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Newsletter

No. 124
JANUARY, 1969

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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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<p>Deadline Dates: No. 125: 3 February 1969 No. 126: 3 March 1969</p>

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

Professor Bernard L. Shapiro
Department of Chemistry
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College Station, Texas 77843

Tel: Oxford 55851
57536
STD Code OOX2

PHYSICAL CHEMISTRY LABORATORY,
SOUTH PARKS ROAD,
OXFORD. OX1 3QZ

26 November 1968

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

Dear Barry,

Brian Sheard, in collaboration with Arthur Peacocke and I, has studied proton magnetic relaxation enhancement in solutions of E.coli ribosomal RNA containing manganese ions. The measurements have been made over a range of temperatures at five magnetic field strengths from 14 MHz to 90 MHz. The effects of the paramagnetic ions are enhanced in the presence of the RNA and this can be interpreted in the usual way in the terms of bindings. As the temperature falls, T_1 and T_2 pass through a minimum value, the magnitude of which is field dependent. The results are certainly not consistent with the simple interpretation in terms of dipolar relaxation; we have interpreted the variation of the relaxation times with temperature in terms of a change in dipolar relaxation mechanism from rotation of the aquo complex to electron spin relaxation of the metal ion. The results indicate that care must be taken in interpreting experiments of this kind and as much experimental information obtained as possible.

We have continued our studies of dynamic nuclear polarisation at high fields; David Taylor and Terry Cannon have been working on the enhancement of carbon-13 resonances in natural abundance, and Raymond Dwek has been working on the enhancement of phosphorus resonances. C-13 resonances have been observed in sixty different compounds; some are strongly enhanced because of scalar coupling to the radical whilst others are inverted because the main interaction is magnetic dipolar. We have attempted to find a qualitative theory to explain why the scalar coupling varies from compound to compound and have been able to obtain some information not already available about some of the compounds studied. Some beautiful examples of the so-called "three spin effect" have been found and the isotope shift in the C-13 spectrum between benzene and deuterobenzene has been measured. A number of phosphorus compounds have been studied and have confirmed that trivalent phosphorus compounds show strong scalar coupling with very large positive enhancements of the resonance whereas pentavalent phosphorus compounds show very weak effects. The phosphorus resonance in a number of inorganic phosphorus compounds has been observed for substances which are so weakly soluble that it would have been very difficult to find the resonances by any other method.

Our Mark I superconducting magnet has been in the persistent mode since last February; the field drift is almost unmeasurable and the homogeneity has not shown any significant change. It has a field of 50 Kgauss with a homogeneity of 3 in 10^7 over a spherical sample of diameter 9 mms. Jim Halliday has been studying caesium resonances in dilute solutions containing other salts and other solvents. He is able to measure the shift to better than 1 in 10^7 at concentrations down to 5 millimolar. He has studied the temperature dependence and the effect on the shift of changing the solvent from water to D_2O and to H_2O . The caesium shifts are extremely sensitive to both temperature and other dissolved materials and we intend to investigate the possibility of using it as a probe in some biological systems.

Yours sincerely,

Rex Richards

Short Title - Proton relaxation enhancement, dynamic nuclear polarisation, and caesium resonances.



PHYSICS DEPARTMENT

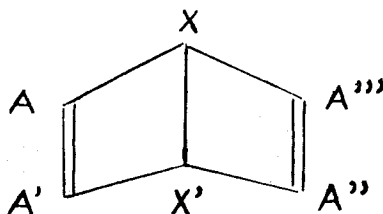
December 2, 1968

Analysis of the $(AA'X)(AA'X)'$ Spectrum of the
Dewar Form of Hexafluorobenzene (C_{2v} - symmetry)

Dear Barry:

I am sorry you had to remind me again of my impending excommunication. With student sit-ins etc., and all the simple things in n.m.r. already done, life has become more complicated. However, one favourable development has been the addition of an IBM 360/50 to our 1620 workhorse in the computing centre. When the chemistry department happened to provide a sample of hexafluorobenzene in the Dewar form, I felt that my chance had come to see if we could analyse a spectrum without double resonance or similar niceties. I am much obliged to Dr. Swalen and Dr. Slomp for providing the programs NMRIT/NMREN and LACNT, respectively.

The molecule



A and X = ^{19}F

has C_{2v} symmetry, and the old-fashioned classification of the spectrum is $AA'A''A'''XX'$ or better, as Dr. Reilly pointed out, $(AA'X)(AA'X)'$. The energy matrix decomposes into 4 submatrices with eigenfunctions belonging to the symmetry species $\alpha_1, \alpha_2, \beta_1, \beta_2$. The corresponding decomposition of the spectrum is shown in Figures 1 and 2. Figure 1 shows the spectrum of the four A fluorines centered 41.11 ppm downfield from normal hexafluorobenzene in a 30°C sample containing the two forms of C_6F_6 in approximately equal proportions, and Figure 2 shows the spectrum of the two X fluorines centered 27.19 ppm upfield from normal C_6F_6 .

The splitting of the strong doublet at the A centre, and of the triplet at the X centre, is $|J_{AX} + J_{AX'}|$. Each A subspectrum contains

an AB pattern with effective chemical shift $|J_{AX} - J_{AX'}|$ and effective coupling $J_{\alpha 1} \dots J_{\beta 2}$, respectively. The same AB patterns also occur twice in each X subspectrum as is indicated in the Figures. The remaining lines in the $\alpha 1$ and $\beta 2$ subspectra can be grouped into sets of 4. Each such set has an "origin", marked 0 in the Figures, and occurs several times due to inversion about that origin and due to reflection at the centre of the A and X spectra. The details may be gathered from the Figures. These 4-line sets permit the $\alpha 1$ and $\beta 2$ subspectra to be identified and they give the value $|J_{AA'} + J_{AA''} + J_{AA'''}|$ as the average shift of sets 2 and 3 from set 1 in the $\alpha 1$ subspectrum of the X fluorines.

It is thus possible to decompose the observed spectrum into the 4 subspectra $\alpha 1 \dots \beta 2$ and to determine

$|J_{AX} \pm J_{AX'}|$, $|J_{AA'} + J_{AA''} + J_{AA'''}|$ and $J_{\alpha 1} \dots J_{\beta 2}$ except for the ambiguity that the $\alpha 2$ and $\beta 1$ subspectra may be interchanged. 8 sets of spin coupling constants may then be derived, and these are related by the permutations and relative sign changes listed in the following Table.

$J_{AA'}$	$J_{AA''}$	$J_{AA'''}$	J_{AX}	$J_{AX'}$	$J_{XX'}$
a	b	c	d	e	f
a	b	c	-d	-e	f
a	b	c	e	d	f
a	b	c	-e	-d	f
b	a	c	d	e	f
b	a	c	-d	-e	f
b	a	c	e	d	f
b	a	c	-e	-d	f
$14.08 \pm .01$	$-3.02 \pm .01$	$0.06 \pm .02$	$-10.02 \pm .01$	$7.09 \pm .01$	$-9.40 \pm .01$ Hz

All these sets, and of course another 8 resulting from the reversal of all signs, produce the same spectrum. One of them may be chosen to start an iterative computer fitting procedure. If NMRIT/NMREN 2 is used the traces $\text{Tr}(\alpha 1) = 3 (J_{AA'} + J_{AA''} + 2 J_{AA'''} + J_{XX'})$

$$\text{Tr}(\alpha 2) = 3 (J_{AA'} - J_{AA''} - 2 J_{AA'''})$$

$$\text{Tr}(\beta 1) = -3 (J_{AA'} - J_{AA''} + 2 J_{AA'''})$$

$$\text{Tr}(\beta 2) = -3 (J_{AA'} + J_{AA''} - 2 J_{AA'''} + J_{XX'})$$

are needed.

In practice, we found it necessary to compute a few trial spectra in order to resolve ambiguities arising from unresolved and from low-intensity lines. The α_1 and α_2 subspectra can be distinguished only with the help of the X spectrum and the A spectrum can consequently be fitted equally well with f in the Table replaced by $-f$.

Some 6 spectra were recorded at various sweep rates and amplitudes but only one was used in the iterative procedure, the r.m.s. experimental frequency error is estimated to be ± 0.2 Hz. 76 transitions are theoretically allowed in the A spectrum, 72 in the X spectrum, and these are all present in the calculated spectrum (weakest intensity 0.002, total intensity 192). 70 transitions were assigned and used in the iteration in the A spectrum, 66 in the X spectrum. One set of parameters representing the computed best fit is listed in the last row of the Table with the probable errors given by LACNT. The r.m.s. error between calculated and observed frequencies is 0.1 Hz

with a maximum deviation of 0.26 Hz for an overlapping line pair in the X spectrum. The error vectors printed out by LACNT do not indicate any dangerous correlation between parameters, and the computed spectrum appears to match the observed one (not shown here) quite well within the experimental accuracy.

The parameter set in the last row of the Table does appear to fit the spectrum but any permutation or sign change listed in the Table, as well as a complete sign reversal, would fit equally well. I would be pleased to receive comments from your readers as to which set would match their expectation.

