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Newsletter

No. 135
DECEMBER, 1969

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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.

Deadline Dates: No. 136: 5 January 1970
No. 137: 2 February 1970

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

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

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 Germany

October 15, 1969

Determination by INDOR of $K_{XH} > 0$ in

$X(CH = CH_2)_n$ (X = Sn, Hg, Pb; n = 4, 2, 4)

Dear Barry:

The analogy of metal-proton coupling constants in methyl-, ethyl-, vinyl- and phenyl-compounds with the corresponding H-H and C-H coupling constants has received further support by our determination of the sign of J_{XH} in the title compounds with respect to J_{HH} in the vinyl fragment. We used the Varian HA 60 which was driven by the 5 MHz frequency of a General Radio frequency synthesizer to synchronize ν_1 , the sweep output of the C-1024 Varian CAT to change ν_2 of the synthesizer and the C-1024 to be able to record $^1H\{-X\}$ INDOR-spectra without distortion by Overhauser-effects, which might otherwise lead to wrong assignments. It is thus quite feasible to record INDOR-spectra by sitting on a 1H -line which is so weak that it may not be visible in the normal one-scan 1H -spektrum.

Assuming positive signs of the J_{HH} 's in the vinyl-fragments we found positive reduced geminal, cis and trans X-H coupling constants, confirming the expectations expressed in Spectrochimica Acta 25A, 1399-1406 (1969). The full paper is expected to appear in Z. phys. Chemie, May 1970.

Sincerely yours,

f w s

PHYSIQUE EXPÉRIMENTALE MOLÉCULAIRE

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69320/RF/MCP

Paris, le 30 octobre 1969

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

TEXAS 77843 (U. S. A.)

"Etude par R. M. N. d'effets intermoléculaires dans le tritertiobutylcarbinol".

Cher Docteur SHAPIRO,

De nombreuses recherches en Infrarouge et R. M. N. (1-4) relatives aux effets intermoléculaires invoquent l'encombrement stérique pour justifier l'absence ou la faiblesse des liaisons intermoléculaires des alcools. Nous sommes intéressés, dans ce travail, au tritertiobutylcarbinol ou tétraméthyl 2-2, 4-4 tert-butyl 3-pentanol : $[(CH_3)_3 C]_3 COH$ (TTBC) qui, à notre connaissance, n'avait pas encore été étudié.

Les mesures ont été effectuées à température variable (Varian A 60), repère interne tétraméthylsilane. Une étude en Infrarouge a été faite par Monsieur MALARSKY.*

RESULTATS :

1. - Autoassociation : Les déplacements de la raie R. M. N. OH vers les champs forts soit par dilution dans CCl_4 (fig. 1), soit par élévation de température (fig. 2) sont en faveur de l'existence de liaisons de type $-OH... O$. En fait, les valeurs de $\Delta\delta = \delta_{pur} - \delta_{\infty CCl_4}$ (0,15 p.p.m.) et $\Delta\delta/\Delta T$ (0,2 Hz/degré) sont faibles par rapport à celles correspondantes du méthanol par exemple (4,33 p.p.m. et 0,54 Hz par degré⁽⁶⁾), du tertibutanol (3,35 p.p.m.)⁽⁵⁾ ou même du ditertiobutyl carbinol (0,87 p.p.m.)⁽⁴⁾. Cependant, nous avons essayé de déterminer les paramètres thermodynamiques de l'équilibre :

$$n(TTBC) \rightleftharpoons (TTBC)_n \quad K_n = C_n / (C_1)^n$$

$$C_1 \quad K_n \quad C_n$$

en supposant que seuls sont en présence des monomères et des n-mères d'une espèce donnée :

$$vC = v_1 C_1 + nK_n C_1^n v_n$$

v fréquence observée.

v_1 fréquence du monomère

v_n fréquence du n-mère.

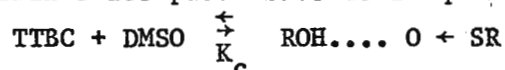
Nous avons introduit dans ces équations des valeurs arbitraires de n , v_n , K_n ; en procédant par itérations successives (9, 10), la meilleure

(*) Z. MALARSKI. - Université de Wrocław - (Pologne) (Bulletin de Société Chimique de Pologne - à paraître).

correspondance entre courbe calculée et courbe expérimentale a été obtenue pour $n = 2$, $K_2 = 0,01 \text{ litre.mole}^{-1}$, et $\nu_2 = 190 \text{ Hz}$ (fig. 3). En raison de la trop grande similitude des résultats à 58° et à 91°C , nous n'avons pas utilisé ces derniers pour la détermination de l'enthalpie ΔH à partir des courbes $\text{Log } K = f(1/T)$.

2. - Complexation : Le déplacement de la raie OH par dilution dans des solvants basiques (DMSO, dibutylamine) traduit la complexation du proton de OH sur l'hétéroatome d'oxygène ou d'azote (fig. 1). Dans le cas de la dibutylamine (de pK relativement élevé : $K_b \neq 10^{-3}$), il faut noter -contrairement au cas des thiols par exemple (7)- l'absence d'échanges rapides de type OH-NH. Seul un léger déplacement de la raie NH vers les champs faibles (0,1 p.p.m.) se manifeste lorsque la concentration en amine décroît. La valeur de $\Delta\delta = \delta_{\text{pur}} - \delta_\infty$ est de l'ordre de 0,9 p.p.m. pour la solution de dibutylamine et de 2,08 p.p.m. pour le DMSO.

En vue de déterminer les paramètres de l'équilibre :



nous avons suivi les variations du déplacement chimique de OH dans le mélange ternaire TTBC + CCl_4 + DMSO aux températures de 33° , 58° , 91°C .

$$K_c = \frac{C_c}{(C_a - C_c)(C_b - C_c)}$$

$$\nu C_a = C_c \nu_c + (C_a - C_c) \nu_a$$

C_a = concentration du complexe

C_b = concentration de ROH

C_c = concentration de DMSO

ν = fréquence mesurée

ν_c = fréquence du proton complexé

ν_a = fréquence du proton libre

Dans l'hypothèse d'un complexe 1/1, par une méthode de calcul itérative (8), nous avons obtenu (fig. 4a) les valeurs suivantes :

$$K_{33^\circ} = 0,29 \text{ litre.mole}^{-1} \quad \nu = 172,5 \text{ Hz}$$

$$K_{58^\circ} = 0,23 \text{ litre.mole}^{-1} \quad \nu_c = 160,7 \text{ Hz}$$

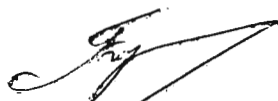
$$K_{91^\circ} = 0,21 \text{ litre.mole}^{-1} \quad \nu_c = 137,3 \text{ Hz}$$

De la courbe $\text{log } K = f(1/T)$ (fig. 4b), nous avons déduit une valeur de ΔH de l'ordre de 1Kcal.mole^{-1} .

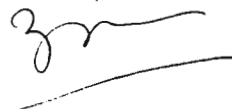
En résumé, il semble donc que, malgré l'encombrement stérique très important autour du groupement hydroxyle, le TTBC soit susceptible de former de faibles liaisons hydrogène avec prédominance de monomères et de dimères dans le produit pur.

.../...

