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Newsletter

No. 148
JANUARY, 1971

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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Deadline Dates: No. 149: 1 February 1971 No. 150: 1 March 1971

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

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



Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

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

Uw kenmerk

Uw brief van

Ons kenmerk

Delft, Nederland, Lorentzweg 1, tel. 01730-33222
December 8. 1970 toestel:

Onderwerp Free-precession-decay for a two spin($\frac{1}{2}$)-system.

Dear Professor Shapiro,

In solid-state NMR much work has been done on measuring free-precession-decays of crystals (1,2). Theoretical expansions, using dipolar broadening as basic interaction, have been given by several authors (2,3,4). They fit the experiments quite well. On the other hand trial-functions have been given for several decays with good results, but with little theoretical background. These trial-functions have the following form:

$$G(t) = F(t) H(t) \quad (1)$$

where $H(t)$ is a Gaussian function. $F(t)$ is given by e.g. $\sin(bt)/bt$ (5) or $2J_1(bt)/bt$ (6). We feel that by giving these trial-functions a more theoretical background we can get more information about what's happening physically than by using a mere mathematical expansion.

Consider a molecule with one pair of identical spins ($\frac{1}{2}$).

The spins in other molecules produce a field $\Delta\omega/\gamma$ at the site of this molecule (intermolecular-interaction). We assume the intermolecular-interaction to be "much" weaker than the intramolecular-interaction.

Now we can write, following Metzger and Gaines (6):

$$G(t) = 2 \int f(\alpha) \cos \alpha t \, d\alpha \int h(\Delta\omega) \cos \Delta\omega t \, d\Delta\omega \quad (2)$$

where α/γ represents the local field due to the intramolecular-interaction. α is given by:

$$\alpha = (3\gamma^2 h/4r^3) (1 - 3 \cos^2 \theta) = p(1 - 3 \cos^2 \theta) \quad (3)$$

$f(\alpha)$ and $h(\Delta\omega)$ are the distributionfunctions of α and $\Delta\omega$ over the sample.

From (1) and (2) it is clear that $F(t)$ and $H(t)$ are the Fouriertransforms of $f(\alpha)$ and $h(\Delta\omega)$. We assume $h(\Delta\omega)$ to be Gaussian like in all trial-functions. If we assume the dipolar axis between the two spins to have equal chance for every direction in space (spherical distribution) we find after some calculation:

$$F(t) = F(pt) = \sqrt{\pi/6pt} \{ \cos(pt)C_2(3pt) + \sin(pt)S_2(3pt) \} \quad (4)$$

where C_2 and S_2 are Fresnel integrals. In the figure the function $F(pt)$ is given, together with $\sin(bt)/bt$ and $2J_1(bt)/bt$. The constants b have been chosen in such a way that all functions have the same first zero point. From the figure it is clear that the functions don't differ much up to this point. Measurements were made on the protons in polycrystalline CH_2Cl_2 and H_2NCN to verify equation (4). Our spin-echo equipment being not ready yet, we had to use the Fouriertransform of a continuous-wave experiment. The zero points for CH_2Cl_2 are in fairly good agreement with the theory, while that of H_2NCN are not (perhaps due to the interaction with nitrogen-atom in the H_2N -group). From the given value of p we calculated the intramolecular distance r . The result for CH_2Cl_2 is $1,93 \pm 0,03 \text{ \AA}$ (literature gives $1,78 \pm 0,03 \text{ \AA}$); for H_2NCN we found $1,81 \pm 0,02 \text{ \AA}$ ($1,62 \pm 0,02 \text{ \AA}$). Our next concern is the assumption of a Gaussian function for the intermolecular interaction, and the intramolecular interaction between different spins.

Sincerely yours,



Chr. Steenberg.

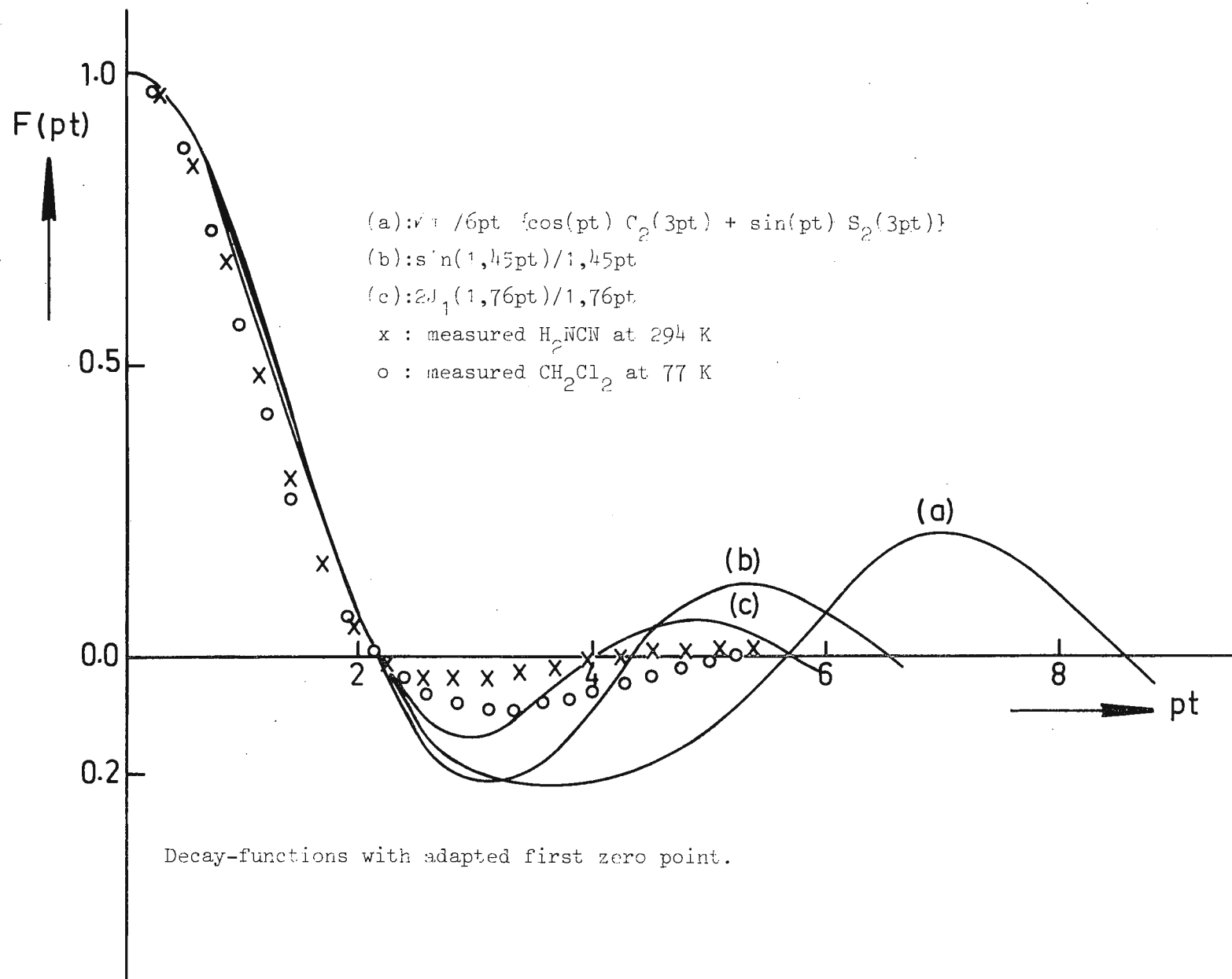


R.A. Wind.

Please, credit this letter to Prof. Dr. Ir. J. Smidt, who thanks you for your reminder.

References:

- (1) D.E. Barnaal and I.J. Lowe, Phys. Rev 148, 328 (1966)
- (2) R.E. Fornes, G.W. Parker, J.D. Memory, Phys. Rev B 1, 4228 (1970)
- (3) J.H. van Vleck, Phys. Rev 74, 1168 (1948)
- (4) I.J. Lowe and R.E. Norberg, Phys. Rev 107, 46 (1967)
- (5) A. Abragam, Principles of Nuclear Magnetism (p.120) (Clarendon, Oxford, 1961)
- (6) D.S. Metzger and J.R. Gaines, Phys. Rev 147, 644 (1966)



Prof. Dr. Ernst G. Hoffmann

MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG

MPI für Kohlenforschung, 4330 Mülheim-Ruhr, Kaiser-Wilhelm-Platz 1

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Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen

Datum

Dr.Ho/Lk

5.12.1970

Lieber Doktor Shapiro!

Obwohl seit 1957 neben anderem auf dem Gebiet der NMR-Spektroskopie tätig, habe ich es bisher noch immer versäumt, von dem außerordentlichen Nutzen Gebrauch zu machen, den der Austausch von NMR-Informationen zwischen Fachkollegen durch Ihre NMR Newsletters bedeutet. Es ist ausschließlich meine Schuld und mein Schaden, denn immer wieder haben mich Kollegen wie Dr. Englert oder Dr. Brügel und jetzt auch nochmals Dr. Dreeskamp auf die Nützlichkeit dieser Informationsquelle aufmerksam gemacht. Darf ich Sie deshalb bitten, mich in Zukunft in Ihre "Mailing List" aufzunehmen und mich mit den seit einiger Zeit üblichen Kosten zu belasten. Über die Einschränkungen, denen der Gebrauch der Mitteilungen der Letters unterworfen ist, weiß ich Bescheid.

Vielleicht akzeptieren Sie als meinen ersten Beitrag eine Mitteilung über eine einfache und schnelle Methode zur Bestimmung der chemischen Verschiebung von Heterokernen:

Seit längerer Zeit benutzen wir eines unserer NMR-Geräte (14,1 kG) im Puls-Betrieb, einerseits um Kinetik über den Spin-Echo-Effekt zu betreiben (über die Behandlung von Viellinienspektren durch doppelte Fourier-Transformation siehe die jetzt im 1. Heft der Zeitschrift für Naturforschung, Band a, 1971 erscheinende Notiz), teils um durch Pulsmodulation stationär Spektren (in der Weise "Time Division" nach Meiboom bzw. "Time Sharing" nach Baker) der verschiedensten Kerne im Haupt- oder Seitenband mit weiten Sweep-Breiten aufnehmen zu können. Die Anwendung der Fourier-transformationspektroskopie betreiben wir schon längere Zeit. Trotz

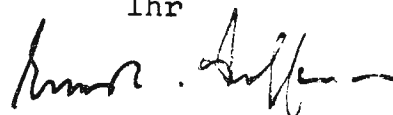
der Verwendung von 5mm-Röhrchen in einer selbstgefertigten Universalprobe (Vorteil: geringer Substanzbedarf und die Möglichkeit der Messung luftempfindlicher Substanzen im abgeschmolzenen Röhrchen) erreichen wir hohe Empfindlichkeiten durch Anwendung einer speziellen Modulationstechnik. Im Augenblick untersuchen wir gerade ^{31}P in Komplexen nach einer sehr einfachen Methode, die nicht einmal eine Fourier-Transformation unbedingt erfordert, wenn außer $^n\text{J}_{\text{P} \dots \text{H}}$ keine weiteren Kopplungen auftreten:

Das von ^1H rauschentkoppelte Sample wird in Schritten von 0,5 - 1 kHz gepulst (0,5 - 1 msec lange Einzelpulse), bis auf dem Oszillographenschirm oder nach ca. 10 Pulsen auf dem CAT ein Signal erscheint. Mit einem VCO-gesteuerten Frequenzsynthetisator (ein sehr preiswertes Modell, das allerdings für den Sweep von uns umgebaut wurde, ist der FS 30 von Schlumberger Overseas, aus dem wir gleichzeitig die Grundfrequenzen für ^1H und ^{19}F entnehmen) verändern wir die z.B. ^{31}P -Frequenz so lange, bis wir die freie Induktion ohne Wiggles bekommen haben. Bei nicht zu verdünnten Samples können wir so unter Umständen bis zu 14 Messungen der Chemical Shift durchführen (externer Standard, externer Fluor-Lock). Damit läßt sich die Resonanzfrequenz an einem Zähler direkt ablesen. Die Standardisierung erfolgt auf Protonenresonanz, nachdem die Rauschmodulation auf eine Time-Division-Modulation umgeschaltet wurde. Natürlich erfordert das System außer Eingangsweichen auch Weichen für die gleichzeitig betriebenen Empfänger ^{31}P etc., ^1H .

