Texas A & M University
N—M—R
Newsletter

No. 120
SEPTEMBER, 1968

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These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.

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Deadline Dates: No. 121: 7 October 1968
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All Newsletter correspondence, etc., should be addressed to:

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

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

9 September 1968

Concerning Financing of TAMU NMR Newsletter

With great reluctance I must revive the annual discussion of financing the [TAMU] NMR Newsletter. I do not find soliciting money a congenial activity, and this will be the first and only general public airing of the problem for the coming year. This year, as last, letters were sent to all companies, government labs, and research institutes receiving the Newsletter, calling for voluntary contributions (amount not specified). Last year, such a scheme worked very well and a list on the back cover of each Newsletter indicated those companies, etc., who have carried the financial load for the past year. Many of these companies have contributed again this year, although in several cases this has been at a reduced rate--which I understand and with which I can, of course, take no exception.

However, the over-all level of response this year has so far been far less than will be required to operate the Newsletter for the entire year. I hope those who have received letters but who have not yet replied will not mind this gentle reminder that we would very much like to hear from them. Those companies, etc., who have somehow been missed are also invited to make their willingness to contribute known. I have made no specific individual pitches to academic recipients on the theory that most academic departments would find it very difficult to provide funds this year. I hope that I am wrong in many cases, and I will look forward to hearing from those academic recipients willing to step forward and join those who have already volunteered. I would point out that it costs approximately $25.00 per year per subscription, even with our low-overhead operation.

Support for the Newsletter can be provided either as a direct contribution or through a subscription fee, for which we can provide invoices where necessary.

We need to raise ca. $4,000 in addition to amounts already received or promised. If we do not, our Newsletter will probably cease publication approximately March, 1969.

B L Shapiro

B. L. Shapiro

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA 90024

August 6, 1968

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

Title: C^{13}-H and vicinal coupling constants in cyclohexane; comments on the letter of Gerhardt Binsch

Dear Barry,

In work with G. Ohmurny and D. Learn, we have prepared cyclohexane-$\underline{d}_{10}$-cis-1,2-$\underline{h}_2$ and cyclohexane-$\underline{d}_{10}$-trans-1,2-$\underline{h}_2$ and have examined the proton spectra (deuterons decoupled) of these compounds at room temperature and at about -100°. Analysis of the AB spectrum in the cis compound and of the C_{13} satellites as ABX spectra in the trans compound gave the following parameters:

$\delta_e - \delta_a$ = 0.477 ppm (-100°, cis)
= 0.480 ppm (-100°, trans)

C^{13}-H isotope shift = 0.006 ppm (-100° and r.t., trans)

J_{ae} = 3.59 Hz (-100°, cis)

J_{ae} = 13.31 Hz (-100°, trans)

J_{ee} = 3.06 Hz (-100°, trans)

$1/2\ (J_{aa} + J_{ee})$ = 8.16 Hz (r.t., trans)

$J_{C^{13}-H_a}$ = 122.6 Hz (-100°, trans)

$J_{C^{13}-H_e}$ = 126.6 Hz (-100°, trans)

$1/2\ (J_{C^{13}-H_a} + J_{C^{13}-H_e})$ = 124.6 Hz (r.t., trans)

The conformational dependence of the C^{13}-H coupling constant is of interest.

Comments on the letter (No. 117-21) of Gerhardt Binsch concerning dynamic NMR studies

We want to take issue with the statement, "People interested in reliable results might in the future want to avoid the excessively simple spin systems.. ...". Since we spend a lot of time and trouble synthesizing deuterated compounds to get simple spectra, it might appear that we have been wasting our time. Such, however, is not the case, as shown by the following discussion:

First of all, one has to determine whether the exchange involves primarily chemical shifts or coupling constants.

If chemical shifts are primarily involved, one should operate as far as possible with an uncoupled system. For example, consider a compound with two protons undergoing intramolecular exchange: If ν_{AB} = 2 Hz, J_{AB} = 20 Hz, the spectrum at fast exchange will consist of a single line and at slow exchange of an AB quartet with the separation of the inner pair of 0.1 Hz and the intensity of each member of the outer pair of only about 0.12% that of the (combined) inner pair. Thus under practical conditions of resolution, sensitivity and compound concentration, no information whatever would be obtained from the nmr spectrum, even though the information is theoretically available. Now contrast this with the situation where we have simplified the spectrum by replacing one proton by deuteron and where we measure the proton spectrum with the deuterons decoupled (this is not strictly necessary because the spectrum is now first order - however, because the rate of quadrupole relaxation varies with temperature, decoupling is very desirable). The slow exchange spectrum is now an equal intensity doublet of separation 2Hz and the coalescence of this doublet into a single line is easily observable. Thus removing the effect of coupling has enabled us to obtain rate constants which are unavailable otherwise.

If coupling constants are primarily involved in the averaging (and this is the example which Binsch presented) then it is obvious that the molecule must contain at least two magnetic nuclei so that a coupling constant can exist. An extreme example is our work on the determination of the rate of bond shift in cyclooctatetraene (J. Am. Chem. Soc., 84, 671 (1962), where bond shift does not change chemical shifts but does change H-H coupling constants. Thus the (normal) spectrum gives no information on rates of bond shift, because coupling constants are not observable in this system.
However, the C^{13} satellites do give information on the H-H coupling constants, and these bands are temperature dependent and do give the rate constant for bond shift. The C^{13} satellite spectra, however, are extremely complex because correct analysis involves a strongly coupled system (ABCDEFGMX at low temperatures). We doubt that the spectrum, which does not show distinct resolved lines, can be analyzed, let alone the temperature dependence of this spectrum. Thus only rough rate constants can be obtained. We are in the process of making cyclooctatetraene-1,2,3,4,5,6-d_6, where the low temperature C^{13} satellite spectrum is the superposition of two ABX systems and the high temperature spectrum is a single ABX system, and which is therefore amenable to analysis.

Thus we believe that it is best, in general, to make the system as simple as possible, but of course of a type where the process being studied causes at

least two lines in the spectrum to coalesce into one line. Since in most proton spectra line widths are largely determined by magnetic field inhomogeneities (in the slow or fast exchange limit) and thus have the same line widths, the most accurate rate data can be obtained with the greatest separation of the lines which coalesce at higher temperatures. Although it may appear (superficially) convenient to have several sets of lines of different separations and thus different coalescence temperatures, this does not result in more accurate rate data than the study of a single pair of lines, provided that is the one with the greatest separation.

Where chemical shifts are being averaged, it is advantageous to obtain spectra at as high a magnetic field as possible since for a given rate constant the line broadening in the region of moderately fast exchange ($T > T_c$) is proportional to the square of the frequency separation in the absence of exchange, whereas magnetic field inhomogeneities depend on instrumental factors and appear to be proportional to the magnetic field, i.e., to the frequency separation for chemical shifts.

In our opinion, in the very simple systems (e.g., cyclohexane-$\underline{d}_{11}$) where sites are equally populated and chemical shifts show only very slight temperature dependence, complete line shape analysis does not give appreciably better results than simple line width measurements. In general, the application of complete line shape analysis is probably a good thing, provided that it does not lead to the belief that such a procedure guarantees correct kinetic parameters, and thus leads to a neglect of other important sources of error.

Yours sincerely,

Frank

F. A. L. Anet

FALA:bgg
Via Airmail

120-4

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

Pittsburgh Coal
Research Center

July 25, 1968

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Position Available

The U. S. Bureau of Mines is interested in interviewing B.S. or M.S. graduates in chemistry or physics (with some electronics background) for a full-time position in the field of electron spin resonance spectroscopy. Contact either of the undersigned for further details.

Sincerely yours,

Herb

H. L. Retcofsky
Research Physicist
Spectrometry

Gus

R. A. Friedel
Project Coordinator
Spectrometry

Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

August 5, 1968

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

Dear Professor Shapiro:

CYCLIST: "ERROR"

Due to a misplaced parenthesis, the standard deviation as computed in early editions of Cyclist is incorrect. Users of Cyclist should check that the line following statement 2001 reads: STDEV(I) = SQRTF (sum/(SN-1.)).

It turns out that the ERROR as originally computed is equal to the new ERROR divided by the square root of the number of spectra in the frequency range minus one,

$$(\text{ERROR})(\sqrt{SN-1}) = \text{STDEV(I)}$$
$$= \text{SQRTF (sum/(SN-1.))}$$

so that the correction can be made in this manner without rerunning the program.

We apologize for this oversight and for the frustration it may have caused users. S.A.T.S.

Sincerely,

Denis

DEW:smm

Denis E. Wisnosky

Bob

Robert J. Kostelnik

120-6

N.V. PHILIPS-DUPHAR
POSTBUS 2 - WEESP - NEDERLAND

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VITAMINE - WEESP

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

Uw ref./Your ref.	Onze ref./Our ref.	Afd./Dept.	Datum/Date
	FVD/AK/71	56632	July 30, 1968

Dear Dr. Shapiro,

Modification of the 4th-order network on the Varian HA-100

On the Varian HA 100 the current adjustment of the 4th order is nonlinear (fig.1, curve A). If a large setting of the 4th order is required, the adjustment is very critical. We have modified the network (figs. 2 and 3) in order to obtain a more linear relation between 4th-order setting and the current (fig.1, curve B). The ASZ 15, together with the other additional components, is mounted, electrically insulated, on a copper heat sink (100 x 70 x 1 mm) screwed to the power supply inside the Homogeneity Control System VK 3531 B.
Plotting the lock signal indicator meter reading (ITT NMR Newsletter 111-1) against the 4th-order setting, after readjustment of curvature and Y gradient, leeds very quickly to the optimum 4th-order setting by a nearly linear interpolation. Instead of the lock signal indicator the recorder of the HA 100, too, can be used, with the shim switch on.

Sincerely yours,

N.V. Philips-Duphar
Research Laboratories, Dept.32

F.W. van Deursen

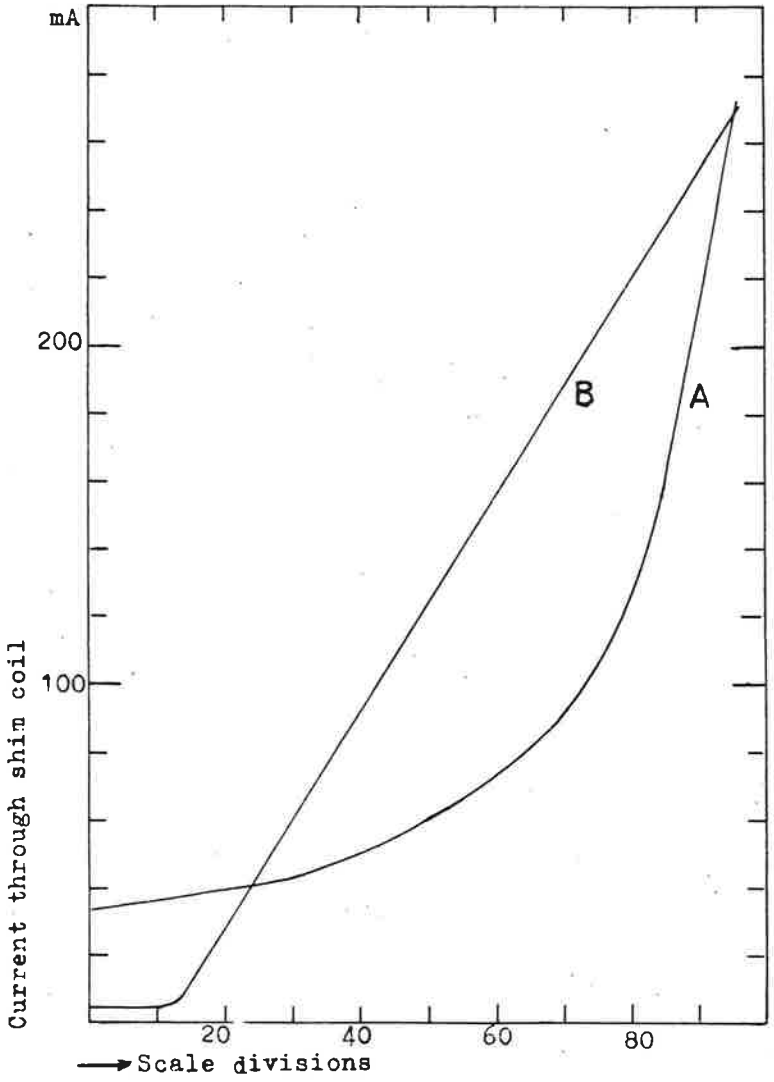


FIG. 1

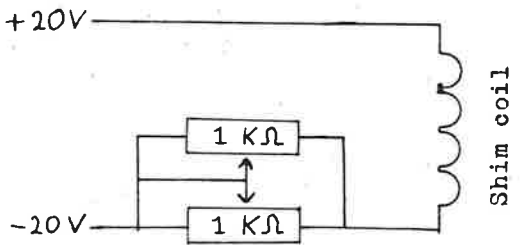


FIG. 2 Original network

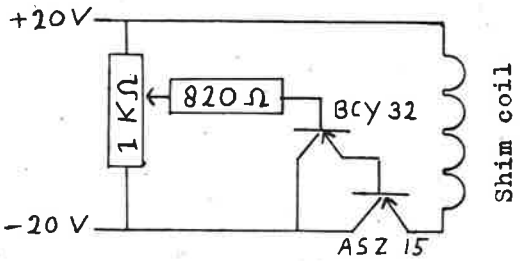


FIG. 3 Modified network

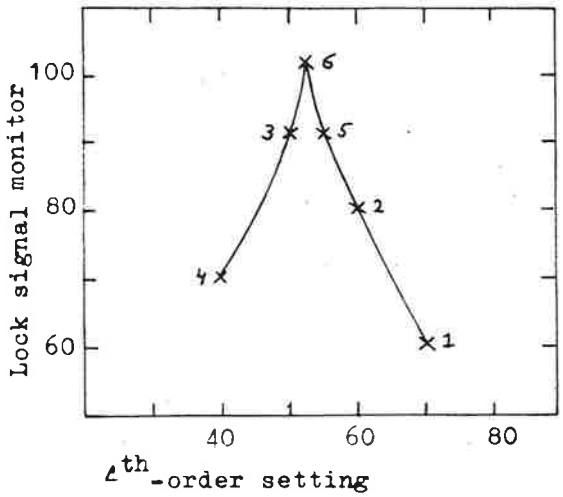


FIG. 4

(The numbers indicate the sequence of the measurements)

120-8

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 – TEL. 430422
VORSTEHER: PROF. DR. P. HUBER

Prof. Dr. P. Diehl
Dr. C.L. Khetrapal

Basel, August 1, 1968/ea

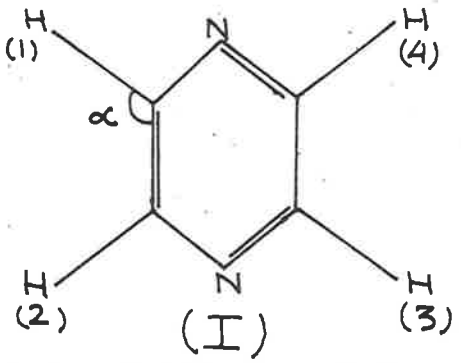
Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University

Stanford, California 94305
USA

Uncertainties in the determination of geometry of pyrazine in the liquid crystalline nematic phases

Dear Barry,

we have investigated pyrazine (I) in the



(I)

liquid crystalline nematic phases from the point of view of studying the geometry of the molecule. The study has been made in a) 30 mole % solution in p-p'-di-n-hexyloxyazoxybenzene at 80° C, b) 9 mole % solution in p-methoxy benzylidene-α-methyl cinnamic acid propyl ester at room temperature (∽ 27° C) and c) 15·4 mole % solution in anisole azophenyl- n-capronate at 55° C. In each case the spectrum consists of two groups of lines placed symmetrically about the centre. The respective intensity distribution is 2:1:4:1, 2:2:3:1 and 2:1:4:1. The following values of the direct couplings are obtained:

a) D_{12} = -317·5 ± 1·0 Hz; D_{14} = -86·0 ± 1·0 Hz; D_{13} =-50·0± 1·0Hz

b) D_{12} = -378·8 ± 0·7 Hz; D_{14} = -30·0 ± 1·5 Hz; D_{13} =-30·0±1·0 Hz

c) D_{12} = -561·7 ± 1·0 Hz; D_{14} = -17·2± 1·0 Hz; D_{13} =-28·4±1·0 Hz

The various direct couplings are related to the ratios of the interproton distances in this molecule by the following equation:

$$D_{14}\, x^5 - D_{13}\,(1+x^2)^{5/2} + D_{12} = 0 \quad \text{where} \quad x = r_{14}/r_{12} \qquad (I)$$

Equation (I) with the D-values reported in (a) above has no solution in the range of positive x but the curve passes through a minimum at x = 1·53. However, if the D-values are changed by 1 Hz, the accuracy of measurement, two solutions are obtained at $x \simeq 1{\cdot}391$ and 1·755. A change of the D-values by the same amount in the other direction again does not give a solution for positive x. This gives a large uncertainty to the value of x under these conditions. The situation could not be improved even by changing the concentration and the temperature. ~~even.~~

In the room temperature liquid crystal spectrum, two lines of relative intensity one each overlap and this corresponds to the fact that D_{14} and D_{13} are equal within limits of resolution. This reduces the accuracy of the determination of the D-values and hence uncertainties in the value of x are quite large ($x \simeq 1{\cdot}56 \pm 0.10$). Assuming the CNC and the CCN angles reported by Coulson and Looyenga (J. Chem. Soc. 6592 (1965)) and the CC and the CN bond lengths given by Wheatley (Acta cryst. 10, 182 (1957) one obtains $\alpha = 124^\circ \pm 4^\circ$.

