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December, 1974

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All Newsletter Correspondence, Etc. Should Be Addressed To:

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

IN REPLY PLEASE QUOTE

REF. NVR.RC

THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W.

DEPARTMENT OF ORGANIC CHEMISTRY.
5th November, 1974.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A&M University,
COLLEGE STATION,   Texas 77843, U.S.A.

Dear Dr. Shapiro,

Subject: Paramagnetic Line-Broadening as an Aid in Assigning ^{13}C N.m.r. Spectra

To assist in assigning ^{13}C n.m.r. spectra, various aids, such as off-resonance proton decoupling, specific deuteration, effects of paramagnetic shift reagents, or use of spin-lattice relaxation times are available, but each is subject to limitations. In certain circumstances, paramagnetic line broadening may prove a useful addition to the armory.

For a substrate present in large excess and capable of only weak or moderately weak binding to the metal atom in a paramagnetic transition-metal complex, there will be fast exchange between substrate molecules in the coordination sphere and those in the bulk medium, and overall relaxation times of a magnetic nucleus in a substrate molecule are then weighted averages of the values for the free and bound molecules. The nuclear relaxation processes involve both contact hyperfine and dipole-dipole interactions of the nuclear and unpaired electron spins, and general expressions for nuclear T_1 and T_2 values have been given by various authors.[1-3] Discussion has been mostly concerned with interpretation of contact and/or pseudo-contact shifts, especially of proton resonances, and line-broadening effects are referred to mainly as causes of difficulty in observing the resonances.

Some metal complexes however show a sharp e.s.r. line at room temperature, and broadening of resonances of magnetic nuclei on complexed substrate in these cases is likely to be dominated by contact interactions, especially for ^{13}C nuclei for which the hyperfine coupling constant $\underline{A}$ may be very large.[4] Linewidth contributions are proportional to $\underline{A}^2$. By analogy with other spin-spin scalar interactions (as, for instance, metal-^{13}C coupling in various covalent metal-hydrocarbon molecules, for which $^3J_{CM} > {}^2J_{CM}$, and values of $^3J_{CM}$ show a Karplus-type dependency), in the metal-complexed amine fragment,
we expect $\underline{A}_1 < \underline{A}_2$, and that values of $\underline{A}_2$ for non-equivalent sites two bonds removed from the nitrogen atom will differ depending upon variations in the dihedral angle between the M-N and C1-C2 bonds.
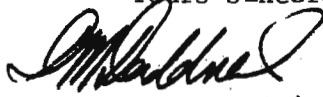
These ideas are supported by ^{13}C n.m.r. spectral results upon progressive addition of small amounts of copper acetylacetonate (up to maximum concn. ca 2×10^{-2}M) to cyclohexylamine, the isomeric cis- and trans-2-, -3-, and -4-methylcyclohexylamines, and n-pentylamine. In each case, the resonances of C2,C6 were the first to broaden, followed by that of C1, then progressively those of carbon atoms three or more bonds removed from the nitrogen atom. For the conformationally fixed trans-2-methylcyclohexylamine, the C2 resonance broadened much faster than that for C6, which suggests strongly that the nitrogen lone-pair and complexed Cu atom are oriented trans to C2 (and its attached methyl group) about the N-C1 bond. A similar differential effect on C2,C6 was not observed for the conformationally mobile cis-2-methylcyclohexylamine. The electronic relaxation rate is such that $T_{1e}^{-1} \ll (\gamma_e/2\pi)\underline{A}_i$, and line broadening was in no case accompanied by chemical shifts of the resonances. Line-broadening studies also proved useful in assigning c.m.r. spectra of some oximes but not that of n-pentanol.

Details of the broadening theory, assignments of the present spectra, and other matters such as amino-group substituent-effect parameters, are given in a full paper (with Dr. A.I.R. Burfitt) to be published in the Australian Journal of Chemistry.

This will probably be our last joint contribution to these Newsletters. One of us (D.M.D.) has abandoned the rustic delights of rural Armidale (population, ca 20K) for the fleshpots of metropolitan Brisbane (pop., ca 0.75M). Each of us hopes to continue our own contributions for some time yet.

Yours sincerely,

D.M. DODDRELL.   N.V. RIGGS.

[1] A. Carrington and D. McLachlan, "Introduction to Magnetic Resonance," p. 221 (Harper and Row, New York, 1967).

[2] D.R. Eaton and W.D. Phillips, Adv.Magn.Res., 1965, 1, 103-148.

[3] G.A. Webb, Ann. Rep. NMR Spectry., 1970, 3, 211-259.

[4] D. Doddrell and J.D. Roberts, J.Amer.Chem.Soc., 1970, 92, 4484, 5255, 6839.

225B Boxwood Rd., Apt. 207
Annapolis, Maryland 21403
November 5, 1974

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

Carbon-13 Shielding Anisotropy in CFCl$_3$

Dear Professor Shapiro,

We have used natural abundance C-13 NMR to determine the shielding anisotropy of CFCl$_3$ in several nematic liquid crystals including EBBA. The spectra were run at Columbia University on a JEOL PFT-100 Spectrometer interfaced with a Nicolet 1080 computer

Because of the long relaxation time, it was necessary to use rather high concentrations of CFCl$_3$ in the nematic phase and to accumulate FT spectra overnight. In Fig. (1) are shown some of the C-13 spectra obtained in EBBA (N-(p-ethoxybenzylidene)-p-butylaniline). Spectra a) and b) are the isotropic and nematic-phase proton-decoupled line patterns. In the isotropic spectrum the 2 CFCl$_3$ peaks are much smaller than the EBBA peaks, due to the longer relaxation time of CFCl$_3$ and the difference between solvent and solute. For certain liquid crystals the solvent interfered with the solute peaks and the systems could not be used. Fig. (1c) is the fluorine-decoupled nematic-phase spectrum of CFCl$_3$. It was recorded in order to verify that the 2 lines observed in b) were in fact those of CFCl$_3$ and to allow a more accurate measurement of the chemical shift in the nematic phase.

The preferred orientation of a nematic liquid crystal in a magnetic field causes a displacement in the chemical shift from its isotropic or rapid rotational value, σ_{Av} or σ_{iso} by an amount depending on the shielding anisotropy and the average degree of orientation S_z. The latter is determined from the direct dipolar coupling, which is obtained as the difference between the nematic- and isotropic-phase C-F splitting. It has been established from the fluorine spectra that the signs of J_{CF} and S_z are negative in EBBA. The fluorine spectra also helped confirm spectral assignments and demonstrated sample stability and reproducibility of results.[1] However it should be noted that unlike F-19, C-13 chemical shifts have been found to have a very small temperature dependence in the isotropic and nematic phases (except of course where S is changing). This allows the so-called "Single-point" to be used for determining the anisotropy.

From the spectra shown were obtained the values $|\Delta v|_{CF} = 239$ Hz, $J_{CF} = 276$ Hz, $S = -0.00436$ and $\sigma_{||} - \sigma_\perp = 33.4 \pm 8$ ppm. Combining these values with data from other liquid crystal samples yields the following for the shielding tensor of CFCl$_3$.

$$\sigma_{||} - \sigma_\perp = 29 \pm 9 \text{ ppm}$$

$$\sigma_{Av} = 76 \pm 8 \text{ ppm}$$

$$\sigma_{||} = 95 \pm 10 \text{ ppm}$$

$$\sigma_\perp = 66 \pm 10 \text{ ppm}.$$

A more detailed discussion of the C-13 shielding trends and spin-rotation constants will be contained in an article currently being prepared jointly with Professor B.P. Dailey of Columbia.

Sincerely,

Bernard R. Appleman

Bernard R. Appleman

1. Appleman,B.R. and Dailey,B.P., J. Magn. Resonance 16, 1974 in press.
2. Bhattacharyya,P.K. and Dailey,B.P., Mol. Phys. 26,1379(1973).

c) Nematic Phase   18,940 Sweeps

T = 25 C   Fluorine Decoupled

CS$_2$

b) Nematic Phase   19,450 Sweeps

T = 25 C   Proton Decoupled

CS$_2$

a) Isotropic Phase

T= 30 C

4096 sweeps

Proton Decoupled

CS$_2$ CFCl$_3$
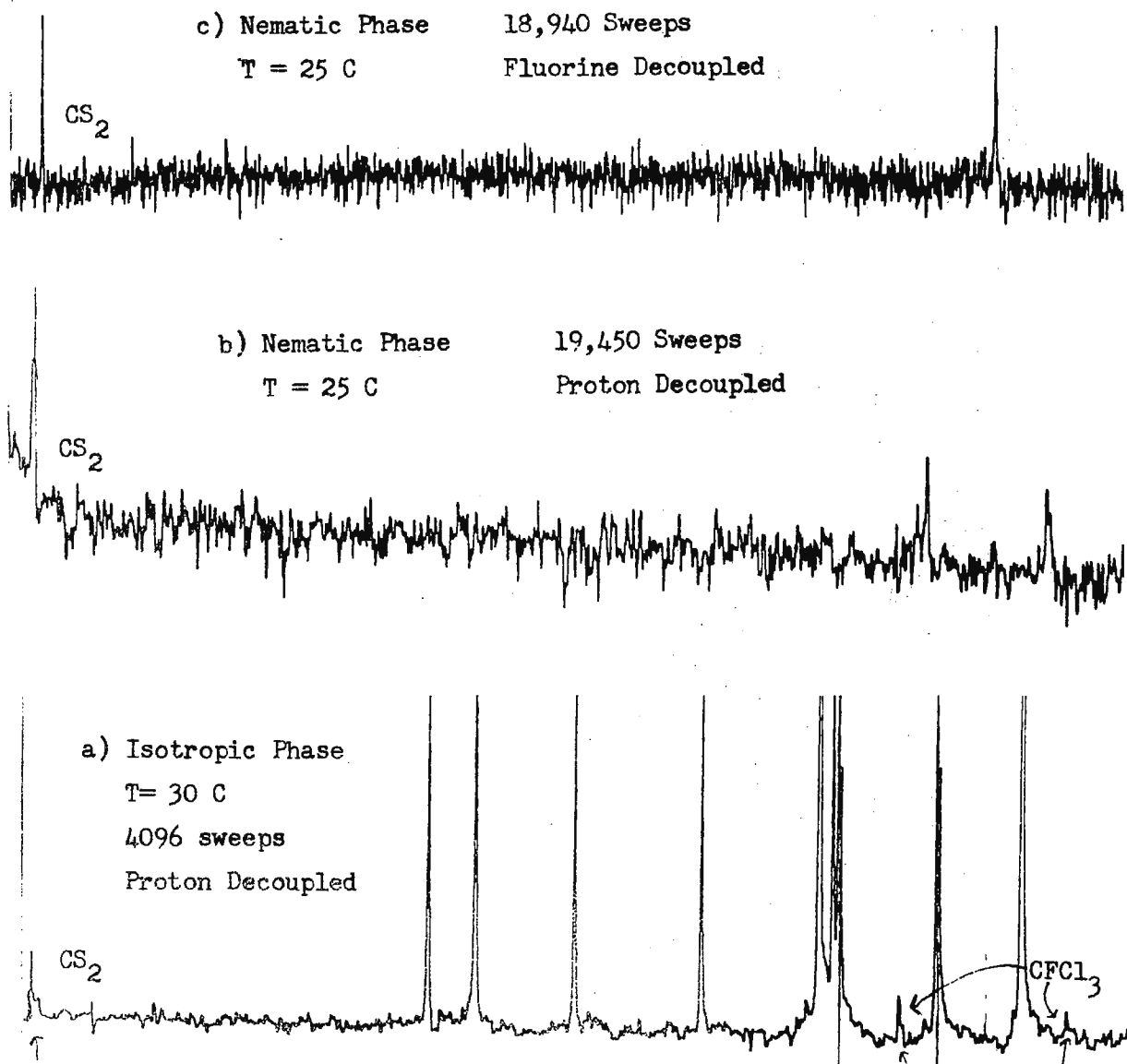
Figure (1) C-13 spectrum of CFCl$_3$ in EBBA; Pulse width 3 sec, Rep. 2 sec Spectrum width 2.5 kHz (complete spectrum not shown in a)

EM Reagents®

^{12}C Solvents Depleted Solvents: Deuterated Compounds

In Fourier transfer ^{13}C NMR spectroscopy, the signal-to-noise ratio, and thus spectrum quality, is often limited by the strongest signal. In a normal sample, there is much more of the solvent present than there is of the substance under test. For this reason, the solvent signal is frequently much stronger than the sample signal; thus the solvent tends to limit the sensitivity and usefulness of ^{13}C NMR measurements .

