Texas A & M University N – M – R Newsletter

No. 145
OCTOBER, 1970

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

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

MONTECATINI EDISON S.p.A.

SEDE IN MILANO - CAPITALE L. 749.000.000.000 INTERAMENTE VERSATO

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DIREZIONE GENERALE RICERCHE E BREVETTI

DIRI
CENTRO RICERCHE DI BOLLATE

Bollate, September 10, 1970

Si prega indirizzare la risposta a:
MONTECATINI EDISON S.p.A.
DIRI Centro Ricerche di Bollate
Via S. Pietro, 50
20021 Bollate (Milano)

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

our ref.: 6408   LC/vr

Subject: <u>NMR spectrum of diiodotetrafluorocyclobutene</u>

Dear Professor Shapiro,

during the sabbatical leave spent this Spring at East Anglia University, where I worked with Dr. R.K. Harris, I tackled a few problems of NMR analysis. I like to report here the results obtained in the analysis of the diiod<u>o</u> tetrafluorocyclobutene.

The normal NMR spectrum of such a molecule consists of a single line resonance at $\phi^* = 113.1$, since all the fluorine nuclei are equivalent. In order to obtain information about the coupling constants we have observed the ^{13}C satellite spectrum of the mole<u>e</u> cule containing one ^{13}C atom on the CF_2 group. The spectrum can be treated as an approximate AA'XX' system[1] where the two geminal coupling constants are equal and large (J^{FF}_{gem} = ca. 200 c/s).

The pattern expected must be a simple five-line pattern with intensities 1:2:2:2:1 if $|L| > |N|$ or 2:1:2:1:2 if $|N| > |L|$. The spectrum of the diiodotetrafluorocyclobutene is of the type $|L| > |N|$, and it is therefore immediately clear that J_{vic} and J'_{vic} (cis and trans coupling constants) are opposite in sign. The low-field $^{13}CF_2$ spectrum at 94.07 Mc/sec is reported in Figu re and is consistent with K and N having the same sign[2], which

./...

Mod. 92/14

MONTECATINI EDISON S.p.A.

Direzione Generale

Ricerche e Brevetti

Centro Ricerche Bollate

must be positive because of the known sign of J_{gem}^{FF}. The results are collected in table with those already known[2] of two related compounds[2]. The assignment of J_{trans} and J_{cis} has been done on the basis of results obtained by Newmark on unsymmetrically substituted cyclobutenes[3].
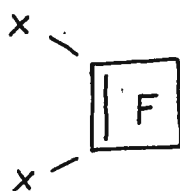
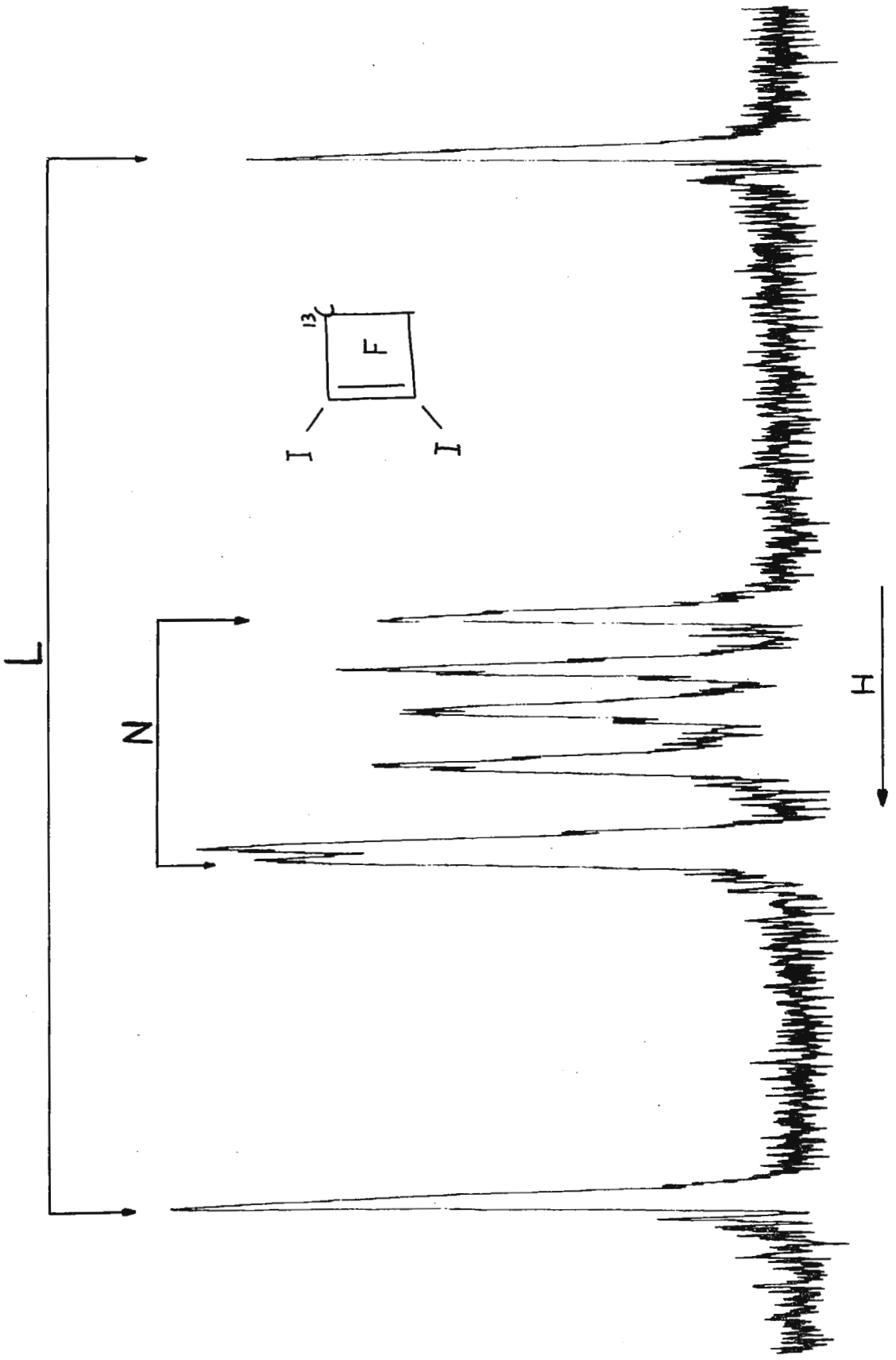| X	$\phi^{*}(CF_2)$	J_{trans}	J_{cis}
I	113.10	24.47	- 15.35
Cl	118.47	25.13	- 12.77
F	120.75	26.50	- 12.27

With best regards,

Yours sincerely,

Luciano Cavalli

L. Cavalli

1) N. Sheppard and J.J. Turner, Proc. Roy. Soc., A 252, 506, 1959

2) R.K. Harris and V.J. Robinson, J. Magn. Res., 1, 362, 1969

3) R.A. Newmark, G.R. Apai and R.O. Michael, J. Magn. Res., 1, 418, 1969

UNIVERSITY OF CALIFORNIA, DAVIS

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DEPARTMENT OF CHEMISTRY   DAVIS, CALIFORNIA 95616

September 5, 1970

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

Si^{29} NMR; Iron in the Probe

Dear Barry:

Recently Roger Scholl of our department has applied the synthesizer-based, C^{13}-centerband-sweep, F^{19} lock system of our modified HA-100 (Bartuska, Nakashima and Maciel, <u>Rev. Sci. Instr.</u>, in press) to Si^{29} magnetic resonance. The attached figure gives an idea of the types of signals he's obtaining.

In the process of probe modification he ran into the difficulty that electronics technicians sometimes forget about the fact that probe components must be non-ferromagnetic. Indeed, some components that "look" as if they shouldn't be ferromagnetic turn out to have this undesirable property. In a tongue-in-cheek attempt to dramatize this fact one of our other students, Mark Bacon, wrote a parody on this experience. It was meant only for local exposure, but I include excerpts here.

Best regards,

Gary E. Maciel
Professor of Chemistry

GEM:mim
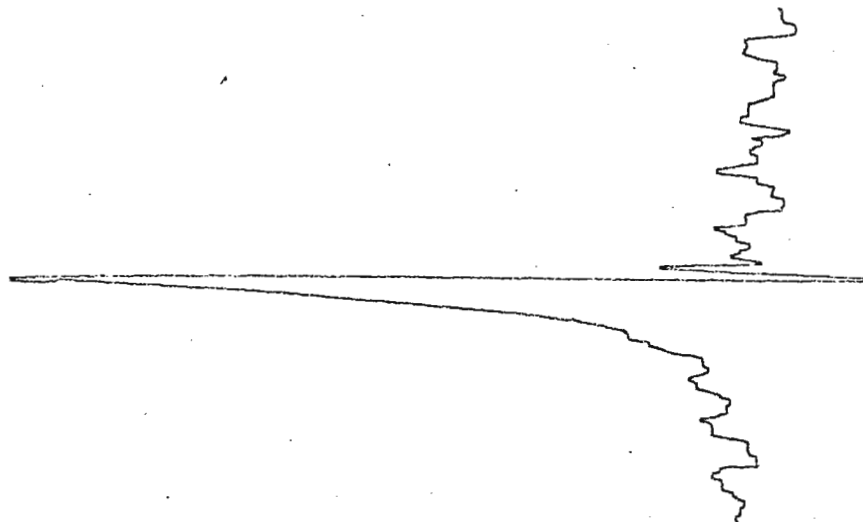
Centerband-sweep Si^{29} spectrum of TMS, using internal F^{19} lock and proton decoupling, natural abundance, eighteen scans, about one Hz line-width.

An Iron Probe for Doing Ultra-Wide-Line NMR(?) Under High Resolution Conditions*
by Roger L. Scholl

ABSTRACT

Herein is described an NMR probe quite unlike any ever before thrown together. Only the probe body is non-magnetic; all internal components were meticulously screened for their ferromagnetic properties. A good initial test of the completed unit is the suck-in test: is the operator yanked off his feet and strained through the magnet polefaces by the field, while trying to slide the probe into the magnet? The author is presently recuperating in a local hospital from the effects of this test.

