

Printed ✓

Illinois
Institute of
Technology
N-M-R
Newsletter

No. 73
OCTOBER, 1964

Diehl	Simpler Subspectra from Complex NMR Spectra	1
Gillies, Randall	Absolute Signs of Some N^{15} Proton Couplings	2
Page, T.F.	Magnet Cabinet; Molecular Weight of Small Samples; A Meeting of C^{13} Resonators?	4
Willis	A Simple NMR Tube Cleaner and Dryer	6
Stothers	A Correction for IITNMR <u>72</u> , 15	8
Berlin, K.D.	P-H Coupling in Acyl- and Aroyl-phosphonates	10
Beach	Modified MOUSE for A-60	11
Ramey	Tacticity of Poly(Vinyl Alcohol), Poly(Vinyl Acetate), and Poly(Vinyl Trifluoroacetate) by NMR	14
Cavalli	Long Range Couplings in the "Conjugated Acrolein Dimer"	17
Andersson, Odberg	On Quadrupole Effects in KBr with Substitutional Cl Ions	20
Lauterbur	Pb^{207} Resonance Studies in Single Crystals; Isotope Effect in Cobalt Spectra	24
Lundin	Electronic Sweep for A60-CAT Operation (Cont'd); Microcells	27
Anderson, W.A., Freeman	Telegraphic Transmissions over Record Distances?	28
Tensmeyer	Calculation of Pyrazole Proton Chemical Shifts	30

modulation transfer via J-coupl.

Deadline Date for Next Issue: 20 November 1964

A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
BASEL, SCHWEIZ - KLINGELBERGSTR. 82
VORSTEHER: PROF. DR. P. HUBER

Basle, September 25th 1964.

Prof. Dr. P. Diehl

Prof. B. L. S h a p i r o
Illinois Institute of Technology
Technological Center
C h i c a g o 60616.

Dear Barry,

Thank you for your kind "letter". I was not quite sure whether you would count IIT N-M-RN 70,33 as my contribution as well.

Since you did not, I am sending you its second part. Again in cooperation with Dr. R. Jones and Dr. H.J. Bernstein I started studying the break down of complex NMR-spectra into simpler subspectra. The result is, that such a break down is always possible if we have at least one pair of weakly coupled nuclei.

As an example we discussed the ABB'-part of the ABB'XX' - spectrum of Pyridine which we showed to be a superposition of two AB₂-type and two ABC-type spectra. The AB₂-type spectra can easily be sorted out and immediately provide the following parameters : δ_{AB} , J_{AB} , J_{AX} , $J_{BX} + J'_{BX}$. The details of the method will be published soon in the Canadian Journal of Chemistry.

Yours sincerely

Peter

P. Diehl.



QUEEN MARY COLLEGE

(UNIVERSITY OF LONDON)

MILE END ROAD · E.1

TELEPHONE · ADVANCE 4811

23rd September, 1964.

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

Dear Barry,

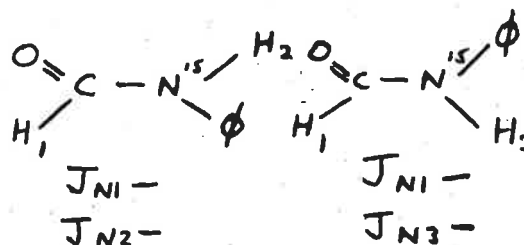
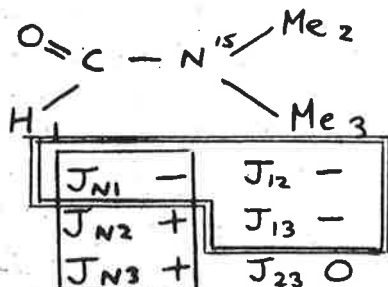
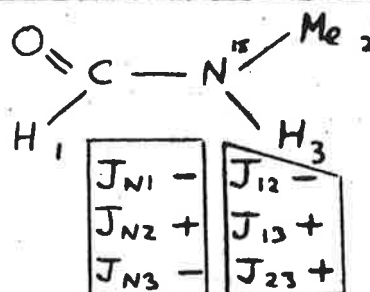
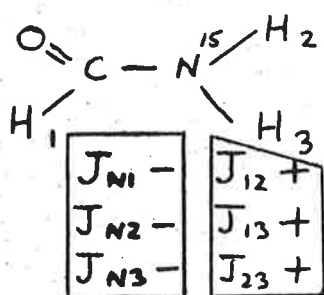
Absolute signs of some N^{15} proton couplings

We were interested to see the contribution on p. 14 of issue No. 71 concerning $H-C-C-^{14}N$ and $H-C-^{14}N$ in $CH_2CH_2N=C$. The assignment of $H-C-C-^{14}N$ as positive and $H-C-N^{14}$ negative based on $H-C-C-H$ being positive agrees with our work on N^{15} substituted formamides. We have now related J_{N1} in NN-dimethyl formamide- N^{15} (1) to J_{12} (H-Me) and J_{13} (H-Me) by irradiation of the ^{15}N lines.

(1) A.J.R. Bourn and E.W. Randall, J. Mol. Spec., **13**, 29 (1964).

We find irradiation of the low field side of the ^{15}N decouples the high field side of both methyl groups (lines 2 and 4). Since ^{15}N has a negative magnetogyric ratio this means that J_{N1} , J_{12} (H-Me), J_{13} (H-Me) all have the same sign. So the accumulated signs are:-

(2) Proton-proton decoupling of formamide- N^{15} , N-methyl formamide- N^{15} to be published in Molecular Physics.



The relative signs in N-phenylformamide were inferred from single resonance spectra.

Relative signs in single boxes found were by $\{H\}$ H, those in the double box by $\{^{15}N\}$ H.

contd./...

- 2 -

The direct couplings J_{N2} and J_{N3} in formamide- N^{15} should both be negative relative to an absolute positive sign for $J_{C^{13}H}$, the reversal of sign being due solely to the presence of one nucleus with a negative . On this basis it then follows that J_{12} , J_{13} , J_{23} in formamide- N^{15} are all positive. The positive signs for J_{12} , J_{13} check well with other sign determination experiments. (3)

-
- (3) P.C. Lauterbur and R.J. Kurland, J. Am. Chem. Soc., 84, 3405 (1962);
A.D. Buckingham and K.A. McLauchlan, Proc. Chem. Soc., 144, 1963.
-

We thus find the geminal coupling J_{N1} to be negative and not positive as suggested on p. 15 of No. 71. We suggest J_{N1} , which is always ~ 15 c/s, is very different in nature to N^{14} -C-H in $CH_3CH_2-N\equiv C$ which looks to be ~ 1.9 c/s from the spectra on p. 16 of issue 71. The N-Me couplings in our molecules are more comparable, ~ 1.2 c/s [0.8 c/s for N^{14}]. They also have an opposite sign to directly bonded N^{15} -H and hence are positive.

This is in agreement with the sign for N^{14} -C-H ethyl isonitrile (negative) since the only difference is the negative γ for N^{15} .

Yours sincerely,

D. Gillies

D. Gillies

Ed Randall

E.W. Randall

Battelle Memorial Institute

5 0 5 K I N G A V E N U E C O L U M B U S , O H I O 4 3 2 0 1

5

AREA CODE 614, TELEPHONE 299-3121

September 23, 1964

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

Dear Barry:

Your final warning catches us at a time when several pieces of work are completed but none is yet in a form so that it can be put on public display. We are thus forced to tell you briefly what we have done to keep on your mailing list and to promise more detailed information in the very near future.

Magnet Cabinet: 9 months ago we built a plexiglass cabinet around our HR-60 magnet to improve the sweep stability and resolution. While we make no pretense that it gives stability equivalent to field-frequency control it does allow one to scan very slowly with good stability and resolution. The attached scan of o-dichlorobenzene is representative of what we can now routinely get. Cost (not including labor) was \$175.00.

Molecular Weight of Small Samples: We have modified the technique of Barcza (J. Org. Chem., 28, 1914-5 (1963)) so that molecular weights of 10-30 mg samples can be measured with an accuracy of \pm one per cent or better to molecular weight 500. This work is being written up and will be submitted to Analytical Chemistry.

Last, but not least, we have finally got our C^{13} probe and rf unit and have it in operation. We have been talking with Dave Grant about the need for a small informal meeting of those doing C^{13} work to discuss C^{13} exclusively. I should be most interested hearing from those who think such a meeting might be profitable.

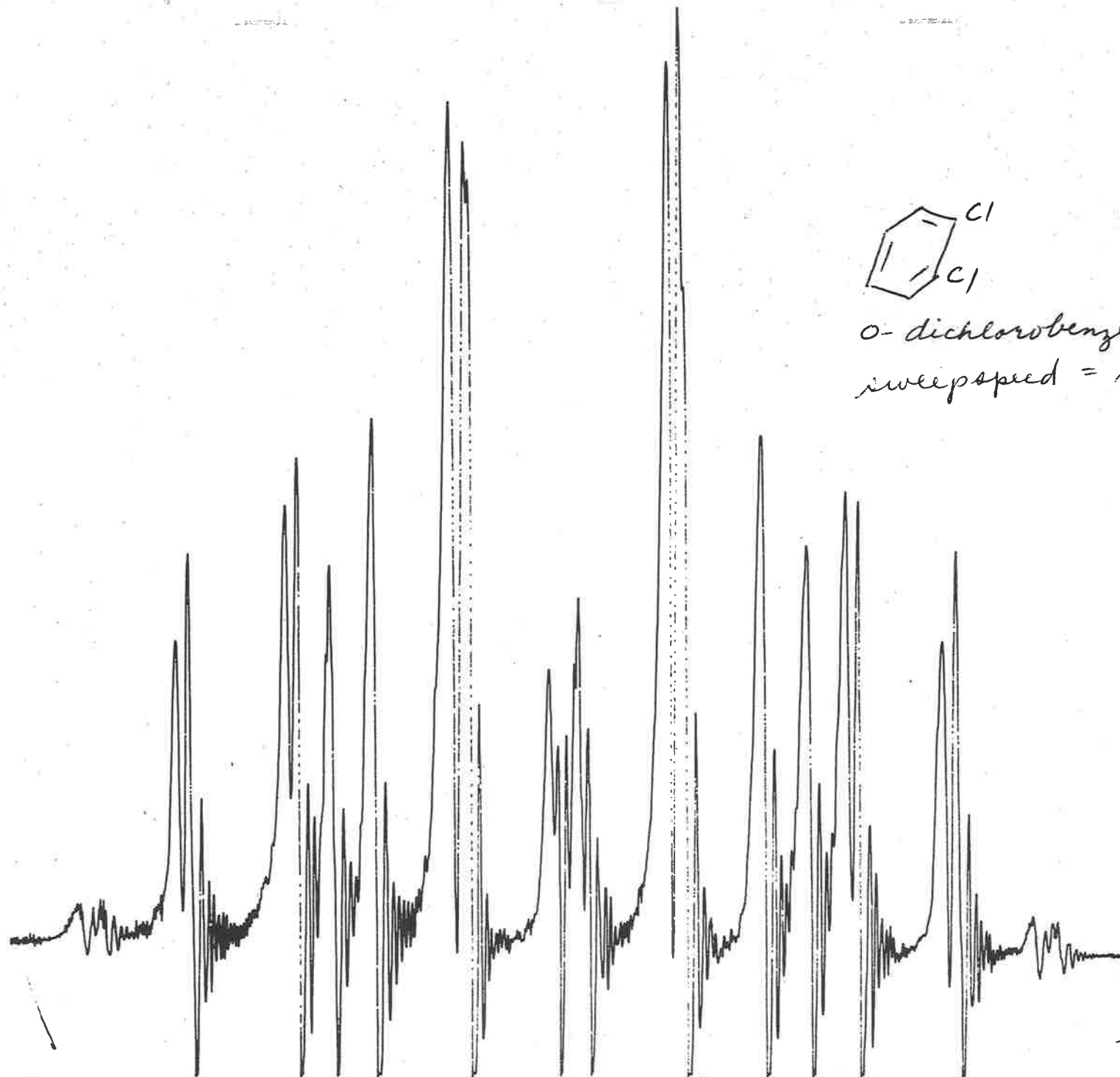
Best personal regards,

Very truly yours,

Tom

Thomas F. Page, Jr.
Research Chemist
Molecular Spectroscopy

TFP/mh



o-dichlorobenzene

sweep speed = ~ 0.2 cps/sec.

