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Newsletter

No. **254**

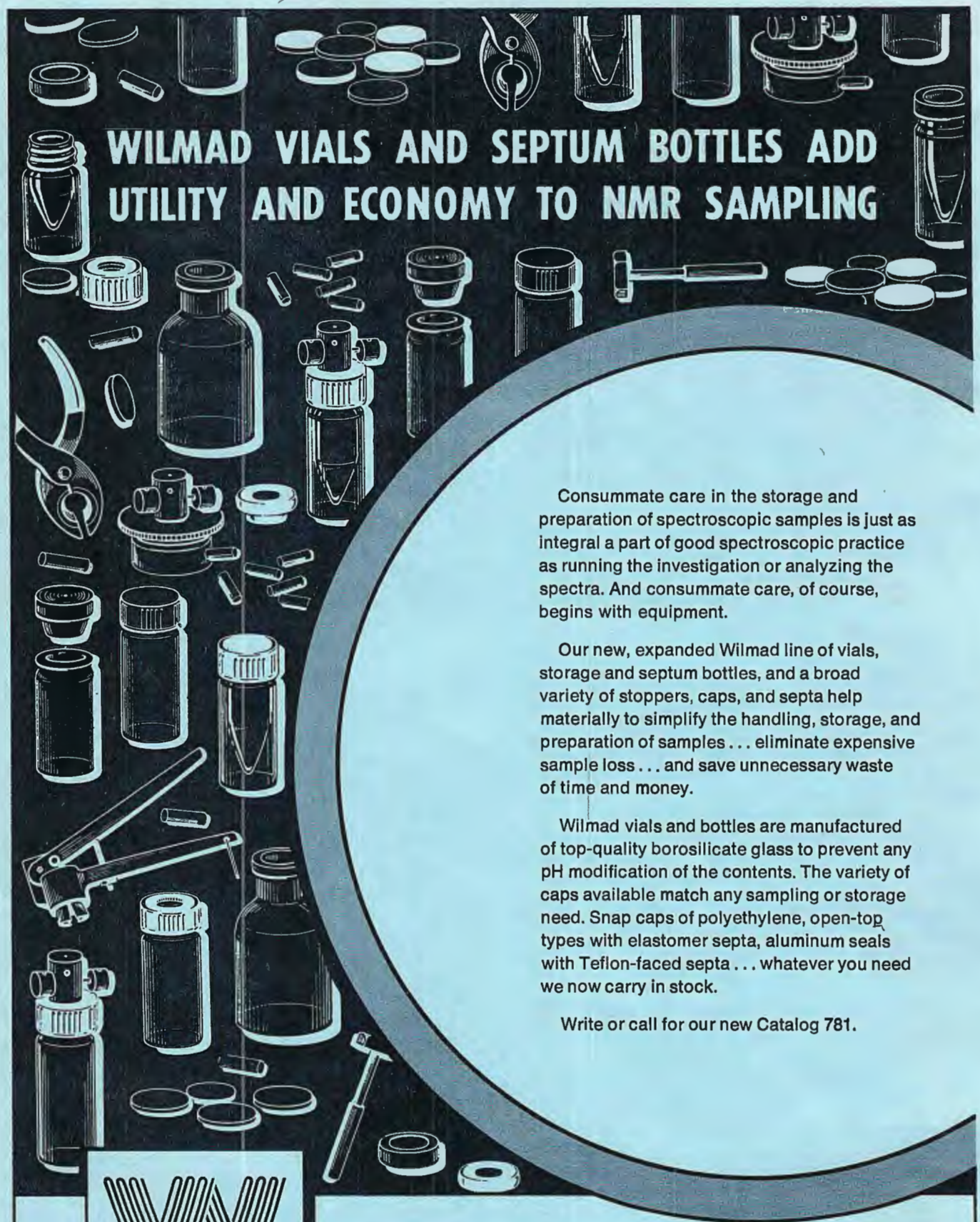
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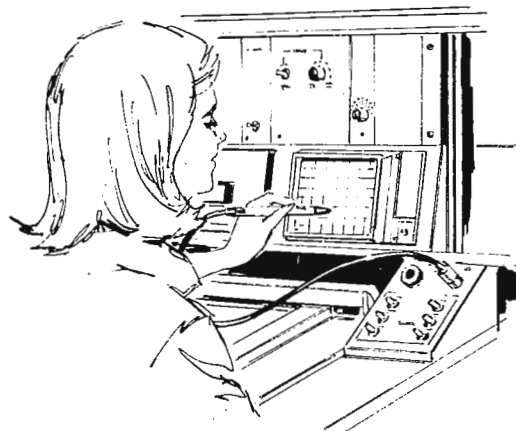
All Newsletter Correspondence, Etc., Should be Addressed To:

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

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

Dear Barry,

"Small is Beautiful"

Most high resolution NMR spectroscopists would like to have a knob on the machine which would boost resolution by a factor of three or four when necessary. Examples of methods for resolution enhancement by data manipulation of the detected signal are legion; we propose an alternative technique which operates on the signal before detection.

The basic idea is to use a very small sample. However, when one tries to do this by confining the sample inside a small container no real improvement is achieved because the interfaces introduce discontinuities in magnetic susceptibility which distort the field. So we use a standard 5 mm spinning cylindrical sample, but greatly reduce the effective sample size.

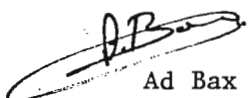

To do this we borrow the techniques of spin mapping, applying a strong field gradient (in the Z direction) and exciting with a selective pulse sequence (1). In this way only a flat disc-shaped volume is excited. The imposed gradient is then removed and the excited spins are allowed to precess freely in a homogeneous magnetic field, essentially unaffected by all natural Z gradients. In principle it should be possible to search for the best part of the field by varying the selective irradiation frequency, and to extend the idea to limit the extent of the sample in all three dimensions.

Experiments were carried out on a 300 MHz superconducting spectrometer in Delft (hence the choice of the Z axis for the imposed gradient, since this is the spinning axis). The spectrum of the low field ring proton of furan-2-aldehyde serves as an illustration (Figure 1), showing the improvement in resolution as stronger and stronger field gradients were used during excitation. The line widths decreased from about 0.6 Hz in trace (a) to 0.08 Hz in trace (d).

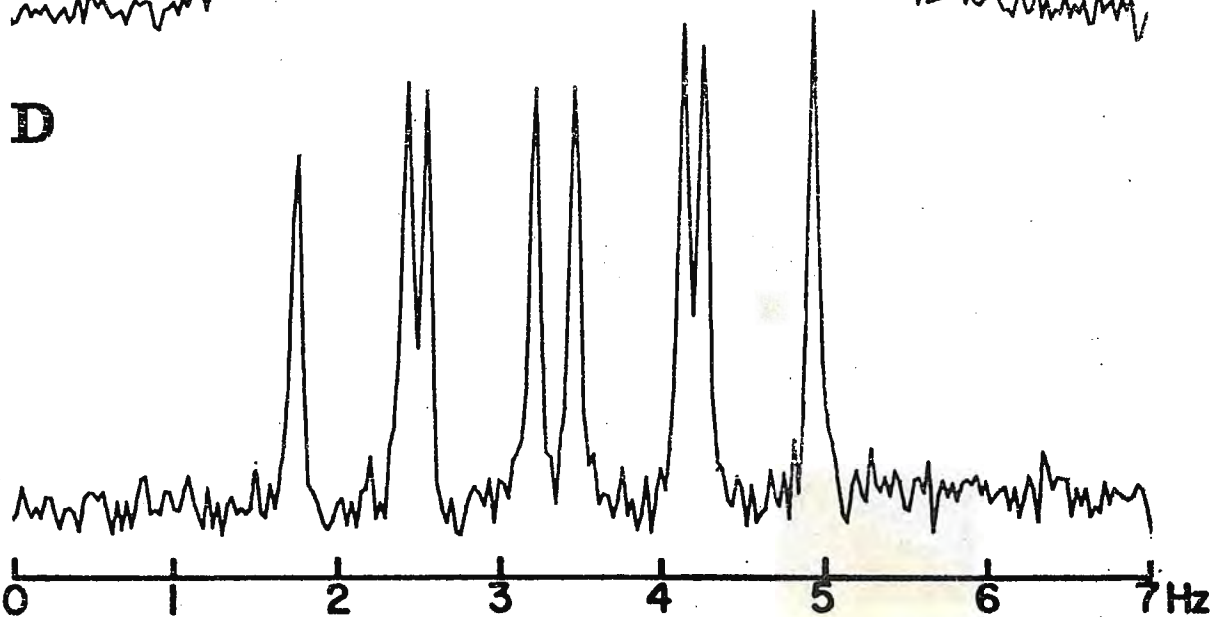
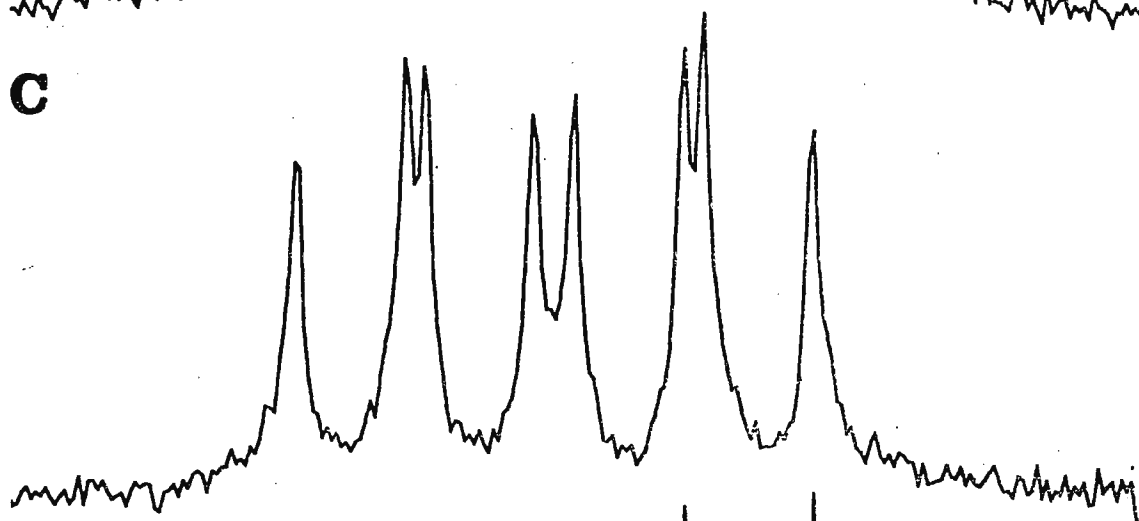
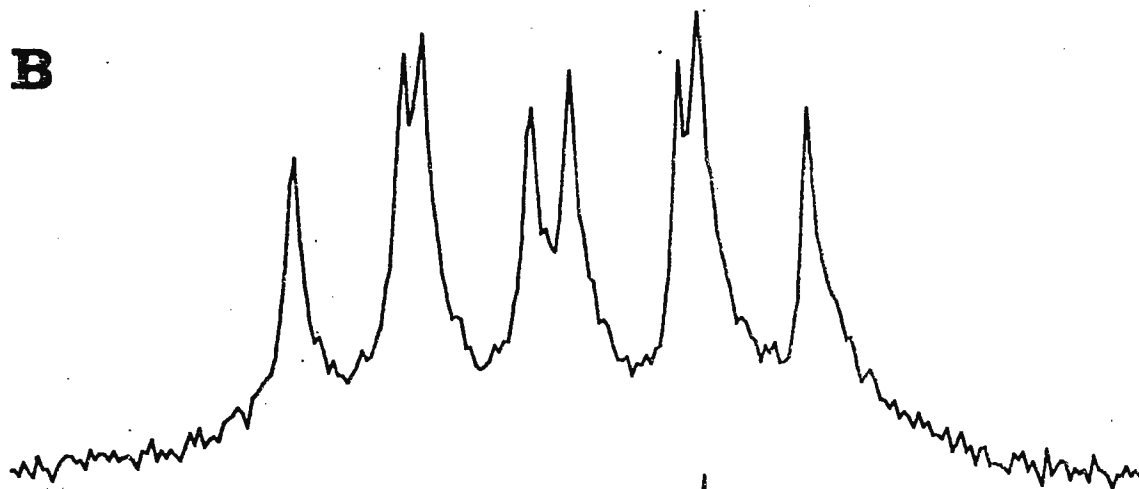
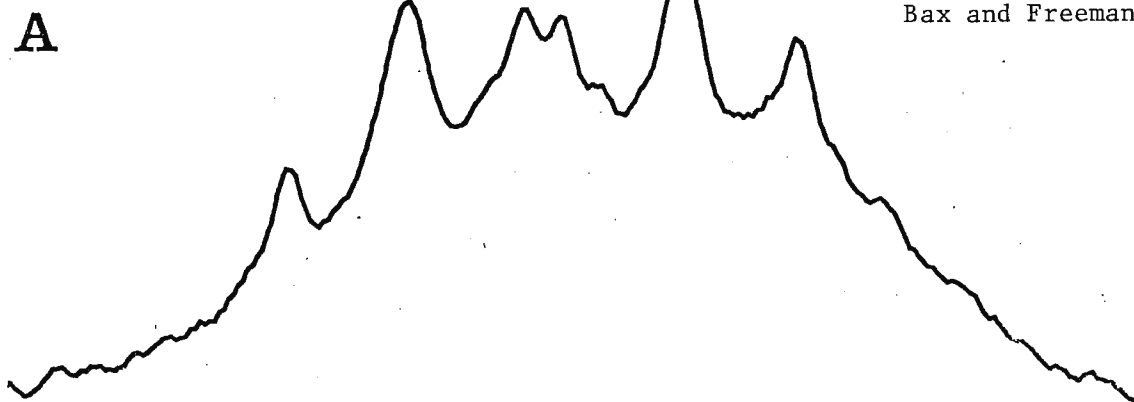
Several experiments which are affected by diffusion might also benefit from such a technique. The preparation pulse would select a restricted sample volume such that any subsequent diffusion would be across only very weak natural gradients; spin echo experiments and inversion-recovery spin-lattice relaxation experiments should then become less sensitive to diffusion.

The experiment is simple to implement. Perhaps we may indeed see a new knob on future spectrometers - it would be labelled RESOLVE (Resolution Enhancement by Selective Observation of Limited Volume Elements).

Yours sincerely,

 
Ad Bax and Ray Freeman

(1) G. Bodenhausen, R. Freeman and G.A. Morris, J. Magn. Reson. 23, 171 (1976); G.A. Morris and R. Freeman, J. Magn. Reson. 29, 433 (1978). The latter reference mentions this application to resolution enhancement.



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Professor B. L. Shapiro
Department of Chemistry
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College Station, Texas 77843

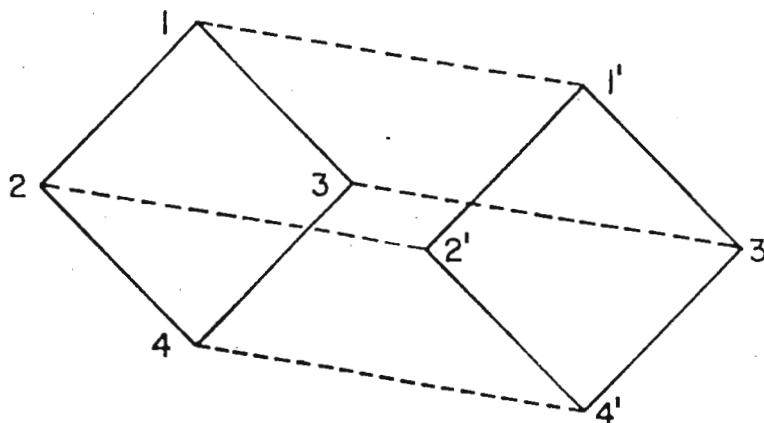
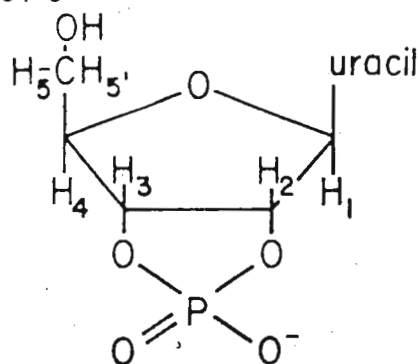
October 25th 1979

Elucidation of the Flip Angle Effect

Dear Dr Shapiro,

In the course of our enduring search for wrinkles in heteronuclear two-dimensional NMR spectroscopy¹, we were recently surprised to find that the spectra can be dependent on the flip angle of one of the pulses used to transfer the magnetization from protons to phosphorus. The experiment involved examining the two-dimensional spectra of 2'3'cyclic uridine monophosphate (2'3'cUMP). This is a rather complicated spin system, the 2' and 3' protons forming an ABX system with the phosphorus nucleus. In addition, both the 2' and 3' protons are coupled to their immediate neighbors in the ribose ring. This implies that all four phosphorus lines should be modulated by a total of sixteen frequencies - eight of which arise from the 2' proton and eight from the 3' proton. The experimental results we obtained in our first attempt did not agree with this analysis at all. In actual fact we observed, as can be seen in Fig.1, that each phosphorus transition was modulated by only eight proton frequencies. Thus, half of the signals expected in the proton dimension were missing. Closer inspection of the Figure shows that the proton frequencies are not the same for all four phosphorus transitions. All of the sixteen proton frequencies do in fact occur, but unlike our naive expectation only half of them are modulating any given phosphorus transition. These rather odd findings lead us to think about what we were actually doing.

In the two-dimensional experiment the first proton pulse tilts the proton magnetization into the x-y plane of the rotating frame. After the magnetizations have freely precessed for a while, the free precession is interrupted and the information is stored in the form of non-equilibrium populations by the application of a second proton pulse. The normal analysis assumes that only ideal 90° pulses are used throughout. The use of a second proton pulse with a smaller flip angle however tends to simplify the reshuffling of the populations. The information about the precession of, say, the (1,2) proton transition will be stored in the populations of the levels 1 and 2. Thus, the proton frequency (1,2) will only modulate the phosphorus transitions (1,1') and (2,2') as can be seen in the energy level diagram, which represents the ABX subunit consisting of the 2' and 3' protons and the phosphorus nucleus (the latter's transitions are indicated by dotted lines.)



A proton flip angle of 90° on the other hand reshuffles the populations in such a way that the modulation due to the (1, 2) proton transition is spread equally over the levels 1, 2, 3 and 4. Thus the proton frequency (1, 2) appears as a modulation in all four phosphorus transitions. If a proton flip angle of about 160° is applied, the proton frequency (1, 2) will appear in the modulation of the phosphorus transitions (3, 3') and (4, 4'), although these transitions do not share a common energy level with the proton transition responsible for the modulation.

Since the flip angle effect complicates the relationship between two-dimensional and conventional proton spectra², it is desirable to remove the flip angle effect. In principle one could use a 90° proton pulse, but the calibration is tedious and the smallest deviation from the ideal angle may severely distort the spectra. The method which we chose to apply was found to be virtually fool-proof. The recipe, based on a detailed population analysis, is to subtract the slice taken from the two-dimensional spectrum at the phosphorus transition (4, 4') from a similar slice at the (1, 1') transition. The resulting spectra are no longer dependent on the flip angle, as can be seen in Figure 3, and agree well with the theoretical spectrum derived from an earlier analysis of 2'3'cUMP³, calculated according to a method described elsewhere². As an added attraction, the signal-to-noise ratio of the difference is at least twice that of the slices themselves. The spectra obtained provide insight into the conformation of cellular phosphates, though the linear combinations described here should be of general utility in two-dimensional spectroscopy.

1. A. A. Maudsley and R. R. Ernst, Chem. Phys. Letters, 50, 368 (1977).

2. P. H. Bolton and G. Bodenhausen, J. Am. Chem. Soc., 101, 1080 (1979).

3. R. D. Lapper and I. C. P. Smith, J. Am. Chem. Soc., 95, 2880 (1973).

Philip Bolton

Department of Chemistry

Wesleyan University

Middletown

Connecticut 06457

Geoffrey Bodenhausen

Francis Bitter National Magnet Laboratory

Massachusetts Institute of Technology

170 Albany Street

Cambridge, MA 02139

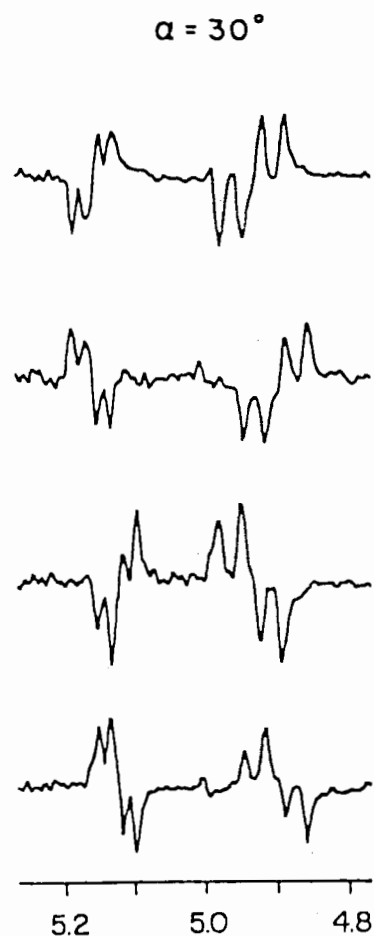


Figure 1

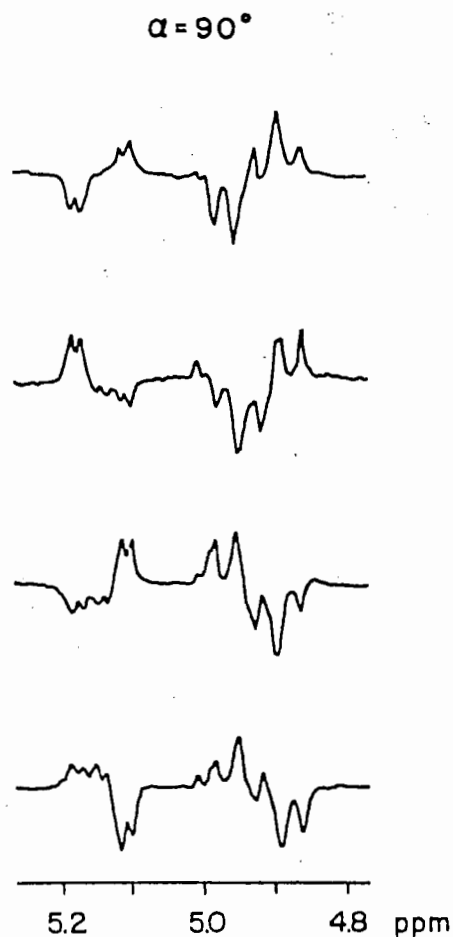


Figure 2

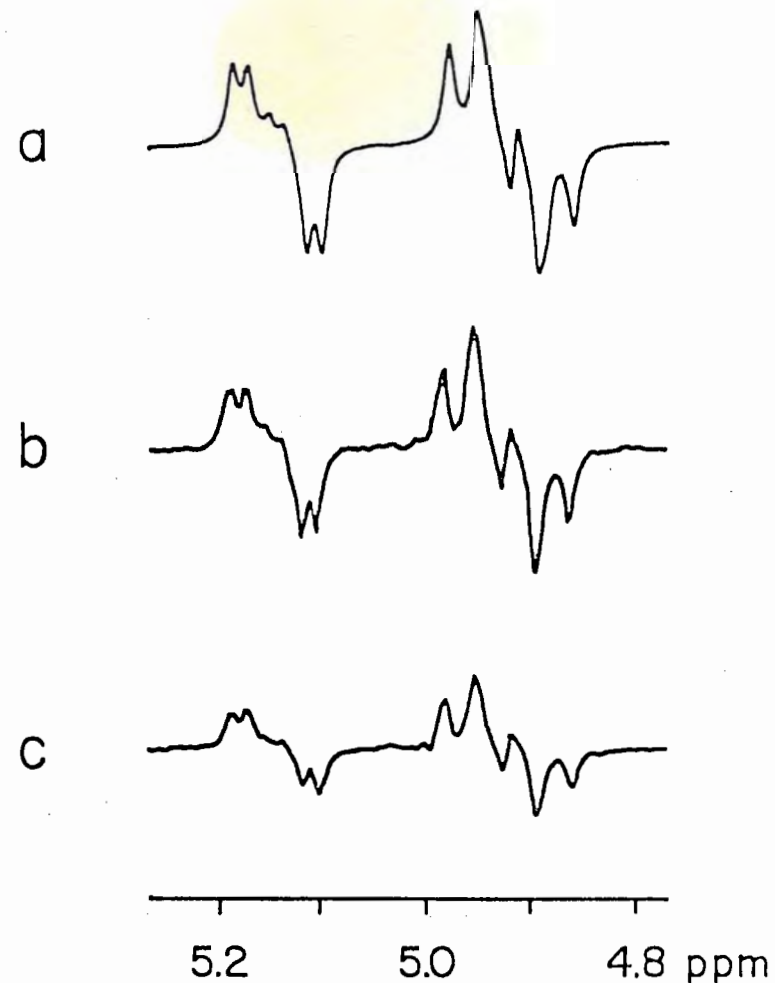


Figure 3

Fig. 1. Phase-sensitive two dimensional spectra of 2'3'cUMP, obtained with a proton flip angle set to 30° . Only eight proton frequencies are observed in these traces, which, stacked in the vertical dimension, correspond to the four phosphorus transitions.