Impedances were matched to within ± 0.01 ohm of the desired value with the aid of a Boonton RX meter, to insure highest sensitivity consistent with ultra-wide lines. This probe gives barely perceptible base line bumps when ordinary high-resolution probes give 0.5 Hz lines. The probe promises to unlock a whole new realm of ultrawide-line NMR under high resolution conditions. This area of NMR has hitherto been scoffed at by even the most naive of NMR practitioners.

ACKNOWLEDGEMENT

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Zürich

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Universitätstrasse
Tel. (051) 32 73 30

9 September 1970

Professor Bernhard L. Shapiro

Department of Chemistry

Texas A+M University

College Station, Texas 77843

Dear Barry,

1. Fourier Difference Spectroscopy

Many people may have gained the impression that Fourier
spectroscopy is rather pretentious with regard to instrumental sophi-
stication. The contrary is true. Except for the indispensable computer
system, Fourier spectroscopy is less demanding than conventional
spectroscopy. At first, it is possible to dispose of the linear field
or frequency sweep because Fourier spectroscopy is a stationary method.
In this letter, I would like to demonstrate a new method which further
allows to eliminate the field-frequency lock, the field modulation
units and even the flux stabilizer.

This method, it may be called "Fourier difference spectros-
copy", is based on the use of a linear or quadratic detector to record
only difference frequencies between a strong reference line and the
weak resonances of the sample to be investigated. These difference fre-
quencies are to a very good approximation independent of variations of
the magnetic field strength.

Usually, we put a 1 mm capillary filled with a suitable
reference substance (TMS, H_2O or H_2SO_4 for proton resonance) into the
sample to be investigated. The radio frequency pulses for the excita-
tion of the free induction decays are selected strong enough to cover
the total frequency range through which the resonance lines could drift
as caused by the variations of the magnetic field. The composite sig-
nal of reference and sample is passed through a diode detector (as it
is already contained in the Varian rf unit V4311) to generate the
difference frequencies. A low-pass filter eliminates the rf frequencies
and passes the desired difference frequencies only, as shown in Fig.1.

The signal consists of an approximately exponential decay caused by the envelope of the reference signal decay and superimposed are the weak difference frequencies caused by the sample resonances. The reference signal is suppressed as shown in Fig. 2 (we use a legendre polynomial approximation to the original signal, Fig. 1, to extract the reference response which is then subtracted). The remaining signal, Fig.2, is equivalent to a free induction decay of the sample signal alone with its zero frequency at the position of the reference line. Its Fourier transform gives a spectrum with enhanced sensitivity equivalent to that of conventional Fourier spectroscopy. Figure 3 shows the Fourier transform of Fig. 2 and may be compared with a single scan recorded in the same total time on the same instrument as shown in Fig. 4.

The operation of this system is extremely simple. The only critical adjustment concerns field homogeneity. But this operation could easily be automated(Rev.Sci.Instr.$\underline{39}$,998,1968). The free induction decay stays for days invariably on the scope. It is quite insensitive to spurious field modulation, like power line frequency modulation. Because of the large dynamic range of the composite signal, some attention must be paid to the digitization error of the A/D converter (compare IIT-NMR Newsletter $\underline{112}$, p.53). We used a 9 bit + sign converter which may be at the lower limit, but it did not affect the results. The spectra are sensitive to spinning side bands of the reference line (Fig.3) and also to possible C^{13} sidebands which may appear to be quite strong.

Fourier difference spectroscopy provides an intriguing possibility to solve the notorious field-frequency lock problems in NMR. It also can easily be adapted to more sophisticated refocussing schemes. A more complete account of this work will be published soon.

2. Postdoctoral Fellowship Available

I would like to mention that there is a postdoctoral fellowship available for doing research in our NMR group which is

concerned with new NMR techniques including pulse experiments, solid state resonance and multiple resonance. The fellowship is granted for one year and the salary amounts to 24'000.- Swiss Francs/year.

Best regards,

Richard

Richard R. Ernst

Fig.1: Sum of 128 free induction decays of 0.2% ethyl ether and of a reference capillary filled with H_2O/D_2O 1:3 as appearing at the output of the diode detector (60 MHz, pulse spacing 2 sec)
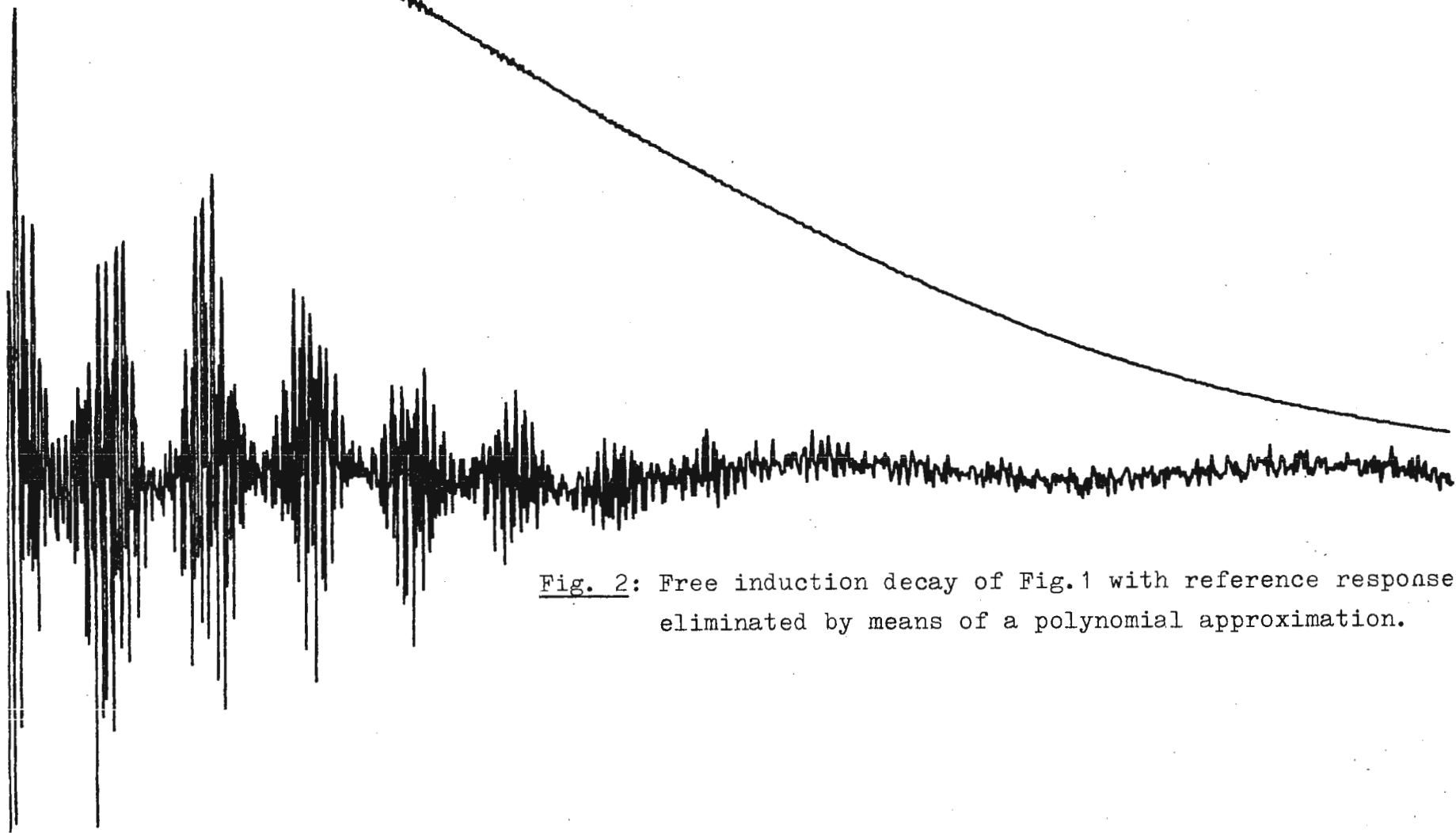
Fig. 2: Free induction decay of Fig.1 with reference response eliminated by means of a polynomial approximation.

