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No.169

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Newsletter

October, 1972

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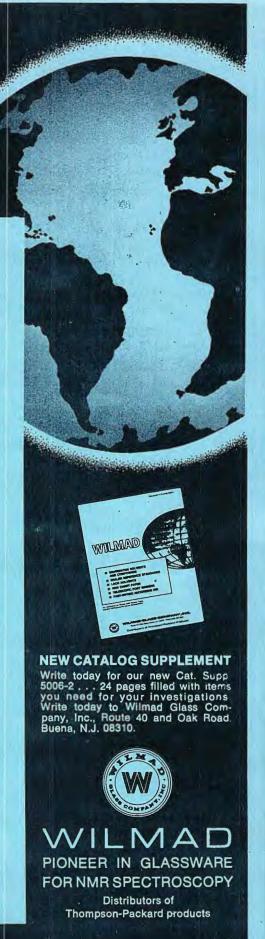
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Deadline Dates: No. 170: 6 November 1972 No. 171: 4 December 1972

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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Ul. Vavilova, 32 Moscow V-312 USSR

May 24, 1972

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77845
U.S.A.

Title: On the Angular Dependence of the Long Range Coupling H-C-C-CH₃.

Dear Barry,

The very similar to proposed by Prof.Sternhell [1] dependence of long range coupling $^4J_{HCCCH_3}$ on dihedral angle might be deduced from empirical equation (2) for $^4J_{HCCCH}$ previously cited in [2]. By averaging this equation for the CH_3 group rotation in fragment $HC-C-CH_3$ it can be found

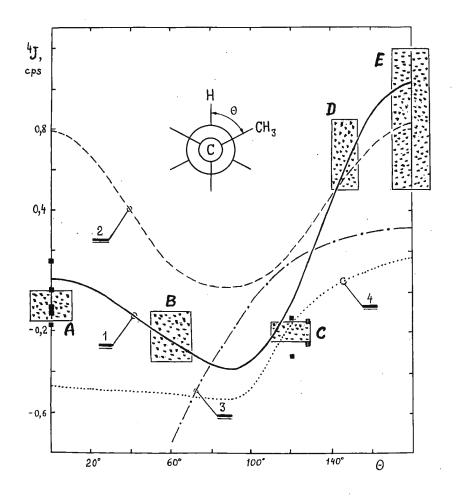
$$^{4}J_{HCCCH_{3}} = 0.41 \cos^{2}\Theta - 0.35 \text{ for } 0^{\circ} \leq \Theta \leq 90^{\circ}$$
 $1.38 \cos^{2}\Theta - 0.35 \text{ for } 90^{\circ} \leq \Theta \leq 180^{\circ}$

or the same in another form

$$^{4}J_{HCCCH_{3}} = 0.9 \cos^{2} \Theta - 0.5 \cos \Theta - 0.35$$

The curve corresponding to this relationship is drawn on the attached figure (Curve 1) together with theoretically calculated curves 2 - 4 and experimental results. It appears that the deduced equation (as well as Prof. S.Sternhell curve [1]) is in better agreement with the experimental results than the theoretical calculations.

For the long range coupling $\text{CH}_3\text{-C-CH}_3$ the above equation gives +0,18 cps in satisfactory agreement with measured 0,2 cps for $(\text{CH}_3)_2\text{CH}_2$ [11] and +0,35 cps for $(\text{CH}_3)_4\text{C}$ [12]. Only the VB calculation (+0,35 cps [3]) also agrees with the experiments.



Angular dependence of the long range coupling ${}^4J_{\text{HCCCH}_3}$. Curves: $\underline{1}$ - this letter; $\underline{2}$ - VB calculations [3]; $\underline{3}$ - MO calculations [4]; $\underline{4}$ - INDO calculations [5]. Experimental results: \underline{A} - from [6,7]; \underline{B} - [8,9]; \underline{C} - [6]; \underline{D} - [7]; \underline{E} - [8,10]; \blacksquare - [1].

The MO [4] and INDO [5] calculations give -0,40 and -0,28 cps correspondingly and disagree even in sign with experiment.

Sincerely yours,

Dr. Vladimir Bystrov

References:

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SAN FRANCISCO, CALIFORNIA 94122

September 7, 1972

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

Dear Barry,

We have recently been looking at water-polyethylene glycol "solutions". PEG is completely miscible with water at sufficiently high temperatures (usually above 40°C), and the resulting solutions have been thoroughly studied by NMR (1). Our concern was with the "solid" that results when these solutions are cooled to room temperature or below. One still observes two resonances (H_20 and the methylene protons of the PEG), usually only 1-100Hz wide. However, the amount of water and PEG contributing to these signals is (generally) less than observed in the liquid phase, indicating some strongly immobilized and slowly exchanging solid is not being detected. The question to be answered is whether the material is a very peculiar type of solid solution or whether two phases (liquid + solid) are present. Area and linewidth data as a function of temperature and composition are given in Figure 1. Figure 2 shows our present working model of a phase diagram which probably fits most of the data at least some of the time. We are now exploring the low temperature part of the diagram.

It appears that I will have some money for a postdoctoral student to pursue the biomacromolecule hydration studies. Anyone interested should contact me in the near future.

Best regards,

Irwin D. Kuntz Associate Professor Chiang Cheng

IDK:bw

(1) K-J Liu and J.E. Anderson, J. Macromol. Sci.-Revs. Macromol. Chem. $\underline{6}$, 128 '70.

Title: Polyethylene Glycol - Water Systems.

Figure 1A. Ratio of water area/PEG area detected on 500Hz A-60 scan as a function of temperature. Several bulk compositions as shown as volume % water.

Figure 1B. Log (linewidth of H₂0) vs. 1/Temperature PEG linewidth (not shown) shows similar behaviour.

Figure 2. Phase diagram for water-PEG Tentative.

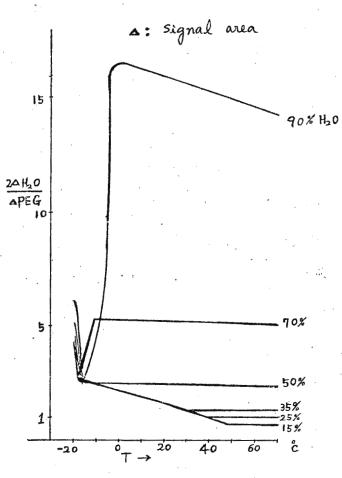


Figure 1a

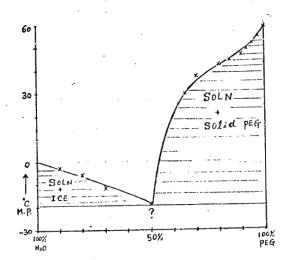
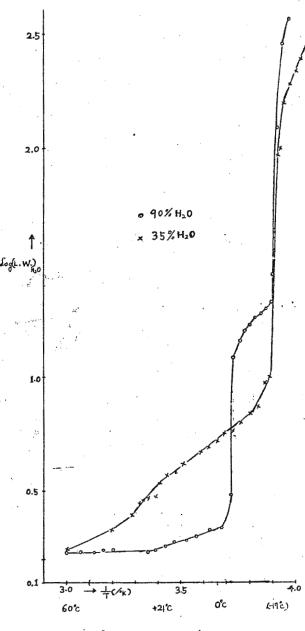


Figure 2



. Figure 1 b



University of Strathclyde

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6th September, 1972

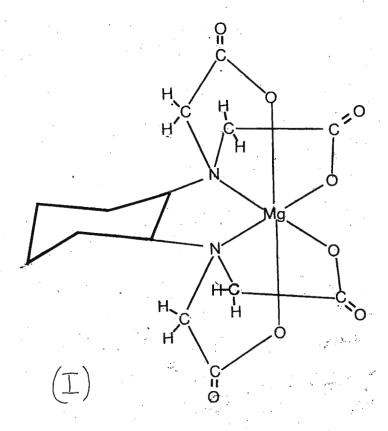
Professor B. L. Shapiro, Department of Chemistry, Texas A and M University College of Science, College Station Texas 77843. U.S.A.

Octahedral Structure of Mg-CDTA Complex

Dear Barry,

As part of a broad spectroscopic study of the solution chemistry of the metal complexes of EDTA and related chelating agents we (Dr. R. H. Nuttall, D. M. Stalker and myself) have looked at the n.m.r. spectrum of the magnesium complex of rac-transcyclo-hexane-1,2-diamine tetraacetic acid [CDTA($\rm H_4$)].

Addition of the correct amount of MgSO₄.7H₂O to a D₂O solution of the tetrasodium salt of $[CDTA(H_A)]$ gave a solution of [CDTAMg]2 2Na which had an n.m.r. spectra consisting of two overlapping AB patterns due to the CH2 protons [chemical shifts (§ scale) A' 3.33; B' 2.91; A' 3.26; B' 2.95 $|J_{A'B'}| = 17 \text{ Hz } |J_{A''B''}| = 16 \text{Hz}$, together with broad resonances due to the cyclohexane methylene and methine protons. This result, which implies the presence of four distinct methylene proton types, among the 'acetic acid' parts of the molecule, can be explained best by formulating the anion as (I), in which the magnesium atom is in an octahedral environment which is stable on the n.m.r. time scale. contrast the disodium salt of EDTA (H_4) shows only one non-equivalent methylene AB quartet, which collapses to a single line on going to the tetrasodium salt. Detailed assignment of CH2 resonances in (I) has not been possible so far, and this point and related studies on other complexes are being further investigated.



