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Illinois Institute of Technology N-M-R Newsletter

No. 91
APRIL, 1966

OVER

Deadline Dates:	No. 92 - 18 May 1966
	No. 93 - 17 June 1966

OKLAHOMA STATE UNIVERSITY • STILLWATER

Department of Chemistry
FRontier 2-6211, Ext. 7215—7218

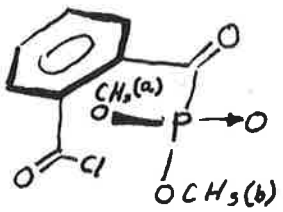
74074

March 21, 1966

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

Dear Dr. Shapiro:

As our contribution to NMR Newsletter we present the following results. The phosphorus ester (acyl phosphonate) I gives an unusual spectrum at 60 Mc in that the methyl resonances are split into a quartet. Apparently the rigid geometry of the system is such to force the one methyl group



over the benzene ring, thereby making it nonequivalent to the other CH_3. The chemical shift for $\nu_{CH_3(a)}$ = 242 cps and $\nu_{CH_3(b)}$ = 220 cps from TMS in carbon tetrachloride. The coupling constants are $J_{CH_3(a) \text{ or } (b)}$ = 10.5 cps. In the corresponding ethyl derivative the CH_2 and CH_3 groups are both split. We are examining other systems to see if hindered rotation is the cause of this long range nonequivalence of alkyl groups.

Sincerely yours,

K. D. Berlin

K. D. Berlin
Associate Professor

KDB:bbm

Short Title: Magnetic Nonequivalence of Alkyl Groups in Hindered Acyl Phosphonates by Virtue of Hindered Rotation.

THE SCHOOL OF PHARMACY

UNIVERSITY OF LONDON

PHARMACEUTICAL CHEMISTRY
PROFESSOR W. B. WHALLEY
D.Sc., Ph.D., F.R.I.C.

WBW/CLS

29/39, BRUNSWICK SQUARE
LONDON, W.C.1.
TELEPHONE TERMINUS 7651/8

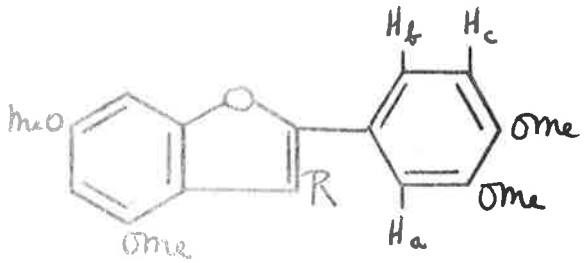
18th March 1966

Dear Dr. Shapiro,

The Conformation of a 2-Phenyl-coumarone

Thank you for your reminder that our "subscription" is due. We should like to tell you about an interesting case of conformational definition we recently encountered, in connection with some work on 2-phenylcoumarones.

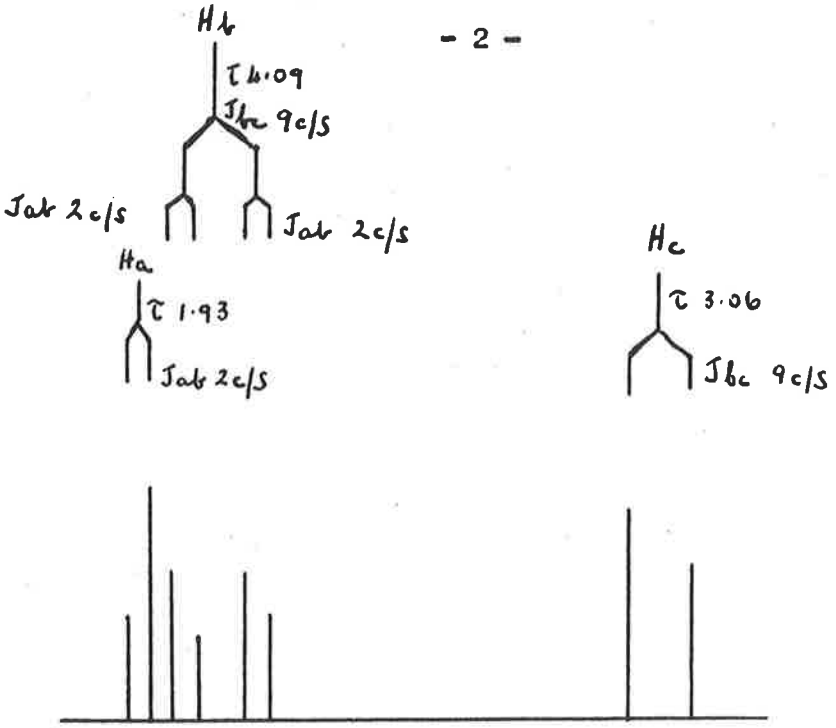
We recently prepared compound (I; R = Me). The n.m.r. spectrum of (I; R = Me) includes signals at τ 3.68 and 3.35 (doublets, J 3 c/s, one pair of meta aromatic protons in ring A), 6.05, 6.10, 6.13 and



(I)

6.18 (singlets, 4 x OMe, 12 protons), and 7.43 (singlet, = C.Me, 3 protons). The signals associated with the aromatic protons of ring B fall into two distinct groups: (i) proton H_c which resonates at τ 3.06 (doublet, J/9 c/s) showing ortho splitting; (ii) the H_a and H_b protons which appear at τ 2.7 as a strongly coupled multiplet. The signals associated with the H_a and H_b protons in (I; R = CHO) appear even further downfield and give the spectrum shown.

/cont.....



This allows definition of the conformation of 2-(3,4-dimethoxyphenyl)-3-formyl-4,6-dimethoxycoumarone as (I; R = CHO) rather than the alternative in which ring B is rotated through 180° about the 1',4'-axis.

We hope to report interesting results upon some new topics shortly.

This work was carried out in conjunction with Drs. D.W. Mathieson and C.A. Anirudhan.

We look forward to remaining on the mailing list for your valuable Newsletter.

Best wishes,

Yours sincerely,

W. B. Whalley

W. B. Whalley

Professor Bernard L. Shapiro,
Illinois Institute of Technology,
Chicago,
Illinois 60616,
U. S. A.

UNIVERSITY OF FLORIDA
GAINESVILLE, 32603

DEPARTMENT OF CHEMISTRY

March 22, 1966

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

Dear Barry:

In order to renew our subscription to IITNMRN, I should like to mention some operating details and system modifications which have proved useful with our Varian DP-60 spectrometer system.

(1) Treatment of recirculated cooling water. Contamination of the cooling water and partial blockage of the magnet coils afforded a serious problem until we began using our present treatment, recommended to us by the local microwave tube manufacturing plant of the Sperry Company. To the water in the tank is added a small amount (approximately 10 ppm) of Nalco 353, and the pH is then adjusted with morpholine to the range 9.0 - 9.5. During a period of about 18 months we have observed no rise in magnet temperature or reduction in flow rate of water.

(2) Modification of the slow-sweep unit. We have added a fourth sweep-rate multiplier position, "Super-Fast." This is a great aid in fluorine work, and has also enabled us to discard the precession field scanning unit for wide-line work. At least in the range of line widths we are concerned with, up to 20,000 cycles, the slow-sweep unit is quite adequate and, of course, much more reproducible.

(3) Replacement of the variable autotransformer in the V2100B Power Supply. Several years ago, the original transformer burned out both brushes and armature. We happened to have a surplus autotransformer of 9.7 KVA capacity with a motor drive

attached. Since this unit was too large to mount inside the cabinet, we built a metal case to protect the terminals on it and placed it on top of the power supply cabinet, in space which serves no other useful function. We also added a voltmeter on the front of the case to monitor the transformer output. This serves the same purpose as the scale formerly attached to the transformer handle: the rise in operating voltage of the 304TL's can be followed as the tubes age. At the same time, we can observe fluctuations in line voltage which are occasionally troublesome. Location of the transformer outside the cabinet reduces the demand on the cooling fan within the power supply, which is also an advantage.

(4) Modification of the probe. It is frequently necessary for us to change frequency from 56.4 to 60.0 mc. or vice versa. To retune the probe in its original form is very convenient, and, while we have two probes, it is preferable to keep one in the high-sensitivity configuration and the other in the variable temperature configuration. Accordingly, we have moved the receiver coil tuning condenser to a small cylindrical housing in front of the probe, where it can be adjusted without disassembling the entire probe. At the same time, we have two r.f. units, one kept at each of the frequencies, and thus we can change between H and F within a few minutes.

Some of these ideas have been suggested before by others, but perhaps not all of your current readers have seen them. If anyone desires more detailed information, we should be happy to supply details.

Cordially yours,

Wallace S. Brey, Jr.

Wallace S. Brey, Jr.
Professor of Chemistry

College of Pharmacy · Department of Chemistry
UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

833 South Wood Street · Chicago, Illinois 60612 · Telephone 663-7245

March 25, 1966

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

Re: Solvent Dependence of C^{13}-H and C^{13}-F Coupling Constants

Dear Barry:

I spent last summer at Argonne National Laboratory working with Steve Danyluk on solvent effects in NMR. Some of the findings which are being sorted out for publication might be of interest to the Newsletter readers.

We studied the solvent dependence of the directly-bonded C^{13}-H and C^{13}-F^{19} coupling constants in cis and trans 1,2-dichlorofluoroethylene in a variety of polar and non-polar solvents.

The spectra for the two isomers are of the simple AX type and the C^{13}-H and C^{13}-F^{19} coupling constants are obtained directly from the satellite lines in the proton and fluorine spectra respectively. A summary of the parameters is given in Table I (cis isomer) and Table II (trans isomer). All of the chemical shifts and observable coupling constants show a strong solvent dependence*; Tables I and II. A slight concentration dependence was also noted for δ_H, ϕ_F and J_{C13-H}; however, the changes were much less than those observed in different solvents.

*A strong solvent dependence was also noted for the C^{13}=C-H and C^{13}=C-F coupling constants.

Table I; Solvent Dependence of Chemical Shifts and Coupling Constants for Cis 1,2-dichlorofluoroethylene[d]

Solvent	δ_H [a,b]	J_{C13-H} [a]	ϕ_F [c]	$J_{C13-F19}$
	c.p.s.	c.p.s.	c.p.s.	c.p.s.
cyclohexane	362.0	195.6	4763	300.0
benzene	323.4	198.0	--	--
carbon disulfide	369.8	195.5	4675	300.0
isopropyl ether	389.4	199.6	--	--
chloroform	372.9	199.6	4746	300.0
acetone	405.5	199.6	--	--
acetonitrile	390.4	198.0	4798	298.6
N,N-dimethylformamide	424.4	202.5	4807	297.0
dimethylsulfoxide	428.8	201.0	4767	298.0

Table II; Solvent Dependence of Chemical Shifts and Coupling Constants for trans 1,2-dichlorofluoroethylene[d]

Solvent	δ_H	$J_{C^{13}-H}$	ϕ_F	$J_{C^{13}-F^{19}}$
	c.p.s.	c.p.s.	c.p.s.	c.p.s.
cyclohexane	325.2	201.7	4501	306.9
benzene	286.3	204.0	--	--
carbon disulfide	333.6	201.8	4468	306.6
isopropyl ether	352.6	205.2	--	--
chloroform	336.2	203.8	4491	306.2
acetone	377.3	205.9	--	--
acetonitrile	355.7	204.5	4558	304.5
N,N-dimethylformamide	390.7	208.6	4565	302.9
dimethyl sulfoxide	394.7	207.1	4518	304.2

a The proton chemical shifts are accurate to ± 0.2 c.p.s. and coupling constants to ± 0.1 c.p.s.

The fluorine chemical shifts and coupling constants are accurate to ± 1.0 c.p.s. and ± 0.5 c.p.s. respectively.

b Proton chemical shifts are for 1% solutions and are relative to internal T.M.S.

c Fluorine chemical shifts are for 50% solutions and are given relative to external Cl_3CF.

d Spectra were measured at room temperature 25 ± 2° C using Varian DA-60 and A56-60 spectrometers. The sweep ranges were carefully calibrated several times.

The proton and fluorine chemical shifts for both isomers show a marked decrease in solvents of higher dielectric constant. In contrast the C^{13}-H coupling constants increase in magnitude while the C^{13}-F^{19} coupling constants decrease in the more polar solvents. Both the proton and fluorine chemical shifts vary linearly** with the respective $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ coupling constants in different solvents. A linear correlation is also noted between the directly-bonded couplings and J_{H-F} over the same range of solvents. These observations indicate that the medium effect acts to change the shieldings and coupling constants by a similar mechanism. Since the chemical shifts follow the trend expected if the reaction field of the solvent is the dominant influence it follows that the changes in coupling constants are also largely due to this effect.

**The pronounced high field shift in benzene is due to the anisotropic diamagnetic susceptibility of the solvent molecules.

The solvent-induced changes in magnitude of $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ can be rationalized in terms of the MO theory of Pople and Santry for directly-bonded coupling constants. Considering the C^{13}-H coupling constant, an increase in the magnitude of the reaction field acting in the region of the C-H bond will tend to increase the s character≠ of the C-hybrid bonding orbital and hence will lead to a more positive value for $J_{C^{13}-H}$; if the sign of $J_{C^{13}-H}$ is positive then $J_{C^{13}-H}$ will increase in more polar solvents as is observed. For the $C^{13}-F^{19}$ coupling, the reaction field acting in the region of the C-F bond will tend to draw the bonding electrons closer to the F Atom. The increased polarity of the bond results in a trend of the $C^{13}-F^{19}$ coupling constant to more positive values; since the sign of $J_{C^{13}-F^{19}}$ is most likely negative the observed coupling constant decreases in magnitude.

The present results show the possibility of determining the signs of directly-bonded coupling constants from their solvent dependence without recourse to double resonance techniques. A similar suggestion was made recently by S. L. Smith and R. H. Cox (J. Mol. Spectroscopy 16, 216 [1965]) in connection with the solvent dependence of the geminal and vicinal couplings in styrene oxide. The usefulness of solvent effects for sign determination is limited, however, to simple systems in which solute-solute and solute-solvent interactions are easily characterized.

≠ Electrostatic repulsion between the bonding electron and the negatively charged reaction field will force the electron closer to the C atom. cf. D. F. Evans, J. Chem. Soc. 5575 (1963).

Sincerely yours,

Charlie

Charles L. Bell
Associate Professor of Chemistry
(with Steven S. Danyluk)

CLB:jf

Glaxo Research Limited

Greenford · Middlesex

TELEPHONE: BYRON 3434 TELEGRAMS: Glaxotha, London, Telex CODE: New Standard, Bentleys

91-9

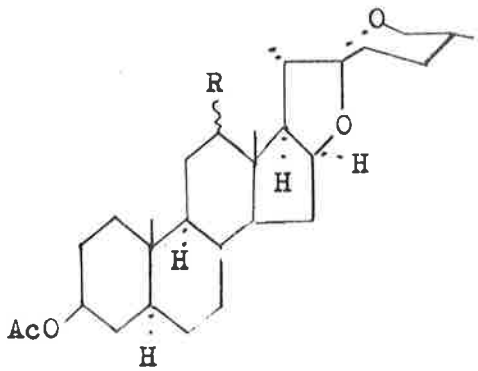
2nd March, 1966.

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

Dear Professor Shapiro,

$\Delta^{9(11)}$-Steroidal 25R-Sapogenins

We have followed our study of the p.m.r. spectra of 11-oxo-steroids (J. Chem. Soc., 1965, 7328) by an examination of the effect of a 9(11)-ethylenic linkage on the p.m.r. spectra of a series of steroidal 25R-sapogenins.



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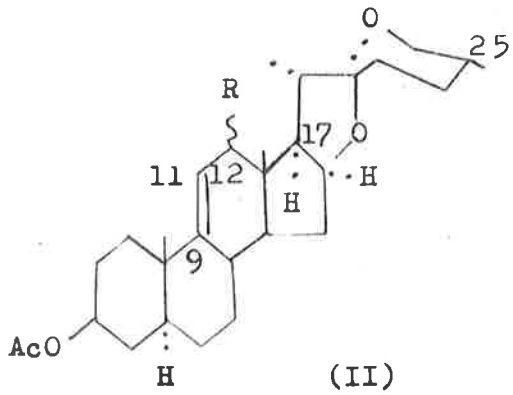


(II)

The 12-proton peaks for tigogenin (I; R = H) and 9-dehydrotigogenin acetates (II; R = H), which are hidden under the general methylene envelope, are displaced downfield and are readily identified when a 12-substituent is introduced. A comparison of the $CDCl_3$ spectra of (I; R = α-Ac) and (I; R = β-Ac) shows that the 12β-proton (equatorial) absorbs at lower magnetic field (τ 5.08) than does the 12α-proton (axial) (τ 5.45). Introduction of a 9(11)-double-bond, however, deshields the axial 12α-proton (cf. II; R = β-AcO) and causes it to absorb at lower field (τ 4.92) than does the corresponding 12β-proton (cf. II; R = α-AcO) (τ 5.05).

A 12α-substituent (cf. II; R = α-AcO), but not a 12β-substituent (cf. II; R = β-AcO), by 1,3-diaxial interaction deshields the 17α-proton, which appears as two doublets centred at about τ 7.75.

Measurements were also undertaken on a series of cyclopseudo--25R-sapogenins and the effect of changing the solvent from $CDCl_3$ to benzene was investigated.

A full account has been submitted for publication in the Journal of the Chemical Society.

Yours sincerely,

James L Page — Dr. J.L. Page

G.F.H. Green

S E Staniforth — S.E. Staniforth

91-10

THE UNIVERSITY OF TEXAS
AUSTIN 78712

THE DEPARTMENT OF BOTANY

March 24, 1966

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

Flavonoid Spectra

Dear Dr. Shapiro:

We recently published over 50 n.m.r. spectra of flavonoids ("Nuclear Magnetic Resonance Analysis of Flavonoids", The University of Texas Publication No. 6418, 1964). A second collection is now in preparation. However, we can provide Xerox copies of the additional spectra now to those interested in flavonoid chemistry.

