, 1000 v oil-filled capacitor.

Poor regulation was initially encountered and this was apparently due to high frequency oscillations that were observed at TB 801-5. The oscillations were reduced (and regulation improved) by replacing the 0.25 μ F capacitor, C710, with a 2 μ F one. Satisfactory operation was finally obtained by disconnecting the switched resistors from the circuit and connecting the 22K resistor directly to TB 801-5 (see schematic). This change was acceptable because the magnet is used only at a fixed field of 23 kG.

We would be interested in learning about experiences that others have had in adopting Pearson's circuit to their power supply units.

Title: Pearson Modification to Varian V2100A Power Supply.

Sincerely yours,

Charlie

C. A. Reilly

SHELL DEVELOPMENT COMPANY
Bellaire Research Center, Houston

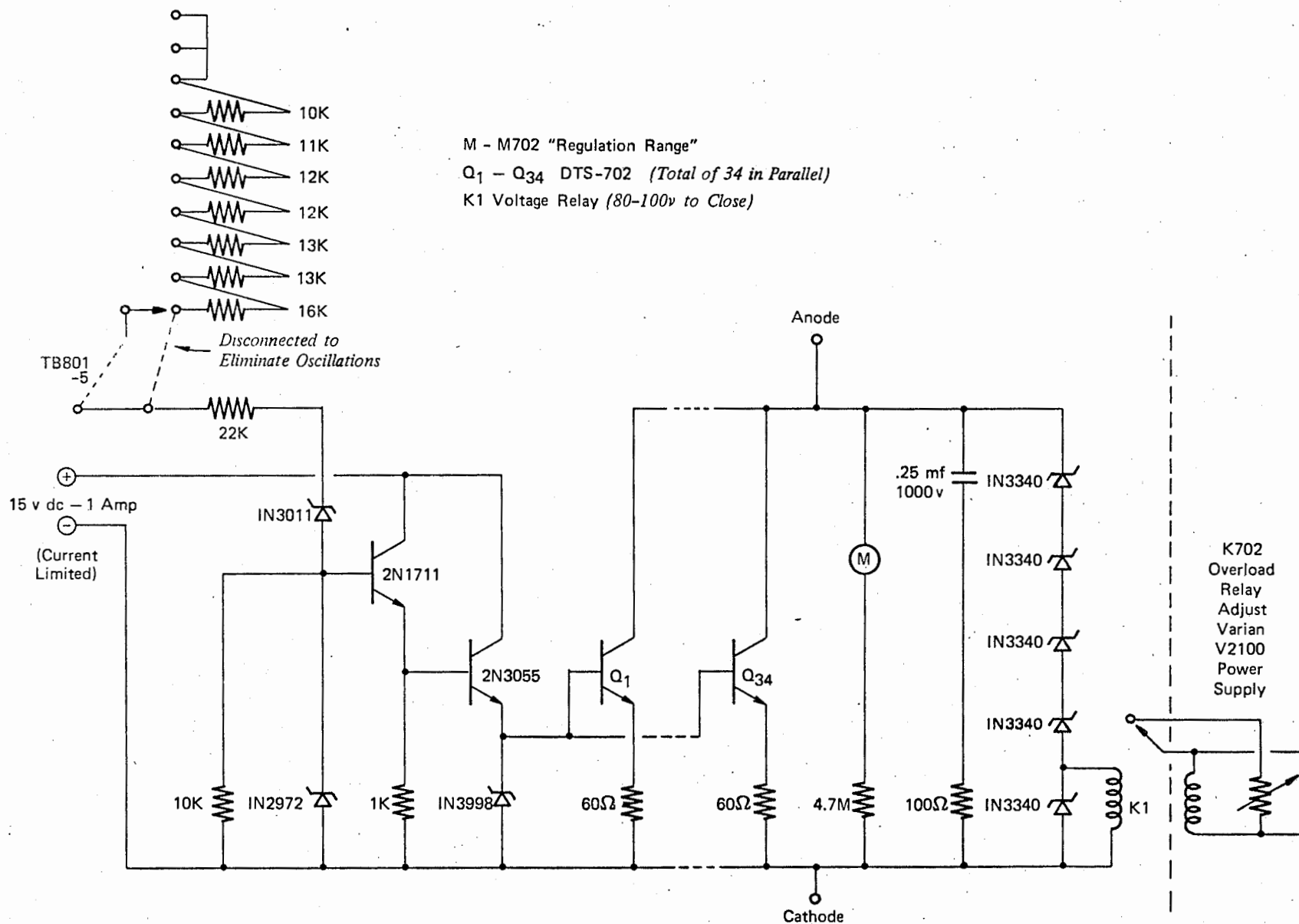


Figure 1. SCHEMATIC WIRING DIAGRAM

PERKIN-ELMER

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June 13, 1972

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

Dear Barry:

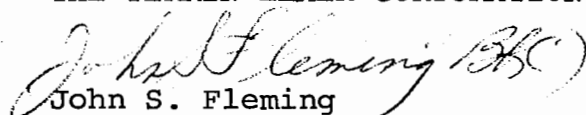
"A SIMPLE HEROIN ANALYSIS"

One set of application and data spectra which we have been running turned out to be of interest to a number of agencies and I thought perhaps some of your readers might be interested in the results. We have been quantitatively identifying heroin in a series of drug samples by measuring the amplitude of the methyl resonances and comparing with the amplitude of the methyl resonances in a series of known concentration standards. Comparison of unknowns ("street samples") with the standards has allowed analysis of the unknown and the analysis compares very well with the percentages obtained from gas chromatography analysis.

The sensitivity is still a limiting factor, but the work has been done with 5 mg of samples with 5 to 15% heroin. This method then allows a simple, quick, but precise method of analysis.

Sincerely,

THE PERKIN-ELMER CORPORATION


John S. Fleming
Nuclear Magnetic Resonance
Product Specialist

JSF:bkc



U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

CHEMICAL SHIFT - DEFINITION?

21 June 1972

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

Dear Barry:

ASTM Subcommittee E-13.7 is presently considering recommendations for standards and practices in high resolution nmr. I believe it is correct to state that many practitioners in the field regard field sweep and frequency sweep nmr to be entirely equivalent. That this is not so has been demonstrated by Rummens¹. Some simple experiments in this laboratory have produced results in complete agreement with Rummens' paper. The results in two tubes are summarized in the table.

There are a number of points to be made about these data. 1) The difference of 1.4 Hz at 164 ppm is easily measurable and far beyond the limits of experimental error. 2) The difference between field and frequency sweep measurements increases four-fold as the shift difference doubles, in agreement with Rummens' calculations. 3) The chemical shift difference is affected by the choice of reference. Note that in tube B, C_6F_6 is not as far upfield (WF_6 reference) as WF_6 is downfield (C_6F_6 reference). This result implies that it will not be correct to bring all chemical shift data to a common base simply by choosing the proper additive constant. Such an adjustment of data can, of course, be accomplished if the original data are available and the necessary algebra is clearly in mind.

The effect discussed above will probably prove to be negligible for all or nearly all cases in proton nmr. However, carbon-13 shifts include the range covered in these experiments and will show the same effects. Obviously, the experimenter must know how his equipment works (field or frequency sweep, if locked -- whether sideband or centerband, if sideband -- whether upper or lower, and the frequency of both the rf unit and the sideband oscillator) in order to convert measured frequency differences into chemical shifts correctly.

Professor Barry L. Shapiro

21 June 1972

The Subcommittee would welcome suggestions from the nmr community as to the best way to define chemical shift. I think the following points should be adhered to: 1) The definition must be clear and unambiguous. 2) The definition should be experimentally realizable, i.e., shifts in terms of a "bare nucleus" are useless for the present purpose. 3) The equipment required should be no more than is available in most nmr laboratories. This probably rules out rf counters, for example.

Yours truly,

R. B.

Rolf B. Johannesen
Inorganic Chemistry Section

¹ Rummens, *Org. Magn. Resonance*, 2, 209 (1970).

TABLE

	Tube A	Tube B
	SiF ₄ + CFCl ₃	C ₆ F ₆ + WF ₆
Upfield peak	SiF ₄	C ₆ F ₆
Separation by Field Sweep, upfield peak = 0	9260.0 Hz 164.062 ppm	18585.7 Hz 329.312 ppm
Separation by Frequency Sweep, upfield peak = 0	9258.6 Hz 164.037 ppm	18579.6 Hz 329.206 ppm
Separation by Field Sweep, downfield peak = 0	9258.6 Hz 164.037 ppm	18579.6 Hz 329.206 ppm

166-34

27 June 1972

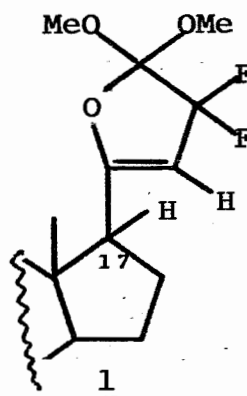
Professor Bernard L. Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, Texas 77843

Dear Barry:

"SOME UNUSUAL H-F COUPLING CONSTANTS"

