Texas A & M University
N-M-R Newsletter

No. 121
OCTOBER, 1968

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

LABORATORIUM VOOR ORGANISCHE
SCHEIKUNDE DER UNIVERSITEIT VAN
AMSTERDAM
NIEUWE ACHTERGRACHT 129
TELEFOON 947174 (5 LIJNEN)

AMSTERDAM, September 10, 1968

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

Measurement of the sample spinning rate on a Varian HA-100

Dear Professor Shapiro,

The 2.5 kHz signal at J-134 of the V4311 RF unit is superimposed by a lower frequency sine wave. The latter has a much higher amplitude (100 - 1500 mV_{p-p} at RF power 10 dB) which permits the direct determination of its frequency using the V-4315 counter*. It is found to be equal to the frequency of the sample spinner. Monitoring this "spinner signal" offers several advantages:

1. it is easier to maintain a constant spinning rate, especially when the probe temperature is varied over a wide range.
2. most of us are at least occasionally plagued by too large spinning side bands, even at optimum field homogeneity. Similarly, in double resonance experiments excessive beat patterns can be quite irksome. Rotating the sample tube with respect to the spinner until the "spinner signal" has a minimum amplitude often cures these troubles.
3. in this manner, batches of sample tubes can be screened for use with a particular spinner without having to run spectra.

Instrument modifications:
Since we installed van Deursen's "continous lock signal meter" (ITTNMRN 111-1) on our instrument, the scope and counter are available for monitoring the "spinner signal" while running spectra. We also made two calibrated auxiliary oscillators for double- and triple resonance (F.W. van Deursen ITTNMRN 102-14). The "spinner signal" and the signals from these oscillators are selected for monitoring by a switch mounted in the auxiliary oscillator panel. The wiper of this switch is wired to the "external" position of S 1306 of V-4354A.

* as on some instruments this amplitude is somewhat smaller, a simple pre-amplifier with filter may have to be installed at the counter input (F.W. van Deursen, private communication).

Sincerely yours,

P.J. van der Haak

K. Spaargaren.

University of East Anglia

School of Chemical Sciences
University Plain
Norwich NOR 85C
Telephone Norwich 52651

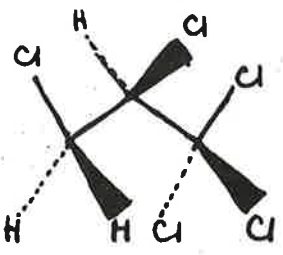
2nd August 1968

Dear Barry,

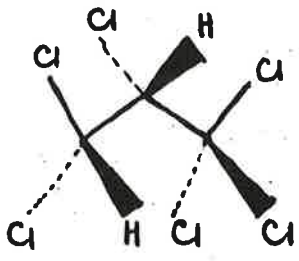
We have recently been carrying out a detailed infra-red and NMR study of a considerable number of chlorinated propanes in order to elucidate details of rotational isomerism for the series as a whole. We offer some of the results as our current contributions to the NMR Newsletter.

For two of the molecules we have studied, 1,1,1,2,3-pentachloropropane ($CCl_3.CHCl.CH_2Cl$) and 1,1,1,2,3,3-hexachloropropane ($CCl_3.CHCl.CHCl_2$), the vicinal coupling constants are rather interesting. In saturated molecules containing carbon-carbon single bonds the process of reorientation between possible rotational isomers is normally fast with respect to the NMR time scale at room temperature, leading to an average value of the vicinal coupling constants. For the two compounds in question the infra-red spectra show that only one rotational isomer is effectively present for each liquid. The NMR spectrum for the first compound is of the ABC type, which is fitted by values of -12.1 Hz for the geminal coupling constant and 9.5 Hz and 2.2 Hz for the two vicinal coupling constants. The second compound gives a vicinal coupling constant of 1.4 Hz.

For each of these two compounds three possible all-staggered rotational isomers are possible in principle. For the first we choose the configuration (I)



(I)

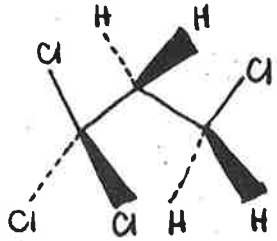


(II)

since it involves least steric strain and, in particular, this is the only conformation that avoids strong steric interaction between parallel C-Cl bonds attached to carbon atoms 1 and 3. We see, therefore, that the values 9.5 Hz and 2.2 Hz refer effectively to trans and gauche vicinal coupling constants respectively; these are close to expected values.

For the second compound the small observed coupling constant of 1.4 Hz shows that the protons must be in a (60°) gauche arrangement or have a dihedral angle between the CH bonds closer to 90°. The staggered conformation, (II) has the least steric strain but there is still one strong steric interaction between the parallel, eclipsed carbon-chlorine bonds of the terminal carbon atoms. It is interesting that the most likely distortion from this all-staggered configuration would be to enable the CH bond of $CHCl_2$ to become approximately staggered with respect to CCl bonds of the CCl_3 group. This would indeed lead to a dihedral angle between the protons that is larger than 60°.

In a third molecule, 1,1,1,3-tetrachloropropane ($CCl_3.CH_2.CH_2Cl$), the AA'BB' spectrum has been analysed to give coupling constants of 10.9 Hz and 4.8 Hz. These can also be interpreted as approximately trans and gauche vicinal coupling constants. Again it is clear from the infra-red spectrum that there is one dominant isomer. Of the three possible all-staggered configurations the conformation below (III) should be particularly stable as the two others would again involve strong parallel (1:3) steric interaction of the terminal chlorine atoms.



(III)

These three molecules may represent the first instances where individual trans and gauche proton-proton vicinal coupling constants have been measured directly around a carbon-carbon single bond at room temperature for a non-ring system. The values obtained are similar to those found for analogous vicinal coupling constants in cyclohexanes.

Yours sincerely,

Brodie Dempster Keith Price Norman

A.B. Dempster. K. Price. N. Sheppard.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305.

Title: "Vicinal Coupling Constants from Preferred Conformation of Chlorinated Propanes".

Southern Research Institute

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

September 17, 1968

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

Subject: Correlation of proton chemical shifts in cis-5,6-disubstituted norbornenes with Taft's inductive substituent constant

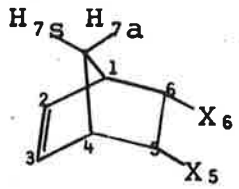
Dear Barry:

Thank you for the reminder that it is time for a contribution to the Newsletter.

We have done additional work on the pmr spectra of cis-5,6-disubstituted norbornenes since our last contribution on that subject in IIT NMR Newsletter No. 111. Recently, we have analyzed the spectra of exo,- and endo,cis-5,6-dihydroxynorbornene.

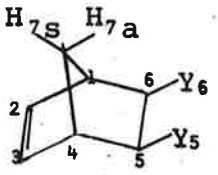
We have used the chemical shift data from our analyses, and additional chemical shift data from the literature,[1,2] to determine that the chemical shifts of H_{7a}, H_{7s}, and $H_1(H_4)$ may be expressed as linear functions of Taft's inductive substituent constant, σ_I.

Chemical shifts were available for the following derivatives:



Endo

X_5	X_6
H	H
Br	Br
OH	OH
OAc	OAc
Cl	Br
Cl	Cl



Exo

Y_5	Y_6
H	H
Br	Br
OH	OH
OAc	OAc
Cl	Br

...TO THE CHAIRMAN
1941 - 1963

For the second compound the small observed coupling constant of 1.4 Hz shows that the protons must be in a (60^{o}) gauche arrangement or have a dihedral angle between the CH bonds closer to 90^{o}. The staggered conformation, (II) has the least steric strain but there is still one strong steric interaction between the parallel, eclipsed carbon-chlorine bonds of the terminal carbon atoms. It is interesting that the most likely distortion from this all-staggered configuration would be to enable the CH bond of $CHCl_2$ to become approximately staggered with respect to CCl bonds of the CCl_3 group. This would indeed lead to a dihedral angle between the protons that is larger than 60^{o}.

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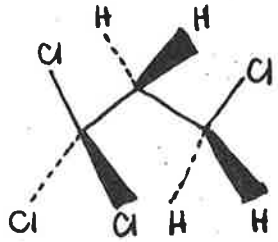

(III)

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Yours sincerely,

Brodie Dempster Keith Price Norman

A.B. Dempster. K. Price. N. Sheppard.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305.

Title: "Vicinal Coupling Constants from Preferred Conformation of Chlorinated Propanes".

Southern Research Institute

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

September 17, 1968

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

Subject: Correlation of proton chemical shifts in cis-5,6-disubstituted norbornenes with Taft's inductive substituent constant

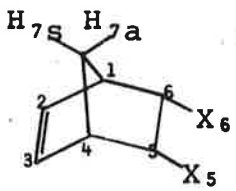
Dear Barry:

Thank you for the reminder that it is time for a contribution to the Newsletter.

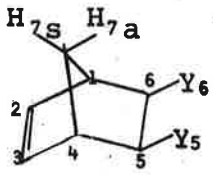
We have done additional work on the pmr spectra of cis-5,6-disubstituted norbornenes since our last contribution on that subject in IIT NMR Newsletter No. 111. Recently, we have analyzed the spectra of exo,- and endo,cis-5,6-dihydroxynorbornene.

We have used the chemical shift data from our analyses, and additional chemical shift data from the literature,[1,2] to determine that the chemical shifts of H_{7a}, H_{7s}, and $H_1(H_4)$ may be expressed as linear functions of Taft's inductive substituent constant, σ_I.

Chemical shifts were available for the following derivatives:



Endo	
X_5	X_6
H	H
Br	Br
OH	OH
OAc	OAc
Cl	Br
Cl	Cl



Exo	
Y_5	Y_6
H	H
Br	Br
OH	OH
OAc	OAc
Cl	Br

ASSISTANT TO THE CHAIRMAN
1941 1961

Southern Research Institute

Professor Bernard L. Shapiro
College Station, Texas 77843
September 17, 1968

For exo,cis-5,6-disubstituted norbornenes,[3] the equations for these relations, the standard deviations of the intercepts and slopes, and the correlation coefficients, r, are:

$$\delta H_{7a} = (1.04 \pm 0.04) + (2.68 \pm 0.12)\sigma_I \qquad r = 0.997$$
$$\delta H_{7s} = (1.31 \pm 0.02) + (1.08 \pm 0.06)\sigma_I \qquad r = 0.995$$
$$\delta H_1 = \delta H_4 = (1.93 \pm 0.29) + (2.44 \pm 0.71)\sigma_I \qquad r = 0.926$$

Here, δH_{7a}, δH_{7s}, and δH_1 are the chemical shifts of H_{7a}, H_{7s}, and H_1 in ppm downfield from internal tetramethylsilane. The solvent employed was either carbon tetrachloride or chloroform-d.

For endo,cis-5,6-disubstituted norbornenes,[3] the equations are:

$$\delta H_{7a} = (1.00 \pm 0.06) + (0.96 \pm 0.15)\sigma_I \qquad r = 0.952$$
$$\delta H_{7s} = (1.28 \pm 0.07) + (0.98 \pm 0.19)\sigma_I \qquad r = 0.934$$
$$\delta H_1 = \delta H_4 = (2.46 \pm 0.06) + (1.73 \pm 0.15)\sigma_I \qquad r = 0.989$$

We are presently preparing an account of this work for journal publication. Meanwhile, I trust that this note will keep us in good standing with the Newsletter.

Sincerely,

Martha C. Thorpe
Research Chemist

mct ss

(1) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Synder, J. Amer. Chem. Soc., 90, 3721 (1968).

(2) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, J. Org. Chem., 30, 2624 (1965).

(3) The equations relating δH_1 to σ_I were derived from data which did not include norbornene itself.

121-6
SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 717451

AMSTERDAM, September 18. 1968.

Uw ref.:

Onze ref.:

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

NMR Spectrum of Oriented Ethene

Dear Professor Shapiro,

The N.M.R. spectrum of ethene, oriented in the nematic phase[1] of 4,4'-di-n-hexyloxyazoxybenzene, has been measured and interpreted. The spectrum can be analysed in terms of a Hamiltonian consisting of the Zeeman-, the direct coupling-, and the indirect (scalar) coupling terms. Because ethene has D_{2h} symmetry, only two motional constants, denoted by $c_{3z^2-r^2}$ and $c_{x^2-y^2}$ in Snyder's[2] notation, are needed to describe the average orientation of the ethene molecule in the nematic solvent.