Ich hoffe, daß Ihnen die Mitteilung als ausreichend für die Aufnahme in die NMR Newsletters dient und muß mich nur entschuldigen, daß ich den Beitrag in deutsch abgefaßt habe, da ich in der Eile keine brauchbare Übersetzung zustande bringe (mein letzter Aufenthalt in USA war 1960).

Mit herzlichen Grüßen

Ihr



(Prof. E.G. Hoffmann)

Max-Planck-Institut
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D-4330 Muelheim/Ruhr
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DEPARTMENT OF CHEMISTRY

December 8, 1970

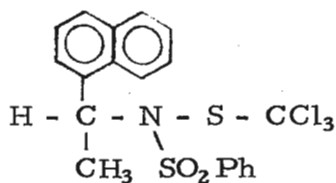
Professor B. L. Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, Texas 77843

Dear Professor Shapiro:

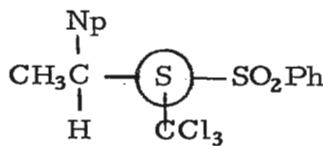
Comments on: Low temperature non-equivalence in a doubly asymmetric hydroxylamine.

In a recent letter¹ Hall discussed the n.m.r. spectra of some trialkylhydroxylamines. Because of the asymmetry of the hydroxylamine grouping^{2,3} and the presence of an asymmetric carbon atom two diastereomers are observed in the n.m.r. spectra at temperatures low enough that stereomutation at the hydroxylamine asymmetric unit is slow on the n.m.r. time scale.

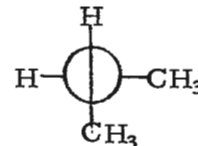
We have examined n.m.r spectra of a number of the sulfur analogues, sulfenamides, and have obtained similar results. As an example the n.m.r. spectrum of 1 features two C-methyl doublets that



1
~



2
~



3
~

arise from the two diastereomers of this compound. The asymmetry of the sulfenamide unit might have been due to the presence of an asymmetric nitrogen atom, or alternatively to the chiral axis of the

Page Two

sulfenamide bond if the conformation of the sulfenamide bond is like that shown in Newman projection $\tilde{2}$. We note that the chiral axis indicated in $\tilde{2}$ brings to mind the Newman projection of 1,2-dimethylallene, $\tilde{3}$, which likewise possesses axial chirality. Likewise two processes are possible for the rate determining step in the interconversion of the two diastereomers of $\tilde{1}$, rotation about the N-S bond or inversion of the nitrogen pyramid.⁴ The structure of $\tilde{1}$ has been determined by X-ray diffraction and features essentially planar substitution at nitrogen and a geometry like that of $\tilde{2}$ for the chiral axis of the sulfenamide bond. The barrier to nitrogen inversion is greatly reduced by the presence of the phenylsulfonyl group which is known to reduce nitrogen inversion barriers in aziridines.

We have succeeded in isolating, by crystallization, the pure (R,R)-isomer of $\tilde{1}$, which is stable at temperatures below -60° and exhibits a single doublet in the n.m.r. spectrum (see upper figure). When the temperature is raised to -50° epimerization, by rotation about sulfenyl S-N bond, begins to occur at a measurable rate until an equilibrium mixture of the two isomers is reached. In sulfenamides without additional asymmetric units diastereomerism is not possible, although chemical shift nonequivalence of diastereotopic protons is observed.

A similar situation is occurring in the hydroxylamine analogues. As we have shown, slow rotation as well as slow nitrogen inversion can lead to diastereomerism and either explanation is in accord with Hall's results. We therefore reject his contention that his results provide information about whether nitrogen inversion or torsion about the N-S bond is slow on the n.m.r. time scale.

In the absence of further information, we might even regard the torsion explanation as more probable in view of the behavior of the

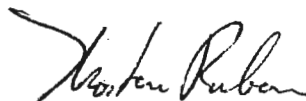
Page Three

sulfur analogues for which the torsion explanation has been firmly established.⁵

Sincerely yours,

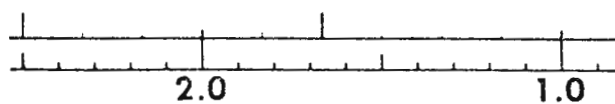
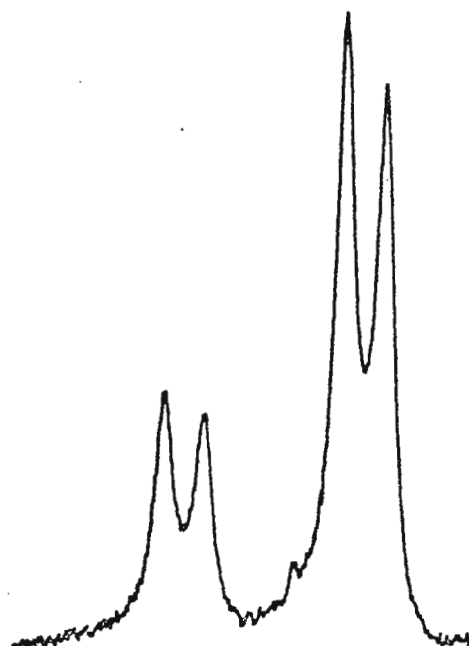
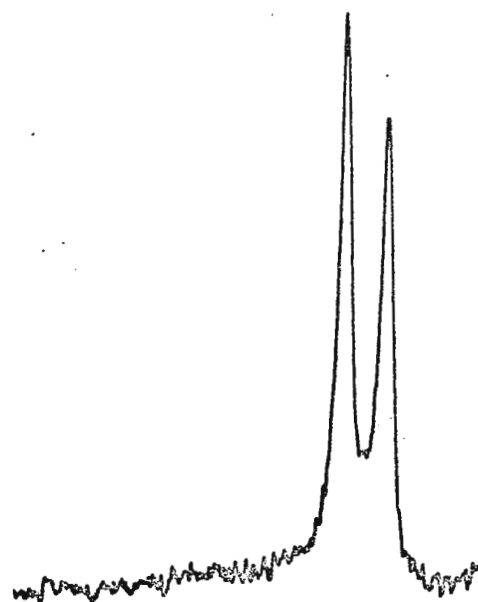


S.K. Lauderback



M. Raban

1. C.D. Hall, TAMUNMR Newsletter, No. 146, 14 (1970).
2. D.L. Griffith and J.D. Roberts, J. Amer. Chem. Soc.,
87, 4089 (1965).
3. M. Raban and G.W.J. Kenney, Jr., Tetrahedron Letters, 1295
(1969).
4. M. Raban, G.W.J. Kenney, Jr., J.M. Moldowan, and F.B.
Jones, Jr., J. Amer. Chem. Soc., 90, 2985 (1968).
5. M. Raban, G.W.J. Kenney, Jr., and F.B. Jones, Jr., ibid,
91, 677 (1969).



N.m.r. spectra of 1 in methylene chloride. The upper spectrum was measured at -50° after dissolution at ca. -70° . The lower spectrum was measured at -50° after dissolution at room temperature.



JET PROPULSION LABORATORY California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103

10 December 1970

Refer to: 326-SLM:lh

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

Dear Barry: A Bond Bending Effect on $^1J_{13}^{C-H}$

Very recently while Dr. M. Ashley Cooper was in our laboratory he carried through some systematic investigations of the proton nmr spectra of a number of alkenes, cycloalkenes and aromatic hydrocarbons. We believe that this work provides a much clearer understanding of various types of steric distortion which affect the magnitudes of proton-proton coupling constants. In the case of the steric contributions to cis-vicinal vinylic coupling, $^3J_{HH}$, both experimental results and approximate theoretical treatments of all the reasonable types of strain-induced molecular distortions suggest that C=C-H bond angle changes provide the major contributions. In the course of this work, Dr. Cooper measured the spectra of both cis-di-t-butylethylene and trans-di-t-butylethylene; these and some related results are given in Table I. The values of $^1J_{13}^{C-H}$ in these former two molecules are the smallest ever observed for the vinylic type. Results to be discussed elsewhere demonstrate a satisfactory correlation between the C=C-C (or C=C-H) bond angles and $^3J_{HH}$ and $^1J_{13}^{C-H}$ and suggest the interesting possibility of obtaining accurate estimates of bond angles from nmr coupling constants.

With best regards,

Sincerely yours,

Stanley L. Manatt
Assistant Section Manager
Bioscience Section

Table I. Summary of Coupling Constant Data from Present Work and Literature.

	$^1J_{^{13}C-H}$	$^3J_{-HH}$	C=C-H Angle in degrees
Ethylene	+156.2 ^a , 156.4 ^b		122.0 (C=C-H) ^c
<u>cis</u> -2-butene	---	+10.88 ^d	125.0 ^e
<u>trans</u> -2-butene	---	+15.09 ^d	---
<u>cis</u> -di- <u>t</u> -butylethylene	+150.4	+14.2	136 ^f
<u>trans</u> -di- <u>t</u> -butylethylene	+149.4	+16.10	---
cyclopentene	+161.6	+ 5.57	111.5 ^g
cyclohexene	+158.4	+10.11	123.3 ^h
cycloheptene	+156.2	+11.02	---
cyclooctene	+156.0	+10.41	---

^aR. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. (London), Sec. A, 269, 386 (1962). ^bD. M. Graham and C. E. Holloway, Can. J. Chem., 41, 2114 (1963). ^cL. S. Bartell and R. A. Bonham, J. Chem. Phys., 31, 400 (1959). ^dR. K. Harris and B. R. Howes, J. Mol. Spectrosc., 28, 191 (1968). ^eT. N. Sarachman, J. Chem. Phys., 49, 3148 (1968). ^fEstimated from data on o-t-butylaromatic molecules. ^gG. W. Rathjens, J. Chem. Phys., 36, 2401 (1962). ^hL. H. Scharpen, J. E. Wollrab and D. P. Ames, ibid., 49, 2368 (1968).

Institut für Physikalische Chemie

der Rhein.-Westf. Techn. Hochschule Aachen
Direktor Prof. Dr. U. F. Franck

51 AACHEN, den 12.12.70

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Dr. R. Kosfeld

Prof. B. L. Shapiro
Chemistry Department
Texas A. + M. University
College Station

Texas - 77843

USA

The Eighth Colloquium on NMR-Spectroscopy
Germany, Aachen, April 14. - 20., 1971

Dear Dr. Shapiro,

Would you please publish the following announcement in the
NMR Newsletters:

Announcement

The Eighth Colloquium on NMR-Spectroscopy, concerned with
"Magnetic Relaxation Phenomena and Internal Kinetics of Fluid
Systems", will take place at the Institut für Physikalische
Chemie - Dozentur für Physikalische Chemie-, Rheinisch-Westfälische
Technische Hochschule, Aachen on April 14 - 20, 1971.

This Colloquium will be performed by support of the "Scientific
Affairs Division" of the "North Atlantic Treaty Organization" in
Brussels.

Prospective participants should address inquiries to:

Dr. R. Kosfeld, RWTH Aachen, D51 Aachen, Templergraben 55.

Sincerely yours



(Kosfeld)

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Prof. Dr. H. Günther

5 KÖLN, Dec. 14, 1970
ZÜLPICHER STRASSE 47
TELEFON: 20 24 22 39

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

Computer Program *YMODI*

Dear Barry,

Your reminder (once again!) and a letter of F. Diehl et al. (TAMU-Letter 146-17) prompts us to report, that one of us (J. B. P.) has developed an iterative computer program *YMODI* that calculates the geometry and orientation parameters of molecules with up to eight protons from the dipolar coupling constants measured in nematic solvents.

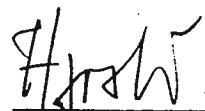
We have tested *YMODI* in the case of benzo-cyclopropene, where explicit expressions for the oriented AA'BB'-system¹ could be used to obtain the values of some interproton distances. The results of both methods were identical.

Listings of the program and a short description are available upon request. A more detailed account will be given in the Ph.D. thesis of J.B.P. that will be available next spring. Results of more chemical interest from our work with nematic solvents will be reported shortly.