Sincerely yours,

Richard

R. Kaiser

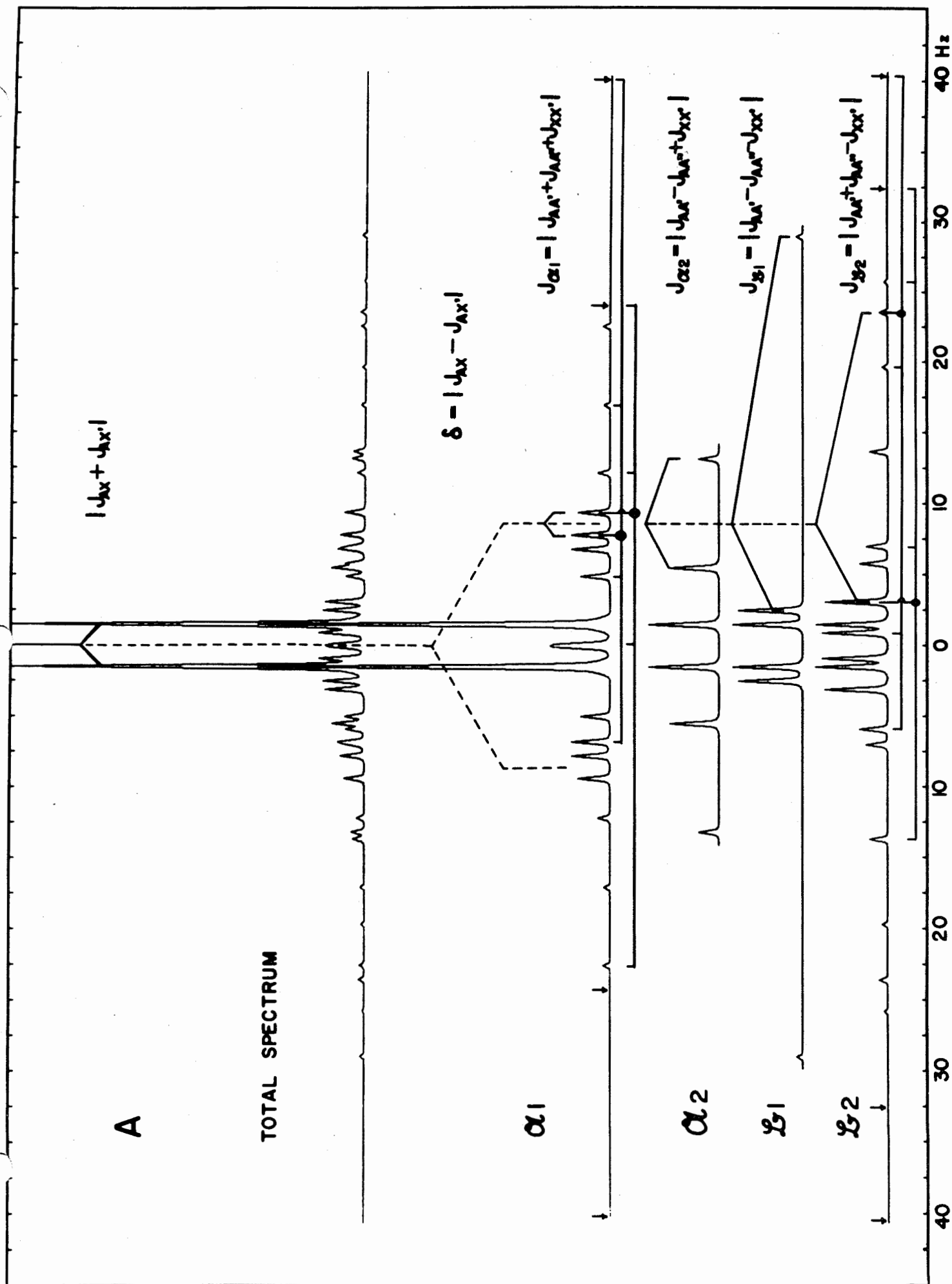


Figure 1

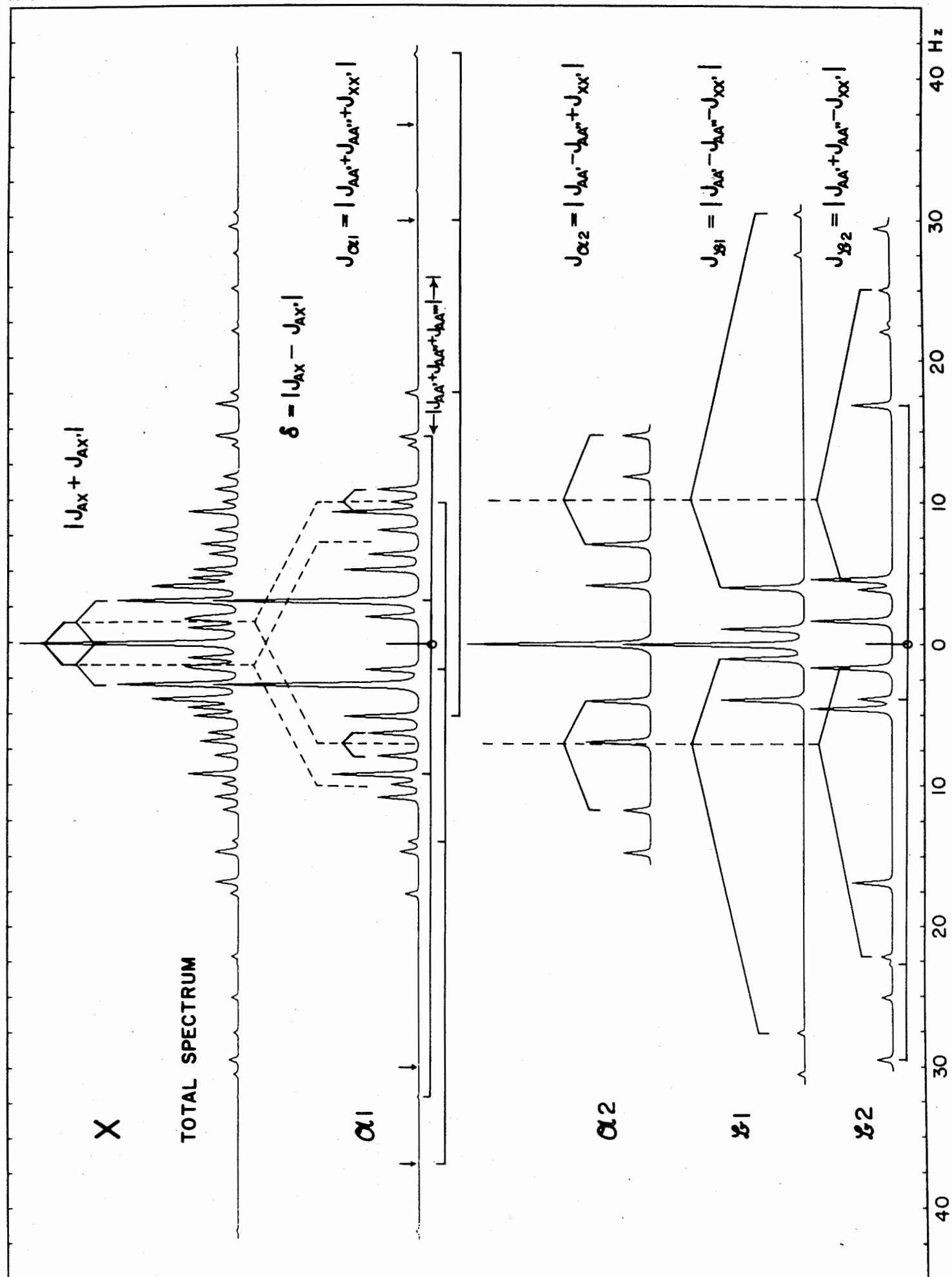


Figure 2

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70
SWEDEN

Cable address: Technology

EF/IB

124-7

Stockholm, December 9th, 1968

Professor
Bernhard Shapiro
Dept. of Chemistry
Texas A & M University
College Station, Texas 77843
USA

Band shape analysis

Dear Barry,

We have, for number of years, made use of a series expansion based on the linear harmonic oscillator wave functions to characterize the band-shape of NMR Wide Line spectra. The advantages of this procedure are, first that the series is rapidly converging, usually calling for less than five terms to achieve a satisfactory approximation, second that the band shape is described by analytical expressions, third that the moments of the band are easily and accurately computed from the expansion coefficients, fourth that the necessary truncation of the band is easily and correctly performed by disregarding the experimental extreme wings of the band and automatically extrapolating the analytical expressions, determined by the main and accurate central part of the band, to the truncated zones of poor signal to noise ratio.

Now, the central limit theorem states - somewhat loosely expressed - that an ensemble of weakly coupled but statistically independent oscillators satisfy a gaussian distribution. Violation of this theorem occurs as soon the mutual interaction between the oscillators or their interaction with a substrate removes the condition of statistical independence.

Since the ground state of the linear harmonic oscillator - that is, the first term in the series expansion - represents a gaussian distribution, the admixture of overtones will indicate the degree of dipolar coupling effects and interdependence of the nuclei involved in the resonance. The easy determination of the fourth moment may similarly be used to reveal the presence of scalar coupling effects.

The old computer program (Acta Chem. Scand. 16, 2149, 1962) several times revised and extended, has now been transcribed to FORTRAN in a new curve-fitting program, WIDELINE, by Kjell-Ivar Dahlqvist of this group, to cover the case of nonisocentric but symmetric four-band structures. Like the old program, WIDELINE makes use of the method of least squares, but the minimization process is now based on the subroutine STEPIT developed by I.P. Chandler, Physics Dept., University of Indiana and available from Quantum Chemistry Program Exchange, I.U. Chemistry Dept., Bloomington Indiana, USA.

The two halves of the spectrum are analyzed separately to permit a check on drift asymmetries and transient effects.

The result of the analysis contains information of:

band shifts,

band widths,

expansion coefficients,

band areas,

areas of the derivatives of the measured and
computed bands

second moments

fourth moments

error sum

mean deviation

Moments of higher order can easily be included and the measured and calculated band shapes plotted as exemplified in Fig. 1 showing a proton spectrum of collagen under tension (work in progress, carried out by P.Lindner of this group).

The squared error sum was 1.91714 cm^2 and the mean deviation of the five-term expansion shown as the full line in Fig. 1 was 0.1679 cm . The computer time on IBM 360/75 was, for the whole spectrum, 5.35 minutes.

WIDELINE is available from

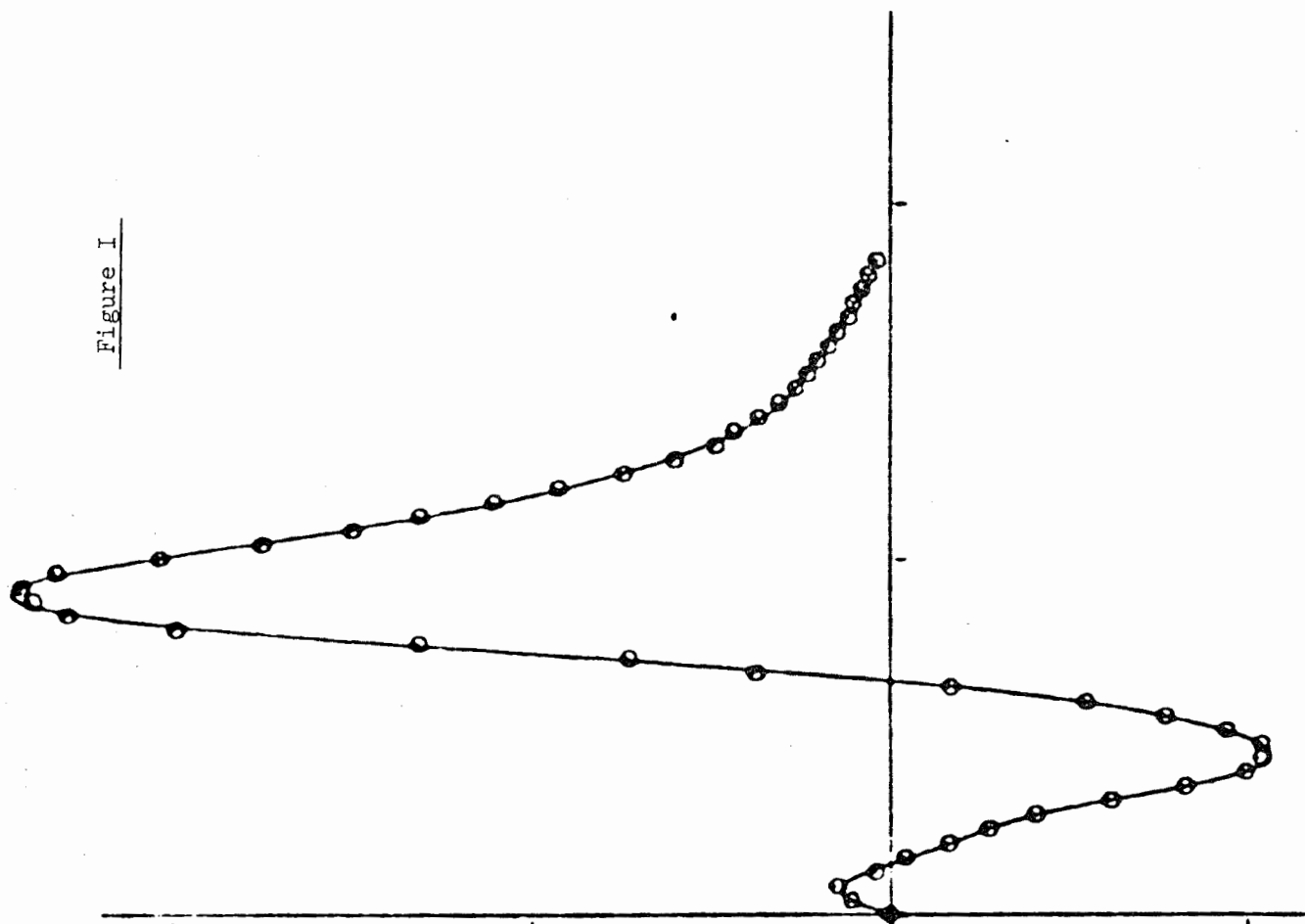
NUCLEAR MAGNETIC RESONANCE GROUP
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70 SWEDEN

Kind regards and best wishes for the New Year,

Yours truly,


Professor Erik Forslind

Figure I



SIMON FRASER UNIVERSITY

DEPARTMENT OF CHEMISTRY



BURNABY 2, BRITISH COLUMBIA

Telephone 291-3111 Area code 604

December, 2, 1968

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

Dear Barry,

Fourier Transform NMR Spectroscopy

It seems to us that since you moved westward your "blues" now arrive earlier. Our regrets about our amnesia.

Recently we have been interested in the application of our NMR Specialties pulse machine to the S/N problem via signal averaging of the free induction decay followed by Fourier transformation. We have modified our 60 Mhz spectrometer to 15 Mhz operation, and use a Fabritek 1064 signal averager for collecting the data. The transformation is done on an IBM 360/40 computer, using a fast transform program kindly supplied by Bob Vold, though it has been modified to reduce frequency dependent phase distortion caused by maladjustment of the rf reference phase, by the finite sampling rate, and by the output filter network.

The figure shows some preliminary results for the Sn^{119} 15 Mhz spectrum in neat liquid $\text{Sn}(\text{CH}_3)_4$. a) is a strip-chart plot of the contents of 2048 memory channels after 128 sweeps at 1 sec interval, sampling every 100μ sec. The sample was contained in a 15 mm non-spinning tube, and the Varian DP60 magnet was not field-frequency locked. The output filter time constant was 10μ sec. b) is the computed Fourier transform of a), from a Calcomp plot. We can detect 11 of the 13 proton-coupled lines, but have not yet located the C^{13} side-bands.

..2..

- 2 -

We have seen by this method natural abundance C^{13} spectra in a variety of compounds, but magnet drift is troublesome over the longer accumulation times necessitated by slow C^{13} relaxation. Arthur Brooke is now putting together a field frequency lock system.

With best wishes to you for '69.

