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Newsletter

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

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

W. H. Stegemann   im Hause

Gesellschaft für Molekularbiologische Forschung mbH
3301 Stöckheim über Braunschweig
Mascheroder Weg 1
Telex 9-52667
Telefon 05 31 / 6 00 71

June 26, 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University

College Station, Texas 77843

U S A

Modified V-2100 B Regulated Magnet Power Supply

Dear Professor Shapiro,

During the operation of our Varian HA-100 NMR spectrometer, we
have been bothered by the frequent breakdown of ballast tubes type
304 TL. These tubes last about one year and must then be re-
placed; occasionally, we have had to replace them at shorter
intervals. One then has to wait at least one day after replace-
ment until the magnetic field stability is attained. We decided,
therefore, to replace the ballast tubes by service-free semi-
conductors.

We hereby describe a modified V 2100 B regulated magnet power
supply system. This modification has the desirable effects of
reducing both the breakdown rate and diminishing the heat pro-
duction; in addition, the voltage requirement is substantially
reduced due to the lower collector voltage of the transistors
compared with the ballast tubes. The V 3505 Chopper-amplifier
is used as before for the control and regulating functions.
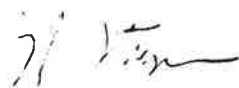
Sixteen groups of power transistors, each group containing
three transistors, are placed in series in order to obtain
the necessary voltage stability; the detailed circuit is re-
produced in an accompanying circuit diagram. The individual

- 2 -

Gesellschaft für Molekularbiologische Forschung mbH
3301 Stöckhelm über Braunschweig

Blatt   2   zum Schreiben June 26, 1969
Prof. Dr. B. L. Shapiro

amplifier plates are mounted on a 4 mm aluminium sheet measuring 295 x 290 mm. The sixteen plates are accomodated on two rods of insulating material mounted at the same place in the power supply which the ballast tubes formerly occupied. Furthermore, the built-in fan can now be used for cooling the transistors. The temperature of the emergent cooling air is <u>ca.</u> 40°C.

The interlock circuit has to be modified as follows: a self holding contact relay is placed in series with the S 201 (high voltage) switch. In this manner the automatic switching on of the magnetic voltage following a mains breakdown is avoided. The microswitch in parallel with the relays is conveniently operated by setting the variable transformer to zero.

Those interested in our modified power supply are invited to write for photographs showing the detailed arrangement of the individual parts.

Sincerely yours,

(W. H. Stegemann)

Anode

10 k 16
10 k 15
10 k 14
10 k 13
10 k 12
10 k 11
10 k 10
10 k 9
10 k 8
10 k 7
10 k 6
10 k 5
10 k 4
10 k 3
10 k 2
10 k

3 x 2N3055

BC 109 A
220 k 500 BC 140
ZF 5.6 5 5 5 BYY 89 10nF

zu Punkt 4 des Chopper-Amplifiers

Kathode

3 x 2N3055
BC 109 A
500 BYY 89
BAY 18

Aufbau der Verstärkerplatten 2 bis 15

Schaltung der transistorisierten

Stromstabilisierung

EASTMAN KODAK COMPANY

ROCHESTER 4, NEW YORK

June 24, 1969

PLEASE ADDRESS REPLY TO
RESEARCH LABORATORIES

TELEPHONE
GLADSTONE 8-1000

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

Dear Barry,

PHASE-LOCKED FIELD-FREQUENCY STABILIZATION OF
100 MHz FOURIER TRANSFORM SPECTROSCOPY

In order to do Fourier transform nmr, we have recently constructed
our own 100 MHz pulse modification for use on a Varian HA-100.

We have found it necessary to devise a low-frequency phase-locked
oscillator. This was done to insure that the lock signal which we
derive from a component of the free-induction decay will not vary from
pulse to pulse. This, of course, is required for coherent accumulation
of signal in a CAT experiment.

Figure 1 shows the connection of the pulse generator units.

In Figure 2 are the details of the low frequency locked oscillator.
The FREQ. ADJ. control varies the RC time constant which determines
the firing rate of the 2D21 Thyratron. A 4.3 v p-p sync voltage obtained
from J1307 (SWEEP OSC. OUTPUT) permits the thyratron to fire only at
the positive peak of each cycle. This locks the phase of the free-
induction decay lock signal from one pulse to the next.

During operation, the R.F. reference phase control on the V-4311
is adjusted for the best lock. This is indicated by minimum jitter of
the Slow Sweep galvonometer.

Some economy and savings in time resulted from the discovery that
our Wavetek (model 114) VCG could be used as a versatile pulse generator.
For use as a pulse generator, the Wavetek 114 (if you happen to have
one around) controls are as follows:

a. Freq. Hz: X10K
b. Sweep width: max counterclockwise
c. Start/Stop point: -90°
d. Trigger mode
e. Slope: +
f. Level: +
g. Sweep rate Hz: off
h. Attenuator: ⎍⎍

The pulse width may be conveniently varied by the frequency dial
and is given (in μ sec) by $\sqrt{500/\text{dial reading (kHz)}}$. Pulse height
can be varied from 0 to $\sim$ 30 volts.

We have obtained and transformed a number of spectra successfully. Some subtle pitfalls in the Fourier technique have appeared, especially when multiple pulse experiments (i.e., signal averaging) are desired. These electronic bugs are in the process of being exterminated and we hope to have some results to report in a few weeks.

                              Very truly yours,

                              Stanley Gross
                              S. Gross

                              Richard E. Grave
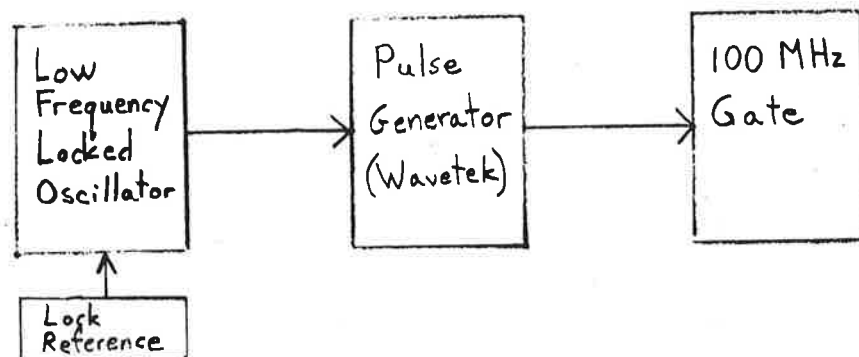   R. Graves

                              Phil Rose
                              P. Rose
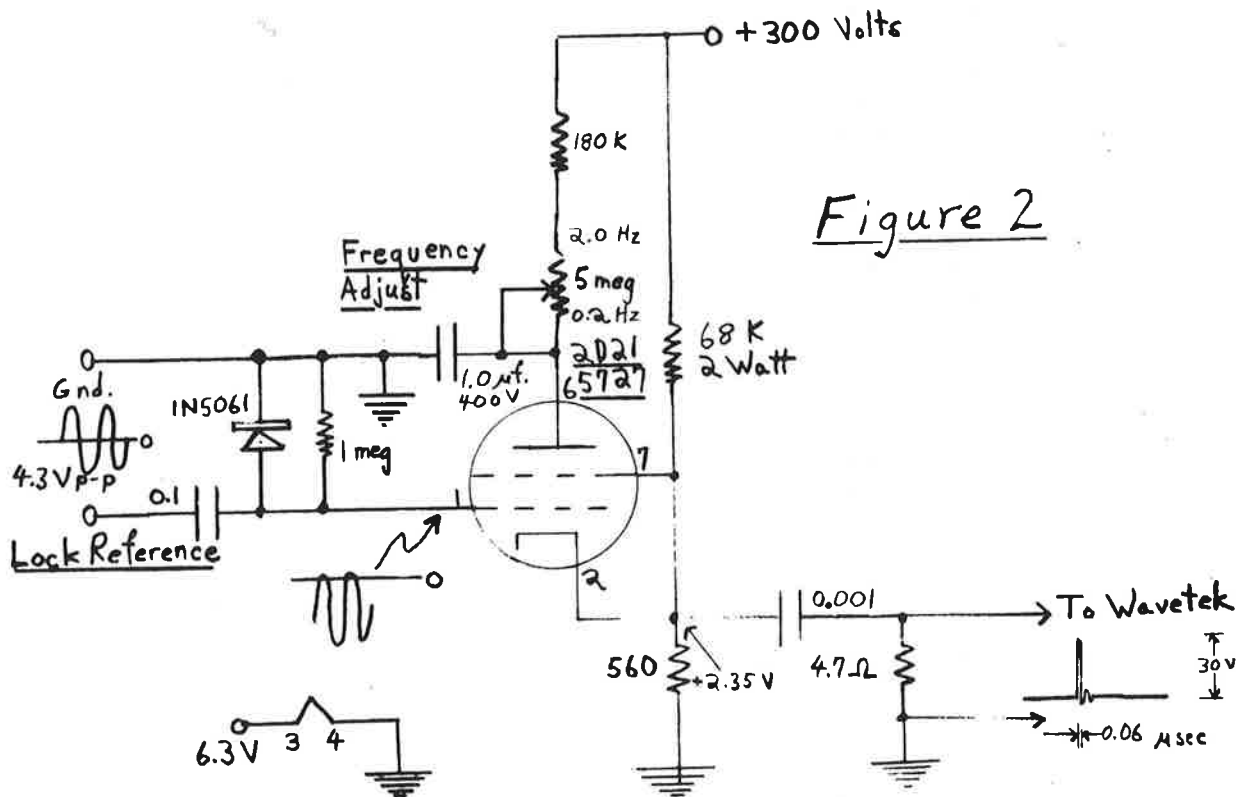   Research Laboratories

PR:djr

Figure 1

Figure 2

Université Libre de Bruxelles

FACULTE DES SCIENCES
Avenue F.-D. Roosevelt, 50

Service : **Organic Chemistry**

Dir.: Prof.R.H.MARTIN

(A rappeler dans la réponse)

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

Réf.: First example of Nuclear Overhauser effect (N.O.E.) between aromatic protons.

Dear Dr. Shapiro,

We wish to report here what we believe to be the first example of an internal nuclear Overhauser effect between aromatic protons.

The molecule chosen for this investigation was dibenz [a, j] anthracene (I) whose N.M.R. spectrum is shown in fig I. In this system, H_{14} is very close to (and thus strongly relaxed by) H_1 and H_{13}. We could thus hope to observe a N.O.E. between these nuclei.

Double irradiation experiments (Bruker HX 90 Mc) were performed on a saturated $CDCL_3$ solution of freshly recrystallised dibenz [a, j] anthracene, which had been thoroughly degazed under high vacuum and sealed in an atmosphere of nitrogen. The integrated area of proton H_7 was used as an internal reference for measurements.

Saturation of the singlet of H_{14} produces an enhancement of 23,8 % of the integrated area of the multiplet of (H_1+H_{13}). The reverse experiment, i.e. saturation at the center of the multiplet of (H_1+H_{13}) results in an enhancement of 40,2 % of the integrated area of proton H_{14}.

No N.O.E. was detectable between peri or ortho protons (internal reference : H_{14}).

These results can be interpreted qualitatively by assuming that proton H_{14} is " protected " by H_1 and H_{13} against intermolecular relaxation effects whereas protons H_1 and H_{13} are more accessible and thus more readily relaxable by an intermolecular mecanism.
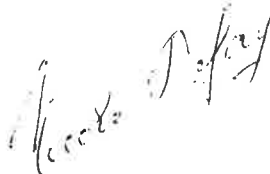
A more detailled account of this work will be published later.

With best regards.