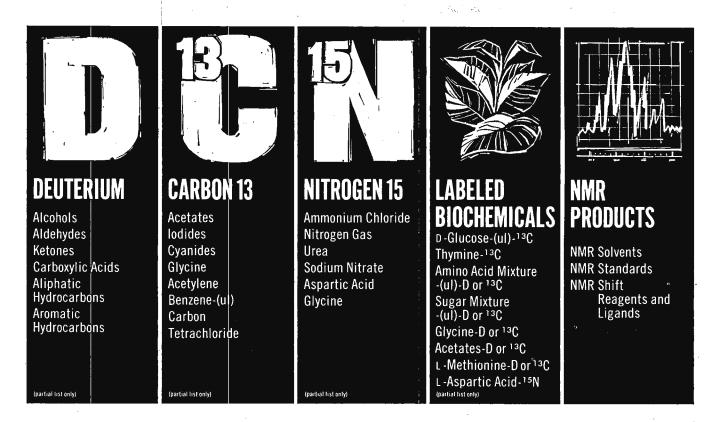
Although magnesium is known from n.m.r. studies of the hydrated ion to be 6-coordinate [S. Nakamura and S. Meiboom, J. Amer. Chem. Soc., 89, 1765 (1967), N. A. Matwiyoff and H. Taube, J. Amer. Chem. Soc., 90, 2796 (1968)], this direct evidence of an octahedral structure in solution is apparently new.

Yours sincerely,

P. Bladon.

Dr. Peter Bladon

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September 19, 1972

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

TITLE: A CALL FOR ²⁹Si SPECTROSCOPISTS; POSSIBLE REFERENCES FOR SILICON-29 CHEMICAL SHIFTS

Dear Barry:

At the recent NATO Advanced Study Institute on NMR of Nuclei Other Than Protons (Tirrenia, Italy, September 1972) Gary Maciel made some suggestions regarding informal establishment of chemical shift references for nuclei that are beginning to emerge from the novelty stage.

Gary suggested that the first person to publish FT experiments on a given nucleus should assemble an informal committee of spectroscopists becoming active with that nucleus. That committee would investigate and suggest possible chemical shift references for the nucleus as well as determine chemical shifts of alternate referencing materials (Experimental References), relative to the tentative reference compound (Standard Reference)1.

The mantle of responsibility apparently being placed on my shoulders for Silicon-29 nmr², I am hereby asking any and all nmr spectroscopists currently doing any ²⁹Si work to please send me a brief note -- with their name and address if nothing else -- so that I may discharge my responsibilities. Further information will be sent to those who respond to this call.

Sincerely,

George C. Levy

Materials Characterization Operation

eorge C. Kevy

¹See for example: ¹³C References -- G.C. Levy and J.D. Cargioli, <u>J. Magn. Resonance</u>, <u>6</u>, 143 (1972).

²G.C. Levy, <u>J. Am. Chem. Soc.</u>, <u>94</u>, 4793 (1972).

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

September 12, 1972

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

Dear Barry:

"Lock System for Bruker 321S Pulsed Spectrometer"

A recent communication in this Newsletter from Professor Kurland regarding a lock system for a Bruker 321S spectrometer prompts us to describe the system that we are currently using.

Earlier this year we installed a pulsed lock system designed for our instrument by Dr. Steven Parks of Tomlinson Research Instruments, Tallahassee, Florida. The TRI lock is for the most part an adaptation of the Packer and Strikel technique except that an internal or external reference sample may be used. It consists of a frequency source phase locked to the spectrometer r.f. source, a gated r.f. transmitter and receiver, a gated integrator for detection of the off-resonance condition and appropriate control circuitry including logic for inhibition of the lock during the observation of the main signal. signal is detected with a dual phase detector whose outputs are adjusted to be in phase and in quadrature with the lock signal immediately following the r.f. The error signal is obtained through integration of the quadrature signal to give both magnitude and direction of any off-resonance condition. feature of the TRI system is that the integration gate is derived from the inphase signal; the gate is initiated when the Bloch decay from the lock sample has fallen to a selectable level and is terminated if the Bloch decay goes negative or at the end of a setable integration period. The resonance condition can thus be achieved from a large initial offset without sacrificing the sensitivity with which the resonance condition is maintained.

We currently are using a sample of doped deuterium oxide as the external reference; it is observed at ~ 8 MHz. while fluorine is observed at ~ 50 MHz. The quality

Professor B. L. Shapiro

September 12, 1972

of the lock is sufficient for relaxation time measurements; no optimization of the lock for other uses such as high-resolution work has yet been attempted.

Sincerely yours,

B Ma oon

G. B. Matson Postgraduate Research Chemist

Ton.

J. T. Gerig Associate Professor

1. K. J. Packer and A. J. Strike, J. Magn. Res., 2, 79 (1970).

JTG:rt



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Catania li 11 September 1972

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

Dear Professor Shapiro:

H NMR spectrum of Bis(4-nitro-2-aminophenyl) disulphide:a case of ABX deceptive simplicity.

In the course of NMR studies on the aromatic protons of model diphenyl disulphide systems, we have run the 60 MHz spectrum of the title compound in diglyme (8 mol%) solution. The obtained spectrum is an excellent example of what have been termed "deceptively simple spectra of ABX type". Fortunately, we resolved this deceptive simplicity by measuring the spectrum in another solvent, i.e. DMSO-d (the remaining only in which the compound is soluble).

The increased number of transition in the AB part of the spectrum to be iterated allowed us to obtain the spectral parameters listed below (r.m.s.error 0.030):

H ₃	457.737	Hz
H ₅	437.303	1 1
^Н 6	442.389	1.1
J 35	2.619	1.1
J 36	0.301	• •
J ₅₆	8,.580	7 1

Many apologies for the long delay.

Yours sincerely, followed Dr/G.C.Pappalardo

^{*}G.C.Pappalardo, D.A.Clemente, Presented at the Vth Symposium on Organic Sulfur Chemistry, Lund, Sweden, June 5-9, 1972.



THE UNIVERSITY OF TEXAS AT AUSTIN AUSTIN, TEXAS 78712

Department of Chemistry

September 13, 1972

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

Dear Barry,

Suggested Title: Used Magnet or Spectrometer: Buy/Share/Sell.

I am in the market for an electromagnet (9" or larger) capable of 30 MHz 1 H or 19 F NMR in a 1 3/4" gap. The principal requirement is time stability suitable for spin echo work. Good homogeneity is not critical but the time stability requirement will, for most systems, dictate high resolution quality, such as a Varian V2100B.

I will also consider purchasing a complete spectrometer such as an HR-60, DP-60, etc. Inasmuch as I would be interested only in the magnet and accessories in such a system, I would urge any parties interested in the rest of said spectrometer (for spare parts, Fourier Transform Conversions, etc.) to contact me; perhaps a three-way deal can be arranged.

I can arrange transportation; demonstrated operation is a necessity.

Thank you.

Yours truly,

Chas. G. Wade

Assistant Professor of Chemistry

(512) 471-1252



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20390

6110-414: WBM: adm 13 Sep 1972

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

Subj: Variable Channel Advance Rate for the Nicolet 1074 Dear Barry:

The sweep times of our Fieldials and HA-100 spectrometer are not fully compatible with the available channel dwell times of our Nicolet 1074. As a result, we have had to accept either fractional sweep accumulations or inefficient sweep rates. These compromises can be avoided by using external channel advance pulses to drive the 1074. We have found that a digital frequency divider, such as the General Radio 1399, serves admirably. The divider has a stable internal clock which is divided down according to the manually preset division dials. Accurate synchronization of the spectrometer sweep time to the desired channel capacity of the 1074 is easily obtained. Depending on the output pulse characteristics of the digital divider, it may be necessary to broaden the pulse using a one shot MV with a suitable time constant (e.g., an SN74121) with R = 3K, C = .025 μ F).

We obtain a reproducible trigger to start the 1074 sweep from the Fieldial x-axis drive ramp, feeding it to the sweep trigger input of the 1074 through a 20K resistor.

Sincerely yours,

W. B. MONIZ, Head NMR Spectroscopy Section

Physical Chemistry Branch Chemistry Division, Code 6110 Professor B. L. Shapiro NMR Newsletter Department of Chemistry Texas A and M University College Station, Texas 77848

Postdoctoral Position Available

Dr. Berliner of our Department has a position available beginning immediately.

The research activities will involve spin label structural investigations of some proteolytic enzymes, microenvironmental studies of polymers, or structure-mechanism studies of selected enzymes by NMR-paramagentic relaxation techniques.

The qualifications desired are preferably persons with experience in magnetic resonance methods (in biology or polymer chemistry); however, persons with a strong interest in physical chemistry or biochemistry will also be considered.

Applicants should include a curriculum vitae, transcripts, names of three persons as references, and an estimate of their approximate date of availability.

Write to:

Professor Lawrence J. Berliner The Ohio State University Department of Chemistry 140 W. 18th Avenue Columbus, Ohio 43210

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Sincerely,

64

Gideon Fraenkel



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HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street

Cambridge, Massachusetts 02138

U.S.A.

