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NOVEMBER, 1971

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READ AND INITIAL

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Have you looked after your 1971-1972 subscription yet? Your promptness will be greatly appreciated.

Deadline dates: No. 159: 6 December 1971
No. 160: 3 January 1972

All Newsletter correspondence, etc., should be addressed to:

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

13 th EXPERIMENTAL NMR CONFERENCE

Chairman: B. L. Shapiro, Dept. of Chem., Texas A&M Univ., College Station, Tex. 77843
Sec.-Treas: E. Lustig, F.D.A. BF-145, 200 C Street, S.W., Washington, D.C. 20204
Committee: R. E. Lundin, Western Reg. Res. Lab., 800 Buchanan St., Albany, Calif. 94710
J. D. Swalen, IBM Research Laboratory, San Jose, Calif. 95114
J. Schaefer, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, Mo. 63166
C. S. Johnson, Jr., Chem. Dept., Univ. of N. Carolina, Chapel Hill, N.C. 27514

The 13th ENC (Experimental NMR Conference) will be held April 30-May 4, 1972 at the Asilomar Conference Grounds in Pacific Grove (Monterey), California. As usual, this conference will be devoted to new developments in advanced instrumentation and experimental techniques. It is not intended as a forum for the presentation of results by standard NMR methods. Although most papers will be invited, there will be a small amount of time allotted for the presentation of contributed talks. Inquiries concerning specific contributed papers should be directed to the Chairman.

All suggestions or inquiries concerning the program will be welcomed, and these should be directed to the conference Chairman or to any member of the organizing committee. The committee is especially interested in opinions concerning desirable topics for discussion at the 13th ENC, as well as the names of suitable speakers - both domestic and foreign - who might be invited to the conference.

This preliminary announcement has been sent to all attendees at recent ENC's. Others wishing to be put on the mailing list for further announcements concerning the program and registration for the 13th ENC at Asilomar are invited to address these requests to the Secretary-Treasurer.

PLEASE POST OR CIRCULATE

ИНСТИТУТ ХИМИИ
ПРИРОДНЫХ СОЕДИНЕНИЙ
АН СССР

Dr.V.F.Bystrov, Vice-Director
INSTITUTE FOR CHEMISTRY
OF NATURAL PRODUCTS
ACADEMY OF SCIENCES OF USSR
Ul. Vavilova, 32, Moscow, USSR

«16» August 1971 г.

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

Title: NMR of Membrane Surfaces.

Dear Barry,

In the course of investigation /Doklady Akad. Nauk SSSR (Proc.Acad.Sci. USSR) 194, 222 (1970)/ of the effect of paramagnetic ions on the NMR spectrum of a sonicated lecithin dispersion in water (Fig. 1A) we have found that addition of $Eu(NO_3)_3$ splits the $N^+(CH_3)_3$ signal in two components (Fig. 1B): a low field one, whose position is the same as for the salt free dispersion and one shifting to higher field, the higher the salt concentration. The integral intensity of the high field $N^+(CH_3)_3$ component is ~1.5 fold that of the low field component. The addition of $MnSO_4$ to this sample broadens the higher field component (Fig. 1C).

We explain these results as being due to the interaction of the paramagnetic Eu^{3+} and Mn^{2+} ions with the polar lecithin termini (probably phosphate groups) situated only on the external surface of the bilayer vesicles (Fig. 2). On resonication the sample gives spectrum indicating that the paramagnetic ions are now both "outside" and "inside" the vesicle cavity. This could have been the result of breakdown of the vesicles on additional sonication followed by their reforming during which they incorporated paramagnetic ions in the internal aqueous phase.

The spectrum of the sample with "external" ions on standing did not undergo change for at least 24 hours. Obviously, paramagnetic ions of themselves do not penetrate into the internal

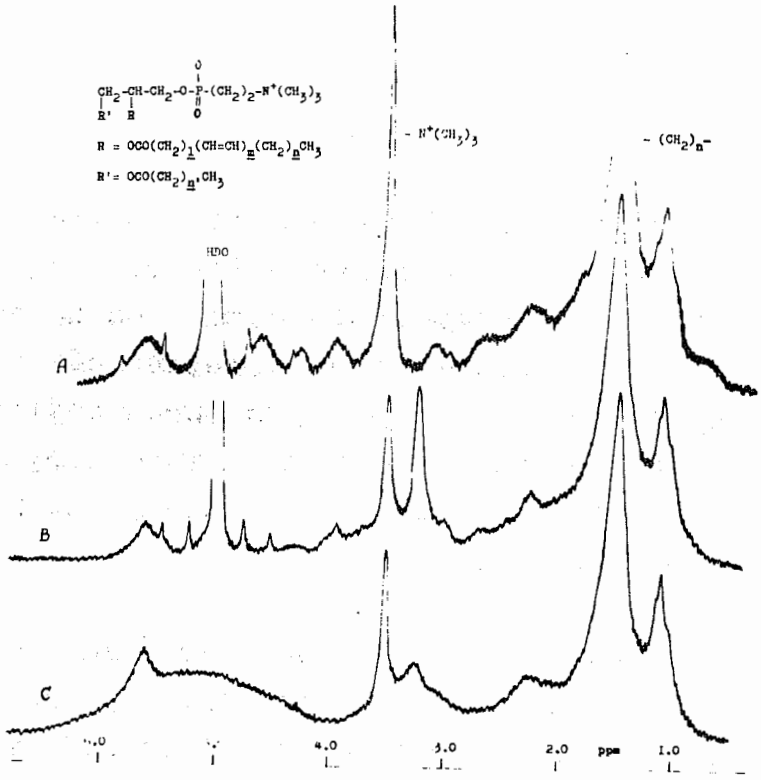


Fig. 1. NMR spectra of a sonicated 5% w/v dispersion of egg yolk lecithin in D_2O (A); after addition of 2.10^{-2} M/l $Eu(NO_3)_3$ (B) and 3.10^{-3} M/l $MnSO_4$ (C).

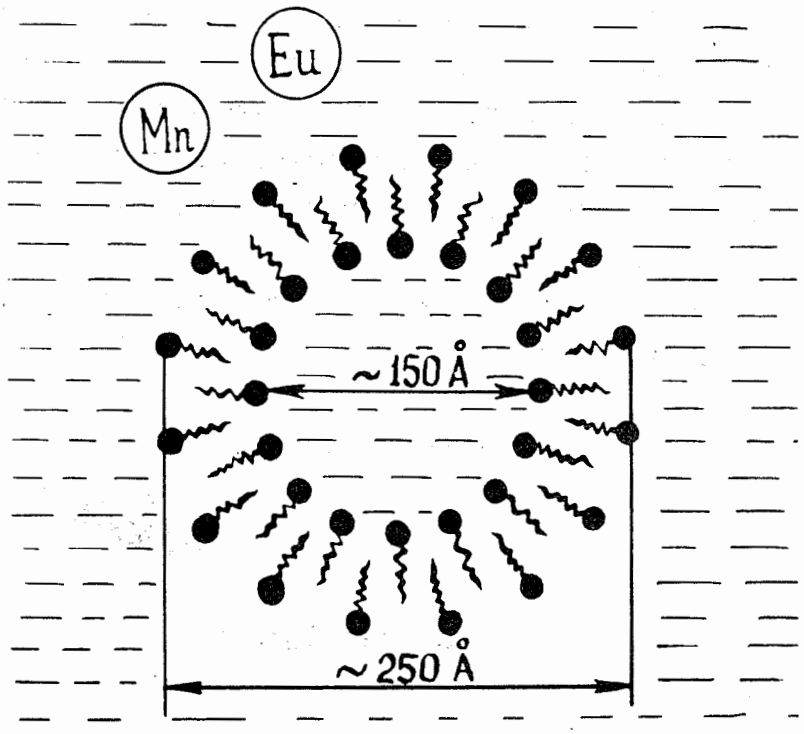


Fig. 2. Schematic representation of lecithin vesicles.

cavity. On the other hand, the water molecules can easily penetrate through the semipermeable membrane. This has been shown by a special experiment with a sonicated lecithin-water (H_2O) dispersion in the presence of "external" $MnSO_4$. The NMR spectrum revealed only a broad and no narrow H_2O signal, which in the absence of the exchange must be due to 0.5% of over all water content incorporated in the internal cavity of the vesicles.

We also have found that the Pr^{3+} and Nd^{3+} ions shift the $N^+(CH_3)_3$ signal from the external surface of the lecithin vesicle in opposite direction than the Eu^{3+} ions, that is in lower field. The effect for the 0.02 M/l salt concentration is: for $Eu(NO_3)_3$ +0.25 ppm, $Pr(NO_3)_3$ — 0.66 ppm and $NdCl_3$ -0.15 ppm.

The use of paramagnetic ions considerably widen the possibilities of NMR spectroscopy in the study of membrane structure, permitting differentiation of the internal and external surfaces of membrane without their impairment. The method thus may find application in studies of structural asimmetry and exchange phenomena in membrane systems.

This investigation has been performed in collaboration with Drs. L.I.Barsukov, N.I.Dubrovina and Prof. L.D.Bergelson.

Sincerely yours,

Vladimir

Vladimir Bystrov

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20390

IN REPLY REFER TO:

6110-429:WBM:vmg
1 October 1971

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

Dear Barry:

About a year ago, a small water leak developed along one lead to the terminal block in a coil of our HA-100 12" magnet. The affected winding showed a resistance to ground of only a few hundred ohms, with the short very close to one end. At the suggestion of Rolf Tschudin, we added one quart of a nationally advertised antifreeze containing anti-leak ingredients to the cooling water. Within a few days, FTC objections notwithstanding, the product functioned as claimed and the leak had stopped. We then permuted the terminal block connections to place the "grounded" coil at the end of the series string. Magnet regulation and homogeneity were unimpaired and the spectrometer performed normally, although the low resistance path to ground caused the current meter of the V2100B to read incorrectly. After moving to our new quarters in May, we replaced the defective coil, so we cannot say how permanent the antifreeze is.

Chet Poranski has modified our closed shell INDO/CNDO MO program (QCPE 144, by Ragle, Gentzler, and Clark) to calculate the individual Q_{AA} and Q_{AB} terms used in Pople's paramagnetic shift equation. We will be happy to forward the Fortran changes to anyone requesting them.

Sincerely yours,

W. B. MONIZ, Head
NMR Spectroscopy Section
Chemistry Division, Code 6110

Title: Stop gap measure for magnet water leak; Calculation of Pople Q's.

WAYNE STATE UNIVERSITY

COLLEGE OF LIBERAL ARTS DETROIT, MICHIGAN 48202

DEPARTMENT OF CHEMISTRY

September 30, 1971

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

Dear Dr. Shapiro:

Long Live Coalescence Measurements!

A recent letter by Dr. Gideon Fraenkel ("No More Coalescence Measurements," TAMUNMR Newsletter No. 156) prompts me to write this letter. In work done recently in this laboratory, we were able to show that ΔG^* values and rate constants obtained by the so called "coalescence method" are in good agreement with complete line shape analysis (D. Kost, E. H. Carlson and M. Raban, Chem. Commun. 656 (1971)). This was shown to be true in the case of uncoupled AB exchange, as well as in unsymmetrical and more complicated systems, such as the coupled AB, coalescence of unequally intense singlets, and the coalescence of doublets (equally and unequally intense). In much more complex systems it is difficult to define a point of coalescence. However, the cases studied by us seem to cover some 95 percent of the exchange phenomena reported in literature.

A "one point kinetics" can be quite accurate when rate constants and ΔG^*'s are measured. It is, of course, of no value in ΔH^* and ΔS^* measurements. The accuracy of these activation parameters measured by line shape analysis is, however, often also doubtful, due to the small temperature range at which the spectrum is affected by exchange processes. For intramolecular exchange reactions such as inversion or rotation about a partial double bond, ΔS^* is expected to be close to zero. In fact, reported values which exceed 10-15 eu for such a reaction are usually rejected as being unreliable and resulting from experimental or systematic errors (cf. J. M. Lehn, Fortschritte der Chemischen Forschung 15, 311 (1970)). With ΔS^* being very small, the temperature dependence of ΔG^* is negligible

so that it can be safely used in making comparisons of barriers within a certain series. Relatively accurate activation parameters are obtained only when measured over a large temperature range, in cases where two methods can be applied or when the chemical shift difference between the exchanging sites is very large.

Being a simple and fairly accurate method as it is, I believe that the coalescence method will continue to be used extensively by chemists in that area.

Sincerely yours,

Daniel Kost

Daniel Kost
Research Associate

srn

Please credit this letter to Morton Raban's subscription.

