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Newsletter

No. 213

June, 1976

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DEADLINE DATES: No. 214: 5 July 1976
 No. 215: 2 August 1976

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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BIOLOGICAL MAGNETIC RESONANCE COURSE: UNIVERSITY OF WISCONSIN-MADISON

An advanced introduction to magnetic resonance spectroscopy and its biomedical applications will be held from August 15-21, 1976, at the Department of Biochemistry, 420 Henry Mall, Madison, Wisconsin 53706. Applications should be sent to Professor William A. Gibbons, Course Chairman, before the registration deadline of June 15, 1976.

Topics will include (1) Proteins and Nucleic Acids - Conformational change, Denaturation, Folding and Self-Assembly of: a) Peptides and Proteins, and b) Nucleosides, Nucleic Acids and Carbohydrates. (2) Binding, kinetics, mechanism studies of enzymes. (3) ESR studies of metalloproteins, free radicals and membranes. (4) NMR studies of membranes, intercellular metals and metabolites and tissue metabolism.

Lecturers will include J. Campbell, R. Deslauriers, R. Dwek, W. A. Gibbons, J. Hyde, P. Hart, D. Kearns, S. Koenig, J. Markley, W. H. Orme-Johnson, J. Peisach, J. Seelig, R. Shulman, and H. Wyssbrod.

The Course will be suitable for advance graduate students, post-doctoral and faculty researchers in biophysics, biochemistry, chemistry and biology.



Laboratoire des Organométalliques

J. C. MAIRE, Professeur.

16th april 1976

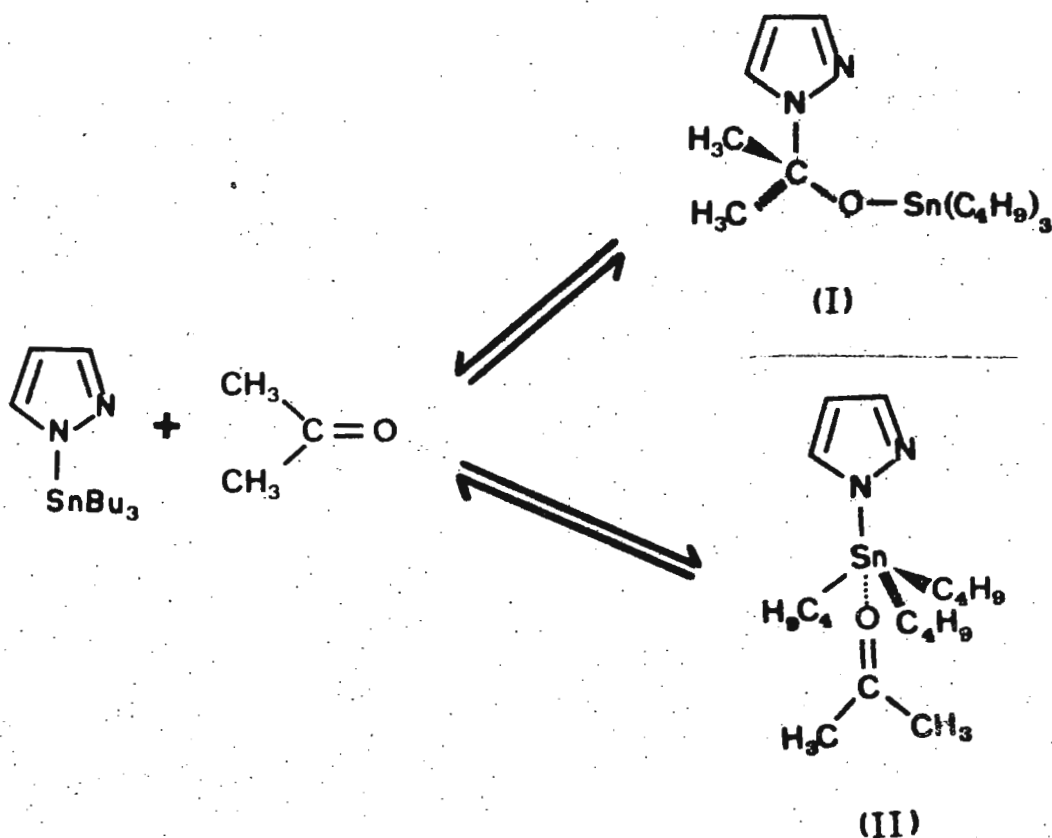
Professor B.L. SHAPIRO
Department of Chemistry
Texas A and M University
College Station
Texas 77843,
U.S.A.

Dear Prof. Shapiro,

Structure of pyrazole tin derivatives :
A low temperature ^1H Nmr study.

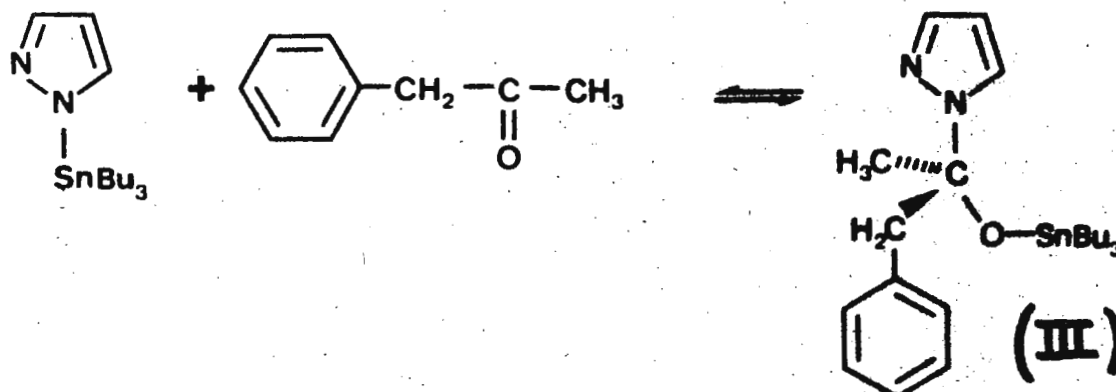
We have shown earlier that N-tributyltinpyrazole was giving, at low temperature, a reversible adduct with ketones.

This adduct could be either a genuine addition compound (I) or a complex between tin and oxygen (II).



In the way to determine the right structure we performed the following experiment using methylbenzylketone (III). In this compound, the benzylic protons are equivalent and give a single line.

As we expected the structure (I) to be the right one, the addition of (III) should give a compound with an asymmetric carbon leading to two non equivalent protons on the benzylic position.



That's what we observed on figure I.

- At +25°C, there is no adduct formed and the benzylic protons give a single line.
- At -50°C part of the N-tributyltinpyrazole has already given the adduct and one can see that :

- protons H₃ and H₅ of the pyrazole ring are no more equivalent in the adduct
- benzylic protons of the adduct give an AB spectrum.

Then, structure (I) was the right one, N-tributyltinpyrazole gives a reversible nucleophilic addition with ketones at low temperature.

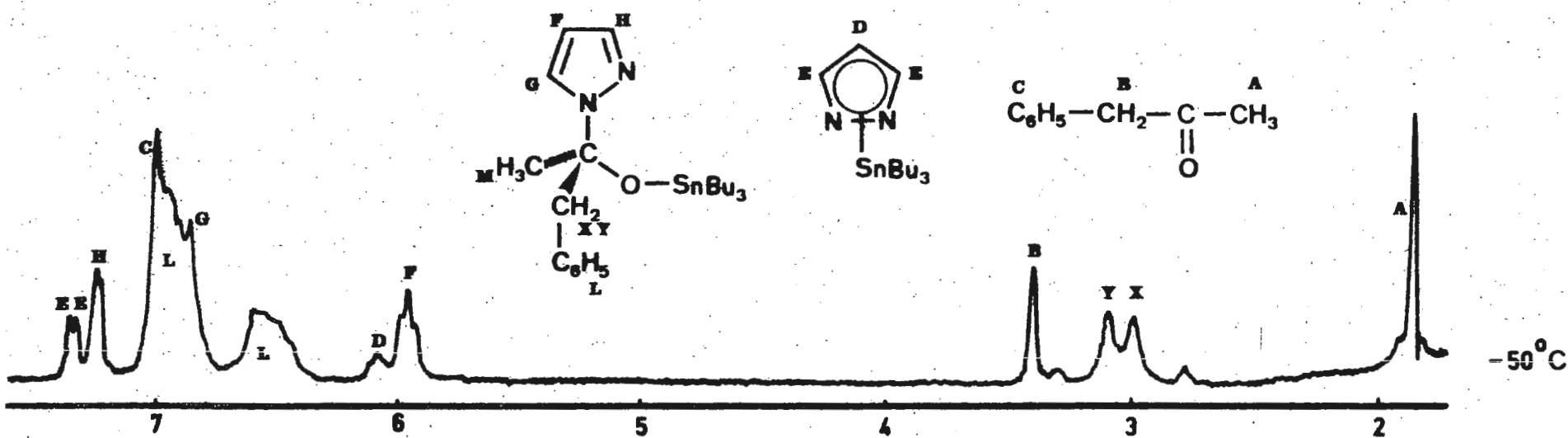
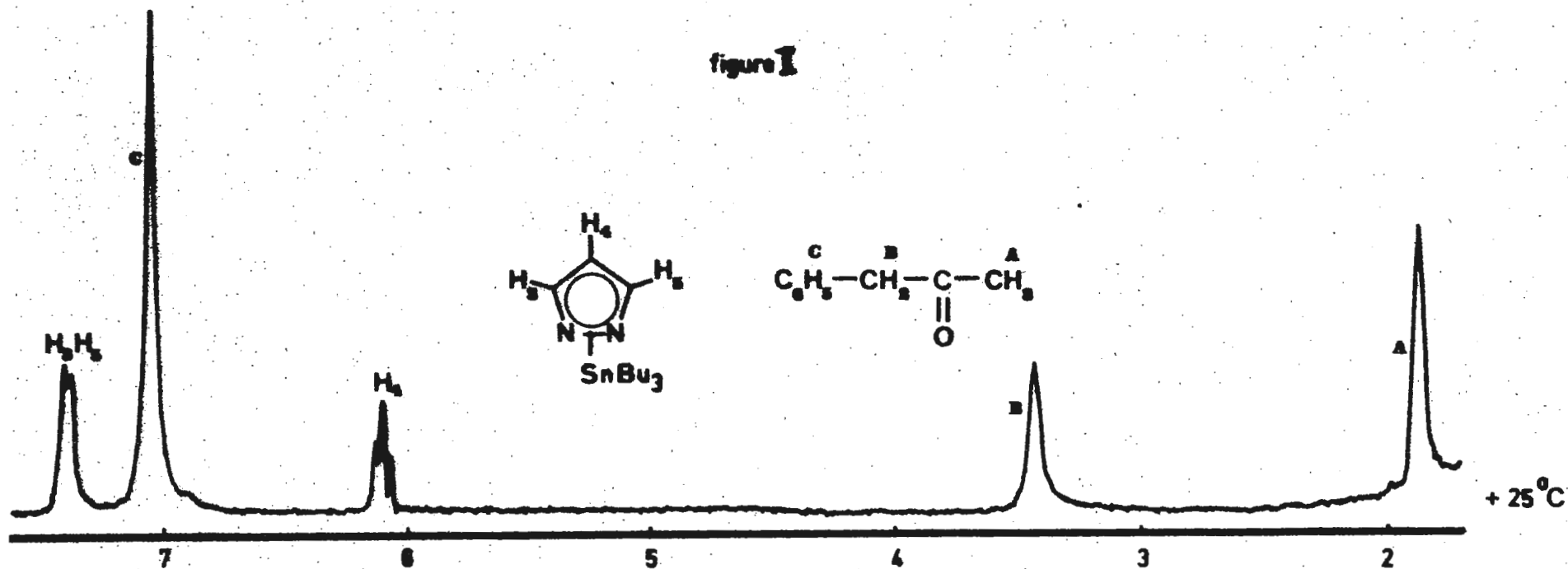
R. GASSEND