The spectrum in anisole-azophenyl-n-capronate is determinated by D_{12} with the result that the |para direct coupling| is larger than the |meta| . This spectrum gives a fairly accurate estimate of the x-parameter (x = 1·66±0.02) corresponding to $\alpha = 120^\circ\ 22' \pm 45'$ under the above assumptions of the ring geometry.

Yours sincerely,

Peter

(P. Diehl)

C. L. Khetrapal

(C.L. Khetrapal)

20-10

PROFESSOR OF ORGANIC CHEMISTRY
W. D. OLLIS

TELEPHONE NO. 78555 EXT. 462

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SHEFFIELD
S3 7HF

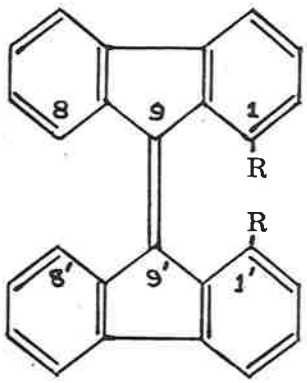
3rd August, 1968

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

Dear Barry,

Configurational isomerism of 9, 9'-bisfluorenylidenes

1, 1'-Disubstituted-9, 9'-bisfluorenylidenes would be expected to adopt non-planar conformations in order to diminish the strain associated with steric interaction between hydrogens or substituents in positions 1, 1', 8, and 8'. Thus, in principle 1, 1'-disubstituted-9, 9'-bisfluorenylidenes could be associated with a number of non-planar chiral conformations related to the cis- and trans-diastereoisomers (I and II).



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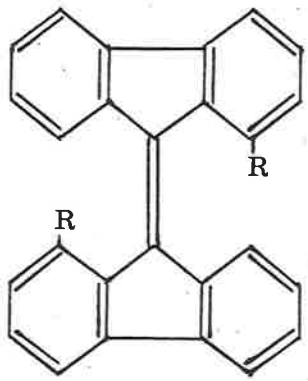

(II)

In order to investigate this situation, the temperature-dependence of the n.m.r. spectra of various derivatives has been studied in which the substituents R contain prochiral groups. Evidence for chirality is provided by the n.m.r. spectrum of the 1,1'-diethoxycarbonyl-9,9'-bisfluorenylidene (R = CO_2Et), whose n.m.r. spectrum shows an ABX_3 system at room temperature which changes to an A_2X_3 system at higher temperatures. The coalescence temperature for this compound in pentachloroethane solution was 111 ± 5^{o} and this corresponds to $\Delta G_{T_c}^{\ddagger} = 19.3 \pm 0.3$ kcal./mole. Similar results have been obtained for other esters and their study has provided evidence for conformational equilibria involving conformers possibly associated with both cis- and trans-configurations (I and II).

It is clear that the conformational behaviour of derivatives of 9,9'-bisfluorenylidenes is rather more complicated than might have been expected, but we are hopeful that the study of their temperature-dependent n.m.r. spectra will provide an understanding of the processes involved.

Yours sincerely,

I. R. Gault W. D. Ollis I. O. Sutherland

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Buenos Aires, 5 August, 1968

Dr. BERNARD L. SHAPIRO.
Texas A&M University.
College Station, Texas 77843.
U.S.A.

Double resonance spectra of some ABX_2 systems.

Dear Dr. Shapiro:

We have been interested recently in trying to determine the magnitudes and signs of the J constants in 2,3 di Cl propene and in 2,3 di Br propene.

a) In the brom derivative no splitting due to J_{BX} was present, and as the halfwidth of the B lines was bigger than of the A lines, we apply the Indor technique for detecting the B lines. The plotting of the average Indor data (fig. 1) indicates that each of the B lines is in fact an almost perfectly overlapping triplet with $J_{BX} = (0.10 \pm 0.01)$Hz, and that the frequencies of the maxima of fig. 1 are the positions of the components of this triplet. Those experimental results are coherent with an ABX_2 energy level diagram with all the J's of the same sign.

b) The 2,3 di chlor propene has a well resolved spectrum but the value of J_{BX} is rather small (0.26 Hz) to allow a sign definition according to the intensity of their external B lines relative to the internal ones. For that reason we made a partial decoupling experiment. We optimize first the values of V_2 and of $\frac{\gamma H_2}{2\pi}$ corresponding to the collapsing of the triplets originated by J_{AX} and J_{BX}. The theoretical

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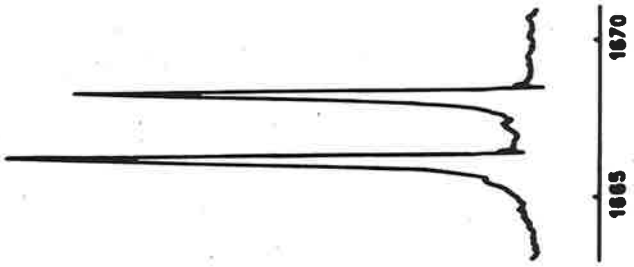
//

D.R. spectra of this substance for different relative signs of the J's were calculated, and the results favoured the same relative signs for all the J's (fig. 2).

Sincerely yours.

Enrique Ferrá

Dora G. de Kowalewski



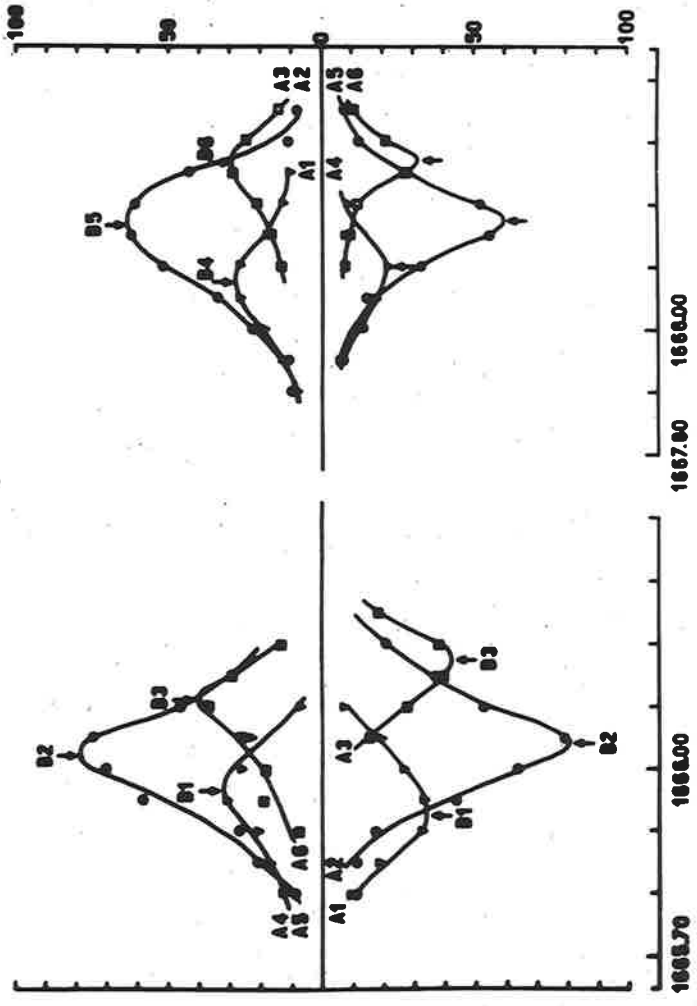
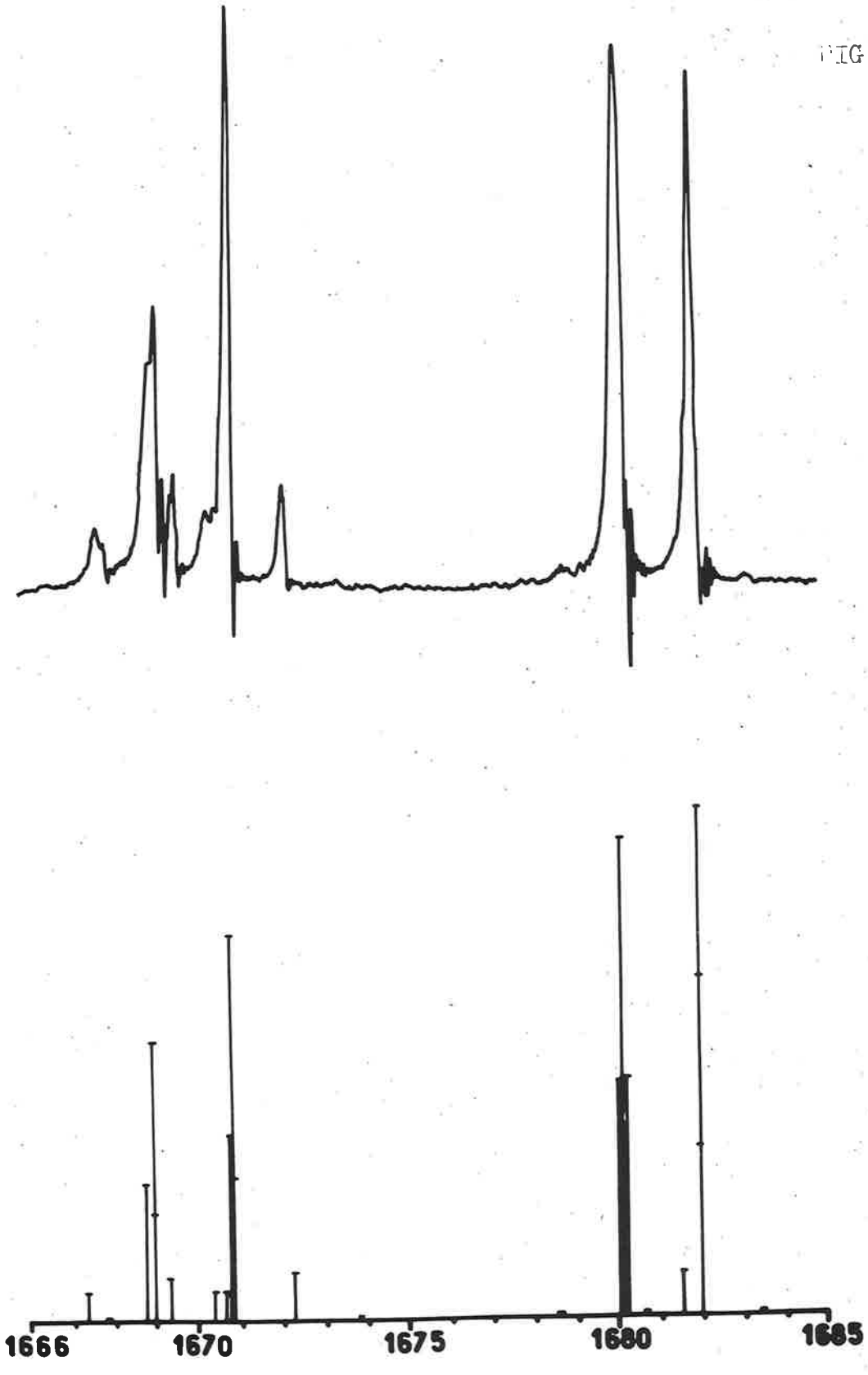


FIG. 1

FIG 2



INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS
CZECHOSLOVAK ACADEMY OF SCIENCE
PRAHA-SUCHDOL 2

August 6, 1968

Prof. B. L. S h a p i r o
Texas A & M University
College Station,
T e x a s 77843

re: NMR parameters vers. electronegativity

Dear Professor Shapiro:

Recently, a referee compelled us to make a small literature survey of the existing linear dependencies of the NMR parameters upon the electronegativity. The survey revealed shocking differences in the values of electronegativity that various (and even the same) authors had used for the same substituent in supposed-to-be the same scales.

As our aim was to determine how significant are the slopes found in these dependencies we repeated the least-square fit calculations after choosing "the best electronegativity values". The results of these calculations are indicated in the two accompanying tables for the cases of J_{cis}'s and internal chemical shifts' dependencies in the classes of compounds which were of our interest (E_{CD} and E_H denote Cavanaugh-Dailey and Huggins electronegativity scales, resp.)

In the tables only the slopes for 1,1-dichlorocyclopropane derivatives are statistically compared with those of other series of derivatives. It was the 1,1-dichlorocyclopropane derivatives for which the intermediate slopes (between those found for saturated and unsaturated series) were claimed by K.L.Williamson and others (J.Am.Chem.Soc. 86, 762 /1964/). The comparison made here shows that the intermediate character is not sufficiently statistically founded.

Sincerely yours,

J. Schraml

Parameters of Least-Square Fit of $E = f \cdot \delta + \varepsilon$ Dependencies

Derivatives of	1,1-Dichlorocyclopropane		Ethane	Hexachloro-norbornene		Norbor-nene	Ethylene	
chemical shift	δ_{cis}	δ_{trans}	δ	δ_{cis}	δ_{trans}	δ_{cis}	δ_{cis}	δ_{trans}
electronegativity scale	E_{CD}	E_{CD}	E_H	E_{CD}	E_{CD}	E_{CD}	E_{CD}	E_{CD}
intercept (elneg.unit)	2.24	2.16	1.77	2.02	1.95	2.08	2.26	2.35
slope x 10^2 (elneg.unit/Hz)	0.95	0.91	1.14	1.19	0.86	0.91	0.79	0.78
correlation coefficient	1.00	0.98	0.96	0.99	0.99	0.98	0.82	0.76
t - test[a]	-	-	-	+	-	-	-	-

[a] Sign + (-) indicates that the difference between the slopes of the given column and that of the corresponding column for 1,1-dichlorocyclopropanes is (is not) significant at 10% significance level.

