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Newsletter

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No. 133 october, 1969

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

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

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

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

September 3, 1969

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

Dear Dr. Shapiro:

New Life for an A-60

During the past couple of years, we have devoted considerable time to improving our A-60 nmr instruments. A program that covers upgrading, tuning, and service has been developed. Our A-60's now have better than double their original signal-to-noise with very little down time. Anyone interested in the program should drop me a line.

Variable Temperature for Other Nuclei

Our needs for nmr other than proton has greatly increased during the past year. We recently modified out HA-60 to handle other nuclei at variable temperature. Figure I shows a modified V-4331 probe with the following features:

- a) The probe will spin a sample tube as large as 15 mm at room temperature.
- b) A sample tube as large as 12 mm will spin at variable temperature.
- c) The probe temperature has been varied from -100° C to +100°C. Temperatures beyond this range will be attempted when the need arises.
- d) The temperature is preset and controlled by a Varian V-4340 temperature controller.
- e) The probe can be used with internal lock or HR mode. External lock is now being considered.

The V-4331 probe was purchased with the receiver coil wrapped on the inside of the faraday shield. The spinner is a SK-431 from Wilmad Glass Company.

2

September 3, 1969

Figure II is an open side view of the variable temperature probe. Inlet A, N^2 is necessary to keep the spinner bearing from binding at low temperature. Inlet B, N^2 is necessary to keep moisture from forming on the outer surface of the dewar.

Figure III is a print of the dewar used in the probe. The dewar was difficult to make because of the thin walls. Our glass shop is credited for the fine craftsmanship.

Please credit this article to the subscription of Prof. William Ritchey of our department.

Sincerely yours,

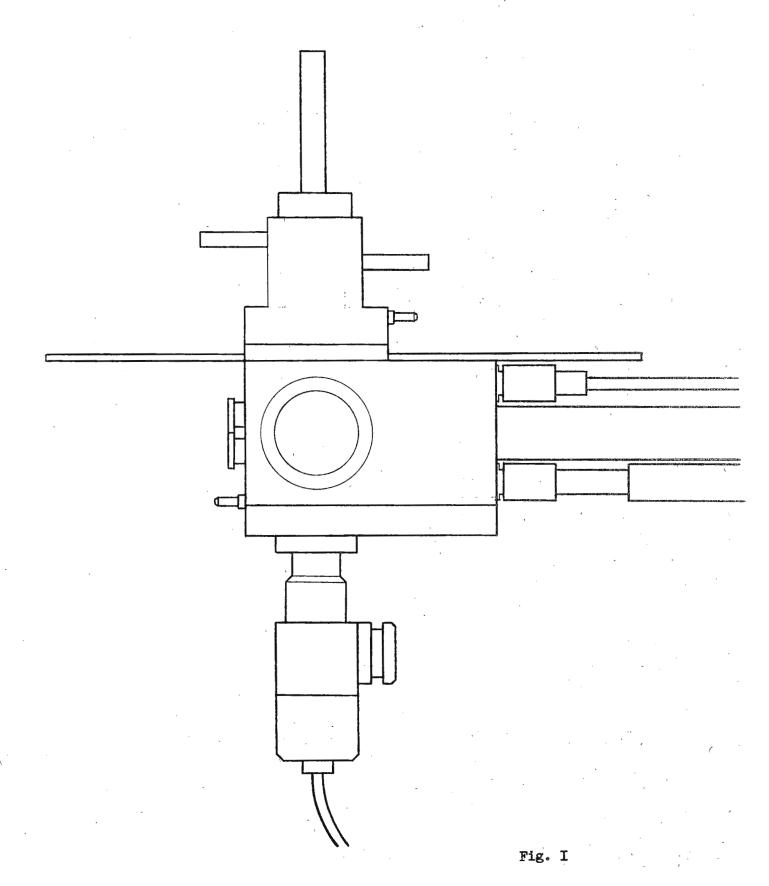
Clarence Gust

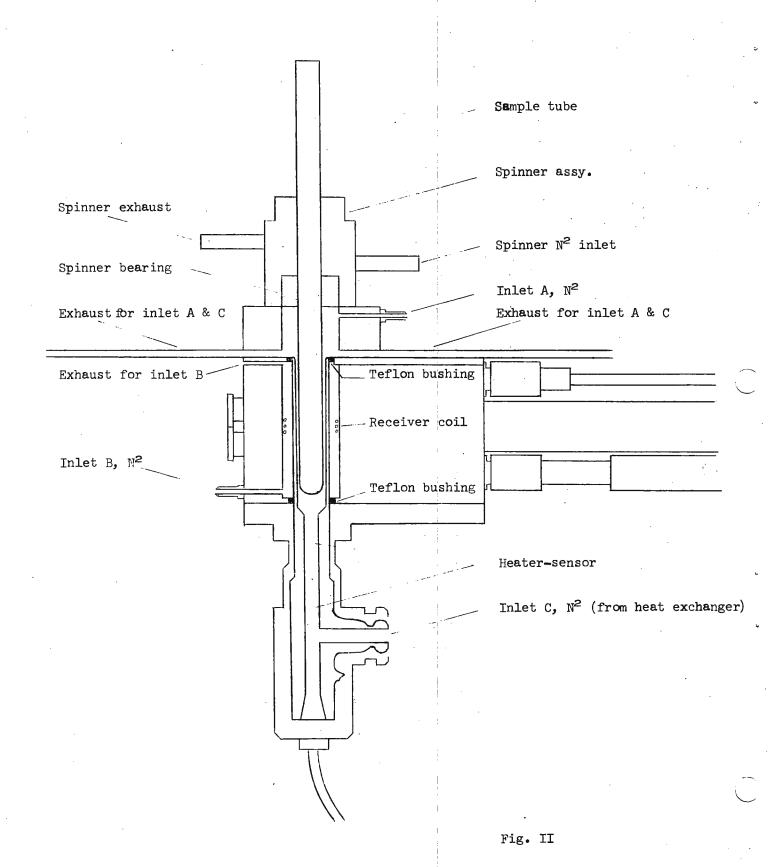
Instructor

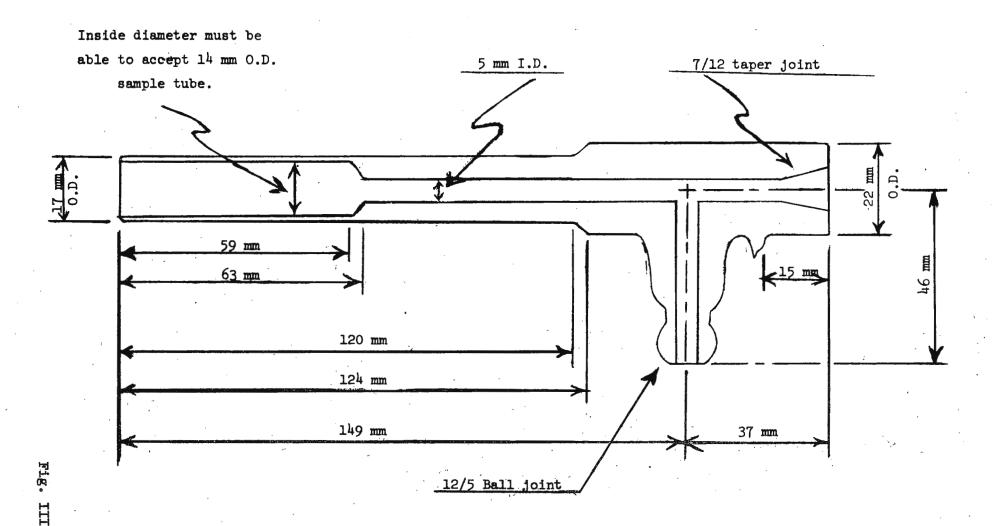
/ Carence

CG:df

Encl: Fig. I, II, III







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September 1, 1969

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

Dear Dr. Shapiro,

We have studied the quadrupole coupling constants (e 2 q $_2$) of Cs 133 and As in a single crystal of CsH $_2$ AsO $_4$ with ferroelectric Curie point T $_c$ = 143 K.