J.C. MAIRE

R. Gassend

J.C. Maire

figure I





THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

May 4, 1976

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

Title: "Pulsed Gradient Diffusion under FT / Position Available

Dear Barry,

In continuing our work¹ on lateral diffusion measurements in model membrane bilayers, we have begun looking at the line intensities of the Fourier Transformed spectrum instead of the echo amplitudes. This has several advantages, especially simultaneous measurement of diffusion coefficients of various components present, and easy phase corrections to compensate for magnet drift. I'd be interested in hearing from anyone who has tried similar experiments.

I have a research leave for Berkeley next year which creates a temporary one year teaching/research position in physical chemistry in our department for the 1976/77 academic year.

Ideally the position involves teaching about one course per semester and interacting with my research group (pulsed NMR of liquid crystals and membranes). In addition, the individual may use my lab and the departmental facilities for his or her own personal research. The course involvement will probably be in a nonscience majors series involving topics from birth control to energy to drugs to pesticides. The salary will be competitive with assistant professor levels.

While we would prefer the ideal situation discussed above, we will certainly consider any good candidates and attempt to modify our desires accordingly.

Potential candidates should call as soon as possible any of the three:

Professor Chas. G. Wade (512) 471-1252
Professor J.M. White (512) 471-3704
Professor W.H. Wade (512) 471-3949

Thanks.

Yours truly,

A handwritten signature in cursive script that reads "Chas G Wade".

Chas. G. Wade
Associate Professor of Chemistry

¹ S. Roeder, E. Burnell, A-L. Kuo, C.G. Wade, J. Chem. Phys. 64, 1848 (1976)

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DEPARTMENT OF CHEMISTRY

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

April 29, 1976

Re.: ^{13}C Shift Reassignments in Alkyl Indoles

Dear Barry:

As a result of some ^{13}C studies which we have made on derivatives of hexahydroechinulin, I, we have reexamined the question of assignments in the ^{13}C spectra of methylated indoles. The original study of Parker and Roberts¹ on a variety of monomethylindoles gave rise to a set of substituent parameters for the effect of a methyl group on ^{13}C shieldings when attached to each carbon of the indole nucleus. This table is reproduced in Stothers' compendium of ^{13}C spectroscopy².

When we examined the shifts in 2,5,7-trimethylindole, those at C_4 and C_6 were very different from those predicted from the table of substituent parameters. We therefore reexamined the assignments for C_4 and C_6 of 5-methylindole by s.f.o.r.d. and proved that the original assignments¹ for C_4 and C_6 should be reversed. Very recently, Gribble, Nelson, Johnson and Levy³ have reported another error in assignments involving C_5 and C_6 of indole and 2,3-dimethylindole. We have therefore revised all the shieldings for the methylated indoles (Table 1) and derived a modified set of substituent parameters (Table 2). It can be seen that the new substituent parameters give much better agreement between predicted and observed shieldings of 2,5,7-trimethyl, 2,3,5-trimethylindole (where only C_2 and C_3 deviate presumably as a result of ortho disubstitution) and also hexahydroechinulin. In addition it is interesting to note the reciprocal character of all these substituent parameters, i.e. the effect of a C_5 -methyl on C_4 is the same as a C_4 -methyl on C_5 .

All spectra were run on Ian C.P. Smith's CFT-20. We are particularly indebted to Ian for performing the off-resonance decoupling experiments.

Best regards,

R.R. Fraser

¹ R.G. Parker and J.D. Roberts, J. Org. Chem., **35**, 996 (1970).

² G.W. Gribble, R.B. Nelson, J.L. Johnson and G.C. Levy, J. Org. Chem., **40**, 3720 (1975).

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	
H	125.2	102.6	121.3	120.3	122.3	111.8	
2-Methyl	[135.7]	100.4	(120.0)	(119.9)	121.1	110.9	TABLE I ¹³ C Shieldings of Indole & Methyl Derivatives
3-Methyl	122.7	[111.4]	(119.4)	(119.6)	122.3	111.7	
4-Methyl	124.2	101.1	[130.2]	120.1	122.2	109.3	
5-Methyl	125.0	102.1	120.8	[128.8]	123.7	111.3	
6-Methyl	124.3	102.3	(120.7)	(121.9)	[131.5]	111.6	
7-Methyl	124.8	103.0	(118.9)	(120.3)	122.7	[120.9]	
1,2-Dimethyl	[138.1]	100.0	(120.0)	(119.6)	120.7	109.2	
2,3-Dimethyl	[131.4]	[106.8]	118.4	119.3	121.1	110.7	
2,7-Dimethyl	[135.1]	101.0	117.7	119.8	121.7	[119.9]	
2,3,7-Trimethyl	[131.2]	[106.3]	118.1	[127.8]	122.5	110.2	
2,5,7-Trimethyl	-	100.5	117.1	[128.9]	123.2	[118.9]	

^a δ_c , ppm from TMS. All shift data, except for the 2,5,7-Trimethyl derivative (0.4M in CDCl₃) is that originally reported (1) and converted using $\delta_c^{CS_2}$ 192.8. Square brackets indicate substituted carbons. Shifts given in parentheses indicate possible assignment reversal.

TABLE 2. Methyl Substituent Effects in the Indole Ring System^a

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
2-Methyl	[10.5]	-2.2	-1.3	-0.4	-1.2	-0.9
3-Methyl	-2.5	[8.8]	-1.9	-0.7	0.0	-0.1
4-Methyl	-1.0	-1.5	[8.9]	-0.2	-0.1	-2.5
5-Methyl	-0.2	-0.5	-0.5	[8.5]	1.4	-0.5
6-Methyl	-0.9	-0.3	(-0.6)	(1.6)	[9.2]	-0.2
7-Methyl	-0.4	0.4	(-2.4)	(0.0)	0.4	[9.1]

^a ppm from indole. Square brackets indicate substituted carbons. Shifts in parentheses are tentative.



DEPARTMENT OF CHEMISTRY
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10th May, 1976

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

Dear Barry,

CANCAN, a computer program for analysis of oriented NMR spectra

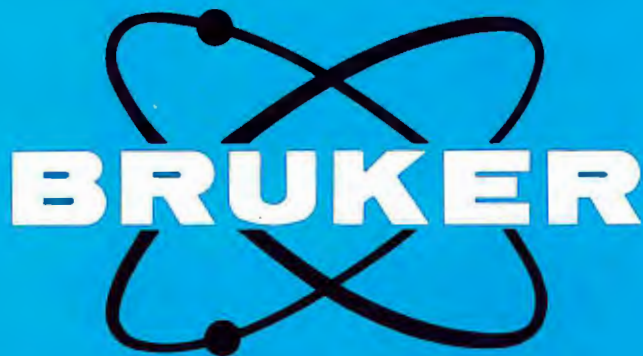
LACX is the title of a FORTRAN computer program, written by C. W. Haigh of University College of Wales at Swansea, for the calculation and analysis of isotropic NMR spectra. This program is more efficient for spin systems containing a plane of symmetry than the various versions of LAOCOON because the basis functions take explicit account of this symmetry. Almost all the molecules which have been studied using NMR spectroscopy in liquid crystal solvents contain at least one symmetry plane and we have therefore modified LACX to include anisotropic direct coupling constants [defined as in Mol. Phys. 15, 333 (1968)]. Iterative calculations are possible varying shifts, J couplings and direct couplings. All the output facilities of the original program have been retained. These include print out of the eigenvalues, partial differentials of transition frequencies with respect to selected parameters and the energy levels associated with each transition. A plotting option is also possible.

Typical of the largest spin systems which we have been investigating are AA'BB'XX'YY' AA'BB'CC'DD' ABB'CC'DD'E.

Running on an ICL 1906A computer, calculation of the proton spectrum of an AA'A"A" BB'B"B" spin system requires about 80 seconds using LACX, an improvement by a factor of 10 over LAOCOON. Listings of the program and details of the data input are available on request from John Lindon and eventually it is intended to include this program in the library of NMR programs available for use with the 1906A computer at the Atlas Computer Laboratory of the Science Research Council. For obvious reasons the program has been named CANCAN.

Best wishes,

Jim Emsley and John Lindon



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May 11, 1976

P.O. BOX 21

TULSA, OKLAHOMA 74102

AREA CODE 918-582-0101

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

Dear Dr. Shapiro:

RE: Sample Preparation Technique for Water-Soluble Polymers

We, at Dowell, received our first NMR spectrometer, a CFT-20, in December, and much of the time since then has been spent becoming familiar with the operation of the instrument and gaining some insight into utilization of the NMR technique to solve problems.

We have obtained ^{13}C spectra of several of our products, including a number of water-soluble polymers. Since these materials form gels at low concentrations, considerable difficulty was encountered in preparing homogeneous samples containing sufficient amounts of polymer material to obtain a spectrum in a reasonable period of time. We have found, however, that by using a high-speed blender to mix the polymer, we can prepare a sample containing higher concentrations of the material and can obtain a good spectrum with considerable savings in time.

In acquiring a spectrum of high molecular weight polyacrylamide, for example, the maximum concentration obtainable by conventional mixing is about 3%, and under our experimental conditions a good spectrum could be produced in about 12-15 hours using this solution. By mixing the polymer for 15 seconds in a blender we prepared a sample containing 25% polymer. The sample was not homogeneous, and was not even a uniform mixture; it contained many air bubbles and was so viscous that considerable effort was required to "stuff" the sample into the NMR tube. Nevertheless, we acquired a good spectrum in 1-2 hours.