Sincerely yours,

Tom J. Mabry

Tom J. Mabry
Assistant Professor

TJM:ja

CALIFORNIA STATE COLLEGE  **AT LOS ANGELES**

Department of Chemistry

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)
Telephone 225-1651 (Area Code 213)

March 24, 1966

Dr. Bernard Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

In addition to continuing our studies of electrolytic solutions, we are investigating complexes of several ions with a variety of organic solvents. We have found that it is often possible to detect separate NMR signals for bulk and complexed solvent molecules, indicating that the complex formed is strong and, consequently, the exchange of molecules among the various environments is slow. A typical example is the $AlCl_3$-Dimethylformamide (DMF) system. In solutions of $AlCl_3$, two sets of methyl doublets, separated by about 15 cps, and two carbonyl proton signals, separated by approximately 50 cps, are observed. The peaks corresponding to the complexed DMF appear downfield from the bulk signals. By comparing the areas of the two carbonyl proton signals, coordination numbers were calculated. We are now studying the appearance of these signals as a function of temperature and hope to obtain rate data for the process DMF (complexed) $\longrightarrow$ DMF (bulk).

We have also completed preliminary studies of several ions, including Be(II), Al(III), Ga(III), Si(IV), Ti(IV) and Sb(V) in solvents such as N,N-Dimethylformamide, N-Methylformamide, N-ethylformamide, and ethylformante.

Sincerely yours,

Anthony Fratiello
Anthony Fratiello

Ronald Schuster
Ronald Schuster

Don Paul Miller
Don Paul Miller

FSM/ml

91-12

CSIRO

AIR MAIL

DIVISION OF PLANT INDUSTRY

P.O. BOX 109, CANBERRA CITY, A.C.T. TELEPHONE 40455. TELEGRAMS CORESEARCH CANBERRA

WPAP:RCC
Ref:

24th March, 1966.

Professor Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
CHICAGO, ILLINOIS 60616, U.S.A.

Dear Professor Shapiro,

Stable C1024 Read-out Times

We have had trouble with instability of the read-out times of our C1024 and recently decided to rectify the matter. Unlike Connors IITNMR 83-34 and Flaut IITNMR 85-20 I was fortunate enough to have circuits and wiring diagrams. Since, as Connors states, the read-in time oscillator is more stable than the read-out time oscillator, I decided to use this to actuate the read-out circuits. This stability is available because small drifts in the nominal 81935 cps., are divided by the binary circuits while the X-Y display oscillator uses large RC components to reduce the nominal 10 KC of the unijunction oscillator down to the range 2-100 cps., for the read-out times. Any drift of this frequency is then multiplied by the read-out time which leads to variations on the pre-calibrated charts.

The read-in oscillator pulse train, after appropriate division, is available at either PC43/U or at read-in time selector switch S8C/6. This pulse train was switched through S3J/6 to S3J/7 (a spare bank on the function selector switch) thence to terminal Y on PC8 (X-Y display oscillator card). It was necessary to make three changes on PC8. The lead to PC8/U was removed and insulated. (This disconnected the trim pots on PC36 and read-out time selector switch). Terminal A and terminal U on PC8 were joined by a 100K ohm. resistor. (This set the oscilloscope sweep generator at approximately 10 KCs). The forward bias on diode gate D5 was increased by joining terminals PC8/Z and PC8/J (-20V) with a 56 K ohm. resistor. In our case the master oscillator (81935 cps.) on PC40 was slightly high resulting in shorter read-out times. This was adjusted by adding capacitance (100 PF) across terminals PC40Z and PC40F. If there are any small residual drifts it may help if the existing tuned collector capacitors are replaced by higher quality silver-mica condensors.

Trusting that this contribution will warrant continuation of our subscription.

Yours sincerely,

W.P.A. Pascoe

(W.P.A. Pascoe)

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

Pittsburgh
Coal Research Center

March 24, 1966

Dear Barry:

C^{13} NMR Signals in Coal Derivatives and Petroleum

Quantitative determination of aromatic to non-aromatic carbons in coal derivatives and petroleum has been achieved using carbon-13 nuclear magnetic resonance spectrometry. Spectrometer calibration was accomplished utilizing spectra of pure alkylaromatic and hydroaromatic compounds (fig. 1). All spectra were obtained by observing the dispersion mode under rapid passage conditions, thus all hindrances such as peak asymmetries, spectral inversion, dispersion mode line broadening, etc. were present. A baseline technique similar to that in common use in infrared spectrophotometry was employed; only singly integrated (as opposed to doubly integrated) spectral intensities were used. Representative spectra are illustrated in figure 2 and typical results shown in table 1.

Many thanks for continuing to send out these most helpful newsletters.

Sincerely yours,

Hal
Gus

H. L. Retcofsky
R. A. Friedel

Table 1.- Carbon-13 nuclear magnetic resonance data

Material	Aromaticity $f_a = C_{aro}/C_{total}$	
	C^{13} NMR	Other
Neutral oil from 700° C cracking of a 450° C carbonization product from coal	0.70 ± .05	0.66 1/
Coal tar pitch; softening point 80°-85° C (Carbon disulfide solubles)	.90 ± .10	.94 1/ .94 2/
Anthracene oil from coal	.95 ± .05	.89 2/ .92 1/
Heavy creosote from coal	.95 ± .05	.93 2/
Ponca City crude petroleum	.15 ± .05	

1/ Proton magnetic resonance data.
2/ Mass spectrometric data.

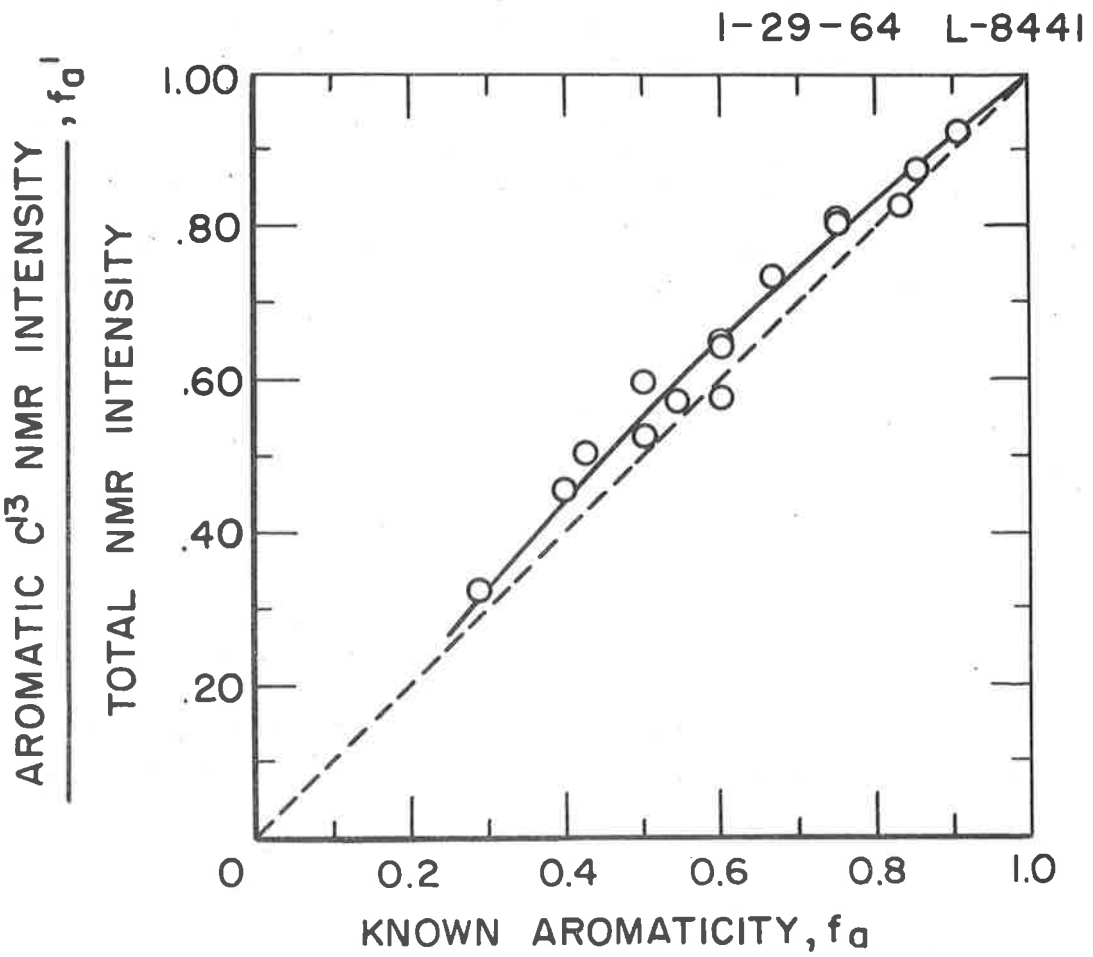


Figure 1.- Aromaticity calibration curve for a C^{13} NMR spectrometer.

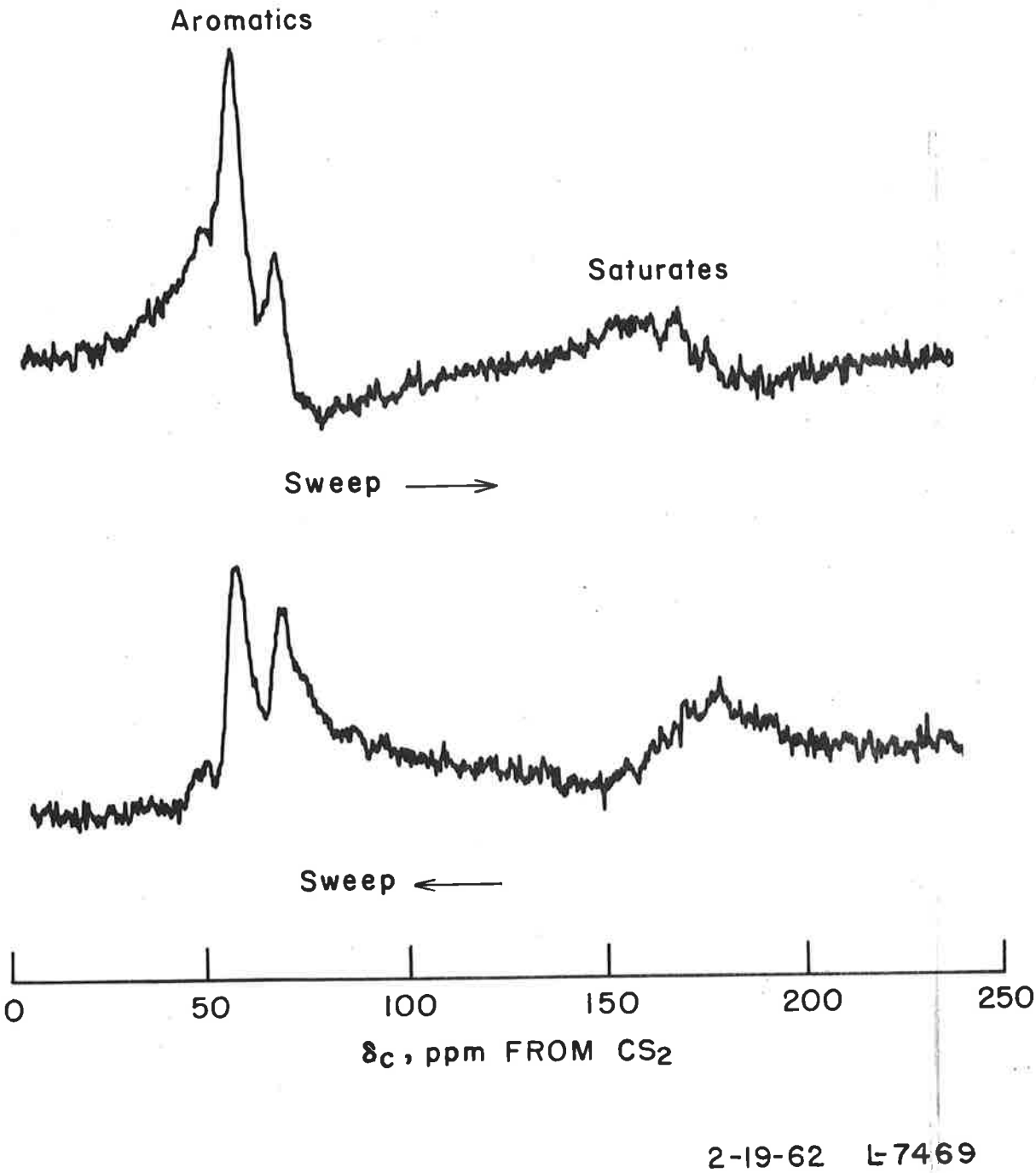


Figure 2.- C^{13} NMR spectra of a neutral oil from 700° C cracking of a 450° C carbonization product from coal.

91-16

INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT WÜRZBURG
VORSTAND: PROF. DR. MAX SCHMIDT

8700 WÜRZBURG, Röntgenring 11
Telefon (0931) 31560/561

23. 3. 1966

Hubert Schmidbaur
Werner Wolfsberger

Herrn
Prof. Dr. B. L. Shapiro
Illinois Institute of Technology
Chicago, 60616, U S A

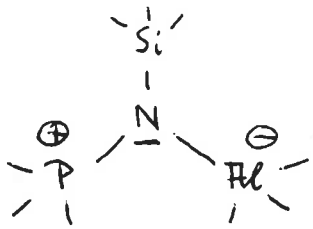
Effect of complex formation on the chemical shifts and coupling constants of the donator molecule.

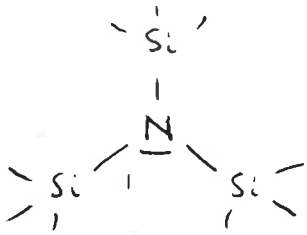
Dear Professor Shapiro,

We are afraid that this contribution to IIT NMR letters will be by far to late to keep our laboratory on your mailing list. There are several reasons for this delay, however, among which our recent moving from the University of Marburg to the University of Würzburg is the most significant one. Would you please change our address and keep the new one on your list ?

Naturally there has not been done much work in our NMR laboratory during the last few month, but we were able to get at least some results, which could be of interest to readers of your monthly letters.

As a part of our investigations on NMR spectra of isoelectronic organometallic molecules we have studied compounds containing the skeleton I, an isostere of the trisilylamin skeleton II:

I: 

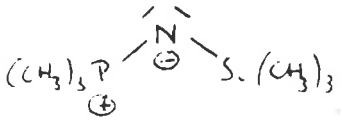
II: 

An example for this is the coordination compound IV, an adduct molecule of the silyl phosphinimine III and $AlCl_3$:

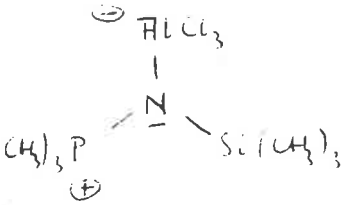
INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT WÜRZBURG

Blatt 2 an Prof. Dr. B. L. Shapiro
vom 23. 3. 1966

III.



IV



III is a very suitable model molecule for our purposes, as all its elements (except for N) exhibit nuclear spins 1/2 for one of their isotopes.

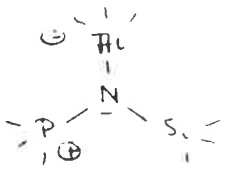
In the table below we are listing the ^{1}H-Chemical Shifts and coupling constants of the free donor molecule III and those of the complex IV. (δ-values in c/s at 60 Mc relative to ext. TMS; Diluted sol. in CH_2Cl_2 as a solvent; 30°.)

	III	IV	
δ $(CH_3)_3Si$	+3.8	-30.5	Δ = -34.3
δ $(CH_3)_3P$	-82.5	-122.5	Δ = -40.0
$J(^1\underline{H}-C-^{29}\underline{Si})$	6.4	6.8	J_{III}/J_{IV} = 1.063
$J(^1\underline{H}-C-^{31}\underline{P})$	12.4	13.25	" = 1.069
$J(^1\underline{H}-^{13}\underline{C})Si$	117	120	" = 1.032
$J(^1\underline{H}-^{13}\underline{C})P$	127	130	" = 1.026

These findings clearly show, that the effect of the acceptor molecule $AlCl_3$ is much more pronounced at the $(CH_3)_3P$- than on the $(CH_3)_3Si$- grouping. For the latter the downfield shift Δ as well as the increase of the J-values (taken as J_{III}/J_{IV}) are smaller than those for the neighbouring $(CH_3)_3P$- group. This may be interpreted in terms of a higher $d_{\pi}p_{\pi}$-bond order of the P-N relative to the Si-N bond. In other words a resonance form V thus should contribute more to the ground state of the molecule than VI or VII.

V:

VI.



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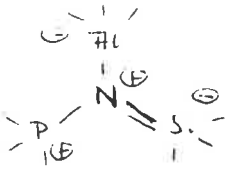

Yours sincerely

H. Schmidbaur W. Wolfsberger

91-18

The Standard Oil Company
(An Ohio Corporation)
Research Department
4440 Warrensville Center Road
Cleveland, Ohio 44128

E. C. HUGHES
VICE PRESIDENT

March 23, 1966

Professor Bernard L. Shapiro
Associate Professor
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Title: (1) Concerning Line Ordering and Tacticity of Polymers and
(2) Determination of Reactivity Ratios in Acrylonitrile Co-Polymers by NMR.

Dear Barry,

For those readers interested in NMR of polymers we would like to briefly mention two papers which should appear in the literature in the near future.

The first paper attempts to provide some sort of rationale to observed line ordering in polymers. Backbone protons alpha and beta to functional groups attached to the chain have been observed to give different chemical shifts for those within isotactic, syndiotactic, or heterotactic triads. In some cases the order of these peaks from low field to high has been s-h-i and in others just the reverse. This is clearly seen in the case of decoupled β-proton bands or in those vinyl polymers having deuterium on the α-carbon. Examples of polymers giving the s-h-i (Ho→) ordering are poly(vinyl alcohol), poly(vinyl methyl ether) and poly(acetaldehyde), and of those giving the i-h-s (Ho→) ordering are poly(vinyl acetate), poly(methyl methacrylate) and polypropylene.

In a third category are a few polymers which exhibit no significant difference in chemical shift (hence no line ordering) of α or β protons. Examples in this case would be polyacrylonitrile, polymethacrylonitrile, and polyvinyl fluoride. It is our contention that observed line ordering (or lack of it) can be predicted from the nature of the functional group attached to the polymer backbone, and consequent anisotropic shielding or deshielding, as the case may be, of backbone protons.