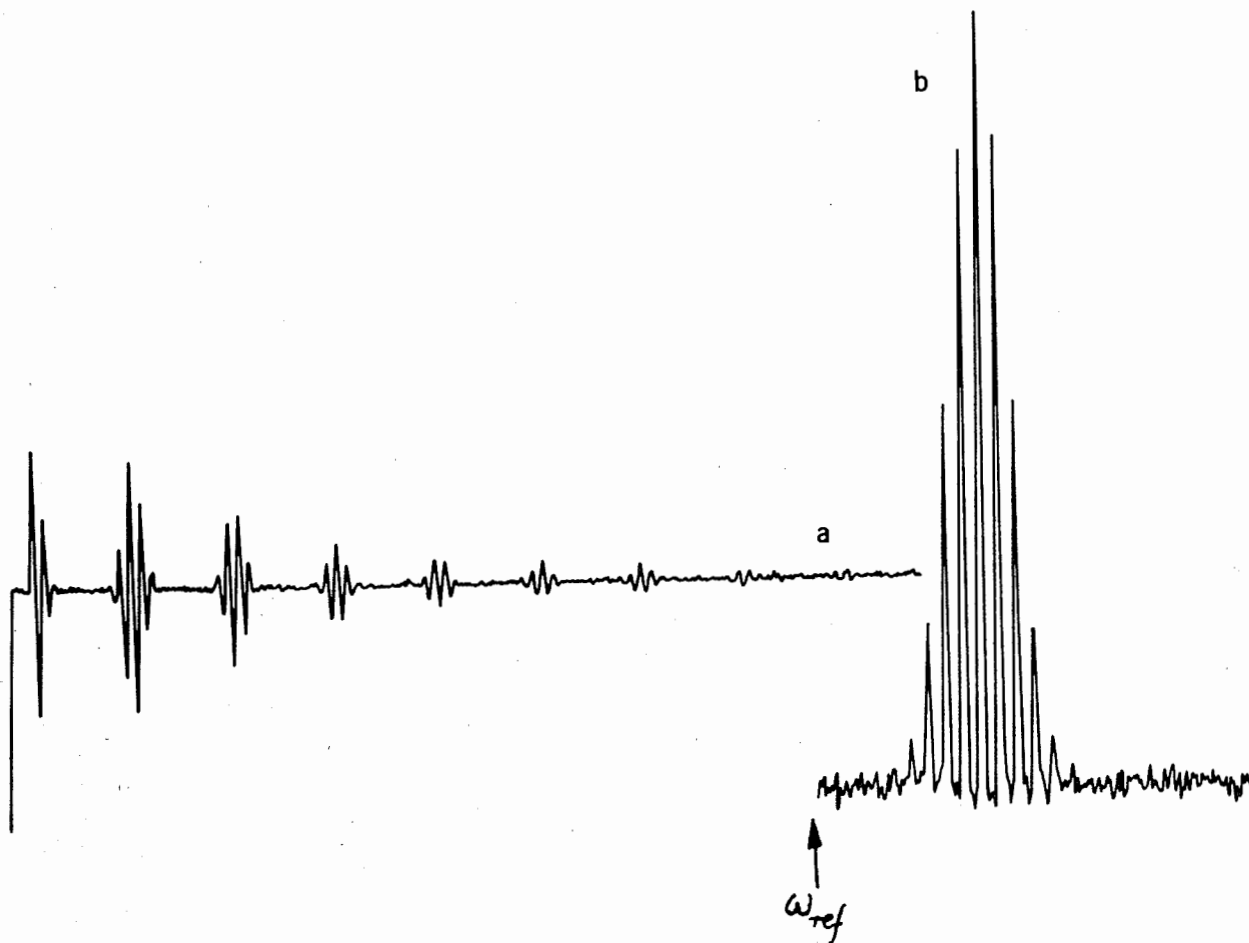
Yours sincerely,

M. Kaplansky
M. Kaplansky

E.J. Wells
E.J. Wells

J.G. Hallett
J.G. Hallett

A.R. Gangadharan
A.R. Gangadharan

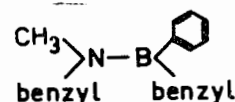


Äquilibrierung von Aminoborane.

Im Rahmen unserer Untersuchungen¹⁾ über die Bindungsverhältnisse in organischen Phosphor - Stickstoffverbindungen²⁾ und Bor-Stickstoffverbindungen synthetisierten wir einige Aminoborane, bei denen in Lösung ein Gleichgewicht zweier Isomere mit Hilfe der PR-Spektroskopie nachzuweisen war.

Beim Methylphenylamino-chlorphenylboran ist das Isomergleichgewicht sehr stark temperaturabhängig. Bei +80°C ist das eine Isomere (A) im Gleichgewicht zu 19% ($K = B/A = 4,4$) vorhanden. Bei +25°C steigt der Anteil des Isomeren (A) auf 44% ($K = 1,36$) und bei -80°C sogar auf 86% ($K = 0,14$). Die freie Aktivierungsenthalpie ΔG_a^* der Umwandlung beider Isomere kann bei dieser Verbindung nicht wie üblich aus der chemischen Verschiebung (Δv) und der Aufspaltungstemperatur (T_a) der PR-Signale bestimmt werden, sondern es muß die Äquilibrierungsmethode³⁾ bei tiefen Temperaturen (-80°C bis -70°C) angewendet werden. Bei dieser Methode wird die Einstellung des Gleichgewichts bei konstanter Temperatur (z.B. -80°C) zeitlich verfolgt (s. Abb.). Aus der Halbwertszeit ($t_{1/2}$) und der Gleichgewichtskonstanten (K) (bei konstanter Temperatur) kann die für diese Temperatur charakteristische Geschwindigkeitskonstante (k) berechnet werden. Für obige Verbindung errechnet sich ein ΔG_{-80}^* -Wert von 14,7 kcal/Mol ($t_{1/2} = 10,5$ Min.; $k_{-80} = 10,3$).

Im Gegensatz zu obigem Aminoboran kann das Methylbenzylamino-benzylphenylboran kristallin erhalten werden. Löst man die Kristalle bei -10°C in Schwefelkohlenstoff, so erhält man das PR-Spektrum eines Isomeren. Bei +22°C stellt sich nach ungefähr acht Stunden das Gleichgewicht zweier Isomere ein ($K = 0,78$; $t_{1/2} = 38$ Min.). Aus der Äquilibrierung folgt ein ΔG_{+22}^* -Wert von 21,2 kcal/Mol.



Da diese Verbindung keine so extreme Temperaturabhängigkeit der Gleichgewichtskonstanten (K) zeigt, wie dies beim Methylphenylamino-chlorphenylboran der Fall ist, kann aus dem Zusammenfließen der entsprechenden Signale der beiden Isomeren bei $+180^{\circ}\text{C}$ zusätzlich ein ΔG_a^* -Wert bestimmt werden. Aus der Aufspaltungstemperatur $T_a = +180^{\circ}\text{C}$ und der chemischen Verschiebung $\Delta\gamma = 22\text{Hz}$ der beiden N-Methylen-signale errechnet sich ein ΔG_{+180}^* -Wert von $23,4\text{ kcal/Mol}$.

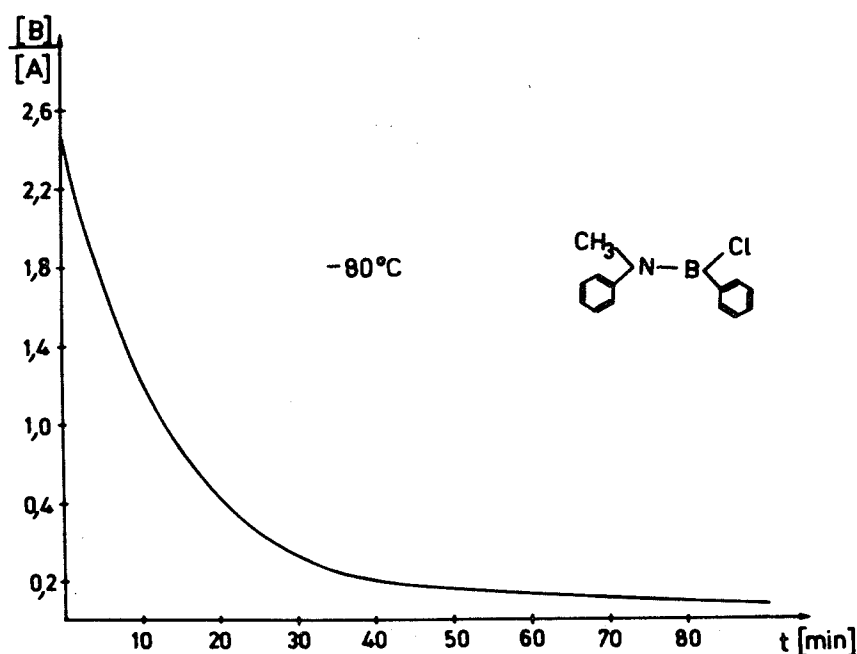


Abb.: Isomerenverhältnis(B/A) des Methylphenylamino-chlorphenylborans aufgetragen gegen die Zeit.

Da in den Aminoborane die vier Substituenten nahezu in einer Ebene liegen, unterscheiden sich die Isomeren durch eine cis- bzw. trans- Stellung der Substituenten. Die relative Stellung der Substituenten der zwei mit PR-Spektroskopie nachweisbaren Isomeren konnte jedoch bisher nicht eindeutig bestimmt werden.

- Literatur:
- 1) Dissertation, D. Imbery 1968.
 - 2) D. Imbery, H. Friebolin, Zeitschrift für Naturf. **23**, 759, (1968)
 - 3) A. Mannschreck, Habilitation 1967.

D. Imbery H. Friebolin



CANISIUS COLLEGE

BUFFALO, NEW YORK 14208

DEPARTMENT OF CHEMISTRY

December 9, 1968

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

NMR SPECTRA OF MERCUROCHROME

Dear Dr. Shapiro:

We recently measured the PMR spectra of several mercury compounds. We also had available structurally related compounds not containing mercury. The influence of the mercury atom on the spectra seemed to be interesting enough for me to present one example.

The traces of the aromatic ring region for two compounds are given in the adjoining figure. The structures are drawn alongside each trace and we note they differ in that the top one does not have the HgOH group and in addition has one less proton than the bottom structure.

Further work must be done to assign the signals but it can be noted the top spectrum has a very sharp singlet signal absent in the bottom one. It is difficult to assign this strong signal to any protons present in the top structure. Perhaps it is the disubstituted benzene ring signal.

Perhaps of more interest is the very weak signal the compound containing mercury gave us. This compound (mercurochrome) is extremely soluble in water but even 10-20% by weight in water gives a broad and weak signal. The spectrum on the opposite page represents the maximum signal we could obtain from mercurochrome. We varied concentration, R. F. field, amplitude, etc. on our A-60 and this was the best we could do. There seems to be little doubt the mercury atom is quenching the signal. Any comments or suggestions on this problem from your readers would be appreciated.

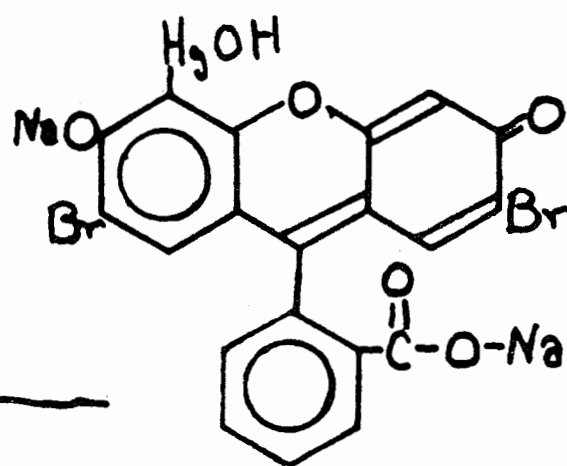
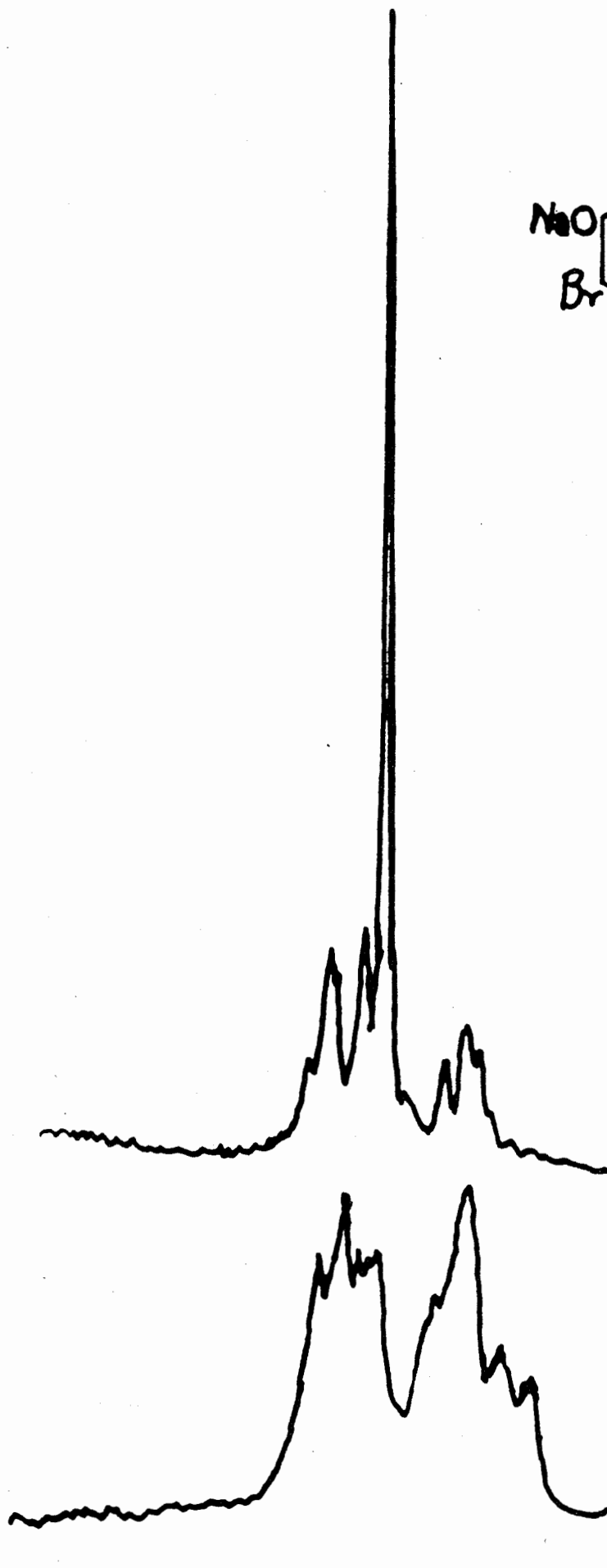
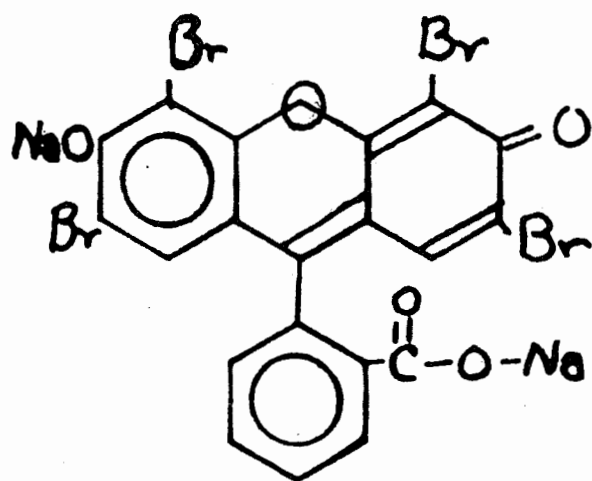
Sincerely,