From the spectrum (figure 1a) three direct coupling constants can be obtained, i.e. D_{gem}, D_{cis} and D_{trans}; they are defined in figure 2. Only one independent parameter concerning the geometrical structure of ethene can be derived from these constants, for instance the ratio $x = \frac{r_{cis}}{r_{gem}}$. The parameters of the spectrum of fig. 1a, which was run at + 83°C, with an estimated concentration of 15 mol %, are collected in the following table:

$D_{gem} = \pm 480.1$ Hz	$J_{gem} = \pm 2.5$ Hz
$D_{cis} = \mp 740.5$	$J_{cis} = \pm 11.7$
$D_{trans} = \mp 199.6$	$J_{trans} = \pm 19.1$

The relative signs and the absolute values of the indirect coupling constants have been reported in the literature[3].
From the data of the table one calculates:

$$x = 1.3199,$$

$$c_{3z^2-r^2} = \mp 0.07337,$$

$$c_{x^2-y^2} = \pm 0.07560.$$

Four spectra, measured at different temperatures and concentrations, give an average value of $x = 1.320 \pm 0.006$.
Electron diffraction[4], infra-red[5], and Raman[6] spectroscopy yield resp. the following data: $x = 1.320 \pm 0.020$

1.330 ± 0.016

1.327 ± 0.009

These results are in good agreement with N.M.R. measurements (if corrections are made for the molecular vibrations[7], the value of x is decreased by about 0.003, which can be neglected in view of the experimental uncertainty).

Fig. 1a and 1b show the observed and computer simulated spectrum. These are only in agreement, if the relative signs of the indirect and direct coupling constants are taken as in the table. If it is assumed, that the planar molecule is on the average aligned parallel to the magnetic field, then $c_{3z^2-r^2}$ is negative, which means that $D_{gem}>0$, $D_{cis}<0$ and $D_{trans}<0$. This implies that the absolute signs of the indirect coupling constants are positive.

Yours sincerely,

(N. Bovée)

(C.W. Hilbers)

(C. MacLean)

(1) A. Saupe, G. Englert; Phys. Rev. Letters 11, 462 (1963).
A. Saupe; Z. Naturforsch. 19a, 161 (1964).
(2) L.C. Snyder; J.Chem. Phys. 43, 4041 (1965).
(3) N. Sheppard and R.M. Lynden-Bell; Proc.Roy.Soc. 269, 385 (1962).
(4) L.S. Bartell, R.A. Roth, and L.D. Hollowell; J.Chem. Phys. 42; 2683 (1965).
(5) H.C. Allen and E.K. Plyler; J.Am.Chem.Soc. 80, 2673 (1958).
(6) J.M. Dowling and B.P. Stoicheff; Bull. Am. Phys. Soc. 3, 313(1958).
(7) L.A. Bartell; J.Chem. Phys. 23, 1219 (1955).

fig 2

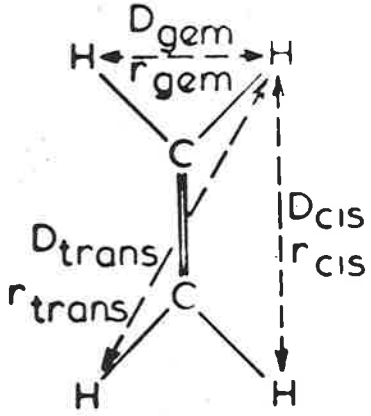
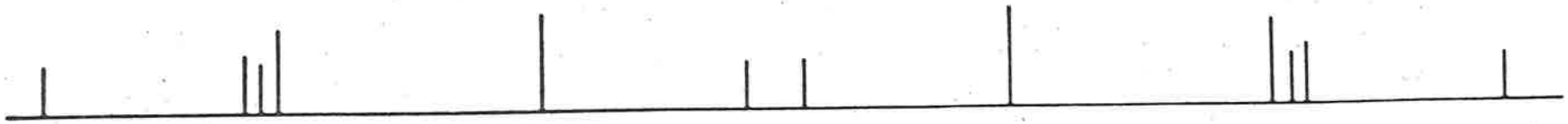


fig 1a

fig 1b



121-10

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)

Bruxelles 5, le September 17th, 1968.

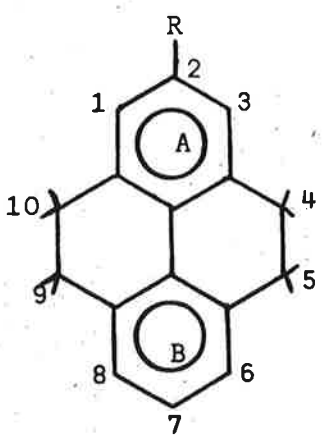
SUBSTITUENT EFFECTS IN 4,5,9,10-TETRAHYDROPYRENE.

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

Dear Professor Shapiro,

Several authors have shown that the chemical shift of the para-protons in monosubstituted benzenes can be linearly related to Hammett's substituent constants σ_H (para) [1-5]. This behaviour has been shown to be due essentially to π-electronic charge modifications at the carbon atom to which the hydrogen is bonded [4,5].

We wish to report here some results of a related investigation on 2-substituted 4,5,9,10-tetrahydropyrene in an attempt to obtain the π-charge modifications from the measured proton chemical shifts in the non-substituted ring B, thus minimizing substituent anisotropy effects [1] and ring-current modifications of the substituted ring [5].



Protons 6, 7 and 8 form an AB_2 system in which υ_A, υ_B and $\Delta\upsilon_{AB}$ are functions of the substituent R present in ring A. The results are summarized in the Table. In the context of the existing theories, these results would indicate that the π-electronic density on the different carbon atoms of ring B closely parrallel the para-substituent Hammett constants σ_H (para) of the groups R, thus seriously questionning the principle based on L.C.A.O.-theory predicting alternation of sign for the π-electronic charges in alternant systems. It seems indeed, for instance, that an electron withdrawing substituent lowers the π-electron density on all the carbon atoms of ring B. Wether this discrepancy is due to extensive σ-π interaction producing a general polarisation of the π-electrons by the substituent or to purely σ-charge density effects can however not be deduced from our results.

TABLE.

Substituent R*	υ_A	υ_B	$\Delta\upsilon_{AB}$	σ_H (para)
$-NH_2$	420.0	420.0	0.0	- 0.660
-H	425.8	423.0	2.8	0
-I**	427.8	423.5	4.3	+ 0.276
$-COCH_3$	430.6	426.0	4.6	+ 0.502
$-NO_2$	434.0	428.2	5.8	+ 0.778

* Spectra recorded at 10% concentration in $CDCl_3$.
** Spectrum recorded at 8% concentration in $CDCl_3$.

Excellent linear relations are observed when υ_A, υ_B or $\Delta\upsilon_{AB}$ are plotted versus σ_H (para), thus indicating the the *"meta"* like positions 6 and 8 are less affected by the substituent of ring A than the *"para"* like carbon atom at position 7. It is further expected that introduction of stronger donor substituents

than the amino-group, should inverse the frequency-order of protons A and B.

Extension of this work is in progress.

With best regards,

Yours sincerely.

R.H.MARTIN. R.FLAMMANG. H.P.FIGEYS.

References:

1) H.SPIESECKE and W.G.SCHNEIDER, J.Chem.Phys.,35, 731 (1961).
2) P.DIEHL, Helv.Chim.Acta, 44, 829 (1961).
3) G.W.SMITH, J.Mol.Spectroscopy, 12, 146 (1964).
4) T.K.WU and B.P.DAILEY, J.Chem.Phys., 41, 2769 (1964).
5) H.P.FIGEYS and R.FLAMMANG, Mol.Phys., 12, 581 (1967).

UNIVERSITY OF ILLINOIS
Department of
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URBANA
61803

The William Albert Noyes Laboratory

24 September 1968

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

Title: Low resolution nmr spectra in liquid crystals; photochemically induced dynamic nuclear polarization?

Dear Barry:

Before departing from Bryn Mawr for a year's leave at Illinois, we pulled together some results on the spectra of some difluorodihalobenzenes in liquid crystals. These molecules were reported in an IITNMR Newsletter last year. The spectra were taken directly on JEOLCO 60 and 100 MHz spectrometers, courtesy of their staff in Nutley, N. J.

The resolution was poor by comparison with other workers (Saupe & Englert, Meiboom, etc.) in the field, but direct couplings and the principal values and axes of the order matrix could be obtained. Copies of a short letter (preprint) on this subject can be had for the asking.

We can reproduce thermally generated benzoyl radicals and chemically induced dynamic nuclear polarization for benzoyl peroxide in cyclohexanone. Attempts were made this summer to generate the radicals photochemically and inside the magnet. A mercury arc focussed on the sample, or led to it by optical fibers does not give a detectable quantum yield. The light of a 2 mw He-Ne laser did give detectable benzene, but perhaps only because the laser heated the sample. Photochemical nmr would be an exciting technique, but how does one illuminate the sample inside an A-60 type probe?

Sincerely yours,

Jay

Jay Martin Anderson
Visiting Lecturer

University of Illinois at Chicago Circle

121-14

College of Liberal Arts and Sciences
Department of Chemistry
(Box 4348) Chicago, Illinois 60680
Telephone: 663-3161

September 23, 1968

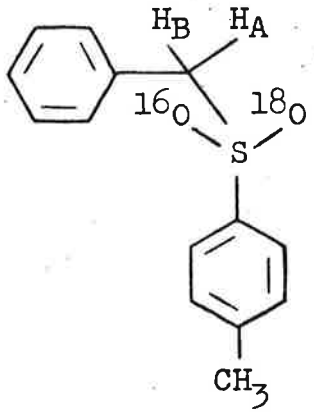
Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

The Equivalence of Diastereotopic Protons in an Isotopically Chiral Molecule

Dear Professor Shapiro:

The chemical and magnetic nonequivalence of geminal diastereotopic protons in chiral molecules is familiar. We wish to report our work on the investigation of this phenomenon in molecules where chirality is due to isotopic differences.[1]

The benzylic protons in the chiral molecule (-)-benzyl p-tolyl [$S^{16}O^{18}O$] sulfone[2] (1) are diastereotopic and therefore anisochronous.



1

It appeared of interest to determine whether their anisochronous nature might be manifested in an observable chemical shift difference. Spectra determined at 60 MH_z and 100 MH_z for $CDCl_3$ of 1 showed only A_2 behavior for the benzylic protons. Similar

results were obtained in several other achiral solvents.

Finally the spectrum of 1 was measured at 220 MH_z.[3] The benzylic protons appeared as sharp completely symmetrical singlet resonances with no tendency towards splitting.

The non-observation of splitting is not surprising in what might be described as a system of mildly diastereotopic protons.

Sincerely,

Robert M. Moriarty

Robert M. Moriarty
University of Illinois
Chicago Circle Campus

C. J. M. Stirling
King's College
University of London
England

RMM:lr

1. For an earlier contribution to this problem see J. Kim and R. M. Moriarty, Illinois Institute of Technology, NMR Newsletter 93, 26 (1966).
2. C. J. M. Stirling, J. Chem. Soc., 5741 (1963).
3. We wish to thank Prof. J. M. Lehn, Institut de Chimie, Strasbourg, for arranging this measurement.

CALIFORNIA STATE COLLEGE AT LOS ANGELES

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)

Department of Chemistry

September 23, 1968

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

Dear Barry:

Two Bond ^{13}CCH Coupling in α-Chlorostyrene

I hope that this contribution does not arrive too late to maintain a continuous subscription to the Newsletter.

In connection with a synthetic effort, we have had occasion to prepare α-chlorostyrene-α-^{13}C and measure its proton resonance spectrum. We thought that some readers might find the vinylic coupling pattern of this compound interesting.[1] The vinylic proton region of a 51% ^{13}C enriched

1. For an excellent review see: J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon Press, New York (1966), pp. 1027-1029.

sample is shown in the attached figure. The region consists of twelve sharp lines in a nearly symmetrical multiplet. The multiplet can be readily interpreted as an ABX spectrum with $\Delta\nu_{H_aH_b}$ = 10.1 Hz, $J_{H_aH_b}$ = 1.6 Hz, $J_{^{13}CCH_a}$ = 6.3 Hz, and $J_{^{13}CCH_b}$ = 5.6 Hz. The assignment can be verified by comparison with the spectrum of an unenriched sample. The ^{13}CCH coupling constants are similar to those reported by Karabatsos[2] some time ago.