T. F. Page Jr.

73-5

A SIMPLE NMR TUBE CLEANER AND DRYER

Donald E. Willis

Central Research Department, Monsanto Company
St. Louis, Missouri

Of practical consideration in NMR studies is a simple method of cleaning NMR tubes. Figure 1 shows the design of a simple, but effective tube cleaner and dryer. This type cleaner provides a means of cleaning both inner and outer surfaces of NMR tubes in one simple operation.

The drawing is self-explanatory as far as construction of the cleaner is concerned. In use, an NMR tube is placed over the 3 mm tube and stopcock 1 turned to apply a vacuum. Various solvents (water, acetone, carbon tetrachloride, acid, or cleaning solution) are dripped down the outside of the tube. As the liquid reaches the open end of the tube, it is drawn into the space between the tubes and then out the center tube to a trap. The NMR tube can be "soaked" in solvent by filling the reservoir (stopcocks closed) to a level above the lower end of the tube, opening the vacuum stopcock slightly to draw solvent into the tube and then closing the vacuum stopcock. After "soaking", the excess solvent is drained off (stopcock 2), the vacuum is again applied and rinsing resumed. Several solvents may be required to clean very dirty tubes, ending with water, acetone and/or carbon tetrachloride. If acid cleaning is required, proper precautions should be taken to insure that an incompatible mixture of acid and organic solvents does not accumulate in the trap. Continued aspiration may be used to dry the tube or stopcock 1 may be turned to pass a slight stream of dry air or nitrogen through the tube.

The Teflon sleeve (a short length of ca. 3 mm o.d. tubing commonly used in gas chromatography) serves as a cushion when the NMR tube is placed on the cleaner and to obtain circulation of liquid and air in the bottom of the tube.

While shown as only a single unit, the cleaner-dryer could be made to contain several units connected to common lines. The dimensions shown are designed for the standard A-60 precision 5 mm thin-wall tubes and may require alteration to accommodate other types of tubes.

/pm

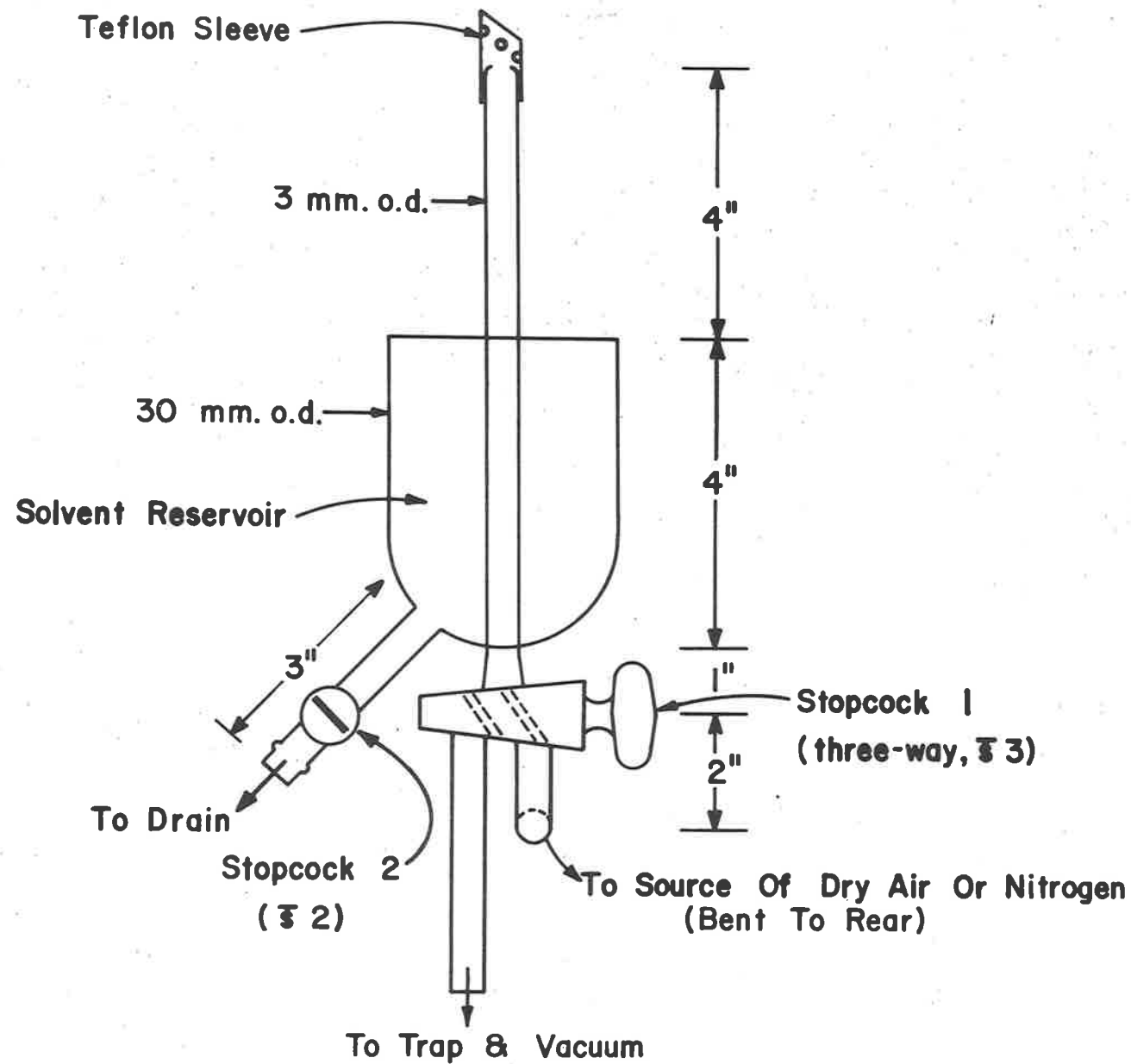


Figure 1. NMR Tube Cleaner And Dryer
(Not Drawn To Scale)

THE UNIVERSITY OF WESTERN ONTARIO
UNIVERSITY COLLEGE
OF ARTS AND SCIENCE



DEPARTMENT OF CHEMISTRY

LONDON, CANADA

October 7, 1964.

Dr. B. L. Shapiro,
Dept. of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago, Ill. 60616
U.S.A.

Dear Barry,

A correction for IINMR 72-15.

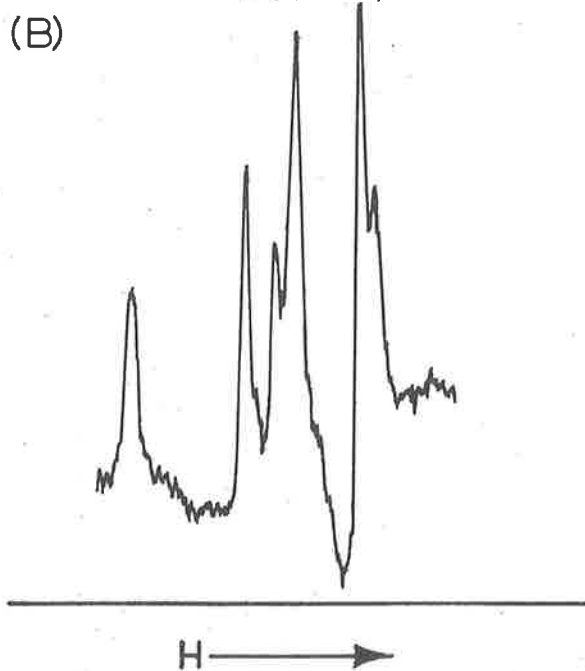
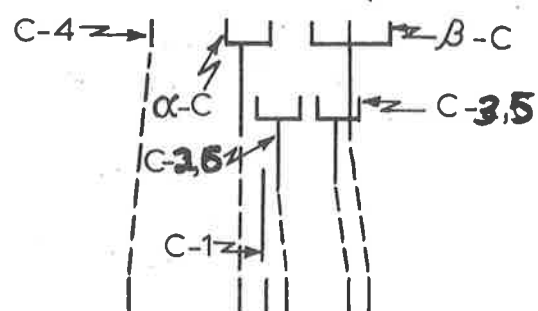
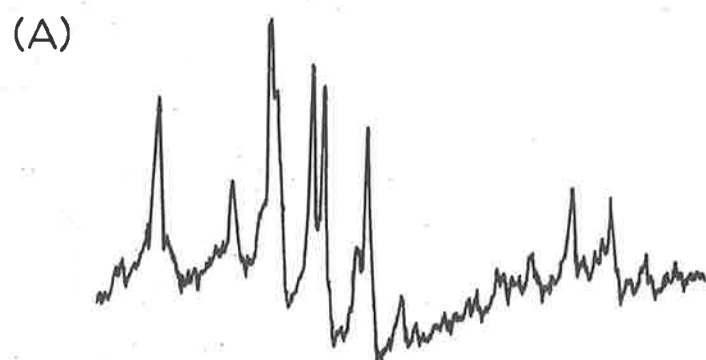
I must apologize for enclosing the wrong figure with my recent contribution on our styrene results. The figure which I intended to include is submitted herewith to show a typical result from a spin decoupling experiment.

Sincerely,

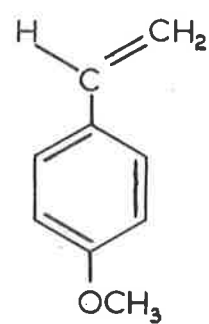
A handwritten signature in cursive script that reads "Joke".

J. B. Stothers
Associate Professor

JBS:vl



15.1 Mc/s
SPECTRA OF



(A) normal

(B) with double
irradiation at
60Mc/s


OKLAHOMA STATE UNIVERSITY • STILLWATER

 Department of Chemistry
 Frontier 2-6211, Ext. 7215-7218

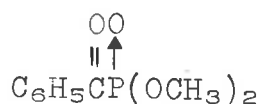
September 25, 1964

74075

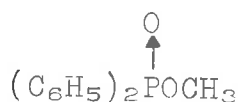
Dr. B. C. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Chicago, Illinois 60616

Dear Dr. Shapiro:

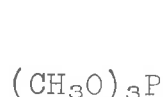
In response to our obligation for a contribution we have been studying the P-H coupling in several acyl- and aroyl-phosphonates. Part of this work will be published shortly. Dimethyl benzoylphosphonate (I) displays a doublet for the methyl group ($J = 11$ cps) as expected ($\delta -3.87$). This is comparable to $J_{P-CH_3} = 12$ cps in methyl diphenylphosphinate (II) ($\delta 3.68$) or in trimethyl phosphite (III) ($J_{P-CH_3} = 10$ cps; $\delta 3.5$). If the phosphorus atom is separated from the methyl group by a carbonyl function, as in diethyl acetylphosphonate (IV) the value of the coupling drops sharply ($J = 5$ cps, $\delta 2.43$). We are investigating several other members in this latter series to determine if the coupling is dependent upon electronic and steric effects.