Fourier transform techniques increase the sensitivity of NMR spectroscopy to such an extent that the natural content of ^{13}C (1.1%) is often sufficient to provide ^{13}C solvent signals that mask the ^{13}C signals of the sample.

In order to minimize the solvent signal, E. Merck has developed a new class of Uvasols, in which the ^{13}C content is less than 10% of the natural level. These are compounds with ^{12}C content of from 99.93 to 99.95%. In addition, these Uvasols are synthesized with a deuteration degree of more than 99.5% in order to eliminate possible Overhauser amplifications in proton-noise de-coupled spectra which could increase solvent-signal amplitudes by a factor of as much as three and which, therefore, could mimic a higher level of ^{13}C than is actually present. Preparation techniques allow the synthesis of many different solvents. For example, chlorinated ^{12}C methanes (CCl_4, $CDCl_3$, CD_2Cl_2), ^{12}C methanol, and ^{12}C methyl halogenides, non proton solvents such as ^{12}C dimethylsulfoxide, ^{12}C dimethylformamide, ^{12}C tetramethyl urea, ^{12}C acetic acid and its derivatives and others in which the carbon atoms in a molecule have the same ^{12}C isotope content. At the present time, five ^{12}C solvents are commercially available from EM Laboratories.

Figure 1 compares the NMR spectrum of methanol with natural ^{13}C content (a) and the spectrum of methanol containing only 5% of the natural ^{13}C content (b). Both spectra were obtained under identical measuring conditions with a Varian XL-100 NMR spectrometer. Spectrum (a) shows the septet of the CD_3 group at 47.05 ppm with a ^{13}C-^{2}H spin coupling of 22 Hz in the region between 40 and 55 ppm relative to TMS. In spectrum (b), the same region is practically signal-free.
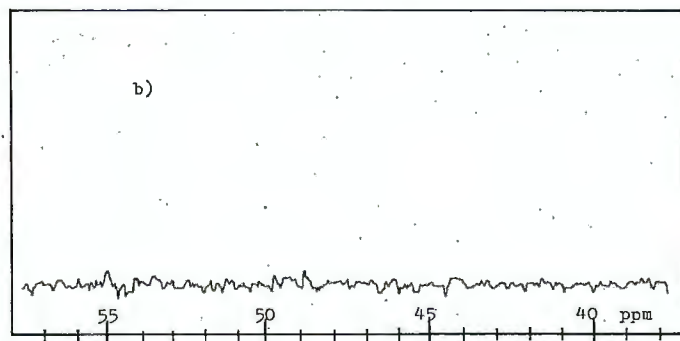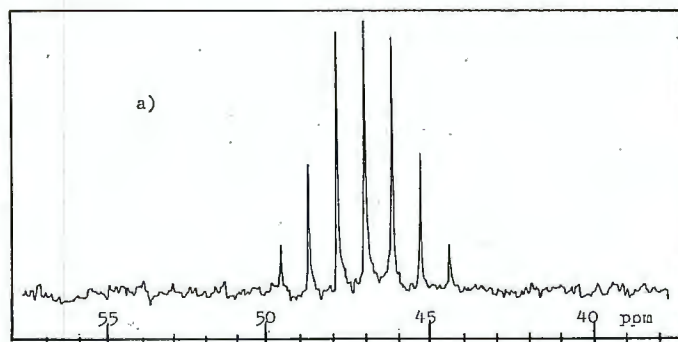
Deuterated Compounds

Deuterochloroform-^{12}C for NMR spectroscopy **Uvasol®**
$^{12}CCl_3D$ MW 120.37

10718-71	1 ml	27.00
10718-7A	10 ml	240.00

Dideuterodichloromethane-^{12}C for NMR spectroscopy **Uvasol®**
$^{12}CCl_2D_2$ MW 86.93

10717-71	1 ml	40.00
10717-7A	10 ml	538.00

Carbon tetrachloride-^{12}C for NMR spectroscopy **Uvasol®**
$^{12}CCl_4$ MW 153.81

2205-71	1 ml	25.00
2205-7A	10 ml	210.00

Tetradeuteromethanol-^{12}C for NMR spectroscopy **Uvasol®**
$^{12}CD_3OD$ MW 36.07

10628-71	1 ml	33.00
10628-7A	10 ml	290.00

Hexadeuterodimethylsulfoxide-^{12}C for NMR spectroscopy **Uvasol®**
($^{12}CD_3)_2SO$ MW 84.17

10781-71	1 ml	81.00
10781-7A	10 ml	735.00

If you would like more information about deuterated solvents, shift reagents, standards, anisotropic solvents, or instrumentation chemicals, write to EM Laboratories.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

September 12, 1974

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

Subject: ASTM Standard for NMR

Dear Barry:

ASTM Subcommittee E 13.07 is currently revising Standard E 386 which
contains definitions, etc. pertaining to nmr spectroscopy. Standard
E 386 is too long to reproduce in the Newsletter, but I will be pleased
to send copies of the proposed revised version to anyone interested.
Everyone on my mailing list was sent a copy within the past few weeks,
so should not ask for another unless he failed to receive it.

I have a computer program to offer specifically to those laboratories
which have a PDP8/E computer interfaced to an FT-1074 with no mass
storage device. It allows the PAL III Assembler and the Editor to be
resident in core at the same time and uses the 1074 memory as a buffer.
It is possible to go back and forth between Editor and Assembler, so that
a paper tape of a source program need not be punched until it can at least
be assembled and perhaps partially debugged.

Yours very truly,

Rolf B. Johannesen
Chairman
ASTM Subcommittee E 13.07

ISTITUTO CHIMICO

della

UNIVERSITÀ DI TORINO

10125 TORINO, November 6, 1974

CORSO MASSIMO D'AZEGLIO, 48

Tel. 65 21 02 - 68 28 92 - 65 58 31 - 65 58 32

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

Dear Professor Shapiro,

^{13}C-n.m.r. of the methinyltricobalt enneacarbonyl derivatives $Co_3(CO)_9CY$

With our new Jeol PS-100-FT machine we are currently investigating
by ^{13}C-n.m.r. some particular aspects of organometallic derivatives,
mainly clusters.

We wish to report the relevant features of the ^{13}C-n.m.r. spectra
of some derivatives with formula $Co_3(CO)_9CY$ (Y = Alkyl, Aryl, Halogen):

a) recently Seyferth et al. (1) reported that they were unable to
observe the resonance of the carbinyl carbon CCo_3 due to the nu-
clear quadrupole broadening of the cobalt. With overnight accumu-
lation we have observed broad resonances for this type of carbons
/ Fig. $Co_3(CO)_9CCH_3$ / (W ½ 80 Hz). The shift is extremally low
field for a sp3 carbon and, depending on the nature of the substi-
tuent Y, is in the range 300 ÷ 260 p.p.m. downfield TMS.

b) the peak of the CO's is also quite broad (W ½ $\sim$ 40 Hz) and is
narrowing by lowering the temperature up to $\sim$ 8 Hz at -90° C. The
same idea couldn't be verified on the apical carbon CCo_3 owing to
the high cost of the ^{13}C enriched starting materials, e.g. $^{13}CCl_4$.

These observations, coupled with those obtained in this laboratory on Mn and other Co derivatives, are promising interesting applications of the thermal decoupling in the case of carbons bonded to metals having spin $> \frac{1}{2}$.

c) one resonance only is observed for the carbonyls even at -100°C, suggesting a fluxional behaviour of this molecule in solution.

Yours Sincerely

S.Aime   O.Gambino   L.Milone

1) D.Seyferth, G.H.Williams, D.D.Traficante - J.Amer.Chem.Soc.,
   1974, 96, 604.

25 ppm

CO

CCo₃
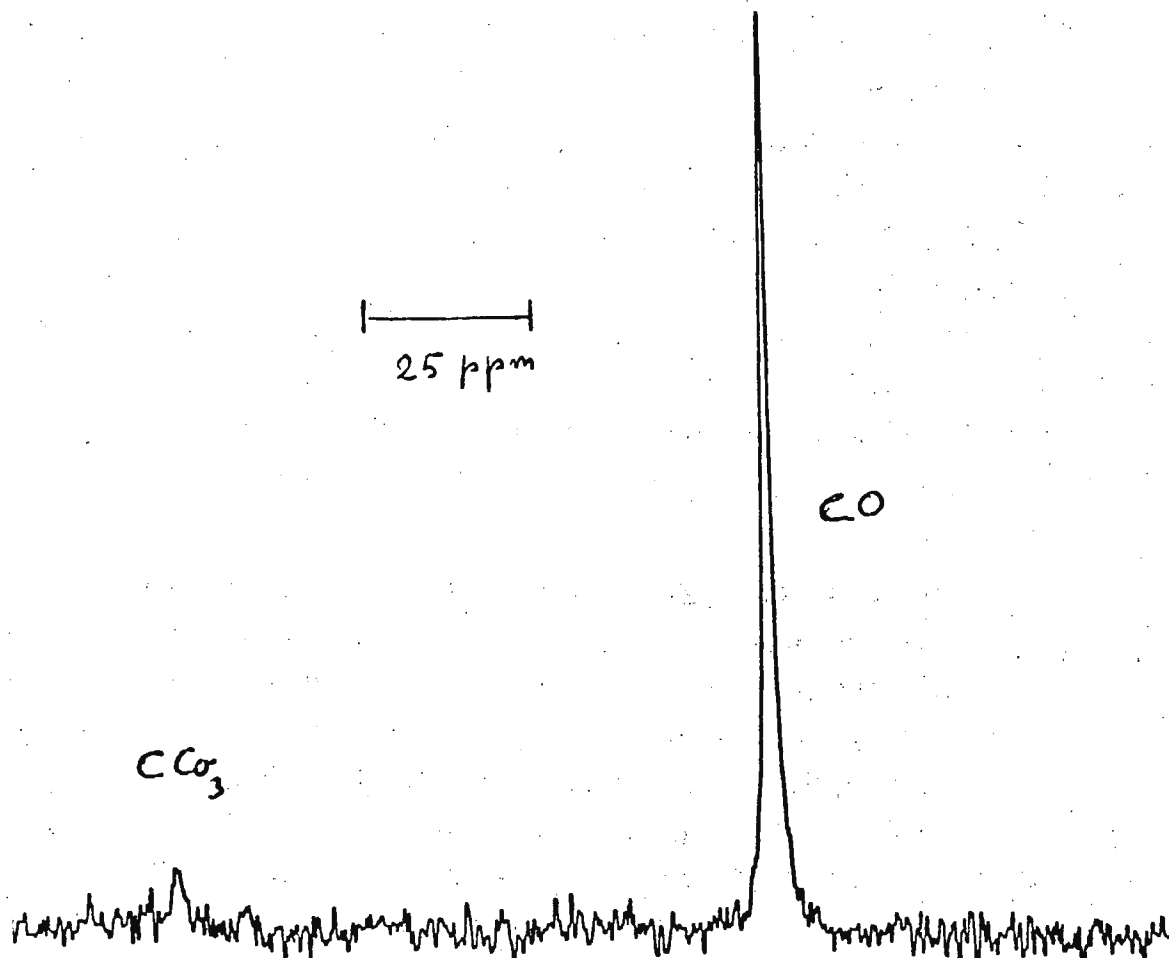
CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

November 11, 1974

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

Effect of Paramagnetic Metal Impurities on
Carbon-13 Spin-Lattice Relaxation Times of Carboxyl Carbons

Dear Barry,

The effect of trace paramagnetic impurities on ^{1}H-nmr linewidths is well known, and shortening of ^{1}H spin-lattice relaxation times (T_1) by such impurities for histidine has been reported recently (1). It now appears that spin-lattice relaxation times of carbon-13 nuclei of carboxyl carbons can be extremely sensitive to trace amounts of paramagnetic metal ions.