September 14, 1972

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

Dear Barry:

We are just completing and writing up for publication a NMR study of the isomers of retinal (all-trans, 9-cis, 11-cis, and 13-cis). We have, in particular, been concentrating on the measurement of nuclear Overhauser enhancements (NOE's) and $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ $\mathrm{T_1}$'s. One interesting feature came up which demonstrates the importance of knowing both NOE's and $\mathrm{T_1}$'s in the determination of molecular structure. The NOE's for the all-trans isomer appear to indicate,

upon inspection, a completely planar structure of the polyene chain. For example, the enhancement of 15H upon irradiation of 13CH $_3$ is 41%; close to the maximum expected value of 50% if the relaxation of 15H is completely dominated by 13CH $_3$ (ie. 15H is close to 13CH $_3$). On the other hand, if one predicts T_1 's based upon the assumption that the relaxation of the protons in all-trans retinal is dominated by intramolecular dipole-dipole interactions, one does quite well (ie. within 20-30%) for all the protons except 15H for which the predicted T_1 is 1.4 seconds and the observed T_1 is 5.7 seconds. We think this indicates that there is considerable motion about the 14-15 bond. Oscillatory motion of 15H would have the effect of lengthening its T_1 , but would not bring it appreciably closer to any other protons so that its relaxation is still dominated by 13CH $_3$ and the observed NOE is not reduced.

Yours sincerely,

fort Lawren

Robert Rowan

Brian D. Sykes

RR:BDS/bam Running title: NOE's and T₁'s

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12th September 1972

Professor B. L. Shapiro Texas A and M University College Station, Texas 77843

Dear Barry:

V-3506 Flux Stabilizer Modification

Several problems encountered by us in the operation of our Varian HA-100 spectrometer have been traced to dirty contacts of the "balance/operate" switch in the V-3506 magnet flux stabilizer. This appears to be a widespread and chronic ailment of these units.

The problem arises with the solid copper sliding switch contacts which switch the pickup coil. In our experience, at approximately 6 to 12 month intervals, the contact resistance increases to ~ 2.5 ohms; dismantling the flux stabilizer and cleaning the switch is then necessary. The symptoms of a dirty switch contact are:

- (1) difficulty in locking the stabilizer (i.e., switching to "operate").
- (2) oscillation of the slow-sweep galvanometer, either occurring spontaneously or when the lock voltage exceeds one volt.
- (3) erratic lock operation in the Fourier mode.
- (4) spontaneous unlocking of the flux stabilizer.

We have eliminated the dirty switch syndrome by rewiring the "balance/operate" switch so that the galvanometer is permanently connected to the pickup coils.

- (a) The lug connected to terminal 3 on SIA is placed under terminal 2 of SIA.
- (b) The 27k resistor, R2, is disconnected from terminal 1 on S1A. In its place, a solid copper (not tinned), insulated wire of at least No. 20 gauge is connected from terminal 1 to the TB2 side of R3.
- (c) A pair of 1N5061 diodes are connected to the unused terminals 1 and 2 of TB2 in order to protect the galvanometer. 1N914b diodes should also work. (King, IITNMR 118, 54 (1968)).

Professor B. L. Shapiro

12th September 1972

An additional source of instability resulted from partial failure of selenium rectifier CR1. We have replaced it with two IN1127 silicon rectifiers, the anodes of which may be soldered directly to A3 and A7 of T3.

The only unpleasant consequence of our modification, and it is a relatively minor one, is the galvo damping, which now results in a period of about five minutes, should the system "unlock." However, stability is so increased that we have experienced only a single "unlocking" incident over a several month period and that due to the loss of power to the magnet!

Please credit this to the account of Dr. P. I. Rose.

Sincerely yours,

S. Gross

Chemistry Division Research Laboratories

SG/mg

DER RUKSUNIVERSITEIT TE UTRECHT CROESESTRAAT 79

POSTGIRO 65985 - TEL.882311

UTRECHT, August 16, 1972

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

- a) SIMEQ II/16
- b) Inexpensive 12 mm microcell assembly

Dear Professor Shapiro,

We have available a version of the spin simulation program SIMEQ (TAMUNMR 150, p 20) for a Varian 16K 620 i or L series computer with the HM/D & EA option. The program is subject to the same limitations as the older version but the simulation procedure is speeded up by 30-70% and two output options are added, namely; an oscilloscope display a parameter list print-out.

Access to AID II for magnetic tape handling is provided. Simulated spectra (2k data points each instead of 1k in the old program) may be stored in three buffers. Each buffer contains the spectrum and its associated parameter list. Manual iterative simulations are possible for the spectra in all buffers, frequencies, intensities and parameterlists are retained for all buffers. The oscilloscope display has many of the features of the Varian ZOOM routines such as spectrum width variation, spectrum shift and continuously variable spectrum amplitude. The spectra in the three buffers may be displayed or plotted in several ways, either individually or summed with independently chosen amplitudes and relative shifts.

Spectra are either normalised for the highest peak or they are absolute value spectra.

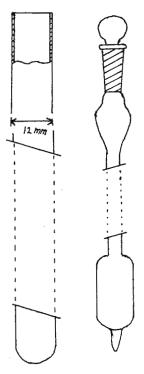
The modified program was written with valuable advice from the original SIMEQ programmer, C.W.F. Kort.

Object tape and operating instructions are available upon request.

A version for 8k corestore of the old SIMEQ using the HM/D & EA option and including an oscilloscope display will be available shortly.

b) Though many microcells have been described by various authors or are available commercially from various sources, here follows the description of still another one. For our purposes the commercial microcells for large diameter tubes (12 mm o.d.) were not satisfactory because of large spinning side bands, difficult positioning and non-optimum sample geometry with the resulting bad sensitivity and/or bad resolution. The cylindrical semi-microcell of fig. 1 fits snugly inside a normal high precision 12 mm o.d. nmr sample tube (Varian or Wilmad). It is made from the inner tube of a Wilmad coaxial cell assembly (Wilmad 516 I/12 mm). The length of this cylindrical microcell with spherical end walls is variable, but optimum sensitivity resolution is obtained for a length of about 18 mm (1 ml sample). Performance is still acceptable for a length of about 12 mm (0.5 ml sample).

Resolution for the longer cell is the same as that of the 12 mm tube. Sensitivity is about 95 % of that of a normal 12 mm tube. Spinning side bands are about 2 %, if the cell is carefully made, at spinning speeds of \sim 30 cps. Material costs of one complete microcell assembly (cell + outer tube) are \$ 10,- .



Sincerely Yours,

M.J.A. de Bie

// you for

J.P.C.M.van Dongen

SCALE 1:1

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000 Instrument Research. September 20th 1972



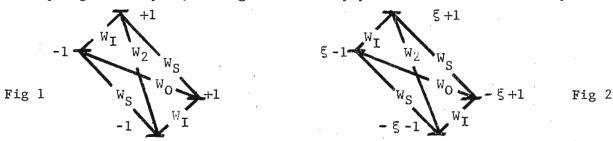
Professor B. L. Shapiro, Department of Chemistry, Texas A. and M. University, College Station, Texas 77843

Dear Barry,

"Nuclear Overhauser Enhancement Factors"

I found your blue note waiting when I got back to California after a minisabbatical in Dr Richards' laboratory in Oxford. One of the concerns of the biochemists there was the possibility of errors in ${}^{\mathsf{T}}\mathbf{T}_{\mathsf{I}}{}^{\mathsf{H}}$ determinations in coupled spin systems, where the recovery curve is not a single exponential, as in the classic experiment of Solomon on HF. Going through the equations for a two-spin system led to the realization that there should be an experimental method of measuring the degree to which dipole-dipole interaction contributes to the total spin-lattice relaxation, simply by measuring two relaxation rates.

Iain Campbell collaborated on these measurements, and being committed to molecules of major biochemical importance, we chose formic acid (a two-spin system with I = ^{13}C , S = ^{1}H , and ξ = $\gamma_{\text{S}}/\gamma_{\text{I}}$ = 3.98). The first measurement is a conventional inversion-recovery performed on the I spins (without decoupling the S spins). Figure 1 shows populations after the 180° pulse.



It is readily shown that the initial rate of recovery is given by:

$$R_{\mathbf{0}}(\widetilde{\mathbf{I}}) = 2W_{\mathbf{I}} + W_2 + W_0 \tag{1}$$

The second measurement applies 180° pulses simultaneously to both I and S spins, driving the cross-relaxation paths W_2 and W_0 harder (Figure 2). As a result the initial rate of recovery of I magnetization is increased if the dipolar mechanism is important, giving:

$$R_0(\tilde{I}, \tilde{S}) = 2W_I + W_2 + W_0 + \xi (W_2 - W_0)$$
 (2)

Using Solomon's expression for the nuclear Overhauser enhancement factor $\eta_{\rm I}$ gives a simple expression for the ratio of these initial rates:

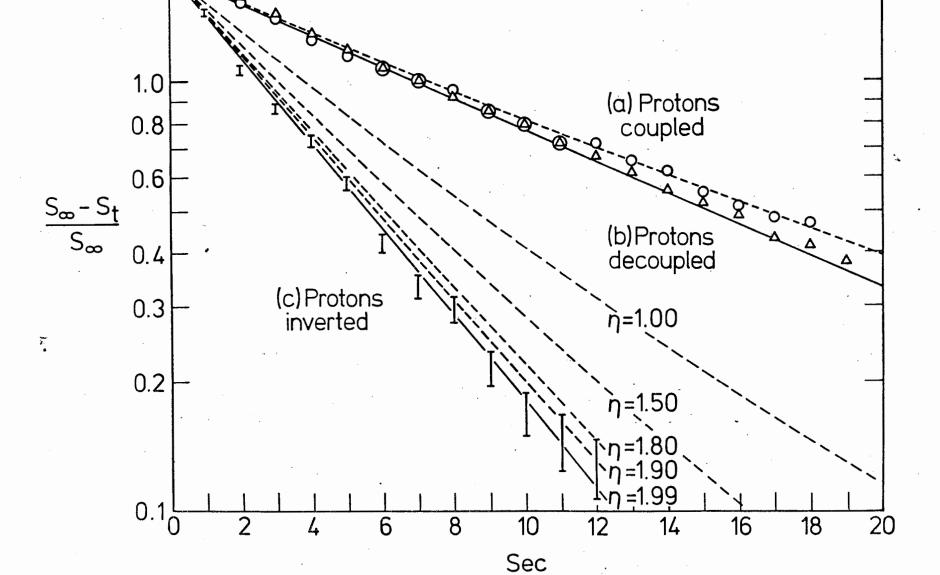
$$\eta_{I} = \xi (W_{2} - W_{0})/(2W_{I} + W_{2} + W_{0});$$
 $R_{o}(\widetilde{I}, \widetilde{S})/R_{o}(\widetilde{I}) = 1 + \eta_{I}$
(3)

As expected the experimental ratio for formic acid is close to three, confirming that the relaxation is essentially dipolar (Figure 3). Since the conventional Overhauser determination often encounters difficulties in the integration of undecoupled ¹³C spectra, we feel that this may well prove a useful alternative technique.

Yours sincerely,

Ray Freeman

l. Solomon, Phys. Rev. <u>99</u>, 559 (1955).



Ray Freeman and Iain Campbell - Figure 3

2.0

Recovery of ^{13}C magnetization in formic acid after a 1800 pulse, compared with theoretical curves.

UNIVERSITÉ CLAUDE BERNARD, LYON I

LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918 69621 - VILLEURBANNE - FRANCE TÉL. (78) 52.07.04 et 52.12.29

Villeurbanne, le 22 Septembre 1972

Doctor B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station Texas 77843
U.S.A.

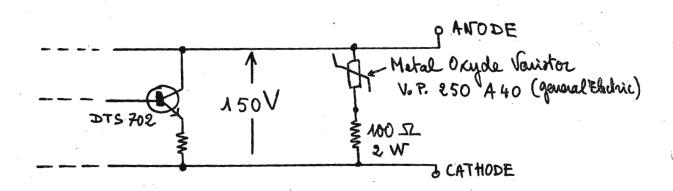
Cher Professeur Shapiro,

Transistorisation de l'alimentation Varian V 2100 B.

A notre tour nous avons renoncé aux 304 TL de l'alimentation V 2100 B de notre HA 100 et comme C.A. REILLY [TAMUNN n°166; p.29, (1972)] nous avons opté pour le montage proposé par J.E. PEARSON [Rev. Sc. Instrum. 42, (5), 713, (1971)]: 34 transistors DTS 702 montés en parallèle remplacent les 8 tubes 304 TL, la polarisation de 15 Volts étant obtenue grâce à un circuit intégré µA 723.

A la suite des fluctuations du courant du réseau, nous avons enregistré nos premières déconvenues (mise hors d'usage de transistors et diodes Zeener) et, à l'occasion d'une panne de courant du secteur ce fut la catastrophe : l'aimant induit alors une forte surtension au niveau des transistors (dont la polarisation est simultanément supprimée) qui n'apprécient guère ce genre de traitement. Nous signalons le remède que nous avons apporté à ces maux car la méthode diffère de celle de REILLY et nous donne depuis six mois toute satisfaction.

Au montage de PZERSON nous ajoutons : 1°) Un circuit de protection décrit ci-dessous qui absorbe les surtensions transitoires



UNIVERSITÉ CLAUDE BERNARD, LYON I

LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43. Bd DU 11 NOVEMBRE 1918 69621 - VILLEURBANNE - FRANCE TÉL (78) 52.07.04 et 52.12.29

 $2^{\circ})$ Un condensateur placé à la sortie du pont redresseur dans l'alimentation de la polarisation des transistors. La valeur doit être choisie de 10 000 μF à 15 000 μF de sorte que la polarisation soit maintenue en cas de coupure.

Le choix du point de fonctionnement des transistors est important. Nous les utilisons sous 150 V. A noter que nous avons conservé en parallèle l'ancien montage des 304 TL pour le cas où ...

Recevez nos sentiments les meilleurs.

A. BRIGUET

J. DELMAU

J.C. DUPLAN

September 18, 1972

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

Dear Barry:

We have been investigating the extremely interesting Rapid Scan Nmr experiment that J. Dadok reported at the 13th ENC. In this experiment, he reported that ringings of a rapidly scanned cw nmr spectrum can be decomposed to yield the standard frequency domain spectrum by cross correlating this spectrum with the response of a single reference line scanned under the same conditions. He also reported that this correlation could be performed using a calculated reference spectrum as well as an experimental one.

This technique is of interest both to people who have insufficient funds for Fourier and to those who need to obtain data of a small region of a spectrum without the problems of foldback encountered in FT-Nmr.

We have repeated this work utilizing the 1080 data system and developed some programs for the correlation procedure. We obtained a rapid scan 500 Hz spectrum of the quartet of acetaldehyde at several data rates and correlated it with the response of the CHC13 line in the TMS-CHC13 sample obtained under the same conditions.

A theoretical spectrum was produced as well, utilizing the function

$$e^{a\omega} \sin^{b\omega^2}$$

as a crude approximation of the Bloch equations, where ω is the frequency, a is related to T_2^* and b is the sweep width. This function appeared to give fairly adequate results compared to the experimental reference spectrum. Spectrum 1 shows the response of the acetaldehyde quartet when sampled at 1000 Hz while swept over 500 Hz at a rate of 4.0 seconds per scan. Thus, 4096 data points were obtained. Spectrum 2 shows the chloroform reference spectrum under the same conditions and spectrum 3 shows the correlated result. Spectrum 4 shows the calculated reference and spectrum 5 the result of the cross-correlation of the calculated reference and spectrum 1.

Dr. B. L. Shapiro September 18, 1972

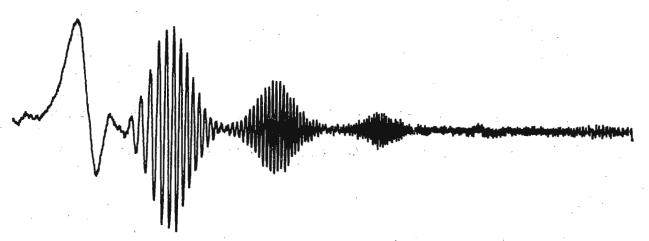
Clearly this is only preliminary work, but we will be happy to share our findings and our programs with anyone who is interested. Dr. Dadok has indicated that both he and others are pursuing this work and he will be glad to discuss his findings as well.

Regards,

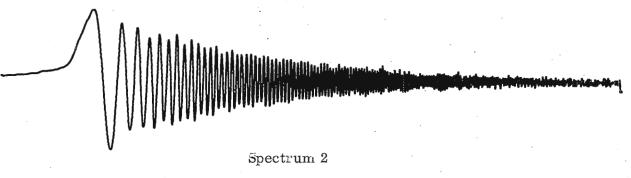
Jack Kisslinger

Jim Cooper

JK:JC:rg

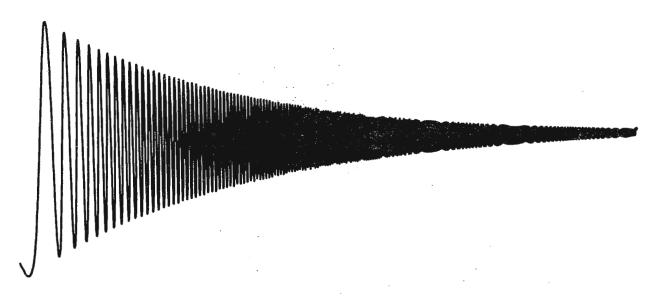


Spectrum 1

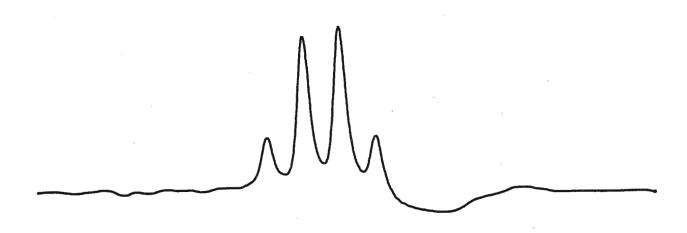




Spectrum 3



Spectrum 4



Spectrum 5

ANORGANISCH-CHEMISCHES LABORATORIUM DER TECHNISCHEN UNIVERSITÄT MUNCHEN

8 MUNCHEN 2, den September 15, 72 Arcisstraße 21, Postfach-Nr. 20 24 20 Ruf-Nr. (0811) 2105/330/331/332 333 (Prof. Fritz)

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

Title: 1H-NMR Evidence for the Bonding of a Cyclic Azo Ligand via one Nitrogen Atom in Transition Metal Complexes.