Fig. 2. Two-dimensional spectra of 2'3'cUMP obtained with a proton flip angle of about 90° .

Fig. 3. (a) Theoretical spectrum calculated with coupling constants and chemical shifts given elsewhere³. (b) Spectrum obtained by subtracting the top trace of Fig. 2 from the bottom trace in the same Figure. (c) Spectrum resulting from the subtraction of the top and bottom traces in Fig. 1. The resulting multiplets are independent of the flip angle and can be analysed by iterative computer programs to extract the various coupling constants in the ribose ring system.



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September 11, 1979

(803) 777-7341

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

Re: TITLE - Boron Chemical Shift Calculations and a Update of the NSF
NMR Facility at the University of South Carolina.

Dear Barry:

As usual your color-coded reminder has arrived about 4 to 6 weeks too early. Therefore, in this contribution I will provide you with a progress report on the status of our nmr facility and a brief summary of our progress on Boron Chemical Shift Calculations.

At the present time our multinuclear WH-400 is in Billerica being fitted with its computer and some minor accessories. We expect installation to start in about two weeks. If no major disasters occur, we should be able to start operation in mid October. Hence, any potential users may write to me to obtain the necessary information and forms that will be required before we can obtain any data for them. When the spectrometer is completely functional, we will formally announce to the nmr community as a whole that we are operational.

Over the past several years we have been interested in the magnetic resonance parameters of boron containing compounds. An obvious aspect of this research is to be able to predict boron chemical shifts from relatively simple molecular orbital calculations. This work has been carried out in collaboration with Professor Paul Dobosh at Mount Holyoke College and a graduate student at the University of South Carolina, Yu Chung Chou. A representative selection of our results is summarized in Table I. Space limitations do not allow a detailed description of how these results were obtained. Briefly, the wave functions were obtained from a perturbed SCF calculation done at the INDO level of approximation. However, all of the integrals involved in the evaluation of the shielding tensor were calculated exactly. This was accomplished by expending the necessary integrals as a sum of gaussians. The level of agreement between the predicted chemical shifts and the experimental data is very good. Those readers who are interested in the details can write me for a preprint of the paper we are currently preparing for publication.

Warmest Regards,

Paul D. Ellis
Professor of Chemistry and
Facility Director

PDE:lep

Table I

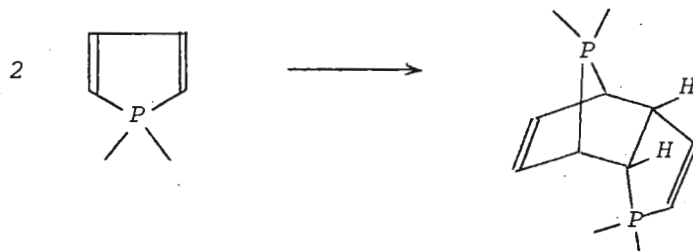
Calculated and Experimental Chemical Shifts for Some Representative Boron Containing Compounds^a

Compound	σ_A^{AA}	σ_A^{CC}	σ_A^{AC}	σ_A^{CD}	σ_A^a	ρ_A^e	$\delta_A(\text{calc})$	$\delta_A(\text{exp})^d$	$\delta_A(\text{exp}) - \delta_A(\text{calc})$
1. $\text{B}_5\text{H}_{11}(\text{B}_1)^e$	30.55	4.86	25.81	29.17	90.39	3.1236	-81.03	-72.8	8.2
2.* $\text{B}_5\text{H}_9(\text{B}_1)^e$	17.70	4.44	17.66	43.68	74.49	3.1494	-65.13	-70.2	-5.2
3.* $\text{B}_4\text{H}_{10}(\text{B}_1)^e$	9.10	3.74	26.63	22.57	62.04	3.0335	-52.68	-59.3	-6.6
4. $\text{B}_{10}\text{H}_{14}(\text{B}_2)^f$	19.54	6.19	16.85	35.31	77.89	3.0133	-68.53	-53.3	15.2
5.* $\text{B}_5\text{H}_9(\text{B}_2)^e$	-2.70	4.22	23.85	23.36	48.45	2.9737	-39.09	-30.6	8.5
6.* $\text{B}_4\text{H}_{10}(\text{B}_2)^e$	-4.42	3.38	29.18	14.16	42.31	3.0132	-32.95	-24.4	8.6
7. $\text{B}_5\text{H}_{11}(\text{B}_3)^e$	-10.32	3.43	26.68	13.13	32.92	3.0594	-23.56	-17.0	6.6
8. $\text{B}_{10}\text{H}_{14}(\text{B}_5)^f$	-4.96	4.73	18.05	25.36	43.19	2.9786	-33.83	-16.8	17.0
9. $\text{B}_5\text{H}_{11}(\text{B}_2)^e$	-11.61	4.73	20.33	20.45	33.90	2.9539	-24.54	-10.0	14.5
10. $\text{B}_{10}\text{H}_{14}(\text{B}_6)^f$	-15.57	4.24	19.15	21.52	29.34	2.9325	-19.98	-7.8	12.18
11. $\text{B}_{10}\text{H}_{14}(\text{B})^f$	-10.23	5.99	9.19	33.15	38.10	2.9390	-28.74	-6.2	22.54
12.* B_2H_6^g	-25.40	2.82	26.43	5.51	9.36	3.0329	0.00	0.0	----
13. $\text{B}(\text{C}_2\text{H}_5)_3^h$	-36.66	-2.96	5.24	1.97	-32.40	2.9439	41.76	37.7	-4.1
14. $(\text{CH}_3)_2\text{BC}_3\text{H}_3^h$	-57.84	1.99	0.69	6.06	-49.10	2.8900	58.46	53.5	-5.0
15. $\text{B}(\text{CH}_3)_3^h$	-69.25	-0.46	-1.44	10.88	-60.26	2.8650	69.62	68.5	-1.1

TERVALENT PHOSPHOLE DIMERIZATION AROUND A MOLYBDENUM CARBONYL MOIETY

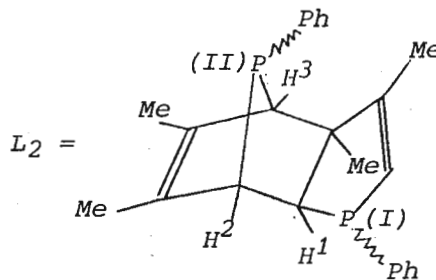
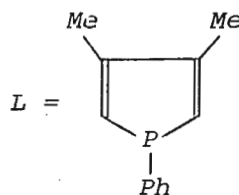
Dear Barry,

Many P(IV) derivatives of simple phospholes are known to undergo a spontaneous Diels-Alder dimerization which gives only one isomer. In one case a X-ray analysis has shown that the rings were fused with the endo relation (1).



On the contrary trivalent phospholes are normally stable toward thermal or photochemical dimerization. In only one instance a photochemical "2+2" dimerization was described with 1,2,5-triphenylphosphole (2) which is now known to be not fully representative of its class.

When irradiating 1-phenyl-3,4-dimethylphosphole/L with molybdenum hexacarbonyl we obtained as the main product a complex with the $L_2Mo(CO)_4$ stoichiometry. However the 1H and ^{31}P NMR spectra of this compound showed quite clearly that it was a complex of the phosphole dimer.

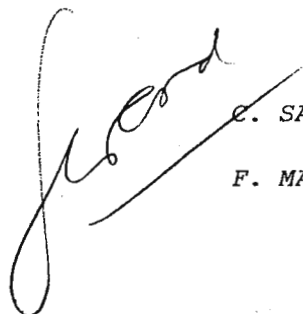


Only the exo structure is compatible with the chelation of molybdenum by this new dimeric ligand. Upon sulfuration the complex yielded the exo dimeric sulfide which was compared with the normal endo dimeric sulfide (obtained by $P=O \rightarrow P=S$ conversion from the corresponding oxide). A full $^1H \{^{31}P\}$ analysis has been performed on these dimers. The data are given hereafter.

	CH ₃		H ¹	H ²	H ³	CH=
L ₂ Mo(CO) ₄	2.0	1.55	2.64	3.01	2.68	6.23
	1.51	1.20	² J(H-P)41.4	² J(H-P)2.2	² J(H-P)5.83	² J(H-P)34.3
			³ J(H-P)6.35	J(H ¹ -H ²)3.19	J(H ³ -H ²)1.90	
(LS) ₂ <u>exo</u>	2.30	1.53	3.70	3.04	2.19-2.04	5.90
	1.47	1.26	² J(H-P)6.94	² J(H-P)2.8	-	² J(H-P)25.3
			³ J(H-P)4.17	J(H ² -H ¹)1.94	-	
(LS) ₂ <u>endo</u>	2.0	1.93	3.71	3.53	3.01	5.76
	1.79	1.45	² J(H-P)4.65	² J(H-P)5.28	² J(H-P)4.5	² J(H-P)26.8
			³ J(H-P)2.37	³ J(H-P)2.43	J(H ³ -H ²)2.08	⁵ J(H-P)5.5
				J(H ² -H ¹)2.57		

Important differences are observed between the endo and exo sulfides but it is difficult to correlate them with the proposed structures. Particularly noteworthy are the 5-bond coupling of the ethylenic proton with P(II) in the endo sulfide and the extraordinary large coupling of H¹ with P(I) in the L₂Mo(CO)₄ complex. A X-ray study of this complex is presently carried out

Best
regards



C. SANTINI,

F. MATHEY,

R. MANKOWSKI-FAVELIER,

G. MAVEL,

- (1) Y.H. Chiu and W.N. Lipscomb, J. Am. Chem. Soc., 91, 4150 (1969)
 (2) T.J. Barton and A.J. Nelson, Tetrahedron Letters, 5037 (1969).

Prof. B. S h a p i r o
Department of Chemistry
Texas A and M University
College Station Texas 77843
USA

Dear Barry,

Solvent effects on the structure of oriented molecules

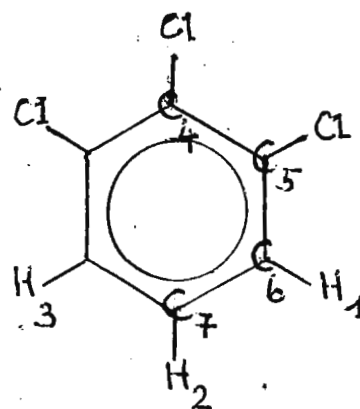
Some time ago we have demonstrated ¹ that the apparently variable distance ratios in the molecule benzene may be attributed to correlation-solvent-effects, i.e. the internuclear distances and angles vary slightly with the angle between the internuclear axes and the liquid crystal axis. The observed effects are in the range of + 0.35 to - 0.52% in the distance ratios.

We have now studied the corresponding effects in the molecule 1,2,3-trichlorobenzene. Unfortunately, in this case, the problem is more complex. Any variation of structure with solvents may be a true structure change, e.g. with corresponding change in the electric dipole moment. In other words we detect effects, but they may be superpositions of correlation and permanent change of structure.

In the Table I present some selected results which demonstrate that in 1,2,3-trichlorobenzene the solvent effects are roughly 3 times larger than in benzene.

Table: Selected solvent effects on distance ratios in the molecule 1,2,3-trichlorobenzene. Changes in % from the solvent Merck ZLI 1167 to Merck Phase IV.

$r(i,j)/r(6,7)$	change in %
$r(1,3)$	$+ 0,66 \pm 0,03$
$r(1,6)$	$+ 0,69 \pm 0,04$
$r(1,7)$	$+ 0,61 \pm 0,04$
$r(2,4)$	$- 0,98 \pm 0,09$
$r(2,5)$	$- 0,87 \pm 0,10$
$r(2,6)$	$- 0,46 \pm 0,09$
$r(3,6)$	$+ 0,62 \pm 0,02$
$r(5,6)$	$- 1,56 \pm 0,12$



We have a certain indication that most effects are true changes in structure. The final geometries, after vibration corrections are additive, whereas large correlation effects should introduce non-additivities.

At any rate the measurements show that solvent effects on the structure of oriented molecules may introduce uncertainties of the data in the range of approximately ± 1 to 2 %.

Sincerely yours

Peter

Peter Diehl

¹P. Diehl, H. Bösigler and H. Zimmermann
J.Magn.Reson. 33, 113 (1979)

GRUPPO LEPETIT ^{spa}*Lepetit*

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20158 Milano, Italy

20124 Milano . Via R. Lepetit, 8
telefoni 27771. interurb.: 279735.6.7
telegrammi: Lepetit . Milano
telex: 32054 Lepetit . Milano
conto corrente postale N. 00589200
casella postale 3698 . 20100 Milano

destinatario:

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

REGISTEREDSPECIAL DELIVERY

nostro riferimento: Dept. of Physical Chemistry data: Milano, October 5, 1979

Title : NMR SPECTRAL DATA OF D-GLUCURONIC ACID

Dear Professor Shapiro,

during our studies in the field of drug metabolism, we often encountered β -D glucuronides as conjugates of drugs or of their metabolites, isolated from biological fluids.

As both the ^1H and ^{13}C NMR lines of β -D glucuronic acid frequently overlap some of those of the metabolite(s) and, to our knowledge, no data on the free acid have been reported, we thought it useful to report the ^1H and ^{13}C NMR data of D-glucuronic acid (1). Since I shows mutarotation, we have studied the 1/1 mixture of the α and β anomers in $\text{Me}_2\text{SO}-d_6$ after equilibration and D_2O exchange.

The ^1H NMR shifts at 270 MHz and the ^{13}C NMR shifts at 67.88 MHz are reported in Table. The assignments were made by $^1\text{H}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ decouplings, starting from the signals at δ 4.95 and 4.35, assigned to H-1 α and H-1 β , respectively. The ^1H NMR shifts well compare with those reported for sodium D-glucuronate (1). Our data show that, as observed e.g. for glucose (2), in the transformation $\beta \rightarrow \alpha$, all the carbons, except C-4, experience a shielding increase, whereas the appended protons, except H-4, become less shielded.

The inversion of configuration at the anomeric center has been reported to introduce a delocalized and concerted polarization of the

LEPETTI

foglio numero

C-H bonds in the molecule (3), but this phenomenon still deserves a theoretical consideration.

Yours sincerely,

Edoardo Martinelli
Edoardo Martinelli

Ambrogio Ripamonti
Ambrogio Ripamonti

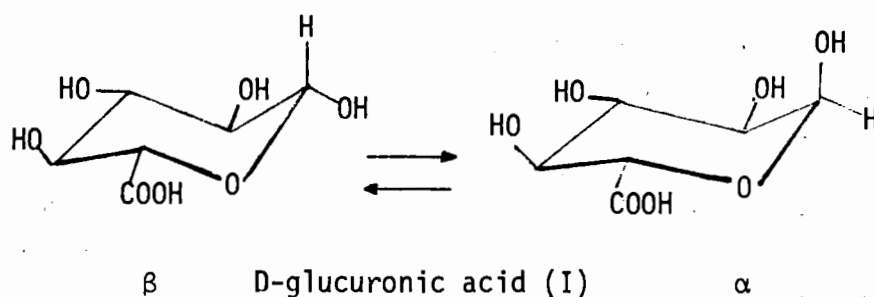


Table - ^1H and ^{13}C NMR chemical shifts of I in $\text{Me}_2\text{SO}-d_6$ (conc. 1.5 M)

	1		2		3		4		5		6	
	α	β	α	β	α	β	α	β	α	β	α	β
^1H	4.95	4.35	3.18	2.93	3.42	3.15	3.29	3.32	3.98	3.58	-	-
$\Delta\delta(\beta-\alpha)$	-0.60		-0.25		-0.27		+0.03		-0.40		-	
^{13}C	93.1	97.7	72.3	75.0	73.1	76.5	71.9	72.3	71.7	76.0	170.5	171.4
$\Delta\delta(\beta-\alpha)$	4.6		2.7		3.4		0.4		4.3		0.9	

References

- 1) F. Heatley, J.E. Scott and B. Casu, Carbohydr. Res., **72**, 13 (1979).
- 2) H.J. Koch and A.S. Perlin, Carbohydr. Res., **15**, 403 (1970).
- 3) A.S. Perlin, B. Casu and H.J. Koch, Canad. J. Chem., **48**, 2596 (1970).

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

14 September 1979

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

Dear Barry

SILICON-29 NMR

Thank you for your successive green and orange letters. Life seems to contain decreasing amounts of time per month available for a suitable response. However, I append a few comments on some of our silicon-29 work, which continues to occupy our time and interest.

Recently we have been endeavouring to ascertain the effects of ring-contraction on ^{29}Si chemical shifts. For the series D_n where D is the dimethylsiloxy unit, $-\text{Si}(\text{Me}_2)\text{O}-$, the shifts from TMS are well known¹ for $n=3$ to $n=6$ and are as follows (in ppm):

D_3 -9.2; D_4 -20.0; D_5 -22.8; D_6 -23.0.

There are variations due to experimenter and solution, and we have reported²:

D_4 at -19.71, D_5 at -22.05 and D_6 at -22.67 ppm.

However, the D_6 signal is definitely to low frequency of the resonance due to D units in long linear polymers ($\delta_{\text{Si}} \approx -22.3$, ref. 2), so a reversal of the shift direction with increasing ring-size must occur, and we set out to find where in the series this happened. Dr J A Semlyen of the University of York has kindly supplied us with mixtures of cyclic oligomers. The figure shows one of the spectra, indicating the remarkable dispersion achieved, and results (from a different sample, with D_4 at -19.64 ppm) are as follows:

D_7 -22.93; D_8 -22.98; D_9 -22.88; D_{10} -22.77;
 D_{11} -22.64; D_{12} -22.54; D_{13} -22.43; D_{14} -22.37.

Peaks due to D_{15} and larger species are unresolved at -22.32 ppm. Large rings and long linear polymers give superimposed resonances when in the same solution in the absence of oligomers.

The results show that ^{29}Si NMR is a valuable tool for discriminating between small rings, and quantitative intensity measurements are feasible. The shift effects are undoubtedly due, at least in part, to conformation restrictions as the ring contracts, and it is probably no coincidence that the shift changes tail off as an all-trans ring becomes possible (estimated³ to be at $n \approx 13$). Reduction in the occurrence of trans conformations would seem to give low frequency shifts, D_8 having the highest shielding. The high frequency shifts for the smaller rings presumably arise from restrictions in g_+g_- conformations and/or angle-strain at Si or O.

I hope this letter keeps us "solvent" for TAMU NMR.

