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No. 175

University

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April, 1973

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Deadline Dates: No. 176: 7 May 1973

No. 177: 4 June 1973

All Newsletter correspondence, etc. should be addressed to:

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

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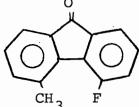
March 5, 1973

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

"Through-Space ⁵J_{CF}"

Dear Professor Shapiro:

We have observed a long-range carbon-fluorine splitting of 18 Hz (in CDCl₃ and CD₃COCD₃) between the methyl carbon and the fluorine in the $^{13}\mathrm{C}$ spectrum of 4-methyl-5-fluorofluorenone, a compound for which we previously reported $^{6}\mathrm{J}_{\mathrm{HF}}$ = 8.3 Hz, between the methyl protons and fluorine. 1



 5 J $_{\rm CF}$ = 18 Hz

This very large coupling between carbon and fluorine, separated by five bonds, but close in space, is consistent with the recent results of Jerome and Servis² with 4-methyl-5-fluorophenanthrene derivatives and further supports the notion of "through-space" coupling in these bridged-biphenyls. ¹

The spectrum was determined with the Varian XL-100-15 system at the General Electric Research and Development Center with the assistance of J.D. Cargioli.

Please credit this contribution to the account of P. R. Shafer.

Sincerely yours,

Jordon W. Mubble
Gordon W. Gribble
Assistant Professor

Kenneth Clark

Assistant Professor of Chemistry

GWG:wo

- 1. G.W. Gribble and J.R. Douglas, Jr., <u>J. Amer. Chem. Soc.</u>, <u>92</u>, 5764 (1970).
- 2. F.R. Jerome and K.L. Servis, <u>ibid.</u>, <u>94</u>, 5896 (1972).

Carr Laboratory, Department of Chemistry MOUNT HOLYOKE COLLEGE

South Hadley, Massachusetts 01075

Telephone 413 538-2214



12 March 1973

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

INCREASING THE POWER OF THE VARIAN V-3512 NOISE DECOUPLER

Dear Barry;

The following modification to our Varian V-3512 Noise Decoupler may be of interest to your readers:

The maximum output of the V-3512 has been increased from a nominal 7 watts into a 100 ohm load to a value of 40 watts into a 50 ohm load. We have found that this modification has enabled us to sufficiently noise decouple the entire proton region with a 20-22 watt output and bandwidth of 1200-1500 Hz. The schematic of the additional amplifier is shown in Figure I. The heart of this amplifier is the RF power transistor (2N5643). Please note that this piece of equipment is easily removed from the decoupler for low power single frequency decoupling. Since we have the Digilab Data and Pulsing system the final stage of the V-3512 required a slight modification to provide a 50 ohm impedance for proper matching to the probe. It is highly recommended that a SWR meter be placed in the line between this amplifier and probe as care must be taken in tuning the system.

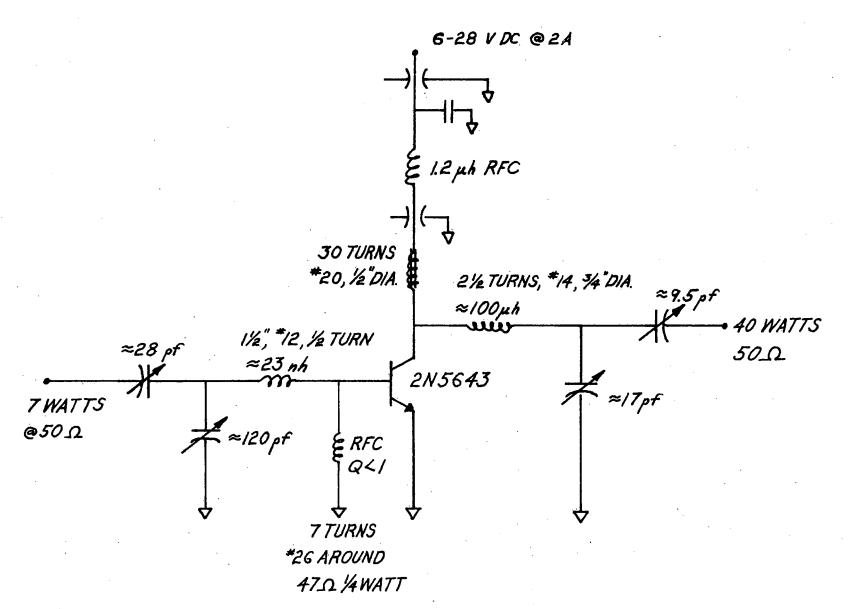
Further details on the design and construction will be furnished upon request.

Sincerely,

D. R. Clutter K. L. Williamson

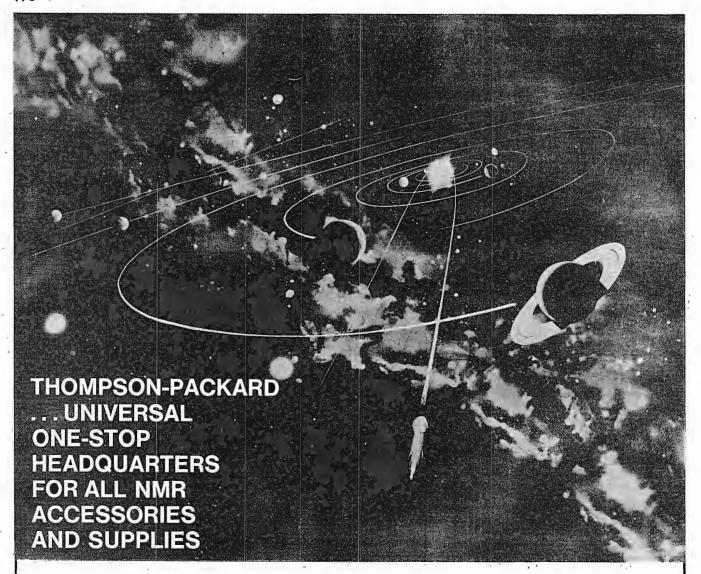
A. Chase

DRC/jrl



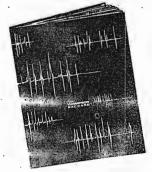
AMPLIFIER FOR VARIAN V-3512 NOISE DECOUPLER Dr. Dale Clutter and Artner Chace Mount Holyoke College

Figure 1



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TEL.: 050 - 11

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

U.S A.

Groningen, 12 March, 1973.

Heat protection for XL-100 probe.

Dear Prof. Shapiro,

The protection described here is used during high power decoupling on a Varian XL-100. It switches the decoupler to low power when the nitrogen-flow, used for cooling, becomes too low, this preventing overheating of the decoupler coil area.

We used the pressure switch S 402 of the variable temperature unit to dectect a too low (or too high) flow. The original diagram of the temperature unit was changed as indicated in the diagram.

The S 705 high power - low power switch has a spare section which is used to switch the base of the BSX 20 transistor. On low power the relay is always energized, independant of the nitrogen flow.