Dear Professor Shapiro,

2,3-Diaza-bicyclo[2.2.1]heptene-2, $C_5H_8N_2$ (I), which is structurally analogous to the mono-olefin norbornene, forms stable transition metal complexes. We have been able to isolate a number of metal carbonyl derivatives containing this cyclic azo compound as a monodentate ligand (e.g. $Cr(CO)_5$ (az), $(\pi-C_5H_5)Mn(CO)_2$ (az), $ArCr(CO)_2$ (az) ($Ar=\pi$ -bonded arene ring of the benzene type) ¹.



(I) "az"

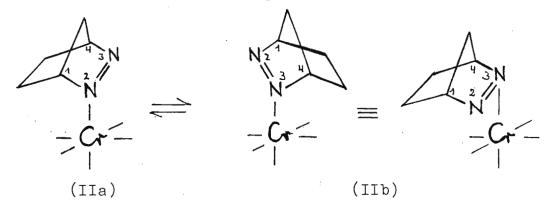
An important problem with these compounds centers around the question, how the azo ligand (I) is attached to the central metal. We have tried to answer this question by studying the $^1\text{H-NMR}$ spectra of $\text{ArCr}(\text{CO})_2$ (az) complexes containing ring-substituted arene ligands.

While the free azo compound (I) shows only a single signal for the bridge-head protons $\mathrm{H^1}$ and $\mathrm{H^4}$ (\mathbf{T} 4.98 in acetone- $\mathrm{d_6}$), the bridge-head protons in complexes of the type $\mathrm{ArCr}(\mathrm{CO})_2$ (az) are observed as two distinct absorptions of equal intensity (35°, in acetone- $\mathrm{d_6}$). If the temperature is raised, the two

¹ M.Herberhold and W.Golla, J.Organometal.Chem. 26(1971)C 27

bridge-head proton signals slowly broaden and eventually coalesce into a single absorption. This temperature dependence of the ¹H-NMR spectra may be interpreted in two different ways:

1. The azo ligand (I) is coordinated to chromium through the lone pair of electrons at one of the azo nitrogen atoms, and therefore the two bridge-head protons are different in the complex,(II), one being next to the metal-bound, the other next to the free nitrogen atom:



2. The azo ligand (I) is coordinated to chromium through the N=N double bond, in a π -olefin-like manner. In this case two stereoisomers are possible which differ according to the relative orientation of the methylene bridge (C⁷) (or the bis-methylene bridge (C⁵-C⁶)) with respect to the rest of the molecule:

As a result of the fast, thermally induced interchange of the coordinated and the free nitrogen atoms in the complex (II), the bridge-head protons H¹ and H⁴ should become averaged to give one single signal in the spectrum. On the other hand, if two isomers of the type IIIa and IIIb are present in equal amounts, the rapid transition of IIIa to IIIb and vice versa

would cause a similar coalescence of the bridge-head proton signals.

Differentiation between the two possibilities (II or III) was found to be possible in the case of the methyl p-methyl benzoate complex, $[CH_3-C_6H_4-COOCH_3]Cr(CO)_2$ (az) (IV). Surprisingly, the four protons of the π -bonded arene ring give rise to an ABXY-type spectrum instead of the well-known AA' XX' pattern which is characteristic of complexed benzene derivatives containing two different p-substituents.

As expected, the two bridge-head protons of the azo ligand appear as two separate signals at normal temperature (in toluene-d₈). They coalesce into a common single absorption at about 95°C, and in the same temperature range the ABXY spectrum of the %-bonded ring changes to an AA^I XX^I type pattern.

The differentiation of the chemically equivalent pairs of arene protons in IV is to be ascribed to a chirality in the complex at normal temparature. Such a chirality is indeed present if the N=N double bond of the azo ligand (I) is unsymmetrically coordinated via the lone pair of electrons at one of the two nitrogen atoms; the two enantiomers are represented by IIa and IIb. The intramolecular change of the coordination site between the two nitrogen atoms which becomes rapid with increasing temperature causes a simultaneous change of the chirality, and both the bridge-head protons (H^1 and H^4) and the two pairs of diastereotopic arene protons (H^2/H^6 and H^3/H^5) become apparently chemically equivalent.

Sincerely yours,

Cornelius G. Kreiter, Konrad Leonhard and Max Herberhold



UNIVERSITY OF SASKATCHEWAN, REGINA CAMPUS

REGINA, CANADA

545 DAZ

DEPARTMENT OF CHEMISTRY

September 26, 1972

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

Dear Barry:

May I use the Newsletter for advertising? I have an opening for a

Post Doctoral Fellow and/or Technician

The pdf I am looking for should be an experienced and mature person who could 1) supervise and (partially) carry out NMR service work, 2) supervise the research of a group of graduate students (during my upcoming sabbatical year), 3) carry out a substantial research project.

Our research is mainly in the areas of medium effects in gases and liquids, conformations of non-cyclic hydrocarbons and in herbicide chemistry (proton FT). We have a Bruker HX-90 spectrometer, with 18" variable field magnet and the Nicolet 1083 FT package ($^1\!H$ and $^{13}\!C$). The post doctoral fellow should be familiar with present-day experimental techniques, particularly FT spectroscopy. Salary is \$710 per month.

The technician should have the equivalent of a Bachelor's degree in Chemistry and should be reasonably competent in electronics. His duties would be 1) the maintenance and repair of the spectrometer, 2) carrying out NMR service work, 3) assisting in the experimental part of the research work of our own NMR group. Some familiarity with modern NMR equipment is desirable, though not essential. Salary negotiable but in the \$6,000 to \$8,000 bracket.

Sincerely yours,

F.H.A. Rummens, D.Sc.,

Professor

FHAR: pmf



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TELEX NO. 13-8840

September 25, 1972

Dr. Bernard L. Shapiro
Dept. of Chemistry
TEXAS A&M UNIVERSITY
College Station, Texas 77843

RECEIVED

SEP 29 1972

TITLE: ¹³C Line Widths as a Function of 'H
Decoupling Power

B. L. SHAPIRO

Dear Barry:

Since Tom Farrar is currently on an extended trip through Europe and Japan, and did not receive your reminder, I would like to briefly outline some of our current research activities here in Cranford.

As was pointed out by R.R. Shoup and D.L. VanderHart (1), 13 C line widths should be a function of the applied Proton decoupling power, due to the effects of C-H scalar coupling. We are currently investigating this effect by measuring T_2 's (Carr-Purcell, phase inversion method) on H^{13} COOH, varying the on-resonance, CW proton decoupling power.

The results of an initial rough study on benzene is reproduced in Fig.1 (we did not have any H¹3COOH, at that time) and shows an increase in the line width by a factor of 2 corresponding to a nominal and uncalibrated decrease in decoupling power by 20db. In our present study on H¹3COOH, we are using $\forall H_2$ of the decoupling field as one of the axes of our plot, however, we had encountered some difficulty in measuring $\forall H_2$ via the residual splitting technique using CW off-resonance decoupling. As was recently pointed out (2), the residual coupling constant and the frequency offset do not obey a linear relationship and instead, $\forall H_2$ is given by ΔY $\sqrt{3\delta} - 3\delta$.

Even using this equation, our plots showed marked deviations and discontinuities, especially at higher frequency offsets (up to 8KHz). The answer to this riddle was finally found when we considered that a) our JEOL PFT-100 system was using 8KHz field modulation and b) our Proton decoupling power was about ten times higher than that used by the authors of (2), causing an additional decoupling effect on the 8KHz Proton sidebands.

When we switched over to our Time Share lock system (eliminating 8KHz field modulation, the formula above gave a reasonably straight line with a γ H2 of 6600Hz.

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contr	1.71116	2d	_		_		

Dr. B. Shapiro Texas A&M University

We hope that this will point out the importance of adequate decoupling power and also the pitfalls associated with measuring γ H2.

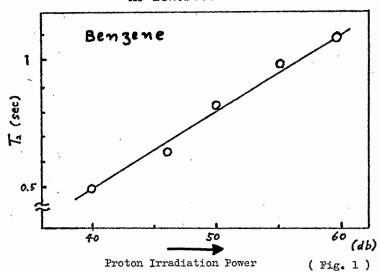
Sincerely,

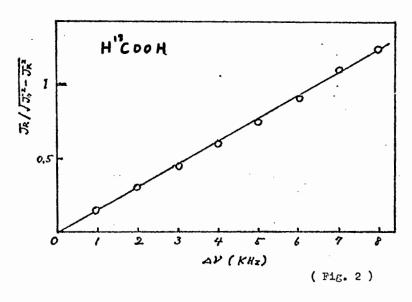
Victor J. Bartuska

Labilia Tabilia

Ko Ishibitsu

/rmh





¹⁾ R.R. Shoup and D.L. VanderHart. <u>JACS</u>, <u>93</u>, 2053 (1971)

²⁾ K.G.R. Pachler, J. Mag. Res., 1, 442 (1972)

Institut für organische Chemie der Universität des Saarlandes

Saarbrücken , den 25.9.72 Telefon: 302.3409

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

Sehr geehrter Prof. Shapiro:

13_{C-NMR}-Spektren von 3aH-Indazolen

Während bei Pyrido-pyrazolen $\underline{1}$ die 13 C-NMR-Spektren des Grund-körpers bekannt sind 1,2 , wurden 3aH-Indazole $\underline{2}$ bis jetzt noch nicht untersucht. Aus diesem Grunde haben wir die 43 C-NMR-Spektren einiger substituierter 3aH-Indazole ($\underline{2a}$ - \underline{c}) untersucht, um eine spektroskopische Unterscheidung von den isomeren Pyrido-pyrazolen $\underline{1}$ zu ermöglichen.

