

Joseph B. Lambert

Illinois
Institute of
Technology
N-M-R
Newsletter

No. 106
JULY, 1967

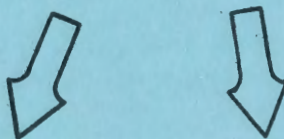
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A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted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

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Deadline Dates: No. 107 - ⑨ August 1967 No. 108 - 8 September 1967

Reminder: For the period August 10, 1967 to August 15, 1968 inclusive, all Newsletter contributions, enquiries, etc., should be addressed as follows:

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



UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

June 12, 1967

Dr. Bernard L. Shapiro
Associate Professor
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

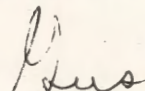
Carbon-13 Magnetic Shieldings in Monosubstituted Pyridines

We have measured carbon shieldings in 26 monosubstituted pyridines. The most interesting results of this investigation are shown graphically in figures 1 and 2. Shieldings of the carbon atoms located para to substituents in 2- and 3-substituted pyridines correlate well with the chemical reactivity parameter σ_p ; the plot (figure 1) is nearly identical to that reported for the corresponding monosubstituted benzenes. Substituent effects at all positions were found to be approximately equal to those of the benzenes except at C-2 for the 2-substituted compounds. Deviations between the two at this position were as large as 21 ppm and were found to correlate reasonably well (figure 2) with the electronegativity of the first atom of the substituent group. Dave Grant indicated at the recent Pittsburgh Conference that such behavior is to be expected on theoretical grounds when a large amount of charge is withdrawn from carbon orbitals.

Many thanks to the participants and attendees of the Symposium on Carbon-13 Magnetic Resonance recently held in Pittsburgh.

Sincerely yours,


H. L. Retcofsky


R. A. Friedel

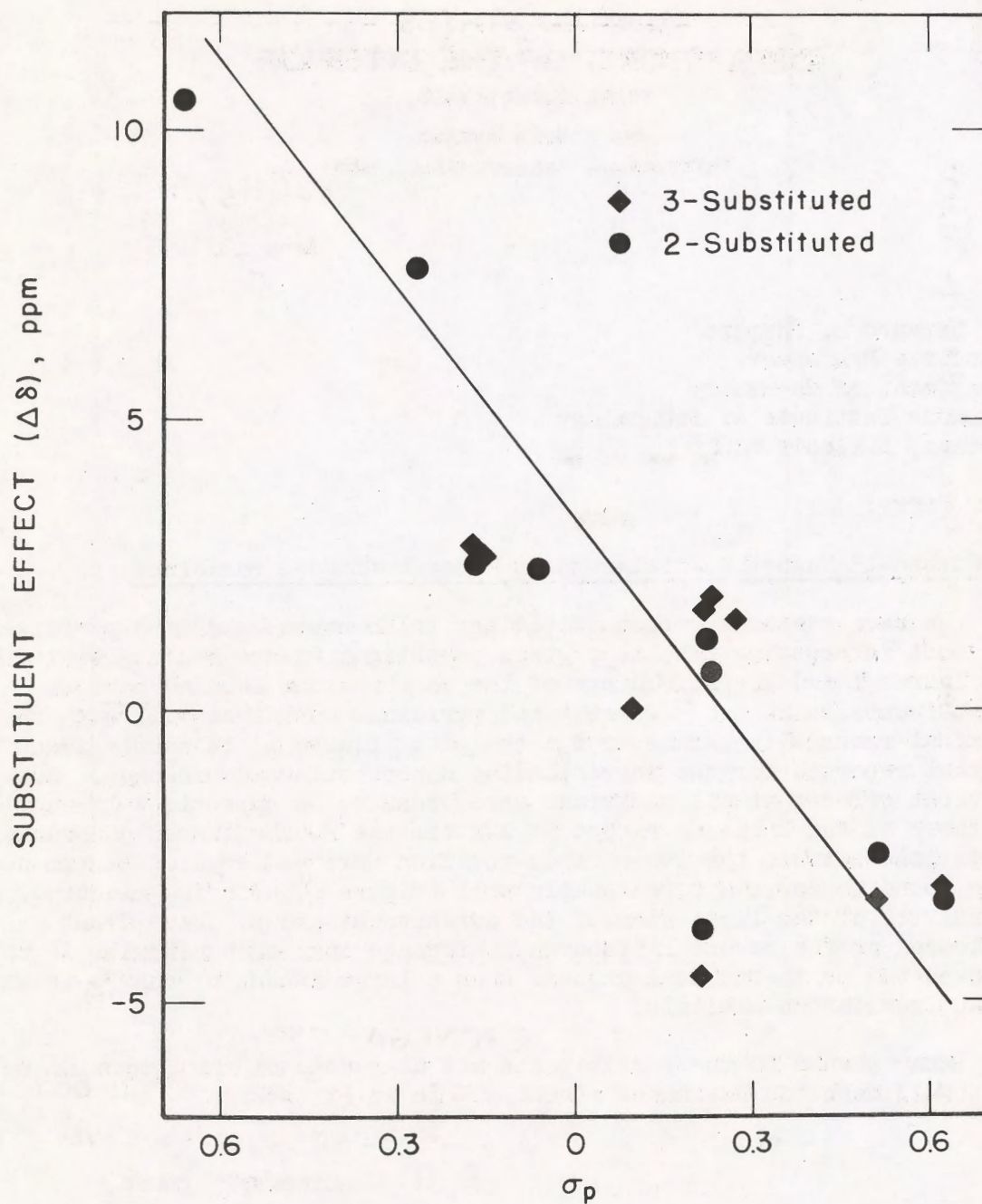


Figure 1 -Magnetic shieldings of carbon atoms *para* to substituents in monosubstituted pyridines vs Hammett σ_p constants.

L-9811

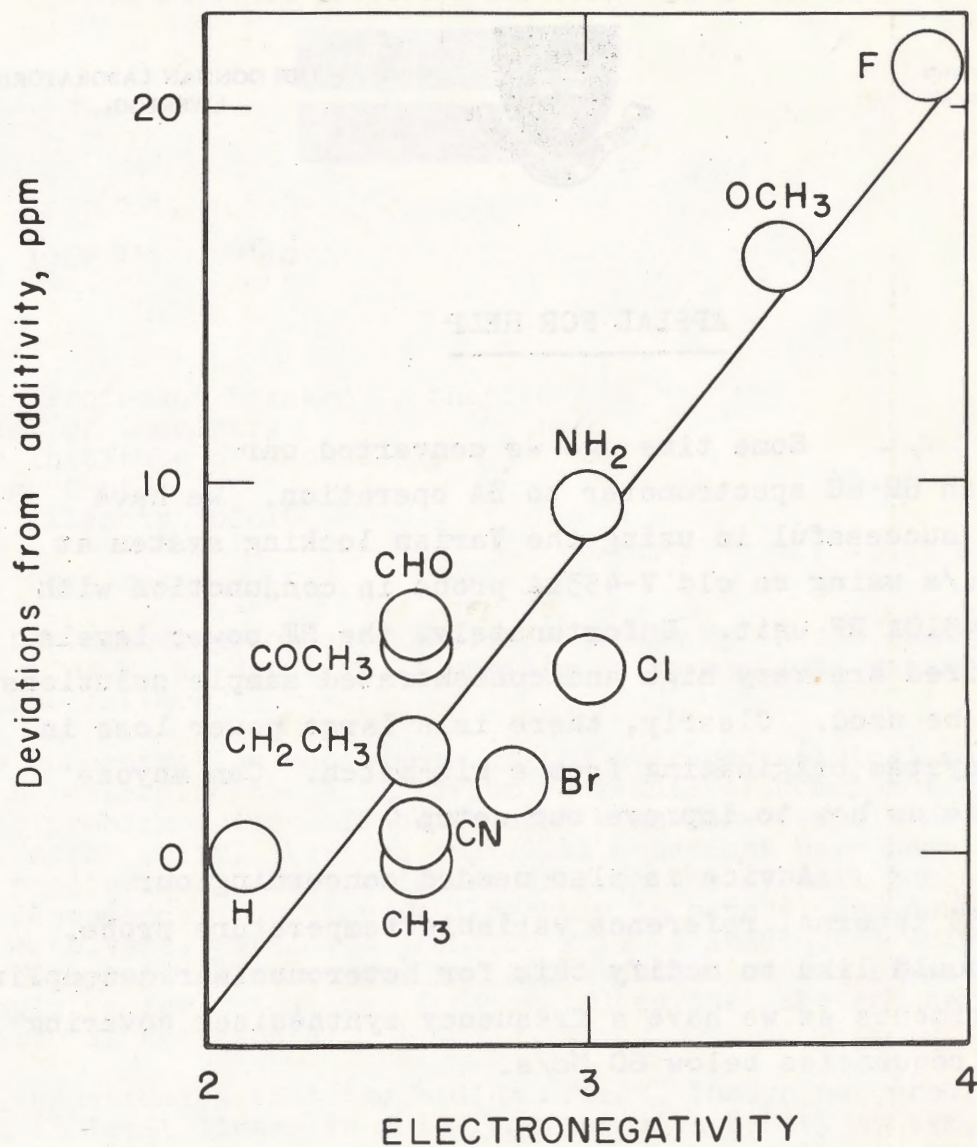


Figure 2 - Deviations from additivity for C-2 carbon shieldings in 2-substituted pyridines vs electronegativities of first atom of substituent.

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

TELEPHONE : ROYAL 6022
Extension 356



THE DONNAN LABORATORIES
LIVERPOOL, 7

APPEAL FOR HELP

Some time ago we converted our Varian HR-60 spectrometer to HA operation. We have been successful in using the Varian locking system at 40 Mc/s using an old V-4331A probe in conjunction with a V-4310A RF unit. Unfortunately, the RF power levels required are very high and concentrated sample solutions must be used. Clearly, there is a large power loss in the system originating from a mis-match. Can anyone advise us how to improve our setup?

Advice is also needed concerning our V-4333 internal reference variable temperature probe. We should like to modify this for heteronuclear decoupling experiments as we have a frequency synthesiser covering all frequencies below 60 Mc/s.

K.W. Jolley

L.H. Sutcliffe

S.M. Walker

DOW CORNING

June 13, 1967

Associate Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr. Shapiro:

I hope the following comments abstracted from my thesis (thesis advisor: Dr. M. W. Hanna) will entitle me to begin to receive IIT NMR Newsletters.

When the concentration dependence of the averaged chemical shift is used to determine the equilibrium constants of complex formation, the problem arises of how to deal with non-specific medium effects on the shift. Various empirical equations have been used to predict and delete this effect from the overall concentration dependence, but they fail because in general any double (solute + solvent) parameter equation will be inadequate unless there is only a single "cause" for non-specific medium effects. For example, a few measurements demonstrated that the Bothner-By equation is not general.

However, by assuming that the medium effect, though not predictable, is at least linear in mole fraction of a binary system, and that the effect is zero for a complex whose proton is buried as in chloroform-aromatic complexes, an equation was obtained from which the equilibrium constant, the shift of the "pure complex", and the medium effect on the uncomplexed chloroform can be found by use of the observed shift-concentration-temperature data.

The equation was applied to the complexes of benzene, toluene, p-xylene, and mesitylene with chloroform. The "complex shift" showed no trend while the equilibrium constant increased as expected with greater aromatic methylation. The "complex shift" results indicate that the aromatic ring current is unaffected by methylation although this issue is complicated by the electric field effect on the shift.

Yours very truly,

Dwight E. Williams

Dwight E. Williams

Chemistry Department,
The University,
Glasgow, W.2.
Scotland.

20th June, 1967.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
Chicago 60616,
Illinois,
U.S.A.