The Standard Oil Company
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In the second paper the utility of compositional analysis of polymers by NMR is demonstrated. Reactivity ratios are determined for three co-polymers of acrylonitrile, with ethyl acrylate, styrene, and methacrylonitrile from Kjeldahl nitrogen analysis and from NMR measurements. In the first co-polymer the reactivity ratios were found to agree with those obtained by classical Kjeldahl methods. In the second case, the Kjeldahl analysis gives results lower than those obtained by NMR. In the last case, in which both monomers contain nitrile groups, the reactivity ratios are obtained with the same ease as before; whereas this would be exceedingly difficult to do by conventional analyses. It is suggested that in the ethyl acrylate-acrylonitrile system both the classical and NMR give agreeable results due to the random nature of the co-polymer. Whereas, in the styrene-acrylo case, this is not true because the acrylo tends to be present in very short sequences (one or two acrylo units); and traditionally, conventional methods of analysis for nitrile-containing polymers have given low results or have been difficult. NMR thus shows itself to be a powerful tool in the analysis of polymer systems.

Sincerely yours,

Bill

W. M. Ritchey

Frank

F. J. Knoll

FJK:clc

FACULTE DES SCIENCES
DE MONTPELLIER

SERVICE CHIMIE M.P.C. 1

R. JACQUIER
Professeur

E.N.S.C.M. 8, Rue de l'Ecole Normale

Tél : (67) 72-14-50

MONTPELLIER, le 22 Mars 1966.

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

ETUDE RMN DE LA STEREOCHIMIE DE LA CINNAMALDAZINE.

Cher Professeur Shapiro,

Ayant déjà examiné (Bull. Soc. Chim. Fr., 1965, p. 877) la configuration d'azines du type RR'C=N-N=CRR', nous donnons ici les résultats de l'étude RMN d'azines dérivant de composés carbonylés $\alpha.\beta$-éthyléniques et plus particulièrement de la cinnamaldazine :

$$C_6H_5-\underset{A}{C}=\underset{B}{C}-\underset{X}{C}=N-N=\underset{X'}{C}-\underset{B'}{C}=\underset{A'}{C}-C_6H_5$$

Si l'on tient compte non seulement de l'isomérie autour des doubles liaisons, mais aussi des simples liaisons et en excluant les isomères s-cis par rapport à la liaison centrale N-N, la cinnamaldazine peut exister sous 36 formes isomères.

D'une façon générale, quel que soit le solvant, le produit ne présente qu'un seul groupe de signaux pour A et A', B et B' et X et X' ce qui exclut les formes dissymétriques ; en plus, quand X= H (aldazines) nos précedentes études montrent que l'azine est toujours syn par rapport à la liaison N-N.

Dans le $CDCl_3$, le DMS et le CH_3NO_2, la proximité des glissements chimiques de H_A et H_B et le fait que $|J_{AB}|$ est grand par rapport à $|J_{AX}-J_{BX}|$ conduisent à des spectres dégénérés ; ainsi dans le $CDCl_3$ à 60 Mc on n'observe que 5 signaux, 3 pour la partie X et 2 pour la partie AB (cf. ABRAHAM et BERNSTEIN, Can. J. Chem., 1961, 39, 216).

Dans le C_6D_6 par contre, la cinnamaldazine présente un spectre normal, les attributions découlant de la comparaison avec les produits méthylés. Le proton H_B est masqué par les signaux du phényle, mais grâce

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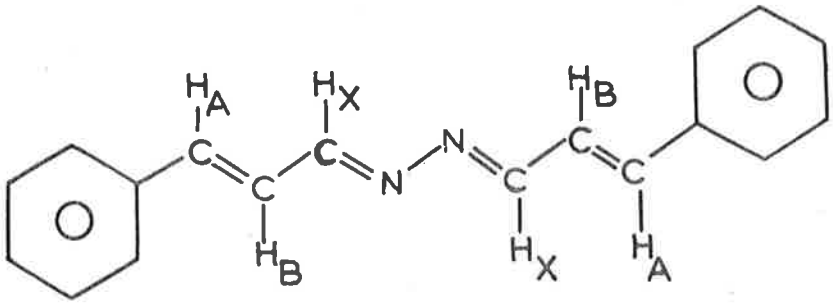
Tél : (67) 72-14-50

MONTPELLIER, le 22 Mars 1966.

à des expériences de découplage de spin à 100 Mc, son glissement chimique a pu être déterminé.

Azine dérivant de	A	B	X	J_{AB}	J_{AX}	J_{BX}
C_6H_5-CH=CH-CHO	H: 3,33(d)	H: 2,82(q)	H: 1,53(d)	16,3	0	9,3
C_6H_5-CH=CH-CO-CH_3	H: 3,11(d)	H: 2,69(d)	CH_3: 7,85	16,5	0	0
C_6H_5-CH=C(-CH_3)-CHO	H: 3,33(m)	CH_3: 7,70(d)	H: 1,57	1,2	0	0

Les valeurs des constantes de couplage montrent que A est trans par rapport à B et B s-trans par rapport à X. Nous avons déjà montré que la cinnamaldazine est symétrique par rapport à la liaison N-N et que H_X est syn par rapport à cette même liaison ; ceci joint au résultat des constantes de couplage donne pour la cinnamaldazine la stéréochimie suivante:



Nous remercions MM. Melera et Scheidegger (VARIAN, Zurich) ainsi que M. Delville (JEOL, Rueil-Malmaison) pour les spectres déterminés à 100 Mc).

R. Jacquier. J. Elguero. C. Marzin.

91-22

P.Niklaus, K.Stich
Sandoz Ltd. Basle,
Switzerland

March 21, 1966

Prof.B.L.Shapiro
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60617
U.S.A.

Dear Dr.Shapiro:

syn/anti isomerism of aliphatic hydrazones

G.J.Karabatsos[1] studied the syn/anti isomerism of phenyl hydrazones and H.A.Staab[2] and his coworkers published recently a paper about isomerism of Schiff's bases. All these compounds contained phenyl groups, which could change the"true" chemical shift of protons near the double bond.

We happened to synthesise some untill now not known hydrazones of aliphatic aldehydes and ketones. The relation of the obtained isomers depends nicely on the bulkyness of the substituents at the carbon and nitrogen atoms - so it is possible to assign the absorptions to the syn and anti forms. We coudn't enrich or separate the isomers, so we think there is a thermal equilibrium of the syn and anti form.e.g.

anti syn

acetaldehyde hydrazone

Some readers may be interested in the isomerism and nmr data of these compounds, so here are a few.

---

1) J.A.C.S. 85, 2784 and 3624, 1963

2) Tetrahedron Letters No.12, 697, 1965

SANDOZ

compound	relation of isom. %	$C-CH_3$	$N-CH_3$	CH=	form*)
1.MeCH=N-NH_2	52	1.68(2)5.5*)		7.1(4)5.5	a
	48	1.75(2)5.5		6.6(4)5.5	s
2.MeCH=N-NHMe	65	1.84(2)5.5	2.70(1)	7.07(4)5.5	a
	35	1.73(2)5.5	2.86(1)	6.65(4)5.5	s
3.MeCH=N-NMe_2	100	1.84(2)5.2	2.65(1)	6.55(4)5.2	a
4.EtCH=N-NH_2	80	1.08(3)		6.99(3)5.0	a
	20	0.97(3)		6.35(3)5.0	s
5.EtCH=N-NHMe	85	1.08(3)	2.75(1)	6.79(3)5.0	a
	15	1.12(3)	2.88(1)	6.26(3)5.0	s
6.EtCH=NMe_2	100	1.05(3)	2.65(1)	6.52(3)5.0	a
7.Me_2C=N-NH_2	-	1.68(1)and 1.84(1)			
8.Me_2C=N-NHMe	-	1.66(1)and] 1.83(1)	2.78(1)		
9.Me_2C=N-NMe_2	-	1.86(1)and] 1.89(1)	2.32(1)		

*) first number: shift in ppm from internal TMS; in brackets: multiplicity; last number: coupling constant in cps;
a: anti, s: syn
solvent: CCl_4 except No.1 and 2 which were taken neat.

P. Nihlans
K. Stoll

91-24

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE

NATIONAL INSTITUTES OF HEALTH
BETHESDA, MD. 20014
AREA CODE 301 TEL: 656-4000

March 28, 1966

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

Dear Barry:

We have been subscribing to the Preston NMR abstracts system since its inception nearly two years ago. With the growth of NMR literature we now have nearly 6000 cards, about half of which contain abstracts of potential use in NMR research. In order to handle the problem of retrieving data from this collection we have enlisted the aid of the digital computer. In spite of your reluctance to mention a commercial enterprise in the Newsletter, I feel that this is the most efficient method to bring this development to the attention of other NMR spectroscopists.

For each abstract card, we have prepared two IBM-type punched cards, each giving the abstract card serial number, one containing the last names of the authors (up to four), and the other containing all the subject codes given on the Preston abstract card. These cards are then read onto a magnetic library tape which can be searched by our computer using a program written by Curt Huntington of the NIH Computation Branch. The program permits searching for either subjects or authors on an "and" or an "or" basis. Printout consists of the abstract card serial numbers and authors' names. A second program permits updating the library tape. We have included only those Preston cards actually containing abstracts; it is possible, however, that Ernest Lustig of FDA will extend the system to the other cards containing literature "listings."

We have had only limited experience with the search system thus far, but it has been helpful and will probably increase in value as the literature grows. Since our programs are written for the Honeywell 800 computer and include non-standard Fortran statements, they may not be useful to others. The program will eventually be rewritten for the IBM 360/65 system. If anyone contemplates a similar automated search system I shall be glad to lend our punched data cards or library tape for duplication.

Best wishes for continued success with the Newsletter.

Sincerely,

Ted

Edwin D. Becker
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

91-26

Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry

28 March 1966

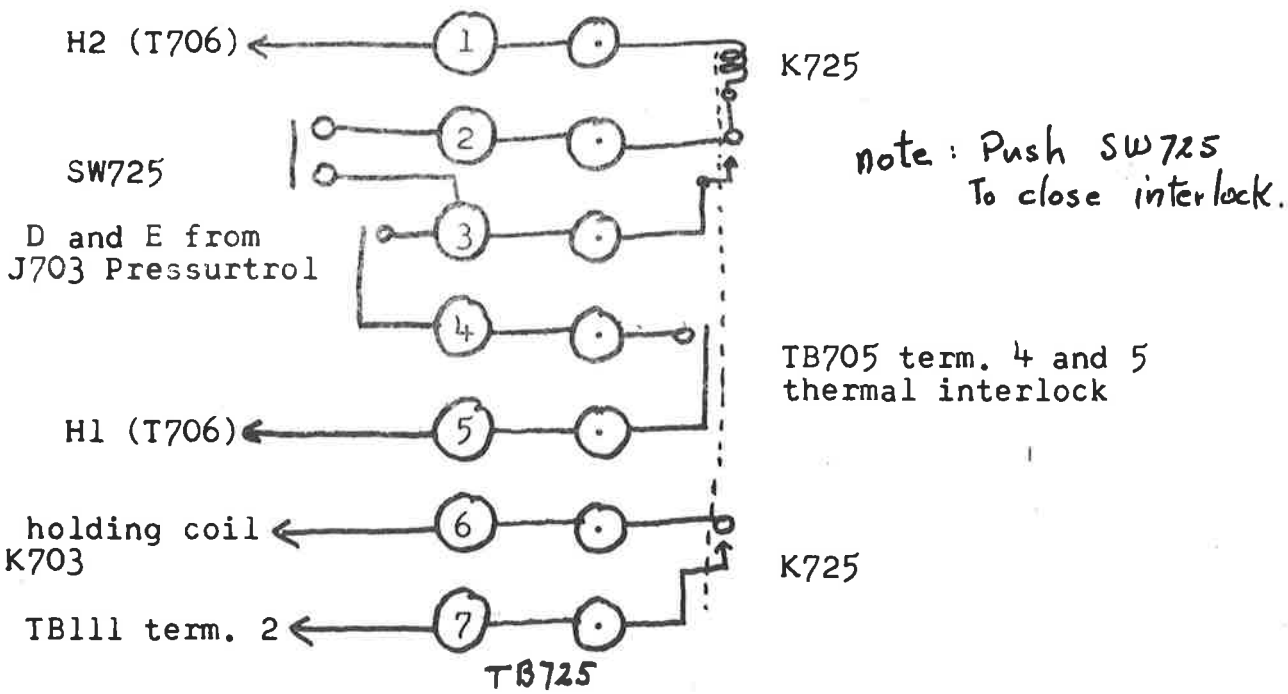
Professor Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois.

Dear Barry:

Enclosed are the changes we have made in the interlock circuit of the V-2100B power supply to prevent intermittant operation of the magnet due to repetitive failure and recovery of power, water pressure or heating and cooling of water or gate tube section. It has proved to be very reliable and fast acting. Essentially all that is done is to relocate (electrically) the Pressuretrol switch and to install a two pole relay. The holding coil of this relay is held on by interlock power through one set of contacts. The other contact closes the line through the holding coil of the main high power contactor, K703.

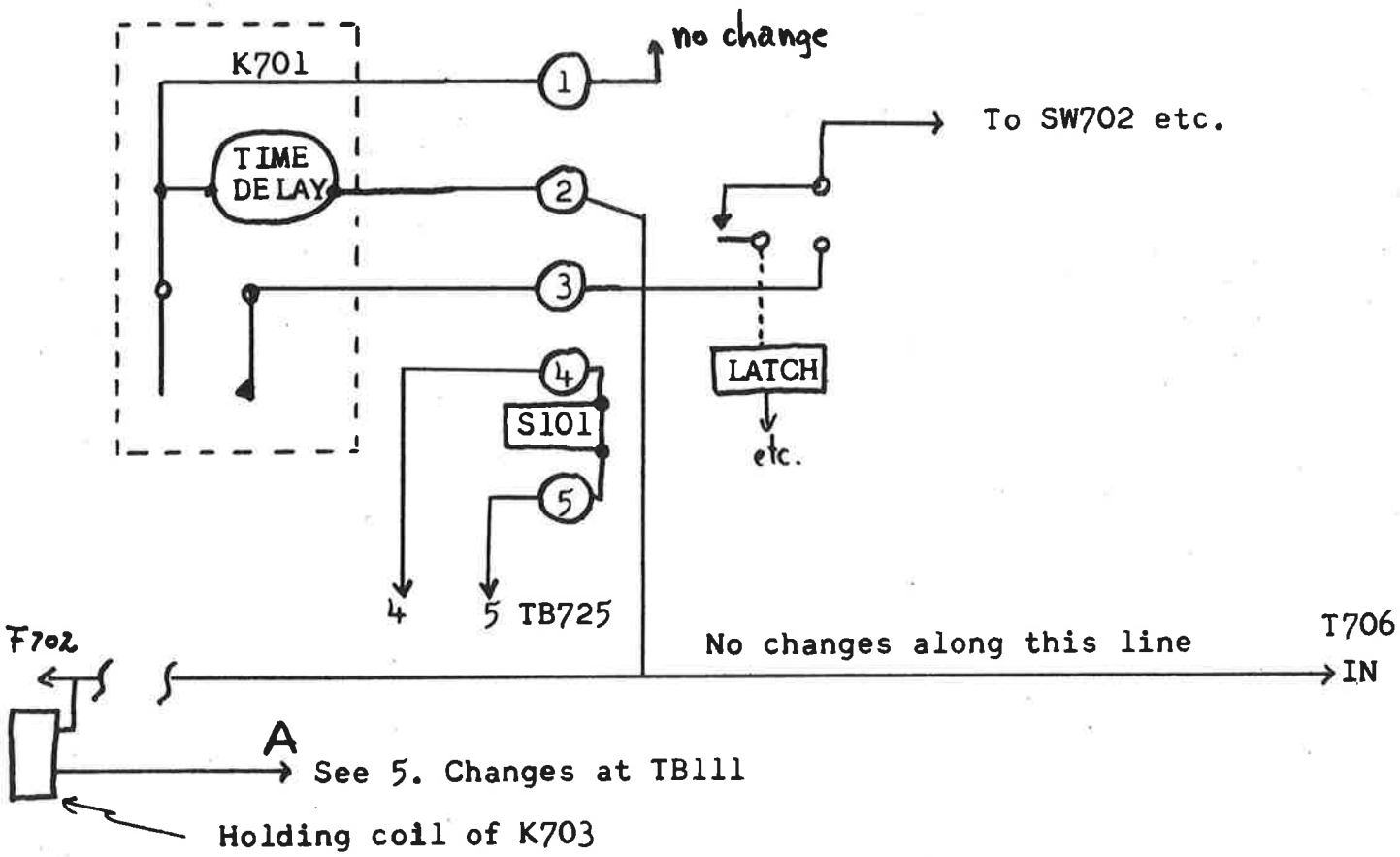
1. New Parts.(Our numbers)
   a) TB725 — 7x2 terminal strip
   b) K725 — two pole-double throw relay with 117VAC coil, e.g. Potter-Brumfield KA11AY (115VAC)
   c) I725 — NE-51H Interlock Failure indicator mtd on front.
   d) SW725 — Normally open single contact push switch.for reset. Install under neon light on front panel.