Parameters of Least - Square Fit of $J_{cis} = \alpha \cdot E_{CD} + \beta$ Dependencies

Derivatives of	1,1-Dichlorocyclopropane	1,1-Dimethylcyclopropane	Hexachloronorbornene	Norbornene	5α-Cholestan-7one	Ethylene
intercept /Hz/	17.52	12.26	12.41	11.12	10.09	22.07
slope /Hz/elneg.unit/	- 2.66	-1.53	-1.36	-0.91	-2.32	-4.50
correlation coefficient	0.96	0.97	0.91	0.90	0.96	0.97
t - test[a]	-	-	+	+	-	+

[a] Sign + (-) indicates that the difference between the slopes of the given column and that of 1st column is (is not) significant at 10% significance level.

OSU

OREGON STATE UNIVERSITY
DEPARTMENT OF AGRICULTURAL CHEMISTRY

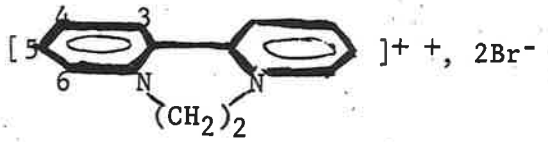
CORVALLIS, OREGON 97331

August 12, 1968

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

Dear Professor Shapiro:

Here is my contribution to the new TAMU NMR News letter. We have completed a proton magnetic resonance study of two biologically active quaternary pyridinium salts and their charge transfer complexes. These compounds are:

Diquat 

Paraquat

As expected from the formula paraquat gave simpler spectra and the coupling constant $J_{2,3}$ = 6.5 Hz. The ring proton spectrum for diquat was very complex and there was considerable overlap of the peaks at 60 and 100 MHz. However, by the courtesy of Dr. L. F. Johnson of Varian Associates we were able to obtain a Spectrum at 220 MHz. The various ring proton coupling constants are:

$$J_{5,6} = 6.0, \quad J_{3,4} = 8.0$$

$$J_{4,5} = 7.5, \quad J_{4,6} = 1.25$$

$$J_{5,3} = 1.5$$

The other proton and the ^{1}H-^{14}N coupling constants were not resolvable. The spectrum also indicated strong ion association between the cation and various anions. For example, I^-, Br^-, $Fe(CN)_6^{-4}$ gave a low field shift of CH_2 proton in diquat and CH_3 proton in paraquat, while the shift was positive when the paramagnetic ferricyanide ion was added. We interpret that the low field shift is due to formation of charge transfer complex between the cation and the anion, while the high field shift in the presence of ferricyanide ion is caused by outersphere ion-pair formation. The existence of charge transfer complex has been confirmed by the observation of charge transfer band in the absorption spectra, where none of the ions show any absorption. We were able to calculate the association constant for this process from the chemical shift changes of $-CH_2$ proton in paraquat, as well as from the optical density measurements.

System	Association Constant K mole^{-1}	
	NMR	Optical Density
Diquat + $K_3Fe(CN)_6$	29	
Paraquat + $K_3Fe(CN)_6$	31	
Paraquat + $K_4Fe(CN)_6$	55	52
Diquat + $K_4Fe(CN)_6$	37	30

Sincerely yours,

R. Haque
Assistant Professor

m11

120-20

G. Englert

c/o F. HOFFMANN-LA ROCHE & CO.

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DEPARTMENT Phy. A.
Eng/hb

15th August, 1968.

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

H-C-H-Bond Angle of Acetonitrile $H_3{}^{13}C$-CN

Dear Dr. Shapiro:

We have previously reported on the measurement of the H-C-H-bond angle of acetonitrile in two nematic solvents (I and II) [1]. In the meantime I have slightly improved the accuracy of these measurements and I should like to give the new results together with those obtained in a third solvent III as follows:

	PMR Data in Solvent		
	I	II	III
∢HCH:	$109^{\circ}(3.5\pm0.5)'$	$108^{\circ}(59.5\pm0.5)'$	$109^{\circ}(11.3\pm1)'$

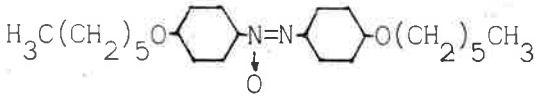
The microwave data [2] were:

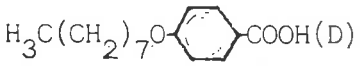
r_o-structure: $109^{\circ}16.5'$

r_s-structure: $109^{\circ}29.5'$

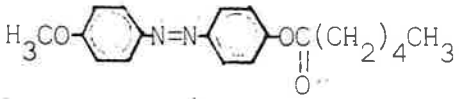
./.

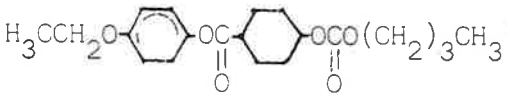
The solvents were:

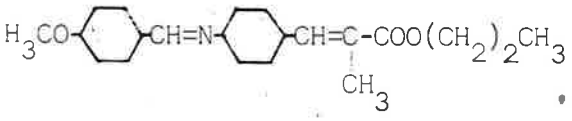
I: 

II: 

III: 3:3:1 mixture of







This mixture was used at 27°C (probe temperature). It is seen that there are small differences in the H-C-H-bond angle, which are believed to be real. The value obtained in solvent III is very close to the r_o-value.

The indirect coupling used for the calculation was $|J_{13_{CH}}| = 136.0$ Hz.

I hope this short contribution will bring me back on your mailing list.

Yours sincerely,

(Gerhard Englert)

1) G. Englert and A. Saupe, Mol.Crystals 1, 503 (1966)
2) C.C. Costain, J.Chem.Phys. 29, 864 (1958)

120-22

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
P. O. BOX 808
LIVERMORE, CALIFORNIA 94550

August 13, 1968

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

Dear Dr. Shapiro:

^{35}Cl NMR of Zinc Complexes

In our last contribution to the Newsletter we described some of our results concerning ^{35}Cl nmr studies of zinc nucleotide diphosphate complexes. We have also extended these studies to nucleotide triphosphate complexes. Perhaps one of the most interesting observations has been the detection of $Zn(NDP)_2$ complexes in dilute solution, i.e., ~5 mM. The presence of these 1:2 complexes, in dilute solution, will require a re-evaluation of nmr data reported in the literature for solutions of much larger concentrations of metal and nucleotides.

We have also extended our ^{35}Cl nmr studies to zinc binding by macromolecules, namely pyruvate kinase. This enzyme catalyzes the following three reactions:

1. ATP + pyruvate $\underset{K^+}{\overset{Mg^{++},\ Mn^{++}}{\rightleftharpoons}}$ ADP + P - enolpyruvate

2. ATP + F^- $\xrightarrow[Mg^{++},\ Mn^{++}]{HCO_3^-}$ ADP + fluorophosphate

3. ATP + NH_2OH $\xrightarrow[Zn]{HCO_3^-}$ ADP + phosphorylated NH_2OH

Mildvan and Cohn (J. Biol. Chem. 241, 1178 (1966) have extensively studied the first two reactions using Mn^{++} as the activating ion and H_2O molecules as the chemical probes. We have studied the third reaction using ^{35}Cl nmr techniques.

The interesting observations are (1) Pyruvate kinase binds four Zn^{2+} ions per molecule as detected in 0.5M KCl solutions, whereas in the identical solution only 2 Mn^{++} ions are bound per molecule of pyruvate kinase. (2) Replacement of the 0.5M KCl by nonactivating 0.5M tetramethylammonium chloride allows pyruvate kinase to bind four Mn^{++} per molecule (Mildvan and Cohn). (3) The chloride ion probe is sensitive to addition of HCO_3^-, indicating a ternary complex in reaction 3, whereas HCO_3^- has no effect on the Mn pyruvate complex.

Sincerely,

Raymond Ward

Raymond Ward
Bert Holder
James Happe

DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
KYOTO UNIVERSITY
KYOTO, JAPAN

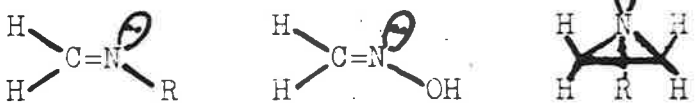
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U. S. A.

August 19, 1968

Dear Professor Shapiro:

The Electronic effect of Lone Pair Orientation on the Nuclear Spin Coupling Constants

It has been accepted that the lone pair electrons on the nitrogen and oxygen atoms affect geminal proton-proton coupling constants in adjacent CH_2 fragment.[1] Recently it has also been reported that there are striking effect of nitrogen lone pair orientation on ^{14}N-C-H and ^{15}N-C-H coupling constants for H_2C = N-R fragments in imines(I) and oximes(II).[2,3]



(I) (II) (III)

We have recently found[4] that the directly bonded ^{13}C-H coupling constant also depends upon the orientation of the nitrogen lone pair electrons in oxime(II) and aziridine(III). And also we would like to note a remarkable effect of the lone pairs on the ^{14}N-C-H and vicinal cis H-H coupling constants for aziridine[4] (Table I).

We are attempting to give a theoretical basis on these definite trend of nuclear spin coupling constants.

DEPARTMENT OF HYDROCARBON CHEMISTRY
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KYOTO, JAPAN

Molecular orbital calculations were carried out for oxime and aziridine by the procedure proposed previously.[5] The evaluation of matrix elements for obtaining molecular orbitals was employed as $H_{rr} = -(I_r + E_r)/2$, where I_r and E_r are the ionization potential and the electron affinity of the rth AO of the valence state. Other parametrizations were taken after the previous procedure. The calculated coupling constants are summarized in Table I where they are compared with the experimemtal results. The trend of the observed coupling constants are well reproduced by the calculation except for the ^{13}C-H and H-H coupling constants in aziridine. Calculations fail to predict the experimental trend of vicinal H-H coupling constants ($J_{cis} > J_{trans}$) for cyclopropane.[5] The reason for these discrepancies in three-membered ring compound is not clear. We are now extending MO calculations of these nuclear spin coupling constants by using a semiempirical SCF-MO theory.

Yours sincerely

T. Yonezawa I. Morishima

T.Yonezawa I.Morishima

References:

(1) J. A. Pople and A. A. Bothner-BY, J. Chem. Phys., 42, 1339 (1965).

(2) B. L. Shapiro, S. J. Ebersole, and R. M. Kopchik, J. Mol. Spectry., 11, 329(1963); C. F. Chang, B. J. Fairless, and M. R. Willcott, ibid., 22, 112(1967).

DEPARTMENT OF HYDROCARBON CHEMISTRY

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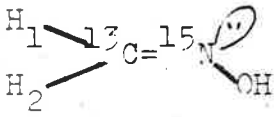
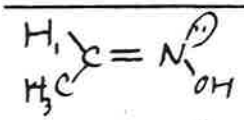
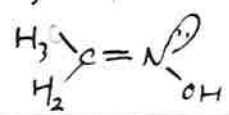
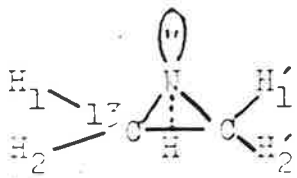
KYOTO, JAPAN

(3) J. P. Kintzingen and J. M. Lehn, Chem. Commun., 660(1967); D. Crépaux and J. M. Lehn, IITNMR, 115, 34(1968).

(4) T. Yonezawa and I. Morishima, J. Mol. Spectry., in press.

(5) T. Yonezawa, I. Morishima, M. Fujii and H. Kato, Bull. Chem. Soc. Japan, 40, 487(1967)

Table I

Molecule	Nucleus	J(Hz) Calcd	J(Hz) Obs	Ref.
	$^{15}N-H_1$	- 11.5	- 13.88	
	$^{15}N-H_2$	- 3.1	+ 2.68	3
	$^{13}C-H_1$	+140.8	—	
	$^{13}C-H_2$	+128.7	—	
	$^{13}C-H_1$	141.2	177	
	$^{13}C-H_2$	131.2	163	4
	$^{15}N-H_1$	- 1.94	$\lvert J^{14}_{N-H_1}\rvert > \lvert J^{14}_{N-H_2}\rvert$	
	$^{15}N-H_2$	- 0.06		
	$^{13}C-H_1$	+125.2	171	
	$^{13}C-H_2$	+127.4	161	4
	H_1-H_1'	+ 2.5	5.3	
	H_2-H_2'	+ 1.7	7.0	
	H_1-H_2	+ 5.1	1.0	

120-26

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DIVISION OF MOLECULAR SCIENCE

19th August 1968

Dear Dr. Shapiro,

N.P.L.N.M.R. News Letter

Another reminder that nine months are not what they used to be. Since no single scientific item seems more appropriate than another for presentation at the moment it might be of interest to record the recent fate of various members of our group and to give a brief resumé of our current interests.

Unfortunately, David Whiffen has just left us for academic pastures in the north of England to be Professor of Physical Chemistry at the University of Newcastle, so we will be without his advice and guiding influence in future. Also, Ron Dean has been lured away by industry having gone to work for Polaron in London a few months ago. This has cut the nuclear resonance portion of the magnetic resonance group down to two (Tony Hartland and myself) and has left us with the embarrassment of a very high spectrometer to operator ratio. We hope that this situation may be alleviated in September however, by a new addition to the staff.

My own current interests involve the use of the rotating frame technique (a new spectrometer now being vigorously operational) to study polymeric materials largely, with particular relation to the effect of polymer morphology on relaxation behaviour.

A number of publications are in preparation and preprints can probably be supplied to anyone who is interested. These are:

1. Polypropylene Oxide. Rotating Frame Proton Spin-Lattice Relaxation Measurements. T.M. Connor and A. Hartland. To be published in 'Polymer'.

2. Rotating Frame Proton Spin-Lattice Relaxation Measurements of Polyethylene Oxides. T.M. Connor and A. Hartland. In preparation.

3. Molecular Motion in Starch. Rotating Frame Proton Spin-Lattice Relaxation Measurements. T.M. Connor. To be published in 'Polymer Letters'.

Further work in progress involves ethylene/methacrylic acid copolymers in ionized forms (ionomers) and a series of very well characterized polystyrenes. The latter work is in conjunction with David Blears (recently employed at the Argonne National Laboratory and now at the Molecular Biophysics Group, Tallahassee, Florida), who also instigated some studies of urea - long chain fatty acid adducts. These show a great many resolvable but as yet unassignable molecular motions, the situation being further complicated by apparent thermal hysteresis effects. These are being investigated by X-ray methods.

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

/contd.

Tony Hartland is concerned with pulsed double resonance experiments and has recently been investigating single crystals of ammonium salts, observing the proton magnetisation as a function of the nitrogen irradiation frequency. It is possible to obtain information about the quadrupole coupling and field assymetry of the nitrogen nucleus. Thus in ammonium thiocyanate this information has been retrieved for both species of nitrogen nucleus. He also has a project in hand for converting our old DP 60 spectrometer into a pulsed Fourier transform spectrometer.

I hope this brief summary of current events makes an acceptable contribution to the newsletter.

Yours sincerely,

Tom Connor

Tom Connor

Fysiska Institutionen, Uppsala, August 20, 1968

Dear Barry,

Simplified ABX analysis, simplified

We are currently engaged in the long term project of writing a guidebook on analysis of high resolution NMR spectra that we intend to make useful also for those chemists who have not been able to save the time for a course in quantum mechanics. In describing a step by step analysis procedure we therefore refrain as much as possible from any reference to basis functions or assignments of observed lines to transitions labelled according to the specific choice of basis functions.

The appended description of the ABX analysis procedure should convey the spirit of our efforts. We beleive that this down-to-earth description may prove even more helpful in instruction courses than the (in principle) totally equivalent procedure described by Reilly in IITNMR 118:20. The appended pages will in fact be handed out to participants of such a course.