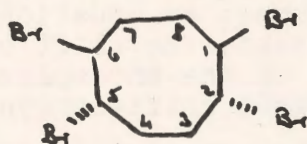
Dear Professor Shapiro,

We are enclosing some information which you might like to include in the I.I.T. N.M.R. bulletin. Please credit it to Dr. Porte's subscription.

Ring Inversion in Tetrasubstituted Cyclooctanes

The temperature-dependent high-resolution NMR spectra of cyclooctane^{1,2,3}, substituted cyclooctanes⁴ and unsaturated cyclooctane derivatives⁵ have been studied producing results with an important bearing on the conformations and on the conformational processes which exist in these molecules in solution.

Recently, we have been carrying out a conformational study of some tetrasubstituted cyclooctanes of which the 1,2,5,6-tetra bromocyclooctane (I) is a typical example.



(I)

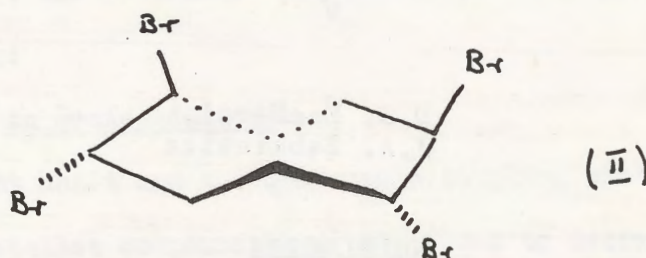
Inspection of molecular models indicates that for a stretched or skewed crown conformation two of the CHBr protons (e.g. those on carbon atoms 1 and 2, H_1 and H_2) occupy axial-type positions and that the other two (H_5 and H_6) are in equatorial-type positions. Although pseudorotation may reasonably be expected to average the magnetic environment of H_1 and H_2 (and also the environment of the

Professor B.L. Shapiro

19th June 1967.

other two protons H_5 and H_6), this process will not bring about complete averaging of all four CHBr proton environments. Ring inversion to give the mirror-image conformer (or ring inversion between two enantiomeric sets of conformers) is required to effect the averaging of chemical shifts of axial-type and equatorial-type protons.

Wagging of one of the eight carbon atoms of a crown form leads to the reversible formation of one of several possible boat-chair forms⁷. However, neither these wagging processes nor possible pseudorotation for boat-chair forms can lead to ring inversion with consequent complete averaging of the CHBr proton chemical shifts. Ring inversion may occur from boat-chair conformations via one of several forms, for example II, which correspond to the centrosymmetric form proposed⁴ as a possible transition state for ring inversion in cyclooctane itself.



The 100 Mc/sec. room temperature proton spectrum of a dilute solution of isomer (I) in CD_2Cl_2 comprises two narrow bands, centered at 5.40τ and 7.50τ with relative intensities 1:2, which correspond to the CHBr and $\text{-CH}_2\text{CH}_2\text{-}$ protons respectively. If the methylene protons are decoupled the CHBr protons give rise to a sharp singlet which implies that ring inversion is sufficiently rapid (on an NMR time scale) to average the magnetic environment of the CHBr protons. In support of rapid ring inversion at room temperature, the $\text{-CH}_2\text{CH}_2\text{-}$ protons give rise to a closely coupled AA'BB' spectrum when the CHBr protons are decoupled.

As the temperature of a solution of (I) in CD_2Cl_2 is lowered, both the CHBr and the methylene resonances broaden markedly owing to the slowing up of ring inversion, and below about -75°C both these resonances show splitting. At the coalescence temperature T_c for the CHBr doublet, $-66.5 (\pm 2)^\circ\text{C}$, one can estimate a rate constant for ring inversion by means of the expression^{8,9}

$$\frac{1}{2\tau} = \frac{\pi(\nu_A - \nu_B)}{f_2}$$

Professor B.L. Shapiro

19th June 1967.

using the value of the doublet separation found at -94°C which is $40\% \text{ c. sec.}^{-1}$. This gives a rate of ring inversion $1/2 \tau$ of 90 sec^{-1} at -66.5°C . It is interesting to note that the rate of ring inversion of the tetrabromide (I) is about two orders of magnitude less than that of the parent cyclic hydrocarbon at the same temperature².

Further studies on this and related systems are being carried out with a view to elucidating the molecular conformations and the kinetic processes occurring in these molecules.

Yours sincerely,

D.D. MacNicol

J.A. Zabkiewicz

D.D. MacNicol,
J.A. ZabkiewiczReferences

1. Harris and Sheppard, Proc.Chem.Soc., 1961, 418.
2. Anet and Hartman, J.Amer.Chem.Soc., 1963, 85, 1204.
3. Anet and St. Jacques, J.Amer.Chem.Soc., 1966, 88, 2585.
4. Anet and St. Jacques, J.Amer.Chem.Soc., 1966, 88, 2586.
5. St. Jacques, Brown and Anet, Tetrahedron Letters, 1966, 5947.
6. Hendrickson, J.Amer.Chem.Soc., 1964, 86, 4854.
7. The most stable boat-chair form is expected to be the one in which (in formula V of ref. 4) the relatively bulky bromine atoms are situated in positions 1e, 2e, 5e and 6e (or 8e, 1e, 4e and 5e). It is of interest to note also that for the present tetrabromide (I) such forms as saddle or tub forms have large transannular bromine-hydrogen interactions and therefore are probably not present to any great extent.
8. Pople, Schneider and Bernstein, "High-resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, p.223.
9. Strictly, of course, this expression is only valid for the coalescence of two lines of equal intensity which have effectively zero line width in the absence of exchange. In the present case, however, the error introduced by its use is probably not large.

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

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DR. R. VIJAYARAGHAVAN

June 22, 1967

Professor B.L. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Chicago 60616 (U.S.A.)

Dear Dr. Shapiro:

Thanks for the reminder. The solid state NMR group is interested in the following:

1. Knight Shift in Semiconductors:

The Knight Shift and the quadropole coupling constant of ^{115}In in In-Bi intermetallic compound have been found to decrease with decreasing temperature. An attempt is made to interpret the results in the light of the structure of the alloy. Professor Lösche may be interested in this work.

2. Conduction electron polarisation in Rare-earth-Platinum alloys:

From the Knight shift, susceptibility and E.P.R. data in R Pt_2 and R Pt_5 compounds, values of interaction constant $J(0)$ have been obtained. The paramagnetic curie temperatures are positive for R Pt_2 and negative for R Pt_5 compounds.

3. F^{19} Resonance in Paramagnetic fluorides:

F^{19} resonance has been observed in Fe F_3 (in antiferromagnetic and paramagnetic phases), Cu F_2 , VF_3 and $\text{Fe F}_3 \cdot 3\text{H}_2\text{O}$. The results will be published soon.

Yours sincerely,

R. Vijayaraghavan
 (R. Vijayaraghavan)

RVcjt



Dr. G. Englert

c/o

F. HOFFMANN-LA ROCHE & CO.**AKTIENGESELLSCHAFT**

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ABTEILUNG Phy. A.
Eng/hb

June 19, 1967.

Prof. B. L. Shapiro
Dept. of Chemistry
Illinois Institute of Technology
Chicago, Ill. 60616Re: Positive sign of $J(\text{CH}_3, \text{CH}_3)$ in 2,4-hexadiyne

Dear Professor Shapiro,

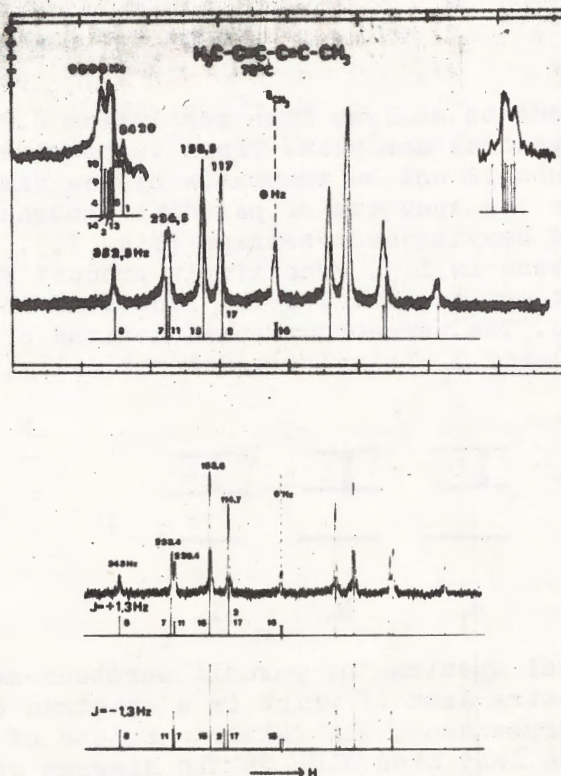
In our last contribution to this Newsletter (No. 99, p. 6) we have reported on the determination of the absolute sign of the coupling constant $J(\text{H}, \text{CH}_3)$ of propyne $\text{H}-\text{C}\equiv\text{C}-\text{CH}_3$ which was shown to be negative as expected. We have continued our investigation on acetylenic compounds oriented in nematic liquid crystals. In this letter I should like to report on the determination of the absolute sign of $J(\text{CH}_3, \text{CH}_3)$ of 2,4-hexadiyne.

The spectrum of this compound dissolved in 4,4-di-n-hexyloxy-azoxybenzene has already been published in ref. 1. In the analysis of the spectrum we did not take into account the indirect J-coupling which was assumed to be negligible ($|J| = 1.3 \text{ Hz}$) compared to the direct couplings (70.2 and 2910 Hz). We have remeasured the spectrum and (besides an error in the calibration of the central part of the previous spectrum) we have found that the sign of J can easily be obtained from the spectrum if the halfwidth of the lines is sufficiently small.

From the anisotropy of the chemical shift of several substituted acetylenes the parallel orientation of the long molecular axis of these compounds with respect to the magnetic field direction is known. The same orientation is assumed here for 2,4-hexadiyne. The corrected spectrum is presented in the upper half of fig. 1 together with a theoretical spectrum calculated with the following parameters (new sign convention for the direct couplings; see ref. 2):

$$\begin{aligned} A(\text{CH}_3, \text{CH}_3) &= -78.3 \text{ Hz} \\ B(\text{CH}_3) &= 2924.2 \text{ Hz} \\ J(\text{CH}_3, \text{CH}_3) &= +1.3 \text{ Hz} \end{aligned}$$

./.



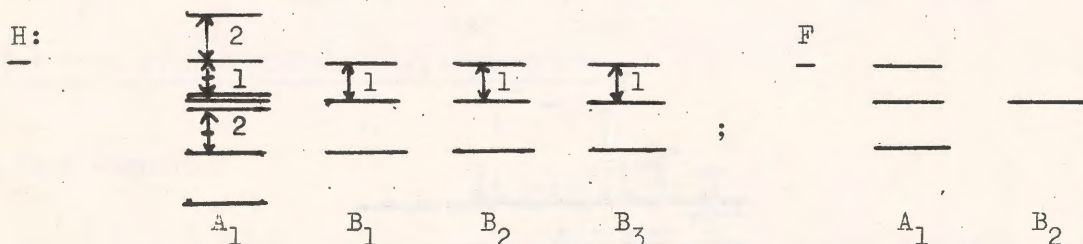
SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairesestraat 174
Telefoon 717451

Amsterdam, June 12. 1967

Dear Dr. Shapiro,

One of the methods to analyse high resolution n.m.r. spectra is the so-called sub-spectral analysis. There is no reason why liquid crystal n.m.r. spectra should not be tractable by the same method¹⁾. As an example consider the spectrum of paradifluorobenzene dissolved in the nematic phase of hexyloxyazoxybenzene (fig. 1.). The symmetry of paradifluorobenzene is D_{2h} . From simple product spinfunctions of the four protons one can construct seven functions that transform as A_1 , three as B_1 , etc. The zero-order spinfunctions of fluorine belong to A_1 (triplets) and B_2 (singlet). Schematically, the energy levels are



The liquid crystal spectrum of paradifluorobenzene is a superposition of three sub-spectra each of which is a spectrum of four protons, such as in paradichlorobenzene. The latter consists of five doublets²⁾. The arrows on the left hand side in the diagram correspond to one half of this spectrum: the numbers refer to relative intensities. The experimental spectrum of paradichlorobenzene shows that dipolar interaction between orthoprotons dominates: $D^o = -4542$; $D^m = +275$; $D^p = -12.6$ Hz (at $+70^\circ\text{C}$ in the same liquid crystal).