October 4, 1971

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

Relaxation time measurement by adiavatic rapid passage on T-60

Dear Professor Shapiro

Adiavatic rapid passage is one of the most simple one to measure rather long spin - lattice relaxation time T_1, as well known. We tried this method with T-60 high resolution NMR spectrometer without any modification of the spectrometer.

Saw tooth voltage from a generater such as Wavetek model 111 was fed into DC sweep coil through pins D and A of J010 which is located on left hand side of the console. Sweep rate and sweep range are determined by frequency and amplitude of the saw tooth. When much bigger rf power is required one can get three times as much power by turning normal-wide line switch of control module to wide line position.

Some of results are reproduced in the figure enclosed.

Spin-lattice relaxation times obtained here coincide satisfactorily with those obtained by the other methods using the same sample.

	present study	other method
cyclohexane	$13.5 \pm 2.0^*$	13.5 ± 1.0
benzene	30.3 ± 2.5	32.7 ± 0.5

*average deviation

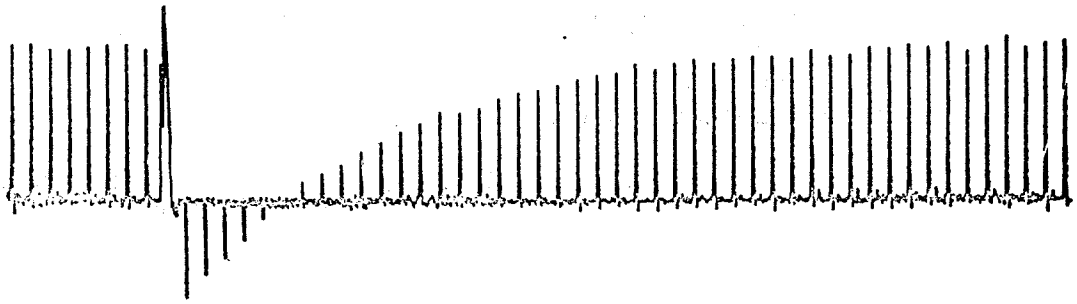
Please credit this contribution to T. Nishida

Yours sincerely,

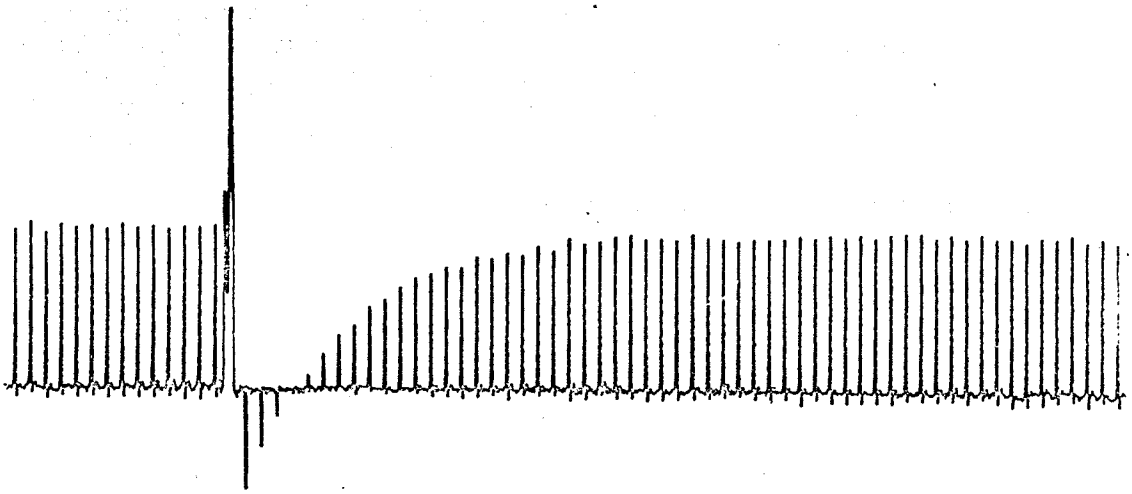
S. Satoh

K. Kushida

SS/sy



(a)



(b)

Recovery of magnetization of (a) benzene (b) cyclohezane in CCl_4 solution of C_6H_6, C_6H_{12}, dioxane and TMS.

YESHIVA UNIVERSITY

BELFER GRADUATE SCHOOL OF SCIENCE

Amsterdam Avenue and 186th Street / New York, N.Y. 10033 / (212) LOrraine 8-8400

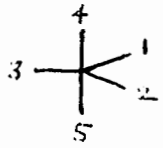
October 5, 1971

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

Title: Modes of Rearrangement in Phosphoranes

Dear Barry:

I have recently studied the possible types or modes of rearrangement in trigonal bipyramid molecules. A molecule



can rearrange with a variety of possible stereochemical consequences which I call "modes." These correspond to rearrangements such as a permutation among an axial and an equatorial ligand denoted as ae, the various permutations among three ligands which would be denoted as aae, aee or eee, etc., although the C_{3V} symmetry makes the permutation description 6-fold degenerate. The distinct modes can be denoted as

$M_0^{(1)} = I,\ eee^{2},\ aaxee^{3}$

$M_1^{(3)} = eaea\ (BPR),\ aexaee^{2}\ (TR)$

$M_2^{(6)} = ae,\ eeea^{3},\ eeaa^{2},\ eexaae\ (TR')$

$M_3^{(1)} = aa,\ ee^{2},\ aaxeee^{2}$

$M_4^{(6)} = aee^{2,3}\ (R),\ aae^{3,4}\ (R'),\ aexee,\ aaee$

$M_5^{(3)} = aexae\ (DPR),\ aeaee$

including the trivial identity, and the numbers in parentheses are the numbers of distinct isomers that can be formed in each mode. The fact that there are different modes of rearrangement- as distinguished from organic chemistry where there is only one, racemization - is due to the possibility of a TBP to re-

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arrange with partial retention of configuration as I discussed at the 1969 meeting in Brussels.

The only experiment that has given unassailable evidence as to mode is that of Whitesides and Mitchell who showed that $(CH_3)_2NPF_4$ rearranges according to either mode $M_{1,5}$ or $M_{3,4}$ or both. All discussions in the literature refer only to mechanism and, in fact, confuse what I have called modes, which have observable stereochemical consequences and are five in number with mechanisms which are infinite in number and can only have the stereochemical consequence of one or more modes. A preprint is available.

Best regards,

Jeremy I. Musher

158-12

MRC
Medical Research Council

MRC Molecular Pharmacology Unit
Medical School, Hills Road
Cambridge CB2 3EF

telephone Cambridge 45171

^{13}C Assignments of Ribose Carbon Nuclei in AMP

Dear Barry,

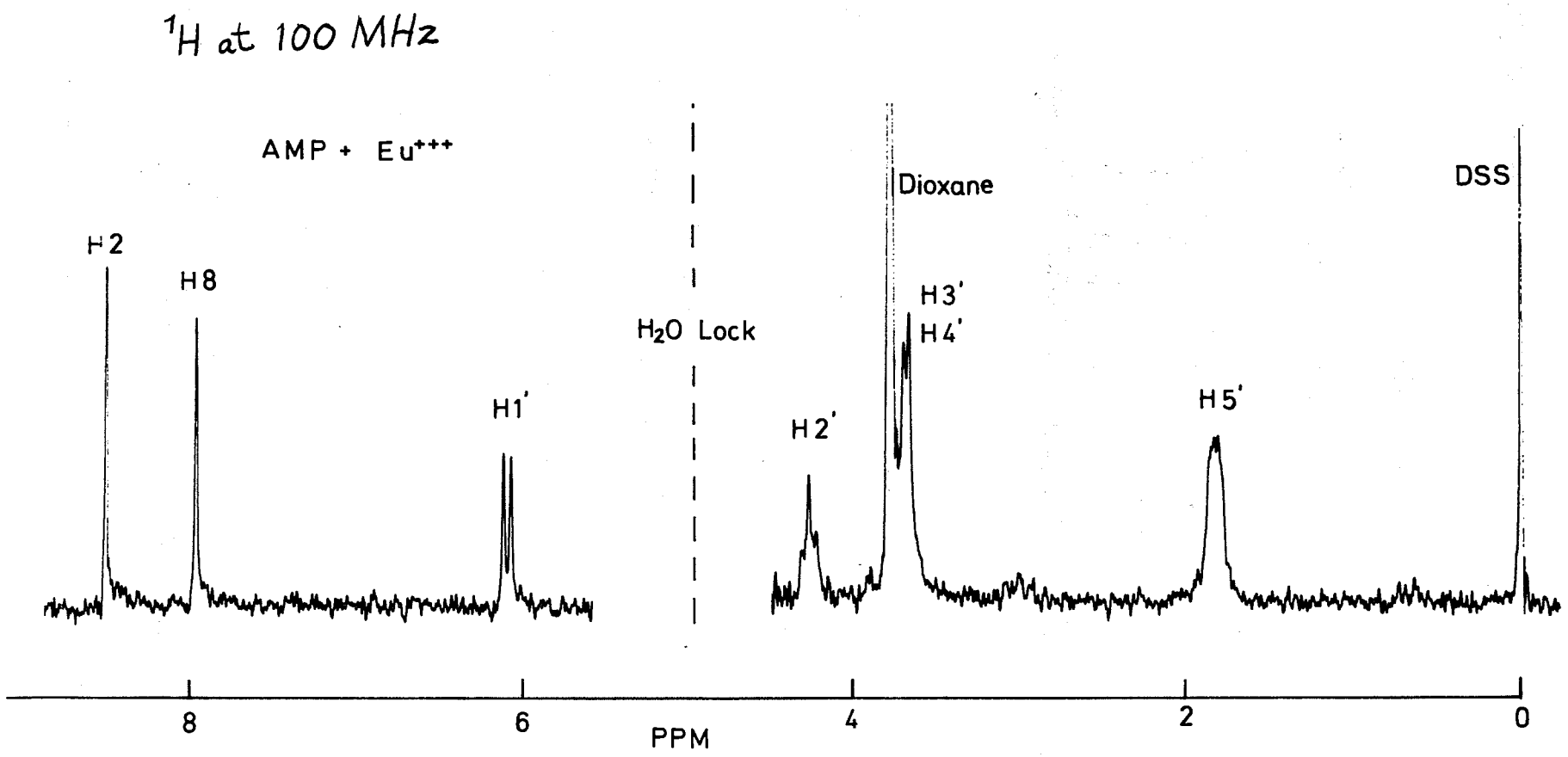
Recently we have been collaborating with J. Glasel, R. J. P. Williams and A. Xavier at Oxford University in exploring the use of lanthanide ion induced pseudo contact shifts to obtain conformational information for nucleotides[1] using both ^{1}H and ^{13}C resonance spectroscopy. In the course of this work we assigned the ^{13}C spectra by using selective C - (H) heteronuclear spin decoupling experiments. This was facilitated in some cases by the increased proton chemical shift differences observed in the presence of Eu^{+++} ions.