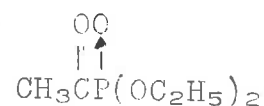
I



II



III



IV

Sincerely yours,

K. D. Berlin

K. D. Berlin
 Associate Professor

KDB:bbm



UNION CARBIDE CORPORATION

PLASTICS DIVISION

RIVER ROAD, BOUND BROOK, N. J. 08805

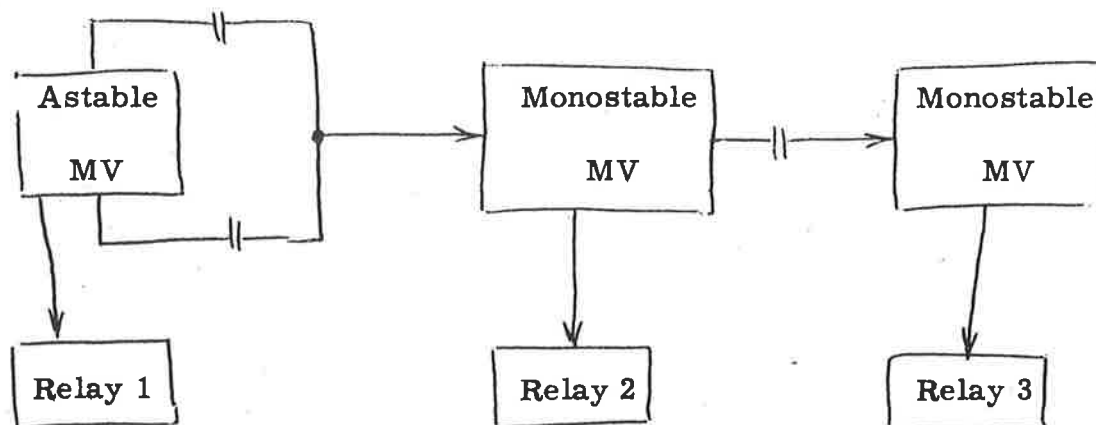
October 1, 1964

Modified MOUSE for A-60

I have read with interest the recent reports of "MOUSING" the A-60. I wish to report the construction of a modified MOUSE [automated SNAIL], which does away with the bar-graph type of data presentation. Besides alleviating the blotting problem, it also eliminates the necessity for carefully balancing the detector zero control.

After allowing the integral to collect for a preset time with the pen up and immobile, the modified MOUSE places the pen down, moves it to the new position, picks the pen up, moves the chart drive to the new position, shorts out the integrating capacitor, and starts to collect a new integral - all in that order. The entire device is not a great deal more complicated than that of Robertson's, and contains more conventional circuitry.

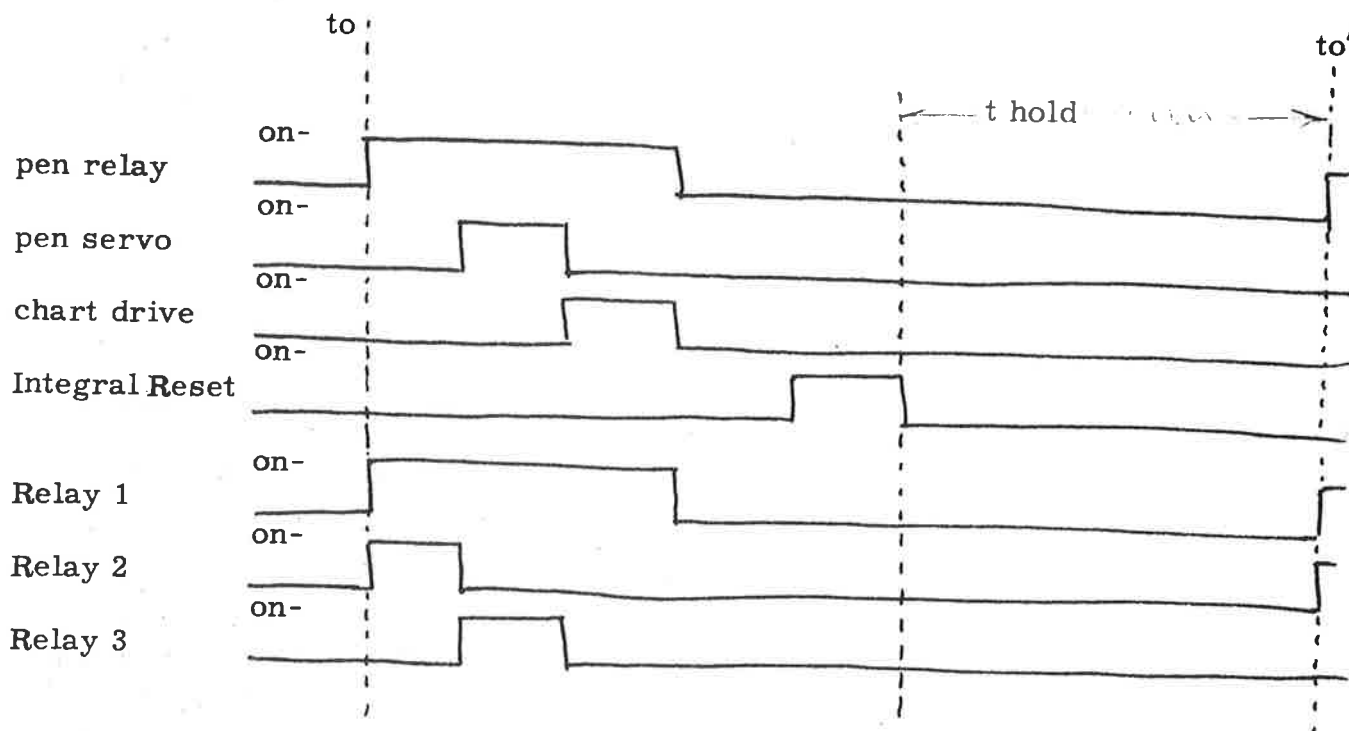
The operation of the apparatus is rooted in an astable asymmetric multivibrator (flip-flop circuit), which on each change of state triggers a monostable multivibrator, which on returning to its original state triggers a second monostable multivibrator. Each of the three multivibrators drives a relay:



The entire system consists of 3 tubes, 3 transistors and 3 relays, plus a power supply. Timing is adjusted via appropriate RC networks.

October 1, 1964

The system logic is as follows:



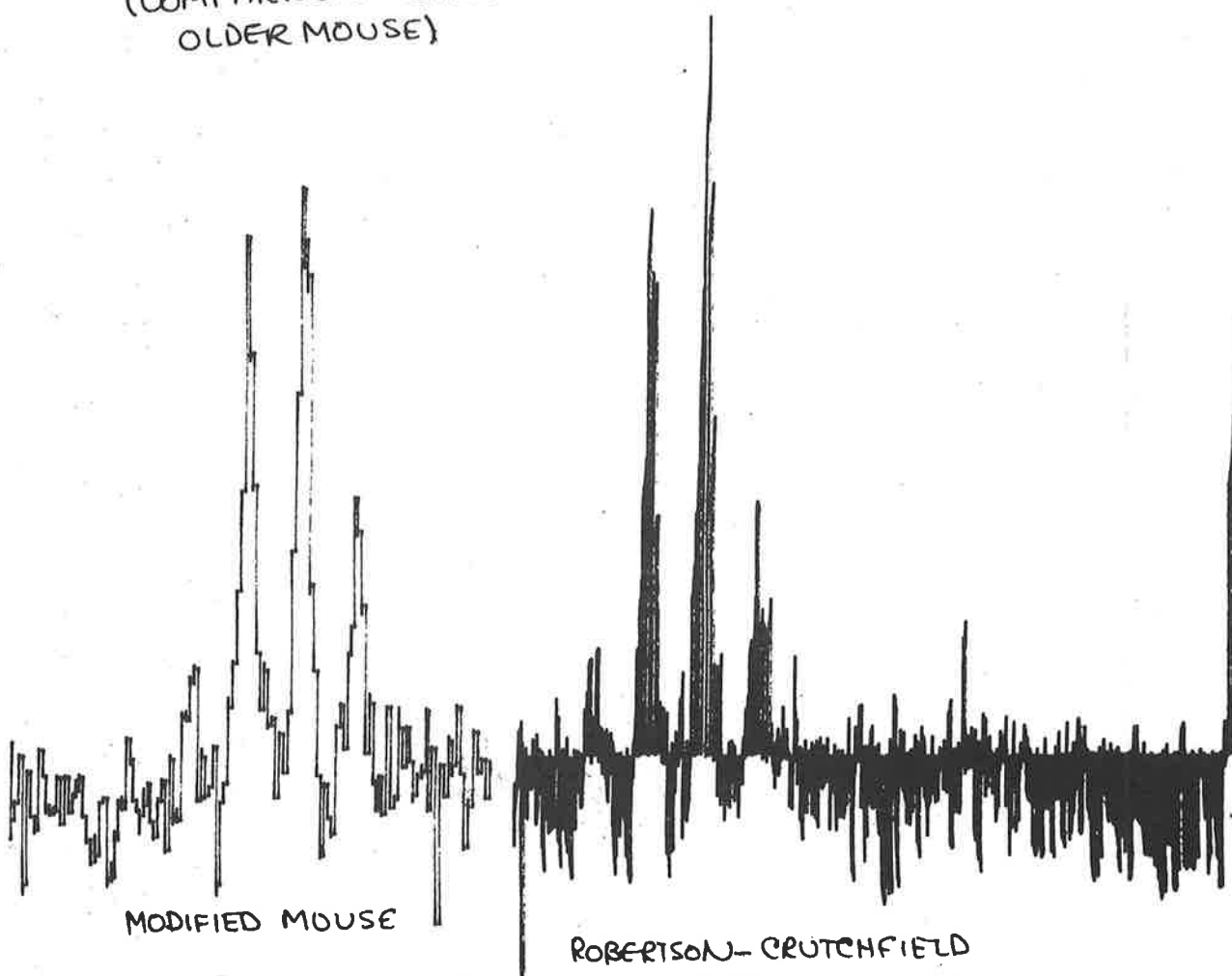
The system functioned well in its initial trials. Although the chart drive pulse accumulates the errors of the timing in all 3 of the circuits, it is of constant duration to within $\pm 3 \times 10^{-3}$ sec. Its utility in S/N enhancement is yet to be evaluated.

Since "brevity is golden," I shall not include details here, but will happily entertain all inquiries and comments concerning the system. A test scan is attached.

W. F. Beach

WFB:MMF
Enc.

SAMPLE SCANS:
(COMPARISON WITH
OLDER MOUSE)



SA = 20.
IA = 80.
RF = .10
SW = 500

SAMPLE: 17% Et ϕ
HOLD TIME: 5 sec./point

WFB 10/5/64



THE ATLANTIC REFINING COMPANY
INCORPORATED - 1870
PETROLEUM PRODUCTS

RESEARCH & DEVELOPMENT DEPARTMENT
RESEARCH DIVISION

500 SOUTH RIDGEWAY AVENUE
P. O. BOX 85
GLENOLDEN, PA.

October 8, 1964

File: 207-2

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

Dear Barry:

The following is a short report on some work that has been submitted to the Journal of Polymer Science. Preprints are available to interested parties.

TACTICITY OF POLY(VINYL ALCOHOL), POLY(VINYL ACETATE), AND
POLY(VINYL TRIFLUOROACETATE) BY NMR

The decoupled high resolution NMR spectra of PVA, PVAc, and PVTFA are readily interpretable in terms of the three triad forms, isotactic, heterotactic, and syndiotactic. The assignment of the three forms was made on the basis of a sample of poly(vinyl methyl ether) of known tacticity which was converted to PVA by reaction with HI. The PVA was converted to PVTFA by reaction with CF_3COOH and to PVAc by reaction with $(\text{CH}_3\text{CO})_2\text{O}$.

In Fig. 1 are shown the spectra of PVTFA in solution in deuterated acetone as obtained at 100 Mc./sec., and at 37°C. The uncoupled spectrum consists of four resonances of which the two labeled α and β are impurities in the solvent and is shown in Fig. 1-A. The resonances with tau values of 4.72 and 7.61 correspond to the α and the β protons, respectively. A slow sweep of the uncoupled and decoupled α proton resonances of samples I, II, and III are shown in Figures 1-B, 1-C, and 1-D, respectively. The spectra clearly shows three components with tau values of 4.63, 4.72 and 4.78. The corresponding spectra of the β protons of Sample II are shown in Figure 1-E.

Sample I was prepared from commercial PVA by reaction with CF_3COOH . Sample II was prepared from the free radical polymerization of vinyl trifluoroacetate at 65°C using azobisisobutyronitrile, and Sample III was prepared from poly(vinyl methyl ether) by reaction with HI followed by CF_3COOH . The concentration of the central monomer units in i , h , and s triads of the PVME used in preparing sample III are 52:33:15. The relative area of the three proton resonances of PVTFA derived from PVME are 48:33:19, as measured from the peak heights. These results provide an unambiguous assignment of the three α proton resonances. The data are summarized in Table I.