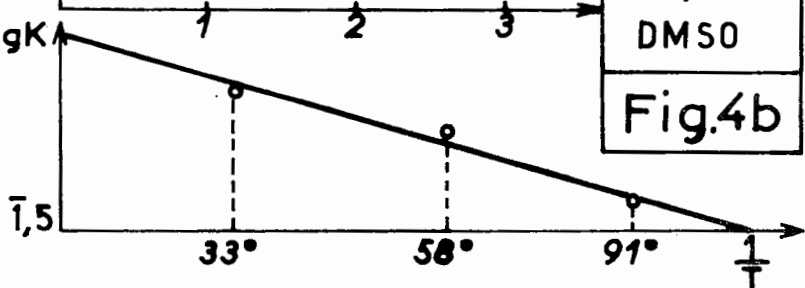
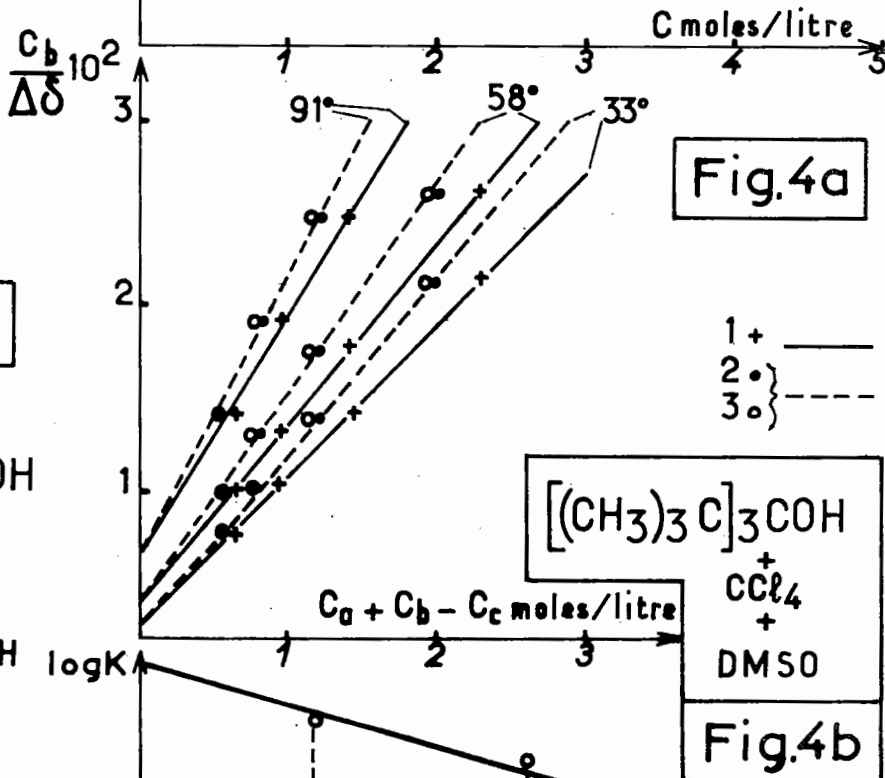
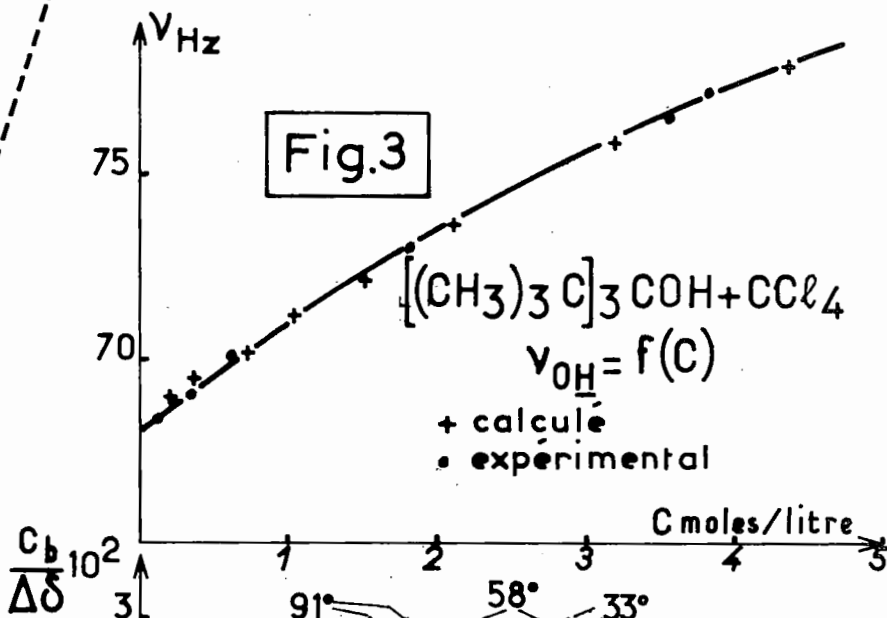
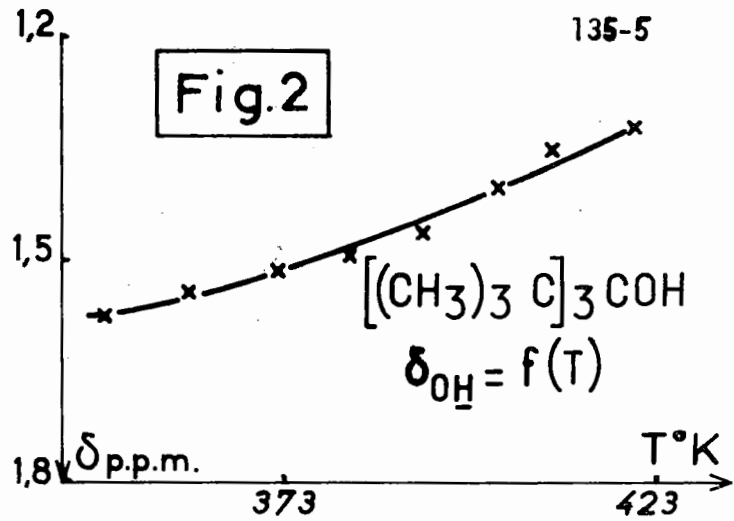
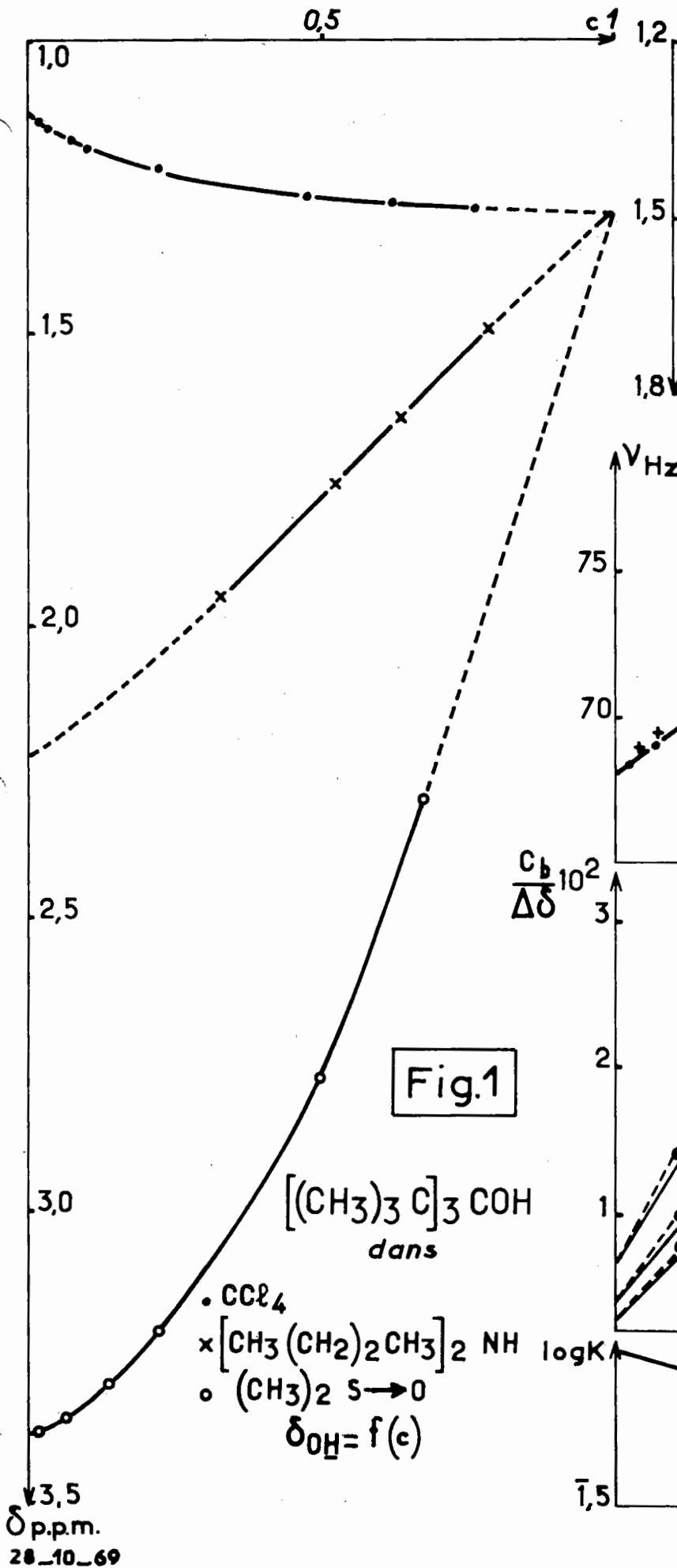
1. - J. S. COOK, J. R. REECE. - Aust. J. Chem. 14, 211, 1961.
2. - B. LEMANCEAU, C. LUSSAN, N. SOUTY, J. BIAIS. - J. Chim. Phys. 195, 1965.
3. - Y. D. SANTOS, P. PINEAU, M. L. JOSIEN. - J. Chim. Phys. 628, 1965.
4. - K. PATTERSON, R. M. HAMMAKER. - J. Phys. Chem. 70, 3745, 1966.
Spectrochim. Acta. - 23 A, 2333, 1967.
5. - M. L. MARTIN. - J. Chim. Phys. 736, 1962.
6. - J. C. DAVIS, K. S. PITZER, C. N. R. RAO. - J. Phys. Chem. 64, 1744, 1960.
7. - M. M. MARCIACQ-ROUSSELOT. - Thèse Paris 1969, C. N. R. S. A.O. N°2901.
8. - M. NAKANO, N. I. NAKANO, T. HIGUCHI. - J. Phys. Chem. 71, 3954, 1967.
9. - S. H. MARCUS, S. I. MILLER. - J. A. C. S. 88, 3719, 1966.
10. - V. S. GRIFFITHS et G. SOCRATES. - J. Mol. Spect. 21, 3,302, 1966.