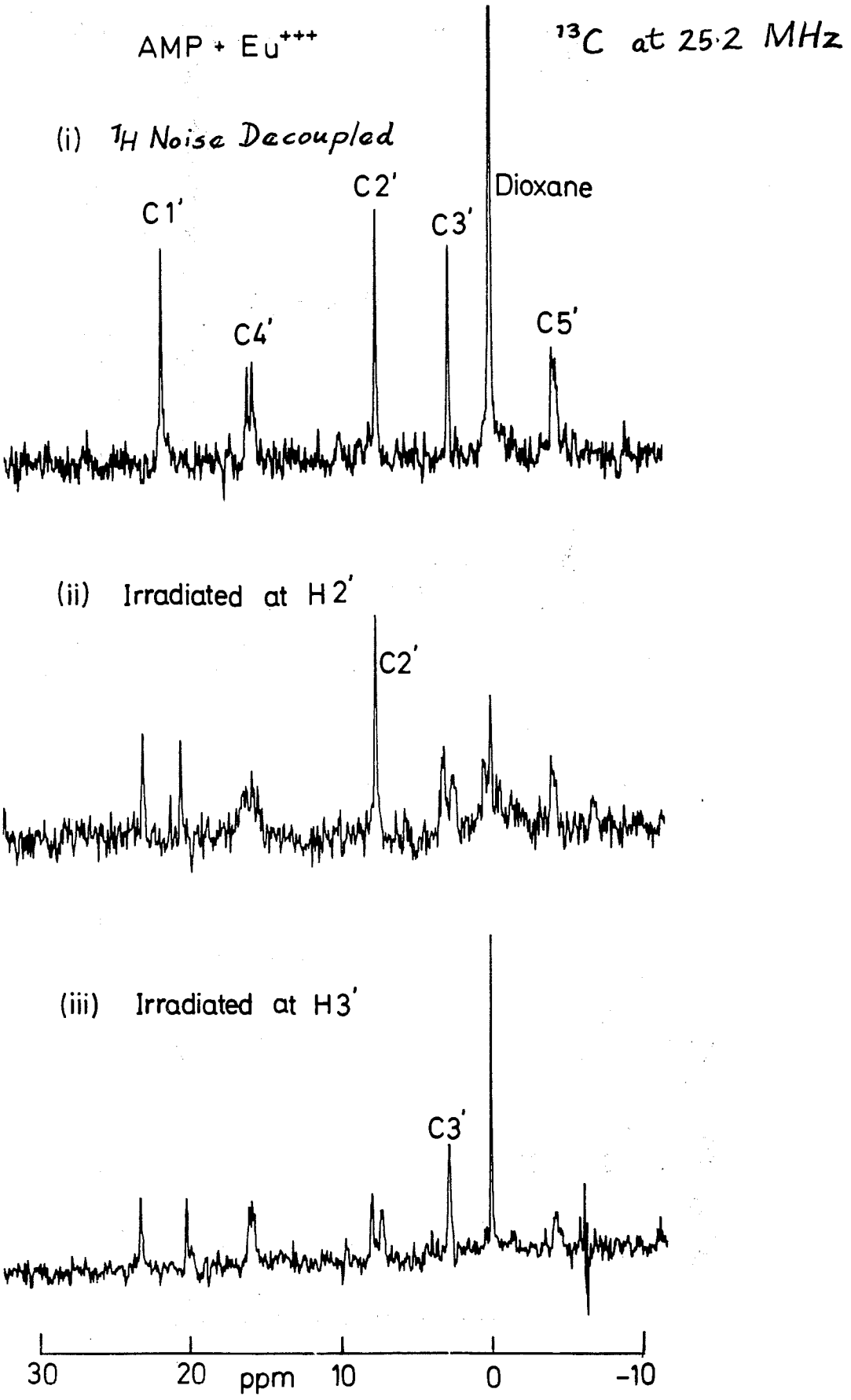
The figures summarise some of our results for AMP; it should be noted that the C2' and C3' assignments are reversed from those reported in earlier studies.[2] It is worth mentioning that the original assignments had first come under suspicion as a result of the Eu^{+++} induced shift calculations and the heteronuclear selective spin decoupling subsequently confirmed that in fact the assignments are as indicated in the figure. The pseudo contact shifts do not cause any of the ^{13}C nuclei to reverse their signal positions and the revised assignments for the ribose carbon nuclei in AMP are: C1', 21.7; C4', 17.5; C2', 7.94; C3', 3.62; C5', -1.99 ppm from dioxane internal reference. The measurements were made using Varian HA100D and XL100 spectrometers.

Best wishes,
Jim Feeney Barry Birdsall
J. Feeney and B. Birdsall,
M.R.C. Molecular Pharmacology Unit.

1. C. D. Barry, A. C. T. North, J. A. Glasel, R. J. P. Williams and A. V. Xavier. Nature 1971. 232, 236.

2. D. E. Dorman and J. D. Roberts, PNAS 65, 19 (1970).


^1H at 100 MHz
AMP + Eu^{+++}
H2
H8
H1'
H_2O Lock
Dioxane
H3'
H4'
H2'
H5'
DSS
8
6
4
2
0
PPM


AMP + Eu+++
13C at 25·2 MHz
(i) 1H Noise Decoupled
C1'
C4'
C2'
C3'
Dioxane
C5'
(ii) Irradiated at H2'
C2'
(iii) Irradiated at H3'
C3'
30
20
ppm
10
0
-10

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UNIVERSITY OF OTTAWA
DEPARTMENT OF CHEMISTRY

October 7, 1971.

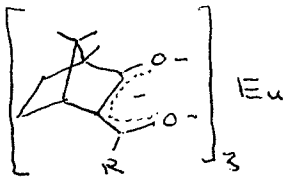
TITLE Shift Reagent Studies

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

Dear Barry:

I thought I'd wait until I received your second "reminder" to satisfy my curiosity as to its format. It certainly has STYLE and IMPACT.

Consequently I would like to summarize some of our current investigations on shift reagents. Perhaps our most notable progress has been made in the synthesis of new optically active shift reagents which are a modification of "Whitesides reagent". Of those made so far, the heptafluorobutyryl derivative of d-camphor, 2, appears to be significantly greater in its ability to resolve signals due to enantiomers than the pivaloyl derivative, 1,



1 R = $-C(CH_3)_3$

2 R = $CF_3CF_2CF_2-$

A summary of these effects is listed in the enclosed table. We are attempting to synthesize other modifications of 1 which may also possess superior "resolving power".

.....2

We have completed an examination of the spectra of a series of sulfoxides in the presence of $Eu(DPM)_3$, for the specific purpose of determining the reliability of making assignments of stereochemistry as the basis of a distance dependence. Briefly, we conclude that the method is reliable in cyclic and bicyclic sulfoxides but not in acyclic sulfoxides. It also appears that bulky substituents adjacent to the s→o group will give some contribution to the shifts by the angular term (as you, in particular, may appreciate). This work will appear in the "International Journal of Sulphur Chemistry" next year.

Best regards,

Bob

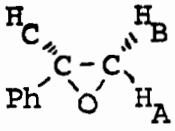
R.R. Fraser.

RRF/ma

P.S. I was very interested in Gideon Fraenkel's comments re coalescence measurements. While I am in qualitative agreement with his ideas I fear that the consequences of his cure may surpass the disease. Banning one point kinetics may result in the encouragement of workers without proper instrumentation or experience to perform line shape studies of an inferior nature which will inevitably appear in the literature. The most important requirement of publishable data is for it to be reliable data. Certainly, overinterpretation of a one-point rate constant should be banned but the data ought to be acceptable if it fulfills other publication criteria.

TABLE 1

Effects of Added 1 and 2 on the NMR Spectra of Racemates.

Compound	Proton	Effect of 1 PS[a]	Effect of 1 $\Delta\nu$[b]	Effect of 2 PS[a]	Effect of 2 $\Delta\nu$[b]
Ph CHNH$_2$ CH$_3$	CH$_3$	6.37	0.19	5.09	0.08
	CH	9.48	0.41	7.57	0.00
	H$_{ortho}$	4.01	0.12	3.25	0.06
Ph CHOH CH$_3$	CH$_3$	2.14	0.00	2.65	0.05
	CH	3.55	0.01	4.64	0.07
	H$_{ortho}$	1.69	0.00	2.27	0.02
CH$_3$CH$_2$CHCH$_A$H$_B$OH CH$_3$	CH$_A$	4.24	0.00	5.55	0.05
	CH$_B$	4.24	0.00	5.54	0.11
	H$_A$	1.13	0.03	4.22	0.15
	H$_B$	1.32	0.03	4.27	0.75
	H$_C$	1.31	0.01	4.69	0.31
PhSOCH$_3$	CH$_3$	1.74	0.09	2.79	0.11
	H$_{ortho}$	1.82	0.02	2.78	0.12
PhCH$_A$SOCH$_3$ H$_B$	H$_A$	2.16	0.00	2.22	0.06
	H$_B$	2.16	0.00	2.26	0.03
	CH$_3$	2.08	0.00	1.92	0.06
Ph CH CHO CH$_3$	CH(O)	0.44	0.00	2.02	0.03
	CH(CH$_3$)	0.25	0.00	1.32	0.01

a The average downfield shift, in ppm of the protons in the two enantiomers in the presence of 0.4 equivalents of 1 or 2. All spectra were measured at 31° on 0.2 - 0.3 M solutions in CCl_4 using a Varian HA-100 spectrometer. Proton-proton spin decoupling was frequently used to simply multiplet absorptions.

b The difference in PS for structurally identical protons in the two enantiomers.

158-18

University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building, Cathedral Street, Glasgow, C1

Telephone: 041-552 4400

6th October, 1971.

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

Dear Barry,

Exchange Effects in Spectra of Allyl Alcohol

We have been intrigued and a little perplexed by some spectra of allyl alcohol. Depending on the solvent and concentration used the spectrum of the proton C can appear as 4 partially overlapping triplets of sharp lines i.e. the normal spectrum (spectrum 1). Under other conditions the outer lines of the triplet are considerably broadened (spectrum 2). We have established that this broadening occurs whenever the chemical shift of the OH proton E is close to that of the methylene protons (D), the concentration at which this happens is of course different for different solvents. The phenomenon can hence be rationalized in part as a case of 'virtual coupling' of proton C to proton E which is undergoing intermolecular exchange at an appropriate rate. In support of this is the observation that D_2O exchange causes reversion to the normal spectrum.

At first glance it is not clear why the broadening should affect only the outer lines of the triplets (indeed the extra coupling might be expected to result in four quartets with splittings of $\frac{2}{3}J_{CD}$; J_{CE} assumed zero). However, computation (LAME) for the two cases does show that the central lines of the triplets are unchanged when the virtual coupling condition is introduced.

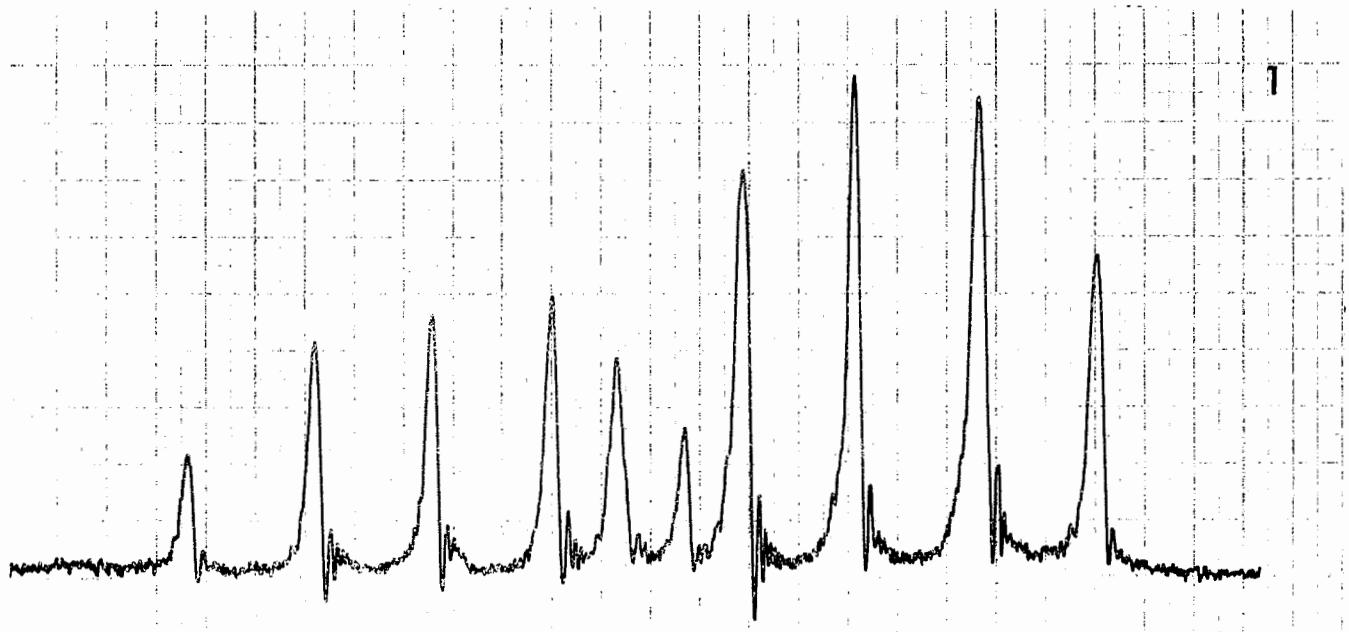
We have surprisingly not been able to find any reference to this phenomenon in the literature and in consequence we are continuing to devote attention to it.