Similar improvements can be expected with other water-soluble polymers. Short mixing times and slow speeds must be used in preparing the sample, however, to prevent shearing of the polymer in the blender.

Sincerely,

David R. Bell

np





THE UNIVERSITY OF ARIZONA

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COLLEGE OF LIBERAL ARTS

DEPARTMENT OF CHEMISTRY

May 4, 1976

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

Dear Barry:

THE DEPENDENCE OF VICINAL COUPLING CONSTANTS ON
 IMPINGING MULTIPLE REAR LOBE (IMRL) EFFECTS

Studies of conformational and substituent dependencies of vicinal ^{13}C - ^{13}C coupling constants in the series of 1-substituted butyl compounds and 11-substituted 1-methyladamantane compounds (carried out in collaboration with Jim Marshall of North Texas State University) show that the values in the butyl series are 1.2 to 1.4 Hz greater in magnitude than those for the trans (180°) arrangement of the corresponding substituted methyladamantane. This was a surprising result and it took a fair amount of time and computation to show that the smaller values for the trans arrangements can be attributed to contributions of negative sign associated with the interactions between the carbon hybrid rear lobes. Calculated INDO-FPT results for the trans arrangements of the carbon atoms in the series butane, methylcyclohexane and 1-methyladamantane are 4.27 Hz, 3.72 Hz, and 3.32 Hz, respectively, and the monotonic decrease in these magnitudes just parallels the increase (2, 3, and 4, respectively) in the number of impinging rear lobes. The situation for methylcyclohexane and methyladamantane is depicted in Figure 1. Not only are these results in agreement with the available experimental data, their recognition removes several apparent anomalies in previous studies of vicinal ^{13}C - ^{13}C coupling constants (1 - 3), e.g., the apparent shift of the maximum vicinal ^{13}C - ^{13}C coupling constant away from the 180° value in the series of labeled carboxylic acids (1).

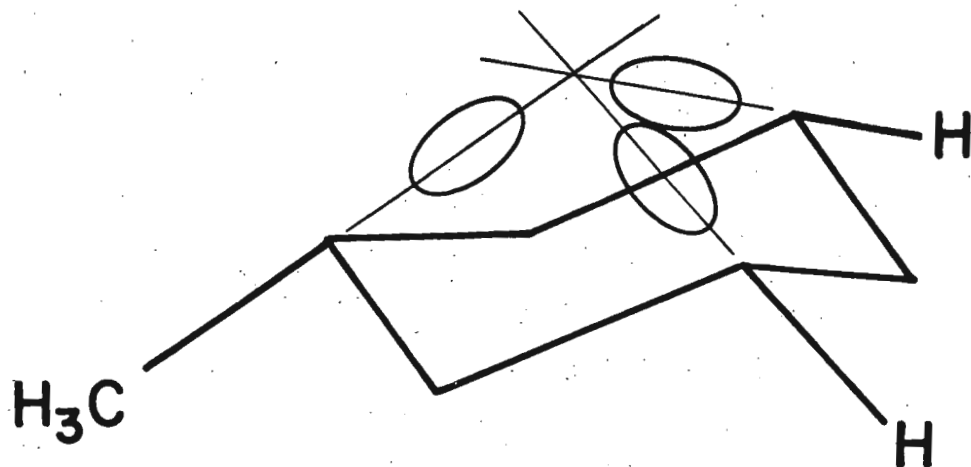
IMRL effects are expected to be quite general, and would be expected to lead to more positive values of $^2J(^{13}\text{C}$ - $^{13}\text{C})$ and $^4J(\text{H}$ - $\text{H}')$. Furthermore, a similar trend is found in the series of vicinal ^{119}Sn - ^{13}C coupling constants in 1-norbornyltrimethylstannane, 2-adamantylstannane, and 1-adamantylstannane with coupling constants of 65.8 Hz, 60.0 Hz, and 51.1 Hz, respectively (4).

- (1) J. L. Marshall and D. E. Miiller, *J. Am. Chem. Soc.*, **95**, 8305 (1973).
- (2) D. Doddrell, I. Burfitt, J. B. Grutzner, and M. Barfield, *ibid.*, **96**, 1241 (1974).
- (3) M. Barfield, I. Burfitt, and D. Doddrell, *ibid.*, **97**, 2631 (1975). Note that the experimental data for compounds 2 and 3 in Table IV should be interchanged.
- (4) D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C. Lee, R. J. Myer, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *ibid.*, **96**, 1640 (1974).

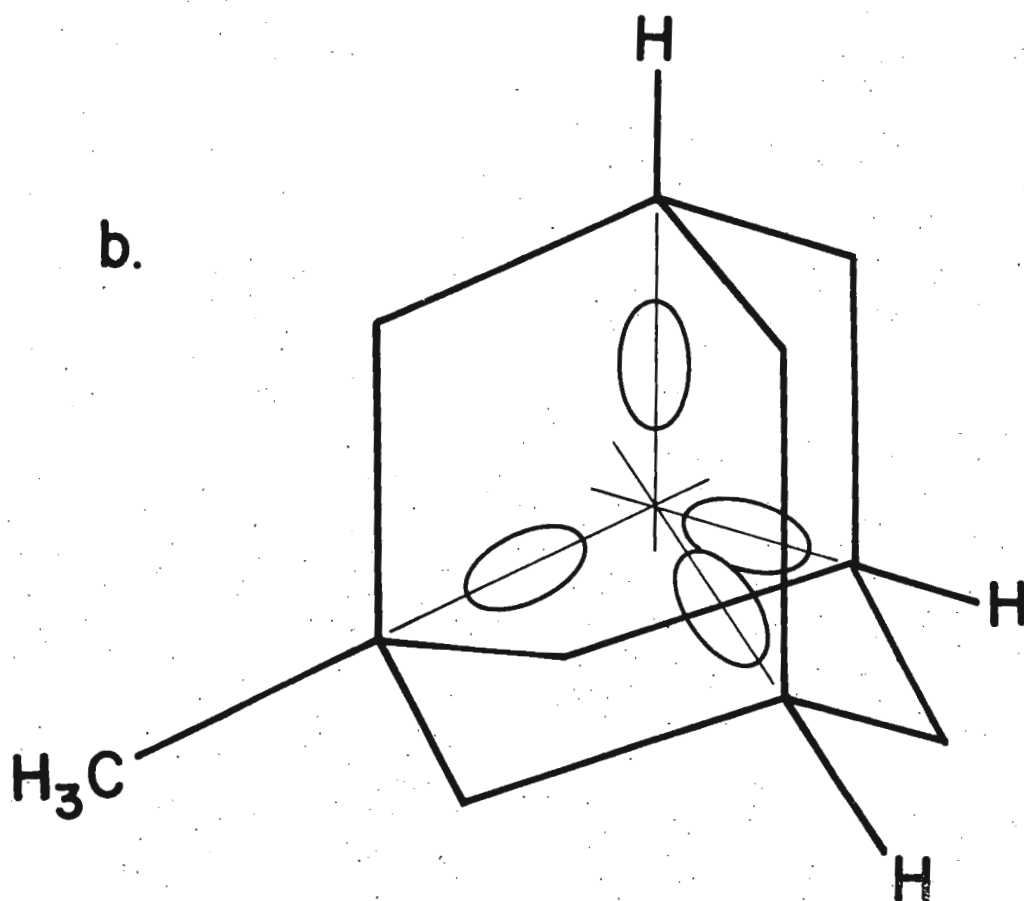
Sincerely,
 Mike Barfield

Figure 1

a.



b.





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DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620813: 974-2144
SUNCOM: 374-2144

May 14, 1976

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

MUCH ADO ABOUT NOTHING or A COMEDY OF ERRORS---

The Temperature Dependence of Lanthanide-Induced Shifts

Dear Barry:

Considerable work has been done over the past few years on the temperature dependence of Lanthanide-Induced Shifts (LIS). In particular, there has arisen considerable disagreement as to whether LIS follow a $1/T$, $1/T^2$, or some other, dependence. What is generally ignored is that equilibrium constants also have a temperature dependence.

Such a case is considered here. Let us first assume 1:1 complex formation (LS complexes only). (This is not unreasonable for bidentate substrates such as β -diketones.) Then if we assume the association equilibrium constant, K , to be 1000 ℓ/mole at 300°K and assume the association entropy to be $\Delta S = -10$ e.u., we get $\Delta H = -7.11$ kcal/mole and are ready to investigate the temperature dependence of LIS.

The observed LIS in such a case is given by

$$\Delta\delta = \frac{\{\beta - [\beta^2 - 4K^2\rho S_0^2]^{1/2}\}}{2KS_0} \cdot \Delta$$

where

$$\beta = 1 + (1 + \rho)KS_0$$

and ρ is the relative moles of LSR to substrate. Finally, Δ is the "bound shift" or the LIS to be expected upon 100% complexation of substrate. In the attached table are given calculations based on an S_0 value (substrate concentration) of 0.2M and a temperature range 200°K-400°K.

Even if it is assumed that the bound shift is a constant (= 1000 here) the changes in the LIS are considerable. In fact, they are quite comparable to those actually observed. Furthermore, it is easily shown that the maximum temperature effects occur at $\rho = 1$. This is a concentration employed by many workers. Curve fitting to these numbers gives temperature dependences very much dependent upon the temperature range and upon the particular ρ -value employed. In fact, conditions can be set up to give "good agreement" with almost any hypothesis imaginable.

Thus, it is obvious that, if one is to attach any significance to the temperature variation of LIS, one should study the bound shift, Δ . *This is the only property which is independent of concentration and thus the only parameter to which meaningful interpretations of LIS temperature dependence can be attached.* Also, since in the usual case, both LS and LS_2 complexes are present, the situation is even more complicated than the simple study given here. In this latter situation, it is necessary to determine two bound shifts in order to have parameters amenable to valid physical interpretation.

Either the intrinsic changes in LIS with temperature are very small (since a constant bound shift can still account for a great deal) or a rather large number of invalid interpretations have been made. Hence, a bi-Shakespearean title.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Assistant Professor of Chemistry

Table: Variation in LIS as a function of temperature and LSR concentration.
($S_0 = 0.2M$; $\Delta = 1000$)

<u>T(°K)</u>	<u>K(l/mole)</u>	<u>$\Delta\delta(\rho = 0.5)$</u>	<u>$\Delta\delta(\rho = 1.0)$</u>	<u>$\Delta\delta(\rho = 1.5)$</u>
200	391513	500.0	996.4	1000.0
225	53518	499.9	990.4	999.8
250	10892	499.5	978.8	999.1
275	2961	498.3	959.7	996.7
300	1000	495.1	931.8	990.3
325	399.1	488.1	894.2	976.6
350	181.6	475.1	847.3	952.1
375	91.81	454.6	792.3	914.9
400	50.54	426.4	731.1	865.2

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Ramsey shielding theory applied to the ^{13}C shift parameters in the alkanes

by Joan Mason, Department of Chemistry, The Open University.