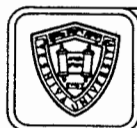
Dr. Herman A. Szymanski
Chairman
Department of Chemistry

HAS:fj

P. S. I have a new address so please send Newsletter to it. The address is:

Dean of Faculty
Alliance College
Cambridge Springs, Pa. 16403





YESHIVA
UNIVERSITY

BELFER GRADUATE SCHOOL OF SCIENCE

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

December 11, 1968

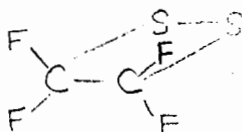
Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

Title: Possible Studies on Carbenes using NMR

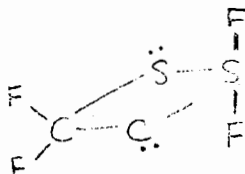
In response to the threatening letters of many colors, I am forced to dig deep into my desk drawer for something of faint relevance to NMR, as I am not desirous of losing my subscription to your worthy newsletter.

The following is but one of many examples of possible experiments that one can devise. Consider the hypothetical molecule



I

and recall that divalent S is unstable relation to tetravalent sulfur (SF_2 is unknown, while SF_4 and SF_6 are stable). This implies the possibility of an equilibrium in which two of the F atoms transfer to one of the sulfurs, leaving a stable carbene



II

where to show the pseudo-symmetry of the problem two dots have been drawn on the S as well. (Recall that this is pseudo-symmetry since there should be 4 dots on the S.) The presence of CF_2 groups instead of the F atoms should stabilize II since they would be sterically unfavorable in I. This should also be relatively unreactive since approach to the carbene should be hindered. Also the S-C-C 90° bond favors the singlet (and presumably more stable) carbene over the triplet. NMR is a unique tool for studying the equilibrium.

Prof. B.L. Shapiro

2

December 11, 1968

Some other NMR studies on short-lived and equilibrating species have been discussed in my article on "hypervalent" molecules to appear in *Angewandte Chemie* in January (?) and all kinds of others can be easily imagined once the unusual behavior of these "hypervalent" molecules (containing non-metallic and metallic atoms in their higher valence states) are appreciated.

Yours sincerely,


Jeremy I. Musher

hn

THE JOHNS HOPKINS UNIVERSITY
SCHOOL OF MEDICINE
725 N. WOLFE STREET · BALTIMORE, MARYLAND 21205

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

December 9, 1968

TELEPHONE 955-5000
AREA CODE 301

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

Title: Micelle Formation in
Synthetic Lecithin

Dear Barry,

I (along with Dr. R. L. Biltonen of this department) have recently investigated the NMR properties of three highly purified synthetic lecithins of chain length C_7 , C_8 , and C_{10} obtained from Dr. L. L. M. von Deenen. The methyl, methylene, and N-methyl resonances of all three compounds were studied as a function of concentration in D_2O . A sudden increase in line-width occurs at 0.25% for C_7 , 0.05% for C_8 , and between 0.01% and 0.05% for C_{10} . These values probably represent the critical micelle concentrations. For the C_7 compound only the methyl resonance broadens, for C_8 both methyl and methylene resonances broaden and for C_{10} all three proton groups are broadened. For the C_7 compound the methyl resonance increase in width from 3 Hz to about 10 Hz while the methylene peak remains at about 10 Hz, its width at low concentration, while the N-methyl resonance remains narrow (~3 Hz). For the C_8 compound the methyl and methylene resonances increase to about 20 Hz in width while again there is no change in the N-methyl peak. In the case of the C_{10} compound all three peaks are dramatically broadened to a value of 75 - 100 Hz. This difference in behavior between the C_{10} compound and the other two may indicate a difference in micelle shape for the larger compound from say a spherical to a bilayer type where surface contact among the sidechains could allow more effective relaxation. We are presently trying to correlate the NMR results with light scattering studies.

Sincerely,



Donald P. Hollis
Assistant Professor

drp



Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry · TEL. (603) 646-2501

December 23, 1968

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


Re: Poor Man's "Frequency
Synthesizer"

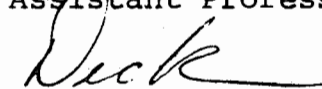
Dear Barry:

One prerequisite for doing high resolution double resonance on an internal lock spectrometer is a highly stable, precisely settable audio oscillator. While the frequency synthesizer is clearly the best answer to this problem in the absence of pecuniary considerations, one needs a realistic solution in the interim. We have come up with a solution based on a Hewlett-Packard 3300A Function generator. The frequency of the oscillator is voltage controlled, so we built a highly stable, precisely settable voltage source. A switch selects the number of mercury batteries (1-8) in series, and the voltage of the last battery added is divided by 3 step decade dividers and a 10 turn pot. Thus, the smallest division on the 10 turn pot corresponds to 1.34 μv . Of course, thermal emf's and changes in contact resistances are probably larger than this, but even without great pains to control temperature and use fancy switches we experience stability of better than three parts in 10^5 over a period of 5 to 10 minutes. This is adequate for most purposes. Considering the amount of engineering one can buy for about \$200 from Leeds and Northrup or General Radio, one would probably be better off buying rather than building the divider, but if anyone would like the circuit it is in the General Radio catalog.

This, of course, is not a frequency synthesizer, but until one comes along it makes a good, cheap substitute. The 3300A is a handy item to have leftover anyway.

Sincerely,


Karl F. Kuhlmann
Assistant Professor


Paul R. Shafer
Professor



EURATOM

CCR

Magnetic Resonance
Dr. H. SpiessckeISPRA
(ITALIA)Ispra, December 11, 1968
HS/mgProfessor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843Very old and old results -compared; nematic spectra of gases.

Dear Barry:

Sorry that I missed the deadline of December 2, but I had to sacrifice a couple of more urgent deadlines on the European altar during the last months.

Long, long ago (IITNMR No 101,22,1967) I published the nematic spectrum of C_2H_4 . In the meantime some more results have piled up and before they will be outdated let's compare them¹⁾.

The table is pretty much selfexplanatory, but some points are worth special comment. I assume that the double bond orients parallel to H_0 in ethylene. Then all J have to be negative. To clarify this point I'm just measuring ethylene-1- ^{13}C . The large discrepancy in the ratio for r_{FF}/r_{HH} in difluoroethylene suggests an appreciable anisotropy of the indirect coupling. The determination of its components will be my next contribution. The ethane spectrum can only be satisfactorily analysed by using the staggered conformation. The differences between the staggered and eclipsed form are readily seen if one compares the theoretical machine drawn spectra. There is no anisotropic contribution to J in trifluoroethane as the small deviation in the nmr and microwave determined ratios shows.

Quite interesting is also the fact that the ratio of r_{14}/r_{12} in cyclopropane, ethylene oxide, and ethylene sulfide is practically the same²⁾.

Best wishes for the next year.

Yours

- 1) Papers given at the NMR Symposium of the Universities Freiburg, Tübingen and Heidelberg, Februar 1968, and 2nd Liquid Crystal Conference, August 1968 Kent, Ohio.
- 2) Symposium on Magnetic Resonance in Chemical Physics, Vancouver, August 1968.

	C_2H_4	$H_2C=CF_2$	$F_2C=CF_2$	H_3C-CH_3 (stagg.)	H_3C-CH_3 (eclip.)	H_3C-CF_3
D_{12}	1230.0	-158.0	1219.0	1360.0	1360.0	717.8
D_{13}	-229.0	-272.4	537.6	-	-	-
D_{14}	-1022.4	-841.4	1529.6	-543.1	-611.8	-109.0
D_{34}^{FF}	-	-133.0	-	-	-	371.6
$C(3Z2-R2)$	0.14191	0.14231	-0.35151	0.147206	0.147206	0.0763
$C(X2-Y2)$	-0.00281	0.09403	-0.35607	-	-	-
r_{FF}/r_{HH} MW	-	1.130	-	-	-	1.211
NMR	-	1.017	-	-	-	1.192
Ra	1.327	-	-	-	-	-
r_{14}/r_{12} NMR	1.318	1.380	1.194	-	-	-
ED	-	-	1.283	-	-	-
MW	-	1.463	-	-	-	-

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

December 16, 1968

LONG-RANGE ^{13}C -H COUPLINGS IN FERROCENE

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

Dear Barry,

Recently we have made a PMR study of the ^{13}C -H satellite patterns of some metallocenes. The spin system of these compounds lends itself very nicely to the analysis of the inner ^{13}C -H satellite patterns, which are only slightly obscured by the intense parent peak. Spectral analysis of this region yields the values for the long range ^{13}C -H couplings, whereas the outer satellites are only dependent upon the differences in these couplings. All of the proton parameters (isotopic chemical shifts, proton-proton-couplings and all ^{13}C -H coupling constants) can be determined from the simultaneous analysis of both the inner and outer satellite patterns. The enclosed figure shows the observed and computer plots of the outer and inner satellite patterns for ferrocene. The parameters obtained are listed in the table. It was found that the difference in the long range ^{13}C -H couplings as determined from the outer satellites were 0.1 Hz smaller than that obtained from including the inner satellite pattern in the iteration and thus calculating their values exactly. These long range ^{13}C -H coupling values of 6.30 Hz and 7.22 Hz for two- and three-bond couplings, respectively, fall within the same range as the corresponding couplings found by Roberts for five-membered heterocyclic rings.

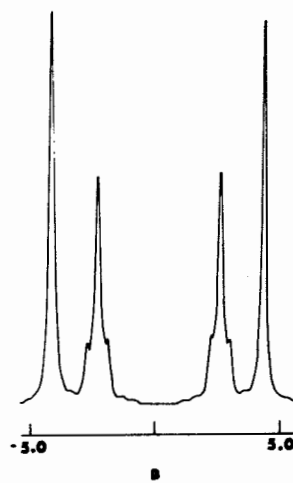
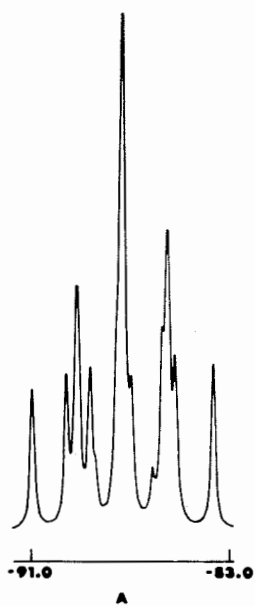
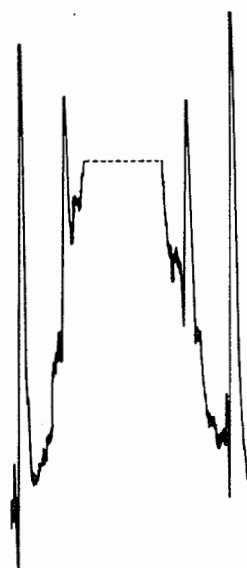
FERROCENE PARAMETERS

V_1	= 0.14	J_{12}, J_{23}	= 2.40	J_{CH}	= 174.81
V_2, V_3	= 0.10	J_{13}, J_{24}	= 1.24	J_{CCH}	= 6.30
V_3, V_4	= 0.08			J_{CCCH}	= 7.22

Sincerely,

*J.H. Goldstein*J.H. Goldstein
R. W. Crecely

JHG:lt



ILLINOIS INSTITUTE OF TECHNOLOGY

CHICAGO, 60616

DEPARTMENT OF CHEMISTRY

December 13, 1968

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

HAMMETT UNCORRELATIONS

Dear Barry:

There are a fair number of chemists who continue to try to correlate the effect of substituents on pmr data with their effect on reactivity. By 1966, we had collected about 30 Hammett correlations (1); we now have about 100 of them. We hope that the negative things we have to say here about these correlations will provoke more critical inquiry, perhaps by other approaches, into the vexing problem of substituent effects on chemical shifts.