Yours sincerely,

M. J. MARCHANT   N. DEFAY   R. H. MARTIN.
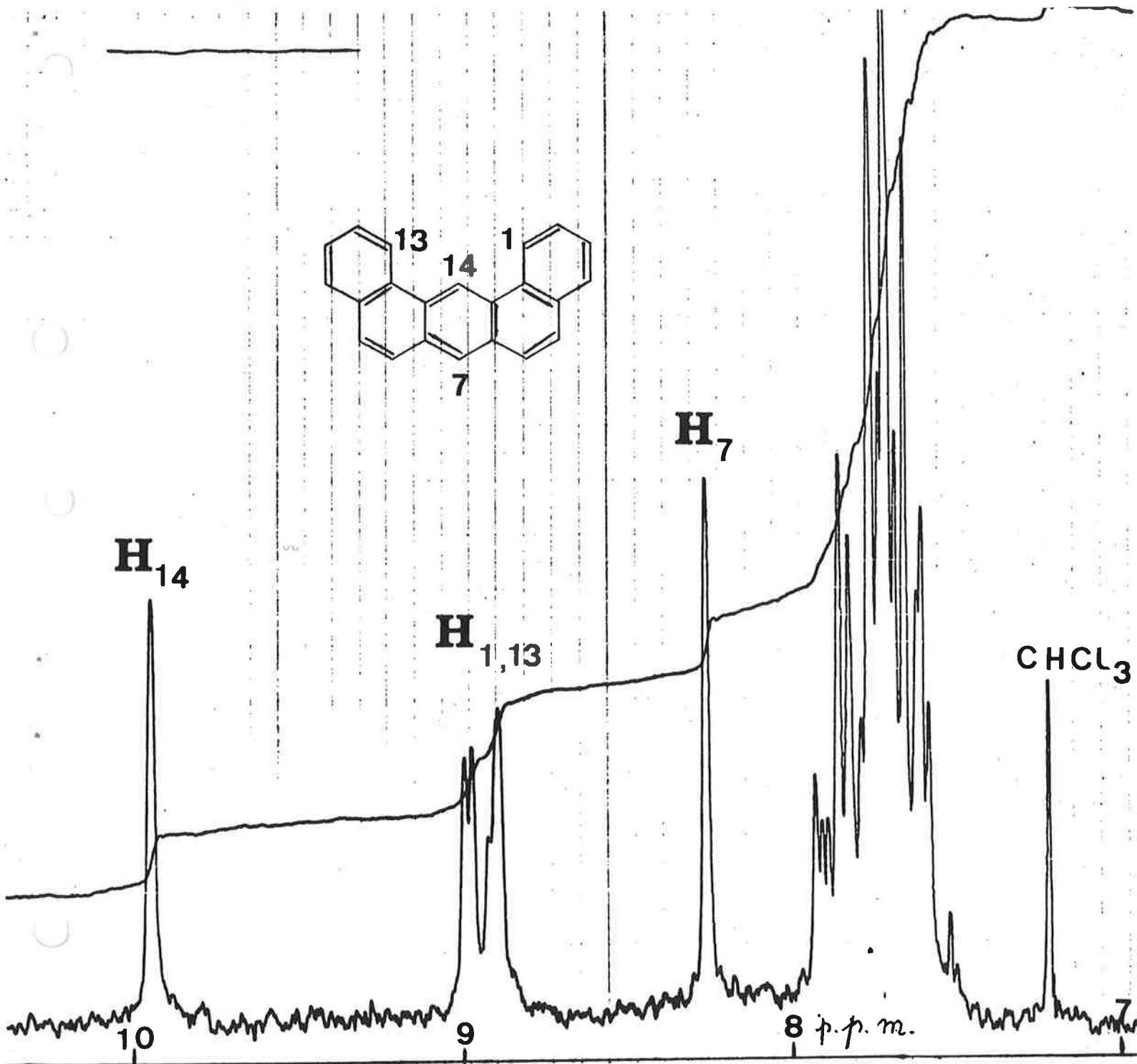
MAGNETIC RESONANCE COMPUTER SYSTEM

The Union Carbide Research Institute at Tarrytown, New York, is develop-
ing a computer system for multi-purpose NMR spectroscopy in a time-
averaging mode. Since a C-1024 computer was already available, they
were interested in incorporating it into their expanded system which
consists of a PDP-8/I Computer, Varian C-1024 Analyzer, Frequency Syn-
thesizer, Nuclear Magnetic Resonance (NMR) Interface Unit and an NMR
Spectrometer. The central element in the system is the PDP-8/I Computer
which is used to control the frequency spectrum of the Synthesizer and
process digital data developed by the C-1024 Analyzer.

The computer, under program control, is capable of selecting up to 1,024
successive frequency settings of the Synthesizer in a predefined sequence.
The output of the Synthesizer in turn is utilized to drive the Spectrometer.
The analogue output of the Spectrometer is sampled and converted to binary
data by the Varian C-1024 Analyzer. It is therefore possible to gener-
ate repetitive programmed frequency scans and achieve enhanced signal-
to-noise characteristics by the utilization of time averaging correlation
techniques. The C-1024 may also be easily detached and used normally in
a remote time averaging experiment, freeing the central computer for
other applications.

Magnetic Resonance Computer System

The NMR Interface Unit, designed by Custom Computer Systems, Inc., Plainview, New York, contains the specialized electronics and control logic required to interface the PDP-8/I computer to the Varian C-1024 Time-averaging computer and the Digitized Frequency Synthesizer. The Interface Unit is designed to accept 17 bit data words from the Varian C-1024 Analyzer, and reformat the data for transfer into the 12 bit word PDP-8/I computer. The Interface Unit also will accept address information from the PDP-8/I computer, which in turn is processed and provided as an input to the Varian C-1024 Analyzer. Special devices in the Interface Unit are utilized to interface the PDP-8/I computer to the Frequency Synthesizer. Noise suppression networks have been included in the Interface Unit to minimize susceptibility to noise transients.

The flexibility that can be achieved by the proposed system will enable researchers to develop varied systems. Both broadline and high resolution resonance patterns can be developed. Furthermore, the data processing capability of the PDP-8/I computer can be utilized to filter, edit and otherwise enhance the quality of the resultant experimental data.

Anyone interested in further details about the system is invited to contact Robert Trocchio, Custom Computer Systems, Inc., 40 South Mall, Plainview, New York 11803.

Robert Trocchio

Iwan N. Stranski-Institut
II. Institut für Physikalische Chemie
der Technischen Universität Berlin
Prof. D ....

Eo .. .. . 11. Juli 1969

3 S

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

U. S. A.

Re.: Impurities in Tetramethylsilane

Dear Professor Shapiro,
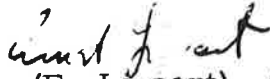
In the course of studying highly diluted solutions with internal standar-
disation by TMS we came across an impurity in the Tetramethylsilane-
standard-substance which proved to be Tetrahydrofurane. This im-
purity for instance is present in Merck-Uvasol-Tetramethylsilane
and in Fluka-Tetramethylsilane.

Fig. 1 is the CAT-1000 output after 40 scans showing the two
multiplets of Tetrahydrofurane being centered at 161.o c/s and
325.9 c/s downfield from TMS at a standard frequency of 90 Mc.
The CAT-1000 was attached to a Bruker KIS HFX 90/60 NMR
Spectrometer operating at 90 Mc.

Studying dilute solutions with the aid of "time-averaging" this
impurity could give rise to erroneous signals which have nothing
to do with the substance under study. Being a cyclic ether tetra-
hydrofurane could interfere when studying association equilibria.

We succeeded to eliminate the Tetrahydrofurande by simple column
chromatography with Al_2O_3 basic, Merck.

Sincerely yours,

(E. Lippert)   (U. Jentschura)

Fig. : 1

* Shifts are in c/s downfield from TMS

Ivan N. St an ' Inst' g
II Instt u fü. F gC
c Tovrisch un itil B

BP

BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

SPECTRUM ANALYSIS USING A DUPONT 310 CURVE RESOLVER

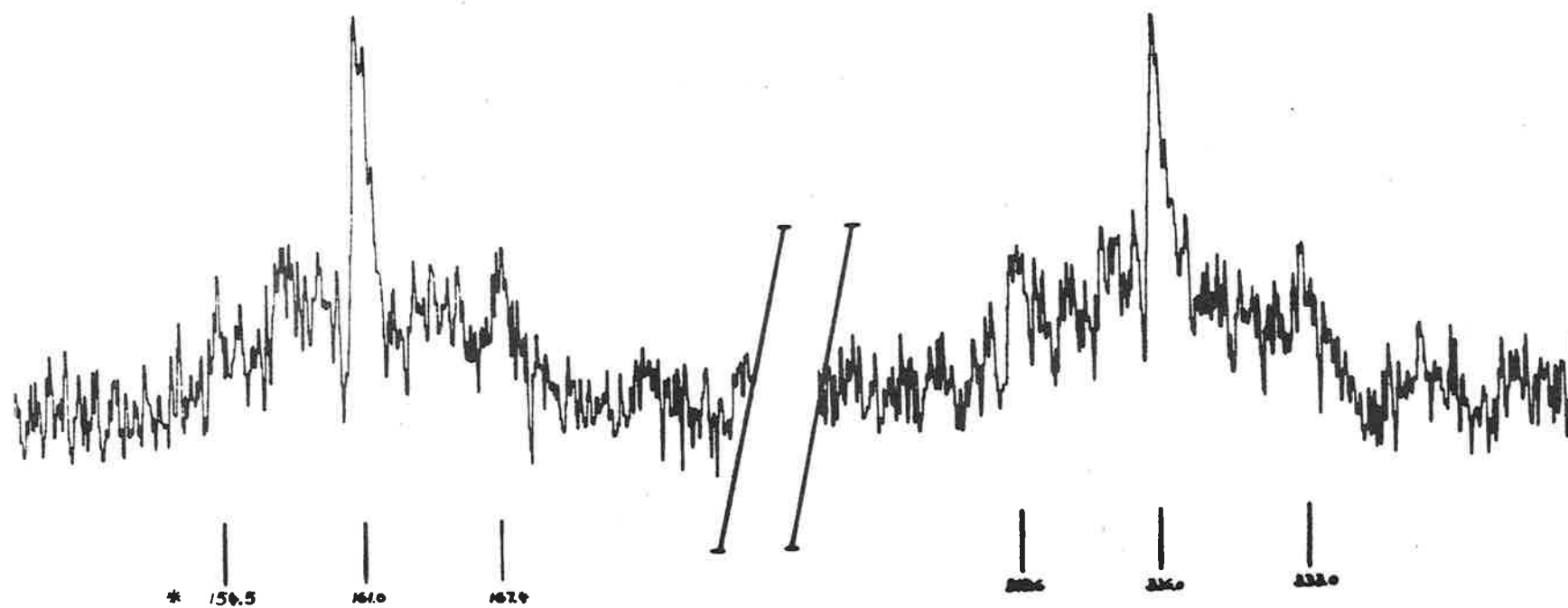In many applications band overlap problems greatly inhibit the extraction of analytical data from NMR spectra. In recent years attempts have been made to overcome these overlap problems using a variety of techniques (1). Where the spectrum of interest consists of a number of overlapping symmetrical bands with the same basic line shape the system can be resolved or at least partially resolved eg by deconvolution methods, (1). However, in many industrial applications spectra given by commercial products, eg petroleum fractions, are usually composed of overlapping bands of very different widths and shapes which makes the application of mathematical methods difficult. To overcome these difficulties we have recently been conducing some experiments with a Dupont 310 Curve Resolver, where the composite (experimental) spectrum is synthesized by summing a number of component peaks which are generated by the instrument. The original spectrum, the matching synthesized spectrum and the component peaks can be readily displayed, superimposed or otherwise on the instrument viewing screen. Further details of the instrument and its operation have appeared elsewhere, (2), (3).

In practice we have found the instrument very simple to use and the changes that can be observed in the synthesized spectrum on the addition of various peaks can be most illuminating. Figure 1 shows a typical analysed spectrum given by a petroleum fraction of which it was desired to know the various concentrations of CH_3, CH_2 and CH groups. Analyses of this kind are not possible at this time by any other method.

While the use of the 310 Curve Resolver is obvious equally obvious is its abuse. Clearly, realistic band shapes must be generated using knowledge gained by the examination of the spectra of suitable reference materials. Also the positioning of bands must be done carefully using reference chemical shift data. If these dangers are realised and accommodated the 310 Curve Resolver can be a most useful aid in spectrum analysis.

We should like to acknowledge the kind co-operation of Mr I.G. Wylie of Dupont Instruments, Hitchin, Herts, England in this work.

S.A. Knight

REFERENCES

(1) R.R. Ernst, Advances in Magnetic Resonance, Vol 2, 50.