In paradifluorobenzene the dipolar couplings between the fluorine spins and the protons are intermediate: $D_{HF}^o + D_{HF}^m = -776$ Hz. If the orientation of the two molecules in the nematic phase is similar, four sub-spectra are expected, two of which coincide (i.e. $(A_1)_o$ and $(B_2)_o$ of fluorine), as observed in fig. 1.

In a more complete analysis one has to consider the representations of the direct product. As an example, the totally symmetric representation A_1 is contained in the direct product through $A_1 \times A_1$ and $B_2 \times B_2$. If (kl) denotes the spinstates of the fluorine spins and protons the energy levels are:

$A_1 \times A_1$:	(1.2)			$B_2 \times B_2$:
	(1.1)	(0.2)		
	(1.0)	(0.1)	(-1.2)	(0.1)
	(1.-1)	(0.0)	(-1.1)	(0.0)
	(1.-2)	(0.-1)	(-1.0)	(0.-1)
		(0.-2)	(-1.-1)	
			(-1.-2)	

Interaction between states with different Zeeman-energies can be neglected. This means, for example, that for $l_z = 1$ only the levels (0,0) interact. One can verify that for this and other cases the splitting is small. The contribution to the sub-spectra of A_1 consists of two doublets; the remaining three doublets are readily traced in B_1 , B_2 , and B_3 of the direct product.

A complete calculation shows that the parameters that describe the orientation of paradifluorobenzene in hexyloxyazoxybenzene at $+10^\circ$ are, in Snyder's³⁾ notation,

$$c_{3z}^2 - r^2 = -0.35$$

$$c_{xz}^2 - y^2 = -0.26^5$$

Sincerely,

J. Pulchuis

J. Pulchuis

C.W. Hilbers

C.W. Hilbers

C. MacLean

C. MacLean

References:

- 1) G. Diehl, private communication.
- 2) G. Englert and A. Saupe, Z.Naturforschung, 19a (1964), 172.
- 3) L.C. Snyder, J.Chem.Phys., 43 (1965), 4041.

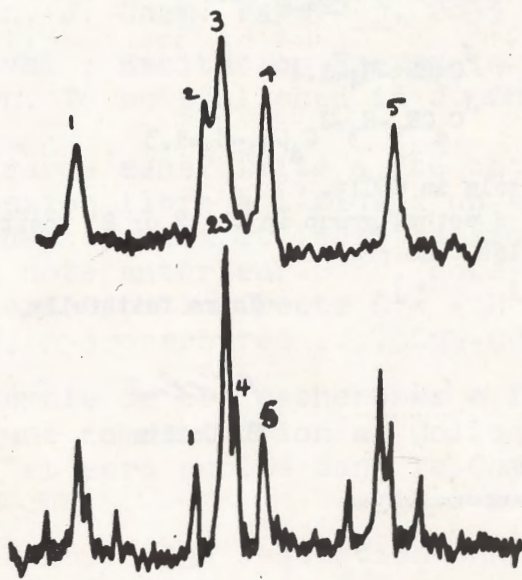


Fig. 1. Low field side of proton spectrum of paradifluorobenzene in hexyloxyazoxybenzene. The central part has been expanded at the top.

Numbers indicate corresponding lines. The separation between lines 3 and 4 is

$$F^H + D^2 = 26 \text{ Hz.}$$

DIVISION OF MINERAL CHEMISTRY — COAL RESEARCH LABORATORY

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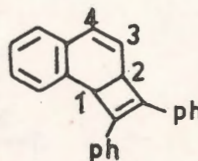
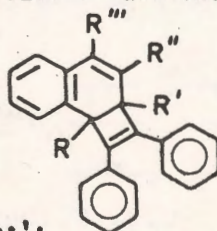
13th June, 1967

Professor B.L. Shapiro,
 Dept. of Chemistry,
 Illinois Institute of Technology, Technology Center,
 CHICAGO...ILLINOIS...60616...U.S.A.

Dear Professor Shapiro,

Thank you for the reminder note - time seems to pass at an ever increasing rate. In this letter we will list some of the pmr parameters of a series of substituted 2,3-benzobicyclo(4.2.0)octatriene.

Heading 2,3-benzobicyclo[4.2.0]octatriene.



Proton numbering system.

Compound.	R	R'	R''	R'''	H ₁	H ₂	H ₃	H ₄
I	H	H	H	H	4.48	4.07	6.20	6.32
II	H	H	H	CH ₃	4.47	4.04	6.06	-
III	H	CH ₃	H	H	4.12	-	6.10	6.33
IV	H	CH ₃	CH ₃	H	4.10	-	-	6.10
V	CH ₃	H	H	CH ₃	-	3.62	6.08	-

Chem. shifts in ppm from TMS

Coupling constants.

Compound.	J _{1,2}	J _{2,3}	J _{2,4}	J _{3,4}	others
I	5.0	4.2	-1.1	9.9	
II	5.1	4.3	-	-	J _{CH₃-H₃} =J _{CH₃-H₂} =1.4
III	-	-	-	9.9	
IV	-	-	-	-	J _{C₃CH₃-H₄} =1.4
V	-	4.5	-	-	J _{C₄CH₃-H₃} =J _{C₄CH₃-H₂} =1.3

The compounds were examined as a 5-10% soln in CDCl₃.

It is of interest to note the effect of a methyl group in the R or R' position on the chemical shift of the remaining cyclobutene proton.

Yours faithfully,

P. Collin

P. Collin

UNIVERSITÉ DE GENÈVE
INSTITUT DE PHYSIQUE EXPÉRIMENTALE
BOULEVARD D'YVOY

Professor B.L. Shapiro
Dept. of Chemistry
Illinois Institute of
Technology
Chicago, 60616

Geneva, June 26, 1967.

Dear Dr. Shapiro,

RMN de haute résolution dans le champ magnétique terrestre

Nous avons mentionné dans une précédente lettre les recherches poursuivies ici en haute résolution dans le champ magnétique terrestre :

- Les mesures en régime permanent sur les esters dérivés de l'acide phosphorique, qui ont permis la mesure et l'interprétation de la grandeur et du signe des constantes $J(H_1^1 - P_{31}^{15})$ séparé par 2 ou plusieurs liaisons sont achevées et en cours de publications aux Helvetica Physica Acta (1967)
E. Duval et G. Béné : Détermination des signes des constantes de couplage $^{31}P - ^1H$ dans quelques composés organophosphorés.
L'interprétation théorique a fait l'objet de plusieurs publications dont les deux plus récentes sont :
E. Duval : Excitation Energy in the Nuclear Spin-Spin Interaction. J. Chem. Phys. 45, 2855 (1966)
E. Duval : Excitation Energy in the Nuclear Spin-Spin Interaction. To be published in J. Chem. Phys. (June 67) as letter.
- Une grande sensibilité a été obtenue par prépolarisation et précession libre à l'aide d'un appareil assurant l'accumulation des signaux et leur transformation de Fourier. Comme il a été noté antérieurement, nous avons pu étudier notamment l'interaction indirecte $C^{13} - H^1$ dans divers dérivés ($CHCl_3$, CH_3OH , hydrocarbures ..., $CH_3-CO-CH_3$...)
L'ensemble de ces recherches a fait l'objet d'une conférence et d'une communication au Colloque Ampère de LJUBLJANA (sept. 1966) et sera publié dans le Compte Rendu des Actes de ce Colloque :
G.J. Béné : High resolution NMR spectroscopy in the terrestrial magnetic field range.
G.J. Béné, M. Merck, R. Secheyay, A. Erbeia : Free precession experiments in terrestrial magnetic field.
North Holland Publ. Co - Amsterdam 1967.

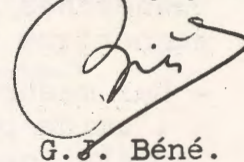
Professor B.L. Shapiro - Chicago - 26.6.67

2.

Le travail de ces derniers mois a porté sur l'analyse précise de la forme des courbes de résonance obtenues par prépolarisation et précession libre dans le champ magnétique terrestre en vue d'en déduire la grandeur des temps de relaxation. L'influence du "Radiation Damping" a été mise en évidence ainsi que celle de l'orientation relative du champ magnétique terrestre et du champ polarisant.

Signalons une technique intéressante pour ces recherches (M. Merck). En utilisant un balayage exponentiel pendant la phase de précession libre, on peut séparer les effets de Radiation Damping (qui n'obéissent pas à une loi exponentielle) des diverses contributions à la relaxation transversale T_2 . Si le "Radiation Damping" est négligeable, la trace de décroissance du signal est presque linéaire (figures ci-jointes).

Sincerely yours,



G.J. Béné.

P.S.: Légende des figures

Le balayage en abscisse (coordonnées de temps) sur l'enregistreur est commandé par la tension d'un condensateur qui se décharge dans une résistance.

La valeur du produit RC (R = résistance, C = capacité) est soigneusement étalonnée.

Lorsque la constante de temps du circuit RC est égale à la constante de temps T_2 de l'exponentielle du signal de précession libre, on obtient une droite.

Sur le graphe ci-joint, nous voyons :

1. le signal de précession de l'eau (non-dégazée) à 20 °C.
2. la courbe redressée, dont la constante de temps n'est pas en accord avec le RC.
3. le signal redressé : une droite.

En fait, on n'obtiendra pas une droite parfaite car le signal de précession n'est pas une vraie exponentielle.

Signal de précession libre
 H_2O , $\theta = 20^\circ C$

①

2.2 sec

1.8 sec

le signal redressé

2.2 sec

②

③

UNIVERSITÉ DE NANTES
FACULTÉ DES SCIENCES
 B. P. 1044 NANTES

Laboratoire de Chimie Organique-Physique
 38, Boulevard Michelet - Nantes

Nantes, le 23 Juin 1967

Professor B.L. SHAPIRO
 Chemistry department

I I T CHICAGO

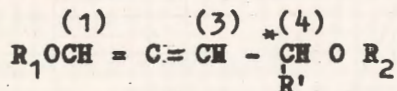
Illinois U.S.A.

N M R evidence for diastereoisomers with axial and centro dissymetries. Magnetic non equivalence.

Cher Professeur SHAPIRO,

Au cours d'études sur la non équivalence magnétique dans les systèmes alléniques (1) nous avons pu montrer que la R.M.N. permet de distinguer des diastéréoisomères dont l'une des dissymétries est de type allénique.

Ainsi, les spectres de composés du type (A) = $R_1OCH=C=CH-\overset{*}{\underset{R'}{CH}}-OR_2$ obtenus par isomérisation de (B) = $R_1OCH_2C\equiv C\underset{R'}{CH}OR_2$ (2) s'interprètent en admettant la présence, en quantités égales, de deux isomères caractérisés par des paramètres R.M.N. très voisins (tableau)



R_1	R_2	R'	δ_1	δ_3	J_{13}	J_{34}	J_{14}
			P.P.M.			Hz	
$(CH_3)_3C$	CH_3CH_2	$CH(CH_3)_2$	6,45 6,39	5,37 5,37	5,55 5,55	7,9 7,9	0,95 1,15

.../...