With best wishes

Yours sincerely

Robin

R K Harris

D J Burton

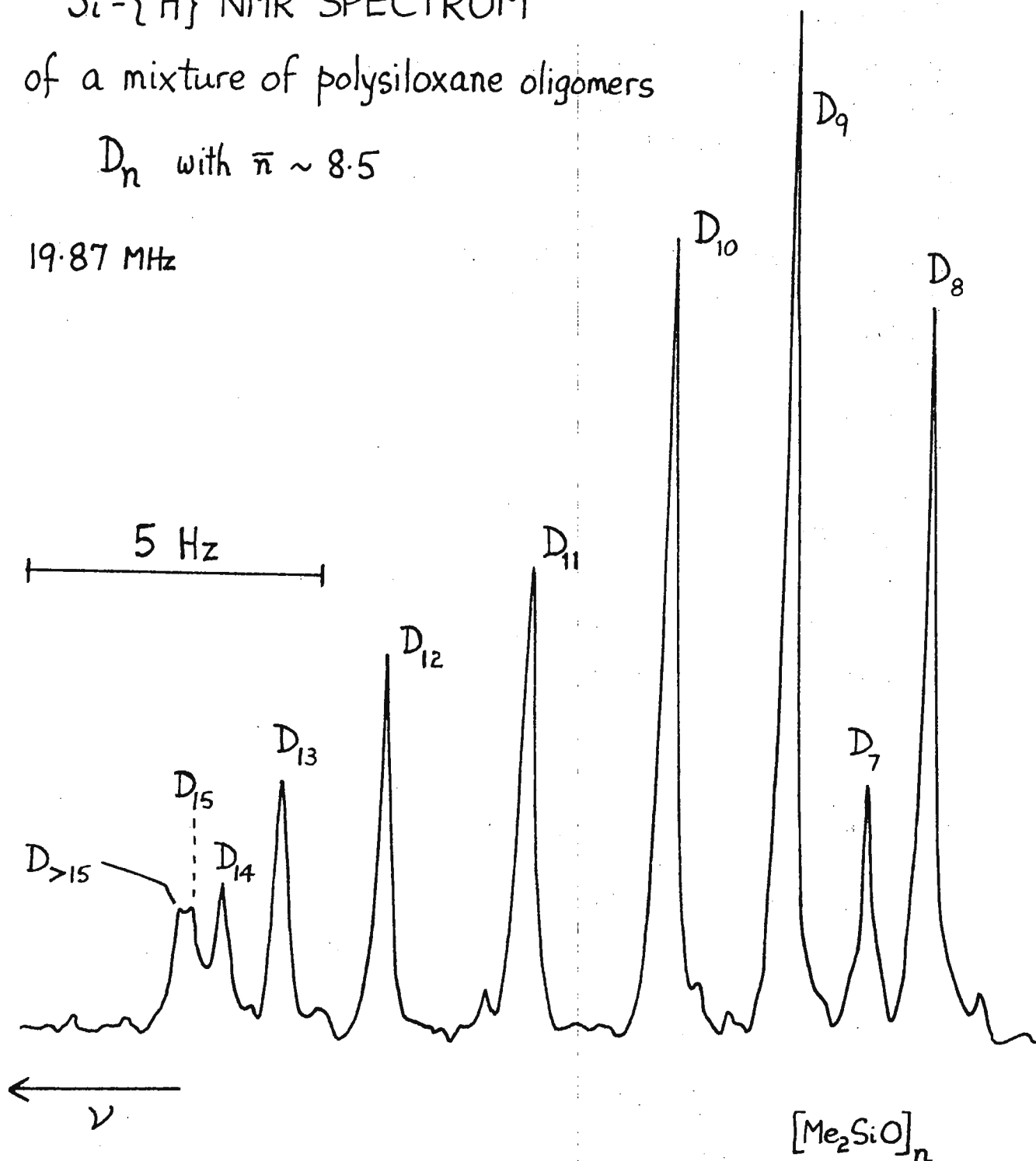
D J Burton

- 1 G Engelhardt, M Mägi and E Lippmaa, J. Organometal Chem. 54, 115 (1973)
- 2 R K Harris and M L Robins, Polymer 19, 1123 (1978)
- 3 L E Scales and J A Semlyen, Polymer 17, 601 (1976)

$^{29}\text{Si} - \{^1\text{H}\}$ NMR SPECTRUM
of a mixture of polysiloxane oligomers

D_n with $\bar{n} \sim 8.5$

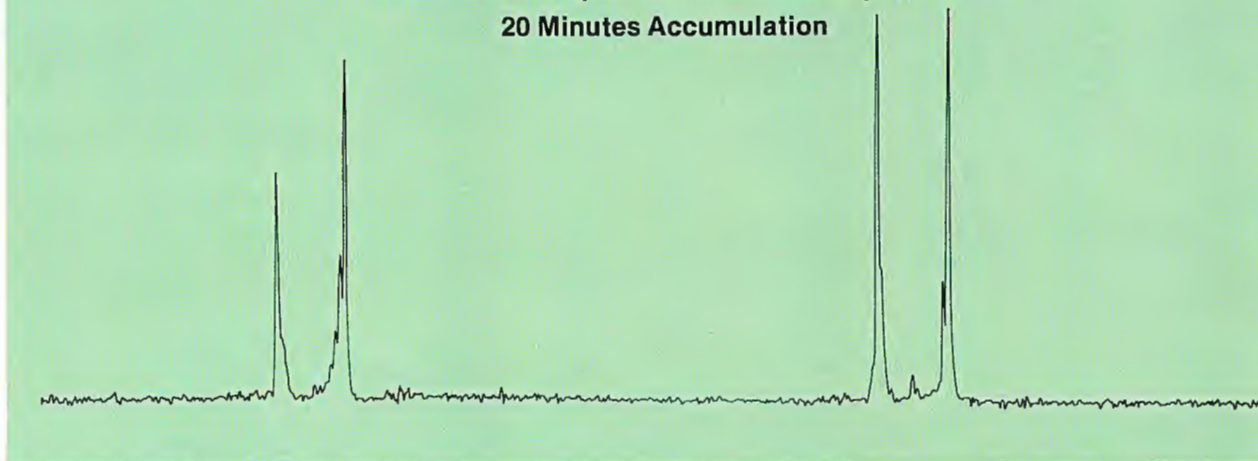
19.87 MHz



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...you just don't have an XL-200!

50-MHz NMR Spectrum of Cured Neoprene
20 Minutes Accumulation



¹³C spectrum of cured neoprene with carbon black* in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the fine structure. The width of the plot is 10 KHz. *Sample courtesy of E. I. Du Pont de Nemours and Company

With the new ¹³C solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 superconducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; generate your own convenient macro-commands;

create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband accessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including ¹³C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.



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**Pharmaceutical Products Division**

Abbott Laboratories
North Chicago, Illinois 60064

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, TX 77840

Dear Professor Shapiro,

Imidazo-thiazole Substitution Assignments
Based on ^{13}C NMR Chemical Shifts

Recently three imidazo-thiazole compounds (3, 4 and 5) were submitted to the NMR laboratory for structural assignment with emphasis on their substitution pattern.

The ^1H NMR of 3 and 4, in addition to two methylene multiplets, showed methyl and carboethoxy resonances. Noise decoupled and coupled ^{13}C NMR spectra were obtained and positional isomers were assigned. A summary of the ^{13}C NMR chemical shifts is given in Table I.

The resonances in the low 160 ppm range are clearly due to the carbonyl of the carboethoxy in 3, 4 and 5. The resonances in the 148.2 to 153.1 ppm range are due to C-8 based on model compound 1. Specific assignments for C-5 and C-6 in 1 can be made by comparison with 2, cognizant of the approximately 13 ppm downfield shift caused by phenyl substitution. Using approximate substituent effects of +10 ppm for CH_3 and +2 for COEt, one can use compound 1 to calculate the two positional isomers:

	3			4	
	Calc.	Obs.		Calc.	Obs.
C-5	127	133 (CH_3)	C-5	119	119 (COEt)
C-6	136	135 (COEt)	C-6	144	152 (CH_3)

The coupled spectrum of 3 and 4 assigned the carbon bearing the methyl group by its characteristic quartet multiplicity ($2J = 6.8$ Hz). Inspection of the calculated versus observed chemical shifts reveals that 3 is the 5-methyl and 4 is the 6-methyl analog.

In compound 5 the coupled spectrum clearly assigned C-8 to the resonance at 150.1 ppm since it is a triplet, the result of two identical couplings ($^3J = 7.5$ Hz). The resonance at 127.6 ppm is clearly a quartet in the coupled spectrum ($^2J = 6.8$ Hz), therefore it must be C-3. The resonance at 109.6 ppm shows a large coupling and a smaller long range coupling with a methyl. Therefore, this resonance has to be C-2. Using approximate substitution effects for a COEt group and compound 1 as a model the singlet resonance at 138.9 ppm can be assigned to C-6 and the doublet resonance at 115.5 ppm to C-5, thereby establishing the compound as 6-COEt substituted.

a

Quite recently 6 and 7 were submitted for identification. A comparison with the other model compounds in Table I clearly establishes 6 as the 6-COEt isomer and 7 as the 5-COEt isomer.

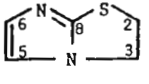
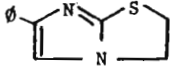
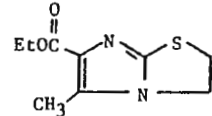
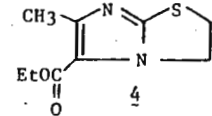
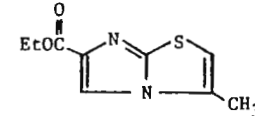
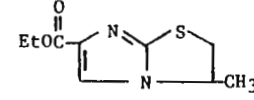
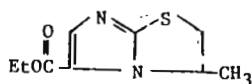
All other resonances in each compound were easily assigned by comparison with other model compounds.

It is interesting to note that in the case of 5 only one isomer was obtained.

Sincerely,

Ruth S. Stanaszek David L. Arendsen Robert W. DeNet
Ruth S. Stanaszek, David L. Arendsen, Robert DeNet

Table I
CMR Chemical Shifts

							
Assignment	1	2	3	4	5	6	7
O C	-----	-----	s 163.3	s 160.3	s 162.8	s 162.3	s 159.4
C-8	s 149.8*	s 150.1	s 148.2	s 153.1	s 150.1	s 150.2	s 154.1
C-5	d 116.7	d 112.4	s 133.1**	s 119.1	d 115.5	d 121.5	s 122.1
C-3	t 46.0	t 46.1	t 44.2	s 47.7	s 127.6**	d 54.3	d 54.9
C-6	d 134.0	s 147.2	s 134.8	s 152.9**	s 138.9	s 138.3	d 141.7
C-2	t 34.8	t 34.5	t 34.5	t 34.8	d 109.6	t 41.9	t 42.3
OCH ₂ (Et)	-----	-----	t 60.1	t 60.2	t 60.8	t 60.3	t 60.5
CH ₃ (Et)	-----	-----	q 14.5	q 14.4	q 14.4	q 14.4	q 14.4
CH ₃	-----	-----	q 10.9	q 15.8	q 13.2	q 19.2	q 18.3

*ORSFD experiment.

**Quartet in coupled spectrum (2J = 6.8 Hz).

Note: All chemical shifts values were measured from internal TMS in CDCl₃.

STANFORD UNIVERSITY

STANFORD, CALIFORNIA 94305

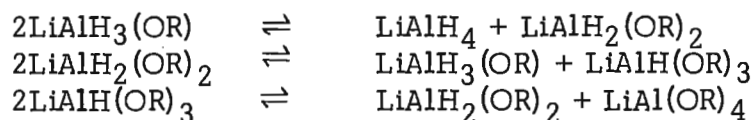
DEPARTMENT OF CHEMISTRY

September 4, 1979

Disproportionation of 1,2-diphenyl-3-methyl-4-dimethylamino-2-butanol Shown by ^{27}Al NMR.

Dear Professor Shapiro:

In the course of our research into chiral lithium aluminum alkoxy hydrides, we investigated their ^{27}Al NMR spectra. The results were extremely interesting and provide a new technique to identify the disproportionation reaction shown below:



Disproportionation has been frequently suggested to explain the behavior of simple alkoxy lithium aluminum hydrides, for example, $\text{LiAlH}_2(\text{OCH}_2\text{CH}_3)_2$.

We were studying the reactions of aminoalcohols with lithium aluminum hydride, specifically analogues of 1,2-diphenyl-3-methyl-4-dimethylamino-2-butanol (Darvon alcohol). These compounds were not expected to undergo disproportionation because of the possibility for chelation by the dimethylamino group. However, when the compound formed by reaction of two equivalents of Darvon alcohol with LiAlH_4 was dissolved in dry THF, the ^{27}Al NMR spectra, at 26 MHz, showed uncomplexed LiAlH_4 , Figure 1, whereas the IR spectrum did not indicate any unreacted LiAlH_4 . Thus, we are forced to conclude that disproportionation was occurring.

These ^{27}Al spectra were extremely easy to obtain on a Varian XL-100 spectrometer equipped with a Nicolet Multi Observe Nuclei Probe (NTC 440) and a TT1010A with a NIC 1180 data system. Each spectrum usually required only 500 acquisitions. Thus, ^{27}Al NMR should prove to be an extremely powerful technique for mechanistic investigations of lithium aluminum hydride species.

Please credit this letter to the account of Professor Oleg Jardetzky, Stanford Magnetic Resonance Laboratory.

Sincerely,

Natalie L. McClure

N.L. McClure

Michael Hogan

M. Hogan

Harvey S. Mosher

H.S. Mosher

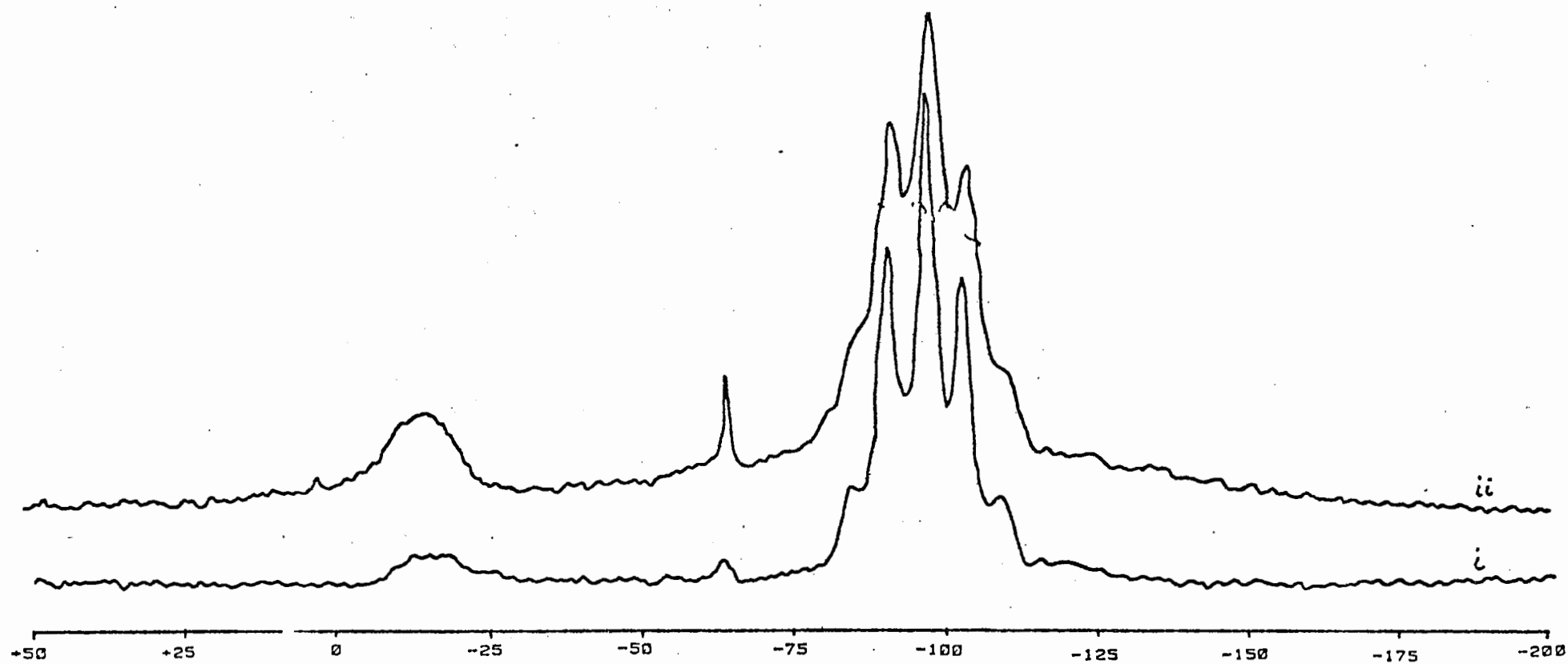


FIGURE 1. ^{27}Al NMR SPECTRA. i) THE NMR SPECTRUM OF LiAlH_4 IN THF.
ii) THE NMR SPECTRUM OF $\text{LiAlH}_2(\text{ODARVON})_2$ IN ETHER.



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DEPARTMENT OF PHYSIOLOGY and BIOPHYSICS

September 24, 1979

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

¹⁷O Magnetic Resonance of Amino Acids and Aryl Ketones

Dear Barry:


It has taken some time to debug our new Bruker CXP-180 spectrometer but we are now able to keep it running around the clock at 24.4 MHz (the frequency of our favorite nucleus--¹⁷O). The high power capabilities are certainly a plus here since ¹⁷O liquid state lines can be as broad as 4 kHz and if you add some paramagnetics--the shifts are out of sight on ordinary spectrometers. We spent several months exploring the possibilities of natural abundance work. However, we have been working primarily with amino acids and aromatic ketones and the broad lines (amino acids usually about 250 Hz and for the aromatics anywhere from 300 Hz to 4000 Hz) in combination with occasional solubility problems require extensive signal averaging to obtain a signal. ¹⁷O natural abundance studies of aqueous amino acids are often particularly difficult and computer memory will fill up at about 15,000 scans depending of course, on the attenuation used. A combination of Bruker's PAPS (phase alternating pulse sequence) program to eliminate mechanical ringing effects in the probe and a solvent suppression sequence would give up to 1.5 Mshots. We were able to obtain several chemical shifts of amino acids using this method but it was clear that any serious relaxation work would


require enriched compounds. Sample tubes are about 3 cm in length and 10 mm in diameter and lie transversely in H_2O . However, the very small volumes available with the enriched compounds provoked us to build a coil for 5 mm tubes. The spectra obtained with this coil have been excellent and most importantly we can conserve on precious ^{17}O labelled compounds.

A typical enriched spectra of m-methoxy acetophenone (54% in ^{17}O) on about 10,000 scans is shown in Figure 1. The need for 10 Kscans is due to the little blip slightly downfield from the water and dioxane peaks--this is the unenriched $-OCH_3$. The carbonyl peak is excellent working material for relaxation studies after 1000 pulses which requires all of 4 minutes to accumulate. ^{17}O relaxation calculations require the quadrupolar coupling constant and we have been exploring the use of liquid crystals to get at this number. The natural abundance signal of water and enriched urea (20%) in the isotropic phase of a lyotropic liquid crystal is given in figure 2a. The ^{17}O ($I=5/2$) quadrupolar splitting gives the typical five lines and the coupling constant is easily obtained from the splittings. The liquid phase spectrum of the urea-water solution is shown directly below in figure 2b.

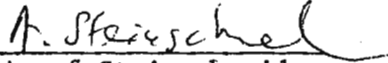
Sincerely,


Daniel Fiat


Thomas St. Amour


M.I. Burgar


Bill Valentine


Assaf Steinschneider

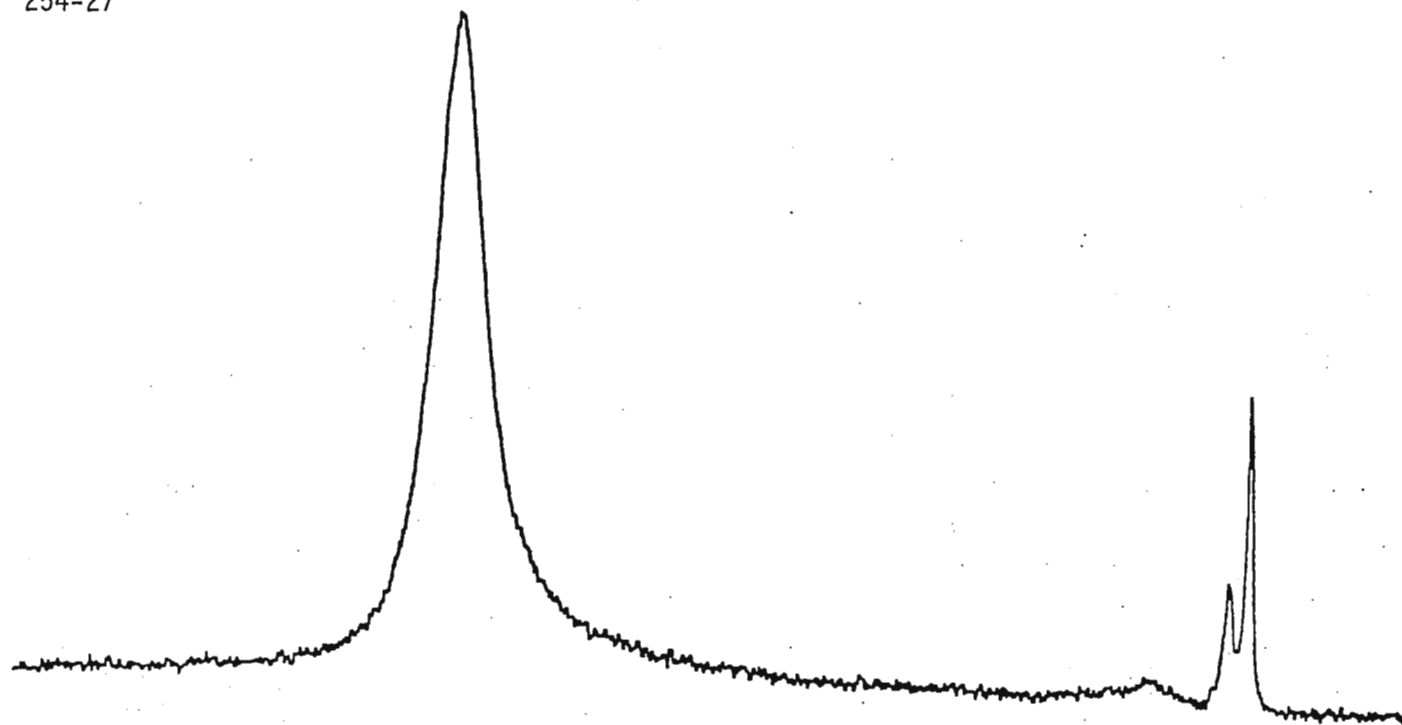
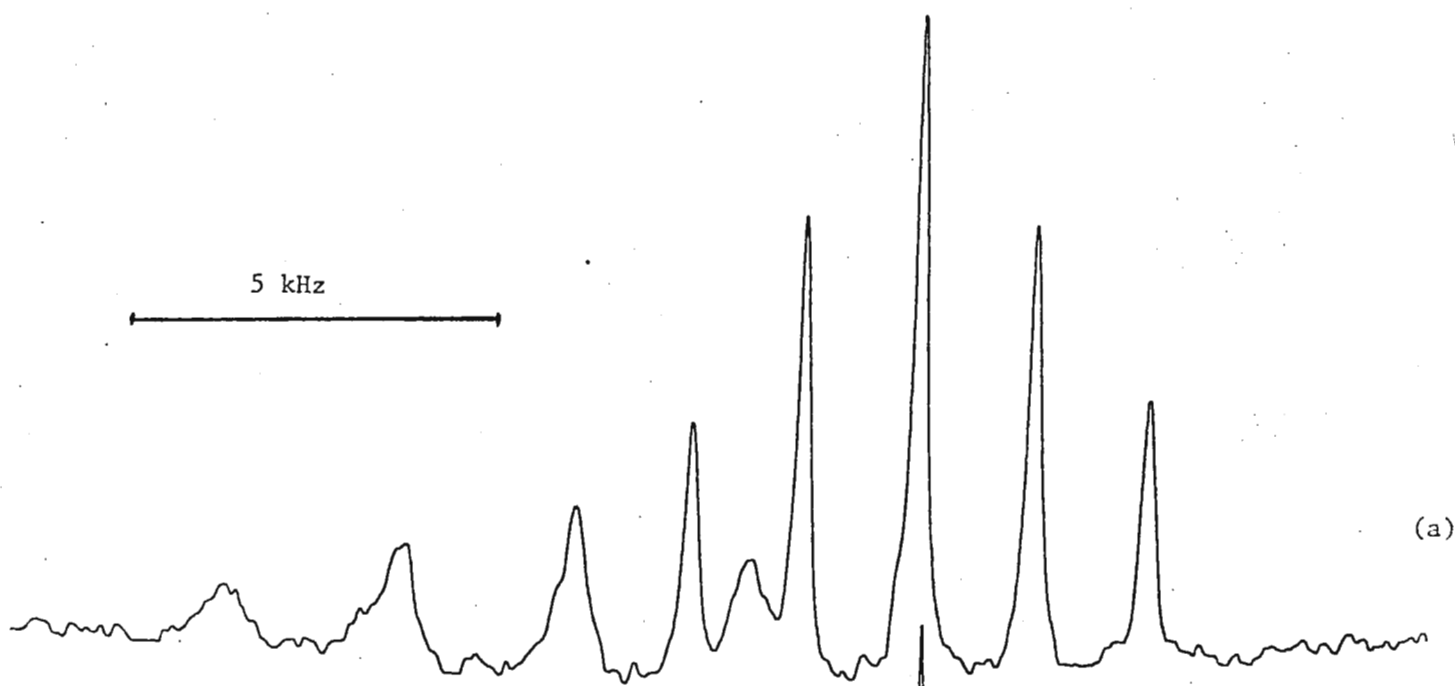