Fig. 3: Fourier transform of Fig. 2

$$S/N = 2.5 \cdot \frac{60}{6} = 25.0$$

Residual reference
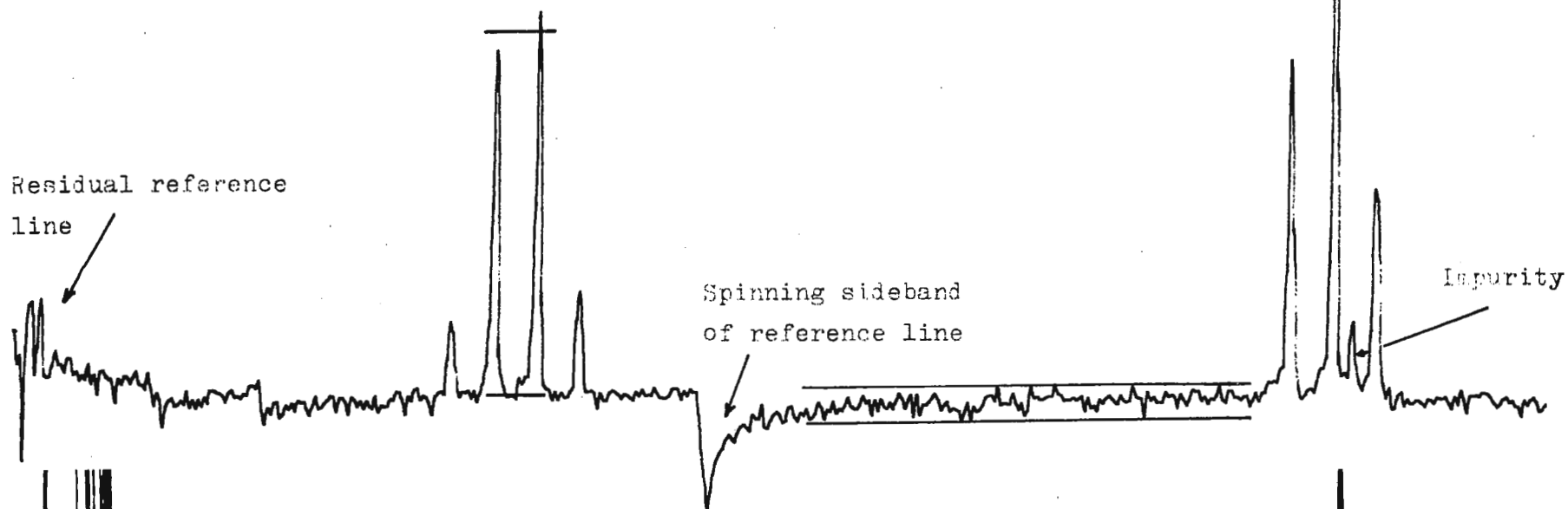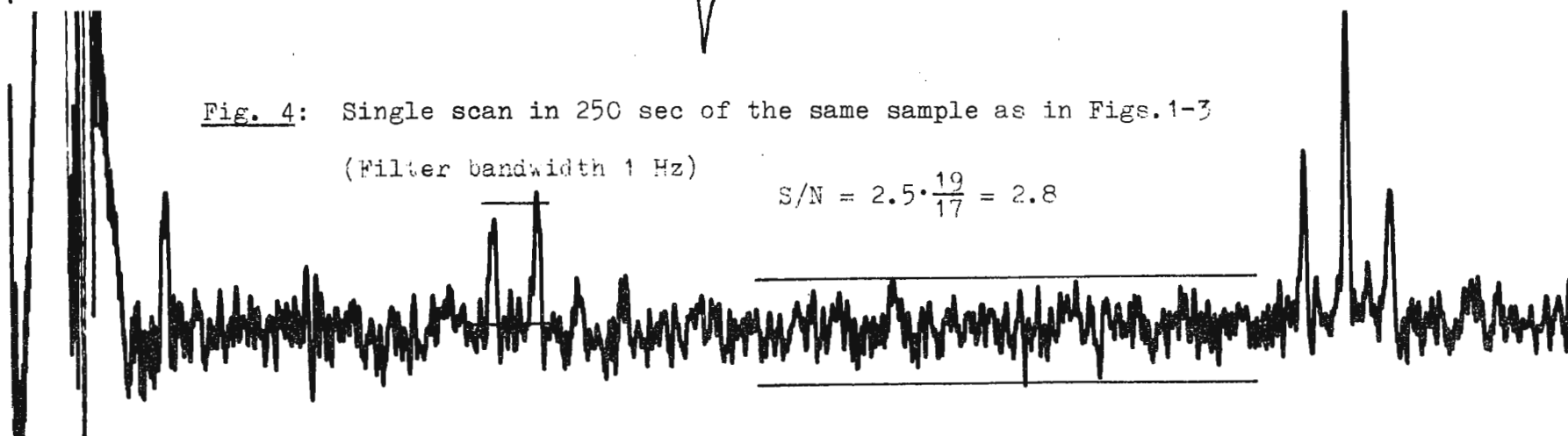line

Spinning sideband
of reference line

Impurity

Fig. 4: Single scan in 250 sec of the same sample as in Figs. 1-3

(Filter bandwidth 1 Hz)

$$S/N = 2.5 \cdot \frac{19}{17} = 2.8$$

UNIVERSITY OF SASKATCHEWAN REGINA CAMPUS

DEPARTMENT OF CHEMISTRY   REGINA SASKATCHEWAN

September 10, 1970.

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

> Titles: 1)   NMR of thiocarbamate herbicides
>   2)   Video-taped Spectroscopy Programs Available

Dear Dr. Shapiro:

sub 1:   On the premise that (research) money is only to be found in polution problems we recently ran NMR spectra (at variable temperature) of eight commercially used thiocarbamate herbicides. For all of these we determined the coalescence temperature t_c for the $S-C-NR_1R_2$ alkyl protons, finding a range from $t_c = +35^\circ$ C (for molinate) to $t_c = -1^\circ$ C (for pebulate). Reasoning that higher t_c values are equivalent to higher polarity in the amide group, we sought to correlate the t_c values with other physical, chemical and biological properties. We found no correlation between t_c and general herbicidal activity and rate of chemical breakdown. There are crude correlations between t_c and solubility, rate of leaching and rate of microbial breakdown. Within a group of chemically similar thiocarbamates (change in alkyl groups) t_c correlates with toxicity. Finally, t_c correlates inversely with adsorptivity (on clay), the inversion probably being due to the negative heat of solution of thiocarbamates in water. A paper (with full details) will be published shortly in J. Agr. Food Chemistry.

sub 2:   In the past year or so I have made a number of videotapes (mix of film, graphies, stills and "live" studio presentation) on the proper operation of spectrometric equipment. They are intended as do-it-yourself instruction. We use them for all our 3rd and 4th year students taking spectroscopy, for newly arrived graduate students and so on via a monitor room where they can dial the required program.

We have considered that we could sell copies of these. We have facilities to dubb onto 2" Quad., 1" Ampex or ½" Sony. We are not certain about prices, but it might be about $5.00 per minute of program plus tape costs. (altogether less than 10% of the production costs!). We can also loan tapes for anyone who considers himself a serious potential buyer.

Professor B. L. Shapiro   September 10, 1970
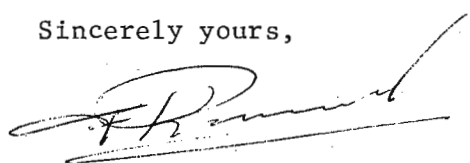
At the moment we have the following programs:
1) Introduction to NMR (40 min)
2) The Varian A-60A; recording a spectrum (36 min)
3) The Varian A-60A; Tuning Procedures (41 min)
4) Atomic Absorption Spectroscopy; the Techtron AA-100 (22 min)
5) Infrared Spectroscopy (42 min)
      a) Recording Spectra with the Beckman IR-8 (19 min)
      b) Sampling Procedures (23 min)

The programs are of professional technical quality (thanks to our excellent AV-TV Centre) while on my side I am preaching my usual gospel "do not touch any knob, until you know what is behind it and what effects it can have on your data".

Anyone interested should write directly to the undersigned.

Sincerely yours,

F. H. A. Rummens,
Associate Professor of Chemistry.

FHAR/ivg

Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry · TEL. (603) 646-2501

September 15, 1970

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

Spin Echoes with a CAT, a BAT, and a Time Shared Computer

Dear Barry:

We have been measuring the fluorine relaxation times of some
p-fluoropolystyrene solutions recently. We are primarily interested
in the molecular weight dependence of the relaxation times. Keizo
Matsuo has prepared samples over a wide range of molecular weights.
It is too early to say anything about the results, but I thought some
of the readers of the newsletter might be interested in the instru-
mental setup we are using to measure T_2 by the Carr-Purcell-Meiboom-
Gill method. The basic idea is to use the Varian C-1024 not only to
record the data, but to control the experiment and to transmit the
digital data directly to the computer.

The data transmission problem was solved for us by a local moon-
light engineering firm (I.D.M. Inc., Hanover, N.H. 03755). The inter-
face lives in a 4x4x6 inch box, including power supply and controls,
plugs with a single cable into a very slightly modified 33 ASR teletype,
and can dump the contents of the CAT into the Dartmouth Time-Sharing
System in about five minutes. The time limitation is the teletype data
transmission rate. Briefly, the thing works by coding the 17 bit word
in each channel of the CAT into two six bit words and one five bit word
in a shift register. The necessary control bits are loaded and then
sent serially to the teletype. The coding of the data is such that each
word is a printable character (including blank), and the output is
divided into 64 lines 16 channels long that look like this:

    "+T(/)*O"+K+]"+]"+X",1",1",?",5",A",8",C",B",A

One could learn to read this if he were willing to learn a 32 digit
number system (=0,!=1,etc.). However, a simple basic program turns
this apparent nonsense into numbers, integrates the echoes, and does
a weighted least squares fit to find T_2 in a little over one second of
central processor time. The 10 minutes required to get from an acceptable
record in the CAT to a T_2 value is peanuts compared to the time required
to work up any type of analogue record. We have been getting T_2 repro-
ducible to about 1 percent on solutions with 24 mg of polymer per ml of
solution (.2M in F).

The technique for using the CAT to control the experiment is based
on the binary output jack on the back. After spending an evening with the
CAT manual and the oscilloscope I figured out what all those pins were
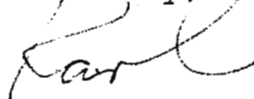doing. Nine of them present a parallel binary channel number.

In our case the interface between the CAT and the Tektronix type 161 pulse generators controlling our modified V-4311 rf unit is a Tektronix 547 dual time-base oscilloscope. A line from one bit of the channel number (which bit depends on how many echoes you want) is connected to the external trigger input of the scope. Suppose the fifth bit is so connected. When the CAT is triggered and address advance pulses begin, nothing happens to bit 5 until 16 pulses have been applied, then it goes on. The CAT has now gathered 16 samples of the baseline. The rising edge of bit 5 going on triggers one time base of the scope which in turn triggers the 90° pulse. This time base is set for a time long compared to the full CAT sweep, and so fires only once. The next 16 samples the CAT gathers are of the tail following the 90° pulse. At the 32nd address advance pulse bit 5 goes off, triggering the other time base with the negative going signal. This time base triggers a 180° pulse and is set for a time short enough that it is ready to fire when bit 5 again goes off 32 address advance pulses later. Thus we get 32 samples of each of 31 echoes. Successive experiments are in perfect registration and the limitation on the number we can accumulate is presently set by field instability. We are using a high resolution magnet with flux stabilizer control.

I have not yet been able to think of a correspondingly simple way to control T_1 measurements.

Please credit this to Dick Shafer's account as usual.