In our studies on fluorinated steroids, the novel ring structure 1 was prepared as a derivative in both the estratriene and androstane series. Analysis of the ^1H and ^{19}F NMR spectra yielded some unusual H-F coupling constants. The signal for the vinylic proton is a doublet ($\delta=5.03$, $J=1.5$ Hz, CDCl_3) and double resonance experiments proved that this proton is coupled only to a proton at $\delta=2.0$ ppm (assumed to be H-17 but obscured by other steroid proton resonances). Similar H-H allylic couplings have been reported. The lack of vicinyl H-F coupling is

estratriene
 or androstane



reasonable when one considers the low $^3J_{\text{HF}}$ in 3,3-difluoro cyclobutenes (1.6-2.5 Hz)¹ and the known decrease of vicinyl H-F couplings with increasing ring size and increasing substituent electronegativity.²

The ^{19}F NMR spectrum of the androstane derivative consists of the AB part of an ABX pattern centered at 103.9 ppm (upfield

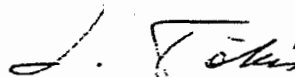
Professor Bernard L. Shapiro

from CFCl_3 , 94.1 MHz) with $\delta_{AB} = 90.35$ Hz, $J_{AB} = 242.5$ Hz, $J_{AX} = 5.9$ Hz, and $J_{BX} = 1.6$ Hz. On the assumption that the fluorines are coupled to H-17 we then have a very large homoallylic H-F coupling (the five bond couplings in 1,1,1-trifluoro-2-butenes are on the order of 2.8 Hz)³ as well as evidence for an angular dependence of $^5J_{\text{HF}}$. We do not believe that through space coupling is significant in this case since the internuclear distances (as measured on Dreiding models) are too large⁴ and the bond vectors are incorrect.

Sincerely,



M. L. Maddox, Ph.D.*



L. Tökés, Ph.D.

-
1. J. D. Park, R. O. Michael and R. A. Newmark
J. Am. Chem. Soc., 91, 5933 (1969)
 2. K. L. Williamson, Y-F. L. Hsu, F. H. Hall, S. Swager and
M. S. Coulter, J. Am. Chem. Soc., 90, 6717 (1968)
 3. R. N. Haszeldine, D. W. Keen, and A. E. Tipping, J. Chem. Soc., (C),
414, (1970)
 4. E. Abushanab, J. Am. Chem. Soc., 93, 6532 (1971)



DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-59122
TELEX 47661

12th June 1972

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

Dear Barry,

Postdoctoral Fellowship Available

For the past two years we have been exploring the possibility of getting useful structural information on organometallic compounds by studying the spectra of partially aligned molecules, so far by using nematic liquid crystals as solvents. Some very interesting systems have been studied and it appears that this technique has considerable scope, particularly for studying mobile systems.

This work is a joint project with Professor I. R. Beattie of this Department, who now has available a Postdoctoral Fellowship for someone to continue work in this field. He is looking for someone capable, and interested, in some preparative work as well as in analysing and interpreting the spectra.

Anyone interested should write to me as soon as possible.

Yours sincerely,

Jim Emsley

J. W. Emsley

Yale University
SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT 06510

SECTION OF PHYSICAL SCIENCES

Tel: 203-436-8100

Dear Dr. Shapiro:

I would like to advertise the following position in TAMU:

Position: ASSISTANT IN RESEARCH

Requirements: B.S. or M.S. in chemistry, knowledge of electronics and computer programming desired.

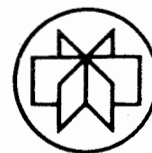
Duties: Engage in carbon-13 Fourier transform studies of biologically important compounds and further development of FT system; some service work necessary.

Salary: \$6800-8100

Starting date: August 15, 1972

Robert J. Cushley
Assistant Professor

PLEASE POST



DEPARTMENT OF CHEMISTRY

FACULTY OF NATURAL SCIENCES AND MATHEMATICS

June 29, 1972

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

Dear Barry:

For the past several months we have been occupied with perfecting a field-frequency control system for our Bruker 321s variable frequency pulsed spectrometer. To this end we have wedded (or at least forced to cohabit) our Varian HA-60 and Bruker spectrometers. The HA-60 lock signal is provided by a doped water sample in a "piggy-back" probe, aligned on the z-axis with the sample for pulsed nmr. In order to avoid field modulation for the lock signal, we have modified the 60 MHz rf unit of the HA-60 for time sharing modulation. Signal averaging for the pulsed nmr signals is effected by means of a PDP-8/I instrument computer. At present, the pulsed nmr and lock frequencies are not coherent, although we plan to modify this feature eventually. The stability, nevertheless, is satisfactory for our purposes: fluctuations over a 12 hour period are slow and less than about 2 mG.

I'll be happy to supply further details about the system, including appropriate schematics, to those interested.

We have been carrying out relaxation studies of various nuclear species using the above system: ^1H , ^7Li , ^{23}Na , ^{87}Rb , ^{11}B , ^{27}Al , ^{51}V , ^{55}Mn and ^{93}Nb . The alkali metal ion studies have been principally concerned with the binding of such ions to gramicidin A. A preliminary report of this work (carried out in collaboration with Dr. Charles Wenner, Roswell Park Memorial Institute) is being written up and preprints will be available for those interested.