2. (a) G. J. Karabatsos, G. D. Graham, and F. M. Vane, J. Phys. Chem., 65, 1657 (1961); (b) G. J. Karabatsos and C. E. Orzech, Jr., J. Am. Chem. Soc., 86, 3574 (1964).

Particularly interesting is the difference in coupling constants (0.7 Hz) between two bond ^{13}C coupling to the two different geminal protons.

Muller[3] has observed very large differences in the $^{13}C{=}CH$ coupling constants

---

3. N. Muller, J. Chem. Phys., 37, 2729 (1960).

---

of cis- and trans- 1,2-dichloroethylene and diethyl maleate and fumarate, but we are not aware that such coupling constants have been reported for styrenes with a geminal CH_2 group.

Sincerely yours,

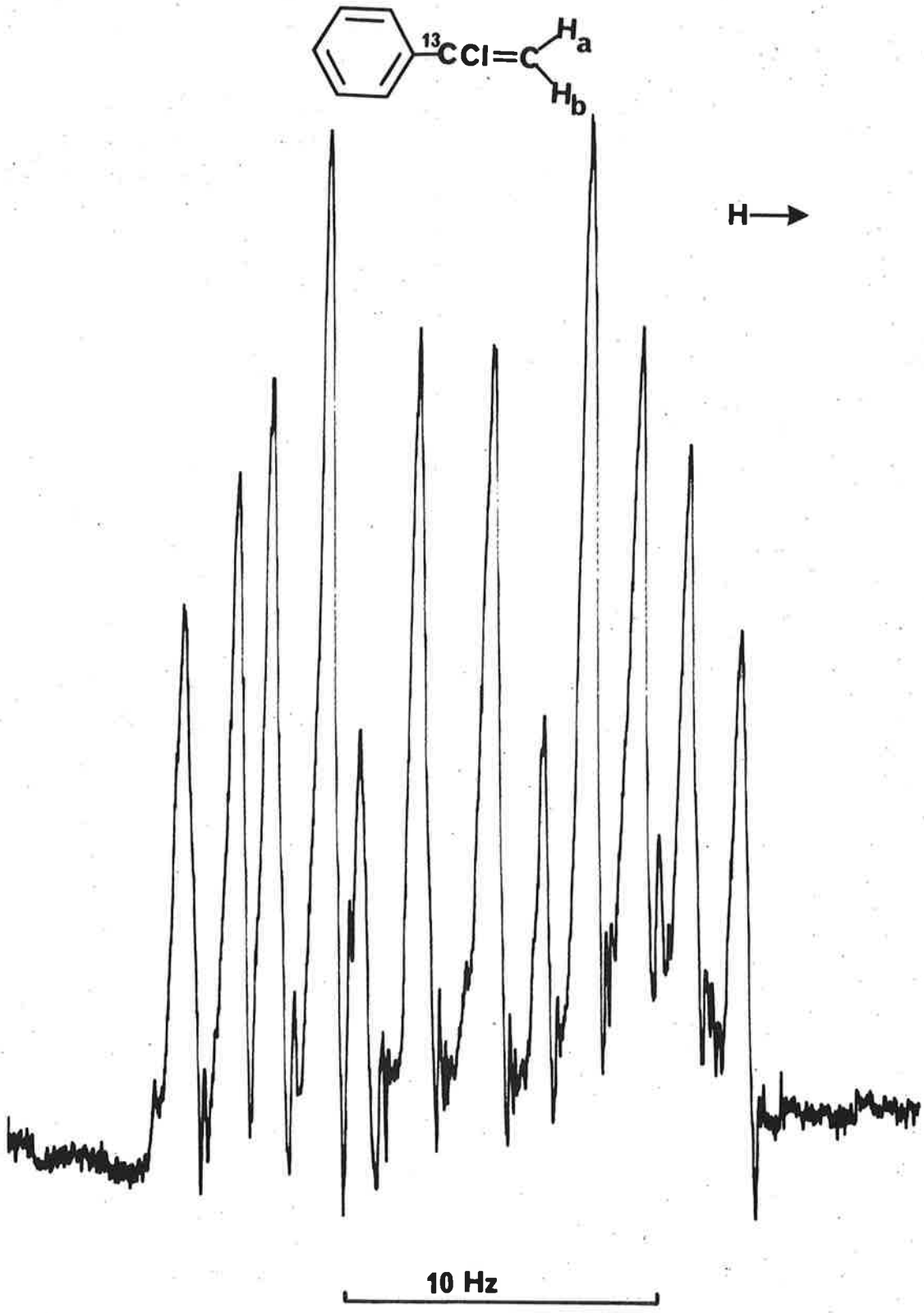
Joseph Casanova, Jr.

Joseph Casanova, Jr.

Randall N. Morris

Randall N. Morris

JC/bm


^{13}CCl=C
H_a
H_b
H
10 Hz

DEPARTMENT OF THE ARMY
WALTER REED ARMY INSTITUTE OF RESEARCH
WALTER REED ARMY MEDICAL CENTER
WASHINGTON, D.C. 20012

IN REPLY REFER TO

MEDEC-ZJB

13 September 1968

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

Dear Barry, A-60 Power Supply Modification

For the past year we have had trouble keeping our 7 year old A-60 on the air. The problem was an intermittent de-tuning of the receiver and transmitter units, along with other minor instabilities. We feel we have recently solved our problem and would like to pass on the modifications made to our magnet power supply. We have been told that this modification has been made on all A-60's produced in the last few years - so only old timers need to check their schematics.

We have removed transistors # Q1622 and Q1623 (2N525) and replaced them with one 2N3133. Resistor R1674 was increased from 150K to 470K or any value to 1 meg. The condition being that position 5 remain stable and minimum oscillation. Reset pot on voltage regulator to center needle on position 5. Lastly we put a 0.47 μf 200V capacitor across resistor R1673. We also put in a new DC-AC chopper (G-1601, Stevens-Arnold CH-BA12 50/60) and in the current regulator we change resistor R1635 from 2.2K to 6.6K to help prevent oscillations.

Regards,

JACK R. LANDIS
Associate Professor
Chemistry Department
CCNY

STEPHEN R. HELLER, Ph.D.
Research Chemist
Department of Biophysics

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY 07030

Department of
Chemistry and Chemical Engineering

September 24, 1968

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

Hydration of HCl and $HClO_4$

Dear Professor Shapiro:

We have recently extended our work on the measurement of hydration numbers from temperature effects on proton resonance to aqueous solutions of strong acids and bases. The following is a brief description of our findings in this area.

A single resonance line appears in the spectrum of such a solution and its shift δ_{sol} is a time average value of the shifts of the proton in its various environments; namely: (1) as the hydrogen ion (or in the hydroxyl ion); (2) in water molecules hydrated to the ions; and (3) in water molecules having a "normal" water structure. Thus

$$\delta_{sol} = X_A\delta_A + (1 - X_A)[X_S\delta_S + X_N\delta_N] \qquad (1)$$

where X_A is the mole fraction of protons which are acidic (or basic), X_S is the mole fraction of water molecules hydrated to the ions, and X_N is the mole fraction of water molecules having a "normal" water structure. δ_A, δ_S and δ_N are the corresponding proton chemical shifts relative to some standard which does not vary with temperature, such as gaseous ethane. The expression in the brackets of equation (1) represents the time average proton chemical shift of all the water molecules in the solution. In employing this equation we are assuming that the acid (or base) is completely dissociated. If we let m represent the stoichiometric molality of the acid (or base) and h represent the total "effective" hydration number of the ions present then $X_A = m/(m + 111.02)$; $X_S = mh/55.51$; and $X_N = 1 - mh/55.51$. Substituting these expressions for X_A, X_S and X_N into equation (1) and rearranging the resulting equation we obtain:

$$\delta_{sol} = \left(\frac{m}{m + 111.02}\right)\delta_A + \left(\frac{111.02}{m + 111.02}\right)\left[\left(\frac{mh}{55.51}\right)(\delta_S - \delta_N) + \delta_N\right] \qquad (2)$$

The total hydration number can then be obtained by taking the derivative with respect to the temperature, T, of both sides of equation (2). Assuming further that only δ_N is a function of temperature, we find

$$h = \left(\frac{55.51}{m}\right)\left[1 - \left(\frac{m + 111.02}{111.02}\right)\frac{d\delta_{sol}/dT}{d\delta_N/dT}\right] \qquad (3)$$

Using Eq. (3) we obtain the following results

	Total Hydration
HCl	3.4 ± 0.4
$HClO_4$	2.6 ± 0.4
NaOH	2.9 ± 0.3

Kind regards

Edmund R. Malinowski

Edmund R. Malinowski

Paul S. Knapp

/jef

Howard Vogrin

References

(1) E. R. Malinowski, P. S. Knapp and B. Feuer: J. Chem. Phys., 45, 4274 (1966); 47, 347 (1967).

(2) E. R. Malinowski and P. S. Knapp: J. Chem. Phys., 48, 4989 (1968).

121-22

Laboratorium
für physikalische Chemie
Eidg. Technische Hochschule
Zürich

Dr. R.R. Ernst
EH

ZÜRICH, 23.9.1968
Universitätstrasse
Tel. (051) 32 73 30

Prof. B.L. Shapiro
Department of Chemistry
Texas A + M University
COLLEGE STATION - Texas 77843
USA

NMR Studies of Fluorine-Substituted Cyclobutanes

Dear Barry,

I would like to report some results obtained from fluorine resonance studies of cyclobutane derivatives which were done partly recently, partly during my stay at Varian. The aim was to investigate the dihedral dependence of vicinal fluorine-fluorine coupling constants. The investigated molecules and the corresponding room temperature data are given in Table I. All molecules, except for $R_1 = R_2 = Cl$, exist in two cis-trans isomers (I and II) which commonly occur to equal amounts in mixture (for their preparation, see Ref. 1). Additionally, because of the non-planarity of the cyclobutane ring, [2,3] each isomer occurs in two rapidly interconverting conformations. The equilibrium between them is affected by the fact that the bulkier substituents (in our notation R_2 and also the Cl) prefer an almost equatorial position. Throughout this investigation, noise decoupling[4] was employed to completely eliminate proton-fluorine couplings.

The principal problem is the assignment of the resonances to the two isomers in mixture. An unique assignment is possible based on the chemical shifts of fluorine nuclei, assuming that the dominant effects are the electric field shift by the neighbouring chlorine[5] and the shift due to the anisotropy of the ring system[6]. The same assignment can be obtained based on long-range H-F couplings and, as well, by means of vicinal H-F couplings.

The chemical shift of the two geminal fluorine nuclei in the two related isomers are plotted in Fig. I as a function of the "equatorial-equatorial" F-F coupling constant J^{I}_{BX} which appears to be a rough measure for the difference in bulkiness of the two groups R_1 and R_2. It is obvious that the chlorine in α-position causes a down-field shift of about 10 ppm of the fluorine resonance in cis position to the chlorine throughout all these compounds. Additionally, there exists a low-field shift of equatorial fluorines which depends on the difference in bulkiness of R_1 and R_2. This is caused by the preference for one conformation for large R_2, such that it becomes possible to distinguish between "equatorial" and "axial" positions. The resulting anisotropy shift reaches a maximum of 10 ppm for cases where one conformation is predominantly occupied.

The vicinal fluorine-fluorine couplings show some interesting tendencies. "Equatorial-axial" couplings (J_{AX} in isomer I) and "axial-equatorial" couplings (J_{BX} in isomer II) with a dihedral angle of about 25° are consistently negative and show no obvious correlation with the asymmetry of substitution. The positive "equatorial-equatorial" coupling (J_{BX} in isomer I) has a pronounced dependence on the substituents. It seems to be markedly different in the two conformations with dihedral angles of about 10° and 150°. The "axial-axial" coupling, on the other hand, is consistently the smallest coupling and can assume either sign. The signs of the coupling constants were related to the geminal F-F coupling constants which are assumed to be positive (tickling experiments with simultaneous noise decoupling).