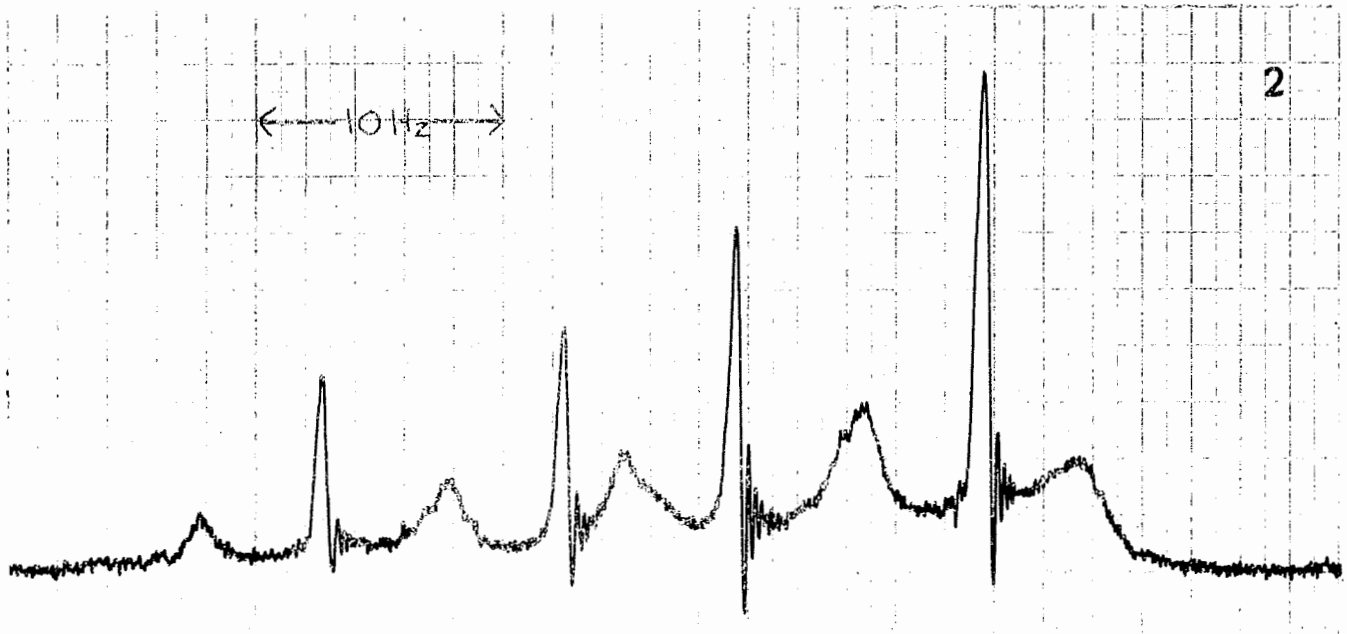
Kind regards,

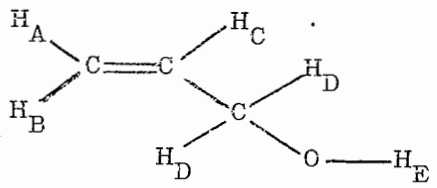
Yours sincerely,

Peter Bladon.

Keith Hardie Peter Bladon







Allyl alcohol in $CDCl_3$ (40% v/v). Proton C resonances.

Spectrum 1. After treatment with D_2O. This corresponds to the spectra obtained at other concentrations.

Spectrum 2. Before treatment with D_2O. This shows the effect of 'virtual' coupling of proton C to proton E.

University of East Anglia

School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR

11th October 1971

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

NMR PROGRAM LIBRARY

Dear Professor Shapiro,

We have been developing an NMR PROGRAM LIBRARY as was first mentioned in the TAMUNMR newsletter in February 1969. This library has been prepared under the auspices of the U.K. Science Research Council for use by British universities employing the ATLAS computer at Chilton, Berks. (1). A fairly wide range of programs are now available, as follows:

LAOCOON 1968 LAOCOON 4-SPIN	}	iterative analysis of general spin systems
UEANMR BASIC	—	non-iterative analysis of spin systems with magnetic equivalence
UEANMR ITERATIVE	—	iterative analysis of spin systems with magnetic equivalence
LAOCOON LC UEANMR LC	}	liquid crystal programmes (non-iterative)

Plotting routines

SHAPE FUNCTION	—	chemical exchange between two non-coupled sites
AB SHAPE	—	chemical exchange between two coupled sites
LACX	—	iterative analysis of spin systems possessing chemical equivalence
QUADRUCALC	—	iterative fit of spin-$\frac{1}{2}$ bandshapes for first order spin systems involving a single quadrupolar nucleus of unit spin.

Other programs are currently under development and should soon become available for general use. These include a program for exchange processes involving exchange between two non-equivalent AB spin systems, and DNMR3 (original author G. Binsch) for chemical exchange between many sites, and BUCF (2) which was written by M. Kinns in order to calculate multiple quantum spectra.

Anybody who is interested should write to one of us at the University of East Anglia, for details and listings of the programs.

Yours sincerely,

Robin Harris M. Kinns

R. K. Harris M. Kinns.

(1) NMR PROGRAM LIBRARY - Manual issued by the ATLAS Computer Laboratory, Science Research Council, Chilton, Didcot, Berks, and references cited therein.

(2) M. Kinns, unpublished work.

158-22

COLORADO
STATE
UNIVERSITY
FORT COLLINS
COLORADO
80521

department of chemistry

October 18, 1971

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

Re: Titles: ^{13}C—^{13}C Coupling Constants
^{13}C Fourier Transform

Dear Barry:

Having been studying ^{13}C—^{13}C coupling constants for some time now, our research group has recently had the good fortune of being able to apply the pulse-Fourier transform approach. While all of our previous efforts, using CW methods, have required dilabelled or monolabelled substances, our current work relies on natural-abundance signals, i.e., the natural-abundance ^{13}C satellites about the natural-abundance ^{13}C signal.

Kim Summerhays has made a study of a series of isopropyl and t-butyl compounds. Using a Bruker HFX-90 spectrometer and Digilab FTS/NMR-3 data system with Digilab pulse unit, we typically obtain satellites with signal-to-noise ratios of 5:1 or better after about 2000 repetitions in a simple pulse-wait-pulse-wait . . . train. Pulse widths of about 40 μsec and wait times of about 2 sec were usually employed. In order to obtain good resolution and precision, either the judicious use of very good filters or a large data storage capacity are needed. We employed 16 K data points, using the disc, and estimate that the results are accurate to ±0.15 Hz.

For $(CH_3)_3CX$ compounds, the results are, for a series of substituents(X): CO_2H, 35.30; $COC(CH_3)_3$, 35.40; CH_3, 35.65; C_6H_5, 35.70; $SSC(CH_3)_3$, 37.55; NH_2, 37.60; Br, 37.80; Cl, 37.95; OH, 39.55: and OCH_3, 40.25 Hz. For $(CH_3)_2CHX$ compounds, the results are: CO_2H, 34.35; $COCH_3$, 34.70; C_6H_5, 34.75; I, 36.70; Br, 37.10; Cl, 37.30: NH_2, 37.25; $NHCH(CH_3)_2$, 38.10; OH, 38.60; OCH_3, 39.90; and $OCH(CH_3)_2$, 39.85 Hz.

We are also examining several other series of compounds by this method.

Sincerely,

Gary E. Maciel

GEM/jb

Institut für Physikalische Chemie
der Rhein.-Westf. Techn. Hochschule Aachen
Direktor Prof. Dr. U. F. Franck
Abt.f.Phys.Chemie d.Kunststoffe
Prof. Dr. Kosfeld

51 AACHEN, den 14. 10. 1971
Templergraben 59 · Fernruf (0241) 422/2750/53
Fernschreiber: 0832/704

2770

Herrn
Prof. B. L. Shapiro
Department of Chemistry
Texas A u. M University

College Station, Texas 77 843
U. S. A.

Betr.: Tunneleffekt von Methylgruppen

Sehr geehrter Herr Shapiro!

An PMMA und PMA haben wir Breitlinienmessungen bis herunter zu 5 K durchgeführt. Mit Hilfe eines Rechenprogramms von Bergmann u. Nawotki (1) wurden aus den gemessenen Absorptionslinien die Anteile der beweglichen und der eingefrorenen Methylgruppen in Abhängigkeit von der Temperatur ermittelt. Die Abbildungen zeigen diese Anteile.

Zwischen 5 K und 20 K hat r_1, der Anteil der eingefrorenen Methylgruppen, einen mittleren Wert von 0,76, d.h., 76 % der Methylgruppen sind bei diesen Temperaturen unbeweglich. Die restlichen 24 % zeigen auch bei diesen tiefen Temperaturen noch Beweglichkeit. Dieses Resultat überrascht, da man, falls es sich bei der Rotation der Methylgruppen um eine thermisch aktivierte Bewegung handelt, bei derart tiefen Temperaturen keine nennenswerten Bewegungen mehr erwarten sollte. Eine Erklärung bietet jedoch die Annahme, daß die Methylgruppen von ihren Schwingungszuständen aus das ihrer Bewegung entgegenstehende Behinderungspotential durchtunneln, wie es bereits von Powles und Gutowsky (2) vorgeschlagen wurde. Da die Tunnelfrequenzen unterhalb 70 K nahezu temperaturunabhängig sind (3), werden demnach auch bei tiefsten Temperaturen genügend viele Methylgruppen die Behinderungspotentiale durchtunneln und so die beobachteten Beweglichkeiten erklären.

Bei einer Erwärmung auf 77 K fällt r_1 auf 0,5 ab, was bedeutet, daß bei dieser Temperatur die Estermethylgruppen des PMMA frei oder nur schwach behindert rotieren, während alle Hauptkettenmethylgruppen noch unbeweglich sind. Erst oberhalb 120 K fällt r_1 weiter und zeigt damit die beginnende Rotation auch der α-Methylgruppen an. Bei weiterer Temperaturerhöhung fällt r_1 auf Null ab, was auf eine vollständige Rotation der

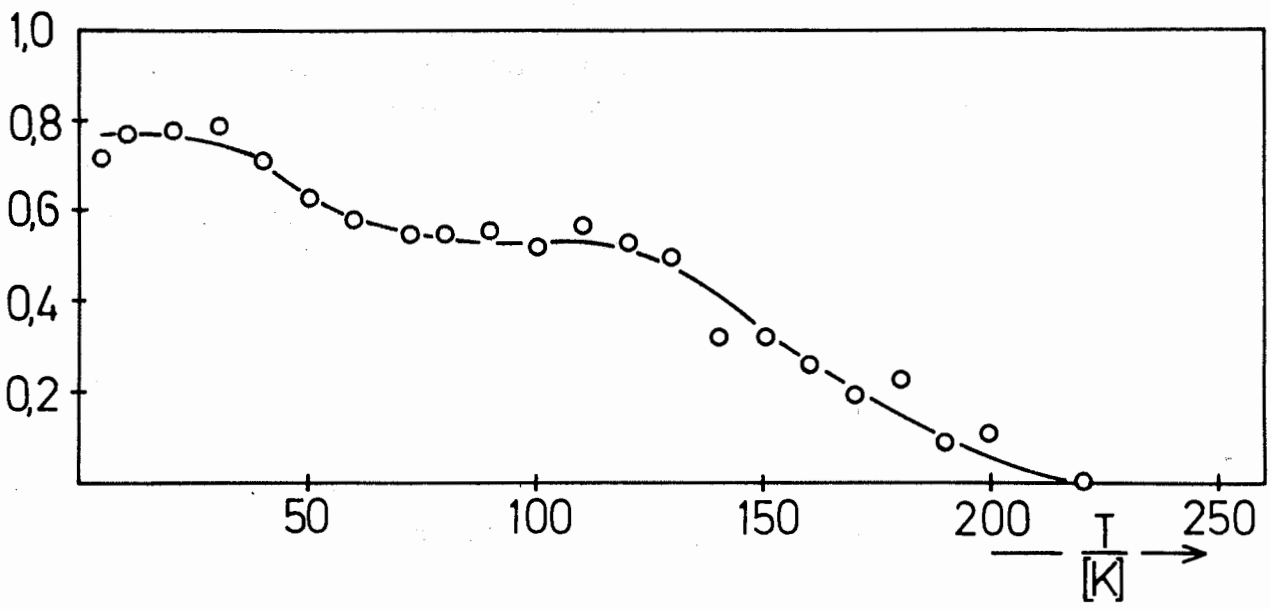
beiden Methylgruppen des PMMA hinweist. Bei PMA fehlt die Hauptkettenmethylgruppe. Die Abbildung zeigt daher nur den Verlauf von r_1 der Estermethylgruppe in Abhängigkeit von der Temperatur. Auch bei dieser Substanz ergibt sich bei 5 K ein Anteil der beweglichen Gruppen von 28 %, was ebenfalls auf den Tunneleffekt der Methylgruppen hinweist.