UNIVERSITÉ DE NANTES
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Laboratoire de Chimie Organique-Physique
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Nantes, le

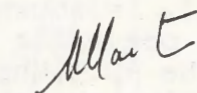
- 2 -

Dans de tels diastéréoisomères on attend effectivement des valeurs très proches des constantes $J_{\text{H-C=C-C-H}}$

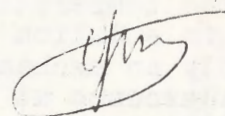
Par ailleurs, le fait que les $J_{\text{H-C}^*\text{-C-H}}$ et les δ soient presque identiques dans les deux structures, suggère que les équilibres conformationnels y sont analogues.

Dans le spectre de la partie méthylénique de $R_2 = \text{Et}$ on peut grouper deux systèmes de transitions correspondant aux parties AB et A'B' de spectres ABC_3 et $\text{A'B'C}'_3$. Une analyse effectuée dans le cas du composé $R' = \text{CH}_3$ conduit aux non équivalences magnétiques $\delta_A - \delta_B = 0,21_0$ et $\delta_{A'} - \delta_{B'} = 0,19_5$. Celles-ci sont inférieures à la valeur correspondante déterminée dans l'éther acétylénique isomère (B).

Nous vous prions de croire, Cher Professeur SHAPIRO, à notre cordial souvenir.



M.L. MARTIN



G.J. MARTIN

(1) M.L. MARTIN, R. MANTIONE, G.J. MARTIN - Tetrahedron Letters
3185-1965 et 3873 - 1966

(2) R. MANTIONE, - Thèse à paraître

SIMON FRASER UNIVERSITY

DEPARTMENT OF CHEMISTRY



BURNABY 2, BRITISH COLUMBIA

Telephone 291-3111 Area code 604

23rd June, 1967.

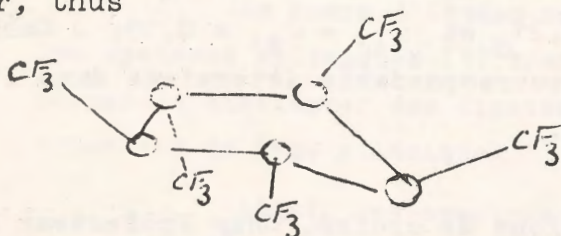
Professor B.L. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Chicago, Illinois 60616

Pseudo-Rotation in $(PCF_3)_5$

Dear Barry,

Thank you for the footnote to your reminder note. We would be honoured to have you visit us, if you could spare the time from Stanford.

Recently Prof. A.B. Burg lectured here on some exotic P compounds he has generated over the last decade, and we thought it might be amusing to examine the nuclear outlook of P and F in $(PCF_3)_5$. The crystal structure has shown the molecule to be non-planar, thus



The temperature dependence of the 56.4 Mhz F^{19} spectrum of $(PCF_3)_5$ in solution with $(PCF_3)_4$ is shown in the diagram. There is apparently an exchange process occurring which has not quite reached coalescence at $+200^\circ C$. The 40.5 Mhz P^{31} spectrum also shows a 2:3 doublet, with inverted relative shift to the F^{19} spectrum, that broadens somewhat on heating. The spectrum of $(PCF_3)_4$ is temperature independent.

We ascribe the scrambling mechanism to pseudo-rotation in the P_5 ring, although other processes have to be considered, i.e. individual P atom inversion, ring opening, CF_3 exchange etc. The minimum value of ΔG^\ddagger of the process is 22.5 kcals. It is probably around 23.5 kcals. We believe that this is the first time that pseudo-rotation has been seen by NMR in simple 5 membered rings.

The details of both the F and P spectra of both the pentamer and tetramer are a mess.

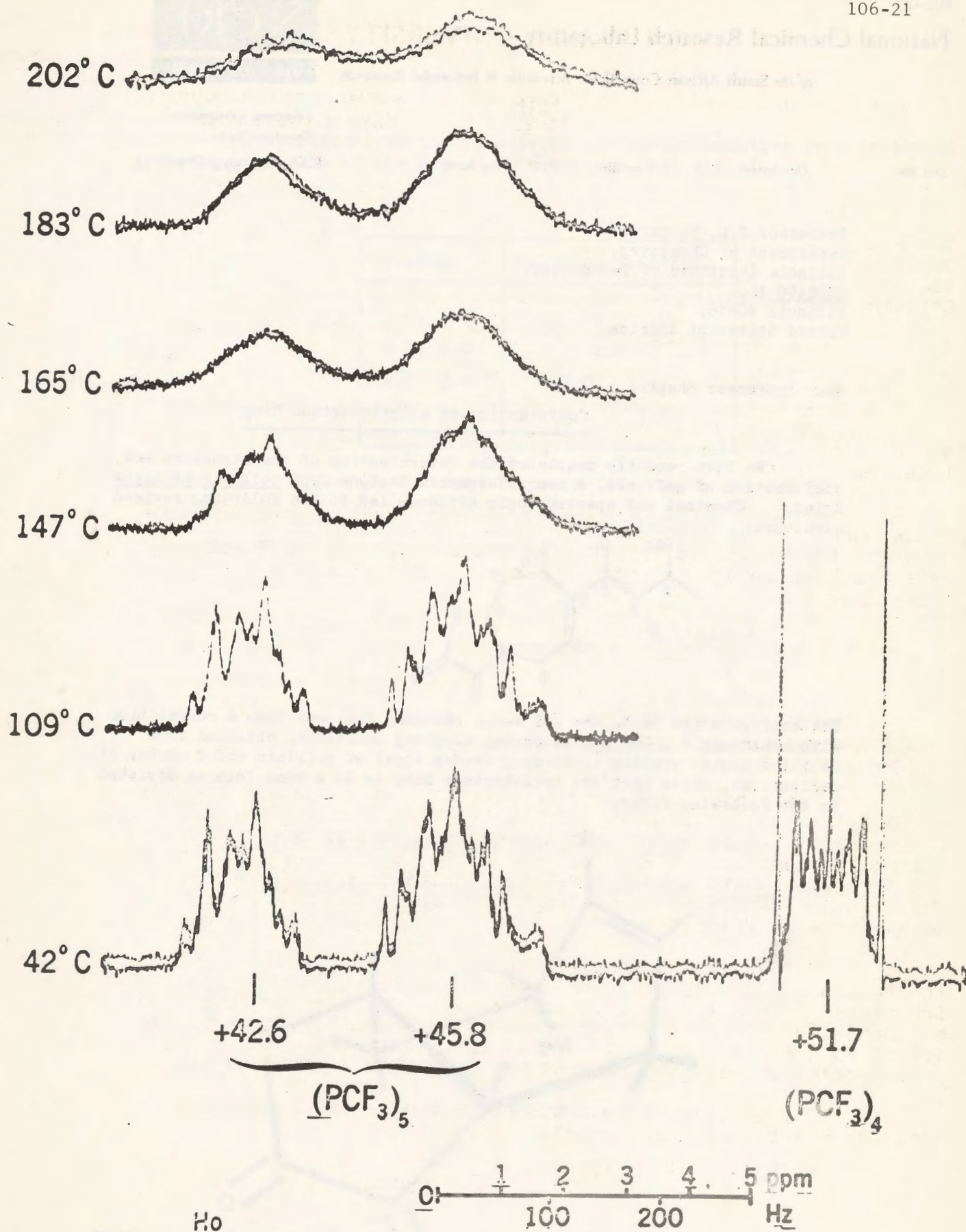
With all best wishes,

Yours,

Ed.

E.J. Wells

EJW/mln



National Chemical Research Laboratory

of the South African Council for Scientific & Industrial Research

NCRL

OF THE CSIR

Telegrams NAVORSCHM

Telephone 74-6011

P.O. Box 395, Pretoria

Our file

Our letter

Your file

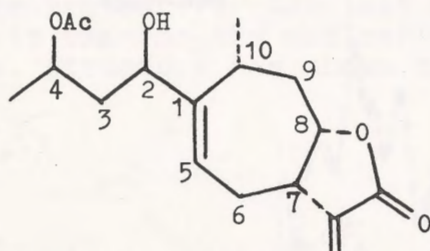
Your letter

Professor B.L. Shapiro,
 Department of Chemistry,
 Illinois Institute of Technology,
 CHICAGO 16,
 Illinois 60616,
 United States of America.

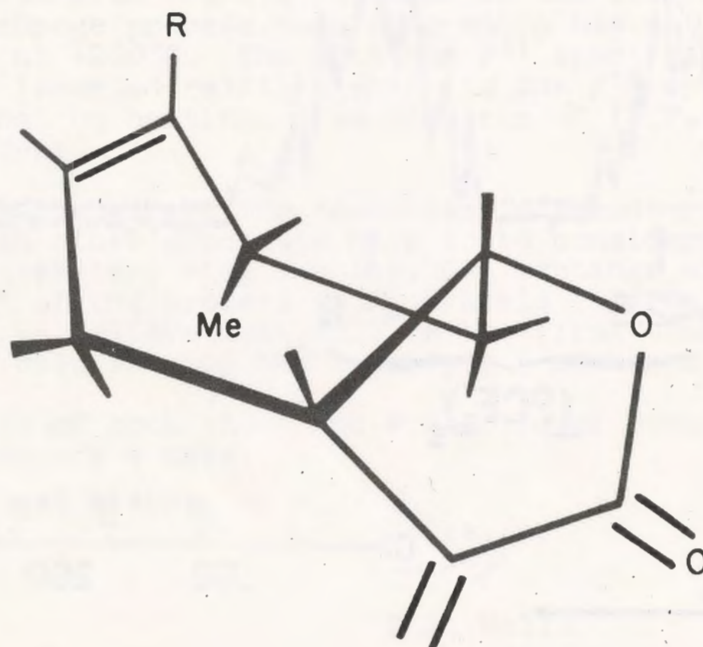
Dear Professor Shapiro,

Conformation of a Cycloheptene Ring

We have recently completed the determination of the structure and conformation of gafrinin, a sesquiterpenoid lactone from *Geigeria africana* Gries.¹ Chemical and spectroscopic evidence led to the following revised structure:



The configuration (α -C₁₀-Me and α -cis lactone) followed from a correlation with Xanthumin.² The proton-proton coupling constants, obtained from detailed n.m.r. studies (including decouplings) of gafrinin and a number of derivatives, shows that the cycloheptene ring is in a boat form as depicted in the following figure:



Distortions from the ideally staggered conformation were indicated by the magnitude of the H-9, H-10 couplings (see Table).

Protons	Coupling Constants
H-6, H-7	6.0, 11.0
H-7, H-8	8.6
H-8, H-9	3.0, 11.6
H-9, H-10	0, 7.5

Yours sincerely,

K. Pachler

K. Pachler
SENIOR RESEARCH OFFICER
CHEMICAL PHYSICS GROUP
NATIONAL CHEMICAL RESEARCH LABORATORY

¹ J.P. de Villiers, J. Chem. Soc. 1961, 2049.

² H. Minato and I. Horibe, J. Chem. Soc. 1965, 7009.

THE UNIVERSITY OF LIVERPOOL
DEPARTMENT OF ORGANIC CHEMISTRY

TELEPHONE: ROYAL 6022



THE ROBERT ROBINSON LABORATORIES,
OXFORD STREET,
LIVERPOOL 7.