The dihedral dependence of the vicinal F-F coupling constants obviously is different from the dependence expected from simple calculations using only the contact term [7]. It seems that for small dihedral angles ($\varphi \sim 0$) and for large angles ($\varphi \sim 180°$), the coupling constants are negative and in the order of 8 Hz,

whereas for intermediate angles ($\varphi \sim 90^{\circ}$) positive values up to 8 Hz may occur. Some related date were reported recently by R.A. Newmark [8]. The complete story has been submitted for publication and part of it was reported at the recent Colloque Ampere in Grenoble.

Sincerely yours

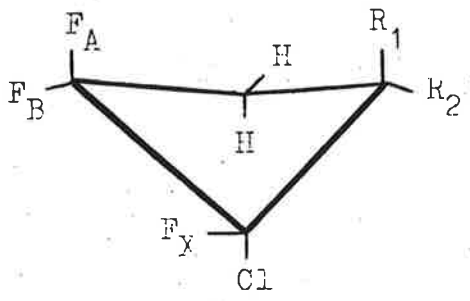
Richard R. Ernst

1. P. Tarrant, R.W. Johnson and W.S. Brey, J.Org.Chem. 27,602(1962)
2. J.B. Lambert and J.D. Roberts, J.Am.Chem.Soc. 85,3710(1963)
3. L.C. Snyder and S. Meiboom, J.Am.Chem.Soc. 89,1083(1967)
4. R.R. Ernst, J.Chem.Phys. 45,3845(1966)
5. J. Feeney, L.H. Sutcliffe and S.M. Walker, Mol.Phys. 11,117(1966)
6. J. Homer and L.F. Thomas, Trans.Faraday Soc. 59,2431(1963)
7. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution NMR Spectroscopy", Vol. 1(Pergamon Press, 1966), p. 189
8. R.A. Newmark, IITNMR 118,39(1968)

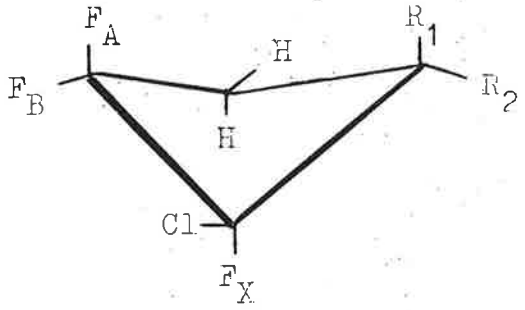
Fig. I: Chemical shifts of the two geminal fluorines plotted as a function of the equatorial-equatorial coupling constant J^{I}_{BX}. The open circles and squares refer to isomer I, the filled circles and squares refer to isomer II. The corresponding substituents R_1 and R_2 are indicated at the top of the figure.

Table I: Collection of chemical shifts (ppm from $CFCl_3$) and fluorine coupling constants (10 Vol.% in $CFCl_3$)

I



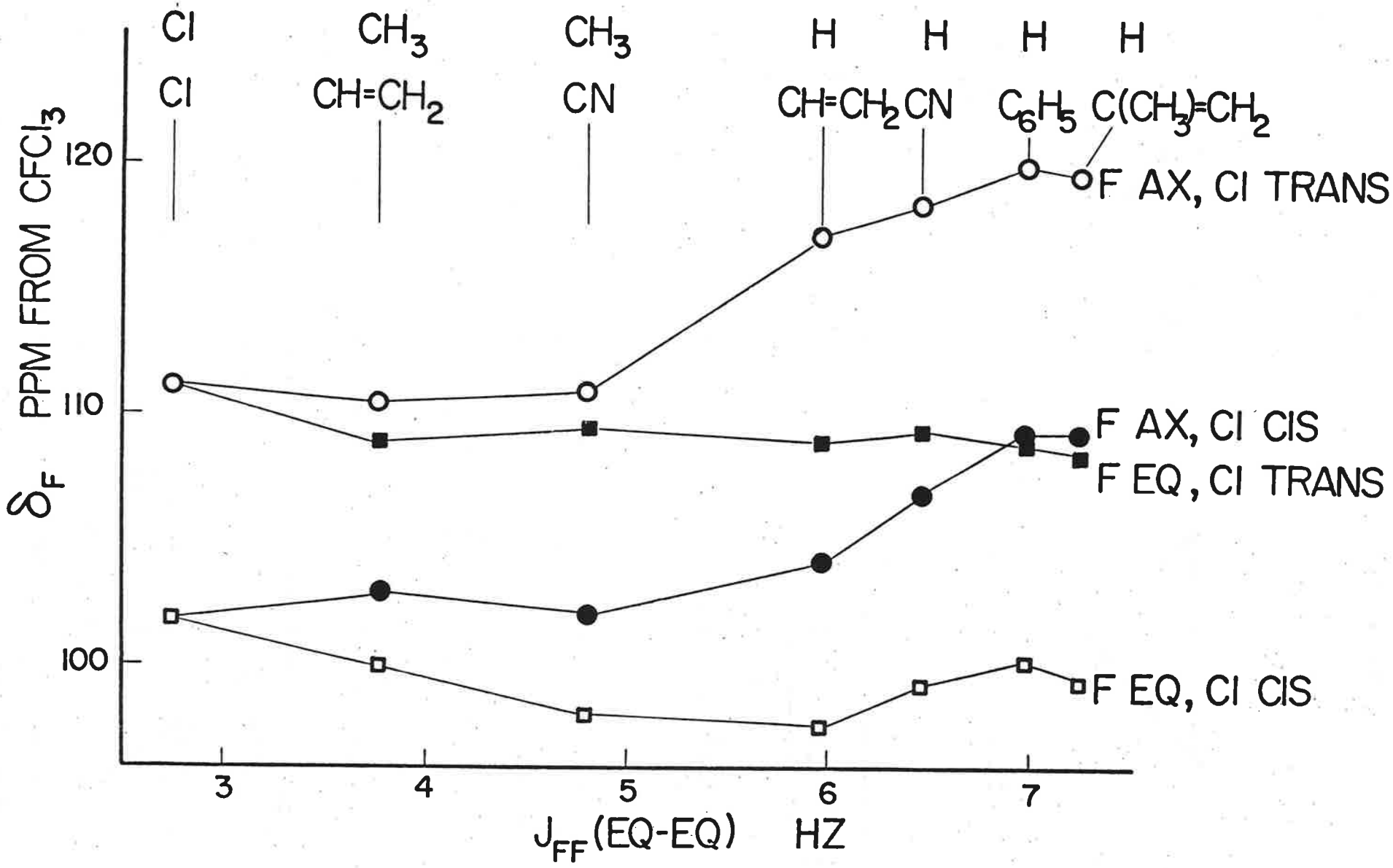
II



		δ_A PPM	δ_B PPM	δ_X PPM	J_{AX} HZ	J_{BX} HZ	J_{AB} HZ
RMS ERROR +)							
SUBSTITUENTS	ISOMER	±0.002	±0.002	±0.003	±0.03	±0.03	±0.12
R_1, R_2 : Cl (Temp.: 36°C)		102.00	111.35	114.47	+2.73	-8.88	202.7
R_1 : CH_3	I	110.51	99.88	124.52	-8.60	+3.78	199.8
R_2 : $CH=CH_2$ (Temp. : 37°C)	II	102.97	108.86	127.57	-0.82	-8.61	202.2
R_1 : H	I	118.42	99.97	111.34	-7.81	+5.94	196.0
R_2 : $CH=CH_2$ (Temp. : 31°C)	II	106.83	109.35	135.71	-1.25	-6.53	199.6
R_1 : H	I	117.24	97.54	112.47	-6.75	+6.46	197.8
R_2 : CN (Temp. : 36°C)	II	104.21	108.49	126.09	+0.76	-6.37	199.6
R_1 : H	I	119.67	99.40	108.69	-7.81	+6.97	195.0
R_2 : C_6H_5 (Temp. : 37°C)	II	109.27	108.31	137.17	-0.20	-9.15	199.6
R_1 : H	I	120.00	100.17	109.68	-7.54	+7.23	192.8
R_2 : $C(CH_3):CH_2$ (Temp.: 37°C)	II	*) 109.39	*) 108.89	139.11	-0.42	-8.07	~ 200

*) 20 Vol.% in 20% $CFCl_3$ + 60% C_6F_6

+) There possibly is an additional systematic error caused by temperature and concentration


Cl
Cl
CH3
CH=CH2
CH3
CN
H
CH=CH2
H
CN
H
C6H5
H
C(CH3)=CH2
F AX, Cl TRANS
F AX, Cl CIS
F EQ, Cl TRANS
F EQ, Cl CIS
δF PPM FROM CFCl3
120
110
100
3
4
5
6
7
JFF(EQ-EQ) HZ

NATIONAL TSING HUA UNIVERSITY

Hsinchu, Taiwan

Republic of China

September 26, 1968

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

NMR Shifts and Electron Density

Dear Professor Shapiro:

Professor Norman C. Li, who is visiting us this summer, has shown me your letter re the TAMU NMR NEWSLETTER, and has asked me to send you an account of some of my NMR work done at Duquesne University in Pittsburgh last summer.

So, here goes. It has been recognized that the NMR shift in aromatic molecules tends to reflect the π-electron density on the carbon atom to which the proton is bonded, and that a simple linear correlation exists between the proton chemical shift, δ, and the local "excess" charge, $\Delta\rho$ (located on the carbon atom), in aromatic systems:

$$\delta = k\,\Delta\rho \qquad (1)$$

In general, there is fairly good correspondence between the experimental density, with k = 10.7 ppm/electron, and density calculated from various molecular orbital methods. In applying eq 1, several perturbing effects are encountered: the magnetic anisotropy of substituents or of hetero atoms in the aromatic ring, ion association, and solvent effects. If we neglect such perturbing effects and adopt k = 10.7 for the imidazole and pyridine systems, the change in electron densities on carbon atoms with formation of the zinc complexes may be calculated, and compared with the corresponding changes on formation of the protonated species.

The chemical shifts of zinc-imidazole complex, δ, relative to those of free imidazole in dimethyl sulfoxide medium[1] have been determined and are listed in column 2 of Table I. Using eq 1, the values of $\Delta\rho$ are calculated. The ρ values of free imidazole[2] are given in column 4, so that the values for zinc-imidazole can be calculated. These are listed in column 5, and compared with the values for imidazolium ion[3], ImH^+.

We have also measured the chemical shifts of 0.1M pyridine in dimethyl sulfoxide in the presence of various concentrations of zinc chloride. By using eq 9 of ref. 1,

we have obtained the chemical shifts, δ, of zinc-pyridine complex, relative to those of free pyridine. Table II summarizes the results. The ρ values for pyridine and pyridinium ion, pyH^+, are taken from ref. 4.

Table I. Imidazole System

	δ, ppm	$\Delta\rho$	ρ_{Im}	ρ_{Zn-Im}	ρ_{ImH^+}
C(2)	-0.47	-0.044	0.991	0.947	0.875
C(4)	-0.23	-0.021	1.104	1.083	1.029
C(5)	-0.23	-0.021	1.072	1.051	1.029

Table II. Pyridine System

	δ, ppm	$\Delta\rho$	ρ_{py}	ρ_{Zn-py}	ρ_{pyH^+}
α	-0.06	-0.006	0.952	0.946	0.899
β	-0.43	-0.040	1.004	0.964	0.927
γ	-0.43	-0.040	0.981	0.941	0.829

From Tables I and II, it is seen that the local "excess" charge with the formation of zinc complex is much less than with the formation of the protonated species. The evaluation of the appropriate values of k to take into account the contribution of magnetic anisotropy of the N atom and the zinc ion is necessary for quantitative results, and the program is in progress.

Sincerely yours,

Sung-Mao Wang /cm

Sung Mao Wang
Head, Department of
Chemistry

References: (1) S. M. Wang and N. C. Li, J. Am. Chem. Soc., 88, 4592(1966); (2) B. Pullman and A. Pullman, "Quantum Biochemistry," Interscience, New York (1963), p.781; (3) R. L. Collin and B. Pullman, Arch. Biochem. Biophys., 108, 535(1964); (4) T. Schaefer and W. G. Schneider, Can. J. Chem., 41, 966(1963).