The Hammett equation and its simple variants take the form,

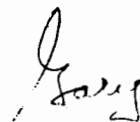
$$v = \rho\sigma + \text{constant} \quad (1)$$

when one examines pmr data of the family, $\text{RC}_6\text{H}_4-\text{T}-\underline{\text{H}}$ (1). If eq.1 is relevant, then one can interpret the slope, ρ , as a measure of the sensitivity of $\underline{\text{H}}$ to the effect of substituents as communicated through the link $-\text{C}_6\text{H}_4-\text{T}-$. Equation 1 often holds for kinetic and equilibrium data. In these cases, ρ may be well-behaved: it is fairly constant for a given chain length T and falls off systematically as T gets longer (2).

We have collected many of the available pmr ρ values in Figure 1. The code numbers refer to families $\text{Ar}-\text{T}-\underline{\text{H}}$, which are identified, in part in ref.1, and in a paper to be published. The ρ values scatter in no obvious pattern and make no obvious sense. Since eq.1 is usually unreliable for pmr data anyway (1), there seems to be little point in using it.

Judging by the number of recent papers in this field, it is questionable whether anything, even Figure 1, can discourage the use of eq.1. But we hope it will.

Yours sincerely,

Sidney I. Miller

Gary R. Wiley, S.J.

References

- (1) S.H. Marcus, W.F. Reynolds, and S.I. Miller, J.Org.Chem., 31, 1872 (1966).
- (2) W.K. Kwok, R.A. More O'Ferrall and S.I. Miller, J.Amer.Chem.Soc., 86, 1507 (1964).

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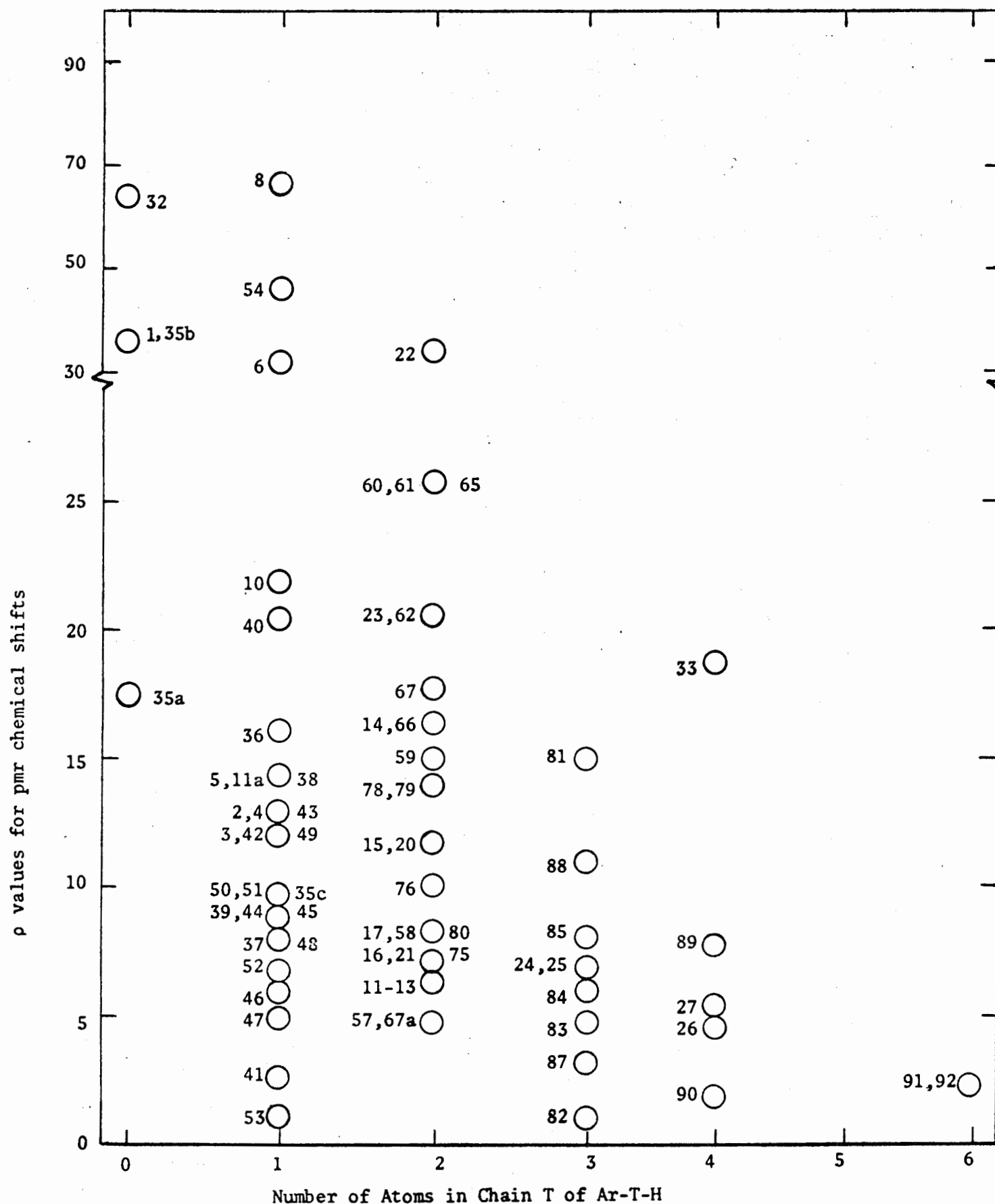


Fig. 6. Transmission of substituent effects and Hammett ρ values. The pmr data are given in Table IV or Ref. 3. ρ values for highly polar solvents are not included here.

ILLINOIS INSTITUTE OF TECHNOLOGY

CHICAGO, 60616

DEPARTMENT OF CHEMISTRY

December 11, 1968

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

Re: SHAPE OF CYCLIC HEXAPEPTIDE RINGS

Dear Barry:

We have shifted our efforts from studies of cyclic dipeptides to studies of cyclic hexapeptides, and have now examined spectra of cyclo-pentaglycyl-L-tyrosyl (I) and cyclo-diglycyl-L-histidylglycyl-L-tyrosyl, plus partially deuteriated versions of these.

For both peptides, in each of the solvents water, trifluoroacetic acid and dimethyl sulfoxide, the six amide protons divide into two groups; there is a lower field group of four and a higher field group of two. An example is shown in Figure I, which shows the amide proton region of cyclo-Gly₃-Gly-d₂-Gly-d₂-Tyr dissolved in dimethyl sulfoxide - 10% water.

The chemical shifts of the lower field set of protons are dependent on solvent, and agree with the chemical shifts of the internal amide protons of non-cyclic pentaglycylglycine. The upper field pair is apparently independent of solvent. The table illustrates this for peptide I.

Chemical Shift of Amide Protons, ppm below Reference

Solvent	Internal Reference	<u>c</u> -Gly ₅ Tyr (I)		H-Gly ₆ -OH
		Set of Two Protons	Set of Four Protons	Internal Amide Protons
DMSO	TMS	7.7-7.8	8.3	8.1
TFA	TMS	7.7	7.85	7.9
H ₂ O	DSS	7.7	8.25	8.15

We conclude from these observations that, at least in these three peptides, the cyclic hexapeptide backbone has the general configuration shown in Figure II. This backbone structure was proposed some years ago by Schwyzer (1) on chemical evidence, and has been found, as one of several arrangements, in the crystal of cyclo-hexaglycyl hemihydrate (2).

Best regards,

Anita Go

Anita Go

Masako Ohnishi

大西 征子

Ken Kopple

K. Kopple

- (1) R. Schwyzer, *Rec. Chem. Progr. (Kresge-Hooker Sci. Lib.)*, 20, 147 (1959); R. Schwyzer, P. Sieber and B. Gorup, *Chimia*, 12, 90 (1958); R. Schwyzer, *et al.*, *Helv. Chim. Acta*, 47, 441 (1964).
- (2) I. L. Karle and J. Karle, *Acta Cryst.*, 16, 969 (1963).

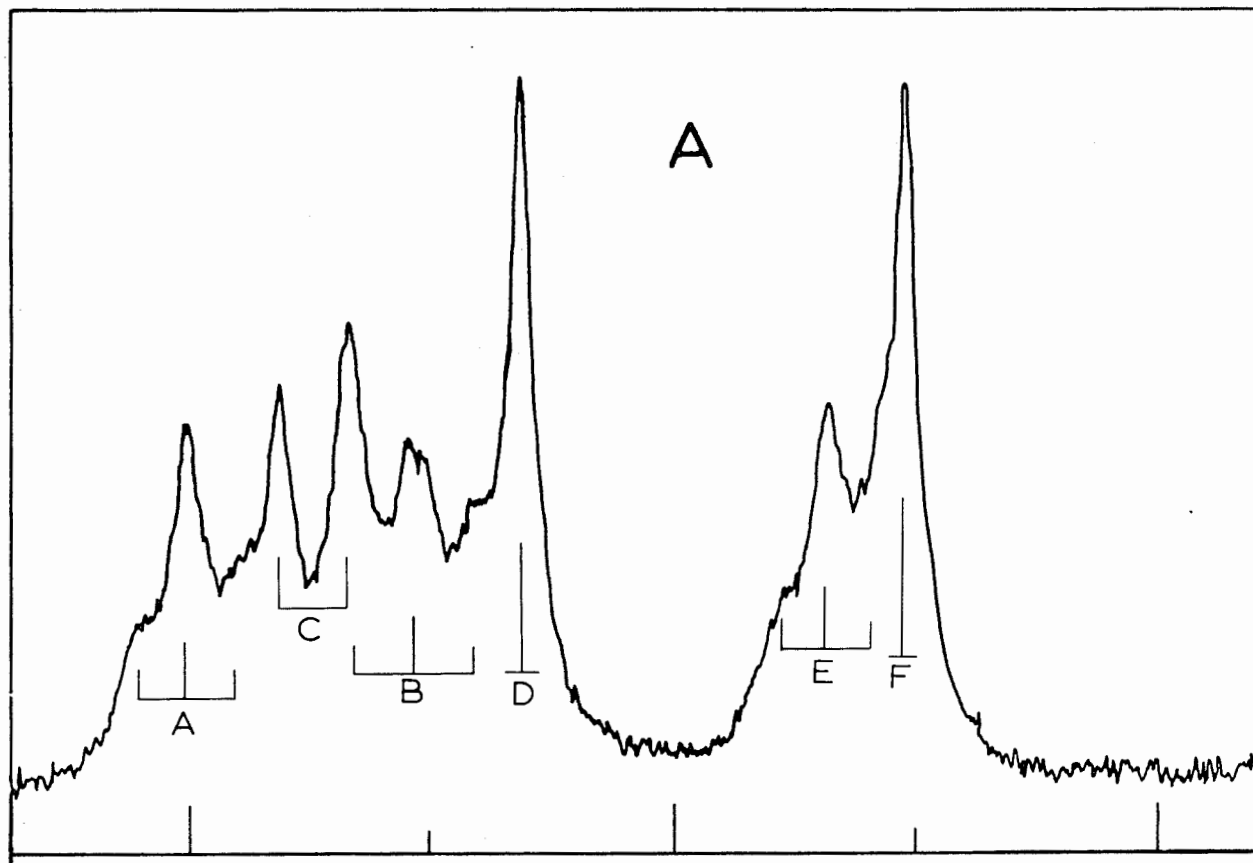


Figure I

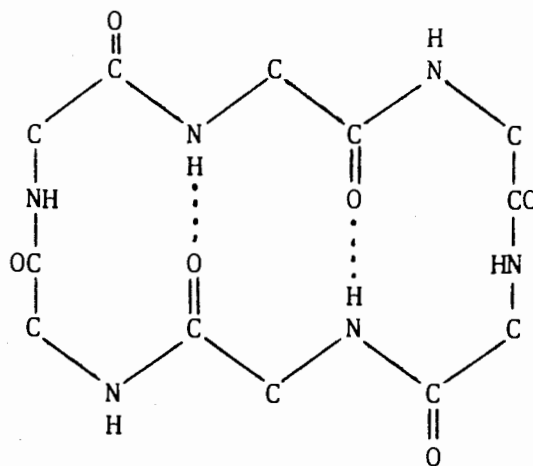


Figure II



ECOLE DE PHYSIQUE

UNIVERSITE DE GENEVE

INSTITUT DE PHYSIQUE
EXPERIMENTALE

BOULEVARD D'YVOY 32

TEL. (022) ~~XXXXXX~~ 241268

GENEVE

GJB/lmg

Genève, le 13 décembre 1968

Professeur Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College of Science

College Station - Texas 77843
U.S.A.

Cher Professeur Shapiro,

RMN haute résolution aux très basses fréquences

Votre lettre de rappel me donne l'occasion de résumer ci-dessous quelques résultats obtenus au cours de cette année 1968. Je rappelle tout d'abord que nous étudions la RMN haute résolution dans des liquides mobiles diamagnétiques - essentiellement pour l'instant résonance protonique - à des fréquences de travail comprises entre 2 et 4 KHz, soit en régime permanent (bobines de Bloch), soit par précession libre après prépolarisation.