Sincerely yours,



J.B. Pawliczek



H. Günther

1) F. Diehl et al., Canad. J. Chem. 46, 2645 (1968).

University of Bristol

School of Chemistry

Telephone: Bristol 24161 Ext.

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Bristol
England BS8 1TS

15th December, 1970.

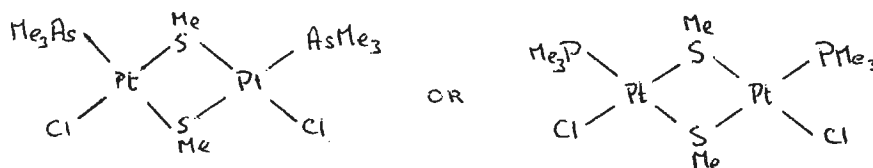
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843,
U.S.A.

Dear Professor Shapiro,

Platinum Satellites

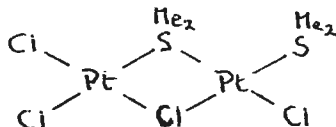
The typical 1:4:1 triplet pattern formed by the satellites due to coupling to the 33% of ^{195}Pt and the main line is well known but in the course of our (i.e. with P.L. Goggin, F.J.S. Reed and B.F. Taylor) studies on platinum complexes we have come across some more complicated examples.

To start with, there is the situation where a proton is equally coupled to two platinum atoms; e.g. the methyl mercapto groups in



For these, a quintet, 1:8:18:8:1 is predicted and sometimes found. Although the outer lines are often too weak to be observed, the relative intensities of the other lines easily distinguish a symmetrical bridging group from a terminal group.

The situation of a bridging group bonded unequally to two platinum atoms should produce four satellites, one quarter of the intensity of the parent at $\pm \frac{1}{2}J_{\text{PtH}}$ and $\pm \frac{1}{2}J_{\text{Pt'H}}$. There should be four more satellites, one sixteenth of the parent at $\pm \frac{1}{2}(J_{\text{PtH}} \pm J_{\text{Pt'H}})$ due to the $(^{195}\text{Pt})_2$ species. One example is the isomer



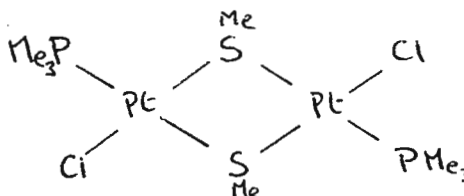
in which the bridging sulphide protons show a double set of satellites $J_{\text{PtH}} = 37\text{Hz}$ and $J_{\text{Pt'H}} = 34.4\text{Hz}$. The outer satellites at $\pm 35.7\text{Hz}$ are just visible. The terminal sulphide group gives a normal single set of satellites $^3J_{\text{PtH}} = 47.9$ so $^5J_{\text{PtH}}$ must be zero.

/over

15th December, 1970.

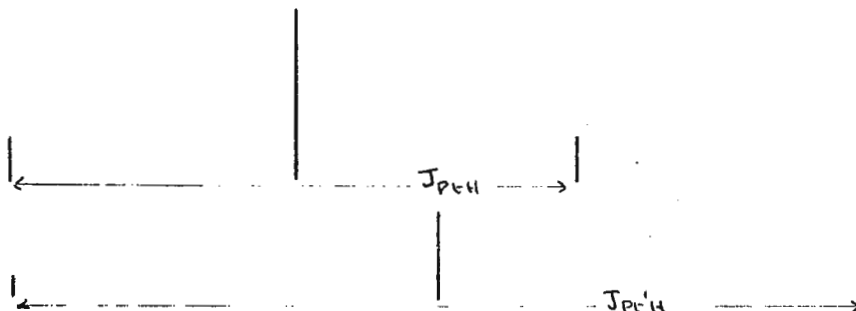
Professor Bernard L. Shapiro,
Texas A & M University.

However, the complex



proved to be not so simple. The spectrum shown has additional peaks due to the cis isomer. The parent band shows, by the presence of additional lines inside the main doublet, the effect of a small P-P coupling (0.5Hz) in this $[AX_3]_2$ system. This description does not apply to the strong set of satellites as the two phosphorus nuclei are not equivalent and the resulting satellites are simple doublets. The outer weak satellites are observed at $\pm \frac{1}{2}(|J_{Pt-H}| + |J_{Pt'-H}|)$. If we assume, as is most likely, that both Pt-H couplings have the same sign, then these satellites correspond to the $\alpha\alpha$ and $\beta\beta$ platinum spin states and should have the same structure as the central band i.e. complex. The spectrum is too weak to be sure about this but it is certainly not ruled out. There is no sign at $\pm \frac{1}{2}(J_{Pt-H} - J_{Pt'-H})$ of the other weak satellites corresponding to the $\alpha\beta$ and $\beta\alpha$ spin states. This can be explained if there is significant Pt-Pt coupling as the system should be described as $[AX_3]_2$ (without including the phosphorus atoms). Such Pt-Pt coupling is not unlikely and I guess that it is sufficiently large compared to $|J_{Pt-H} - J_{Pt'-H}| = 39.1\text{Hz}$ to result in these satellites appearing under the central band.

Another case of 'anomalous' satellites occurs with $(PMe_3)_3PtCl.NO_3$. The main proton peaks consist of a triplet with a broad central line for the trans $(PMe_3)_2Pt$ group and a doublet for the remaining phosphine. The latter shows a splitting of 0.6Hz from the ^{31}P 's of the other phosphines but a similar splitting is not observed on the trans $(PMe_3)_2Pt$ resonances. All the platinum satellites resemble their parents except for the downfield one of the single phosphine. This consists of a doublet of doublets instead of a doublet of triplets. Apparent doublets can occur if the coupling between the two different types of phosphine is similar in magnitude to the shift between them. This could be effectively produced in one set of satellites by the different coupling of platinum to the two types of phosphorus. The ^{31}P spectrum should thus be (omitting P-P splitting)-



We have not got round to measuring the phosphorus spectrum yet to check this deduction.*

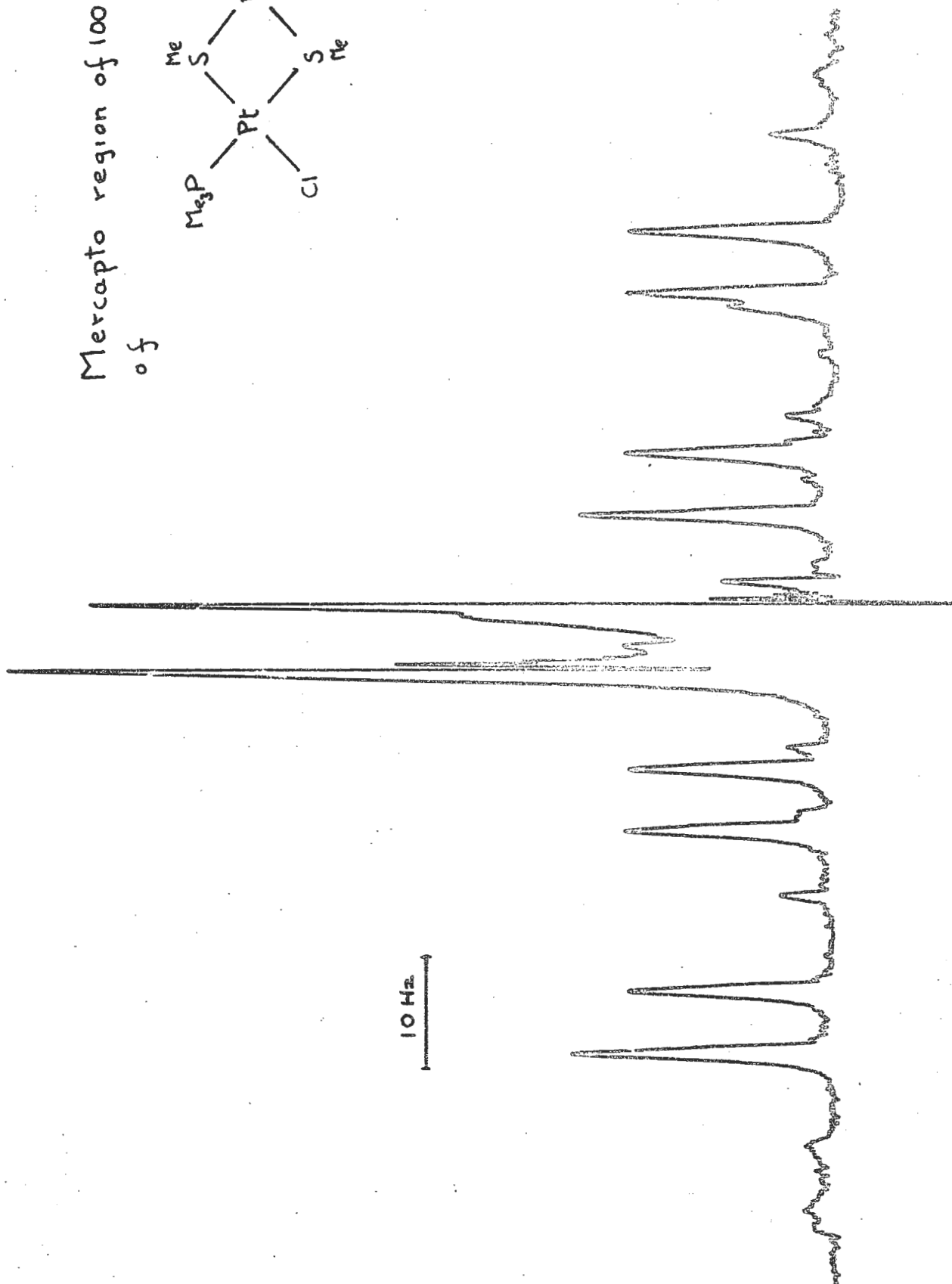
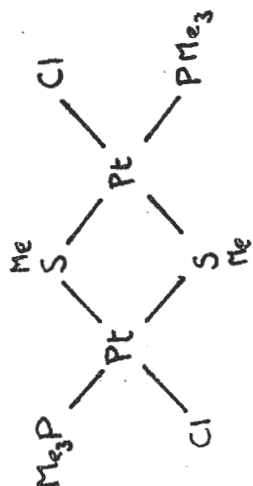
Yours sincerely,

R.J. Goodfellow

Robin Goodfellow

* Power cuts and nmr spectrometers don't go well together.

Mercapto region of 100 MHz spectrum
of



RUTGERS UNIVERSITY *The State University of New Jersey*

SCHOOL OF CHEMISTRY
Ralph G. Wright Laboratory
New Brunswick, New Jersey 08903

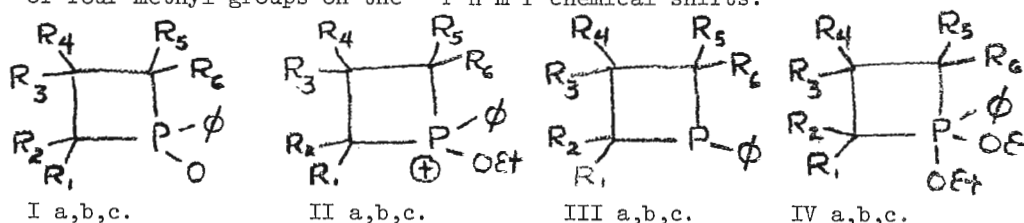
December 16, 1970

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

³¹P
P NMR Chemical Shifts of Four Membered
Ring Phosphorus Containing Compounds

Dear Dr. Shapiro:

We are interested in the chemistry of phosphetanes and related compounds. During the last year, or so, we have accumulated considerable ³¹P n m r data on these materials. In general the substances differ only in the degree and position of substitution on the four membered ring. Despite these relatively small structural alterations one finds rather substantial differences in chemical shifts within a series. In particular one notes the effect of α substitution of four methyl groups on the ³¹P n m r chemical shifts.



a: $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$, $R_5 = R_6 = \text{H}$

b: $R_1 = R_2 = R_3 = \text{CH}_3$, $R_4 = R_5 = R_6 = \text{H}$

c: $R_1 = R_2 = R_5 = R_6 = \text{CH}_3$, $R_3 = R_4 = \text{H}$

³¹P chemical shifts relative to 85% H₃PO₄

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
a	- 50	- 91	- 8	+ 36
b	- 38	- 83	- 1.5	+ 36
	- 45	- 95	- 2.5	
c	- 51	- 98	- 44	+ 22

Clearly there are interesting effects, probably steric in origin, which cause these variations.