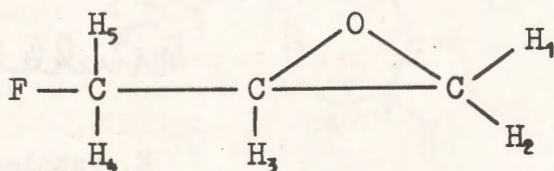
28th June, 1967.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616,
U.S.A.

Dear Barry,

Spectral Data for Epifluorohydrin

For my contribution to the Newsletter, may I quote some preliminary results obtained from the 100 Mc/s and 94.1 Mc/s spectra of epifluorohydrin ($\sim 20\%$ in CDCl_3). From this rather spectacular spectrum, first order couplings and shifts were obtained, and fed into LAOCOON II, which converged rapidly to give the following data:-



$W_1 = 266.312$ (c/s from TMS)	$J_{12} = 4.900$	$J_{25} = -0.013$
$W_2 = 285.457$	$J_{13} = 2.642$	$J_{2F} = 3.671$
$W_3 = 324.880$	$J_{14} = 0.196$	$J_{34} = 5.882$
$W_4 = 428.765$	$J_{15} = 0.306$	$J_{35} = 2.556$
$W_5 = 465.082$	$J_{1F} = 1.218$	$J_{3F} = 12.249$
$\delta_F = +6,070$ (c/s from C_6F_6)	$J_{23} = 4.245$	$J_{45} = -10.752$
	$J_{24} = -0.026$	$J_{4F} = 47.167$
		$J_{5F} = 47.611$
RMS error = 0.025 c/s		

- 2 -

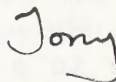
The proton-proton couplings compare favourably with those reported for epichlorhydrin,¹ except for the long range couplings which are reduced as expected, with no resolvable splitting between H_2 and H_4 or H_5 .

The analysis shows $J_{4,5}$ and $J_{4,F}$ (or $J_{5,F}$) to be opposite in sign, but further work is in progress to establish the other relative signs, that of the four bond H-F couplings being of particular interest. Tickling experiments should establish such information shortly. It is hoped to examine the rotational isomerism in this compound by studying the spectrum in solvents of different polarity.

I hope this letter will keep me on the list for a few months.

With best regards

Yours sincerely,



W.A. Thomas.

¹ G. Aruldas and V. Nayar, Ind. J. App. Phys., 1966, 4, 361 (and references therein)

INSTITUT FÜR PHYSIKALISCHE CHEMIE DER
TECHNISCHEN HOCHSCHULE STUTTGART

Doz. Dr. Herbert Dreeskamp

7 STUTTGART N

Wiederholdstraße 15

Telefon 2997 8393

May 30, 1967

Spin-coupling in XMe_4 -compounds

Dear Barry:

At last I found the time to complete a manuscript on the work we have been doing on the tetramethyl-compounds. You may recall that I talked about this at the 7th ENC in March 1966. So here is a table with the coupling-constants in group IV compounds given in cps:

Isotope	J_{CH}	$J_{\text{X-C}}$	$J_{\text{X-C-H}}$	$J_{\text{C-X-C-H}}$	$J_{\text{H-C-C-H}}$
X	± 0.3	± 3	± 0.2	± 0.1	± 0.05
C^{13}	+ 124.2		± 3.7	+ 4.4	± 0.35
Si^{29}	+ 118.4	- 50	+ 6.5	+ 2.0	+ 0.2
Sn^{119}	+ 127.8	- 336	+ 54.0	+ 1.5	± 0.1
Pb^{207}	+ 133.9	+ 249	- 61.2	± 1.0	< 0.05

The signs are relative to a positive $J_{\text{C-H}}$ and were determined by either H-{C}, H-{X} or H-{H} double resonance experiments. Apparently the one-bond normalized coupling constants are positive and their values are reasonably proportional to $\varphi_{\text{X}}^2(o) \cdot \varphi_{\text{C}}^2(o)$. Furthermore, from a negative sign of $J'_{\text{X-C-H}}$ follows the experimental proof of $J'_{\text{X-H}} > 0$ in XH_4 compounds. For some time (Z. Naturforschg. 19a, 139 (1964)) I had hoped this would be true. Finally $J_{\text{C-X-C-H}}$ is quite closely $= \gamma_{\text{C}} \cdot \varphi_{\text{C}}^2(o) (\gamma_{\text{H}} \cdot \varphi_{\text{H}}^2(o))^{-1} \cdot J_{\text{H-X-C-H}}$ in $\text{HX}(\text{CH}_3)_3$, which did not surprise us a bit.

Sincerely yours,

H. Dreeskamp

THE UNIVERSITY OF WESTERN ONTARIO
FACULTY OF ARTS AND SCIENCE
COLLEGE OF SCIENCE



DEPARTMENT OF CHEMISTRY

LONDON, CANADA

June 29, 1967

Dr. B. L. Shapiro,
Dept. of Chemistry,
Illinois Institute of Technology,
Chicago, Ill. 60616, U.S.A.

Dear Barry,

Some time ago, Dhami and Stothers reported the ^{13}C spectra of a large number of substituted anisoles (1).

1. K. S. DHAMI and J. B. STOTHERS, Can. J. Chem. 44, 2855 (1966).

Having the compounds at hand, I thought it might be instructive to look at the directly-bonded CH couplings in the methoxy group. I hoped to observe some conformational dependence.

The data for twelve anisoles (neat liquids), plotted against the methoxy carbon shifts, fall into two separate correlations, involving:

- 1) unsubstituted and ortho-substituted anisoles,
- 2) di-ortho-substituted anisoles.

Presumably, di-ortho-substitution forces the methoxy group out-of-plane and out of conjugation with the ring, thereby attenuating the sensitivity of the coupling constant to changes in the electron density at carbon (as reflected in the carbon shift). This is understandable if the major cause of electron redistribution is conjugative interaction with the aromatic ring.

Consider the following data:

R	$J(^{13}\text{CH})$	$\delta(\text{CH}_3\text{O})$
H	143.7	138.1
Me	142.7	134.3
i-Pr	142.3	132.1
t-Bu	141.8	128.9

As the size of the 2,6-substituents increases, the degree of coplanarity is decreased, and with it the contribution from canonical forms having a positive charge at oxygen. Hence the electron density at the methoxy carbon should increase, along with the carbon shift. The coupling constant should decrease as the effective nuclear charge at carbon decreases (2), as is observed.

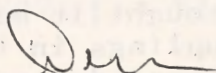
2. D. M. GRANT and W. M. LICHTMAN, J. Am. Chem. Soc., 87, 3994 (1965).

There still seems to be no good explanation for the anomalous shift changes of the methoxy carbons.

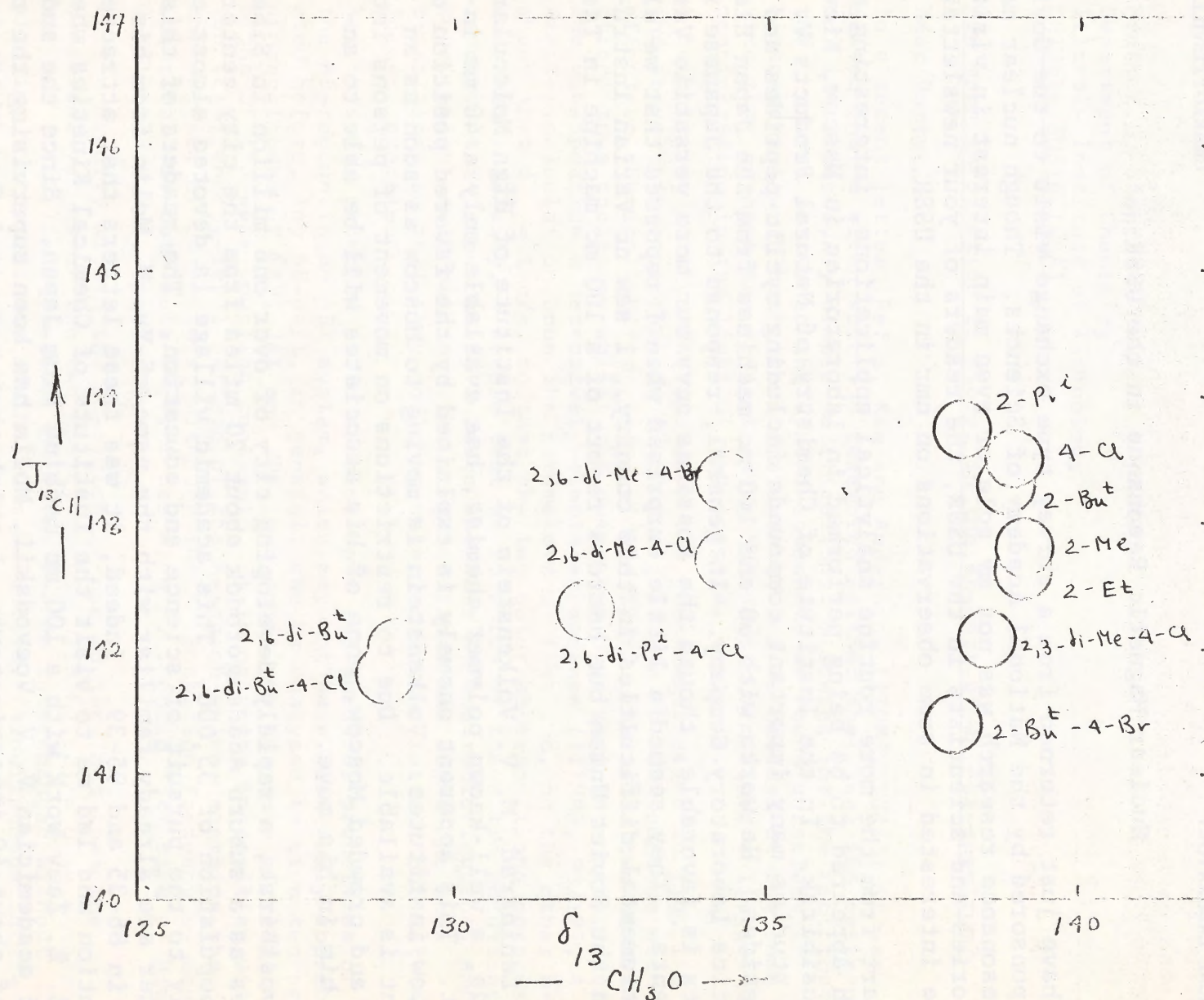
Please credit this contribution to my subscription,
c/o Chemistry Department, Boston College.

Short Title: Conformational Effects on $J(^{13}\text{CH})$.

Sincerely,



D. J. Sardella



UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY

COBB CHEMICAL LABORATORY

CHARLOTTESVILLE, VA.

Nuclear Magnetic Resonance in the USSR

I have just returned from a survey type exchange visit to the Soviet Union sponsored by the National Academy of Sciences. Though nuclear magnetic resonance research was not my sole or even main interest in visiting laboratories and scientists in the USSR, the readers of your newsletter might be interested in some observations on nmr in the USSR.

Apart from the more routine analytical applications, interesting nmr research appeared to be being performed in laboratories in Moscow, Kiev, and Novosibirsk. In the Institute of Chemistry of Natural Products V. F. Bystrov studies many important compounds including cyclic peptides and depsipeptides. He works with 60 and 100 mc machines from the Japan Electron Optics Laboratory Company. In general, response to the Japanese instruments is favorable, though the Russians envy our more versatile Varian instruments. They seemed a little surprised when I reported that we also had instrumental difficulties in this country. I saw no Varian instruments in the Soviet Union but heard a report of a 100 mc machine in Tashkent.

