Texas A & M University
N - M - R
Newsletter

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All Newsletter correspondence, etc. should be addressed to:

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

FYSISCH CHEMISCH LABORATORIUM
RIJKSUNIVERSITEIT GRONINGEN
BLOEMSINGEL 10
Telefoon (05900) 3 48 41*
Groningen, The Netherlands.

GRONINGEN, 7 January 1972

Onze ref.: Drs. H.T.Edzes

Uw ref.:

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

Betreft: COHERENT AVERAGING OF QUADRUPOLAR SPLITTINGS.

Dear Dr. Shapiro,

During the last few years pulsed NMR techniques have been developed to diminish the effect of dipolar interactions on the NMR signals of solids (1,2,3). The same theory also applies to quadrupolar interactions, but I am not aware of any published experiment to demonstrate the effect of pulse trains on quadrupolar interactions.

In cooperation with Dr. A.Rupprecht (Institute of Inorganic and Physical Chemistry, University of Stockholm, Sweden), I am studying the interaction of alkalimetal ions with hydrated fibers of DNA. The fibers are very well oriented, as they are prepared by a wet spinning method (4). The NMR spectra of the counterions Na and Li show a quadrupolar splitting. This splitting is much smaller than in solids, due to a rapid exchange of the quadrupolar nuclei between different surroundings.(6).

I want to show the effect of some pulse sequences on the decay signals of ^{7}Li in a sample of LiDNA. The sample used has a maximum quadrupolar splitting of about 300 mG., when the fiber is oriented parallel to the magnetic field. The pulse experiments were performed on a home-built pulse NMR system. The signals were accumulated on a signal averager (Datalab 101S) with a special integrater input to increase the signal-to-noise ratio to its optimum. A special pulse programmer (5) makes the pulse sequence wished, and drives the averager. The operating RF frequency is 14 MHz., the 90° pulse length is 9 μsec., and the results are an average of 128 or 256 measurements.

The ^{7}Li wide line NMR spectrum of the sample studied is shown in the insert of the figure. The curves show the results of the pulse trains used.

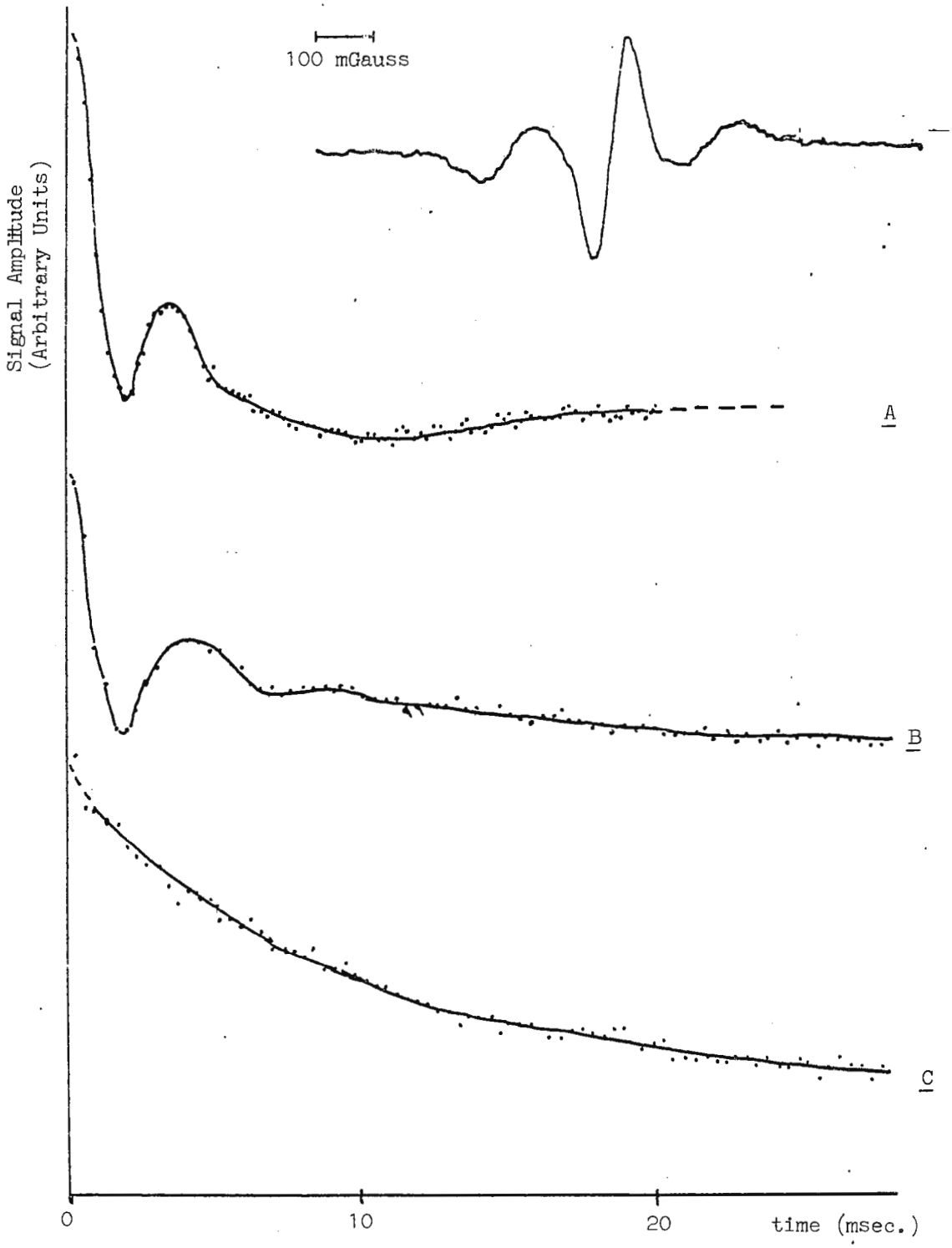
Curve A shows the free induction decay, with the central peak slightly off resonance. The quadrupolar splitting shows up as a strong modulation in the beginning of the decay; the resonance offset bends the last half below zero. Curve B shows the echo amplitudes in a normal CPGM pulse sequence, 90°_{90} - (t - 180°_{0} - t - echo-)$_n$. The effects of field inhomogeniety and resonance offset then disappear, but the quadrupolar interaction still shows up in the decay as a strong modulation of the first half of the signal pictured. The decay continues beyond the figure, due to the long relaxation time of the central peak of the ^{7}Li spectrum.
Curve C shows the effect of a modification of the CPGM sequence to 90°_{90} - (t - 90°_{0} - t - 'echo'-)$_n$ (MCP sequence). This pulse sequence was shown (1,2) to affect the quadrupolar interaction so as to render it ineefective on the decay, in addition to the effects of the normal CPGM sequence on field inhomogeniety, chemical shift, and resonance offset on the decay. There clearly exists no longer any modulation in the signal due to quadrupolar interaction, nor to resonance offset and field inhomogeniety.

As it is a prerequisite to pulse much faster than the decay time, applications of this technique are only possible for small quadrupolar interactions. In solids this happens very rare. In general difficulties arise when the system studied is not rigid (3). The case presented here seems to be illustrative for a number of systems, where motions are the reason that coherent averaging yet is possible. If a rapid exchange of the quadrupolar nuclei results in a small effective quadrupolar splitting with a fixed direction, then coherent averaging becomes possible. Similar behaviour probably exists in several water-clay systems, as some two-pulse experiments performed show that the dipolar (for H_2O) or the quadrupolar (for D_2O) interaction can be influenced by pulses (7).

Yours sincerely,

Hommo T. Edzes

References:
1. J.S.Waugh, and L.M.Huber, J.Chem.Phys. 47, 1862 (1967).
2. U.Haeberlen, and J.S.Waugh, Phys.Rev. 175, 453 (1968).
3. U.Haeberlen, and J.S.Waugh, Phys.Rev. 185, 420 (1969).
4. A.Rupprecht, Biotechnol.Bioeng. 12, 93 (1970).
5. H.T.Edzes, Proc. XVI Colloque AMPERE, Bucharest, 1970. In the press.
6. H.T.Edzes, A.Rupprecht, and H.J.C.Berendsen, to be published.
7. D.E.Woessner, B.S.Snowden Jr., and G.H.Meyer, J.Chem.Phys. 51, 2968 (1969).