Milton Keynes, MK7 6AA. Great Britain.

Grant and Paul¹ have shown that ^{13}C shifts in alkanes can be predicted from a set of empirical parameters (α - ϵ). These are given (as S_k) in the Table so as to represent increments in the shielding (i.e. positive upfield) of an alkane carbon for substitution of α , β , γ ,... hydrogen by alkyl carbon. The fall-off of these parameters with distance from the resonant nucleus is unexpected, for $\alpha \approx \beta$, γ is opposite in sign to the others, and δ and ϵ are not negligible, i.e. the long-range contributions are much larger than those calculated by the dipole approximation from neighbouring bond anisotropies.¹

Grant and Paul gave further additive parameters for chain branching, but these are unnecessary if an atom-plus-ligand local term which we now call σ_d^{AL} is used as diamagnetic correction of the observed shifts.² With the resonant nucleus (A) as gauge origin, σ_d^{AL} is summed over the atom A and its α -substituents (L for ligand) according to Flygare's equation.³ Subtraction of σ_d^{AL} from the shielding σ (obtained by referring the chemical shift δ to an absolute scale) gives an atom-plus-ligand paramagnetic term σ_p^{AL} which shows better 'chemical' correlations, such as additivity of substituent effects, or periodic variation with atomic number of the ligand, than the Saika-Slichter (atomic) local term σ_p^{A} , or the shift δ .

We now extend this argument to cover all (α , β , γ ,...) substitution by alkyl carbon. The Flygare equation³ gives the molecular (Ramsey) diamagnetic term as $\sigma_d(\text{A}) = \sigma_d(\text{free atom}) + \frac{e^2}{3mc^2} \sum_k \frac{Z_k}{r_k}$, where Z_k is the atomic number, r_k the distance from the nucleus A of the k th nucleus, k runs over all nuclei in the molecule except A. and free atom terms are taken from ref. 4. Thus the substituent contributions α_d , β_d , γ_d ... to $\sigma_d(\text{A})$ are additive, and so then must be the corresponding paramagnetic contributions (α_p , β_p , γ_p ,...) by difference from the observed shielding parameters. Therefore the Ramsey (molecular) terms⁵ for the ^{13}C nucleus A are given by $\sigma(\text{A}) = \sigma_d(\text{A}) + \sigma_p(\text{A})$, where $\sigma_d(\text{A}) = \sigma_d(\text{CH}_4) + \sum_k D_k$ (the D_k being the diamagnetic parameters α_d ,...) and $\sigma_p(\text{A}) = \sigma_p(\text{CH}_4) + \sum_k P_k$ (the P_k being the paramagnetic parameters α_p ,...).

We thus extend Grant's parameterisation $\sigma(\text{A}) = \sigma(\text{CH}_4) + \sum_k S_k$ by setting

$S_k(\text{obs.}) = D_k(\text{calc.}) + P_k$ (i.e. $\alpha = \alpha_d + \alpha_p$, and similarly), calculating the D_k by Flygare's equation, and obtaining the P_k by difference from the observed increment in shielding. $\sigma(\text{CH}_4)$ is obtained by referring the chemical shift to an absolute scale based on Ramsey's measurement⁶ of the spin-rotation constant for ^{13}CO , and the ^{13}CO chemical shift,⁷ with σ_d calculated as before.³

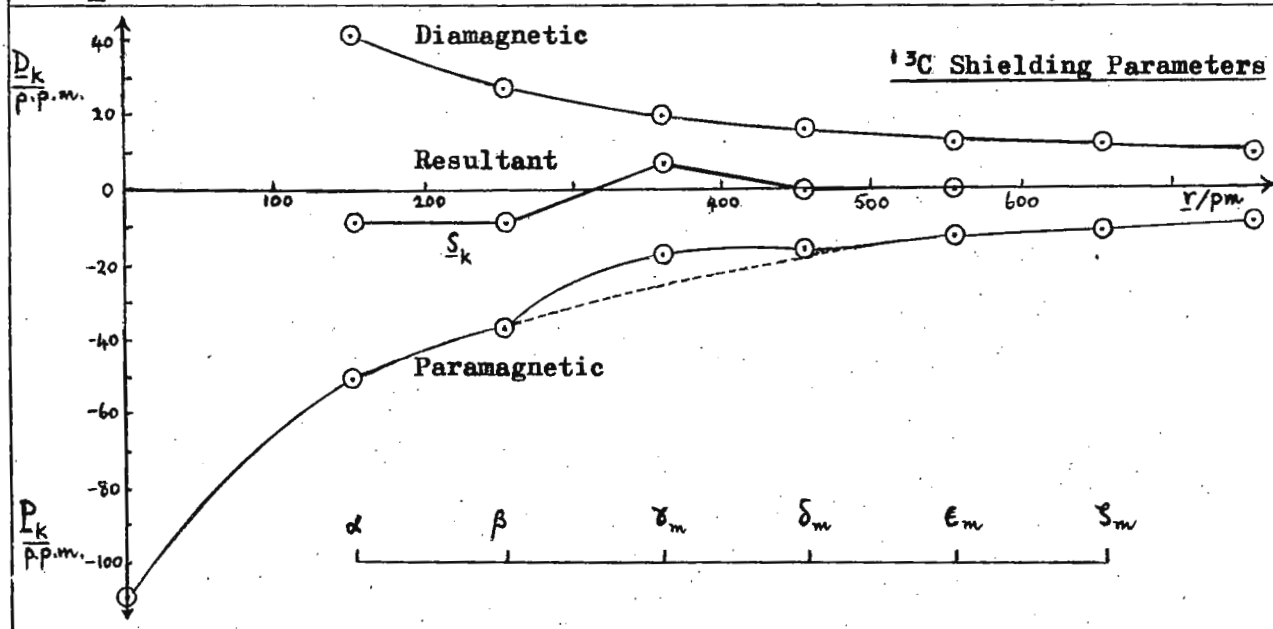
The contribution of the replaced hydrogen is important in the derivation of the substituent parameters: thus α_d is the difference between the diamagnetic contribution of $\alpha\text{-CH}_3$ (50.0 p.p.m.) and that of $\alpha\text{-H}$ (8.6 p.p.m.), and so on. Different parameters are obtained for rings because of the hydrogens lost with ring closure and the effects of conformation, so we restrict ourselves to acyclic alkanes. The γ , δ , and ϵ parameters depend on conformation, and γ_m , δ_m , and ϵ_m are the mean values for liquids at 27 °C. The weighting of the anti (a) and gauche (g^+) states given in the Table, and used to calculate the diamagnetic terms, was obtained from Flory's statistical mechanical studies of n-alkanes,⁸ as were the molecular dimensions. The Figure is a plot of the parameters S_k , D_k , and P_k against the distance r of the substituent carbon from the resonant nucleus. D_k falls off smoothly as (r^{-1}), and so too does P_k beyond the γ -substituent at which the two shielding contributions become equal and opposite. The Figure thus illustrates the cancellation of long-range shielding contributions in large molecules which forms the basis of local-term approximations, and shows the observed variation of the neighbouring contributions (α - ϵ) as arising from the difference in fall-off of the diamagnetic and paramagnetic parts.

That the fall-off of the P_k is not smooth, probably arises from the differences in orientation of the successive substituent groups. Although the dipole approximation for neighbouring contributions to 'other-nucleus' shielding gives smaller values than those observed, the angular dependence seems to be relevant to the irregularities in the P_k curve, since the geometric factor $(1 - 3\cos^2\theta)$ becomes positive for $\theta > 54.7^\circ$, as for γ_g , $\delta_{g^+g^+}$, or δ_{ag^+} . The Table shows that γ_d increases by 5.6 p.p.m. as the substituent moves closer from anti to gauche, but γ for rigid molecules⁹ increases by 6.4 p.p.m., i.e. the paramagnetic parameter has become slightly less negative. When, therefore, sector rules can be developed for long-range shielding,¹⁰ we may find that regions of higher shielding for e.g. gauche conformations of the substituents account for the deviation of γ_p , δ_p , and ϵ_p from the smooth curve that can be drawn through

the other P_k . Taking the molecule as a whole we should perhaps expect a numerically smaller σ_p (though a larger σ_d) for the more compact conformers.

Table Substituent parameters for ^{13}C shielding in the acyclic alkanes

Substituent (weighting)	r/pm	$S_k/\text{p.p.m.}$ (obs.)	$D_k/\text{p.p.m.}$ (calc.)	$P_k/\text{p.p.m.}$ (by difference)
α	153	-9.1	41.4	-50.5
β	254	-9.4	27.3	-36.7
γ_g (40%)	311	6.4	23.6	-17.2
γ_m	357	2.5	20.2	-17.7
γ_a (60%)	390	0.0	18.0	-18.0
$\delta_{g^{\pm}g^{\pm}}$ (12%)	390		17.7	
$\delta_{ag^{\pm}}$ (28%)	450		16.8	
$\delta_{g^{\pm}a}$ (28%)				
δ_m	455	-0.4	16.1	-16.5
δ_{aa} (32%)	507		14.3	
ϵ_m	555	-0.2	12.5	-12.7



- ¹ D.M. Grant and E.G. Paul, *JACS* 1964, 86, 2984.
- ² Joan Mason, *JCS (A)* 1971, 1038.
- ³ W.H. Flygare and J. Goodisman, *JCP* 1968, 49, 3122.
- ⁴ G. Malli and C. Froese, *Int. J. Quantum Chem.* 1967, 1s, 95.
- ⁵ N.F. Ramsey, *Phys. Rev.* 1950, 78, 699.
- ⁶ I. Ozier, L.M. Crapo, and N.F. Ramsey, *JCP* 1968, 49, 2314.
- ⁷ R. Ettinger, P. Blume, A. Patterson, and P.C. Lauterbur, *JCP* 1960, 33, 1597.
- ⁸ A. Abe, R.L. Jernigan, and P.J. Flory, *JACS* 1966, 88, 631.
- ⁹ D.K. Dalling and D.M. Grant, *JACS* 1972, 94, 5318.
- ¹⁰ A.D. Buckingham and P.J. Stiles, *Mol. Phys.* 1972, 24, 99.