The temperature coefficient of as 75 - $_{\rm q}^2$ (= 5.0 \pm 0.1 Mc/s at room temperature and γ = 0.) exhibits an 'anomalous' behaviour, namely, its increase with decrease of temperature is too large to be accounted for by the 'normal' lattice thermal contraction. The line width of $_{\rm q}^{75}$ - $_{\rm p}^{12}$ - $_{\rm p}^{12}$) into transition increased as the temperature of the crystal was lowered and eventually it broadened beyond detection at about 150 K.

Was observed at 128° K, 15° below Tc, in few selected orientations. A rotation pattern of the spectrum (with c-axis as the rotation axis) yieleded the following values of the quadrupole coupling tensors for the two physically non-equivalent Cs-sites (with respect to the a-b-c. Crystalline frame of reference).

| site | 9 _{xx} | Gar | \mathcal{G}_{zz} |
|------|-----------------|------------|--------------------|
| a . | + 360 hc/a | 0 | <u>+</u> 360 Kc/s |
| р | . 0 | + 360 Kc/s | <u>+</u> 360 Kc/s |

It should be noted that the average of the two tensors at the two sites is equal to the tensor in the paraelectric phase. We believe that these results

throw some light on the mechanism of ferroelectricity in the crystals of the $\mbox{KH}_2\mbox{PO}_4$ family.

Yours sincerely,

R. Vijayangham.

L.C. Gupta

Title NMR of Cs 133 and As 75 in ferroelectric Cs H2AsO4.

McMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY

September 2, 1969

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

Dear Barry:

Modification of V-4354A "Lock Box" on Varian DA60-IL Spectrometer for ¹⁹F Spectra

As Dr. R. Goodfellow writes in IIT NMR Newsletter No. 101, the basic step in converting a DA60 (or HA100) for fluorine spectra is to substitute an external oscillator, e.g., a Muirhead-Wigan Decade Oscillator DA-890-A for the manual oscillator of the lock box. When lock signals are desired, considerable difficulty is then experienced with phasing, which Dr. Goodfellow gets round by two banks of switched capacitors, one at the reference input to the audio amplifier and phase detector and one at the reference input of the control amplifier and phase detector.

A different method has been used here and involves a second basic step, which is to have the external oscillator supply the audio frequency in two phases, which can be varied relative to one another over 360°. A circuit which does this conveniently is given herewith and this can be easily adapted to any other oscillator which has an output not less than approximately ten times the 1 volt peak to peak which is required for both modulation and reference sources. Another (the third) new input is made at the rear of the lock box. The "manual oscillator" input is as before, but the new 'manual oscillator phase detector reference" input now supplies the branch from the tapping point of R1304 which does not go to the attenuator. A six position switch with capacitors is used at the input to the control amplifier and phase detector (R of J1323) and switched to the appropriate value for the manual oscillator frequency in uses as follows: .005 μF (200-750 Hz), .002 μF (750 Hz - 1.5 KHz), .001 μF (1.5-3.5 KHz) (normal) 470 pf (2.5-5 KHz), 300 pf (5-10 KHz), 120 pf (10-20 KHz and higher). It is important that too large a capacitor is not switched in for the manual oscillator frequency being used as a 90° phase shift would not be obtained.

A few words on the operation may be helpful. The steps to give an HA frequency sweep spectrum are as follows:

Using a manual oscillator frequency of 2.5 KHz to 3.5 KHz and zero manual oscillator frequency phase shift, an unlocked field sweep sideband spectrum is run using the slow sweep unit. Corrections to the RF reference phase control are made sidebands give absorption signals.

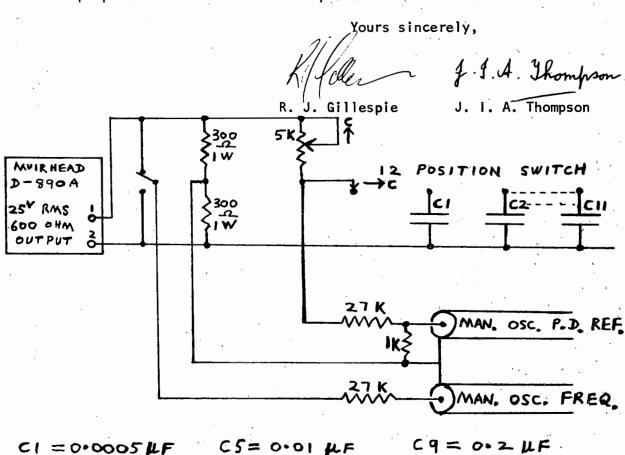
C2 =0.001

C3 =0.002

C4 = 0.004

- 2. Adjust the manual oscillator frequency to that required for the lock signal frequency. Switch capacity at control amplifier to appropriate value.
- 3. Using the slow sweep unit, run an unlocked field sweep spectrum. Select first upper sideband of lock signal and adjust the manual oscillator phase detector reference phase so that a good absorption signal is obtained. (Turn the 5K variable resistor maximum clockwise (see diagram) and switch in increasing capacitors until over correction is obtained. Then turn back the 5K as necessary. The switch gives 180° phase shift.)
- 4. Using the slow sweep unit, run to the peak of the (absorption of the) lock signal, which will be appearing on the oscilloscope as a sine wave of manual oscillator frequency when the signal monitor switch is at "RCVR". Switch to "frequency sweep" and put lock to "on". The sine wave oscilloscope signal should remain on the screen.

Lock signals of 15-20 KHz have been obtained. So far the maximum lock frequency used has been 8667 Hz and the minimum 1141 Hz. As the system is so versatile, only "clear thinking" is necessary to lock on to either upper or lower sideband signals with an appropriate frequency. The auto-shim should also continue to function correctly, although this has not been checked. HA field sweep spectra should also be easily obtained.



C6 = 0.02

C8 = 0.1

C7=0.04

C10 = 0.4

C11 = 1.0

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY LOS ANGELES, CALIFORNIA 90024

September 2, 1969

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

Title: 250 MHz Proton Spectra at -150°

Dear Barry:

I would like to describe some preliminary low-temperature proton spectra which we have obtained on a superconducting solenoid spectrometer (deuteron spectra obtained with this spectrometer were presented at the Tenth Experimental NMR Conference, Pittsburgh, February, 1969). Because of viscosity broadening at low temperatures, it is very advantageous to operate at the highest frequency possible. Unfortunately, commercially available superconducting solenoid spectrometers have been limited, until now at least, to sample temperatures of not much lower than -60°.

In a joint project with Dr. W. L. Mock of the Mellon Institute, we have been interested in determining the barrier to inversion in the completely conjugated seven-membered ring molecule, thiepin 1,1-dioxide. We chose to study 3-isopropyl-6-methylthiepin 1,1-dioxide (I), in which the methyl groups of the isopropyl chain are diastereotopic because of the non-planarity of the ring.

September 2, 1969 Page Two

Therefore, if ring investion is fast (on the nmr time scale) only a single chemical shift will be observed for these methyl groups. Spin coupling with the adjacent methine proton will then result in a doublet, as is in fact observed at room temperature. When ring inversion is slow there should be two chemical shifts, and hence two doublets. In a study of this compound carried out by Dr. Mary Brown and Mr. Craig Bradley, spectra were measured at 60, 100, and 250 MHz from room temperature down to about -150°. Spectra at -150° at these three frequencies are given in the Figure. Only the 250 MHz spectrum clearly shows the presence of two chemical shifts for the (isopropyl) methyl groups. The calculated spectra shown on the right in the Figure were obtained with the following parameters: $\delta = 0.10$ ppm; J (to adjacent methine H) = 6.9 Hz; line width in the absence of ring inversion = 7 Hz (8.5 Hz at 250 MHz); rate constant for ring inversion = 10 sec -1 (corresponding to a free energy of activation of 6.4 kcal/mole). There is satisfactory agreement between the experimental and calculated spectra at all three spectrometer frequencies.