Sincerely,

Dorothy Z Denney

Dorothy Z. Denney

148-18



NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Telephone 74-6011 Telegrams NAVORSCHEM

AIR MAIL

P. O. Box 395

OUR FILE

YOUR FILE

PRETORIA

60/6-Pach

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

Dear Professor Shapiro,

Comparison of ^1H N.M.R. parameters for
2-pyrone and 2-thiopyrone

We must apologise for the delay in offering a contribution. Your blue letter has been passed between here and Basel, Switzerland, where Dr. Pachler is spending a year's leave, and it has finally ended up on my desk for answering.

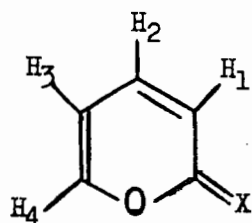
...

The accompanying table shows a comparison of the chemical shifts, coupling constants and ASIS, obtained from analyses of the 100 MHz spectra of 2-pyrone and 2-thiopyrone. Although the spectra are little perturbed from first order, the tabulated data are from the usual iterative calculation.

Yours sincerely,

A.A. Chalmers
RESEARCH OFFICER
NATIONAL CHEMICAL RESEARCH LABORATORY

AAC/JW



X = O, S

	X = O			X = S		
	in CCl ₄	in C ₆ D ₆	ASIS	in CCl ₄	in C ₆ D ₆	ASIS
W1	618.5	579.6	38.9	707.0	677.0	30.0
W2	719.3	613.4	105.9	692.4	578.3	114.1
W3	608.1	505.1	103.0	635.6	516.9	118.7
W4	743.9	650.0	93.9	770.4	658.5	111.9
J12	9.54	9.48		9.19	9.14	
J13	1.15	1.11		1.13	1.28	
J14	1.20	1.25		1.50	1.31	
J23	6.32	6.33		6.56	6.55	
J24	2.24	2.25		1.69	1.77	
J34	5.20	5.20		5.08	5.12	

All solutions 3 mole %

All parameters in Hz, chemical shifts from internal T.M.S.



Medical Research Council

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

telephone Cambridge 45171

reference

16th. December, 1970.

Water Band Removal Using Double Resonance Technique

Dear Barry,

Recently we observed an interesting double resonance effect involving exchange of magnetisation which enables us to effectively remove the residual H_2O absorption band in some D_2O solutions. During the NMR investigation of a series of catecholamines we obtained the ^1H resonance spectrum of isoprenaline part of which is illustrated in the figure. On irradiation at $\delta = 8.21$ ppm there is a dramatic decrease in the intensity of the water band which enables us to see clearly the previously obscured $\beta\text{-CH}$ triplet. Obviously we are irradiating protons in slow chemical exchange with the water protons. Since the spectrum was recorded in 99.8% D_2O solution there will be a very small fraction of the exchangeable groups in isoprenaline still bearing protons which could be involved in slow exchange with the residual protons in the solvent. Examination of the 100 MHz ^1H spectrum of isoprenaline in H_2O solution reveals a broad band at 8.21 ppm attributable to the NH_2^+ protons. When we have characterised this effect further, it might prove of use not only in removing unwanted water proton bands but also in the assignment of exchangeable protons in solution.

Best wishes,

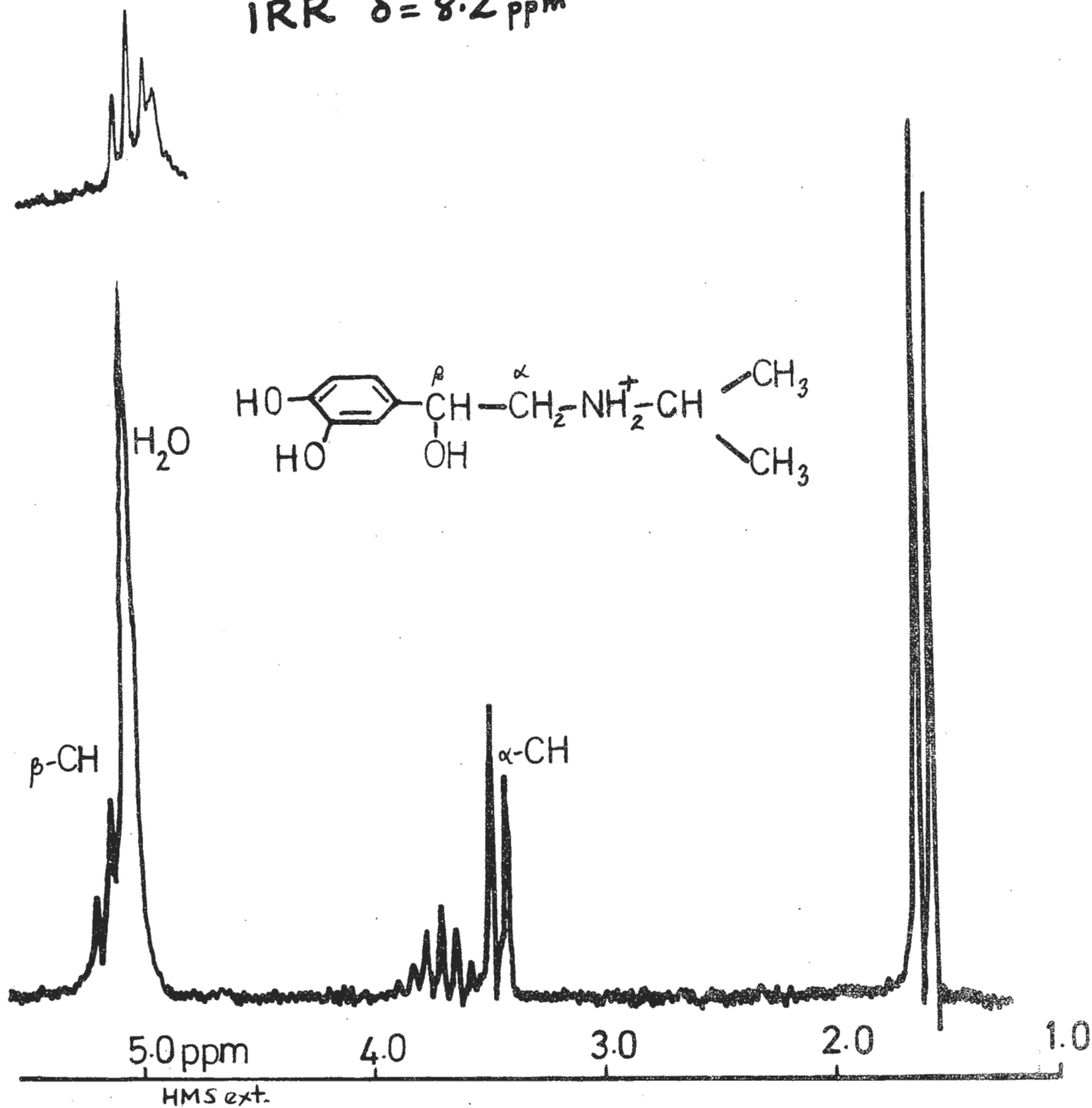
A handwritten signature in cursive script, appearing to read 'Jim'.

J. Feeney

A handwritten signature in cursive script, appearing to read 'Gordon Roberts'.

G.C.K. Roberts.

IRR $\delta = 8.2$ ppm



INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS
CZECHOSLOVAK ACADEMY OF SCIENCE
PRAHA 6 - SUCHBOL 2

December 16th, 1970

A/2443

Professor B. L. S h a p i r o
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Re: The leakage(CCl_4) through pressure caps

Dear Professor Shapiro:

In the course of recently completed study of association of $\text{Me}_3\text{M}(\text{CH}_2)_n\text{OH}$ alcohols ($\text{M} = \text{C}, \text{Si}, \text{Ge}; n = 1 - 4$) it was necessary to prepare a large series of solutions of these alcohols in carbon tetrachloride in NMR tubes.

In our laboratory, similarly as in many others, NMR tubes are usually closed with standard caps or with pressure caps made of poly(vinyl chloride). These caps, while they can stand some overpressure, appear permeable to some solvent vapours. In our test the caps (pressure caps sold by NMR Specialties, Inc.) let 31 mg (in average) of CCl_4 escape from a tube a day if the tubes were kept in a dry box at room temperature. This leak away cannot be suppressed by storing the tubes with the solutions in CCl_4 atmosphere. Then the tubes gain weight due to the difference of partial pressure. Fortunately, the caps are not permeable to water.

Sincerely yours,


Jiří Dědina


Jan Schraml

P.S. The paper on association of the alcohols will be published in Coll. Czech. Chem. Commun.

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

School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR
18th December, 1970.

STEADY-STATE HIGH-RESOLUTION NMR DETERMINATIONS
OF RELAXATION TIMES

Dear Barry,

Your usual reminder provokes a letter on the above topic, in which we have become increasingly interested. In particular we are convinced that steady state methods have much to recommend them, because under equilibrium conditions every resolved NMR line has clearly defined (in an experimental sense) effective relaxation times $T_{1\text{eff}}$ and $T_{2\text{eff}}$ i.e. Bloch-type equations are valid. Non-equilibrium methods do not yield experimental parameters in such a simple fashion.

Steady-state high-resolution NMR methods yield $T_{1\text{eff}}$ and $T_{2\text{eff}}$ essentially from saturation effects and linewidths respectively [from here on we will drop the "eff" subscripts for our own convenience!]. The determination of T_1 requires either prior knowledge of T_2 or calibration with a sample of known T_1 . The equilibrium conditions are obtained most conveniently for cases with short values of T_2 ; such cases have the added advantage that problems of field or frequency inhomogeneity are minimal. Values of T_1 may be obtained conveniently by plotting $B_m/S(0)$ vs. B_m^2 - the ratio of the slope to the intercept is $\gamma^2 K^2 T_1 T_2$ (for the meaning of B_m and K see below; $S(0)$ is the signal height at the Larmor frequency). However, in practice this method requires the accurate location of the baseline for each spectrum. Consequently we are now employing total lineshape fitting in a manner which does not require prior determination of the baseline (see the figure).

The sample we have chosen for detailed study is one of 2,6-difluoro-3,4,5-trichloropyridine in CCl_4 , plus a little CFCl_3 . It can be shown that the presence of two magnetically equivalent fluorine nuclei does not affect the problem. The presence of the quadrupolar nitrogen nucleus makes T_2 short, but T_1 remains long, thus giving an ideal situation. The table shows the results of fitting seven spectra at different levels of power in the radio-frequency field (at ambient temperature). This power, B_1 ,

/may be

may be expressed in terms of modulation power, B_1 , measured on the C.R.O. in arbitrary units, as $B_1 = KB_m$, where K depends on the radiofrequency attenuation. The constant K was determined using the Torrey oscillation method on a sample of CFCl_2 with CFCl_3 lock. An HA100 spectrometer, operating at 94.075 MHz on ^{19}F resonance, was used throughout the experiments. The bands were digitized using a d-mac Ltd. pencil follower to give ~ 200 points over sweep width 100 Hz; this operation will be computerized shortly.

The spectra were obtained under varying degrees of partial saturation. They were shown to be accurately Lorentzian - governed by a "relaxation time" $T_{2\text{sat}}$ $T_2/[1 + \gamma^2 B_1^2 T_1 T_2]^{1/2}$. The true T_2 was found by plotting $T_{2\text{sat}}^2$ vs B_m^2 - the intercept is T_2^{-2} , giving 0.0354 ± 0.0004 sec. for T_2 . Each value of $T_{2\text{sat}}$ then yields an estimate of T_1 (see the table). The errors in $T_{2\text{sat}}$ increase with B_m largely because of errors in signal phase, for which we make no correction as yet. Therefore we regard the best estimate of T_1 to be 14.8 ± 0.3 s.

Currently we are extending this work to investigate the solvent and temperature-dependence of T_1 for this molecule. When our 620/i computer is installed and operating we envisage that we will be able to obtain accurate values of relaxation times fairly readily by this method.

Best wishes,

Robin Harris

R.K. Harris.