Literatur:

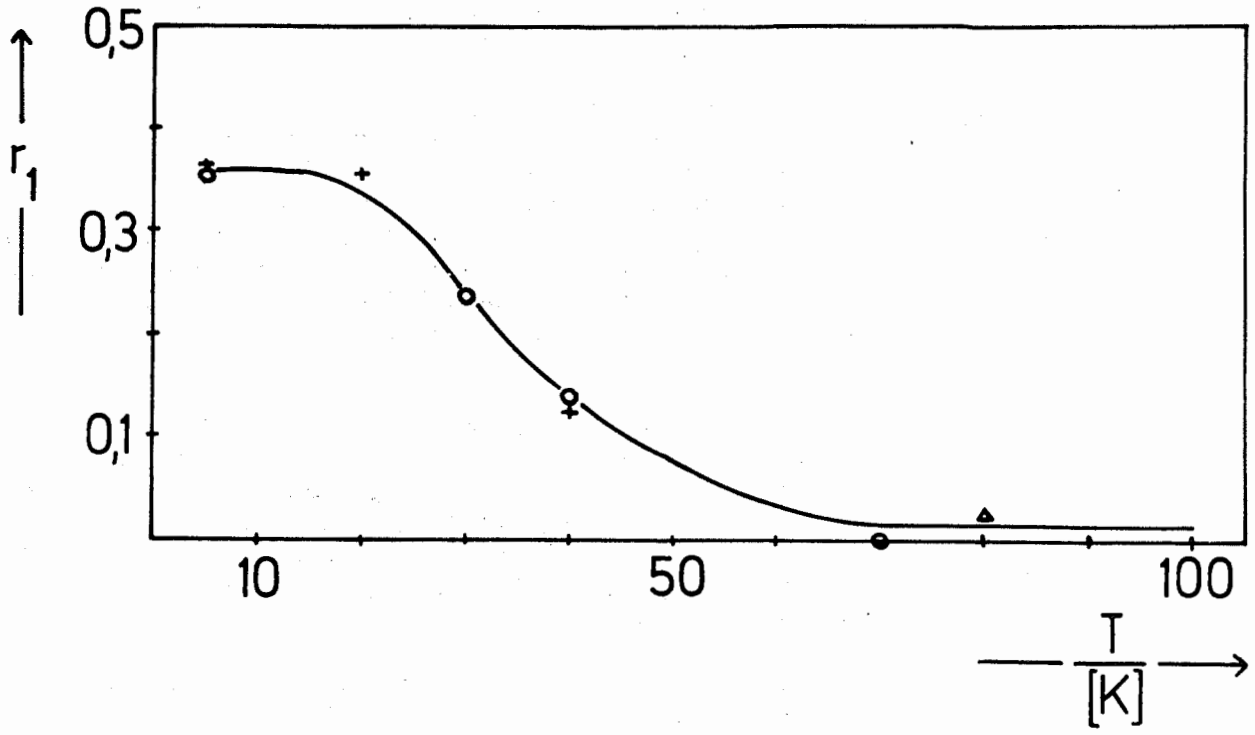
1) Bergmann, K.
"NMR, Basic Principles and Progress"
Vol. 4 p. 233 ff.
Springer Verlag, Berlin, Heidelberg
New York 1971
2) Powles J.G., H.S. Gutowsky
J. Chem. Phys. 23, 1692 (1955)
3) Stejskal, E.O., H.S. Gutowsky
J. Chem. Phys. 28, 388 (1958)

Mit besten Grüßen
Ihre

(Kosfeld) (v. Mylius)



Anteil der unbeweglichen Methylgruppen beim PMMA



Anteil der unbeweglichen Methylgruppen beim PMA

158-26

UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C. 29208

Department of Chemistry

October 12, 1971

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

Title: High Resolution Boron-11 nmr on an XL-100

Dear Barry:

Thank you for your little blue reminder sheet. I would like to briefly outline some of the boron-11 nmr research that is currently being undertaken at the University of South Carolina. This work is being done with the collaboration of Dr. Jerry Odom of our department and a graduate student, Mr. Douglas W. Lowman, who is under our joint supervision.

We have applied the high power decoupling technique previously described for pentaborane (9)[1] to a series of 1-substituted pentaboranes, B_5H_8X, in order to study the effect of substituents on the directly bonded boron-boron coupling constants. To date, we have looked at the compounds where X = H, CH_3, C_2H_5, Cl, Br, I, and Si $(CH_3)_3$. The experimental results for J_{BB} are presented in Table I. In addition to the results mentioned above, Table I also contains the upper limits for J_{BB} in diborane (6), 1,1-dimethyldiborane (6), and tetraborane (10), and for comparison the values of J_{CC} for a series of related acetyl compounds[2].

Examination of Table I reveals a 30% change in J_{BB} for the B_5H_8X compounds. This is comparable to the 30% change observed in J_{CC} for the same substituents. From the ratio of $\gamma 11_B/\gamma 13_C$ one would expect that J_{BB} would be larger than J_{CC}, all other factors being equal. In contrast to this, the values of J_{BB} seem to be attenuated in magnitude. It is also important to note that there is not an obvious monotonic relationship between J_{BB} and J_{CC} as a function of the substituent, e.g. note the halogens.

A clue to this observed attenuation effect for J_{BB} can be obtained from the values of J_{BB} for diborane (6) and tetraborane (10), i.e. 6 and 2.5 Hz,

respectively. Simple arguments concerning small quadrupole effects and qualitative molecular orbital considerations lead one to expect that these couplings should be zero. This arises because of the lack of any significant amount of two-electron two-center bonding between the borons in these molecules. Simple bonding arguments for B_5H_9 show that the amount of two-center two-electron character attributed to the B(apex) - B(base) bond is about 50%.[3] Hence, an attenuation of J_{BB} compared to a full two-center two-electron bond.

Within the limited set of data presented here it seems that boron-boron coupling constants enjoy the same sensitivity to substituent effects as carbon-carbon coupling constants. However, values of J_{BB} may also allow one to deduce the fractional two-electron two-center character of a particular bond and consequently become a powerful tool in investigating structures in boron hydrides.

Sincerely,

Douglas W. Lowman

Jerry D. Odom
Asst. Professor
of Chemistry

Paul D. Ellis
Asst. Professor
of Chemistry

References:

1. J. D. Odom, P. D. Ellis, and H. C. Walsh, J. Amer. Chem. Soc., 93, 3529 (1971).

2. G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, J. Mag. Res. 1, 41(1969).

3. W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin and Company, New York.

Table I

Directly Bonded ^{11}B - ^{11}B Coupling Constants in 1-B_5H_8X Compounds

X	J_{BB} (±0.5Hz)
$CH(CH_3)_2$	18.6
CH_3	18.9
C_2H_5	19.0
$Si(CH_3)_3$	<19
H	19.4
Cl	24.4
Br	25.1
I	26.7

Directly Bonded ^{13}C - ^{13}C Coupling in Substituted Acetyl Compounds

X	J_{CC} (±0.2Hz)
CH_3	40.1
C_2H_5	38.4
H	39.4
Cl	56.1
Br	54.1
I	46.5

Compound	J_{BB}(Hz)
1,1-dimethyldiborane (6)	<7
diborane (6)	<6
tetraborane (10)	<2.5

ORGANISCH CHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT TE UTRECHT
CROESESTRAAT 79
POSTGIRO 65985-TEL. 82311

UTRECHT, 21 October 1971
(NEDERLAND)

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

a ^{13}C NMR of neopentyl derivatives
b An easy method to determine accurately the offset of the ^{1}H-lock-reference on XL-100 systems.

Dear Professor Shapiro,

In the course of our investigations on long-range coupling constants in saturated systems, we synthesized a number of neopentyl derivatives.It seemed worthwhile to investigate also the ^{13}C nmr spectra of these compounds. In the table ^{13}C shifts, relative to CS_2, of the carbon atoms of the neopentyl group are given. Noise decoupled spectra were obtained from 40% $^{v}/_{v}$ solutions in aceton d_6/CCl_4 1:2 while locking on deuterium. In this solvent the CS_2 resonance offset position was determined in a separate experiment and found to be 78,276.6 Hz for a deuterium-lock frequency of 15,401,000 Hz.
The δ values of the observed peaks were then calculated from the measured resonance offset positions:

$$\delta\ (\text{ppm}) = \frac{78{,}276.6 - \dfrac{15{,}401{,}000 \times \text{obs.offset}}{^{2}\text{D-lock frequency}}}{25.165}$$

We could not find a reasonable correlation of the ^{13}C shifts of the α and β carbons of the neopentyl group with the Huggins electronegativity of the first atom of the substituent or with the $^{1}J_{^{13}C-H}$ of the neopentyl methyl groups. A reasonable correlation with the Huggins electronegativity was found for the internal shift ($\delta C_\gamma - \delta C_\beta$), but in that case the electronegativity of the hydrogen atom was quite low. Reasonable group electronegativities are found from the C_γ shifts.

The experimental data for the aldehyde differ very much from the expected values. However it is possible that the aldehyde has polymerised in the course of our experiments, then the data would fit quite nicely.
We will extend this ^{13}C study to a larger number of neopentyl derivatives as soon as our 16k FT system, that is being installed on our XL 100 spectrometer is fully operational.

Table: $\delta^{13}C$ in $(C_\gamma H_3)_3 C_\beta C_\alpha H_2-X$

X	δC_α	δC_β	δC_γ	$^2J(^{13}C_\gamma H)$	$E_x^{(1)}$	$E_x^{(2)}$
H[3]	162.7	166.7	162.7		1.73	2.24
cyclohexyl	140.90	161.6	162.64	124.5	2.46	2.23
neopentyl	163.43	162.66	163.04	123.6	2.36	2.35
fenyl	142.41	160.99	163.30	124.2	2.64	2.44
C≡N	161.07	162.22	163.97	122.4	2.56	2.65
$N^{\oplus}\equiv C:^{\ominus}$	138.98	161.26	166.14	125.4	3.02	3.36
COCl	132.77	161.00	163.97	124.6	2.71	2.60
$COCH_3$	137.45	162.12	163.15	121.7	2.46	2.39
COOH	145.20	162.32	163.19	124.8	2.43	2.40
$COOCH_3$	145.36	162.25	163.26	124.5	2.45	2.42
J	167.51	161.39	163.80	123.5	2.65	2.60
Br	145.12	160.51	164.92	125.3	2.95	2.96
Cl	135.89	159.74	165.67	127.5	3.15	3.21
OCH_3	109.33	160.71	166.04	124.8	3.08	3.33
OH	120.14	160.06	166.44	124.4	3.23	3.45
CHO[4]	120.17	167.01	166.48	123.9	2.23	3.45

Notes: 1: $E_x = 0.143\ (\delta C_\gamma - \delta C_\beta) + 2.31$

2: $E_x = 0.326\ \delta C_\gamma - 50.80$

3: From: H.Spiesecke, W.G.Schneider, J.Chem.Phys. 35, 722 (1961)

4: Probably polymerised

b. The determination of the exact (which means with an accuracy of 0,001 H_z) offset position of the internal homo-nuclear-lock reference line is difficult for most spectrometer systems,but not on the XL 100 system. In the XL 100 all frequencies are derived from a master oscillater, hence

it is a matter of simple arithmetics (and a 100 MHz counter) to determine the exact lock-offset. For protons the lock-offset is found from the lock-transmitter frequency (about 100.1 MHz) as follows:

$$\text{Lock offset} = \frac{85}{101653} \times \text{R.F. lock}$$

This formula can be extended to other nuclei if one knows the divisors in the frequency controllers.

Yours sincerely,

M.J.A. de Bie P.Boer J.P.C.M. van Dongen J.W.Zwikker

158-32

Prof. Dr. E.G. Hoffmann
MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG

MPI für Kohlenforschung, 4330 Mülheim-Ruhr, Kaiser-Wilhelm-Platz 1
Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843
U.S.A.

4330 Mülheim a. d. Ruhr
Kaiser-Wilhelm-Platz 1
Telefon Sa.-Nr. ~~3 40 21~~ 30 61
Durchwahl: 306 .....

Ihr Zeichen	Ihre Nachricht vom	Unser Zeichen	Datum
			21.10.1971

Routine NMR-Service with a Remote Large Time-Sharing Computer.

Dear Dr. Shapiro,

I am really sorry for being so late with my contribution, but hope that I am not yet "locked out" of your mailing system.

One of our problems in the past two years has been how to use a big time-sharing computer for routine service in NMR. Years ago, efficient dedicated systems were not yet on the market, on the other hand our institute had acquired a PDP-10 time-sharing system with multiplexed analog inputs, that has since been publicised* as "Mülheimer System" by some of our people here. At first it was intended to serve mainly the X-ray laboratory, but the inclusion of analytical tasks (MS, GC, NMR etc.) justified the expansion to the present size.

The distance from our lab to the computer and its ADC's (a multiplexed slow one and a single-user fast one) is about 300 meters. The analog and control lines have to be distributed among the many users, leaving only a few for NMR and EPR.