Yours sincerely,

F. A. L. Anet

FALA: ems Attach:

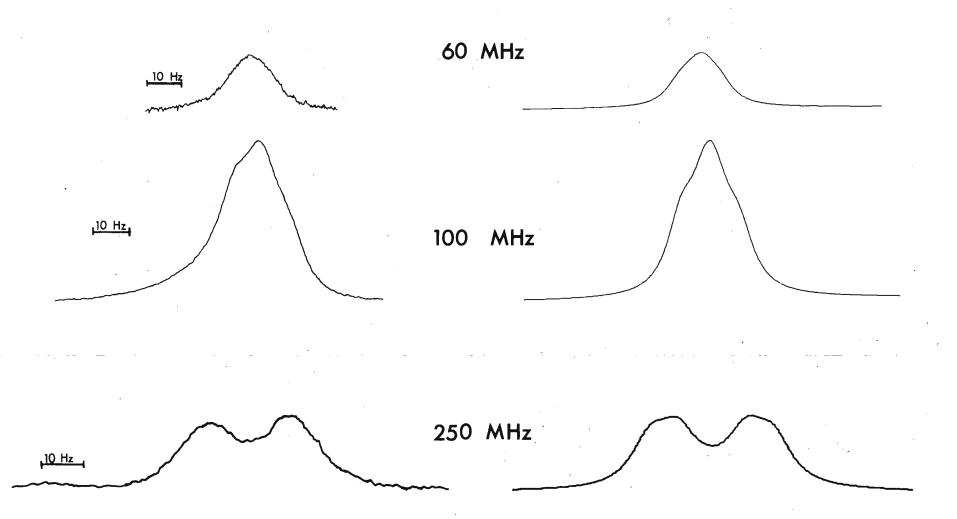


Figure. Experimental and calculated methyl bands of the isopropyl group in I at $-150\,^\circ$ for various spectrometer frequencies.

TELEPHONE OI-580 3583-4-5



61 NEW CAVENDISH STREET LONDON W.1

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

16th July, 1969

Dear Professor Shapiro,

I would be very grateful indeed if you will kindly give publicity in your IITNMR Newsletter concerning the 5th Conference on Molecular Spectroscopy as per/the attached.

C.H. MAYNARD

Administrative Secretary

s sincerely

5TH CONFERENCE ON MOLECULAR SPECTROSCOFY

The Hydrocarbon Research Group of the Institute of Petroleum is arranging to hold its next Conference on Molecular Spectroscopy in Brighton from 20th - 24th September, 1971. As at previous conferences it is the intention to deal with a number of the most important aspects of spectroscopy with particular attention being paid to the rapidly developing new techniques in the field. An exhibition of spectroscopic equipment will be incorporated in the arrangements.

im Hause

Gesellschaft für Molekularbiologische Forschung mbH 3301 Stöckheim über Braunschweig Mascheroder Weg 1 Telex 9-52667 Telefon 05 31 / 600 71

September 10, 1969

Dear Professor Shapiro,

Recently we introduced some technical modifications in the Varian HA 100 NMR-instrumentation which might be of interest to others.

1. A facility for securing signals when operating with a timeaverage computer.

When using the HA 100 instrument in conjunction with the timeaverage computer, it is necessary to maintain the lock during the entire time of registration. Quite frequently this prerequisite is not met, so we had to devise a system which interrupts computer storage of signals as soon as the lock signal has been lost.

As illustrated in the diagram, a Schmitt-trigger is controlled by a photodiode in front of the window of a Leeds & Northrop galvanometer.

Short term disappearance of the light beam will switch the relay replacing the normal time average switch and at the same time shunting the galvanometer precluding any damage to these parts.

2. Modification of the V 4343 variable temperature controller.

There is no safe way to check wether or not the selected temperature in the V 4343 variable temperature controller is in fact maintained inside the probe.

Thus we introduced direct measurement of the temperature inside the probe.

The input bridge of the temperature controller was modified in the following fashion.

The resistance thermometer PT 56 was connected with a cross coil DC meter. The thermometer plus current path of the cross coil are now one branch of the bridge. An additional branch was formed from the previously used set point temperature potentiometer and a preresistor. The circuit so formed is operated on DC in contrast to the original design.

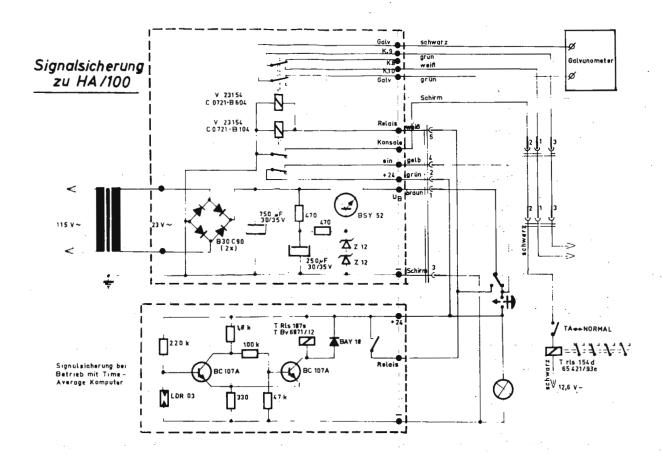
In this manner a change in the temperature will unbalance the bridge producing an alternating current by means of a chopper, which itself is coupled to the regular amplifier already present.

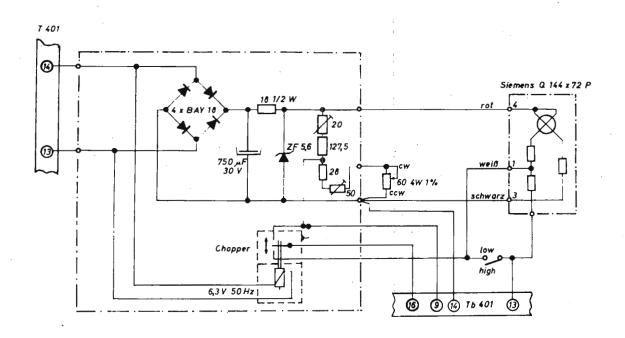
Thus, the same thermometer serves for recording the experimental temperature as well as for regulating the temperature.

Resistors should be adjusted to the cross coil type used. The circuit diagram is given enclosed.

Sincerely yours

(H. Stegemann)





Modifikation zum Anschluß eines Quotienten-Temperaturmeßwerkes in der Eingangsbrücke des V6040 Temperatur-Controllers

LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918 69 - VILLEURBANNE

TÉL. (78) 52.07.04 et 52.12.29

Villeurbanne, le 15/9

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

Titre: Mesures de T, sur Varian A.60.A

Cher Professeur Shapiro.

Pour la détermination de T, nous utilisons habituellement un HA-100 sur lequel les mesures s'effectuent facilement. Désirant opérer à un champ différent, nous avons été amenés à rechercher une méthode qui nous permette d'employer, à ca même effet, un A-60-A.

Pour observer l'évolution d'une résonance à la fréquence ω , nous affichons une fréquence Ω sur le spin decoupleur V6058A.

Il est possible de renverser la magnétisation des noyaux qui résoneront à la fréquence ω lorsque le chariot, qui se déplace à la vitesse V (Hertz/s), parvient à une distance Ω de la résonance. Le chariot passe par cette résonance après un temps $t = \Omega/V$ et l'on observe alors un signal proportionnel à l'intensité de l'aimantation à cet instant.

Il suffit de faire varier pour reconstituer, point par point, l'évolution de la magnétisation longitudinale en fonction du temps.

Les temps de relaxation qui nous interessent (dans des liquides avec $T_1#T_2$ $_{\sim}$ qq.secondes), la condition de passage adiabatique $_{\sim}/_{T_c}$ $_{\sim}/_{H_c}$ el $_{\sim}/_{AL}$ $_{\sim}/_{H_c}$ est réalisée si l'on prend10Hz/s comme vitesse du chariot et 3m.gauss comme intensité du champ de radiofréquence H_2 .