I recall that various descriptions of solid state modifications of the Varian V2100/magnet power supplies have been given in TAMU/NMR over the last several years. Unfortunately, a number of my back issues have disappeared, so I can't find the appropriate letters. I'd appreciate very much receiving information from TAMU/NMR readers on such modifications: replacement of the 872A rectifiers and/or the 304TL's by solid state elements.

Sincerely,

Bob

Robert J. Kurland

SUGGESTED TITLE: Field-Frequency Control for Bruker 321s Spectrometer*; Request for Information

*Or: "An Experiment in Misalliance".

Yale University

SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT 06510

SECTION OF PHYSICAL SCIENCES

July 3, 1972

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

Dear Professor Shapiro:

Long-range ^{13}C - ^1H Spin-Spin Coupling Visualized by Pulsed
Double Resonance

In the course of our ^{13}C Fourier transform studies on aromatic and heterocyclic compounds we have become aware of some interesting long-range ring and side chain-ring ^{13}C - ^1H couplings. In order to better delineate these effects we have had cause to construct a Digital Gate Width Control unit for pulsed double resonance studies (1,2). Our needs were the usual - to observe small ^{13}C - ^1H splittings while cutting down scanning time by utilizing Overhauser enhanced signals due to pulsed double resonance effects.

The first figure entitled "Gated Proton Decoupling" gives the timing chart for gating the proton noise-decoupling frequency (IRRAD). The timing should be compared with that of Figure 2 in the paper describing our complete computer controlled FT system which appeared recently in Analytical Chemistry (3). Briefly, the leading edge of the receiver gating pulse triggers the Gate Width Control unit whose pulse length is selected by thumb wheels. The decoupling pulse is delayed for a period just greater than required to accumulate 8192 data points at rates (in the present instance) as low as 2.5 KHz.

Concomittant with the IRRAD pulse, the next rf pulse is delayed by a time greater than the IRRAD pulse length, using the program delay inherent in the routine NIN10 (3).

We have operated at duty cycles as low as 0.5 with model compounds and still find NOE's > 2 .

Yale University

SCHOOL OF MEDICINE

NEW HAVEN, CONNECTICUT 06510

SECTION OF PHYSICAL SCIENCES

The first pulsed double resonance ^{13}C -FT spectrum shown is that of 4-picoline(4-methylpyridine); resolution 1.25 Hz. The $\text{C}_{2,6}$ peaks on either side of the C_4 sextet show a unique coupling pattern demonstrated on the following spectrum depicting that region. The resolution was decreased to 0.31 Hz (8K data set; 2.5 KHz digitizing rate) and clearly shows the outermost lines as pentets while the innermost lines remain doublets. The C_3, C_5 peaks, not shown, resolve into 14 lines indicating a 4-bond coupling to the methyl protons. As well, the methyl resonance consists of broadened quartets of triplets, indicating a small (< 0.3 Hz) 4-bond coupling between the side-chain methyl carbon and the 2,6 - protons.

The next pulsed double resonance ^{13}C -FT spectrum (4-cyanopyridine) shows an altered $\text{C}_{3,5}$ region, illustrated in the following 0.3 resolution segment. The expected 8 line multiplet for each peak of the doublet is shown and reinforces the assignment for 4-picoline. The ^{13}C resonance for the cyano group, although broadened by the quadrupolar nitrogen, does show a triplet of triplets indicating side chain carbon to ring hydrogen coupling of 4-bonds.

These studies are continuing and will be communicated in full.