2. TB725 wiring diagram.

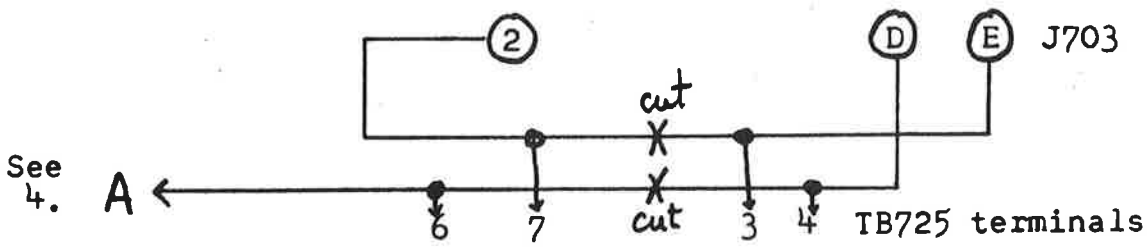


3. I725 - connect to terminals 1 and 6 of TB725

4. Changes at K701 and TB705



5. Changes at TB711. (No changes at terminals 1, 3 and 4).



6. Changes at T706. At the IN side of the Sola, add leads to TB725 terminals 1 and 5.

Cheers, Karl Dick

Kuhlmann and Shafer

91-28

PHYSIKALISCHES INSTITUT
DER KARL-MARX-UNIVERSITÄT

LEIPZIG C 1, den 4.3.1966
LINNÉSTRASSE 5 · FERNSPRECHER 32480
35682
65150

Herrn

Prof. B.L. S h a p i r o
Dept.of Chemistry
Illinois Institute of Technology
Technology Centre
C h i c a g o / Ill. / USA

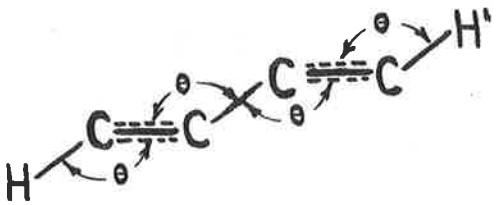
Untersuchung der weitreichenden H-H-Kopplung über fünf Bindungen in planaren Kohlenwasserstoffen

Sehr geehrter Herr Professor Shapiro!

Wir haben uns in der letzten Zeit mit der Untersuchung der weitreichenden H-H-Kopplungskonstanten über fünf Bindungen in planaren Kohlenwasserstoffen beschäftigt.

Molekültheoretische Berechnungen dieser weitreichenden Kopplungskonstanten sind bisher unter Berücksichtigung der π-Elektronen von Karplus /15/ und Mc Connell /16/ durchgeführt worden. In beiden Arbeiten werden jedoch die Kopplungsbeiträge der σ-Elektronen von vornherein vernachlässigt.

Ausgangspunkt unserer Arbeit war deshalb die Berechnung auch des σ-Elektronenbeitrages zur weitreichenden H-H-Kopplung. Da aus den experimentell gemessenen weitreichenden Kopplungskonstanten über planare Kohlenwasserstoff-Bindungsstrukturen bekannt ist, daß die Kopplungskonstanten über sogenannte zick-zack- (oder besser trans-trans-trans-)-Bindungsstrukturen am größten sind, wurde den Berechnungen ein solcher Bindungstyp mit gleichen Bindungswinkeln θ (gleicher Hybridisierung) für alle Kohlenstoffatome in einer solchen Kette zugrunde gelegt:



Die Berechnungen haben wir mit Hilfe der Dichtematrixmethode nach Mc Weeny /17/ durchgeführt. Aus der Dichtematrix R für die betrachtete

III 16 910 Lp G 541 36

Molekülstruktur und den Werten der Bindungswellenfunktionen am Ort der koppelnden Kerne (hier als Spaltenvektoren $\phi(H)$ und $\phi(H')$ geschrieben) erhält man die Kopplungskonstante nach der Formel

$$J^{cont}_{HH'} = \frac{1}{\hbar}\left(\frac{16\pi\mu_B\hbar}{3}\right)^2 \gamma_H^2 \frac{1}{\Delta E}\left[\phi^T(H)\, R\, \phi(H')\right]^2 .$$

Die in Abhängigkeit vom Bindungs- und Hybridisierungswinkel Θ berechneten σ-Elektronenbeiträge zu $J_{HH'}$ sind in der beigefügten Abbildung als Kurve d eingezeichnet (ΔE=9eV). (Bei der Auswertung hat sich gezeigt, daß es günstig ist, die experimentell gemessenen und die theoretisch berechneten Kopplungskonstanten in ihrer Abhängigkeit vom Produkt über die Kohlenstoff-2s-Charaktere $\prod_1^k\left(-\frac{\cos\Theta_i}{1-\cos\Theta_i}\right)$ zu betrachten, wobei die Hybridisierungswinkel der C-Atome berücksichtigt werden, über die die Kopplung vermittelt wird.)

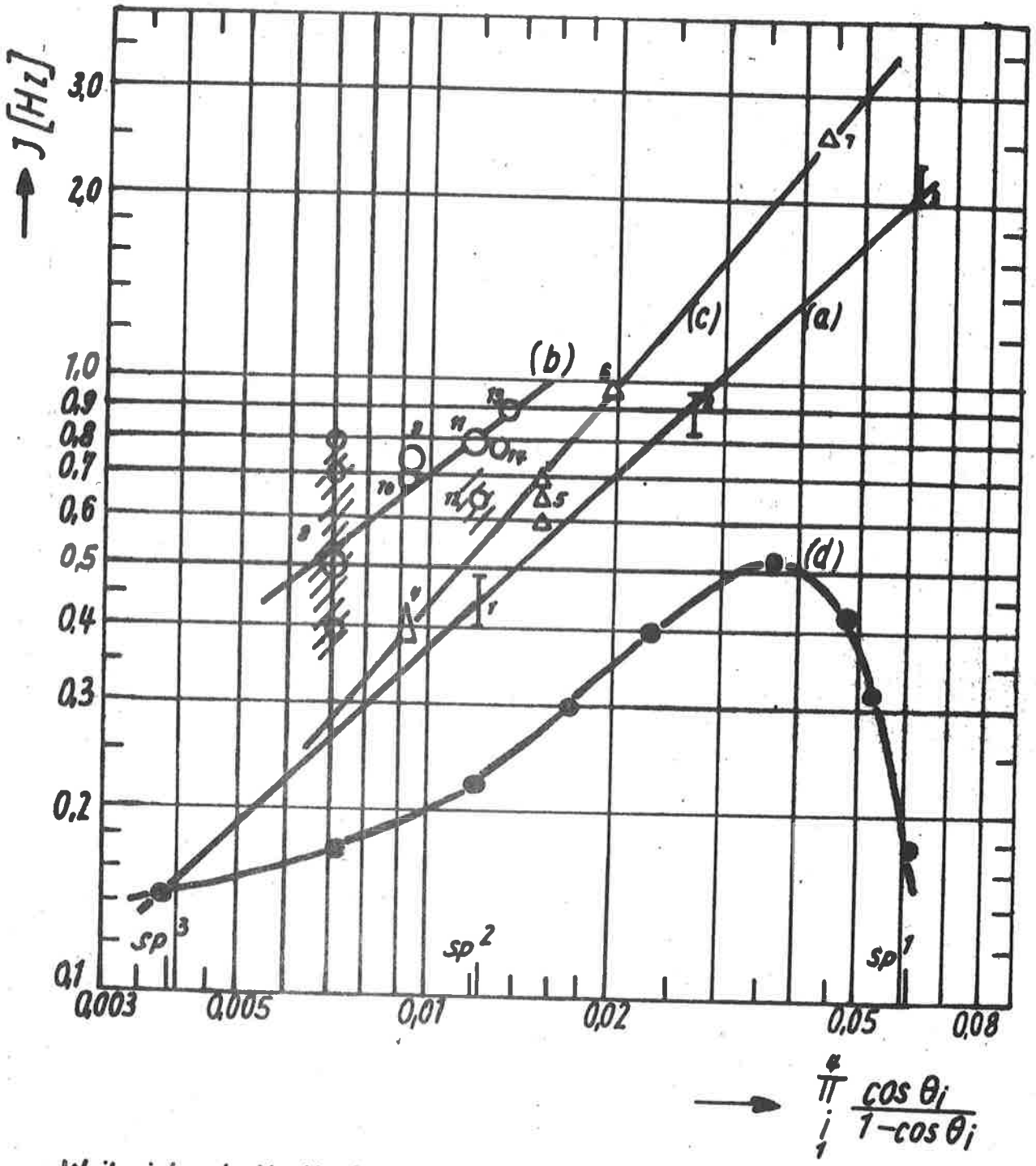
Beim Vergleich der berechneten σ-Elektronenbeiträge mit den in entsprechenden planaren Molekülstrukturen experimentell gemessenen Kopplungskonstanten hat es sich gezeigt, daß man bei den betrachteten Kopplungskonstanten drei Kopplungstypen unterscheiden muß (Kurven a, b, c der Abb.)

Aus den einzelnen Kurven lassen sich folgende Schlußfolgerungen ziehen:

1.) Über eine planare (!) zick-zack-Struktur mit sp^3-hybridisierten C-Atomen müßte sowohl nach Extrapolation der Kurve a als auch nach unseren Berechnungen eine weitreichende H-H-Kopplungskonstante von (0,15...0,20) Hz gemessen werden.

2.) Im Bereich sp^2-hybridisierter C-Atome (Θ=120°...130°, $\prod_i\left(-\frac{\cos\Theta_i}{1-\cos\Theta_i}\right)$=0,012...0,030) ist die Differenz der Kurven a und d in jedem Punkt annähernd mit dem berechneten σ -Elektronenbeitrag (Kurve d) identisch. Das heißt, daß die weitreichende trans-trans-trans-Kopplung über "rein hybridisierte" Bindungsstrukturen in diesem Bereich zur Hälfte durch die σ-Elektronen und zur Hälfte durch die π-Elektronen der betreffenden Bindungsstruktur vermittelt werden.

3.) Die weitreichende H-H-Kopplung über acetylenische Bindungsstrukturen (Θ =180°) wird ausschließlich durch die π -Eletronen der betreffenden Bindungen vermittelt. Das stimmt auch mit den Beobachtungen überein, wo über



Weitreichende H -H -Kopplungskonstanten in Abhängigkeit vom Produkt der Kohlenstoff-2s-Charaktere

a) in rein hybridisierten Molekülen
b) in aromatischen Molekülen
c) in Molekülen mit hyperkonjugierten Methylgruppen
d) berechneter σ-Elektronenbeitrag zur betrachteten Kopplung

solche Bindungsstrukturen weitreichende H-H-Kopplungskonstanten bis über 9 Bindungen beobachtet wurden /7/.

4.) Bei Kopplungen über aromatische Bindungsstrukturen (Kurve b) bewirken die delokalisierten π-Elektronen eine Vergrößerung der Kopplungskonstante um (0,25...0,40)Hz gegenüber Kurve a. Wir haben mit Hilfe der HMO-Methode und der Formel von Mc Connell /16/ einen Kopplungsbeitrag der aromatischen π-Eletronen von 0,33 Hz berechnet. Das stimmt mit den experimentell erhaltenen (0,25.... 0,40)Hz sehr gut überein.

Mit freundlichen Grüßen

H. Frischleder

(Dipl.-Phys.H.Frischleder)

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91-32

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March 31, 1966

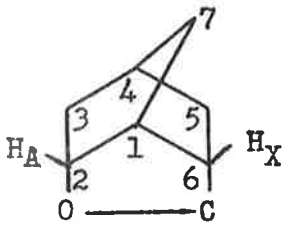
File: 000-17

Dr. Bernard L. Shapiro
Associate Professor
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry: Title: Long-Range Couplings

Some recent work on long-range coupling may be of interest to some of the readers.

Recently we(1) have observed an unusually large long-range coupling between the protons H_A and H_X for a series of bicyclo(2,2,1) and bicyclo(2,2,2) derivatives bearing a bridged oxygenated unit spanning the 2,6 positions (Table 1)



The first obvious feature about the long-range coupling phenomenon for compounds I-VI is that protons H_A and H_X conform to the "W pattern". This arrangement of the nuclei, which is apparently a prerequisite for optimal long-range coupling, could allow for overlap between the small lobes of the sp^3 orbitals at C_2 and C_6. A second factor of importance in the internuclear distance between C_2 and C_6. Compression of this distance due to the C_2-C_6 bridge would expectedly have the effect of causing more efficient overlap.

These factors are consonant with the "through space" mechanism for rationalization of the large values of $^4J_{H-H}$. However, consideration of all $^4J_{H-H}$ values reported to date seems to indicate a second mechanism which appears to be more reasonable than the through space.

Large values of $^4J_{H-H}$ have been found for the bicyclo(2,1,1)-hexane derivatives(2,3). The values for these compounds range from 6.7-8.1 c.p.s. and the interacting protons not only conform to the W pattern, but they are

also associated with a four membered ring system. Numerous values of $^4J_{H-H}$ have been reported for protons located in six membered ring systems(4). The values are, however, relatively small ranging from 0.5-2.0 c.p.s. The collective data for the four, five and six membered ring systems seems to indicate that the large values of $^4J_{H-H}$ are related to the presence of steric strain in the system which could cause appreciable π-electron density, and that the interaction may take place via a σ-π mechanism as suggested by Musher(5).

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Very truly yours,

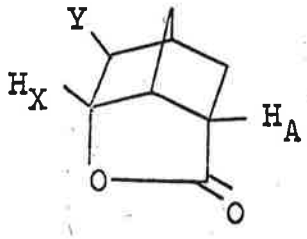
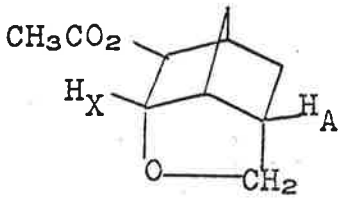
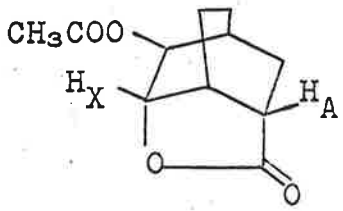
Kermit C. Ramey

Kermit C. Ramey

KCR:LH

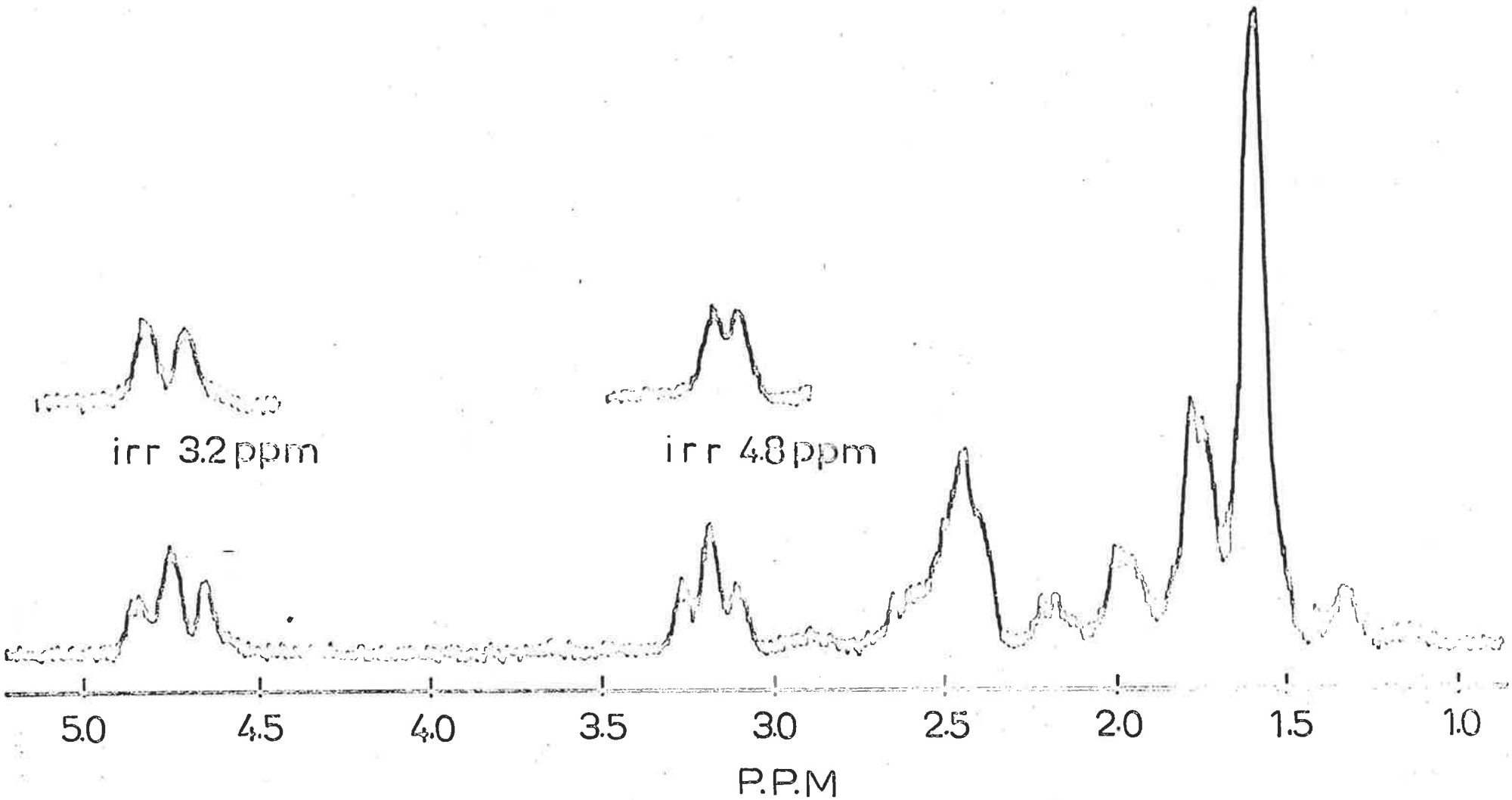
TABLE 1

Chemical Shifts and Coupling Constants for 2,6-Bridged Bicyclic Systems[a]

Compound		H_A p.p.m.	H_X p.p.m.	$J_{HA}J_{HX}$ c.p.s.
				
	Y			
I,	H	3.18	4.78	5.0
II,	I	3.20	5.10	5.0
III,	Br	3.24	4.90	5.4
IV,	$OCOCH_3$	3.20	4.52	5.0
 V		2.67	4.09	5.0
 VI		2.57	4.37	5.2

(a) Chemical shifts refer to dilute $CDCl_3$ solutions relative to TMS as internal standard

DOUBLE IRRADIATION SPECTRUM OF COMPOUND I IN CARBON TETRACHLORIDE SOLUTION AT 60 Mc./Sec.