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

Frick Chemical Laboratory

September 26, 1968

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

Dear Barry,

COUPLING CONSTANTS AS PROBES INTO DIGNITY

There have been many reported instances of solvent dependence of coupling constants, in most cases polar solutes have been studied in either polar or non-polar solvents and correlations were attempted with dielectric functions like the reaction field term $\frac{\epsilon-1}{2\epsilon+a}$ or with the Stark term $\frac{(2\epsilon+1)(\epsilon-1)}{\epsilon}$. These studies are characterized in general by great scatter of the experimental points with regard to the correlation lines.

It is possible to devise an experiment to demonstrate that coupling parameters display a simple dependence upon the bulk properties of the solution. By choosing a centro-symmetric solute, such as tetramethyltin, it is possible to eliminate all but the non-specific van der Waals interactions. The resulting changes in the coupling constants, albeit small, are significant and correlate extremely well with McRae's formulation of dispersion forces. Bayliss and McRae (1) have shown the proportionality of dispersion forces to the term $\frac{n^2-1}{2n^2+1}$ where n is the refractive index of the medium. We have played a little with tetramethyltin (Table I).

TABLE I

Solvent variation of the heteronuclear ^2J coupling constants in tetramethyltin.

Solvent	n	$^2J_{^{119}Sn\text{-}C\text{-}H}$ (Hz)	$^2J_{^{117}Sn\text{-}C\text{-}H}$ (Hz)
heptane	1.3883	54.01	51.63
heptane-carbon disulfide (4:1 v/v)	1.4260	53.87	51.53
heptane-carbon disulfide (1:1 v/v)	1.4924	53.77	51.51
heptane-carbon disulfide (1:4 v/v)	1.5645	53.60	51.25
carbon disulfide	1.6154	53.46[5]	51.15

The origin of this dependence remains obscure. Changes in the mean excitation energy ΔE for the Fermi contact term cannot yet be calculated with the necessary precision. Also, we do not seem to have gained much understanding about the nature of dispersion forces in solution since 160 years ago when Dalton was writing: "Each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity, or otherwise, are disposed to encroach upon it, at a respectful distance."(2)

With best personal regards,

Sincerely yours,

Pierre Laszlo

Arnold Speert

PL/mb

(1) N.S. Bayliss, J Chem. Phys., 18, 292 (1950); E.G. McRae, J. Phys. Chem., 61, 562 (1957); M.E. Baur and M. Nicol, J. Chem. Phys., 44 3337 (1967).

(2) J. Dalton, A New System of Chemistry, Manchester 1808, Chapter 3.

121-32

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129

Department of Chemistry

September 27, 1968

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

Dear Barry: Chemical Shift Correlations in the 2-X-Pyridines

I have managed to refrain myself from starting this note off with some choice Aggie jokes which are popular here and, instead, welcome you to the ranks of Texas Resonators.

Recently we have completed the spectral analyses of a series of 2-substituted pyridines done in dilute carbon tetrachloride solution and the shifts for the corresponding cations taken in 1:1 trifluoroacetic-acetic acid. The former were analyzed completely using nitrogen decoupled spectra while the chemical shifts of the latter were estimated from the similar splitting patterns of the free bases (also a number of these were close to first order). The data are given in Tables I and II.

The chemical shifts of H_3 in both series followed the Q relation quite closely (see J. Am. Chem. Soc., 89, 5018 (1967) and I.I.T.N.M.R. 112-14) with correlation coefficients of 0.987 and 0.994 for the free bases and cations respectively. Just as in the monosubstituted benzenes, the shifts at H_5 follow σ_p. The electronic perturbation introduced by protonating the nitrogen does not affect this.

Protons H_4 and H_6 in both series are meta to the various substituents. H_4 shows a fair correlation with the meta porton shifts in the monosubstituted benzenes. One hastens to add "for whatever that means" since such meta shifts seem to correlate with nothing. In the 1-X-2-Y-benzenes (X constant and Y varied) there is a correlation of H_6 with σ_m. We suggested (vide infra) that the intervening substituent at C-1 was insulating H_6 from the field effect of Y. Your new colleague, Ed Meyers once suggested just the opposite i.e. the polarizable X relayed the field effect of Y to H_6 and that was why the σ_m relation obtained. H_6 in the protonated pyridines does not correlate well with σ_m. However, the correlation is good for the free bases. Furthermore, we have some evidence that the magnitude

TABLE I. Parameters for 2-Substituted Pyridines[a]

2-X	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}	τ_3	τ_4	τ_5	τ_6	RMS[b]
NH_2	8.37	1.01	0.98	7.17	1.97	5.05	3.65	2.74	3.53	2.06	0.020
CH_3O	8.35	0.98	0.81	7.09	2.06	5.08	3.38	2.57	3.27	1.94	0.032
CH_3	7.71	1.17	0.93	7.50	1.89	4.88	2.99	2.58	3.04	1.63	0.048
F	8.23	0.91	0.78	7.23	2.10	4.95	3.12	2.23	2.85	1.81	0.030
Cl	8.08	0.98	0.80	7.41	2.06	4.86	2.76	2.42	2.85	1.69	0.029
Br	8.03	0.94	0.79	7.39	2.09	4.81	2.60	2.54	2.83	1.69	0.013
I	7.75	1.25	0.82	7.45	2.06	4.82	2.35	2.73	2.80	1.72	0.031
CN	7.80	1.19	0.96	7.85	1.74	4.84	2.30	2.12	2.45	1.31	0.041
NO_2	8.26	1.05	0.86	7.38	1.86	4.62	1.84	1.94	2.32	1.41	0.029

a. Dilute solutions in carbon tetrachloride. Coupling constants in c.p.s.

b. Root mean square error in line positions.

of effects at H_6 depend on the polarizability of the intervening substituent, and the nitrogen lone pair shows the largest effects of all.

Yours sincerely,

Bill

W. B. Smith
Chairman
Department of Chemistry

WBS/dc

TABLE II. Chemical Shifts for Protonated 2-Substituted Pyridines[a]

2X	δ_3	δ_4	δ_5	δ_6
NH_2	4.94	5.72	4.77	5.79
CH_3O	5.38	6.38	5.39	6.20
CH_3	5.76	6.39	5.67	6.49
F	5.35	6.26	5.55	6.37
Cl	5.92	6.45	5.89	6.64
Br	6.03	6.30	5.89	6.69
I	6.32	6.13	5.92	6.69
CN	6.14	6.44	6.05	6.88
NO_2	6.29	6.16	5.76	6.67

a. Solutions (10% V/V) in 1:1 trifluoroacetic acid-acetic acid. Chemical shifts are in p.p.m. from the acetic acid methyl protons which served as an internal reference.

Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

30 September 1968

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

Dear Barry:

In recent issues of the Newsletter, George Slomp (1)(116-36) and Charlie Reilly (2)(118-22) presented analyses of the spectrum of 5-hydroxynaphthoquinone. Using the LAOCOON program George found two different sets of parameters corresponding to the same line assignment of the spectrum as expected from the theory of three-spin spectra. Of the two solutions, he selected the "true" one on the basis of a better agreement between calculated and observed line intensities.

It is worth noting that the reported difficulties in using the LAOCOON program and the necessity of choosing an arbitrary separation of 0.2 cps between the lines of the unresolved doublet would not have occurred with more accurate measurements of the line frequencies; indeed in the latter instance the true separation between the two close lines could have been determined by using the repeated spacings rules. No statistical analysis of the errors associated with the parameters was reported. The latter would have shown that while the "true" solution is most likely the nearest one to the "correct" set of parameters (as indicated by the comparison between experimental and calculated intensities), the probable error of each spectral parameter in the two sets is of the same order of magnitude, if not larger, than the difference between corresponding parameters of the two sets. In plain language this means that the accuracy of the experimental measurements is, in this case, inadequate to determine sets of parameters more accurate than those given by the LAOCOON program, which however, still indicates correctly the occurrence of a double solution to the problem.

In his communication (2) to the Newsletter, Charlie Reilly misses this point. In comparing the NMRIT program and LAOCOON, he notes that, starting with Slomp's experimental data, the NMRIT program converges to a unique set of parameters, which behavior, he implies, any self-respecting program should have in the case of an ABX spectrum. Unfortunately for the argument however, the spectrum of 5-hydroxynaphthoquinone is at the border-line between the ABX and the ABC type and it can be demonstrated theoretically that two solutions to the problem always exist for this case too. To do so in the most straightforward way and to avoid the complications which arise because of the experimental errors in the line measurements, we have

(1) first calculated the spectrum corresponding to the parameters given by NMRIT, (2) then submitted the resulting calculated spectrum to an analysis with the EXAN II program. The results of the calculations are summarized in Table I, where we have reported the two sets of parameters obtained from the EXAN analysis, the calculated frequencies (necessarily identical for the two sets of parameters) and the corresponding intensities. The first solution is identical to the one given by NMRIT and which was used to calculate the theoretical spectrum in the first place. The second solution is the one missed by NMRIT. By the way, it is interesting to note that the latter set of parameters is closer to Slomp's "true" solution and fits the experimental intensities better than the first one does. In conclusion therefore the NMRIT program not only missed one of the two possible solutions, but also converged to the one most likely to be incorrect; the latter result, however, must be purely accidental.

Best regards from all of us,

S. M. Castellano

A. A. Bothner-By

Suggested title for this letter:

"Habeat scabiem quisquis ad me venerit novissimus"

Table I. Coningate sets of spectral parameters of 5-hydroxynaphthoquinone as calculated from Reilly's data (IIT N-M-R Newsletter 118, 20, (1968).

	I	II
W(1)	434.799	434.834
W(2)	454.297	454.426
W(3)	456.904	456.739
J(1,2)	1.305	1.097
J(1,3)	8.295	8.469
J(2,3)	7.499	7.532

Frequencies	Intensities (I)	Intensities (II)
425.2807	.0676	.0748
429.1325	.6077	.6025
432.8882	.7039	.6842
435.0987	.8347	.8173
438.8545	1.4745	1.4703
442.7062	.3119	.3511
446.0802	.0185	.0355
449.8360	.3742	.3787
453.4573	2.4714	2.4699
453.6877	2.3738	2.3620
457.2130	1.3798	1.3920
459.6540	1.2332	1.2236
461.0647	.0028	.0002
467.0310	.1457	.1377
478.0125	.0003	.0002

121-38

DIVISION OF APPLIED CHEMISTRY
DIVISION DE CHIMIE APPLIQUÉE

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OTTAWA 7.

September 23rd, 1968

Exchange Phenomenon between a Carbonium Ion and its Parent Molecule

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

Dear Professor Shapiro,

I hope that this letter will put me on your mailing list of TAMU-NMR Letters. However since I will be leaving Canada soon I would prefer to receive the letters at my permanent address: Università di Bologna, Facoltà di Chimica Industriale Risorgimento, 4 Bologna, Italy.

For the past year I worked at N.R.C. with Syd Brownstein and we investigated the possibility of observing exchange between a simple carbonium ion and its parent molecule. We found out that $CH_3CO^{(+)}$ AsF_6^- was the most suitable compound and CH_3COF the best generating molecule. The shape of P.M.R. spectrum of a solution 0.1 molal in both the species as function of the temperature is reported in fig. 1. The solvent used is SO_2, the internal reference is CH_2Cl_2 and the spectrometer is a Varian 100 MHz. In order to obtain good values of the lifetime from the doublet of CH_3COF we arranged a computer program that can reproduce the spectral shape as function of the lifetimes. The activation energy was found to be 10.3 kcal/mol from the doublet of CH_3COF and 11.3 from the singlet of $CH_3CO^+AsF_6^-$. This difference is believed to be within the experimental errors so $10.8 \pm .5$ kcal/mol is probably the correct result. Further work is in progress to find out the steps through which the equilibrium takes place. So far it appears that the equilibrium is 0 order in respect of CH_3COF and 1/2 order in respect to CH_3CO^+ AsF_6^-.