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ИНСТИТУТ КИБЕРНЕТИКИ
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№ 26

14th May 197 6

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

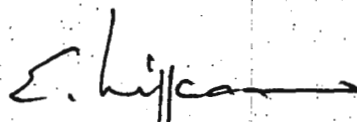
Dear Professor Shapiro,


High resolution ^{13}C NMR in solids with polarization transfer, decoupling and magic angle spinning

The combination of spin decoupling and polarization transfer with rapid magic-angle sample spinning, as first proposed by Waugh and Haeberlen, is a very promising new technique for the study of the NMR spectra of rare nuclei in solids. Schaefer and Stejskal were the first to show the practicability of this approach and now we can do it too, not just with some specially machined pieces of plastics, but with anything, including solutions of the same polymer (if soluble). The rotation frequencies go up to 4 kHz in a 25 kHz decoupling - polarization transfer field. Polarization transfer to the non-protonated carbons is very efficient and is not much suppressed by rapid rotation at the magic angle. The 65 Hz resolution achieved can certainly be improved, because the low-field line measured actually consists of three resonances at 153.1; 150.4 and 149.5 ppm and the decoupling field used takes only a fraction of the total rf power available.

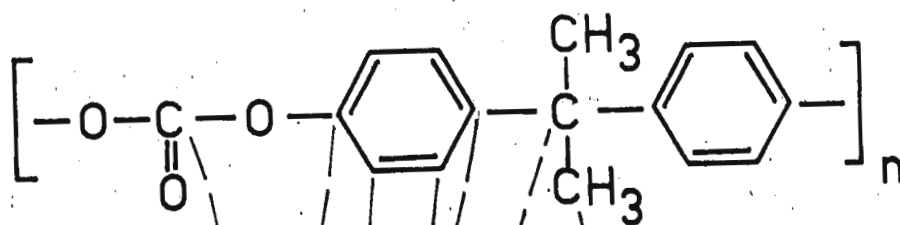
With all good wishes,

Yours sincerely

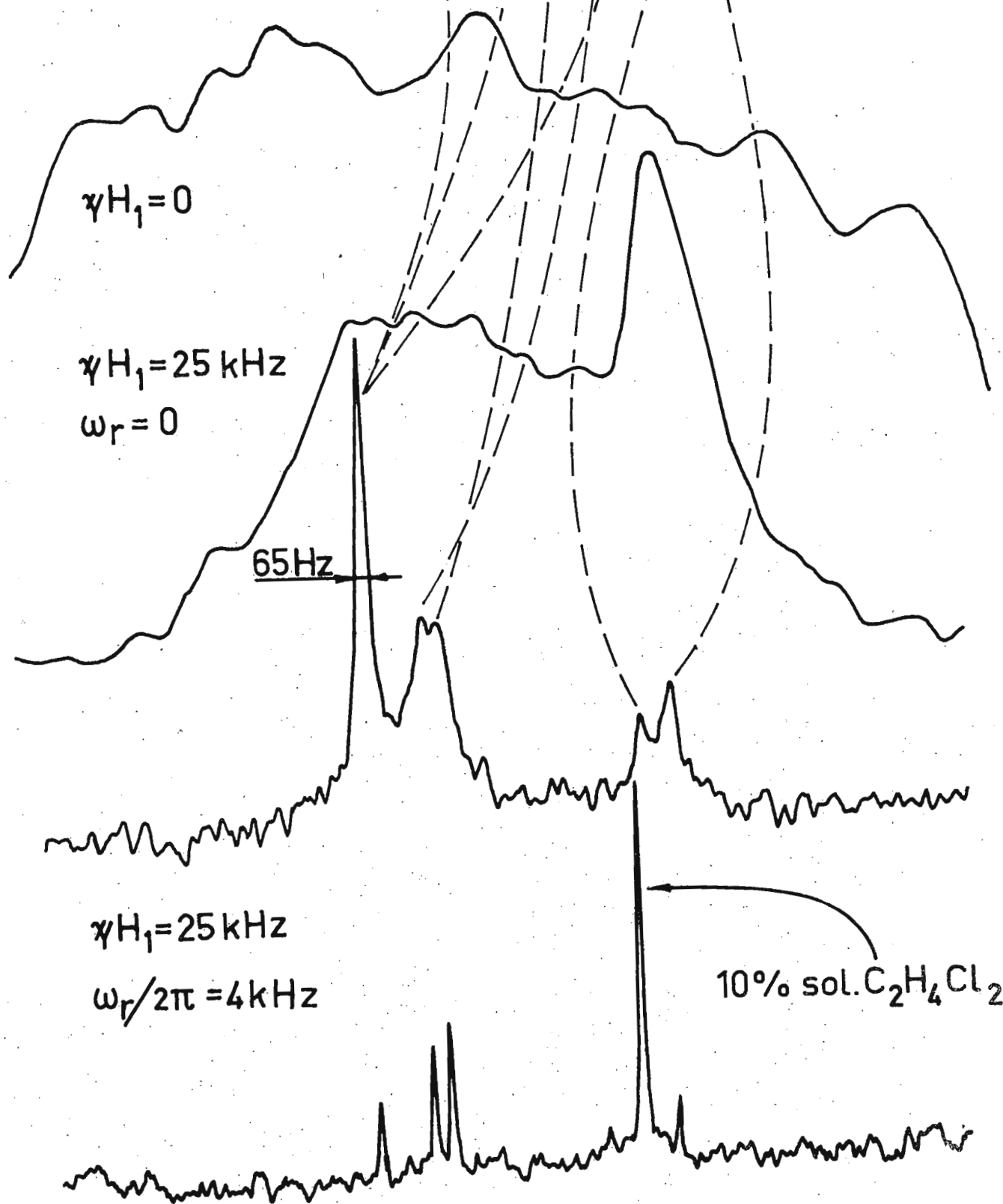

E. Lippmaa


M. Alla

LEXAN

 $\gamma H_1 = 0$ $\gamma H_1 = 25 \text{ kHz}$ $\omega_r = 0$

65 Hz

 $\gamma H_1 = 25 \text{ kHz}$ $\omega_r / 2\pi = 4 \text{ kHz}$ 10% sol. $\text{C}_2\text{H}_4\text{Cl}_2$ 

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

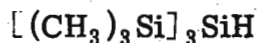
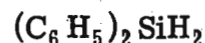
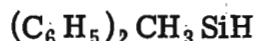
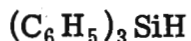
DEPARTMENT OF CHEMISTRY

May 17, 1976

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

Dear Barry:

Two recent reports claim the production of silicenium (R_3Si^+) ions, which would comprise the first silicon analogues in solution of the carbenium ion (R_3C^+).^{1,2} We have used these authors' method of hydride abstraction ($R_3SiH + (C_6H_5)_3C^+-ClO_4 \longrightarrow "R_3Si^+-ClO_4" + (C_6H_5)_3C-H$), to examine a number of silyl hydrides:



On the basis of four lines of evidence, we conclude that silicenium ions are not formed in any of the systems studied to date by this method.

1. All of the systems, including the dihydride, react with triphenylmethyl perchlorate to give isolable triphenylmethane and a silicon species (the "intermediate") that on reduction with $NaBD_4$ ($"R_3Si^+-ClO_4" + NaBD_4 \longrightarrow R_3Si-D$) gives back R_3Si-D (hydride replaced by deuteride). The triphenyl, diphenylmethyl, and diphenyl systems are known by many other tests not to give silicenium ions, so that the reports^{1,2} of replacement of Si-H by Si-D via this two-step procedure do not prove that the intermediate is R_3Si^+ . What other possibilities are there?
2. The methyl resonance of diphenylmethylsilane moves down-field only 0.4 ppm on reaction with triphenylmethyl perchlorate ($CH_3(C_6H_5)_2SiH + (C_6H_5)_3C^+-ClO_4 \longrightarrow "CH_3(C_6H_5)_2Si^+-ClO_4"$). In fact the nmr spectrum of the "intermediate" can be obtained at room temperature with considerable ease. The small size of the shift is not consistent with a methyl group adjacent to an electron deficient center.

3. The above nmr shifts were observed with both CH_2Cl_2 and 1/1 $\text{CH}_3\text{CN}/1,4\text{-dioxane}$ as solvent. Had ionic species been involved, the nmr shifts in the two solvents should have been quite different.
4. The same solutions that gave the above nmr data were found to be entirely nonconducting. Only when excess triphenylmethyl perchlorate was present did the solutions exhibit a measurable conductance.

On the basis of the chemical, nmr, and conductance results, we conclude that hydride abstraction on a silane produces a covalent material, $\text{R}_3\text{Si-O-ClO}_3$, or possibly an undissociated tight ion pair. We find no evidence for trivalent silicon cations.

Sincerely,



Joseph B. Lambert

Hsiang-ning Sun

1. J. Y. Corey, J. Am. Chem. Soc., 97, 3237 (1975).
2. J. Y. Corey, D. Gust, and K. Mislow, J. Organomet. Chem., 101, C7 (1975).

Title: There still are no silicenium ions in solution.

THE UNIVERSITY OF GEORGIA

Department of Chemistry 404-542-2626

ATHENS, GEORGIA 30602



May 17, 1976

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

Title: Dimerization and Restricted Rotation in Nitrosobenzenes

Dear Barry:

During the past year we have been investigating the temperature dependence of the ^{13}C spectra of para-substituted nitrosobenzenes. Three rate processes are detectable, depending on the substituent: (a) tautomerization, $\text{X} = \text{OH}$; (b) dimerization, $\text{X} = \text{H}, \text{Cl}, \text{CH}_3$; and (c) restricted rotation about the C-N bond, $\text{X} = -\text{N}(\text{CH}_3)_2, \text{NH}_2, \text{OCH}_3, \text{CH}_3, \text{H}$, and Cl . Although some of these compounds have been examined previously by ^1H NMR¹ and ^{13}C NMR², the dimerization has not been treated previously. Equilibrium constants for the dimerization processes at 25°C are $\text{H} = 3.73 \times 10^{-3}$, $\text{Cl} = 1.05 \times 10^{-5}$, and $\text{CH}_3 = 4.62 \times 10^{-2}$. Activation energies for the barrier to rotation correlate well with the σ^+ value of the substituent.

In another ^{13}C investigation with Lou Allinger, we have been studying the rotation of the phenyl ring in [n] paracyclophanes. With the $n = 12$ alcohol, the coalescence temperature is $\sim 95^\circ\text{C}$. We have not been able to detect any rotation with the $n = 10$ alcohol. At present, we are examining the $n = 11$ and 13 alcohols.

Sincerely yours,

Richard H. Cox
Associate Professor

RHC:mjd

1. I. C. Calder and P. J. Garratt, *Tetrahedron*, **25**, 4023 (1969).
2. Y. K. Grishin, N. M. Sergeyen, O. A. Subbotin and Y. A. Ustynyuk, *Mol. Phys.*, **25**, 297 (1973).