Figure 1



(a)

Figure 2



(b)

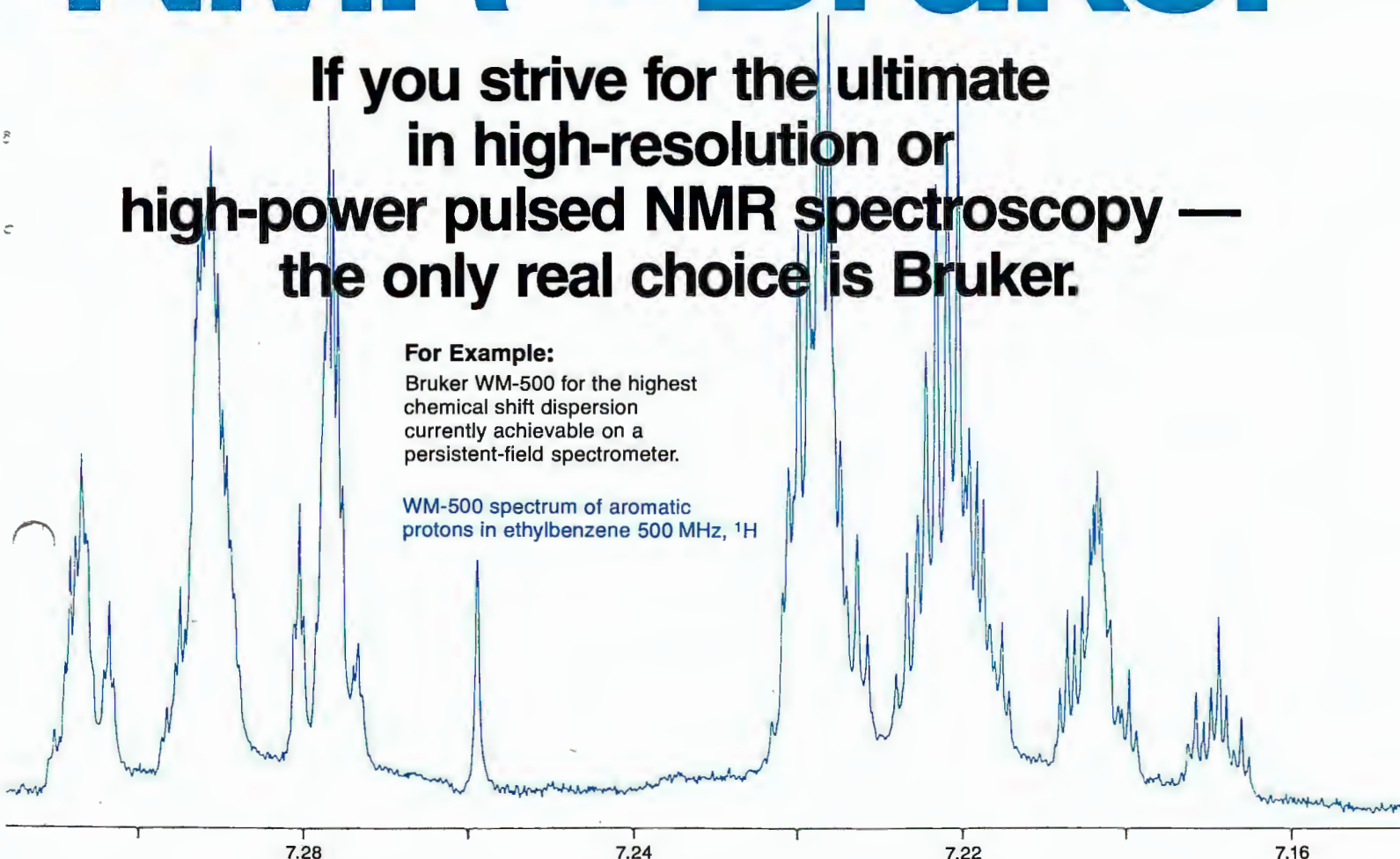
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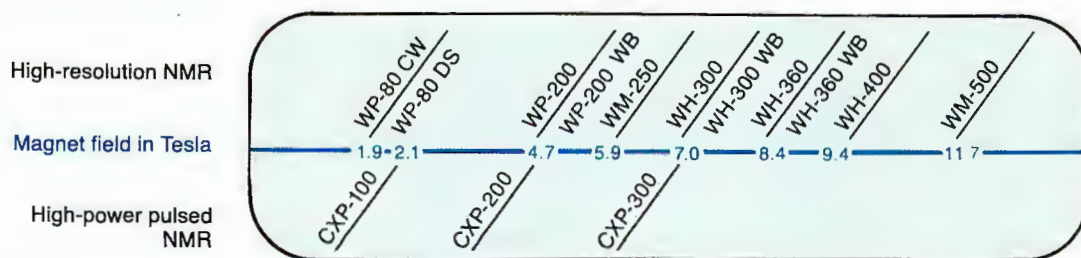
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(301) 762-4440

1603 Darwin Court, Wheaton, IL 60187
(312) 668-4441

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

Dilithium s-Indacenyl Dianion - A 14- π - Electron System
with Localized Charges

Dear Barry,

The most commonly accepted model in predicting the aromaticity of polycyclic ions is a peripheral model where the charge density is delocalized over the entire diatropic system. We have recently prepared dilithium s-indacene and studied its ^1H - and ^{13}C NMR spectra by varying the solvent. Comparisons of the absolute shifts (^1H and ^{13}C) of this dianion with those of indenyl- and cyclopentadienyl-lithium indicated qualitatively that the negative charges were localized to the five-membered rings (Figure). Additionally, increasing the π -polarizing cationic fields (THF: HMPT \rightarrow THF) causes just minor changes of the ^{13}C chemical shifts of the indacenyl dianion. A similar change, having the indenyl system, induced significant upfield changes for the five-membered ring carbons, while the proton-bearing benzenoid carbons moved downfield. Thus, the indicated charge localized structure of the indacenyl dianion is not due to the cationic fields. Our ab initio MO calculations (total charge densities) of the free dianion confirmed the experimental observations.

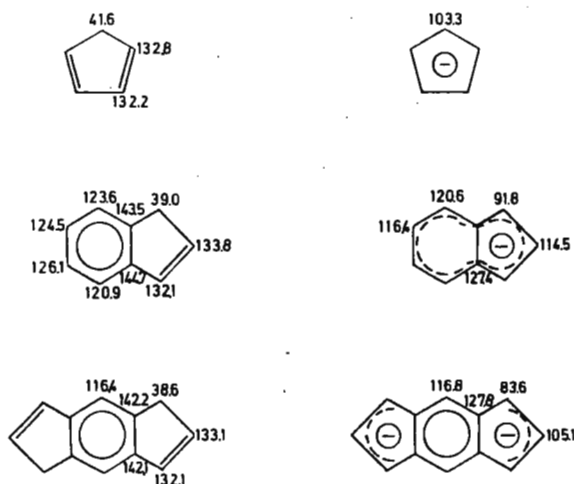


Figure ^{13}C NMR chemical shifts of cyclopentadienyllithium, indenyllithium, s-indacenyl dilithium (obtained under contact ion pair conditions) and the corresponding carbon acids (CDCl_3).

Best regards



Ulf Edlund

Monsanto

CORPORATE RESEARCH LABORATORIE

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

October 8, 1979

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

Dear Barry:

Magic-Angle C-13 NMR of Carbon-Fiber Precursors

One route for the production of a carbon fiber starts by a low-temperature pyrolysis in air of fibers made from polyacrylonitrile homo- or copolymers (Figure, left). Carbon fibers are then produced by a subsequent high-temperature carbonization. While the characterization of the initial fibers and the intermediate partially aromatized, or oxidized, material is difficult by conventional spectroscopy, we have found that analysis by magic-angle cross-polarization ^{13}C nmr is a practical matter. The spectrum of Orlon 42, which is predominantly polyacrylonitrile, consists of a high-field line arising from the aliphatic main-chain carbons, and a low-field line from the nitrile carbon (Figure, top right). The latter is broadened by ^{13}C - ^{14}N coupling not removed by magic-angle spinning. The extent to which the pyrolyzed Orlon carbon-fiber precursor retains aliphatic character can be estimated by the intensity of the high-field line (Figure, bottom right). With suitable model compounds and with various fiber precursors pyrolyzed to different degrees, we feel we could ultimately make some sense out of the observed four or five aromatic-carbon lines. These assignments might also be important in understanding the carbonization process itself. (The effects of ^{14}N broadening are nasty however. One way out of that dilemma is to perform single and double-cross polarization experiments on fibers made from ^{15}N -polyacrylonitrile, since 2-kHz spinning will remove completely ^{13}C - ^{15}N dipolar broadening.)

Sincerely,

Jacob Schaefer

E. O. Stejskal

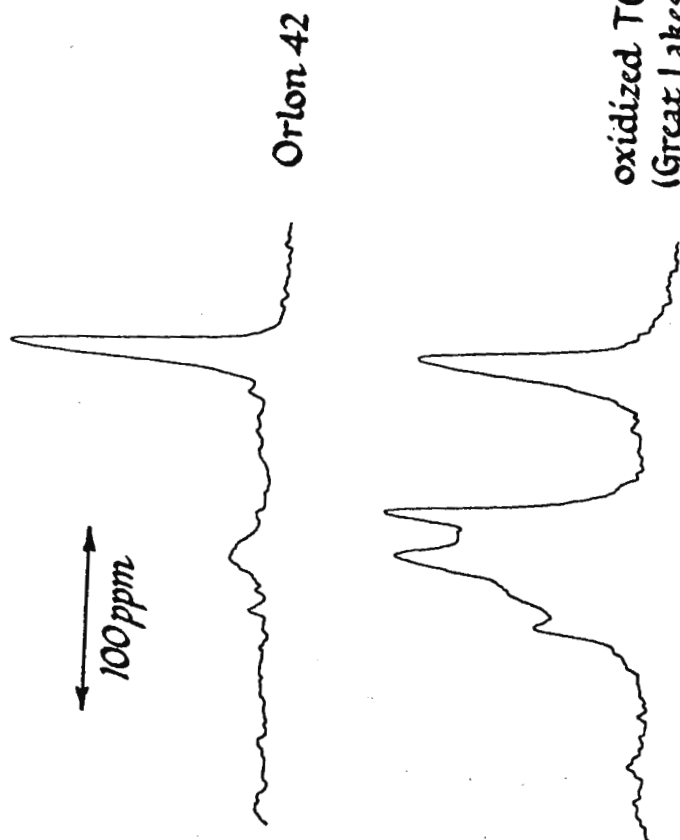
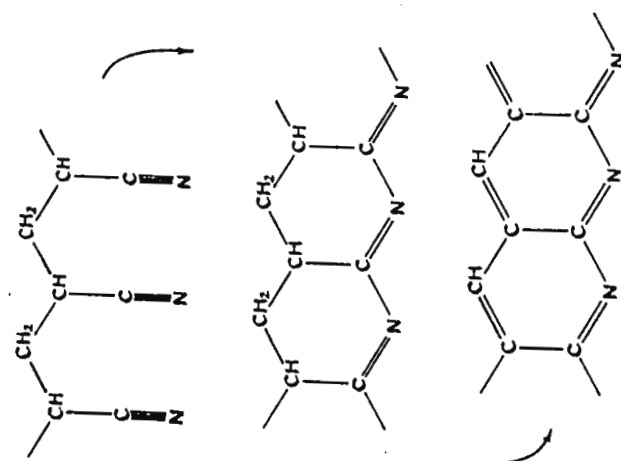
R. A. McKay

Jake

Ed.

Bob

/ct



oxidized TOW
(Great Lakes Carbon Co.
stabilized fiber)



**EIDG. TECHNISCHE HOCHSCHULE
ZÜRICH**

**Laboratorium
für Physikalische Chemie**

Prof. Dr. R. R. Ernst

RIER/mü

CH-8006 Zürich, Oct. 18, 1979
Universitätstrasse 22
Tel. (01) 32 62 11

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

POSTDOCTORAL POSITION AVAILABLE FOR NMR SPECTROSCOPIST

Dear Barry,

For the continuation of an interdisciplinary research project on the application of Overhauser effects and cross-relaxation to biomolecules, we are looking for a

NMR spectroscopist

with a good theoretical background and with experimental experience in relaxation studies and/or biological NMR.

The desired starting date is May to August 1980. The initial employment would last for one full year, but it is renewable. The salary will be equivalent to that of an Assistant I according to ETH regulations.

Inquiries should be sent to

Prof. Kurt Wüthrich
Institut für Molekularbiologie
und Biophysik
ETH-Hönggerberg
8093 Zürich, Switzerland

or Prof. R.R. Ernst
Laboratorium für
Physikalische Chemie
ETH-Zentrum
8092 Zürich, Switzerland

Sincerely yours

Richard R. Ernst



THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

October 2, 1979

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

RE: Senior Staff Position in NMR

Dear Barry:

The Chemistry Department has an opening at the senior staff level for an NMR spectroscopist. We are looking for a graduate engineer or a Ph.D. in one of the physical sciences. Recent NMR experience is essential.

The responsibilities include operation and supervision of NMR equipment (WH-90 and WM-250 Multinuclear FT NMR spectrometers). Collaboration with faculty and instrument development are strongly encouraged.

We would like to make this appointment before May 1, 1980. The starting salary will be \$20,000 or higher, depending on qualifications. Applicants should send a resume and three letters of recommendation to me at the above address.

The University of Arizona is an Equal Employment Opportunity/Affirmative Action/Section 564 Employer.

Sincerely yours,

A handwritten signature in cursive script that reads "Mike".

Michael Barfield
Professor

MB:jlh

Universität Regensburg
FACHBEREICH CHEMIE UND PHARMAZIE
Institut für Chemie
M. Milun,
A. Mannschreck

8400 REGENSBURG, Sept. 25, 1979
Universitätsstraße 31 - Postfach
Telefon (0941) 9431
Telex: 065658 unire d

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

DIASTEREOMERIC ELECTRON-DONOR-ACCEPTOR (EDA) ASSOCIATION
COMPLEXES

Dear Professor Shapiro:

We have recently shown¹⁾ some ^1H shift effects caused by EDA interactions between chiral molecules: Changes of chemical shifts and additional splitting compared with the spectra of the free components. Additional splittings appear in the spectra of the racemic substrate in the presence of an optically active partner. Fig. 1 shows the effect of temperature on the shifts and on the splittings of aromatic proton signals of the acceptor (*RS*)-1 in the presence of the donor (+)-2²⁾. Use of a *non-racemic* mixture of (*R*)- and (*S*)-1 enabled us to assign the two sets of signals of 1 (Fig. 1). The additional splittings disappear, as expected¹⁾, when *both* components are applied as racemates. We hope that the splittings, combined with the above shift changes, will result in a model for the relative orientation of the components in the complex.

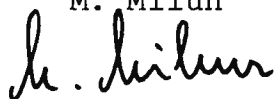
One of our EDA donors is N,N,2-trimethyl-2,3-dihydro-quinoxaline, (+)-3. In the spectra of (*R*)-1 + (+)-3 and of (*RS*)-1 + (+)-3 we have observed broadening of the aromatic protons of 1 or of the aliphatic protons of 3, respectively. When we went down from 299 K to 200 K, the affected signals became sharp, reversibly. When the same samples were measured after a few weeks, the same effect was observed. This is not the first time that such phenomena appear in the spectra of 1 mixed with some donor, but the broadening usually disappeared one day after mixing. — We are interested to learn about

any experience of this kind as well as about possible explanations for this effect.

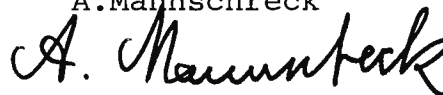
Further n.m.r. problems dealt with in our group include chiral cation-anion association complexes³⁾ as well as internal rotation in substituted acetophenones⁴⁾, benzamides⁴⁾, and enamides⁵⁾.

Sincerely yours,

M. Milun



A. Mannschreck



-
- 1) A.Mannschreck, P.Roza, H.Brockmann jr., and T.Kemmer, Angew.Chem. 90, 995 (1978); Angew.Chem.Int.Ed.Engl. 17, 940 (1978).
 - 2) Kindly provided by Dr. H. C. Anderson, Syntex Corporation, Palo Alto, California.
 - 3) F.Lefèvre, C.Rabiller, A.Mannschreck, and G.J.Martin, J.C.S. Chem.Comm. 1979, in print; T.Burgemeister, H.Koller, and A.Mannschreck, unpublished results.
 - 4) M.Holík and A.Mannschreck, Org.Magn.Resonance 12, 28, 223 (1979).
 - 5) H.Ahlbrecht, G.Becher, J.Blecher, H.-O.Kalinowski, W.Raab, and A.Mannschreck, Tetrahedron Lett. 1979, 2265.

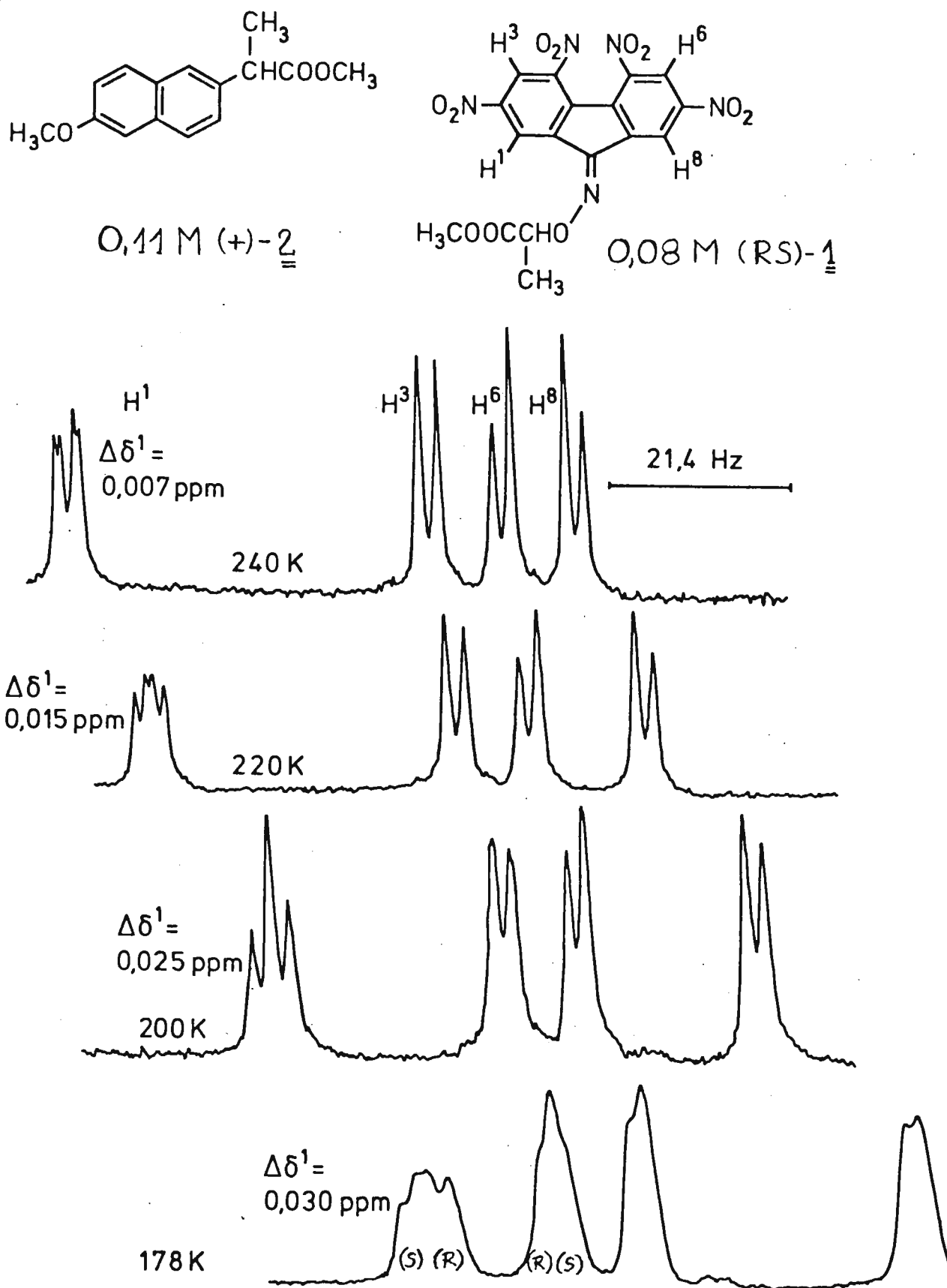


Fig. 1. Effect of temperature on the shifts and on the signal splitting $\Delta\delta^1$ for H^1 of (RS)-1 in the presence of (+)-2. $[D_6]$ acetone; 90 MHz. Shifts at 240 K: $\delta = 9.42$ (H^1), 8.96 (H^3), 8.86 (H^6), 8.77 ppm (H^8). For the spectrum at 178 K, the assignments (see text) of (R)- and (S)-1 are indicated.

varian / instrument group

25 hanover road / florham park / new jersey 07932

telephone (201) 822-3700



October 16, 1979

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

PHOSPHORUS USERS BEWARE!

Dear Barry,

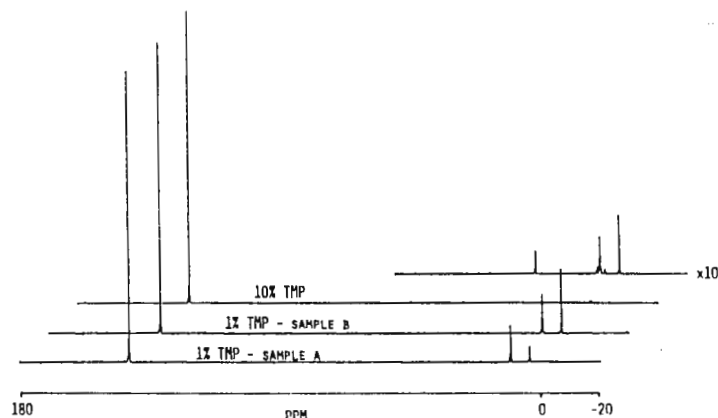
Trimethylphosphite has long been the phosphorus sensitivity standard for P-31 nmr. Normally, a relatively narrow spectral width is chosen for the signal-to-noise test. Choice of a spectral width which encompasses the entire range of P-31 resonances unfortunately reveals a serious problem with this compound, namely, sample purity.