On high power decoupling, an and gate formed by D₁ and D₂ allows only energizing of the relay if lamp DS 402 is on. DS 402 is only on when the flow is normal. When the flow becomes too low DS 402 is short circuited by the pressure switch. The relay is de-energized and switches from high to low power. When the flow is brought back to normal the relay can be energized again by quickly switching S 705 form high power to low power and back to high power.

When the used relay is very fast or when it is preferred to leave S 705 on high power it is possible to install a reset switch (see dotted lines in the diagram).

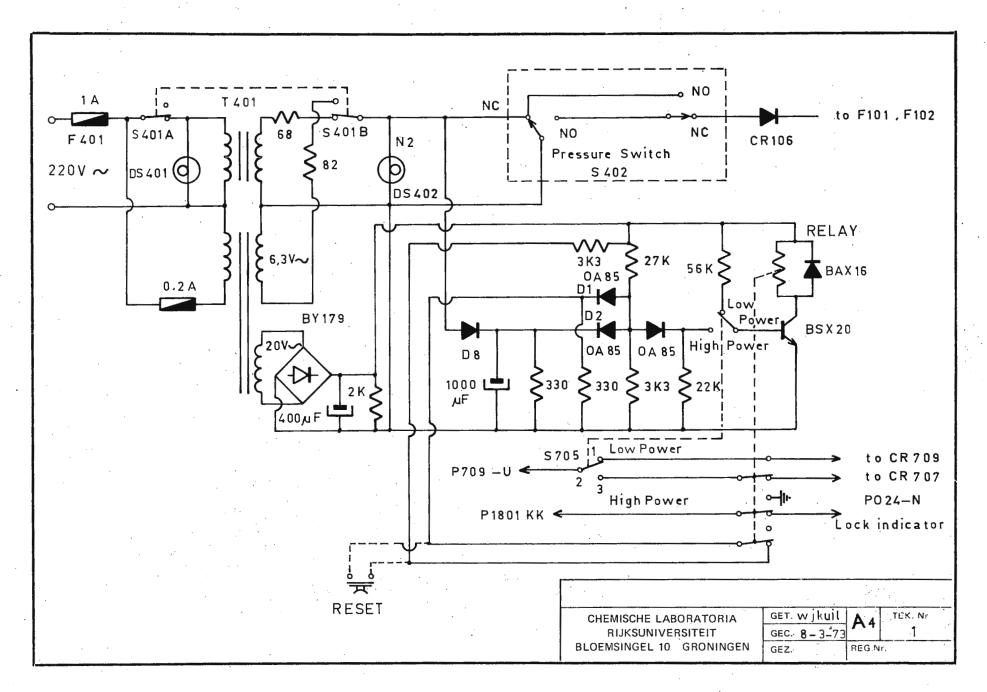
When the protection switches from high to low power, accumalation of spectra is stopped by interrupting the lock indicator line (see diagram).

Sincerely yours,

Mr de Rapper

M. de Rapper.

J. Runsink.



UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

DEPARTMENT OF CHEMISTRY

March 5, 1973

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

Dear Barry:

We have recently used our JEOL PFT-100 13 C probe to measure 51 V and 23 Na resonances. These experiments were performed using internal 2 H lock at 15.3584 MH_z and a frequency synthesizer to generate the 26.29 and 26.45 MH_z Signals needed for these two nuclei. Neither the probe nor any of the preamps were returned so the S/N of the spectra have not been optimized, but the results clearly show that good spectra for these two nuclei can be obtained with a 13 C probe at no extra expense if a frequency synthesizer is available. Spectra are shown in Figs. 1 and 2. The 51 V was present as 1M VO $_4$ in 1M KOH in D $_2$ O. 23 Na was in 1M NaCl in D $_2$ O.

Best regards,

mel

M. W. Hanna

Professor Chemistry

Title: ⁵¹V and ²³Na NMR Using a JEOL ¹³C Probe.

51 V AS VO4 1 M IN 1 M KOH 26,29 MHZ 32 SCANS Δν=78.1 HZ

23 Na IN IM NaCC/D2O 26.45 MH2 32 SCANS AVI : 12,2H2 ABBOTT LABORATORU V AGIENTITIC DIVISIONS NORTH CHICAGO VILINOIS 60064

March 19, 1973

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

Dear Dr. Shapiro,

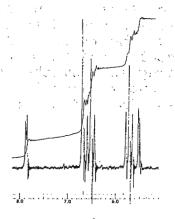
A CASE OF HETERONUCLEAR VIRUTAL COUPLING

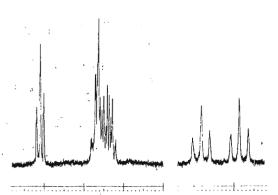
The 'H nmr spectrum of neat 2-chloro-1,1,2-trifluoroethyl difluromethyl ether,

HC1FC-CF $_2$ -O-CF $_2$ H, exhibits an unusual feature which caused us some concern when first observed. The proton of the chlorotrifluoroethyl group gives rise to a doublet of triplets multiplet (6.11 ppm; $J_{H-C-F} = 42.0 \text{ Hz}$; $J_{H-C-C-F} = 4.5 \text{ Hz}$) as expected; however, the triplet expected for the difluoro-

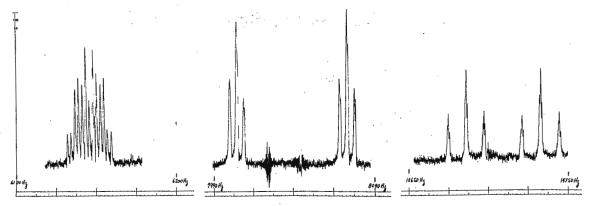
methyl group (6.78 ppm; J_{H-C-F} = 69.5 Hz) has additional fine structure on the outermost lines.

An explanation for this phenomenon was suggested when the 19 F nmr of the same neat sample was examined. The resonances of the CF_2 and CHClF groups of the chlorotrifluoroethyl group are overlapping and since these groups are strongly interacting a $^{19}\mathrm{F}^{-1}\mathrm{H}$ virtual coupling between the CHClF proton and the CF_2 group arises. LACCN3 calculations using suitable parameters reproduce the fine structure and confirm the explanation.





A complete analysis of the $^{19}{\rm F}$ spectrum is possible in DMSO- d_6 solution where there is no overlap.



Group	Position (ppm $\frac{1}{4}$)	Coupling Cons	stan	ts	
C-CF ₂ -O	+ 65.3	J _{F-C-F}	not Δν		served 2.0 Hz
		J F-C-C-F		=	11.4 Hz
	•	J _{F-C-C-F} J _{F-C-C-H}		=	4.5 Hz
$C\underline{F}_2H$	+ 85.4	J _{F-C-H}		=	69.0 Hz
-		J _{F-C-O-C-F}		=	4.5 Hz
		J _{F-C-O-C-C-F}		=	0.6 Hz
CHC1 <u>F</u>	+156.2	J _{F-C-H}		=	46.5 Hz

^{*} upfield from internal CFC13.