Recevez, cher Professeur, nos sentiments les meilleurs.

A.Briguet

J.C Duplan

J.Delmau

MAND

- Julie



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Genève, le 15 septembre 1969

Professeur Bernard L. SHAPIRO Department of Chemistry Texas A & M University College of Science

College Station, Texas 77843

Cher Professeur Shapiro,

Résonance magnétique nucléaire et précession libre dans les champs très faibles

Votre lettre de rappel - je m'excuse de l'avoir attendue - me donne l'occasion de résumer quelques résultats obtenus au cours de cette année dans ce domaine.

- 1) Communications à la Société Suisse de Physique (mai 1969) :
- Forme de la courbe de décroissance du signal en précession libre après prépolarisation (A. Erbéia, J. Perrenoud et G.J. Béné)

Nous proposons une analyse phénoménologique de signaux de précession libre obtenus dans le champ magnétique terrestre après prépolarisation perpendiculaire dans un champ de 12 Gauss.

- L'évolution de l'enveloppe du signal protonique est interprétée dans les cas du benzène et de l'eau désoxygénés, en fonction des temps de relaxation T_1 et T_{\sim} .
- Il en ressort qu'une mesure directe de $(1/T_1 + 1/T_2)$ est obtenue à partir de la pente de l'enveloppe à l'origine et qu'une mesure indépendante de T_1 et de T_2 peut se déduire de la forme de cette enveloppe.
- Mise en évidence simple et quantitative de l'équivalence entre un champ magnétique et une rotation (E. Hiltbrand, B. Borcard et G.J. Béné)

L'équivalence d'un champ magnétique et d'une rotation est mise en évidence de manière indirecte et non quantitative dans les gyromètres basés sur la résonance magnétique nucléaire.

La rotation ω_B de la bobine de prépolarisation et de détection de la précession libre ainsi que de l'échantillon qu'elle contient permet, dans une expérience de précession des protons dans le champ terrestre de déterminer directement la fréquence de Larmor résultant du champ appliqué (le champ terrestre $H_T = \omega / \chi$) et de l'équivalent en champ de la rotation ω_B de la bobine. Lorsque l'axe de rotation est parallèle au champ terrestre, la fréquence de Larmor mesurée est, selon le sens de la rotation : $\omega_D + \omega_B$. Si l'axe de rotation forme un angle α avec la direction du champ terrestre, on observe la fréquence de Larmor correspondant à la composition vectorielle du champ terrestre et de l'équivalent en champ de la rotation.

Professeur B.L. Shapiro, College Station - Texas 77843 - 15.9.1969

- NMR Haute Résolution dans le Champ Magnétique Terrestre : Analyse d'Interactions Indirectes de Spins de Protons avec N₁₅ et C₁₃ à la concentration naturelle de ces noyaux (B. Borcard, F. John et G.J. Béné)

Une amélioration appréciable de la sensibilité d'un spectromètre fonctionnant par précession libre de noyaux dans le champ magnétique terrestre après prépolarisation dans un champ perpendiculaire de grande intensité a permis à l'aide de cette technique l'analyse des interactions indirectes des protons avec le carbone 13 et l'azote 15 à la concentration de ces noyaux dans les composés liquides

| C,H' | Chloroforme | AB |
|---|--|-----------------|
| C ₁₂ -H i | Dichlorométhane | ABZ |
| C _{1,2} -H' | Alcool méthylique | AB |
| C ¹³ -H' C ¹³ -H' N ₁₅ -H' | Nitrate d'ammonium en solution aqueuse | AB [→] |

Cette méthode permet d'isoler le spectre résultant de l'interaction de nucléides de nature différente et d'en déduire avec précision la valeur de la constante d'interaction indirecte J.

- 2) Note aux C.R. Acad. Sc. Paris, t. 268, p. 1446-1448 (2 juin 1969) Série B:
- Echos rotatoires à fréquence zéro (B. Borcard, E. Hiltbrand et G.J. Béné)
 Nous décrivons une méthode nouvelle qui nous a permis d'observer pour la première fois des échos de spins nucléaires sans impulsions de radiofréquence

Puis-je profiter de cette lettre pour annoncer le prochain Colloque Ampère qui aura lieu à Bucarest (Roumanie) du ler au 6 septembre 1970. Des détails vous seront envoyés ultérieurement.

Croyez, cher Professeur Shapiro, à mes meilleurs sentiments.

dans de faibles champs inhomogènes.

Prof. G.J. Béné

Koninklijke / Shell - Loboratorium, Amsterdom
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Tear Ir. Shapiro.

IM. B.in -allylpalladium complexes

In 1963 Forsén and Hoffman reported an elegant method, making use of nuclear magnetic double resonance (NMDR), for the study of chemically exchanging nuclei. With this technique considerably longer lifetimes can be studied than with the line-shape method and in addition the exact pathway of the exchange in many-site systems can be determined. Only a limited number of applications have been reported. As shown here, NMDR can be very useful in the study of fluxional organometallic compounds.

Briefly, the method is as follows. In a many-spin system with chemical exchange the signal intensity at one site is reduced if another signal of an exchanging site is saturated. The demagnetization depends on the chemical lifetimes and the spin-lattice relaxation times. Relaxations should be independent, and cases without spin-spin coupling are most easily interpreted.

The experiments were done on a Varian HA-100 spectrometer in the frequency-sweep mode; only steady-state spectra are shown. When the saturating audio-oscillator was turned on, an overall decrease in intensity and a small Block-Siegert shift were observed. To prevent these interfering effects the oscillator was kept on while the spectra were taken. Resonance condition is ther. met by slightly changing the audio frequency (about 30 Hz upfield or downfield stepwise).

The example given here (see figure) is an asymmetric π -methallyl-palladium complex² with four different proton signals that broaden simultaneously in the NAR spectrum when the temperature is raised. By means of NMDR it is easily found that proton (1) only exchanges with (4) and (2) exchanges with (3); saturation of (1) leads to demagnetization of (4) (fig. B) and so on. Thus, the exchange path is established if assignments are known. More examples and experimental details will be published.

Please credit this contribution to Dr. E.L. Mackor.

Yours sincerely,

P.W.N.M. van Leeuwen

A.P. Praat

1. 3. Forsén and R.A. Hoffman, Acta Chem. Scand. 17 (1963) 1787.

E. M. Urieze, A.F. Praat and P. Cossee, J. Organometallic Chem. 12 (1968) 533.

- A AUDIOFIELD $\rm H_2$ SET 25 Hz ABOVE THE RESONANCE FREQUENCY OF H (1) SET ON THE RESONANCE FREQUENCY OF H (1) SET ON THE RESONANCE FREQUENCY OF H (2) IRRADIATION OF H (4) AND H(3) YIELDS SIMILAR PICTURES



SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

September 15th, 1969

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

Dear Barry,

ISOLATION AND ISOMERIZATION OF DIASTEREOMERIC ROTATIONAL ISOMERS

Your reminder notice arrived while I was in the process of making my move from the University of Rochester so I have been rather slow in getting my contribution organized.

We have been using n.m.r. to study restricted rotation in a number of compounds which show biphenyl-like isomerism and which also contain an asymmetric carbon atom. Since two centres of dissymmetry are present in these compounds, the rotational isomers are diastereomers. In most of the cases we have looked at the n.m.r. spectra of the diastereomeric rotamers show very distinct differences. Since we have usually been dealing with an equilibrium mixture of the isomers, we have seen the superimposed spectra of the two forms. Provided that the barrier to rotation is not too high (or too low) the spectra are temperature dependent, and in certain cases we have been able to determine activation parameters by complete line shape analysis.