One of us (R.A.H.) wants to apologize for having again required a reminder to contribute, and we ask you to credit the present contribution to Uppsala.

Finally we wish to back up an earlier suggestion for the title of your excellent newsletter, viz.

N M R
Early
Warning
System

which probably is as adequate as any other and which could be retained in case of future changes of affiliation. The sponsorship of your department could conceivably be indicated in a prominent subtitle.

Sincerely yours,

Ragnar A. Hoffman Sture Forsén

I Basic structure of an ABX spectrum.

A. The spectrum of a genuine ABX spin system displays two distinct bands, viz. a symmetrical six line pattern in the X basic multiplet and an eight line pattern in the AB basic multiplet. Noise and overlap may reduce the number of actually observed lines in an experimental ABX spectrum.

The centre of symmetry of the X basis multiplet corresponds to ν_X. (The centre of gravity of the AB basic multiplet corresponds to $\frac{1}{2}(\nu_A+\nu_B)$, but ν_A and ν_B are better evaluated in the step-by-step analysis).

B. The AB basic multiplet may always be decomposed into two subspectra and the total intensity of the multiplet is shared evenly by the two subspectra.

The four line pattern of each one of the two subspectra displays a mirror image symmetry and has the same intensity ratio between inner and outer lines as that of a two spin AB spectrum. The apparent A-B coupling constants of the two subspectra are equal and both given by J_{AB}, the actual A-B spin coupling constant of our ABX spin system.

C. The AB basic multiplet is invariant under an interchange of the magnitudes of $|\nu_A-\nu_B|$ and $|J_{AX}-J_{BX}|$. The transition frequencies of the X basic multiplet are also in variant under such an exchange but their relative intensities are not.

D. The spectrum remains unchanged if we change the signs of J_{AX} and J_{BX} simultaneously and also if we change the sign of J_{AB}. We shall arbitrarily choose an analysis procedure that always yields positive values for J_{AB} and for the larger one of J_{AX} and J_{BX}. The relative signs of J_{AX} and J_{BX} are usually obtained through the analysis.

II. Step by step analysis of an ABX spectrum

In our procedure labels A and B are always chosen to yield $\nu_A > \nu_B$.

Step 1. Pick out the two subspectra of the AB basic multiplet by use of the rules under I.B above.

Step 2. Measure the centre frequencies $\bar{\nu}_1$ and $\bar{\nu}_2$ and the frequency intervals a_1, b_1 and a_2, b_2 of the two subspectra. (Cf. the appertaining

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Figure 1). Always choose labels so that $\bar{\nu}_1 > \bar{\nu}_2$.

Step 3. Evaluate the parameters Δ_1 and Δ_2 according to

$$\Delta_1 = \sqrt{a_1 b_1} \tag{1}$$

$$\Delta_2 = \sqrt{a_2 b_2} \tag{2}$$

and the angles φ_1 and φ_2 which are defined by

$$\text{Sin } 2\varphi_1 = \frac{a_1 - b_1}{a_1 + b_1} \tag{3}$$

$$\text{Sin } 2\varphi_2 = \frac{a_2 - b_2}{a_2 + b_2} \tag{4}$$

and chosen in the interval $0^o < \varphi < 45^o$

Step 4. Prior to a comparison of calculated and observed X multiplet intensity distributions we must, according to I.C. above, in principle accept two different sets of NMR parameters. In set (i) we assume that $|\nu_A - \nu_B| > \frac{1}{2}|J_{AX} - J_{BX}|$ and in set (ii) this inequality is reversed. The parameters of set (i) are given by:

Set (i)

$$J_{AB} = \tfrac{1}{2}(a_1 - b_1) = \tfrac{1}{2}(a_2 - b_2) \tag{5}$$

$$\nu_A = \tfrac{1}{2}(\bar{\nu}_1 + \bar{\nu}_2) + \frac{1}{4}(\Delta_1 + \Delta_2) \tag{6}$$

$$\nu_B = \tfrac{1}{2}(\bar{\nu}_1 + \bar{\nu}_2) - \frac{1}{4}(\Delta_1 + \Delta_2) \tag{7}$$

$$J_{AX} = (\bar{\nu}_1 - \bar{\nu}_2) + \tfrac{1}{2}(\Delta_1 - \Delta_2) \tag{8}$$

$$J_{BX} = (\bar{\nu}_1 - \bar{\nu}_2) - \tfrac{1}{2}(\Delta_1 - \Delta_2) \tag{9}$$

and ν_X is given by the centre of symmetry of the X basic multiplet.

In set (ii) the NMR parameters are given by the same set of equations with the sign of the smaller one of Δ_1 and Δ_2 reversed in equations (6) to (9).

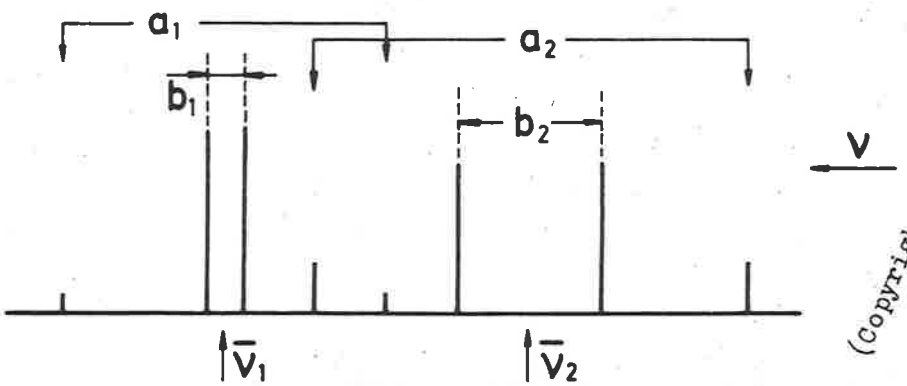

Fig. 1

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Step 5. Before discussing the X-part spectrum we must distinguish between spectra where the AB and X basic multiplets are recorded at one and the same nominal value of the magnetic Ho-field (as will always be the case if A, B and X are of the same isotopic species) and spectra where the AB-part is recorded at a field of Ho and X at a field of Ho'. In the latter case the parameter $\nu_A - \nu_B$ assumes different values in the two spectra and the entities a_n, b_n (n=1 or n=2) when occurring in equations (3) and (4) above and in the expressions of step 6 below must accordingly be replaced by

$$a_n' = \sqrt{J_{AB}^2 + a_n b_n (Ho'/Ho)^2} + J_{AB}$$

$$b_n' = \sqrt{J_{AB}^2 + a_n b_n (Ho'/Ho)^2} - J_{AB}$$

before executing step 6.

Step 6. In order to compare the calculated and observed intensities of the three pairs of X multiplet lines centered at ν_X we shall first normalize the total intensity of the X basic multiplet to 4 units.

One pair of lines, that will always be strong, is separated by a frequency interval of

$$|J_{AX} + J_{BX}| = 2|\bar{\nu}_1 - \bar{\nu}_2| ,$$

and each one of these transitions has an intensity of unity.

A second pair displays an interval of

$$\tfrac{1}{2}|a_1 + b_1 - a_2 - b_2|$$

and the intensity of each line equals $\mathrm{Cos}^2(\varphi_1 - \varphi_2)$ if set (i) is correct but is equal to $\mathrm{Sin}^2(\varphi_1 + \varphi_2)$ if set (ii) is the correct one.

The third pair displays a larger splitting of

$$\tfrac{1}{2}|a_1 + b_1 + a_2 + b_2|$$

and the intensity of each line must equal $\mathrm{Sin}^2(\varphi_1 - \varphi_2)$ if set (i) is correct but equals $\mathrm{Cos}^2(\varphi_1 + \varphi_2)$ if set (ii) is correct.

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THE QUEEN'S AWARD TO INDUSTRY 1966

THE QUEEN'S AWARD TO INDUSTRY 1968

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

Your Ref:

Our Ref: A.R.G./B5
Research Department

21st August, 1968

Dear Professor Shapiro,

NITROGEN-14 COUPLING IN DIMETHYLNITRAMINE

The observation that the methyl proton signal at 3.41δ of dimethylnitramine, $(CH_3)_2N.NO_2$, shows a triplet splitting of 1.5 c.p.s. was made first by Lamberton et al (J. Chem. Soc. (B), 1968, 6.) and they stated that this splitting must be due to ^{14}N coupling. Nitrogen-14 double irradiation experiments with the equipment we have described previously (NMR Newsletter 95, 1) confirm this and in the figure we show (a) the normal appearance of the triplet in $CDCl_3$ solution at 100 Mc/s and 40°C and (b) the collapse of the triplet upon simultaneous irradiation at the ^{14}N frequency $\sim$ 7.22 Mc/s, other conditions being unchanged.

From the critical ^{14}N frequency producing the maximum sharpening of the singlet, the ^{14}N chemical shift of the ^{14}N nucleus causing the splitting can be ascertained. This is 21.8 $\pm$ 1.5 ppm (with respect to nitrate ion). Such a value is typical of nitro group nitrogen nuclei, but is over 100 ppm different from amino group nitrogen values. Clearly therefore, the observed splitting is due to a three bond coupling between the protons and the nitro group nitrogen. The shape of the methyl triplet is governed by the ^{14}N quadrupole relaxation rate. Under the conditions in the figure, this relaxation rate must be slow, but already some partial collapse of the two outer lines can be seen. This collapse can be accentuated by lowering the temperature and vice versa.

The figure also shows integrals taken across the normal and ^{14}N decoupled methyl group signals under identical conditions. It can be seen that the areas are not equal, an increase in area of about 65% being found for the decoupled signal compared to the undecoupled signal. The most probable explanation of this involves an Internal Nuclear Overhauser Effect between the protons and the ^{14}N nuclei and further work is in progress on this and similar systems.

Yours sincerely,

P. Hampson A. Mathias.

P.HAMPSON. A.MATHIAS.

PH/AM/LA.

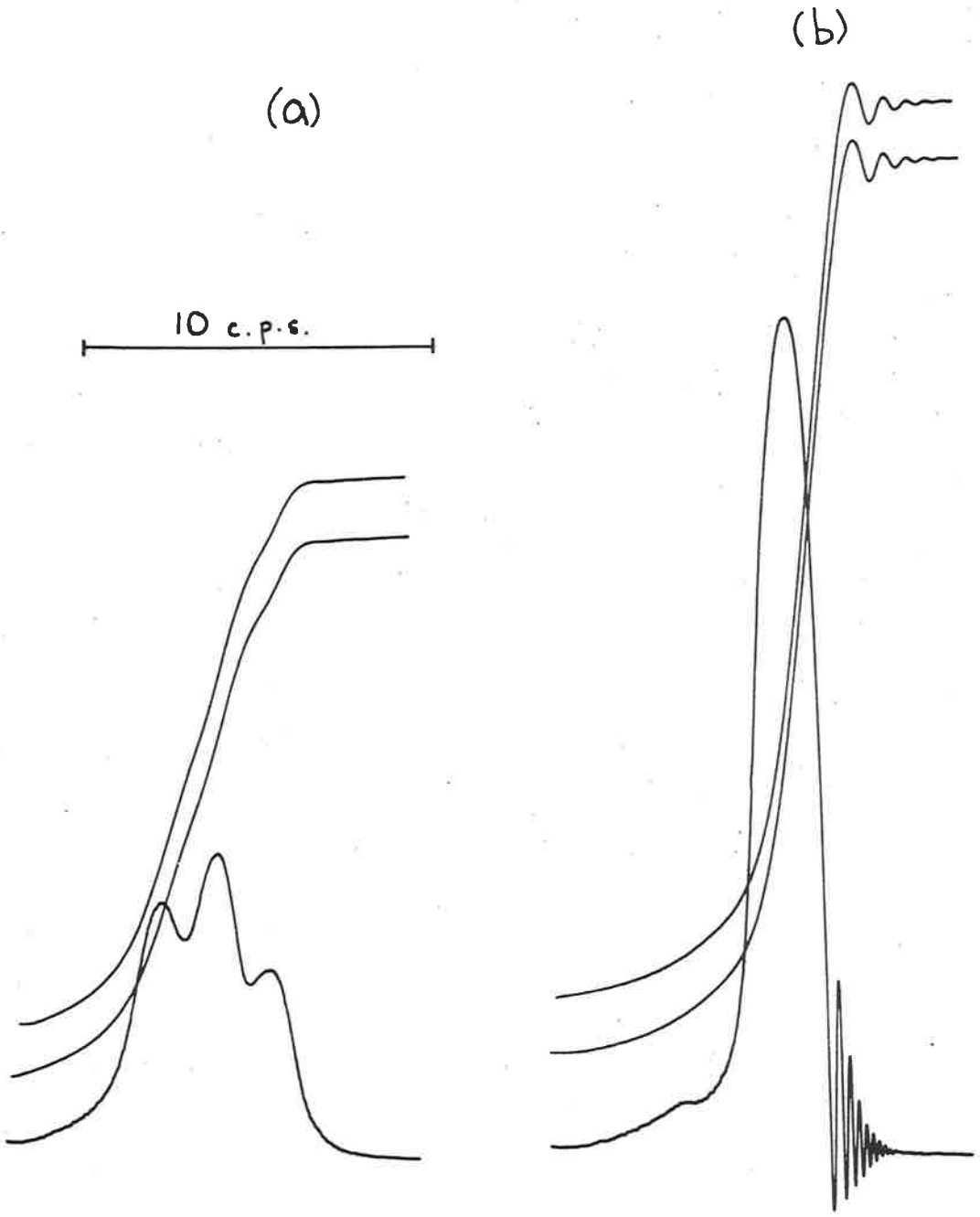
TELEPHONE: CHEETHAM HILL 1460 TRUNK DIALLING 061 CHE 1460 TELEX: 66152/3/4 TELEGRAMS: BRIDYCOR, MANCHESTER

DIMETHYL NITRAMINE $(CH_3)_2N.NO_2$

CH_3 PROTON SIGNAL AT 3·41δ

(a) NORMAL

(b) WITH ^{14}N IRRADIATION



120-34

POLITECNICO DI MILANO
ISTITUTO DI CHIMICA
Piazza Leonardo da Vinci, 32 - MILANO 20133
TEL. 292.109 - 292.110

Milano, July 22, 1968

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

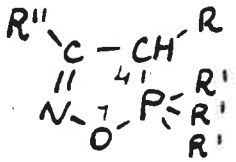
Subject: ^{1}H nmr spectra of a new series of phosphorus pentacovalent compounds and their corresponding phosphonium salts. An unusually strong change in $^2J_{P,H}$ with C-methylation.

Dear Dr. Shapiro,

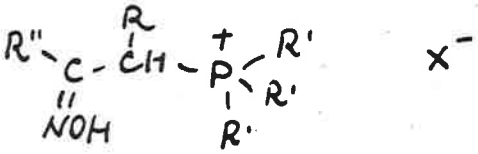
I am sorry that you had to send me two reminders for my contribution. I am completely out of date now. My work was interrupted for more than one month at the beginning of the year. Then I have been involved in structure determination of some natural products: Daunomycin, Narciclasine, Neoantimycin, indole alkaloids, some of which are already published (1), the others will appear soon.

Here is our contribution for the last 8 months! (Is it possible to receive the old Newsletter from December 1967 ?)
Next contribution ("nmr spectra of pyrrolinones") will follow in a few weeks.

We have studied the ^{1}H spectra of 8 compounds of type I together with their corresponding salts of type II :



I



II

In tab. only some data are reported. Fig 1 shows the spectrum of Ia, fig. 2 the spectrum of Id.
The spectra at 60 and 100 Mc are identical except for chemical shift difference. The two protons at C-4 are magnetically equivalent in salts as well as in cyclic compounds. Coupling constants are not solvent (+) and temperature dependent over a range from +30° to -50°C ; this interval is limited by decomposition and low solubility of the products.