Singerely,

Richard S. Egan nmr 1ab, D-482

msg



The University of Sydney

SYDNEY, N.S.W. 2006

IN REPLY PLEASE QUOTE:

Department of Organic Chemistry

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

2nd March, 1973

Dear Barry,

Comparative Performance of 23.5 kG, 12" Narrow Gap Varian Magnets

When we first took delivery of our XL100/12 system we were rather disappointed with its resolution, which was not significantly better than that of our HA100D operating in frequency sweep mode. A survey, summarized in the attached table, of a significant proportion of XL100/12 owners - a rare breed - convinced us that our machine was not too bad and that for a really good performance you should take an axe to one of the magnet coils (see footnote 2). We have also carried out informal enquiries among XL100/15 owners and found that the resolution is not much better, but line-shape may be. A very careful comparison of the five HA100 systems in Australia showed that the resolution was fairly uniform, with our system a clear winner by a nose, once the polarities were properly connected (after two years). With research samples, of course, sample preparation (i.e., degassing, filtering, removing paramagnetic impurities, good tubes) is critical.

In our constant battle to achieve and retain resolution, we have concluded that tents and super air conditioning appear to be of marginal value, but that mechanical shimming, probe positioning, spinner housing alignment, coil positioning, spinning rate, dirt in the probe and - above all - patience with shimming, are important. On occasions when our resolution fell significantly below the sort of figures shown in the table, a fault or error of some sort was to blame and we believe that line widths of more than 0.3 Hz at 500 seconds sweep time with the title magnets are not acceptable, even if the system is quite old.

With best regards,

Yours sincerely,

Seo Stember

S. STERNHELL

J.C. Broply.

E NEMODEN

P.S. We are anxious to receive any comments concerning resolution.

Institution	Best resolu	ution (ODCB) 1 (Hz) for	XL100/12
	500 sec	1000 sec		2500 sec
New York University	0.25	-		-
Standard Oil of Ohio	0.25	0.20		
Fordham University	0.3	<u>-</u>		_
Carleton University	0.23	0.18		-
Ajinomoto Co.	<u>-</u>	- ;		0.14
Sydney, Magnet I	0.27	0.22		-
Sydney, Magnet 12	0.21	0.16		0.11
Sydney, Magnet II ³	0.25	0.19		0.13
Sydney, Magnet II	0.20	0.15		0.12
Sydney, HA100D ⁵	0.26	0.21		0.16

¹Varian sample 943346-26, standard settings, ¹H lock.

Sweep with 25 Hz and lower RF power. At sweep time 5000 seconds the signal normally used for monitoring resolution splits into a doublet resolved to ca. 33% of height while the small inner lines of the AA'BB' spectrum are fully resolved (as shown here) with W₁ of individual components of ca. 0.07 Hz, i.e., we see all 24 lines and approach natural line-widths.

Varian sample 943346-11, standard settings, frequency sweep. At sweep time 5000 seconds 0.14 Hz. Using Varian sample 943346-26, frequency sweep, time of 500 seconds and optimized RF gives 0.26 Hz, i.e., for all practical purposes identical with the XL100/12 system, while the inner lines of the AA'BB' spectrum are split to ca. 50%. This machine is now 6 years old and these resolution figures (best ever) were obtained recently.



²After patching up temporarily a major leak in the cooling plate with a giant brass C-clamp and amateur repositioning of the coils etc., by the undersigned.

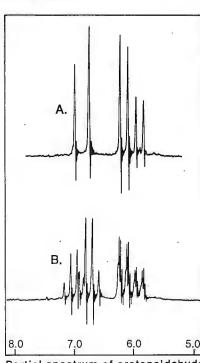
 $^{^{3}}$ Replacement for Magnet I.

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



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STAB ODER EINHEIT: ÉTAT-MAJOR OU UNITÉ: STATO MAGGIORE O UNITÀ:

March 11, 1973

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

Dear Barry:

Don't be afraid, I did not become a prefessional as the heading of this letter may suggest. But even here in military service, one is not exempted from your blue reminders! Unfortunately, I am not allowed to disclose to you against whom we are preparing our next war, So let me tell you something about my real interests. Actually, it is hard to remember anything intelligent in this unpleasant atmosphere.

Relation between Absorption and Dispersion Mode Signal in Fourier Spectroscopy

It is generally claimed that absorption and dispersion mode spectra of linear time-independent systems are connected by a Hilbert transformation or by the Kramers-Kronig relations. This is not necessarily true for Fourier spectra obtained by a digital Fourier transformation.

Let's assume that the free induction decay is represented by N (usually N = 2^{n}) samples. The fast Fourier transform routine produces N/2 + 1 cosine coefficients forming, for example, the absorption signal and N/2 - 1 sine coefficients forming the dispersion mode signal. Obviously, the two signals must be independent as the N degrees of freedom have been distributed among the two signals. Here, no Kramers-Kronig relation can hold.

It is wellknown that it is possible to interpolate Fourier spectra by transforming an arrey consisting of the original N sample values supplemented by N zeros. In this manner, twice as many values for the absorption and the dispersion mode signal are obtained, the new values being centered between the original values. It



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can easily be shown that the interpolated absorption and dispersion mode signal are related by a discrete periodic Hilbert transform which is similar to the wellknown continuous Hilbert transform. Thus, each of the two signals contains the entire information content of the original free induction decay. This 'interpolation process' has produced new information as far as one of the two signals is considered only. The odd-numbered values of the absorption mode signal represent the information contained in the original dispersion mode signal.

On the other hand, any further interpolation obtained by transformation of the original arrey of sample values supplemented by $k \cdot N$ zeros, k > 1, does not increase the information content but is entirely equivalent to a trigonometric interpolation process which at most may improve the visual appearance of the spectrum. A detailed analysis by Enrico Bartholdi and myself is in press in the Journal of Magnetic Resonance.