K. M. Worvill

K. M. Worvill.

RKH/MAL

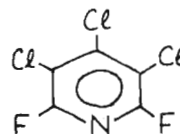
RESULTS FOR 2,6-DIFLUORO-3,4,5-TRICHLOROPYRIDINE

B_m^+	B_1	T_{2sat}/s	% error on T_{2sat}	T_{2eff}/T_{2sat}	T_{1eff}/s	saturation parameter*
10	0.0293	0.0312	1.0	1.14	15.0	0.29
20	0.0585	0.0242	1.0	1.46	14.8	1.13
30	0.0877	0.0188	2.0	1.88	14.9	2.56
40	0.117	0.0152	3.6	2.33	14.6	4.45
50	0.146	0.0134	6.0	2.64	12.5	5.98
60	0.176	0.0112	10	3.16	13.0	8.97
70	0.205	0.0098	15	3.61	12.8	11.95

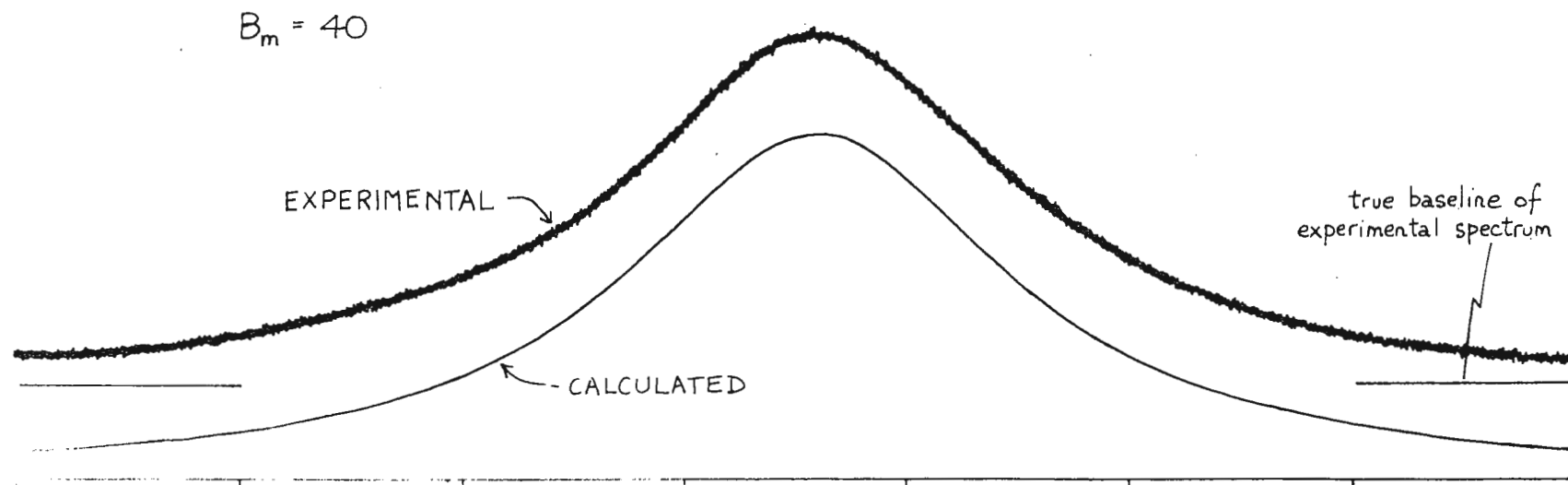
⁺ In arbitrary units (-25 dB radiofrequency attenuation was used).

* $\gamma^2 B_1^2 T_{1eff} T_{2eff}$

SATURATION EXPERIMENT ON



[the frequency scale at the bottom is in units of 100 Hz]



Unilever Research

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Olivier van Noortlaan 120
Vlaardingen
postbus 114

telefoon 010-353 000
telex 23261



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

gww:rp

CC/0828/as

toestel

datum 17 Dec 70

Dear Professor Shapiro,

Re: Vortex Formation in Spinning Sample Tubes

The formation of vortices in spinning NMR tubes has always been recognised as one of the hazards in high resolution NMR, and has become more important with the use of very high spinning speeds in the superconducting magnet systems. This prompted us to measure these vortices in an NMR sample tube, setting up a test rig with an HA-100 spinnerhousing, a travelling microscope and a stroboscope (for measuring spinning speeds). The figure shows a few of the results in a plot of ΔZ (depression of the liquid surface) against spinning frequency. In all cases the normal spinning speed in electromagnet systems (ca 30 cps) presents no problems, but at the 70-80 cps employed in the HR 220 the vortices become of the order of 2 cm. This means that about half of the normally used 4 cm column of solution is flung up the sides of the sample tube, and does not contribute to the NMR signal.

The vortex formation differs from the simple theory ($\Delta Z = \omega^2 a^2 / 4g$) through the capillary effects, and whilst we have not pursued the quest for an all-embracing equation, the vortex decreases as the term density/surface tension decreases.

We have been obtaining useful S/N enhancements on the HR 220 by employing plugs in the tubes to eliminate these vortices and using only 2 cm of liquid. The problem should also be resolved by using capillary and spherical microcells, and we are currently investigating their use on the HR 220.

Encl.

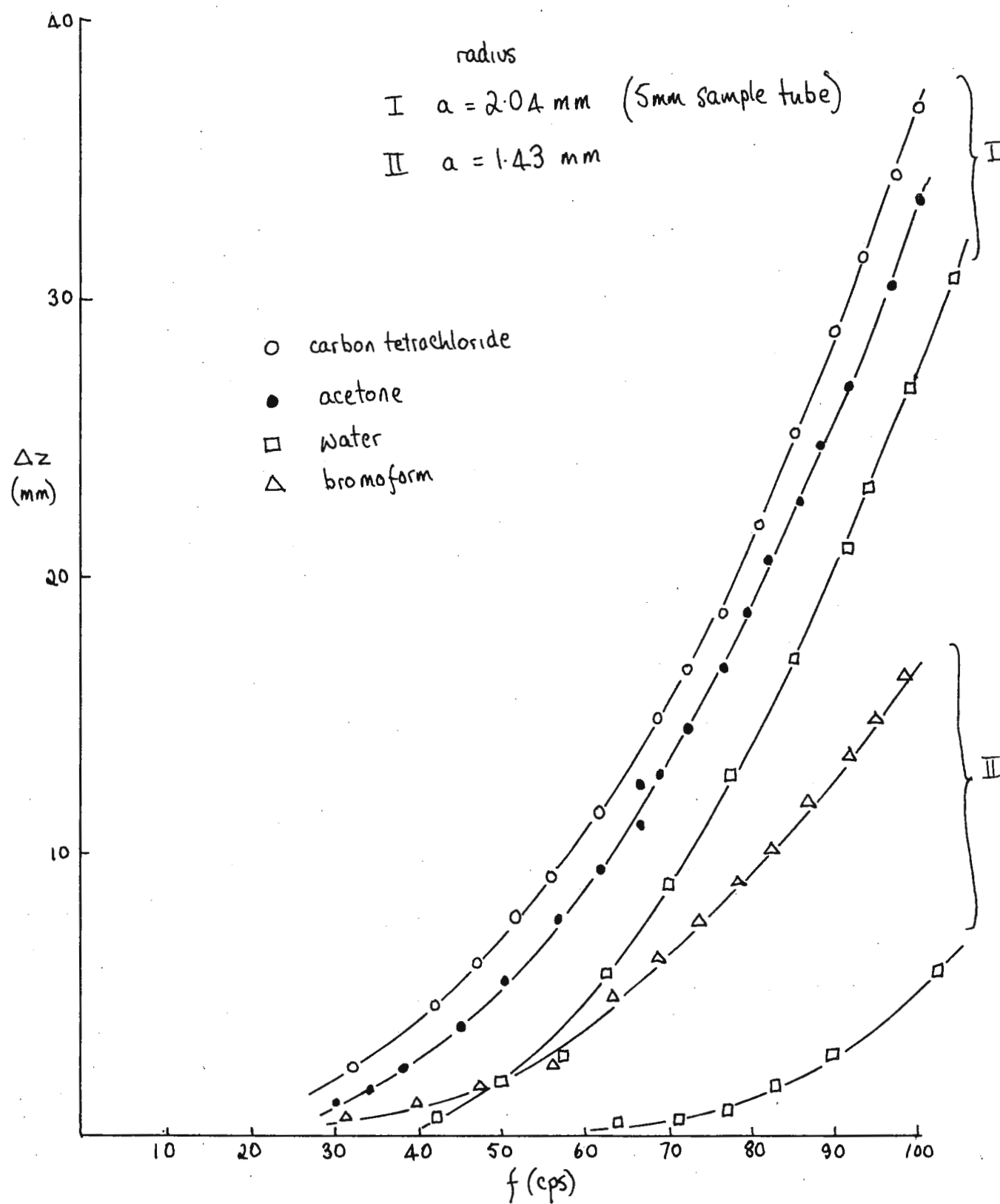
Yours sincerely,

UNILEVER RESEARCH VLAARDINGEN

David Frost

D.J. Frost

Vortex Formation (Δz) as a Function of Spinning Frequency.





The University of Western Ontario, London 72, Canada

Faculty of Science
Department of Chemistry

December 18, 1970.

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

Dear Barry,

Some Parameters for Estimations of Olefinic ^{13}C Shieldings

In reluctant response to your multicolored nagging notes, I can describe a set of parameters generated by linear regression analysis, which have been useful for rough estimates of the effects of alkyl substitution on olefinic ^{13}C shieldings in various alkenes. This is really a modification of the original list described by Friedel and Retcofsky in 1963, but may be of interest in view of the set recently described by Lippmaa et al (1) for polyhalosubstituted acrylic acids. Most of the data were taken from the literature and since most are rapid-passage results one cannot expect a tremendously good correlation. The results listed in Table I, however, seem surprisingly "good". Hopefully these may be useful to others. The superscript indicates the mode of transmission to the carbon of interest i.e. through a σ -network or through the π -bond. The gem factor represents the effects at a fully substituted olefinic carbon (gem $^{\alpha}$) and its neighbor (gem $^{\beta}$) while mult $^{\sigma}$ and mult $^{\pi}$ are the effects of branching at the α -carbon. The constant factors are satisfyingly close to the ethylene shieldings as one would hope. These parameters are in terms of the TMS shielding scale so that a positive value represents a downfield shift. A specific shielding is estimated from the relation $\delta_{\text{C}}^{\text{i}} = K + \sum nA_j$ where all appropriate coefficients, A $_j$, are summed a la Grant's treatment of the alkane shieldings.

A similar treatment of the data for an assortment of α,β -unsaturated carbonyl derivatives gave the results in Table II. The systems are restricted to planar ones since steric inhibition of conjugation affects the olefinic shieldings. The major difference is that the α - and β -carbons were treated separately to achieve a fit. Finally we have a set corresponding to that of Lippmaa but for a series of monohalocarboxylic acids and their methyl esters which is given in Table III together with the Lippmaa parameters. It is interesting that the shieldings in the acids and esters are very similar (within 1 ppm for similar substituents).

I hope this rescues my subscription.

Best regards to Lee.

Sincerely,

J.B. Stothers
Professor of Chemistry.