- 2 -

Table I

<u>Polymer</u>	<u>Source</u>	<u>Tacticity</u>					
		<u>triads</u>			<u>diads^a</u>		
		<u>s</u>	<u>h</u>	<u>i</u>	<u>s</u>	<u>i</u>	
PVME	General Aniline & Film Corp.	15	33	52	31.5	68.5	
PVTFA	From PVME above by reaction with HI followed by CF ₃ COOH	19	33	48	35.5	64.5	
PVTFA	Free radical polymerization	34	51	15	59.5	40.5	
PVTFA	From PVA below by reaction with CF ₃ COOH	31	43	26	52.5	47.5	
PVA	duPont Elvanol 72-60	36	42	22	57.0	43.0	

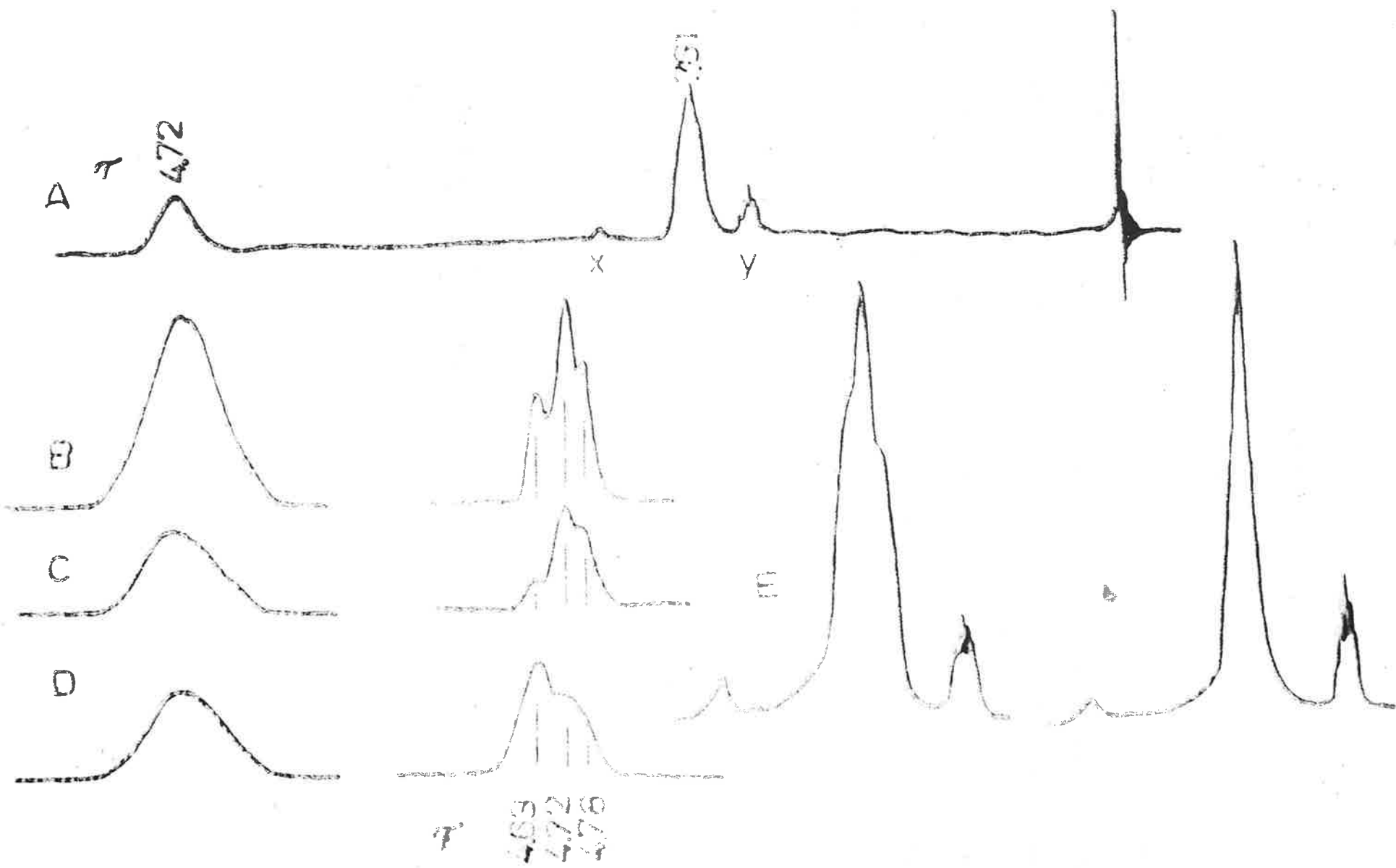
^a Calculated from triads

Similar results were obtained for PVA and PVAc.

Very truly yours,

Kermit C. Ramey
Kermit C. Ramey

KCR:LH



SOCIETÀ EDISON

SOCIETÀ PER AZIONI CON SEDE IN MILANO
CAPITALE SOCIALE L. 375.000.000.000 - INTERAMENTE VERSATO
LABORATORIO RICERCHE DI BOLLATE

AZIENDA CHIMICA

BOLLATE ~) October 1964

Località Traversagna - Telefoni 2910 - 2919
Casella Postale N. 15

Nella risposta citare il N° 2891/Cav/td

Associate Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago - Illinois 60616

Subject: Long range couplings in the "conjugated acrolein dimer"

Dear Professor Shapiro,

your letter of August 12 prompts us to send
an extra contribution hoping to obtain a few back issues of the
Newsletter.

Recent publications on long-range couplings
between protons separated from one another by four and five bonds
(allylic and homoallylic coupling in unsaturated systems) give us
the opportunity to report similar observations in the NMR spectra of
5,6-dihydro-2N-pyran-3-carboxaldehyde, the so-called "conjugated
acrolein dimer". (I)

The spectrum of such a compound in CCl_4
solution (50% in volume) consists of five separate bands (see figures
hereby enclosed) which, because of their shifts and intensities,
can be assigned to the aldehydic proton ($\tau = 0.64$), the A proton
($\tau = 3.05$), the B ($\tau = 5.81$), C, ($\tau = 6.29$) and D ($\tau = 7.60$)
protons. As it is shown in the theoretical spectrum we have observed
long-range couplings between the protons of the B group and those of the
A and D groups, with values respectively of $J_{AB} = 1.8$ and $J_{BD} = 2.6$
c.p.s.

In addition the aldehydic proton is shown to
be coupled by 0.4 c.p.s. to those of the B group through a 4-
bonds coupling.

All of the coupling constants can be obtained
by simple first order interpretation of the spectrum.

./.

SOCIETÀ EDISON
AZIENDA CHIMICA

Foglio N. 2Seguito al N. 2891 del 5.10.64

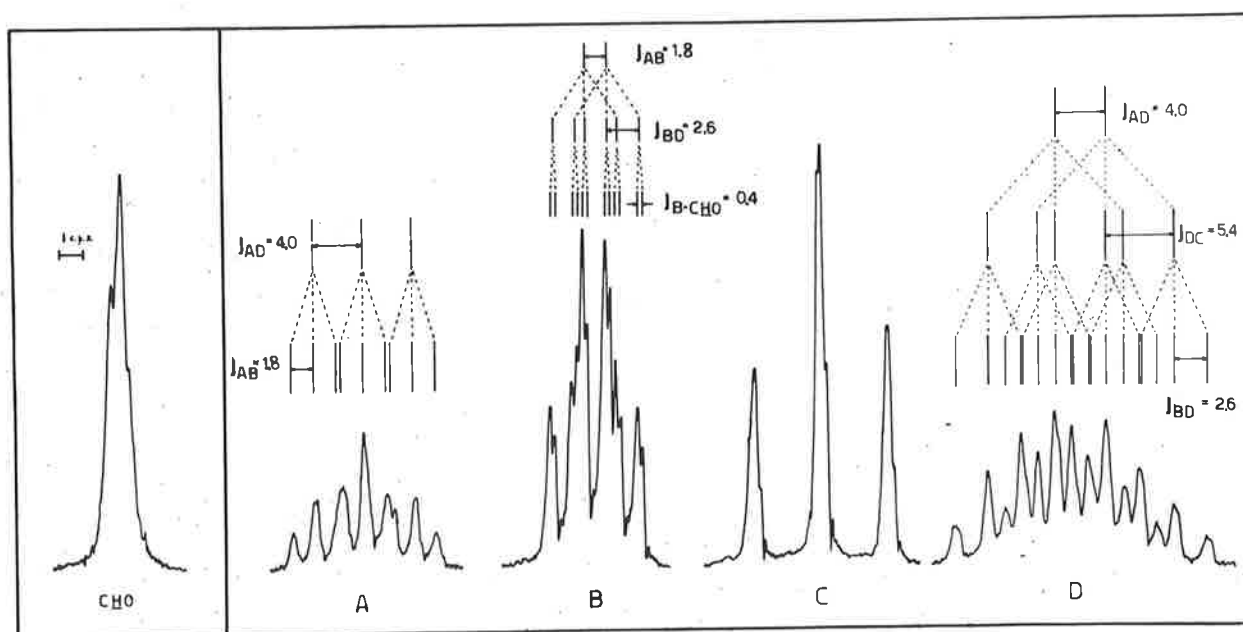
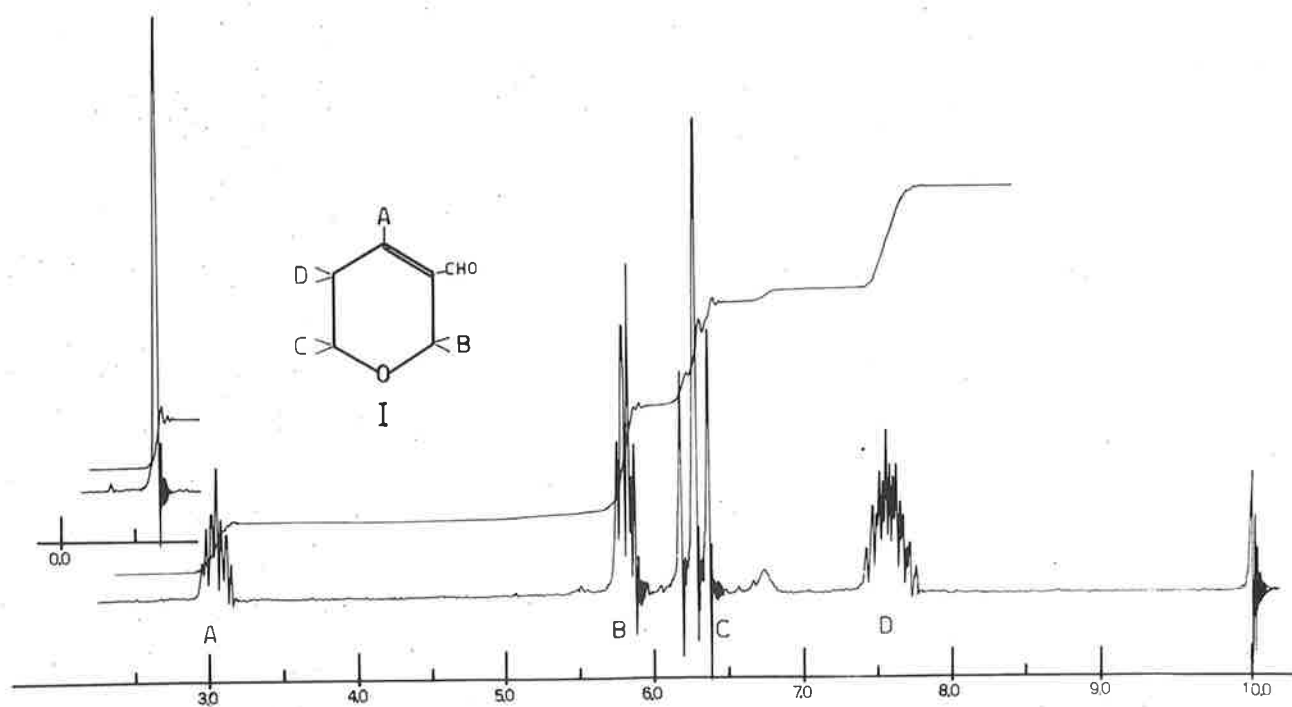
The broadening of the triplet of the aldehydic proton suggests additional small couplings with other ring protons probably that located at the A position.