R. FREYMANN



M.M.MARCIACQ-ROUSSELOT



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10 November 1969

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

A sample tube for pressure
work with gases.

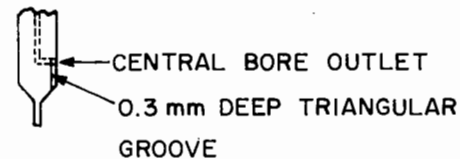
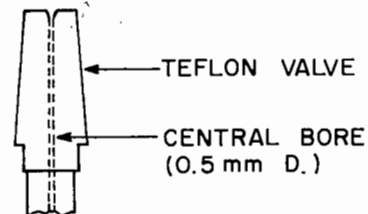
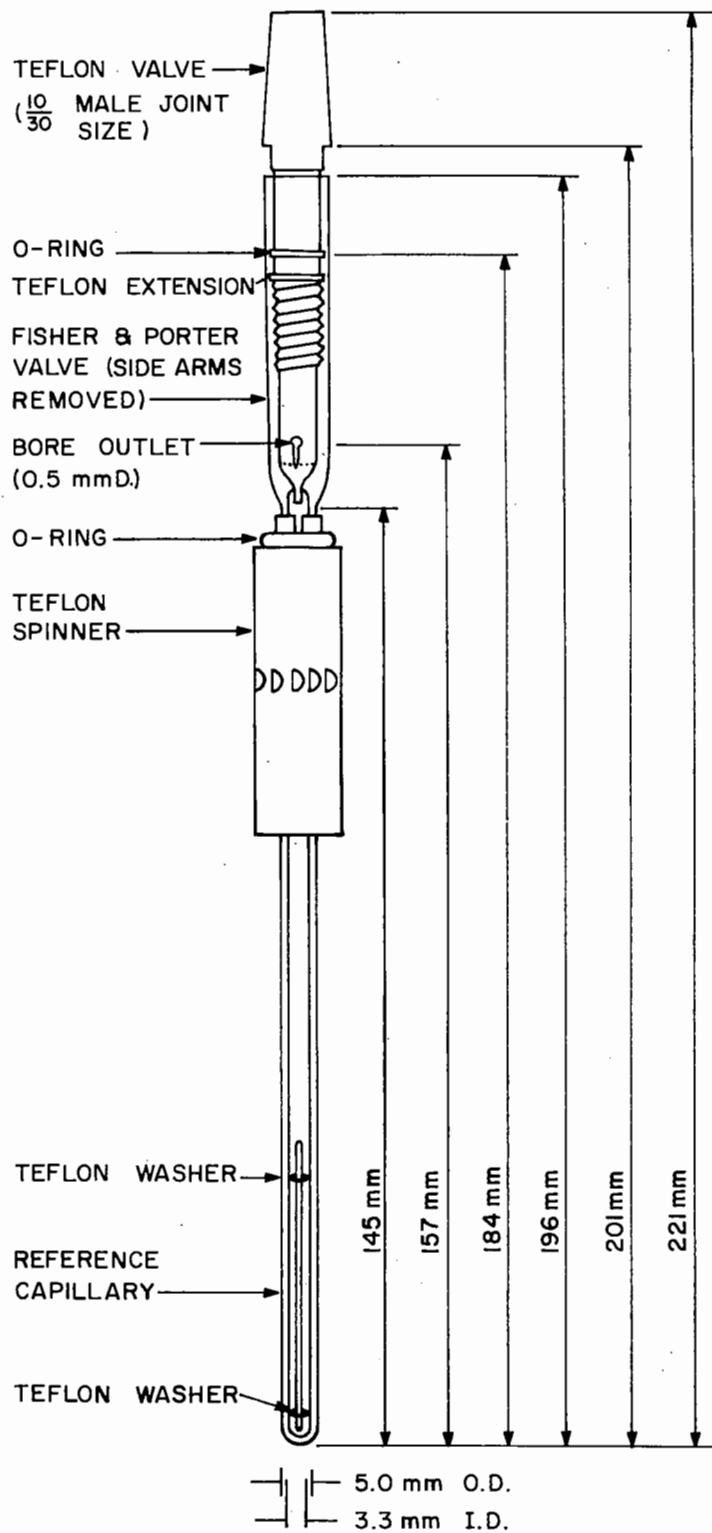
Dear Barry,

We have designed a gas-tight sample tube that is satisfactory for NMR studies up to a pressure of 60 atmospheres. We have been working with such a tube for quite sometime and believe, it may be of interest to other investigators who intend to work on gaseous samples in this pressure range. The tube is shown in the figure and the exact dimensions are given to facilitate construction. The tube could be of pyrex glass with 5 mm O.D. and 3 mm I.D. and 14.5 cm in length. It is sealed at one end to give an uniform round bottom and the other end is joined to the bottom of a Fisher & Porter Teflon valve of $1 \frac{1}{4}$ mm bore - the two side arms of this valve having been previously removed. [The same company is now manufacturing these valves without side arms]. The usual teflon valve is replaced by a slightly modified valve (see figure) which has a central hole for the passage of the gas sample. The conical section of the teflon valve at the bottom spills over the glass surface when the contact between the two surfaces is good. The gas is completely sealed by such an arrangement. We have checked the gas leakage by chemical shift measurement and found no noticeable change even after a week. The conical tip of the teflon valve should be polished properly for good sealing. The top of the valve is designed to fit a KLMAX $\frac{10}{11}$ female joint in a vacuum system.

Such a tube can also be used for temperature work. The usual pressure cap used in the Varian V-4341 variable temperature unit should be extended by at least 4 cms to fit this pressure tube.

S. Mohanty
S. Mohanty

H.J. Bernstein
H.J. Bernstein



A SAMPLE TUBE FOR PRESSURE WORK WITH GASES

BRYN MAWR COLLEGE
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DEPARTMENT OF CHEMISTRY

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13 November 1969

Prof. B. L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station TX 77843

Dear Barry:

Although the computers-for-NMR drum may be well-beaten already, let me offer these two short news items which may nonetheless be of interest to some.