TABLE I

Regression analysis of olefinic ^{13}C shieldings in acyclic alkenes

Shielding Parameter	Linear alkenes		Acyclic alkenes	
	Coefficient (ppm) A_j	No. of Examples	Coefficient (ppm) A_j	No. of Examples
α	$+10.8 \pm 0.4$	36	$+11.0 \pm 0.4$	76
β^π	-6.8 ± 0.4	36	-7.1 ± 0.4	76
β^σ	$+7.1 \pm 0.4$	28	$+6.0 \pm 0.3$	52
γ^π	-1.5 ± 0.4	28	-1.9 ± 0.3	52
γ^σ	-1.1 ± 0.4	22	-1.0 ± 0.3	30
δ^π	$+0.4 \pm 0.4$	24	$+1.1 \pm 0.3$	32
δ^σ	0.0 ± 0.4	16	$+0.7 \pm 0.4$	16
ϵ	$+0.5 \pm 0.3$	26	$+0.2 \pm 0.3$	26
<u>cis</u>	-1.2 ± 0.2	17	-1.2 ± 0.3	37
<u>gem</u> $^\alpha$			-4.9 ± 0.5	13
<u>gem</u> $^\beta$			$+1.2 \pm 0.5$	13
<u>mult</u> $^\sigma$			$+1.3 \pm 0.6$	5
<u>mult</u> $^\pi$			-0.7 ± 0.6	5
R^2	0.997		0.997	
σ	0.64		0.90	
Const. (K)	121.6		122.1	

TABLE II

Substituent parameters for alkyl substitution in

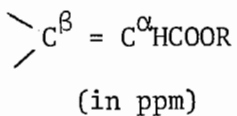
 α, β -unsaturated carbonyl compounds, $\text{>C}^\beta = \text{C}^\alpha\text{COX}$

(in ppm)

Parameter A_j	α -C	No. of examples	β -C	No. of examples
α	7.5 ± 0.4	13	13.7 ± 0.6	26
β^π	-5.4 ± 0.4	26	-5.6 ± 0.6	13
β^σ			5.5 ± 0.9	4
γ^π	-1.7 ± 0.6	4		
<u>gem</u> $^\beta$			-2.2 ± 1.0	5
<u>cis</u> alkyl	-1.3 ± 0.6	8	-0.5 ± 0.7	8
carbonyl	-2.3 ± 0.6	9		
X = Me	-1.5 ± 0.6	11	-10.3 ± 0.9	11
OH	-10.1 ± 0.6	7	-7.6 ± 0.9	7
OMe	-10.2 ± 0.6	7	-9.1 ± 0.9	7
Constant, <u>K</u>	138.3		139.2	
Standard error	± 0.7		± 1.0	
Multiple correlation coefficient	0.998		0.996	

TABLE III

Substituent parameters for some β -substituents on the olefinic
 ^{13}C shieldings of α, β -unsaturated carboxylic acids and esters.



Substituent parameters $\underline{A_j}$	$\alpha\text{-C}$		$\beta\text{-C}$	
	This work	Ref. 1	This work	Ref. 1
Me	-5.6 \pm 0.7	-4	13.5 \pm 1.2	10
Cl	-3.1 \pm 0.7	-4	5.8 \pm 1.2	4
Br	-0.4 \pm 0.7	1	-3.3 \pm 1.2	1
I	8.8 \pm 0.7	11	-29.6 \pm 1.2	-35
<u>cis</u> -Me	-2.3 \pm 0.5	-2	1.4 \pm 0.9	2
<u>cis</u> -Cl	-4.1 \pm 0.6	-2	-4.6 \pm 1.0	-5
<u>cis</u> -Br	-3.5 \pm 0.6	-6	-6.1 \pm 1.1	-12
<u>cis</u> -I	-6.5 \pm 0.6	-9	-3.7 \pm 1.0	-4
<u>gem</u> Me, X	1.8 \pm 0.7		1.6 \pm 1.3	
R = H	0.6 \pm 0.3		1.0 \pm 0.5	
= Me	0.0		0.0	
Constant, \underline{K}	128.1		130.4	
Standard error	0.8		1.3	

PARIS, le 18 DECEMBRE 1970

Docteur Bernard L. SHAPIRO

Department of Chemistry
Texas A et M University
College Station

70.497 - RF/AP

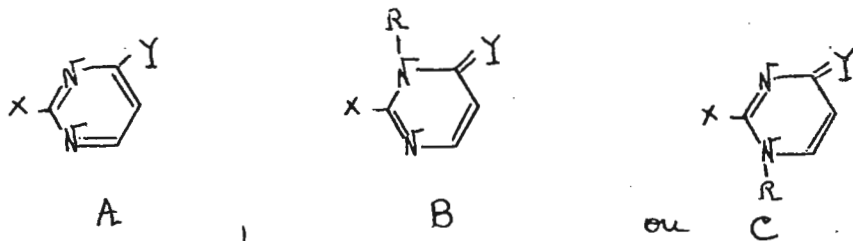
TEXAS 77843

Cher Docteur Shapiro,

Etude de certains dérivés de la pyrimidine.

Nous avons étudié la structure de pyrimidines substituées ou non en -2 par un groupement méthyle ou phényle et en -4 par divers groupements fonctionnels.

Les composés de base synthétisés sont du type :



X = H, CH₃ ou C₆H₅

R = H ou CH₃

Y = O, S, OCH₃, SCH₃, NHR, NHCOR, N(CH₃) COCH₃.

Dans le cas des composés du type C, avec X = H et R = CH₃, le couplage méta (J 2,6) à travers l'atome d'Azote I est grand (2,0 à 2,6 Htz), alors qu'il est faible dans le cas des composés du type A ou B (0,4 à 0,8 Htz).

La valeur du couplage ortho (J 5,6) augmente quand le caractère aromatique du cycle pyrimidique est détruit (composés B) et surtout lors d'une substitution de l'Azote I (composés C) avec X = H.

Dans le cas où X = CH₃ ou ϕ , les valeurs de J_{ortho} sont également plus élevées dans les composés du type C.

Nous remarquons de plus que, en général, le déplacement chimique du proton en -5 est le plus affecté lors du déplacement d'un atome d'oxygène par un atome de soufre en position -4 (δ à champ plus faible). Les protons en -6 ou en -2, de même que les substituants en -2 (-CH₃ ou ϕ) voient leurs déplacements chimiques peu affectés par une telle substitution.

Lorsque X = C₆H₅, dans le cas des composés du type B ou C, le signal du groupement phényle est un singulet. Ceci est à rapprocher des résultats que nous avons déjà obtenus lors de notre étude d'autres hétérocycles (thiazole, oxadiazole-1,2,4 ...)

Cette étude de composés de bases dérivés de la pyrimidine nous permet de fixer

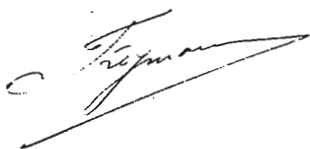
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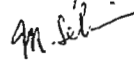
la structure de composés plus complexes synthétisés dans nos laboratoires dans le but de leur étude pharmacologique.

Avec nos sentiments cordiaux.

R.FREYMANN



M.SELIM



M.SELIM



CHEMICAL CENTER

PHYSICAL CHEMISTRY 2

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

Dear Dr. Shapiro:

Overhauser studies
of 2-acetylfuran at low temperatures

Recently we reported a study of the activation parameters for the conversion $I \rightleftharpoons II$ in 2-acetylfuran¹⁾.



At low temperatures ($< -100^{\circ}\text{C}$), the 3-proton exhibits two quartets, one from each conformer, with a chemical shift difference of 0.222 ppm. If the assignment of these signals to the conformers I and II is done according to the "Pople-Jackman model"²⁾ for the diamagnetic anisotropy of the carbonyl group, the low field H-3 quartet should arise from conformer I. On the other hand the application of the model proposed by Karabatsos et al.³⁾ predicts the low field H-3 quartet to belong to conformer II.

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In order to be able to make an unambiguous assignment of the low temperature spectrum of 2-acetylfuran we have performed Overhauser studies at $\sim -130^{\circ}\text{C}$. By simultaneous irradiation of both CH_3 signals, the low field H-3 quartet showed a nuclear Overhauser enhancement of 30% relative to the high field one, which proves that these signals belong to conformer II. This seems to indicate that the carbonyl group has a shielding effect on the H-3 proton in conformer I.

Difficulties of the above type also arise in the assignment of the low temperature spectrum of 2-furan-aldehyde and thus Overhauser studies have also been carried out on this molecule. However, no Overhauser effect have as yet been observed in this case.

Yours sincerely

Kjell-Ivar Dahlqvist
Kjell-Ivar Dahlqvist

Anna-Britta Hörnfeldt
Anna-Britta Hörnfeldt

References:

- 1) L.Arlinger, K.I.Dahlqvist and S.Forsén,
Acta Chem. Scand. 24 662 (1970).
- 2) L.M.Jackman and S.Sternhell, Applications of Nuclear
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2 nd Ed. Pergamon Press, Oxford 1969, Cap. 2-2.
- 3) G.J.Karabatsos, G.C.Sonnichsen, N.Hsi and D.J.Fenoglio,
J.Am.Chem.Soc. 89 506 (1967).

UNION CARBIDE CORPORATION

TARRYTOWN TECHNICAL CENTER

SAW MILL RIVER ROAD AT ROUTE 100C, P. O. BOX 65, TARRYTOWN, NEW YORK 10591

December 18, 1970

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

Dear Professor Shapiro:

As part of a study of the structures of several vinyl silanes, we have reinvestigated the proton NMR spectrum of trichlorovinylsilane. At 60 MHz its spectrum in CCl_4 is reported to consist of a single line in the vinyl region with symmetrical silicon-29 satellites and a Si-H coupling of 4.0 Hz (R. Summitt, J. J. Eisch, J. T. Trainor, and M. T. Rogers, J. Phys. Chem., 62, 2362 (1963)). However further splitting of the main line becomes apparent when the spectrum is observed in other solvents, while at 220 MHz this region more closely resembles an ABC pattern.

The carbon-13 satellite spectrum of the vinyl protons consists of two overlapping ABX patterns. These give in each satellite four and eight lines for the two isotopic species, respectively. Analysis of these spectra provide approximate values for the three H-H coupling constants and proton chemical shifts. The following H-H coupling constants gave a computed spectrum (NMRIT) in good agreement with the 220 MHz main band spectrum of trichlorovinylsilane

$$J \text{ (Geminal)} = 2.5 \text{ Hz}$$
$$J \text{ (Trans)} = 20.2 \text{ Hz}$$
$$J \text{ (Cis)} = 14.1 \text{ Hz}$$

We are now attempting to obtain values for the various Si-H coupling constants in this and several other vinylsilanes.

Please credit this contribution to Earl Whipple's overdue account.

Sincerely yours,


Paul J. Green

PJG/m



JAPAN ELECTRON OPTICS LABORATORY CO., LTD.

NEW TOKYO BLDG., 3-3-1 MARUNOUCHI, CHIYODA-KU, TOKYO 100, JAPAN

Telephone: 211-8611

Cable address: JEMSCOPE TOKYO

Telex: 222-3608

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

S.C.M. Aided Carbon-13 Pulsed Fourier Transform Spectroscopy

Dear Professor Shapiro,

There are two main reasons for adopting a Super Conducting Magnet (SCM) for Carbon-13 NMR: 1) Signal to Noise (S/N) enhancement and 2) Chemical Shift enhancement. Of the two, in the case of Fourier Transform (FT) NMR, the S/N enhancement is the more important since the gains achieved in Chemical Shift enhancement are often compromised due to practical considerations such as the size and state of one's pocketbook, which, in turn, places a limitation on the memory size of the computer used.

We have recently used a SCM for polarization¹ of a sample and observed the C-13 resonance on a conventional electromagnet via FT techniques. The sample is left in a strong SCM field (56,800 gauss) for a time which is long compared to the sample T_1 . It is moved adiabatically to the conventional spectrometer, which is operated at 14,100 gauss, as quickly as possible. The sample spinner is started immediately, a $1/2$ pi pulsed is applied and the free induction decay (FID) signal is read directly into a mini-computer and Fourier Transformed.

We have attained S/N enhancement factors of two to three compared to the spectra obtained without the aid of a SCM. Since the maximum enhancement factor expected in this experiment is four (the ratio of the magnetic fields), these results are reasonable if one considers that because of relaxation during the transportation time of the samples the polarization decays somewhat.

Under the present experimental conditions (a temporary set-up), the observing spectrometer (a C-60HL) is located about 3 meters from the SCM, and it takes at least 7 sec. to transfer the sample from the SCM to the C-60HL. For this reason, a sample with a long relaxation time such as $^{13}\text{CS}_2$ ($T_1 \approx 45$ sec) shows bigger enhancement than $\text{CH}_3^{13}\text{COOH}$ ($T_1 \approx 18$ sec) which has a shorter relaxation time. (See Figs. 1 and 2).



Refocussing techniques such as super-DEFT² or SEFT³ might be very important for time-averaging S/N enhancement since the decay time of the polarization is about the same as the relaxation time, T_1 . Of course, the higher the SCM the better. Another consideration here is that the homogeneity of the SCM field is not important.