Sincerely,

Karl F. Kuhlmann
Assistant Professor
of Chemistry

KFK/blw

SIMON FRASER UNIVERSITY

Department of Chemistry

BURNABY 2, BRITISH COLUMBIA
Telephone 291-3111 Area code 604

21st September, 1970.

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

Dear Barry,

Bromide Ion Probe Studies of Haemoglobin

Following Stengle and Baldeschwieler's work with Cl^- [J.A.C.S. 89, 3045, (1967)] we have recently been investigating the use of Br^{79} and Br^{81} as probes for determining the properties of mercury binding sites in proteins by signal averaging the Br free induction decay at 15 Mhz. Our conclusions on equine haemoglobin are:

1) There are approximately two active - SH groups capable of binding mercury in the haemoglobin tetramer, although variations in this number (1.5 - 2.6) are noticeable between different samples from the manufacturer (Pentex Inc.). This is in agreement with the results of Stengle and Baldeschwieler and with most other workers using standard analytical techniques.

2) The appropriate transverse relaxation rate expression for halogen X ($I = 3/2$) probe experiments is:

$$R_2 - R_{2,o} = \left\{ \tau_{ex} + 10\left(\frac{\hbar}{e^2qQ}\right)^2 (1/\tau_{ex} + 1/\tau_c) \right\}^{-1} [Hg]/[X^-] = \alpha[Hg] \qquad (1)$$

for a suitably homogeneous magnet, where $R_{2,o}$ and R_2 are the relaxation rates before and after the addition of HgX_2 to the protein - halide solution; $\tau_{ex} = \{k_1[X^-]\}^{-1}$ is the mean lifetime for bound halogen, and τ_c is the correlation time for reorientation of the Hg-Br bond at the bound site. Three limiting regions for the exchange follow from this equation:

..2..

i) $\tau_{ex} \gg T_{2,bound}$,   <u>slow</u> exchange limit, τ_{ex} only obtainable

ii) $\tau_c \ll \tau_{ex} \ll T_{2,bound}$,   <u>fast</u> exchange limit, τ_c only obtainable

iii) $\tau_{ex} \ll \tau_c$,   <u>extreme</u> exchange limit, τ_{ex} only obtainable

Region ii) has been assumed by all workers concerned with probe techniques to date. We find that this assumption may not always be valid with chloride probes. For bromide, the marked decrease in $T_{2,bound}$ due to larger $(e^2qQ)^2$ places the two Br isotopes in the intermediate region between i) and ii). Here it is possible in principle to extract <u>both</u> τ_c and τ_{ex} from the $[X^-]$ dependence of α, with a check from comparison of the two isotopes.

The region between i) and ii) has been discussed by O'Reilly et al. [J. Chem. Phys. <u>39</u>, 1756, (1963)] and that between ii) and iii) by Marshall [J. Chem. Phys. <u>52</u>, 2527 (1970)].

3) The $[Br^-]$ dependence of α^{-1} is not linear in the i)-ii) region as predicted by Eq.(1). We interpret this salt effect on haemoglobin as being due to a decrease of τ_c with NaBr concentration at constant pH. This conclusion is at variance with that of Stengle and Baldeschwieler on Cl^-, caused we think by their neglect of the (small) effects of the exchange rate.

4) Both τ_c and τ_{ex} are influenced by pH. k_1 decreases slightly from pH 7 to pH 10.5.

5) Not enough is known about e^2qQ in the Protein-S-Hg-Br environment to be certain about the true average value of τ_c. Using $e^2qQ = 320$ Mhz estimated for solid $HgBr_4^=$ complexes [O'Reilly et al.], we estimate τ_c for haemoglobin in 1M NaBr at pH 7 to have the remarkably small value 10^{-10} sec. This is about an order of magnitude smaller than that measured by Stengle and Baldeschwieler with Cl^- and may indicate a differential salt effect between Cl^- and Br^- on the overall conformation of the protein.
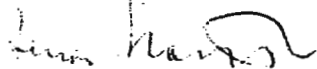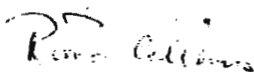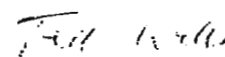
A more detailed report is being prepared.

With best wishes,

Z. Starcuk   R. Collins   E.J. Wells

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

September 23, 1970

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

Dear Barry:

High-resolution C-13 Spectrum of Acetone

During the past several months we have been working intensively
with high-resolution C-13 spectra. These have been obtained on
our Bruker HFX-90, using a Fabri-Tek 1074 for time averaging.
During the course of this work we had occasion to evaluate our
resolution and sensitivity under appropriate operating condi-
tions.

The inclosed figure illustrates the performance we are able to
obtain under the conditions detailed in the caption. This is
the spectrum of the lower-field of the two central resonances
of the large (methyl) quartet in acetone. This small quartet
shows a long-range coupling, $^3J_{CH}$, of 1.48 Hz. The line width
at half height is within 0.5 Hz, which is typical of the results
we have been obtaining by time-averaging on natural abundance
samples.

No especial or unusual steps were taken in preparing the sample.
The acetone used was the Matheson-Coleman-Bell product trans-
ferred from the bottle to the sample tube without out-gassing or
sealing.

We would like to learn what resolution has been obtained in
other laboratories on natural abundance C-13 spectra with time
averaging.

Sincerely,

A. R. Tarpley   J. H. Goldstein

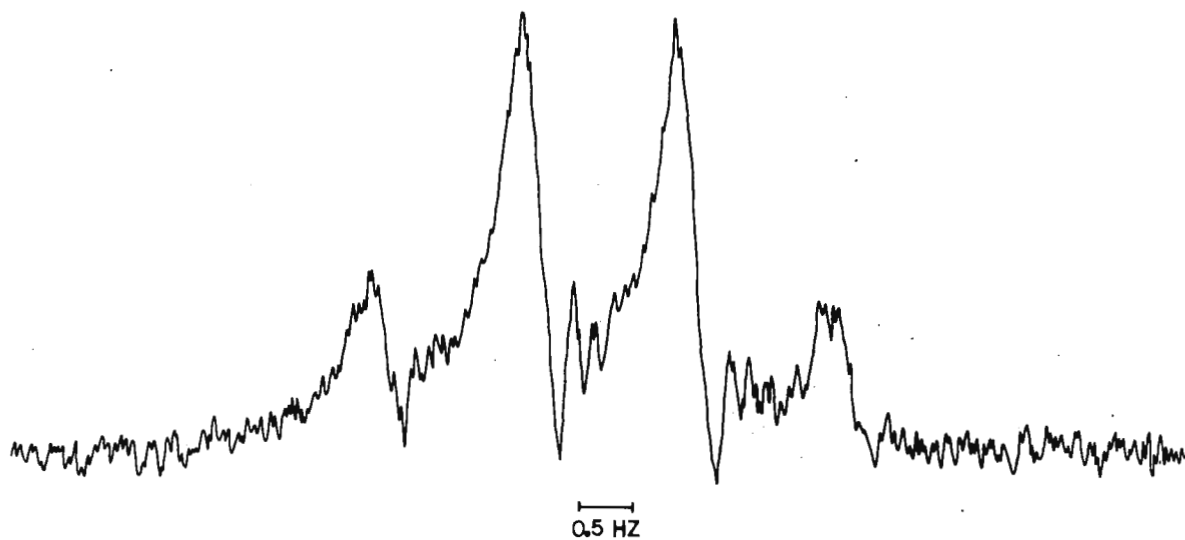JHG:lt

0.5 HZ

Figure 1.   The natural abundance carbon-13 spectrum of the small
            quartet in neat acetone. The spectrum was time
            averaged for 32 scans at a sweep width of 0.2 Hz/cm
            and a sweep time of 3.3 sec/Hz in a 13 mm sample tube.
            Proton stabilization on the methyl resonance of ace-
            tone was employed.

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September 23, 1970

Prof. B.L. Shapiro
Department of Chemistry
Texas A.& M. University

College Station, Texas 77843

USA

"Homonuclear INDOR for Structure Elucidation"

Dear Barry:

INDOR experiments have been performed in hetero- and homo-
nuclear systems. Applications however are rather scarce and
according to a recent review article on the subject [1] have
been focussed either on the determination of chemical shifts
of nuclei other than protons or on the determination of relative
signs of coupling constants and energy level diagrams. We do
not know about an application of $^1H,^1H$-INDOR to solve a comp-
lex structural problem.

Recently we modified our HA-100 spectrometer according to the
instructions of Varian AG Switzerland [2] and we have started
to investigate the potential of this double resonance method
for structural studies.

As a first example we wish to present the complete structure
elucidation of a dimer of 11,13-dioxo-12-methyl-12-aza[4.4.3]
propellane 1.

$\underline{1}$ $\underline{2}$ $C_{26}H_{22}O_4N_2$
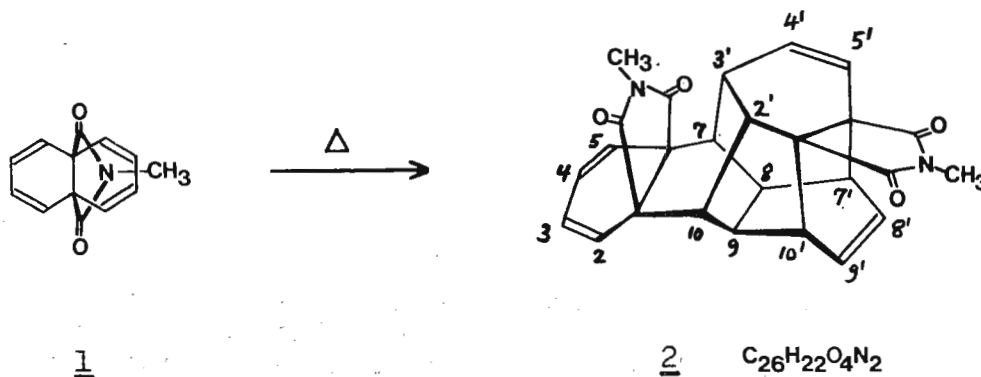
The 100 MHz and 220 MHz spectra of the dimer (fig. 1) are very complex and do not permit an analysis by conventional double resonance techniques. In the 100 MHz spectrum only <u>four</u> protons exhibit resonances which are clearly resolved whereas the signals of <u>twelve</u> protons show extensive overlap in the vinylic region and in the two aliphatic regions. Two N-methyl signals indicate that the dimer has an unsymmetrical structure.