Rapid ring inversion has to be responsible for the equivalence of the methylene protons respectively in the B, C e D groups.

Yours faithfully,

Lucio Cavalli

Luciano Cavalli



THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70

SWEDEN

Cable address: Technology

NUCLEAR MAGNETIC RESONANCE GROUP
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70 SWEDEN

Stockholm, September 22, 1964.

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago Ill. 60616

U S A

LOA/BR

On Quadrupole Effects in KBr with Substitutional Cl Ions

Dear Dr. Shapiro,

In a letter by Andersson and Forslind reproduced in Mellon NMR No. 42 was reported the observation of shifted resonance lines in the wings of the I^{127} resonance line of a KI single crystal. The assumption that the shifts were caused by Na ions in substitutional positions in the lattice has later been proved by activation analysis and by observing the same shifts in KI crystals doped with Na.

The shifted resonance lines arise in the following way. In a perfect NaCl type lattice with cubic symmetry no quadrupole coupling effects appear since the electric field gradient is zero at the positions of the nuclei. The distortion of the lattice caused by the dislocations in a real crystal is, however, so great that for nuclei such as Br and I with large quadrupole moments, the quadrupole effect smears out the contribution to the resonance line from all transitions except the one between the states with $m = 1/2$ and $m = -1/2$, which is unaffected by the quadrupole coupling to the first order approximation. In the immediate neighbourhood of a substitutional ion the lattice is considerably distorted and the quadrupole coupling constants for nuclei in this region are so large that second order effects become important. When the number of substitutional impurities is sufficient to give an observable number of neighbour nuclei in identical field gradients the second order shifts of the $m = 1/2 \leftrightarrow m = -1/2$ resonance lines for these nuclei can be measured. The lines observed have been subjected to such second-order shifts deriving from different nuclei neighbouring the impurity. The computations needed to determine the field gradient tensor and its orientation at the nuclei surrounding a substitutional ion in a NaCl-type lattice have recently been set down in a paper by Andersson and Forslind soon to be published in Arkiv för Fysik together with the results of measurements on a KI crystal grown with 0.1 mole per cent Rb I.

Here we report the results from an investigation of a KBr crystal with Cl ions in substitutional positions. The bromine nuclei closest to the Cl impurity ion are those in the $\{1, 1, 0\}$ positions, the curly brackets indicating that all the positions $(1, 1, 0)$, $(1, 0, 1)$, $(\bar{1}, 1, 0)$ etc. are included. The numbers are measured in units of the interionic distance

along the crystal axes. The largest shifts are expected to be observed for the $\{1, 1, 0\}$ nuclei. In Fig. 1 the shifts for the Br^{81} resonance at 16 MHz have been plotted and a rotation pattern for $\{1, 1, 0\}$ nuclei has been fitted to the points. The pattern has been computed for the case that the crystal is rotated around a crystal axis perpendicular to the magnetic field and that the field gradient tensor at the nucleus $(1, 1, 0)$ has two equally large principal axes in the $[110]$ and $[\bar{1}10]$ directions while the principle axis in the $[001]$ direction is zero. θ is the angle of rotation from a position where the magnetic field is parallel to a crystal axis. The shifts are represented by the quantity $D = \nu_0(\nu - \nu_0)$ where ν and ν_0 are the resonance frequencies for respectively the disturbed and the undisturbed nuclei. The theoretical expression for the D values is independent of the resonance frequency at which the shifts are observed, which simplifies the comparison between different measurements. For this reason also the shifts of the Br^{81} resonances have been transformed to D values for Br^{79} resonances. We obtain for the magnitude of the largest principle axes of the field gradient tensor at the $\{1, 1, 0\}$ nuclei the value $\text{eq.} = (29,6 \pm 0,4) \cdot 10^{15} \text{ V/cm}^2$.

A representative spectrum is shown in Fig. 2 where the resonance line from the undisturbed nuclei is attenuated 100 times. The positions of the $\{1, 1, 0\}$ resonances are indicated by arrows. To make it possible to eliminate such false lines caused by noise as the one observed to the extreme left the recording of the spectra has to be repeated many times for each angle.

In Fig. 3 the D values for the shifts observed at the frequencies 8 MHz (\bullet) and 6 MHz (Δ) for the Br^{79} resonance have been plotted. The rotation pattern for the $\{2, 0, 0\}$ nuclei has been fitted to the points. In this case the field gradient tensor is axially symmetric and we find $\text{eq.} = (13,3 \pm 0,3) \cdot 10^{15} \text{ V/cm}^2$.

For small values of θ resonance lines for nuclei more distant from the impurity have been observed as can be seen from Fig. 3. These lines may be attributed to the $\{2, 1, 1\}$ or the $\{2, 2, 0\}$ nuclei. From the similarity with the rotation pattern for the $\{1, 1, 0\}$ nuclei we suppose that these are $\{2, 2, 0\}$ lines. If the orientation of the field gradient tensor is the same as in the $\{1, 1, 0\}$ case we obtain $\text{eq.} = 4,3 \cdot 10^{15} \text{ V/cm}^2$.

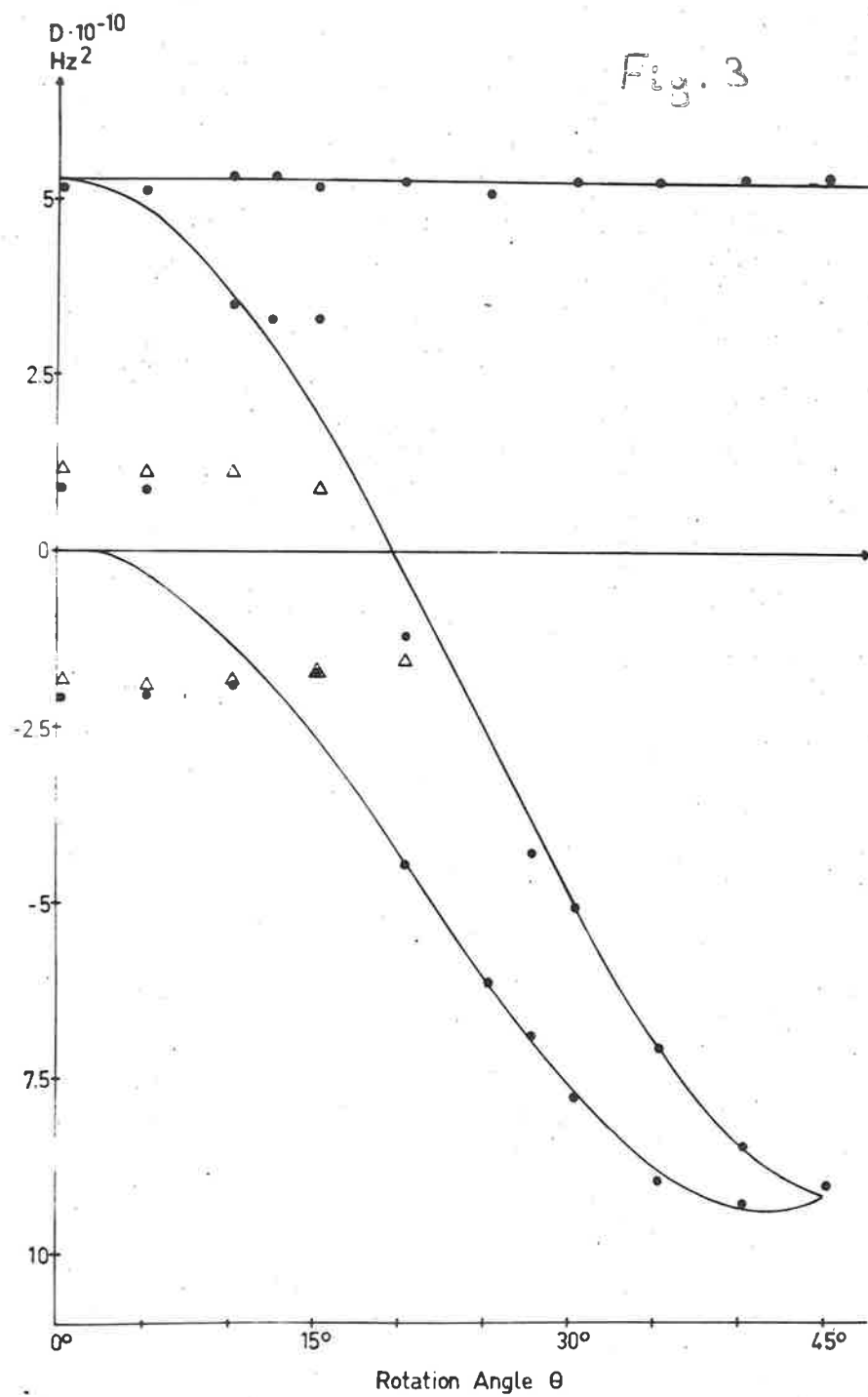
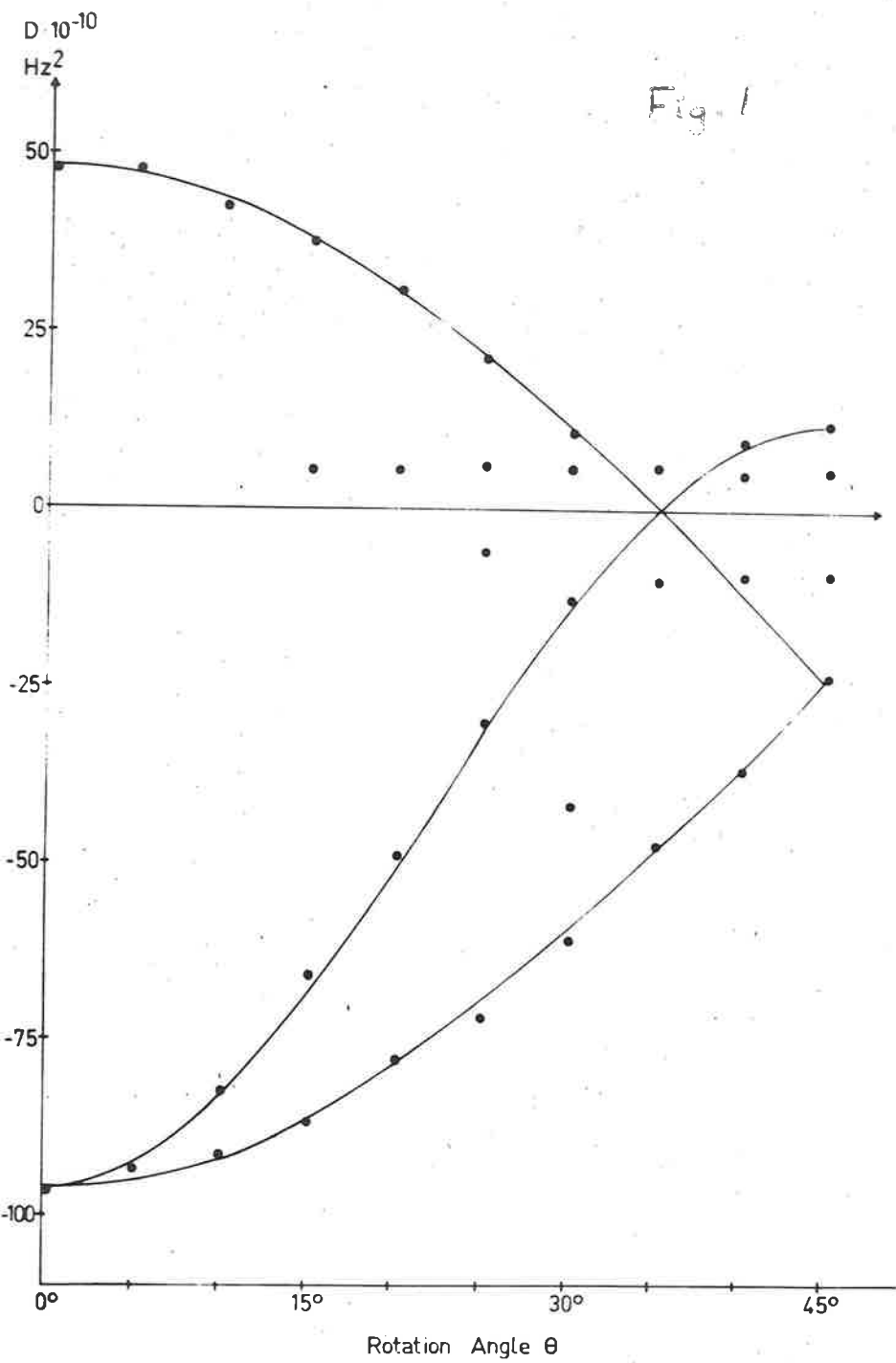
Yours sincerely