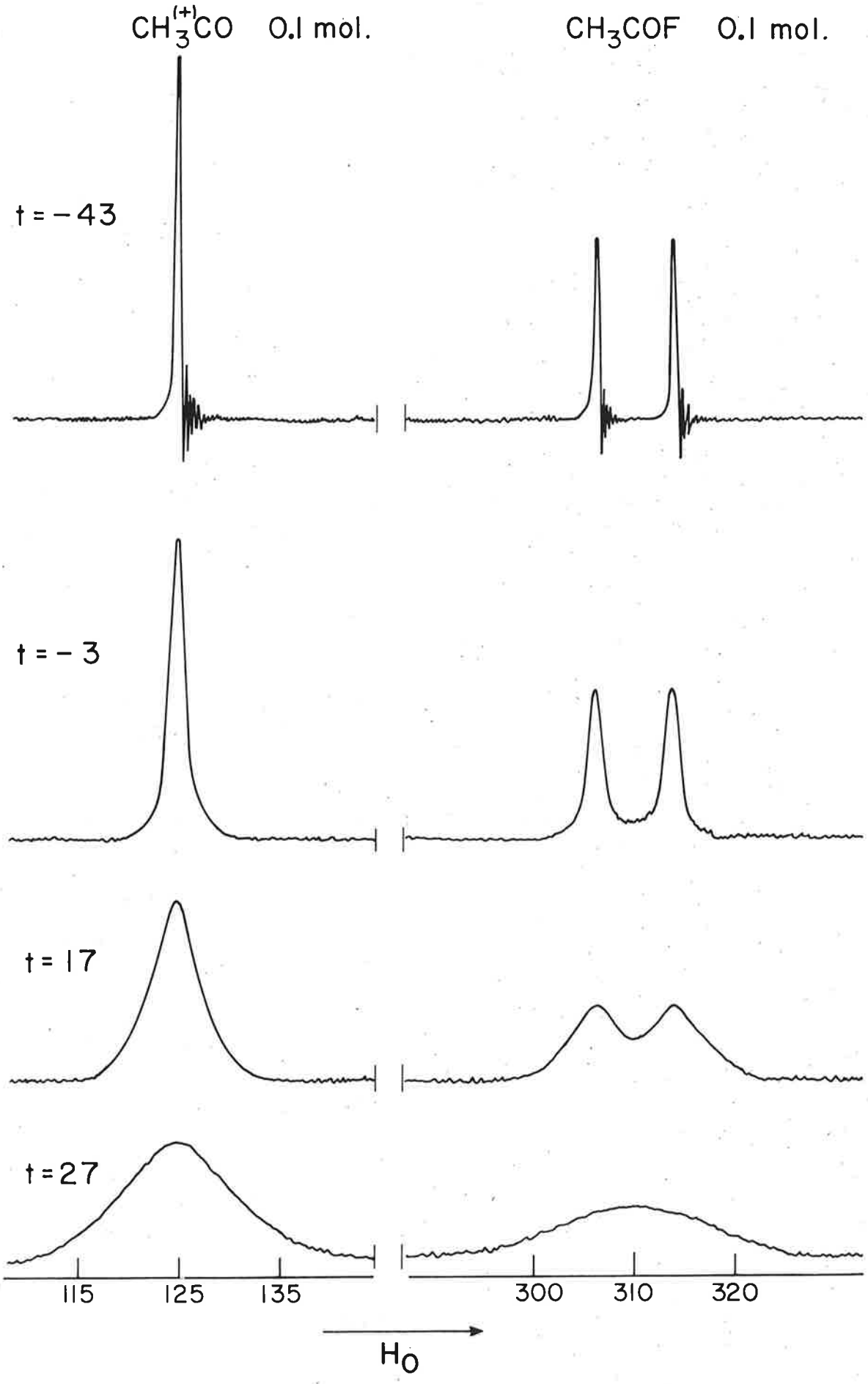
Part of this work has been presented to the XXIII Symposium on Structure and molecular spectroscopy held in Columbus, Ohio.

With my best regards,

Yours truly,

Lodovico Lunazzi

LL/md


$CH_3^{(+)}CO$ 0.1 mol.
CH_3COF 0.1 mol.
t = −43
t = − 3
t = 17
t = 27
115
125
135
300
310
320
H_0

121-40

THE UNIVERSITY OF GEORGIA

Department of Chemistry

ATHENS, GEORGIA 30601

September 27, 1968

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

Dear Barry:

We recently became interested in the mechanism of metalation of weak carbon acids. The reaction of several substituted fluorenes (in d_8-THF) with potassium metal to produce the corresponding carbanion were followed by an NMR in situ technique.

The NMR parameters for the carbanion are given in the Table. Chemical shifts and coupling constants are quite different in the carbanions, compared to the neutral compounds. Proton 4 is desheilded whereas protons 1,2 and 3 are more sheilded in the carbanions. The downfield shift of proton 9 on forming the carbanions is consistent with a change from sp^3 to sp^2 hybridization for the C-9 carbon.

From simple Huckel calculations, there is a correlation between bond-orders and coupling constants[1,2], but not with electron densities and chemical shifts. We are investigating the correlations further along with the parameters for other carbanions and will keep you informed.

1. N. Jonathan, S. Gordon, and B.P. Dailey, J. Chem. Phys., 36, 2443 (1962).

2. W.B. Smith, W.H. Watson, and S. Chiranjeevi, J. Am. Chem. Soc., 89, 1438 (1967).

Title: NMR Spectra of Carbanions

Sincerely yours,

Dick

Richard H. Cox
Assistant Professor

RHC:bab

NMR PARAMETERS OF FLUORENYLCARBANIONS

X	$\nu_{1,8}$ [a]	$\nu_{2,7}$	$\nu_{3,6}$	$\nu_{4,5}$	ν_9	$J_{12,87}$ [b]	$J_{13,68}$	$J_{14,58}$	$J_{23,67}$	$J_{24,57}$	$J_{34,56}$
CH_2 [c]	7.41	7.16	7.24	7.65	3.82	7.25	1.25	0.7	7.4	0.85	7.65
C-H	7.27	6.81	6.44	7.86	5.89	8.11	0.92	0.86	6.69	1.16	7.81
$C-CH_3$	7.22	6.83	6.39	7.82	2.47	8.19	1.05	0.80	6.58	1.22	7.76
C-Ø	7.85	6.92	6.58	7.91	--	8.17	1.03	0.77	6.70	1.22	7.76
$1-CH_3$,C-H	2.45	6.65	6.42	7.71	5.87	--	--	--	6.72	1.07	7.87
	7.30	6.79	6.43	7.81		8.10	1.07	0.81	6.64	1.20	7.79
$2-CH_3$,C-H	7.05	2.35	6.31	7.72	5.79	--	1.55	0.75	--	--	7.93
	7.23	6.76	6.41	7.77		8.11	1.06	0.80	6.63	1.20	7.77
N	7.60	7.15	6.75	7.95	--	8.09	1.08	0.74	6.86	1.37	7.63

a. In ppm from TMS.

b. In Hz.

c. K.D. Bartle and D.W. Jones, J. Mal. Structure, 1, 131 (1967).

UNIVERSITY OF Minnesota

DIVISION OF ORGANIC CHEMISTRY
335 CHEMISTRY BUILDING · MINNEAPOLIS, MINNESOTA 55455

October 2, 1968

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

Title: proton couplings in cyclohexane

Dear Barry:

Analysis of the deuterium decoupled AA'BB' (at -103^{o}) and ^{13}C-H satellite (at 38^{o}) spectra of cyclohexane-$\underline{d_8}$-1,1,2,2,-$\underline{h_4}$ (I) gave the parameters collected in the Table. They may be compared with those parameters given by Anet in TAMU NMR Newsletter 120-1.

Sincerely yours,

Ed

Edgar Garbisch

Mike

Michael Griffith

EG/MG/ms
encl.

Proton Chemical Shifts and Coupling Constants for I in cps.[a]

Spectrum	Proton Chemical Shifts[b]		Proton Coupling Constants				
	equatorial(e)	axial(a)	geminal	trans		cis	^{13}C—H
				(a,a)	(e,e)	(a,e)	
AA'BB' (-103^{o})[c]	96.96	68.20	-13.05	13.12	2.96	3.65	—
^{13}C—H Satellite (38^{o})[d]	83.92[e]		f	8.07[g]		3.73	125.00[h]

a) The tabulated parameters are considered accurate to 0.05 cps. The probable errors for the parameters, that arise from the least squares analysis, fall between 0.01 and 0.02 cps.

b) Cps downfield from TMS at 60 Mcps.

c) 5% of I in CS_2 (mole/mole).

d) Neat I.

e) $\frac{1}{2}(\nu_a + \nu_e)$.

f) Not accurately determined from the analysis.

g) $\frac{1}{2}(J_{a,a} + J_{e,e})$

h) Neither the least squares frequency fit nor the relative transition intensities are affected significantly by varying $J_{^{13}C\text{-}C\text{-}H}$ between 10 and -10 cps.

121-44

THE UNIVERSITY OF MANITOBA

DEPARTMENT OF CHEMISTRY

WINNIPEG, CANADA

October 2, 1968.

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

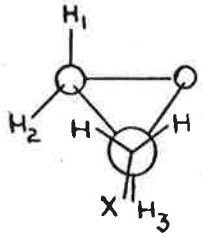
Dear Barry,

Short Title: Shift and Coupling Constant Parameters for the epihalohydrins in benzene solution.

Dr. Christopher Macdonald has recently analyzed the PMR spectra at 60 MHz of the epihalohydrins (I; X = H, F, Cl, Br, I) as 10 mole % solutions in benzene. Extensive tickling experiments determined the relative signs of the coupling constants. The peak positions, fed into LAOCOON III, converged to the parameters given below. The final parameters, except for X = F, had RMS errors <0.015 Hz; computed probable errors in parameters <0.01 Hz; worst fit for any resolved peak (width at half height ≈ 0.12 Hz) within the uncertainty in peak position measurement (±0.03 Hz). When X = F there was some difficulty in resolving peaks from H_1, H_2, H_4 and H_5. This gave a RMS error = 0.025 Hz with the worst fit being ±0.07 Hz. Because of this and because of the differences in the signs of several 4-bond couplings from a previous report (1), confirmation of the results for X = F is being made.

Several preliminary conclusions can be reached on the basis of these results. First, several chemical shifts and coupling constants differ from previous values (2,3), the discrepancies not being wholly due to the choice of solvent. The results for propylene oxide agree well with those of Elleman, Manatt and Pearce (4). Second, the experience with these compounds reinforces recent caveats on the reliability of machine-fitted data. For example, equally "valid" machine fits with experimental peak positions and intensities are found for X = F where the signs of J_{14} and J_{15} are interchanged with J_{24} and J_{25}.

Finally, the 4-bond couplings, ^4J are of interest. J_{14} and J_{15} are negative while J_{24} and J_{25} are positive. If the conformation found for epichlorohydrin by microwave spectroscopy (5) is assumed to exist for the benzene solutions (X=Cl,Br,I) then neither of the two formulations (6,7) previously suggested for the variations in ^4J with dihedral angle is directly applicable to the epihalohydrins.



$$^4J = 0.7\ (\cos^2\phi^1 + \cos^2\phi^{111}) - 0.3 \qquad (6)$$

$$^4J = A_i \cos^2\phi^1 \cos^2\phi^{111} - B \qquad (7)$$

Yours sincerely,

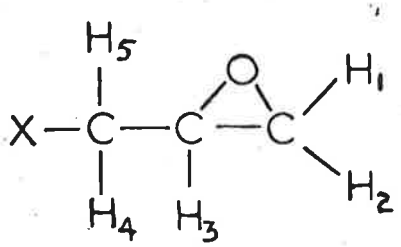
Chris Macdonald.