Sincerely yours,

Michael

Prof. Richard R. Ernst

DIVISION OF PHYSICAL CHEMISTRY THE ROYAL INSTITUTE OF TECHNOLOGY STOCKHOLM 70 SWEDEN

Cable address: Technology

Stockholm March 23, 1973

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

Wide-line NMR clarifies dielectric relaxation mechanisms

Dear Barry,

In our studies of intercrystalline water adsorption in clay mineral aggregates we have shown that the scalar coupling between unlike spins - the water protons and the nuclei of the exchangeable cations - gives rise to band width enhancements localized in narrow temperature ranges characteristic of the state of hydration and the type of cation present. Since the hydration of hydrophilic clays occurs as one or several water layers intercalated between the clay crystallites some 10 Å thick, it is possible at temperatures below 0°C to find out in what layer the nonresonating but relaxing cation is situated and how it is coupled to the water lattice. It turns out that the ions preferentially couple to the intermolecular hindered translation mode around 170 cm⁻¹ modulated by the imposed dielectric field. The ensuing relaxation band is structureless but can now be resolved in great detail making use of the temperature dependence of the scalar ionwater interaction in an NMR spectrum. The method also easily distinguishes between stabilizing and disruptive ion-water

Yours Sincerely,

Professor E. Forslind

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN Urbana, Illinois 61801

School of Chemical Sciences

Department of Chemistry

March 13, 1973

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

77843

Dear Barry:

Re: Pulsed NMR Studies of Fluorine Relaxation in MPF6

Shmuel Albert in our group has been brave enough to take another, more detailed look at a phenomenon which Gerry Miller first discovered several years ago [Miller and Gutowsky, J. Chem. Phys. 39, 1983 (1963)]. This is the sensitivity to physical state and thermal history in KPF₆ and RbPF₆ of the PF₆ reorientations. Gerry looked at the F-19 line shapes and second moments; Shmuel has looked at the T₁.

In particular, he has observed T_1 in polycrystalline Na, K, Rb, and Cs hexafluorophosphates at temperatures between 77° and 476°K by pulsed NMR methods. In each case a discontinuity occurs in the temperature dependence, at 276°, 275°, 210° and 82°K, respectively, those for the K and Rb salts corresponding to previously reported phase transitions. The temperature dependence of T_1 observed in the low-temperature phase of the Na, K, and Rb salts has a minimum and an asymmetric shape which are attributed to dipolar relaxation by thermally activated, random reorientations of the PF₆ ions, the activation energy E_a being smaller on the low-temperature side of the T_1 minimum than on the high side.

Typical data, those for RbPF6, are reproduced in Figure 1. The temperature of the T_1 minimum and E_a decrease with increasing size of the cation, as does the transition temperature (See Table I). The Ti's are very sensitive to the physical state of KPF 6 and RbPF 6 and to thermal cycling in RbPF 6. Powdering the sample broadens the T1 minimum, shifts it to lower temperatures by 2° to 8°, reduces its value by about 25 percent, and decreases the low-temperature E2. These effects are analogous to those reported in Miller's line-shape studies and are consistent with the two+phase model proposed in that connection. One phase consists of relatively perfect crystalline domains, with a high Ea, and the other of domains with defects which lower Ea. Spin exchange between the two types of domains is fast enough to average out the different T1's in the two phases and produce exponential relaxation.

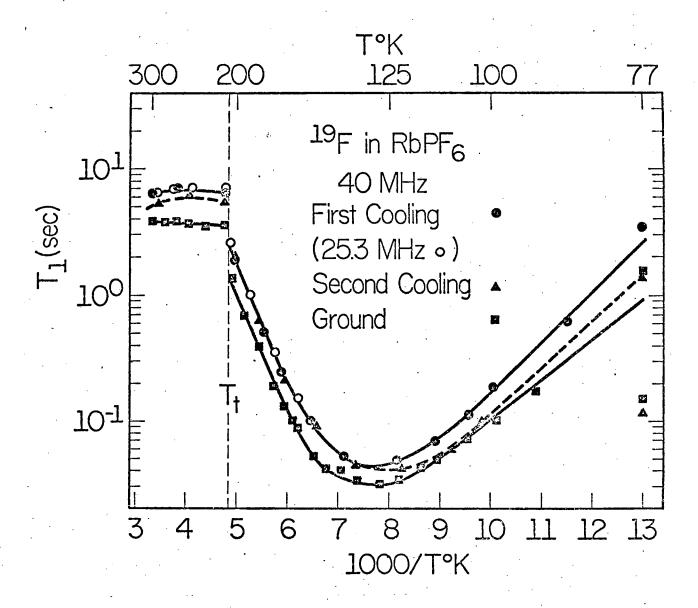


Fig. 1 The temperature dependence of the fluorine spin-lattice relaxation time T₁ observed at 40 MHz in RbPF₆. The circles are for the original granular sample which had not been previously cooled (or heated) beyond the temperature of measurement (open circles are a few data at 25.3 MHz). The triangles are for a sample which had previously been cycled to liquid nitrogen temperature and back to room temperature. The squares are for the original sample after it was finely powdered.

Table I. The minimum T_1 's and temperatures at which they were observed for the Na, K, and Rb hexafluorophosphates at 40 MHz, and the activation parameters obtained from the temperature dependence of T_1 on the high- and low-temperature sides of the minima.

	Physical	Min. T _i	T(min)	High-tem	p. parameters	Low-temp. parameters		
Salt	state	msec	°K	E _a (kcal)	To(sec)	E _a (kcal)	To(sec)	
Na	powder ^a	22 <u>+</u> 1.5	245 <u>+</u> 2	7.9 <u>+</u> 1.5	(3 <u>+</u> 2)×10 ⁻¹⁶	6.9 <u>+</u> 0.5	(2 <u>+</u> 0.5)x10 ⁻¹⁵	
K	recryst.	41 <u>+</u> 3	213 <u>+</u> 2	11.1 <u>+</u> 0.7	(9 <u>+</u> 3)×10 ⁻²	5.5 <u>+</u> 0.4	(5 <u>+</u> 2)x10 ⁻¹⁵	
	granular ^a	21 <u>+</u> 2	211 <u>+</u> 3	11.7 <u>+</u> 0.7	(2+0.5)×10 ⁻² 1	5,5 <u>+</u> 0,4	(5 <u>+2</u>)×10 ⁻¹⁵	
	powdered	14.5 <u>+</u> 1.5	206 <u>+</u> 3	11.0 <u>+</u> 0.7	(5 <u>+2</u>)×10 ⁻² 1	5,1+0,4	(9 <u>+</u> 3)x10 ⁻¹⁵	
Rb	granular ^a	~44	~131	4.3+0.3	~2×10 ⁻¹⁶	1.8 <u>+</u> 0.3	~2.5x10 ⁻¹²	
٠.	cycledb	~40	~129	4.3 <u>+</u> 0.3	~1×10-16	~1.7	~3.5x10 ⁻¹²	
**	powdered	32 <u>+</u> 2	128 <u>+</u> 4	4.2 <u>+</u> 0.3	(2 <u>+</u> 1)×10 ⁻¹⁶	1.5 <u>+</u> 0.4	(9 <u>+</u> 5)x10 ⁻¹²	

^aThe original form of the sample. b The powder produced by a thermal cycle from 300° to 77°K.

However, in finely powdered RbPF₆ at 77°K non-exponential relaxation was observed (Fig. 1) and is attributed to paramagnetic impurities. In the high-temperature phase of all four salts, T_1 exhibits a broad frequency-independent maximum of 4 to 7 sec which is attributed to relaxation by $\overline{\text{spin-rotation}}$ interactions within the rapidly reorienting $\overline{\text{PF}_6}$ ions.

I hope this pays up my subscription for a while!