(2) 310 Curve Resolver, Instrument Products Division,
     E.I. Du Pont de Nemours and Co. (Inc), Wilmington, Delaware
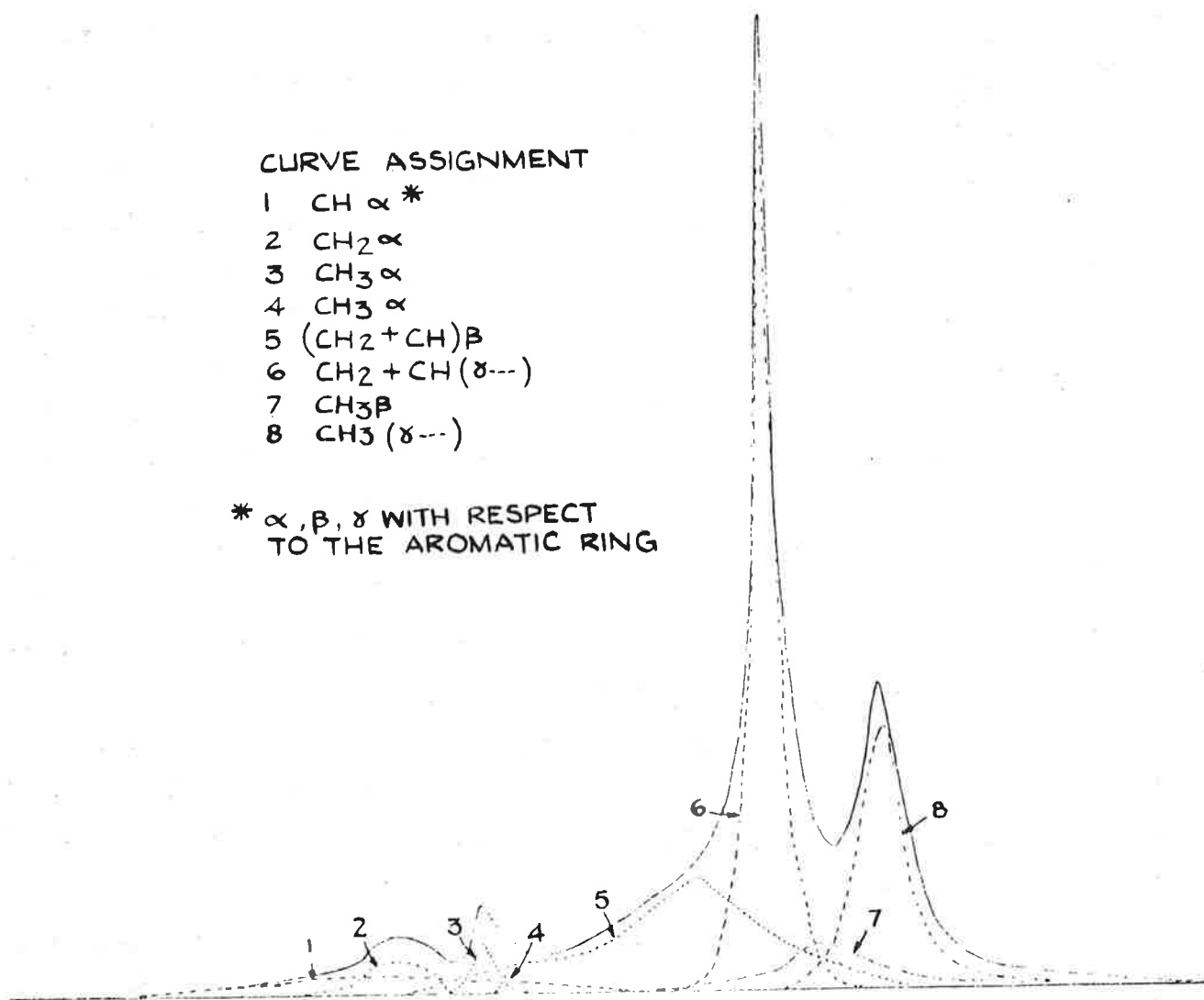   19898.

(3) Chem and Eng News 1965, 43, 50.

ALKYL REGION OF HYDROGEN-NMR SPECTRUM
OF AN AROMATIC PETROLEUM FRACTION

FIG 1

CURVE ASSIGNMENT
1 CH α *
2 CH$_2$ α
3 CH$_3$ α
4 CH$_3$ α
5 (CH$_2$ + CH) β
6 CH$_2$ + CH (γ---)
7 CH$_3$ β
8 CH$_3$ (γ---)

* α, β, γ WITH RESPECT
  TO THE AROMATIC RING

Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich

PD Dr. R.R.Ernst

ZÜRICH,
Universitätstrasse
Tel. (051) 32 73 30

7-7-69

Prof. B.L.Shapiro
Dept. of Chemistry
Texas A and M University
College Station, Texas 77843

COMPUTER INTERFACE FOR TIME AVERAGING DEVICE

Dear Barry,

One of the main handicaps for using computers in connection
with spectrometers is to get the necessary interfaces. We were faced
with the situation having a good computer (Varian 620i) and several
spectrometers (A60D, DA60, HR220 and a self-made one) but no inter-
face to connect them. We decided to use our C1024 time averaging
device to accumulate the data from the spectrometers and, later, to
transfer them to the computer for data handling. Actually, for many
people, this may be one of the easiest ways to feed NMR spectra into
a computer. Even if a direct interface is available (we got ours in
the mean time from Varian), it can well be justified to use a C1024
for tedious time averaging instead of blocking a computer for the
entire time (we want to use, for example, the computer at the same
time for IR interferometry). At present, we are using this system
for stochastic resonance experiments, employing noise to excite the
resonances.

The attached scheme should be self-explanatory. The inter-
face connects the binary output of the C1024 to the I/O bus of the 620i.
Except for the levelconverters, integrated circuits from Texas Instru-
ments are used. It is important to interconnect pins 32 and 48 at the
C1024 connector P1, otherwise, the address advance does not work. The
address of the interface arbitrarily was selected to be 15_8.

The following little routine will load 1024 words from
the C1024 into the computer memory starting at address FADDR. The
C1024 controls are switched to BINARY READ OUT mode.

```
        ,LDB    ,FADDR      load address of first memory location
        ,LDXI   ,1024       load number of words to be transfered
START   ,CIA    ,015        transfer one word into A register
        ,CPA    ,           complement content of A register
        ,STA    ,0,2        store content of A register
        ,IBR    ,           form next address
        ,DXR    ,           count transfered words
        ,JXZ    ,STOP       stop if 1024 words transfered
        ,JMP    ,START      go to next transfer
STOP    ,HLT    ,           halt
```

This shows that it is not too difficult to build simple interfaces
yourself.

                        With best regards

                        Richard

                        Richard R. Ernst

INTERFACE
C1024 - 620i

7-7-69 R.E.
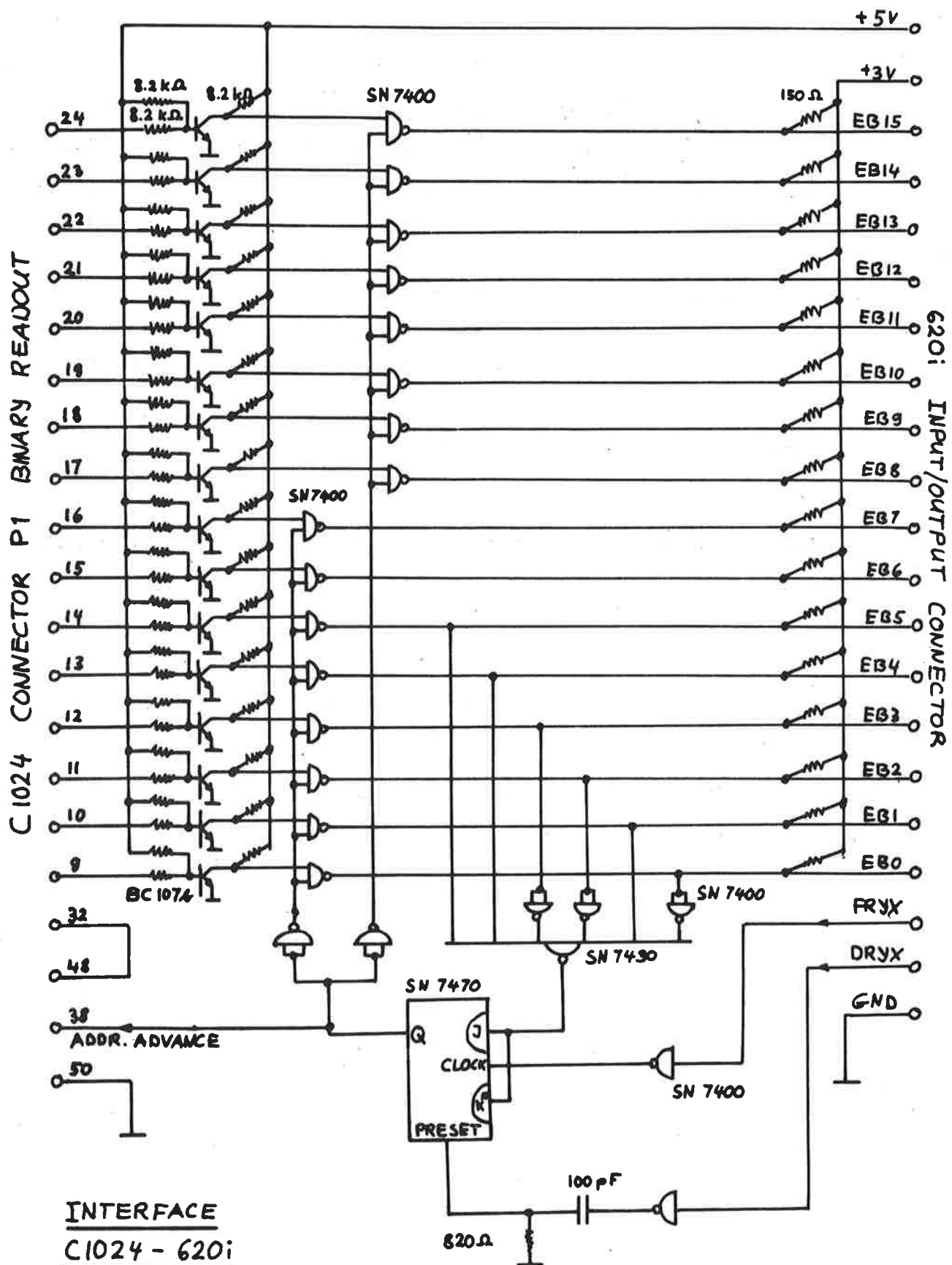
Southern Research Institute

2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35205
TELEPHONE 205-323-6592

July 11, 1969

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

Some Observations of Proton-Fluorine Coupling Constants

Dear Barry:

In 1965 we reported observation of spin-spin coupling between H_6 and H_8 and between H_2 and H_6 of the purine cation.[*] We have since observed spin-spin coupling of H_8 of 9-benzyl-2,6-difluoropurine, I, with at least one of the fluorines, presumably F_6.
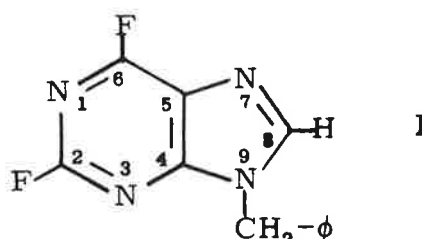
It was not possible to resolve the H_8 peak sufficiently well to determine whether H_8 is coupled to both fluorines, but the broadness of the "doublet" suggests that this may well be so. This coupling was observed on the neutral molecule in $CDCl_3$, whereas that reported for purine was not observable on the neutral molecule, but only on the cation. $J(F_6, H_8)$ of I is approximately 1.6 Hz, whereas $J(H_6, H_8)$ of the purine cation was found to be about 0.3 Hz.

Over a period of several years, we have had occasion to determine the pmr spectra of 23 nitrosoureas of the form
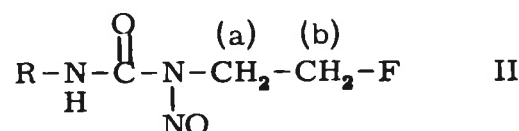
Professor Bernard L. Shapiro
July 11, 1969

-2-

where R varied among aliphatic and aromatic groups. In all cases
the proton spectrum of the 2-fluoroethyl group was of the general
form (eliminating some fine structure on the "triplets"):

$H_o \longrightarrow$
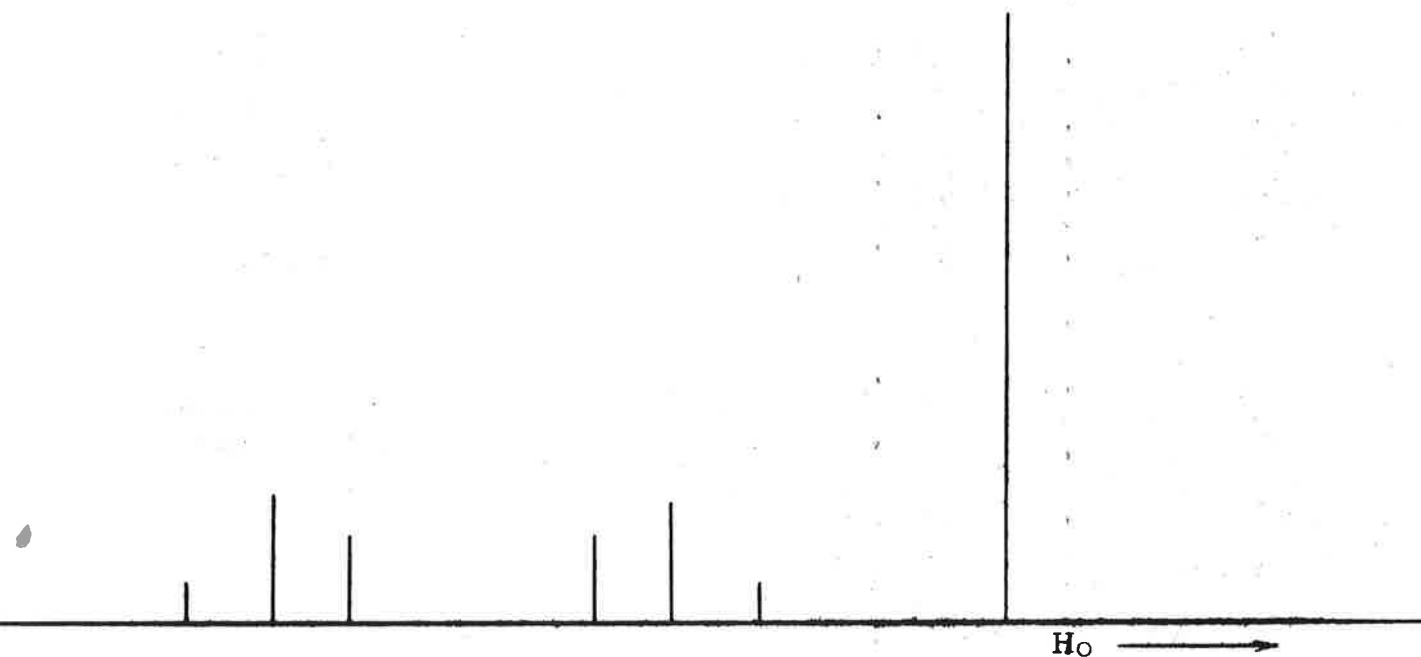
The (a) and (b) protons are practically insensitive to the nature of R,
both as to δ's and J's. In all such spectra which we have obtained

$$\delta_a - \tfrac{1}{2} J(H_a, F) \cong \delta_b - \tfrac{1}{2} J(H_b, F),$$

thus giving rise to the upfield singlet which represents half of the total
absorption from the (a) and (b) protons. As measured from the center peaks
of the "triplets" to the singlet: $J(H_a, F) \approx 22$ Hz, $J(H_b, F) \approx 49$ Hz, with
variations of 1-2 Hz over the range of 23 compounds.