C.J. Macdonald

Ted Schaefer

T. Schaefer

1. W.A. Thomas. IITNMR. No. 106, p 24.
2. G. Aruldhas and V. Nayar. Ind. J. App. Phys., 4, 361 (1966)
3. E. Lippert and H. Prigge. Ber. Bunsenges. Physik. Chem., 67, 415 (1963)
4. D.D. Elleman, S.L. Manatt and C.D. Pearce. J. Chem. Phys., 42, 650 (1965)
5. M. Igarashi. Bull. Chem. Soc. Japan., 28, 58 (1955)
6. M. Barfield. J. Chem. Phys., 41, 3825 (1964)
7. V.F. Bystrov and A.U. Stepanyants., J. Mol. Spectry., 21 241 (1966)



I

	H	F	Cl	Br	I
δ_1	-2.001	-2.031	-2.009	-1.994	-1.966
δ_2	-2.326	-2.193	-2.218	-2.273	-2.325
δ_3	-2.577	-2.675	-2.674	-2.719	-2.696
δ_4	-0.975	-3.737	-2.964	-2.744	-2.490
δ_5		-4.049	-2.962	-2.824	-2.664
δ_X		-	-	-	-
J_{12}	5.33	5.13	5.04	5.05	5.08
J_{13}	2.53	2.55	2.39	2.37	2.36
J_{14}	-0.38	-0.24	-0.27	-0.26	-0.23
J_{15}		-0.29	-0.35	-0.33	-0.36
J_{1X}		-1.45	-	-	-
J_{23}	3.83	4.25	3.85	3.82	3.80
J_{24}	0.52	0.19	0.06	0.01	0.02
J_{25}		0.03	0.56	0.67	0.81
J_{2X}		3.80	-	-	-
J_{34}	5.15	6.00	4.75	5.44	6.46
J_{35}		2.55	6.00	6.18	5.94
J_{3X}		11.83	-	-	-
J_{45}	insensitive	-10.65	-11.63	-10.58	-10.13
J_{4X}	to this	47.40	-	-	-
J_{5X}	parameter	47.88	-	-	-

δ in p.p.m. from TMS

J in Hz

121-46

Gulf Research & Development Company

A. Bruce King
DIVISION DIRECTOR
PHYSICAL SCIENCES

P. O. Drawer 2038
Pittsburgh, Pa. 15230

October 2, 1968

Reference: 6251AA10-1

Via Air Mail

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

Dear Professor Shapiro:

For the purpose of renewing our subscription to the TAMU NMR Newsletter, I am submitting a brief summary of some work, a full account of which is scheduled to appear in THE JOURNAL OF PHYSICAL CHEMISTRY.

QUADRUPOLAR RELAXATION OF ^{27}Al NMR IN ALUMINUM ALKYLS

The line width of the ^{27}Al NMR line has been recorded for many neat, and solutions of, aluminum alkyls in hydrocarbons over wide temperature and concentration ranges. The dominant line-width determining relaxation mechanism is the interaction of nuclear electric quadrupole moment with the electric field gradient at the nucleus. The observed line widths vary from 3-46 gauss at 11.09 MHz, and correspond to nuclear quadrupole coupling constants which are reasonable for the aluminum nucleus. The correlation times are calculated variously including the use of the Debye equation and the microviscosity models. It is shown that the use of the Debye relation to obtain correlation times must be made with considerable caution. There is a linear dependence of line width on macroscopic viscosity. For similar molecules of comparable viscosity, the ratio of line width to the product of viscosity and molar volume is fairly constant indicating that the Debye relation may be used for determination of relative correlation times and for making comparisons. The constraints on the applicability of the Debye equation, however, are severe. At zero viscosity, there is a residual line width, and the temperature dependence of the line width results in non-Arrhenius behavior. The use of the microviscosity model yields some improved agreement with experimental correlation times. However, the detailed experimental examination points to the need for possible theoretical re-evaluation of the models that are being used for determining correlation times.

Sincerely yours,

Leonidas Petrakis, Supervisor
Molecular Spectroscopy Section

THE UNIVERSITY OF UTAH
SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

October 5, 1968

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

Re: Paramagnetic Ring Currents in Biphenylene

Dear Barry:

We would like to report the carbon-13 chemical shifts for several related aromatic compounds and draw attention to what we feel is an interesting variation in these shift values. The compounds biphenylene (I), triphenylene (II), and naphthalene (III), are similar to one another in that each has three magnetically non-equivalent carbons--a bridgehead and α and β carbons in a six-membered aromatic ring. Despite this similarity, biphenylene exhibits the somewhat unique chemical shift values given in the following table:

Carbon-13 Chemical Shifts (ppm relative to benzene)

	C-1	C-2	C-3	Total Range
I	+10.71	-0.07	-23.23	33.94
II	+ 4.95	+1.13	- 1.52	6.47
III	+ 0.44	+2.56	- 5.20	7.76

In view of the theoretical (CNDO-SCF-MO) result that biphenylene (I) has charge densities and free valencies which are much more similar to benzene than those calculated by the same method for naphthalene, it is evident that the total chemical shift range for biphenylene is unusual. Furthermore, chemical shift variations arising from ring strain in the four-membered ring in biphenylene would seem to be dismissed by the observation that the methylene carbon in butane (103.7 ppm) and cyclobutane (105.4 ppm) show no marked differences attributable to ring strain.

The +4.95 ppm upfield shift at C-1 in triphenylene was noted at C-4 in phenanthrene where the geometrical features are the same as in triphenylene. This shift is attributed to a steric effect arising from the proximity of the directly bonded hydrogens. The same steric arguments are not valid for explaining the larger upfield shift at C-1 in biphenylene. The paramagnetic ring current expected for the four membered ring in the biphenylene molecule[1] appears to be the best remaining explanation for the anomaly. This explanation rests on the assumption that the α-carbons and bridgehead carbons lie, respectively, outside and inside of the toroidal path of π-electron paramagnetic current.

Sincerely yours,

David M. Grant

Alan J. Jones

[1] H. P. Figeys, Chem. Comm., 495, (1967).

121-48

THE UNIVERSITY OF ARIZONA

TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS

DEPARTMENT OF CHEMISTRY

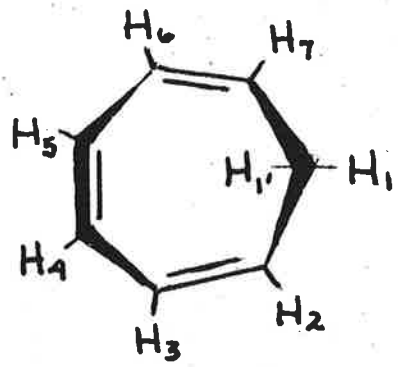
October 4, 1968

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

Title: Calculations of π-Electron Coupling Constants in Cycloheptatriene

Dear Barry:

Calculations of π-electron contributions to the coupling constants in the cycloheptatriene molecule are based on a formalism (1) which uses the generalized product approximation and intergroup configuration interaction. Results are entered in Table I along with experimental data (2,3). Two different conformations were assumed for the fragments since microwave (4) and x-ray diffraction (5) studies gave different results for the angle β between the planes formed by C_3-C_4-C_5-C_6 and C_2-C_3...C_6-C_7.



Of the two sets of calculated values only that for $\beta = 0^\circ$ appears to be completely consistent with experiment. For example, if we consider the addition of +1.2 Hz (6) to the four bond coupling constants for the $\beta = 0^\circ$ conformation, then there results $J_{24} + J_{25} = +1.30$ Hz, $J_{35} = 0.73$ Hz. Since any additional σ-electron contributions to $^5J_{36}$ are expected to be positive, the calculated value for $\beta = 40^\circ$ is at least too big by a factor of 2. It appears, therefore, that the $\sim 0^\circ$ for β is the correct one for cycloheptatriene in solution.

1. M. Barfield, J. Chem. Phys., to be published
2. H. Günther and R. Wenzl, Z. Naturforsch. A226, 389 (1967)
3. H. Günther, M. Gorlitz and H. H. Hinrichs, Tetrahedron, 24, 5665 (1966)

Sincerely yours,

Mike

Mike Barfield

MB/re

4. S. S. Butcher, J. Chem. Phys. 42, 1833 (1965)
5. J. P. Dunitz and P. Pauling, Helv. Chim. Acta, 43, 2188 (1960)
6. M. Barfield, J. Chem. Phys. 41, 3825 (1964)

TABLE I Cycloheptatriene

HH'	$J^{\pi}_{HH'}$(Calc.) Hz		$J_{HH'}$(Expt.)
	$\beta=40^{\circ}$	$\beta=0^{\circ}$	Hz
12	0.93	0.86	6.7
13	-0.91	-0.82	< 0.4
14	0.50	0.04	< 0.1
23	2.48	2.33	8.9
24	-1.64	-1.04	1.48
25	0.55	1.14	
26	-0.34	-0.42	...
27	0.09	0.51	...
34	3.06	0.95	5.51
35	-1.99	-0.47	0.72
36	1.26	0.36	0.69

121-50

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
800 BUCHANAN STREET
ALBANY, CALIFORNIA 94710

September 16, 1968

AIRMAIL

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

Scheme for Obtaining a Fixed 100 MH_z Output
from General Radio Frequency Synthesizer
for Use in HA-100

Dear Barry:

Since more and more people seem to be getting frequency synthesizers both as a frequency source for their spectrometers and for use as a homo-hetero spin decoupler, I thought some of your readers might be interested in the scheme we employ to reference the 100 MH_z output of our HA-100 to a General Radio 1164-A synthesizer.

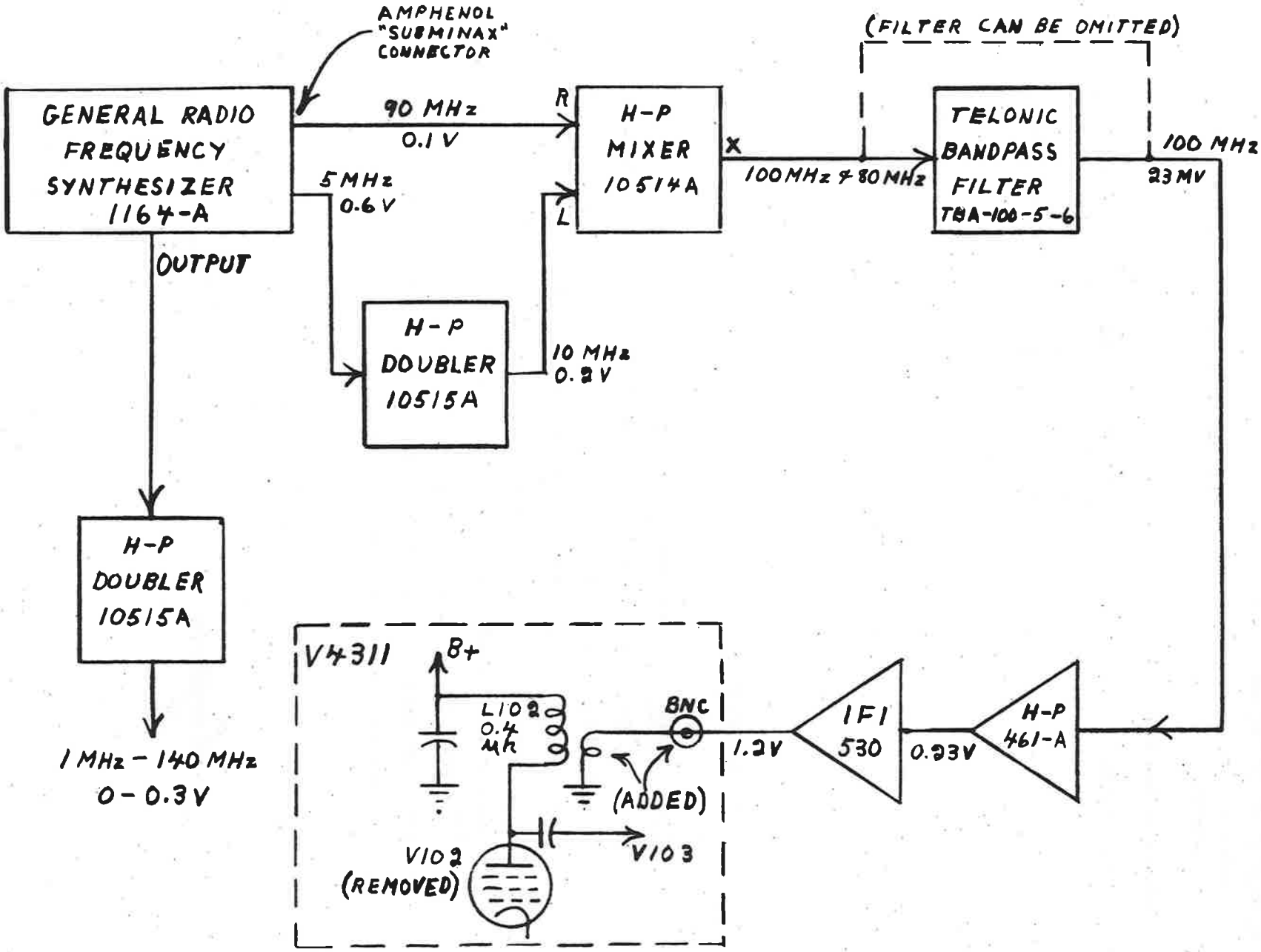
The fixed 5 MH_z and 90 MH_z outputs at the rear panel of the synthesizer can be simply combined to yield 80 and 100 MH_z as shown on the attached diagram. After amplification (apparently the filter shown on the diagram is not necessary) these frequencies are loop-coupled to the plate coil of the second stage of the 4311 transmitter. In our unit this stage was tuned to 50 MH_z so four of the six turns of the coil had to be removed in order to obtain resonance at 100 MH_z. I understand in newer units this stage is already tuned to the higher frequency. I'm sure that by coupling into the grid circuit of the second stage after tuning it for 100 MH_z, one could operate with an appreciably lower drive level, thus eliminating the need for the second amplifier.