Recently, we have been interested in preparing more highly hindered compounds of this type in order to obtain diastereomeric rotational isomers with sufficient conformational stability to be isolated. We have planned to use n.m.r. to follow the separation and, at a later stage, to monitor the isomerization of the individual rotamers to the equilibrium mixture. One such compound that we have studied.

$$\begin{array}{c|c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & & \\$$

has been obtained through the co-operation of Dr. Andre Rosowsky of the

Children's Cancer Research Foundation, Boston.

Isolation of one of the rotational isomers of this compound proved to be surprisingly easy, since it was obtained, with only slight contamination by the other isomer, on ordinary work-up following synthesis. The portions of the spectrum which are most sensitive to rotation of the tolyl group about the C-N bond are the doublet and quartet arising from the CH3-C-H group on the hetero ring. Conversion of the pure isomer to the equilibrium mixture can be followed readily at a particular temperature by recording the growth of an additional methyl doublet produced by the second isomer 0.185 p.p.m. to high field of the original doublet. At 100 MHz this separation is sufficient to enable us to follow the isomerization by repeated integration.

In this case, the barrier to rotation is too high for a significant temperature dependence of the line shape of the equilibrium mixture to be observable at attainable temperatures (using perfluorobutyric acid solutions).

Yours sincerely,

L.D. Colebrook,

Department of Chemistry.

LDC/mp



GENT, September 17th 1969.

KRIJGSLAAŅ 105 (België - Europa) Tel. (09) 22.60.95

Some long-range couplings involving fluorine atoms.

Dear Prof. Shapiro,

In a general study on 1,3-dioxanes, we observed several long-range couplings (ref. 1,2) in the N.M.R. spectra. However couplings over more than four bonds are often to small to be studied. Some trifluoromethyl-substituted-1,3-dioxanes were now prepared in view to study dipolar interactions in those molecules. The knowledge of the occurence of some new long range paths in those 1,3-dioxane systems was very helpfull in the assignation of their configurations. More over the specific long-range couplings, encountered in other alkyl-substituted 1,3-dioxanes (ref. 3)($^5J_{2e}$ _ 5e) are also encountered in 4-CF₃-1,3-dioxanes. It is noteworthy that an axial 4-CF₃ has a much greater ability for long-range coupling than an equatorial 4-CF₃, as illustrated in table I.

Table I.

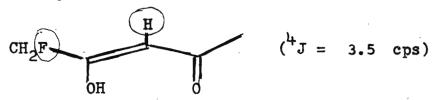
| | ⁵ J _{2a} - ^{6a CF} 3 | | ⁵ J _{4a} - 6a CF ₃ | ⁵ J _{2a} - 6a CF ₃ |
|--|--|----------|--|--|
| trans 4-t-butyl-6- CF3-1,3-dioxane | 1.85 cps | 0.85 cps | 1.7 cps | ~1 cps |
| $\frac{\text{trans}}{\text{CF}_3}$ 4- \emptyset -6- $\frac{1}{3}$ -dioxane | 1.55 cps | 0.55 cps | H _{l+} over- | \sim 1 cps |
| trans 4-CF ₃ -6-CH ₃ -1,3-dioxane | | 0.7 cps | | \sim 1 cps |



September 17th 1969. GENT. KRIJGSLAAN 105 Tel. (99) 22.60.95

(België - Europa)

During the preparation of those types of compounds we also found a allylic long-range (F19) coupling in (enolized) 1-F-acetylacetone:



Remarkable was the fact that clearly no analogous long-range coupling is observed, involving CH2F-hydrogens. This could indicate a high preference of one of the rotamers, over the two others, around the C1-C2 bond, due to dipolar interaction.

References.

- (1) Gelan J., Anteunis M., Bull.Soc.Chim.Belges, 77 (1968) 447-454.
- (2) Swaelens G., Anteunis M., Bull.Soc.Chim.Belges, 2,4-dioxabicyclo 3.3.1. -nonane. (in press).
- (3) Ramey K.C., Messich J., Tetrah.Letters no 49, 4423 (1965).

G. SWAELENS and M. ANTEUNIS.

EMORY UNIVERSITY ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

September 24, 1969

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

Title: Furan Revisited

Dear Barry:

Over the past few years furan has received considerable attention from NMR spectroscopists. The reason for this, in part, has been due to the steady progress that has been made in instrumentation allowing better resolution and sensitivity, hence better data with which to solve the problem. The most recent analysis of the proton spectrum of furan (Newsletter #131-22) predicts a set of four lines in the center regions of each of the two proton patterns, with spacings of approximately 0.06, 0.1, 0.1 and 0.1, 0.1, 0.06 Hz from low to high field. Because of our past interest in this molecule we thought that this system would provide a reliable test of the resolution of the Bruker HX - 90 spectrometer. The spectra we obtained, shown in Figure 1, do indeed consist of four identifiable peaks in each region.

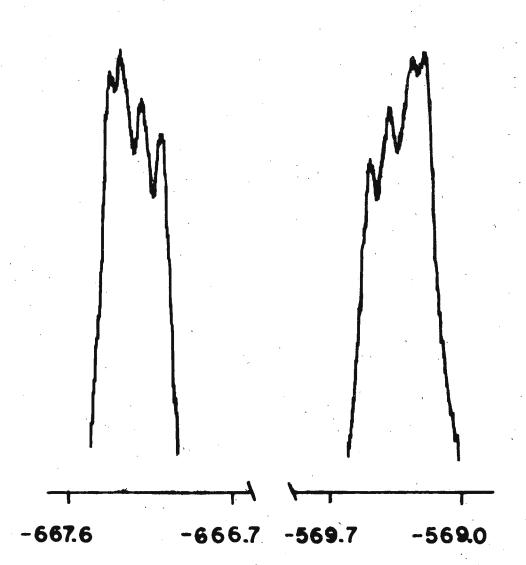
No special techniques were used in preparing the sample (40% in acetone) other than to degas the solution. The Bruker HX - 90 operating at 90 MHz was locked on the TMS resonance while slowly sweeping (5000 seconds) the regions of interest utilizing a narrow sweep width of 0.2 Hz/cm. The splittings were obtained consistently on repeated sweeps. By fitting a Lorentz line shape to the calculated spectrum, the line width at half-peak height appears to be between 0.08 and 0.09 Hz. This attainment in resolution seems to be due to the excellent stability and design of the spectrometer system.

Sincerely yours,

R. W. Crecely

L. H. Altmayer

J. H. Goldstein



CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
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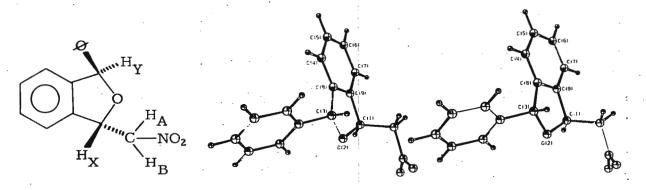
September 19, 1969

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

Correlation of Conformation about a C-C Bond Observed for the Crystal and in Solution.

Dear Barry,

In the area of stereochemical analysis, X-ray diffraction studies on a single crystal have proven to be very valuable. However, there is always a problem as to whether the conformation in the crystal corresponds to the average conformation in solution. In connection with work on the stereochemistry of 1,3-disubstituted phthalans carried out in conjunction with Dr. F.J. Petracek of the Riker Laboratories, one of us (R.G.P.) and J. Bordner have determined the crystal structure of trans-1-(nitromethy1)-3-phenylphthalan, I. In the crystal, Figure 1, the dihedral angle between the C-H_X and C-NO₂ bonds is observed to be 90°.



1

Figure 1. Stereoprojection of the X-ray structure for trans-1-(nitro-methyl)-3-phenylphthalan.

The 220 MHz spectra of I in deuteriochloroform is shown in Figure 2. Analysis of this ABXY pattern by LAOCOON III gave the following coupling constants:

| • | J | Hz | | |
|-----------|----|-------|-------|-------|
| | AB | -12.6 | | |
| | AX | +8.2 | | |
| | BX | +3.1 | | |
| | XY | ±3.0 | • | |
| , 10 Hz | M | M | M. | 10 Hs |
| | | | | |
| XY Region | | | AB Re | gion |

Figure 2. 220 MHz spectra in deuteriochloroform, observed and calculated for <u>trans-l-(nitromethyl)-3-phenylphthalan</u>.