T_1 values of less than 15 sec for the carboxyl carbon of glycine (about 2 m in D_2O) have been reported (2, 3). Routine precautions to avoid contamination were taken in these studies (2), and analyses for trace metal ions in our samples by atomic emission spectroscopy were reported to be negative. Subsequently, Bob Vold and his group at the University of California, San Diego, informed us that they had measured considerably longer T_1 values for the glycine carboxyl carbon. We therefore obtained new metal analyses, and these indicated that paramagnetic metal ions on the order of 10^{-5} M were in fact present in our original samples. A reinvestigation was undertaken.

After purification, a sample of 2 m glycine (90% ^{13}C enriched at the carboxyl carbon) in D_2O was obtained which had a T_1 of 79 sec. This dramatic increase in T_1 resulted from the following procedure. The glycine was sublimed (bath temperature 150°) at 0.1 mm. The D_2O used as solvent was distilled and then extracted five times with a 0.05% solution of dithizone in carbon tetrachloride. (These treatments are necessary because the D_2O sold in glass bottles is supplied to the vendors by the Atomic Energy Commission in steel drums.) After the glycine solution was made up, it was washed an additional five times with dithizone solution, and EDTA (about 10^{-3} M) was added. The solution was degassed by bubbling argon through for 5 min. The nmr tube, vortex plug, and glassware were soaked overnight in alkaline EDTA solution

and rinsed with double-distilled water before use. In some cases, the T_1 values of carboxyl carbons have decreased markedly on standing, and this may be due to leaching paramagnetic metals out of the glass. (One should remember that precision-bore tubes are formed on metal mandrels.)

Despite all of this, the value of 79 sec for T_1 may have to be regarded as a minimum value if significant amounts of paramagnetic material still were not removed by the above treatment. The NOE yields a T_{1DD} of 131 sec and $T_{1(other)}$ of 290 sec. The $T_{1(other)}$ could be due to spin rotation, if it is not due to residual metal-induced relaxation. However, it is possible that the glycine is, in fact, clean now, because both the concentration dependence (2) and the pD dependence (2, 3) reported earlier for D_2O solutions of glycine were not observed with the purified samples.

In light of these disturbing results, we emphasize that extreme precautions in sample preparation are required if reliable carboxyl carbon T_1 values are desired. Paramagnetic impurities may lead not only to T_1 values which are too short, but also to spurious dependencies on concentration and pH.

With all good wishes,

Very truly yours,

Harry Pearson

Devens Gust

John D. Roberts

References:

(1) R. E. Wasylishen and J. S. Cohen, Nature, 249, 847 (1974).
(2) I. M. Armitage, H. Huber, H. Pearson, and J. D. Roberts, Proc. Nat. Acad. Sci. USA, 71, 2096 (1974).
(3) H. Saito and I. C. P. Smith, Arch. Biochem. Biophysics, 163, 699 (1974).

Natural Abundance ^{13}C NMR Spectrum
0.012M HEW Lysozyme, Molecular Weight 14,314

CARBONYL
11-ARGININES
2-TYROSINES
1-TYROSINE
AROMATIC
ALIPHATIC
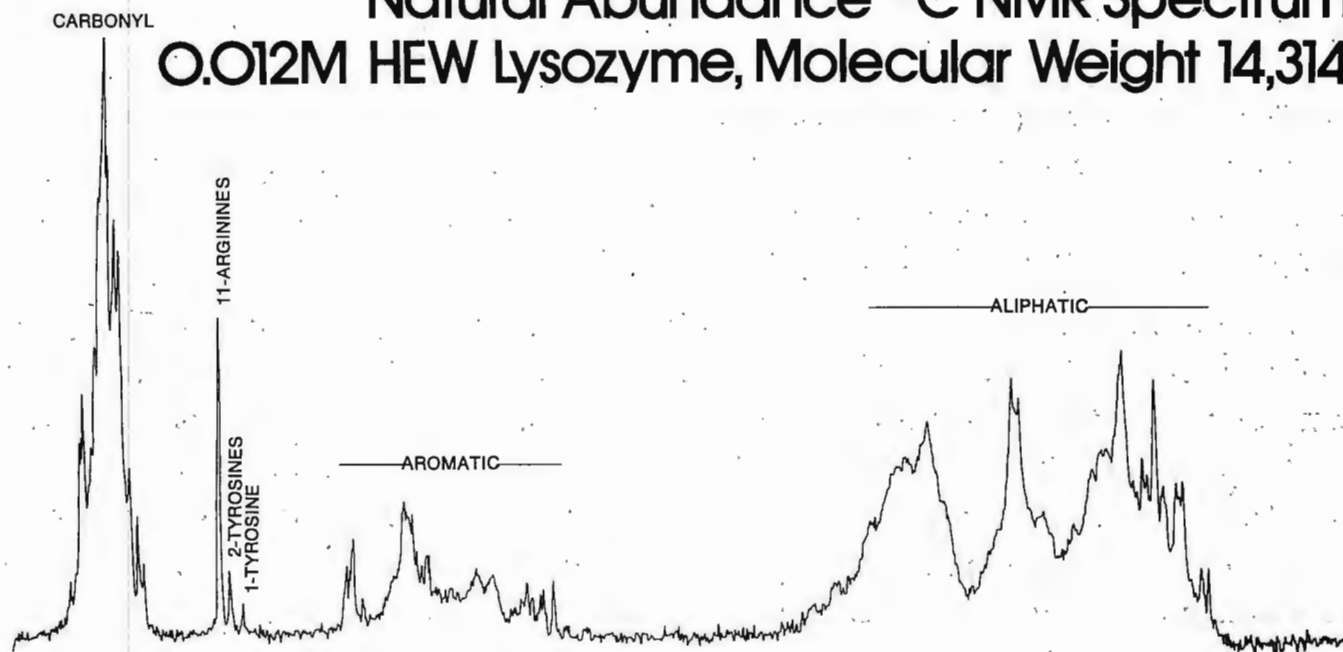
Proton-decoupled natural abundance ^{13}C spectrum of hen egg white lysozyme in 0.15M NaCl in 9:1 H_2O/D_2O, pH 4.0, 45°C. Recorded with a TT-14 system[1] at 15.08 MHz using a 20 mm sample tube; 37,107 90° pulses; 4096 time-domain points; and 1.165 Hz digital line broadening. This spectrum demonstrates that in a small protein, single carbon resonances such as the one assigned above to C^ζ in a single tyrosine residue, can be observed after only five hours of signal averaging with use of the 20 mm sample technology developed at Indiana University by Dr. Adam Allerhand.[2,3]

1. Sample run at the University of Chicago, courtesy of Dr. Philip Keim, Pritzker School of Medicine.
2. A. Allerhand, R.F. Childers, E. Oldfield, J. Magn. Resonance, *11*, 272 (1973).
3. E. Oldfield and A. Allerhand, Proc. Nat. Acad. Sci. USA, *70*, 3531 (1973).

HIGH SENSITIVITY CARBON-13 FT-NMR
with a TT-14 System

The TT-14 FT NMR System combines a state-of-the-art solid state console, Nicolet NMR-80 computer, 20 mm sample probe developed by Dr. Adam Allerhand, and a time-proved Varian 14 kilogauss magnet into the highest sensitivity carbon-13 performance available today. Features of this system are:

- internal deuterium lock;
- proton decoupler with pulse delay gating capability;
- observe, lock, and decoupler frequencies derived from a single master oscillator;
- 10 mm insert available for studies of limited sample quantities;
- readily convertible to other nuclei studies, e.g. ^{15}N, ^{31}P, or even ^1H;
- multipulse capability, including automatic T_1 measurements;
- disk memory unit for program and data storage;
- excellent software package, including versatile quantitative measurement capability, automatic calculation of T_1 values with error limits, iterative 6-spin spectrum calculation, and new software as developed at no cost;
- available as an add-on for existing 14 kilogauss magnet system owners.

Please phone or write for additional information on the versatile TT-14 System.
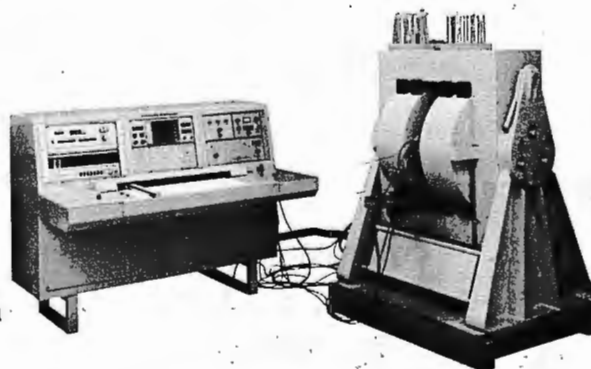
NTC NICOLET TECHNOLOGY CORPORATION

145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076
(formerly Transform Technology Inc.)

DEPARTMENT OF PHYSICS

November 8, 1974

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.
· Canada

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

Dear Barry,

Radiation damping was a nuisance in earlier days when
samples used to be so rich in nuclear magnetism that they could
almost serve as compass needles. The trouble with these bar
magnets, spinning transversely at 4×10^7 rev/sec in the receiver
coil, was that they performed too well as power generators. The
work output reduces the magnetic energy of the sample and the
magnetization swiftly aligns itself with H_o, frustrating the
skillful effort of the transmitter trying to nutate it into the
transverse plane. The results were broad lines and short FID's,
wherefrom the misnomer radiation 'damping' arose. Although such
'damping' is rare in the days of C^{13} spectroscopy, the subject
continues to be intriguing in its quantum mechanical aspects,
especially because of its relation to two-level maser oscillators,
superradiant states, giant pulses, etc.

A brief survey of the literature (1) shows that observable
phenomena may be classified by the value of the radiation time
constant $T_r = [2\pi M G \eta \gamma]^{-1}$ in comparison with T_2 and T_c, where
G=gain, Q=quality factor, and T_c = time constant Q/Ω of resonant
structure in radiation feedback loop operating at frequency Ω,
M=sample magnetization, η=filling factor, γ=gyromagnetic ratio.
The circle drawn below is an image of the T_r axis from $-\infty$
to $+\infty$ and defines 6 ranges 'a - f'. In high resolution nmr,
$T_2 > T_c$ will usually apply. For normal spectrometers, G=Q and
$T_c = Q/(\gamma H_o)$ refer to the resonant receiver coil, and T_r is in
range 'a' with appreciable damping for strong resonances only.
For H^1 resonances in neat water, benzene, TMS, etc, T_r can be in
range 'b' where the maser threshold is exceeded for an inverted
magnetization. This implies that inversion is not possible by means
of a 180° pulse, rapid adiabatic passage, etc. To go further
(or even this far with weaker samples) requires increased feed-
back gain G by means of an electronic feedback loop added to the
spectrometer. In range 'c', the maser oscillations are 100%
amplitude modulated giving emission pulses which have been
interpreted as coherent spin echoes.