Die ¹³C-NMR-Spektren von <u>2</u>2 - <u>c</u> wurden nach der Puls-Fourier-Transform-Methode aufgenommen. Die Substanzen waren in CDClz gelöst, TMS wurde als innerer Standard zugefügt. Die chemischen Verschiebungen sind daher auf TMS bezogen. Als Messgerät diente ein Bruker HX-90-Gerät mit Puls-Fourier-Transform-Einheit für ¹³C.

Tab. 1: 13C-NMR-Spektren der 3aH-Indazole 2a - c in CDCl3

C-Atom	<u>2</u>	<u>a</u>		<u>b</u>	<u>(</u>		
8	$_{ m Hz}$	ppm	Hz	ppm	. Hz	ppm	
3 3a 4 5* 6* 7 8	3685 1797 2828 2891 2936 3267 3369	162.8 79.4 124.9 127.7 129.7 144.4 148.8	3685 1801 2825 2947 3050 3260 3529	162.8 79.6 124.8 130.2 134.7 144.0 155.9	3664 1782 2532 2886 3043 3175 3376	161.9 78.7 111.9 127.5 134.4 140.3 149.2	

* austauschbar

Interpretation des ¹³C-NMR-Spektrums von 2b:

Bei höchstem Feld tritt das Signal des sp'-C-Atoms auf, dessen hohe chemische Verschiebung durch seine hohe Elektronendichte erklärt werden kann (1801 Hz; 79.6 ppm&). Bei tieferem Feld befinden sich Peaks von Kohlenstoffatomen, deren Elektronendichte durch elektronenziehende Substituenten vermindert wird. So tritt bei tiefstem Feld, 3685 Hz, 162.8 ppm6, ein Peak auf, dem das C3-Atom zugeordnet werden muß. Es ist erstens an den elektronegativen Stickstoff gebunden, zweitens trägt es einen stark elektronenziehenden Substituenten. Bei 3529 Hz (155.9 ppm 6) liegt das zweite, einem Stickstoff benachbarte, C-Atom (C8). Auch bei C' macht sich der elektronenziehende Effekt des Stickstoffatoms noch bemerkbar. Das Signal erscheint bei 3260 Hz (144.0 ppm 6). Das C4-Atom ist an ein sp3-C-Atom gebunden und trägt im Gegensatz zu C3 in nächster Nachbarschaft keine entschirmenden Gruppen. Es erscheint von den noch zuzuordnenden C-Atomen 4, 5, 6 bei höchstem Feld, bei 2825 Hz (124.8 ppm 8). Bei 2947 Hz und 3050 Hz liegen zwei Peaks ähnlicher Verschiebung. Es handelt sich um die C-Atome 5 und 6. Eine endgültige Zuordnung kann in diesem Falle nicht getroffen werden.

Der Substituenteneinfluß auf die chemischen Verschiebungen von $2\underline{a}$ - \underline{c} ist, wie Tabelle 1 zeigt, nicht besonders groß. Die $3\overline{a}H$ -Indazole 2 können jedoch aufgrund ihrer 13C-NMR-Spektren sofort von den isomeren Pyrido-pyrazolen 1 unterschieden werden. In $2\underline{a}$ - \underline{c} tritt das 3a-C-Atom bei höchstem Feld (δ = 78-79 ppm) $\overline{a}\overline{u}$ f und unterscheidet sich in seiner chemischen Verschiebung eindeutig von dem C-Atom bei höchstem Feld in Pyrido-pyrazolen 1. Hier liegt das C-1-Atom bei höchstem Feld im Bereich von δ = 94 - 117 ppm $^{1-3}$. Während in den Pyrido-pyrazolen 1 das freie Elektronenpaar am Stickstoff delokalisiert ist \overline{u} nd das System 1 aromatischen Charakter besitzt, liegt in 2 ein 1-System vor.

C / hn (H. Dürr) W SamolA

(W. Schmidt)

R. J. Pugmire, M. J. Robins, D. M. Grant und R. K. Robins, J. Amer. chem. Soc. <u>93</u>, 1887 (1971).

H. Dürr, R. Sergio und V. Formacek, TAMU-NMR-Letter 1972,

H. Dürr, R. Sergio und W. Schmidt, Liebigs Ann. Chem. in Vorbereitung.

UNIVERSITY OF DELAWARE

NEWARK, DELAWARE

DEPARTMENT OF CHEMISTRY

September 20, 1972

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

Title: A Simple Modification to a Bruker HFX-90 for Counting Δf_1 in FT Mode

Dear Professor Shapiro:

Our Bruker HFX-90 is equipped with a Bruker BSV-2 unit for pulse operation. As installed by Bruker, the fifrequency offset (Δ fl) could not be read on the built-in frequency counter when operating in pulsed mode.

In the Bruker system a 30 MHz + 1/3 Δ fl frequency is pulsed by a gate in the BSV-2 (see figure). This pulsed 30 MHz + 1/3 Δ fl is then routed to the transmitter where it is converted to 90 MHz + Δ fl and thence to a X frequency. Also located in the transmitter is a "frequenzzählung" board which receives the 30 MHz + 1/3 Δ fl input. When the frequenzzählung board receives a cw 30 MHz + 1/3 Δ fl, its circuits will produce a continuous square wave output equal to Δ fl. This square wave is then fed to the counter. When a pulsed 30 MHz + 1/3 Δ fl is fed to the frequenzzählung board, no usable output is obtained for the counter.

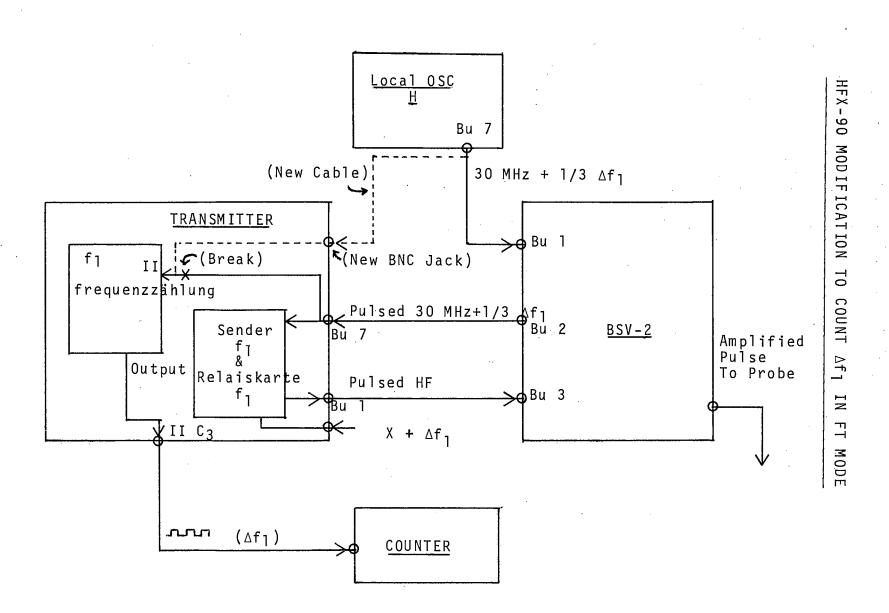
This problem can be overcome by a minor wiring change in the transmitter. First, install a BNC jack at the rear jack panel of the transmitter. Next break the wire at input II of the fl frequenzzählung and connect this input by means of a shielded cable to the new BNC jack at the rear. This now gives a separate input to the fl frequenzzählung board. A BNC "Tee" inserted at Bu 7 of the L.O.H. unit and connected to this new input on the transmitter will enable the built-in counter to function in both cw and FT modes.

Credit this contribution to the account of L. M. Venanzi.

Sincerely, Freeman

Walter J. Freeman

WJF:11b Enclosure





Section de Physique

CH - 1211 GENÈVE 4

Professeur Bernard L. SHAPIRO Dept. of Chemistry Texas A & M University College of Science College Station, Texas 77843 U.S.A.

V/RÉF.

N/REF. GB/co

GENÈVE, LE

le 12 septembre 1972

Cher Professeur Shapiro,

Merci beaucoup de votre lettre de rappel du 6 septembre.

- 1) Nouvelles du Groupement Ampère.
 First Specialized "Colloque Ampère"
 Krakow (Poland) August, 28-Sept. 1, 1973
 (First Circular) Voir annexe.
- 2) Travaux récents dans le domaine du magnétisme nucléaire.

Communications à la séance de printemps de la Société Suisse de Physique - Berne 21-22 avril 1972 - R. Sechehaye, B. Borcard, E. Hiltbrand et G.J. Béné "Effet Overhauser en champ faible ou quasi nul".

Résumé: Evaluation précise du facteur d'amplification Overhauser, le signal étant visible en l'absence d'excitation des spins électroniques.

- G.J. Béné et B. Borcard "Techniques nouvelles d'observation des échos de spins".

Résumé: On utilise soit des impulsions de champ constant l'onde RF étant permanente, soit des "anti-impulsions" (programme inverse d'impulsions classiques) ces dernières donnant des échos dans le référentiel tournant.