91-36

Eidg. Technische Hochschule
Laboratorium für Organische Chemie
Zürich

8006 Zürich,
Universitätstr. 6
Tel. 051 / 32 73 30

March 8, 1966

Dr. H. Gerlach

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

Dear Professor Shapiro,

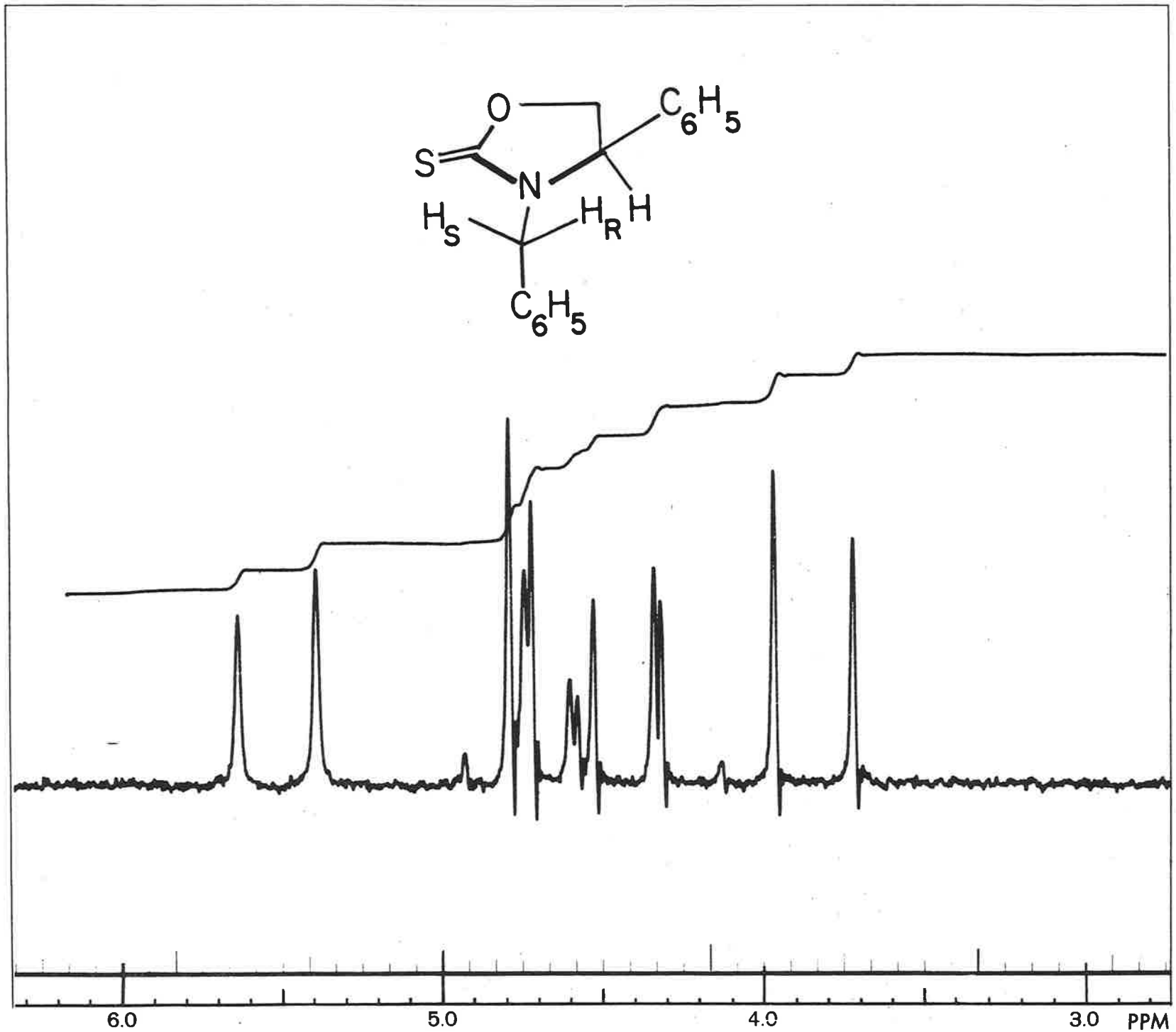
In the course of some work in progress, we were faced with the problem of distinguishing between the two geminal hydrogens of the methylene group in benzylamine. If benzylamine is converted into N-benzyl-4-phenyl-oxazolidine-2-thion the task can be solved by nmr spectroscopy. In the nmr spectrum of the latter derivative in $CDCl_3$ (cf. fig.), the doublet at δ 5,52 (J = 15) corresponds to the benzylic proton that is nearer to a strongly deshielding group, whereas the doublet of the second benzylic proton appears at δ 3,85 (J = 15). The corresponding signals in N-benzyl-4-phenyl-oxazolidone-2 appear at δ 4,78 (J = 15) and δ 3,60 (J = 15). Thus the signal assigned to the proton nearer to the strongly deshielding group is shifted appreciably more upfield ($\Delta\delta$ 0,74 ppm) when the sulfur in the thiocarbonyl compound is replaced by oxygen than is the signal assigned to the second proton.

If the reasonable assumption is made that both compounds possess in solution a similar distribution of conformations, one can conclude that the strongly deshielding group is the thiocarbonyl or the carbonyl group respectively.

With the additional assumption that the conformational equilibrium is mainly determined by the repulsion between the two bulky phenyl groups, one can draw a most probable "average conformation" (cf. formula in fig.) with the phenyl group of the benzyl residue and the phenyl group in the 4-position on opposite sides of the plane defined by the five-membered oxazolidine ring. Hence the signal at lower field corresponds to the proton H_S, which is nearer to the strongly deshielding thiocarbonyl group.

Sincerely yours

H. Gerlach



91-37

QUEEN MARY COLLEGE
(UNIVERSITY OF LONDON)
MILE END ROAD · LONDON · E.1.
Telephone: ADVANCE 4811

DEPARTMENT OF CHEMISTRY

PROFESSOR K. W. SYKES, M.A., B.Sc., D.Phil.
PROFESSOR B. C. L. WEEDON, D.Sc., Ph.D., F.R.I.C.
PROFESSOR D. C. BRADLEY, D.Sc.

30 March 1966

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
CHICAGO, Ill.
U. S. A.

Inequivalent Methylene Protons (or some are more equal than others

Dear Barry:

In the last letter from Queen Mary College we claimed the world record of 11.2 p.p.m. for inequivalent methylene protons by resorting to the paramagnetic compound $ReCl_4(PEt_2Ph)_2$. May we now claim 0.72 p.p.m. as the record for inequivalent methylene groups in a diamagnetic compound? The cases in question are $RhCl_3(PEt_2Ph)_3$, $IrCl_3(PEt_2Ph)_3$.

The spectrum is shown in the figure and is in the literature (Mol. Phys., 10, 41, 1965) as having an inequivalence of only about 0.1 p.p.m. in the methylene protons. This was based on the assignment by areas of the group centred at -2.12 p.p.m. to the CH_2' protons and the group at -2.92 p.p.m. to the CH_2 protons. While doing some comparisons of the Varian and Jeol 100 Mc/s spectrometers, we decided to use their homonuclear decoupling facilities to check this assignment. Irradiation of the peak at -2.92 p.p.m. affected not only the CH_3 proton resonance as expected but also the group at -2.12 p.p.m. (no matter which instrument was used!). Further examination indicated that the low field peak was 'half' the CH_2 resonance and the higher field peak was the other 'half' of CH_2 plus CH_2'. This assignment also leads to the area ratio being 2:1, but was not considered before because of the high degree of inequivalence inferred.

This inequivalence apparently due to the lack of symmetry around the P atoms extends in the paramagnetic case of $Re[P(CH_2CH_2CH_3)_2Ph]_3Cl_3$ to the β CH_2 protons. The shift difference is 0.7 p.p.m. Each is shifted approximately 5 p.p.m. downfield relative to the diamagnetic analogue.

Dr. Sales' calculations (à la La Mar) on pseudo contact shifts indicate that the large methylene inequivalence can be accounted for this way. However the shifts relative to diamagnetics require an additional mechanism which for alkyl groups could be rationalised as a σ propagated (isotropic) contact shift.

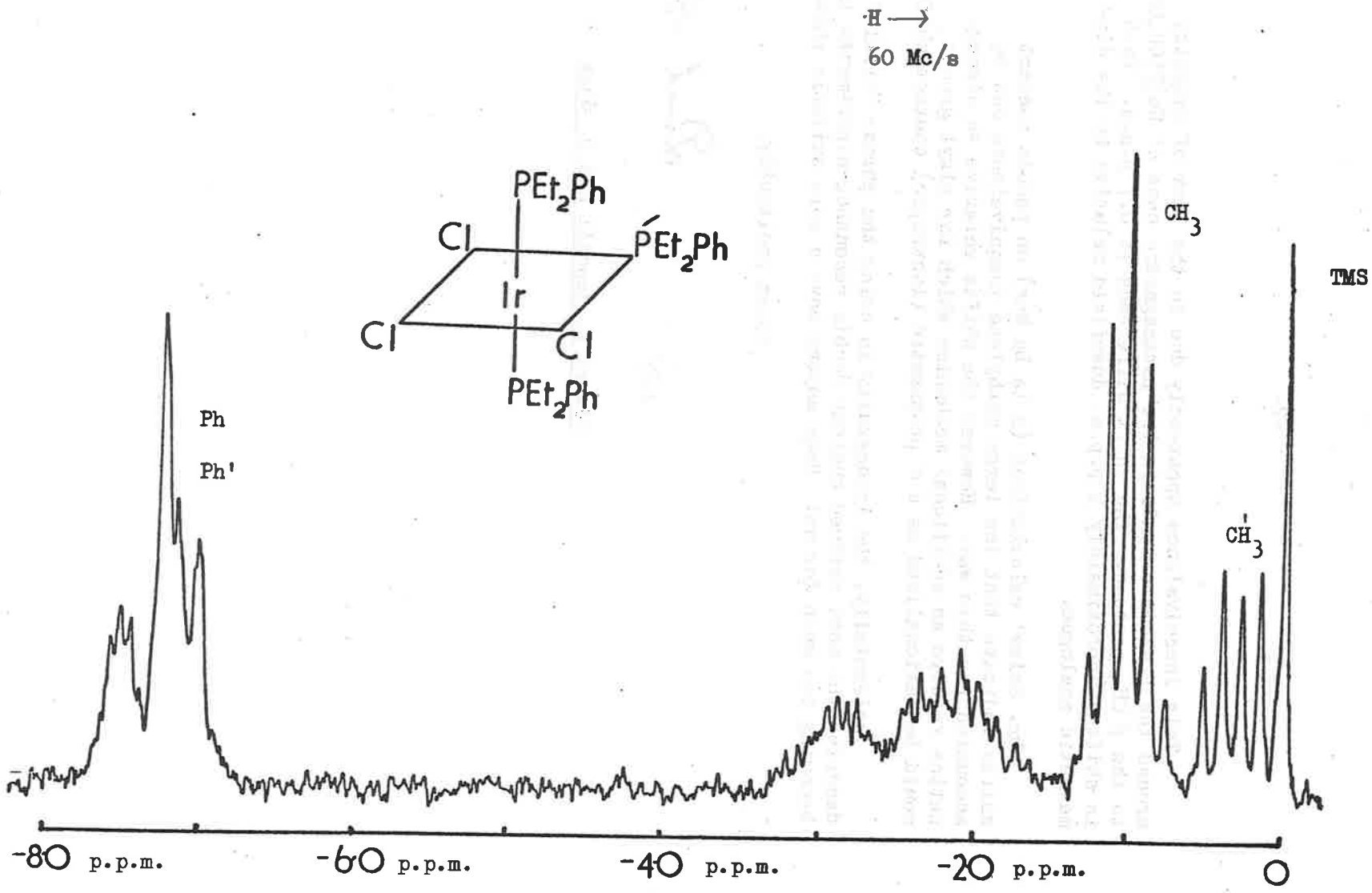
Incidentally, the incongruity in using the phrase "tickle" to describe the most refined nuclear double resonance experiments is becoming too much for us! Does anyone have a more suitable phrase?

Yours penitently,

Dick Shaw

Ed

Edward W. Randall and D. Shaw


H ⟶
60 Mc/s
PEt2Ph
Cl
PEt2Ph
Ir
Cl
Cl
PEt2Ph
Ph
Ph'
CH3
CH'3
TMS
-80 p.p.m.
-60 p.p.m.
-40 p.p.m.
-20 p.p.m.
0

COMUNITA EUROPEA
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La Commissione
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EUROPÄISCHE
ATOMGEMEINSCHAFT
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EUROPESE GEMEENSCHAP
VOOR ATOOMENERGIE
De Commissie
GEMEENSCHAPPELIJK CENTRUM
VOOR ONDERZOEK

Magnetic Resonance

Ispra, 1 April 1966
HS/mg

Prof. Dr. Bernard L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago/Illinois

Title: Orientation of $H^{13}CN$ in nematic phases

Dear Professor Shapiro:

Some time ago I succeeded to get spectra of oriented $H^{13}CN$ in p-capronyloxy-p'-ethoxy-azobenzene. The splitting at 63°C with a concentration of approx. 10 mole % $H^{13}CN$ is 1112 cps. With J_{CH} 270 cps in $H^{13}CN$ and positive the degree of order S_ξ of the longitudinal axes is: (see Englert, Saupe, Z. f. Naturf. 19a, 172 (1964)

$$S_\xi = \frac{B_{1,2} \cdot r^3}{60} = 0.017$$

$B_{1,2}$ = 1112 - 270 = 0,842 kcps = direct dipolar coupling constant. r_{HC} = 1.0646 Å

Surprisingly enough an experiment with p-capronyloxy-p'-ethoxy-azoxybenzene yielded a splitting of 116 cps (S_ξ = -0.003) only. With a positive sign for the indirect coupling constant J_{CH} this can only be explained with a negative sign for the direct coupling constant B which would amount to a perpendicu-

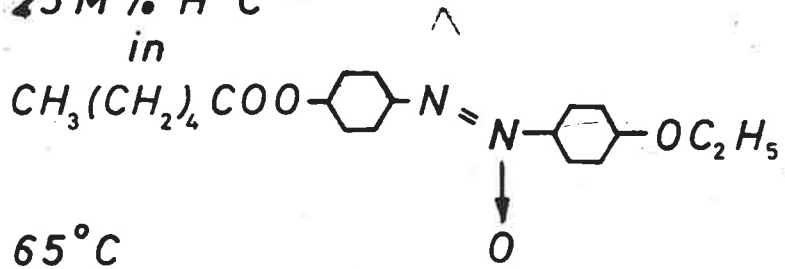
lar orientation of $H^{13}CN$ with respect to the longitudinal axes of the nematic host substance. A reduction of J_{CH} in the azoxy derivative due to beginning proton exchange is unlikely since in the isotropic phase at 150°C the normal splitting of 270 cps was determined. Besides there does not seem to be a dipolar association in the nematic phases as in liquid HCN since the spectrum is typical for an isolated two spin system.

Yours sincerely,

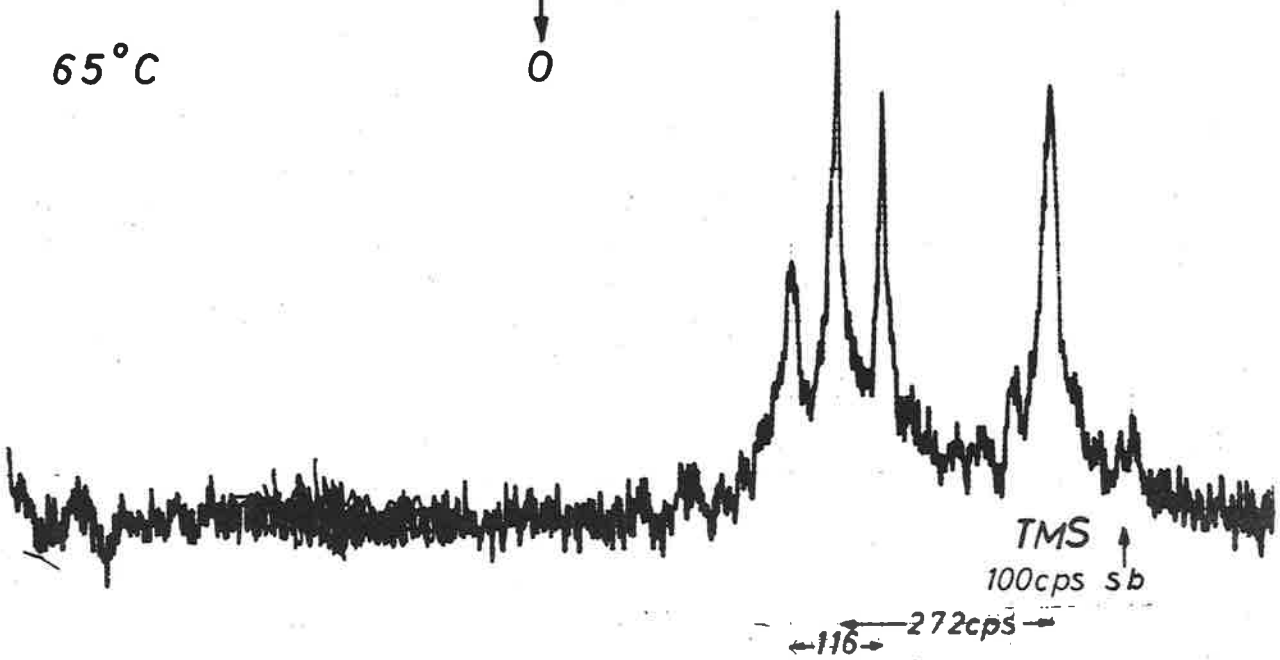
H. Spiesecke

25 M% $H^{13}CN$

in

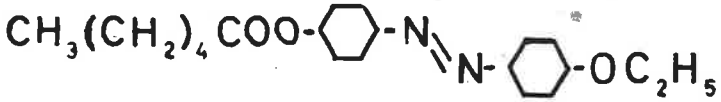


65°C

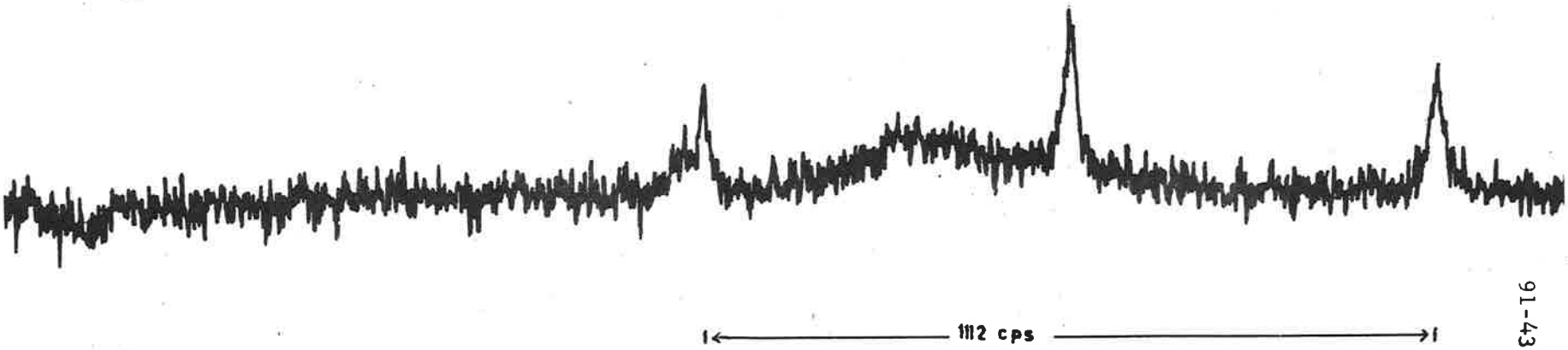


10 M% $H^{13}CN$

in



63°C



91-44

Institut für physikalische Chemie
der Rhein.-Westf.Techn.Hochschule
Aachen, Direktor Prof.Dr.U.Franck

51 Aachen, den 4.3.1966
Klosterbongard 12
Fernruf 422 2154

Mr.
Dr. Bernard L. S h a p i r o
Illinois Institute of Technology

C H I C A G O , 60616, U S A

Sehr geehrter Dr. S h a p i r o !