An expanded spectrum (fig. 2) of the 8 vinylic protons illustrates how the hidden resonance lines of H-5' can be located precisely by INDOR using lines of H-4' as monitor transitions. Similarly, using H-8' as a monitor proton, hidden lines of the vinylic neighbour H-9' and of the two aliphatic protons H-7' and H-10' could be determined (fig 3a).

An important extension of the technique is illustrated in fig. 3b. A hidden line of H-9' which has been determined by INDOR can be used as a monitor line for consecutive INDOR experiments. The importance of consecutive INDOR for structure elucidations is demonstrated in fig. 4 which shows that it was possible, starting from only three directly observed protons, to determine the chemical shifts and coupling constants of eleven of the twelve skeletal protons of the dimer. The vicinal coupling constants obtained are in good agreement with torsional angles estimated from a model of the dimer <u>2</u>.

The technique of consecutive INDOR has also been successfully applied to determine the parameters of the four diene protons H-2, H-3, H-4 and H-5. The signals of three of these protons are hidden. Starting from only six primary monitor lines, we have been able to obtain 32 INDOR lines which were used to analyse the four-spin system.

A detailed account of this work is in press [3] and we are engaged in further studies on carbohydrates and peptides.

With best wishes,

Yours sincerely,

W.von Philipsborn   O.Sciacovelli

[1] V.J.Kowalewski in: Progress in NMR Spectroscopy, Vol.5,1969

[2] U. Scheidegger, TAMU NMR Newsletter No. 126, 28 (1969)

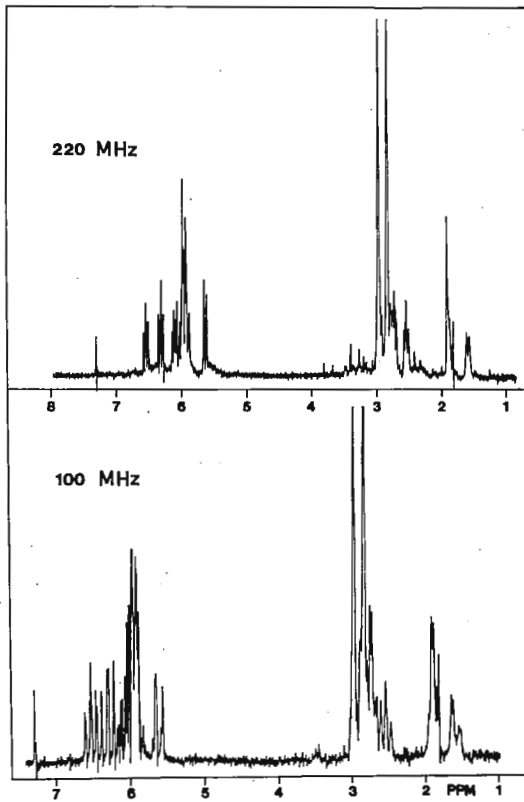[3] O. Sciacovelli, W.von Philipsborn, C. Amith & D. Ginsburg, Tetrahedron <u>19</u>, 4589 (1970)

220 MHz

100 MHz

fig. 1

H-8'   H-4'

650   600   550

640,3
632,8   590,8

                                   590,0
599,9
                                            H-5'

599,0

fig. 2

a)
J_{8'9'}
J_{10'9}   J_{7'8}
J_{10'8'}   J_{7'8}

H-8'
655,1

H-9'   H-10'   H-7'
VINYLIC   ALIPHATIC

10 Hz

b)

H-9'
588,8

J_{10'8}   J_{7'9}
J_{10'9'}   J_{7'8}
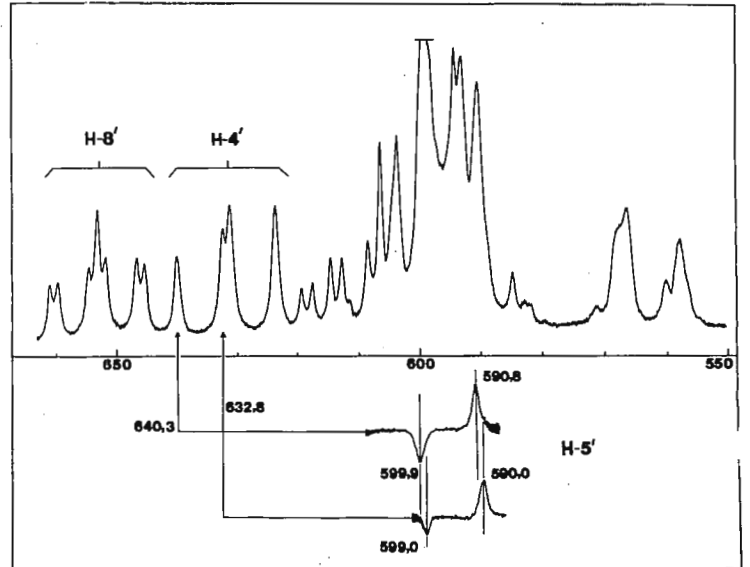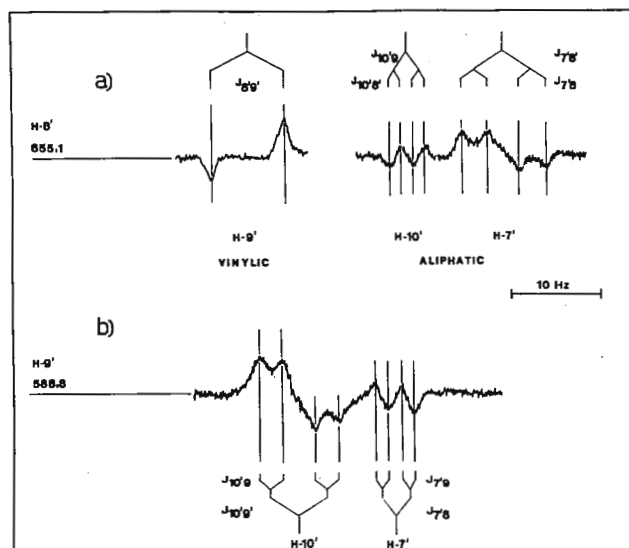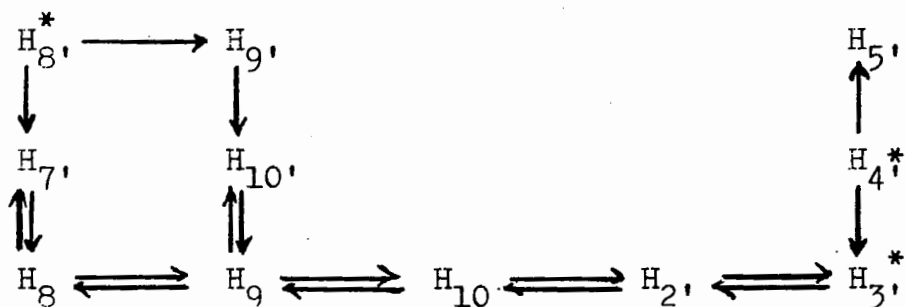H-10'   H-7'

fig. 3

fig.4 Sequence of protons as derived from INDOR
       * indicates directly observed protons

H-C(3')	2.55 ppm	J(3'2')	5.5 Hz;	J(3'5')	0.9 Hz
H-C(4')	6.32	J(4'5')	8.9	J(4'3')	7.8
H-C(5')	5.95				
H-C(7')	2.77	J(7'8') 6.5 J(7'8) 2.8		J(7'9')	1.2
H-C(8')	6.53	J(8'9')	8.1	J(8'10')	1.3
H-C(9')	5.97	J(9'10')	6.2		
H-C(10')	2.85	J(10'9)	2.8		
H-C(8)	1.91	J(8 9)	10.5		
H-C(9)	1.60	J(9 10)	2.0		
H-C(2')	2.95	J(2'10)	6.1	J(2'9)	2.0
H-C(10)	2.71				
H-C(2)	5.63	J(2 3)	9.5	J(2 4)	0.8
H-C(3)	6.10	J(3 4)	5.6	J(3 5)	1.0
H-C(4)	5.99	J(4 5)	9.5		
H-C(5)	5.90	J(5 2)	1.1		

BAT SHEVA SUMMER SCHOOL ON MOLECULAR DYNAMICS IN LIQUIDS

A Summer School on Molecular Dynamics in Liquids sponsored by the Bat-Sheva de Rottschild Foundation will be held at the Technion, Haifa, Israel between September 1-17, 1971.

Lectures and discussions will be held on the theoretical and experimental aspects of the study of molecular motions in the liquid phase. Special emphasis will be given to modern approaches to the study of relaxation phenomena in liquids through such techniques as light scattering, IR lineshapes, nmr and esr dielectric dispersion, etc.

Amongst those who have agreed to attend are:

A. Ben Reuven (Rehovot) - Orientational Motion in Liquids

M. Bixon (Tel-Aviv), Polymer Dynamics in Solutions

P.G. de Gennes (Orsay) - Dynamical Properties of Liquid Crystals

D. Kivelson (UCLA) - Spin Relaxation

T.A. Litowitz (Washington, D.C.) - Light Scattering and Sound Absorption

I. Oppenheim (MIT) - Generalized Hydrodynamics

R. Zwanzig (Maryland) - The Linear Response Theory

The School is open to Research Scientists and Graduate Students interested in the field. For application and further information please write to:

A. Loewenstein
Department of Chemistry
Technion, Haifa, Israel

before January 31st, 1971.

Registration fee is I.L.140 ($40) and includes communal lunch. Accommodation and other meals are not included but will be available at moderate rates in the Students' Residence. A very limited number of grants may be available upon request.