Professeur Bernard L. SHAPIRO, Dpt. of Chemistry -

- B. Borcard, E. Hiltbrand, R. Sechehaye et G.J. Béné "Effets de cohérence par impulsions apériodiques en magnétisme nucléaire".

<u>Résumé</u>: Interprétation des pseudo-échos observés antérieurement et déclenchement de la précession libre par une impulsion apériodique.

Le soussigné a rédigé (en français) une mise au point sur "Méthodes nouvelles d'Impulsions et d'échos de spins", Preprints ou tirés à part disponibles.

Meilleurs sentiments.

Prof. G.Béné

28th AUGUST KRAKÓW POLAND



1ST SPECIALIZED COLLOQUE AMPERE

The purpose of this conference is to bring together specialists interested in modern NMR methods and their applications to solids.

SCIENTIFIC PROGRAMME

Nuclear magnetic resonance in solids with special reference to pulse methods, high resolution, spin dynamics and related phenomena.

SCOPE

The programme will include short communications on original work and invited lectures. Four days of the conference will be devoted to sessions and the fifth to a common excursion. All sessions will be plenary and enough time will be left for informal discussions.

TIME AND LOCATION

Cracow, Poland, 28th August — 1st September 1973.

LOGAL ORGANIZER

The Institute of Nuclear Physics acting on behalf of the Ampére Group in collaboration with the Jagiellonian University, the Polish Physical Society, and the Spectroscopy Commission of the Polish Academy of Sciences.

SCIENTIFIC ADVISORY COMMITTEE

Professors: S.A. Altshuler, USSR; F.R. Andrew, England; G.J. Bene, Switzerland; R. Blinc, Yugoslavia; M. Bloom, Canada; R. Freyman, France; L. van Gerven, Belgium; L. Giulotto, Italy; C.J. Gorter, Holiand; E.L. Hahn, USA; K.H. Hausser, German Federal Rep.; G. Hertz, German Federal Rep.; V. Hovi, Finland; A.Z. Hrynkiewicz, Poland; J.A. Janik, Poland; A. Kastler, France; R. Kubo, Japan; K. Leibler, Poland; A. Lösche, German Democratic Rep.; Z. Pajak, Poland; H. Pfeifer, German Democratic Rep.; A. Piekara, Poland; J. Pietrzak, Poland; J.G. Powles, England; I.I. Rabi, USA; M. Rákoš, Czechoslovakia; T. Skaliński, Poland; B. Staliński, Poland; J. Stankowski, Poland; B.J. Trzebiatowska, Poland.

DEADLINES

for application 31st March, 1973 for communications 31st May, 1973

LANGUAGE

In principle English, French, German, and Russian, but the organizers express their hope that if possible the speakers will employ English.

PROCEEDINGS

The proceedings of the Conference will be published in a special issue of the Reports of the Institute of Nuclear Physics.

ATTENUARCE

Those expecting to attend the Conference are kindly requested to submit the attached questionnaire in order to receive further information about the conference and a final application form. They will be mailed in January 1973.

MAILING ADDRESS OF THE COMMITTEE

Dr J. W. Hennel INSTITUTE OF NUCLEAR PHYSICS

KRAKÓW 23, POLAND

UL. RADZIKOWSKIEGO 152

I am interested in the 1st Specialized Colloque Ampére to be held in Cracow in 1973 and would like to receive further information.

(Block letters, please)

NAME

ORGANIZATION

ADDRESS

I think the following person(s) would be interested in receiving information (give relevant addresses).

University of Bristol

School of Chemistry

Telephone: Bristol 24161 Ext.

Cantock's Close Bristol England BS8 ITS

27th September, 1972.

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

Dear Professor Shapiro,

Applications of ¹H { ¹⁹⁵Pt} INDOR Spectroscopy

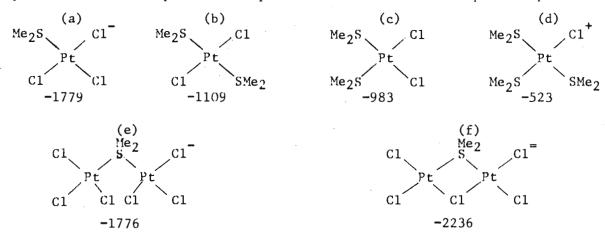
Our heteronuclear INDOR set up using a Schomandl ND 100 M frequency synthesizer with the HA 100 is working well and is now a routine technique (e.g. figure A). Whilst we have got results with several nuclei, we have been particularly interested in ^{195}Pt . Rather than define some arbitrary compound as the reference for platinum shifts, it seems far better to use a standard frequency related to the more universal standard -TMS. Thus for ^{195}Pt , the obvious choice is 21.4 MHz when TMS is at 100 MHz exactly. The observed shifts, $\delta(\text{Pt})$, lie either side of this and high frequencies are taken as negative shifts.

To establish the variability of $\delta(Pt)$ for a compound under different conditions, we have studied two complexes in several solvents and at various temperatures and concentrations. There does not seem to be any significant concentration effect below 0.1 Molar in methylene chloride. For a 0.05 M solution $\delta(Pt)$ varies more for the ionic species than the neutral complex.

Solvent	trans	PtBr ₂ (SMe ₂) ₂	$Pr_4^n NPtC1_3 PMe_3$			
C_6D_6		-625.4p.p.m.	-			
CC14		-615.8	-			
CDC13		-632.1	-1025.7			
CH ₂ CĬ ₂		-633.3	-1029.2			
$(\overline{CD}_3)_{2}^{-}CO$		-629.9	-1050.2			
CD ₃ NO ₂		-631.6	-1031.5			
С ₆ Й ₅ NŌ ₂		-626.6	-1038.2			
cĎ ₃ ŏp ~		-618.7	–			

The effect of temperature is more notable, approx +0.25 and +0.5 p.p.m. per $^{\circ}$ C for the two complexes respectively. From rough measurements over the range -60° to +30°C this appears to be linear. However, as the shifts of different compounds range over several thousands of p.p.m. these effects are relatively small. Thus $\delta(Pt)$ is a good characterising measurement of a platinum complex.

An example of the chemical usefulness of $\delta(Pt)$ measurements is the study of the mixture produced when Ph4PC1 is added to Pt2Cl4(SMe2)2. The proton n.m.r. shows four different types of terminal sulphide groups and two different bridging sulphide groups. Although the total concentration of this solution was less than 0.05 M we obtained $\delta(Pt)$ for all these signals. The platinum shifts of possible components were obtained from pure samples as:-



Three of the terminal sulphide groups have shifts of -1776, -1111 and -982 p.p.m. and are easily identified as (a), (b) and (c) whilst the bridged species with $\delta(Pt)$ of -2338p.p.m. is clearly (f). The remaining bridging group is coupled to two different platinum nuclei with shifts -1710 and -1008p.p.m. The last terminal group resonance has the same integral as this bridging group and $\delta(Pt)$ = -1007 indicates it is coupled to the upfield platinum atom of the two bridged by this group. To judge from the shifts of (a) and (e), $\delta(Pt)$ is very little affected by the coordination of a second metal ion to the sulphide i.e. only the actual donor atom is important. On this basis, the values of $\delta(Pt)$ correspond to platinum environments of types (a) and (b) or (c) - J(Pt-H) favours (b) so the likely structure is:-

This lack of importance of other groups attached to the donor atom is illustrated by the results of McFarlane (Chem.Comm. 1969, 439). When one sulphide in (b) or (c) is replaced by dimethylsulphoxide, $\delta(Pt)$ only changes by +77 and +8p.p.m. respectively. Thus it seemed surprising to us that the compound reported as $PtCl_2(DMSO)_2$ should have a shift of -1532p.p.m. (on our scale) - a more likely compound to have this shift would be $KPtCl_3(DMSO)$. We have now prepared $Pr_4^2NPtCl_3(DMSO)$ and its shift of -1534p.p.m. confirms this deduction

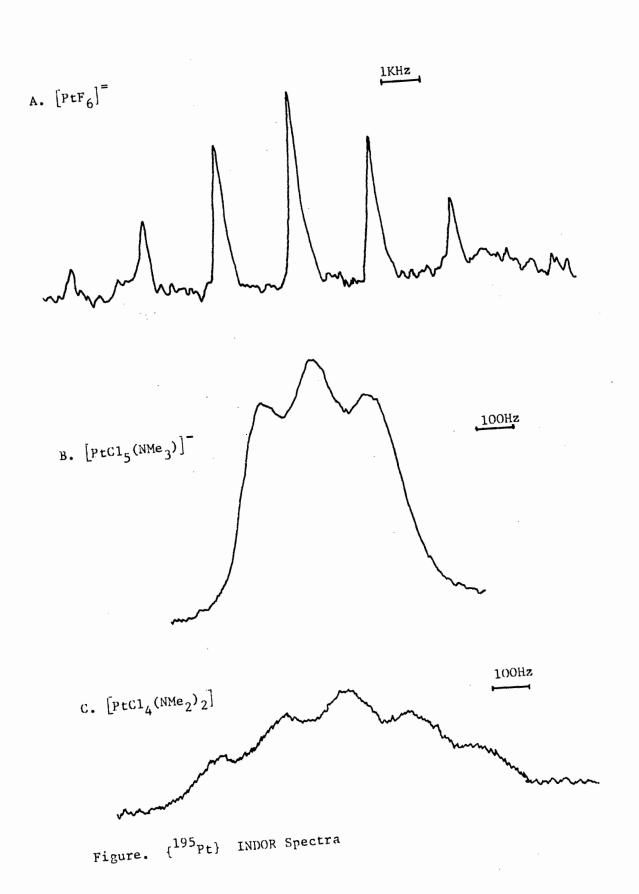
The 1 H { 195 Pt} INDOR spectra of trimethylamine complexes gave an unexpected bonus (Figure B and C). Pt-N coupling is clearly visible although the spectrum is not sufficiently resolved, due to nitrogen relaxation, for accurate evaluation of J(PtN). In view of the uncertainty of the relationship between the lineshape of the INDOR spectrum and that of the true spectrum, curve fitting does not seem justified even in the complexes containing only one amine ligand.