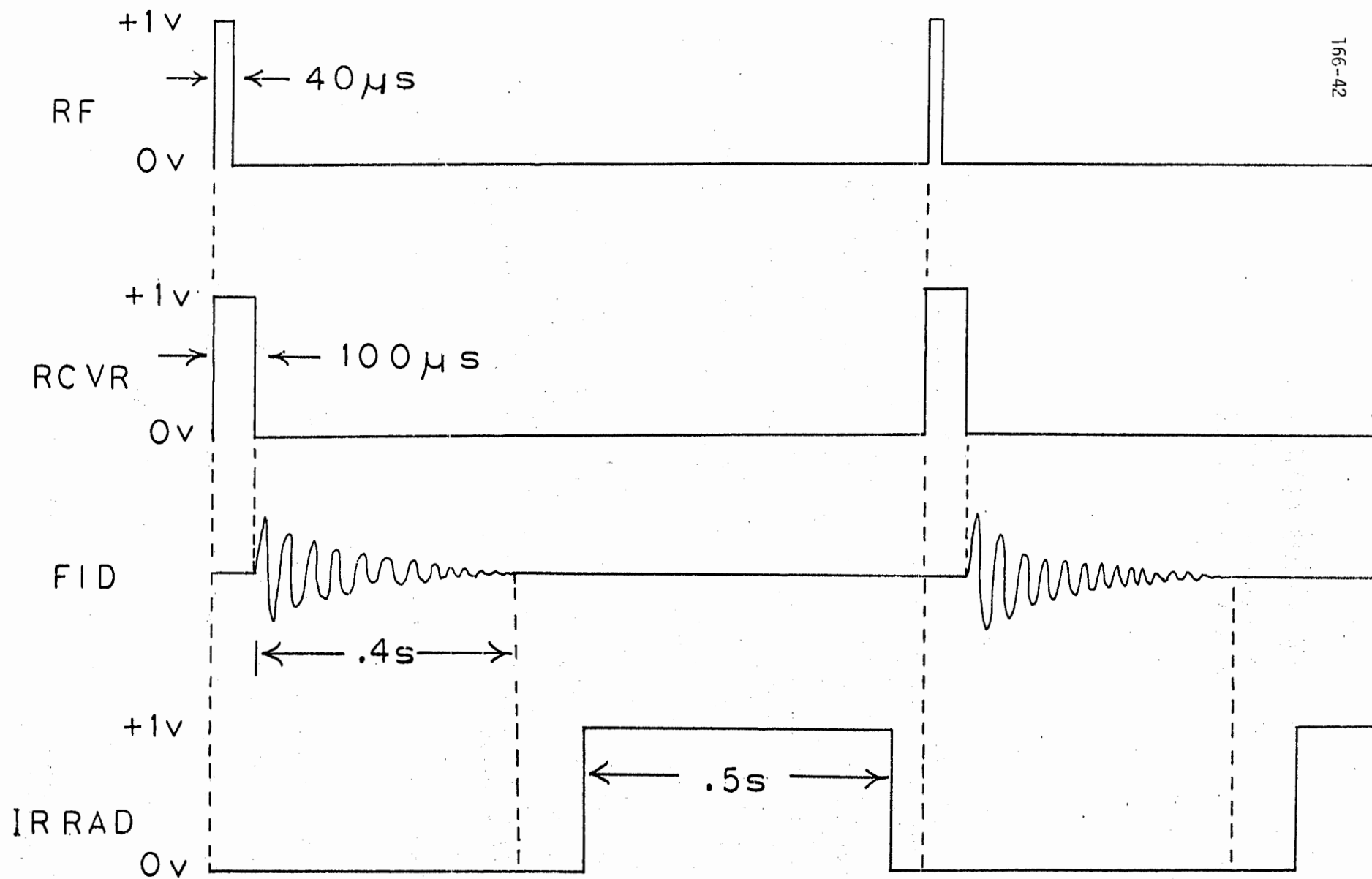
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3. R.J. Cushley, D.R. Anderson and S.R. Lipsky, Anal. Chem. 43, 1281 (1971)

Sincerely yours,

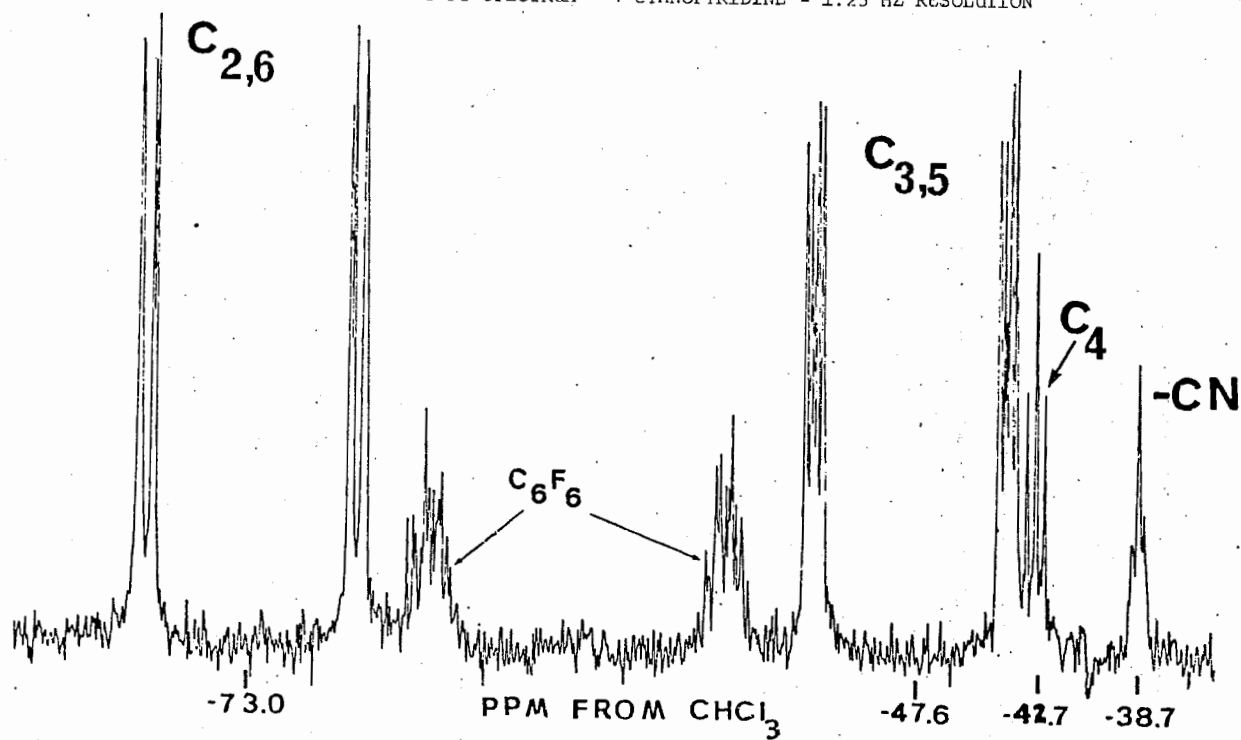
Robert J. Cushley
Robert J. Cushley
Assistant Professor