Three different samples of trimethylphosphite were run on a Varian XL-200 with SW=20000, NT=128, PW=30°, a repetition rate of 1 second, and using broadband proton decoupling. The spectra reveal impurities in all samples, and significant levels of impurities in two out of three samples. Rough integration of the worst sample showed only 65% of the total phosphorus in the sample in the form of trimethylphosphite. This has clear implications insofar as signal-to-noise measurements are concerned.

The source and exact identity of these impurities is unknown. But the wide variation in impurity level from sample to sample suggests that the user is wise to measure any trimethylphosphite sample under these conditions before using it for signal-to-noise measurements.

Sincerely,

Steven L. Patt
NMR Applications Chemist





NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6110-766:BSH:kvk

11 October 1979

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

Dear Professor Shapiro:

Re: ¹⁵N NMR Study of Polyamides Using J Cross-Polarization Techniques

Recently, we have used J Cross-Polarization (JCP) techniques in liquids to overcome the formidable sensitivity problems connected with natural abundance ¹⁵N NMR. (1,2) The signal gathering efficiency of JCP for ¹⁵N NMR is 15 to 300 times greater than that of conventional FT NMR. (2)

It has been shown that the ¹⁵N chemical shifts of polypeptides containing glycyglycine units and polyamides are substantially more sensitive to sequence lengths than are the ¹³C shifts. (3) We looked at ¹⁵N chemical shifts of polyamides in solutions of 20% concentrations in sulfuric acid, formic acid, trifluoroacetic acid, and hexafluoroisopropanol (all samples and solutions were provided by Dr. R. C. Ferguson of DuPont).

The JCP experiments were run at 23 kG on a modified Varian HA-100 with external fluorine lock. Experimental conditions were: 5 mm spinning sample, 25°C, 8 msec cross-polarization time, broadband proton decoupling, 1000 accumulations at 2 sec intervals (experiment time, 48 minutes), 1200 Hz sweep width/quadrature detection, 2K data points, 2 Hz exponential line broadening. A S/N of 4-5 was typical. The sensitivity improvement achieved in the present study can be appreciated by examining the following tabulation:

<u>Method</u>	<u>Amt. Polyamide</u>	<u>Sample Tube</u>	<u>Field</u>	<u>Accum. Time</u>
FT ⁴	1.5g	20mm	21kG	0.5-2 hr.
JCP	0.15g	5mm	23kG	0.8 hr.

Please credit this contribution to Dr. William B. Moniz's account.

Sincerely,

Brenda S. Holmes
 BRENDA S. HOLMES
 Polymer Diagnostics Section
 Chemical Diagnostics Branch
 Chemistry Division

References

1. R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, J. Am. Chem. Soc. 100, 5228 (1978).
 2. R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, J. Magn. Reson. 32, 465 (1978).
 3. H. R. Kricheldorf and W. E. Hull, J. Poly. Sci. Poly. Chem. 16, 583 (1978).
 4. H. R. Kricheldorf and G. Schilling, Makromol. Chem. 179, 2667 (1978); H. R. Kricheldorf, *ibid.*, 179, 2675 (1978).
-

Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

(212) 570-5666

October 18, 1979

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

Dear Barry:

Postdoctoral Positions Available

I have two postdoctoral openings available in my group, one immediately and one shortly after the first of the year. Both positions involve continuing applications of ¹⁵N nmr spectroscopy in organic chemistry, so I am seeking people with a good background in organic chemistry. It would be desirable if at least one person has some experience with Fourier transform nmr spectroscopy. The salary, paid from grant funds, would be \$11-12,000, depending on experience. Applicants should send me a curriculum vitae and publications list, and arrange for 2-3 letters of recommendation to be sent. Hunter College and the Research Foundation of CUNY are Equal Opportunity employers.

Sincerely yours,



Robert L. Lichter
Associate Professor
Chairman



McGill
University

Department of Chemistry
Pulp and Paper Building

October 12, 1979.

Dr. W.H. Dawson

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

A Method of Cooling the Probe for Low Temperature NMR

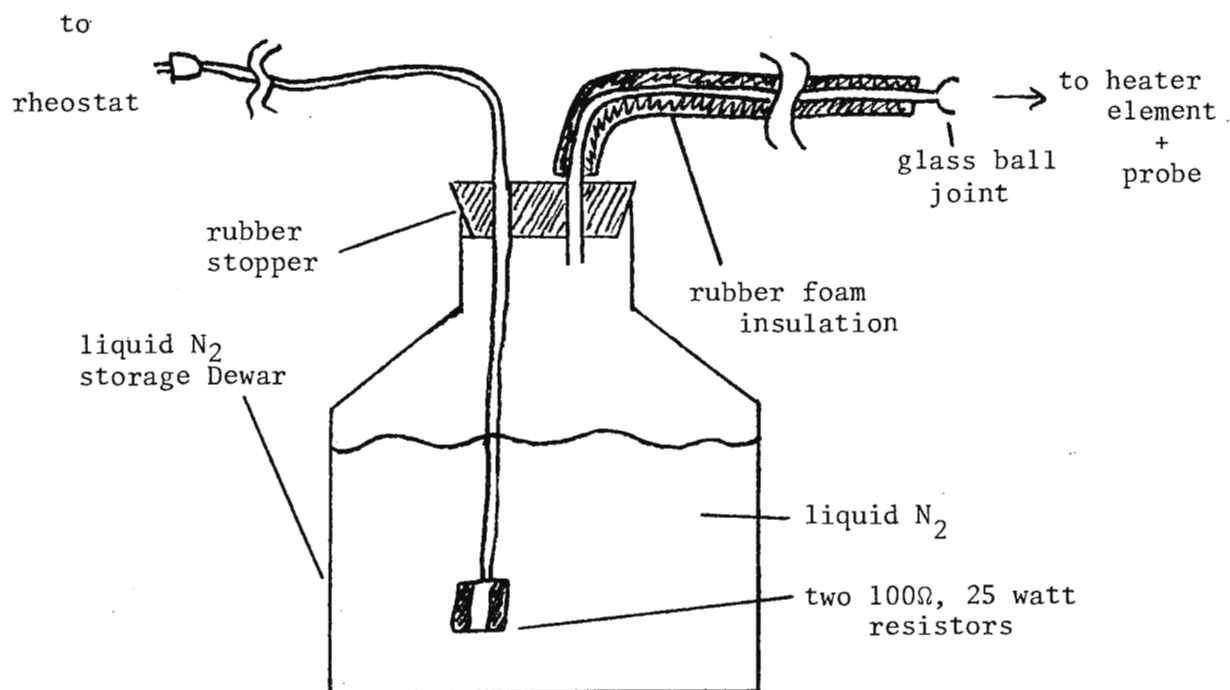
Dear Barry:

We would like to bring to the attention of your readers a method of cooling NMR probes for low temperature experiments. It is one that we have been using for some time now and is an alternative to the coil-immersed-in-liquid-nitrogen method commonly used for cooling the stream of nitrogen that flows past the probe insert. The set-up is shown in the figure. The two 100 Ω , 25 watt resistors (Ohmite Mfg. Co., Skokie, Illinois, cat. no. 0200F) are connected in parallel and the rheostat is of the usual lab variety ("Powerstat", Superior Electrical CB., Bristol, Conn.). The Dewar we used has a 6 cm wide mouth. By applying a current to the resistors under control of the rheostat it is possible to regulate the nitrogen boil off rate, hence the amount of cold nitrogen gas reaching the probe.

We prefer this method because it consumes less liquid nitrogen and requires less attention, the latter because it avoids the need to periodically top up the liquid nitrogen level. The unit supplies very dry nitrogen gas to the probe and at a very stable flow rate. The amount of heater regulation required is therefore reduced and more stable temperatures are possible. We find that the apparatus is easier to set up and disassemble than the coil-immersion unit and moderately low temperatures (-120°) are easily achieved.

We secure the rubber stopper to the Dewar with a piece of wire during operation. At times, however, a lot of nitrogen will vent off in a hurry (e.g. just after immersing the resistors in the liquid nitrogen or upon making a large rheostat adjustment). Until you have gained experience with the unit, proceed with caution.

..... cont'd



Bill

W.H. Dawson

Gord.

G.K. Hamer *

Please credit this contribution to Dr. A.S. Perlin's subscription.

* Present address: Xerox Research Centre of Canada
2480 Dunwin Drive, Mississauga, Ontario

**Instruments, Inc.**

MANNING PARK
BILLERICA, MASSACHUSETTS 01821
(617) 667-9580

2 October 1979

Dr. Barry L. Shapiro
Editor TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77843

"Can C-13 NMR break the millimole concentration barrier?" or

"High-Field ¹³C NMR, a tool for conformational analysis of synthetic polymers?"

Dear Barry,

We have recently started evaluation of our newly installed Demo Lab WH-360 Widebore Spectrometer, an instrument which has specifically been designed for those requesting the ultimate in sensitivity at a given concentration. Applications are numerous in such fields as characterization of synthetic and naturally occurring macromolecules, structural studies on scarcely soluble organic molecules, detection and identification of minor constituents in production processes, impurities in waste water, etc.

Obtention of a sufficiently large volume of homogeneity and complete decoupling of protons across the full chemical shift band in spinning sample tubes of 20 mm diameter were the two most challenging problems which had to be solved beforehand.

We were particularly intrigued by answering the question as to the limiting concentration affording proton-decoupled carbon spectra in a tolerable experimental time. First experiments on the popular 10 mM sucrose sample suggested a practical detection limit of approximately 2 mM, an estimate, which turned out to be too conservative.

The spectrum in Figure 1 of 2 mM cholesteryl acetate, recorded in four hours total time, exhibits an average signal-to-noise ratio of about 35:1. If a somewhat lower signal-to-noise ratio is accepted, one readily recognizes that spectra on 1 mM solutions become feasible overnight. It should be noted that under the recording conditions used the quarternary carbons 5, 10 and 13 are clearly discernible and all carbons are uniformly decoupled.

The actual gain in dispersion in spectra of macromolecules at high as opposed to low magnetic field has been a subject of considerable controversy. The intervention of frequency-dependent T_2 mechanisms such as chemical shift anisotropy, though shown to be existent, does not seem to be a substantial contributor to the line widths at high field and therefore does not seem to affect line widths adversely. In order to test the dispersive power of the instrument, we examined the spectra of a commercial sample of polyvinyl chloride (2% in 9:1 ODCB/deutero-benzene at 45°C). Whereas on the methine resonance pentad splittings could be partially resolved (as they can at much lower fields) the methylene peaks at lower frequency clearly show fine structure assignable to hexad splittings on the rrr, rnr, and mmm tetrad resonances. The necessity for high signal-to-noise (Figure 2 a) is dictated by the requirement for resolution enhancement techniques such as exponential multiplication in conjunction with Gaussian apodization, which we found to be most appropriate for obtaining spectra with minimal degree of distortion, as shown by the trace in Figure 2 b. An attempt to further enhance resolution by increasing temperature (as we naively thought would be the key to success) failed. To our surprise, however, the habitus of the spectrum changed in a different fashion, viz. in that distinctive line displacements occurred within each group of lines. This is most conspicuous for the center line of a group of resonances assignable to mnr and mrm tetrads respectively. This line has been found to gradually shift to high field upon raising the temperature (Figure 3 a-d).

The relative shielding changes, albeit not quantifiable at this point, may be explained in terms of long-range shielding contributions arising from increased populations of high-energy conformers. More systematic experiments need to be performed in order to fully understand the effects observed, but the preliminary data indicate that high-field C-13 NMR may offer a unique tool for the study of polymer conformation in solution.

Sincerely yours,

Bruker Instruments, Inc.



Dr. Felix W. Wehrli



Mark Mattingly

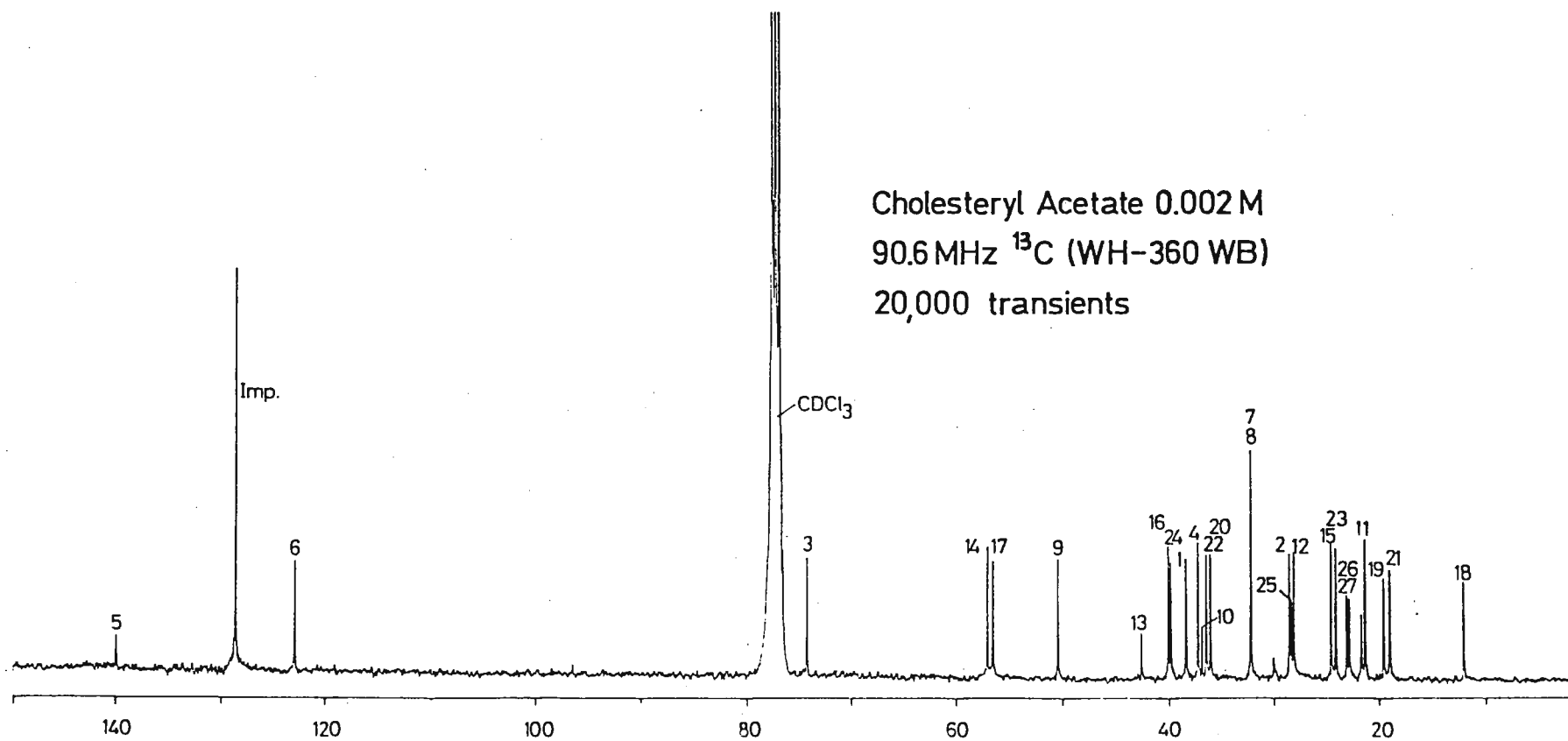


Figure 1.

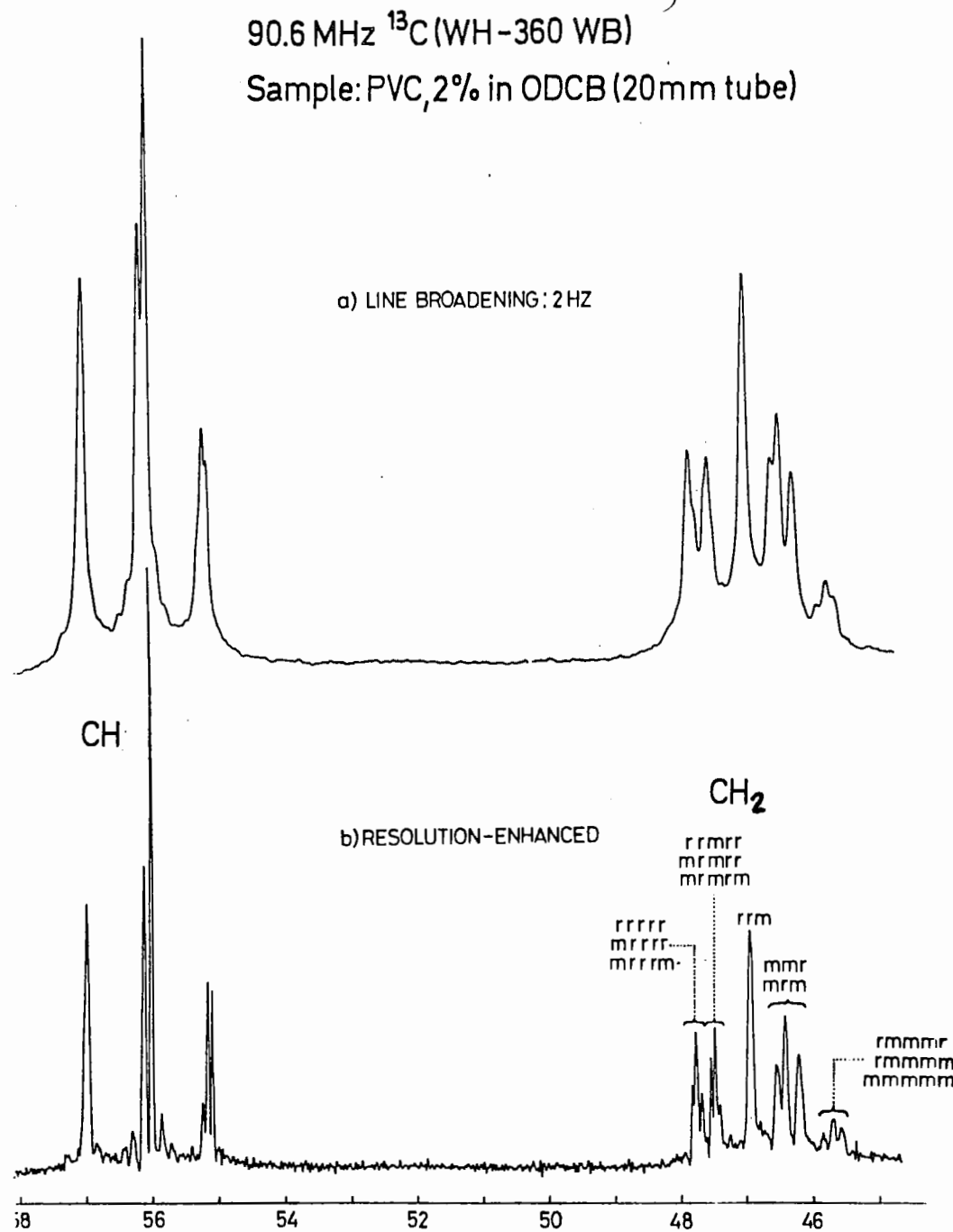


Figure 2.

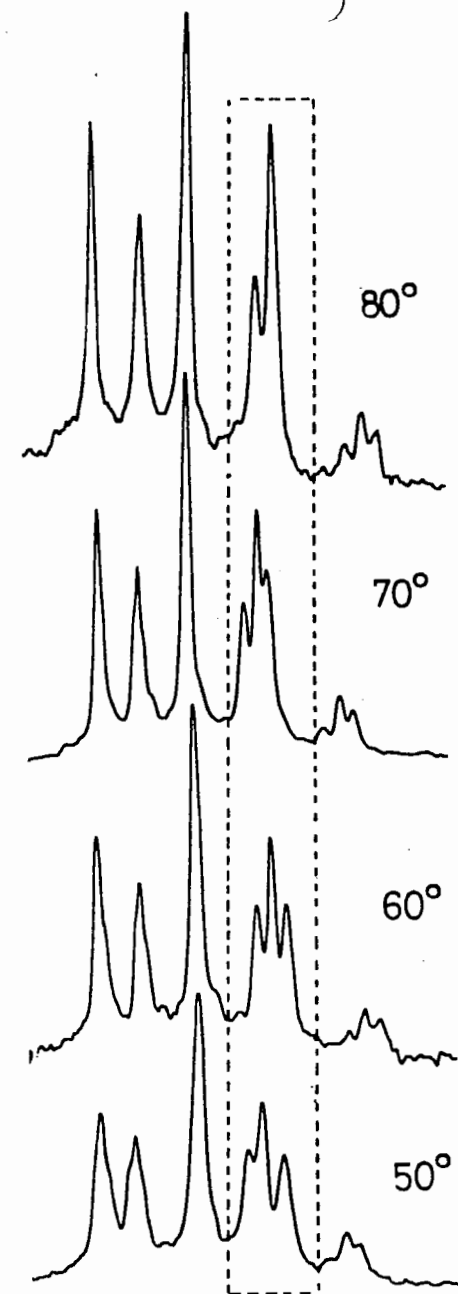


Figure 3.

THE INSTITUTE FOR CANCER RESEARCH

7701 BURHOLME AVENUE

FOX CHASE · PHILADELPHIA, PENNSYLVANIA 19111

(215) 342-1000 · CABLE ADDRESS: CANSEARCH

October 12, 1979

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

Dear Barry:

HOMONUCLEAR PHOSPHORUS DECOUPLING OF ATP

The enclosed spectra establish a point which is probably too pedantic to publish, but which is nevertheless satisfying. By continuous homonuclear phosphorus decoupling we have established that the splittings in the ^{31}P spectra of ATP (50 mM, pH 7.0) are indeed due to ^{31}P - ^{31}P spin coupling as has long been reasonably assumed (Cohn, M. and Hughes, T. R., J. Biol. Chem. 235, 3250 (1960)). No ^{31}P - ^{31}P Overhauser enhancements are detected in these preliminary studies suggesting that dipolar interaction between ^{31}P nuclei does not solely contribute toward their relaxation.

The FT spectra were obtained at 121.5 MHz without proton decoupling on the Bruker 300 MHz instrument at Billerica, Mass., in collaboration with Bruce Hawkins.