^{7}Li decay signals in wet LiDNA, in some pulse sequences.

A. Free induction decay, central peak slightly off resonance.

B. 90°_{90} - (t - 180°_0 - t - echo -)$_n$, t= 171 μsec., same resonance field.

C. 90°_{90} - (t - 90°_0 - t - 'echo'-)$_n$, t= 85 μsec., same resonance field.

Insert: Wide Line NMR quadrupolar spectrum of ^{7}Li.

Glaxo

Glaxo Research Ltd, Greenford, Middlesex

Telephone: 01-422 3434
Telegrams: Glaxotha, London
Telex: 22134
Code: New Standard, Bentleys

~~Please address reply to:~~

Prof. B.L. Shapiro,
Texas A & M University,
College Station, TEXAS 77843.

16th November, 1971

Dear Professor Shapiro,

Lanthanide Shift Reagents

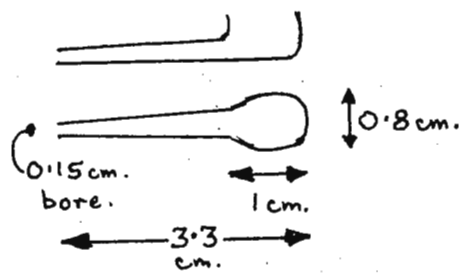
We have used the various lanthanide shift reagents that are commercially available to examine the reproducibility of shift parameter values (i.e., the downfield shift in p.p.m. that would be observed with a shift reagent/substrate molar ratio of unity) for morpholine (cf. H. Hart and G.M. Love, Tetrahedron Letters, 1971, 625). A liquid, such as morpholine, is not ideal for a quantitative test of this kind; a crystalline solid, such as p-nitrobenzyl alcohol that can be easily purified and dried, should have considerable advantages. However, our shift parameter values (see Table) indicate the "scatter" to be expected.

Shift Parameters for $CDCl_3$ solutions of morpholine at 34°

Lanthanide Reagent	Molar conc. of morpholine	Shift parameters (p.p.m.)		
		OCH_2	NCH_2	NH
$Eu(dpm)_3$	1.15	24	54	180
$Eu(dpm)_3$	a	22	48	170
$Pr(dpm)_3$	1.15	-36	-72	-210
$Pr(dpm)_3$	a	-33	-71	-210
$Eu(fod)_3$	1.15	16	39	130
$Pr(fod)_3$	1.09	-40	-79	-220
$Eu(fod)_3-D_{27}$	1.18	18	42	140
$Pr(fod)_3-D_{27}$	1.26	-33	-62	-170

(a) cf. Hart and Love, loc.cit.; molar conc. and temperature

During the measurement of shift parameter values, it is necessary to accurately weigh and transfer to the spinning tube without loss small quantities of dry lanthanide reagent. We have found that these transfers are facilitated by using small glass "boats" about 3 cm long and weighing about 1 g (see Figure). The dimensions of the "boat" are not critical, but the neck of the "boat" should fit easily into the open end of the spinning tube and should have an internal diameter of about 1.5 mm, i.e., wide enough to avoid trapping particles of reagent. In this way 5 mg samples of reagent can be handled.



May we enquire as to when and where the report on your A.F.M. data survey of n.m.r. spectra is to be published? Incidentally, what does A.F.M. stand for? Is it armoured fighting machine?

Yours sincerely,

J.E. Page R.A. Fletton G.F.H. Green

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

December 30, 1971

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

Dear Dr. Shapiro:

May we open our "account" by reporting some observations concerning the carbon resonances of some group Va derivatives.

Utilizing our recently acquired Bruker-HFX spectrometer equipped with Fourier Transform capabilities, we have measured the proton decoupled natural abundance carbon-13 spectra of the compounds shown in the Table.

Assuming the position of the para carbon resonance to be a reflection of the degree of overlap of the lone-pair with the π-system, it may be seen that P, As and Sb do not interact strongly with the aromatic-π-system. In contrast, the C-4 resonance of triphenylamine appears at considerably higher field in keeping with the recognized relatively low basicity of this amine.

Sincerely,

L. M. Venanzi

L. M. Venanzi, Chairman and
E. I. duPont de Nemours
Professor of Chemistry

P. S. Pregosin
Postdoctoral Fellow

LMV:PSP/sma
Enclosure

Compound

Ph_3X: Chemical Shift*

X	C_{-1}	C_{26}	C_{35}	C_4
N	147.8	124.1	129.1	122.6
P	137.1	133.5	128.3	128.4
As	139.6	133.6	128.6	128.4
Sb	138.4	136.1	128.8	128.8

*Chemical sifts were measured from the central peak of the deuteriochloroform triplet and have been corrected to TMS using the relation:

$$\delta \text{ TMS} = \delta \text{ CDCl}_3 + 77.0$$

Values are estimated to be correct to ±0.1 ppm.

$\delta C_6H_6 = 128.4$

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Boite postale nº 1
91 - Vert le Petit
téléphone : 496.22.21

Dr B.L. SHAPIRO
Department of CHEMISTRY
Texas A & M University
College of Science
College Station, Texas 77843

U.S.A.

Vert le Petit, le 14 Janvier 1972

N° 153 B. GM/mg COl

Europium-induced ^{31}p shifts in $(Me_2N)_3PO$

Dear Barry,

We have been in much trouble (which explains the delay in answering your blue note, which rapidly turned to pink) when trying to obtain significant data on contact and pseudo-contact contributions in lanthanide nitrate induced ^{31}P shifts on trisdimethylaminophosphine oxide. From observations on d_6-acetone solutions reported by J. K. M. Sanders and D. H. Williams (Tetrah. Letters, 1971, p. 2813), we contemplated the possibility of using triphenyl phosphine as an internal standard ; as we prefered to use water solutions, it occured that this phosphine precipitated quite easily in the presence of $Eu(NO_3)_3$. Thus, we had to rely on P_4O_6 as external standard and investigate the Eu-dependence of phosphorus shift in 1 : 2 $(Me_2N)_3PO$ - H_2O mixtures, up to a molar ratio $[Eu]/[(Me_2N)_3PO]$ of 0.07.* Representative results are presented hereafter

$[Eu]/[HMPT]$	Chemical shift (high field VS. P_4O_6)
0.	84.5 **
0.030	87.2
0.043	89.7
0.057	95.6
0.070	95.4

.../

.../...

This yields a ^{31}P- gradient of ca. 165 ppm which is greatly lower than that observed (in acetone solutions) for $(MeO)_3PO$, $(EtO)_3PO$ and $(EtO)_2P(O)Et$, VIZ. 500 ± 50.

This may be an indication of a phosphoryl deactivation by the amino groups or of a competition between nitrogen and phosphoryl (and water) sites*** Extension to other lanthanide (Yb, Dy, Ho, Er, Nd and Gd) is planned but we have first to solve the problem of solvent effects.

With very best regards.

G. MAVEL

R. MANKOWSKI-FAVELIER

Z.W. WOLKOWSKI

* Samples are prepared first by dissolving $Eu(NO_3)_3\ 6\ H_2O$ in water and then adding $(Me_2N)_3PO$. Precipitation occurs at ca. 0.097

** This shift is significantly different (ca - 5 ppm) from pure HMPT.

*** Relevant ^{14}N investigation is to be done in Prof. Witanowski laboratory (Warsaw).

161-10

TELEPHONE: 660 0522.

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

January 14, 1972

The University of Sydney
Department of Organic Chemistry
SYDNEY, N.S.W. 2006

IN REPLY PLEASE QUOTE:

LONG RANGE COUPLING ACROSS FOUR SINGLE BONDS INVOLVING METHYL GROUPS

Dear Barry,

With the exception of data for some three-membered ring derivatives, the majority of the results available[1-3] for $^4J_{Me-C-C-H}$ refer to dihedral angles of 180 and 60°. Dr. P. W. Westerman and Miss Alison M. Dean prepared the compounds listed below and obtained their NMR parameters. Coincidentally, Dr. D. H. Hunter of the University of Western Ontario has also analysed the spectra of the two isomeric dimethylacenaphthenes and obtained similar results.