Carlos Ortiz
Carlos Ortiz

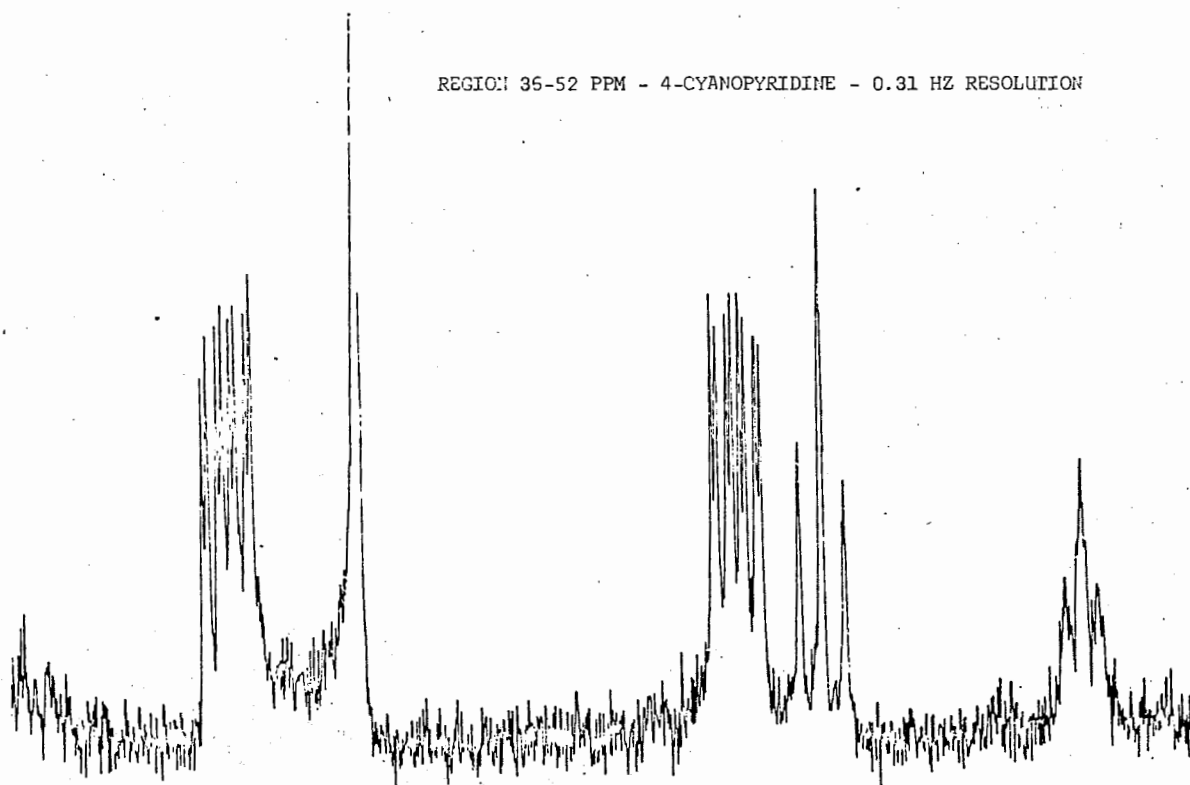


GATED PROTON DECOUPLING

¹³C-FT SPECTRUM - 4-CYANOPYRIDINE - 1.25 HZ RESOLUTION



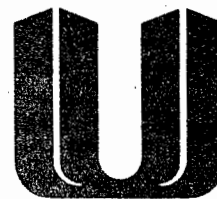
REGION: 35-52 PPM - 4-CYANOPYRIDINE - 0.31 HZ RESOLUTION



Unilever Research

Port Sunlight Laboratory
Unilever Limited
Port Sunlight
Wirral Cheshire L62 4XN

Telephone 051-645 2000
Telex 627235



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

30 MAY 72

Dear Professor Shapiro

As our latest contribution to TAMU NMR we have outlined some of the projects currently underway in the laboratory that utilise NMR.