Sincerely yours,

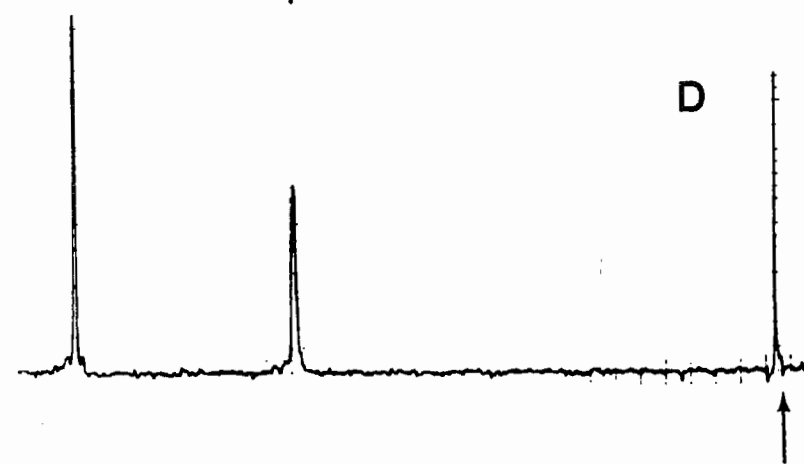
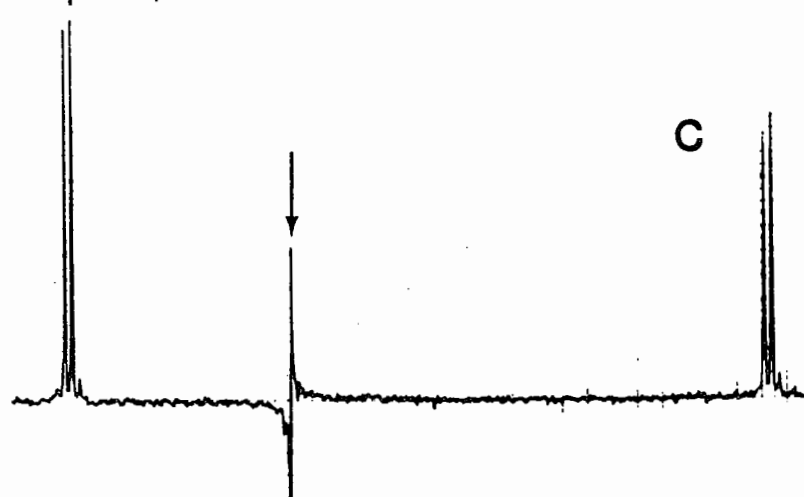
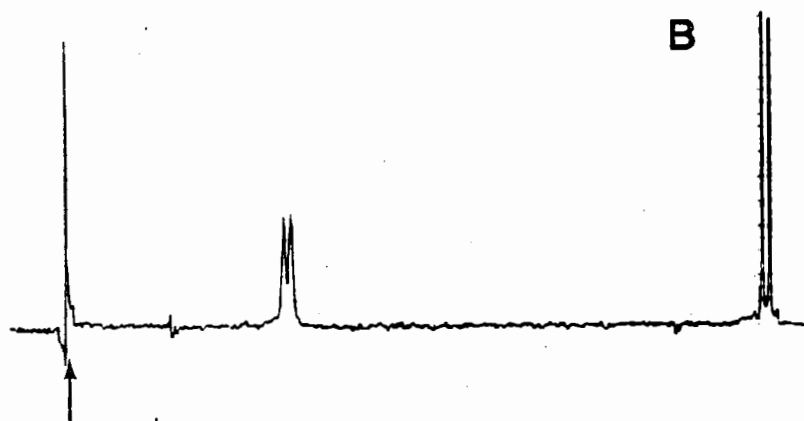
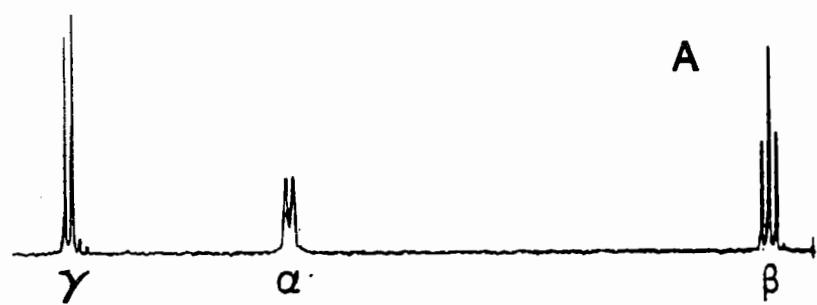


Albert S. Mildvan



Raj K. Gupta

jdi
encl:



GBF Mascheroder Weg 1 D-3300 Braunschweig-Stöckheim

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

GBF

Gesellschaft für
Biotechnologische
Forschung mbH

Abteilung

Physikalische Meßtechnik
Dr. Ernst Lustig

Ihre Nachricht vom

Telefon 05 31/70 08-1

Telefondurchwahl

Datum

05 31/70 08 362

16.10.79

Suppression of spinning side-bands

Dear Professor Shapiro,

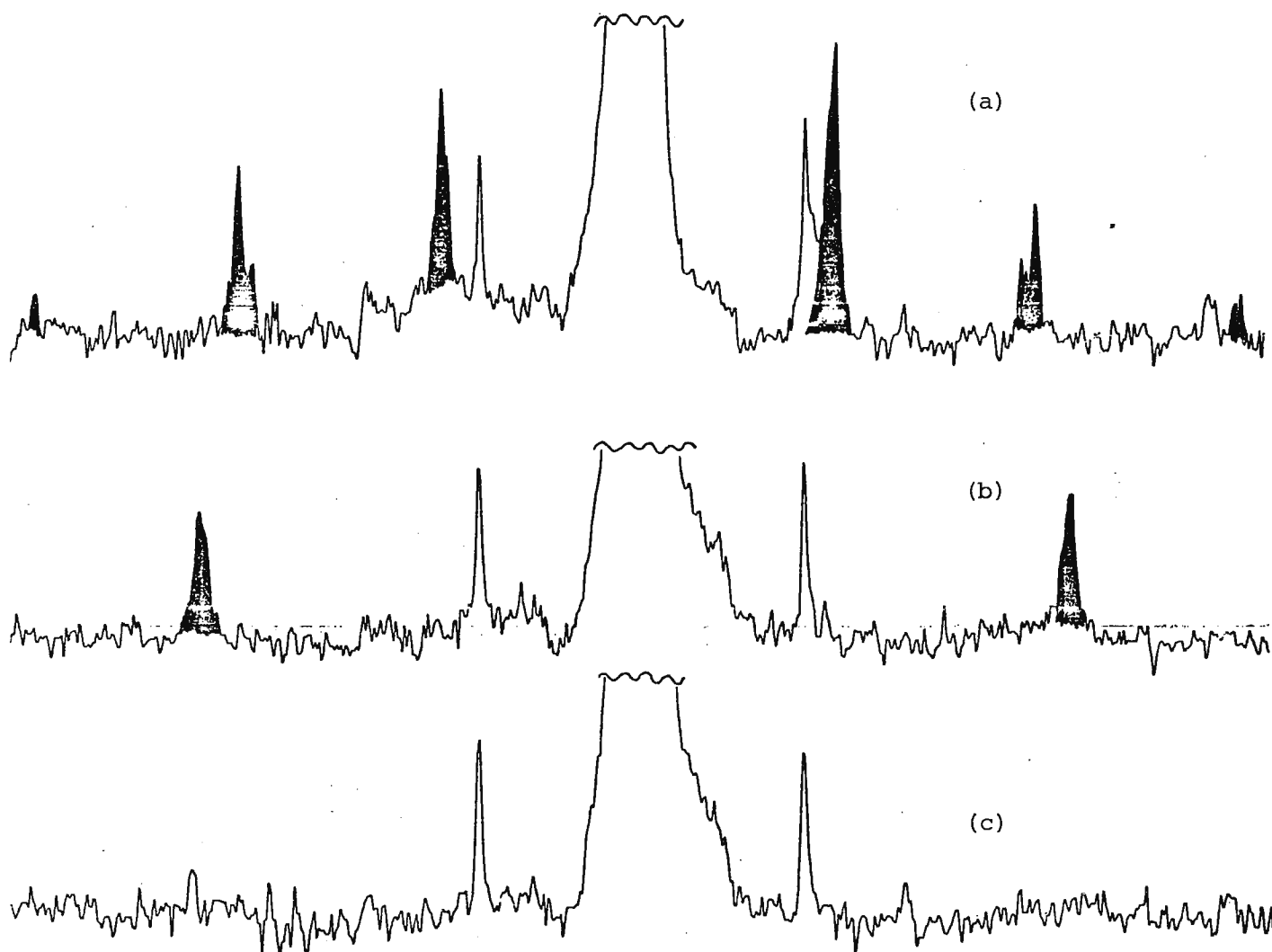
We have recently been interested in studying carbon-carbon spin-spin coupling constants from natural-abundance C-13 spectra on our CFT-20. In other than simple systems, spinning side-bands often interfere with the C-13 satellites. In order to overcome this problem we have modified a peristaltic pump which allows a continuous variation of the air pressure applied to the spinner for sample tube rotation¹. The advantages of such a system are seen in the accompanying figure.

Yours sincerely,

Victor Wray Ludger Ernst David N. Lincoln

Victor Wray, Ludger Ernst and David N. Lincoln

1. German Patent Application 28 16 225.6 (14th. April 1978) and foreign applications.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the methyl carbon of ethanol taken under the same pulse conditions on a Varian CFT-20 spectrometer (a) with a normal spinning speed of 23 rps, (b) with a spinning speed of 50 rps, and (c) with a continuously variable spinning speed (30-60 rps).

Uppsala, October 17, 1979

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

"Quantitative off-resonance studies made easier"

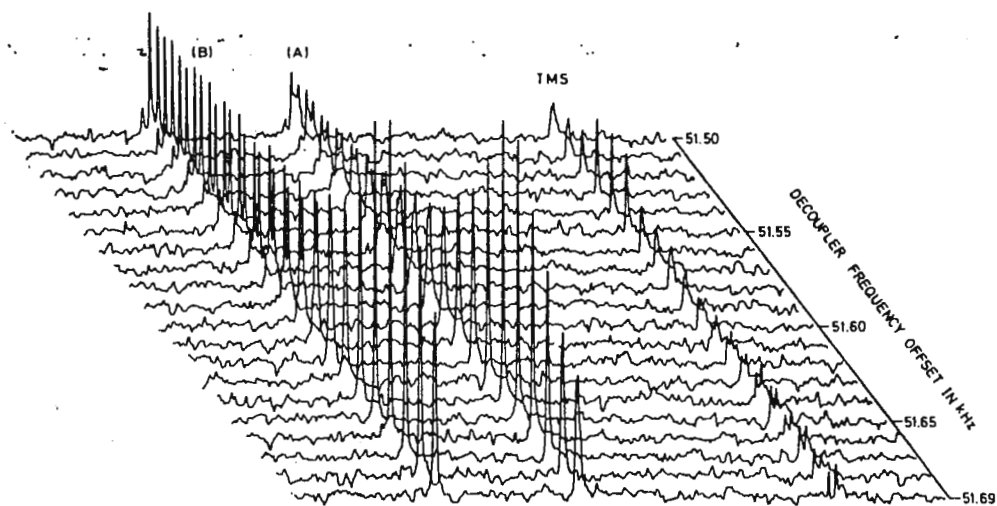
Dear Professor Shapiro,

In reply to your yellow reminder I would like to submit a note concerning an improved method for the evaluation of $^{13}\text{C} - \{^1\text{H}\}$ off-resonance decoupling experiments. Anyone who has tried to evaluate residual spin couplings from such experiments for subsequent plotting vs. the decoupler frequency has probably noted several difficulties related to peak overlap, second-order effects, poor S/N and so on. Fig. 1 illustrates an alternative approach; measuring peak heights vs. decoupler frequency. It is immediately apparent that the resulting "intensity bandshapes" look very familiar. Indeed, to first approximation, they should be Lorentzian since they are functions of the linearly changing overlap between approximately Lorentzian bands. Fig. 2 illustrates the non-linear least-squares fits. The statistical errors are small, despite the relatively poor S/N. Some further arguments for the method can be found in a note, which was submitted for publication in August.

Yours sincerely,

Peter Stilbs

Peter Stilbs



stilbs, Fig 1.

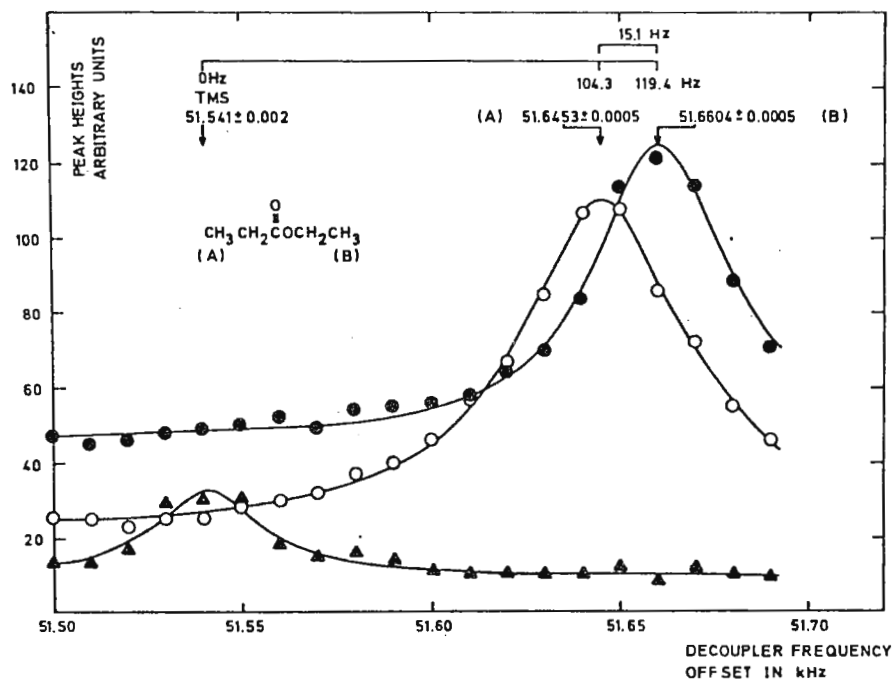


Fig. 2



UNIVERSITY OF STOCKHOLM
ARRHENIUS LABORATORY
Physical Chemistry

October 17, 1979

Dr. Bernard Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77840

Title: Vicinal proton-proton coupling constant in ethane

Dear Dr Shapiro,

In answer to your multicoloured reminders, we would like to report on a continuation of our work on the finite perturbation-configuration interaction calculations of the Fermi contact contribution to the nuclear spin-spin coupling constants [1,2]. This time we have applied our method to a problem of major chemical interest, the dihedral angle dependence of the vicinal proton-proton coupling constant in ethane. The purpose of our work has been two-fold. First, we wanted to find how important the correlation effects are for a three-bond coupling constant as compared to one-bond and two-bond couplings [2]. Our second interest is related to the functional form of the dihedral angle dependence, eq. (1), originally derived by Karplus [3] using simple valence bond theory.


$$^3J_{HH} = A + B \cos\phi + C \cos 2\phi \quad (1)$$

The aims have been to check whether our calculations could be fitted faithfully to this equation and whether our thus obtained values of A,B and C would agree with the empirically determined constants.

The results are presented in the figure. The triangles correspond to the values calculated at the Hartree-Fock level, the circles to correlated results. The lines are the plots of eq. (1) using the least-squares fitted values of A,B and C. We can see that it really is important to include the correlation effects and that our data fit well the Karplus relation. The A,B and C values, including the correlation, are 6.9, -1.1 and 6.1, respectively, which may be compared to the empirical A=7, B=-1 and C=5, obtained for substituted cyclohexanes [4]. Our J(average) = 7.0 Hz compares also nicely to the experimental value of 8.0 Hz, measured by Lynden-Bell and Sheppard [5].

Yours sincerely


Jozef Kowalewski

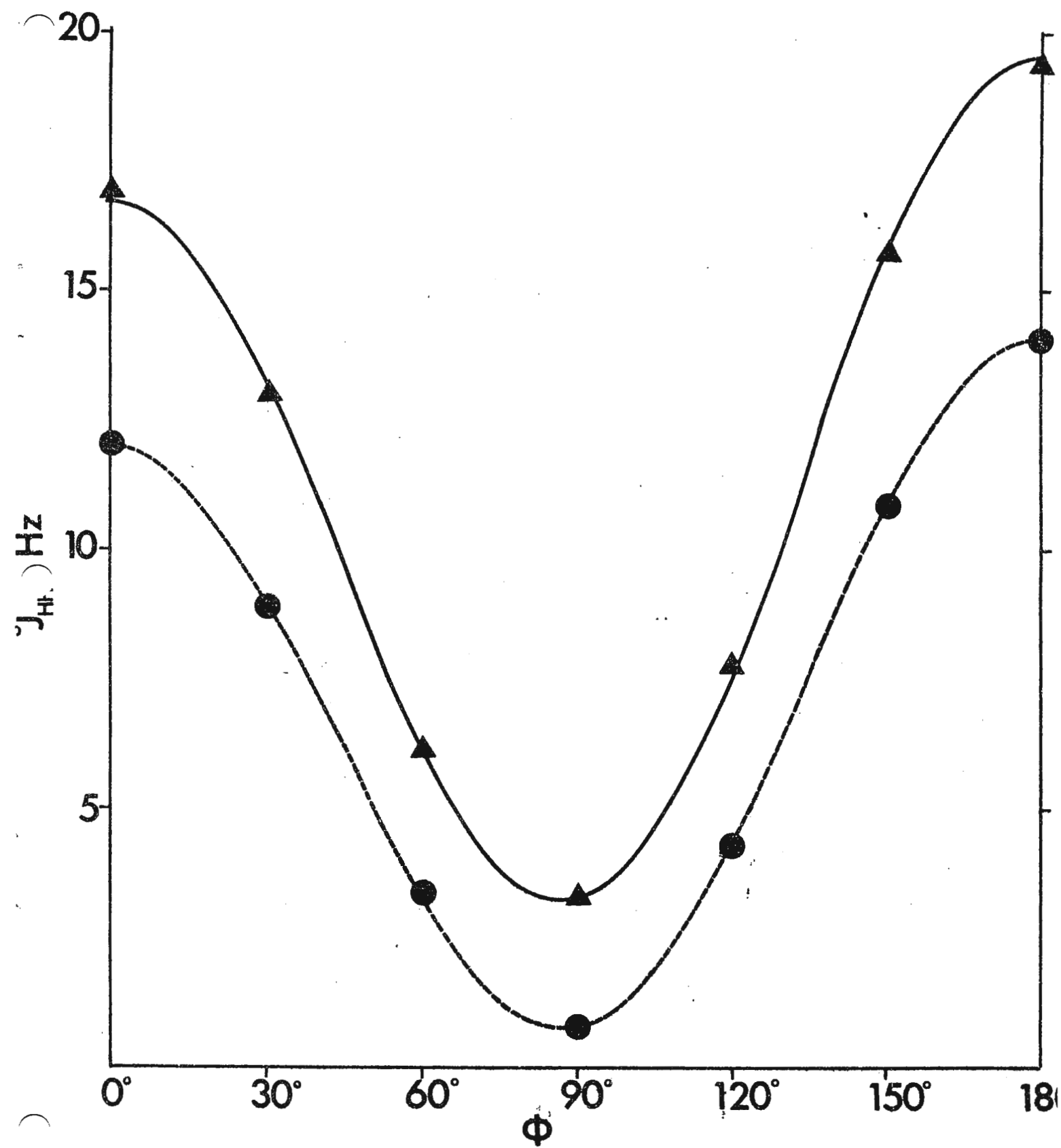

Aatto Laaksonen

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5. R.M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. A269, 385 (1962)

Postal address
Fack
S-104 05 STOCKHOLM
Sweden

Street address
Bergiusvägen 65
Frescati
Tel. 15 01 60 (exchange)



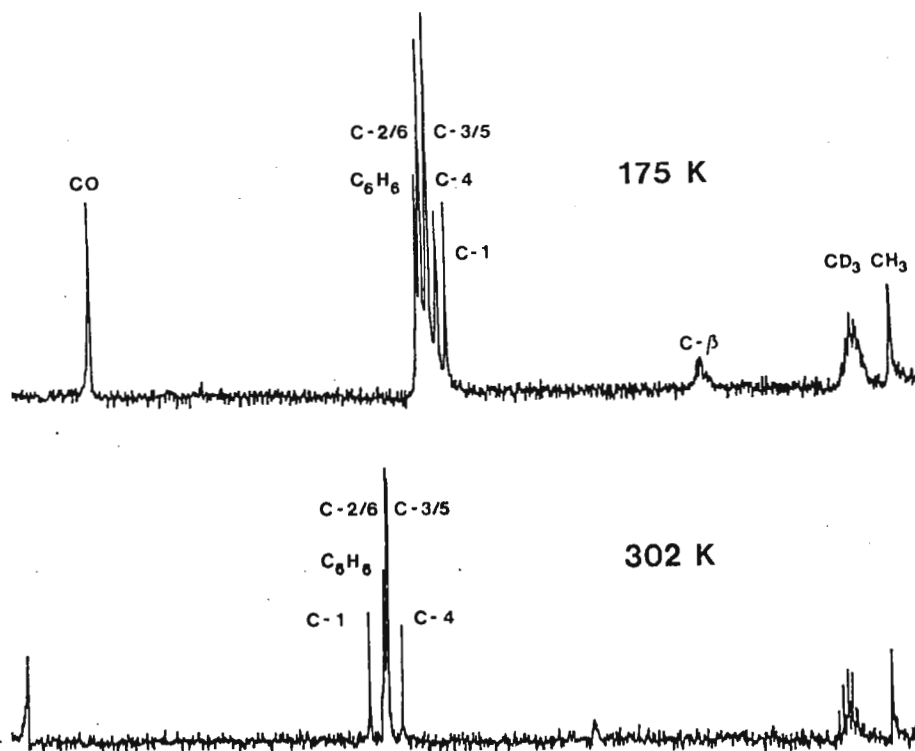
Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

Title: Disorganizing ^{13}C signals
of aromatic compounds

Dear Professor Shapiro!

There is little doubt that the ^{13}C nmr spectrum of toluene now exists in every laboratory's collection of spectra and you may be astonished to have news from it. In fact, the problem I want to mention today escaped our attention for quite some time since one usually does not carefully look at the signals of a solvent.

Much to our surprise we found out during temperature dependent paramagnetic nmr studies of cobaltocenes that at least the C-1 signal of toluene- d_8 is wandering around. In order to get more insight in this phenomenon we simplified the spectrum by switching to ordinary toluene and prepared a concentrated solution of 1,1'-diethylcobaltocene in a mixture of toluene, benzene and acetone- d_6 . The figure shows the solvent signals at two different temperatures (the only ^{13}C signal of the cobaltocene appearing in the usual diamagnetic range is C- β). You will notice a considerable change in signal



ordering and in aliphatic/aromatic carbon shift difference. Similar behavior is found for the acetone C=O resonance.

Further studies showed that these spectral changes are also present in ^1H nmr and that they are concentration dependent. We thus propose a specific time averaged orientation of cobaltocene and aromatics (as well as some other anisotropic molecules). This gives rise to susceptibility shifts which may not be compensated by internal referencing.

Some consequences of our findings are:

- Cobaltocenes may serve as ^{13}C and ^1H shift reagents even for aromatic compounds.
- A precise determination of paramagnetic nmr shifts of e.g. metallocene radicals must include the sample concentration.
- Errors may arise in the measurement of magnetic moments with the nmr method.