September 23, 1970

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

Dear Doctor Shapiro:

In this laboratory the aromatic proton spectra of a variety of naphthalene
sulfonic acid derivatives and their salts have been measured using a Varian
A-60 spectrometer. The usual solvents for this work were H_2O or dimethyl-
sulfoxide-d_6 but, occasionally, because of low solubility in DMSO-d_6 or inter-
ference from the strong H_2O signals, D_2O was used. Except for minor shifts due
to differences in sample concentration the aromatic proton spectra in D_2O and
H_2O were usually identical for a given compound. In DMSO-d_6 the chemical
shifts can differ markedly from those in the aqueous solvents but the overall
patterns of the signals are similar.

Recently the spectra of 2-aminonaphthalene-6,8-disulfonic acid (Amino G-Acid),
were prepared in all three solvents. In both H_2O and DMSO-d_6 this compound
gave similar patterns for the five aromatic protons consisting of overlapping
ABX (for protons 1, 3 and 4) and AB (for protons 5 and 7) subspectra. The
disodium salt of this compound also gave the expected patterns for the five
aromatic protons in H_2O. The observed shifts are given in the attached table.

In D_2O the spectra were anomalous; signals were observed for only four protons,
forming two separate AB subspectra. The signal for proton 1 was absent in the
spectra of both the free acid and the salt (see table). When the D_2O solutions
were evaporated to dryness and redissolved in H_2O the signal for proton 1
reappeared, giving the familiar ABX subspectrum.

Dr. B. L. Shapiro   September 23, 1970

This facile exchange of an aromatic proton with D_2O had not been observed
with any of the naphthalene sulfonic acids previously examined. However, other
examples of this phenomenon may have been overlooked since D_2O was not usually
used as the solvent. Compounds with related structures, such as the isomeric
Amino J-Acid (2-naphthylamine-5,7-disulfonic acid), the sodium salt of the
monosulfonate (2-naphthylamine-8-sulfonic acid) and the di-potassium salt of
the naphthol analog (2-naphthol-6,8-disulfonic acid), do not exhibit this
exchange with D_2O.

Very recently preliminary measurements were made on the sodium salt of Gamma
Acid (8-hydroxy-2-naphthylamine-6-sulfonic acid) but signal assignments have
not been completed. One of the aromatic protons of this compound exchanges
with D_2O and it appears probable that either proton 1 or proton 7 is affected.

The exchange of an aromatic proton with D_2O does not seem to be a common
phenomenon and too few examples have been observed to permit prediction of
the occurrence of a labile proton in this class of compounds. It is known
that position 1 in β-naphthols and β-naphthylamines is generally the most
active site for substitution reactions. This experience indicates that
compound identification or structural assignments of naphthalene sulfonic
acid derivatives should not be based solely upon spectra prepared using D_2O
as the solvent.

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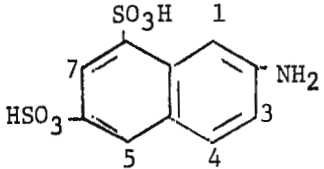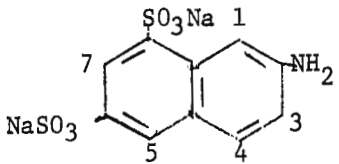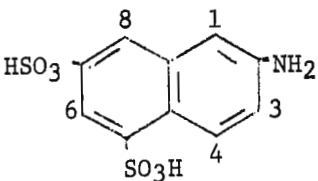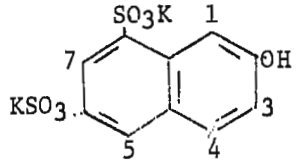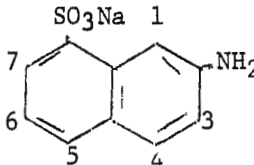Company (Dr. J. Lancaster).

Sincerely yours,

Jessie L. Gove
NMR Laboratory

Suggested Title: Aromatic Proton Exchange in Naphthalene Sulfonic Acids

JLG/mmcp
Attach.

Table I: Chemical Shifts of Naphthalene Sulfonic Acid Derivatives

Compound	Solvent	T (1)	T (3)	T (4)	T (5)	T (6)	T (7)	T (8)
SO₃H, NH₂ naphthalene (HSO₃ at 6)	D_2O	–	2.76	2.50	1.91	–	1.50	–
	H_2O	1.50	2.76	2.42	1.95	–	1.58	–
	DMSO-d₆	1.02	2.43	1.82	1.71	–	1.53	–
SO₃Na, NH₂ naphthalene (NaSO₃)	D_2O	–	2.62	2.33	1.77	–	1.46	–
	H_2O	1.45	2.63	2.32	1.77	–	1.46	–
HSO₃, NH₂, SO₃H naphthalene	D_2O	2.22	2.30	1.31	–	1.38	–	1.71
	H_2O	2.23	2.30	1.31	–	1.38	–	1.72
	DMSO-d₆	1.92	2.39	1.03	–	1.58	–	1.74
SO₃K, OH naphthalene (KSO₃)	D_2O	1.95	2.68	1.97	1.50	–	1.50	–
	H_2O	1.92	2.69	1.99	1.47	–	1.48	–
	DMSO-d₆	1.82	2.87	2.17	1.72	–	1.91	–
SO₃Na, NH₂ naphthalene	D_2O	2.03	2.90	2.33	2.19	2.69	1.84	–
	H_2O	2.07	2.89	2.38	2.18	2.70	1.87	–

Department of Chemistry   September 25, 1970

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

Short Title: "Topomerism" - a new term.

Dear Barry:

We would like to propose a system of nomenclature for the important situation where ligands are found in different chemical and/or magnetic environments through an exchange of position without alteration of the chemical species involved. A typical example is the exchange of the equatorial and axial fluorine atoms in 1,1-difluorocyclohexane, in this case by ring inversion. Names have been coined for the process of exchange, notably "degenerate isomerization", "isodynamic change" (1) and "automerization" (2); and the species which undergo the exchange have been called "automers" (2). We feel that all these terms leave something to be desired, the first because the process is obviously not an isomerization (the structures involved are the same, not isomeric) and the second because it relates to energy rather than to structure. "Automerization" is more apt, but, in our opinion, focusses attention on the uninteresting part of the phenomenon (the sameness of the structures involved) rather than on the interesting aspect, and the one which deserves description, namely the fact that the process of interchange puts structurally identical ligands in different environments (using the word structure in its most general sense of constitution plus configuration plus conformation).

Recently, a nomenclature has been coined (3), and is becoming accepted and extended (4, 5), designating ligands in stereochemically different environments as "enantiotopic" or "diastereotopic" (3), the overall term for the two cases being "heterotopic" (4) or stereoheterotopic (5); in contrast, ligands in identical surroundings are called "homotopic" (4, 5).* We therefore propose that the process leading to exchange of ligands of the same structure, which differ in "topicity" (derived from Greek topos = place) be called "topomerization" and that the indistinguishable species being involved in this exchange be called "topomers". Common examples from the current literature are shown below; many additional examples have recently been discussed by one of us (8). It is to be noted that the new terms can be used regardless of whether the interchange in question comes about by rotation, inversion, bond shifting or by some other process; this is particularly advantageous in cases where the actual mechanism of exchange is not known (8).

---

* For prochiral enantiotopic and diastereotopic ligands (3) we use the designations L_R and L_S defined elsewhere (4, 6). For heterotopic ligands in an olefin (cis or trans to a given group at the other end of the double bond) we use the symbols L_Z and L_E (cf. 7) according as to whether the ligand is cis (Z) or trans (E) to the group of higher Cahn-Ingold-Prelog sequence.

I (9, 10)

II (11)

III (12)

IV

V (13)
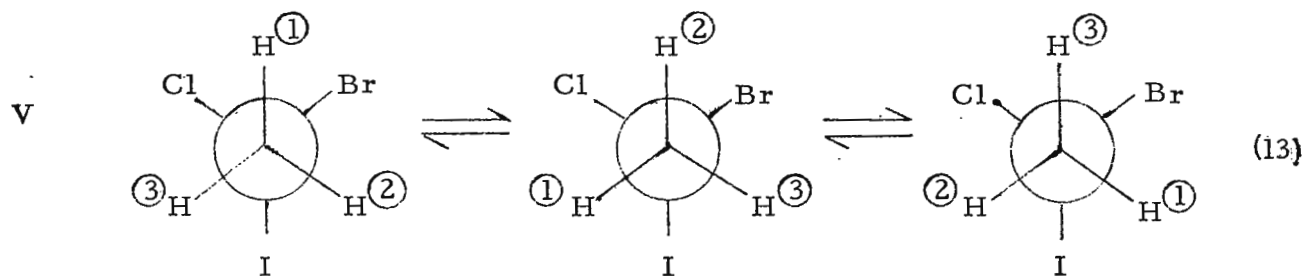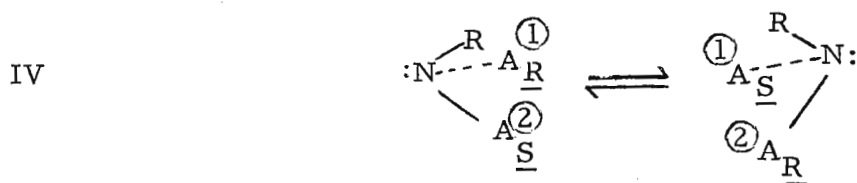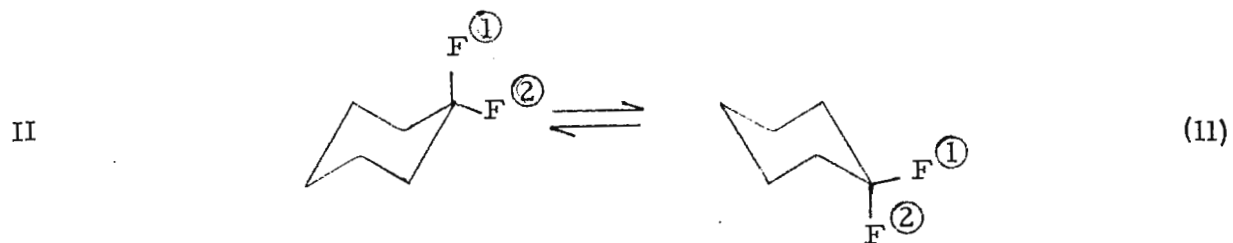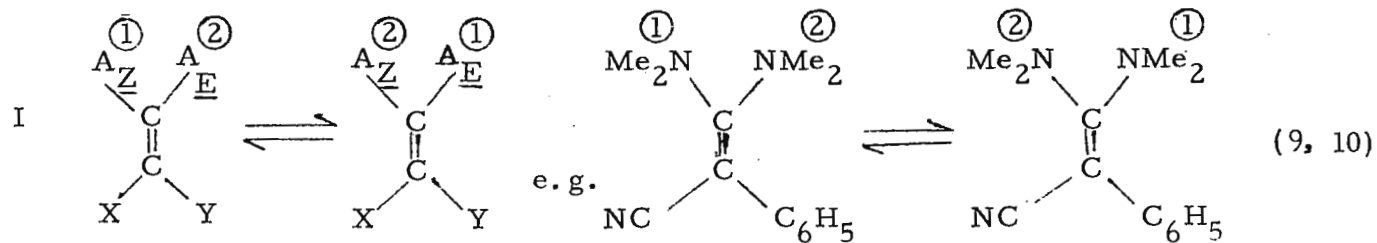
Topomers can be classified just as isomers into constitutional topomers (e.g. valence bond topomers, III) and stereotopomers. The latter may be diastereotopomers (I, II) or enantiotopomers (IV). Case I represents cis-trans topomerization or diastereotopomerization, since A_Z and A_E are diastereotopic groups; similarly case II represents diastereotopomers by virtue of exchange of equatorial and axial fluorine. Case III (bullvalene) represents valence bond topomerization; the topomers are constitutional since one and the same ligand (carbon, hydrogen) is placed in chemically different positions (allylic, two kinds of vinylic and cyclopropanoid). Case IV is one of enantiotopomerism; the enantiotopic groups A_R and A_S might, in principle, be distinguishable in a chiral solvent when inversion is slow. Case V as case II may be described as one of conformational diastereotopomerism since the three conformations differ in the location of designated hydrogen ligands.*