Short titles:- NMR of liquid crystals, protein-surfactant interactions, and micellar solutions

Lyotropic Liquid Crystal Phases

Our research into water molecular motions of lyotropic l c phases has been continued with a study of the alkyl trimethylammonium bromide (CTAB)/water hexagonal phases. Deuterium and proton T_1 , T_2 and line width measurements have been made for C_8 , C_{12} and C_{16} TAB/water samples. The T_1 values indicate that water rotational motions are restricted far more in this system than in other l c phases that we have examined, although no formal hydrogen bonding between CTAB head groups and water molecules is possible. Also splittings of some of the deuterium and proton resonances are observed. The deuterium splittings are quadrupolar in origin while the frequency (field) independence of the proton splittings indicates a dipolar mechanism. Only C_8 TAB samples showed this dipolar coupling on the water (proton) resonance, and while most samples gave powder spectra a few well resolved doublets were obtained (Fig). Presumably these were the result of some macroscopic orientation of the sample. (G J T T).

Protein-Surfactant Interaction

High resolution NMR and spin labelling have been used to study the binding of a range of surfactants to proteins (Bovine Serum Albumin, B S A, a globular protein and gelatin, random coil). Surfactant NMR spectra are an average of 'free' and 'bound' molecules and indicate together with the ESR results, that surfactant molecules become tightly bound to the protein. Relaxation rates of protons adjacent to the surfactant head group are preferentially increased over those for the main alkyl chain protons suggesting restricted mobility of the head group. An anionic surfactant (SDS) was bound more strongly than a cationic surfactant (C_{12} TAB). It can be concluded that

surfactant head groups bind to oppositely charged ionic groups on the protein. Chemical shift measurements indicate that the surfactant head group was at the surface of the protein while the alkyl chains reside in a more hydrophobic environment. Lysolecithin appears to be exceptional in that while the head group is also bound to the protein surface by ionic or polar binding, the alkyl chains probably have markedly restricted motion.

The NMR spectra of proteins in the presence of surfactants exhibit a general broadening of resonances, SDS having the largest effect. No differential broadening of protein resonances was observed in the native protein, or in urea denatured protein. Thus no information about the identity of specific binding sites on the protein was obtained. (J O).

Micellar solutions

Earlier work on the binding of sodium ions to charged micelle surfaces is being followed by similar experiments using different counterions, such as lithium, caesium and rubidium. Preliminary results show that in contrast to the sodium ion, the hydration layer around the lithium ion is unchanged when adsorbed from the bulk solution to the charged micelle/water interface.

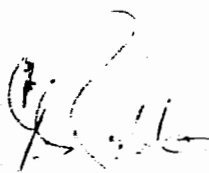
Presumably the stronger electrical field of the smaller lithium ion is sufficient to prevent distortion of its hydration layer.

The results of the experiments should be useful in explaining the difference in adsorption properties of various ions. (I D R).