Students are coming back from holidays now, a fact which considerably limits our research activities. Nevertheless I hope to communicate details of this work soon.

Yours very sincerely

Frank J. Jolani



SIMON FRASER UNIVERSITY, BURNABY, B.C., CANADA, V5A 1S6
DEPARTMENT OF CHEMISTRY; 291-3345

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

18th October, 1979.

Dear Barry,

SINGLE COIL PROBE PROBLEMS

Recently we have been attempting to run broadband DMR on our XL-100 system. In order to obtain the short pulse times and high sensitivity necessary for these experiments we have constructed a high Q. 12 mm., single coil probe. The coil consists of 9 turns, AWG #24 copper wire, 13 mm. I.D. and 9 mm. in length, glued to the inside of a 15 mm. glass tube. The Q is 100 when matched to 50 Ω at 15.4 MHz. Using this probe we have obtained a $\Pi/2$ pulse time of 6 μ s with a transmitter power of 200 watts and a sensitivity(S/N) double that of the Varian V4412 12 mm. probe.

As anticipated, the high Q and single coil geometry cause pulse ringdown problems. With no sample in the probe and the probe removed from the magnet gap we observed approximately 300 μ s of ringing following a 6 μ s pulse, after 1000 acquisitions. This response is due to the dissipation of stored energy in the magnetic field of the coil and cavity. A very effective active₁ probe damper has been designed which has totally eliminated this problem. The damper uses a V-FET connected across the end of a $\lambda/4$ transmission line to reflect a variable impedance to the 50 Ω match point of the coil tuning circuit.

With the active damper in place there is no evidence of ringing phenomena in 100,000 acquisitions of the experiment described above.

As soon as the probe is placed in the magnet gap, however, a new ringing phenomena occurs. This ringing is phase coherent with the driving R.F., and persists for approximately 600 μ s. The peak amplitude is approximately 50 times larger than thermal noise after 4000 acquisitions, and is proportional to the D.C. magnetic field squared, directly proportional to the driving R.F. amplitude, but insensitive to frequency over a range of 30 KHz. We believe that the probable cause is acoustic resonance²⁻⁵. This is the generation of ultrasonic resonant modes controlled by the geometry and composition of the probe walls and/or sample coil, followed by the re-emission of R.F. energy.



/Cont.....

We have tried all of the suggested cures for this "coil disease":

- rigidly fixing all conductors in the probe,
- variations in the size and composition of the coil wire,
e.g. stranded, solid, ribbon, copper, silver, etc.,
- variations in the size and geometry of the coil and probe cavity,
- coating the coil and sideplates in acoustically lossy substances
e.g. RTV
- removing all of the probe except the naked coil, coil former and
connecting co-axial cable from the magnetic field.

None of these attempts produced any significant change in the amplitude of the ringing.

The only success we have had is to use a pulse sequence which causes the F.I.D. to be 180° out of phase with the last applied R.F. pulse before acquisition. For a simple "one-pulse" experiment we use the T1SM experiment from the NTCFT software - i.e.

1. 90° - sample and add - delay
2. 180° - τ - 90° - sample and subtract - delay

This experiment adds the F.I.D.'s while, due to the phase dependence of the ringing, allowing us to subtract the ringing effects in the first acquisition from those in the second. The technique works, but the complications introduced, such as less bandwidth and inaccuracies in the 180° pulse, make it at best a stop-gap solution. If anyone has suggestions to help us with this problem, we would appreciate your communication.

Yours sincerely,

A. Brooke
A. Brooke

T.F. Openshaw
T.F. Openshaw

Bob
R.J. Cushley
Professor

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University of Waterloo



Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Chemistry
519-885-1211

October 19, 1979

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

Dear Barry:

Subject: Micelle Motion in Lyotropic Nematic Phases.

For several years, this laboratory has been involved in a study of lyotropic nematic liquid crystalline phases which spontaneously align in applied magnetic fields.¹ These phases have been classified into two main classes, Type I ($\Delta\chi > 0$) and Type II ($\Delta\chi < 0$) which align such that the director or uniaxis of the liquid crystal is parallel or perpendicular, respectively, with respect to the field. These unique lyotropic liquid crystals are structurally related to hexagonal H_o and lamellar L_o phases in that Type I systems are composed of cylinders of finite length, while Type II systems are composed of disc-shaped micelles of bilayer thickness, and greater than 1000 Å in diameter.^{1,2,3}

A Type I mesophase based on the amphiphile, potassium laurate may be prepared in equilibrium with the hexagonal phase, while a Type II mesophase based on decylammonium chloride may be prepared in which it is in equilibrium with a lamellar phase.⁴ The related co-existent phases have ²H NMR order profiles of the hydrocarbon chains which differ by a constant factor for each position in each of the two cases. The order profile is lowered in the nematic liquid crystals because the micelle units are finite in size and their symmetry axes can oscillate about the director of the mesophase. The accompanying ²H NMR spectrum shows the co-existence region of lamellar decylammonium chloride and Type II disc micelle (DM) decylammonium chloride phases. The lamellar phase which has been aligned by a heating and cooling cycle in the field is assigned on the right half of the symmetrical spectrum, while the spontaneously aligned Type II DM phase is assigned on the left.

An upper limit for the oscillation angle can be estimated to be 27° in the case of the Type II disc shaped micelles and 23° in the case of the finite cylindrical micelles.

-continued-

Sincerely,

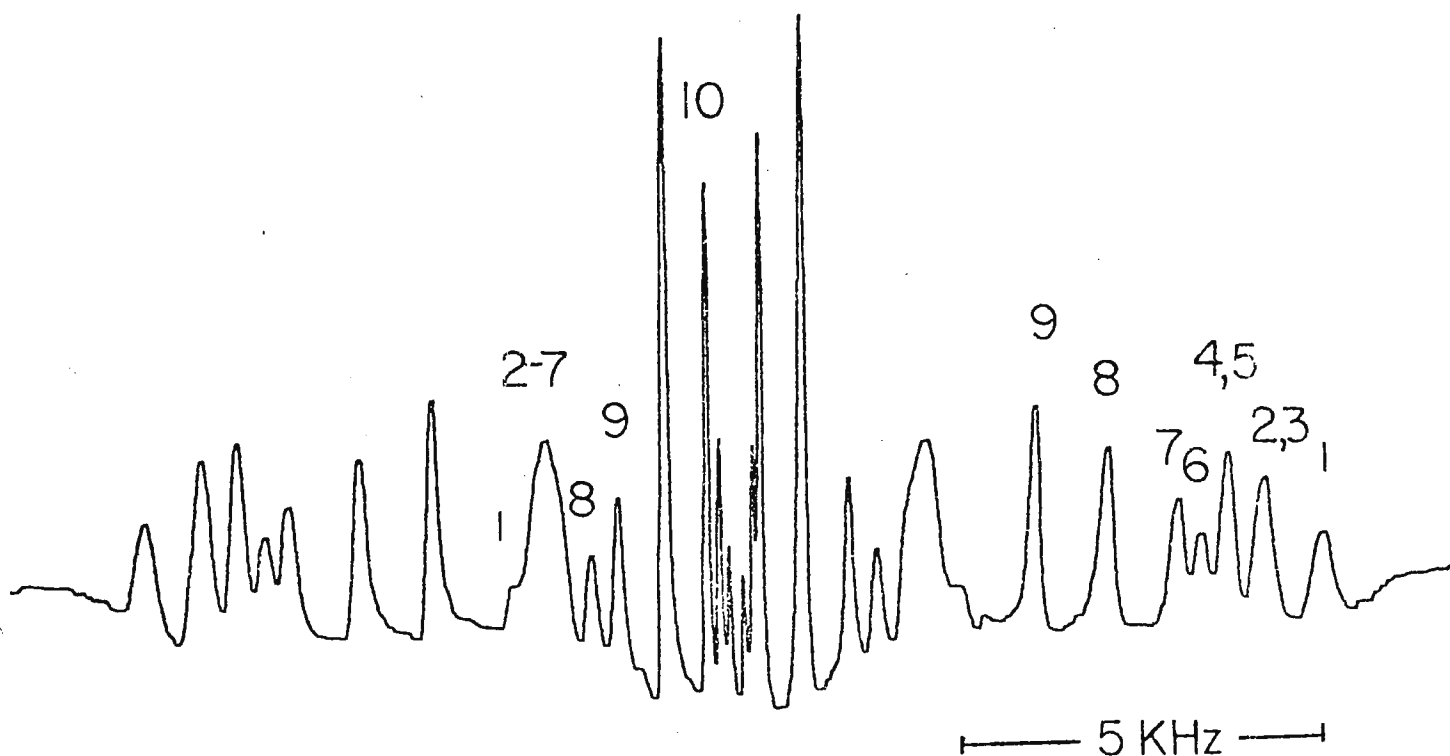
pps B.J. Forrest
 Bruce J. Forrest

L.W. Reeves
 Leonard W. Reeves
 Professor of Chemistry

References

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B-9000 GENT, October 19, 1979

KRIJGSLAAN 271 - S 4
(België-Europa)

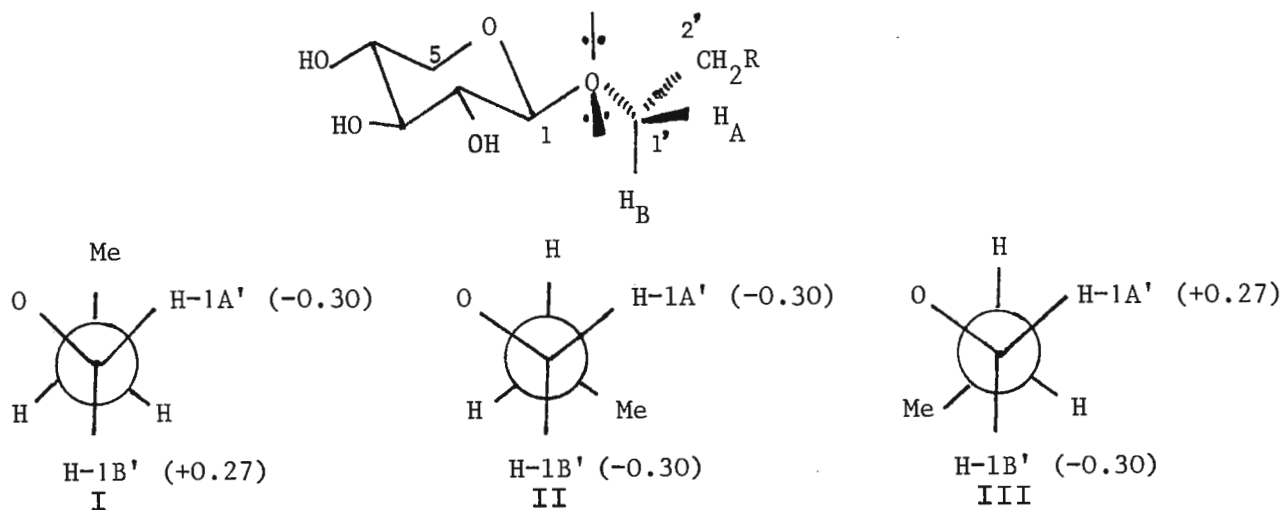
Tel. 22 57 15

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

Dear Barry,

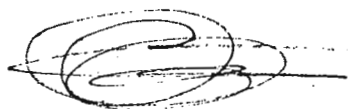
Lopsided rotation around C(1')-C(2') in alkyl osides?

For some years now we have tried to correlate the chemical shifts of the protons in carbohydrates with the effects of the substituents (increments). Although we have shown that this is possible for the conformationally relatively simple O-Methyl osides¹, this is less trivial for higher O-Alkyl chains. Even the chemical shifts of the protons in the chains are not easy to correlate, as f.i. the chemical shifts of H-1A' and H-1B' in Et and n.Pr β -D-xylopyranoside. The non equivalence of H-1A' and H-1B' in both compounds should be viewed as resulting from the contributions of i.a. the rotameric states around C(1')-C(2'), as shown in the figure.

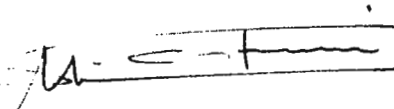


We calculate with the aid of earlier determined increments³ (figure, data between brackets) that both H-1A' and H-1B' should suffer from the same upfield effect of -0.11 ppm in the n.Pr oside. We find for H-1A' -0.17 ppm and for H-1B' -0.12 ppm. A slight lopsided rotation around C(1')-C(2') (e.g. 31% I, 46% II and 23% III) would account for this. Unequal rotor-populations around ω were also noticed in gentiobiose⁴.

Sincerely yours,



André DE BRUYN.



Marc J.O. ANTEUNIS.



LABORATORIUM
VOOR
ORGANISCHE CHEMIE

B-9000 GENT, 18.10.1979

KRIJGSLAAN 271 - S 4
(België-Europa)

Tel. 22 57 15

REFERENCES:

1. A. De Bruyn, M. Anteunis and P. Kovac; Collection Czechoslov. Chem. Comm. 42 (1977) 3057.
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4. D.A. Rees and W.E. Scott; J. Chem. Soc. (B) (1971) 469.

TABLE. The chemical shifts in δ from TMS-internal of Et and n.Pr β -D-xylopyranoside in wet CDCl_3 , at 360 MHz, conc. $\sim 2\%$.

Chemical shifts	H-1	H-2	H-3	H-4	H-5A	H-5B	H-1A'	H-1B'	Δ	CH_2	CH_3
Et β -D-xylopyranoside	4.27 ₅	3.38 ₀	3.50 ₃	3.66 ₆	3.90 ₆	3.28 ₈	3.91 ₁	3.61 ₁	0.30	—	1.25
n.Pr β -D-xylopyranoside	4.28 ₀	3.39 ₇	3.50 ₇	3.67 ₇	3.96 ₇	3.26 ₉	3.74 ₁	3.49 ₄	0.24	1.64	0.92

University of Illinois at Urbana-Champaign

School of Chemical Sciences
Urbana, Illinois 61801

October 23, 1979

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

Dear Barry:

NSF Midwest Regional Instrumentation Facility:
Positions Available.

We have recently been funded by NSF to establish a Regional Instrumentation Facility in Nuclear Magnetic Resonance Spectroscopy, to serve primarily the Midwestern United States, and as a result a number of positions are now available.

The equipment available to the Facility will include the following supercon systems:

1. 500 MHz 2" bore FT system for ^2H , ^{13}C and ^1H
2. 360 MHz widebore FT system for ^{13}C , ^2H and solid-state NMR
3. 360 MHz narrowbore FT system (NT-360) for ^1H , ^{13}C solution studies
4. 250 MHz widebore FT system for ^{13}C in solids, large sample multinuclear NMR
5. 220 MHz widebore FT system for ^2H in solids
6. 220 MHz narrowbore system (HR-220) for solution ^1H FT NMR
7. 150 MHz widebore system for ^{13}C in solids and liquids

In addition, a variety of other systems (multinuclear large sample XL-100, HA-100, FX-60, two EM-390's, T-60, wideline, X and Q-band EPRs) will be accessible to Facility users.

The positions currently available are as follows:

1. Spectroscopist, (\$22,000). We require a Ph.D. level NMR spectroscopist to assist in the construction of the 500 MHz, and 250 MHz "solids" NMR instruments. Candidates should have demonstrated a capability in the construction of FT NMR instrumentation, and will be expected to maintain an active program of instrumentation development to keep the Facility current in terms of new capabilities as they are developed in other research centers and at Illinois. This position will be of a continuing nature.

2. Research Associate (\$12-13,000). A two year appointment as an instrumentation-specialist postdoctoral Research-Associate is available for work on probe and spectrometer developments (cooled-coil and preamp high-sensitivity probe; sensitivity optimization for high-field sideways-spinning and magic angle experiments) and demonstration of improved capabilities on a variety of chemical and biochemical systems.
3. Assistant Spectroscopists (B.S. level; 2 positions; \$11-12,000). Two positions are available for B.S. level employees to be responsible for obtaining spectra for Facility users. Candidates should have some experience in operation of NMR instrumentation, preferably using Fourier transform techniques. These positions will be of a continuing nature.

Applicants should submit a curriculum vitae and arrange for three letters of recommendation to be sent to me as soon as possible. It is hoped that the Facility will begin operation in the Spring of 1980.

Yours sincerely,



Eric Oldfield
Assistant Professor
of Chemistry

E0:kjb

Northern Illinois University 
DeKalb, Illinois 60115

The Michael Faraday Laboratories
Department of Chemistry
815 753 1181

October 24, 1979

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

ISOTROPIC SHIFTS IN NATIVE CYTOCHROME C PEROXIDASE AND COMPOUND-I;
POSITION AVAILABLE: ELECTRONICS ENGINEER.

Dear Barry:

For the past nine months professor James Erman and I have been studying the properties of cytochrome c peroxidase. This enzyme is isolated from yeast, contains an Fe^{3+} -heme and reacts with H_2O_2 . The reaction with H_2O_2 produces CcP-I, compound I, which is formally at an oxidation state two equivalents above the native state and is formulated as an Fe^{4+} -heme accompanied by an oxidized amino acid side chain which appears as a free radical. The subsequent in vivo reaction of CcP-I is viewed as a return to the native state by way of consecutive one electron transfers from molecules of reduced cytochrome c.

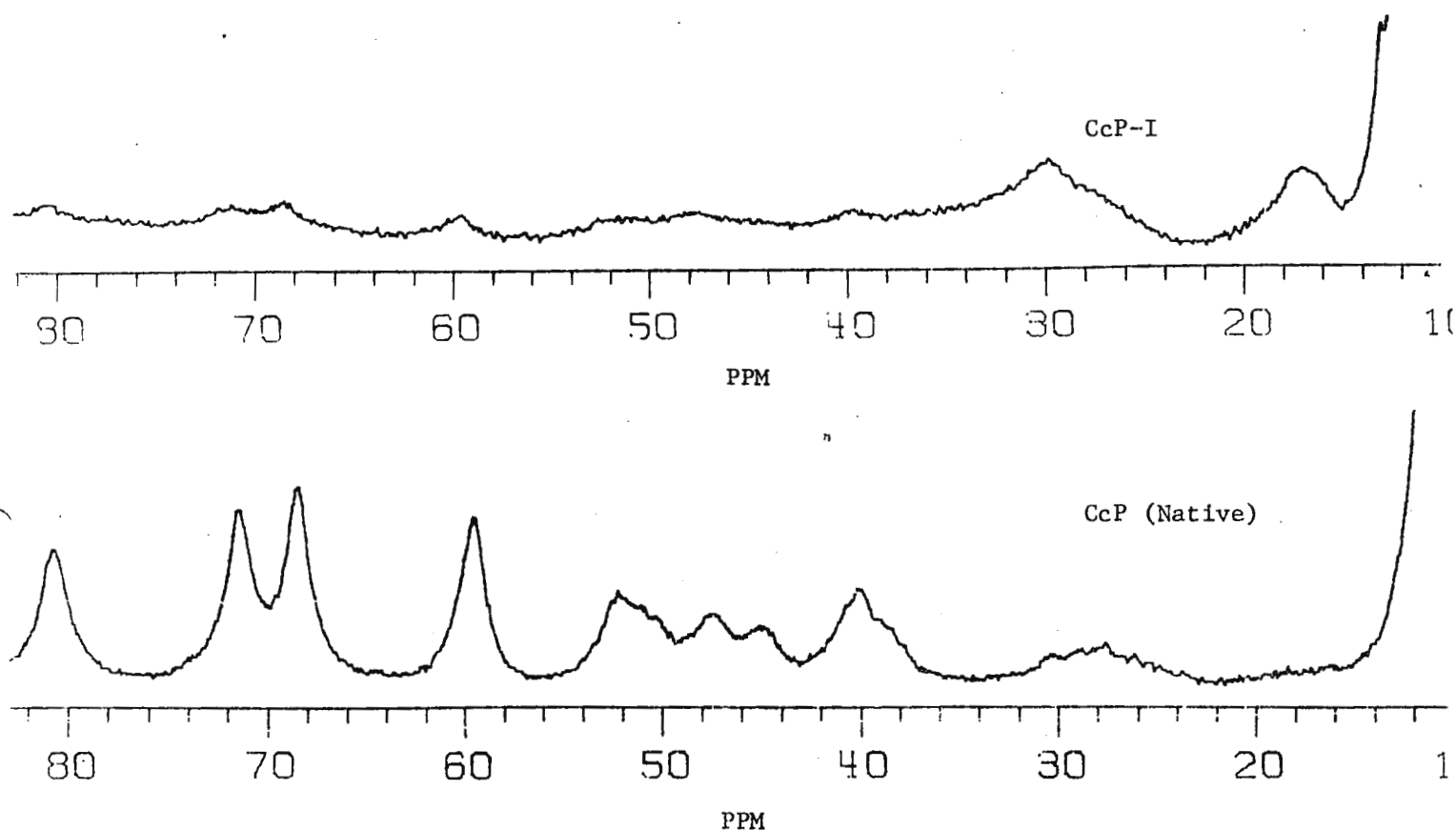
With the chemistry of iron porphyrins being rapidly expanded to include stable Fe^{4+} compounds we have sought to characterize the compound-I form of CcP by nmr. The figure shows that the isotropic resonances characteristic of the high spin Fe^{3+} -heme native protein are lost upon oxidation with H_2O_2 and are replaced by at least two other isotropic resonances 30 and 16 ppm downfield from dss. The resonance pattern we observe for CcP-I is quite different than that observed for horseradish peroxidase compound-I and because of this we believe that CcP-I is a low spin species. We should also like to point out that to our knowledge these are the first CcP nmr spectra to appear in print.

Please note that we have a position available for a person to support our nmr and laser facilities as described below. Please credit this contribution to the NIU-NMR group.

Sincerely,



James D. Satterlee
Assistant Professor of Chemistry



ELECTRONICS ENGINEER

Creative, highly-motivated person sought to interact with and support a chemistry faculty engaged in NMR, laser, micro/mini-computers, and other research programs. Design capabilities in modern digital, analog, RF electronics required. Involves some supervisory responsibility. Send resume to Professor Peter Daum, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. Northern Illinois University is an Affirmative Action/Equal Opportunity employer.

CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY



October 29, 1979

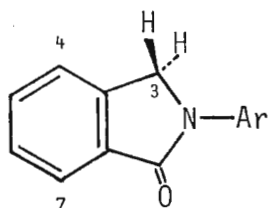
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Dear Barry:

Proton Spin-Lattice Relaxation of N-Aryl Heterocycles

On my recent leave, which I spent working with Laurie Hall at the University of British Columbia, my experimental work involved ^1H spin-lattice relaxation studies. These were carried out using the 270 MHz "home-built" spectrometer (TAMU NMR Newsletter, 238, 19 (1978)) and the inversion-recovery pulse sequence.

Among the compounds we looked at were some of our N-aryl-substituted heterocyclic compounds which may show biphenyl-like isomerism, and for which we have been examining inter-ring interactions. These included a series of N-aryl isoindolinones (prepared by M.A. Khadim), which have low barriers to internal rotation, and which do not show splitting of the diastereotopic 3-methylene signals as low as -150° (100 MHz).