We plan to use SCM fields of 75 kGauss or more and to shorten the transfer time to 1 sec or less in order to further improve the S/N enhancement. Since the ^{13}C relaxation time of ordinary organic compounds lie within the range of 10 to 100 sec⁴ such experiments should be of practical value.

Best regards

Yours Sincerely,

T. Kase

T. Kase

M. Takeuchi

M. Takeuchi

Reference;

- 1) Some suggestion will be found in "Sensitivity Enhancement in Magnetic resonance" by R.R.Ernst of "Advances in Magnetic Resonance Vol.2" edited by J. S. Waugh. (1966)
- 2) T. Farrar Private communication (1970), DEFT is proposed by E.D.Becker, J.A. Ferretti, T. Farrar, 7784 91 J. Am. Chem. Soc. (1969)
- 3) A. Allerhand, D.W. Cochran, 4482 92-14 J. Am. Chem. Soc. (1970)
- 4) Maciel, et al. Private communication "Carbon-13 Pulse Nuclear Magnetic Resonance" (to be published) (1970).

Fig. 1

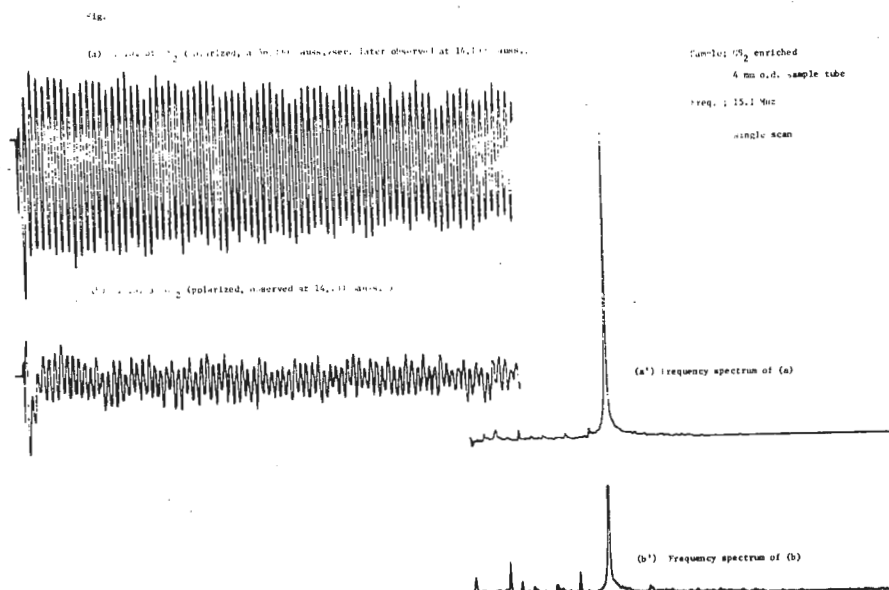
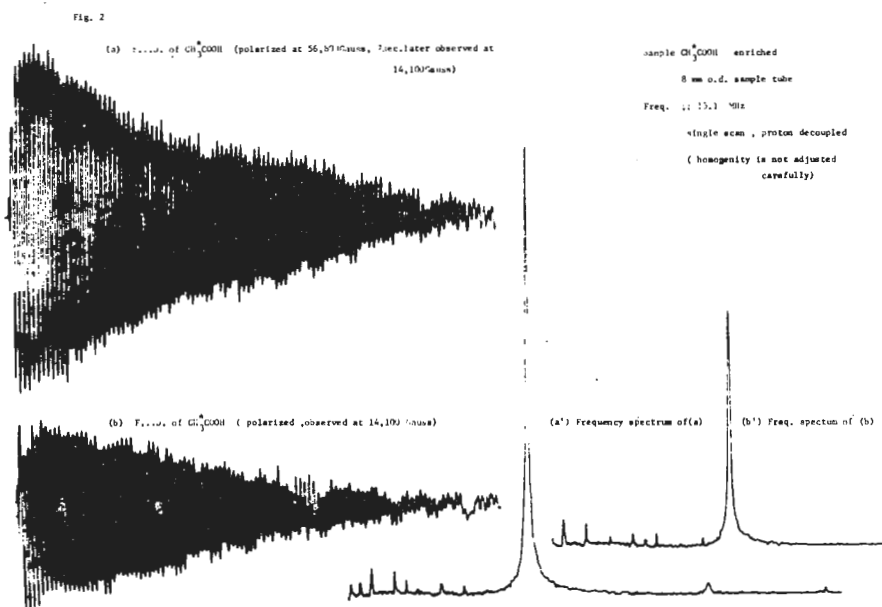


Fig. 2





United States Department of the Interior

BUREAU OF MINES

4800 Forbes Avenue
Pittsburgh, Pennsylvania 15213

December 21, 1970

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

Dear Barry:

Our present ^{13}C NMR investigations are concerned almost exclusively with measurements on solid samples. Some recent work on an anthracitic coal and solid adamantane has led to a

CONFIRMATION OF THE HIGH AROMATICITY OF ANTHRACITE
BY BROADLINE CARBON-13 MAGNETIC RESONANCE SPECTROMETRY

Spectra of Dorrance anthracite (92.7% moisture and ash-free carbon) and adamantane are shown in the accompanying figure. A chemical shift correlation chart indicating the general spectral regions of absorption by aromatic and saturated carbon atoms in selected hydrocarbons appears near the bottom of the figure.

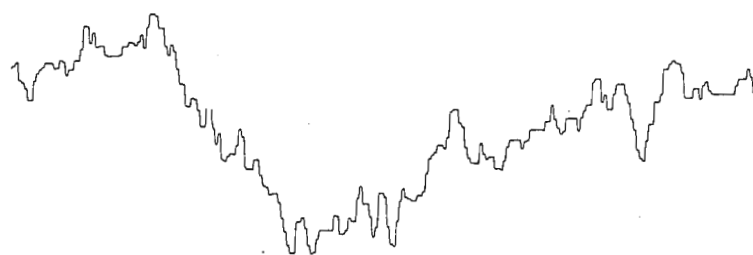
The chemical shift of the anthracite sample (53 ppm with respect to neat carbon disulfide) plus the fact that little if any absorption occurs in the spectral region attributed to resonances of saturated carbon atoms attest to the high aromaticity of the material. The purpose of obtaining spectra of solid adamantane was to extend the region of saturated carbon atom absorption to include the effects of at least some dipolar line broadening. The present work also suggests that measurements made with more sophisticated spectrometers operating at higher magnetic fields should eventually lead to quantitative determination of the aromaticity of coals and other solid substances.

Sincerely yours,

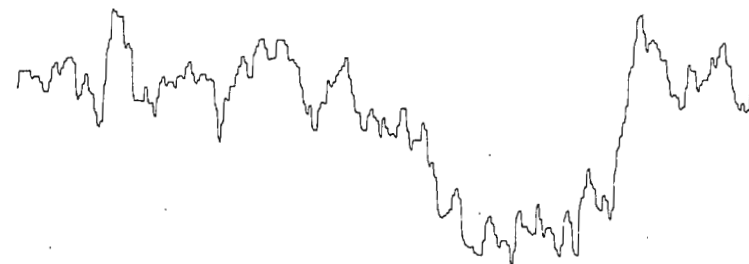
H. L. Retcofsky

R. A. Friedel

DORRANCE ANTHRACITE

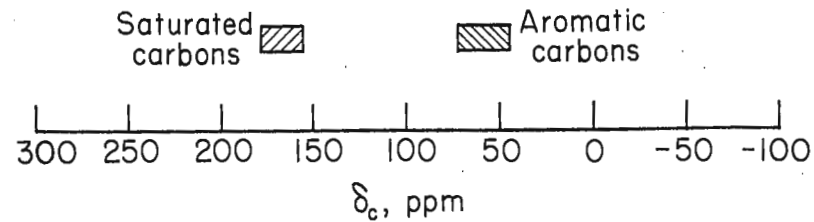
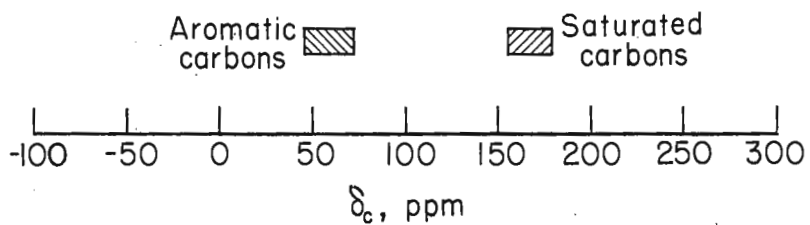
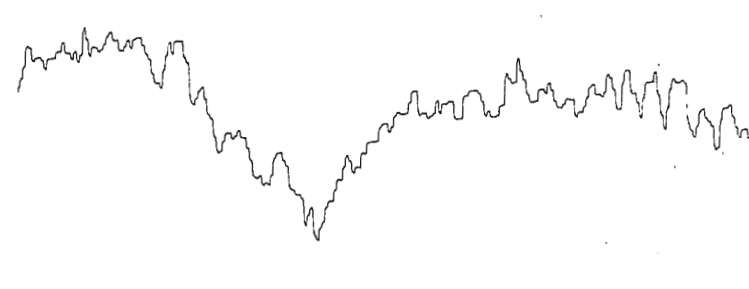
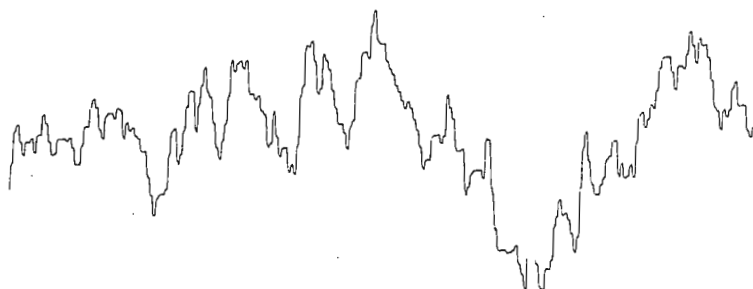


Increasing field sweeps



Decreasing field sweeps

ADAMANTANE



^{13}C NMR spectra of Dorrance anthracite and solid adamantane.



University
of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building Cathedral Street, Glasgow, C.1
Telephone: Bell 4400 STD 041-552 4400

28th December, 1970.

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

Linking Elliott 905 Computer to R10 Spectrometer

Dear Barry,

I am afraid that we had no startling chemistry to report this time and all I can give is an interim account of our activities. Our efforts at the moment are directed towards interfacing an Elliott 905 computer [8K x 18bits] to our nmr spectrometers (R10 and R14). This is available to us for this purpose when it is not in use for on-line mass spectrometer work - this means in practice the overnight period.

We^x are aiming to provide the usual signal enhancement facilities, together with the ability to frequency-sweep the spectrometers via a computer controlled frequency synthesizer (Schlumberger SFD 120). We are contemplating trying Fourier-transform techniques, the main difficulty in this connection may be the distance between the nmr instruments and the computer (160 ft.).

Our most spectacular success so far has been resolution enhancement; a very simple program which subtracts repetitively a proportion of the second differential from a stored spectrum displaying the result after each subtraction on an oscilloscope. The amount of second differential incorporated can be adjusted by means of sense-keys on the computer until particular unresolved lines are made to appear and before the results are punched out or plotted. The technique is devised from an earlier FORTRAN program we had written for a large computer. Here a predetermined proportion of the second derivative was used. As an added bonus in both programs we get a print out of the frequencies of the resolved lines.

Yours sincerely,

Peter Bladon

Dr. Peter Bladon

^x 'We' should not be taken as the royal plural but is meant to include Mike Foreman (late of Dundee) and Keith Hardie, both of whom are on a well-earned holiday and so cannot sign this letter.

DOW CORNING

December 29, 1970

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

Quantitative Analysis by NMR

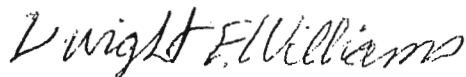
Dear Barry:

Despite the antiquity of the technique, we seem to have found a previously undescribed source of serious error in the quantitative analysis by NMR of certain samples. Use of a weighed internal integration standard is the method of choice for NMR quantitative analysis. However, this method cannot be used for many samples due to physical (phase) or chemical incompatibilities of otherwise suitable internal standards. For these samples, an external integration standard in a different (but equal!) sample tube must be used.