De telles résonances ne présentent une structure que si des noyaux de nature différente A et B présentent une interaction indirecte (couplage J).

Si $\Delta \nu_L$ = différence des fréquences de Larmor des noyaux couplés
 J = constante de couplage indirect
 ΔH = largeur naturelle des raies de résonance
 δ = déplacement chimique interne

On a les relations $\Delta \nu_L \approx J$ et $\Delta H \gg \delta$

1) Etude en régime permanent à 4000 Hz, interaction $P_{15}^{31} - H_1^1$.

Sur chacune des composantes du doublet protonique, A. Erbeia et P. Dreyfuss ont mesuré le temps de relaxation transversale T_2 ce qui a permis, par application de la théorie de Redfield, d'attribuer à l'interaction dipolaire au moins 80% des effets de relaxation.

2) Etude en régime transitoire dans le champ magnétique terrestre.

Nous avons observé le multiplet protonique résultant de l'interaction indirecte des noyaux N_7^{15} et H_1^1 dans l'ion $(NH_4)^+$ à la concentration naturelle des nucléides N_7^{15} . Non seulement cette analyse nous a permis une nouvelle détermination de la constante d'interaction J proton-azote 15 plus précise, mais en bon accord avec les mesures antérieures, nous avons été en mesure de calculer avec précision les positions et amplitudes des composantes protoniques des systèmes

$$A - B, \quad A - B^2, \quad A - B^3, \quad A - B^4$$

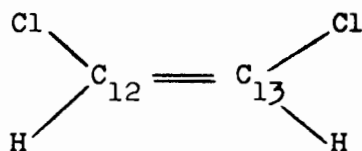
lorsque A et B sont des noyaux de nature différente et que les noyaux B sont magnétiquement équivalents.

Professeur B.L. Shapiro, College Station - Texas 77843 - 13.12.1968

Dans les mêmes lignes nous terminons actuellement l'étude

- 1) de la relaxation longitudinale en régime permanent sur le même système $P^{31}-H^1$
- 2) de systèmes A A' B (interaction protons, carbone 13 dans les dichlorethènes ci et trans).

Noter ici le changement de nomenclature par rapport à la haute résolution conventionnelle



Avec mes meilleurs sentiments

Prof. G.J. Béné



Imperial Chemical Industries Limited

PETROCHEMICAL & POLYMER LABORATORY

P.O. Box No. 11, The Heath, Runcorn, Cheshire

Telephone: RUNCORN 3456

Trunk Dialling: OWA 853456

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Telex: 62655 ICIMONDIVHQ, RCN

20th December, 1968.

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

Your Ref.

Our Ref. JKB/CEW

Dear Barry,

Thank you for your reminder. May we offer the following:

"Paramagnetic benzene": some thoughts and a non-observation

A simple classical picture of the familiar ring-current effect in a benzene molecule is a system in which six π -electrons are constrained to move along a circular path, with no resistance to this tangential motion. Application of a magnetic flux density B_0 along the ring axis produces a temporary accelerating force on the electrons which is easily shown to result in a total ring current $i = \frac{3 e^2 B_0}{2 \pi m c}$. This current

persists as long as the flux density along the symmetry axis is maintained at the steady value B_0 . The expression obtained can be used to predict the ring-current contribution to the diamagnetic susceptibility, and hence the anisotropy; the value predicted is $8.1 \times 10^{-29} \text{ cm}^3$, in quite good agreement with the experimental value of $9 \times 10^{-29} \text{ cm}^3$ (crystalline benzene, Krishnan et al., 1933).

What happens if benzene is synthesised in a strong magnetic field? Two alternatives need to be considered: either the π -electron system at the instant of its creation carries a ring current appropriate to the instantaneous magnetic flux through the ring (taking into account the orientation of the molecule), or the π -electron system carries no initial current, acquiring a ring current only when the flux through it is changed. Classically the second alternative appears more likely, and this would have the interesting consequence that on removal from the magnetic field the benzene molecules would each carry a trapped ring current depending on their orientation at the instant of formation.

Classical theory predicts that a benzene molecule formed in a field of 10^4 gauss along its symmetry axis should have a built-in magnetic moment of about 10^{-4} Bohr magneton (rather less than $1/10$ the magnetic moment of a proton). The effect on static magnetic susceptibility and relaxation times would be too small to measure, and in a random liquid any spin-spin coupling or chemical shift effects would average to zero. It appears, therefore, that the best chance of detecting special properties in benzene prepared in a magnetic field is to look at it in a liquid crystal solvent.

FROM: J.K. Becconsall.

SHEET NO.: 1

TO: Professor B.L. Shapiro.

DATE: 20th December, 1968.

We have made some preliminary attempts to observe "paramagnetic benzene". In the first experiment, benzene was prepared by dehydrogenation of 1,4-cyclohexadiene, using N-bromosuccinimide in carbon tetrachloride, in a field of about 3000 gauss provided by an electromagnet. The benzene was separated by g.l.c. from the resulting mixture, and was then examined in our HR-220 spectrometer as a nematic solution in 4,4'-dihexoxy-azoxybenzene. In the second experiment a sample of benzene was irradiated with ultra-violet light for 30 minutes in a magnetic field of the same strength as that used previously, in the hope that temporary excitation of π -electrons to higher levels followed by reversion to the ground state would result in ring current trapping. The benzene was then dissolved in 4,4'-dihexoxy-azoxybenzene and examined as a nematic solution.

In both experiments we were unable to find any differences between these samples and ordinary benzene.

We have not so far tried to work out a quantum-mechanical description which might give an answer to this problem, and we would be interested to hear from any theoreticians who can present reasons why the experiment should, or should not, be expected to work.

We feel sure that this contribution must qualify for the "wild theories" category!

Best wishes,

Yours sincerely,

Jack Becconsall

J.K. Becconsall

J.G. Kenworthy

J.G. Kenworthy

M.C. McIvor

M.C. McIvor

J.D.R. Vass

J.D.R. Vass

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7. 23 December 1968

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

Title: NMR TUBE FOR GAS PHASE
STUDIES.

Dear Barry,

Recent work in these labs has prompted us to design an NMR tube amenable to gas phase studies.

The valve assembly shown in Figure I consists of a modified Fisher-Porter valve where the side arms were carefully removed and a glass tube was sealed on close to the seat. For external references, a capillary fitted with teflon spacers to keep it centered, was inserted before the tube end was sealed off at the correct length.

The valve cylinder consists of a piece of teflon, machine-tooled to the original specifications but whose top section is machined to a standard 14/40 taper. Finally, a 1 mm bore is drilled through the center and emerges at right angles approximately 1 mm above the seat.

A good seal can be seen when the teflon seat flows under pressure when the valve cylinder is screwed down. (Pressure up to 40 atmospheres have been used in the tube without noticeable leakage).

We found that the 14/40 ground glass adapter on the vacuum line had to be greased since teflon to ground glass makes a poor seal. With the specifications given in the figure, the tube fits exactly in our HA-60 probe and in spite of the added weight, no spinning problems were encountered.

Sincerely,

Arthur Grey

H.J. Bernstein.

AAG/HJB/mn

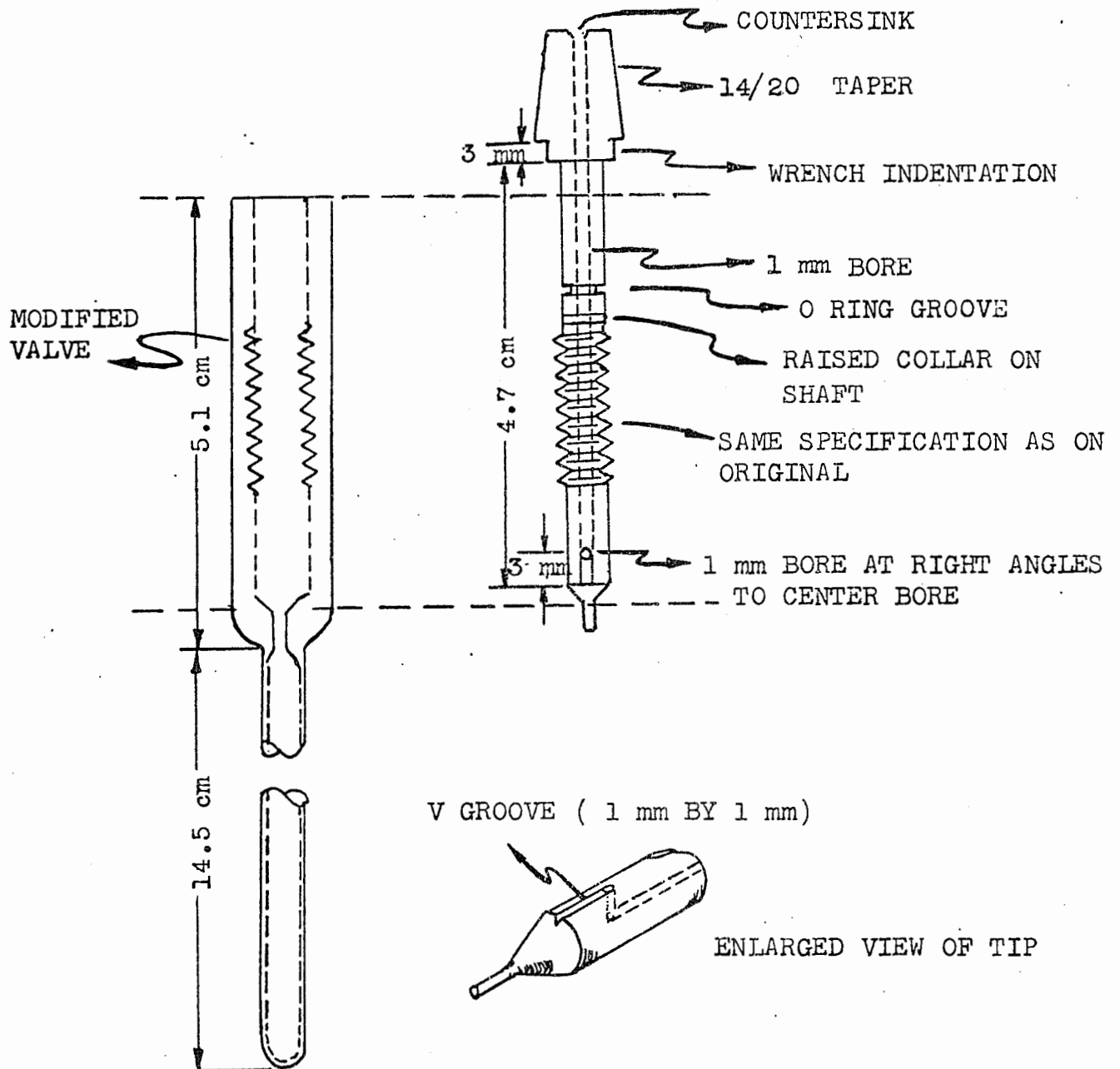


FIGURE 1

INSTITUT DE CHIMIE

Boîte postale 296 / R 8
Téléphone 36.30.02 à 07

J.M. LEHN

STRASBOURG, le 20 Décembre 1968
1, rue Blaise PASCAL

Prof. B.L. SHAPIRO
Department of Chemistry
Texas A and M University
COLLEGE STATION
Texas 77843
U.S.A.

Dear Barry,

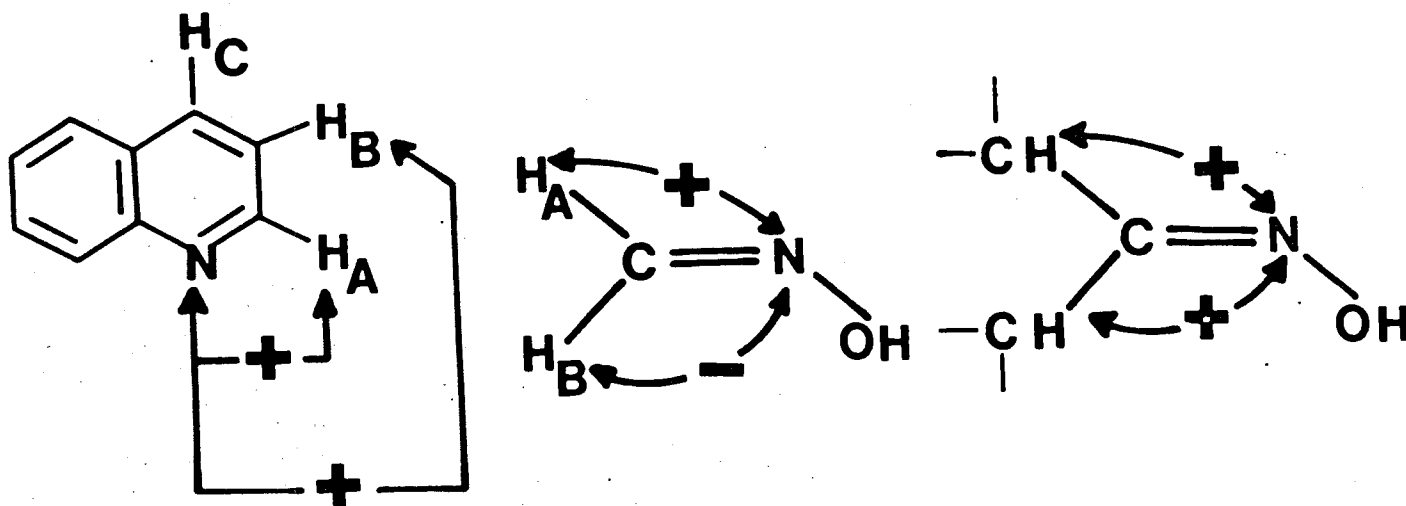
We again met the dead-line. This makes we feel that I must unconsciously like that pretty blue colour.....