The series, whose members differ in their N-aryl group substitution patterns, show a 4.3-fold dynamic range of ^1H R_1 values. Since the molecular tumbling rates are affected by changes in substitution on the aryl group, a normalization procedure is necessary to minimize correlation time effects if relaxation rates of compounds within the series are to be compared. In this case, the R_1 values were normalized with respect to that of the remote 7-proton within the invariant isoindolinone moiety, on the assumption that this proton would not be directly affected by changes in the aryl group.

The 3-methylene protons are the fastest relaxing; the isolated aromatic protons, e.g. H-7, are the slowest. We could identify the effects of methyl and methoxyl groups on relaxation rates of aryl group protons. The normalized rates show that a significant inter-ring relaxation pathway exists between the 3-methylene protons and ortho-substituents on the aryl group.

Relaxation rates were measured by the null point method and, in a number of cases, also by non-linear regression calculations; in general, good agreement was obtained.

Best regards,

Yours sincerely,

A handwritten signature in cursive script, appearing to read "Laurie".

L.D. Colebrook
Professor of Chemistry

LDC/ac

UNIVERSITY OF CALIFORNIA, DAVIS
NUCLEAR MAGNETIC RESONANCE FACILITY
Davis, California 95616

"SYMPOSIUM ON BIOLOGICAL AND BIOMEDICAL NMR SPECTROSCOPY"
March 27 - 28, 1980

October 3, 1979

Dear Barry:

The University of California, Davis marks the installation of a new high field biological NMR facility and the appointments of E. M. Bradbury and G. N. LaMar as facility co-directors by sponsoring a program on biological applications of NMR.

An excellent group of speakers has been included in the symposium sessions, to ensure that both scientists with extensive NMR experience and workers with future interest in NMR as a tool in biological and medical sciences will benefit from the conference.

The scientific program will consist of four sessions featuring invited speakers plus a poster session for submitted papers. A partial list of participants include:

I Nucleic Acids

D. R. Kearns	"Dynamics and Conformational States of DNA"
R. Hurd	" ¹ H NMR Studies of Transfer RNA in Solution"
D. J. Patel	"Structure and Dynamics of Drug Nucleic Acid Interactions in Solution"
E. M. Bradbury	"Interaction of Chromosomal Proteins with DNA"

- continued -

REGISTRATION

A preliminary registration form is attached below. Please use this form to indicate your intention to attend the conference and to ensure that your name will be included on the mailing list when further notices are mailed. If others in your laboratory group also plan to attend, please indicate their names on this registration form. Final registration forms will be mailed at a later date. See reverse side for further information.

Preliminary Registration Form

Name _____
(last) (first)

Title _____

Name of Institution or Company _____

Address _____

I (do) (do not) wish to present a paper at the poster session. Give title if you wish to present.

Others from laboratory who plan to attend _____

II Peptides and Proteins

- W. A. Gibbons "Studies of Conformation and Hydrogen Bonding in Complex Peptides Using Proton Relaxation Spectroscopy"
- T. Miyazawa "NMR Studies of Molecular Conformations, Hydrogen Bonding and Thermodynamics of Protons"
- G.C.K. Roberts "NMR Studies on the Specificity in Small Molecule Binding to Dihydrofolate Reductase"
- O. Jardetzky "Protein Internal Motions"

III Metalloproteins

- B. D. Sykes "Determination of the Structure of Parvalbumin in Solution from Lanthanide Induced H-1 NMR Shifts"
- I. M. Armitage "Cd-113 and C-13 NMR Studies of Metallothionein"
- G. N. LaMar "H-1 NMR Studies of Iron Heme-Protein Interactions"
- J. L. Markley "NMR Studies of Electron Transport Proteins"

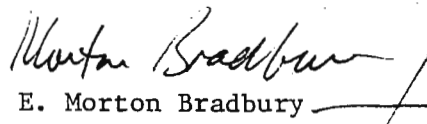
IV In - Vivo

- J. Schaefer "Magic Angle N-15 NMR Studies of Plant Metabolism"
- R. G. Shulman "C-13 and P-31 NMR Studies of Cells and Tissues"
- R. C. Lauterbur "NMR Zeugmatographic Smaging Employing H-1 and P-31"
- E. R. Andrew "NMR Imaging in Biology and Medicine"
- D. P. Hollis "Phosphorous NMR Studies of Myocardium"

Yours truly,



Jerry L. Dallas



E. Morton Bradbury

For further information or aid in arranging registration or accommodations, contact members of the organizing committee:

E.M. Bradbury, Department of Biological Chemistry (916) (752-2927)
 G.N. La Mar, Department of Chemistry (916) (752-0958)
 R.S. Criddle, Department of Biochemistry (916) (752-1949)
 J.L. Dallas (Symposium Secretary), UCD NMR Facility (916) (752-7677)

Place
Stamp
Here

J.L. Dallas
 NMR Facility
 Department of Chemistry
 University of California
 Davis, CA 95616
 U.S.A.

You are invited...

to participate in a workshop on High Resolution Nuclear Magnetic Resonance with emphasis on the latest experimental and theoretical developments in multinuclear, high field and solid state NMR. This meeting will take place on the campus of Case Western Reserve University, Cleveland, Ohio, December 18-19, 1979. The sponsor of this workshop is the Materials Research Laboratory with participation of the Chemistry, Macromolecular Science and Pharmacology departments.

WORKSHOP ON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Program

Dec. 18, 1979

Millis Lecture Hall

9:00-10:00 AM Registration

Session I: Opening Plenary Session

10:00-10:15 Opening Remarks, J.L. Koenig, Chairman

10:15-10:30 Welcoming Remarks

E. Baer, Dean, Case Institute of Technology

A. Heuer, Director, Materials Research Laboratory

10:30-11:45 Plenary Lecture Chairman: H. Sternlicht, CWRU
"Principles and Application of Two Dimensional NMR Spectroscopy"

R. Ernst

Eidgenössische Technische Hochschule

Zurich, Switzerland

Luncheon

Session II: High Field NMR Chairman: R. Mooney, SOHIO

1:15-2:00 PM Invited Lecture
"Pulse FT and NOE Study of t-RNA"

A. Redfield

Brandeis University

2:00-2:40 "Application of NMR in Studies of Drug Action"
H. Sternlicht and J. Mieyal
Case Western Reserve University

2:40-3:00 Coffee break

3:00-3:45 Invited Lecture
"Application of Scaling Techniques in the Simplification of ^{13}C Spectrum"
R. Ernst

4:00-4:45 "Reductive Methylation using ^{13}C -formaldehyde: A Probe for Biological Amino Groups"

T. Gerkin

Case Western Reserve University

4:45-6:00 Open House--NMR Facilities

High Resolution NMR for Solids

Department of Macromolecular Science, 207 Olin Bldg.

MAIF Multinuclear NMR Facility

Department of Chemistry, 206N Millis Science Center

High Field NMR Facility

Department of Pharmacology, W344 Medical School

Dec. 19, 1979

Session III: Multinuclear NMR Chairman: C. Carman, B.F. Goodrich
 8:30-9:15 AM Invited Lecture
 "NMR of the Low Frequency Metal Nucleides"
 O. Gansow
 Michigan State University
 9:15-10:00 Invited Lecture
 "NMR of Inorganic Glasses"
 P. Bray
 Brown University
 10:00-10:15 Coffee break
 10:15-10:45 "Dynamic ^{77}Se and ^{31}P NMR Studies of Transition Metal Complexes"
 J. Fackler
 Case Western Reserve University
 10:45-11:30 Invited Lecture
 "Application of Saturation Transfer and Isotopic Perturbation
 Techniques to Dynamic NMR"
 J. Faller
 Yale University
 11:30-12:00 "Application of ^{17}O and ^{15}N NMR to Studies of Water, The
 Hydronium Ion and Nucleic Acid Bases"
 G. Mateescu
 Case Western Reserve University

Luncheon

Session IV: NMR of Solids Chairman:
 1:30-2:15 Invited Lecture
 "Application of Solid State ^{13}C NMR in Semicrystalline
 Polymers: Expectations for Resolution using Magic Angle
 Sample Spinning"
 D. L. VanderHart
 National Bureau of Standards
 2:15-3:00 Invited Lecture
 "Variable Temperature High Resolution NMR of Organic Solids"
 C.S. Yannani
 IBM Corp.
 3:00-3:30 Coffee
 3:30-4:00 "Multiple Field Studies of Solids"
 W. Ritchey
 Case Western Reserve University
 4:00-4:30 "High Resolution ^{13}C NMR of Polymers"
 J. L. Koenig
 Case Western Reserve University

For further information contact Dr. Jack L. Koenig
 Department of Macromolecular Science
 Case Western Reserve University
 Cleveland, Ohio 44106
 (216) 368-4176

Standard Oil Company (Indiana)

Amoco Research Center
P.O. Box 400
Naperville, Illinois 60540
312-420-5111

October 22, 1979

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

Carbon-13 NMR Study of Polymer Melts

Dear Barry:

One of the problems we frequently encounter in our laboratory is the analysis of polyolefins such as polypropylene, polyethylene and ethylene-propylene copolymers using ^{13}C nmr. This analysis is generally carried out on 10% (w/v) solutions of the polymer in ortho-dichlorobenzene or 1,2,4-trichlorobenzene at 130°C. On our instrument (CFT-20) we found that the signal-to-noise of the spectrum was severely instrument limited. Figure 1 shows two spectra of the methyl region of an ethylene-propylene copolymer. The top spectrum represents the transform of 8K transients. The bottom spectrum represents the transform of only the first 4K transients of the total 8K transients collected. Not only does the S/N not increase by $\sqrt{2}$ in the 8K spectrum, the noise pattern in both spectra is identical! This implies that useful signal averaging was completed before 4K transients were acquired. We attribute this effect to dynamic range limitation caused by the large intensity of the solvent resonances relative to the small intensity of the polymer resonances.

Our first solution to this problem was to run all samples as 10% solutions in tetrachlorothiophene because all the carbon atoms in this solvent have long T_1 's which greatly reduce the solvent resonance intensities. This allowed us to do real signal averaging for longer times. However we still required overnight acquisitions to obtain sufficient S/N to carry out quantitative experiments. In order to reduce the experimental times we have been acquiring data on "melts." The polymer is placed in an nmr tube with about 10% (v/w) of trichlorobenzene. The tube is then placed in an oil bath at 160°C until the sample is molten. The solvent helps decrease the viscosity and also aids in the removal of trapped air bubbles which can be eliminated by applying a house vacuum to the molten sample. Finally, a lock signal is obtained from a 4 mm o.d. capillary of perdeuteroethylene glycol which is coaxially centered in the 10 mm sample tube using Wilmad Teflon sleeves. We find that by using melts we are able to reduce our

experiment time from 16 hours to 1 hour per sample. Figure 2 shows a 10% solution spectrum acquired in 16 hours at 130° and a melt spectrum obtained in 1 hour at 160°C for an ethylene-propylene copolymer. Although the melt spectrum shows some loss in resolution due to viscosity, it is not sufficient to interfere with the analysis.

Finally, we have found that a combination of running melts at 160° plus using a double precision acquisition program supplied by Steve Patt of Varian is necessary to detect chain branching in high density polyethylene. Figure 3 shows the spectrum of a high density polyethylene under the trade name DMDJ 7006. A spectrum of the same material was recently given by Spevacek¹ who used 20% solutions at 120° and 16 hour acquisitions. The S/N shown here is at least an order of magnitude better for the same time. Not only are the branch carbons clearly observed but resonances due to chain termination are also easily discerned.

Yours very truly,

Joe

G. J. Ray
Mail Station F-9

GJR/jh
Att

¹ J. Spevacek, Polymer, 19, 1149 (1978).

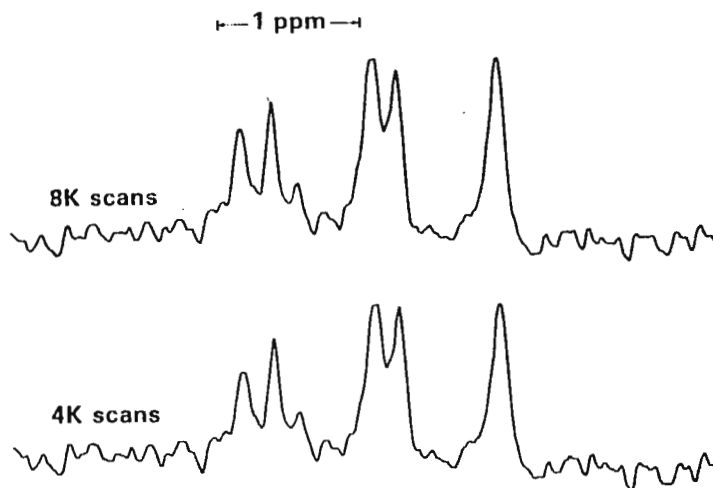


Figure 1. The ^{13}C nmr spectrum of the methyl region of an ethylene-propylene copolymer.

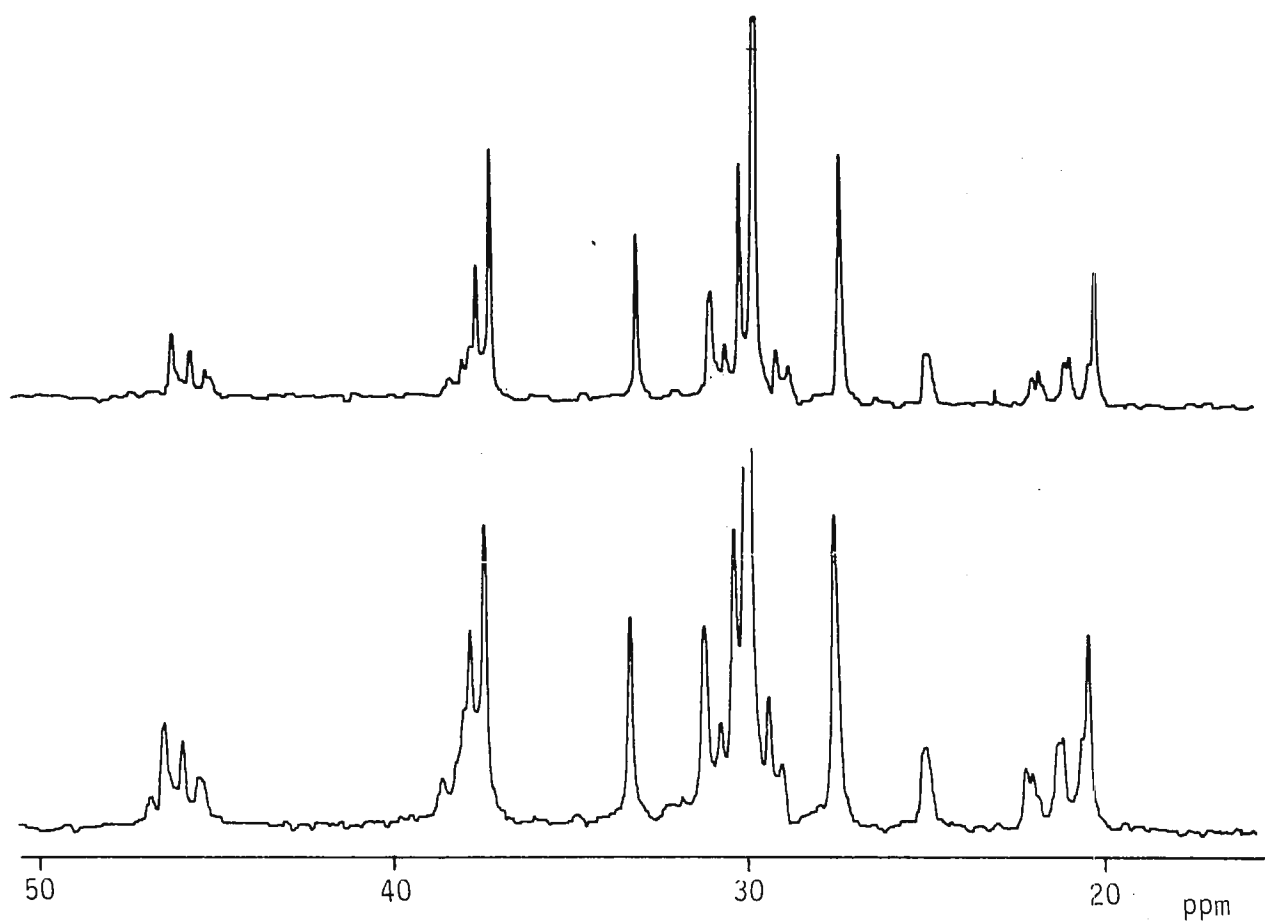


Figure 2. The ^{13}C nmr spectra of an ethylene-propylene copolymer.
 Top: 16 hour acquisition on a 10% solution.
 Bottom: 1 hour acquisition on a melt.

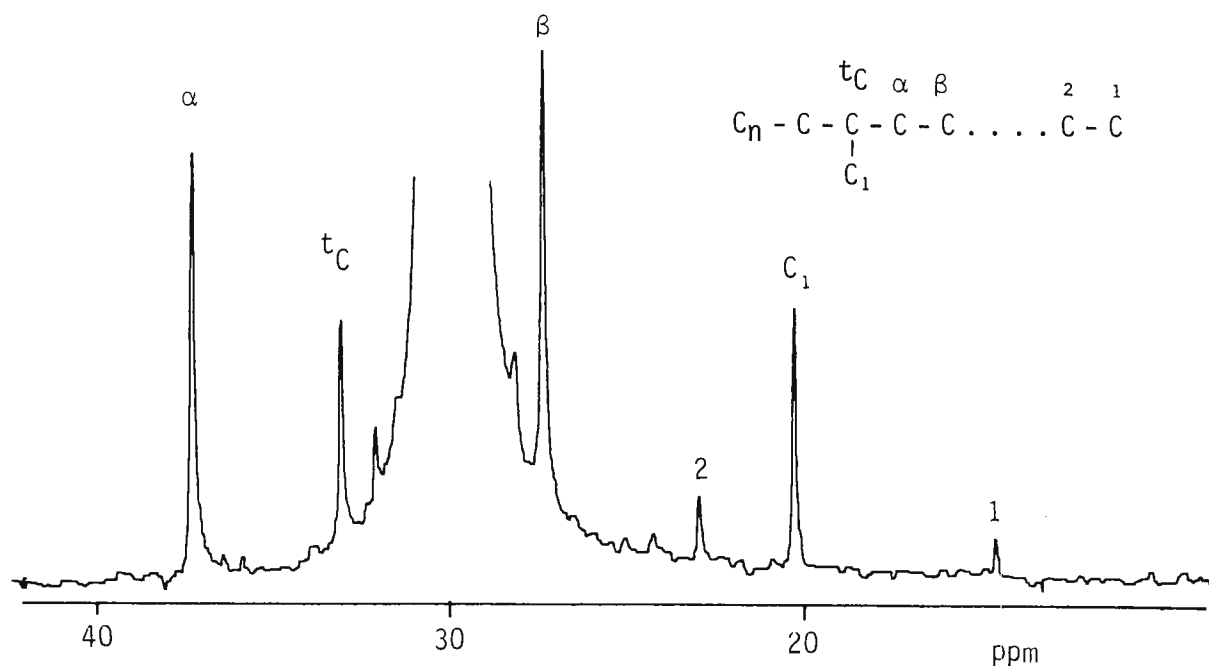


Figure 3. The ^{13}C nmr spectrum of a polyethylene sample - 16 hour acquisition on a melt.

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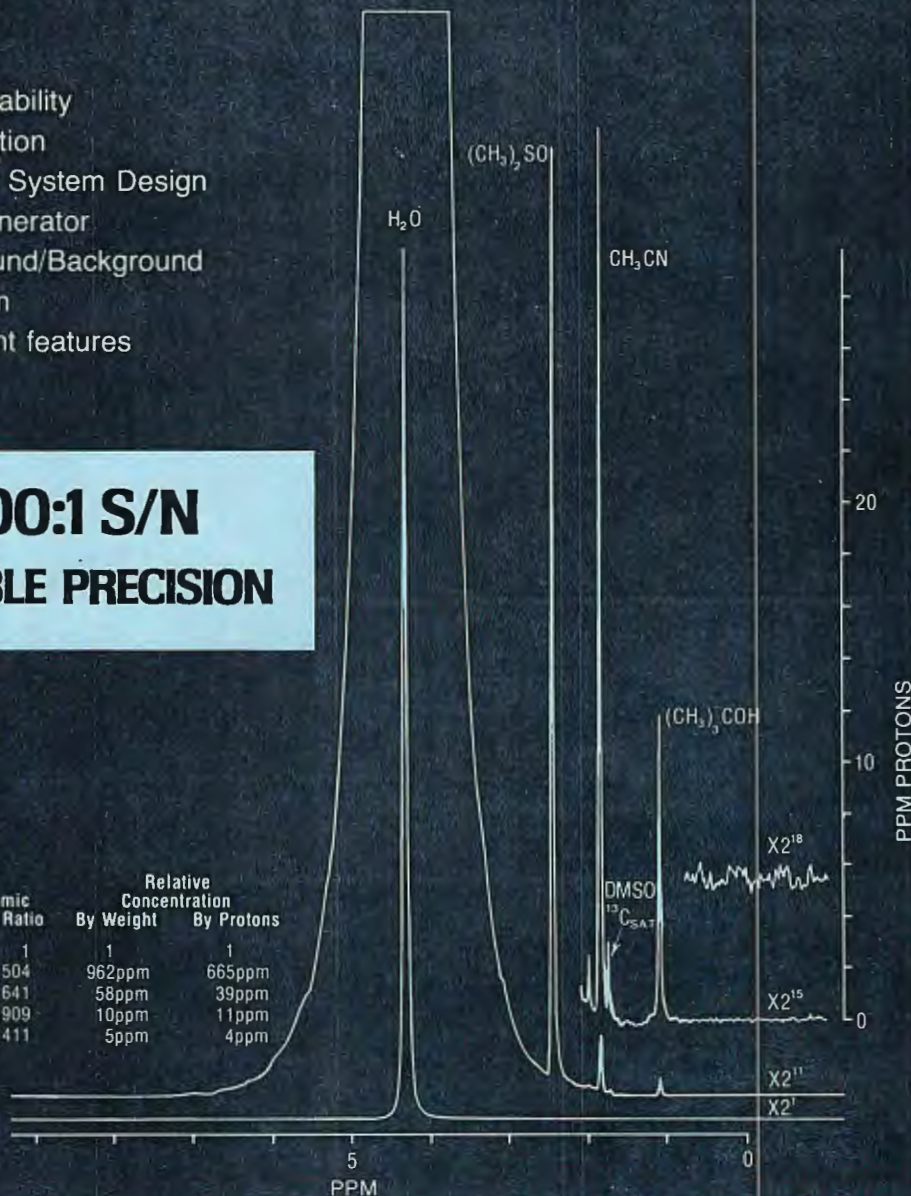
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Acetonitrile	0.06	0.0039%	25,641	58ppm	39ppm
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