TIME-SHARED LAOCOON

Upon returning to Bryn Mawr, we have made some use of the Laocoon program on our batch-mode computer, but have also found it worthwhile to reprogram the Laocoon program for time-sharing use. I have used P. J. Black's modification of Bothner-by's tried-and-true program which includes direct (dipolar) coupling for those who are investigating spectra in anisotropic solvents. A version for six spins now operates written in Xtran, an extended Fortran II language offered on the Com-Share system.

Listings and brief documentation will be sent to any interested parties. Other Com-Share users can, I believe, copy the programs directly from my files with a minimum of effort.

NMR SPECTRUM SIMULATION ON THE TYPAGRAPH

The Typagraph (Typagraph Corp., 7525 Convoy Ct., San Diego CA 92111) is a plotting teleprinter; that is, it is a modified teletype with .02 inch resolution achieved through control of a stepping motor in both horizontal and vertical directions. At Bryn Mawr, we have experimented with the Typagraph in simulating nmr spectra; a sample is attached.

Listings and documentation for the nmr plotting program are also available on request. Typagraph software is maintained on most time-sharing services.

Sincerely yours,

Jay.

Jay Martin Anderson

+GO

NO. OF LINES: 4

WILL YOU READ IN FREQ AND INTENS FROM TERMINAL? YES

- 50. 1.
- 45. 3.
- 40. 3.
- 35. 1.

OFFSET IN HZ: 0.

SWEEP WIDTH IN HZ: 100.

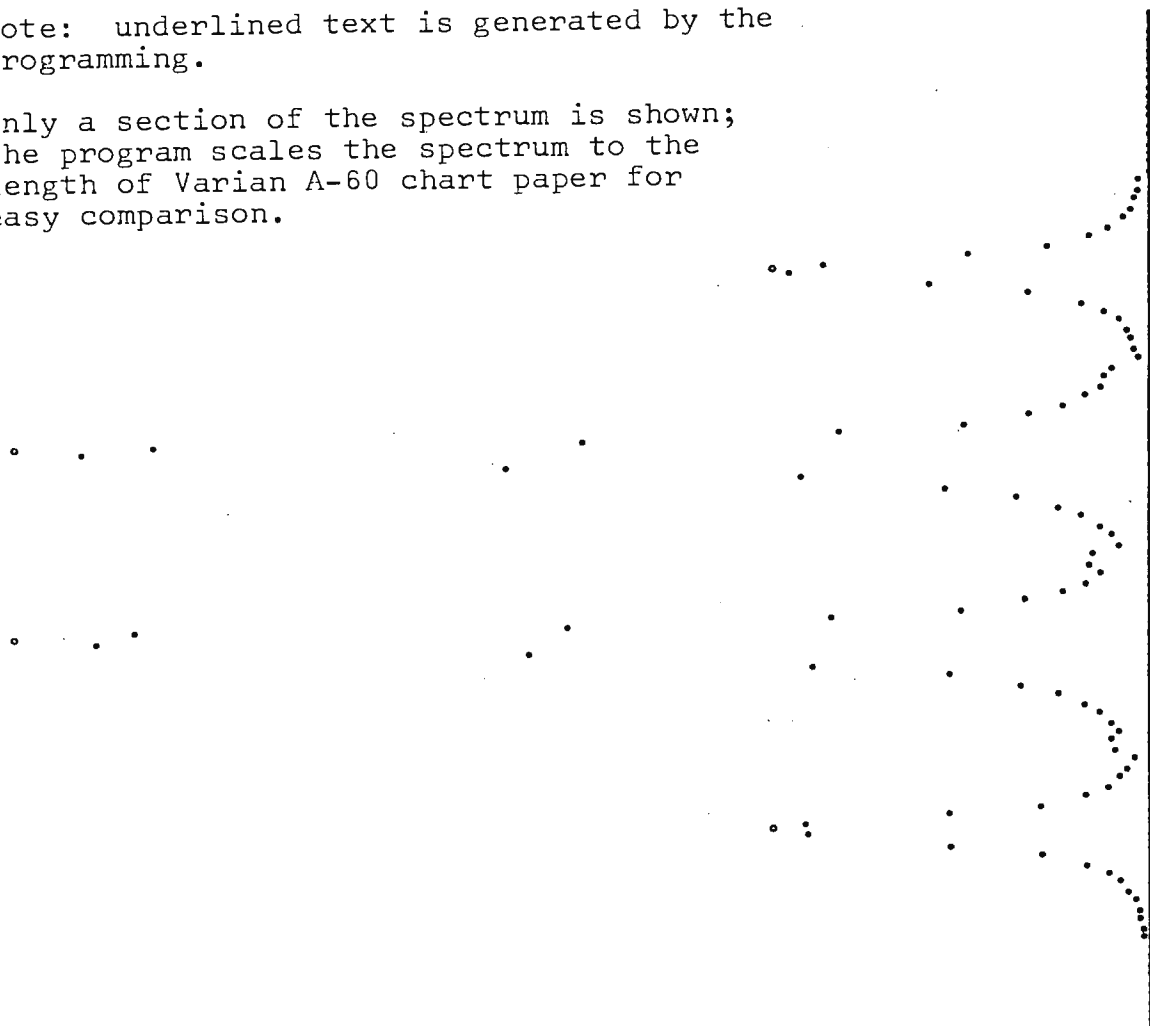
LINE WIDTH IN HZ: 0.4

THERE ARE 4 LINES ON THIS PLOT.

CHECK PLOT MODE

Note: underlined text is generated by the programming.

Only a section of the spectrum is shown; the program scales the spectrum to the length of Varian A-60 chart paper for easy comparison.





13 November 1969

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

Title(Short): Electron transfer $K_4Mo(CN)_8 - K_3Mo(CN)_8$

Dear Barry,

Your "blue" reminders are great promoters of nmr research.

Thank you!

We have studied the rate electron transfer between $K_3Mo(CN)_8$ (paramagnetic) and $K_4Mo(CN)_8$ (diamagnetic) in aqueous solution by the ^{95}Mo and ^{14}N resonances. In both cases the lifetime broadening of $K_4Mo(CN)_8$ (0.5-1M) through addition of $K_3Mo(CN)_8$ was observed. The slow exchange approximation was assumed (although we have slight doubts whether it is valid for the ^{14}N). The results at room temperature are $k=1.2\pm 0.5 \times 10^5 \text{ mole}^{-1} \text{ sec}^{-1}$ from ^{14}N measurements and $k=1.1\pm 0.5 \times 10^5 \text{ mole}^{-1} \text{ sec}^{-1}$ from ^{95}Mo measurements. Measurements of temperature dependence have also been attempted but difficulties were encountered due to the low ^{95}Mo sensitivity and the decomposition of $K_3Mo(CN)_8$.

We are currently investigating relaxation processes in various inorganic complexes in solution.

Yours sincerely,

H. Gilboa Aharon.

H. Gilboa

A. Loewenstein

**THE UNIVERSITY OF NEW BRUNSWICK**

FREDERICTON, N.B.

November 18, 1969

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

Short title:
Noise stimulated spectrum

Dear Barry:

Many readers of the Newsletter must have wished they could turn off the noise generator that all manufacturers supply free of charge with their spectrometers. Of course, nature has cleverly provided good thermodynamic laws to prevent such a simple solution of our practical problems, and to lead us up the square root path of signal averaging. It is thus hardly surprising that noise is generally considered a nuisance, yet I believe that this isn't quite fair. Richard Ernst has shown that noise irradiation acts in a manner similar to chemical exchange or relaxation, and the following will show, I hope, that it is possible to obtain an unperturbed spectrum (albeit noisy with our present technique) by stimulating the spin system with noise.