The dihedral angles of $C-H_A$ and $C-H_B$ with respect to $C-H_X$ were calculated from the observed coupling, J_{AX} and J_{BX} . The standard Karplus equation was used as derived for ethane. This form of the Karplus relationship was chosen on the basis of the following considerations. The large number of strongly electronegative groups attached to the two carbons of interest should reduce the value of J_{vic} by several Hz relative to ethane. On the other hand, the oxygen atom in the five-membered heterocyclic ring with the electrons in the p-orbitals coplanar with the adjacent $C-H_X$ bond has been observed to enhance the value of J_{vic} by as much as +2.3 Hz. Thus, these two opposing factors operating on J_{vic} should cancel to a first approximation.

The dihedral angles calculated from the NMR data indicate that the average orientation of the $C-H_{\overline{X}}$ and $C-NO_2$ bonds is ca. 90°. It is interesting that the average orientation in solution (CDCl₃) is the same as the orientation determined by X-ray analysis of crystal.

With all good wishes,

Very truly yours,

Robert A. Smith

Richard G. Parker

Beckerd G. Parker

John D. Roberts

References:

- 1. S. Sternhell, Quart. Rev., 23, 236 (1969).
- 2. R.J. Abraham and K.G.R. Pachler, Mol. Phys., 7, 165 (1962).
- 3. M. Antenunis, <u>Bull. Soc. Chem. Belg.</u>, 75, 413 (1966).

Hooker Research center

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September 22, 1969

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

Possible Factors in the Solvent Dependence of Certain Vicinal Coupling Constants

Dear Dr. Shapiro:

In our last newsletter (TAMU NMR No. 122, p.44) we described several halonorbornenes in which trends in the vicinal coupling constant were revealed on the successive replacement of chlorine with bromine and iodine on the proton bearing carbon(s). Among these, in the <u>trans-5,6-dihalo-1,2,3,4,7,7-hexachloronorbornenes, A, Fig. 1, an increase in the vicinal proton-proton coupling constant with increasing size of the halogen was noted and was attributed to the enlargement of the approximately 120° dihedral bond angle between hydrogens.</u>

Analyzing the proton spectrum of endo-5-nitro-1,2,3,4,7,7-hexa-chloronorbornene, B, Fig. 1, we noted a marked variation in the vicinal coupling with the change of solvent. Thus its trans coupling constant of 3.64+0.02 cps in hexadeuteriobenzene increased to 4.44+0.02 cps in hexadeuterioacetone and increased further to 4.96+0.06 cps in deuteriochloroform. Utilizing the Karplus relationship and the argument described above, an increase in the trans coupling can indicate an increase in the hypothetical 120°



dihedral bond angle and thus it might relate to an increase in the effective size of the solvated nitro group. This, on expansion due to solvation, exerts increased torsional force on the carbon attached to it and pushes the exo hydrogen on the same carbon more toward the bridge, thus affecting or distorting the symmetry of the norbornene carbon skeleton. The apparent increase in the size of the solvated nitro group on going from benzene to acetone to chloroform might be due to an increase in the size or the number of the solvating molecules, or both.

As expected, the effect observed is not isolated from the rest of the nmr parameters of the molecule. While changes in the chemical shifts are more difficult to interpret due to the anisotropy of the solvent molecules (benzene, expectedly, effects shielding on all protons relative to chloroform and acetone), variations in the cis coupling constants seem to support the steric argument advanced above. The torsional force which increases the trans dihedral angle increases also the cis H-C-C-H dihedral angle, which is assumed to be near zero in the least solvated species. The anticipated decrease in the cis coupling thus was found to run roughly parallel with the increase in the trans coupling and the relationship is illustrated in Fig. 2.

We thank Professor Wayland Noland, University of Minnesota, for the sample of pure endo-5-nitro-1,2,3,4,7,7-hexachloronorbornene used in these analyses.

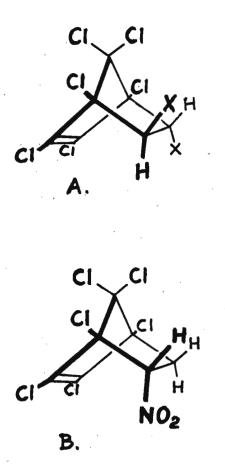
Sincerely,

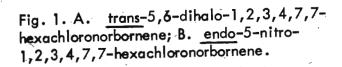
Victor Mark

Senior Research Associate

Victor Mark

VM/srd





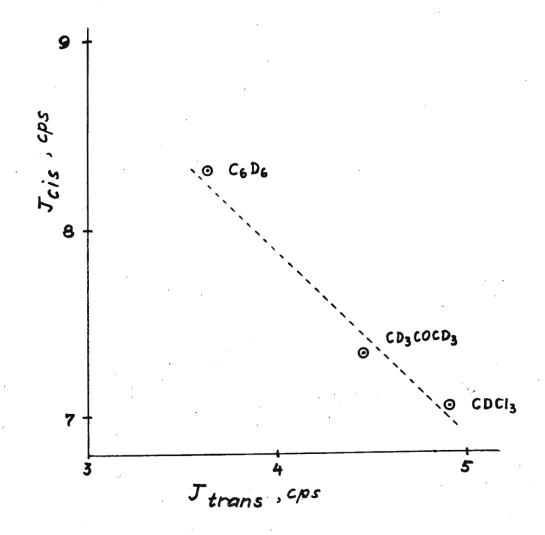


Fig. 2. Correlation diagram between cis and trans coupling constants in B.





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

Your Ref:

Our Ref: FL/ARS-B4 Research Department

22nd September 1969.

Derr Professor Chapiro,

HA-100 Recorder Modification

Readers may be interested in the sample modification we have made to our mini-step digital recorder to provide us with a selection of "fast sweep" times, similar to those of the "normal sweep" times. Thus, when using the spectrometer in conjunction with the C-1024 computer for /I enhancement, we have a choice of 10, 25, 50, 100, 250, 500 or 1,000 secs. For the recorder sweeps-back time, instead of the standard 10 secs. Two main benefits are derived from this system.

- (a) hen working with a small locking signal in the field swept mode, the use of a longer sweep back time prevents the loss of lock which sometimes otherwise occurs.
- (b) The spectrometer can be set to accumulate a spectrum scanned in both directions. We find this particularly useful when carrying out quantitative analyses involving the comparison of closely spaced peaks in weak solutions. Movable limit microswitches (described by hr.1.Commor in MR Newsletter No.83) are used to limit the extent of the scan. With the "fast sweep" time set equal to the "normal sweep" time, a sweep width, between microswitches, is chosen so that the sweep time for one forward and one reverse sweep, is just greater than the computer sweep time. The accumulated spectrum is that of the region of interest recorded in both directions, side by side.

The only components required are a two-pole wafer switch and five diodes which we have mounted on the switch. Our switch is mounted on the recorder control panel. A diagram of the circuit modification is given.

Yours sincerely,

A.Mathies

P.Hempson

F::/J::

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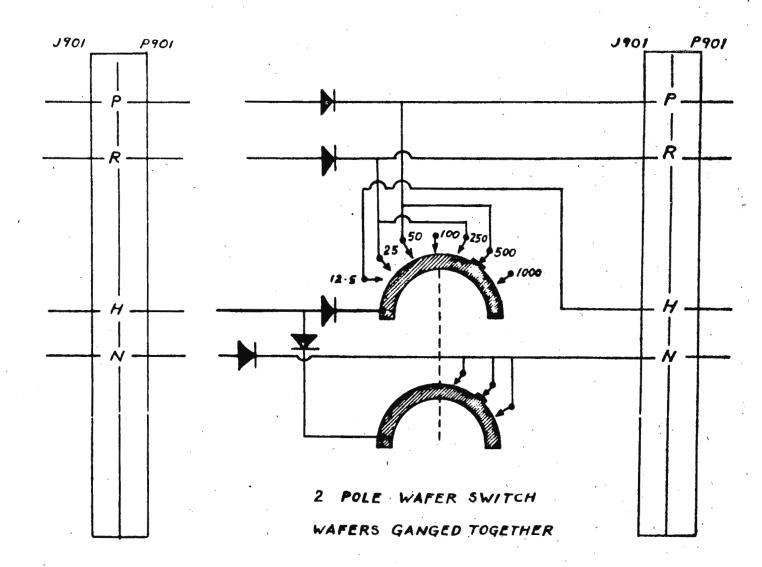
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- ORIGINAL -

- MODIFIED
CIRCUIT



South Parks Road,

Oxford.