The phenomenon of topomerization is, obviously, of particular importance in NMR spectroscopy, since, depending on its time scale, the ligands interchanged in the process may be isochronous or anisochronous (3) and/or magnetically equivalent or nonequivalent and the rate of topomerization is frequently ascertained by NMR line-shape studies.

So far, the nomenclature has dealt with ligands which are, in principle, structurally non-equivalent. However, for completeness and maximum usefulness, it should be able to deal also with cases of nuclei which are structurally equivalent but, in principle, magnetically non-equivalent. The most general case of such ligands is shown in example VI. Here the three hydrogens (and also the three fluorines) are, of course, structurally equivalent, not only in the case

VI

VII

(14)

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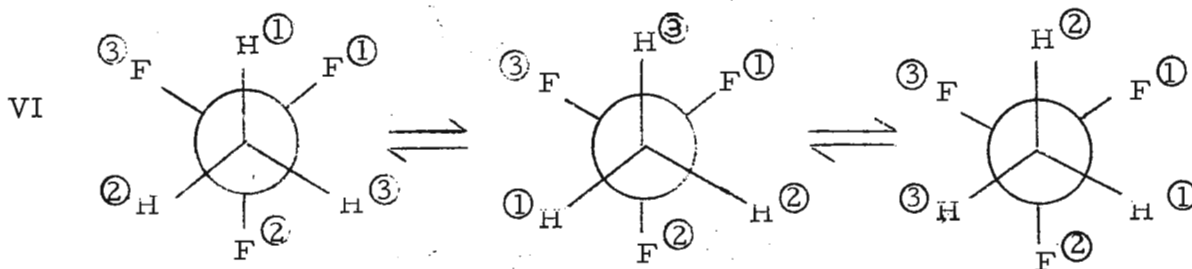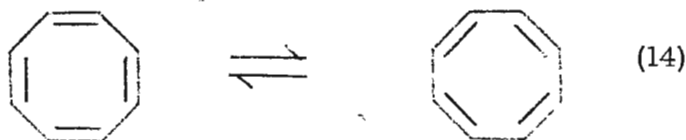
* Topomerization by rotation about the carbon-carbon bond of V is confined to cyclic permutations (123 ⇌ 231 ⇌ 312); the remaining permutational possibilities (213 ⇌ 132 ⇌ 321) are inaccessible by rotation. The situation could be characterized by an extension of the Cahn-Ingold-Prelog rules, where the labeling determines the priority sequence and the "configurational" symbol is enclosed in square brackets. In the topomers of V the methyl group then belongs to the [R] family.

VIII

$$H_S^{①}-C-H_R^{②} \quad \rightleftharpoons \quad H_S^{②}-C-H_R^{①} \qquad (15)$$

with MgCl at top and:

VIII

MgCl		MgCl
$H_S^{①}-\overset{\mid}{C}-H_R^{②}$	$\rightleftharpoons$	$H_S^{②}-\overset{\mid}{C}-H_R^{①}$
$H-\overset{\mid}{C}-H$		$H-\overset{\mid}{C}-H$
$C(CH_3)_3$		$C(CH_3)_3$

(15)
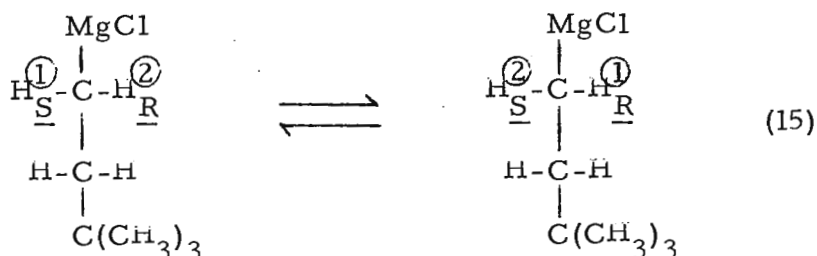
when rotation about the C-C bond is fast, but also when it is slow on the time scale
of the experiment. However, the magnetic equivalence which exists in the limit
of fast rotation (system A_2X_2) is lost in the limit of slow rotation (system
AA'A''XX'X''), since a distinction now exists between the gauche H/F coupling
and the anti H/F coupling. Thus, although the nuclei hydrogen (or fluorine) cannot
be distinguished even in the case of slow rotation (since they are equivalent), their
magnetic non-equivalence can be recognized in the spectral pattern. We propose
to label the case represented by example VI one of "homotopomerization" and call
the three interconverting structures "homotopomers". It should be noted that,
whereas the exchanging ligands in ordinary topomers (which, for the sake of
distinction, may be called "heterotopomers" if necessary) are heterotopic, either
constitutionally or stereochemically, the exchanging ligands in homotopomers are
constitutionally and stereochemically equivalent, their only non-equivalence being
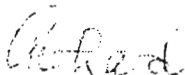of the magnetic kind.

Another interesting case of (constitutional) homotopomerization is represented
by the bond shift process in cyclooctatetraene (VII). Here (at least in the average
planar model) all nuclei are equivalent but ^{13}C coupling reveals the difference of
adjacent carbon atoms being linked by a single or a double bond (14).*

Case VIII, though similar to case VI, differs in that protons H_R and H_S are
enantiotopic rather than homotopic. Thus this is a case of enantiotopomerization,
but, in distinction to case IV, in this instance in the limit of slow exchange H_R
and H_S can be distinguished by their magnetic nonequivalence through unequal
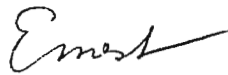coupling with the adjacent methylene protons (15).

---

* It should be noted that this case is not dependent on the simultaneous presence
of ^{12}C and ^{13}C in the cyclooctatetraene. Rather, the presence of two magnetic nuclei
(^{1}H and ^{13}C) makes it possible to see the coupling of vicinal protons; the same
phenomenon (albeit complicated by additional ^{13}C coupling) would be seen in
cyclooctatetrane-per-^{13}C; cf. R. M. Lynden-Bell and N. Sheppard, Proc. Roy.
Soc., Ser. A, 269, 385 (1962). Thus this is truly a case of homotopomerization.

We realize that the introduction of new jargon in chemistry is usually not greeted with universal joy. We therefore solicit comments (both sweet and sour) regarding the usefulness and propriety of the terms here proposed from TAMUNMRN readers.

Sincerely yours,

Gerhard Binsch   Ernest L. Eliel   Horst Kessler*

* Chemisches Institut der Universitat Tübingen, Wihelmstr. 33, 74 Tübingen, Germany.

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(15) G. M. Whitesides, M. Witanowski and J. D. Roberts, J. Amer. Chem. Soc., 87, 2854 (1965).

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DEPARTMENT OF CHEMISTRY

TELEPHONE:
544 0611

28 September, 1970

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

Dear Barry,

LAOCOON versus HYDRA

Some time ago we decided to compare the n.m.r. parameters of some of our pet compounds with those of dibenzothiophene. At that time only an approximate analysis existed[1] so we undertook a more thorough study. Our normal analytical method is LAOCOON III but out of interest we also performed a direct analysis based on the ABMX approximation, with the AB part close to the deceptively simple limit. (The sample was a 5% solution in CCl_4.) Although a small difference in these two results was expected, the disagreement was a bit disturbing. Specifically, LAOCOON III had the magnitude of J_{12} and J_{34} (and of J_{13} and J_{24}) in the reverse order to the direct solution, and that expected on empirical grounds. (J_{12} is usually larger than J_{34}.) Further investigation showed that LAOCOON III was extremely sensitive to the input parameter and the experimental data. Unless trial parameters were carefully chosen, the iteration diverged or converged to a false solution due to the extensive line label changes in the region where $\delta_{23} \approx 0$. Secondly, the final parameters were very sensitive to the separation of lines which were unresolved (marked * in the spectrum). The experimental separations had been estimated from line widths. When the estimates were increased from an average of 0.08 Hz to 0.16 Hz the coupling constants changed from those in column 2 to those in column 3 of the table below. More reliable values are probably those in column 4 where all unresolved lines have been omitted from the input data. Surprisingly the direct ABMX calculation is fairly insensitive to these line positions. During the course of this work, Clin and Lemanceau[2] published the results of their analysis of dibenzothiophene. They used the Reilly and Swalen iterative method and their results (column 6) were substantially different. Their value for $(J_{24} + J_{34})$ was also significantly different, whereas all our solutions give the same value of 9.22. The results indicate that iterative methods of analysis should be used with caution in cases where shifts and/or coupling constants become similar in magnitude. The program should be checked for sensitivity to the experimental line positions and if possible, another analytical method used as a double check. A similar warning has been given by MacDonald and Schaefer[3] who found the same sensitivity in the spectrum of epichlorohydrin. It seems this effect is more widespread than is commonly supposed.