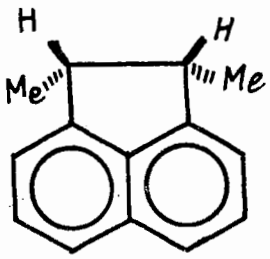
It can be seen that for dihedral angles of approximately 0 and 120°, $^4J_{Me-C-C-H}$ takes up small absolute values. It is now possible to draw an approximate experimental curve for the angular dependence of $^4J_{Me-C-C-H}$ and compare it with the VB[3,4] and INDO[5] calculations. It appears from the attached figure that the VB results seem better for the region near $\phi=180°$, but that the INDO curve is closer to our new data and to the region of $\phi=60°$. From the structural point of view, it is important to note that large values of $^4J_{Me-C-C-H}$ can now be taken as uniquely indicative of the antiperiplanar relationship with the coupled proton.

With best regards, yours sincerely

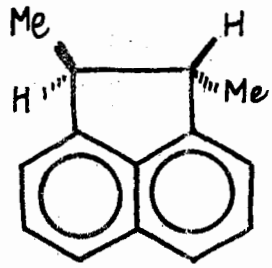
Sev Sternhell

S. Sternhell

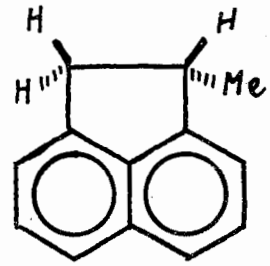
[1] Jackman and Sternhell, "Applications of NMR spectroscopy in organic chemistry", Pergamon 1969, Ch. 4-4. [2] Sternhell, Quart. Revs., 23, 236 (1969). [3] Barfield and Chakrabarti, Chem. Revs., 69, 757 (1969). [4] Barfield, J. Chem. Phys., 41, 3825 (1964). [5] Barfield, J. Am. Chem. Soc., 93, 1066 (1971).



$^{128}J = -0.26$

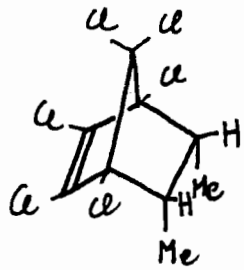


$^{0}J = -0.08$

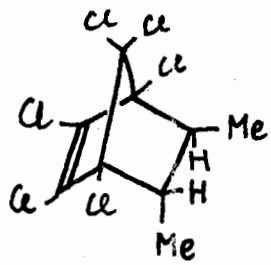


$^{128}J = -0.15$

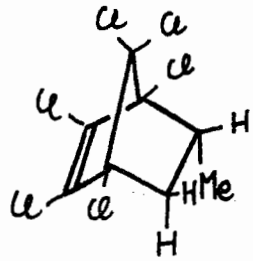
$^{0}J = +0.01$



$^{120}J = -0.32$

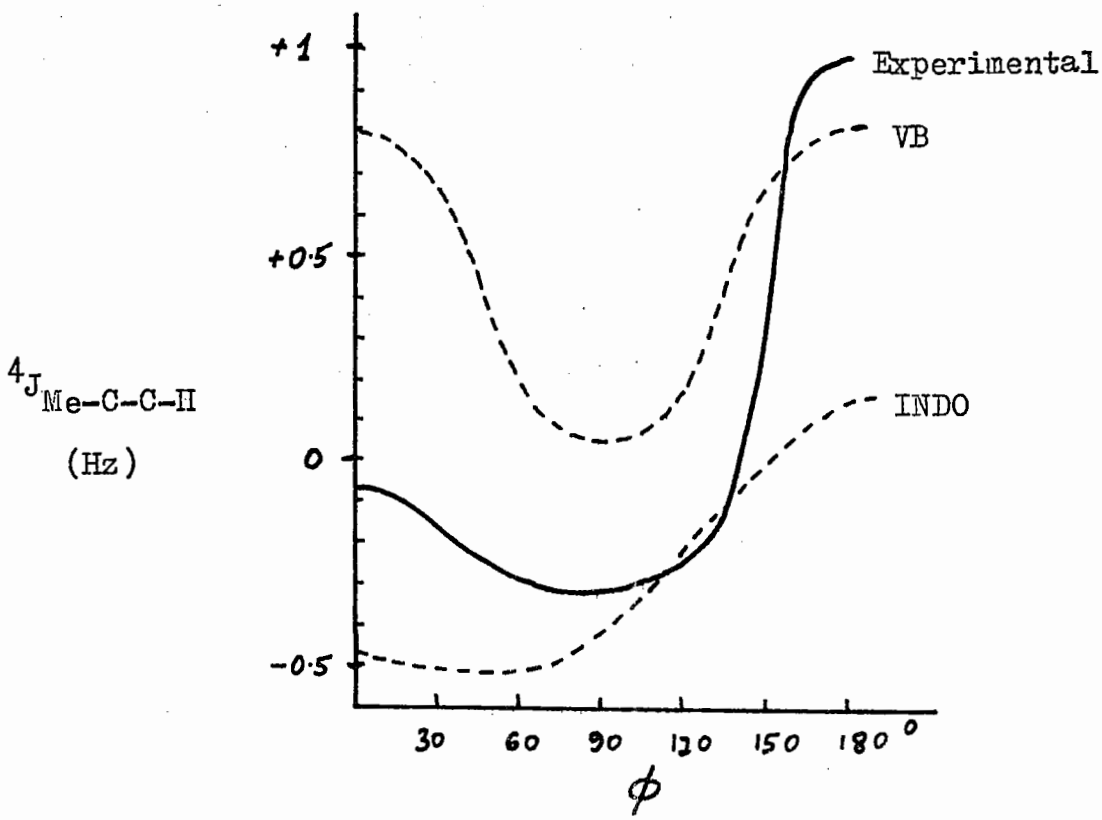


$^{0}J = +0.15, -0.10$



$^{120}J = -0.13$

$^{0}J = -0.17$



CHEMISCHE LABORATORIA DER RIJKSUNIVERSITEIT
ZERNIKELAAN, PADDEPOEL, GRONINGEN

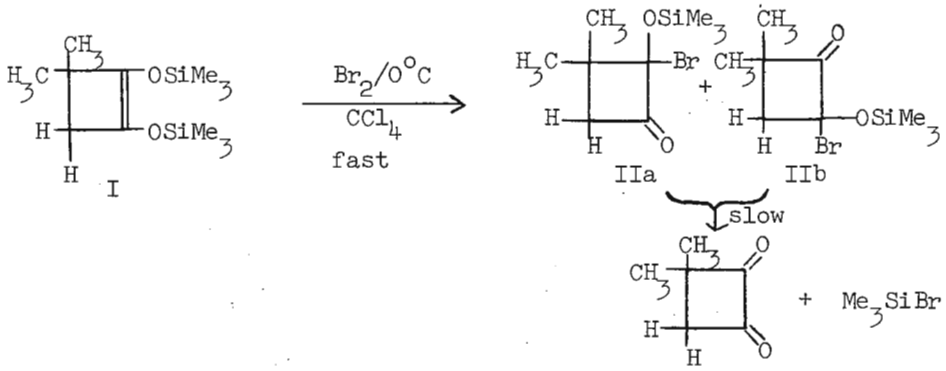
ORGANISCH CHEMISCH LABORATORIUM

7 January 1972

Determination of the structures of two isomeric substituted cyclobutanones.

Dear Professor Shapiro,

In the reaction of I with bromine at 0°C in carbontetrachloride a mixture of products is formed, that is slowly converted into the dione III. This conversion can be stimulated by heating or by addition of a polar solvent. 60 Mhz PMR spectra of the reaction mixture suggested that the initially formed products were IIa and IIb in a ratio of 3:1 (τ = 7-8: two AB spectra; τ = 8.5-9: four signals with unequal intensities; τ = 9.45: singlet of $(CH_3)_3SiBr$; τ = 9.72: singlet). The assignment of the peaks in this spectrum was very difficult. Compounds IIa and IIb should both give seven lines: an AB quartet, two methyl signals and a strong peak for the trimethylsilyl group.