In Leningrad, M. V. Volkenstein of the Institute of High Molecular Compounds, a well-known polymer chemist, has available only a 40 mc instrument. This apparent anomaly is explained by the favored position of the Moscow institutes. Volkenstein is moving to Moscow as soon as an apartment is available. Due to restrictions on movement of persons into popular and crowded Moscow, none of his associates will be able to accompany him in his move.

Novosibirsk, a rapidly developing city of over one million in Siberia, possesses as a suburb Akademgorodok about 20 miles from the city center with a population of 35,000. This academic village is devoted almost exclusively to the pursuit of science and education. The readers of this newsletter are already familiar with the name of Yu. N. Molin from his letters in 86-35 and 95-39. Indeed, it was these letters that attracted my attention and led me to visit the Institute of Chemical Kinetics where he and E. E. Zaev work with a 100 mc machine from Japan. Since the sudden death of academician V. V. Voevodskii, Molin has been supervising the research of about 40 investigators. I think that personnel from this group would benefit greatly if given the opportunity to perform nmr research in this country.

Bruce Martin

R. Bruce Martin
Professor of Chemistry

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

Basel, 29 June 1967

Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 60616 (USA)

How much information is stored in the AB-part of an ABX-spectrum?

Dear Barry,

In a recent letter (Ref.1, Kim and Anderson, IITNMR, 104/3) it was stated that a given spectrum resembled neither the usual ABX pattern, nor its deceptively simple modifications. Allowing for the fact that the C proton perturbed the system somewhat, we found ourselves in disagreement with both these statements, and we decided at the same time that perhaps the AB-part in an ABX spectrum merited a little more consideration in the light of sub-spectral analysis.

A calculation of the ABX-type upon the parameters given in fig. 1 b of the above reference reveals a truly degenerate ab-sub-spectrum with the effective chemical shift $\delta_{ab} = \delta_{AB} - \frac{1}{2}(J_{AC} - J_{BC}) = 0$. The inner two ab transitions thus coalesce, whilst the outer two have zero intensity, giving the sub-spectrum a deceptively-simple appearance (IITNMR, 88/12). A similar calculation upon the parameters of fig. 1 c, on the other hand, shows that $\delta_{ab} = 1$ c/s, so that the two outer ab transitions possess non-zero intensity. A simple test as to which of these two solutions is correct is provided by a large increase of the radiofrequency amplitude, which would saturate the stronger lines and boost the weak transitions so that they could be observed in the latter, but not the former, example.

All this has prompted us to discuss some sub-spectral properties of the AB-region in an ABX system, which may not have been fully appreciated before. Any AB-part, in general, can be analysed to give two sets of magnitudes of δ_{AB} , J_{AX} and J_{BX} , and sometimes two sets of relative signs of the weak coupling constants. It is only the intensities within the (2:2) energy-level pattern of the X-region which determine the correct set of parameters, although the X transition frequencies are identical for both sets (Ref. 2 See also P.L. Corio "Structure of High Resolution N.M.R. Spectra").

This ambiguity within the AB-region is due to the fact that the numerical values of the two energy levels with $F_z(AB) = 0$ in either of the two (1:2:1) energy-level patterns may be interchanged without altering the appearance of the ab-sub-spectra. (Simultaneous interchange of both sets of energy-levels merely results in a relabelling of the A and B nuclei).

The consequences of this are displayed in fig. 1 for different AB-regions, where the effective chemical shifts of the two ab-sub-spectra range from the case of no overlap (non-eclipsed type), through partial and degenerate overlap, to the case where one shift is completely contained within the other (totally-eclipsed type). In each case the relative signs of the weak coupling constants are given, and it is

- 2 -

immediately obvious that in each of the two possible analyses, δ_{AB} , J_{AX} , J_{BX} possess totally different magnitudes, although, of course, $|J_{AB}|$ remains unchanged. Only one example of degeneracy is given (where incidentally, an example of the misleadingly-termed "virtual-coupling" is shown), since the other type has been mentioned above (ie when one of the effective shifts is zero), when one ab-sub-spectrum consists of only one strong line. In the latter case, an interchange of energy-levels will, at most, merely re-label the nuclei, and not alter the parameter magnitudes.

The cases in fig. 1 and the other degenerate cases include all possible types of AB-regions arising from ABX spectra, and can therefore be used to elicit information by inspection. For example, ref. 1, fig. 1 b corresponds to the non-eclipsed type, so that the signs are necessarily positive, whereas fig. 1 c is an example of the above fig. 1(4), where either the relative signs are negative, or else $J_{BX}=0$.

In general, one of the ambiguous possibilities can often be rejected on account of an atypical coupling constant magnitude, otherwise a computer-type approach to the intensities of the X-region is required in order to unambiguously assign the correct parameters.

Yours sincerely,

Peter

Roderick J. Chuck

Peter Diehl
R.J. Chuck

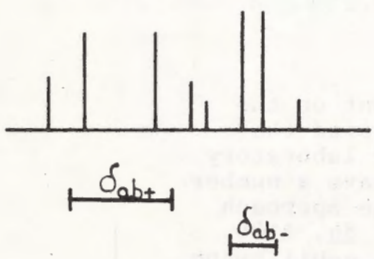
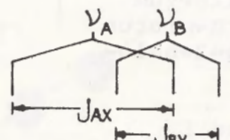
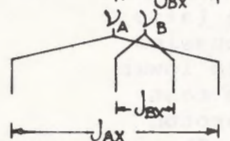
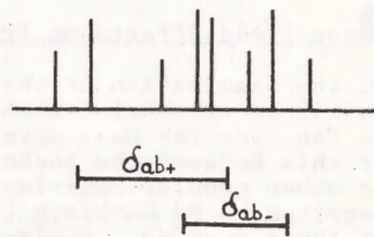
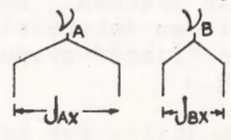
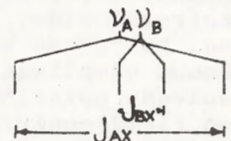
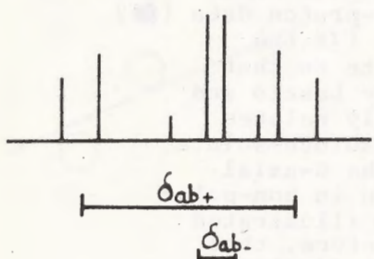
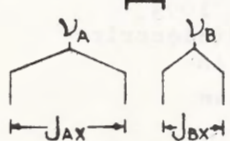
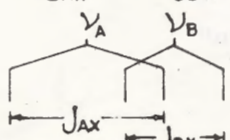
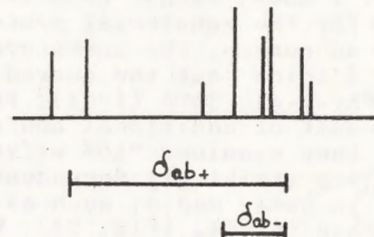
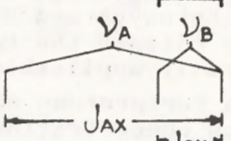
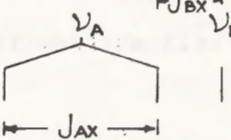
AB-part of ABX-spectrum	Rel. signs J_{AX}, J_{BX} .	AB-part of ABX-spectrum	Rel. signs J_{AX}, J_{BX} .
<p>1. Non-eclipsed</p>  <p>a. </p> <p>b. </p>	alike	<p>2. Partially-eclipsed</p>  <p>a. </p> <p>b. </p>	alike
<p>3. Totally-eclipsed</p>  <p>a. </p> <p>b. </p>	opposite	<p>4. Degenerate</p>  <p>a. </p> <p>b. </p>	opposite

Fig. 1: AB-parts of ABX spectra, where $\delta_{ab\pm} = (\nu_A - \nu_B) \pm \frac{1}{2} (J_{AX} - J_{BX})$

ν_A, ν_B are the chemical shifts of nuclei A and B respectively.

THE UNIVERSITY OF WESTERN ONTARIO
FACULTY OF ARTS AND SCIENCE
COLLEGE OF SCIENCE



DEPARTMENT OF CHEMISTRY

LONDON, CANADA

July 4, 1967

Dr. B. L. Shapiro,
Dept. of Chemistry,
Illinois Institute of Technology,
Chicago, Ill. 60616, U.S.A.

Dear Barry,

Reaction Field Effects on Proton Shieldings

As you know, the examination of the effects of solvent on the conformational equilibria of α -halocyclohexanones has occupied the talents of Yuh-Hsu Pan over the past several months in our laboratory. NMR was chosen for this because the technique appears to have a number of advantages over other popular experimental methods. The approach has been fully described by Ed Garbisch [J. Am. Chem. Soc. **86**, 1780 (1964)] for one of these systems. Besides the data on the equilibrium constants, etc. there is an interesting feature revealed by the α -proton (CHX) shieldings of the "fixed" systems, i.e. the cis- and trans-2-halo-4-t-butylcyclohexanones.

We measured these shifts for ketones having X = Br, Cl, and F in cyclohexane, carbontetrachloride, chloroform and acetonitrile (also in p-dioxane and benzene, but these won't enter the present discussion because of other well-known complications) and noted the trend to lower field with increasing solvent polarity. It seemed worthwhile to test for evidence of reaction field contributions by plotting the α -proton shieldings vs. $[(\epsilon-1)/(\epsilon+1)]$. These plots are shown in Fig. 1. The shielding data are "infinite dilution" values obtained from plots of the α -proton shifts vs. concentration over the range 1.5 - 30 mole % (except for cyclohexane solutions in which solubility limits the available range). Fig. 1 shows linear behavior for the axial α -proton data (●) with more scatter for the equatorial proton results (○). (If the latter were drawn as curves, the curvature would be opposite to that commonly found.) I think that the curved plots obtained by Laszlo and Musher [J. Chem. Phys. **41**, 3906 (1964)] for two very closely related compounds are a result of additional contributions due to solute-solute association since they examined "10% wt/vol" solutions. The α -axial proton shieldings are strikingly dependent on concentration in non-polar solvents (but not in polar media, such as acetonitrile) as illustrated for the α -chloro case in CCl₄ (Fig. 2). We conclude, therefore, that the recently proposed [Kotowicz and Schaefer, Can. J. Chem. **45**, 1093 (1967)] proportionality between the reaction field effect and [dielectric constant]^{1/2} is not generally applicable. The potential dangers in interpreting shift data for protons of polar solutes in non-polar media even at fairly low concentration seems clear from Fig. 2.

I hope that this will suffice to continue my "subscription" for a few more months.

Best regards.