Yours sincerely,

Robin Goodfellow Brain Eagler.

R.J. Goodfellow

B.F. Taylor



INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY

RECOMMENDATIONS FOR THE PRESENTATION OF NMR DATA FOR PUBLICATION IN CHEMICAL JOURNALS

Adopted at Washington, DC, USA during 21–23 July 1971

LONDON BUTTERWORTHS

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY†

RECOMMENDATIONS FOR THE PRESENTATION OF NMR DATA FOR PUBLICATION IN CHEMICAL JOURNALS

The extensive use of nuclear magnetic resonance spectroscopy in chemical research makes it desirable to encourage the presentation of n.m.r. data in a uniform manner. Commission I.5 (Molecular Structure and Spectroscopy) therefore recommends that the following conventions should be followed in the graphical presentation of n.m.r. data in chemical journals.

A. CONVENTIONS RELATING TO PROTON SPECTRA

(1) The dimensionless scale factor for chemical shifts should be 10⁶, i.e. parts per million, for which p.p.m. is a convenient abbreviation.

(2) The unit for measured data should be hertz (cycles per second), for which Hz is the appropriate abbreviation, and the frequency scale should run in the same direction as the dimensionless scale.

- (3) The unit for spin-spin coupling constants should be hertz (cycles per second).
- (4) The graphical presentation of spectra should show the frequency decreasing to the right (applied field increasing to the right), absorption increasing upwards, and the standard sweep direction should be from high to low frequency (low to high field).
- (5) Whenever possible the dimensionless scale should be tied to an internal reference, which should normally be tetramethylsilane. The proton resonance of tetramethylsilane should be taken as zero; if some other internal reference is used that reference, and the conversion shift used to convert the measured shifts to the tetramethylsilane reference scale, should be explicitly stated. The dimensionless scale should be defined as positive in the high frequency (low field) direction. The scale in parts per million based on zero for tetramethylsilane should be termed the δ scale. A shift measured on this scale should be given as, for example, $\delta = 5.00$, not $\delta = 5.00$ p.p.m. The symbol $\delta_{\rm H}$ may be used if there is ambiguity about the nucleus under investigation.

[†] Titular Members: R. N. Jones (Canada) (Chairman); A. R. H. Cole (Australia) (Vice-Chairman); F. A. Miller (USA) (Secretary); Members: M. A. Elyashevich (USSR), Th. Förster (Germany), A. Hadni (France), Y. Morino (Japan), N. Sheppard (UK); Associate Members: E. Fluck (Germany), E. R. Lippincott (USA), R. C. Lord (USA), S. Nagakura (Japan), J. Plivá (Czechoslovakia), Sir Harold Thompson (UK), D. W. Turner (UK), Advisory Counsellor: G. Herzberg (Canada); National Representative: T. Urbanski (Poland).

PRESENTATION OF NMR DATA

- (6) When the spectra are submitted for publication, additional information should include:
 - (a) The name of the solvent used.
 - (b) The concentration of the solute.
 - (c) The name and concentration of the internal reference.
 - (d) The name of the external reference if one is used. Water should not normally be so used because of the temperature dependence of its resonance.
 - (e) The temperature of the sample.
 - (f) The procedure used to measure the peak positions.
 - (g) The radio-frequency at which the measurements were made; alternatively the magnetic field should be stated if the spectrum was obtained by a frequency sweep method.

Other information should be added where appropriate or necessary, e.g. the sweep rate, the magnitude of the H_1 fields, data pertinent to the use of spin decoupling, and whether oxygen has been removed from the sample. Solvent and impurity bands, carbon-13 satellites, or spinning sidebands should be indicated as such.

If single resonances or part spectra are presented as diagrams there should be a graphical indication of the distance corresponding to a suitable range of Hz so that fine-structure spacings, or widths of broad resonances, can be estimated.

B. CONVENTIONS RELATING TO SPECTRA FROM OTHER NUCLEI

At this stage the Commission does not wish to make definite recommendations relating to n.m.r. spectra of other nuclei. However, increasing interest in the use of double resonance techniques to relate chemical shifts of other nuclei to the proton resonance of tetramethylsilane suggests that it may become advantageous to adopt the same conventions for other nuclei.



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE

FOOD AND DRUG ADMINISTRATION WASHINGTON, D.C. 20204

October 2, 1972

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

NMR PROGRAMS FOR USE ON REMOTE COMPUTER TERMINALS

Dear Barry:

The rapid proliferation of remote computer terminals prompted me to write or adapt programs for nmr calculations. In fact we are, at present, using an IBM 2741 terminal for almost all our nmr computer applications. Two programs of general interest are described below.

- A. SIMULATE2: A simulation program (up to five spins) based on matrix-oriented algorithms(1). The program is coded in APL/360.
 - 1. Input.
 - a. Chemical shifts.
 - b. Indirect coupling constants (J's).
 - c. Direct coupling constants (D's; optional).
 - d. Plotting parameters (optional).
 - 2. Output.
 - a. Eigenvectors (optional).
 - b. Relative levels identified by the corresponding 1st-order basis functions (optional).
 - c. An ordered list of transitions, intensities and connections.
 - d. A "tickling table" showing progressive and regressive connections (optional).
 - e. Any number of stick plots of any selected portion of the spectrum - all lines are labelled, and the abscissa is in ppm.

This program is highly interactive and should be immediately usable by anyone versed in nmr.

B. LAOCOON4: An iterative simulation program (up to six spins) which mathematically is equivalent to LAOCN3(2). It is coded in CALL OS/360 FORTRAN.

The operation of this program is well described in the above reference - only the major modifications will be described.

- 1. Input.
 - a. All input has been made interactive parameters are requested as needed.
 - b. Most input is free-form (unformatted); the exception is the parameter sets for iteration which are in (12,4(1x,12)) format.
- 2. Output.
 - a. The unordered transition list has been deleted.
 - b. The ordered transition list includes connections.
 - A list of levels identified by 1st-order basis functions has been added.
 - d. Format statements have been modified to be usable on teletype as well as the IBM 2741 terminal.
- 3. File handling.
 - a. All tape I/O instructions have been rewritten to be CALL OS/360-compatible.
 - b. Two scratch files ("SCRATCH1" and "SCRATCH2") must be initialized by the user.

A listing of the source programs for either or both of these programs can be obtained upon request. By the way, the editing routine that has typed this letter can also be supplied.

Sincerely yours,

D. n. Lincoln

David N. Lincoln

References:

- (1) Diehl, P., Kellerhals, H. and Lustig, E., "Computer Assistance in the Analysis of High-Resolution NMR Spectra", Vol. 6 of "NMR Basic Principles and Progress", Diehl, P., Fluck, E. and Kosfeld, R., editors (Springer-Verlag: New York Heidelberg Berlin) 1972.
- (2) Castellano, S. M., "LAOCN3", in "Computer Programs for Chemistry", Vol. 1, DeTar, D. F., editor (Benjamin: New York) 1968, p. 10.

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For the kind of pulse required in tomorrow's NMR research, we have the perfect heart today. It's our PFT-100 Fourier Transform system. A system designed with incredible power, unusual versatility.

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When You Need an NMR System, See Varian First.

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometer systems; from low cost systems designed to solve the typical problems of industrial and academic laboratories to the ultimate in research NMR systems.

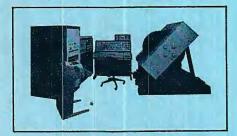
Our basic systems are briefly described here. Ask us what's new for any one, since we're continually expanding the flexibility and research capability of NMR instrumentation.

HR-220 and HR-300



These offer the highest performance in commercially available high resolution NMR spectrometers. The HR-220 (220 MHz) and HR-300 (300 MHz) spectrometers are engineered for use in those applications requiring the highest magnetic field strengths such as liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of ¹H, ¹³C, ¹⁹F, ³¹P, ¹¹B, and ²H in both the continuous wave and Fourier transform modes.

XL-100



A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz, and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments.

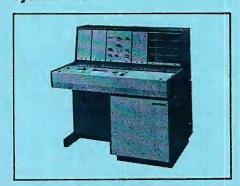
Locking flexibility for homo- or heteronuclear internal lock on ¹H, ¹⁹F, and ²H, and external lock on ¹H and ¹⁹F are provided. Fourier transform operation, T₁ measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

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System T-60



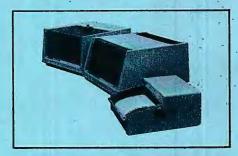
The most versatile instrument in the low-to-modestly priced end of Varian's NMR line, the T-60 features high performance and modular accessories. The basic instrument is excellent for routine applications. Accessories such as ¹⁹F, ³¹P, variable temperature and spin decoupling expand its capability into many complex research applications.

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