Zur Bestimmung des Diffusionskoeffizienten D_s mit Hilfe der Spin-Echo-Technik wird ein über die gesamte Probe linearer Feldgradient benötigt. Im Gegensatz zu bekannten Meßmethoden benutzen wir einen impulsförmigen Feldgradienten. Diese Maßnahme hat den Vorteil, daß sich die Probe im Zeitintervall von $t = -\infty$ bis $t = 0$ im thermischen Gleichgewicht befindet, und dieses Gleichgewicht nicht durch den vorhandenen Feldgradienten gestört ist (siehe Zitat 1). Dabei befindet sich die Probe im homogensten Teil des konstanten Magnetfeldes H_o, so daß die Inhomogenität des konstanten Magnetfeldes H_o praktisch zu vernachlässigen ist. Gleichzeitig mit dem hochfrequenten Impuls wird der Feldgradient dem homogenen Feld überlagert.

Zur Erzeugung des Gradientenimpulses wird die in Abb. 1 wiedergegebene Schaltung verwendet. Zur Gradientenspule ist ein Ohmscher Widerstand in Serie geschaltet. Hiermit wird die Anstiegsdauer des Gradientenimpulses auf den kleinsten Wert eingestellt. Die Anstiegs- und Abfallzeit (bis auf 90 %) des Gradientenimpulses ist bei der hier wiedergegebenen Schaltung 30 μs.

In der Abb. 2 sind die Diffusionskoeffizienten wiedergegeben, die von uns mit konstanten und mit impulsförmigen linearen Feldgradienten erhalten wurden. Diese Meßergebnisse sind mit den Werten von SIMPSON und CARR (2) und mit Ergebnissen verglichen, die mit Hilfe der Tracermethode (3) bestimmt wurden.

(1) Stejskal E.O., J.E. Tanner, J. Chem. Phys. 42, 288, (1965).
J. Sci.Instr. 36, 1086, (1965).

(2) Simpson J.H., H.Y. Carr, Phys. Rev. 111, 1201, (1958).

(3) Wang J.H., C.V. Robinson, J.S. Edelman, J. Am. Chem. Soc. 75, 466, (1953).

Mit besten Grüßen

Dr. Kosfeld L. Oehlmann

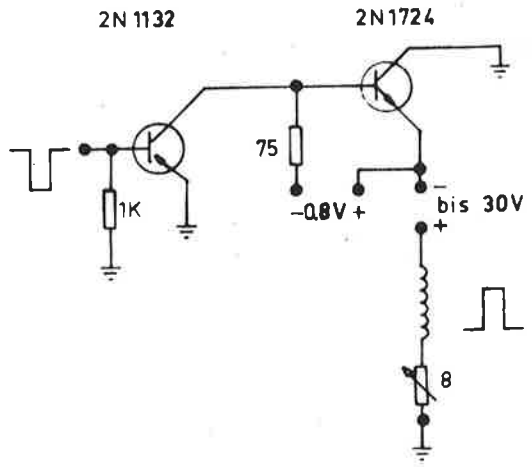


Abb. 1 Schaltskizze zur Erzeugung eines impulsförmigen Feldgradienten.

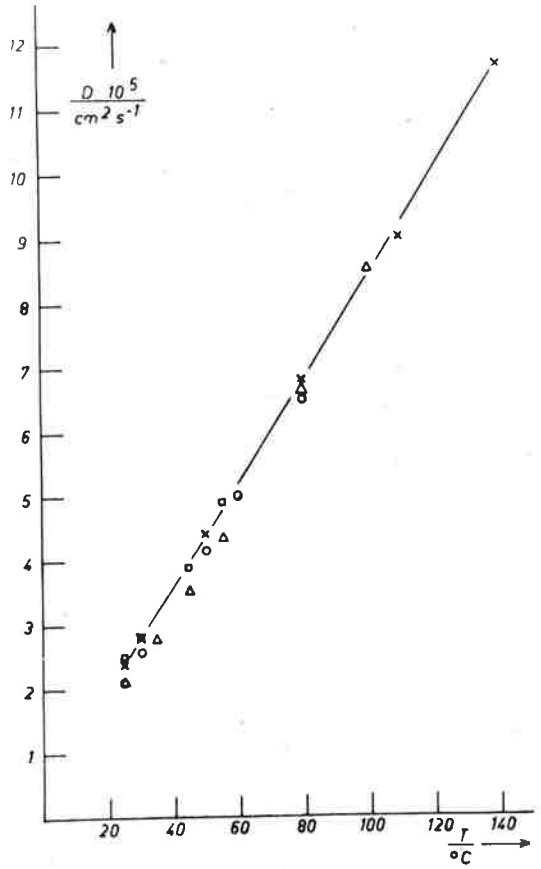


Abb. 2 Selbstdiffusionskoeffizient von Wasser in Abhängigkeit von der Temperatur.
X Eigene Messung mit impulsförmigen Feldgradienten.
O Eigene Messung mit konstanten linearen Feldgradienten.
Δ Werte nach SIMPSON, CARR (2).
□ Werte nach WANG, ROBINSON, Edelman (3).

91-46

UNION CARBIDE

UNION CARBIDE CORPORATION

P. O. BOX 278, TARRYTOWN, N. Y.

UNION CARBIDE
RESEARCH INSTITUTE

April 12, 1966

Professor B. L. Shapiro
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

We received a C-1024 a few months ago, and have so far been more interested in its potential as an analog to digital convertor than in its performance in signal enhancement, although the latter has been useful on occasions. One trick we have tried is to selectively cancel spectra of components in mixtures. If, for example, we have two fractions containing amounts X_1 and X_2 of a component, A, then we might enter the first fraction X_2 times and the second X_1 times in reverse polarity, thereby cancelling the spectrum of A. This is of course inefficient in practice, so we in fact utilize different gain settings, and look to the day when the scaling is done entirely in a computer. It may also be necessary to use fairly dilute solutions to minimize solute-solute interactions, whereupon cancellation of signal aggravates signal to noise problems. These effects are often smallest in mixtures most difficult to separate, however, so that the situation doesn't appear altogether hopeless. As an example, I've attached (top and bottom) spectra of two mixtures of erythro and threo isomers of 1, 2, 3-trichlorobutane, and between them one combination designed to subtract out one of the components.

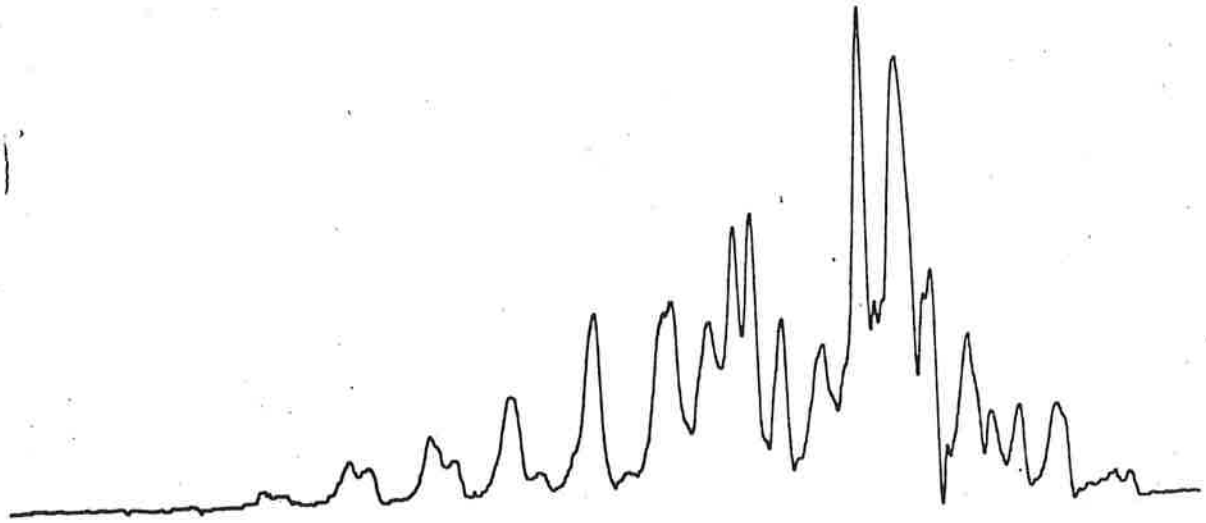
I hope this gets me reinstated on your mailing list.

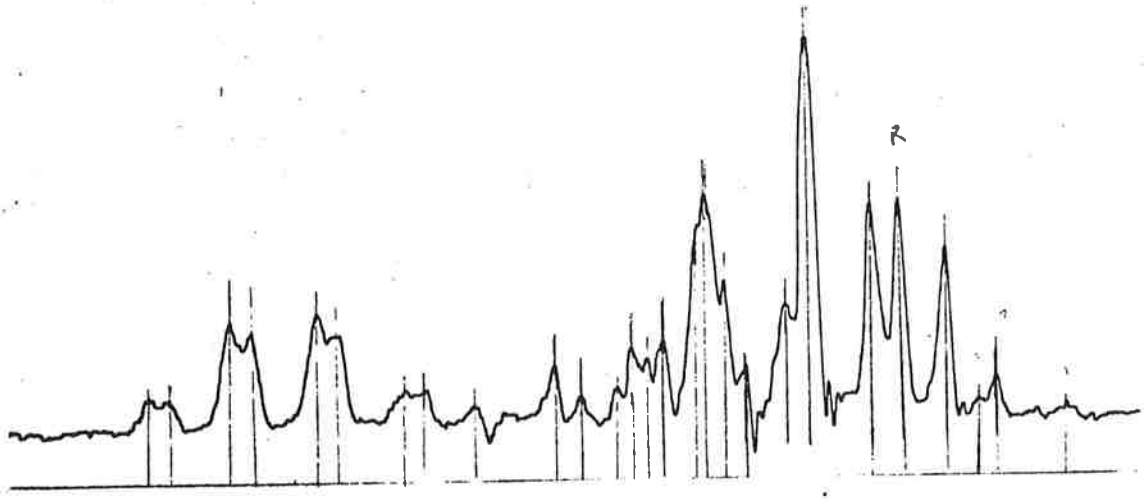
Sincerely yours,

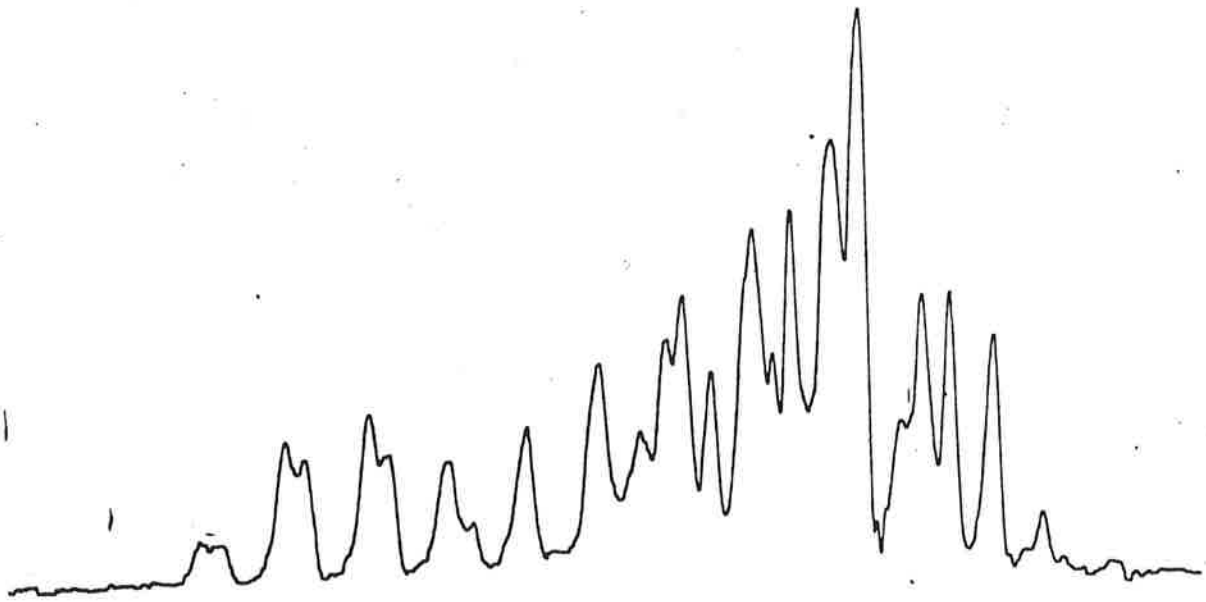
E. B. Whipple

EBW:nt
Encl.

Selective Cancellation in the C-1024







91-48

Max-Planck-Institut für Biochemie
Dr. J.Sonnenbichler

München 15, den 18. 3. 66
Goethestraße 31
Fernruf 59 42 61/63
Postschließfach 64

Herrn
Dr.Bernard L.Shapiro
Illinois Institute of Technology
Chicago, 60616

Lieber Herr Dr. Shapiro!

Als kleiner Beitrag zu den IITNMR-Letters möchte ich heute auf die Probleme der Biochemiker zu sprechen kommen:

Messungen mit kleinsten Substanzmengen.

An unserem Institut wird viel an der Strukturaufklärung organischer Naturstoffe gearbeitet. Dabei stehen wir häufig vor dem Problem, mit unserem A-60 Messungen mit 1 - 2 µMol (200 - 500 γ) durchzuführen. Selbstverständlich verwenden wir nur Mikro-sample-tubes. Jetzt haben wir den alten 3-turn insert unseres A-60 gegen den neuen 6-turn insert der neueren Geräte ausgetauscht ohne die Shimspulen auszuwechseln. Unsere sensitivity für den 1%-Äthylbenzolstandard hat sich dadurch von 7:1 auf 15:1 verbessert. Wir können diesen Austausch allen Besitzern eines alten A-60 wärmstens empfehlen.

Zusammen mit dem TAD konnten wir in den vergangenen Tagen mit 300 γ Substanz eines seltenen Nukleosids aus S-RNA gute Spektren aufnehmen und die Konstitution beweisen.

Wir sind für alle Tips dankbar, die eine weitere Verbesserung der sensitivity bringen. Von den Firmen wird ja im allgemeinen mehr Wert auf die Verbesserung der Auflösung als auf eine Erhöhung der Empfindlichkeit gelegt.

Mit freundlichen Grüßen

Ihr

Johann Sonnenbichler

Institut für Elektrowerkstoffe

GEMEINNÜTZIGES FORSCHUNGSINSTITUT DER FRAUNHOFER-GESELLSCHAFT

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

Prof. B.L. Shapiro
Illinois Institute
of Technology

Chicago, Illinois 60616
USA

TELEFON 0761 45514

78 FREIBURG I. BR.
ECKERSTRASSE 4

Ihre Zeichen | Ihre Nachricht vom | Unser Zeichen

April 6, 1966

H^1 - and F^{19}-Spectra of 1,3,5-Trifluorobenzene Dissolved in a Nematic Liquid Crystal

Dear Professor Shapiro:

Recently we investigated the proton and the fluorine NMR spectra of 1,3,5-trifluorobenzene oriented in a nematic solution of 4,4'-di-n-hexyloxy-azoxy-benzene. From the analysis of the spectra taken at 60 and 56.4 Mcps we obtained the following results:

1. 1,3,5-trifluorobenzene in a nematic solution is more oriented than benzene and less than hexafluorobenzene. Characteristic values of the degrees of order S for the different substances are: benzene S = -0.10, 1,3,5-trifluorobenzene S = -0.15, hexafluorobenzene S = -0.26 ($S = 1/2 \langle 3\cos^2\theta - 1\rangle_{AV}$, where θ is the angle between the magnetic field and the molecular symmetry axis normal to the molecular plane).

2. The scalar coupling constants J_{HH}^{meta}, J_{FF}^{meta} and J_{HF}^{ortho} are positive, J_{HF}^{para} is negative. The values and the relative signs of the constants have recently been published by Jones, Hirst and Bernstein[1]. Interesting is the comparison with hexafluorobenzene[2], where J_{FF}^{meta} has about the same absolute value, but a negative sign.

3. Comparing the ratios of the measured coupling constants for the anisotropic part of the total (direct + indirect) spin-spin-interaction with those calculated for the direct spin-spin-interaction, we conclude that there exist noticable contributions of the indirect spin-spin-interaction to the anisotropic FF(meta), HF(ortho) and HF(para) couplings. Such Anisotropic contributions

to FF couplings have already been reported by Snyder and Anderson[2] for hexafluorobenzene. (Their results for C_6F_6, including the sign of J_{FF}^{meta} mentioned above could be confirmed by us.)