Best regards,

H. S. Gutowsk

Professor of Chemistry

HSG:cfh

P.S. Post-doctorate Openings. I will have an opening or two for postdoctorates. Areas of interest include NMR of solids and Fourier-transform, high resolution studies. Attention is called to these openings as part of the efforts of the University of Illinois to ensure that such appointments do not discriminate for reasons of sex, race or ethnic group.

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Dr. V.F. Bystrov

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UI. Vavilova, 32 Moscow V-312 USSR

February 27, 1973

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

<u>Title</u>: Refinement and Theoretical Calculation of the Peptide NH-C H Coupling Constant.

Dear Barry,

With the accumulation of more data on the conformation of peptides it has now become possible to refine the earlier proposed Karplus-like dependence of the peptide NH-C $^{\circ}$ H vicinal coupling constant of the dihedral 0 angle (or the torsion Ø angle). The new dependence, presented by hatched area on Fig. 1 lies within the region of one proposed earlier, but confines permissible angles for a given experimental $^{3}J_{NHCH}$ (corrected on electronegativities of the C $^{\circ}$ neighbouring atoms according 1) to narrower limits and more definitely discriminates between the cis and trans orientation of the NH-C $^{\circ}$ H protons.

Recently it appeared that choice of the model compounds for plotting the $^3J_{\rm NHCH}$ angular dependence has an important bearing on the numerical parameters of the curve, especially for the $0 \sim 0^\circ$ ($\emptyset \sim 60^\circ$) region. In particular if one takes compounds with transamide bonds the $^3J_{\rm NHCH}$ for $0 = 0^\circ$ turns out to be 8.0 - 9.0 Hz (Fig.1), whereas for the set of compounds which contains also cisamides the same angle corresponds to a value of 6.4 Hz 2 or even 5.6 - 6.0 Hz 3 .

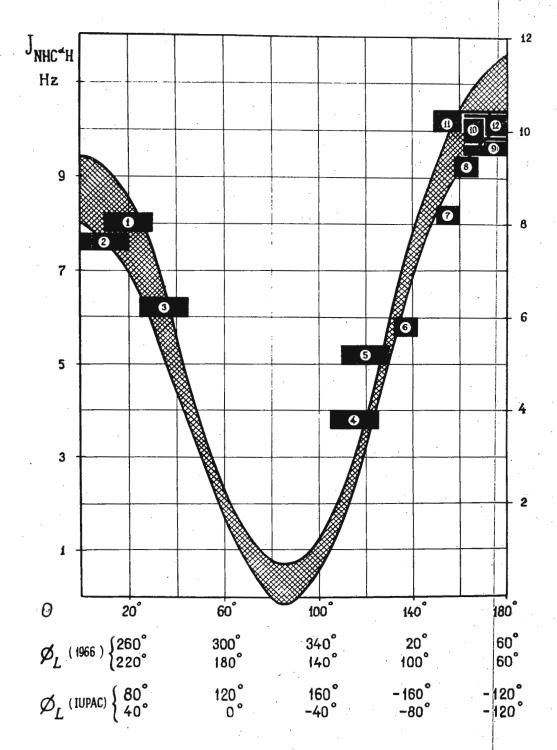


Fig. 1. Experimental data are: 1 and 3, D- and L-Val of valinomycin in the "bracelet" conformation; 10 and 2, the same in the "propeller" conformation; 4, 9, 11 and 12, D-Phe, L-Orn, L-Leu and L-Val of gramicidine S; 5, L- and D-Val of K⁺-valinomycin complex; 6-8, L-Orn, 2,3 of alumichrome (X-ray diffraction data for ferrichrome A).

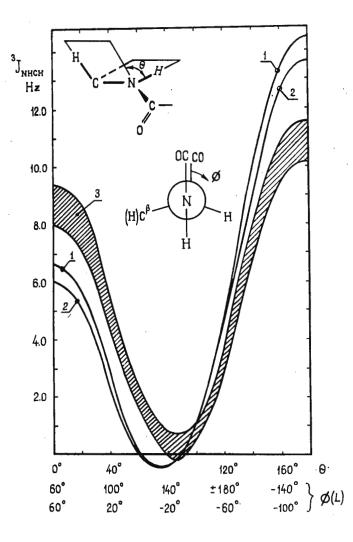


Fig. 2. Theoretical dependence of the $^3J_{\rm NHCH}$ coupling constant on the rotational states about the N-C° bond for the trans- (1) and cis-isomer (2) of NFA at ψ = 180°. (3) - Empirical dependence for peptides (see Fig. 1).

In order to find an explanation for this discrepancy and to provide a theoretical basis for the shape of the $^3J_{\rm NHCH}$ angular dependence, Dr. V.Solkan has made a theoretical INDO calculation of the vicinal NH-C H coupling in N-formylaminoacetaldehyde (NFA) O=CH-NH-C H₂CHO, considered as a model of the N-C -C(=0) fragment of the aminoacid residue.

The general shape of the theoretical $^{3}J_{\mathrm{NHCH}}$ dependence on the dihedral 0 angle is that of a Karplus-like curve (Fig. 2, curves 1 and 2), confirming the basic assumption underlying the empirical approach $^{1-3}$.

It should be particularly noted that the calculated $^3J_{\mathrm{NHCH}}$ are smaller for the <u>cis-</u> than for the <u>trans-</u> isomers of NFA. A similar result has been obtained for the averaged $^3J_{\mathrm{NHCH}_3}$ constant in N-methylformamide (NMF): 4.7 and 5.1 Hz respectively (experiment gives 4.45+0.05 and 4.85+0.05 Hz). This difference is evidently the reason for the above mentioned discrepancy between the stereochemical $^3J_{\mathrm{NHCH}}$ relation for peptides with <u>trans-amide bond</u> (ref. 1 and Fig. 1) and for the set of compounds with cis-amides 2 , 3. Since the data used for plotting the latter in the region of $\theta \sim 0^\circ$ ($\phi \sim 60^\circ$) were based mainly on the <u>cis-amides</u> it is just this region that the low $^3J_{\mathrm{NHCH}}$ values were most clearly manifested.

Best regards,

Vladimir Bystrov

Wadimir

References

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- 2. G.N.Ramachandran, R.Chandrasekaran and K.D.Kopple, Biopolymers 10, 2113 (1971).
- C.M. Thong, D. Canet, P. Granger, M. Marraud and J. Neel,
 C.r. Acad. Sci., Ser. C, <u>279</u>, 580 (1969); J. Neel, Pure Appl. Chem. <u>31</u>, 201 (1972).
- 4. J.A.Pople, J.W.McIver, Jr. and N.S.Ostlund, J. Chem. Phys. <u>49</u>, 2960, 2965 (1968).



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March 20, 1973

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

Dear Dr. Shapiro,

We have read in the Dec. 1972 issue the interesting communication of Sievers and Cunningham (171-32) on the crystal data of some lanthanide shift reagent complexes, indicating that the Eu-0 bond distance ranges between 2.3 and 2.7 Ao.