Negative T_r result from a reversal of the sign of G in the
feedback loop, which is then of the type described for the
nuclear sideband oscillator (2). Phenomena in ranges 'd - f'

correspond to those in 'a - c', respectively, except that the roles of the thermal equilibrium state and of the inverted state are interchanged with respect to radiation 'damping'. Thus, in range 'e', the thermal equilibrium state is unstable against maser oscillations (nuclear sideband generator) as the inverted state was unstable in range 'b'. Some observations with T_r in range 'f' have been briefly reported earlier (3), and some H^1 spectra for range 'd' are shown in the second row of the following figure. The top row gives comparison resonances with the unmodified spectrometer ($T_r \simeq +\infty$), the lines are broad due to chemical exchange. The first example exhibits a promising radiation narrowing corresponding to the broadening in 'a', but the second example demonstrates the associated amplitude non-linearity with a quartet that is not quite 1:3:3:1 first order. Some partially overlapping lines were chosen for the third example to demonstrate that the line shape is no longer a Lorentzian absorption mode. These three effects: narrowing, amplitude non-linearity, change of line shape, match the analysis given by Bruce and Bloom (1) for range 'a' except that they are reversed in sign.

Sincerely yours,

R. F. Hobson

Reinhold

R. Kaiser
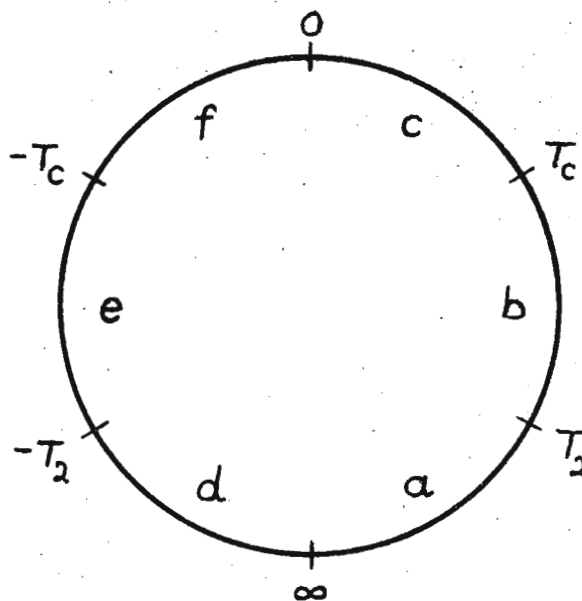
(1) N. Bloembergen, R.V. Pound, Phys. Rev. 95, 8 (1954)
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    K.W. Gray, I. Ozier, Phys. Rev. Letters 26, 161 (1971)
    Yu.S. Konstantinov, A.M. Smirnov,
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(3) R. Kaiser, IITNMR 87, 38 (1965)
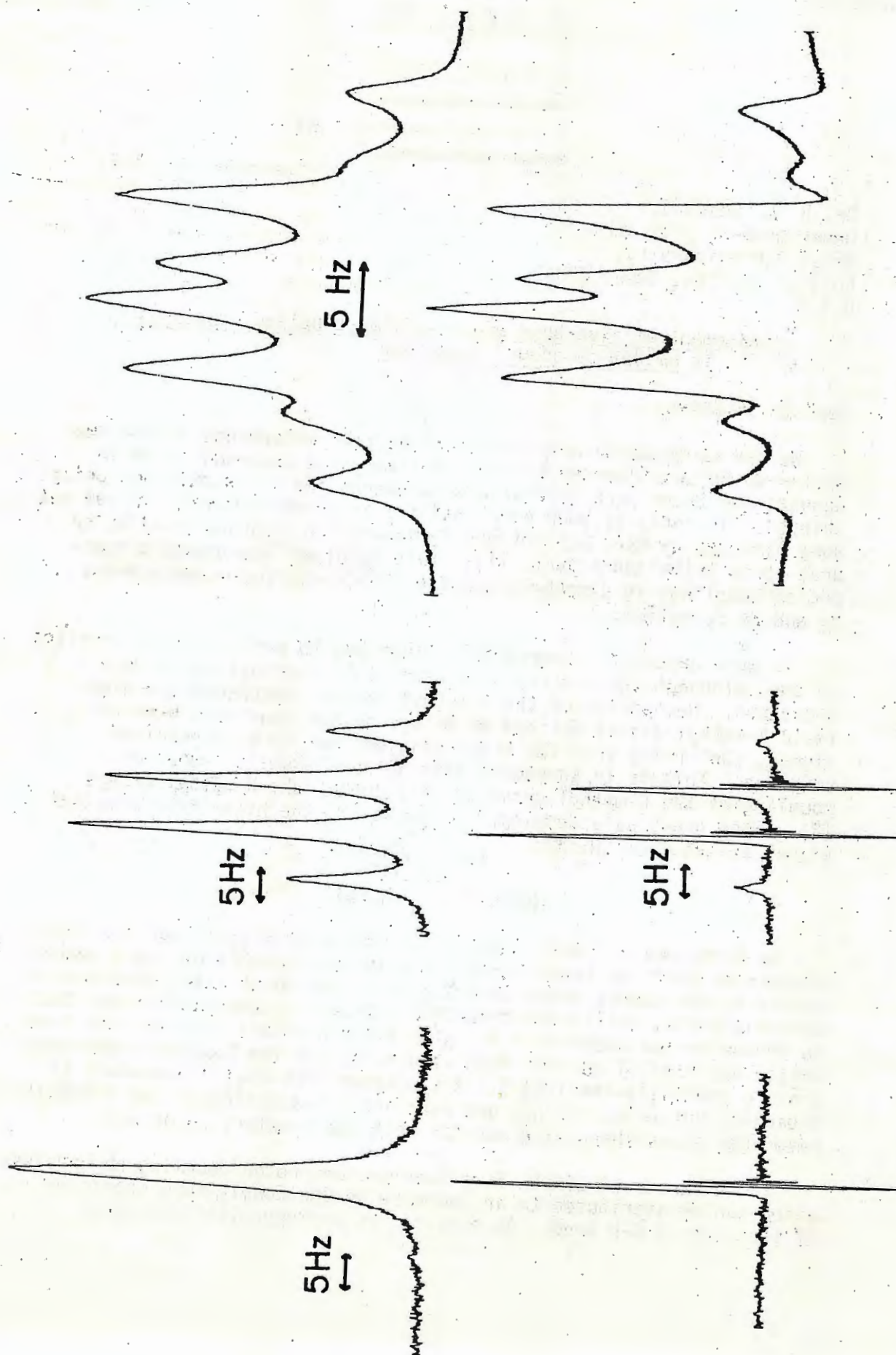
BROCK
University

St. Catharines, Ontario L2S 3A1.

November 13, 1974.

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

Enhancement of five-bond proton-proton coupling constants in amides by adduct formation

Dear Dr. Shapiro:

We had hoped to be able to report on the performance of our new
Bruker WP-60 spectrometer by now. Delivery was supposed to be in
August, but there were several postponements and it is only now being
shipped. In reply to your pink letter I am reporting work carried out
some time ago by Gary Schrobilgen in connection with our studies on
urea-boron trihalide adducts (1). This involves long-range proton-
proton couplings in dimethylacetamide (DMAC) and their enhancement
by adduct formation.

We were unable to observe splittings due to proton-proton coupling
in DMAC although the C-methyl and high-field N-methyl peaks were
broadened. Decoupling of the C-methyl protons sharpened the high-
field N-methyl signal but had no effect on the low-field N-methyl
signal, confirming that the broadening was due to an unresolved
coupling. This is in agreement with de Kowalewski's report of
coupling of the C-methyl group to only one of the N-methyl groups
(2). From previously developed criteria (3) the high-field N-methyl
signal arises from $CH_3(a)$:

$$\underset{(c)H_3C}{\overset{O}{\diagdown}} C = N \overset{CH_3(a)}{\underset{CH_3(b)}{\diagup}}$$
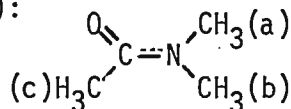
On formation of the 1:1 adduct of DMAC with BF_3, all of the DMAC
resonances shift to lower field. The non-equivalence of the N-methyl
groups in the adduct shows that oxygen is the donor atom. The adduct
proton signals, unlike the free-DMAC signals, do show splittings due
to proton-proton coupling. The high-field N-methyl peak arising from
$CH_3(a)$ has 1:3:3:1 quartet fine structure, and the C-methyl resonance
shows a partially-resolved 1:3:3:1 quartet. The $CH_3(b)$ resonance is
broadened but no splittings are resolved. Decoupling of the C-methyl
resonance gives sharp singlets for both the N-methyl resonances.

The enhancement of the five-bond proton-proton coupling on complex-
ation can be attributed to an increase in the double-bond character
of the central C-N bond. As expected by analogy with long-range

Nmr Parameters of DMAC and its BF_3 Adduct in CH_2Cl_2

	^1H chemical shifts (δ)			^1H-^1H coupling constants (Hz)	
	$CH_3(c)$	$CH_3(b)$	$CH_3(a)$	b-c	a-c
DMAC	2.02	2.98	2.89	0.0	*
DMAC.BF_3	2.42	3.25	3.20	*	0.7

*broadening due to unresolved coupling

---

couplings in olefins, the trans methyl protons couple more strongly than the cis methyl protons. The four-bond proton-proton coupling between the two N-methyl groups, which would be unaffected by the nature of the central C-N bond, remains too small to detect. While this work was in progress similar five-bond couplings were reported in protonated DMAC and in DMAC.$SbCl_5$ (4).

Yours sincerely,

J. S. Hartman,
Associate Professor.

1. J. S. Hartman and G. J. Schrobilgen, Inorg. Chem., 13, 874 (1974), and references therein.

2. D. G. de Kowalewski, J. Phys. Radium, 23, 255 (1962).

3. W. E. Stewart and T. H. Siddall, III, Chem. Reviews, 70, 517 (1970).

4. Q. Appleton, L. Bernander, and G. Olofsson, Tetrahedron, 27, 5921 (1971).

UNIVERSITY OF GRONINGEN DEPARTMENT OF PHYSICAL CHEMISTRY

ZERNIKELAAN, PADDEPOEL, GRONINGEN, THE NETHERLANDS

Tel.: 050 -

GRONINGEN, November 14, 1974

Prof. B.L.Shapiro

Department of Chemistry

Texas A&M University

College Station, Texas 77843, U.S.A.

Dear prof. Shapiro,

LORCO, a computer program for Lorentz convolution

Sorry for your bleu letter.

Recently I wrote a program which may be of interest for those having access to a Varian 620 computer with MK II interface. This program is written in assembler language and needs the lowest 7 K of memory. It is designed to generate a theoretical NMR spectrum.

J couplings are not considered, but up to 64 lines may be entered with freely choosen height, in proton units, frequency, in PPM, and linewidth, in Hz. The ith point on the theoretical spectrum is calculated according to:

$$S(i) = \sum_{j=1}^{N \leqslant 64} int(j) \times \frac{SLW}{LW(j)} \times \frac{1}{1 + (\frac{2\Delta ji}{LW(j)})^2}$$

where,

  int(j) : height of line j in proton units

  SLW   : general linewidth, can be used for those lines having the same width

  Lw(j)   : linewidth of line j

  Δ_{ji} : frequency difference between point i and the position of line j

There are 22 commands available to control the program. They are entered as in the case of the Varian FT programs.