100 Mhz Spectra (on a Varian XL-100) made a better assignment possible. All peaks were now resolved (see Table 1). As IIb was present in a relatively low concentration, the signals due to IIb were small compared with those of IIa and III. The peaks of IIa are named a to g, those of IIb 1 to 7.

Most lines were singlets, only lines a and b appeared as quartets (J = 0.7 Hz) and line f was a doublet (J = 0.7 Hz). The assignment was chequed with the aid of INDOR and Double Resonance techniques. In the INDOR spectrum, monitoring of line d gave an "up" for line a and a "down" for line b. Monitoring of line c gave the mirror image of the former spectrum. The INDOR spectrum of line

Table 1. A 100 Mhz spectrum of the reaction mixture.

Peak	τ	Multiplicity
a	6.97	quartets
b	7.13	$J = 0.7$ Hz, $J_{gem} = 16.3$ Hz
1	7.15	singlets
2	7.28	$J_{gem} = 13.1$ Hz
III (CH_2)	7.30	S
3	7.57	S
c	7.68	S
4	7.70	S
d	7.84	S
e	8.48	S
5	$\Delta\nu = 0.9$ Hz	S
III (CH_3)	8.67	S
6	8.78	S
f	8.84	doublet $J = 0.7$ Hz
$(CH_3)_3SiBr$	9.44	S
g	9.72	S
7	$\Delta\nu = 0.7$ Hz	S

2 gave an "up" for line 3 and a "down" for line 4. So the lines a to d are an AB spectrum, due to the CH_2 group in IIa, the lines 1 to 4 are another AB spectrum, due to the CH_2 of IIb. The geminal coupling constants are 16.3 and 13.1 Hz respectively. Irradiation on line f caused the two quartets a and b to collaps to singlets. In the major product IIa therefore a long range coupling exists between one of the hydrogen atoms of the CH_2 group and one of the CH_3 groups.

The two absorptions for III were easily recognised by their slowly increasing intensity; this was confirmed by the PMR spectrum of pure III.

The geminal coupling constant in cyclobutanone derivatives[1,2] is normally -10.9 to -14.4 Hz, but in systems with an adjacent carbonyl group it is increased to -15 to -17 Hz. We therefore concluded that IIa has a carbonyl group adjacent to the CH_2 group and IIb has not.

A long range coupling constant over four bonds normally follows a W-mechanism. In a planar cyclobutane ring such a W-structure is not present between any of the methyl substituents and a hydrogen atom. When the ring is strongly puckered, however, a W-structure can exist when a C-CH_3 and a C-H bond are in one plane and the two substituents are in a trans position towards each other. As such a coupling was observed in the main product, this compound therefore has the most puckered and consequently the most crowded structure IIa.

Sincerely yours,

J. Runsink, H. Reiffers.

1. J.W. Emsley, J. Feeney and L.H. Sutcliffe, Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 5, page 205 (Pergamon Press).

2. I. Fleming and D.H. Williams, Tetrahedron 23, 2747 (1967).

Oregon Graduate Center
for Study and Research
19600 N.W. Walker Road · Beaverton, Oregon 97005 · 503/645-1121

January 17, 1972

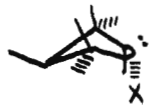
Professor Barry Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Change of Address; Stereospecific $^2J_{PCC}$

Dear Barry:

Effective mid-February I'll be at Varian's Eastern Applications Laboratory, 25 Highway 22, Springfield, New Jersey 07081, as Applications Chemist. The lab will be equipped with an XL-100-15-FT. I am looking forward to making new acquaintances both within and outside of the NMR community.

To put a little more meat in this I'll report on a stereospecificity we've found for $^2J_{PCC}$ in four-membered phosphorus heterocycles. This very closely patterns the $^2J_{PCH}$ stereospecificity in phosphines (J. P. Albrand, D. Gagnaire, and J. B. Robert, Chem. Commun., 1968, 1469). The stereospecificity noted for $^2J_{PCC}$ will prove especially useful in cases where the $^2J_{PCH}$ is difficult to obtain from complicated ^1H spectra.



$^2J_{PCC}$ (α-methyls)

	axial	equatorial	axial	equatorial
X = C_6H_5	31.8	2.5	4.9	27.8
X = CH_3	30.5	2.1	4.3	26.9
X = Cl	37.1	0.0	2.5	33.5

Sincerely,

George A. Gray
Assistant Professor of Chemistry

GAG:nw

19th January 1972

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

Dear Professor Shapiro,

SOLVENT AND TEMPERATURE EFFECTS ON THE SYN-ANTI ISOMERISM OF ACETALDOXIME.

The population ratio for the syn-anti isomers of acetaldoxime

Syn anti

pure liquid and in various solvents, at room temperature, has been determined from their proton NMR spectra, being

Solvent	Syn/anti
pure liquid	0.61 ± 0.01
CCl_4	0.60 ± 0.01
C_6H_{12}	0.56 ± 0.02
C_7H_{16}	0.52 ± 0.01
$CDCl_3$	0.65 ± 0.02
C_6H_6	0.61 ± 0.02
CH_3OH	0.68 ± 0.02
$(CH_3)_2CO$	0.72 ± 0.02
T.F.A.	~0

The study is now being extended to low and high temperatures, in order to obtain the appropriate thermodynamic functions.

Please credit this letter to V.M.S. Gil.

Yours sincerely,

J.J. Romão de Sousa

M. Madalena Caldeira

V.M.S. Gil

SIMON FRASER UNIVERSITY BURNABY 2, B.C., CANADA
DEPARTMENT OF CHEMISTRY; 291-3111

January 20, 1972

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

Dear Barry:

Ge^{73} Spin Relaxation in Liquid GeF_4

Apologies for my tardiness in maintaining my "participatory subscription" to your worthwhile news letter.

We have been continuing our studies of relaxation mechanisms of high-Z nuclear spins in liquids, and recently Mrs. M. Tracey has been investigating the Ge^{73} relaxation pathways in neat liquid germanium tetrafluoride. The possible mechanisms have been classified according to the rank of the spherical tensor spin operators that arise in the expansion of the various possible spin-lattice interactions in the fluctuating hamiltonian. Within this classification, the Ge^{73} ($I = 9/2$, 7.61% abundant) in the tetrahedral GeF_4 species is of interest because

a) the nuclear g-factor of Ge^{73} is small, reducing the importance of first rank, magnetic dipole interactions (viz. heteronuclear dipole-dipole, spin-rotation interactions, etc.)

b) by symmetry, the static electric field gradient at Ge^{73} vanishes in a tetrahedral species, removing the possibility of static second rank, electric quadrupole interactions; thus leaving open

c) the possibility that the relaxation pathway is via higher order fourth rank electric hexadecapole (and for completeness, but unlikely, third rank magnetic octupole) interactions.

We have monitored the Ge^{73} Zeeman state lifetimes by observing the individual linewidths of the F^{19} spin-coupled decet at 56.4 and 94.1 Mhz, with advantages over the normal direct T_1 measurement of

a) sensitivity, and

b) selectivity. It should be emphasized that in the limit of slow relaxation ($R_1 \ll 2\pi J$) the multiplet component linewidths are a measure of the relaxation transitions out of a given M state, $\sum_{M^1} P_{MM^1}$, whereas the T_1 measurement is an average of this quantity over all M states, ie $\sum\sum_{MM^1} P_{MM^1}$

For an interaction of spin tensor rank Ω, the individual relaxation transition probabilities P_{MM^1} are proportional to $|\langle I,M'|T(\Omega)|I,M\rangle|^2$ and the complete relaxation matrix can easily be evaluated for given Ω, $I = 9/2$ by appeal to the 3j tables of Rotenberg et al.[1] Fig 1 shows the multiplet peak height patterns predicted by this procedure in the slow relaxation limit (valid here, where $J_{Ge^{73}-F} = 179$ hz) for Ω values through 4. Rank zero interactions include all those troublesome effects in the F^{19} spectrum that are independent of the M-state of Ge^{73}, such as H_0 inhomogeneity effects (assumed constant across the multiplet- a dubious assumption due to thermal drifts in external lock operation at temperatures away from ambient) F^{19} T_1 effects, and F^{19} T_2 effects (as occasioned by possible catalyzed intermolecular F^{19} chemical exchange).