25 September 1969

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

Dear Barry,

I am writing to describe briefly some measurements of caesium resonances which have been made in my laboratory by Jim Halliday and Robert Sharp. The caesium resonances were measured on a 50 Kg superconducting magnet with a digitally swept spectrometer which has now been described in the literature. The measurements were made at about 30 MHz and we were able to fix the chemical shift to -1.5 Hz.

Caesium salts with chloride, bromide, iodide, hydroxide, and nitrate were measured as a function of concentration in the range 5 mM to 3 N, in water, D_2O , H_2 O and in a number of other solvents. The temperature dependence of the shifts was also measured.

We found that the chemical shifts could be rationalized very satisfactorily in terms of a simple theory for the radial distribution function of ions around the central ion and for the radial dependence of the chemical shift. The radial distribution function assumes that the ion is normally surrounded by water and that when another ion approaches it, a stable distribution is achieved either when the ion is in direct contact with the central ion, or when it is separated from the central ion by a single shell of water molecules. It is assumed that intermediate positions are unstable. Furthermore we treat the solvent as a continuum beyond the first hydration shell. Various contributions to the radial dependence of the chemical shift were considered and for caesium salts the overlap mechanism is by far the most important. these assumptions the absolute value of the chemical shift can be found within a factor of 2, and if the calculated shifts are adjusted to fit one experimental point, the concentration dependence over the range measured is very accurately predicted. If the dielectric constant of the solvent is changed, the theory predicts a different concentration dependence and the predictions are well obeyed for solvents of reasonably high dielectric constant. Mixtures of water with glycine, ethanediol, ethanol, pyridine and methanol all behaved very well, but the low dielectric constant mixtures of water with sulpholane are not well described by the This is probably as a result of ion pairing. The theory also predicts a small temperature dependence with chemical shifts and the predictions are within experimental error the same as those measured. The theory and the detailed results will appear before long in a paper in the Proceedings of the Royal Society.

With best wishes,

Yours sincerely,

Por Richards

Short title: Caesium Chemical Shifts in Salt Solutions



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October 2nd, 1969.

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

Hindered Rotation in "Benzoxazine-like" Molecules

Dear Barry,

In the last contribution I described some studies of hindered rotation in molecules with the structure (I) TAMUNMRN #124. Now I would like to describe some further work with vaguely similar molecules. Structures II and III.

$$R_1$$
 CH_2
 R_3
 R_4
 R_5
 R_4
 R_7
 R_8
 R_9
 R_9

It appears that the N-H hydrogen bond in structure II gives sufficient rigidity to the molecule that hindered rotation about the nitrogen-aromatic carbon bond is observed when R_3 = t-butyl and R_5 = H. We have not yet completed the rate analysis as a function of temperature but assuming ΔS = 0, as found previously, ΔH for the t-butyl compound of structure II is 16.7 k.cal/mole compared with 16.9±0.3 k.cal/mole for a similarly substituted compound of Structure I. When R_3 = R_5 =H no hindrance to free rotation is observed.

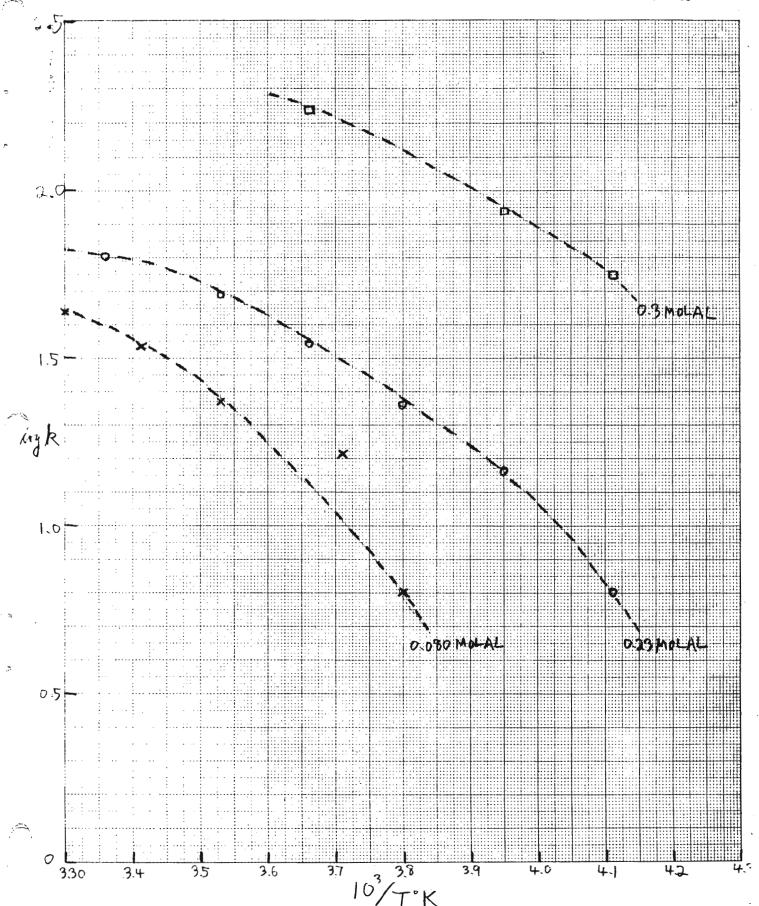
Exchange between the hydrogens on oxygen and nitrogen were observed in carbon-disulfide solution for compounds of Structure III. The results for the compound where $R_1=R_2=t-buty1$, $R_3=R_4=hydrogen$ and $R_5=methy1$ are shown on the accompanying graph. The observed rate of exchange seems to be the sum of an intramolecular and an intermolecular step.

Yours truly,

S. Brownstein

SB:d1

P.S. I am on Sabbatical at Laval, but continue my subscription at N.R.C.





THE UNIVERSITY OF OKLAHOMA

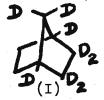
September 24, 1969

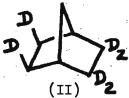
Professor Bernard L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

CALCULATION OF JHH VALUES IN NORBORNANE

Dear Dr. Shapiro,

In connection with our recent interest in nmr spectra of rigid ring systems, we have prepared the specifically-deuterated norbornanes, I and II, below, and we have calculated their nmr spectra (LAOCOON III).





The observed and calculated deuterium-decoupled 100 MHz nmr spectra along with the isotopic analysis (mass spec.) of compound I are shown in figure 1. The shaded areas in the observed spectrum are due to the presence of isotopic impurity, i.e., 1 H in the 2- or 3- positions.

Various $J_{\rm HH}$ values have been calculated for the AA'BB' system in I and for the more complex six-spin system in II. The results of these calculations are tabulated below:

| • | | |
|------------|-----------------|-------------------|
| Coupling | g Constant, JXY | Calcd. value, Hz. |
| <u>x</u> | <u>Y</u> | |
| ī | <u>T</u> | O (assumed)* |
| 2n | 3 n | 9.05 ± 0.10 |
| 2 x | 3 x | 12.22 ± 0.10 |
| 2n | 2 x | -11.79 ± 0.08 |
| 2n | 3 x | 4.62 ± 0.07 |
| 1 | 2n | 2.07 ± 0.12 |
| 1 | 3n | 0.51 ± 0.12 |
| 2n | 7 s | ±0.22 ± 0.12 |
| 2n | 7a | + 3.06 |
| 1 | 7s | 1.59 ± 0.11 |
| 7s | 7a | -12.50 (assumed)* |
| , - | | |

^{*}Spectrum is insensitive to J787a, and to J1,4

Sincerely,

Of particular significance in the above table are the observation that $J_{2n3n} \neq J_{2x3x}$ despite the equivalence of their respective dihedral angles (= 0), and the observation of the small, but finite coupling, J_{2n7s} .