Ureas without the nitroso group, of the form

$$\underset{\substack{| \\ H}}{R-N}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\substack{| \\ H}}{N}-\overset{(a') \;\; (b')}{CH_2-CH_2}-F \qquad III$$
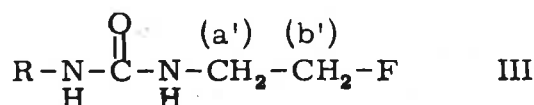
Professor Bernard L. Shapiro
July 11, 1969

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give more complex and predictable spectra, since δ_a' is smaller, and $J(H_a', F)$ greater ($\sim$27 Hz), than in compounds of type II.

Sincerely yours,

Martha Thorpe, Research Chemist
Molecular Spectroscopy Section

MT fh

*W. C. Coburn, Jr., M. C. Thorpe, J. A. Montgomery, and K. Hewson, J. Org. Chem., **30**, 1110 (1965).

Department of Chemistry

BROCK
University

St. Catharines, Ontario   July 11, 1969.

Glenridge Campus
684-7201 Ext. 317

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

ADDUCTS OF MIXED BORON TRIHALIDES

Dear Dr. Shapiro:

With this contribution I would like to begin a subscription
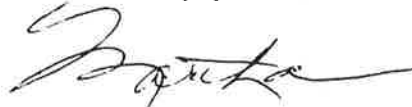to the TAMU NMR Newsletter. Brock University's small n.m.r. group,
consisting primarily of Dr. Jack Miller and myself and our students, is
mainly concerned at present with the study of Lewis acid-base complexes.
We have an A-60 with CAT and spin decoupler at Brock, and have had
access to more extensive n.m.r. facilities through the courtesy of
McMaster University's Chemistry Department.

We have recently observed low-temperature proton, fluorine
and boron-11 n.m.r. spectra of the mixed boron trihalide adducts
$Me_2O.BF_2Cl$ and $Me_2O.BFCl_2$. These form readily through halogen
scrambling when a methylene chloride solution of the adducts $Me_2O.BF_3$
and $Me_2O.BCl_3$ is warmed briefly to room temperature. Adducts of the
mixed boron trihalides do not appear to have been reported previously
although the mixed trihalides themselves, which are unstable to dis-
proportionation, are well known.

As expected, the proton complexation shifts of the mixed
adducts are intermediate between those of the BF_3 and BCl_3 adducts;
however they do not vary linearly with the number of chlorines.
(Me_2O complexation shifts in p.p.m: BF_3, 0.59; BF_2Cl, 0.65; $BFCl_2$,
0.78; BCl_3, 0.96). Trends in the fluorine spectra of the adducts
resemble trends in the free mixed trihalides:

	^{19}F Chemical shifts (ppm from $CFCl_3$)		$J_{^{11}B - ^{19}F}$ (Hz)	
	free trihalide (1)	$Me_2O.BX_3$	free trihalide (1)	$Me_2O.BX_3$
BF_3	124.2	158.2	15	~0
BF_2Cl	73.5	132.6	34	26
$BFCl_2$	36.0	116.2	74	56

- 2 -

If the ^{19}F chemical shift pattern of the free trihalides is attributed to Π bonding, survival of much of the Π bonding in the adducts is indicated, in line with recent calculations (2).

We attempted boron - 11 resonance at 11.46 MHz to verify the coupling patterns seen in the fluorine - 19 spectra. We did not get sufficient resolution for this. However, in related work with solutions containing $Me_2O.BCl_3$ and $Me_2O.BBr_3$, boron - 11 resonance provided evidence for the existence of the mixed complexes $Me_2O.BCl_2Br$ and $Me_2O.BClBr_2$.

Preliminary studies show that the mixed boron halide adducts of a number of other Lewis bases form readily by halogen scrambling. We are investigating the scope and limitations of this reaction.

Yours sincerely,

Steve Hartman

J. S. Hartman.

JHS:nd

References:

(1) T. D. Coyle and F. G. A. Stone, J. Chem. Phy., 32, 1892 (1960).

(2) D. G. Brown, R. S. Drago, and T. F. Bolles, J. Am. Chem. Soc. 90, 5706 (1968).

Istituto di Chimica Organica e di Chimica Industriale
dell'Università di Bologna

Dr. Bernard L. Shapiro
Dept. of Chemistry
Texas A and M University
College Station
Texas, 77843 (U.S.A.)

24/7/1969

li ....

Viale Risorgimento, 4 - Tel. 42.18.80
c.a.p. 40136

<u>Title</u>: A further lifting of the deceptive simplicity
in the p.m.r. spectrum of the molecule of the
furan.

Dear dr. Shapiro,

        I have been recently interested in measuring the 60 MHz. spectra of
a series of mercury-furan derivatives in concentrated DMSO solutions, and thus I also
measured the furan itself in the same solvent . I observed that in a 50% solution in
DMSO the central peaks of the two triplets of its spectrum are actually resolved in
three bands, each other separated by 0.11 Hz. Furthermore also the bands of much
smaller intensity have been detected, so that the whole spectrum displaied 18 out of
the 24 theoretical bands of an AA'BB.
The spectrum of the furan is normally formed by only two triplets and for such a
reason was at first believed to be an A_2X_2 system. Abraham and Bernstein [Can. J. of
Chem. <u>39</u>, 216, 905, (1961)] pointed out however that it had to be considered a case of
deceptive simplicity and later Reddy and Goldstein [J. Am. Chem. Soc., <u>84</u>, 583, (1962)]
by resolving in a doublet each of the central peaks of the triplets, observed an 8
band spectrum. Grant, Hirst and Gutowsky, enhancing the bands of very small intensity,
obtained a 14 bands spectrum [J. Chem. Phys., <u>38</u>, 470, (1963)].
In the present case a still more resolved spectrum is displaied and therefore
mesurements of the greatest precision hitherto atteined for the furan could be carried
out by means of the LAOCN III computing program.

Tables with the chemical shifts (referred to the DMSO which is 151.87 Hz. downfield
in respect to TMS) and J coupling constants as well as the experimental and calculated
frequencies are reported.
Only very few lines are still degenerate in the present spectrum, as it can be seen
in the figure in which the upfield symmetrical half spectrum is reported (upper)
together with the calculated one (below), drawn for greater convenience in a twice
enlarged scale.

It can be thus concluded that in such conditions of solvent and resolution (band
width = 0.15 Hz.) the deceptive simplicity of the 60 MHz. spectrum of the furan
is completely removed.

Yours sincerely

(Lodovico Lunazzi)

TABLE 1 - Chemical shifts (in Hz. in respect to DMSO) and J_{HH} coupling constants for the 60 MHz. spectrum of the furan.

	Present work	Ref. 2	Ref. 3
$\nu_1 = \nu_4 =$	$306.89_2 \pm .009$		
$\nu_2 = \nu_3 =$	$236.02_8 \pm .009$		
$J_{12} = J_{34} =$	$1.75_2 \pm .030$	1.75	1.8
$J_{13} = J_{24} =$	$0.81_4 \pm .030$	.85	0.8
$J_{14} =$	$1.48_6 \pm .012$	1.4	1.5_5
$J_{23} =$	$3.27_1 \pm .014$	3.3	3.5_3
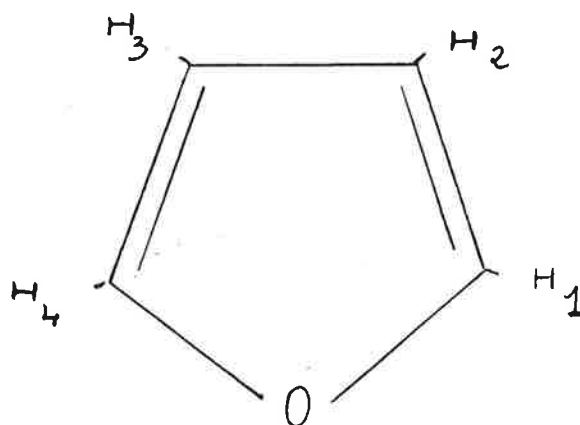
TABLE 2 - Experimental and calculated 60 MHz. spectrum of the furan.

Transitions	Calculated frequencies	Intensity	Experimental frequencies
33	231.203	0.017	231.15
48	234.125	0.109	234.14
54	234.722 }	1.928	234.76
42	234.742 }	1.929	
28	235.909 }	1.879	235.90
5	235.960 }	1.977	
29	236.050	1.982	236.01
52	236.141	1.891	236.13
2	237.288 }	2.072	237.34
13	237.308 }	2.074	
27	237.925	0.121	237.99
6	240.807	0.022	240.76
34	302.113	0.022	302.07
22	304.995	0.121	305.00
37	305.612 }	2.074	305.62
53	305.632 }	2.072	
47	306.779	1.891	306.81
11	306.870	1.982	306.92
30	306.960 }	1.977	307.03
21	307.011 }	1.879	
8	308.178 }	1.929	308.17
1	308.198 }	1.928	
51	308.795	0.109	308.75
12	311.717	0.017	311.67
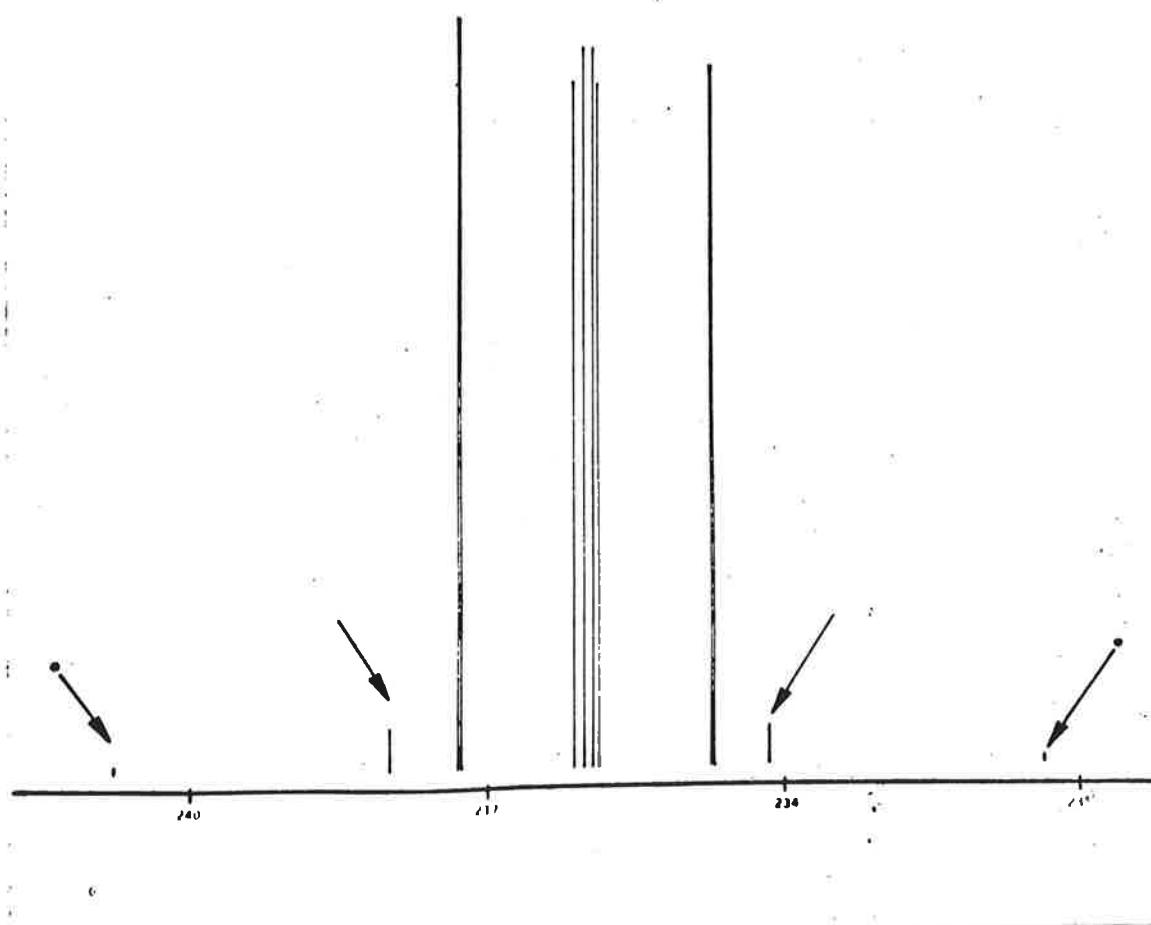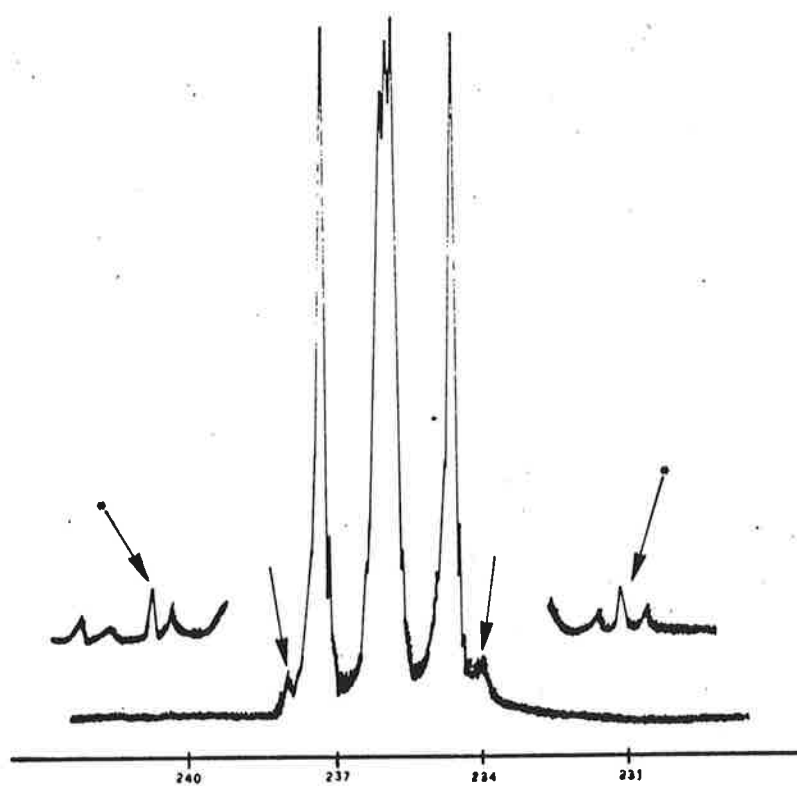
PROFESSOR OF ORGANIC CHEMISTRY