Our 1959 model V-4302 spectrometer was locked in the usual way by means of a few drops of TMS in the otherwise neat sample of o-dichlorobenzene so that the r.f. carrier was about 60 Hz below the center of the approximately 35 Hz wide spectrum of o-dichlorobenzene. A stochastic voltage with zero mean, closely Gaussian amplitude probability density and almost flat power density spectrum from 10 Hz to 115 Hz (lower corner frequency given by noise generator, upper by second order filter with damping factor near 0.6) was applied to the modulation coils through a filter to correct the 6 db/octave attenuation caused by the modulation index so that uniform, weak modulation sidebands were produced. Trace (a) in the figure below shows a 1.65 sec long segment of this input signal taken ahead of the 6 db/octave correction. Trace (b) shows the resulting 1.65 sec segment of the spectrometer output voltage at the output of a 115 Hz low pass filter following the r.f. phase sensitive detector. It is possible to obtain the modulus or the absolute square of the o-dichlorobenzene spectrum by feeding this output into a narrow band scanning audio spectrum analyzer, and it may also be possible to separate the absorption and dispersion modes by feeding both input and output into a scanning audio phase

Prof. B. L. Shapiro
November 18, 1969

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sensitive detector through tracking narrow band pass filters in the signal and reference channels. Either method leads to a single channel noise spectrometer whose resolution is determined by the detector bandwidth, and neither method looks terribly attractive. To obtain the advantage of multichannel operation we sampled and digitized both the input and output signals to do the subsequent processing on a digital computer. The computer hardware requires that the signals be divided into records of finite length, and the processing is relatively simple by means of the usual steady state Fourier transform methods if a record is used that allows a periodic extension in time. We therefore used a relay switch at the input to the spectrometer modulation coils to periodically turn the input signal on for 14 sec and off for 14 sec. A computer record starts with the "on" period and is 22 sec long. The following Traces show some results for a single such record of 22 sec length. No averaging was done other than in the final recording of the Traces to smooth the sampled structure of the computer output. Trace (c) gives the output power spectrum of the 50 Hz wide region of interest, (d) shows the real and (e) the imaginary part (dispersion and absorption mode) of the o-dichlorobenzene spectrum. Finally, Trace (f) shows for comparison the absorption mode spectrum of the same sample taken in the locked field sweep mode on the same spectrometer with a scan time of 12 minutes.

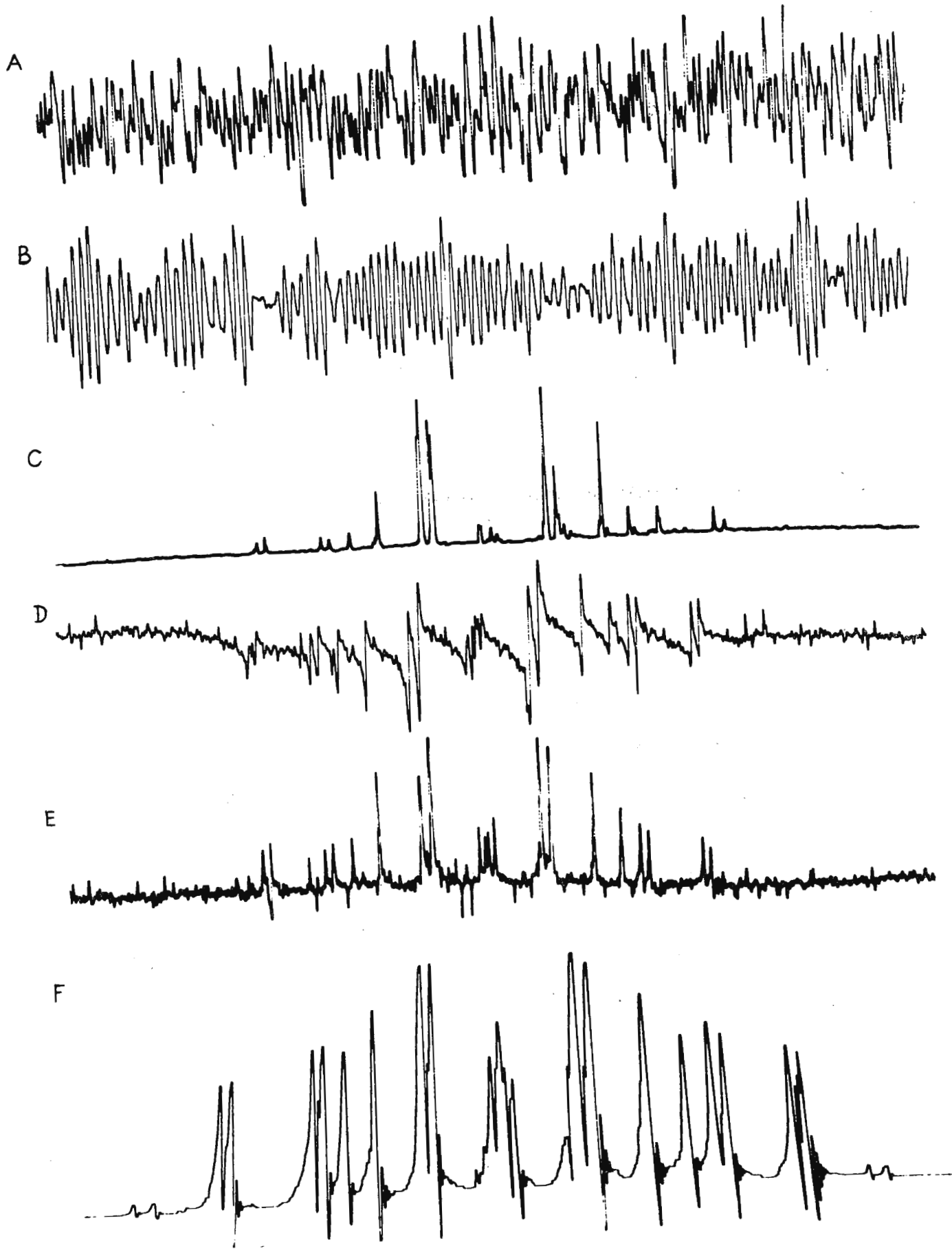
It is clear that our technique needs some improvements. We are working on these and on the averaging of spectra from several records. Comments, suggestions, etc. are always welcome.

Sincerely yours,



R. Kaiser, Professor

RK:seb




THE DOW CHEMICAL COMPANY

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November 17, 1969

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

RADIATION DAMPING IN THE A56/60

During the course of some NMR studies on our Varian A56/60 we have encountered a little publicized effect, radiation damping, which should be brought to the attention of those who aren't aware of the possibility of its appearance in all high resolution instruments. The ramifications of radiation damping in most NMR experiments have been adequately treated by several authors.¹⁻⁴ Some loss of energy to the receiver coil occurs upon detection of the resonant magnetization. This manifests itself by the addition of a third term to that used to express the effective transverse relaxation time, T_2' , of a resonance line

$$\frac{1}{T_2'} = \frac{1}{T_2^0} + \frac{1}{T_2} \Delta H_0 + \frac{1}{T_{2RD}}$$

where

$$T_{2RD} = (2\pi \mathcal{N} M_0 Q)^{-1} ;$$

\mathcal{N} is the filling factor, M_0 is the equilibrium magnetization of a particular transition, and Q is the quality factor of the coil. Since Q and \mathcal{N} are usually fixed there are only two handles for minimizing the contributions from T_{2RD}^{-1} ; diluting the sample and detuning the capacitor in the receiver coil.⁵

In the instruments having multinuclei capabilities the magnitude of broadening can vary from day to day depending upon the frequency being used and who tuned the probe last. In the proton spectrum of neat methyl iodide we have found the ratio of the parent peak width to the natural abundance ¹³C satellite peak width

Dr. Bernard L. Shapiro
Texas A & M University

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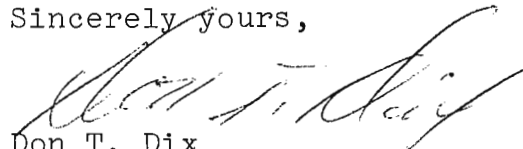
$$\frac{\Delta\nu^{12}\text{CH}_3\text{I}}{\Delta\nu^{13}\text{CH}_3\text{I}}$$

to vary from 5.0 to 1.0 with some loss in S/N in the latter case. Thus optimum resolution isn't achieved in concentrated samples; integrations can also be affected. The ^{13}C satellite peak provides a good reference line width as radiation damping is virtually absent due to its smaller Mo. Particular care should be exercised by those who use a solvent peak or any other strong resonance to obtain the natural line width in chemical exchange studies.