4. The anisotropies of the proton and fluorine chemical shift turned out to be

$$\Delta\sigma_H = (-2.50 \pm 0.20).10^{-6}$$
$$\Delta\sigma_F = (+99 \pm 5).10^{-6}$$

(with $\Delta\sigma = \sigma_{zz} - 1/2(\sigma_{xx} + \sigma_{yy})$, z-axis perpendicular to the molecular plane, y-axis parallel to the CF bond). The shift anisotropy of the protons in 1,3,5-trifluorobenzene is nearly the same as in benzene[3] $(-2.9 \pm 0.2) \cdot 10^{-6}$. In contrast, $\Delta\sigma_F$ differs strongly from the value obtained for hexafluorobenzene[2] $(+154 \cdot 10^{-6})$.

Combining our value of $\Delta\sigma_F$ with the shielding anisotropy of monofluorobenzene given by Snyder[4] we obtain the following relations for the shielding tensor components of a fluorine nucleus of monofluorobenzene or 1,3,5-trifluorobenzene

$$\sigma_{xx} - \sigma_{zz} = -157 \cdot 10^{-6}$$
$$\sigma_{yy} - \sigma_{zz} = -41 \cdot 10^{-6}$$

This procedure seems to be justified, since there is no great difference between the scalar shielding constants of CH_3F_3 and CH_5F.

The observed differences of the shielding tensor components can be explained by the theory of Karplus and Das[5] with reasonable values for the degree of ionisation and of the double bond character of the CF bond. For a further study of the CF bond we intend to investigate some other fluorobenzenes oriented in nematic solutions.

At the end of this contribution to ITTNN we should like to mention a problem we have with our F^{19}-measurements. For a more exact determination of $\Delta\sigma_F$ we need an internal F^{19}-standard which should have as high a symmetry as TMS, and which gives only one line in the nematic and the isotropic solution. We have tried to get $Si(CF_3)_4$ or $C(CF_3)_4$, or at least to find a prescription to make them ourselves, but without succes. Perhaps readers of ITTNN can give

us advice?

Up to now we determined $\Delta\sigma_F$ by measuring the shift of the nematic spectrum against the isotropic spectrum. We applied the following simple method using the sidebands of a 2000 cps modulation: After recording the main signal of the nematic phase we heated the sample so that the following sideband belonged to the isotropic phase. The main signal position ν in the isotropic phase then is $\nu = \nu_{sideband} - 2000$.

We are indebted to Professor G.C.Finger, Urbana, Illinois for giving us 1,3,5-trifluorobenzene.

Sincerely yours,

J. Nehring A Saupe

(J. Nehring) (A. Saupe)

1) R.G.Jones, R.C.Hirst, H.J.Bernstein, Can. J. Chem. 43, 683 (1965)
2) L.C.Snyder, E.W.Anderson, J. Chem. Phys. 42, 3336 (1965)
3) A.Saupe, Z. Naturf. 20a, 572 (1965)
4) L.C.Snyder, J. Chem. Phys. 43, 4041 (1965)
5) M.Karplus, T.P.Das, J. Chem. Phys. 34, 1683 (1961)

91-52

UNIVERSITY OF HOUSTON
CULLEN BOULEVARD
HOUSTON, TEXAS 77004

CHEMISTRY DEPARTMENT

April 7, 1966

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60611

Dear Barry:

ANOTHER EXAMPLE OF LINE BROADENING CAUSED BY OXYGEN

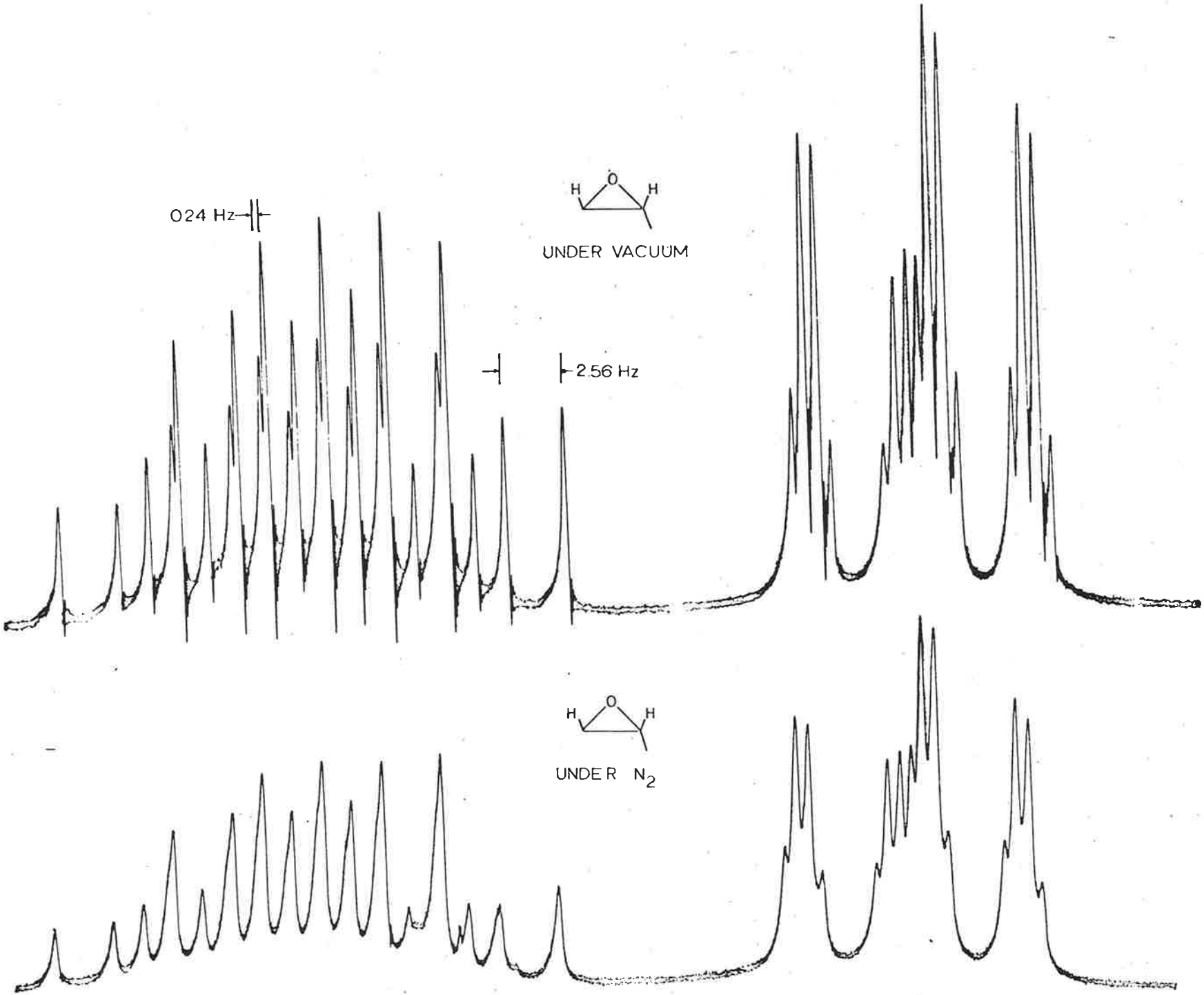
Since we are just learning to operate our HA-100 we thought we would like to share one of our experiences with readers of the Newsletter. Ray Ettinger of Varian Associates suggested propylene oxide to us as a good compound for checking spectrometer performance. In particular, the proton adjacent to the methyl group provides a forest of closely spaced lines that demands a good field-frequency stabilization unit to obtain a resolved spectrum. While Ray Ettinger was visiting with us we prepared a propylene oxide sample by bubbling nitrogen through a neat sample containing benzene, and sealed the sample tube with a plastic pressure cap. On the day of sample preparation we obtained a reasonable spectrum, but the quality depreciated rapidly until on the third day we obtained the enclosed spectrum of two of the protons labeled "Under N_2". We then decided to use a vacuum degassed sample and found immediately the resolution, stability, and signal/noise improved as demonstrated by the other spectrum labeled "Under Vacuum". It is obvious that some oxygen diffused through the cap, and that this oxygen is a trouble-maker. Needless to say we have routinely used vacuum sealed samples for any work other than casual examination of reaction mixtures. Even though the effect of oxygen broadening is well-known, we had to be reconvinced and we therefore would suggest to Newsletter readers that they be exceedingly particular about excluding oxygen in samples of critical interest.

Sincerely yours,

Bob — Billy J. Fairless

M.R. Willcott — Billy J. Fairless

Enclosure


0.24 Hz
2.56 Hz
UNDER VACUUM
UNDER N_2

FUNDAMENTAL PRINCIPLES OF

n.m.r. SPECTROSCOPY

SPONSORED BY: The UCR Department of Chemistry and University of California Extension, Riverside

WHEN: Wed.-Fri., June 8-10, 1966

WHERE: Chemistry Building, University of California, Riverside

Purpose and for whom intended: An intensive short course designed to introduce the participants to the basic theoretical and practical fundamentals of N.M.R. spectroscopy. It is aimed primarily to instruct personnel from industry, although it may be equally valuable to persons in academic and government laboratories. The material will be of interest not only to those directly involved in the use of N.M.R. spectrometers, but also supervisory personnel interested in the potential usefulness of N.M.R. spectroscopy.

COURSE DESCRIPTION: The course will be conducted at a basic rather than advanced level and will be composed of a series of lectures and laboratory sessions. In the laboratory sessions, each participant will learn the fundamentals of operation of a basic N.M.R. spectrometer and be given demonstrations of specialized auxiliary equipment and advanced spectrometers. Open laboratory sessions on Thursday evening and Friday afternoon will allow participants to further familiarize themselves with the instrumentation of N.M.R.

CREDIT: This course is set up as a one unit course under the title "Chemistry X 400." For those desiring credit a final examination will be given at the end of the course. All participants who complete the course, whether or not they take the final examination, will be given a "certificate of completion."

LECTURES AND LABORATORIES

FIRST DAY, Wednesday, June 8

9:00- 9:30	Introductions
9:30-10:30	An Introduction to and the Basic Principles of N.M.R. *Professor John Baldeschwieler, Stanford University*
10:45-12:00	Basic Instrumentation *Mr. Roy Ettinger, Varian Associates, Palo Alto*
2:00- 2:30	Laboratory Lecture *Mr. Roy Ettinger, Varian Associates, Palo Alto*
2:30- 5:00	Operation of A-60 (Laboratory)
6:30	Dinner (Speaker)

SECOND DAY, Thursday, June 9

9:30-10:30	Chemical Shift *Professor John D. Roberts, California Institute of Technology*
11:00-12:00	Spin-Spin Splitting *Dr. Stanley Manatt, Jet Propulsion Laboratory, California Institute of Technology*
1:30- 2:30	Applications of N.M.R. to Structure Determination *Professor Marjorie Caserio, University of California, Irvine*
2:30- 5:00	Demonstration Laboratory Sessions*
Evening	Special Lecture and Open Laboratories

*Demonstration laboratories will include Variable Temperature Operation, CAT, Spin-decoupling, Introduction to HA-100, Spectral Interpretation, and HA-100 Demonstrations

THIRD DAY, Friday, June 10

9:00- 9:45	Boron-11 N.M.R. *Professor M. F. Hawthorne, University of California, Riverside*
9:45-10:30	Fluorine-19 N.M.R. *Professor Robert Taft, University of California, Irvine*
10:45-12:00	Kinetics of Fast Processes *Professor Frank Anet, University of California, Los Angeles*
1:30- 5:00	Open Laboratories
4:00- 4:45	Final Examination (Optional)

ENROLLMENT: To insure full opportunity for individual participation, the total number of students accepted will be limited. Enrollments will be accepted in the order in which they are received. Enrollments may be made by individuals or organizations. Any number of persons from a single organization may enroll as long as there are vacancies.

FEES: $125.00 (includes banquet). No refunds will be granted after the opening of the program. Housing: To assist participants in securing their own accommodations, a list of housing facilities located near the campus will be sent immediately to each registered applicant for the course.

LOCATION: The University of California, Riverside, is located in the City of Riverside approximately 60 miles east of Los Angeles, and may be reached by two major freeways. Bonanza Airlines services Riverside from Los Angeles International Airport and Phoenix, Arizona. Frequent helicopter service (Los Angeles Airways) is available between L.A. International and Riverside. Adequate parking is available on campus.

INFORMATION: For information please write, phone or wire Roy Dull, University Extension, University of California, Riverside, California. Phone (Area Code 714) 787-5741. Co-ordinator: Professor Robert C. Neuman, Jr., Department of Chemistry, UCR.

ENROLLMENT FORM

Fundamental Principles of N.M.R. Spectroscopy — Chemistry X 400

Mail to: University of California Extension, University of California, Riverside, California 92502.

Enclose: Check made payable to The Regents of the University of California in the amount of $125.

Name _____ Social Security No. _____

Position _____

Mailing Address _____

Telephone _____

Home Address _____

Organization _____

PROGRESS IN CHEMICAL APPLICATIONS OF n.m.r.

SPONSORED BY: The UCR Department of Chemistry and University of California Extension, Riverside

WHEN: June 6 & 7, 1966

WHERE: Chemistry Building, UCR

PROGRAM: The UCR Department of Chemistry, in cooperation with UC Extension, Riverside, is pleased to present a distinguished group of chemists who will discuss recent developments in their research involving chemical applications of N.M.R. spectroscopy.

This conference is intended to appeal to chemists actively engaged in N.M.R. research.

CONFERENCE PROGRAM

FIRST DAY, Monday, June 6

8:30 a.m.—Registration—Chemistry Building

9:30 a.m.—Opening Remarks

9:45 a.m.—Welcome

10:00 a.m.—Applications of N.M.R. to Studies of Conformation and Conformational Changes
Professor Frank Anet,
University of California, Los Angeles

1:30 p.m.—Applications of Spin-Decoupling to Spectral Analysis
Dr. Stanley Manatt,
Jet Propulsion Laboratory,
California Institute of Technology

3:00 p.m.—Carbon-13 Magnetic Resonance and Molecular Structure
Professor David M. Grant,
University of Utah

6:00 p.m.—Banquet

SECOND DAY, Tuesday, June 7

10:00 a.m.—Halide Ions as Chemical Probes for N.M.R. Studies of Protein
Professor John D. Baldeschwieler,
Stanford University

1:30 p.m.—*para*-Fluorophenyl N.M.R. Shielding as a Prognosticator of Acid-Base Interactions
Professor Robert Taft,
University of California, Irvine

3:00 p.m.—Some Miscellaneous N.M.R. Problems
Professor John D. Roberts,
California Institute of Technology

REGISTRATION AND FEE: The registration fee of $20.00 includes the banquet on Monday evening. In order to achieve maximum interaction between speakers and participants, attendance may be restricted. (No refunds will be granted after the opening of the program.)

HOUSING: To assist participants in securing their own accommodations, a list of motels and hotels located near the campus will be sent immediately to each person who registers or requests this list.

LOCATION: The University of California, Riverside, is located in the City of Riverside approximately 60 miles east of Los Angeles, and may be reached by two major freeways. Bonanza Airlines services Riverside from Los Angeles International Airport and Phoenix, Arizona. Frequent helicopter service (Los Angeles Airdays) is available between L.A. International and Riverside. Adequate parking is available on campus.

INFORMATION: For information please write, phone or wire: Roy Dull, University Extension, University of California, Riverside, California. Phone (Area Code 714) 787-5741. Co-ordinator: Professor Robert C. Neuman, Jr., Department of Chemistry, UCR.

ENROLLMENT FORM

Progress in Chemical Applications of N.M.R.
Mail to: University of California Extension, University of California, Riverside, California 92502.

Enclose: Check made payable to The Regents of the University of California in the amount of $20 (includes banquet.)

Name _____ Social Security No. _____

Position _____

Mailing Address _____

Telephone _____

Home Address _____

91-55

91-56

UNIVERSITÉ D'OTTAWA
FACULTÉ DES SCIENCES PURES ET APPLIQUÉES

UNIVERSITY OF OTTAWA
FACULTY OF PURE AND APPLIED SCIENCE

OTTAWA 2, CANADA

DÉPARTEMENT DE CHIMIE
365, RUE NICHOLAS

DEPARTMENT OF CHEMISTRY
365 NICHOLAS ST.

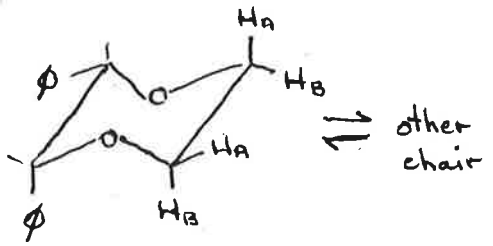
April 15th, 1966

Title: Stereochemistry of Dioxanes and Abortive attempts at Differentiation of Enantiomers.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago 60616, Ill. U.S.A.

Dear Barry,

We have been continuing to analyse the A_2B_2 spectra of some additional 2, 3-disubstituted dioxanes. The spectrum of 2, 3-diphenyl-1, 4-dioxane, m.p. 132° gave the following parameters. The equality of J_A and J_B

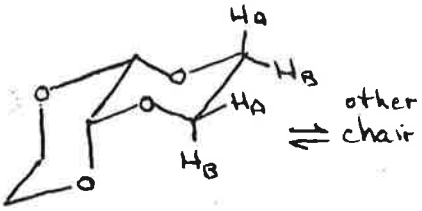


$J_A = J_B = 2.8$ cps.
$J_{Gem} = -11.7$
$J'_{AB} = 6.4$
$\delta_{benzene} = 32.7$

require the compound to have the cis configuration, and to (see Can. J. Chem., 43, 3445 (1965) for the complete argument as applied to cis dichlorodioxane) be undergoing rapid chair-chair interconversions. This conclusion like that for the dichloro derivative corroborates the original assignment and negates the conclusions of Caspi and Lefevre. Perhaps more surprising was the result obtained from the analysis of naphtho-dioxane. This compound, m.p. 134-136 was assigned the trans stereochemistry on the basis of X-ray analysis (Hassel, Acta. Chem. Scand., 10, 136 1956). Yet we obtained the following result from the

... 2

A_2B_2 analysis.



$$J_A = J_B = 2.9$$
$$J_{Gem} = -11.7$$
$$J'_{AB} = 6.4$$
$$\delta = 13.6$$

Again the compound must be cis and interconverting!! To check our assignments we ran the spectrum at 100 mc. (courtesy of Varian's Leroy Johnson) and the above parameters gave a calculated spectrum in good agreement (<0.3 c.p.s.) with the observed. We have just learned from Dr. Altona at Leiden that he analysed the same compounds and obtained results in good agreement with ours. He has submitted a paper for publication in Tetrahedron. We therefore plan to proceed directly to the analysis of two new dioxanes which were synthesized by Dr. Belleau of our department. I don't believe anyone can scoop us on these.