W. D. OLLIS

TELEPHONE No. 78555 EXT. 462

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY

SHEFFIELD

S3 7HF

14th July, 1969

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

Dear Barry,

Diastereoisomeric N, N'-diacylhydrazines

Hindered rotation about the N—N' bond of the N, N'-diacyl-hydrazines (I) results in the possible existence of three racemates (Ia, Ib, and Ic) associated with enantiomers having the indicated absolute configurations. The Cahn—Ingold—Prelog designations used in the formulae (Ia, Ib, and Ic) refer in the following order to the chirality of (i) the acyl residue on the left, (ii) the N—N bond, and (iii) the acyl residue on the right.

$$\text{PhCHX—CO} \qquad \text{CO—CHXPh}$$
$$\text{N—N}$$
$$\text{Me} \qquad\qquad \text{Me}$$
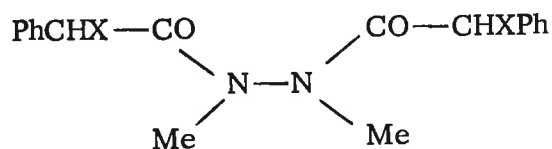
(I)

(a) RRR : SSS

(b) RRS : RSS

(c) RSR : SRS

This possibility of associating the formula (I) with three racemates has been examined by treating N, N'-dimethylhydrazine with (±)-2-phenyl-

propionyl chloride. This yielded two compounds, A, m.p. 87-90°, and B, m.p. 116-119°. The compound A in pentadeuterionitrobenzene solution at 140° showed a doubling of all the signals assignable to the N$-$CH$_3$, CH$-$Me, and CH$-$CH$_3$ groupings. This identifies compound A as giving the racemate (Ib; X = Me) in solution and appropriate coalescences are observed in its nuclear magnetic resonance spectrum at 200° due to a more rapid equilibration between the enantiomers (Ib, RRS) and (Ib, RSS). Compound B gives a nuclear magnetic resonance spectrum in C$_6$D$_5$NO$_2$ solution at 140° showing that it is an equilibrium mixture derived from the racemates (Ia and Ic; X = Me) in a 4 : 1 ratio; it is not yet possible to determine which of the two racemates (Ia or Ic; X = Me) predominates. At higher temperatures (200°) the changes in the nuclear magnetic resonance spectrum of compound B correspond to a more rapid interconversion of the racemates (Ia and Ic; X = Me) resulting in an N$-$Me singlet and a C$-$Me doublet.

The temperature-dependence of the nuclear magnetic resonance spectra of compound A depends upon the rate of interconversion between the enantiomers (Ib, RRS) and (Ib, RSS), whereas for compound B, the temperature-dependence involves the equilibrium between the racemates (Ia) $\rightleftharpoons$ (Ic). Both these phenomena involve N$-$N bond rotation and the rotational barrier determined for both cases is of the same order as that found for other N,N'-diacylhydrazines (G. J. Bishop, B. J. Price, and I. O. Sutherland, Chem.Comm., 1967, 672). Below 140°, spectra were as expected further complicated by the consequences of hindered rotation about the N$-$CO bond.

Similar results have been obtained by acylation of N, N'-dimethylhydrazine with (±)-2-phenylbutyryl chloride giving the compounds (I; X = Et). In this case the configurational assignments have been checked using optically active S-(+)-2-phenylbutyryl chloride as the acylating agent.

We feel that these results are of general interest in that they indicate a new approach for the examination of certain processes involving bond rotation and ring inversion.

Yours sincerely,

R. P. Gellatly   W. D. Ollis   I. O. Sutherland

Organisch-Chemisches Institut
der
Technischen Universität Berlin

Direktor: Prof. Dr. F. Bohlmann

1 Berlin 12, den **July 15, 1969**
Straße des 17. Juni Nr. 115 (Chemiegeb.)
Fernruf: ~~XXXXXXXXXX~~ 314 2252
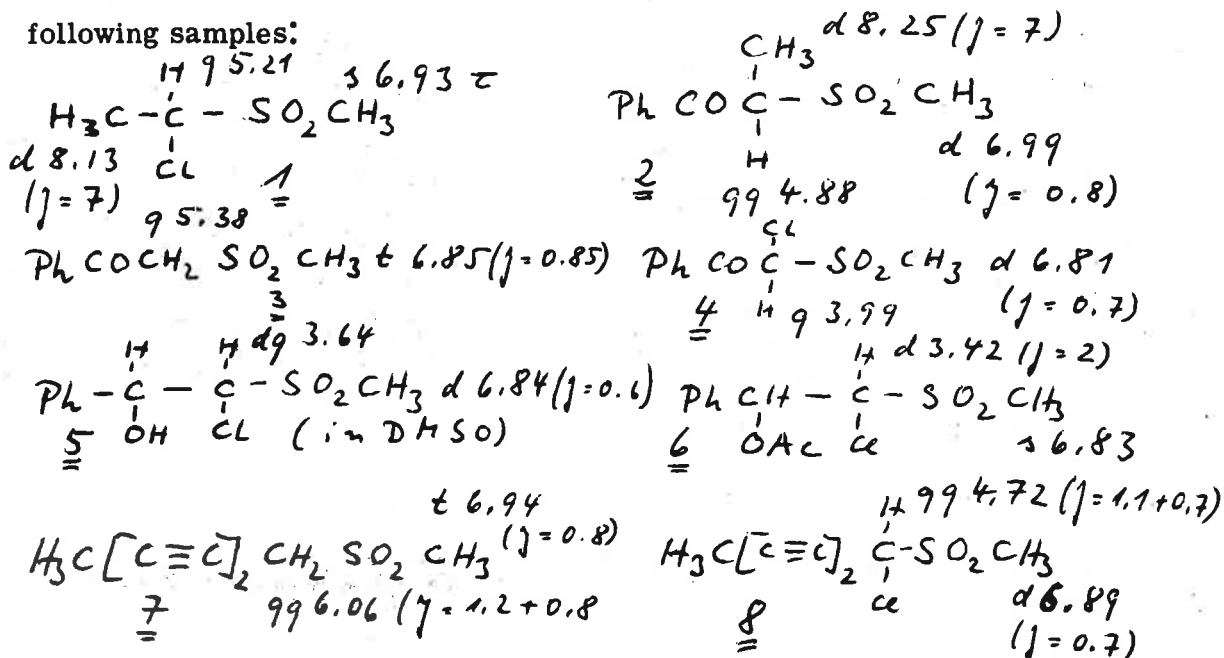
Prof. Dr. B. Shapiro
Department of Chemistry
Texas University
College Station
U.S.A.

Dear Professor Shapiro:

Long range coupling in sulfones

In connection with synthetic work on epoxysulfones we have measured the
NMR-Spectra of several unsymmetrical sulfones. It turns out that in most
cases a long range coupling could be observed as seen in the data of the
following samples:

$H_3C - \overset{H \; q \; 5.21}{\underset{Cl}{C}} - SO_2CH_3 \quad \overset{\searrow 6.93 \; \tau}{}$

$\alpha\,8.13 \; (J = 7) \quad q\,5.38 \quad \underline{\underline{1}}$

$Ph\,COCH_2\,SO_2\,CH_3 \quad \tau\,6.85\,(J = 0.85)$

$\underline{\underline{3}}$

$Ph - \overset{H}{\underset{OH}{C}} - \overset{H \; dq \; 3.64}{\underset{Cl}{C}} - SO_2CH_3 \quad \alpha\,6.84\,(J = 0.6)$

$\underline{\underline{5}} \quad (in\;DMSO)$

$H_3C\,[C \equiv C]_2\,CH_2\,SO_2\,CH_3 \quad \overset{\tau\,6.94}{(J = 0.8)}$

$\underline{\underline{7}} \quad q\,6.06\,(J = 1.2 + 0.8)$

$\overset{CH_3 \; \alpha\,8.25\,(J = 7)}{Ph\,CO\,\underset{H}{\overset{|}{C}} - SO_2\,CH_3} \quad \alpha\,6.99$

$\underline{\underline{2}} \quad qq\,4.88 \quad (J = 0.8)$

$Ph\,CO\,\overset{Cl}{\underset{}{C}} - SO_2\,CH_3 \quad \alpha\,6.81$

$\underline{\underline{4}} \quad H\,q\,3.99 \quad (J = 0.7)$

$Ph\,\overset{H \; \alpha\,3.42\,(J = 2)}{\underset{OAc}{C}H} - \overset{}{\underset{Cl}{C}} - SO_2\,CH_3$

$\underline{\underline{6}} \quad \searrow 6.83$

$H_3C\,[C \equiv C]_2\,\overset{H \; qq \; 4.72\,(J = 1.1 + 0.7)}{\underset{Cl}{C}} - SO_2\,CH_3$

$\underline{\underline{8}} \quad \alpha\,6.89 \quad (J = 0.7)$

Only in the spectra of $\underline{\underline{1}}$ and the acetate $\underline{6}$ no coupling could be observed.
There is one further point which might be of interest: The extremely down-
field shift of the dq. 3.64 in compound $\underline{\underline{5}}$ in DMSO. In $(CD_3)_2CO$ this signal
is located at 4.69 τ , while all the other signals are nearly unchanged. Per-
haps in DMSO the following solvate may be the reason:

$Ph \diagdown \overset{Cl}{\underset{H}{\diagup}} SO_2CH_3$
$H \diagup \overset{}{\underset{}{}} H$
$\overset{O}{\underset{S}{}} \diagup O$
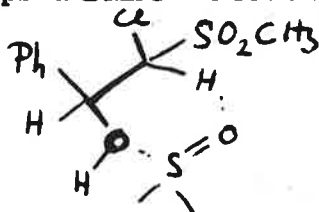
Yours sincerely

F. Bohlmann

PHYSIQUE EXPÉRIMENTALE MOLÉCULAIRE

FACULTÉ DES SCIENCES

9, Quai Saint-Bernard - 75 - PARIS (5e)

Tour 32 - 2e étage

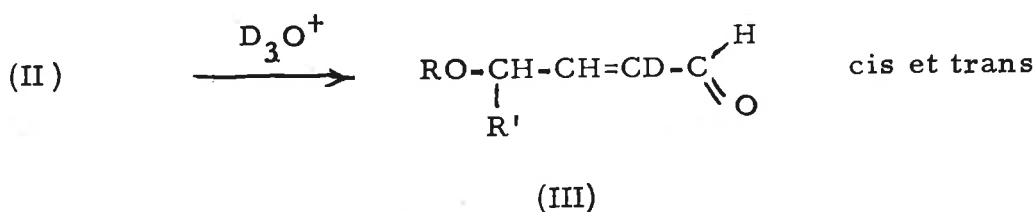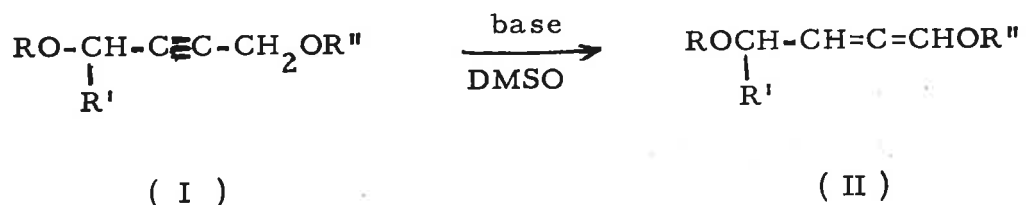Tél. : 336-25-25 - Poste 40-53

Paris, le 22 juillet 1969

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

TEXAS 77843   (U. S. A.)