There is no doubt about the advantage of having the capabilities of a large computer at hand for such applications as accumulations of long spectra, simulations and iterations, line shape, FT and spin-echo computations. While a satelite system would make some tasks easier, there is no chance for us to buy one now, so let me describe what we could achieve with the large time-sharing

system alone, today with our HA-100 system, later with a home built multi-nuclei-FT system.

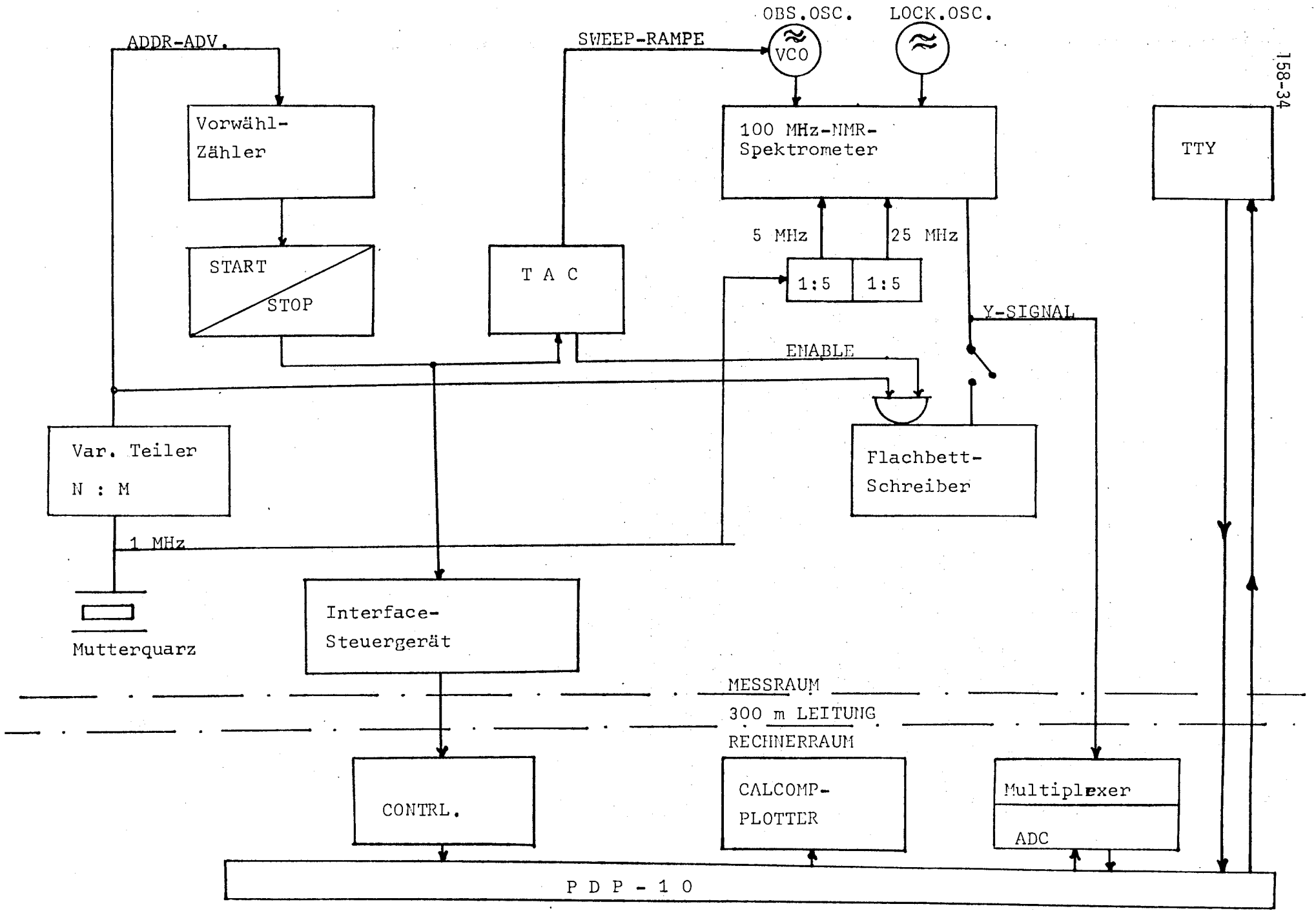
The HA-100 uses one input of the multiplexed slow ADC. Spikes are no more a problem after the multiplexer was properly adjusted. Synchronisation has to rely on the accuracy of the time bases both at the computer and at the spectrometer, because there is no timing control line available.

As the spectrometer time base we use the Xtal frequency of a precision counter, that is properly divided to give the address advance pulses to a TAC. The sweep ramp of the TAC controls a home built high precision VCO (cf. the block diagram) which replaces the internal oscillators of a V4354. These addr. adv. pulses are also counted separately, and start/stop the computer input and the flat bed recorder at two pre-selecteable counts (e.g. 100 and 1123 = $(2^{10}-1)+100$). The stop pulse at 1123 resets the counter and the sweep ramp and initiates another sweep. Thus time averaging can easily be done if needed and further data processing and evaluation is done (see attached sample run) by the large computer.

Sincerely yours,

* e.g. E. Ziegler, D. Henneberg and G. Schomburg
Analyt. Chem. 42, 51A (1970)

Max-Planck-Institut
fuer Kohlenforschung
Phys. opt. Laboratorien
D-4330 Muelheim/Ruhr
Kaiser-Wilhelm-Platz 1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OBS.OSC.
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ADDR-ADV.
SWEEP-RAMPE
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100 MHz-NMR-
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TTY
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Interface-
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PLOTTER
Multiplexer
ADC
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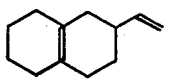
NMRAN 1-MAR-71

PROBE: SELBECK 8847
PROTONENZAHL/START-/STOPPFREQUENZ/LOCKSIGNAL: 18/590.2/90.2/10
CATAUSWERTUNG ? (RETURN=NEIN,1=036,2=SUMS2): 1
SCHAERFE/BREITE/ENGE/PLOT? (Z.B.:1/10): 1/10

*

1-MAR-71 SUS*8
ANZAHL DER LINIEN : 24
ANZAHL DER SPIKES : 24
ANZAHL DER PUNKTE : 5121
ANSTIEG DER NULLINIE: 3840.



SIGNALLAGEN IN PPM = TAUWERTE BEZOGEN AUF 10.00
GEMESSENER BEREICH = 4.10 BIS 9.10 TAU

NR	SIGNALLAGE IN HZ	IN PPM	BEGRENZUNG FUER INTEGRATION BEGINN	ENDE	PROTONEN	GESAMT-INTEGRAL
1	-581.80	4.18	-582.97	-581.12	0.07	0.05
2	-575.26	4.25	-576.43	-574.58	0.06	0.10
3	-571.65	4.28	-573.02	-571.06	0.08	0.17
4	-564.81	4.35	-566.67	-563.84	0.21	0.34
5	-558.08	4.42	-559.35	-557.30	0.11	0.44
6	-554.46	4.46	-556.81	-553.78	0.17	0.57
7	-547.92	4.52	-549.49	-547.24	0.16	0.71
8	-492.47	5.08	-494.32	-491.78	0.20	0.87
9	-490.90	5.09	-491.78	-489.54	0.35	1.14
10	-489.15	5.11	-489.54	-488.75	0.08	1.20
11	-480.75	5.19	-482.70	-477.23	0.59	1.69
12	-475.09	5.25	-476.65	-474.50	0.16	1.81
13	-473.72	5.26	-474.50	-472.45	0.23	2.00
14	-471.77	5.28	-472.35	-471.18	0.14	2.11
15	-470.50	5.30	-471.18	-469.91	0.17	2.24
16	-469.42	5.31	-469.91	-466.98	0.24	2.44
17	-198.38	8.02	-199.46	-198.19	0.07	3.65
18	-175.93	8.24	-186.57	-163.92	10.10	12.44
19	-161.77	8.38	-162.84	-160.89	0.45	12.97
20	-156.40	8.44	-159.72	-156.20	0.85	13.83
21	-150.93	8.49	-154.64	-141.46	3.24	16.69
22	-137.07	8.63	-137.94	-135.89	0.21	17.13
23	-114.32	8.86	-114.90	-113.54	0.04	17.96
24	-111.48	8.89	-112.07	-111.09	0.01	17.97

*

STITUTO DI CHIMICA GENERALE
DELL'UNIVERSITÀ DI CATANIA
CITTÀ UNIVERSITARIA - VIALE A. DORIA
5125 CATANIA (ITALY) - TEL. 336317

Catania, li Oct. 21, 1971

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

Dear Professor Shapiro:

NMR Spectra of N-methylphenylhydrazones

We have just run the NMR spectra (60 Mc sec^{-1}) of the hydrazones $ArCH=N-NMe-C_6H_4.NO_2$-p where Ar- = C_6H_5-; 4-ClC_6H_4-; 4-BrC_6H_4-; 4-FC_6H_4-; 4-$CH_3C_6H_4$-; 4-$CH_3OC_6H_4$-; 3-ClC_6H_4-; 2-ClC_6H_4-; 2-BrC_6H_4-; 2-FC_6H_4-; 2,6-$Cl_2C_6H_3$-; 2,4,6-$CH_3C_6H_2$-; synthesized according to the method recently described in lit. { *F.L.Scott et al.,J.Chem.Soc.B,1411 (1971)* }.

Only the syn-form of the hydrazones is present in solution and the N-*methyl* protons,in each compound,give rise to a doublet signal arising from a long-range "stereospecific" coupling to the methine proton (^5J = 0,7 Hz). These features have been previously detected on N-methylphenylhydrazones type $R_1R_2C=N-NMe-Ph$ (R_1=H and R_2=alkyl) { *G.J.Karabatsos et al.,Tetrahedron 23,1097 (1967)* }.

Anomalous high field shifts have been observed in aromatic,disc-shaped solvents,presumably as a consequence of large σ_A and σ_W values.

Photochemical and UV studies,carried out by Dr.G.Condorelli,are in course on these compounds.

Yours sincerely,

G.C.Pappalardo

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

25 October 1971

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

Dear Barry:

FREE ENERGIES OF ACTIVATION FROM THE COALESCENCE OF AN UNEQUAL DOUBLET

During the course of our studies on the barrier to pyramidal inversion at phosphorus in phospholes, it became necessary to determine rate constants at the coalescence temperature for the exchange of two uncoupled, unequally populated sites.[1] Shanan-Atidi and Bar-Eli have recently addressed this problem, and have presented[2] a graphical solution to the analytic expression

$$P_A - P_B = \Delta P = \left(\frac{X^2-2}{3}\right)^{3/2}\frac{1}{X} \qquad \text{(eq 1)}$$

where

$$X = 2\pi\delta\nu\tau \qquad \text{(eq 2)}$$

and

$$k_A = \frac{1}{2\tau}(1-\Delta P);\ k_B = \frac{1}{2\tau}(1+\Delta P) \qquad \text{(eq 3)}$$

We have found the following procedure, although equivalent, to be more convenient. Thus, solution (Newton-Raphson method) of eq 1, a sixth order polynomial, for each value of ΔP from 0.00 to 1.00 in 0.01 increments resulted in no more than two real and positive roots for each value of ΔP. Choice of the proper root was obvious by inspection. From the resulting tabulation of roots (Table I), the value of X corresponding to a particular value of ΔP is easily extracted, and τ and hence k_A and k_B may be easily calculated (eq 2 and 3, above). The free energies of activation at the coalescence temperature, $\Delta G_A^{\ddagger}$ and $\Delta G_B^{\ddagger}$, may then be calculated by use of the Eyring

equation. Alternatively, the above computations may be conveniently preformed by the following program written in BASIC, for which a sample output is included. Input to the program consists of a value for the coalescence temperature (°C), the value of ΔP (0.00-1.00), and the value of the limiting chemical shift separation (in Hz).

Yours sincerely,

Bill

Joe Andose, Bill Egan, Kurt Mislow

(1) W. Egan, R. Tang, G. Zon, and K. Mislow, J.Amer.Chem.Soc., in press.

(2) H. Shanan-Atidi and K. H. Bar-Eli, J.Phys.Chem., 74, 961 (1970).