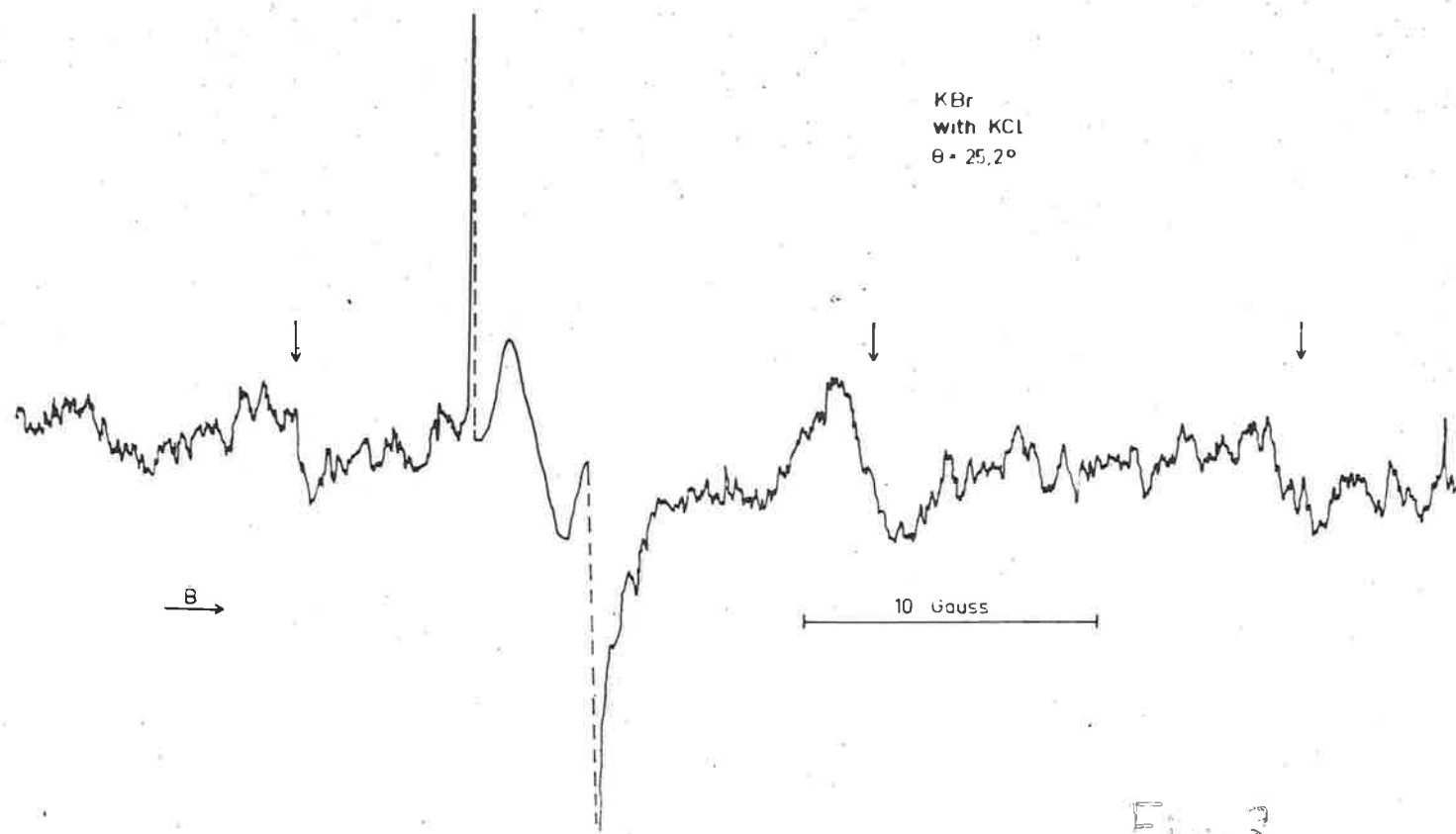
Lars-Olov Andersson

Lars Olov Andersson

Lars Ödberg

Lars Ödberg





STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

DEPARTMENT OF CHEMISTRY

October 13, 1964

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

Dear Barry:

Some of the readers of IITNMRN may be interested in an interim report on our work on the Pb^{207} resonances in single crystals and on studies of isotope effects in cobalt spectra. John Burke and I have completed the analysis of the single crystal spectrum of wulfenite, lead molybdate. We used natural crystals, red-orange in color, from the Red Cloud mine, Yuma, Arizona. Wulfenite is tetragonal, with space group $I4_1/a$ (C_{4h}), and each Pb^{2+} ion is surrounded by

eight O^{2-} ions in such a way that the axially symmetric lead shielding tensors are all equivalent and identically oriented. We find that $\sigma_{\parallel} = -63$ ppm, $\sigma_{\perp} = 126$ ppm, $\sigma_{\text{av}} = -97.4$ ppm relative to saturated aqueous $\text{Pb}(\text{NO}_3)_2$. The σ_{\parallel} and σ_{\perp} are components of the traceless part of the shielding tensor, and σ_{\parallel} is parallel to the c-axis of the crystal. The shielding may be interpreted, following Orgel, as a consequence of the mixing of Sp and p^2 states into the d^{10}s^2 configuration of Pb^{2+} by the non-centrosymmetric environment. I have not yet been able to make a convincing quantitative calculation of this effect, and it may be that other influences, such as covalent bonding, are not negligible.

Dr. Shapiro

-2-

October 13, 1964

Measurements on the C^{13} and N^{15} isotope effects in the $Co(CN)_6^{3-}$ ion are summarized in the following table.

Isotope Shifts in the Co^{59} Spectrum of $K_3Co(CN)_6$

	n	$\Delta\sigma$ (ppm)	$\frac{\Delta\sigma}{n}$
$K_3Co(C^{13}N^{14})_n(C^{12}N^{14})_{6-n}$			
	0	0	--
	1	$0.914 \pm .004^*$	$0.914 \pm .004$
	2	$1.832 \pm .026$	$0.916 \pm .013$
	3	$2.743 \pm .013$	$0.914 \pm .004$
	4	$3.659 \pm .020$	$0.915 \pm .005$
	5	$4.580 \pm .014$	$0.916 \pm .003$
	6	$5.463 \pm .065$	$0.910 \pm .011$
$K_3Co(C^{12}N^{15})_n(C^{12}N^{14})_{6-n}$			
	0	0	---
	6	$1.18 \pm .04$	$0.197 \pm .007$

*95% confidence limits

An approximate calculation of the effect has been made by considering the effect of the change of zero-point energy in the ground and excited electronic states with isotopic substitution on the effective excitation energies used in the perturbation theory of the paramagnetic shielding term. Treating the ion as an XY_6 molecule, I calculate an isotope effect in $Co(C^{13}N^{14})_6^{3-}$ of 7.8 ppm, fairly close to the observed one of 5.5 ppm. Refinement of the calculations by including the effects of all

Dr. Shapiro

-3-

October 13, 1964

vibrational modes is under way. In particular, it is hoped that a more complete vibrational calculation will explain a large part of the difference between the C^{13} and N^{15} effects, which are nearly equal in the XY_6 model. The $Co^{59} - C^{13}$ spin-spin coupling is 126 cps, and the $Co^{59} - N^{15}$ coupling is 3.3 cps. Both signs are, of course, unknown.

A number of other experiments are in progress in both the areas mentioned above, and I shall keep you posted as we get definite results.

Keep up the good work.

Yours truly,



Paul C. Lauterbur
Associate Professor

PCL:jc

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

October 16, 1964

AIRMAIL

Professor Bernard Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

Electronic Sweep for A60-CAT operation (Cont'd)

In the February 64 Newsletter we described the circuitry we were using to couple our A-60 to a 1024 channel CAT. After the equipment had been in operation a few weeks, we found that the sweep circuit as described was unsatisfactory both as to stability and linearity. The trouble was quickly and completely cured by increasing the size of the integrating capacitor from 0.1 to 1.0 ufd. and increasing correspondingly the magnitude of the integrated voltage. The maximum voltage now provided by the "ramp adjust" potentiometer is 16 mv. We would be glad to send detailed schematics to anyone interested. Incidentally, the sweep circuit works equally well with the "high-Z" sweep modification to the A-60.

Microcells

We have been most pleased with the performance of the NMR Specialties* all-glass microcell. We have obtained exceedingly good resolution from them with very little effort provided that the sample was completely free of debris (filter fibers, etc.). Using a 1% TMS solution, a signal enhancement of 7.5 over a Varian* precision sample tube was obtained.

Sincerely yours,



R. E. Lundin, Chemist
Fiber Physics Investigations
Wool and Mohair Laboratory

*



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

Oct 16th, 1964

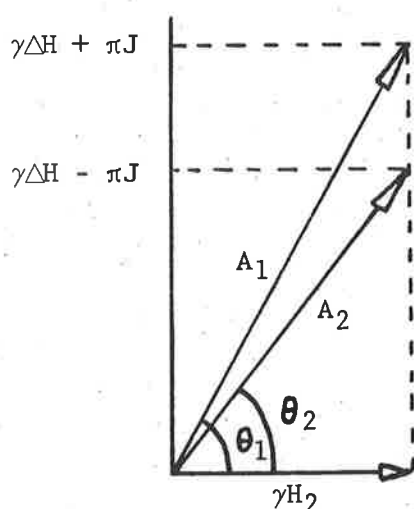
Dear Barry,

You know in your heart these letters are from Varian - the Xerox-insensitive letterheads are used merely to reduce the amount of adverse criticism.

'Telegraphic Transmissions over Record Distances?'

Several years ago some double resonance experiments were started in this laboratory involving the transfer of modulation information through nuclear spin-spin coupling [W. A. Anderson, J. Chem. Phys. 37, 1373 (1962)]. Since then the theory and experiment have evolved sufficiently to show reasonable agreement, and at last the story has been written up for J. Chem. Phys. A few ponderous preprints are available (surface mail only).

Consider a group of nuclear spins ($I = \frac{1}{2}$) coupled through JIS to a second group of spins ($S = \frac{1}{2}$) that are irradiated with an rf field H_2 which may be modulated either in frequency (FM) or in amplitude (AM) at an angular frequency ω_m . For economy of space and frames of reference, let us consider here only a simple-minded pictorial description of the experiment. In a



frame of reference rotating about OZ at a frequency ω_2 , the two S transitions will experience effective fields A_1 and A_2 , where $A_1 - A_2$ is the splitting between the two S lines and (because of the repeated spacing rules) also the splitting between the two I lines. (When $H_2 \rightarrow 0$ or when ΔH becomes very large, $A_1 - A_2 = J$.) This is one way of visualizing how irradiation of the S spins causes the I doublet to coalesce. Now in modulated double resonance a sinusoidal variation of ΔH (in FM) or of H_2 (in AM) causes a modulation of the angles θ_1 and θ_2 ; that is,

the precessing S spins nutate at a frequency ω_m . The quantity $A_1 - A_2$ is similarly modulated and thus modulates the frequencies of the I transitions. This is really a selective modulation of the magnetic field, since only those nuclei that are coupled to the S spins are affected. We might define an 'effective modulation index' for this process, and although it may turn out



- 2 -

to be a rather small quantity, it may be compensated by the use of a fairly strong observing rf field H_1 .