In most spectrometers $\frac{1}{T_{2\text{RD}}}$ might be small compared to $\frac{1}{T_{2\text{H}_0}}$, yet

it could still be much larger than $\frac{1}{T_2}$ and consequently must be reckoned with in relaxation studies.^{5,6} In adiabatic fast passage experiments, for example, a delayed power peak might appear and in more severe cases the magnetization might be prevented from reaching the desired tipping angle.²

Sincerely yours,


Don T. Dix

pat

- (1) C. R. Bruce, R. E. Norberg, and G. E. Pake, Phys. Rev. 104, 419 (1956).
- (2) S. Bloom, J. Appl. Phys. 28, 800 (1957)
- (3) A. Szöke and S. Meiboom, Phys. Rev. 113, 585 (1959)
- (4) A. Abragam, "Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.
- (5) R. Freeman and S. Wittekoek, J. Mag. Res. 1, 238 (1969)
- (6). E. J. Wells and K. H. Abramson, ibid. 1, 362 (1969).

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Dear Professor Shapiro,

QUADRUPOLEAR BROADENING AS A STRUCTURAL PROBE

The quadrupole moment associated with magnetic species having $I > \frac{1}{2}$ which leads to quadrupolar broadening of resonance lines is, in most applications, unwanted and unappreciated. The resulting broadening tends to obscure resonance lines and prevents the observation of fine structure. To overcome this difficulty, heteronuclear spin decoupling techniques have been widely applied.

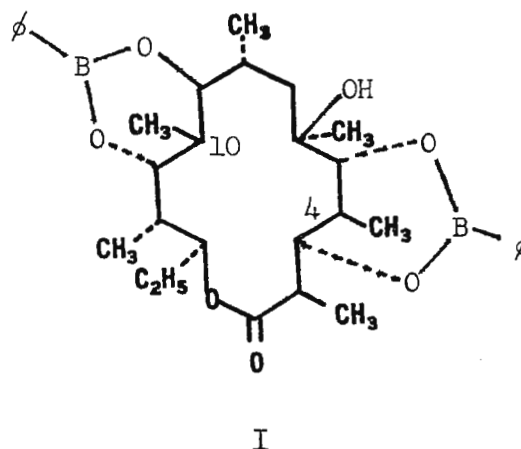
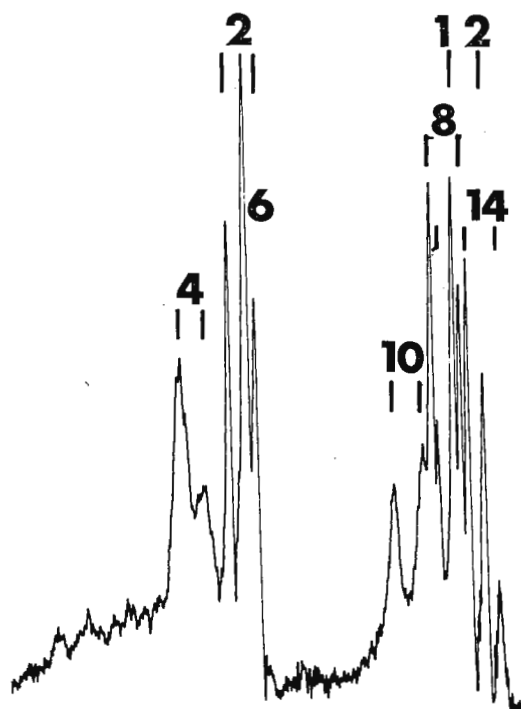
Some positive features have been noted in the past. Among them is the ease, in some cases, in which NCH groupings, usually in aromatic heterocyclic systems, can be detected by the broad resonance lines of the proton caused by the ^{14}N quadrupole. We wish to present a case in which ^{11}B quadrupolar can be used as a structural probe.

A series of phenylboronic acid esters of 9-dihydroerythronolides have been prepared in our laboratories for conformational studies in progress (1,2,3). Complete identification of ring protons and methyl groups was aided by long-range ^{11}B quadrupolar broadening.

In the spectra of 9S-9-dihydroerythronolide B bisphenylboronate (I), the resonances of both the protons and methyl groups situated proximate to the ^{11}B atoms (i.e. at positions 4 and 10) are broadened thereby permitting their assignment. When the spectra is determined is determined at 110° in pyridine- d_5 , the resonances of unaffected methyls have a width at half height of 1.0 Hz while the resonances of the 4- and 10-methyls have widths at half height of 2.5 Hz (cf the figure, the methyl resonances of I). As a result of this quadrupolar broadening, the doublets assigned to the 4- and 10-methyl groups have considerably lower peak intensity. The resonances of the ring protons at these positions were similarly affected. The assignments of the substituent and proton at C-4 and C-10 in these compounds were verified by spin decoupling and are unequivocal. Molecular models confirm the proximity of the boron atoms to the affected groups in these compounds.

It is thought that phenylboronic acid esters might be of value in other cyclic polyols having suitable stereochemistry. This is also an interesting example that points out the "through space" nature of quadrupolar coupling. The number of intervening σ -bonds is too large to explain this phenomenon by a "through Bond" effect. Protons separated from the boron atoms by fewer bonds are not affected.

- (1) T.J. Perun and R.S. Egan, Tetrahedron Letters, 387 (1969)
- (2) T.J. Perun, R.S. Egan, and J.R. Martin, Tetrahedron Letters, accepted for publication.
- (3) R.S. Egan, T.J. Perun, and P.H. Jones, Abstracts, Interscience Conference on Antimicrobial Agents and Chemotherapy, 9, 21 (1969)



Sincerely,

Richard S. Egan
nmr lab D-408

Thomas J. Perun
experimental chemistry
D-482



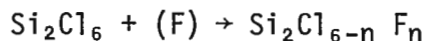
20 November 1969

Dr. B. L. Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, Texas 77840

EXAMPLE OF INDOR FOR STRUCTURE DETERMINATION

Dear Barry:

You will be interested to hear that we are having a look at the fluorination of Si_2Cl_6 under various conditions:



It is convenient to look at the reaction products in an nmr tube. In many instances all possible mixed chlorofluorides are present and nmr can provide information on the course of the reaction without the need of separating the products.

Most of the species obtained can be identified from their multiplet patterns, either in the main ^{19}F spectrum (e.g., $\text{SiF}_3\text{SiF}_2\text{Cl}$) or from the ^{29}Si satellites in the ^{19}F spectrum (e.g., $\text{SiFCl}_2\text{SiFCl}_2$). There remain three molecules, namely the monofluoro-, 1,1-difluoro-, and 1,1,1-trifluoroperchlorodisilanes whose ^{19}F nmr spectra are superficially identical: a single central peak with satellites due to ^{29}Si around ± 35 Hz and ± 180 Hz. (Having identified these materials, vide infra, we can now of course refer to measured values of δ and J .) If we "sit" on one of the ^{29}Si satellites in the ^{19}F spectrum and sweep the ^{29}Si frequency, the multiplet pattern observed gives the desired identification immediately. The values of J and δ observed are solvent-dependent, but typical values in the mixtures we observe are as follows:

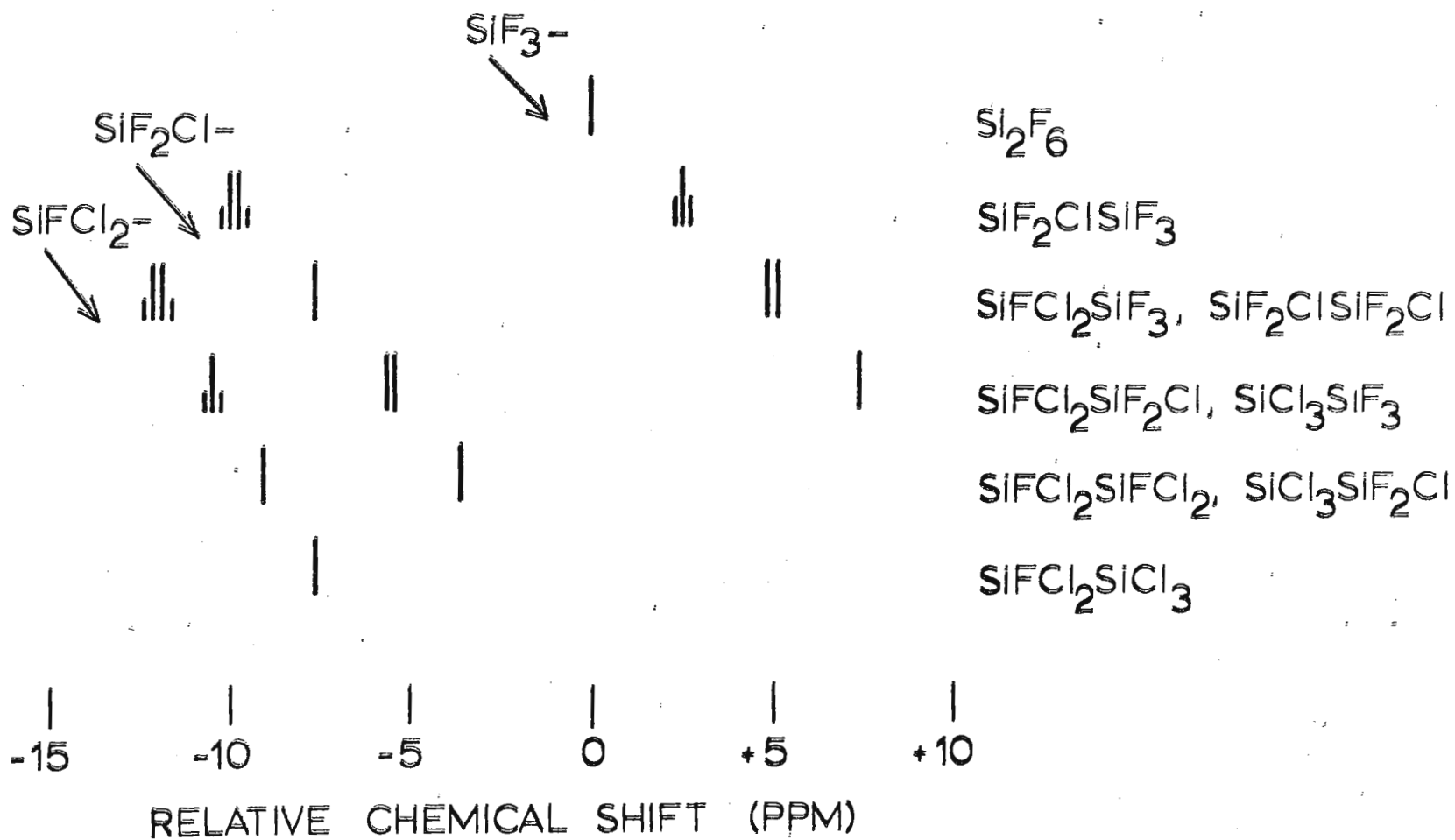
Species	δ	J_{SiF}	J_{SiSiF}
$\text{SiF}_3\text{SiCl}_3$	-49.5 ppm	341 Hz	80 Hz
$\text{SiF}_2\text{ClSiCl}_3$	-38.6	365	72
$\text{SiFCl}_2\text{SiCl}_3$	-34.8	384	65

+ SiF_4 = 0 ppm, negative δ means downfield shift.

Yours very truly,

Rolf B. Johannesen

Rolf B. Johannesen
 Inorganic Chemistry Section





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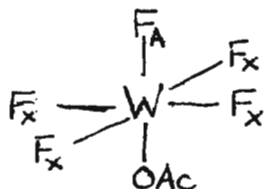
November 19, 1969

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

Dear Barry,

Title: An AX_4 spectrum of a Tungsten derivative

As a desperate attempt to save my TABUNMR (sic) subscription, let me tell you of the ^{19}F NMR spectrum I have obtained on what appears to be $\text{WF}_5\text{OCOCH}_3$. The chemistry is not at all finished on isolating or establishing the structure of this and the series of related compounds made by reacting WF_6 with organic acids and their silver salts but we have obtained a spectrum consistent with the following assignment:



$$\delta(\text{F}_A) = 86.6 \text{ (CFCl}_3 = 0)$$

$$\delta(\text{F}_X) = -50.1$$

$$J_{\text{F}_A\text{F}_X} = 53 \text{ cps}$$

$$J_{\text{WF}_X} = 71 \text{ cps}$$

$$J_{\text{WF}_A} \text{ was unobservable due to concentration limitations}$$

These values are similar to, but different from, those reported by Muetterties [Inorg. Chem. 7, 1968] for WF_6O^- . The only known related compounds of tungsten are WF_6Cl_2 , $\text{W}(\text{OPh})_6$ and the very recently prepared $\text{WF}_5(\text{OR})$ [Chem. Comm. 1969, 151] and $\text{W}[\text{N}(\text{CH}_3)_2]_6$ [Chem. Comm. 1969, 1261]. My interest in these stems from my concern for "hypervalent" molecules [Angew. Chemie 8, 54 (1969)] and my argument that transition metals can be treated in a similar manner. We are thus working simultaneously (and very slowly) on molecules of P, I, Xe and W.

Yours sincerely,

Jeremy I. Musher

JIM:vas

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

November 24, 1969

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

Dear Barry:

Nitrogen Inversion Without Retarding Factors

Slow nitrogen inversion has been observed by DNMR techniques only in systems where either angle strain or electronegative substituents are present. We have measured the activation barriers to nitrogen inversion in two cases in which these effects are minimal and the ambiguity between atomic inversion and bond rotation is eliminated.

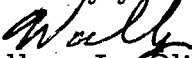
Samples of N-methylpyrrolidine (I) and N-methylhomopiperidine (II) in CHClF_2 (Freon 22) were observed at low temperature on our Bruker HFX-10 90-MHz spectrometer. As the temperature is lowered, the α -proton




resonances reversibly broaden and produce two well-separated groupings, corresponding to the protons *cis* and *trans* to methyl. The coalescence temperature for I is about -100° ($\nu_{AB} = 1.08$ ppm), and for II it is about -125° ($\nu_{AB} = 0.49$ ppm). These data indicate that the free energies of activation are about 8 kcal/mole for I and 7 kcal/mole for II. These values correspond to the barrier to nitrogen inversion unconstrained by small valence angles or lone-pair bearing substituents.

The possibility that the process observed is pseudo rotation of the five- and seven-membered rings was ruled out by observing that the spectra of the parent compounds, pyrrolidine and homopiperidine, are unchanged down to -150° . We are in the process of carrying out a complete line-shape analysis on I.

Sincerely yours,


 Wallace L. Oliver, Jr.


 Joseph B. Lambert

WLO/kc



Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackcly, Manchester, 9

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

Your Ref:

Our Ref: PL/ARS/B5

25 Nov 69

Dear Professor Shapiro,

CATNAPS (A Cat Safety Device)

The letter from Herr Stegemann in the NMR Newsletter No 133 regarding his HA 100 modification prompts us to report a similar modification of ours which also causes the CAT to Neglect Any Pernicious Spectra if the locking signal is lost.

Our modification utilises the Continuous Lock Signal Indication System described by D.Greatbanks and F.W.Barclay in the NMR Newsletter No 123. This consisted of a simple circuit to generate direct current from the audio frequency locking signal so that the locking signal could be displayed as a reading on a microammeter.

The only additional item required for the CATNAPS system is a moving coil relay. The 'coil terminals' are wired in series with the microammeter and the 'contact terminals' are wired in the lead from the N.O. terminal of the left-hand limit switch of the recorder to pin P of P 903. When the locking signal falls below a certain level the relay opens and cuts off the triggering pulses to the C-1024.