OTTAWA, CANADA

K1S5B6



DEPARTMENT OF CHEMISTRY

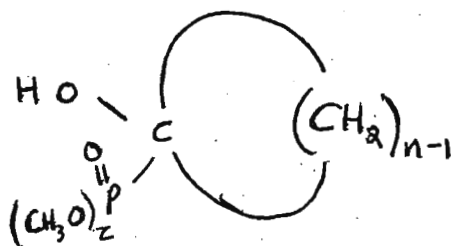
May 18, 1976.

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

Title: "¹³C-³¹P Couplings In Cyclic Hydroxy Phosphonates"

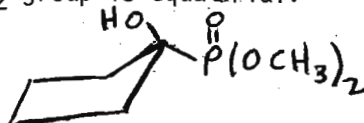
Dear Barry,

In response to your pink letter here are some preliminary results re vicinal C-P couplings in Carbocyclic hydroxy phosphonates obtained by Fred Morin in the course of his fourth year honours project.



<u>n</u>	<u>³J</u>
4	6.5
5	13.0
6	11.2
7	10.9
8	8.8
11	6.7
12	5.7

For the 5-membered ring we interpret the results in terms of the considerable preference for the envelope conformation in which the P(O) (OCH₃)₂ group is equatorial.



The 6-membered ring system shows a temperature invariant ¹³C-spectrum to -120° indicative of a high preference of the P(O)(OCH₃)₂ function for the equatorial position.

Variable temperature studies on the larger ring compounds are in progress as well as the synthesis of the simpler phosphonates which will permit an assessment of the influence of the OH group on the observed J's. In compounds of fixed geometry such a perturbation is substantial, especially when the OH is trans -coplanar to a terminus of the coupling path⁽¹⁾. Best regards.

1. Buchanan & Benezra. Can. J. Chem. 54 231(1976).

Sincerely,

G.W. Buchanan,
 Associate Professor.



Eidg. Technische Hochschule
Zürich-Hönggerberg

Institut für Molekularbiologie und Biophysik

CH-8049 Zürich

Prof. Dr. K. Wüthrich

Tel. (01) 57 57 70

8049 Zürich, May 17, 1976

KW/as

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

Dear Barry:

Some recent pH titration studies of proteins by ^1H NMR at 360 MHz made us aware that the internal reference TSP (2,2,3,3-tetradeutero-3-(Trimethylsilyl)-propionic acid-sodium salt) shows itself a readily measurable pH dependence. This was further investigated in a D_2O solution containing TSP, acetone and dioxane. It is readily apparent from Fig. 1, where the chemical shifts of HDO, dioxane and TSP are plotted vs. that of acetone, that dioxane is as pH-independent as acetone, HDO shows some pH-dependence, and TSP shows a long-range (across six bonds) manifestation of the carboxyl titration (pK from least-squares fit: 5,00; pK of propionic acid: 4,87). In contrast, a similar study of a D_2O solution containing acetone, dioxane and DSS (3-Trimethylsilyl-propane sulfonic acid, sodium salt) showed that the methyl resonance of DSS is essentially independent of pH (Fig. 1). These observations suggest that while DSS and the inert compounds acetone and dioxane are good references for studies of pH-dependent chemical shifts, the water soluble reference TSP should be used with great care for such investigations.

Sincerely yours,

Antonio de Marco

P.S. Please credit this contribution to the subscription of Prof.
K. Wüthrich.

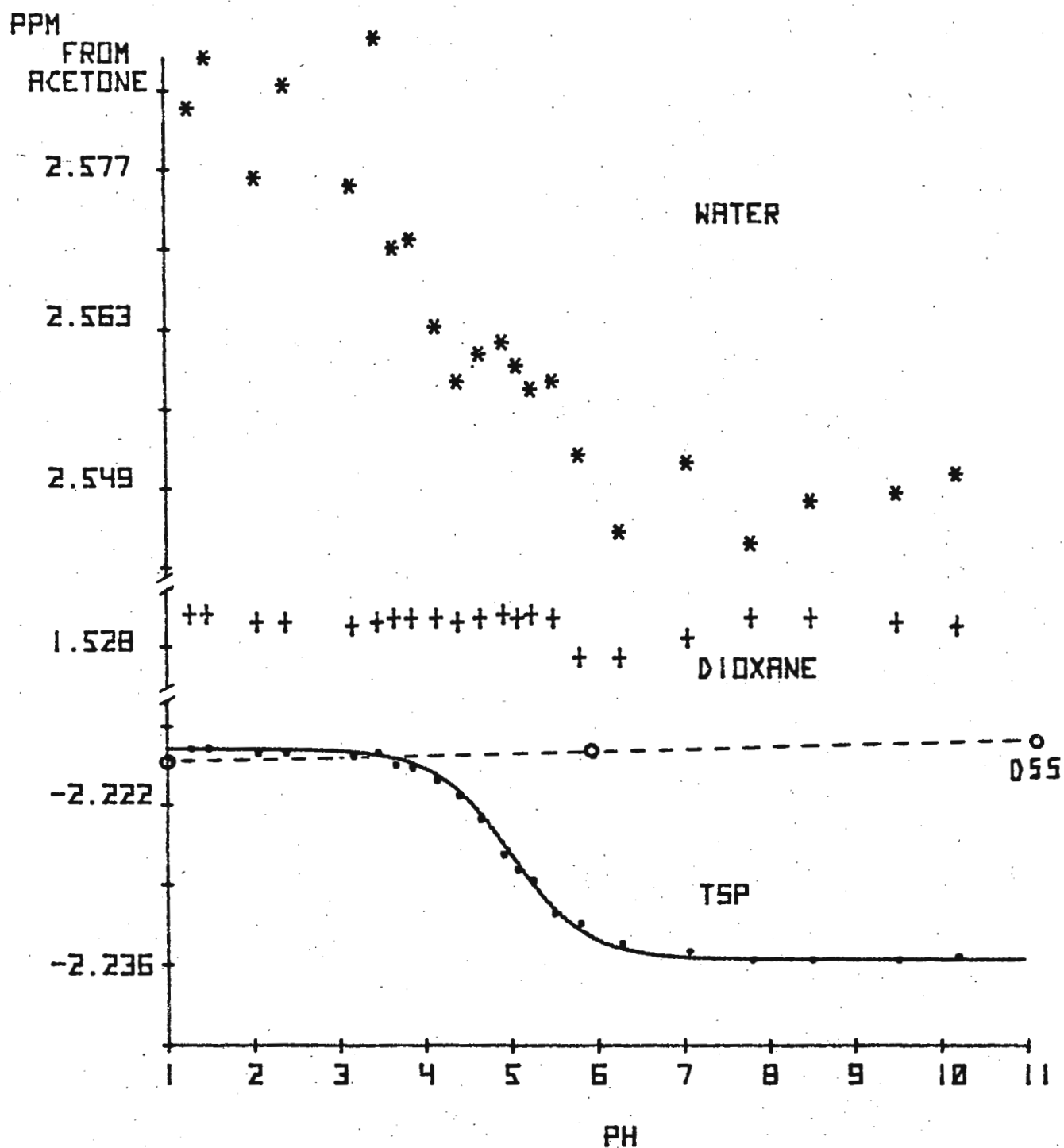


Fig. 1 Plots of the chemical shifts from acetone for HDO (*), dioxane (+), DSS (o) and TSP (•) vs. pH at 25°. The data were obtained at 360 MHz in dilute D₂O solutions of acetone, dioxane and DSS, and acetone, dioxane and TSP, respectively.

БЪЛГАРСКА
АКАДЕМИЯ НА НАУКИТЕ
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

BULGARIAN
ACADEMY OF SCIENCES
INSTITUTE OF ORGANIC CHEMISTRY
1113, Sofia, Bulgaria

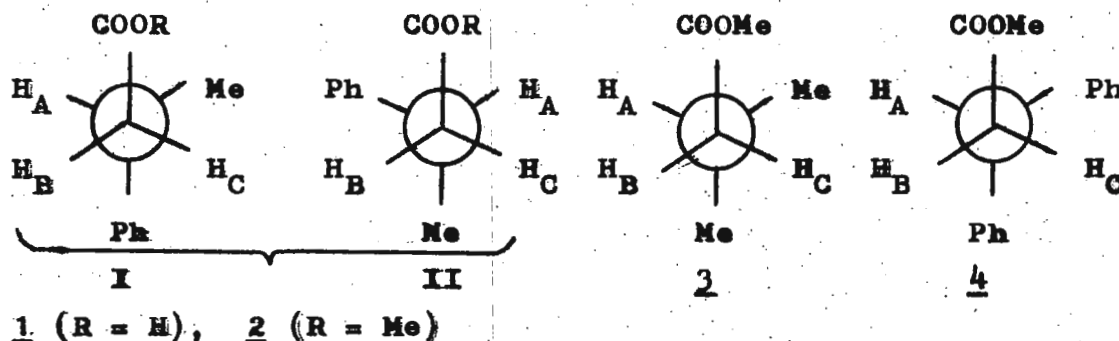
Sofia, 18 May 1976

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

A POSSIBLE APPROACH FOR CONFORMATIONAL ANALYSIS USING LIS

Dear Professor Shapiro,

In collaboration with Dr John Ladd from Salford University we have studied the conformational distribution about the C_2-C_3 bond for 3-phenylbutyric acid (1) and its methyl ester (2).



Computer analysis of the proton spectrum gave $J_{AC} > J_{AB}$ and hence the populations are $p_I > p_{II}$. The assignment of the geminal protons B and C was achieved by stereoselective deuteration¹.

We tried to obtain some independent conformational evidence also by LIS studies. The only proton groups whose induced shifts are likely to depend upon the conformer ratio I/II are Me and Ph. Since of course their induced shift values cannot be compared directly as has been done in other cases², we thought that the use of the Me esters of isovaleric (3) and 3,3-diphenylpropionic (4) acid as models might be helpful.

The $\text{Eu}(\text{fod})_3$ -induced shifts G for the three esters are given on the Table (0.4 M in CDCl_3 ; extrapolated to 1:1 molar ratio). The close values of $G_{\text{CH}_3\text{O}}$ and G_{CH_2} is an indication that the molecular geometry and complexation constants for all

three compounds are very similar. Then, for $p_I > p_{II}$, G_{CH_3C} for 2 should be larger than for 3, and G_{o-Ph} for 2 should be smaller than for 4, which is indeed the case. If $p_I < p_{II}$, the opposite would be true. In order to minimize the effects due to differences in geometry and complexation constants as well as to experimental errors, the use of LIS ratios given in the last two columns of the Table might be preferable.