Best regards,

Sincerely yours,

R. E. Lundin, Research Chemist
Molecular Structure Investigations
Wool and Mohair Laboratory

Enclosure


AMPHENOL
"SUBMINAX"
CONNECTOR
(FILTER CAN BE OMITTED)
GENERAL RADIO
FREQUENCY
SYNTHESIZER
1164-A
90 MHz
0.1 V
R
H-P
MIXER
10514A
X
100 MHz ± 80 MHz
TELONIC
BANDPASS
FILTER
TBA-100-5-6
100 MHz
23 MV
5 MHz
0.6 V
L
OUTPUT
H-P
DOUBLER
10515A
10 MHz
0.2 V
H-P
DOUBLER
10515A
1 MHz - 140 MHz
0 - 0.3 V
V4311
B+
L102
0.4
μh
BNC
1.2 V
IF1
530
0.93 V
H-P
461-A
(ADDED)
V102
(REMOVED)
V103

121-52
DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

Cable address: Technology

RH SF/BE

Stockholm, October 2nd, 1968

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

Dear Barry,

Simplified ABX analysis, oversimplified!

In our manuscript of August 20, 1968 we described a six step analysis procedure for ABX spin systems. To our original elaborations was added a last minute amendment, viz. Step 5, to cater for those people who like ourselves prefer to change the H_o field when going from ^{1}H NMR to ^{19}F NMR rather than retuning the r.f. unit. Unfortunately this amendment turned out to be erroneous and we include an erratum which we deem this time to be correct.

Sincerely yours,

Ragnar Hoffman

Sture Forsén

Erratum:

ABX analysis, Step 5

Before discussing the X-part spectrum we must distinguish between ABX spectra in which the AB and X basic multiplets are recorded at one and the same nominal value of the magnetic H_o field (as will be the case if AB and X are of the same isotopic species) and spectra in which the AB basic multiplet is obtained at a magnetic field of H_o and the X basic multiplet at a (different) field of H_o^1. In the former case step 6 may be executed as it stands, and the remaining paragraphs of step 5 may then be ignored.

In the latter case, however, the parameter $\nu_A-\nu_B$ assumes different values in the two spectra and the change in $(\nu_A-\nu_B)$ will entail changes in the entities (a_1+b_1) and (a_2+b_2) in equations (3) and (4) above and in the last two expressions for the splittings in the X-part spectrum listed in step 6 below.

To obtain the values of (a_1+b_1) and (a_2+b_2) appropriate at the field H_o^1 we use the relationship

$$a_n+b_n = \{[\nu_A-\nu_B \pm \tfrac{1}{2}(J_{AX}-J_{BX})]^2 + J_{AB}^2\}^{\frac{1}{2}} \qquad (10)$$

where n=1 and n=2 corresponds to the upper and lower signs in the bracket or vice versa. The identification of indices n=1 and n=2 with the appropriate sign "+" or "-" may be obtained by evaluating equations (10) with the parameters obtained at H_o from equations (5)-(9) above. The values for (a_1+b_1) and (a_2+b_2) appropriate at the field H_o^1 are then obtained by re-evaluating equations (10) with the parameter $(\nu_A-\nu_B)$ scaled by a factor of H_o^1/H_o. It will be noted that the adjusted values of (a_1+b_1) and (a_2+b_2) at H_o^1 in set (i) will be different from those of set (ii) and the theoretical X basic multiplet evaluated according to step 6 for sets (i) and (ii) will therefore differ not only in their intensity distributions but also in their transition frequencies.

121-54

University College of Swansea

Department of Chemistry

Professor C H Hassall PhD ScD FRIC
Professor and Head of Department
Professor J H Purnell BSc PhD MA PhD
Professor of Physical Chemistry

SINGLETON PARK SWANSEA
TEL SWANSEA 25678

4th October, 1968

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

Dear Dr. Shapiro,

A New Iterative Computer Programme:
LAME (LAOCOON with Magnetic Equivalence)

About a year ago, I was near the end of an extensive revision of a Reilly-Swalen type programme when I read the letter of Professor J. D. Roberts (IITNMR 105-29). This forced me to make a very detailed re-appraisal of the relative merits of LAOCOON (S. Castellano and A. A. Bothner-By, J.Chem. Phys. 41, 3863 (1964) - hereafter BBC) and the approach initiated by J. D. Swalen and C. A. Reilly (ibid. 37, 21 (1962) - hereafter RS), and extended by R. C. Ferguson, D. W. Marquardt and R. M. Stanley (ibid. 41, 2087 (1964) - hereafter FMS), and further modified by J. S. Martin, G. R. de Maré and F. Birss (IITNMR 101-18 - hereafter MMB) and also by Prof. Roberts' group (IITNMR 95-28). I find myself in entire agreement with Prof. Roberts' comments. In addition, I found the BBC approach to be superior for the following reasons:

(a) Their iterative technique takes fully into account the dependence of both diagonal and off-diagonal terms in the Hamiltonian on the parameters, whereas RS only consider their effect on the diagonal elements. As the off-diagonal elements become more important in precisely those highly coupled cases where computers are likely to be used, this fully accounts for the much better convergence observed with the BBC algorithm.

(b) The statistical analysis used by BBC is unassailable. That of RS (at least in the form of MARIP - but see also Freeman, Bhacca and Reilly, J.Chem.Phys. 38, 293 (1963)) I have found to give curious results. That of FMS, while elegant, involves, I have now discovered, errors of principle: as a result, it underestim-

ates the standard deviations of all parameters to a greater or lesser extent, and gives correlation coefficients between them which are simply invalid.
(c) I have nothing to add to the Mellon group's own comments (IITNMR 112-60) concerning LAOCOON's superiority in handling chemical equivalence.

However, the work of FMS and successors does have one great advantage over that of BBC: in cases where magnetic equivalence occurs, this is fully utilised to factorise the Hamiltonian, with potentially greater efficiency both in computation time and in core utilisation. This favourable feature I have now incorporated into LAOCOON; I have called the result by the code name of LAME (LAocoon with Magnetic Equivalence). I wish to acknowledge that in doing so, I have also made extensive use of work both of FMS and of MMB. [Two other groups have done work along these lines. J. A. Musso and M. Azzaro (Bull.Soc.Chem.Fr., No. 10b, supplement, sep.1968, p. 3-4; and private communication) have employed an extremely similar approach, but dimensioned for smaller computers. I believe the East Anglia group have now made their earlier programme (Harris and Woodman, Mol.Phys. 10, 437 (1966)) iterative; it is dimensioned for larger computers.]

Although the essential logical structure of LAOCOON has been retained, considerable re-organisation has occurred, and the following points may be of interest:
(a) The utilisation of core has been improved, particularly by the effective elimination of the largest matrix. In addition, the programme has been divided into sets of routines which can be linked or over-laid (where this is necessary for large problems); as a result, although the total size of the programme has necessarily been increased by the inclusion of magnetic equivalence factorisation, the actual maximum core store required by the programme has been reduced. The consequence of these two changes is that a computer which, using LAOCOON3, could handle at best a six-spin system, can, with LAME, solve e.g. ABCDEFG and A_4B_4CD systems.

(b) Less precise or overlapping transitions may be included in the Least Squares refinement with a lower weight (see also P. J. Black and M. L. Heffernan, Austr. J. Chem. 16, 1051 (1963); and H. J. Bernstein, K. Schaumburg and D. Gillies, Can.J.Chem. 46, 503 (1968). Both groups incorporated this feature.)
(c) As an option, the eigenvalues may be printed. The programme identifies the pairs of eigenvalues between which transitions occur, which is useful in connection with spin-tickling etc.
(d) I personally feel that the inter-relation between the final refined parameter values, which certainly requires more than the printing of the standard deviations, is more helpfully indicated by producing a correlation matrix (FMS' method) than by indicating the principal axes of the error ellipsoid in multidimensional parameter space. Some of the negative correlation coefficients found have been more negative than -0.5, and it is important to realise the implications of this. Accordingly, I suggest that to Ray Abraham's list (IITNMR 114-29) of desiderata for published computer analyses one should add: "(vi) any numerically large correlation coefficient between parameters, or equivalent information."
(e) Another option, which saves time for large problems, is the temporary storage on a suitable output medium of those quantities calculated during a first non-iterative run

which are needed for the succeeding iterative run with the same starting parameters. For small problems it is easier not tobother with this.
(f) For very difficult problems, where assignment of lines is far from easy, the number of non-iterative runs needed can be reduced by the use of another option, which allows the calculation and printing out of the partial differentials of (selected) transition frequencies with respect to (some or all) sets of parameters. This also gives a perhaps more readily assimilated picture of the quantum-mechanical structure of the problem than would the actual eigenvector matrices.

The use of the programme requires, by way of peripherals, an input unit and a lineprinter, and two magnetic tapes. If the option (e) is implemented, an extra input and an extra output channel are required. A further output channel may be used to punch out transition details (for subsequent use by a separate plotting programme). The programme is written in a neutral dialect of FORTRAN IV which should require minimal adaptation for use on other machines.* The computer referred to in (a) above is an I.C.T. 1905 with a central processor of 32,000 24-bit cores (which uses two cores to store one floating point variable): detailed instructions are provided for adjusting dimensions both for smaller and for larger computers. It will be a pleasure to send listings to potential users.

Sincerely yours,

C. W. Haigh

P.S. Listings of the programme MAGN, mentioned in my opening sentence, are also available for devotees of the rival firm. Essentially based on MMB, its most important modification lies in its use of all possible trace relations as proper constraints on the solution: this improves both accuracy and convergence.

* For the solution of a possible query on the IBM 360/30 see IITNMR 116-39.

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

3 October 1968

Missing Pages for TAMU NMR Newsletter

It has come to my attention that occasionally a particular copy of the Newsletter may have a blank page instead of one full of the goodies it was meant to display. This is, I assume, extremely rare and reflects only the expected human imperfections of both our excellent printer and his equipment. (It does not reflect as Ted Becker suggested, I assume with tongue in cheek, the fact that I am using such a devious method to exercise an editorial function.)

Two pages known to have been left blank in at least some copies are:

1.) IIT NMR Newsletter, 117, 20 (June, 1968) - contribution by E. D. Becker.

2.) TAMU NMR Newsletter, 120, 30 - contribution of Hoffman and Forsén.

Please let us know if any of your pages are blank, as we will be happy to supply Xerox copy replacements.

B. L. Shapiro

B. L. Shapiro

121-58

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PUBLIC HEALTH SERVICE

NATIONAL INSTITUTES OF HEALTH
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Bldg. 2, Rm. B2-02C

October 4, 1968

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

Dear Barry:

10th ENC - Preliminary Announcement

Readers of the Newsletter may be interested in knowing that the 10th Experimental NMR Conference will be held at the Carnegie-Mellon University (Mellon Institute), Pittsburgh, Pa., Feb. 27, 28 and March 1, 1969. (The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held in Cleveland the following week.)

As usual, the emphasis at the ENC will be on new NMR instruments and techniques. The Committee is now formulating the conference program; we would welcome suggestions for topics to be covered. The outline of the program will be announced in the Newsletter in about six weeks. Procedures for registration and submission of contributed papers will be given at that time.

Suggestions for the program or questions regarding the Conference may be addressed to the undersigned (Bldg. 2, National Institutes of Health; phone 301-496-2194) or to any other member of the committee.

Sincerely,

Ted.

Edwin D. Becker
Chairman, 10th ENC

Committee:
J. M. Anderson
A. A. Bothner-By
T. J. Flautt
P. R. Shafer
B. L. Shapiro
K. L. Williamson

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