Two unique precautions must be taken to obtain reliable results by the external standard method:

1. Sample tubes must be selected to give equal integrations.
2. The NMR spectrometer must have an "effective rf power" X rf gain feedback clamp so that changes in non-resonant rf power losses due to changes in the sample will be compensated. We have run samples on spectrometers without this feature which show errors of 50% due to this cause. In particular, the Varian HA-60 and T-60 NMR spectrometers do not have this feature and do not give good results by the external integration standard method. However, the older Varian A-60, which has this feature, performs this kind of analysis well. This may be a case of reverse serendipity: Apparently the newer rf transmitters are sufficiently stable so that a power x gain feedback clamp is no longer needed to compensate for amplitude noise in the transmitter.

Very truly yours,



Dwight E. Williams

jh



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

December 31, 1970

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

Title: Histidine C2-H Resonances as Monitor of Protein Structure and Function

Dear Barry:

Thank you so much for your gracious reminder. I will briefly summarize two topics on which we are currently working.

We have obtained 220 MHz spectra of the downfield histidine region of staphylococcal nuclease (1) through its acid denaturation (2). Selective effects are observed for the four histidine C2-H resonances. Fluorescence data for the single tryptophan residue has also been obtained. The results indicate that this denaturation process is reversible and occurs via a multi-stage equilibrium, as opposed to the two-state equilibrium hypothesis.

Our studies on the titration curves of the active site histidines of ribonuclease (3) are continuing. We have programmed and curve-fitted two further mechanistic models which assume an interaction of histidines 12 and 119 either with each other or separately. Preliminary results indicate that the histidines do not interact with each other, but rather with a third group which has a low pK and is probably the carboxyl of Asp-121 (4).

Best regards, and Happy New Year to all,

A handwritten signature in black ink, appearing to read "Jack", with a long horizontal flourish extending to the right.

Jack S. Cohen

References:

1. J. S. Cohen, R. I. Shrager, M. McNeel and A. N. Schechter, Nature 228, 642 (1970).
2. H. Epstein, J. S. Cohen and A. N. Schechter, in preparation.
3. J. S. Cohen, R. I. Shrager, M. McNeel and A. N. Schechter, Biochem. Biophys. Res. Comm. 40, 144 (1970).
4. J. S. Cohen, A. N. Schechter, R. I. Shrager, D. Sachs and S. Heller, unpublished results.



148-45

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

PIGGYBACK PROBE; SYMMETRY-FACTORING COMPUTER PROGRAM

December 31, 1970

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

Dear Barry:

1. We are contemplating an nmr system which is externally locked to, e.g., TMS for observation of heteronuclei under field-frequency lock conditions. If anyone has available a suitable probe (piggyback?) which is surplus to his operation, we would like to know about it and might be willing to make an offer to buy.

2. We are contemplating an nmr program which makes use of symmetry factoring to reduce the size of the problem and hence the running time in cases where certain nuclei are symmetry equivalent but not magnetically equivalent. ODCB is a fairly trivial example of such a system. In case anyone else is working along these lines, I would very much like to hear about it in order to avoid a wasteful duplication of effort.

With best wishes for a happy new year,

Rolf

Rolf B. Johannesen
Inorganic Chemistry Section



U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

December 30, 1970

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

Dear Barry:

This letter is prompted by Professor Kaiser's letter (TAMUNMR 146-12) regarding replacement of 304TL's with transistors.

We have built two such units, each with 16 stages. The first has been in operation since mid-June controlling the current to a 14 kg. 12 inch Varian magnet. It has given no trouble, and has survived several interruptions caused by thunderstorms. A second unit, supposedly identical, does not work properly and our electronics instrumentation section is presently searching for the problem. I will write again when the problem is solved.

The units were built on heat sinks supplied by Wakefield Engineering. These are of modular construction so that as many as desired can be mounted into a large package for cooling by a suitable fan. Since the modules are insulated from one another, and since all collectors in a given module are electrically connected, mica washers are eliminated entirely with resulting simplicity of construction.

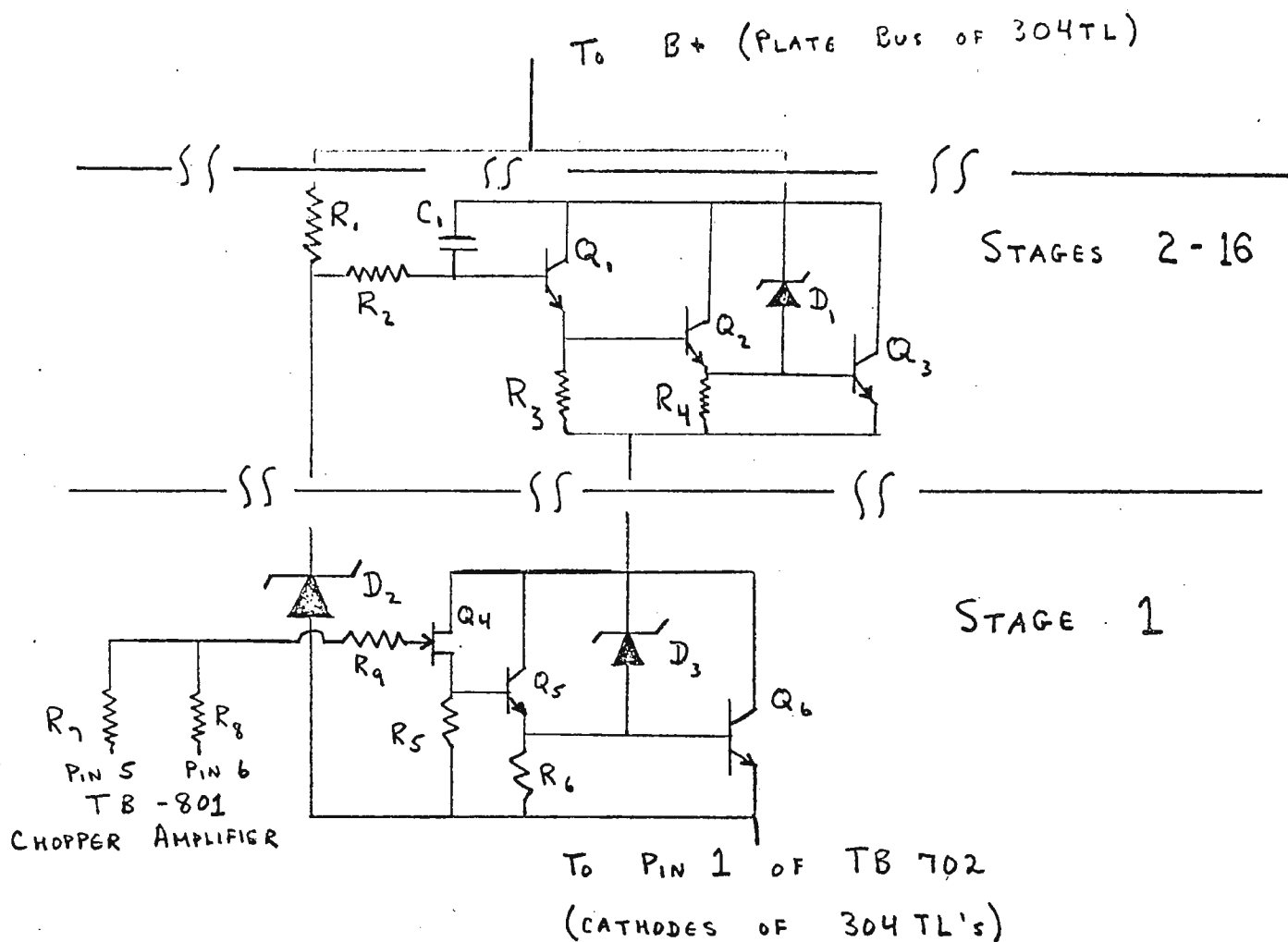
The "regulation range" meter of the magnet power supply as furnished is connected through a dropping resistor to the grid terminals of the 304TL's. Due to the pentode-like characteristics of transistors, we found the voltage at this point to be virtually constant. In order to get a visual indication of circuit conditions, the "regulation range" meter was connected through a dropping resistor (about 5 M is appropriate) to the top of the transistor pass bank (meter polarity must be reversed).

A diagram of the circuit that we used is included. It is not greatly different from the circuit of Stegemann (TAMUNMR 131-1) but the specification of American part numbers for the units may help readers in this country. The second circuit shows an overvoltage protection device. It will trip if the voltage reaches 640 volts, due for instance to a rise in line voltage. The relay contacts are connected into the primary interlock circuit in the magnet. The interlock circuit has been modified to include a latching relay. Thus, if the power to the magnet goes off due to overvoltage in the supply, it will not come on again (which could initiate a vicious cycle) until the latch is released.

Yours truly,

Rolf

Rolf B. Johannesen



$R_1, R_2, R_3, R_5 - 10 \text{ k}\Omega$

$C_1 - .001 \text{ mfd.}$

$R_4, R_6 - 1 \text{ k}\Omega$

$R_7 - 100 \text{ k}\Omega$

$R_9 - 1 \text{ meg}$

$R_8 - 5 \text{ to } 6 \text{ k}\Omega$ (chosen to give 150-200 volts at TB-801-5)

$Q_1 - 2N5209$

$Q_3 - 2N3772$

$D_1 - 1N4756A (47 \text{ v.})$

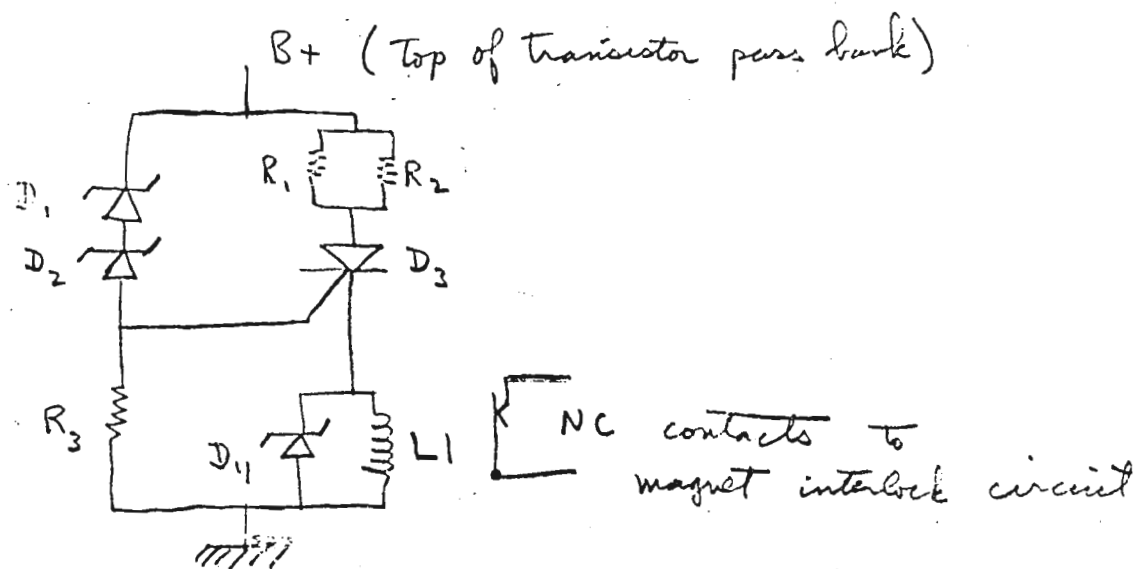
$Q_2, Q_5, Q_6 - 2N5191$

$Q_4 - 2N3687$

$D_2 - 1N4738A (8.2 \text{ v.})$

$D_3 - 1N4790A (10 \text{ v.})$

TRANSISTORIZED CURRENT REGULATOR



R_1, R_2 - 300 Ω 2.5 W

R_3 - 10 K $\frac{1}{2}$ W

L1 - 6 V DC relay

Potter-Brunfield KRP-11 DG

D_1 - UZ 5228 (280V-) Unithode

D_2 - UZ 5236 (360V-) "

D_3 - 2N 3525 (SCR)

D_4 - 1N 2970 B (12V-)

OVERVOLTAGE PROTECTION

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