Compound	G_{CH_3O}	G_{CH_2}	G_{CH}	G_{CH_3C}	G_{o-Ph}	$G_{m,p-Ph}$	$\frac{G_{CH_3C}}{G_{CH_3O}}$	$\frac{G_{o-Ph}}{G_{CH_3O}}$
<u>2</u>	10.6	10.9	9.6	4.3	3.0	0.7	0.406	0.283
<u>3</u>	10.3	10.9	8.8	4.1	-	-	0.398	-
<u>4</u>	10.6	10.6	10.1	-	3.4	0.8	-	0.321

At present we are testing this very approximate approach on other compounds as well as by computations based on the Robertson - McConnell equation.

Sincerely yours,

Stefan

Stefan L. Spassov

1. S.L.Spassov, A.S.Orahovats, S.M.Mishev and J.Schraml, Tetrahedron 30, 365 (1974).
2. G.E.Wright, Tetrahedron Lett. 1097 (1973).

THE EPPLEY INSTITUTE
for
RESEARCH IN CANCER

May 18, 1976

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

Dear Professor Shapiro:

Title: Detection of an Intramolecular Acetal Formation by
¹³C NMR.

A metabolite of N-nitroso-bis(2-oxopropyl)amine (BOP) a potent pancreatic carcinogen in the Syrian golden hamster (1) has been isolated and identified as N-nitroso-2-hydroxypropyl-2-oxopropylamine (HPOP)(2). The cmr spectrum of this compound is shown in Chart A. Treatment of HPOP with acidic methanol yielded a single product whose cmr spectrum is shown in Chart B. This spectrum is consistent with the cyclic acetal structure (Ib). The C₂ resonance at 97.45 ppm is similar to those of the acetal resonances of glucose and other pyranoses (3). The assignments of the other resonances are based on the noise decoupled and off resonance decoupled cmr spectra of trans-2,6-dimethyl-4-nitrosomorpholine. The double resonance for each carbon is a general characteristic of the cmr spectra of nitrosamines and is attributable to distinct syn- and anti-conformations of the nitroso group as the result of restricted rotation about the N-N bond.

The spectrum of HPOP (Chart A) is consistent with an equilibrium mixture of the acyclic and cyclic structures (Figure I). The most striking feature of the cmr spectrum is the presence of both the carbonyl (203.8 and 200.90 ppm) and acetal (94.82 and 94.63 ppm) resonances. The other resonances have been assigned via comparison with the acetal, BOP and N-nitroso-bis(2-hydroxypropyl)amine. Full details of this study will be published shortly.

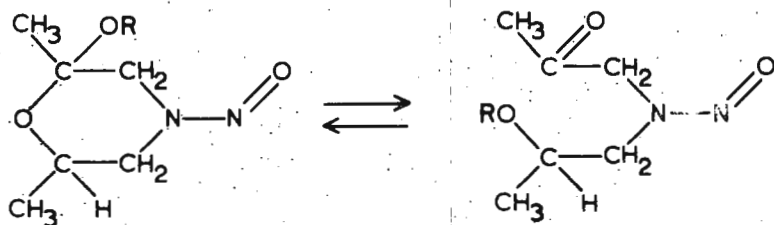
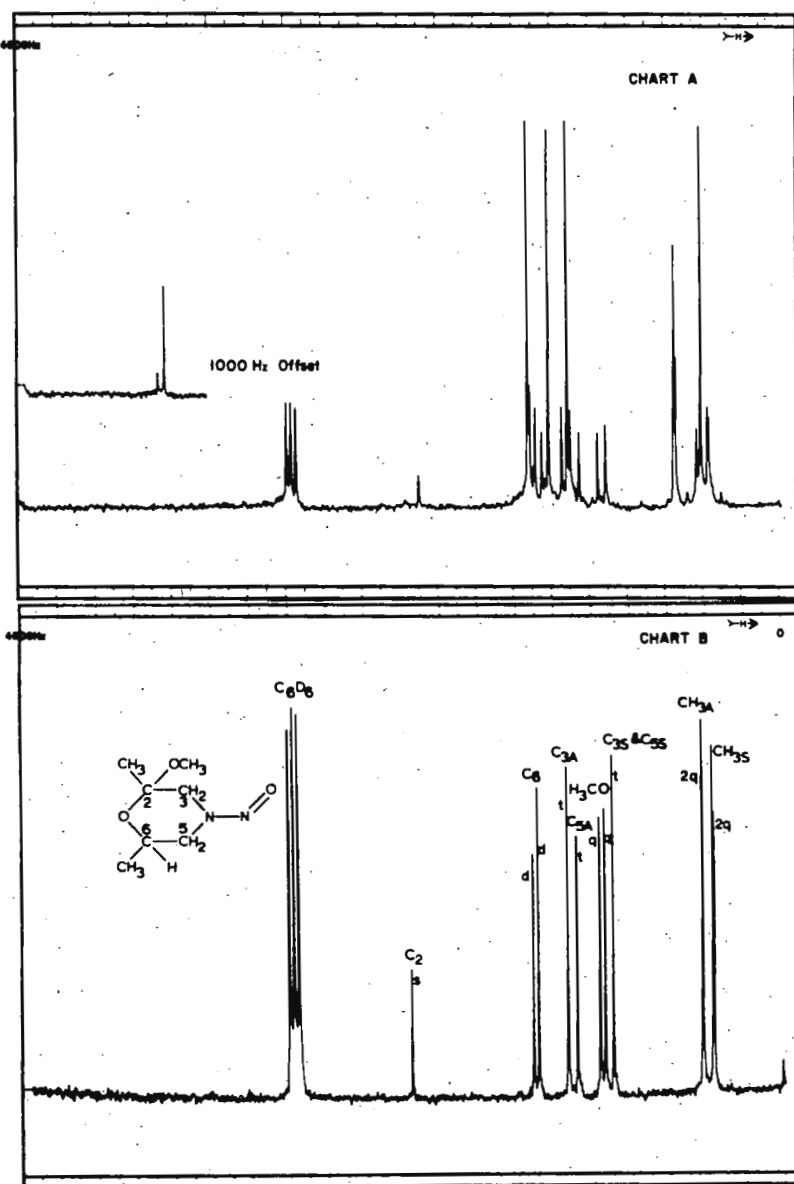


Figure I: Ia, R = H
Ib, R = OCH₃

IIa, R = H



¹P. Pour, et al., Cancer Letters 1, 3 (1975).

²R. Gingell, et al., J. Natl. Cancer Institute, in press.

³L.F. Johnson and W.C. Jankowski, "Carbon-13 NMR Spectra",
Wiley Interscience, New York, NY (1972).

Sincerely,

D.L. Nagel
D.L. Nagel

L. Wallcave
L. Wallcave

R. Kupper
R. Kupper



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DEPARTMENT OF CHEMISTRY

May 20, 1976

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

Dear Professor Shapiro:

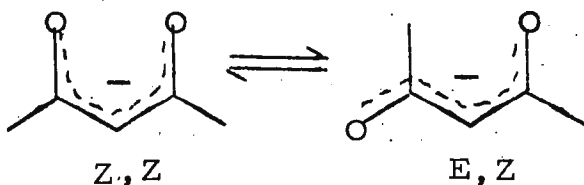
Sulfenamides, Lithium Acetylacetonate, Postdoctoral Opening

A number of years ago, we discovered that nitrobenzene sulfenamides exhibit large barriers to torsion about the N-S formal single bond. The first three entries in the table illustrate the increase in the barrier as the number of nitro groups is increased. We have now succeeded in preparing the fourth compound in the series. We had hoped that the

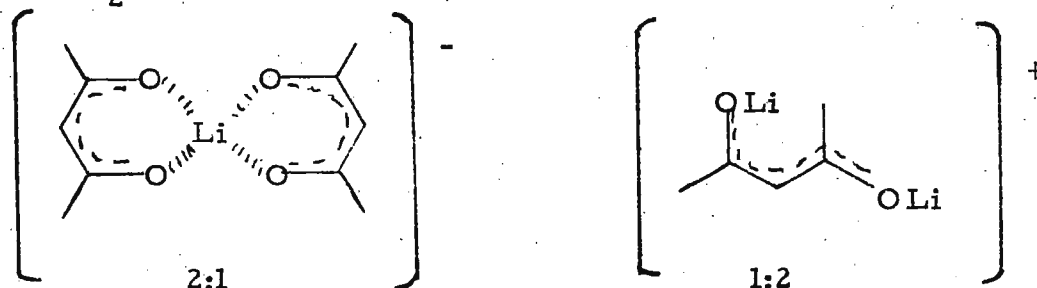
$\text{RSN} \begin{cases} \text{CHCH}_3 & \text{C}_6\text{H}_5 \\ \text{SO}_2 & \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_3 \end{cases}$	R =	ΔG_c^\ddagger (kcal/mol)
	C_6H_5	13.0
		14.7
		19.7
		13.8

barrier would be high enough to permit isolation of torsional diastereomers. Surprisingly, the introduction of the third nitro group removes the electronic effect of the first two. We suppose that a significant change in conformation has occurred which effectively deconjugates the aromatic ring. Further work is underway to elucidate this striking phenomenon.

The equilibria between E, Z and Z, Z configurations of acetyl acetate (AcAc^-), as determined by low temperature nmr spectroscopy, can provide



valuable information about interactions of these anions with metals (J. C. S. Chem. Comm., 1976, 165). Measurement of the spectra of Na AcAc in methanol in the presence of added lithium perchlorate indicates that small amounts of added lithium lead to the formation of a very stable 2:1 complex $\text{Li}(\text{AcAc})_2$ which we suppose has a tetrahedral arrangement at lithium.



We found no evidence for a 1:2 complex $\text{Li}_2 \text{AcAc}$ which has been proposed to exist in acetonitrile (Hiller *et. al.*, J. Inorg. Nucl. Chem., 31, 765 (1969), even when up to 2.5 equivalents of lithium have been added to a methanol solution.

There will be an opening for a post-doctoral research associate in our group. Some experience with ^{13}C spectroscopy, while not necessary, would be desirable since we will acquire an additional Fourier transform spectrometer with probes for ^{13}C , ^1H and ^{19}F within the next few months. Wayne State University is an equal opportunity employer and applications from women and minorities are especially encouraged. Those interested should send a resume and publications list and should arrange for three letters of recommendation.

Sincerely yours,

Morton Raban
Professor of Chemistry

Gaku Yamamoto
Research Associate

/cf



May 26, 1976

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

Dear Barry:

Selective Spin-Locking Experiments

The use of a modulated sequence of non-selective pulses for the selective irradiation of resonance lines has proved valuable for the measurement of Overhauser enhancements and longitudinal relaxation times in homonuclear spin systems (1, 2). An important feature of this, or any other, modulation technique is that the phase of the effective rf field is proportional to the phase of the modulation. A selective spin-locking sequence can therefore be generated by using a modulation pattern containing a 90° phase shift. The modulation pattern is stored in a computer and the length of the sequence before the 90° phase shift is chosen to produce a 90° rotation of the magnetization of the spins of interest, while the pulse sequence following the phase shift provides the spin-locking field. Relaxation during the sequence may be monitored by Fourier transforming the free induction signals following sequences of different lengths.