The most interesting feature is the strong variation in coupling constant value ($^2J_{P,H}$) upon alkylation at C-4; while this change in phosphonium salts falls in the same range as reported (2), in cyclic compounds this change is drastic :

Ia 11.9 cps Id 3.5 cps Ie 3.5-4 cps

Selective decoupling experiments (fig. 2) on Id, showed that $^2J_{P,H}$ and $^3J_{P,H}$ have opposite relative sign. As all the three-bond couplings were found so far to be positive (2,3), also $^3J_{P,H}$ in Id can be taken positive. Consequently $^2J_{P,H}$ should be negative. $^2J_{P,H}$ in Ia, as well as in IIa-e, are assumed to be negative on account of their large modulus and in agreement with geminal P-H couplings in phosphonium salts (2,3). The change in $^2J_{P,H}$ from Ia to Id-e (-11.9 → -3.5 , positive shift) is strong, and can hardly be explained only in terms of the increase of s character of the carbon bonding orbital to phosphorus due to the effect of the electronegativity of the substituent. This is because of the small difference in electronegativity between hydrogen and alkyls .

A similar positive shift of $^2J_{P,H}$ was indeed reported (4) for some phosphonium salts, where however the substituent is much more electronegative than hydrogen:

$Ph_3P^+-CH_3$ J^- $\qquad$ $^2J_{P,H} = |13.2|$ (assumed negative sign)

$Ph_3P^+-CH_2OMe$ J^- $\qquad$ $^2J_{P,H} = |4.0|$

Moreover, if one considers the electronegativity of substituents (H and CH_3), the inverse trend is observed in Ia-d,e with respect to alkylphosphines (3). Obviously the interpretation given for trivalent phosphorus compounds or salts may not be valid in pentacovalent derivatives. Others factors, of course, than electronegativity of substituents may play an important role in determining the magnitude of these couplings (3).

A tentative explanation could be found admitting P-covalent character in Id,e to be higher than in Ia, which implies in the former a more important sp^3d hybridization of the P orbitals. (**)
A change in s character of carbon orbital to phosphorus, in Id,e, due to steric interactions could also be invoked. Nevertheless the strong change with methylation is indeed surprising.

In the forthcoming paper (5) we will discuss also the effect of substituents and positive charge on chemical shifts.
Comparing coupling constants and chemical shift values in phosphonium salts and in their corresponding cyclic derivatives (upfield shift and resp. increase of $^2J_{P,H}$ from salts to cycles), it can be deduced for the latter ones a high contribution of pentacovalent phosphorus structure ($\sim sp^3d$).

(**)

^{31}P chemical shifts are measured only for compounds Ia : + 37.0 ppm, $CHCl_3$ (6).

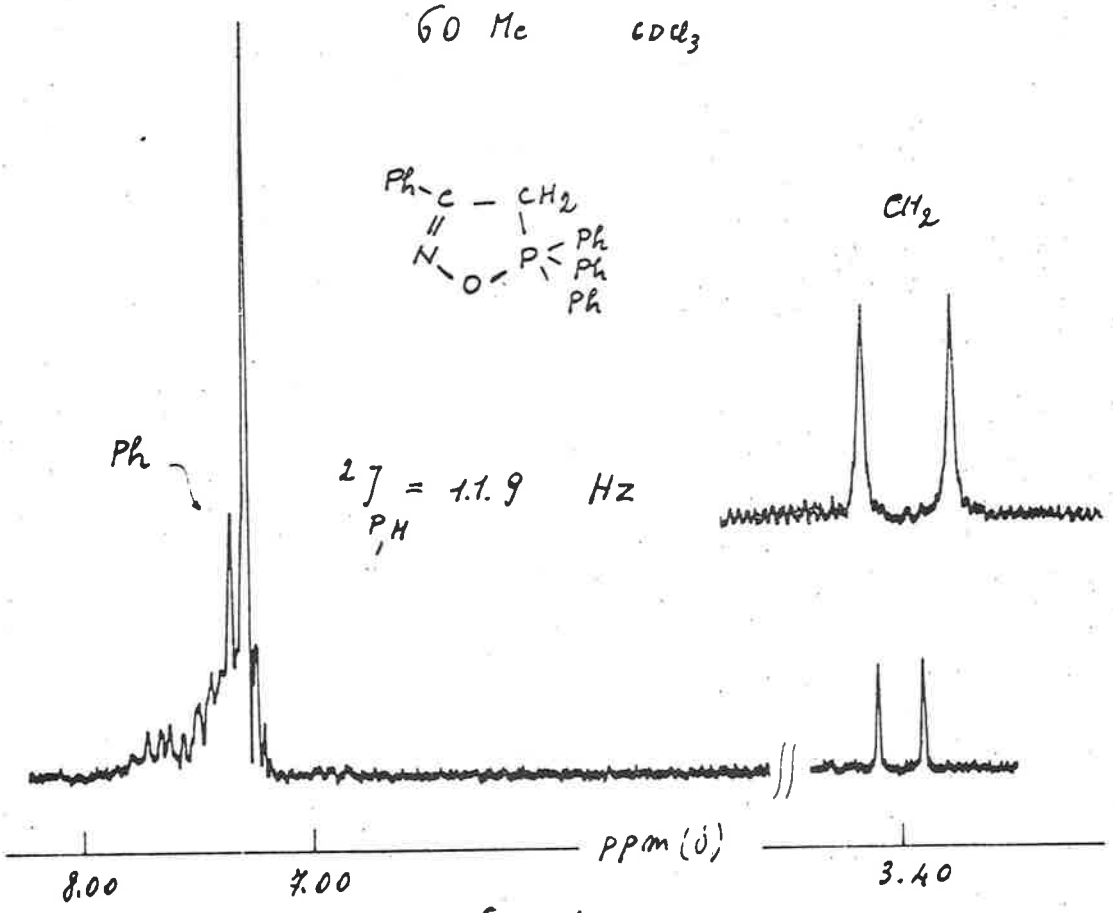


fig. 1

sincerely yours

R. Mendelli

(1) F.Arcamone, G.Cassinelli, G.Franceschi, P.Orezzi, R.Mondelli "The structure of Daunomycin" "The total absolute configuration of Daunomycin" Tetrahedron Letters, 3349, 3353 (1968).

F.Piozzi, C.Fuganti, R.Mondelli, G.Ceriotti "Narciclasine and Narciprimine" Tetrahedron 24, 1119 (1968).

(2) G. Mavel in "Progress in NMR Spectroscopy" Oxford 1966

(3) S.L.Manatt, G.L.Juvinall, R.I.Wagner, D.D.Elleman J.Am. Chem.Soc. 88, 2689 (1966).

(4) D.W.Allen, I.T.Millar, J.C.Tebby Tetrahedron Letters 715 (1968).

(5) G.Gaudiano, R.Mondelli, P.Ponti, C. Ticozzi, A. Umani-Ronchi J.Org.Chem. in press.

(6) R. Huisgen, J.Wulff, Tetrahedron Letters 917 (1967)

	R	R'	R"	J, cps				δ, ppm		
					$CDCl_3$	$DMSO-d_6$	$Pyr-d_5$		$CDCl_3$	$DMSO-d_6$	$Pyr-d_5$
Ia	H	Ph	Ph	$^2J_{P,H}$	11.9	11.9	–	CH_2P	3.40	3.88	–
Ib	H	Ph	Ph	$^2J_{P,H}$	12.2	11.5	11	CH_2P	3.03	3.39	3.29
				$^4J_{H,Me}$	0.7	–	–	Me	2.08	1.96	2.11
Ic	H	n-But	Ph	$^2J_{P,H}$	12.0*	–	–	CH_2P	2.50*	–	–
Id	Me	Ph	Ph	$^2J_{P,H}$	3.5	3.6	3.5	CHP	3.34	3.78	3.70
				$^3J_{P,Me}$	19.7	19.5	19.8	Me	1.66	1.54	1.67
				$^3J_{H,Me}$	7.3	7.3	7.2				
Ie	n-Prop	Ph	Ph	$^2J_{P,H}$	3.5–4	–	4.0	CHP	3.55	3.96	3.93
								Me	0.73	0.66	0.62
IIa	H	Ph	Ph	$^2J_{P,H}$	–	16.8	15.0	CH_2P^+	–	5.16	5.37
IIb	H	Ph	Me	$^2J_{P,H}$	–	14.0	13.5	CH_2P^+	–	4.99	5.76
								Me		1.84	2.29
IIc	H	n-But	Ph	$^2J_{P,H}$	16.7	16.9	16.8	CH_2P^+	4.20	4.04	4.80
IId	Me	Ph	Ph	$^2J_{P,H}$	13.5	13.5	10.6	CHP^+	4.91	5.16	5.26
				$^3J_{P,Me}$	19.0	18.5	19.0	Me	1.80	1.83	2.01
				$^3J_{H,Me}$	7.0	7.0	7.1				
IIe	n-Prop	Ph	Ph	$^2J_{P,H}$	13	13.0	–	CHP^+	5.01	5.21	5.46
								Me	0.83	0.86	0.78

(*) In CCl_4 solution.

(+) with the exception of the salts in pyridine solution, probably because of an acid-base equilibrium.

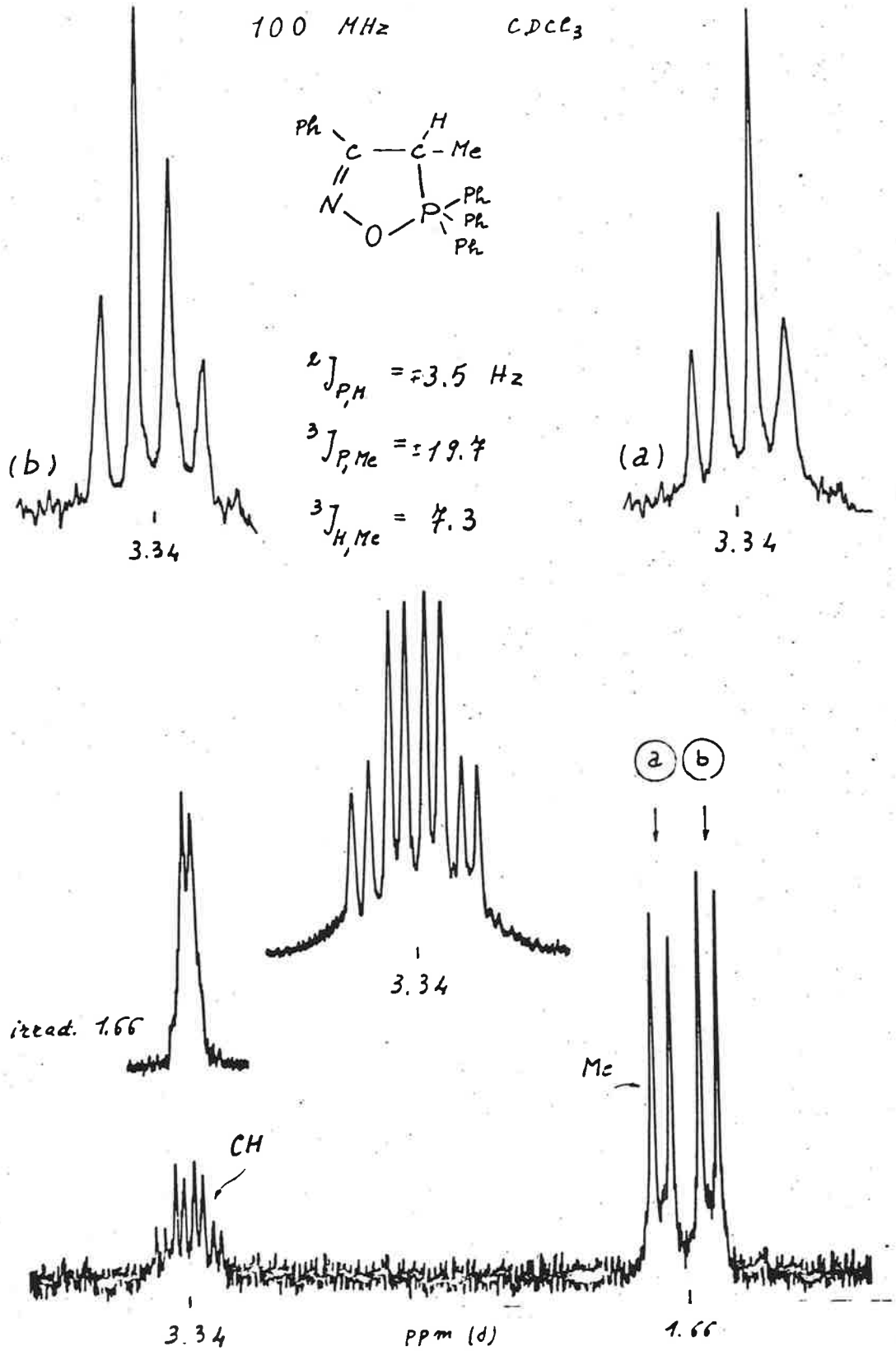

100 MHz
CDCl3
Ph
H
C
C - Me
N
O
P
Ph
Ph
Ph
(b)
3.34
(a)
3.34
2J P,H = ±3.5 Hz
3J P,Me = ±19.7
3J H,Me = 7.3
3.34
irrad. 1.66
a
b
Me
CH
3.34
ppm (δ)
1.66

Fig 2

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

KATHOLIEKE UNIVERSITEIT
NIJMEGEN

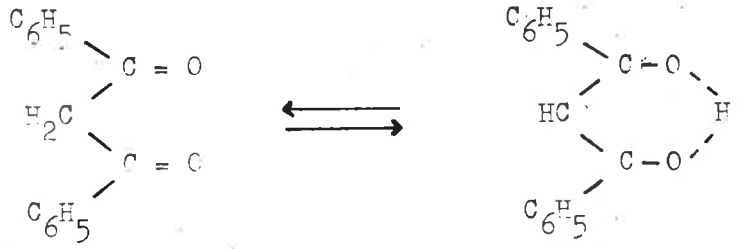
Driehuizerweg 200, Nijmegen
Telefoon (08800) 5 83 33
Afdeling Physical Chemistry

Geadresseerde Professor Shapiro Ons kenmerk 1205/FP/RR Datum 23-8-1968

N.M.R. - study on β-diketones.

We are engaged in a N.M.R. study on β-diketones which can be obtained as mono-, di-, and trinegative ions, and wish to report here some results of measurements on dibenzoyl methane (D.B.M.).

1 The 100 Mc proton spectrum of neutral D.B.M., dissolved in tetrahydrofuran (T.H.F.) demonstrates that the molecule is in its enol configuration (B) in the temperature range from -80°C to +80°C.



A B

The aromatic protons produce two signals with an intensity-ratio of 6 : 4 (see table 1).

Increasing of the temperature results in a line broadening of the enol proton signal. This line broadening is interpreted as resulting from a proton jump from one oxygen to another, as well inter as intra molecular. Assuming a slow exchange process, we calculated from Arrhenius plots an activation energy of about 5 kcal.mole^{-1}, which is in accordance with hydrogen bridge formation ($\Delta H^{\neq}$ = 2.5 à 4.0 kcal.mole^{-1}). The pre-exponential factor of the Arrhenius relation is not constant, due to intermolecular proton jumps. The reaction rate increases with the concentration however not linearly, indicating that higher concentrations favour the inter molecular process.

2 The shape of the methine proton signal of neutral D.B.M. dissolved in T.H.F. depends on temperature and on concentration (see Fig. 1).

We did not yet succeed in correlating the methine signal behaviour with the enol-proton line broadening. From proton-deuterium exchange measurements with D_2O it is seen that both protons are involved in the exchange process.