In general these commands can be divided into three groups:

1. Commands for parameters such as spectrometer frequency, general linewidth, spectral width etc.

2. Commands to add lines to the line table or to manipulate those already entered.

3. Commands for display on the oscilloscope, the spectrometer recorder or an XY-recorder.

   A stick spectrum or a baseline with PPM markers is plotted easily by use of the appropriate commands.

I am enclosing an example of a calculated spectrum, together with the parameter-list defining it.

Program description and listings are ready and, if the interest is not too overwhelming, I'll be glad to send copies of the description and the binary papertape. Copies of the source listing (82 pages), the source deck (only on cards) or the binary file on a compu/corder-100 tape are only available at costprice.

I thank Varian and Dr. C.W.F. Kort (Org.Chemistry Dept., University of Amsterdam) for the permission to use important parts of their software.

Yours truly,

Henk Koekoek


```
> PA
SPEC FREQ (MHZ) =  100
SWEEP (PPM)  FROM :   -     6.00
             TO   :   -     1.90
WIDTH (HZ) =            15.00
Y-AMPL (MM) =    50
PLOT WIDTH (MM) =  100
PLOT TIME =     5

LINES =   6
```

N	INT	FREQ (PPM)	WIDTH (HZ) *
1	1.00	- 5.00	20.00
2	1.00	- 4.50	
3	1.29	- 4.40	
4	1.00	- 4.80	
5	2.00	- 3.50	30.00
6	1.00	- 3.00	

* NO ENTRY IS 15 HZ.
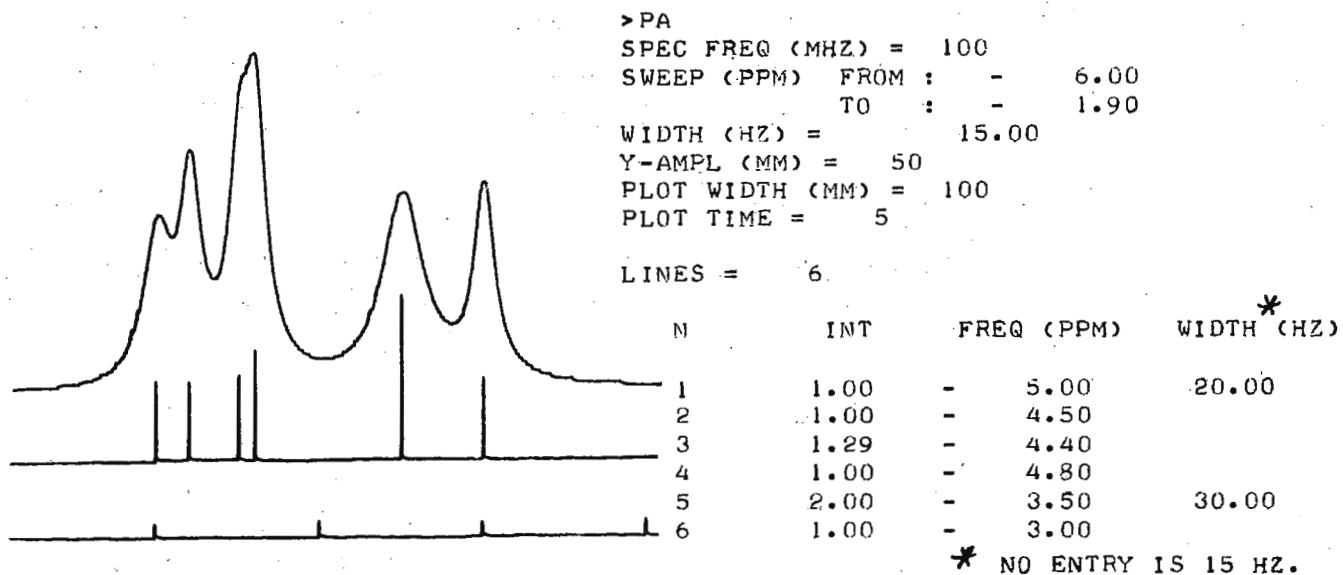
Department of Chemistry
THE UNIVERSITY OF WINNIPEG

WINNIPEG, CANADA   R3B 2E9   November 18, 1974

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

Title: ^{13}C NMR Chemical Shifts in some Isothiazoles.

Dear Barry:

While I was working in Ted Becker's laboratory at the National Institutes of Health we measured the carbon-13 chemical shifts of several 4-substituted iso-thiazoles (see (I) below).

The influence of substituents* on the ^{13}C chemical shifts of C_4 in (I) roughly parallels that on the substituted carbon, C_1, of the corresponding mono-substituted benzenes. The greatest departure was found for X=Br, where the C_4 resonance in (I) is 16.4 ppm to high field of the value in isothiazole. In bromo-benzene, the substituent effect is 5.5 ppm to high field (1). It is interesting to note that a similar large upfield substituent shift of 16.5 ppm has been observed for C_3 in 3-bromothiophene (2). In the case of 3-bromopyridine however, the substituent shift for C_3 was only 2.9 ppm upfield (3).

The ^{13}C chemical shifts for C_3 and C_5 in (I) are given in figure 1. The relative sensitivity of C_3 and C_5 to the various substituents can be _qualitatively_ accounted for by consideration of the following valence bond structures:

(I)
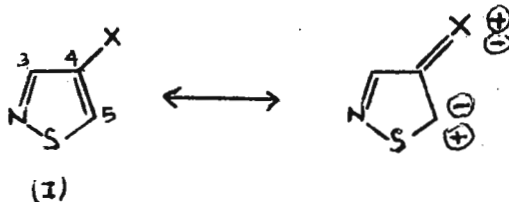
Finally, CNDO/2 calculations on a large number of 4-X-isothiazoles predict the total charge densities at C_5 to vary over a range of approximately twice that calculated for C_3.

A more complete account of this work will appear in Can. J. Chem.,

Sincerely yours,

Rod Wasylishen

Rod Wasylishen

---

*Substituent effects on the ^{13}C chemical shifts are given relative to the parent compounds where X=H.

References:

1. G.L. Nelson, G.C. Levy and J.D. Cargioli. J. Am. Chem. Soc. 94, 3089 (1972).
2. H.L. Retcofsky and R.A. Friedel. J. Phys. Chem. 72, 290 (1968).
3. K. Takahaski, T. Stone and K. Fujieda. J. Phys. Chem. 74, 2765 (1970).
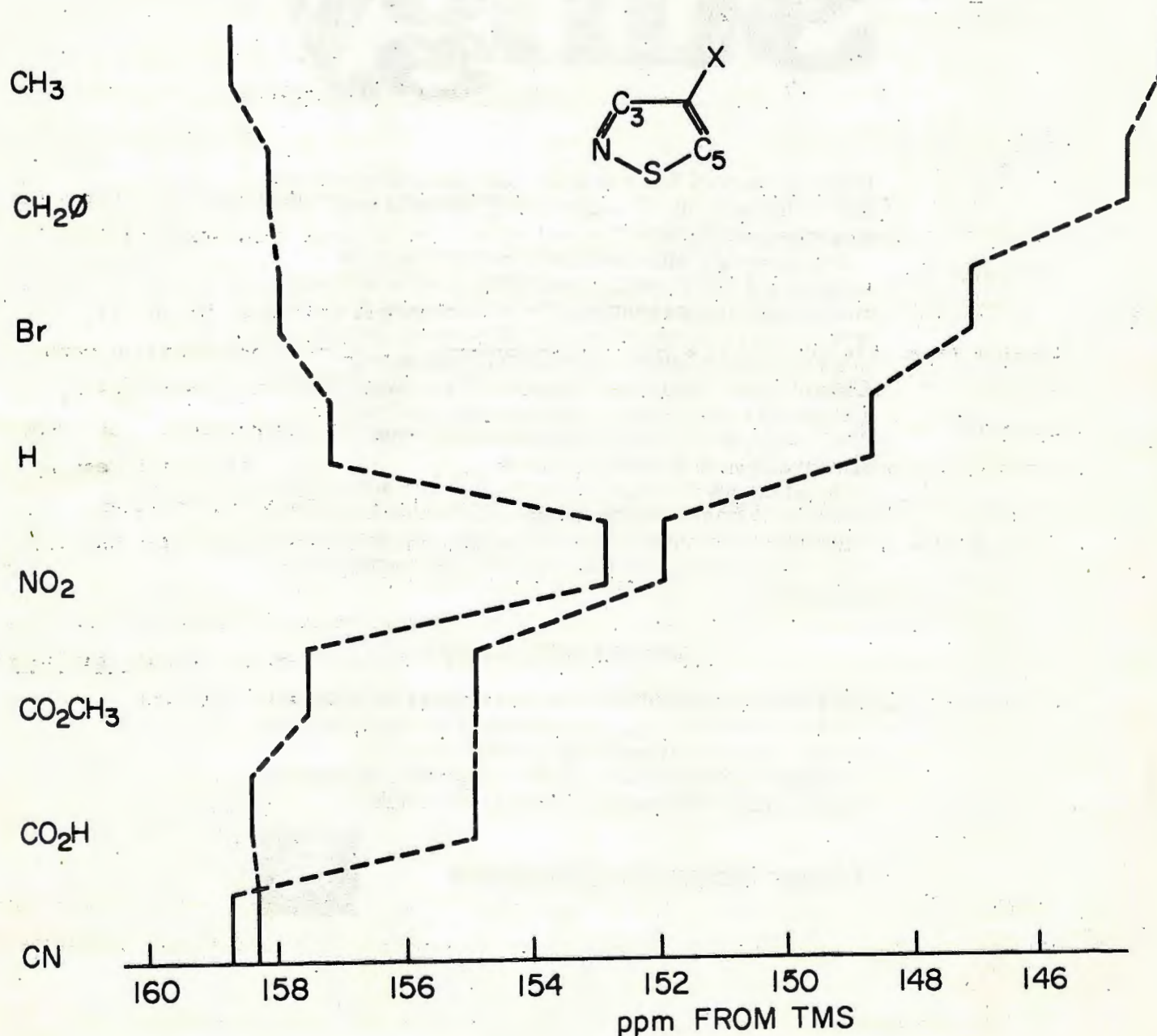
Figure 1. ^{13}C chemical shifts of C_3 and C_5 in some 4-monosubstituted isothiazoles. C_5 is to high field of C_3 in all cases except for X=CN.

Stingy

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NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

November 27, 1974

Dear Fisher,
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Title _____

Institution or company _____

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City _____

State _____ Zip _____

Challenging position in the Chemistry Department Analytical Laboratory for a professional with experience in the operation, development, and maintenance of NMR spectrometers and/or expertise in high-frequency analog and digital electronics. Some knowledge of organic chemistry desirable. Current NMR instrumentation includes a Bruker HFX-90, a Perkin-Elmer R-20B, and a Varian T-60. In addition, it is hoped that a CFT-20 and a 270 MHz superconducting system will be acquired. Possible to work with other lab instrumentation, which includes IR, UV, XPS, fluorescence, and mass spectrometers, and laboratory minicomputers. Excellent benefit program includes opportunity for course work. Send resume to:

Personnel Department
Northwestern University
1812 Chicago Avenue
Evanston, Illinois 60201

Sincerely,

Joseph B. Lambert

JBL/kp

Short title: Position available

UNIVERSITY OF DELAWARE
NEWARK. DELAWARE
19711

DEPARTMENT OF CHEMISTRY

November 19, 1974

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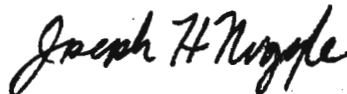Texas A & M University
College Station, Texas   77843

TITLE: TWUNRHO'S: POST-DOCTORAL OPPORTUNITY

Dear Barry:

Our efforts to measure $T_{1\rho}$ by FT have born fruit,
and the results should appear shortly. In the meantime, I
enclose a "typical" (Pines' definition) spectrum of a mixture
of phosphorous halides which will not be in our forthcoming
publication; indeed, we haven't gotten around to analyzing our
results yet. When working, we find that our automated $T_{1\rho}$
set-up fills a notebook a week and, in three weeks, did more
measurement than an average graduate student (like you or I)
a few years ago did in three years. Unfortunately, that idiot
computer won't write the paper. The numbers in brackets on
the figure are the measured $T_{1\rho}$ for that species.