Fig 2 shows the experimental F^{19} multiplet spectrum at -20°C from our XL-100 spectrometer. A glance at the predicted spectra shows the dominant mechanism to be second rank quadrupolar. Over the temperature range studied (+31° to -25°C) the various multiplet linewidths ranged from 6 to 20 hz of which approximately 1 hz is due to rank zero effects and the remainder, according to a computer decomposition is due to rank two interactions. Within our accuracy, we find no evidence for ranks one, three or four contributions. The activation energy for the rank two contribution is 1.5 ± 0.3 kcals $mole^{-1}$.

Various fluctuating distortions of GeF_4 from T_d symmetry have been considered that enable the $T^{(2)}$ pathway - asymmetric vibrations, centrifugal distortion, asymmetric chemical complexation, collisional distortion - and it is concluded that it is the last that is operative, quite analogous to the situation in gaseous Xe^{131} discussed in the early days of NMR by Staub[2] and more recently in liquid $Mo^{97}F_6$ studied here by Brooks[3]. This mechanism then yields a handle on

yet another correlation time in liquids - the collisional correlation time.

Our work on GeF_4 leads to some interesting comparisons with the liquid GeH_4 system communicated briefly by Sackmann and Dreeskamp[4]. It becomes evident that

a) they misassigned their mechanism. In $Ge^{73}H_4$, the Ge^{73} is now seen to relax by a first rank, magnetic dipole interaction (spin-rotation interaction?).

c) the difference in the Ge^{73} relaxation mechanisms in the two systems is due to differential van der Waals distortion on collision, with the GeF_4 molecule being much more polarizable.

The results then allow one to classify GeH_4 as a "hard sphere" liquid and GeF_4 as a "soft sphere" one.

Best wishes for 1972.