3 Dissolving of neutral D.B.M. in liquid NH_3 results in formation of the monobasic ammonium salt: The enol signal disappears and is not restored upon a change in solvent from NH_3 to T.H.F. The other signals are shifted to high field (see table 1).

Prolonged reduction results in a N.M.R. spectrum which is attributed to the trinegative ion of D.B.M.: The aromatic protons yield one broad line with two maxima; all signals are shifted to high field.

Remarks:

It is well known that negative charges cause upfield shifts. The upfield shifts observed for D.B.M. - ions do not correlate with Hückel charge densities

120-40

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Afdeling: Physical Chemistry.

Geadresseerde Professor Shapiro Ons kenmerk 1205/FP/pp Datum 23-8-1968 Blad No 3

e.g. the charge density on the methine carbon atom does not change going from the mono- to the trinegative ion, whereas we found a shift of 0.91 p.p.m.

The Hückel calculation predicts the signal of the four meta protons at higher field than that of the para and ortho protons, which according to the calculated charge density should resonate at about the same field. Experimentally we found the 4-ortho proton signal at lower field which probably is caused by the deshielding effect of the magnetically anisotropic C=O group*).

The values of the chemical shifts of the ions depend on solvent and on concentration. Ion-pair formation could be responsible for this behaviour.

Measurements on solutions of the para magnetic dinegative ion of D.B.M. up to now did not give reproducible results.

*) ref. G.J. Heisswolf and H. Kloosterziel, Recueil 86, 1345-1355 (1967).

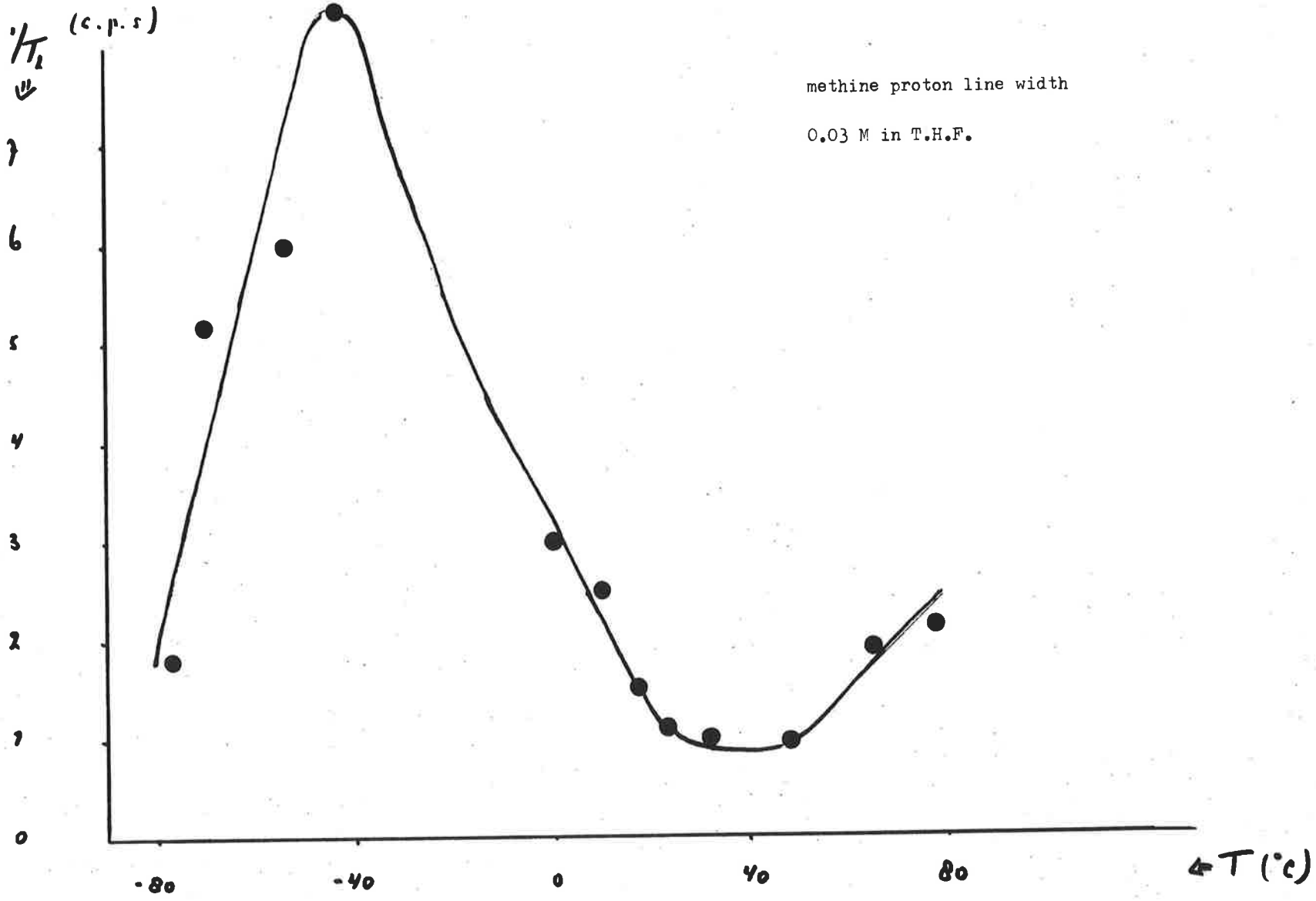
Table 1

Experimental chemical shifts of D.B.M. (p.p.m. T.M.S. - scale)

Conditions	neutral molecule	mononegative ion	mononegative ion	mononegative ion	trinegative ion
Solvent	THF	THF	NH_3	NH_3	NH_3
Counterion	-	Na^+	Na^+	NH_4^+	Na^+
Concentration(M)	0.36	0.38	0.55	0.38	0.35
Temperature (^oC)	-20	-20	-20	-30	-20
Positions(p.p.m.)					
Methine proton	6.22	5.51	5.47	5.27	4.36
six proton group	6.60	6.26	6.51	6.33	6.1
four proton group	7.24	6.94	7.00	6.82	6.4
Enol proton	16.60	-	-	-	-

Sincerely yours,

(Dr. F.W. Pijpers).



methine proton line width

0.03 M in T.H.F.

Figure 1

120-42

Max-Planck-Institut für Biochemie
Dr. J. Sonnenbichler

8 München 15, den 25.7.1968
Goethestraße 31
Fernruf 59 42 61/63
Postschließfach 64

Sehr geehrter Herr Dr. Shapiro!

Der Umbau unseres A-60 und die Installation eines HA-100 hat uns in den vergangenen Monaten einige Mühe gekostet und wir hatten längere Zeit keine Möglichkeit, Spektren zu registrieren. Nach einigem Shimen hat unser HA-100 jetzt "für Biochemiker einigermaßen brauchbare" Werte. Auflösung 0.3 Hz, Signal-Rauschverhältnis (1 % Äthylbenzol) 90:1.

Wir möchten heute ein Experiment beschreiben, das uns wieder zeigte, wie bedingt Referenzsignale als Referenz brauchbar sind:
Bei der Untersuchung der

Bindung von Lysolecithin an Albumin

wird das CH_2-Signal der Fettsäure des Lysolecithins mit steigender Menge Albumin im Gemisch signifikant verbreitert. Das Signal der Trimethylammoniumgruppe wird relativ wenig beeinflußt (Fig. a).

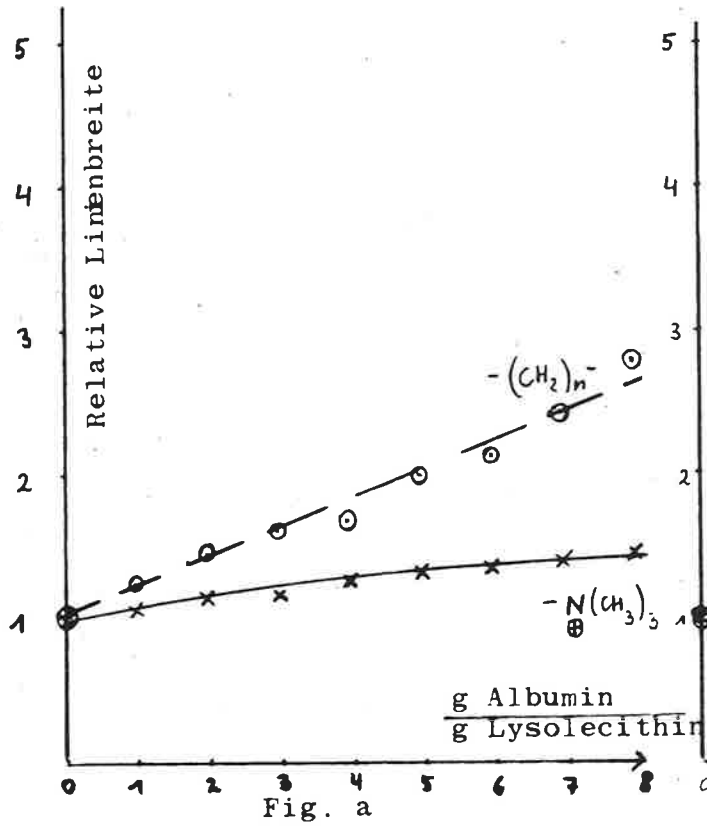


Fig. a

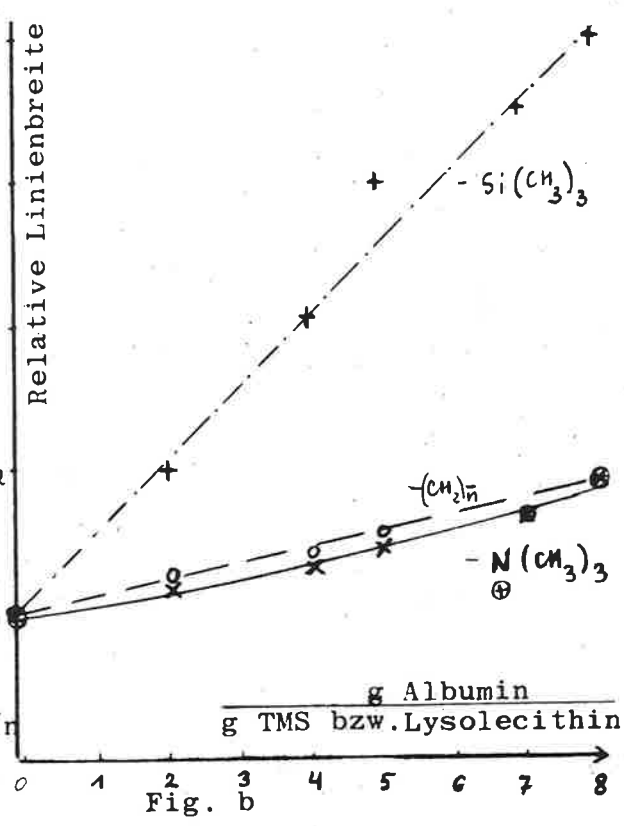


Fig. b

Max-Planck-Institut für Biochemie
Dr. J. Sonnenbichler

2. Blatt zum Schreiben vom 25.7.68 an Herrn Dr. Shapiro

Das Lysolecithin wird also offensichtlich nicht ionogen über die polare Ammoniumstruktur, sondern durch hydrophobe Kräfte über die Fettsäurekette an das Albumin gebunden.

Im Parallelversuch hatten wir als Referenz Trimethylsilylpropiosulfonat zugegeben; mit steigender Menge Albumin im Gemisch wird das Methylsignal dieser Verbindung deutlich verbreitert (Fig. b); d.h. auch das TMS-sulfonat tritt mit dem Albumin in Wechselwirkung und zwar ähnlich wie das Lysolecithin - durch hydrophobe Bindung der Alkylreste an das Albumin.

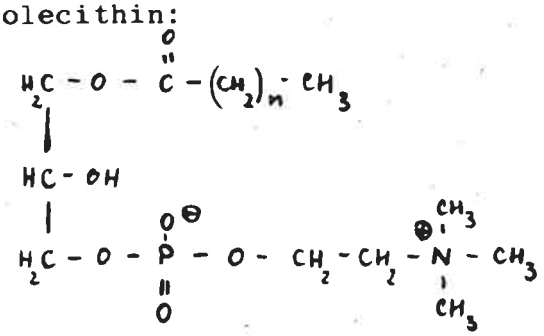
Die Methylgruppen des TMS-sulfonats und die Fettsäurekette des Lysolecithins könnten bei dieser Annahme um die Receptorstellen am Albumin konkurrieren. Dies bestätigt die wesentlich geringere Zunahme der Linienbreite des $-CH_2$-Signals der Lysolecithin-Fettsäurekette in Gegenwart äquimolarer Mengen Trimethylsilylpropiosulfonat.

Unsere Messungen erfolgten in Zusammenarbeit mit Professor Ruhenstroth-Bauer (Max-Planck-Institut für Biochemie, München) und werden in erweiterter Form publiziert.

Mit freundlichem Gruß

Johann Sonnenbichler

Lysolecithin:



120-44

Institut für Physikalische Chemie
der Rhein.-Westf. Techn. Hochschule Aachen
Direktor Prof. Dr. U. F. Franck
Dozent Dr. R. Kosfeld

51 Aachen, den 27. August 1968
Templergraben 59 · Fernruf (0241) 422/2150
Fernschreiber: 0632/704

Herrn
Prof. Bernard L. Shapiro
Department of Chemistry
Texas A a. M. University
College of Science

College Station, Texas 77843
U. S. A.

Sample thermostating in Spin-Echo-Experiments

Dear Professor Shapiro:

Thank you for your letter from August 6, 1968.
In connection with our measurements of the nuclear relaxation times T_1 and T_2 and of the coefficients of self-diffusion D_s in pure liquids we have developed a better method for sample thermostating in Spin-Echo-Experiments.

Figure 1 shows a schematic diagram of the probe. The thermostating is effectuated by a liquid, which does not contain protons and which flows around the sample directly within the coil. Hereby the thermal contact is very good over the entire sample surface, a high stability is attained and a temperature gradient is completly eliminated within the sample region. This is particularly important when diffusion in liquids is to be investigated. A gradient would lead to the appearance of additional convectional motions in the sample.

Figure 2 shows the relaxation time T_1 as a function of temperature for chloroform. According to the theory of the translational Brownian motion of spherical particles, the translational diffusion coefficient can be expressed as $D = kT/f$, where f is given by the Stokes expression $f = 6\pi a \eta$. With these assumptions one can write $\frac{T_1 \cdot \rho \cdot \eta}{T} = C$ when the intermolecular dipol-dipol interaction contributes only to the relaxation rate $1/T_1$ (see also: P.S. Hubbard, Phys.Rev. 131, 275 (1963)) (see Fig. 2).

Our experimental results are in contrast to the data by J. Blicharski (Extrait du Bulletin AMPERE, 9e, fasc. special, 452, 1960). He explains that a decrease of $\frac{T_1 \cdot \rho \cdot \eta}{T}$ with increasing temperature for chloroform is effected by spin-rotation interactions. But our experiments show that in chloroform the decrease of $\frac{T_1 \cdot \rho \cdot \eta}{T}$ with increasing temperature is effected by a temperature gradient within the sample.