Sincerely,

Jake

J. B. Stothers
Professor of Chemistry

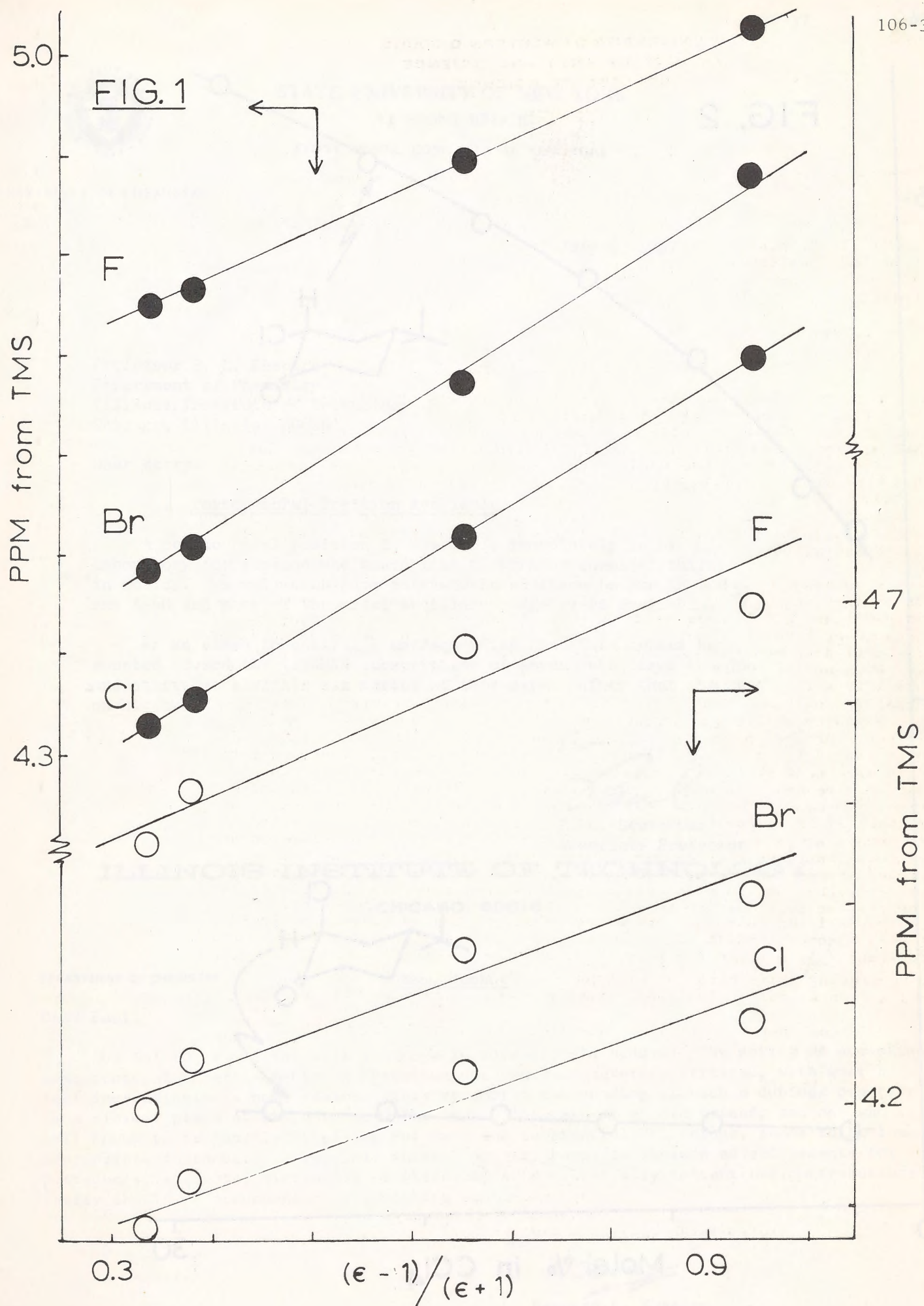
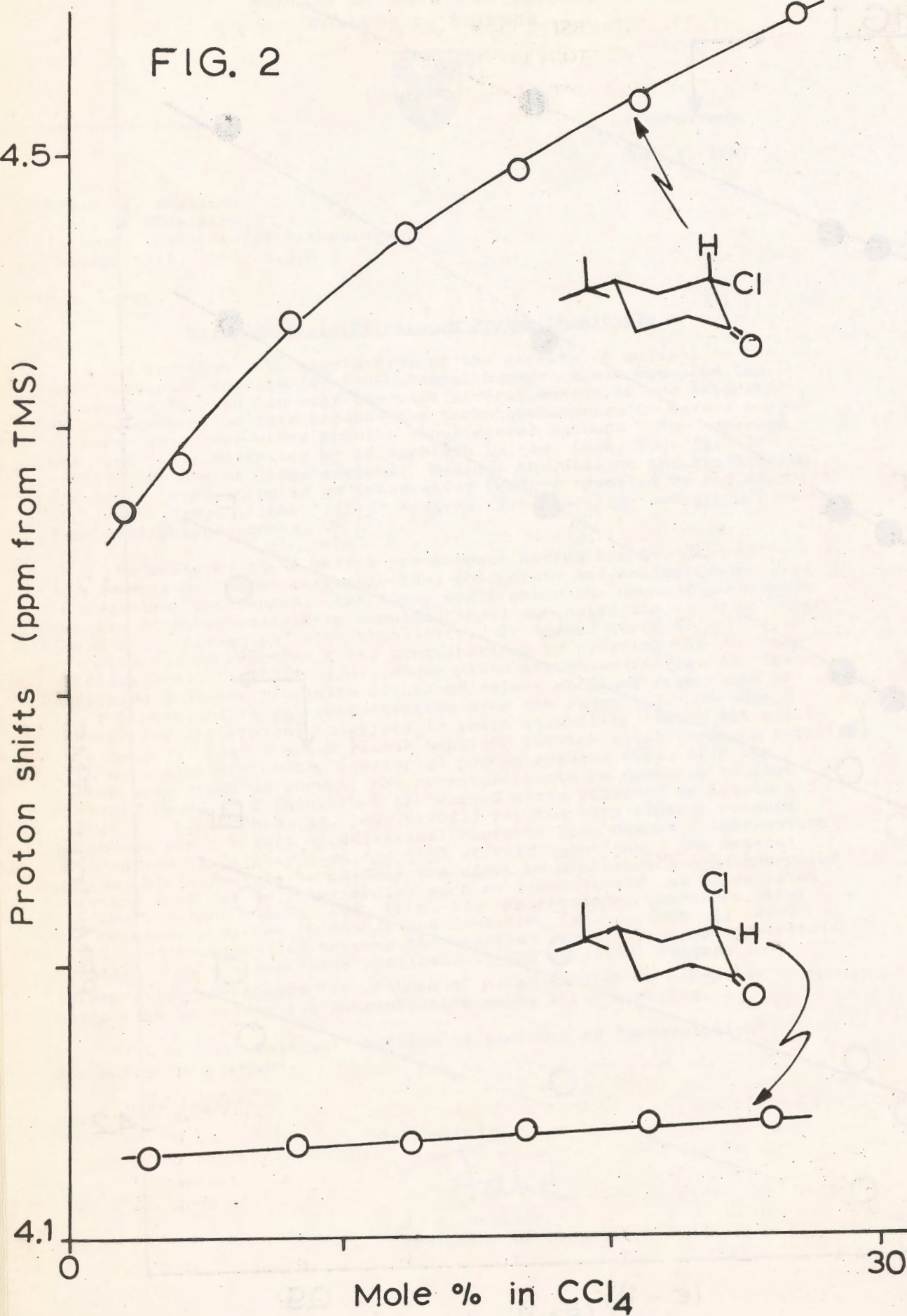


FIG. 2





STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

11790

DEPARTMENT OF CHEMISTRY

July 5, 1967

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

Dear Barry:

Postdoctoral Position Available

A postdoctoral position is available immediately in my laboratory for someone who would like to work on chemical shifts in solids. We will soon have an HR-60 in addition to our HR-100 and A-60 and most of the usual ancillary gadgetry is available.

As an added incentive, I am requesting that this letter be counted toward the IITNMRN subscription of anyone who takes the job and starts work within six months of this date. After that, he is on his own.

Yours truly,

P. C. Lauterbur
Associate Professor

ILLINOIS INSTITUTE OF TECHNOLOGY

CHICAGO, 60616

DEPARTMENT OF CHEMISTRY

Bah, Humbug

Dear Paul;

No! No! 10^n x no! (As well you knew in advance, old buddy.) The policy of accepting post-doctoral advertisements as contributions has been severely critized, with what I feel increasingly is some reason. This attempted compounding of such a dubious practice is a minimal place at which to draw the line. The case of an old friend, and one who is well known to be capable of giving out many and substantial NMR things, seems to be the appropriate instance. In general, while I am very happy to include advertisements for post-doc's, students, mistresses or whatever, such essentially contentless contributions really should be accompanied by something echt.

Y'r sometimes ob'd't s'v't,

Bernard L. Shapiro
Associate Professor

BLS:afc

INSTITUT DE CHIMIE

Boîte Postale 296 / R 8

Téléphone 36.63.51 à 53

Dr. J.M. LEHN

STRASBOURG, le June 9, 1967

1, rue Blaise PASCAL

Dr. B.L. SHAPIRO

IITNMR

Department of Chemistry

Illinois Institute of Technology

CHICAGO Illinois 60616

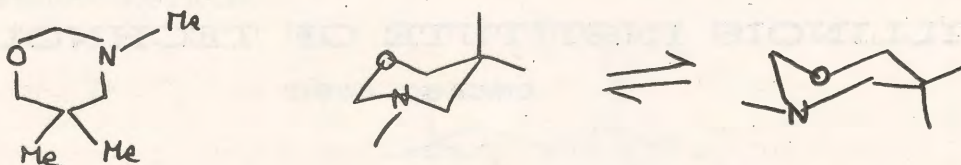
Dear Barry,

May be, after having sent off this contribution, I shall feel myself less guilty

Ring Inversion in Oxazines (with P. Linscheid and F.G. Riddell)

We have studied the ring inversion process in some oxazines and have obtained the corresponding activation parameters .

Lineshape-analysis of the three superimposed AB patterns and of the $C(CH_3)_2$ doublet as a function of temperature leads to the following values : $\Delta G^*(-50^\circ) = 10.7 \pm 0.2$ kcal/mole ; $\Delta H^* = 10.3 \pm 1.0$ kcal/mole and $\Delta S^* = -2 \pm 4$ eu (solvent CH_2Cl_2) , for the following compound :

Influence of lone pair orientation on ^{15}N - 1H coupling (with J.P. Kintzinger)

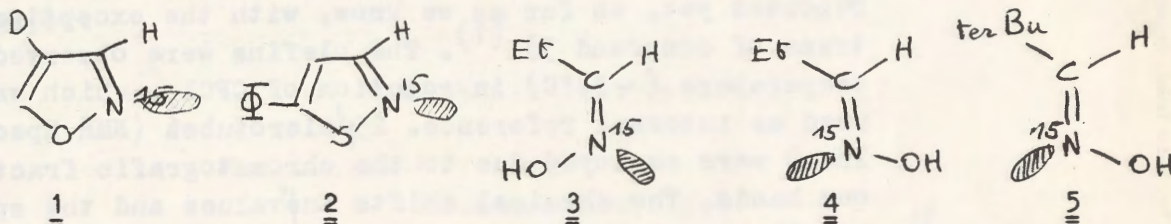
We are studying a number of ^{15}N containing compounds and we have found a very marked effect of lone pair orientation on ^{15}N -C-H coupling . Some results are given in the Table .

It is seen that the ^{15}N -C-H coupling is strongly dependent on the lone pair orientation . A large coupling (14-16 Hz) is found when H and lone pair are cis, a small coupling (3-5 Hz) is found when they are trans .

In SO_4H_2 solution, where the lone pair has been removed by protonation, compounds 2 and 5 show similar couplings (3-4 Hz). We are studying the origin and the applications of this effect.

Compound	Solvent	$J(^{15}\text{N}=\text{C}-\text{H})$ in Hz.
<u>1</u>	DMSO	15
<u>2</u>	CDCl_3	14.2
	SO_4H_2	4.2
<u>3</u>	CH_2Cl_2	16.2
	Pentane	15.5
<u>4</u>	Pentane	3.0
<u>5</u>	Pentane	3.0
	SO_4H_2	3.5

(Compound 2 has been obtained from Roy Olofson at Penn. State U.)