Cher Professeur SHAPIRO,

"Mise en évidence, par R. M. N., de la structure d'alcoxy-aldéhydes α éthyléniques α deutériés".

Des alcoxy-aldéhydes α éthyléniques α deutériés avaient été préparés par la méthode suivante (1)(2) :

$$RO-\underset{\underset{R'}{|}}{C}H-C\equiv C-CH_2OR'' \xrightarrow[\text{DMSO}]{\text{base}} RO\underset{\underset{R'}{|}}{C}H-CH=C=CHOR''$$

(I)   (II)

$$(II) \xrightarrow{D_3O^+} RO-\underset{\underset{R'}{|}}{C}H-CH=CD-C\overset{H}{\underset{O}{\diagdown}} \quad \text{cis et trans}$$

(III)

La chromatographie en phase vapeur n'avait pas permis de différencier les composés deutériés de leurs homologues hydrogénés. Par R. M. N., nous prouvons immédiatement que la deutériation s'est bien effectuée et, de plus, nous définissons sans ambiguïté la position du deutérium dans la molécule.

.../...

En effet, alors que dans le composé hydrogéné (III) on observe un doublet pour le proton aldéhydique 1 par couplage avec le proton 2 (J_{1-2} = 7, 6 Hz trans ; J_{1-2} = 7, 3 Hz cis), dans l'homologue deutérié, il apparaît un triplet de constante de couplage très faible ($J \sim 1$ Hz), qui témoigne de la présence d'un deutérium en position 2.

D'autre part, la R. M. N. distingue les isomères cis et trans pour lesquels le déplacement chimique du proton aldéhydique est différent :

$$\delta_1 \text{ cis} = 10, 08 \text{ p. p. m.}$$

$$\delta_1 \text{ trans} = 9, 54 \text{ p. p. m.}$$

La figure ci-jointe représente les spectres obtenus pour R = R' = CH_3 sur un appareil Varian A 60, à température ambiante.

-=-=-=-=-=-=-=-

Références :

(1). - R. MANTIONE : Thèse Paris 1967

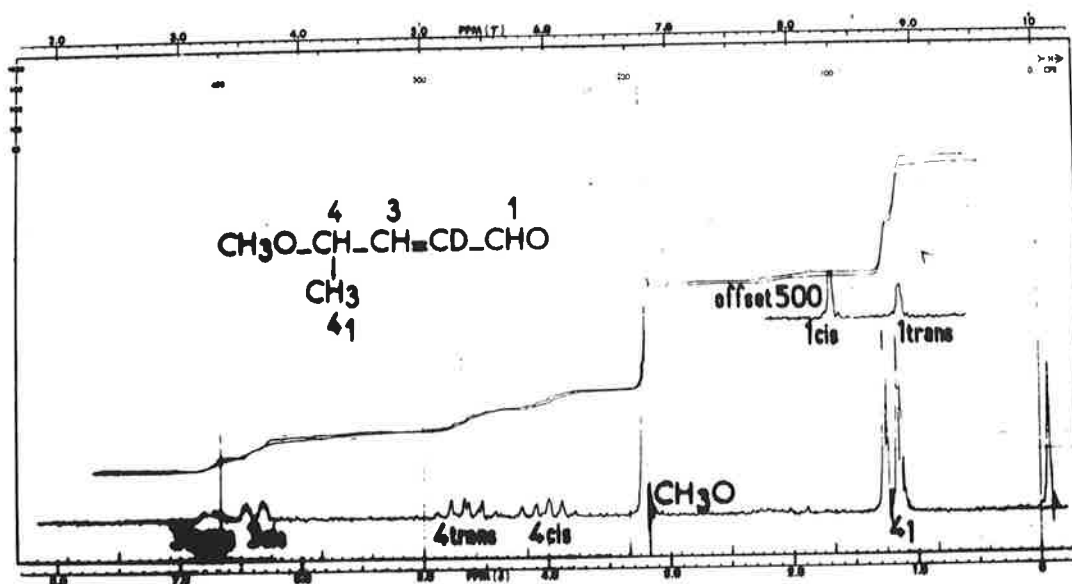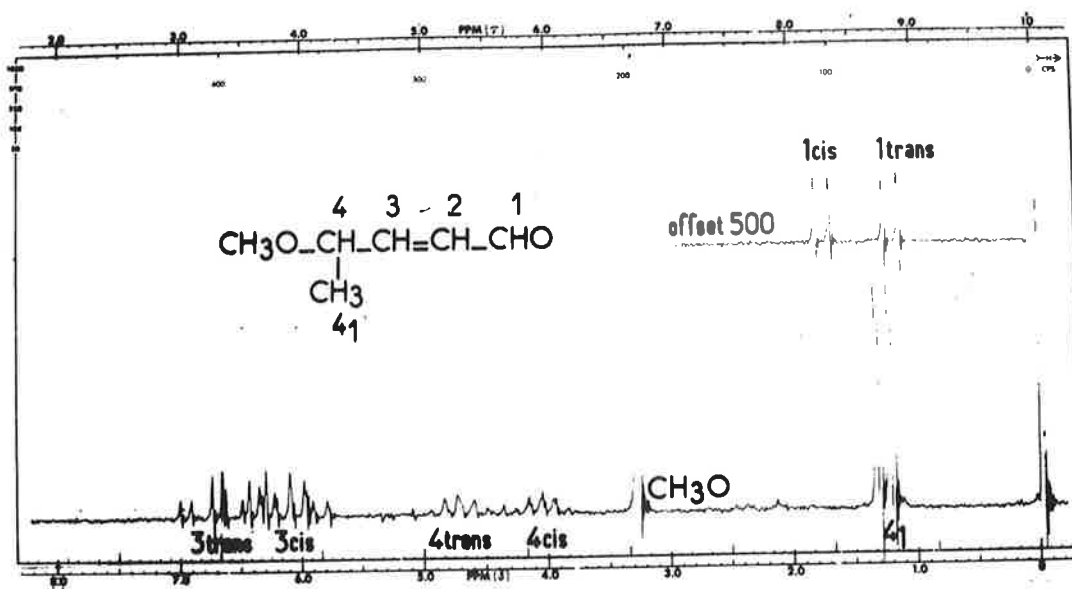(2). - R. MANTIONE : Bull. Soc. Chim. (à paraître)

Bien cordialement,

R. FREYMANN   pour R. MANTIONE   G. MARTIN

CH3O_CH_CH=CH_CHO
            |
           CH3
           4₁

1cis   1trans
offset 500

CH3O

3trans 3cis   4trans 4cis   4₁

CH3O_CH_CH=CD_CHO
          |
         CH3
         4₁

offset 500
1cis   1trans

CH3O

4trans 4cis   4₁

THE UNIVERSITY OF GEORGIA

Department of Chemistry

ATHENS, GEORGIA 30601

July 17, 1969

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

Dear Barry:

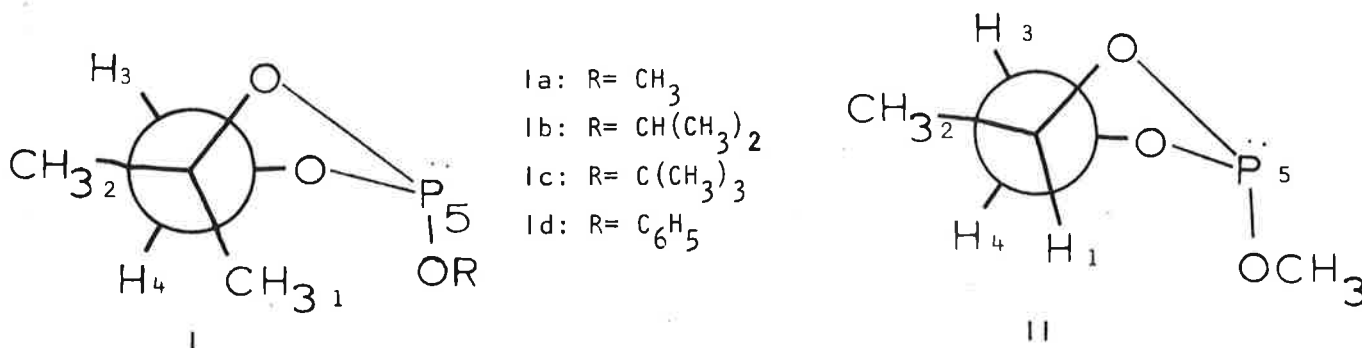"Conformation of Five-membered Ring Phosphites"

The interest in the synthesis of cyclic five-membered ring phosphate esters from analogous phosphite precursors has lead Gary Newton and myself to examine the stereochemistry of trivalent phosphorus, and the conformational preferences in these systems. Previous nmr studies of cyclic phosphites have agreed that inversion at phosphorus is very slow.[1-4] Furthermore, it has been shown that ethylene phosphites[3], ethylene chlorophosphite[2,3] and propylene phosphites[4] possess non-equivalent protons. However, two explanations have been offered for the different magnetic environments in these compounds: (1) a stable pyramidal stereochemistry at phosphorus with a planar five-membered ring[1,2,4] and (2) a twist-envelope conformation of the five-membered ring with a O-C-C-O dihedral angle of $30°$.[3]

We have examined the nmr spectra of a series of isobutylene phosphites I a-e and propylene phosphites II. The data obtained from a detailed analysis of these spectra are given in Table I. The P-O-C-H couplings constants observed in I are considerably different from those observed in ethylene phosphites[3]. It has been suggested that the different P-O-C-H couplings in ethylene phosphites are due to the orientation of the protons with respect to the lone-pair on phosphorus in a planar ring[2]. At least two factors are not consistent with this interpretation for the compounds reported here. (1) If the ring were planar, expected P-O-C-H couplings in the iso-butylene phosphites, 1, would be of similar magnitude as those observed for the ethylene phosphites[3]. The larger P-O-C-H couplings observed in 1 (13.0 vs 9.0 Hz) are incompatible with a planar ring. (2) Replacement of a proton cis to the phosphorus lone pair with a methyl group, as in II, should not alter the overlap of the remaining cis proton. However, significantly different

Professor Bernard L. Shapiro
July 17, 1969
Page 2

P-O-C-H couplings are observed in II.

Thus, the nmr data for I and II are not consistent with a planar ring, but are in accord with a twist - envelope conformation for the five-membered ring similar to that proposed for methyl ethylene phosphite[3] (a twist of $\sim 30°$). The coupling constants in II are consistent with this value whereas the larger P-O-C-H couplings in I suggest a somewhat larger degree of twist.

Ia: R= CH_3
Ib: R= $CH(CH_3)_2$
Ic: R= $C(CH_3)_3$
Id: R= C_6H_5

	v_1[a]	v_2	v_3	v_4	J_{34}[b]	J_{35}	J_{45}
Ia	1.447	1.248	3.796	3.802	-8.45	13.43	0.29
Ib	1.437	1.228	3.738	3.826	-8.32	12.99	0.27
Ic	1.440	1.206	3.714	3.874	-8.25	13.20	0.32
Id	1.479	1.336	3.723	3.803	-8.32	13.12	0.31
II	4.486	1.217	3.368	4.167	-8.22	8.17	1.94 (J_{15} = 0.40)
methyl ethylene phosphite[c]	3.656	3.405	3.405	3.656	-8.44	8.97	1.87

a. In ppm downfield from TMS.   b. In Hz.   c. Reference 3.

Sincerely yours,

Dick

Richard H. Cox
Assistant Professor

RHC:jlw

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4. H. Goldwhite, Chem. and Ind., 495 (1964).