Yours sincerely

(Dr. Kosfeld)

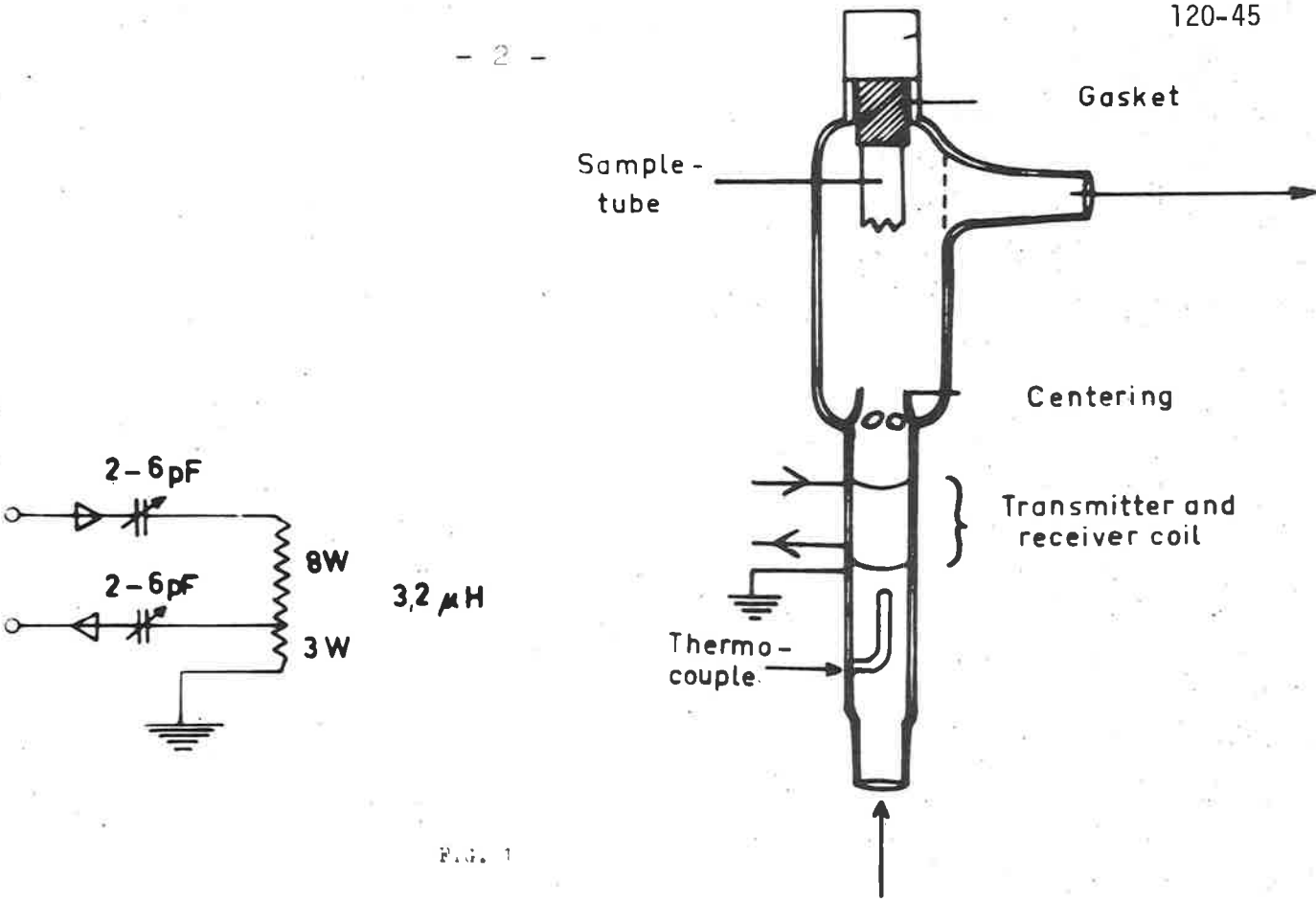
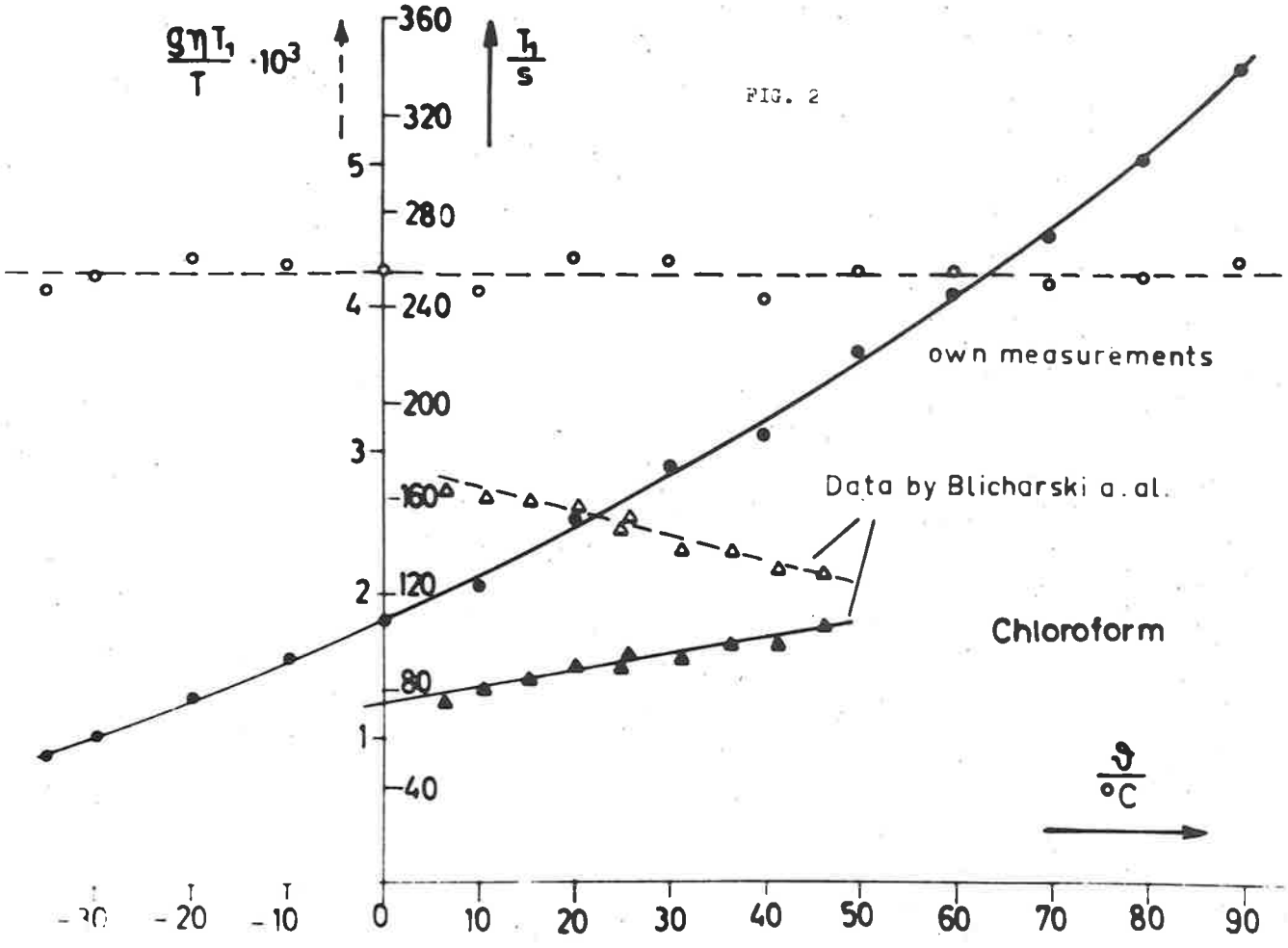

Gasket
Sample-
tube
Centering
Transmitter and
receiver coil
Thermo-
couple
2-6pF
2-6pF
8W
3W
3,2 μH

FIG. 1

FIG. 2


$\frac{g\eta I_1}{T} \cdot 10^3$
$\frac{I_1}{s}$
360
320
280
240
200
160
120
80
40
5
4
3
2
1
own measurements
Data by Blicharski a. al.
Chloroform
$\frac{\vartheta}{°C}$
-30
-20
-10
0
10
20
30
40
50
60
70
80
90

120-46

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

27 August 1968

Refer to: 328-SLM:js

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

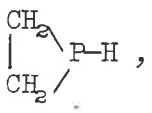
Dear Barry:

For this contribution I would like to present some results from several studies in progress or nearly finished.

Recently we (in collaboration with Dr. Michael T. Bowers) completed the analysis of the rather complex spectrum of hexafluoro-1,3-butadiene(1). Our assignment for 1 was achieved via a very classical means (i.e. from computed trial spectra). Because of the strongly coupled nature of this spectrum and the test spectra we have calculated we believe the set of parameters given in Table 1 has a high probability of being unique.

We (in collaboration with Dr. Edward A. Cohen) have prepared a sample of heptafluoro-β-naphthol(2) and looked at its ^{19}F spectrum. Although the 56.4 MHz spectrum of 2 is complicated, in the 94.1 MHz spectrum it is possible to identify the four peri-fluorine nuclei as two sets of AB quartets which exhibit J_{AB} couplings of approximately 65 Hz! We believe these results provide further new evidence suggesting the reinstatement of the importance of "through-space coupling" between proximate fluorine atoms.

The analyses of the 100 MHz and 40.3 MHz spectra of phosphiran(3),



are nearly complete (with Dr. Michael T. Bowers). An interesting result thus far is the fact that the two P–C–H couplings in 3 are of opposite signs and rather different magnitudes (-2.7 and +16.5 Hz). At present we have not tried to identify which P–C–H is which. These results were obtained from $^{1}H-[^{31}P]$ and $^{31}P-[^{1}H]$ experiments using a proton lock and a double-tuned receiver insert; a more detailed description of this modification of our HA-100 will perhaps be the subject of another letter.

I hope this spattering of results will serve to sustain our subscription.

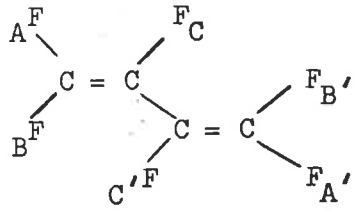
With best regards,

Stan

Stanley L. Manatt
Physics Section

Telephone 354-4321 *Twx 213-449-2451*

Table 1. Final Iterated Parameters for Hexafluoro-1,3-butadiene: coupling constants in Hz and chemical shifts in p.p.m. from internal CCl_3F and internal C_6F_6; estimates of error and other parameters given are those usually calculated in NMRIT (see ref. 25), results were obtained from iteration on 194 transitions.



J_{AB}	J_{AC}	J_{BC}
+50.737 ± 0.006	-118.577 ± 0.006	+31.911 ± 0.006
$J_{AB'}$	$J_{AC'}$	$J_{BC'}$
+2.449 ± 0.006	+2.409 ± 0.005	+14.195 ± 0.006
$J_{AA'}$	$J_{BB'}$	$J_{CC'}$
+4.800 ± 0.008	+11.313 ± 0.008	-30.305 ± 0.008
$\varphi_A^{CCl_3F}$	$\varphi_B^{CCl_3F}$	$\varphi_C^{CCl_3F}$
+93.8586 ± 0.0009	+107.9558 ± 0.0009	+179.6853 ± 0.0009
$\varphi_A^{C_6F_6}$	$\varphi_B^{C_6F_6}$	$\varphi_B^{C_6F_6}$
-73.7340 ± 0.0004	-59.6346 ± 0.0004	+13.0445 ± 0.0004

Sum of squares of residuals 0.054 (8th iteration).
Sum of squares of energy level errors 0.0148.
Average deviation of observed minus calculated line positions 0.026 Hz.
Maximum deviation for two weak lines +0.092 and +0.074 Hz.

120-48

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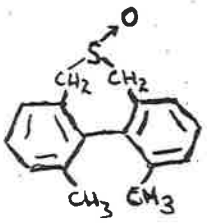
UNIVERSITY OF OTTAWA
DEPARTMENT OF CHEMISTRY

August 27, 1968

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



I

Dear Barry:

I have somewhat hesitantly decided that one more example of non-equivalence might be permissible in view of its unique character and potential value as a source of information on several problems.

The compound in question (I) gave the spectrum (at 100 MHz) shown in the attached figure. It can be seen that all four geminal protons have substantially different shieldings. In this compound we hope to be able to make assignments to each individual proton with the help of NOE's. This information could then be of use in ascertaining the ΔX's for a sulfoxide group. Chemical exchange of the protons is being currently investigated. It is also interesting to note that the non-equivalence of the two methyl groups is detectable in spite of their distance (about 7 Å) from the S → O function. The effect of stereochemistry on the geminal couplings is substantial, i.e. $-J_{Gem}$ = 11.4 and 13.8 and can be used to make tentative assignments to the two methylene groups.

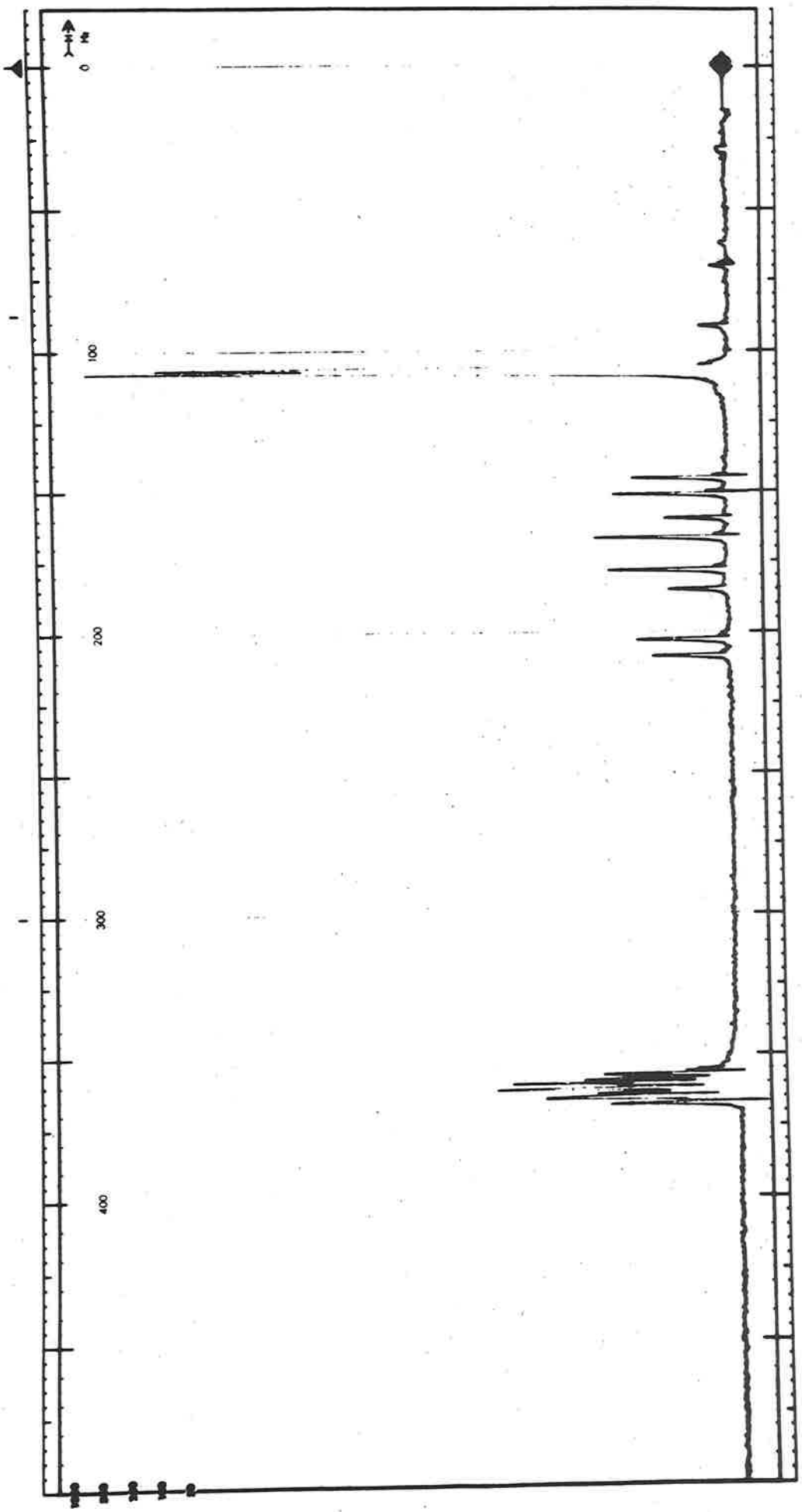
Yours sincerely,

Bob Fraser

R. R. Fraser

RRF;ae

Title: Chemical Shift Non-Equivalence: A Double Dose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August 27, 1968

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

Dear Barry:

Because of a trend which seems to be emerging, and your new address, I would like to suggest the name, "Touring Articles about Magnetic Undertakings", for the Newsletter. Anyway, good luck at your new residence.