Yours sincerely,

E. J. Wells
Associate Professor

EJW/md

1. Rotenberg, Bivins, Metropolis and Wootin "The 3-j and 6-j symbols" Technology Press, Cambridge, Mass. (1959).

2. Staub, Phys. Rev. 93, 904, (1954); Helv. Phys. Acta 29, 246, (1956).

3. S. Brooks, M.Sc. thesis, Simon Fraser University (1969).

4. Sackmann and Dreeskamp, Z. f. Naturforsch 21, 852, (1966).

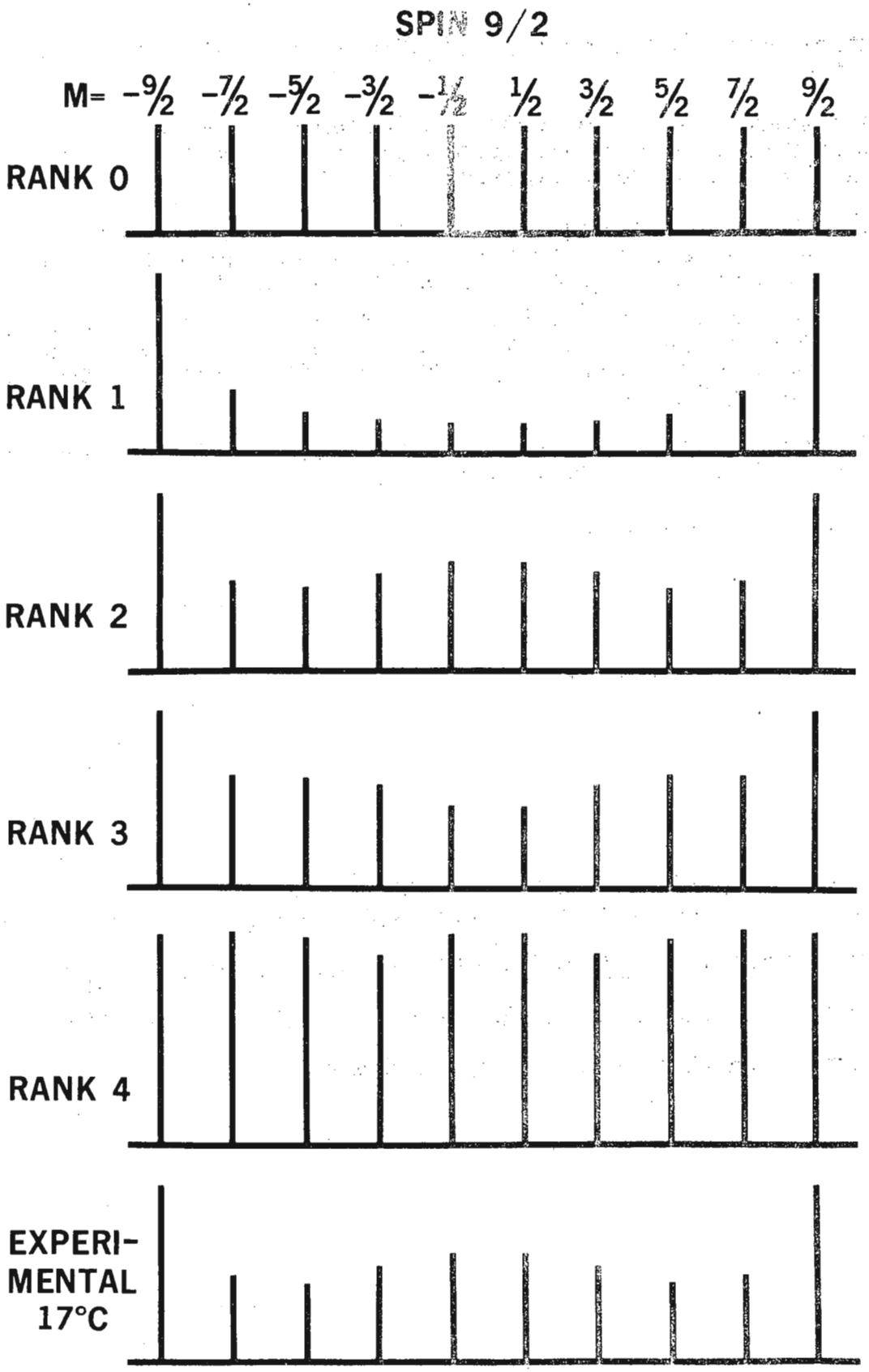

SPIN 9/2
M= -9/2 -7/2 -5/2 -3/2 -1/2 1/2 3/2 5/2 7/2 9/2
RANK 0
RANK 1
RANK 2
RANK 3
RANK 4
EXPERI-
MENTAL
17°C

FIG 1

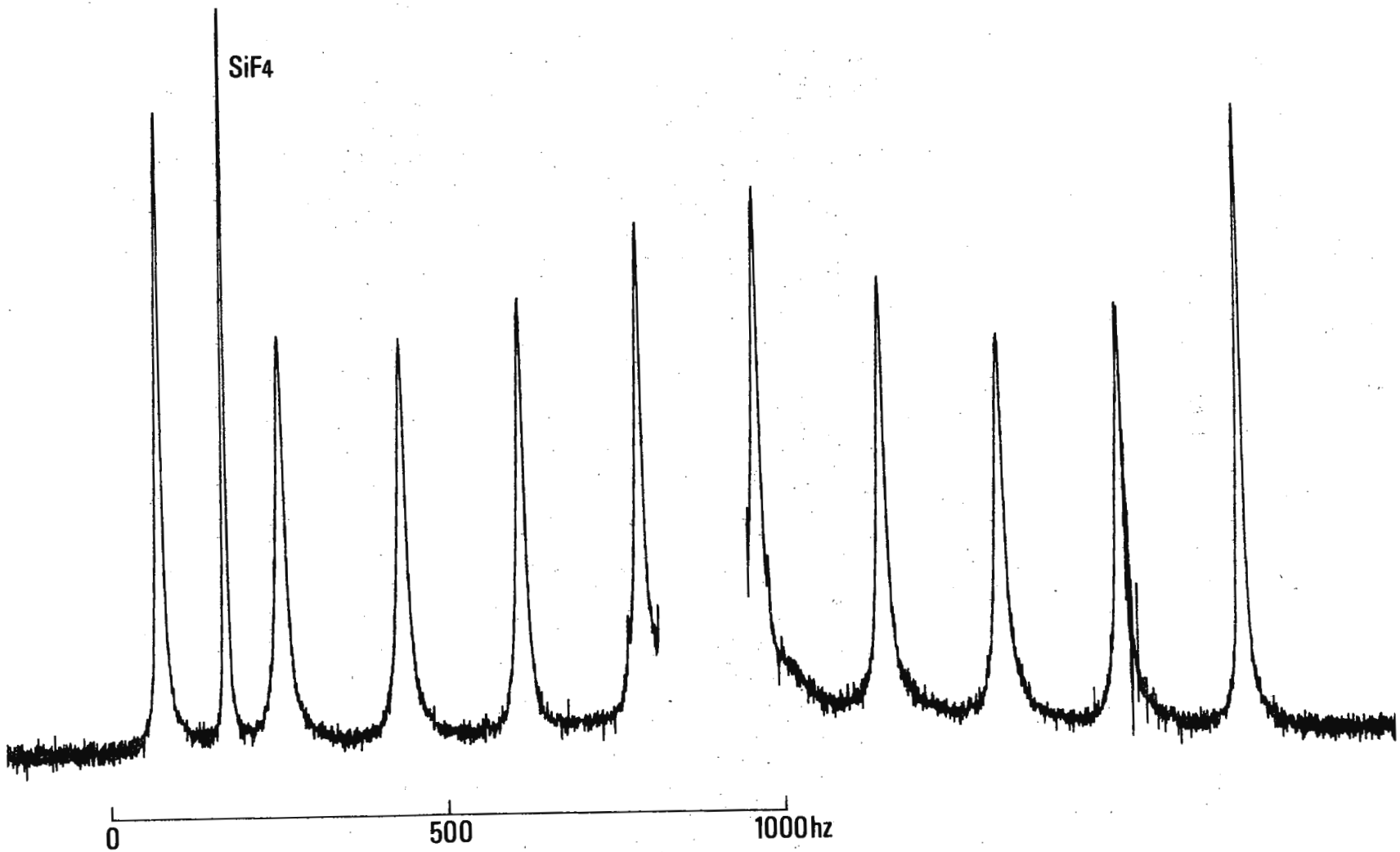


FIG 2.

Gas. 1 Mhz F^{19} decpt due to Ge^{73} in liquid GeF_4 at -20°C

Southern Illinois
University

CARBONDALE, ILLINOIS 62901

Department of Chemistry and Biochemistry

January 19, 1972

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

TITLE: Deuterium Isotope Effects in
Lanthanide Induced Shifts

Dear Barry:

A deuterium isotope effect has been observed in the shifts induced by lanthanide chelate complexes in the nmr spectra of alcohols in which deuterium is substituted for hydrogen geminal to the hydroxyl group.[1] In such cases, proton resonances of the deuterium substituted alcohol are shifted further than those of the unsubstituted alcohol. The effect is readily observed in mixtures of deuterium substituted (labeled) and unsubstituted (unlabeled) alcohols as a doubling of all resonance peaks concomitant with the shifts induced by the lanthanide complex. Similar effects have not been reported for alcohols in which the deuterium substitution is remote from the hydroxyl group. In this paper we report data obtained from additional systems.

Two suggestions have been offered as to the origin of the effect. The first is hydrogen bonding between the geminal H (or D) and one of the oxygen atoms in a metal chelate ring. This has been proposed because, like the mountain, it is there. Analyses of shift magnitudes indicate that the alcohol hydroxyl group coordinates with the metal chelate in a nearly eclipsed conformation relative to the geminal hydrogen. This conformation facilitates hydrogen bonding between the geminal H (or D) and the ring oxygens of the metal chelate ligands. Such secondary hydrogen bonding could contribute to differences in association of the labeled and unlabeled alcohols.

Table. Percent Differences of Lanthanide Induced Shifts of Deuterium Substituted Alcohols Versus Shifts Observed for Unlabeled Molecules.

Alcohol	Shift % Difference
CH_3CHDOH	1.3
CH_3CD_2OH	2.5
HCD_2OH	2.7

A second suggestion is that geminal deuterium substitution increases the bacisity of the alcohol hydroxyl oxygen and thus increases the metal complex-alcohol association constant. Some of our data indicates this; in particular, the effect observed with 1,1-dideuterioethanol is just twice that found for 1-deuterioethanol (Table).

Dr. Jacob Scheafer (Monsanto, St. Louis) suggested that our observations might be related to the deuterium isotope effects found in ^{13}C NMR studies by Reilly.[2] Reilly reports that deuterium substitution on a carbon results in a shift of that carbon ^{13}C resonance upfield (more shielding). Similar electronic effects acting in the compounds in our study could result in increased bacisity of the deuterium substituted alcohol over that of the unlabeled molecule.

Sincerley,

C. C. Hinckley W. A. Boyd G. V. Smith

1. G. V. Smith, W. A. Boyd, and C. C. Hinckley, J. Am. Chem. Soc., 93, 6319 (1971).

2. C. A. Reilly, TAMUNN, No. 156, September 1971.

161-24 Dr. W. Brügel c/o
Badische Anilin- & Soda-Fabrik AG
Hauptlaboratorium

BASF

Telefon (0621) 601 (Vermittlung)
Telex 464811 basf d (Zentrale)
Telegramme: BASF Ludwigshafenrhein
Bankverbindung: Landeszentralbank
6700 Ludwigshafen, Girokonto 545 07300

BASF · 6700 Ludwigshafen

Luftpost

Prof. Dr. B.L. Shapiro

Department of Chemistry
Texas A & M University

College Station, Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Telex	Ludwigshafen
		WH/PV Brü/Dr	(0621) 60- 8401	464-	21. Jan. 1972

Betreff

Beobachtungen am HR-220

Sehr geehrter Herr Professor Shapiro!

Ihr "blauer Brief" vom 3. Januar 1972 trifft uns in einer vergleichsweise schlechten Lage an. Herr Dr. Friebolin hat uns am 31. Dezember 1971 wieder verlassen, um an die Universität (Heidelberg) zurückzukehren. Ich selbst habe mich seit etwa 2 Jahren mehr Fragen der Röntgenphotoelektronenspektroskopie (XPS oder ESCA) zugewandt. Dadurch ist das NMR-Labor zur Zeit sozusagen verwaist. Natürlich wird eine Menge Arbeit erledigt, aber es handelt sich dabei mehr um Routineaufgaben, über die es nichts zu berichten gibt. Aber vielleicht können wir unserer Verpflichtung durch die Mitteilung der folgenden kleinen Beobachtung an unserem HR-220 nachkommen:

Vor über 1 Jahr war das Feld bei diesem Gerät so weit weggedriftet, daß die Veränderungsmöglichkeit des Offset nicht mehr ausreichte, Feld und Sender in die richtige Beziehung zueinander zu bringen. Es war vielmehr notwendig, das Feld neu einzurichten. Dazu wurde die supra-

leitende Solenoidspule stromlos gemacht. Überraschenderweise verblieb ein merkliches magnetisches Restfeld (nachgewiesen durch seine Anziehung auf eine an einem Faden aufgehängte eiserne Büroklammer). Nach Warmfahren der Spule verschwand dieses Restfeld, trat jedoch nach Abkühlung bis zur Supraleitung, Erregung der Spule bis zum Höchstfeld und erneutem Stromlosmachen wiederum auf. Zur Erklärung nahmen wir einen Schluß zwischen einigen Spulenwindungen an, der es unmöglich machte, die betroffenen Teile im supraleitenden Zustand stromlos zu machen, während bei Verlassen der Supraleitung der Widerstand den nun nicht mehr genährten Strom und damit sein Magnetfeld vernichtete. Aus äußeren Gründen ließen wir damals die Sache auf sich beruhen und machten das Instrument wieder meßbereit. Es zeigte sich, daß ein merklicher, nicht mehr direkt beeinflußbarer z_1-Gradient vorhanden war, der die Herstellung der notwendigen Feldhomogenität sehr erschwerte. Den Herren Dr. Friebolin und Ing. Heft gelang es aber mit viel Arbeit und Mühe, einen brauchbaren Meßzustand herzustellen.