I read with interest the report by Pirkle on the observance of two signals for racemic trifluoromethylphenylcarbinol in optically active α-phenethylamine. I might as well report our lack of success in this area. We synthesized an appreciable quantity of optically active p-tolylethyl sulfoxide but have not been able to differentiate enantiomeric alcohols in this solvent. We had hoped that enantiomers might exhibit different values of $J_{\substack{C-O \\ | \quad | \\ H-H}}$ but in all cases the OH signal of our alcohols was a broad singlet in spite of our lacking precautions to ensure dry solvent and solute.

Yours sincerely,

Robert R. Fraser.

RRF/cg

91-58

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

April 6, 1966

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

Current NMR Studies at Purdue

Dear Barry:

For the benefit of readers of the NMR Newsletter, here is a brief report of some work which should be reaching the preprint stage within the next several months.

1. Dick Hughes has reinvestigated the dilution shifts of benzoic acid in benzene, using extreme care to eliminate water and analyzing the data by the method of Davis and Pitzer. He finds that the OH shift of benzoic acid monomers is about 1 ppm upfield from benzene at room temperature, and it seems to move to higher fields as the temperature is raised. The OH shift for the dimers also moves upfield at higher temperatures, starting at about -6.8 ppm from benzene at 30°C.

2. Paul Simon has been looking at the hydrogen-bond shifts in the three component system CCl_4-dioxane-water, at very low water concentrations where H_2O dimers and polymers are absent. Neither the H_2O monomer nor the H_2O-dioxane complexes appear to have temperature independent chemical shifts, but we hope to be able to unravel the data and obtain some ΔH and K values.

3. As reported at the recent Pittsburgh ACS meeting, Ron Birkhahn has made several fluorine-labelled soaps of the type $CF_3(CH_2)_nCOONa$. Because of the relatively enormous solvent-sensitivity of F^{19} shifts, these solutions show drastic spectral changes when the solute ions aggregate to form micelles, and we are very excited about the possibilities of using this method to obtain additional insight into the physical chemistry of detergent solutions.

With best regards.

Sincerely,

Norbert Muller
Associate Professor

ml

1816–1966

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

Pittsburgh
Coal Research Center

April 15, 1966

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

Dear Dr. Shapiro:

C^{13} NMR of Diene-Iron Tricarbonyl Complexes

H. S. Gutowsky, E. N. Frankel, and I have completed a study of the C^{13} NMR spectra of butadiene-iron tricarbonyl and methyl octadecadienoate-iron tricarbonyl to aid in the elucidation of the structures of these complexes. The C^{13}-H coupling constants indicate that all of the C-H bonds in the butadiene complex are essentially sp^2 hybrids. This observation, the C^{13} and H^1 chemical shifts, the H-H coupling constants, and other data are consistent with a structure in which the bonding of Fe at C-2,3 in the diene complexes is very similar to that in ferrocene, but in which the terminal CH_2 or CHR groups are slightly rotated about the C_1-C_2 and C_3-C_4 bonds of the ligand. This steric distortion of the ligand from planarity makes the bonding at C-1,4 differ somewhat from that at C-2,3, but both instances involve π-orbitals on the carbons. The data for 1,3-butadiene and its iron tricarbonyl complex is summarized in table 1. Low signal-to-noise in spectra of the ester complex precluded measurements of the coupling constants; heteronuclear double resonance experiments, however, revealed two doublets centered at 108 ppm and 129 ppm.

This material has been accepted for publication by the Journal of the American Chemical Society and will appear in a future issue.

Sincerely yours,

H. L. Retcofsky

Table 1.- Carbon chemical shifts and C^{13}-H coupling constants in 1,3-butadiene and its iron tricarbonyl complex

Position		Butadiene	Butadiene-iron tricarbonyl
C-1,4	δ_C, ppm from CS_2	76.2	151.7
	J_{C-H}, cps	158	160 ± 5
C-2,3	δ_C, ppm from CS_2	55.6	107.0
	J_{C-H}, cps	158	170 ± 5
C-O	δ_C, ppm from CS_2	--	-18.9

91-60

PHYSIKALISCHES INSTITUT

Associate
Professor B. L. Shapiro
Department of Chemistry
Illinois Insitute of Technology
Technology Center
Chicago 16, Illinois
U S A

LEIPZIG C 1, LINNÉSTR. 5 · TEL.: SAMMELNR. 64511

am 8.3.1966 Az.: Arnd/Hpf.

Sehr geehrter Herr Professor Shapiro!

Für viele Probleme ist es notwendig, die hochaufgelösten Spektren exakt zu analysieren. Es wurden in der Vergangenheit einige Verfahren angegeben, die den Einsatz von elektronischen Rechenmaschinen vorsehen und vielen Laboratorien stehen entsprechende Rechenprogramme zur Verfügung. Es war nun leider nicht möglich, schon vorhandene Programme direkt für unseren Rechenautomaten vom Typ ZRA 1 umzuschreiben. Das größte Hindernis bildete dabei der relativ kleine Speicherraum (4096 Speicherplätze).
Wir haben ein Programm nach der von Ferguson und Marquardt[1)] angegebenen Methode geschrieben, die eine Erweiterung des Verfahrens von Reilly und Swalen[2)] ist.
Einige Besonderheiten des Programmes, die sich aus der Notwendigkeit der Einsparung von Speicherplätzen ergeben, sind folgende:

1. Verzicht auf die Fehlerrechnung.

2. Alle Hauptprogramme (Berechnung der experimentellen Energieniveaus, Iteration, Berechnung der Linienformen) werden nacheinander eingegeben.

3. Für die Berechnung neuer Parameter nach jedem Iterationsschritt konnten explizite Gleichungen gefunden werden:

$$\nu_i' = \frac{1}{\sum_{j,k,\ell_k} (m_{jk\ell_k})_i^2} \sum_{j,k,\ell_k} \left\{ (m_{jk\ell_k})_i \sum_{\nu} S^2_{jk\ell_k\nu} E_{jk\nu} \right\}$$

$$J_{ii'} = \frac{1}{\sum_{j,k,\ell_k} \left\{ (m_{jk\ell_k})_i (m_{jk\ell_k})_{i'} \right\}^2} \sum_{j,k,\ell_k} \left\{ (m_{jk\ell_k})_i (m_{jk\ell_k})_{i'} \sum_{\nu} S^2_{jk\ell_k\nu} E_{jk\nu} \right\}$$

(Bedeutung der Symbole und Indizes siehe [1)])

4. Die Koeffizientenmatrix des Gleichungssystems zur Bestimmung der experimentellen Energieniveaus aus den Frequenzen ist positiv definitiv und deshalb kann das einfache Verfahren von Cholesky zur Auflösung benutzt werden.

5. Wenn das Spektrum sehr viele Übergänge enthält, verzichten wir auf die Anordnung der Frequenzen nach der Größe und drucken sie sofort aus (Die Intensitäten sind immer von selbst auf n 2^{n-1} normiert).

6. Die resultierenden Linienformen werden durch Annahme von Gaußkurven für die Einzellinien berechnet.

Wir können mit unserem Programm Systeme mit maximal 6 nichtäquivalenten Spins behandeln. Bisher haben wir es auf 4- und 5-Spinsysteme angewendet[3), 4)]. Voraussetzung für eine erfolgreiche Durchführung der Iteration ist ein gut aufgelöstes Spektrum, in dem viele Einzellinien beobachtet werden. Diese Bedingung war nicht immer bei den von uns untersuchten 5-Spinsystemen erfüllt, und in solchen Fällen konnte durch die Iteration keine Verbesserung des Ausgangsspektrums erreicht werden. Kann man aber genügend Linien zuordnen, so kommt man mit der Methode sehr schnell zu guten Ergebnissen.

Mit vielen Grüßen

K. Arnold

(K. Arnold)

1) R. C. Ferguson, D. W. Marquardt J. Chem. Phys. 41, 2078 (1964)

2) J. D. Swalen, C. A. Reilly J. Chem. Phys. 37, 21 (1962)

3) E. Mühle Ann. d. Phys. (im Druck)

4) G. Klose, K. Arnold Mol. Phys. (im Druck)

91-62

University of Toronto
TORONTO 5, CANADA

DEPARTMENT OF CHEMISTRY

14 April, 1966.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616,
United States of America.

Cis-trans Isomerism versus Tautomerism in Thioanilides

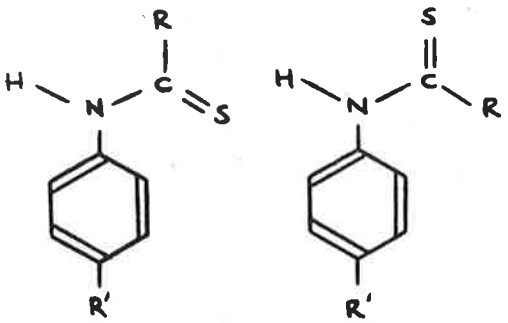
Dear Dr. Shapiro,

I recently had occasion to record the p.m.r. spectrum of thioaceto-p-toluidide and noted that it was unexpectedly complex. In particular, the aliphatic methyl protons gave rise to two signals, as did the aromatic methyl protons. I thought at first that I had observed a case of thioamide-thiolimidic acid tautomerism (this explanation had also been suggested to explain the complexity of the thioacetanilide spectrum[1]) but further work has shown that the phenomenon under observation is cis-trans isomerism of the thioamide group.

The data in the table show that a thiolimidic acid tautomer is not involved because
(a) neither of the aliphatic methyl proton signals approximates that of the fixed tautomer, methyl N-p-tolyl thiolacetimidic acid, and
(b) the aromatic protons of the thioamide occur at lower field than those of the thiolacetimidic ester.

The two isomers are present in about equal proportions in the thioacetyl derivatives, no doubt because of the similarity in size of the sulphur atom and the methyl group. If the size of the alkyl group is reduced (thioformanilide) the thioamide exists wholly in one form; if it be increased (thiopivalotoluidide), wholly in the other. This finding is nicely corroborated by the stretching frequencies of the N-H bonds in the infrared.[2] The situation recalls that in anilides themselves, where, because of the smaller size of the oxygen atom, it is the formanilides which exist in two isomeric forms while the acetanilides exist almost completely in the form with the carbonyl oxygen oriented towards the ring.

The splitting of the aromatic methyl proton signal mentioned above is no doubt due to the long range effects of the thiocarbonyl group. A similar effect (although smaller, 0.65 c/s) is observed in the two forms of p-methyl formanilide. It seems reasonable that the thioamide group should have a greater effect than an amide[3-5], but this is not evident in the ring-proton shifts for the thiopivalotoluidide. This point is under further investigation.

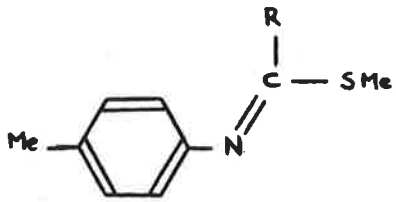


I R = Me, R' = Me

II R = Me, R' = H

III R = H, R' = H

IV R = CMe_3, R' = Me



V R = Me

Compound	Proton Resonances					Infrared	
	N-H	aromatic	R	Ar-Me	Me-S		
I	528-592 (br)	425-456 (mult)	101,148	140 142	-	3385	3324
II	525-621 (br)	430-465 (mult)	100,149	-	-	3393	3359
III	not ident.	429-433 (mult)	391[x]	-	-		3337
IV	" "	429, 435, 441, 450 (A_2B_2)	87	141	-	3400	
V	-	393, 401, 422, 430 (A_2B_2)	142	138	118		

---

x doublet, J = 14.8 c/s; collapses with D_2O

N.m.r. spectra measured for dilute solutions in deuterochloroform at ambient temperature on a Varian A 60 spectrometer. Figures quoted are c/s downfield from t.m.s. internal standard. Infrared spectra measured in chloroform solutions on a Beckman IR-8 spectrophotometer. Figures quoted in wave numbers.

Yours sincerely,

Ian D Rae

(Ian D. Rae)

References

1. A.J. Speziale and L.R. Smith, J. Org. Chem. 28, 5492 (1963).

2. R.A. Russell and H.W. Thompson, Spectrochim. Acta 8, 138 (1956).

3. R. Greenhalgh and M.A. Weinberger, Can. J. Chem. 43, 3340 (1965).

4. M. Shamma, R.W. Legally, P. Miller and E.F. Walker, Jr., Tetrahedron 21, 3255 (1965).

5. P.L. Southwick, J.A. Fitzgerald, and G.E. Milliman, Tetrahedron Letters 1965, No. 18, 1247.

18 April 1966

IIT NMR Newsletter Mailing List

Computerization has come (as it seems it must to nearly everything sooner or later) to be the best way to deal with the logistics of handling and mailing the IIT NMR Newsletter. Accordingly, please force-fit your name and complete mailing address (including name of the country, in English) to the format designated below, so that our computer can spew forth the labels necessary to get the Newsletter to you.

Note: (1) U.S. addresses must have a zip-code, and if you don't know yours, please ascertain it and include it in your address. There are now so many Newsletter subscribers that we cannot undertake to find your zip-codes for you.

(2) ALL Newsletter recipients must send us this new address format. There are NO exceptions. Newsletter Number 91 and all subsequent issues will be sent only to those from whom we have received new addresses by May 15, 1966.

Name (maximum of 28 letters plus spaces)

Address (maximum of 4 lines of 35 letters plus spaces each)

BLS

B. L. Shapiro
Department of Chemistry
Ill. Inst. of Tech.
Chicago, Ill. 60616

"N.M.R. Chemical Shifts of F in Crystals and Solutions" (in Chinese)
I. Chiu Wang
Acta Physica Sinica 20, 41 (1964)

"Addition von Triphenylstannyl-diphenylphosphin an Mehrfachbindungen"
H. Schumann, P. Jutzi und M. Schmidt
Angew. Chem. 77, 912 (1965)

"Nuclear Magnetic Resonance Studies"
V. The Tautomerism of Tasmanone and Belated β-Triketones"
I. R. C. Bick and D. H. S. Horn
Austr. J. Chem. 18, 1405 (1965)

"Carnaubadiol, A Triterpene from Carnauba Wax"
C. S. Barnes, M. N. Galbraith, E. Ritchie, and W. C. Taylor
Austr. J. Chem. 18, 1411 (1965)

"The Chemistry of the Euphorbiaceae"
XII. Compounds Derived from a New Beyeria Species"
P. R. Jefferies and T. G. Payne
Austr. J. Chem. 18, 1441 (1965)

"Extractives of Australian Timbers. VI. Ebelin Lactone"
R. A. Eade, L. P. Rossler, H. V. Simes, and J. J. Simes
Austr. J. Chem. 18, 1451 (1965)

"2-Alkylidene-1-Phenyloxazolidine-4,5-Diones"
K. R. Markham and I. D. Rae
Austr. J. Chem. 18, 1497 (1965)

"Nuclear Magnetic Resonance Spectra of Pyrrolizidine Alkaloids"
I. The Spectra of Retronecine and Heliotridine"
C. C. J. Culvenor, M. L. Heffernan, and W. G. Woods
Aust. J. Chem. 18, 1605 (1965)

"Nuclear Magnetic Resonance Spectra of Pyrrolizidine Alkaloids
II. The Pyrrolizidine Nucleus in Ester and Non-Ester Alkaloids and Their Derivatives"
C. C. J. Culvenor and W. G.Woods
Aust. J. Chem. 18, 1625 (1965)

"Constituents of MELICOPE SARCOCOCCA LAUT"
II. A New Flavanone"
W. Brune and T. A. Geissman
Aust. J. Chem. 18, 1649 (1965)

"Lactic Acid Racemization in Clostridium butylicum. Evidence for a Direct Internal Hydride Shift"
S. S. Shapiro and D. Dennis
Biochemistry 4, 2283 (1965)

"Reactions of Cyanate with Functional Groups of Proteins. IV. Inertness of Aliphatic Hydroxyl Groups. Formation of Carbamyl- and Acylhydantoins"
G. R. Stark
Biochemistry 4, 2363 (1965)

"Nuclear Magnetic Resonance Studies of Cytochrome c. Possible Electron Delocalization"
A. Kowalsky
Biochemistry 4, 2382 (1965)

"The Hydrogen Bond in the Diols. I."
T. Yonezawa, H. Saito, S. Matsuoka and K. Fukui
Bull. Chem. Soc. Japan 38, 1431 (1965)

"The Reaction of Tropoids with Quinone Derivatives. VIII/ The Reaction of Several Tropolones with p-Benzoquinone-monobenzenesulfonimide"
Y. Nishiyama
Bull. Chem. Soc. Japan 38, 1484 (1965)

"^{63}Cu- and ^{65}Cu-^{31}P Spin-Spin Coupling in Copper(I) Tri-alkyl Phosphite Complexes"
R. W. King, T. J. Huttemann and J. G. Verkade
Chem. Commun. 561 (1965)

"The Rearrangement of 9-Hydroxymethyloctalin"
Y. Kikino and P. De Mayo
Chem. Commun. 550 (1965)

"The Interaction of 1,3,5-Trinitrobenzene and Aliphatic Amines"
M. R. Crampton and V. Gold
Chem. Commun. 549 (1965)

"Reactions of Benzenesulphonylcarbene"
R. A. Abramovitch and J. Roy
Chem. Commun. 542 (1965)

"Photochemical Transformations of Dichloromethyl- and Trichloromethyl-cyclohexadienones"
J. King and D. Leaver
Chem. Commun. 539 (1965)

"The Synthesis of Glaucine, O-Methylcorydine, and Pseudo-corydine via Phenolic Oxidative Coupling"
M. Shamma and W. A. Slusarchyk
Chem. Commun. 528 (1965)

"The Structure of Abieslactone, a Methoxy-tetracyclic Triterpene Lactone"
S. Matsunaga, J. Okada, and S. Uyeo
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