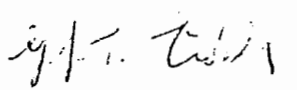
Yours sincerely



J Oakes

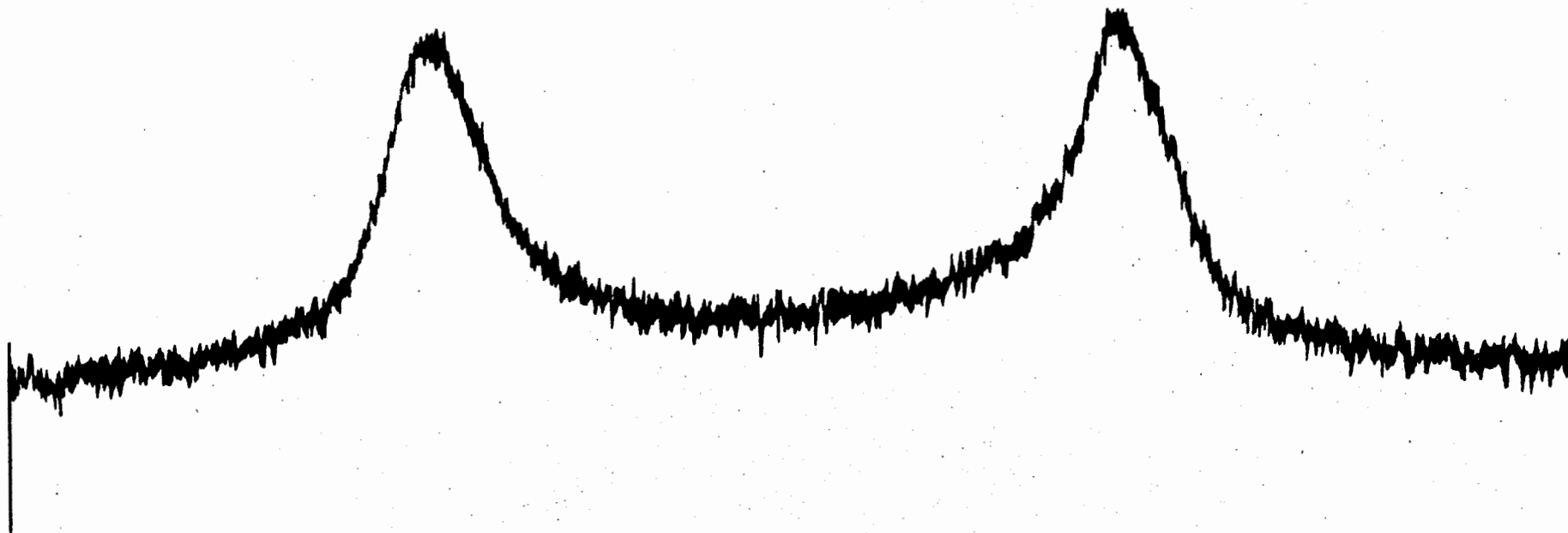


I D Robb



G J T Tiddy

C_8TAB/H_2O 298° 40 Mhz
MOL FRACTION $C_8TAB = 0.258$
← 80hz →



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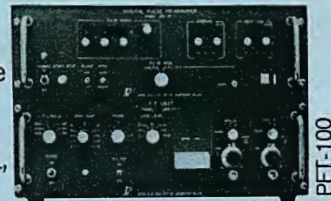
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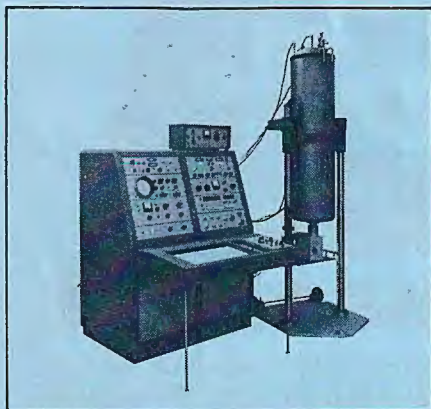
NMR Spectrometers/Mass Spectrometers/ESR Spectrometers/Laser Raman Spectrophotometers/Laboratory Computers/Scanning Electron Microscopes/Electron Microscopes/X-ray Diffractometers/Amino Acid Analyzers.

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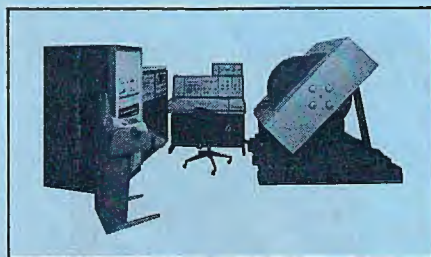
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These offer the highest performance in commercially available high resolution NMR spectrometers. The HR-220 (220 MHz) and HR-300 (300 MHz) spectrometers are engineered for use in those applications requiring the highest magnetic field strengths such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

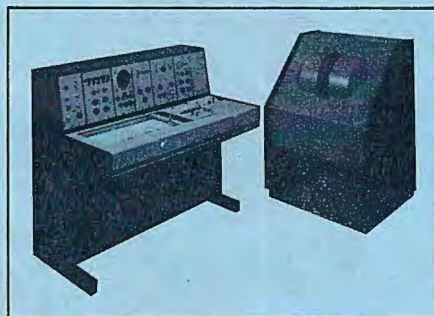
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Locking flexibility for homo- or heteronuclear internal lock on ^1H , ^{19}F , and ^2H , and external lock on ^1H and ^{19}F are provided. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are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

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System T-60



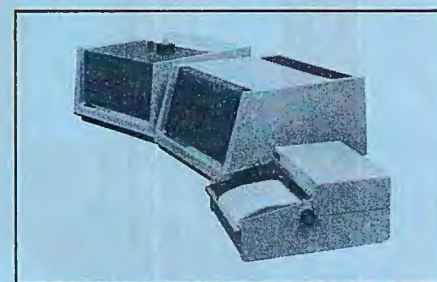
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