Zu Weihnachten 1971 mußten wir wegen unerträglich gewordener Heliumabdampfrate - wir vermuteten Wasser im He- und N_2-Raum (wie es auch der Fall war) - die Spule zwecks Reinigung des Instruments erneut warmfahren. Diesmal entnahmen wir den Solenoid dem Dewar, und siehe da: die beiden Anschlußklemmen eines sog. persistent switch hatten sich gelockert und gaben keinen Kontakt mehr, so daß der in den betroffenen

Badische Anilin- & Soda-Fabrik AG

Empfänger	Unsere Zeichen	67 Ludwigshafen am Rhein	Blatt
Prof. Shapiro	WH/PV Brü/Dr	21. Jan. 1972	3

Betreff

Spulenteilen fließende Strom im supraleitenden Zustand nicht mehr zu beeinflussen war. Dies war die Ursache für das auch diesmal wieder von uns beobachtete Restfeld bei angeblich stromloser Spule. Nach Festdrehen der Klemmschrauben verschwand bei entsprechendem Test das Restfeld, und das Instrument konnte in normaler Weise meßbereit gemacht werden. Es arbeitet jetzt wieder sehr zufriedenstellend mit einer Linienbreite von etwa 0,5 Hz (gemessen an TMS). Die zugehörigen Arbeiten wurden von meinem langjährigen Mitarbeiter Herrn Ing. Heft ausgeführt.

Mit freundlichen Grüßen

(Dr. W. Brügel)

MONTECATINI EDISON S. p. A.
STABILIMENTO PETROLCHIMICO
PORTO MARGHERA

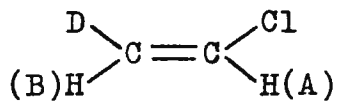
Porto Marghera 25 january 1972

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

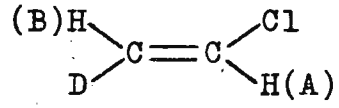
Centro Ricerche Petrolchimiche
Montecatini Edison S.p.A.
Stabilimento Petrolchimico
Via dell'Elettricità, 41
30175 Porto Marghera (Venezia)
ITALY

Subject: Stereochemistry of the addition of DCl to Acetylene.

Recently we have analyzed by NMR spectroscopy the reaction products of the addition of DCl to CH≡CH . This reaction was performed at 140°C in presence of $HgCl_2$ carried on active carbon.
By MS analysis, in synthetised deuterated vinyl chloride, only C_2H_2DCl species were detected. As consequence exchange reactions between reagents and products should be excluded.
The NMR spectrum of the reaction products shows the presence of two isomeric deuterated species :



(cis)



(trans)

Both the isomers present an AB spin system.
Agreement for calculated and experimental lines and intensities was obtained.
In table 1 are reported the values of the parameters obtained for both species. The parameters of trans isomer, made allowance for the temperature, are in agreement with Whipple data.
NMR data of cis isomershave not yet been reported.
Moreover from the peak areas of the B proton, a 9/1 cis/trans isomer ratio was calculated.

Yours sincerely

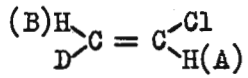
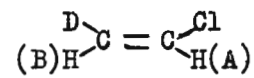
Adelio Rigo
(Adelio Rigo)

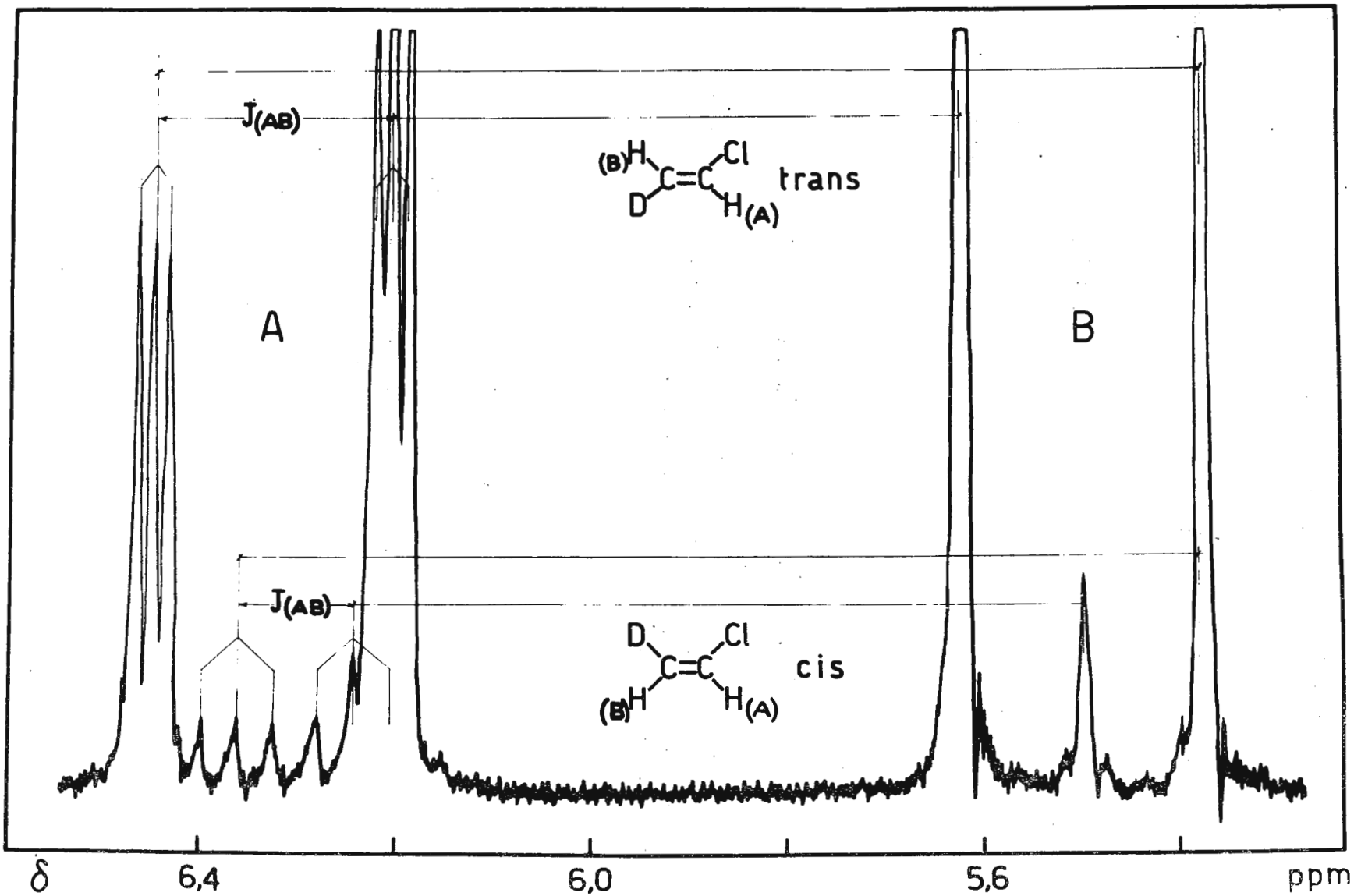
Giorgio Gurato
(Giorgio Gurato)

Reference: E.B.Whipple, W.E.Stewart, G.S.Reddy, J.H.Goldstein
J.Chem.Phys. 34, 2136 (1961)

Table 1. - NMR parameters of cis and trans vinyl chloride β -d_1

(the chemical shifts are expressed in ppm and the coupling constants in Hz).