I expect to have a post-doctoral position available
for next academic year. Some teaching is involved so foreign
candidates must have a good facility in the English language.
Otherwise, we are an equal opportunity employer and minority
individuals are invited to apply.

Yours very truly,
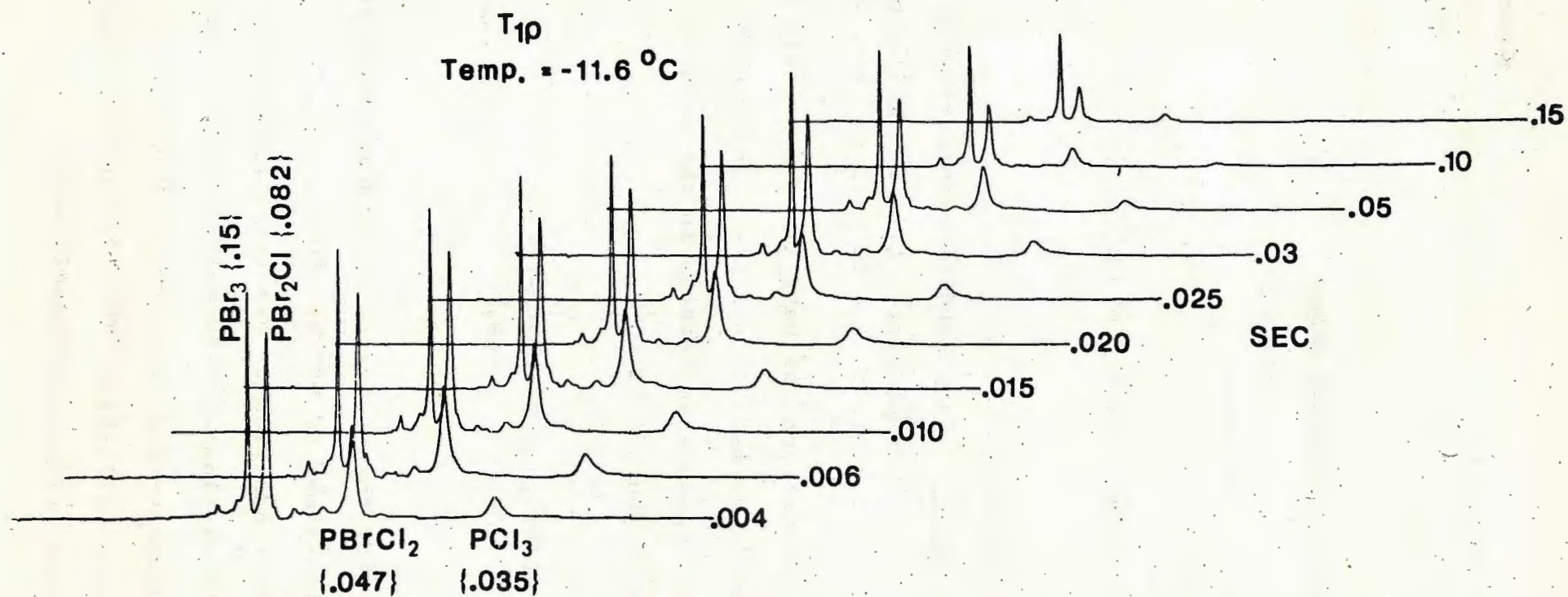
Joseph H. Noggle
Thomas K. Leipert
Walter J. Freeman
David L. Dalrymple

ag

Enclosure

$T_{1\rho}$
Temp. $= -11.6$ °C

PBr$_3$ {.15}

PBr$_2$Cl {.082}

PBrCl$_2$ {.047}

PCl$_3$ {.035}

.15
.10
.05
.03
.025
.020
.015
.010
.006
.004

SEC

195-24

FACHBEREICH CHEMIE
### DER PHILIPPS-UNIVERSITÄT
Marburg/Lahn

Fachbereich Chemie 3550 Marburg/Lahn, Lahnberge

Professor Bernard L. Shapiro

Department of Chemistry

Texas A and M University

College of Science

College Station, Texas 77843

Dear Dr. Shapiro:

Title: ^{13}C-Spin-Lattice-Relaxation-Times as a Probe for

Complexation of n-Butyllithium

At Caltech, we have tried to obtain more insight into the
mechanism of asymmetric synthesis involved in the addition of organo-
metallic compounds to ketones in the presence of 1,4-dimethylamino-
2,3-dimethoxybutane (DDB)[1].

$$(CH_3)_2 \; N-CH_2-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{CH}}-CH-CH_2-N \; (CH_3)_2$$
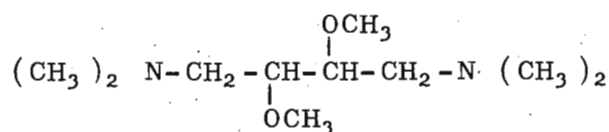
1

For this purpose, we have measured the ^{13}C-spin-lattice
relaxation-times of DDB at -50° in $CD_3(-CH_2)_4-CD_3$ as solvent[2] with
and without addition of n-butyllithium. The measurements were made
on our 'Brukarian'-DFS-60 using both inversion recovery and the
McDonald pulse-sequences. The solutions used were 0.6 M both in
DDB and n-butyllithium. The results are shown below and indicate
a very large effect of complex formation.

	T_1 of DDB [sec]				T_1 of $CD_3-(CH_2)_4-CD_3$	
	-CH-	-CH_2-	-OCH_3	-$N(CH_3)_2$	C_2	C_3
DDB alone	1.3	0.8	1.85	0.7	5.2	6.2
with BuLi	0.22	(0.13)	(0.13)	0.15	4.7	4.9

The effect of the change in viscosity on the T_1 values caused by addition of n-butyllithium does not seem large judging from the small changes for C_2 and C_3 of the solvent. The effects could be due to paramagnetic impurities although atomic absorption analysis indicated no significant amounts were present. Unfortunately, the resonance lines of the CH_2 and the methoxy groups coincided after the addition of the organometallic reagent which prevented a differentiation of the complexing effect on the heteroatoms attached to these carbons. That the change in relaxation is so large - six to tenfold drop suggests that higher aggregates may have been formed. Studies of this kind seem to have a potential to become a valuable tool for probing complex formation.

Please credit this communication to S.B. at the University of Marburg.

Very truly yours,

Stefan Berger
Fachbereich Chemie der Universität

355 Marburg
Lahnberge

Albert Beck

Dieter Seebach
Institut für Organ.Chemie
Fachbereich 14
63 Gießen
Ludwigstraße 21

John D. Roberts
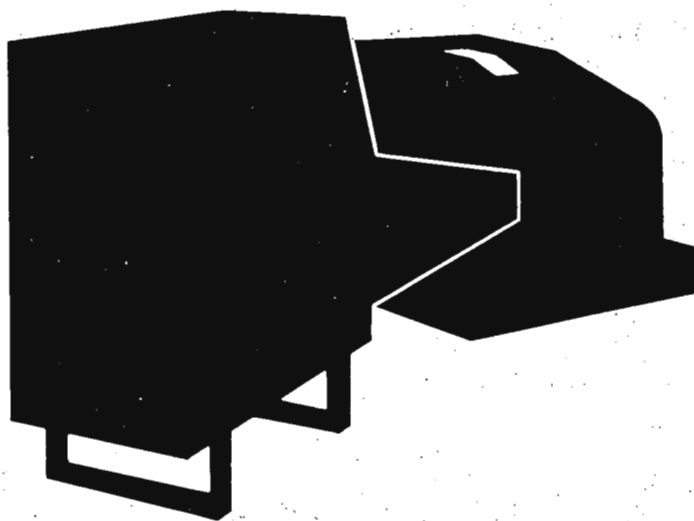California Institute of Technology
Pasadena, Cal 91109

1) D. Seebach, H.Dörr, B.Bastani and V.Ehrig, Angew.Chem. 81, 1002 (1969)
2) $CD_3-(CH_2)_4-CD_3$ was synthesized starting from adipic acid ester via standard methods.

TITLE: SIGNS OF LONG-RANGE CARBON-CARBON COUPLING CONSTANTS

North Texas State University

Denton, Texas 76203

Department of Chemistry

December 3, 1974

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

Dear Barry:

Ever since we started our studies of long-range carbon-carbon coupling constants a few years ago, people kept nagging us when we were going to determine some of the signs. As you may well imagine, the experimental difficulties of determining long-range carbon-carbon coupling constants would be much greater than for, say, carbon-proton and carbon-phosphorous coupling constants. To tell the truth, we could interest no graduate student in attacking the problem. Hence, we could gather data which made it look as if carbon-carbon couplings were similar to carbon-proton and/or proton-proton couplings *if* the respective signs were the same.

However, Denis Miiller (who has just left for a postdoctoral stint with Gary Maciel) has just completed such a study. He synthesized triple-labeled tetrolic ester (1) and did a number of selective spin-decoupling experiments which established the signs to be the same as for the geometrically equivalent propyne (2). Thus, at least for this system carbon-carbon and carbon-proton couplings relate quite well.

We are now planning to convert 1 to other compounds for similar studies.

1

$$\overset{*}{C}H_3-\overset{*}{C} \equiv C-\overset{*}{C}O_2CH_3$$

+20.3

+1.84

2

$$CH_3-C \equiv C-H$$

+50.8

+3.6
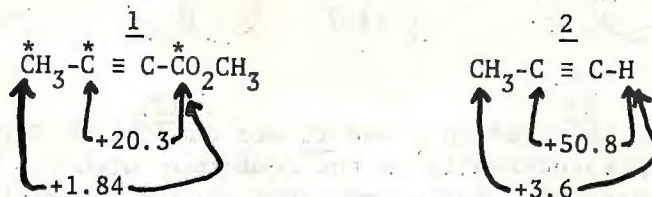
These results, and more details, will appear shortly in JACS.

Sincerely,

Jim

James L. Marshall
Associate Professor

November 20, 1974

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

Effects of Steric Interaction and H-Bonding on the Vicinal Coupling Constant between the Carbinol Hydrogens of the Aromatic Dihydrodiols.

Dear Professor Shapiro:

In the course of the assignment of relative stereochemistry to the dihydrodiols formed from naphthalene and phenanthrene, we have noted that the vicinal coupling constants between the carbinol hydrogens in the trans isomers of these diols are very sensitive to the structure of the remaining aromatic ring. For examples, the coupling constants are found being 10.1, 11.7 and 2.0 Hz for I, II and III, respectively.

$$J_{12}=10.1 \qquad J_{12}=11.7 \qquad J_{34}=2.0$$
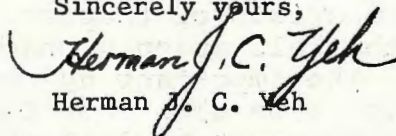
I II III
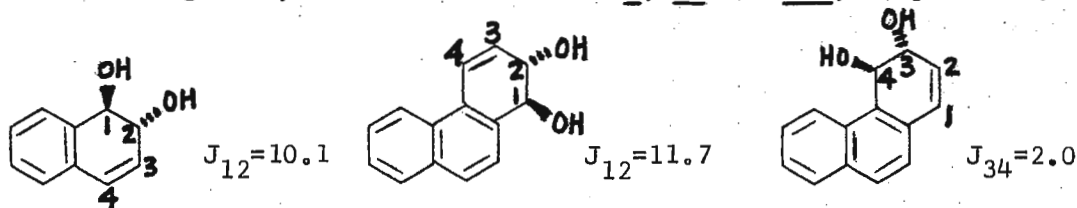
The large coupling constants observed in I and II are due to the fact that these molecules exist preponderantly in the conformer with the OH occupying quasiequatorial positions. Any unfavorable steric interaction between the OH group at C-1 and the peri ring hydrogen at C-8(in I) or C-10(in II) is presumably overcome by internal hydrogen bonding. In III the steric interaction between the hydroxyl group at C-4 and the peri ring hydrogen at C-5 is far more important than the internal H-bonding. Thus, the molecule exists mainly as the conformer with the OH occupying quasiaxial positions. A small coupling constant(~ 2 Hz) was found for this molecule.