TABLE I

Values of X obtained by solution of $X^6 - 6X^4 + (12 - 27(\Delta P)^2)X^2 - 8 = 0$ for given values of ΔP.[26]

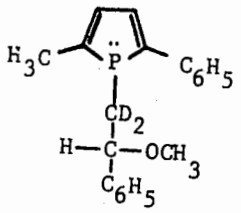
ΔP	X	ΔP	X	ΔP	X	ΔP	X
0.00	1.4142						
0.01	1.4767	0.26	1.9820	0.51	2.3128	0.76	2.5910
0.02	1.5137	0.27	1.9968	0.52	2.3247	0.77	2.6013
0.03	1.5450	0.28	2.0115	0.53	2.3366	0.78	2.6117
0.04	1.5731	0.29	2.0259	0.54	2.3483	0.79	2.6220
0.05	1.5990	0.30	2.0403	0.55	2.3600	0.80	2.6322
0.06	1.6233	0.31	2.0544	0.56	2.3717	0.81	2.6424
0.07	1.6463	0.32	2.0685	0.57	2.3832	0.82	2.6526
0.08	1.6684	0.33	2.0823	0.58	2.3947	0.83	2.6627
0.09	1.6896	0.34	2.0961	0.59	2.4061	0.84	2.6728
0.10	1.7100	0.35	2.1097	0.60	2.4175	0.85	2.6828
0.11	1.7299	0.36	2.1232	0.61	2.4287	0.86	2.6928
0.12	1.7492	0.37	2.1366	0.62	2.4400	0.87	2.7027
0.13	1.7679	0.38	2.1498	0.63	2.4511	0.88	2.7126
0.14	1.7863	0.39	2.1629	0.64	2.4622	0.89	2.7225
0.15	1.8042	0.40	2.1760	0.65	2.4732	0.90	2.7323
0.16	1.8218	0.41	2.1889	0.66	2.4842	0.91	2.7421
0.17	1.8390	0.42	2.2017	0.67	2.4951	0.92	2.7518
0.18	1.8559	0.43	2.2144	0.68	2.5060	0.93	2.7615
0.19	1.8725	0.44	2.2270	0.69	2.5168	0.94	2.7712
0.20	1.8888	0.45	2.2395	0.70	2.5276	0.95	2.7808
0.21	1.9049	0.46	2.2520	0.71	2.5383	0.96	2.7904
0.22	1.9208	0.47	2.2643	0.72	2.5489	0.97	2.8000
0.23	1.9364	0.48	2.2766	0.73	2.5595	0.98	2.8095
0.24	1.9518	0.49	2.2887	0.74	2.5700	0.99	2.8190
0.25	1.9670	0.50	2.3008	0.75	2.5805	1.00	2.8284

```
5  DIM B[101]
10  PRINT "DELTA G ACTIVATION FOR UNEQUAL DOUBLET"
20  PRINT "H.SHANAN-ATIDI AND K.H.BAR-ELI"
30  PRINT "J. PHYS. CHEM., VOL. 74, 961 (1970)"
40  PRINT
50  PRINT " TO HALT EXECUTION, TYPE 'STOP' "
60  PRINT
70  FOR I=1 TO 101
80  READ B[I]
90  NEXT I
91  REM R7=GAS CONSTANT; B7=BOLTZMANN CONSTANT; P7=PLANK CONSTANT
92  READ R7,B7,P7
95  RESTORE
100  DATA 1.4142,1.4767,1.5137,1.545,1.5731,1.599
101  DATA 1.6233,1.6463,1.6684,1.6896,1.71
102  DATA 1.7299,1.7492,1.7679,1.7863,1.8042
103  DATA 1.8218,1.839,1.8559,1.8725,1.8888
104  DATA 1.9049,1.9208,1.9364,1.9518,1.967
105  DATA 1.982,1.9968,2.0115,2.0259,2.0403
106  DATA 2.0544,2.0685,2.0823,2.0961,2.1097
107  DATA 2.1232,2.1366,2.198,2.1629,2.176
108  DATA 2.1889,2.2017,2.2144,2.227,2.2395
109  DATA 2.252,2.2643,2.2766,2.2887,2.3008
110  DATA 2.3128,2.3247,2.3366,2.3483,2.36
111  DATA 2.3717,2.3832,2.3947,2.4061,2.4175
112  DATA 2.4287,2.44,2.4511,2.4622,2.4732
113  DATA 2.4842,2.4951,2.506,2.5168,2.5276
114  DATA 2.5383,2.5489,2.5595,2.57,2.5805
115  DATA 2.591,2.6013,2.6117,2.622,2.6322
116  DATA 2.6424,2.6526,2.6627,2.6728,2.6828
117  DATA 2.6928,2.7027,2.7126,2.7225,2.7323
118  DATA 2.7421,2.7518,2.7615,2.7712,2.7808
119  DATA 2.7904,2.8,2.8095,2.819,2.8284
120  DATA 1.98683,1.38054E-16,6.62560E-27
130  PRINT
140  PRINT "THIS SPACE FOR COMPOUND FORMULA"
150  FOR F=1 TO 6
151  PRINT
152  NEXT F
153  PRINT TAB(6);"SOLVENT ="
154  FOR F=1 TO 4
155  PRINT
156  NEXT F
160  PRINT "  ENTER THE TEMPERATURE AT COALESCENCE (C)";
165  INPUT T
170  PRINT "  ENTER DELTA P";
175  INPUT P
176  LET I=INT(100*P+.5)+1
177  LET X=B[I]
180  PRINT "  ENTER DELTA V";
185  INPUT V
190  LET T1=273.15+T
200  LET F1=B7/(P7*3.14159)
210  LET F2=T1/V
220  LET G1=R7*T1*LOG(F1*F2*(X/(1-P)))
221  LET G1=G1/1000
230  LET G2=R7*T1*LOG(F1*F2*(X/(1+P)))
231  LET G2=G2/1000
240  LET K1=((3.14159*V)/X)*(1-P)
250  LET K2=((3.14159*V)/X)*(1+P)
260  LET G1=INT(10*G1+.5)/10
261  LET G2=INT(10*G2+.5)/10
262  LET K1=INT(10*K1+.5)/10
263  LET K2=INT(10*K2+.5)/10
270  PRINT
275  PRINT
280  PRINT
281  PRINT "G1  EQUALS DELTA G MORE TO LESS STABLE"
282  PRINT "G2  EQUALS DELTA G LESS TO MORE STABLE"
283  PRINT "K1  EQUALS RATE MORE TO LESS STABLE"
284  PRINT "K2  EQUALS RATE LESS TO MORE STABLE"
285  PRINT
286  PRINT
290  PRINT TAB(1);" TEMP (C)";TAB(15);"DELTA G1 (KCAL/MOL)";TAB(41);
291  PRINT "DELTA G2 (KCAL/MOL)"
310  PRINT
320  PRINT TAB(3);T;TAB(20);G1;TAB(46);G2
321  PRINT
322  PRINT
323  PRINT TAB(15);"RATE K1 (SEC-1)";TAB(41);"RATE K2 (SEC-1)"
324  PRINT
325  PRINT TAB(20);K1;TAB(46);K2
326  PRINT
327  PRINT
328  PRINT "* * * * * * * * * * * * * * * * * * * * * * * * * * * * * "
329  GOTO 60
330  END
```

DELTA G ACTIVATION FOR UNEQUAL DOUBLET
H.SHANAN-ATIDI AND K.H.BAR-ELI
J. PHYS. CHEM., VOL. 74, 961 (1970)

TO HALT EXECUTION, TYPE 'STOP'

THIS SPACE FOR COMPOUND FORMULA



SOLVENT = $CFCl_3$

ENTER THE TEMPERATURE AT COALESCENCE (C)? 1.3
ENTER DELTA P? 0.099
ENTER DELTA V? 2.0

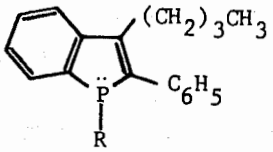
G1 EQUALS DELTA G MORE TO LESS STABLE
G2 EQUALS DELTA G LESS TO MORE STABLE
K1 EQUALS RATE MORE TO LESS STABLE
K2 EQUALS RATE LESS TO MORE STABLE

TEMP (C)	DELTA G1 (KCAL/MOL)	DELTA G2 (KCAL/MOL)
1.3	15.4	15.3

RATE K1 (SEC-1)	RATE K2 (SEC-1)
3.3	4

* *

THIS SPACE FOR COMPOUND FORMULA



SOLVENT = $1,2\text{-}(CD_3)_2C_6H_4$

R = $(\underline{d1})\text{-}CD_2CH(OCH_3)C_6H_5$

ENTER THE TEMPERATURE AT COALESCENCE (C)? 165.0
ENTER DELTA P? 0.091
ENTER DELTA V? 8.5

G1 EQUALS DELTA G MORE TO LESS STABLE
G2 EQUALS DELTA G LESS TO MORE STABLE
K1 EQUALS RATE MORE TO LESS STABLE
K2 EQUALS RATE LESS TO MORE STABLE

TEMP (C)	DELTA G1 (KCAL/MOL)	DELTA G2 (KCAL/MOL)
165	23.7	23.5

RATE K1 (SEC-1)	RATE K2 (SEC-1)
14.4	17.2

* *

UNIVERSITY OF WALES

J. H. PURNELL, Sc.D.,
Professor of Physical Chemistry,
Tel. SWANSEA 25678.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SWANSEA,
SINGLETON PARK,
SWANSEA, SA2 8PP

26th October, 1971.

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

Dear Professor Shapiro,

'Ring Current' Calculations

The recent contribution by Jacobus (This Newsletter 155 - 24) prompts us briefly to summarise some related work of ours, which was presented at the International Symposium on N.M.R. at Birmingham in July 1969. Whereas Jacobus was largely interested in 'ring current' effects in methyl protons, we have concerned ourselves chiefly with aromatic protons. We have just submitted three papers for publication. These are entitled: "P.M.R. of non-planar condensed benzenoid hydrocarbons" I. "Spectra of 3,4-benzophenanthrene, pentahelicene and hexahelicene"; II "Theory of Chemical Shifts"; and "New Tables of 'ring current' shielding in P.M.R." In the first, we report chemical shifts and coupling constants for the three title compounds at infinite dilution in CCl_4. In the second, we formulate a new theory of 'ring current' effects in such non-planar situations, in extension of the earlier quantum-mechanical work of McWeeny[1]. We compare the chemical shifts of paper I with values calculated both by our new theory and (in part) by the semi-classical Johnson-Bovey[2] theory. In the third paper, we present a pictorial comparison of the two theories for a general three-dimensional position in space of a proton, and in an appendix provide our set of tables in the same type of format as that used for the earlier semi-classical tables.[3]

Tables 1, 2 and 3 include a selection of our results. The following conclusions emerge.

(a) The comparatively low-field non-overcrowded protons of Tables 1 and 2 are in the lateral deshielding region of the rings. Their shifts are well predicted by our theory; but the deshielding is seriously over-estimated by the semi-classical approach. Both conclusions are in accord with earlier work on planar hydrocarbons.[4,5]

(b) The comparatively high-field protons are all in the shielding region of one or more rings. Our quantum-mechanical theory under-estimates this shielding effect: this we ascribe to a type of integral approximation originally due to London.[6] This approximation seems to be unreliable in the present context, and has also recently been criticised by others.[7] The Johnson-Bovey theory fares somewhat better, but also under-estimates the shielding.

(c) For the overcrowded protons of table 3, additional downfield steric terms of the order of 1 p.p.m. can probably be ascribed largely to carbon-hydrogen non-bonded interactions. These are analogous to a hydrogen-hydrogen term found in planar aromatics[4,5] and in the birdcage hydrocarbons evidenced by Jacobus.

It is clear that our evaluation of Johnson-Bovey calculations differs markedly from that of Jacobus. In cyclophanes, calculated shifts can be critically dependent on assumed molecular geometries. In the one case where our calculations are directly comparable with those of Jacobus (2,2 metacyclophane) this may well be the explanation of the large discrepancy observed between our two sets of semi-classically calculated shifts. (We used the X-ray geometry of ref.8).

Sincerely yours,

C. W. Haigh

R. B. Mallion
(Christ Church, Oxford)

C. W. Haigh
(Swansea)

P.S. Preprints are available on request (from C.W.H. in Swansea). A limited number of copies of the Tables (as computer output) is also available; but preliminary agreement has been reached with the Editor of "Organic Magnetic Resonance" for the Tables to be published in full.

1. R. McWeeny, 1958, Mol.Phys. 1, 311.
2. C. E. Johnson and F. A. Bovey, 1958, J.Chem.Phys. 29, 1012.
3. e.g. F. A. Bovey, 1969, 'Nuclear Magnetic Resonance Spectroscopy', London and New York, Academic Press; appendix.
4. C. W. Haigh, R. B. Mallion and E. A. G. Armour, 1970, Mol.Phys. 18, 751.
5. R. B. Mallion, 1971, J.Chem.Soc.B, p.681.
6. F. London, 1937, J.Phys.Radium (Paris), 8, 397.
7. A. T. Amos and H. G.ff.Roberts, 1971, Mol.Phys. 20, 1073; 1081; 1089.
8. C. J. Brown, 1953, J.Chem.Soc., p. 3278.
9. e.g. R. Flammang, H. P. Figeys and R. H. Martin, 1968, Tetrahedron, 24, 1171.