This system offers the following advantages:-

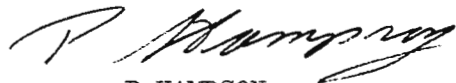
- (i) it is simple to instal for anyone already having the previous modification.

- 2 -

- (ii) it protects for any loss of locking signal, not just loss of locking signal when the flux stabiliser loses control.
- (iii) if the lock signal amplitude is restored then accumulation is continued.

A suitable moving coil relay can be obtained in England from Sangamo Weston Limited, Model S115 Series No 1. The nominal operating current is 50 uA, but satisfactory contact appears to be made at about half this current.

Yours sincerely,



P. HAMPSON.



A. MATHIAS.

PH/LG.

CZECHOSLOVAK ACADEMY OF SCIENCE
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

FLEMINGOVO NÁM. 2

PRAHA 6

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

November 26, 1969

Computer-construction of the dual representation of
energy-level-diagram

Dear Professor Shapiro:

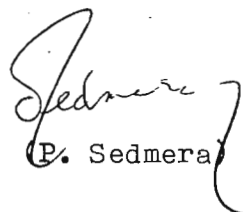
Thank you very much for the reminder. Recently, Castellano and Bothner-By (1) have presented an interesting idea for using the dual representation of the conventional energy-level diagram in high-resolution analysis. We have found that the matrix-representation of the n transitions

$$v_{ij}^{(n)} = E_i - E_j ,$$

which is easily constructed using the selection rules, appears to be a superposition of two dual representations. As an example the same case of a four-spin system with $I=1/2$ presented by Castellano and Bothner-By is shown on the next page. In this way the dual representation can be easily obtained directly as the output of the computer for arbitrary numbering of energy-levels used in various programs. The program-adaptation is available on request.



(Z. Samek)



(P. Sedmera)

(1) S.M. Castellano and A.A. Bothner-By, J.Chem.Phys. 47,
5443 (1967).

	E_0	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}	E_{11}	E_{12}	E_{13}	E_{14}	E_{15}
E_0		1	2	3	4											
E_1	1					5	6	7	8	9	10					
E_2	2					11	12	13	14	15	16					
E_3	3					17	18	19	20	21	22					
E_4	4					23	24	25	26	27	28					
E_5		5	11	17	23							29	30	31	32	
E_6		6	12	18	24							33	34	35	36	
E_7		7	13	19	25							37	38	39	40	
E_8		8	14	20	26							41	42	43	44	
E_9		9	15	21	27							45	46	47	48	
E_{10}		10	16	22	28							49	50	51	52	
E_{11}						29	33	37	41	45	49					53
E_{12}						30	34	38	42	46	50					54
E_{13}						31	35	39	43	47	51					55
E_{14}						32	36	40	44	48	52					56
E_{15}												53	54	55	56	

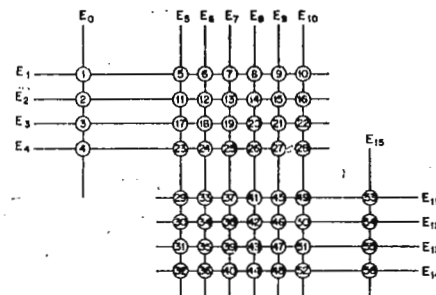


FIG. 2. Dual representation of diagram shown in Fig. 1.

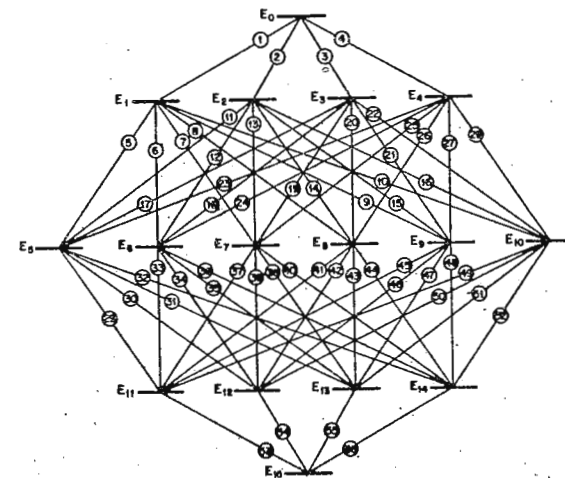


FIG. 1. Conventional energy level and transition diagram for a system of four spin- $\frac{1}{2}$ nuclei.

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AARHUS UNIVERSITET
DANMARK

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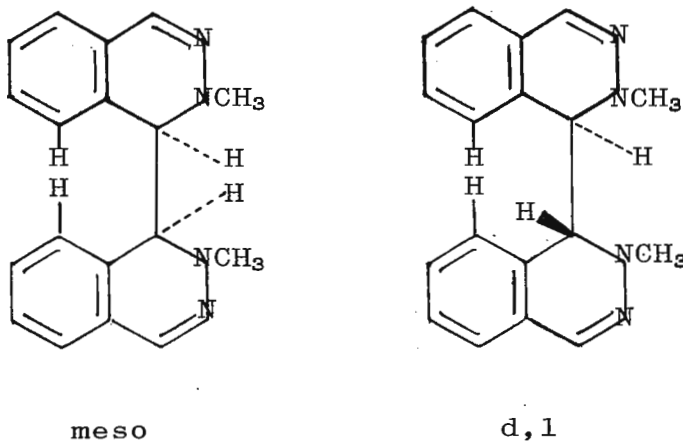
HENNING LUND

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

Dear Dr. Shapiro,

ANISOTROPY SHIFT IN A d,1-MESO PAIR

From a controlled potential electrolysis of 2-methylphthalazinium iodide (borate buffer, $E = -1,2$ V vs SCE) two one-electron reduction products, A and B, were obtained, both dimerized at C-1; they are supposed to be the meso- and the d,l-forms, respectively.



-2-

One of the forms (A) showed the expected spectrum:

$$\begin{aligned}\delta &= 2.80(\text{s}) & \Sigma\text{H} &= 6; \\ \delta &= 4.50(\text{s}) & \Sigma\text{H} &= 2; \\ \delta &= 6.8-7.4(\text{m}) & \Sigma\text{H} &= 10,\end{aligned}$$

whereas the isomer B had a PMR spectrum:

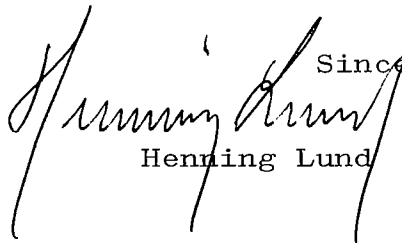
$$\begin{aligned}\delta &= 3.39(\text{s}) & \Sigma\text{H} &= 6; \\ \delta &= 4.29(\text{s}) & \Sigma\text{H} &= 2; \\ \delta &= 5.98 & \Sigma\text{H} &= 2; \\ & \text{(broadened} \\ & \text{doublet,} \\ & \text{J}_0 &= 7.0 \\ & \text{Hz)} \\ \delta &= 6.8-7.3(\text{m}) & \Sigma\text{H} &= 6; \\ \delta &= 7.32(\text{s}) & \Sigma\text{H} &= 2\end{aligned}$$

in which one of the aromatic protons in each ring was shifted about 1 p.p.m. upfield.

An explanation for this anisotropy effect could be that H-8 of isomer B comes, during the rotation around C₁-C_{1'}, very close to the center of the other benzene ring of the molecule. Examination of models suggests that it is the meso-form in which such a situation occurs; in the d,l-form steric hindrance prohibits such a passage of H-8 through the field of the other benzene ring.

2-Isopropylphthalazinium iodide yields similar reduction products; besides the upfield shift of H-8 of isomer B' there is a large difference (1.18 p.p.m.) in the chemical shifts of the methine protons of A' and B'; furthermore, a large non-equivalence of the isopropyl methyl protons (~0.40 p.p.m.) is observed.

Sincerely yours,


Henning Lund


Hans Jørgen Jakobsen

○

1

2

○

3

4

○

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