These authors express same concern about the diffused practice to assume values of the Eu-O bond distance of about 3.0 A in the LIS simulation work.

We have available some data bearing on this point.

In the enclosed table are shown the results obtained assuming the Eu-O bond distance in the range 2.0-3.4 Ao in the case of a computer LIS simulation performed on the dimethylacetamide-Eu (fod) 3 complex.

Symbols and parameters used to define the Eu ion spatial location in the space around the amide are shown in the Figure.

The error level between observed and calculated LIS has been expressed in terms of Hamilton agreement factor (A,F.), as proposed recently by Wilkcott, Lenkinski and Davis.

From data reported in the table it can be seen that the Eu position in the complex appears unchanged by the variation of R and that the corresponding A.F. values denote an excellent degree of LIS simulation over all the range of R explored.

On this basis, we feel that the choice of any Eu-O bond distance in the range 2.5.-3.0 A° cannot affect crucially the LIS simulation process.



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Since there are definite differences in the Ld-O bond distances by changing both ligand and lanthanide, the practice to assume 3.0 Ao offers the advantage of a standardisation in the calculations.

Anybody willing to quote this information may directly refer to it as personal communication from us.

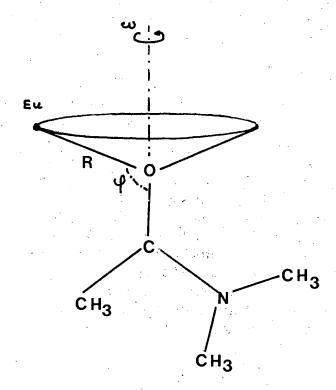
- 1) G.Montaudo and P.Finocchiaro J.Org.Chem., 37, 3434 (1972)
- 2) M.R., Willcott, R.E.Lenkinski and R.E.Davis, J.Amer.Chem.Soc., 94, 5325 (1972)

Title: G.Montaudo, S.Caccamese, V.Librando. Eu-O bond distance in LIS simulation work.

Giorgio Montaudo

Montando

R (A°)	Ą	ω	A.F.
2.0	1100	1000	0.044
2.2	1100	100°	0.037
2.4	1100	100°	0 .03 0
2.6	1100	1000	0.023
2.8	1100	100°	0.016
3.0	1100	1000	0.010
3.2	1100	1000	0.008
3.4	1100	1100	0.005



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March 6, 1973

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

Dear Prof. Shapiro:

To assist the determination of molecular formula which is fundamentally important in the structure elucidation of organic compounds, the number of carbon in the organic compound has been directly and automatedly counted by the feeding ¹³C NMR spectrum.

Suppose the heights of each signal are h_1 , h_2 , h_3 , ..., and h_n (h_i) and h_{min} is the smallest value among them in the proton decoupled 13C NMR spectrum showing n signals, H_{min} is set as $H_{min} = 0.85 \times h_{min}$. Then the following computation continues under the assumption that height of anyone among n signals corresponds to the real strength of 1 carbon. The integer values resulted by dividing hi by Hmin one by one are called a1, a2, a3,, and an (ai) for convenience' sake. When the sum total of a; is compared with 2n, the smaller one is called b. The following relationship will be possible among b, NC (number of carbon atoms), and n.

 $b \ge NC \ge n$

If it is assumed that NC is equal to n, hone obtained by dividing the sum total of hi by NC may be considered as the mean value of the height strength of 1 carbon. d2, d3,, and dn (di) obtained by dividing hi by hone are made into integers by the use of parameters prepared by us and these integers are referred to e1, e2, e3, ..., and Finally the sum total of ei agreed with NC assumed above, can be taken as the reply. Similar operation is carried out by increasing the assumed value of NC from n, n+1, n+2, · · · until it becomes equal to b and all total sums among the calculated values which agree with the assumed values can be taken as replies. In case of feeding the 13C NMR of fenchone as an example, the computation proceeds as shown in the Table.

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hi	h <u>1</u>	h ₂	hз	h4	h5	h6	h7	h8	h9	h ₁₀
111	7.92	8.28	8.90	7.90	8.38	8.36	7.90	8.62	7.61	5.71
h _{min}	·		٠.		5.71			·		
H _{min}				0.85	x 5.7	71 = 4.	85			
	1.63	1.71	1.84	1.63	1.73	1.72	1.63	1.78	1.57	1.18
ai	1	.1	_1	1	1	1	1	1	1	1
b					10					
Assumption					NC ≥ r n = 1					
Hone					7.95			-		
di	0.99	1.04	1.11	0.99	1.05	1.05	0.99	1.08	0.95	0.71
ei	1	1	1	1	1	1	1	1	1	1
Sum of ei	1	0 (Agr	eed wi	th the	assum	ption,	NC =	10)		

The results were mostly satisfactory for 50 spectra of the known compounds.

Sincerely yours,

S. Ochiais

Shukichi Ochiai JEOL, Tokyo, Japan

Shin-ichi Sasaki Miyagi University of Education Aoba, Sendai, Japan

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25.3.73

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

A contribution by Christiane (6) to photo-CIDNP.

Dear Barry:

while lecturing on CIDNP last term I thought it might be very instructive if my students could actually watch a CIDNP-experiment performed and witness an emission signal appear. Of course anything like drilling a hole in a probe-head or constructing an elaborate flow system was impossible. So I figured if we took a system where the substance formed has a long T_4 (long compared to the time necessary to insert a probe into a spectrometer and run the interesting part of an CW-spectrum) we might have a chance. So I borrowed a little toy- horse-shoe magnet off our daughter Christiane (now 6) installed a 150 Watt high pressure mercury lamp about 2m next to an A-60 and took the famous dibenzoylperoxid system (0.1m in d6-acetone plus anthracene as senthisizer -see Kaptain et al. Chem. Comm. 1687 1970). We irradiated the sample inside the field of the little magnet with the focused light of the Hg-lamp for 10 - 60 sec, swiftly moved probe and magnet close to the spinner head of the A-60(beware of letting loose the little magnet) where there is a reasonably strong stray field, inserted the probe and within 10 sec ran a spectrum of the phenyl-region. To everyones surprise the benzene appears in emission!

As implied in the title this experiment is highly instructive though exceedingly simple. I hope this letter will stimulate others to try it.

Sincrely yours

tenon.

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No. 11

6th March 197 3

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

SUBSTITUENT EFFECTS ON THE ²⁹Si CHEMICAL SHIFTS IN SOME ORGANOSILICON COMPOUNDS

Dear Professor Shapiro,

Thank you for your reminder.