Hoping you will find a way of maintaining IITNMR and thanking you very much for all you have already done to keep it going,

With our best wishes,

J.P. Kintzinger

J.M. Lehn

P. Linscheid

F.G. Riddell

F. G. Riddell

SOCIETÀ EDISON

SOCIETÀ PER AZIONI CON SEDE IN MILANO
CAPITALE SOCIALE L. 375.000.000.000 - INTERAMENTE VERSATO

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BOLLATE, July 5, 1967

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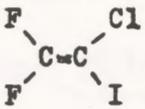
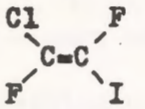
Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago - Ill. 60616

U.S.A.

Subject: F^{19} NMR parameters of some
fluoro-ethylenes and of
some "Dewar" type deriva-
tives.

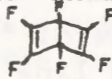
Dear Professor Shapiro,

as our new contribution to IIT NMR Newsletter we like to give here a preliminary account of our research work in the F^{19} NMR field. We have recently recorded with our A56/60 spectrometer the spectra of some fluoro-ethylenes, the NMR parameters of which have not been reported yet, as far as we know, with the exception of J^{FF} trans of compound 3) ⁽¹⁾. The olefins were observed at room temperature ($\sim 37^\circ C$) in solution of $CFCl_3$, which was also used as internal reference. 25 μ microtubes (NMR Specialites Inc.) were employed due to the chromatographic fractions in our hands. The chemical shifts in ν values and the spin-spin coupling constants are reported below:

	δ^* Chemical shift-	Coupling constant (c/s)
1) $CF_2=Cl_2$	63.9	$J_{C^{13}CF}=37$ $J_{C^{13}F}=296$
2) 	75.6 78.6	$J_{gem}^{FF} = 24.0$
3) 	110.0 120.1	$J_{trans}^{FF} = 142.8$

Compound 1), $CF_2=Cl_2$, was identified observing the weak satellites symmetrically displaced to either side of the single main resonance ($\delta^* = 63.9$) and due to splittings

by the C^{13} isotope in natural abundance (1.1%). The $C^{13}.F^{19}$ spin-spin couplings found are in agreement with literature data (2). The chemical shift assignments of compounds 2) and 3), cannot be done on reliable basis. The $F^{19}.F^{19}$ gem. coupling constant and the chemical shifts of geminal fluorines in compound 2) are found to be in agreement with the relationship of Reuben & al. (3).

We have recently completed a piece of work on some derivatives of "Dewar" isomer of perfluorobenzene. The title of the paper, which appears in J. Chem. Soc. B, 384, 1967, is: "The F^{19} NMR spectra of para-bonded isomers of the diethoxytetrafluorobenzenes". A few reprints are available on request. In cooperation with Prof. G. Rigatti (Istituto Chimica-Fisica, Università di Padova) we have also succeeded in the $AA'XX'X''X'''$ analysis of the parent compound, the hexafluoro isomer, , which will be the subject of a forthcoming paper.

With all best regards.

Yours sincerely,

L. Cavalli

L. Cavalli

- (1) M.G. Barlow, Chem. Comm. 703, 1966
- (2) J. Reuben, A. Demiel, J. Chem. Phys. 44, 2216, 1966
- (3) J. Reuben, Y. Shvo, A. Demiel, J. Am. Chem. Soc. 87, 3995, 1965



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

June 29, 1967

IN REPLY REFER TO: 313.06

* Professor Barry Shapiro
Illinois Institute of Technology
Department of Chemistry
Chicago, Illinois 60616

Title: A. Frequency dependent ^1H broad-line NMR spectra.
B. Standard reference materials and standard reference data.

Dear Barry:

In some recent proton broad-line studies of $^1\text{H}^{11}\text{B}(\text{OC}^2\text{H}_3)_2$ we have found experimentally that the proton line shape is frequency dependent. This effect arises from an indirect quadrupole interaction which is important only when the ratio of the Zeeman to the quadrupole resonance frequencies is about 5 to 1 or less. Due to a lack of axial symmetry line shape calculations are not tractable for this system, so we have proceeded to simpler systems.

The National Bureau of Standards has a general program to furnish standard reference data and standard reference samples. Is there a need in NMR spectroscopy for standard reference samples, for example, to calibrate spectrometers or to check the linearity and stability of field sweep ^{19}F spectra? If anyone has any comments or suggestions I would appreciate hearing from them.

Best regards,

Tom

Thomas C. Farrar

MICHIGAN STATE UNIVERSITY EAST LANSING · MICHIGAN 48823

COLLEGE OF NATURAL SCIENCE · DEPARTMENT OF CHEMISTRY · CHEMISTRY BUILDING

July 5, 1967

Professor B. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

CALIBRATION OF NMR THERMOMETER

Our experience with the use of methanol and ethylene glycol chemical shifts, along with the Varian calibration curves [Varian A-60 Temperature Accessory Manual 87-202-001], for measurement of sample temperature may be of interest to those using NMR in rate studies. We found that plots of the values of $\log \tau$ vs $1/T$ for N,N-dimethyltrichloroacetamide, where 2τ is the lifetime of a methyl proton at one site, showed a discontinuity in going from the glycol to the methanol temperature ranges [Fig. 1, upper two lines].

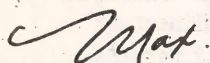
Calibration of the chemical shifts of ethylene glycol and methanol as functions of temperature were therefore carried out in our HA-100 system using conditions approximating those used for sample observation. A thermocouple placed in a small capillary tube was supported centrally in a regular thin-wall sample tube containing the solvent in such a way that temperatures could be measured while spinning the tube. Temperatures were recorded on a specially modified Sargent recorder using a thermocouple which had been calibrated at several temperatures against a Bureau of Standards thermometer. Varying the height of the thermocouple changed the temperature less than $+0.2^\circ$ and all measurements were therefore made with the thermocouple at the vertical position corresponding to the center of the receiver coil. The resulting measurements were fitted to an equation of the form $t^\circ\text{C} = a\delta + b$, where a and b were found from a least-squares fit of twenty or so points and δ is in Hz at 100 MHz in our work. Although this calibration was carried out using reagent grade chemicals in open tubes it was transferred, by the substitution method, to the sealed samples provided by Varian for routine use.

In the high temperature range our values of temperature were somewhat lower than given by the Varian charts for methanol and somewhat higher in the case of ethylene glycol. This accounts for the discontinuity in the upper plot of Fig. 1 and the new curve using our calibration is reasonably linear (lower curve, Fig. 1). In actual practice δ was found at each temperature by substituting a sample of solvent before and after the spectrum of the amide was obtained. Simultaneous observation using a concentric capillary of solvent would be preferable but, even using Teflon spacers, always gave poorer line shapes for the amide. This might not be true at 60 MHz.

Prof. B. Shapiro - July 5, 1967 - page 2

The use of the NMR thermometer is certainly a great convenience in kinetic studies but we conclude that each laboratory interested in reasonable precision of temperature measurement (perhaps $\pm 0.3^\circ\text{C}$) should consider carrying out a calibration under conditions close to those in routine use. The Varian calibrations are, of course, adequate ($\pm 2^\circ\text{C}$) for all but the most precise work.

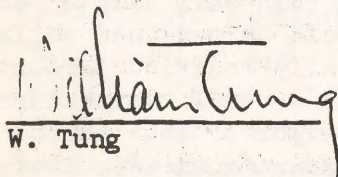
Yours sincerely,



M. T. Rogers

大西 征子

M. Ohnishi



W. Tung

nh

Fig.1 - Plot of $\log \tau$ vs $10^3/T^\circ K$ for N,N-Dimethyltrichloroacetamide.

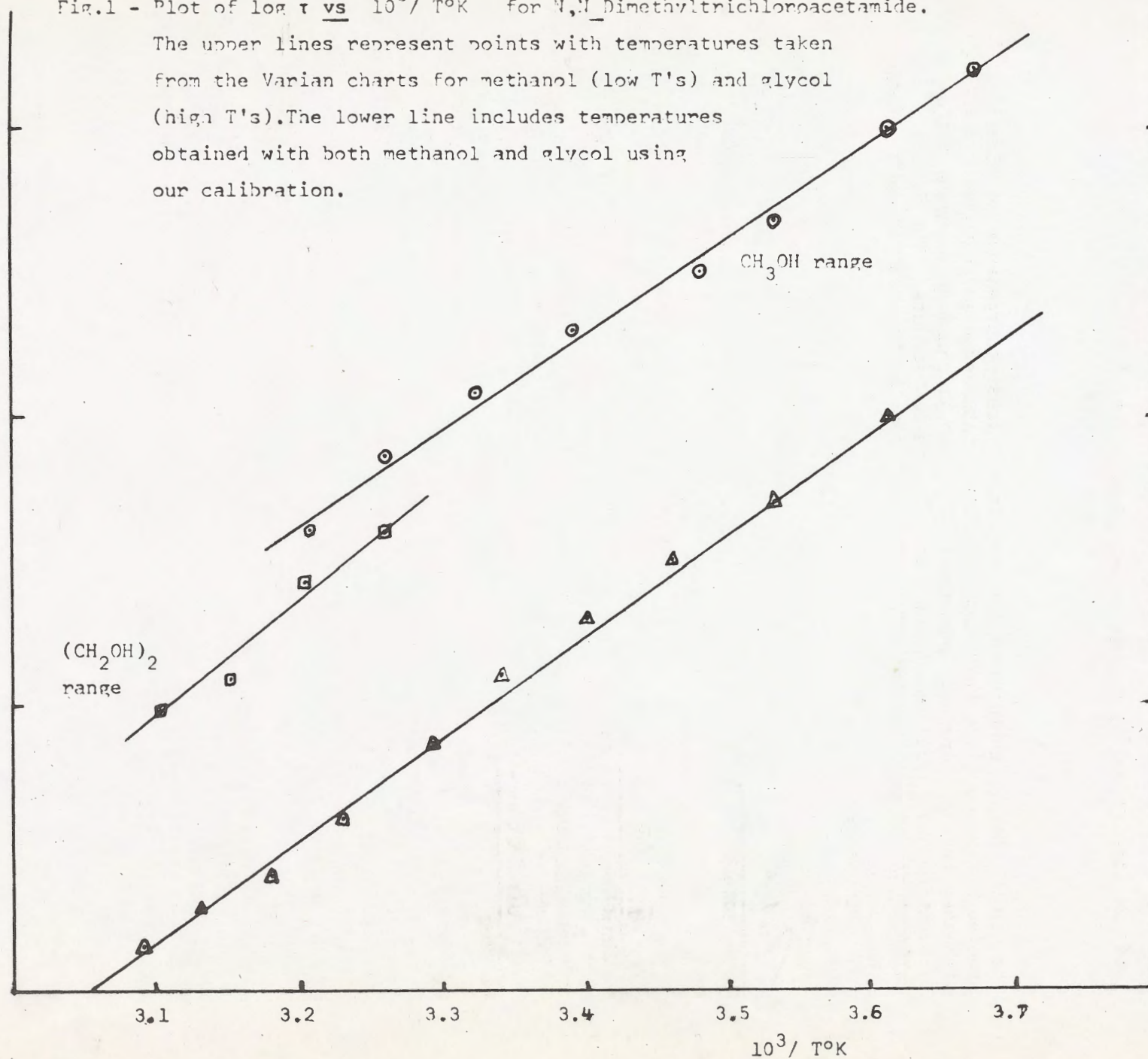
The upper lines represent points with temperatures taken from the Varian charts for methanol (low T's) and glycol (high T's). The lower line includes temperatures obtained with both methanol and glycol using our calibration.

$\log \tau$
(upper
curves)

0.0
 $\log \tau$
(lower
curve)

$(CH_2OH)_2$
range

CH_3OH range



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Beginning with next month's issue, this space will contain a list of the names of those companies, universities and other organizations who will be participating with IIT in sponsoring the Newsletter for the coming year.

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