Digital Voltmeter Internal Lock Monitor

For several years a portion of my time has been devoted to structure identification of compounds isolated from a variety of natural products by another chemist. (For example, J. Org. Chem. 31, 1797 (1966). Currently we are working on identification of sex attractants of pine beetles. Obtaining NMR spectra of compounds isolated from the beetles normally requires time-averaging and microcell sample handling. A 100 μg sample is "large".

To optimize the spectrometer lock and to avoid saturation, we use our digital voltmeter. Connection of the voltmeter to the vertical (Y) axis of the oscilloscope with the diode probe normally used to tune the rf unit conveniently yields the required rectified signal. Variation in the lock amplitude can be continuously monitored (to ± 0.001 volt) by using a fast "sampling rate" on the voltmeter.

Quite simply, the sample signal is optimized for a given sample when the amplitude of the D. C. voltage is as large as possible--without variation of more than ± 1 or 2 millivolts on the voltmeter and with "look signal" spectrometer adjustments at or near maximum. One can thus peak homogeneity controls for individual microcell samples to obtain better signal to noise and to detect small irratic variations in lock voltage not observable using the shim switch. Irratic voltages always occur with saturation but can also arise from nonuniform spinning, traces of dirt in the sample, or presence of strange, yet unidentified things that come from bugs.

In addition to routine spectrometer operation, the digital voltmeter monitor enables one to determine stability of very weak lock signals; especially those from ^{19}F experiments where large sweep offsets (~ 10 KHz) are required. Lock signals from CF_3COOH capillaries can be quite small (15-25 millivolts D. C.) but quite stable.

Best personal regards.

Yours truly,

Tom

Thomas F. Page, Jr.
Research Spectroscopist
Organic & Polymer Characterization

TFP:jec

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

August 30, 1968

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

Dear Barry:

We would like to announce that we have for sale an A-60 spectrometer that has been completely reconditioned during the last 15 months.

Anyone interested in this spectrometer should contact me by mail or phone.

Sincerely,

J. H. Goldstein
Professor of Chemistry

JHG/jd

hooker research center

NIAGARA FALLS, NEW YORK 14302, PHONE (716) 284-9965

July 19, 1968

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

Dear Dr. Shapiro:

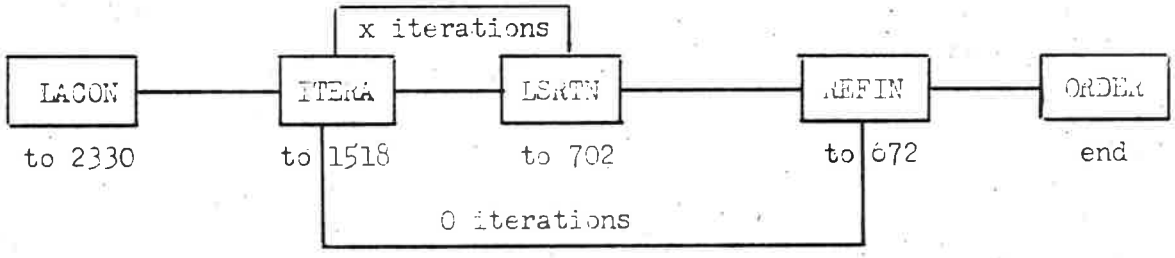
Title: LAOCN 3 ON THE IBM 1130 COMPUTER

After minor difficulties we have been able to adapt the Bothner-By and Castellano LAOCN 3 program for running on an IBM 1130 system with an 8,000 word storage. With the necessary changes, the program will now run two to six spin systems without iteration, and as many as four spins with iterations. The six spin - zero iteration program, requires about twelve minutes including printout, and the four spin with iterations requires about four minutes.

The output is either in a stick form or shaped presentation (obtained by M.P. Williamson while at the Mellon Institute). We are updating the core storage to 16,000 words next month which will increase the ultimate size of the spin system. At that time we will further modify our program and introduce the use of data switch input to vary input parameters. A copy of our present program is available to those interested.

If anyone would like to modify their own program it is quite simple.

For the iterative use, the LAOCN 3 mainline is divided into five parts each of which is connected by a CALL LINK. In this, and the zero iteration modification below, all dimension statements were scaled down to the minimum size needed, all unreferenced statement numbers were removed, format statements were added to the pertinent section, and rewind statements were taken out. Each section contains only their necessary DIMENSION statements and they were put into COMMON.



To LAOCN were added statements 61202 (from the iterative part of LAOCN 3).

ITERA needs minor index changes to adapt to a random access machine (tape vs. disk). Introduce two working storage files (i.e. DEFINE FILE) for storage of VA and VB generated by MATRIX.

LSRTN drops the argument list in 519 (CALL ERROR 9) because it is being carried in a COMMON block.

REFIN requires indexing change and introduction of DEFINE FILE statements as in ITERA.

ORDER required writing MIN Ø (to check total line output).

The zero iterations calculation is run in two parts (MLACO and MREFI) connected by a CALL LINK. The DIMENSION statements are for a six spin maximum and as above other general changes for linking parts are observed.

The first section is called MLACO. Since no iterations are to be performed, statements 8379 to 24 and 2240 to 2330 are deleted. The rough diagonalization from statements 500 to 512 are removed and at 515 a CALL LINK brings in the second part MREFI. This skips the least squares and starts at statement 601 and goes to end.

Please delete my name (JGC) from the mailing list and add Dave Marrs' as he is now in charge of our NMR facilities.

James G. Colson Gerald A. Penna David H. Marr

120-54

DEPARTMENT OF CHEMISTRY TUFTS UNIVERSITY MEDFORD, MASSACHUSETTS 02155

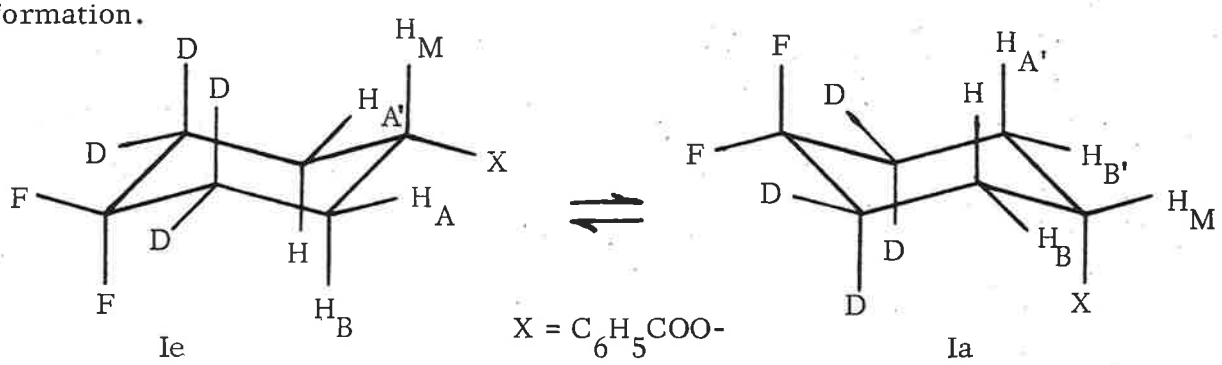
August 30, 1968

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

Dear Barry:

FIVE BOND HCCCCF LONG RANGE COUPLING IN 4,4-DIFLUOROCYCLOHEXYL-3,3,5,5-d_4 BENZOATE.

Long range proton-fluorine coupling may be of some use in structure determination and in conformational studies. For example, we have found that J_{HCCCCF} must vary significantly with molecular geometry. We would be interested in learning the results of other studies involving the dependence of long range proton-fluorine coupling upon structure and conformation.



At both 60 and 100 MHz, a 100 mg sample of 4,4-difluorocyclohexyl-3,3,5,5-d_4 benzoate (I), mp 54-55° (prepared for this work by Thomas W. Giants), in 0.3 ml of CCl_4 at ca. 32° gave a deceptively simple proton resonance spectrum. The C-1 proton (5.12 PPM) appeared as a quintet (splitting 4.8 Hz) of doublets (splitting 3 Hz). The four ring protons at C-2 and C-6 (1.95 PPM) appeared as a doublet (splitting 4.8 Hz). Therefore, this AA'BB'MXY spin system approaches AA' A"A"'MXY with $(J_{AM} + J_{BM})/2 = 4.8$ Hz, where M is the C-1 proton, a quintet, split further into a quintet of doublets by long range FCCCCH coupling. Irradiation to decouple the C-2 and C-6 protons causes the C-1 quintet

of doublets to collapse to a doublet (splitting 3.3 Hz). This residual coupling in the three spin (MXY) system is attributable to long range (five bond) fluorine-proton coupling. Computer analysis using LAOCOON I suggests $J_{MX} = 3.4 \pm 0.4$ Hz, $J_{MY} = 0.5 \pm 0.3$ Hz. The small coupling, not resolved, was estimated from the line shape within the doublet. Since $J_{MX} \gg J_{MY}$, long range FCCCCH coupling must vary greatly with molecular geometry.

With an HA-100 and NMR Specialties HD-60B Heteronuclear Spin Decoupler, irradiation of fluorine caused the C-1 proton quintet of doublets to collapse to a quintet (splitting 4.8), confirming the analysis above for compound I. The C-1 proton band width, $W = 19.2 \pm 0.2$ Hz at ca 31° with fluorine decoupled, when compared with appropriate model compounds, is consistent with a conformational equilibrium favoring Ia, the axial conformer. This conclusion is in agreement with the independent determination of the conformational equilibrium, Ie $\rightleftharpoons$ Ia, $G^\circ_{-104^\circ}$, -0.35 ± 0.04 kcal/mole, determined earlier this year by direct integration of fluorine resonance peaks for Ia and Ie at -104°.[1]

Compounds related to I and model compounds for Ie and Ia are being investigated.

Sincerely yours,

Bob

Robert D. Stolow

(1) R. D. Stolow, T. W. Giants, and J. D. Roberts, Tetrahedron Letters, in press (1968)

120-56

Dr. Ludwig Pohl
c/o
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Herrn
Professor Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

Ihre Zeichen	Ihr Schreiben vom	Hauruf	Unsere Zeichen	DARMSTADT
				2. Sept. 1968

$(CH_3)_3SiCD_2CD_2COONa$, ein neuer wasserlöslicher Kernresonanzstandard

Sehr geehrter Herr Professor Shapiro!

Der bisher benutzte wasserlösliche Kernresonanzstandard $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$, das sogenannte Tiersche Salz, besitzt die allgemein bekannten Nachteile, neben dem allein interessierenden $(CH_3)_3Si$-Signal bei δ = 0,015 ppm 3 störende Resonanzbereiche zwischen δ = 0,3 und 3,1 ppm aufzuweisen.

Wir haben daher einen neuen Standard entwickelt, der diese Nachteile nicht zeigt. Es ist das Natriumsalz der Trimethylsilyl-tetradeuteropropionsäure

$(CH_3)_3SiCD_2CD_2COONa$.

Diese Verbindung ist säure- und basenstabil und besitzt gegenüber dem bisherigen Standard folgende Vorteile:

1) Das $(CH_3)_3Si$-Resonanzsignal liegt bei genau δ = 0,00 ppm (in H_2O und Methanol gemessen).
2) Außer dem Standardsignal sind keine weiteren, störenden Signale im Spektrum vorhanden.
3) Die Löslichkeit in H_2O ist größer als die des Tierschen Salzes.

- 2 -

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4) Das Verhältnis $(CH_3)_3Si$- zu Rest des Moleküls ist günstiger als im bisherigen Standard, so daß z.B. bei gleicher Substanzeinwaage ein größeres Standardsignal zur Verfügung steht, was besonders bei Geräten mit internem Lock von Vorteil ist.

Man kann natürlich auch die einfacher herzustellende nichtdeuterierte Verbindung verwenden, bei der dann Vorteil 2) wegfällt, weil zwei störende Resonanzbereiche zwischen δ = 0,7 bis 0,9 ppm und δ = 2,0 bis 2,3 ppm im Spektrum auftauchen.

Mit freundlichen Grüßen

Ihr sehr ergebener

L. Pohl

(L. Pohl)

120-58

UNIVERSITY OF SUSSEX
THE CHEMICAL LABORATORY FALMER BRIGHTON BN1 9QJ
Telephone Brighton OBR 3 66755

5th September, 1968.

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

Deuterium Isotope effect on geminal couplings between proton and fluorine nuclei

Dear Professor Shapiro:

We have measured coupling constants in fluoroform and silyl fluoride and their fully deuterated derivatives at a variety of concentrations in cyclohexane in order to obtain an estimate of the isotope effect on $^2J_{HF}$. Line positions were measured in pairs (using the internal frequency counter on our HA-100) to minimise the effects of instability, and measurements on all possible pairs of lines in both ^1H and ^{19}F resonance were utilised. The good agreement between the ^1H and ^{19}F values and the fact that no significant difference was detected between values obtained from different pairs of lines (i.e. at different fields) for the same sample, indicated that errors due to the magnetic field sweep non-linearity are less than the errors quoted.

For silyl fluoride, there was no concentration dependence over the 10-20 mole % range studied whilst for fluoroform $^2J_{HF}$ increased with increasing concentration probably due to changes in hydrogen bonded self-association. A brief summary of the results is given below.

$$J = {}^2J_{HF} \text{ or } {}^2J_{DF} \times \gamma_H / \gamma_D$$

J (Hz) in cyclohexane, 25 ± 1°C

SiH_3F	45.764 ± 0.015	
SiD_3F	45.611 ± 0.050	
CHF_3	79.339 ± 0.015	30 mole %
CDF_3	79.261 ± 0.046	

UNIVERSITY OF SUSSEX
THE CHEMICAL LABORATORY FALMER BRIGHTON BN1 9QJ
Telephone Brighton OBR 3 66755

These give estimates for the isotope effect of 0.153 ± 0.052 Hz for silyl fluoride and 0.078 ± 0.048 Hz for fluoroform (30 mole %). In both cases the effect was such that deuteration caused a decrease in the absolute magnitude of the coupling constant.

We hope to make some sense of these numbers from the Theoretical studies being carried out at the moment.

Yours sincerely,

J.N. Murrell

J.N. Murrell.
C.N. Banwell
M.A. Turpin

4 September 1968

Position Available

A major corporation in the Midwest has asked me to announce an opening for a spectroscopist to take charge of the NMR operation in their Research Division. They are seeking a man with at least a B.S. Degree in Chemistry and three or more years working experience in NMR, preferably in industrial laboratories; experience in IR and instrumentation electronics is desirable, but not essential. Anyone potentially interested in such a position should write or telephone Dr. B. L. Shapiro, Department of Chemistry, Texas A & M University, College Station, Texas 77843, (Area Code 713: 845-5545). All inquiries will be strictly confidential and B.L.S. will serve only to establish an immediate connection for the inquirer with the company.

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