From 1972 our work in the field of 29 Si NMR spectroscopy that was begun in 1970 is becoming more intensive. In collaboration with Dr. J.Schraml of the Institute for Chemical Process Fundamentals of Czechoslovak Academy of Sciences we have been studying the 29 Si and 13 C spectra of compounds of general formula 29 Si and 13 C spectra of the investigation of compounds 29 Me $_{3-n}$ X $_n$ Si(CH $_2$) $_m$ Y. The results of the investigation of compounds 29 Me $_{3-n}$ X $_n$ SiCH $_2$ Y (X = OEt. OAc, Cl, F and Y = OAc, Cl, Ph) reveal that the β -substituent effect of Y on the 29 Si chemical shift, i.e.

$$\Delta \delta_{Si} = \delta_{Si} (Me_{3-n} X_n SiCH_2 Y) - \delta_{Si} (Me_{4-n} X_n Si)$$

is not constant with the same X and increases markedly with increasing number of group X capable for $(p \rightarrow d)_{\pi}$ -interaction with silicon. As a typical example, we present here the ²⁹Si chemical shifts of the series Me_{3-n} (OEt)_nSiCH₂OAc (positive values correspond to downfield shifts):

n -	δ _{Si} (ppm from		
	Me _{3-n} (OEt) nSiCH ₂ OAc	Me _{4-n} (OEt) _n Si	Δδ _{Si} (ppm)
0	+0.3	0	+0.3
1	+9.0	+13.5	-4.5
2	-16.1	-6.1	-10.0
3	-58.2	-44.5	-13.7

In some cases (X = OAc, Y = OAc) $\Delta\delta_{\rm Si}$ increases more than 40 ppm when n increases from 0 to 3! To reveal correlations between the electronic character of Y and $^{29}{\rm Si}$ chemical shifts the work is in progress (more details will be published in Journal of Organometallic Compounds), but it is clear, that generally one cannot find even roughly constant substituent increments for CH₂Y-groups in $^{29}{\rm Si}$ NMR.

Please credit this contribution to the account of Prof.E.Lippmaa.

Sincerely yours

M Magi)

STATE UNIVERSITY OF NEW YORK AT STONY BROOK

DEPARTMENT OF CHEMISTRY

STONY BROOK, N.Y. 11790

AIR MAIL

March 26, 1973

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

Dear Barry:

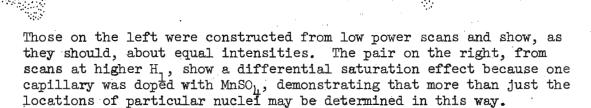
Title: NMR Zeugmatography

Magnetic resonance is peculiar, if you stop to think about it. Other forms of spectroscopy are associated with image-forming techniques. From radio astronomy through radar, optical pyrometers, eyes, ultraviolet microscopy, X-ray radiography and scintigraphy, as well as acoustic and particle spectroscopies, the interactions responsible for spectra are also used to make pictures. But who ever heard of an NMR picture?

A pointless parallel, you may say. A moment's reflection reveals that the wavelength of 60 MHz radiation, for example, is about 5 meters, and who but a geologist or an astrophysicist would be interested in pictures of something with 5 meter resolution? Besides, how are you going to maintain a 1.4T field over that volume? That last comment, however, contains the key to a solution to our heretofore unformulated problem. For magnetic resonance is also distinguished from other forms of spectroscopy in a more fundamental way. It depends upon the presence of two fields, and that fact makes the usual Abbe resolution criterion irrelevant. If the magnetic field is inhomogeneous within an object, the Larmor condition will be satisfied for a given frequency only within certain surfaces of constant field, restricting the interaction between the object and the radiation field to regions that may be very small compared with the wavelength.

It is now obvious that it should be possible to use NMR to make pictures of things - only the details remain to be worked out. Several methods appear to be possible, including one that requires only a standard NMR spectrometer (an A-60, for example) and a pencil and paper. The example shown below was obtained by slightly less primitive techniques, involving

an extra field gradient control box attached to the A-60, and a small computer program on the Departmental IBM 1800. The necessary data were obtained by turning the sample to several known orientations relative to a field gradient and scanning through the broadened peaks. Each scan represents a one-dimensional projection of the signal intensity in a different direction, and by appropriate mathematical manipulations a representation of the object that produced the projections may be constructed. The images in the figure below are those of two 1 mm capillaries of H₀0 in a 5 mm 0.D. tube of D₀0.



It is not possible, of course, to do more than just touch upon these matters here or to discuss techniques, algorithms, or applications. Even those curious about the title of this TAMUNRN contribution will have to await the first paper (in NATURE) or write for a preprint. Just a hint on pronunciation, though. It is ZEU as in ZEUS (ZOOS).

Yours truly,

PCL/sb

Paul C. Lauterbur Professor of Chemistry

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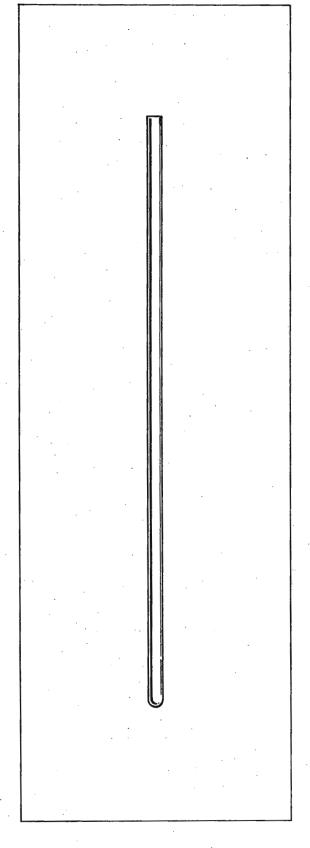
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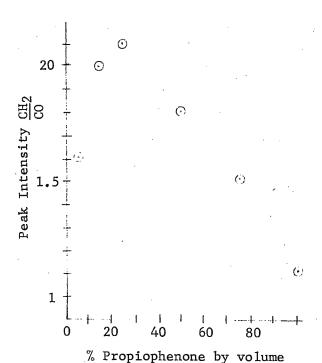
March 26, 1973

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

Dear Dr. Shapiro:

Those familiar with cmr are well aware that the magnitude of the Overhauser enhancement in proton decoupled ¹³C spectra varies for different ¹³C nuclei. Therefore, one can seldom rely on intensities in assigning peaks in a spectrum. In some instances, sample concentration will affect the Overhauser enhancement, as in the case of propiophenone. We obtained spectra of propiophenone at various concentrations in chloroform and plotted the ratio of the peak intensities of methylene/carbonyl carbons as a function of dilution. As you can see in the graph below, optimum methylene peak enhancement occurs at approximately 25% propiophenone concentration. Similar results are obtained using methanol and carbon tetrachloride as solvents. Thus, not only can one get different intensities for different single carbon resonances of a compound, due to variable Overhauser enhancement and relaxation time differences, but the magnitude of intensity differences appear to also depend upon solvent and concentration.

Yours truly,



THE PROCTER & GAMBLE COMPANY
Research & Development Department

Charles D. Sazavsky

Suggested Title: "13C Intensity Anomalies."