Table 1 : Chemical Shifts (τ)

Molecule	Proton	Calculated by New Theory	Exptal
I	2	2.35	2.40
	4	2.11	2.07_5
	6	2.16	2.26^5
II	2	2.57	2.79_5
	4	2.16	2.14_5
	6	2.24	2.21_5

Table 2 : Chemical Shifts (τ)

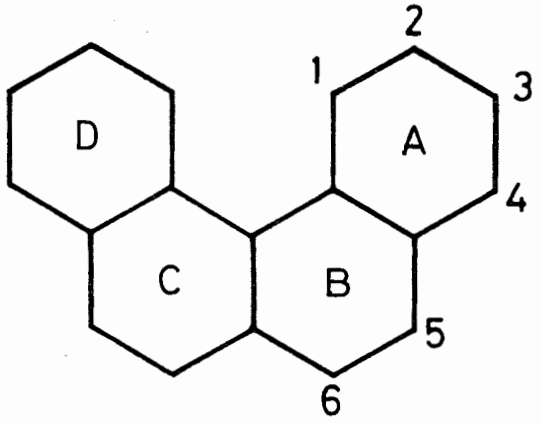
Molecule	Proton	Calculated		Exptal.
		New Theory	Johnson-Bovey	
III	2	2.86	3.03	3.39
	3	2.61	2.45	2.87
	4	2.18	1.64	2.28
	5	2.23	1.43	2.16
	6	2.22	1.30	
	7	2.1_2	1.0_1	2.10
	8	2.1_6	1.22	
IV (2,2-meta-cyclophane)	H_b^*	3.9	4.8	5.75[+]

*Using the notation of Jacobus (loc.cit.) for the methyl-substituted compound.

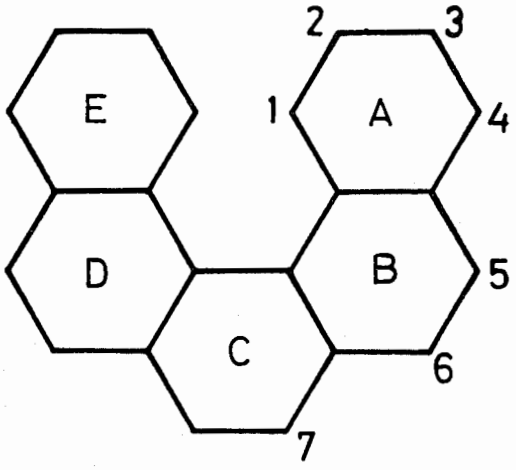
+ref.9.

Table 3 : Chemical Shifts (τ) of Overcrowded Protons

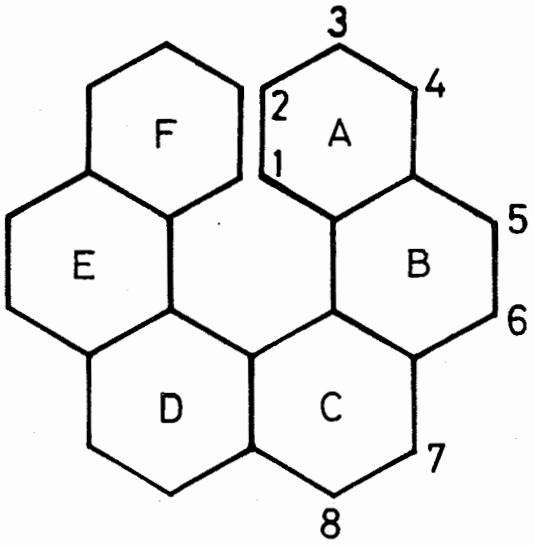
Molecule	Proton	Calculated by New Theory	Exptal.
I	1	2.11	0.92_5
II	1	2.71	1.54^5
III	1	3.09	2.47_5



I



II



III

158-46

UNIVERSITY OF BRISTOL

Telephone Bristol 24161 (Ext.)

SCHOOL OF CHEMISTRY
CANTOCK'S CLOSE
BRISTOL
BS8 1TS.

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

26th. October 1971.

Dear Professor Shapiro,

More Platinum Satellites.

Some years ago when we were examining the p.m.r. spectra of some trimethylphosphine and trimethylarsine complexes of platinum and palladium, we had the impression that the ^{195}Pt satellites of the arsine complexes were abnormally broad. This was emphasised when we examined some trimethylstibine compounds prepared by J.R. Knight here. For these, the satellites were so broad that a previous study[1] had missed them and reported the platinum coupling as zero. We were not moved to investigate this further until a year ago, the same effect was found with trimethylarsine complexes of mercury prepared by S.R. Haddock. Exchange of ligands between metal atoms seemed an unlikely explanation as the central line showed no broadening, lowering the temperature made the satellites broader rather than narrower and because the effect was observed over such a range of compounds. An alternative possibility was an abnormally short relaxation time T_1 for the metal nucleus. As it was only observed when a quadrupolar nucleus (i.e. ^{75}As, ^{121}Sb, or ^{123}Sb) was attached to the metal, the rapid relaxation of the quadrupole was presumably significant. The quadrupolar nucleus (L) can relax the spin of the metal (M) by means of the scalar coupling between them [2]: the relaxation time of the metal is then -

$$\frac{1}{T_1}_M = DD + \frac{8\pi^2 J^2}{3} \frac{I(I+1)\,\tau}{1 + (\omega_M - \omega_L)^2 \tau^2}$$

- DD represents the contribution from dipolar coupling, J the coupling constant between M and L, τ the relaxation time of L and $(\omega_M - \omega_L)$ the difference between the resonant frequencies of M and L. The second term will only be significant if J is large, τ is small and $(\omega_M - \omega_L)$ not too great. For Pt and As, J should be at least 1000 Hz to judge from platinum-phosphorus coupling, τ about 10^{-6} sec., and for a field of 23.5 kgauss, the frequency difference is nearly 4 MHz. which are in keeping with the broadening of ca. 0.5 Hz observed on the proton spectra. For Hg and As, the frequency difference is only 0.75 MHz. which explains the greater broadening which we observed; whilst for Pt and Sb, the main effect will be due to the ^{121}Sb nucleus which has I = 5/2 and a greater quadrupole moment (hence faster relaxation) than aresenic. Other pairs of nuclei for which the frequency difference, J and τ

/Continued.....

could be right for this effect to occur are Pt - I, Hg - I and Pt - Br. We have observed it for the first two but not for the last. To judge from the broadening produced, J(PtI) is much less than J(PtAs) and a small value for J(PtBr) probably accounts for the lack of any observable effect in this case.

We have further pursued this by studying $[PtCl_3AsMe]^-$ at 60 MHz, 40.5 MHz and 32.1 MHz. Assuming that DD is small enough to be ignored, we have got an approximate value of 1400 Hz for J(PtAs) and 1 x 10^{-7} sec. for τ As. Looking at our plot and at other platinum systems, it is likely that DD is of the order of 10 sec and, hence, not strictly ignorable. We would like to get better values for this system together with some for the other systems and to this end we are starting to collect digitised spectra on paper tape and process them on the University's I.C.I. 4/75 computer.

The effect of temperature changes is difficult to evaluate as the viscosity of the solvent makes a vital contribution to the relaxation rate of the quadrupole. Reliable values for the viscosity of methylene chloride below 0°C seem difficult to find, but using approximate values there would appear to be a sensible relationship between the broadening and the viscosity.

We have now got the information on the ^{31}P spectrum of $[PtCl(PMe_3)_3]^+$ which was mentioned in our last contribution (No. 148, p.15). The separation of the low field ^{195}Pt satellites, calculated from the rest of the spectrum, would be only 30 Hz whilst $^2J_{PP}$ is 22 Hz which agrees with our explanation of the 'anomalous' satellite in the proton spectrum. We obtained the ^{31}P results by INDOR using a recently acquired Schomandl ND 100 M frequency synthesizer. Although this system is not going fully yet, it seems very promising.

Yours sincerely,

Robin Goodfellow

Brian Taylor

1. H.P. Fritz and K.E. Schwarzhans, J.Organometal.Chem., 1966, 5, 104.

2. A. Abragam, "The Principles of Nuclear Magnetism", p.331. (We cannot get the examples in Abragam to work out properly. This is not too surprising as the data differs from that of the source, F. Winter, Compt.Rend., 1959, 249, 1346, but we can't get that to work out either!)

Research Laboratory

International Business Machines Corporation

Monterey & Cottle Roads
San Jose, California 95114
408 / 227-7100

October 25, 1971

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

Dear Barry:

We have agreed to write a review article for Charley Poole's Magnetic Resonance Review on computer programs in magnetic resonance, and wish to ask the assistance of TAMU NMR Newsletter readers. Many different computer programs have been written and are currently in use.

So that we may be as complete as possible and realistic about what the leaders in NMR are doing, would the readers, and by necessity the contributors to TAMU NMR, please write us a postcard or letter stating what programs they are using, the amount of usage, who the programmers were and any comments, such as relevant details and opinions.

Thank you.

Sincerely,

T. R. Lusebrink

J. D. Swalen

TRL/JDS:mar

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

October 30, 1971.

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

Dear Barry,

NMR Temperature Measurements - another Non Solution

We have been trying some variable temperature ^{13}C studies on the XL 100. This has raised the hoary old problem of how to best measure the sample temperature since there is no ^{13}C thermometer. We thought we had found a solution with the new Wilmad long stem 5 mm. thermometers. The method involves the simple interchange of the sample tube and the thermometer. This seems to work well for 5 mm. tubes provided the thermometer has been checked and the usual precautions regarding equilibration etc. are observed. The 12 mm. story is very different. There is a difference of as much as 20° between the temperature measured by interchanging sample and thermometer and by placing the thermometer in the sample. The difficulty can be quickly traced to the change in the partitioning of the gas flow between the sample and the probe with the change in "tube" size. We have been forced to return to the standard thermocouple procedure for accurate work.

A number of tests at high and low temperatures have shown, somewhat to our surprise, that the presence or absence of proton noise decoupling has no effect on the sample temperature (within about 0.5°) provided the gas flow is 20 - 30 scfh or greater.

We have been looking at variable temperature ^{13}C spectra of (a) some rearranging carbonium ions, (b) some bullvalene systems and (c) the cycloheptatriene - norcaradiene equilibrium in phenyl cycloheptatriene. The (a) and (b) studies have run into major sensitivity problems and we have postponed detailed studies until our Fourier system is completed. The cycloheptatriene study is in the early stages, but has shown evidence for a small amount of the norcaradiene component. We will present a fuller account of this study when we have done some more work. Please credit this contribution to Dr. Miller's account.

Yours sincerely,

John B. Grutzner

John B. Grutzner

158-50

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KETTERING-MEYER LABORATORY
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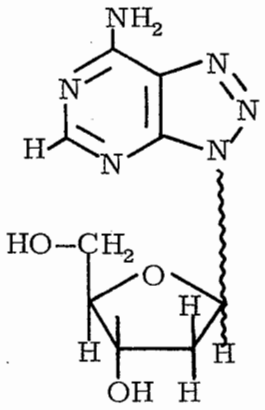
November 2, 1971

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

Dear Barry:

For some time we have been able to identify quite successfully the α- and β-anomers of 2'-deoxyribofuranosyl nucleosides based on the peak width, appearance, and first-order coupling constants of the anomeric proton as first described by Robins and Robins.[1] We have occasionally observed β-anomers which departed considerably from the appearance of a "triplet", but the distinction between the α- and β-anomers was, nevertheless, clear-cut because of the difference in multiplet width (about 14 Hz for the β-anomer, 10 Hz for the α-anomer).

Recently, however, we worked with the anomers of



and found that both anomers gave the appearance of β-anomers. In chemical shift, appearance ("triplet"), and multiplet width (~14 Hz), the anomeric proton absorptions were nearly the same. This was a disturbing development, and we hope that it will not prove true of all anomeric pairs when the base is an 8-azapurine. We cannot help feeling that the 8-nitrogen in the purine ring has been the source of this difference, although Robins and Robins[1] reported that the nature of the base does not affect the splitting of the anomeric proton.

We finally proved the identity of the α- and β-anomers by chemical means, which was not spectroscopically very satisfying.

Sincerely yours,

Martha C. Thorpe
Senior Chemist

MCT:br

[1] M. J. Robins and R. K. Robins, J. Amer. Chem. Soc., 87, 4934 (1965).

Suggested title: "Determination of the Anomeric Configuration of Purine Nucleosides"

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