Duke University
DURHAM
NORTH CAROLINA

DEPARTMENT OF CHEMISTRY

July 23, 1969

POSTAL CODE 27706
TELEPHONE 919-684-2414

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

Dear Dr. Shapiro:

"Decoupling" of ^{31}P-^{1}H in a Phosphine by Complexation
with Nickel Chloride

We wish to describe a particularly striking case where complexation of trivalent phosphorus with Ni^{++} results in complete disappearance of ^{1}H-^{31}P coupling. Such "decoupling" in metal complexes of phosphines is not unknown, although not well understood [for a recent discussion, see Fackler, et al, J. Am. Chem. Soc., 91, 1941 (1969)]. Our case is of interest in demonstrating the valuable simplification of the spectrum that results, and we point it out thinking that others unaware of the effect may find it useful in studying nmr spectra of phosphines. The spectrum may also interest those studying the spectra of complexes.

The spectrum of 1-methyl-3-phospholene is reproduced in Fig. 1. ^{31}P-Coupling causes the methyl group and the vinyl protons to appear as doublets, and the non-equivalent methylene protons to appear as an ABX signal. Fig. 2 is the spectrum of the $NiCl_2$ complex of this phosphine. The complex forms readily, although its analysis suggests a ratio of phosphine to $NiCl_2$ between 2 and 3. The spectrum shows the complete absence of any coupling to ^{31}P. Singlets are now present for the P-CH_3 group and the vinyl protons. The ABX of the methylenes is reduced to an AB signal. The result is precisely what would be expected for the phosphine under hetero-nuclear decoupling.
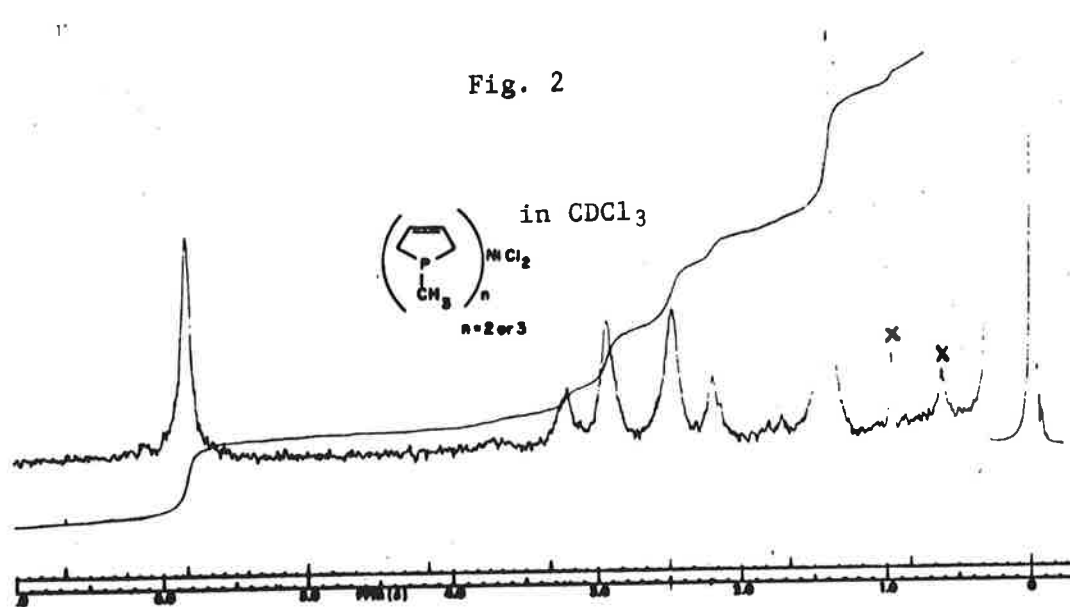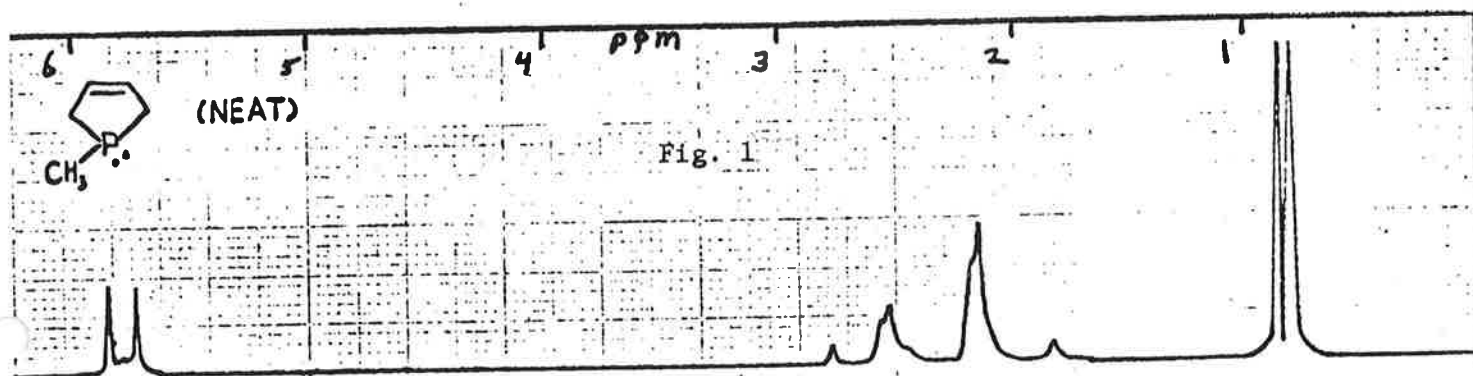
The same effect has been noted for 3,4-dimethyl-3-phospholene, which forms an exact 2:1 complex with $NiCl_2$.

Please credit this submission to Dr. Peter W. Jeffs, Department of Chemistry, Duke University.

Louis D. Quin   Jay G. Bryson

Fig. 1

(NEAT)

Fig. 2

in CDCl$_3$

n = 2 or 3

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT
Afd.: Dr.H.R.Buys

Wassenaarseweg
Postbus 75
Leiden
Telefoon 4 83 33
Tst.

LEIDEN, ...July 25...... 19..69..

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

Dear Professor Shapiro,

Geometry of the 1,3-oxathiane ring as found from NMR

In our laboratory, an extensive investigation into the geometry of cyclic organic compounds has been carried out[1], mainly by means of X-ray analysis. One of our present interests is to correlate the physical properties (viz.dipole moments, vibration spectra and coupling constants) with the geometrical arrangement of the atoms in non-aromatic ring compounds[1-4]. Recently, the so-called "R-value method", introduced by Lambert[5], was extended as follows[4]: For cyclic compounds having two equivalent conformers (i.e. conformer population ratio is 1:1, viz. 6-rings with two equivalent chair forms) and having a $-CH_2-CH_2-$ or a $-CH_2-CHR-$ moiety for which two vicinal proton coupling constants (J_{trans} and J_{cis}) can be evaluated from the NMR spectrum, the ratio

$$R = J_{trans}/J_{cis} \approx (3 - 2\cos^2\psi)/4\cos^2\psi \qquad (1)$$

ψ is the ring dihedral angle in the $-CH_2-CHR-$ fragment. The results for more than 20 compounds indicate[4] that the ψ values calculated from the experimental vicinal coupling constants with the aid of eq.(1) agree with the results from diffraction analyses within about $2°$.

We are currently interested in investigating saturated 1,3-dihetero six-membered rings and in this paper the results of the NMR analysis of 6,6-dimethyl-1,3-oxathiane (see Figure) are reported.
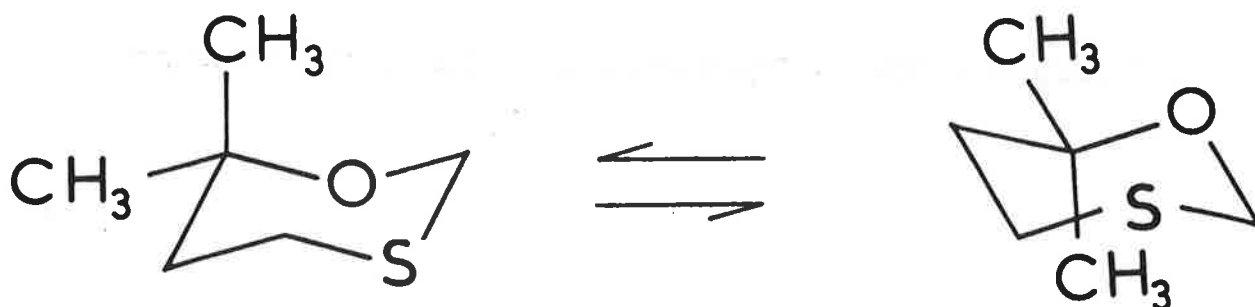
The AA'BB' spectrum of the C_4-C_5 moiety (taken at 100 Mc/s with a Varian HA-100 and at 60 Mc/s with a Jeol JNM-MH-60) yields: ν_A (protons at C_5) = 1.7 ppm, ν_B (protons at C_4) = 2.7 ppm, L = 5.3, M $\approx$ 0, N = 12.4 c/s.

K cannot be extracted from the spectrum. The low value of M is not un-
expected, as the geminal coupling constant in the $-CH_2-S-$ (thiane[6]) and
in the $-CH_2-CH_2-$ moiety (cyclohexane[7]) has about the same value (-13 c/s).
The vicinal couplings in the $-CH_2-CH_2-$ moiety follow from N and L and are,
thus, 8.8_5 and 3.5_5 c/s, respectively. This yields for R 2.49 and for the
ring dihedral angle $\psi = 60°$ (consistent with a normal chair geometry).

The corresponding 1,3-dioxane and 1,3-dithiane ring geometries are
known from X-ray analyses[8,9] on 2-substituted derivatives. The ring dihedral
angles in the $C_4-C_5-C_6$ moiety are 62° in the sulfur compound and 55° in the
oxygen compound, the latter value being in fair agreement with the R-value
for 1,3-dioxane and its 4,4-dimethyl derivative[4]. The geometry found from
NMR for the 1,3-oxathiane ring is, thus, intermediate between those of the
1,3-dioxane and the 1,3-dithiane systems, a trend also observed in the case
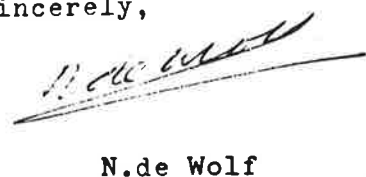of the corresponding 1,4-dihetero rings[1].

Syntheses of other derivatives of 1,3-oxathiane are in progress in or-
der to evaluate the ring dihedral angle about the C_5-C_6 bond, whereas an
X-ray analysis on 2-p-chlorophenyl-1,3-oxathiane will be carried out[10]
for obtaining the entire ring geometry and for a further test of the validi-
ty of the "R-value method".

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Yours sincerely,

H.R.Buys   N.de Wolf

𝕌𝕟𝕚𝕧𝕖𝕣𝕤𝕚𝕥𝕪 𝕠𝕗 ℕ𝕠𝕥𝕣𝕖 𝔻𝕒𝕞𝕖

College of Science

Notre Dame, Indiana 46556

Department of Chemistry

July 28, 1969

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

DNMR III Computer Program

Dear Barry:

Today just a brief progress report on our general NMR line-shape computer program DNMR (cf. TAMUNMRN 117-21).

Those of your readers who have obtained copies will have noticed that the original (loc. cit.) matrix diagonalization routines were replaced by ALLMAT (this version is now referred to as DNMR II). This change resulted in a tremendous boost in efficiency. Just to convince ourselves of what the program is now capable of doing we have performed a sample calculation on a ABCD $\rightleftharpoons$ EFGH exchange problem, a copy of which is attached. One such spectrum consumes 14 minutes of CPU time on our second-generation computer, and we are told that this will be reduced to about 1 minute once our new machine becomes operational (shall we believe it?).

In the meantime we have done more work on this program. We are reasonably convinced that the last bugs are now removed from an updated version (called DNMR III) that can handle magnetic equivalence and "twofold" symmetry, both in conjuction with mutual exchange if desired. Computation times can be reduced much further in cases where these options are applicable, and the extension to a greater number of spins becomes economically feasible. For example, treatment of an exchanging AA'BB' system now takes only 16 seconds. The theory is presently being written up for publication, and we plan to submit DNMR III to QCPE around Christmas time.