An example of the technique applied to the measurement of the transverse relaxation of the protons in 1, 1, 2-trichloroethane is shown in the figure. An effective rf field of 25 Hz was used, applied only to the triplet in (a) and only to the doublet in (b). The measured relaxation times for these two groups were 16.0 seconds and 9.2 seconds respectively. In (c) a 25 Hz spin-locking field was applied to each group simultaneously. Here the doublet is inverted because the complete modulation pattern at its frequency was inverted relative to that for the triplet. The measured relaxation times were 9.8 seconds for the doublet and the outer lines of the triplet while the central line of the triplet was characterized by a double exponential with time constants of 9.8 and 16.0 seconds. Thus there is averaging of the relaxation times among transitions having similar symmetry, just as in a non-selective spin-locking experiment (3).

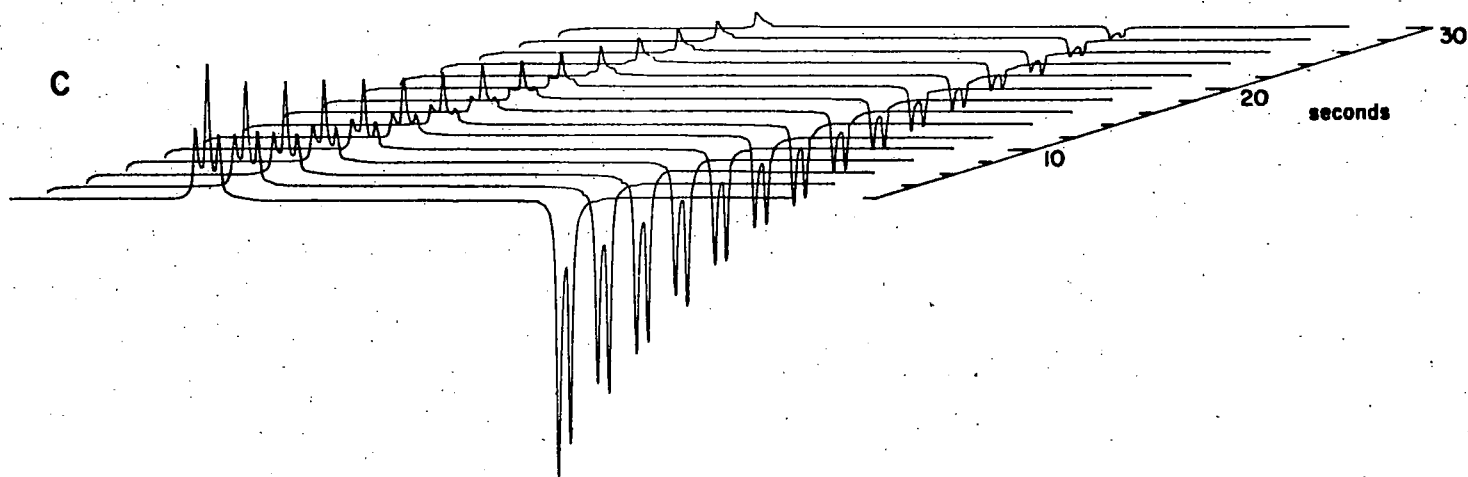
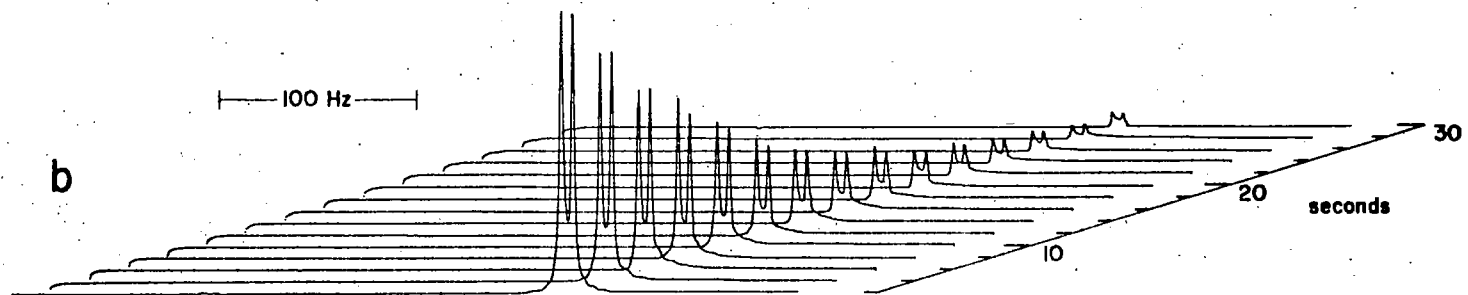
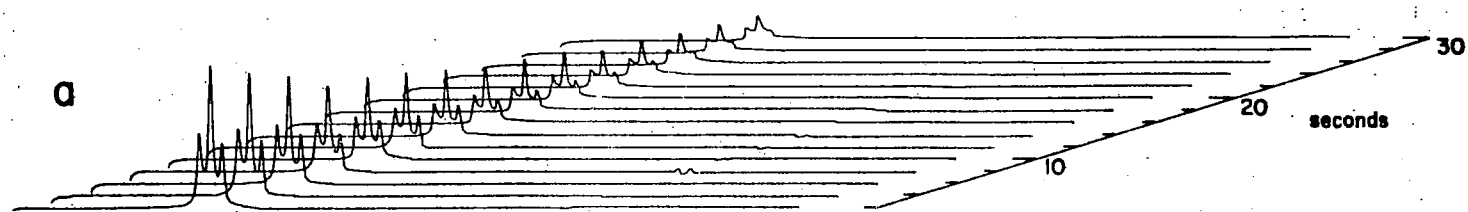
The method seems to provide a useful alternative to non-selective Carr-Purcell experiments which are complicated by the modulation of the echoes in homonuclear coupled systems. A different kind of modulation can still occur in the selective spin-locking experiments. In the spectrum (c), the two groups of spins have the same "spin temperature" in their respective rotating frames. If they are prepared with different spin temperatures, which can be done easily, there is an oscillatory transfer of energy between the two groups of spins as described by Hartmann and Hahn (4).

Yours sincerely,

Howard

H.D.W. Hill

- (1) R. Freeman, H.D.W. Hill, B.L. Tomlinson and L.D. Hall, J. Chem. Phys. **61**, 4466 (1974)
- (2) H.D.W. Hill, TAMUNMR **191**, 55; L.D. Hall and H.D.W. Hill, JACS, **98**, 1269 (1976)
- (3) R.L. Vold and R.R. Vold, J. Chem. Phys. **61**, 2525 (1974)
- (4) S.R. Hartmann and E.L. Hahn, Phys. Rev. **128**, 2042 (1962)



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TELEFONO 292.109 - 292.110

Milano, May 20th, 1976

Errata corrige for the TAMU NMR Newsletter by R. Mondelli, No. 212 (May '76)
pp. 18-19.

δ - effects				
	V - IV	VI - IV	V - IV	VI - IV
$\Delta\delta_{C_{14}}$	+ 2.7	+ 3.7	+ 7.5	+ 3.5
		Me		
ξ - effects				
	II - I	V - IV	VI - IV	
$\Delta\delta_{C_9}$	+ 1.5	+ 2.9	+ 2.3	
$\Delta\delta_{C_{13}}$		+ 2.9	+ 4.1	

I apologize and thank you very much

R. Mondelli
R. Mondelli

New 18-mm Probe for the XL-100

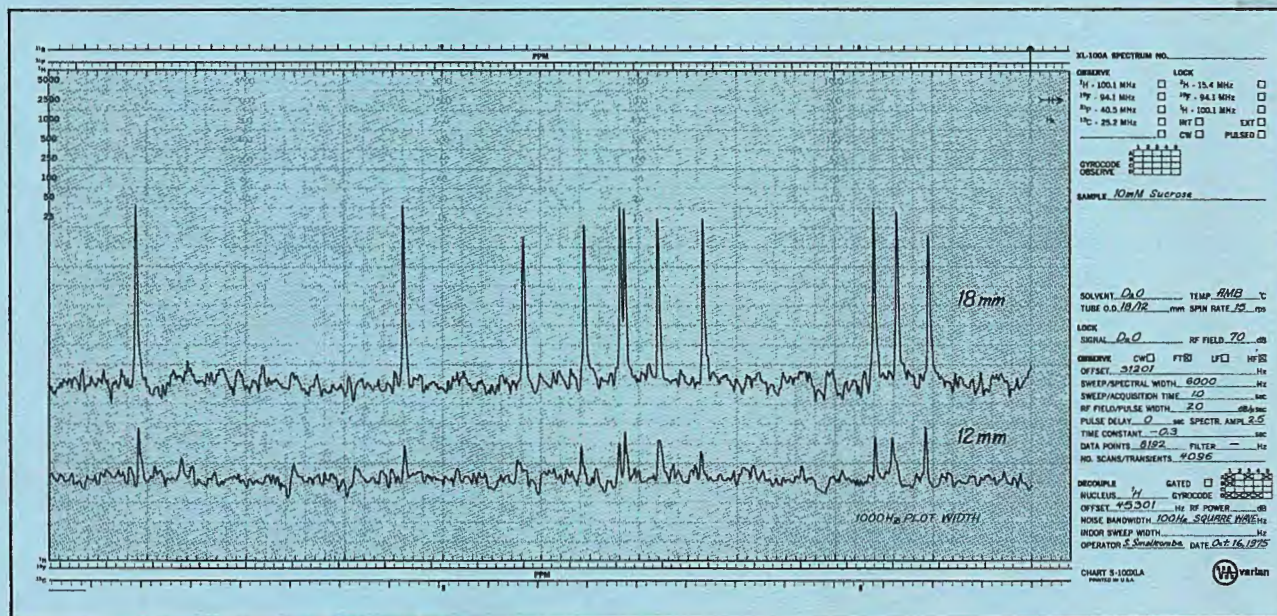
^{13}C Spectra 10 Times Faster

Now Varian XL-100 users can run natural abundance ^{13}C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose — clearly this new probe could extend the application of ^{13}C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs ^{13}C spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10—with results second to none.

Not only is the absolute sensitivity of the V-4418 Probe outstanding, it also offers excellent sensitivity per milliliter of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

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Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D_2O , one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.

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Benzylmalonate

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(10 min.)

^1H

FX 60 C/H DUAL PROBE

1mm
(1 hour)

^{13}C

5 mg
of
CHOLESTEROL

FX 60 C/H DUAL PROBE

10mm
(24 hours)

^{13}C

3,600 PULSES 86,400

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