	TRANS ISOMER 	CIS ISOMER 
Isotopic Purity	≃100	≃100
Reference	TMS	TMS
Solvent	$CDCl_3$	$CDCl_3$
Concentration	50 % in volume (45 % trans isomer and 5 % cis isomer)	50 % in volume (5 % cis isomer and 45 % trans isomer)
Temperature	-19°C	-19°C
δ (A)	6.31	6.30
δ (B)	5.50	5.44
δ (A) - δ(B)	0.81	0.86
J(A•B)	14.70	7.00
J(B•D)	-0.22	-0.22
J(A•D)	1.00	2.20


J(AB)
(B)H
Cl
C=C
D
H(A)
trans
A
B
J(AB)
D
Cl
C=C
(B)H
H(A)
cis
δ
6,4
6,0
5,6
ppm

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

EGF/BLM

28th January, 1972.

Dear Professor Shapiro,

Perkin-Elmer R10 60 MHz NMR Instrument For Sale

Due to a reorganization of the NMR facilities at these laboratories, we have available for sale a 1963 Perkin-Elmer R10 60 MHz high resolution NMR Spectrometer. This instrument has been well cared-for , and is capable of giving excellent results. Among the star attractions offered are

* Flux stabilizer
* Double resonance accessory
* ^{31}P probe and r.f. source
* The excellent Perkin-Elmer variable temperature facility.

If anyone is interested, or knows of anybody who might be interested, please contact me at the above address.

Yours sincerely,

DR. E.G. FINER.

THE UNIVERSITY OF NEW MEXICO | ALBUQUERQUE, NEW MEXICO 87106

DEPARTMENT OF CHEMISTRY
TELEPHONE 505: 277-2821

January 31, 1972

^{15}N SPECTRA OF 5-PHENYLTETRAZOLES

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

Dear Dr. Shapiro:

Over the past ten years I have been aware of the NMR letter which you publish but unaware of how to get on the mailing list. Recently I learned that this can be done simply by sending a letter containing recent work in NMR which might be of interest to NMR spectroscopists. To this end I enclose the following:

5-Phenyltetrazole is a ring molecule containing four adjacent nitrogen atoms. Recently, in studying a problem on rearrangements, I was able to obtain two spectra of this molecule which might be of interest. These spectra were run on an XL-100-15 spectrometer with FTS (620-L) with the help of Bill Jankowski of Varian Associates. The first is the ^{15}N spectrum of 5-phenyltetrazole with no decoupling. The downfield peak ($N_{2,3}$) is 26 ppm upfield of aqueous acidified $^{15}NO_3^-$ in NH_4NO_3 while the broad upfield peak ($N_{1,4}$) is 58.8 ppm away from the other peak. Proton noise decoupling shows that the two kinds of nitrogen atoms are both being relaxed significantly by the protons by means of a dipolar process. The $N_{1,4}$ nitrogens show the greatest effect which is to be expected. The NOE is -3.86 for $N_{1,4}$ and -0.69 for $N_{2,3}$. As can be seen from the sign of the NOE, the negative magnetogyric ratio of nitrogen leads to inversion of the peak upon decoupling. The magnitude of the NOE also suggests that the ring proton is possibly migrating around the ring and spending some time on the nitrogens since the dipolar contribution to relaxation does not follow the normal r^{-6} dependence.

The sample was prepared by dissolving 200 mg of 5-phenyltetrazole in 1/2 ml of DMSO. There is reason to believe that there would be some solvent effect in the shifts of the nitrogens. No correction for bulk susceptibility has been made. In addition, the enrichment of the nitrogens was 100% in any given position for any given molecule but the enrichment was only done for one position at a time. Therefore, the effective enrichment was about 25%. The 5mm sample tube was placed inside a 12mm tube containing D_2O (for locking purposes) and spun.

I hope this is sufficient for a contribution and "subscription" to the NMR newsletter.

Sincerely,

Wm. M. Litchman

WML:bje

QUEEN MARY COLLEGE
UNIVERSITY OF LONDON

DEPARTMENT OF CHEMISTRY
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Professor B. C. L. Weedon, Ph.D., D.Sc., F.R.I.C.
Professor D. C. Bradley, B.Sc., Ph.D., D.Sc., A.R.I.C.

MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811

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

1st February, 1972

ONE YEAR'S FOURIER ON ^{13}C AND ^{15}N

Dear Barry,

We have been operational on our Bruker for just over a year, and (apparently) like most other groups in the ^{13}C Fourier area to judge from your letters we have endeavoured to work around the clock on a 7 day week.

Our National ^{13}C service to other University Groups went operational, officially at least, on 1st June, 1971 with the posting by the Science Research Council of 'brochures' to all U.K. Universities. We had 'serviced' some Groups before then to get the feel of the problems associated with extramural activities, and to phase the service organisation in slowly along with the technical know how.

We have tended to keep our noses to one particular configurational grindstone in an endeavour to educate ourselves to stay operational in a given mode without indulging in frequent changes of configuration. We thought that we would degrade the spectrometer enough during our apprenticeship without inviting trouble by repeatedly changing every 'plug-in' in sight, as a good spectroscopist with a new toy might be tempted to do. In retrospect I am convinced this was the best way. There are enough problems of technique and organisation with seven or more operators without inviting trouble by introducing half a dozen spectrometer modes as well.

Our normal configuration has been ^{13}C, 10mm tube, ^{19}F lock (internal and capillary), ^{1}H noise decoupling, Fourier (1). Even so we have been adventurous enough to have successfully demonstrated the feasibility and something of the utility of ^{15}N Fourier studies even in natural abundance (2) (3). Ed. Rosenberg has conducted a ^{13}C survey of organometallics (4), and John Briggs has successfully noise-decoupled ^{19}F from ^{13}C in the archetypal fluoroaromatics, using an ^{1}H lock. Bruker installed our ^{2}D lock early, and a single coil attachment gratis.

We have had our share of collaboration: from Dr. Moss and Dr. Hart of shift reagent fame on Lanthanide induced ^{13}C shifts (5); with visits from John Sogn (permission of Willie Gibbons at Rockefeller) for ^{15}N; Erkki Rhakamaa (Oulu, Finland) for ^{13}C - ^{15}N couplings, the Kowalewskis (who precipitated our first ^{13}C natural abundance spectra for an oriented sample); Luciano Milone (Turin) with an exciting Rutherium carbonyl cluster compound; and Robert Baert (from Professor van Binst's group in Belgium) who kept us cheerful during a breakdown.

The score on spectra has been about 1650 in one year (Jan.1971 - Jan.1972). 1350 were ^{13}C and 300 ^{15}N. The service, run by Les. Farnell and Eira Hughes, so far has been only on ^{13}C and accounts for about 450 spectra. The average overall is thus about 4 per day which, amazingly, is about the figure forecast in the grant application. We have not, need I say, restricted ourselves to short favourable runs.

The down-time has been about 25%. I do not know how this compares with experience elsewhere, but from the honest but guarded phrases concerning troubles in other letters, I suspect not badly. It is a figure on which we might improve if our reparative expertise increases faster than the decay rate of the spectrometer. Otherwise, breakdown may be a term applicable not only to the spectrometer.

Our qualified success would not have been possible without the skill, goodwill and cooperation of all members of the group, and I should like to acclaim them for their record, including exiles like Paul Pregosin now in Delaware.

Best Wishes,

Ed

E. W. Randall

(1) P.S. Pregosin, E.W. Randall, Chem. Comms. 399 (1971)
(2) J.M. Briggs, L.F. Farnell, E.W. Randall, Chem.Comms. 680 (1971)
(3) P.S. Pregosin, E.W. Randall, A.I. White, Chem.Comms. 1602 (1971)
(4) L.F. Farnell, E.W. Randall, E. Rosenberg, Chem.Comms. 1078 (1971)
(5) J. Briggs, F.A. Hart, G.P. Moss, E.W. Randall. Chem.Comms. 364 (1971)

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