Sincerely yours,

Daniel A. Kleier

Gerhard Binsch

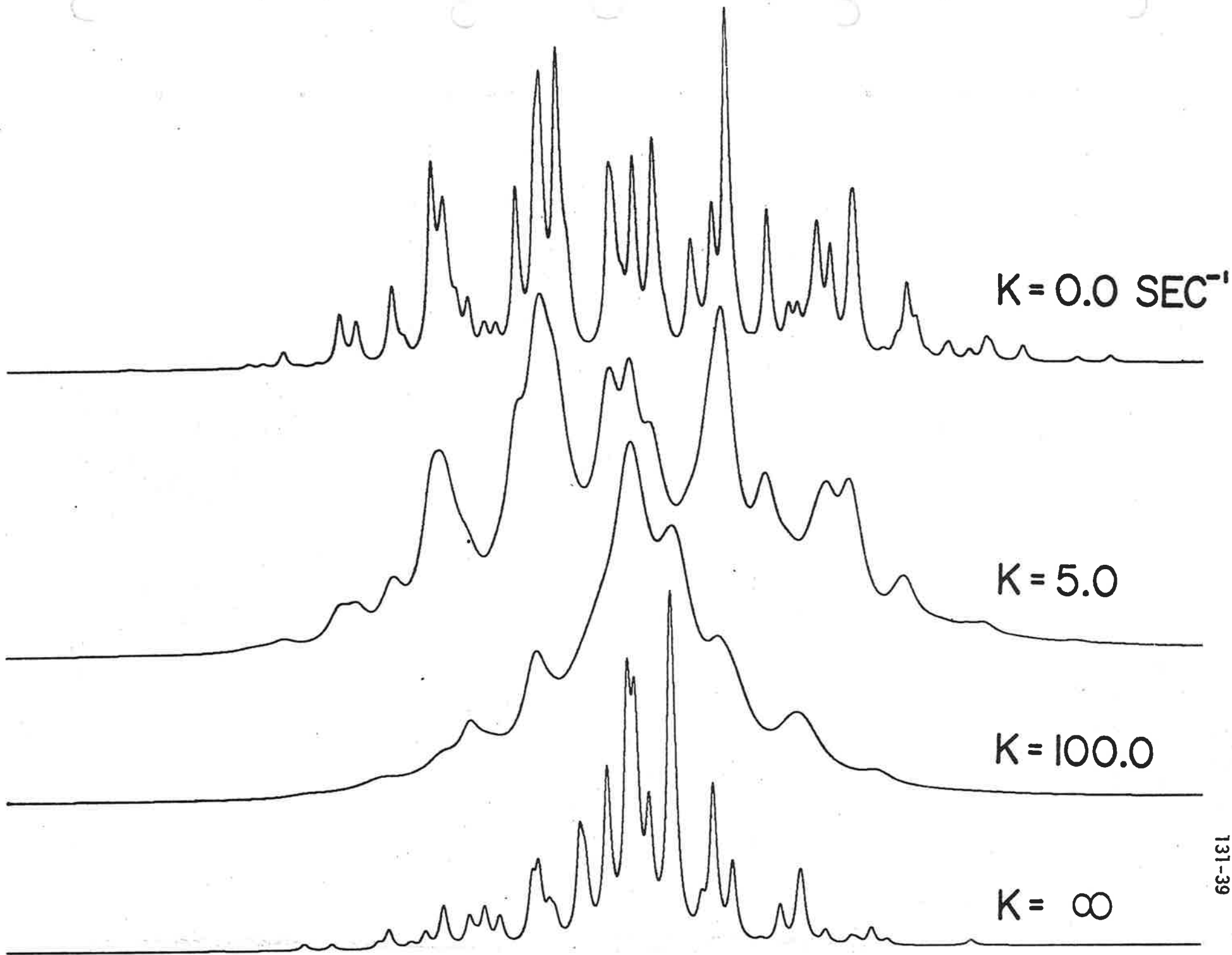DAK:GB:sk

Attachment

K = 0.0 SEC⁻¹

K = 5.0

K = 100.0

K = ∞

131-39

Eidg. Technische Hochschule
Laboratorium für Organische Chemie

Universitätstr. 6/8
CH-8006 Zürich
051 / 32 62 11

Zürich,   25. Juli 1969   fo

Herrn
Prof. Bernard L. Shapiro
Dept. of Chemistry
Texas A&M University
College Station, Texas 77843
U S A

Einfluss eines Porphyrinderivates auf die chemischen Verschiebungen
der Protonen von DSS

Sehr geehrter Herr Professor Shapiro,

In der Protonenresonanzspektroskopie wässriger Lösungen werden die chemischen
Verschiebungen heute generell bezüglich des Methylsignals von Natrium-2,2-
dimethyl-2-silapentan-5-sulfonat (DSS) gemessen. Bei der Verwendung von DSS
besteht jedoch die Gefahr, dass spezifische Assoziationen zwischen Referenz
und Probe die chemische Verschiebung des Referenzsignals beeinflussen. Dieser
Effekt kann besonders bei der Untersuchung aromatischer Protonen gross sein.
So ist z.B. das Signal der Methylgruppen von DSS in einer 0,8-molaren wässrigen
Lösung von 1,3-Dihydroxy-naphtalin gegenüber dem in reinem Wasser gemessenen
Wert um 48 Hz (vermutlich bei 60 MHz) nach höherem Feld verschoben. (E. S. Hand
und Th. Chohen, JACS 87, 133 (1965)).

Bei der Untersuchung des folgenden Porphyrinderivates (I) hat sich gezeigt, dass
eine derartige Verschiebung des Referenzsignals grösser als 1,5 ppm sein kann.

- 2 -
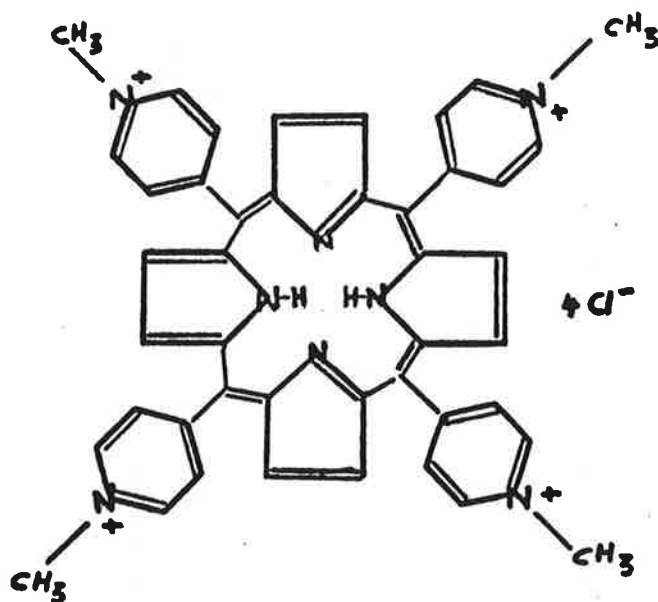
Die Konzentrationsabhängigkeit der chemischen Verschiebungen der Signale
von DSS (vgl. Tabelle 1) weist darauf hin, dass die beiden Verbindungen ein
Assoziat bilden. Die bezüglich einer externen TMS-Referenz gemessenen che-
mischen Verschiebungen wurden mit der Volumensuszeptibilitätskorrektur auf
Daten bezüglich interner Referenz umgerechnet. Die Volumensuszeptibilität
der Lösung wurde gleich der von reinem D_2O angenommen.

Bei der Untersuchung von 1,4-Dimethylpyridiniumjodid konnten keine derartigen
Effekte beobachtet werden. Dementsprechend sind die Effekte auf die chemische
Verschiebung von Protonen in DSS bei der Untersuchung des Porphyrinderivats
I nicht nur auf das Vorhandensein von N-Methylpyridiniumgruppen in dieser Ver-
bindung zurückzuführen.
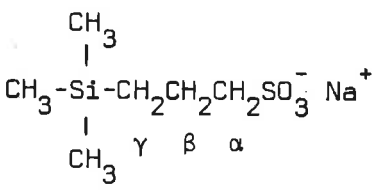
Mit freundlichen Grüssen

R. Scholer   K. Kläutschi   E. Pretsch

<u>Tabelle 1</u>   Konzentrationsabhängigkeit der chemischen Verschiebungen
der Protonen von Natrium-2,2-dimethyl-2-silapentylsulfonat

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_2CH_2CH_2SO_3^- \; Na^+$$
$$\gamma \quad \beta \quad \alpha$$

(δ in ppm; siehe Text)

$\dfrac{[DSS]}{[Porphyrin]}$	δCH_3	$\delta CH_2(\alpha)$	$\delta CH_2(\beta)$	$\delta CH_2(\gamma)$
1,2	- 1,49	--	--	--
2	- 1,04	1,91	--	--
3,9	- 0,95	2,07	0,91	--
4,7	- 0,9	2,18	1,01	--
5,7	- 0,8	2,36	1,18	--
8,6	- 0,61	2,59	1,40	- 0,09
15	- 0,48	2,72	1,56	0,14
28	- 0,21	2,9	1,72	0,44
ca. 10^3	0,06	3,04	1,87	0,66

STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

DEPARTMENT OF CHEMISTRY

July 16, 1969

STONY BROOK, N.Y. 11790

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

After Many a Letter Lives the Cheetah!

Dear Barry:

I am only mildly surprised that someone as completely
urbanized as you are (or would like to be) should be unaware
of the fact that a Cheetah may be trained for hunting. For
your information, therefore, I enclose a copy of the appropriate
page from a book for the "general reader" (Desmond Morris, "The
Mammals", Harper & Row, New York, N.Y. 1965; note picture of
topless Cheetah). Those desiring a deeper introduction to the
subject, should consult M. Chasseur and A. Nimrod, "The Hunting
Felidae, being a Disquisition on the Capture, Handling, Diseases,
and Dietary Proclivities of Acinonyx Jubatus and Divers Small
Cats of the Genus Felis, with Particular Attention to Their
Training in Duties Useful to Man, as is Done in Eastern
Countries, and with Especial Consideration of Their Possible
Importation into These Islands for the Purposes of Augmenting
the Sport of Hunting with a New Pursuit Similar to That of the
Falconers, and Reducing the Population of Noxious Vermin",
Venery and Sons, London, 1873.

The main point of this letter, however, is that I am more
than a little shocked, and, indeed, deeply concerned, that you,
to whose taste I have always deferred in all matters, particularly
those concerning cheesecake of any variety, should have been
so desperately in search of something to say to fill the bottom
of the page as to have penned the last sentence of your comment.
Say it isn't so, Barry! To show that you are not beyond redemption,
your first step on the long way back to a State of Grace might
be to publish the kind of picture that really turns you on
(if it still does). Are you game?

Yours in sorrow,
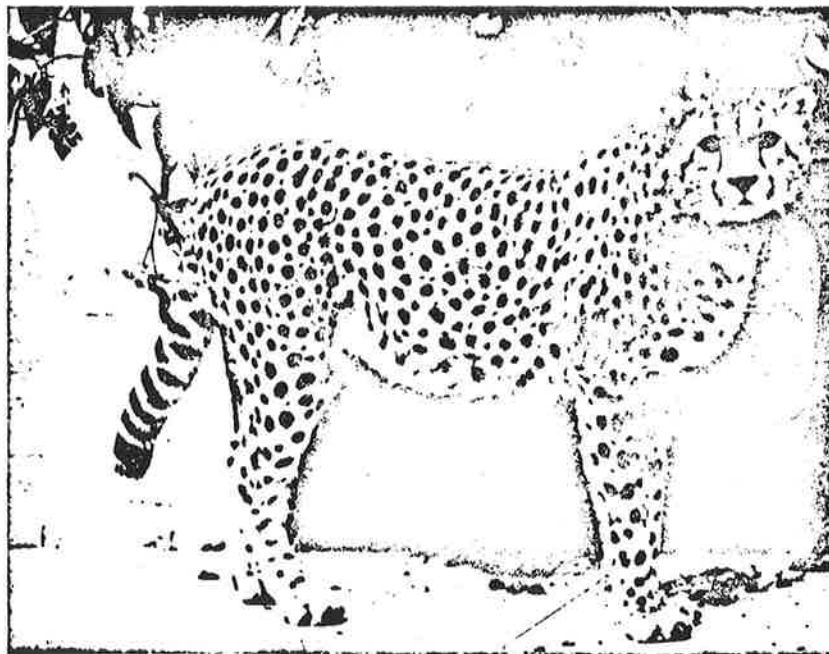
Paul C. Lauterbur
Associate Professor of
Chemistry

PCL:st

Enc.

*Title provided by BLS.

Family FELIDAE   L 252

CHEETAH

Acinonyx jubatus

(Grasslands and semi-deserts of Africa and South-west Asia)

Although dogs are the typical running hunters, the fastest four-legged animal, the Cheetah, is a member of the cat family. Most cats have to bound up to their quarry once they have stalked it. The Cheetah too uses stealth to approach the prey initially, but because it lives in open country it cannot get very close in this way, and is compelled to make its final onslaught from a greater distance. Because of this, it has become specialized as a lanky, powerful sprinter, and has often been described as the most dog-like of the cats. The adult Cheetah is the only cat with permanently extended claws.

Over a distance of up to 400 yards it can reach speeds of about 60 miles an hour, but it lacks stamina and if the prey is not caught inside this distance it soon slows down to await a more favourable opportunity. Cheetahs often hunt in pairs or family groups, usually during the cooler parts of the day. The prey consists of gazelles, Impala, Waterbuck or Ostriches.

Man has used tame Cheetahs as hunting animals for hundreds of years and it is therefore remarkable that this was the last of the large cats to be bred successfully in captivity. Even today it has only been bred in zoos in a few instances, the first occasion apparently being as late as 1960, at Krefeld. Young Cheetahs have a characteristic silver mane that runs down the whole length of the back. This mane, or crest, disappears after the tenth week, at the same time that the cubs lose the ability to retract their claws.

Christian-1; Lions, Cheetahs-1; Non-Editor-0

Attention: P. Christian Lauterbur:

    Uncle!

              B. L. Shapiro

P.S. Suzie - wherever you are - HELP!!

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