Alan P. Marchand Nancy W. Marcha

Alan P. Marchand

Assistant Professor
Chemistry Department
University of Oklahoma

Nancy W. Marchand University of Oklahoma Oklahoma Medical Research Foundation

Auna L. Segre

Anna Laura Segre

Istituto di Chimica Industriale

del Politecnico

Milan, Italy**

**Present address: Carnegie-Mellon University, Mellon Institute, Pittsburgh, Pa. 15213.
***Please credit to APM's subscription.

CALCULATED 100 MHz NMR SPECTRUM

1,2,2,3,3,4,7,7-Octadeuterionorbornane

5n = 6n

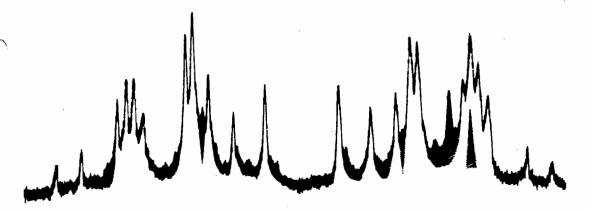
112.54 ± .05

 $v_{5x} = v_{6x}$

143.13 ± .05

ISOTOPIC ANALYSIS

-- % di 0.8% di 1.8% di 3.0% di 6.4% di 17.9% di 35.4% di 35.0% di



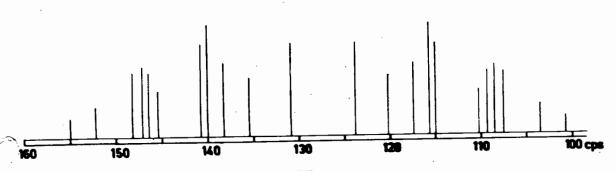


FIGURE 1.



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

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Building 2, Room B2-02

September 30, 1969

Prof. Bernard L. Shapiro Department of Chemistry Texas AAM University College Station, Texas 77843

Dear Barry:

In connection with double resonance studies of 15 N, we have investigated the effect of 14 N/ 15 N isotopic substitution on nitrogen chemical shifts. Since changes in zero point vibrational amplitudes could in principle cause an isotopic shift, it seemed interesting from a theoretical viewpoint and important in practice to determine whether any significant effect exists.

Since I wanted to use the double resonance method in order to refer both ¹⁴N and ¹⁵N chemical shifts to TMS, it was necessary to find compounds where (a) the ¹⁴N coupling to some proton in the molecule can be observed and (b) the ¹⁵N analog can be synthesized readily. In addition I wanted to cover several chemically distinct nitrogens so as to observe the effect over a range of chemical shifts. During the past year we have studied four such isotopic pairs. Ted Axenrod at City College of New York suggested using and synthesized several of the ¹⁵N compounds, and Bob Bradley actually ran the spectra. The data are summarized as follows:

| Compound | $v(^{15}N)/v(^{14}N)$ | δ _N (ppm) | |
|--|--------------------------------------|----------------------|--|
| N(CH ₃)4I | 1.40275706 ± 6x10 ⁻⁸ | 0 | |
| C ₆ H ₅ CH ₂ NC | $1.40275680 \pm 10 \text{x} 10^{-8}$ | 126 | |
| CH ₃ ONO ₂ | 1.40275700 ± 6x10 ⁻⁸ | 298 | |
| (CH ₃) ₂ NNO ₂ | $1.40275684 \pm 6 \times 10^{-8}$ | 312 | |

There is thus no consistent variation of this ratio with nitrogen chemical shift; hence $\sigma(^{14}N) = \sigma(^{15}N)$ to a high degree of precision.

Ed Randall has long been interested in isotope effects on nitrogen chemical shifts and reported earlier (Newsletter, No. 123) values for the frequency ratio for two compounds. His result for NH_4^{-} , 1.40275711, is in quite good agreement with our results. However, his value for CH_3NC (1.40275786) is rather far from the ratios for our samples, and could have led to an expectation of larger isotope effect.

Prof. Bernard L. Shapiro September 30, 1969 Page 2

We have measured ¹⁵N chemical shifts and ¹⁵N-H coupling constants in a series of nitroso compounds and in a number of substituted anilines. But I'll write about that later.

Sincerely,

Ted

Edwin D. Becker
Laboratory of Physical
National Institute of Arthritis
and Metabolic Diseases

P.S. After seeing all the blank space left on this page, I felt compelled to add something in order to forestall a comment by the "non-editor."

You might be interested in knowing that Raman Newsletter (known to some of us as "son of NMR Newsletter") will celebrate its first birthday next month. Even though there are fewer workers active in Raman spectroscopy than in NMR, the mailing list is about 150, and the Newsletter has been widely accepted in the field. It is very frankly patterned after TAMUNMRN—imitation is the sincerest form of flattery, isn't it? We have many of the same problems as you and require occasional dunning letters, though not as yet on pink and blue paper. Thus far financial support has come principally from several of the Raman spectrometer manufacturers. We haven't yet received a rash of contributions on "how to clean your laser windows," but I suppose they will come.

Title: Isotope effect on nitrogen chemical shifts; "Son of TAMUNEUN"

БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

Sofia, the Sept. 29 196.9

BULGARIAN
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INSTITUTE OF ORGANIC CHEMISTRY
Sofia 13

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

Dear Professor Shapiro,

Rotational barriers in some conjugated N,N-dimethylamides

Some times ago we joined the many others studying rotational barriers about C-N bonds by NMR. Here are some results on the activation parameters of N,N-dimethylamides RCONMe₂ (0.5 M solution in CDCl₃) obtained at 60 MHz using the line-shape method of Nakagawa /1/.

| <u>R</u> | $\underline{\mathbf{T}_{\mathbf{o}}(\mathbf{o}_{K})}$ | $\Delta V(Hz)$ | $\Delta G_0^{\dagger}(kcal)$ | $\Delta G_{298}^{\pm}(\text{kcal})$ | ΔH ₂₉₈ | <u>∆8</u> ≠ |
|--------------|---|----------------|------------------------------|-------------------------------------|-------------------|-------------|
| Ph | 297 | 7.8 | 15.7 | | (kcal) | (eu) |
| p-BrC6H4 | 295 | 6.9 | 15.7 | | | |
| PhCH=CH | 304 | 5•5 | 16.3 | 16.5 | 17.5 | +3 |
| MeCH=CH | 267 | 4.6 | 14.3 | 14.9 | 9.0 | - 9 |
| MeCH=CHCH=CH | 300 | 4.5 | 16.2 | 16.2 | 17.7 | +5 |

The (preliminary) results for the two benzamides are in agreement with those obtained by other authors (PhCONMe₂: ΔG_{298}^{\pm} = 15.7, CHCl₃ /2/; 15.78, CDCl₃ /3/; 15.50, MeCN /4/; p-BrC₆H₄CONMe₂: 15.69, CDCl₃ /3/; 15.53, MeCN /4/). Further studies on other N,N-dimethylamides are in progress.

Sincerely yours,

Stefan L. Spassov)

/1/ T.Nakagawa, Bull.Chem.Soc.Japan 39, 1006 (1966).

/2/ C.W.Fryer, F.Conti, C.Franconi, Ric.Sci.Rend.Sez.A 35,788(1965).

/3/ P.K.Korver, Dissertation, University of Amsterdam, 1966.

/4/ L.M.Jackman, T.E.Kavanagh, R.C.Haddon, Organic Magnetic Resonance
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