Signs of $^{15}\text{N},\text{H}$ coupling constants (with D. Crépeux).

We have recently completed our study of the relative signs of geminal $^{15}\text{N},\text{H}$ couplings in ^{15}N -aldoximes by an investigation of the absolute signs of these geminal couplings as well as of related vicinal couplings.

The absolute signs have been determined with the aid of $^{15}\text{N},\text{H}$ spin-tickling experiments performed by Dr. Dean.

The results are as follows (the absolute sign indicated is for the reduced $^{15}\text{N},\text{H}$ coupling; ^{15}N has a negative gyromagnetic ratio):

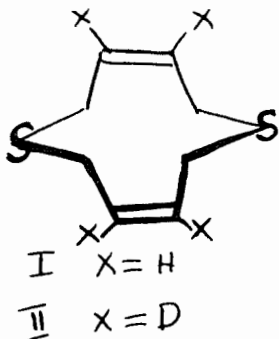


..../..

A study of these couplings in acid medium, showed that the protonation effect shows an alternation leading to a positivation, a negativation and a positivation of the one-bond, geminal and vicinal reduced $^{15}\text{N}, \text{H}$ couplings respectively. These results have been submitted for publication in Molecular Physics.

Ring inversion in a cyclodecadiene-1,6 (with A. Feigenbaum).

Some time ago we have determined the barrier to ring inversion in 4,9-dithia-cyclodecadiene-1,6. The conformation of this molecule as given by an X-Rays structure determination is depicted in I.



The activation parameters of the interconversion have been determined for the tetradeutero-compound II.

The results are (CS_2 solution):

$$\Delta H^\ddagger = 11.6 \pm 0.5 \text{ kcal/mole}$$

$$\Delta S^\ddagger = -2.5 \pm 2 \text{ eu}$$

Best wishes for the New-Year and much success for TAMUNMRNL.....

Cordially yours,

D. Crepau

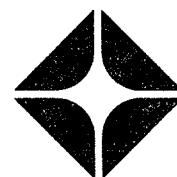
D. CREPAUX

A. Feigenbaum

A. FEIGENBAUM

J.M. Lehn

J.M. LEHN



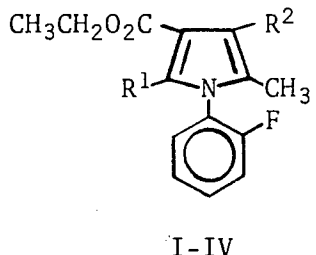
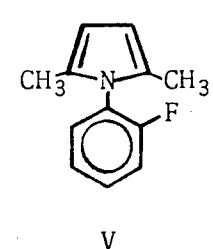
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Dear Barry,

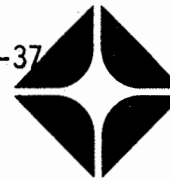
Title: Angle Dependent Long Range H-F Coupling

The angle dependence of long range hydrogen-fluorine coupling over a 4 or 5 bond interval has been noted by several workers.¹ We have observed an interesting example of the angle dependence of long range hydrogen-fluorine coupling over 6 intervening bonds.

The coupling constant, $J_{CH_3, F}$, in the series of 1-(2'-fluorophenyl)pyrroles as shown below, appears to be sensitive to the spatial orientation of the methyl and fluorine groups. This can be illustrated from the hydrogen-fluorine coupling of $J_{CH_3, F} = 1.3$ Hz for compounds I and II, and $J_{CH_3, F} = 0.7$ Hz in the case of compounds III through V. In addition, we have determined the corresponding barriers to rotation about the N-phenyl bond in these compounds as $\Delta F^\ddagger < 11$ Kcal/mole for compounds I and II, and $\Delta F^\ddagger > 25$ Kcal/mole for the compounds III through IV.

 I-IV	Compound	R ¹	R ²	$\pm J_{CH_3, F}$
 V	I	H	H	1.3
	II	H	Cl	1.3
	III	Cl	H	0.7
	IV	Cl	Cl	0.7
	V			0.6

Thus, a minimum average coupling constant of 0.7 Hz is observed when there is a large contribution of a conformation in which the phenyl-pyrrole rings are perpendicular, as in compounds III through V. For those structures in which the rotational energy barrier is relatively low, and there is an increased contribution of a conformation in which the C-CH₃ and C-F bonds are more coplanar, a larger coupling constant is observed. The long range methyl-fluorine coupling constants thus appear to be dependent upon the dihedral angle between the C-CH₃ and C-F bonds. The maximum possible coupling



is probably somewhat greater than the 1.3 Hz observed in the compounds I and II which have an average dihedral angle of about 30°.

The NMR work was done on a Varian HR-60 instrument and the long range hydrogen-fluorine coupling in these compounds has been confirmed by both double resonance and selective deuteration. Please credit this letter as the contribution of F. F. Caserio of ARCO Chemical Company. This work was done at the State University of New York at Buffalo.

Sincerely,

R. A. Smith

R. A. Smith

K. M. Wellman²

1. J. Burdon, Tetrahedron Letters, 21 1101 (1965); P. C. Myhre, J. W. Edmonds, J. D. Kruger, J. A. C. S., 88 2459 (1966); A. H. Lewin, J. A. C. S., 86 2303 (1964).
2. Current address: Chemistry Department, University of Miami, Miami, Florida.

БЪЛГАРСКА
АКАДЕМИЯ НА НАУКИТЕ
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

Dec. 26 8
Sofia, the 196

BULGARIAN
ACADEMY OF SCIENCES
INSTITUTE OF ORGANIC CHEMISTRY
Sofia 13

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

Dear Dr. Shapiro:

Thank you for the reminder. I hope that this contribution does not arrive too late to maintain a continuous subscription to the Newsletter.

Determination of the relative configuration of diastereomers
by N.M.R.

We have measured the N.M.R. spectra of the erythro and threo forms of the acids $C_6H_5CHXCH(C_6H_5)COOH$ (solvent $DMSO-d_6$) and their methyl esters (solvents $CDCl_3$ and $DMSO-d_6$), with $X = OH, OOCCH_3, NH_2, NHCH_3, NHC_6H_5, NHCONH_2, NHCONHCOCH_3$ and Br . The following two features of the spectra were noted and may be used for determination of the relative configuration of compounds of this type as well as for quantitative analysis of mixtures of diastereomers.

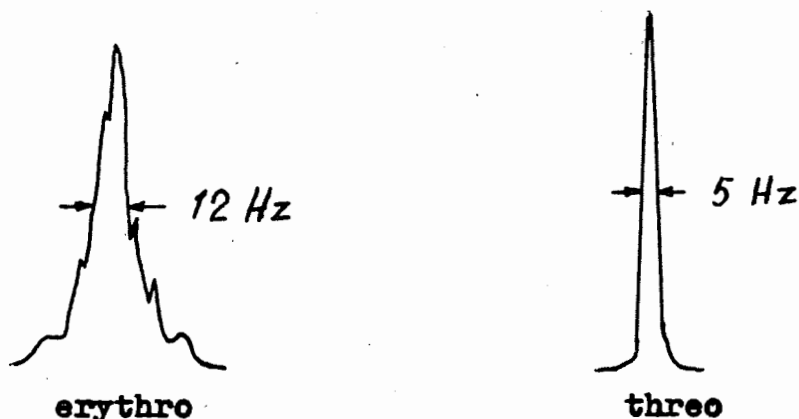
1.(Esters) In all cases the signal of the ester methyl group is in the range 3.35-3.50 ppm (downfield from internal TMS) in the case of erythro forms, and at 3.60-3.70 ppm. for the threo forms, regardless of the solvent ($CDCl_3$ or $DMSO-d_6$).

2.(Acids and esters) In most cases the signal of the phenyl protons in the erythro isomers is much broader and with more pronounced multiplet structure than the signal of the threo isomer (see figure for the respective signals of erythro and threo $C_6H_5CH(OH)CH(C_6H_5)COOH$ in $DMSO-d_6$).

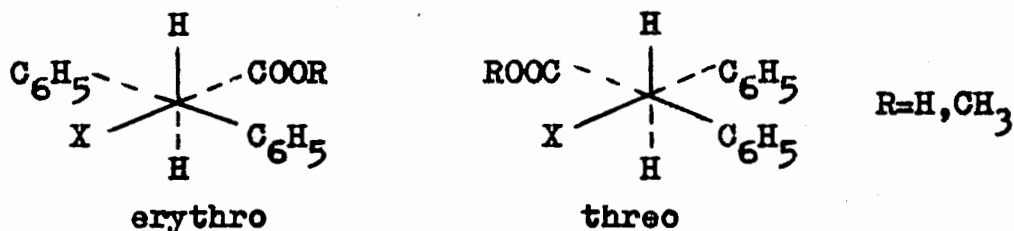
These features can be connected with the conformation of the compounds in question. As already pointed out for some of these diastereomers^{1,2,3}, the vicinal coupling constants are in the

Prof. Bernard L. Shapiro

Page 2



range 7.5-11.5 Hz both for the erythro and threo isomers, suggesting favored conformers with antiperiplanar protons:



It seems that the shielding of the ester methyl group in the erythro forms results from the proximity of the phenyl group, whereas the apparent "equivalence" of the phenyl protons in the threo form is due to their more symmetrical location and absence of gauche polar substituents.

-
- 1) N.D. Berova and B.J. Kurtev, C.R. Acad. Bulg. Sci. 21, 557 (1968).
 - 2) M. Lyapova and B.J. Kurtev, in press.
 - 3) A.R. Katritzky, M.R. Nesbit, B.J. Kurtev, M. Lyapova and I.G. Pojarlieff, in press.

Happy New Year!

Yours sincerely,
Stefan L. Spassov
 Stefan L. Spassov

University of Notre Dame

College of Science

Notre Dame, Indiana 46556

Department of Chemistry

December 31, 1968

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

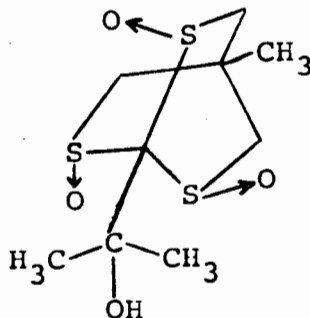
Intrinsically Anisochronous Nuclei; Position Available

Dear Barry:

I am well aware that you have come to hate "news" about just another case of magnetic nonequivalence almost as much as the ominous magnet cooling coils. Maybe you will agree that the following is not "just another case", or maybe you won't. Anyway, here goes.

It has been recognized for some time that the time-averaged chemical shift difference between geminal nuclei or groups of nuclei in molecules of the type RCG_2CXYZ is partly due to differences in conformer populations and partly due to an intrinsic effect ("intrinsic diastereotopism"), but their relative importance has been open to speculation and controversy. Morton Raban's (TL 3105 (1966)) calculation for $CF_2BrCFBrCl$ and $CF_2BrCHBrCl$ provides the only unambiguous evidence for an intrinsic contribution. Challenged by a statement made by Drs. Martin in their review article "... ce terme est très difficile à évaluer expérimentalement l'égalité des populations conformationnelles ne pouvant être obtenue qu'à haute température", Gerald R. Franzen in my laboratory has synthesized a series of "propeller" molecules of the general formula $RCG_2C(X^*)_3$, where the X^* are identical chiral substituents having the same configuration. In these compounds the conformer populations are exactly equal by symmetry and the measured time-averaged chemical shift difference can therefore arise only from intrinsic diastereotopism.

Here is an example. The AA'A"BB'B" spectrum of the ring methylene

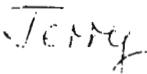


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protons proves the desired propeller stereochemistry of the sulfoxide groups. The geminal methyl groups show up as a doublet with a solvent-dependent chemical shift difference, $\Delta\nu$ in Hz at 60 MHz: pyridine, 1.96; DMSO, 0.90; D₂O, 0.40; CDCl₃, <0.2.

I expect to have an opening for a postdoctoral position in September 1969 for somebody who would like to get involved in some rather sophisticated dynamic studies by NMR. Preferred consideration will be given to individuals with a solid background in NMR and computer programming and with some working knowledge of electronics. Interested applicants should write to me as soon as possible.