To confirm that these molecules are in fast equilibrium between two extreme conformations(OH quasiequatorial v.s. OH quasiaxial) at room temperature, a temperature experiment was conducted in I. The value of the vicinal coupling increases on cooling an acetone solution

of the diol to -70° as anticipated for the increase in the population of the state in which both hydroxyl groups are quasiequatoril. At -70° interconversion between both forms is slow on the nmr time scale, and the presence of both conformers can be detected by inspection of the hydroxyl proton signals. Since the proportion of the minor conformer (both OH quasiaxial) is small($< 10\%$), and the signals due to protons attached to carbon in this form are obscured, the coupling constant J_{12} for this isomer can not be obtained. However, the low temperature coupling constant J_{12} for the pure quasiequatorial(OH) form is found 12.0 Hz.

Study on the energy barrier for the interconversion of this system will be carried out in the near future.

Sincerely yours,

Herman J. C. Yeh

Herman J. C. Yeh

INDIANA UNIVERSITY

Department of Chemistry

CHEMISTRY BUILDING

BLOOMINGTON, INDIANA 47401

TEL. NO. 812—337 5513

November 29, 1974

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

TITLE: RELAXATION PROPERTIES OF NONPROTONATED AROMATIC CARBONS
         OF NATIVE PROTEINS

Dear Barry:

It is becoming increasingly apparent that the resonances of
nonprotonated aromatic carbons provide the greatest opportunities,
in terms of resolution, for using natural-abundance ^{13}C Fourier
transform NMR in studies of individual atomic sites of native
proteins in solution.[1] In collaboration with Dr. Eric Oldfield
and Dr. Raymond S. Norton, I have made a systematic study of the
linewidths, spin-lattice relaxation times, and nuclear Overhauser
enhancements of nonprotonated aromatic carbons (Fig. 1) of some
proteins.[2] A comparison of theoretical and experimental results
indicates that the relaxation mechanism is, in general, predominantly
^{13}C-^{1}H dipolar. The important hydrogens are those two bonds removed
(Fig. 1). In Fig. 1 we also show C^ζ of Arg, because the resonances of
this type of carbon have chemical shifts comparable to those of C^ζ
of Tyr residues. The distances (in Å) of Fig. 1 are based on
published data for amino acids and peptides. Calculated linewidths,
T_1 values, and NOE values are in good agreement with experimental
ones.[2] One useful observation is a uniform lack of appreciable
NOE ($\leqslant$ 30%), in spite of the ^{13}C-^{1}H dipolar relaxation mechanism,
because the effective rotational correlation time is long.[3] As a
result, one does not have to worry about different NOE values for
different nonprotonated aromatic carbons when using integrated
intensities for making a carbon count. However, segmental motion
does introduce some increase in NOE in the case of C^ζ of some Arg
residues.

Differences in T_1 values arise from a different number of
hydrogens two bonds removed (Fig. 1). We have taken advantage of these
differences to identify the resonances of $C^{\delta 2}$ and $C^{\varepsilon 2}$ of Trp
residues[4] by means of the PRFT method.[5] For the identification of
$C^{\varepsilon 2}$ resonances, we use D_2O as solvent, for an obvious reason (Fig. 1).

Best regards,

Adam Allerhand
Professor of Chemistry

References

[1] A. Allerhand, R. F. Childers, and E. Oldfield, Biochemistry, 12, 1335 (1973); E. Oldfield and A. Allerhand, Proc. Nat. Acad. Sci. USA, 70, 3531 (1973); A. Allerhand, R. F. Childers, and E. Oldfield, Ann. N.Y. Acad. Sci., 222, 764 (1973); A. Allerhand, R. F. Childers, and E. Oldfield, J. Magn. Res., 11, 272 (1973).
[2] E. Oldfield, R. S. Norton, and A. Allerhand, to be published.
[3] J. R. Lyerla and D. M. Grant, "Magnetic Resonance," Series One, Vol. 4, C. A. McDowell, Ed., University Park Press, Baltimore, Md., 1972, p. 155.
[4] E. Oldfield and A. Allerhand, J. Amer. Chem. Soc., in press.
[5] R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, J. Chem. Phys., 48, 3831 (1968).
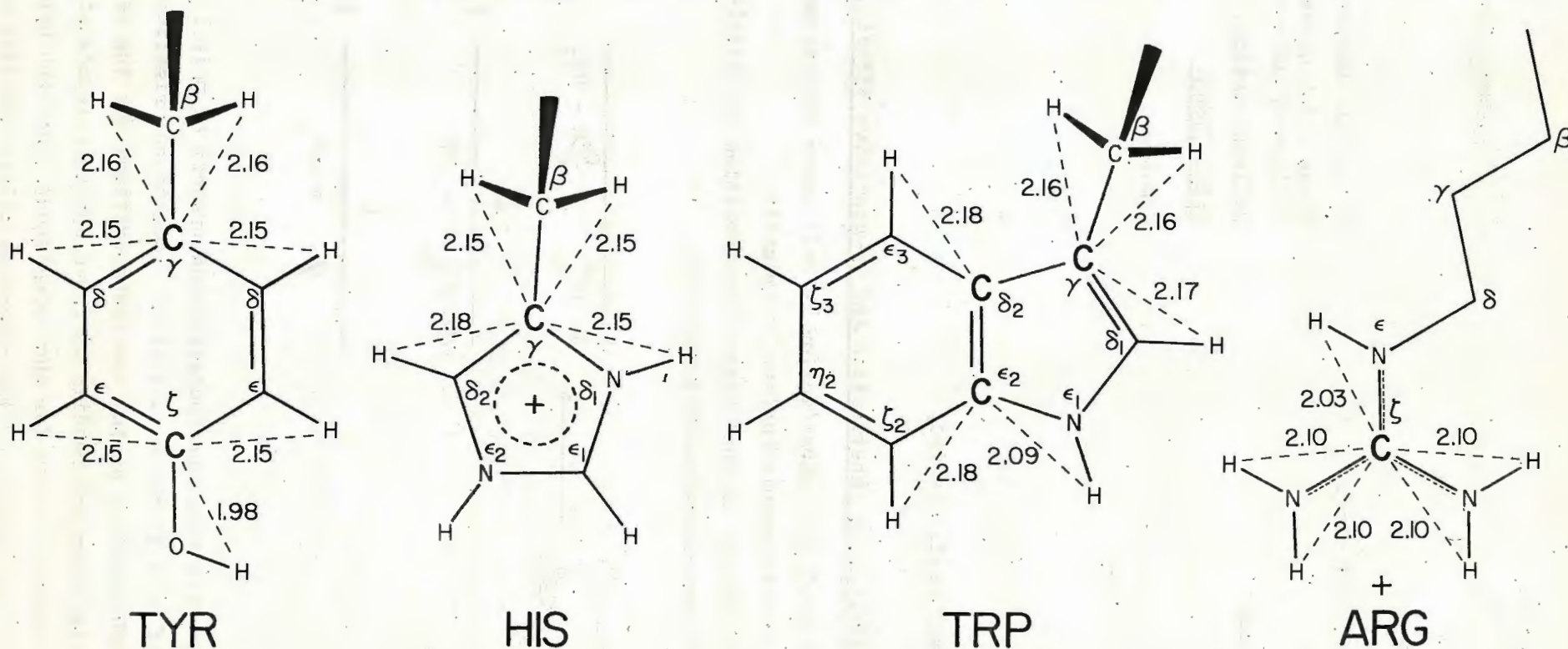
NOT SHOWN: PHE Cγ

Allerhand Figure 1

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT

Afd.:
Wassenaarseweg
Leiden
Telefoon 4 83 33

LEIDEN, 26-11- 19 74.

Drs. J.A. den Hollander,
P.O. Box 75,
Leiden,

The Netherlands.

Prof. B.L. Shapiro,

Texas A & M University,
College of Science,

College Station,

TEXAS 77843.

U.S.A.

Dear Prof. Shapiro,

CIDNP: Pair Substitution and Co-operative Effects.

Radical pair substitution is well known phenomenon in Chemically
Induced Dynamic Nuclear Polarization [1].
An example is the thermal decomposition of acetyl-benzoyl peroxide [2]
in hexachloro-acetone solution.
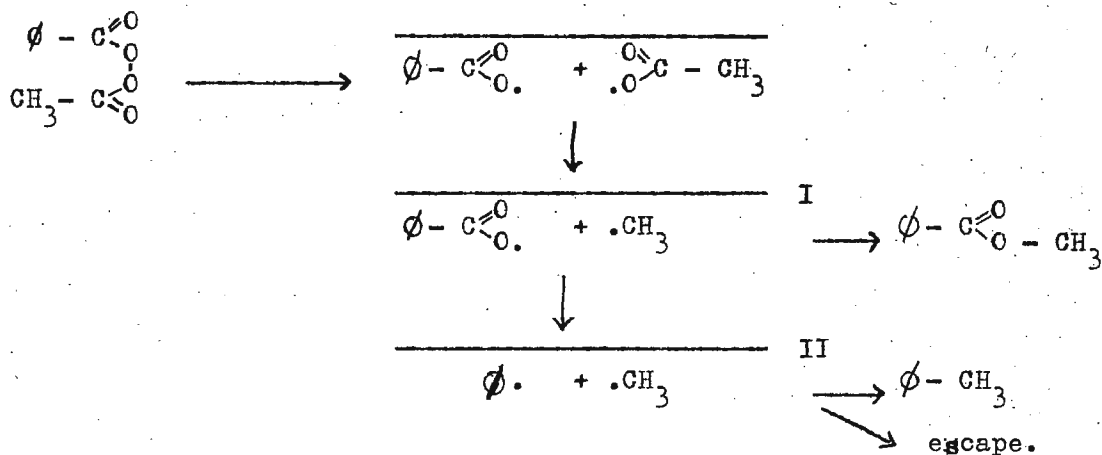
In this case the recombination product of pair I is methylbenzoate,
of pair II toluene. In both products polarizations are observed in the
NMR spectrum during the decomposition. For the methylbenzoate the pola-
rizations are readily assigned using Kaptein's simple rules [3]: we
expect emission for the methylgroup since the hyperfine coupling constant
of the protons of the methylradical is negative and the g-factor of the
benzoyloxy radical is expected to be larger than the g-factor of the

methylradical. The polarizations in the phenylprotons of methylbenzoate
are unimportant, because the hyperfine interactions of the protons in the
benzoyloxyradical are small.