	LAOCOON III	LAOCOON III	LAOCOON III	LAOCOON III/C_6D_6	C + L
W(1)	224.84 *	225.23	225.24	225.26	247.84	
W(2)	266.19	265.82	265.80	265.78	287.49	
W(3)	267.13	266.86	266.88	266.89	283.39	
W(4)	197.19	197.43	197.43	197.42	216.34	
J_{12}	8.48	7.92	8.06	8.17	8.10	8.7
J_{13}	0.71	1.24	1.08	0.96	1.02	0.5
J_{14}	0.71	0.70	0.70	0.71	0.69	0.9
J_{23}	7.14	7.20	7.21	7.20	7.19	7.7
J_{24}	1.65	1.08	1.23	1.35	1.26	1.1
J_{34}	7.57	8.14	7.99	7.87	7.96	7.7
$J_{12} + J_{13}$	9.19	9.12	9.14	9.13	9.12	9.2
$J_{24} + J_{34}$	9.23	9.22	9.22	9.22	9.22	8.8
	RMSE=0.022	RMSE=0.021	RMSE=0.012	RMSE=0.023	

* in Hz measured upfield from the origin of the τ-scale.

To confirm that the parameters in column 4 are approximately correct the spectra in C_6D_6 (column 5), acetone and $CDCl_3$ were also analyzed. In C_6D_6 solution $\delta_{23} = 4.1$ Hz and the results are less sensitive to the measured frequency. As a further check, studies of C^{13} satellite spectra are under way. If this fails, we will have to resort to something truly Heraclean; fire brands perhaps?
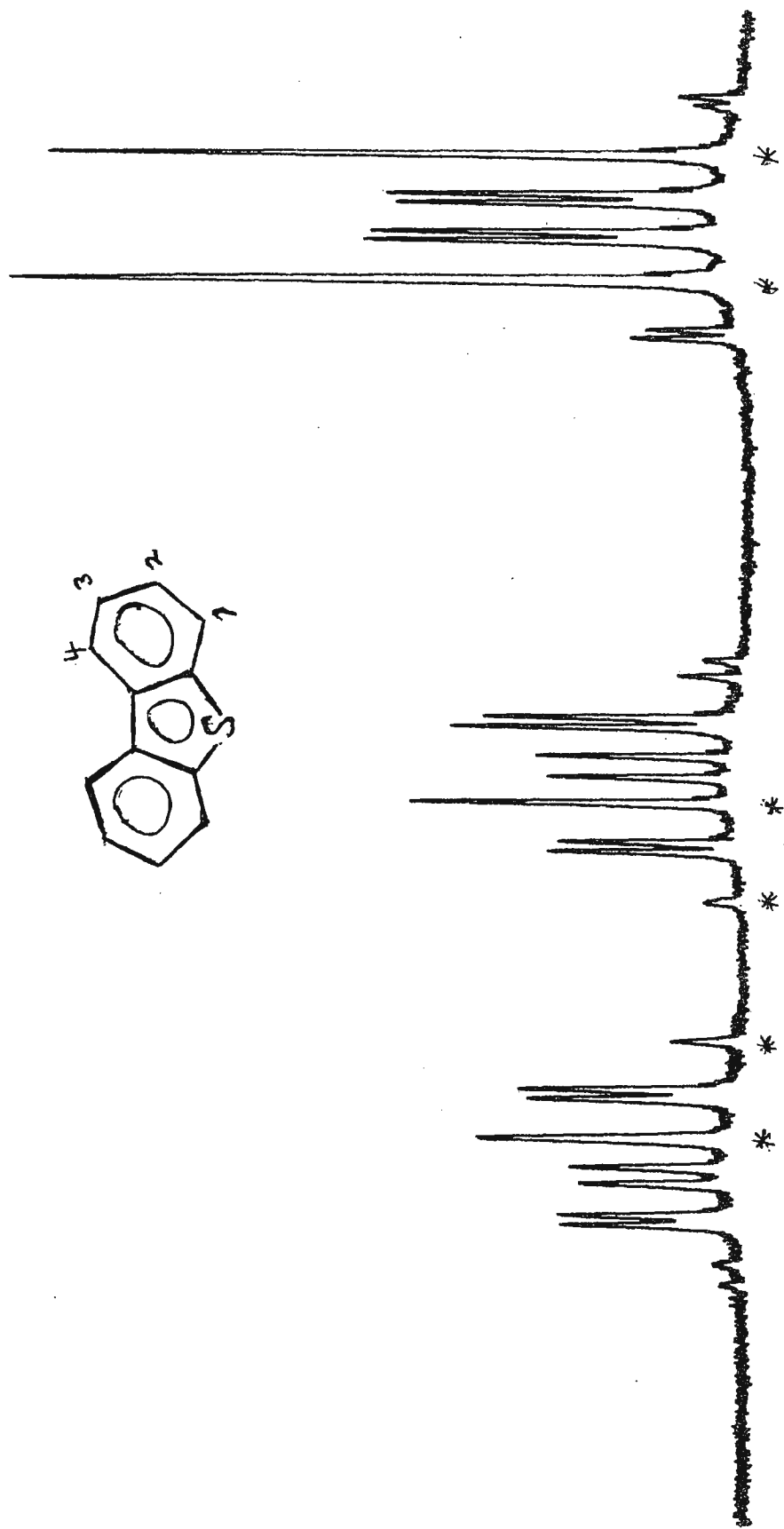
Best wishes,

M. L. Heffernan   F. Balkau

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ATTN OF: AFML (MAYH/R. E. Rondeau/255-2280)   28 September 1970

SUBJECT:

TO: Texas A&M University
Attn: Prof. B. L. Shapiro
College Station, TX 77843

Chemical Shift Assignments in Oximes

Dear Prof. Shapiro:

The magnetic non-equivalence of syn and anti protons in oximes has been
known for a long time. Several NMR studies have established and exploited
the fact that a proton attached to an alpha carbon syn to the hydroxyl
group in the oxime resonates at lower field than an anti proton on an
alpha carbon. However, stereochemical assignments based on this generality
can only be made if the NMR spectra of both stereoisomers can be obtained.

We have found (serendipity again) that the addition of small amounts of
concentrated hydrochloric acid vapor to a benzene solution of a ketoxime
caused the alpha proton syn to the hydroxyl group to shift to higher
field, while the anti-alpha protons were shifted to lower field. Using
dialkyl, cycloalkyl and alkylphenyl ketoximes of known stereochemistry,
we found that in every case, the addition of ten ml of the reagent to
approximately 1 ml of oxime solution produced shifts large enough to
be unambiguously recognized and measured.

The technique involves recording the spectrum of a benzene solution of
the ketoxime and measuring the chemical shift of the alpha protons.
Hydrochloric acid vapor is then withdrawn from the atmosphere in a
concentrated HCl reagent bottle by means of an eyedropper long enough
to reach to the bottom of the NMR sample tube. The gas is then slowly
bubbled through the sample. The spectrum is recorded and the chemical
shifts measured after each addition of HCl.

The method is not only simple and inexpensive, but it also obviates the
need for comparing one's own experimental data with previously compiled
values.

ROGER E. RONDEAU
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September 30, 1970

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

Dear Professor Shapiro:

Please credit this letter to Jim Engle's subscription. The work described will appear in the Proceedings of the Wenner-Gren Symposium on the Structure and Function of Oxidation-Reduction Enzymes, Stockholm, 1970.

<u>Proton Relaxation Enhancement with Protein-Bound Flavin Radicals</u>

by Graham Palmer, Biophysics Research Division, University of Michigan and Albert S. Mildvan Institute for Cancer Research, Fox Chase.

Previous work has shown that enzyme-bound nitroxide radicals and paramagnetic ions, in which the unpaired electrons are well localized, are effective in enhancing the nuclear relaxation rates of the protons of water and substrates. To determine the effects of radicals with highly delocalized spins, such as flavin semiquinones, the proton relaxation rates of water solutions of a free flavin radical, 5-ethyl-10-methyl-lumiflavin semiquinone (LSQ) and a protein-bound flavin radical, flavodoxin semiquinone (FSQ) were studied. At 24.3 MHz, the longitudinal ($1/T_1$) and transverse ($1/T_2$) molar relaxivities of LSQ are equal (133 M^{-1} sec^{-1}) but are less than those of Cu^{2+} (875 M^{-1} sec^{-1}). The immobilization of the flavin semiquinone in flavodoxin causes a 3.6-fold enhancement of $1/T_1$ and a 7.1-fold enhancement of $1/T_2$. Both relaxation rates decrease with increasing temperature (E_a = 1.1 KCal/mole), indicating that water protons exchange at a rate $>10^5$ sec^{-1} into a site which is in contact with the bound flavin. Hyperfine coupling of the order of 0.04 gauss consistent with hydrogen bonding is detected. The average distance between water protons and the unpaired electron of FSQ is $2.5(q)^{1/6}$ where q is the "coordination number" for exchangeable protons on or near the FSQ. Reasonable distances (3.2 ± 1.0 Å) are obtained if q = 4 ± 2, consistent with the results of ENDOR and optical spectroscopy. Hence the accessibility of water protons to enzyme-bound flavin radicals may be studied by relaxation enhancement.

Sincerely yours,

Albert S. Mildvan

ASM/deh

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