Sincerely yours,


Gerhard Binsch

GB:mm

3 January 1969

varian/611 hansen way/palo alto/california 94303/u.s.a./415/326-4000



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

Theoretical Spectra from a Small Computer

Dear Barry,

One attractive solution to the perennial spectrum analysis problems that beset the NMR spectroscopist is to program a small dedicated computer to calculate theoretical NMR spectra. Provided that calculation and display are fast enough, one can dispense with the normal iterative procedure by making small manual adjustments to the input parameters until the experimental spectrum can be fitted satisfactorily. This could also be made to serve a didactic function, giving the operator an almost intuitive grasp of the relations between molecular parameters and the form of complex spectra.

Hanspeter Benz has programmed a Varian 620i computer for this purpose. Matrix diagonalization is accomplished by the Givens-Householder (GH) method, since this is considered to be much faster than the more common Jacobi rotations method (JR) because each iteration of the JR routine involves three square root operations (each of which takes as long as 1/2 millisecond), whereas the GH routine has only one square root operation per iteration. It is also estimated that the GH method gives a higher accuracy for limited word length since the total number of iterations is much less than in the JR routine. Provision can be made for first-order features by putting the relevant off-diagonal elements equal to zero.

The calculation is performed in floating point arithmetic with the exception of the storage of the eigenvectors. A general four-spin calculation takes about 3 seconds, while a five-spin case takes about 10 seconds. A 4K memory is required for a five-spin calculation with plot routine, or for a six-spin calculation without plotting or ordering of the spectral frequencies. The accuracy of the frequencies is about 0.1%, and of the intensities about 2%.

Spectra are plotted typically on an HA100D recorder using a Lorentz line shape with variable width, arbitrary range and scaling, and a program which slows down the horizontal sweep while recording peaks ('constant pen speed'). We hope to have oscilloscope presentation soon.

We show as example the theoretical proton spectrum of trivinylphosphine calculated as an ABCX case (using the 'first-order' approximation for couplings to X) compared with the two ABC subspectra obtained through the 'effective Larmor frequency' approximation.

Yours sincerely,

Ray

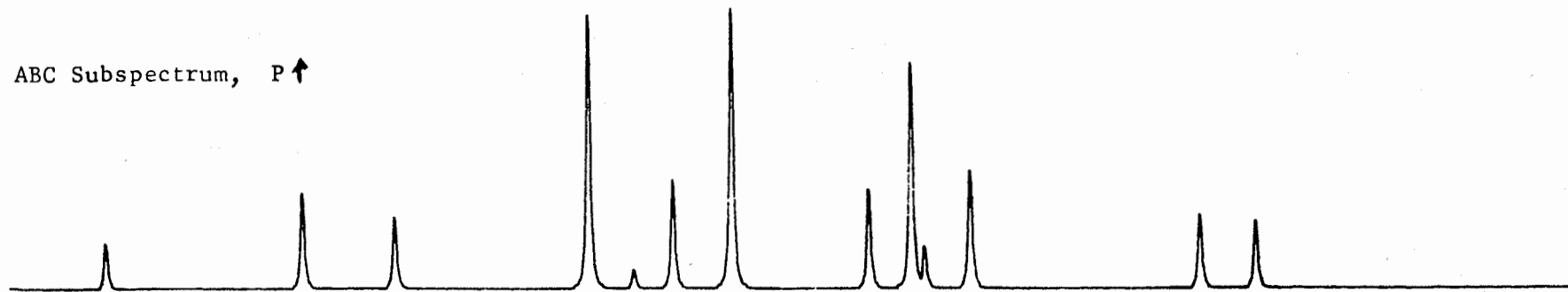
Ray Freeman

H. Benz

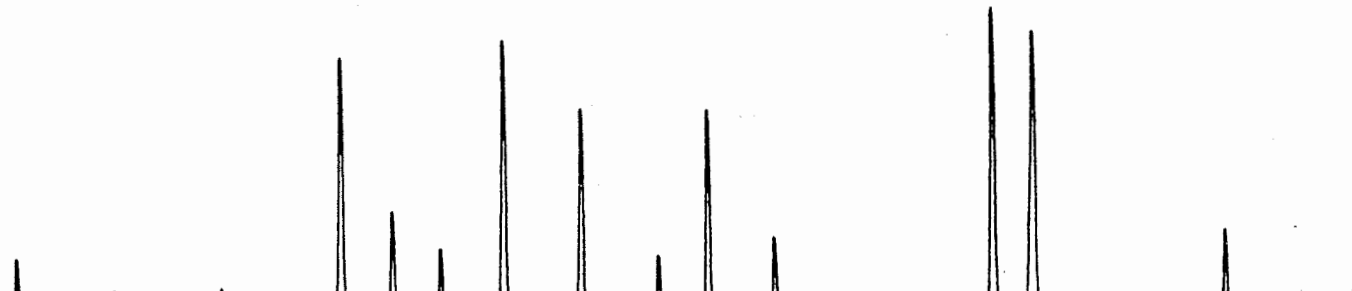
Hanspeter Benz

PROTON SPECTRA OF TRIVINYLPHOSPHINE

ABC Subspectrum, $P \uparrow$



ABCX Spectrum



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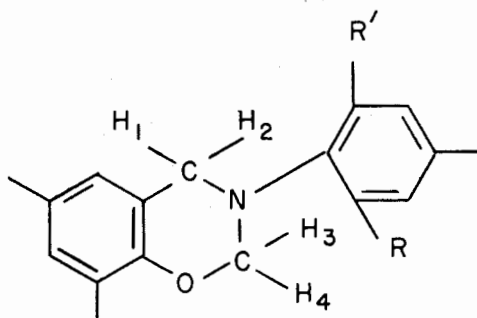
December 31, 1968

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

Dear Barry:

Hindered Rotation in Aryl Substituted Benzoxazines

In a recent letter from Fehlner and Colebrook (TAMUNMRN #123) they described hindered rotation in substituted quinazolinones. Drs. K.U. Ingold and E.C. Horswill have been interested in the chemistry of some similar ring compounds and I looked at the hindered rotation.



- I, $R=R^1=CH_3$
 II, $R=CH_3$, $R^1=H$
 III, $R=(CH_3)_2CH$, $R^1=CH_3$
 IV, $R=(CH_3)_3C$, $R^1=H$

In addition t-butyl groups are located at some of the positions shown by the lines in the different compounds.

No hindrance to rotation (i.e. single lines for protons 1 and 2 and protons 3 and 4) could be observed in the proton resonance of I and II even at $-80^\circ C$. For compound III hindered rotation could be observed at low temperature while compound IV had to be heated in order to observe free rotation. In the limit of slow rotation a pair of well resolved AB quartets could be observed for compounds III and IV.

- 2 -

Compound III	$\delta 1$ and 2	3.87 and 4.65	$J_{1-2}=17.3$ Hz
	$\delta 3$ and 4	4.87 and 5.10	$J_{3-4}=10.2$ Hz
Compound IV	$\delta 1$ and 2	3.95 and 4.61	$J_{1-2}=16.8$ Hz
	$\delta 3$ and 4	4.88 and 5.03	$J_{3-4}=9.7$ Hz

In all the compounds protons 1 and 2 give significantly broadened lines both at the limits of rapid rotation and slow rotation. We attribute this to long range spin coupling to a proton or protons on the adjacent aromatic ring.

The rate data were obtained by comparison of experimental and computer generated spectra. The theoretical spectra were generated for a given lifetime and then broadened by a convolution integral corresponding to the line width in the absence of exchange. Thermodynamic parameters were obtained from the averaged rate data of the two AB sets for each compound.

Compound III $\Delta H^\ddagger = 10.8 \pm 0.6$ kcal/mole $\Delta S^\ddagger = -4 \pm 2$ e.u.

Compound IV $\Delta H^\ddagger = 16.9 \pm 0.3$ kcal/mole $\Delta S^\ddagger = 0.4 \pm 0.2$ e.u.

The change in activation enthalpy is what one might expect in going from an isopropyl to a t-butyl group. The activation entropies are normal in marked contrast to those reported in the previously quoted contribution.

Yours truly,



S. Brownstein.

SB/dn

THE UNIVERSITY OF LIVERPOOL
DEPARTMENT OF INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY

TELEPHONE: ROYAL 6022
Extension 356



THE DONNAN LABORATORIES,
THE UNIVERSITY,
LIVERPOOL L69 3BX.

INTER-RING F - F COUPLING IN PENTAFLUOROPHENYL COMPOUNDS OF GROUP IV ELEMENTS

The ^{19}F line widths of the above compounds have been shown^{1,2} to increase progressively as the number of pentafluorophenyl groups in a compound is increased. There appear to be three possible explanations: (i) there is hindered internal rotation of the pentafluorophenyl groups (ii) the T_2 values for the ^{19}F nuclei are small when extensive fluorine substitution is present (iii) F-F coupling between the rings is taking place. Explanation (i) has been eliminated because we have found that the line widths are independent of temperature over the range 20 - 70°C. T_2 values have been obtained by assuming $T_1 = T_2$ and by measuring T_1 using the saturation-recovery technique.³ Line widths were calculated from the equation $\Delta\nu = (\pi T_2)^{-1}$ and the values are listed in the table:

T_1 Values (± 0.5 sec) of Perfluorophenyl Group IV Compounds

Compound	$^1\text{H}^*$	^{19}F ortho	^{19}F meta	^{19}F para	$\Delta\nu_{\text{calc}}$ (cs^{-1})
$(\text{C}_6\text{H}_5)_3\text{GeC}_6\text{F}_5$	2.7	3.0	2.6	3.1	0.1
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{C}_6\text{F}_5)_2$	3.1	2.5	2.2	3.1	0.1
$\text{C}_6\text{H}_5\text{Ge}(\text{C}_6\text{F}_5)_3$	2.8	4.4	4.0	4.4	0.08

*It is not possible to distinguish between ortho, meta and para positions at 56.4 Mc s^{-1} .

It may be seen that the calculated line widths are much smaller than those observed but in any case decrease, if anything, with increased pentafluorophenyl group substitution. We are left with explanation (iii) to account for the line broadening. The necessary F - F coupling would only have to have a magnitude of about 0.5 cs^{-1} . From a study of the contact shifts of triphenyl germanium (IV) NN'-diethylaminotroponeimineates, Eaton and McClellan⁴ concluded that there is no conjugation between the aromatic ligands. Thus it seems likely that the F - F long range coupling is transmitted via a sigma or a through-space mechanism. While on the topic of through-space coupling, we were surprised to read in Manatt's recent contribution (TAMUNMRN 120/46) that this effect requires "reinstatement".

In the course of this investigation we obtained the ^{19}F chemical shifts of $\text{C}_6\text{H}_5\text{Ge}(\text{C}_6\text{F}_5)_3$ and these are reported below.

^{19}F Chemical Shifts (± 0.1 ppm) of $\text{C}_6\text{H}_5\text{Ge}(\text{C}_6\text{F}_5)_3$

	Ortho	Meta	Para
Referred to internal CFCl_3	124.4	159.5	148.7
Referred to internal C_6F_6	37.9	2.8	13.7

The value of the para minus the meta shift (10.9 ppm) is very close to the value predicted (Figure 3 of reference 2) earlier.

L.H. Sutcliffe G.J.T. Tiddy.

1. D.E. Fenton, A.G. Massey, K.W. Jolley and L.H. Sutcliffe, Chem. Comm. 1967, 1097.
2. K.W. Jolley and L.H. Sutcliffe, Spectrochim. Acta, 1968, 24A, 1191.
3. A.L. van Geet and D.N. Hume, Anal. Chem., 1965, 37, 983.
4. D.R. Eaton and W.R. McClellan, Inorg. Chem., 1967, 6, 2134.

11 Garran Sheineona,
Santry, Dublin 9, Eire.

December 30, 1968.

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

Title: Vinyl Proton Shifts

Dear Barry:

Your reminder of impending surgery reached me at a most embarrassing time. Could you offer at least one credit to a subscriber who is temporarily unemployed?

The following may interest some of your readers. I acknowledge herewith observations of Steven Danyluk.

In compounds of the general type $R_nR'_mMV_{14-m-n}$ the shieldings (and couplings, although of less significance) of the vinyl protons are related by equations of the type

$$\delta_\alpha = K_\alpha + N_p\phi_\alpha + N_mMe_\alpha + N_eCl_\alpha + N_vVi_\alpha$$

where R, R' are phenyl, methyl or chloro groups and M is C, Si, Ge, Sn or Pb; where K is a constant for a given M; N_p, N_m etc. represent the number of phenyl, methyl etc. groups and ϕ, Me , etc. is the shift of the α proton resonance attributable to the presence of one ϕ, Me group etc. attached to M. If the proton labelling used in IITNMRN No. 113 by the writer is adopted then α stands for proton a, b or c.

If the shift due to a Vi group is taken to be zero, K's may be determined from the tetravinyl compounds. The constants ϕ, Me etc. can be determined from a list of data such as given in the reference above and are found to be of either sign.

It may be easily verified that relation (1) obtains where M=Si from the data referred to above. It appears to be true for M=C and Sn and also for other attached groups such as H and ethyl. If in fact this linearity proves to be true for all M indicated above and can be extended to other groups it is obvious that cataloguing of shift data could be greatly facilitated. The shifts can be predicted to within about 2 parts in 10^8 . We will report later when the constants are more precisely evaluated and more data collected.

Sincerely yours,

Sean Cawley. *Sean*

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