The assignment of the signals in the toluene product is less straight-
forward. The g-factor difference between the phenyl- and methylradical is
very small and can not be responsible for the net effects in toluene.
Some years ago the idea of "memory effect" was proposed [4]: the polarization
due to the singlet-triplet mixing which occurred in pair I shows up in the
products of pair II.
In this way we can easily understand the polarization of the methylgroup
of toluene: is should have the same sign as the polarization of the methylgroup
of methylbenzoate.
However, this "memory effect" model fails to explain the observed emission
for the phenylprotons of toluene: the effects in the phenylprotons of
methylbenzoate are very small, whereas the effect of the phenylprotons
of toluene is in the same order of magnitude as the effect of the methyl-
group of toluene.
Our conclusion is that the "memory effect" model breaks down in this case:
a number of cases are described properly by that model, but it is not
capable to describe all cases.
Therefore we reconsidered the problem of pair substitution. In our new
model we calculate first the singlet-triplet mixing in the first pair and
the spin state function at any time t'. Then we assume that at time t' the
radical pair reacts to pair II and the singlet-triplet mixing goes on from
the spin-state at time t'. We also incorporated the possibility of a second
substitution. In this way we get as a result that the polarisation of
products of pair II is a co-operative effect of the singlet-triplet mixing
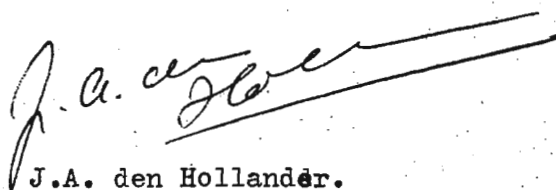in both pairs.
Using this idea it is very straightforward to make qualitative predictions
using Kaptein's simple rules: we should add the ESR parameter of pair I
and pair II together and use the resulting numbers for the prediction.
So in the case of the polarisation of the phenylprotons of toluene we get
as a result: the g-factor difference is large in the benzoyloxy / methyl
radical pair, whereas the hyperfine coupling constants is important in
the phenylradical (this is positive). From this it follows that we have to

expect emission for the phenyl protons of toluene $(\mu \varepsilon \Delta g \, \textit{Æ} \; -+++=-)$.

We want to point out that our idea of "co-operative" effect is more general than the "memory effect" model: all cases explained by the "memory effect" model can also be explained as a "co-operative effect". A paper on this subject will be published shortly. Herein we treat our model in more detail, together with some computer simulations.

Yours sincerely,

J.A. den Hollander.

1) R.A. Cooper, R.G. Lawler, H.R. Ward.
   J. Amer. Chem. Soc. 94, 552 (1972).

2) A.V. Kessenikh, A.V. Ignatenko, S.V. Rykov, A.Ya. Shteinshneider.
   Org. Mag. Res. 5, 537 (1973).

3) R. Kaptein.
   Chem. Comm. 732 (1971).

4) R. Kaptein.
   J. Amer. Chem. Soc. 94, 6262 (1972).

ISTITUTO DI CHIMICA GENERALE
DELL'UNIVERSITÀ DI CATANIA
VIALE A. DORIA, 8 - 95125 CATANIA (ITALY)

CATANIA, 28 November 1974
TEL. 330.533

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

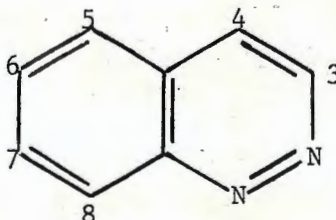Long-range inter-ring couplings in cinnoline.

Dear Professor Shapiro,

We have recently carried out a study of the 250 MHz spectrum of
cinnoline. High-resolution and double resonance experiments
allowed us an accurate analysis of this complex 6-spin system.
The following inter-ring couplings could be detected:

J_{45} = -0.45 Hz;

J_{46} = 0.50 Hz;

J_{47} =-0.36 Hz;

J_{48} = 0.90 Hz.

Theoretical INDO calculations reproduce well in magnitude and
sign the above values.

Best wishes.

Yours sincerely,

G.C.Pappalardo

Now the XL-100A NMR Spectrometer lets you think small.

Thanks to another Varian first, a 1-mm Insert Accessory for the XL-100A Pulsed-Fourier Transform NMR Spectrometer, scientists such as biochemists and pharmaceutical chemists who have to work with limited sample quantities can obtain rapid proton NMR analysis of microgram samples.

Using the insert, it's possible to run spectra of 50 μg or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of Δ^9-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 μg of sample in a 1-mm tube) and Spectrum C (20 μg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.
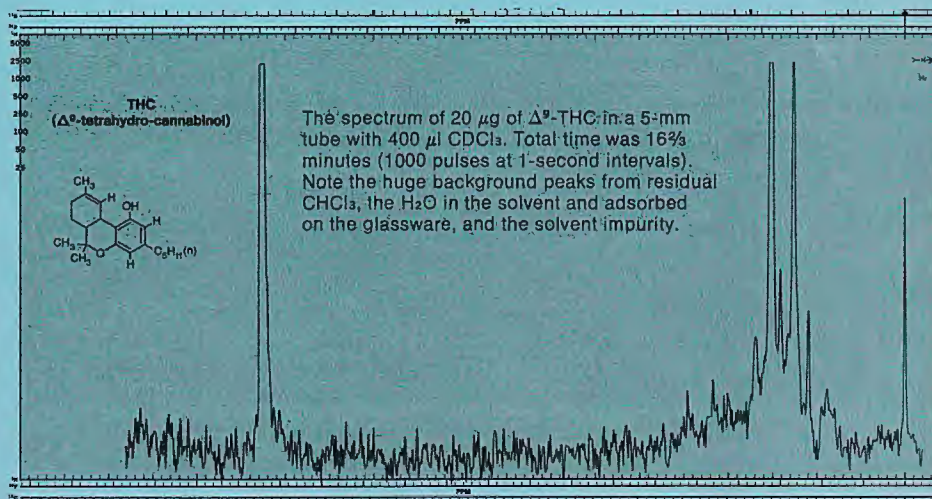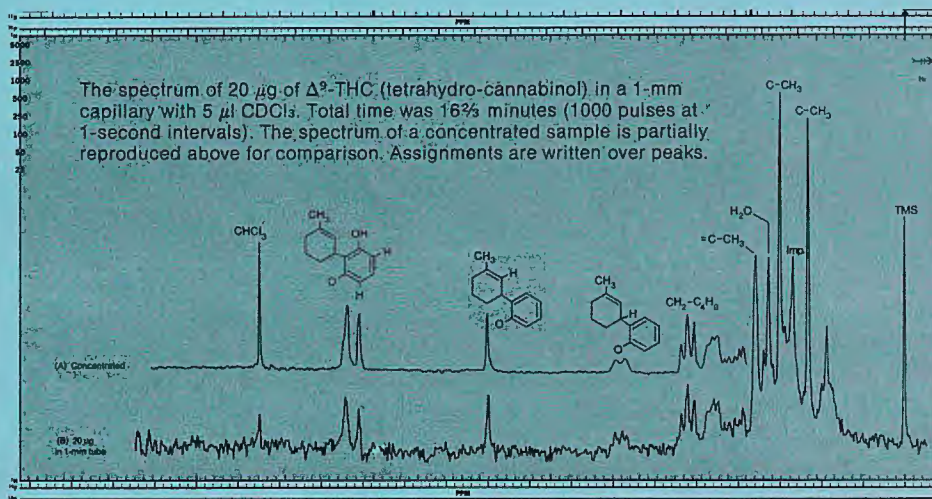
This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5 μl of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

The sample volume in the 1-mm Insert is so much less than the 400 μl required for 5-mm tubes that use of deuterated species becomes more economical.
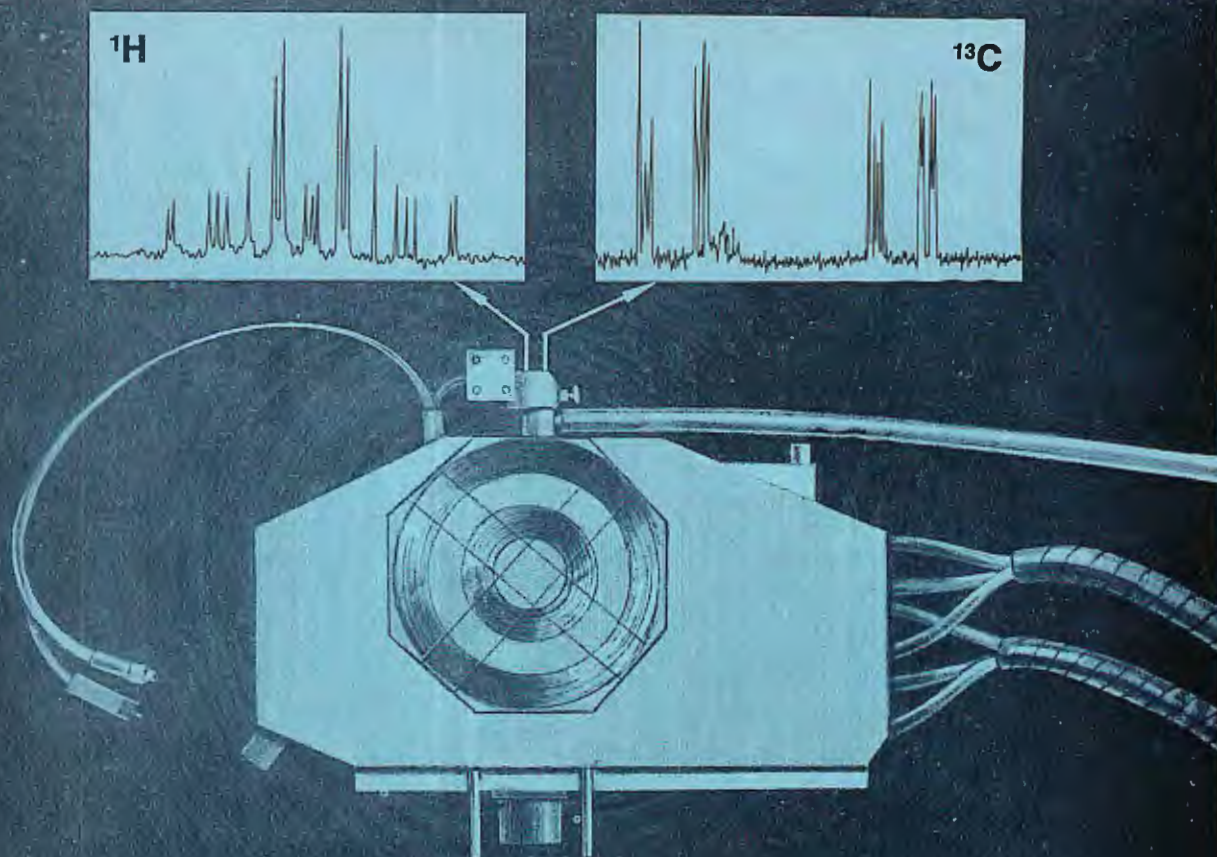
The 1-mm capillary has its own spinner turbine attached. Unlike other existing techniques designed to accommodate small quantities of samples, there are no plugs to adjust and no sample positioning is necessary. Proper positioning is automatic thereby assuring reproducible homogeneity.

Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.

The spectrum of 20 μg of Δ^9-THC (tetrahydro-cannabinol) in a 1-mm capillary with 5 μl CDCl3. Total time was 16⅔ minutes (1000 pulses at 1-second intervals). The spectrum of a concentrated sample is partially reproduced above for comparison. Assignments are written over peaks.

(A) Concentrated

(B) 20 μg in 1-mm tube

THC (Δ^9-tetrahydro-cannabinol)

The spectrum of 20 μg of Δ^9-THC in a 5-mm tube with 400 μl CDCl3. Total time was 16⅔ minutes (1000 pulses at 1-second intervals). Note the huge background peaks from residual CHCl3, the H2O in the solvent and adsorbed on the glassware, and the solvent impurity.