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3280 ROSS ROAD ■ PALO ALTO, CALIFORNIA 94303 ■ PHONE (415) 969-2076

March 29, 1973

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

Dear Barry:

ON THE MEASUREMENT OF 12c-13c ISOTOPE SHIFTS

In looking at the spectra accompanying Charlie Reilly's recent TAMUNMR letter (174-46), it appears to me that Charlie has taken the midpoint of the ^{13}C satellites as measurements of chemical shifts. This leads to considerable error since the δ /J ratios for the two sets of $^{13}\text{C-}^{13}\text{C}$ doublets are only 5.9 in each case.

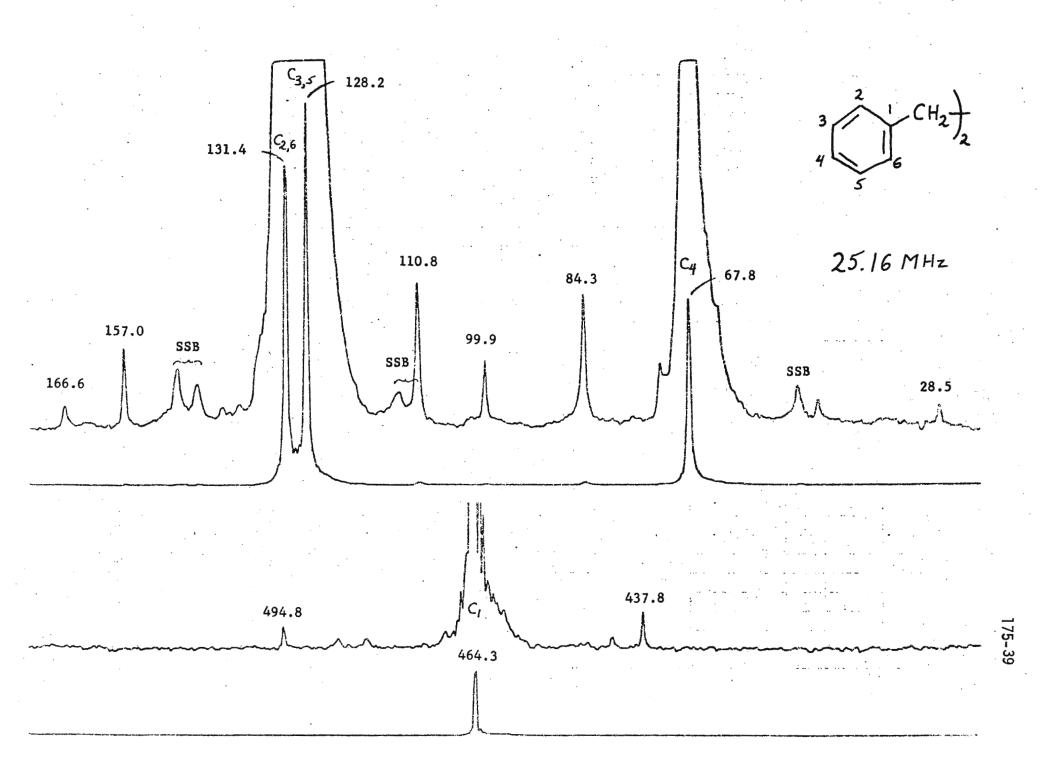
By estimating 13 C satellite frequencies from Charlie's spectra, and using AB analysis I calculate that the 12 C- 13 C isotope shifts are only about 0.2 Hz (0.01 ppm). All are towards lower frequency, which is normal for isotope shifts when a heavier nucleus is introduced.

About a year ago, I measured ¹³C satellites in the proton decoupled ¹³C FT spectrum of dibenzyl in order to confirm assignments for the two pairs of equivalent aromatic carbons. In the enclosed figure, the satellites at 166.6, 110.8, 84.3, and 28.5 Hz (from carrier) form an AB set which have chemical shifts at 127.8 and 67.3 Hz, and thus isotope shifts of 0.4 and 0.5 Hz (ca. 0.02 ppm). The peaks at 494.8, 437.8, 157.0, and 99.9 Hz form another AB set (less perturbed) having chemical shifts at 463.9 and 130.9 Hz. Here again, the isotope shifts are 0.4 and 0.5 Hz.

These isotope shifts are consistant with those seen in other compounds.

Best regards,

LeRoy F. Johnson



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IN REPLY PLEASE QUOTE REF. DD . RC .



THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.
DEPARTMENT OF ORGANIC CHEMISTRY.
29th March, 1973.

Professor B.L. Shapiro, Department of Chemistry, Texas A and M University, COLLEGE STATION, Texas 77843. U.S.A.

Dear Professor Shapiro:

Thank you for your blue letter. I thought your readers may be interested in some more of our \$^13\$C-metal coupling constant\$^1\$ results hence find enclosed data on some tin and lead derivatives of furan and thiophene - work performed as a joint study with Professor Lewis of this department and Bill Kitching at the University of Queensland.

The value of the coupling constants are strongly influenced by the number of alkyl groups attached to the metal atom - the one-bond \$^{13}C_{119}S_{1

These results suggest that the electronegativity of the groups bonded to the metal atom strongly influence the $^{13}\text{C-Metal}$ coupling constants through charges in metal atom effective nuclear charge values. It would be difficult to rationalise the gross changes solely in terms of changes in the s-character of the carbon-metal bond.

It is likely then that Z* values are very important in determining ¹³C-metal coupling constants and serves warning to the many investigators who persist in relating carbon-heteroatom coupling constants to the s-character of bonds.²

Please credit this to the University of New England account.

D. DODDRELL.

- P.S. This work has been written up and preprints are available.
- 1. TAMUN Newsletters No.165, 1 (1972).
- 2. cf. D.M. Grant and W. Litchman, J.Amer.Chem.Soc., 87, 3994 (1965) for a discussion of the variation of J_{CH} with Ξ^* .

Suggested Title: Some More ¹³C-Metal Coupling Constants.

TABLE

			J_{M-13C} (Hz)	
Compound	C2	С3	C4	C5
([]) Sn Mes	507.5	72.4	28.6	24.6
(Sn Mez	589.4	77.7	31.3	27.8
(Tol) + Sm	818.1	100.9	41.6	41.1
(sn Mes	406.9	31.7	17.4	47.0
([s]) sn	647.5	45.7	28.4	65.9
(Tolly Pb	933.3	160.4	67.7	59.0
(Pb	656.1	75.3	39.1	110.3

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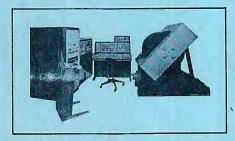
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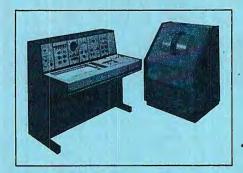
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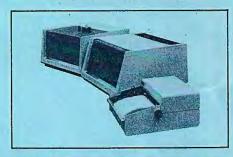
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