The technique can be used to transmit rude messages over a distance of approximately 1 Å (so far no replies have been received), but perhaps a more useful application is in a device that might be called a ' C^{13} filter'. The spectrometer is operated on a modulation sideband response with synchronous detection, but no modulation is applied to the static field H_0 , and cross-modulation of the two radiofrequencies is scrupulously avoided. Consequently, when the C^{13} nucleus is irradiated with a modulated H_2 , the only protons which receive modulation information are those coupled to C^{13} , and there is strong rejection of the 'normal' proton spectrum. The filter may be used in two ways. In one sweep mode it is possible to record the complete C^{13} satellite spectrum with the multiplets due to long-range C^{13} -H coupling clearly revealed. Other experiments, where ω_2 is swept through the C^{13} spectrum at constant ω_1 , give a fairly accurate measure of the C^{13} shift that may be related to the resonance frequency of protons in TMS in the same applied field. This is just a spin decoupling experiment in which the displacements of the proton lines can be followed without interference from the inherently strong signals from C^{12} molecules, and in this sense may be likened to the experiment of V. Royden [Phys. Rev. 96, 543 (1954)] on a C^{13} -enriched sample of methyl iodide. The modulation transfer technique benefits from the high gyromagnetic ratio of protons and their more favorable relaxation times, accepting the restriction of 1.1% natural abundance.

Applied to molecules that contain the appropriate 'triangle' of coupling constants, the method measures the 'effective chemical shifts' of C^{13} and H^1 for a particular spin state of a third nucleus. For example inspection of the modulated double resonance spectrum of $C^{13}H_3CH_2OEt$ indicates that the sign of $J(HH)$ is the same as that of $J(C^{13}H)$, but opposite to that of $J(C^{13}CH)$. It also demonstrates that ether is a suitable medium for the transmission of electromagnetic waves.

Sincerely yours,

W. A. Anderson

W. A. Anderson

Ray Freeman

R. Freeman

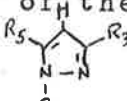
THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY • INDIANAPOLIS 6, U.S.A. • 317-MELROSE 6-2211

October 8, 1964

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

Dear Dr. Shapiro:

We have found an additive relationship for calculating the chemical shift of the 4-proton in 1, 3, 5-tri-substituted pyrazoles, . The relationship takes

the form: $\delta_{4H} = \delta_{4H}(S) + \alpha_1 + \alpha_3 + \alpha_5$ (1) where $\delta_{4H}(S)$ is the shift of 1, 3, 5-trimethyl pyrazole in a particular solvent, S; α_1 , α_3 , and α_5 are empirical constants representing the effect of replacing a CH_3 group by another group at positions 1, 3, and 5, respectively. $\delta_{4H}(S)$ for CDCl_3 is 5.79 ppm.

Enough data are available to obtain α values for the following substituents:

	α_1	α_3	α_5
$-\text{CH}_3$	0	0	0
$-\text{C}_2\text{H}_5$	0.03	0.02	0.02
$-\text{H}$	0.03	0.21	0.23
$-\text{C}_6\text{H}_5$	0.22	0.51	0.30
$-\text{CO}_2\text{Me}$	(0.19)	0.73	0.79
$-\text{CO}_2\text{Et}$	0.20	0.76	0.83
$-\text{CO}_2\text{nPr}$	(0.20)	0.77	0.84
$-\text{CO}_2\text{H}$	Unstable	0.84	0.99
$-\text{CH}_2\text{CO}_2\text{Et}$	0.08	-	-
$-\text{COC}_6\text{H}_5$	0.28	-	-
$-\text{CONHCH}_3$	0.09	-	-
$\text{mNO}_2-\text{C}_6\text{H}_4-$	0.28	-	-
$\text{mNH}_2\text{C}_6\text{H}_4-$	-0.05	-	-

Numbers in parentheses for α_1 were not determined empirically, but were estimated from other members of the series.

A. Agreement with measured δ values.

Equation (1) has been tested with twenty-one N-CH_3 compounds as well as three $\text{N-C}_2\text{H}_5$, three N-phenyl , and two each of

Dr. Shapiro

- 2 -

Oct. 8, 1964

N-CO₂Et, N-benzoyl and N-CH₂CO₂Et. The relationship readily distinguishes the isomers produced by reversing the substituents at the 3 and 5 positions. Agreement of calculated with observed shift values is ± 0.01 ppm. in practically all of the examples tested. No deviations greater than ± 0.03 ppm. occurred.

A similar calculation of 4-proton shifts in N-H pyrazoles indicates that certain N-H pyrazoles occur predominantly in one of the two possible tautomeric forms. These 3-phenyl compounds are precisely those adjudged as such by von Auwers⁽¹⁾, using molecular refraction data.

B. Some interpretations of α values

The values of α_1 form a consistent pattern, in consideration of their respective Hammett σ constants. The effect of R₁ is thus primarily inductive. Magnetic anisotropic effects on the 4-proton by substituents at the 1-position are small due to the distances separating the 4-proton from the 1-substituents. Changes in electron density at the 4-carbon by varying the 1-substituent (for any fixed 3,5 substituents) seem to be accurately reflected in the 4-proton chemical shift. This relationship is being investigated by molecular orbital calculations in our laboratory.

Magnetic anisotropic effects on the 4-proton by 3,5 substituents are discernable. The general trend for α_5 to be slightly larger than α_3 , is clearly reversed for the phenyl group. Also of interest are the relative effects of H, CH₃, and C₂H₅. The inductive effects (α_1) for these three are approximately the same. In contrast a CH₃ or C₂H₅ group at the 3 or 5 position moves an adjacent 4-proton ~ 0.22 and ~ 0.20 ppm. upfield as compared with the H atom at the 3 or 5 position.

C. Solvent effects

The position of the 4-proton is very stable with respect to dilution in CCl₄ and CDCl₃. The 4-proton occurs consistently at lower field in CDCl₃ by 0.13 ± 0.01 ppm. as compared to CCl₄. Preliminary results suggest that DMSO as the solvent shifts the 4-proton 0.06 ppm. higher field from CCl₄. Thus the term $\delta_{4H}(S)$ may have an additive solvent dependence as:

$$\delta_{4H}(S) = \delta_{4H}(\text{ref.}) + \beta(\text{solvent}) \quad (2)$$

Finar and Mooney⁽²⁾ noted an essentially constant downfield shift of 0.73 ± 0.03 ppm. for the 4-proton positions on acidification in TFA. This large shift is readily included as a solvent-ionic charge effect in equation (2).

D. Other pyrazole protons

An attempt was made to find a simple equation for calculating the 3 or 5 proton shifts in several substituted pyrazoles. No such relationship was found for either 3 or 5 protons.

In the N-H pyrazoles, the N-H shift is found to be concentration dependent. The dimeric N-H (concentrated solutions) is found near 13 ppm; the monomeric N-H obtained upon dilution is somewhere higher field than 7 ppm. It is very broad at 0.05 M solution in CDCl₃ or CCl₄.

Oct. 8, 1964

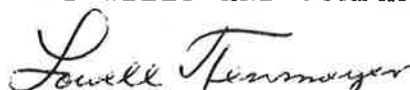
E. Conclusion

With the tabulated α constants and equation (1), the 4-proton shift can be calculated for some 600 compounds in several solvents. The concept is thus subject to extensive testing.

This report is intended to meet the subscription requirements of Paul Landis for Eli Lilly and Co. It was accomplished in co-operation with Cameron Ainsworth, with the excellent help of John Klemm, Larry Spangle, and Paul Landis.

Yours very truly,

ELI LILLY AND COMPANY



Lowell G. Tensmeyer
Chemical Research Division

jb

- (1) K. von Auwers, Ann. 508, 51 (1933)
- (2) I. L. Finar and E. F. Mooney, Spectrochimica Acta, 20, 1269 (1964)

"Synthesis of four Ethyl-dimethylbenzenetriols in Relation to a new Phenolic Metabolite of Penicillium baarnense"
I. Ljungerantz and K. Mosbach
Acta Chem. Scand. 18, 638 (1964)

"Bacterial Carotenoids. XIV. The Carotenoids of Rhodomicrobium vanniellii"
L. Ryvarden and S. L. Jensen
Acta Chem. Scand. 18, 643 (1964)

"Formation of the 1-Thia-2-selena-cyclopentane Ring System from the Thiacyclobutane Ring"
A. Biezaïs and G. Bergson
Acta Chem. Scand. 18, 815 (1964)

"The Genometrical Structure of 3- β -Indolylacrylic Acid"
C. Rappe
Acta Chem. Scand. 18, 818 (1964)

"Isolation from Birch Wood of an Aliphatic Oligoterpene Alcohol, a Methyl Ester of a Hydroxy-triterpene Carboxylic Acid and a Triterpene Alcohol"
B. O. Lindgren
Acta Chem. Scand. 18, 836 (1964)

"Spin Echoes and their Application"
N. M. Pomerantsev
Adv. Phys. Sci.(USSR)(English Transl.) 65, 94 (1958)

"Kupfersalz-Katalysierte Homologisierung von Benzolderivaten mit Diazomethan zu Cycloheptatrien-Derivaten"
E. Müller, H. Kessler, H. Fricke und W. Kiedaisch
Ann. Chem. 675, 63 (1964)

"Zur Kenntnis atherischer Ole, III. Die α -Verbindungen Acyclischer Monoterpene"
G. Ohloff, J. Seibl und E. sz. Kováts
Ann. Chem. 675, 83 (1964)

"Dehydrierung von Steroiden, IX. Abhängigkeit der Dehydrierung mit Chinonen vom Chinon, Reaktionsmilieu und Steroid"
H. Dannenberg und H.-G. Neumann
Ann. Chem. 675, 109 (1964)

"Application de la Spectrographie R.M.N. à l'Attribution de Configuration Géométrique: Styrenes Substitués"
M. Barbieux, N. Defay, J. Pecher et R. H. Martin
Bull. Soc. Chim. Belg. 73, 716 (1964)

"N. M. R. Experiments on Ketals. Part II. A New Possibility for Conformational Analysis"
M. Anteunis
Bull. Soc. Chim. Belg. 73, 731 (1964)

"A Remark on the Isotope Shift in Nuclear Magnetic Shielding"
A. Saika and H. Narumi
Can. J. Phys. 42, 1481 (1964)

"Nuclear Magnetic Resonance in Metal Single Crystals. I. Tin and Aluminum"
E. P. Jones and D. L. Williams
Can. J. Phys. 42, 1499 (1964)

"The Nuclear g Factor of the First Excited State of Pt¹⁹²"
J. A. Cameron
Can. J. Phys. 42, 1680 (1964)

"Polyacetylenverbindungen, LXII. Über natürlich vorkommende Thiophenacetylenverbindungen"
F. Bohlmann, K.-M. Kleine und C. Arndt
Chem. Ber. 97, 2125 (1964)

"Polyacetylenverbindungen, LXIII. Über neue Polyine aus dem Tribus Heliantheae"
F. Bohlmann, H. Bornowski und K.-M. Kleine
Chem. Ber. 97, 2135 (1964)

"Über methylenierte Metallhalogenide, IV. Cyclopropan-Bildung aus Olefinen mit Bis-halogenmethyl-zink"
G. Wittig und F. Wingler
Chem. Ber. 97, 2146 (1964)

"Beiträge zur Chemie des Bors, XXX. Zur Kenntnis von monomerem Bis(dimethylamino)-diäthylphosphino-boran"
H. Nöth und W. Schrägle
Chem. Ber. 97, 2218 (1964)

"endo- und exo- Δ^3 -Norcaren-carbonsäure-(7)"
H. Misso und U. Biethan
Chem. Ber. 97, 2282 (1964)

"Über Kurchi-Alkaloide, VI. Die Strukturaufklärung des Holonamins"
R. Tschesche und H. Ockenfels
Chem. Ber. 97, 2326 (1964)

"Acid-catalysed Hydrogen Exchange of Pyridine 1-Oxides"
A. R. Katritzky, B. J. Ridgwell and A. M. White
Chem. Ind. 1576 (1964)

"Dimethyl Acetylenedicarboxylate—Indene Adduct: A Novel Diels-Alder Reaction"
K. W. Muir, G. A. Sim, P. Strachan and C. F. Huebner
Chem. Ind. 1581 (1964)

"Expérience de Mesure Absolue de la Polarisation Nucléaire dans une Cible de Grande Dimension."'
M. Chapellier
Compt. Rend. 259, 112 (1964)

"Effets de Solvants sur la Largeur des Bandes d'Absorption Infrarouge et sur le Déplacement Chimique en Résonance Magnétique Nucléaire"
P. Jouve, M. Teulier et G. Lévi
Compt. Rend. 259, 119 (1964)

"Quelques Nouveaux Composés Présentant une Bande d'Absorption γ (P-H) double Vers $2\ 350\text{ cm}^{-1}$ "
D. Houalla et R. Wolf
Compt. Rend. 259, 180 (1964)

"Polarisation Dynamique des Noyaux de Fluor d'un Liquide Baignant un Charbon"
J.-P. Grivet
Compt. Rend. 259, 776 (1964)

"Étude par Résonance Magnétique Nucléaire de gaz Hydrogénés Adsorbés sur un Charbon"
J. Conard
Compt. Rend. 259, 1107 (1964)

"Époxyhexanes 2.3 cis et trans et Hexanes Diols 2.3 Érythro et Théo"
D. Gagnaire et P. Monzeglio
Compt. Rend. 259, 1128 (1964)

"Résonance Magnétique Nucléaire de ^{201}Hg , Aligné par Pompage Optique en Utilisant la Raie 1850 Å "
I. M. Popescu et L. N. Novikov
Compt. Rend. 259, 1321 (1964)

"Long Range Coupling in Some Cyclic Compounds"
C. R. Narayanan and N. K. Venkatasubramanian
Indian J. Chem. 2, 274 (1964)

- "Proton Magnetic Resonance Study of the Structure of Manganous Sulphate Tetrahydrate"
C. R. Rao
Indian J. Pure Appl. Phys. 2, 172 (1964)
- "The Proton Nuclear Magnetic Resonance Spectra of Silicon Analogs of Simple Ethyl Compounds."
C. H. Van Dyke and A. G. Mac Diarmid
Inorg. Chem. 3, 1071 (1964)
- "Boron-Nitrogen Compounds. XVI. Some New Boron-Nitrogen Heterocycles"
K. Niedenzu, P. Fritz and J. W. Dawson
Inorg. Chem. 3, 1077 (1964)
- "Disilanylphosphine and Disilylphosphine"
S. D. Gokhale and W. L. Jolly
Inorg. Chem. 3, 1141 (1964)
- "A Study of the Reaction of Boric Acid with Amines: Hydroxyboroxin-Amine Salts"
B. D. Vineyard and H. C. Godt, Jr.
Inorg. Chem. 3, 1144 (1964)
- "Raman, Infrared, and Nuclear Magnetic Resonance Spectroscopic Studies on Aqueous Solutions of Dimethyltin(IV) Compounds: Structure and Bonding of the Aquodimethyltin Ion"
M. M. McGrady and R. S. Tobias
Inorg. Chem. 3, 1157 (1964)
- "Synthesis and Characterization of Fluorimododisulfuryl Fluoride, $(\text{FSO}_2)_2\text{NF}$, and Difluoramidosulfuryl Fluoride, FSO_2NF_2 "
M. Lustig, C. L. Bumgardner, F. A. Johnson and J. K. Ruff
Inorg. Chem. 3, 1165 (1964)
- "Chemistry of Boranes. XIII. Chloromethyltrimethylamino Derivatives of B_{10}^{-2} and $\text{B}_{12}\text{H}_{12}^{-2}$ "
W. R. Hertler
Inorg. Chem. 3, 1195 (1964)
- "Chemistry of Boranes. XVI. A New Heterocyclic Boron Compound"
N. E. Miller and E. L. Muetterties
Inorg. Chem. 3, 1196 (1964)
- "Reactions of Triethylamine with Copper Halides. II. Internal Oxidation-Reduction of Dichlorobis(triethylamine)-copper(II)"
J. F. Weiss, G. Tollin and J. T. Yoke, III
Inorg. Chem. 3, 1344 (1964)
- "Chemistry of Boranes. XVIII. Oxidation of $\text{B}_{10}\text{H}_{10}^{-2}$ and its Derivatives"
B. L. Chamberland and E. L. Muetterties
Inorg. Chem. 3, 1450 (1964)
- "Long-Range Effect of an Asymmetric Grouping on the Magnetic Equivalence of Methylene Group Protons"
J. C. Randall, J. J. McLeskey, III, P. Smith and M. E. Hobbs
J. Am. Chem. Soc. 86, 3229 (1964)
- "Vibrational Assignment for cis- and trans-1,2-Dichloro-1-fluoroethylenes: $\text{FClC}=\text{CClH}$ and $\text{FClC}=\text{CClD}$ "
W. C. Craig, G. Y. Lo, C. D. Needham and J. Overend
J. Am. Chem. Soc. 86, 3232 (1964)
- "Novel Acetylene Tungsten Carbonyl Complexes"
D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross and J. G. Grasselli
J. Am. Chem. Soc. 86, 3261 (1964)
- "Preparation and Properties of Some Duroquinone π -Complexes of Cobalt, Rhodium, and Iridium"
G. N. Schrauzer and K. C. Dewhirst
J. Am. Chem. Soc. 86, 3265 (1964)
- "Mechanisms of α -Elimination. Nitrobenzylsulfonium, -ammonium, and -phosphonium Ions Reacting with Aqueous Hydroxide"
I. Rothberg and E. R. Thornton
J. Am. Chem. Soc. 86, 3296 (1964)
- "Photochemical Transformations of 1,5-Cyclooctadiene"
R. Srinivasan
J. Am. Chem. Soc. 86, 3318 (1964)
- "The Synthesis of Three Monodeuterionorbornanes, and the Stereochemistry of Acid-Catalyzed Cleavage of Nortricyclene"
A. Nickon and J. H. Hammons
J. Am. Chem. Soc. 86, 3322 (1964)
- "Synthesis and Study of Pseudoaromatic Compounds. I. The Synthesis of 8-Vinylheptafulvene"
D. J. Bertelli, C. Golino and D. L. Dreyer
J. Am. Chem. Soc. 86, 3329 (1964)
- "Stereochemical Evidence for Bridged Radicals. Photobromination of cis- and trans-4-Bromo-t-butylcyclohexane"
P. S. Skell and P. D. Readio
- "Stereochemical Assignments for β -Ketols Formed by Aldol Addition of Three Simple Ketones to p-Nitrobenzaldehyde"
M. Stiles, R. R. Winkler, Y.-L. Chang and L. Traynor
J. Am. Chem. Soc. 86, 3337 (1964)
- "Synthesis and Stereochemistry of Indolizidine and Pyrrolizidine Methosalts"
W. L. Meyer and N. Sapianchiay
J. Am. Chem. Soc. 86, 3343 (1964)
- "Structural Studies by Nuclear Magnetic Resonance. VIII. Ring-Substituted Phenylhydrazones, Semicarbazones, and Thiosemicarbazones"
G. J. Karabatsos, F. M. Vane, R. A. Taller and N. Hsi
J. Am. Chem. Soc. 86, 3351 (1964)
- "Calabash Curare Alkaloids. Specific Deuterium Labeling and Nuclear Magnetic Resonance Studies"
M. Grdinic, D. A. Nelson and V. Boekelheide
J. Am. Chem. Soc. 86, 3357 (1964)
- "The Nuclear Magnetic Resonance Spectra of the Angular Proton in Benzofuran- and Indolofuran-quinolizidines"
M. Uskokovic, H. Bruderer, C. von Planta, T. Williams and A. Bossi
J. Am. Chem. Soc. 86, 3364 (1964)
- "Coenzyme Q. LVI. Novel Cyclization of Quinones to Chromanols and Possible Iron-Coenzyme Q Complexes"
H. W. Moore and K. Folkers
J. Am. Chem. Soc. 86, 3393 (1964)
- "Dimerization of Cyclooctatetraene. I. Structure of the 'Three Double Bond' Dimer"
H. W. Moore
J. Am. Chem. Soc. 86, 3398 (1964)
- "Chemistry of Boranes. XIV. Amination of $\text{B}_{10}\text{H}_{10}^{-2}$ and $\text{B}_{12}\text{H}_{12}^{-2}$ with Hydroxylamine-O-sulfonic Acid"
W. R. Hertler and M. S. Raasch
J. Am. Chem. Soc. 86, 3661 (1964)
- "Steric Effect on Deshielding of the Aromatic C_4 -Proton by a C_5 -Proton in an Octahydrophenanthrene Series"
W. Nagata, T. Terasawa and K. Tori
J. Am. Chem. Soc. 86, 3746 (1964)
- "Small-Ring Compounds. XLI. The Formolysis of Allylcarbinyl Tosylate"
K. L. Servis and J. D. Roberts
J. Am. Chem. Soc. 86, 3773 (1964)

"Organic Sulfur Compounds. XIV. Oxidative Addition of Thiol Acids to Unsaturated Hydrocarbons. Cooxidation of Thio-lacetic Acid and Indene by Molecular Oxygen"
A. A. Oswald, K. Griesbaum and W. Naegele
J. Am. Chem. Soc. 86, 3791 (1964)

"Photochemical and Thermal Valence Tautomerization of 2,3-Diphenylindenone Oxide. II."
E. F. Ullman and J. E. Miles
J. Am. Chem. Soc. 86, 3814 (1964)

"General Base Catalyzed Ethanolysis of Ethyl Trifluoroacetate"
S. L. Johnson
J. Am. Chem. Soc. 86, 3819 (1964)

"The Effect of Methylmercapto, Methylsulfinyl, and Methylsulfonyl Groups on the Equilibrium in Three-Carbon Prototropic Systems"
D. E. O'Connor and W. I. Lyness
J. Am. Chem. Soc. 86, 3840 (1964)

"The Reactions of Aroyl Halides with Phosphites. Esters of Aroylphosphonic Acids"
K. Darrell Berlin and H. A. Taylor
J. Am. Chem. Soc. 86, 3862 (1964)

"Spin-Spin Coupling in Binuclear Complexes"
W. E. Hatfield and J. S. Paschal
J. Am. Chem. Soc. 86, 3888 (1964)

"Thionosulfites. A New Class of Cyclic Esters Containing Branch-Bonded Sulfur"
Q. E. Thompson, M. M. Crutchfield and M. W. Dietrich
J. Am. Chem. Soc. 86, 3891 (1964)

"Solvent Effects on the C¹³ Chemical Shift of the Substituted Carbon Atom of Phenol"
G. E. Maciel and R. V. James
J. Am. Chem. Soc. 86, 3893 (1964)

"Formation and Capture of a Reactive Intermediate Related to Dimethylpseudoindene"
J. A. Berson and M. Pomerantz
J. Am. Chem. Soc. 86, 3896 (1964)

"Paracyclophanes. IV. A Multilayered [2.2]₂Paracyclophane"
D. T. Longone and H. S. Chow
J. Am. Chem. Soc. 86, 3898 (1964)

"Isolation of Tetramethylcyclopropanone Ethyl Hemiketal from Photolysis of Tetramethylcyclobutanedione"
H. G. Richey, Jr., J. M. Richey and D. C. Clagett
J. Am. Chem. Soc. 86, 3906 (1964)

"Steroid Synthesis Based on Oxonium Intermediates. I. Application to 20-Ketosteroids"
J. P. Dusza, J. P. Joseph and S. Bernstein
J. Am. Chem. Soc. 86, 3908 (1964)

"Electron Donor Ability of 7-Oxabicyclo[2.2.1]heptane"
M. Tamres, S. Searles, Jr. and J. M. Goodenow
J. Am. Chem. Soc. 86, 3934 (1964)

"Studies on Nickel(II) Complexes. VII. A Nuclear Resonance Investigation of Mixed Ligand Complexes"
A. Chakraborty and R. H. Holm
J. Am. Chem. Soc. 86, 3999 (1964)

"Steroids. CCLX. Spectra and Stereochemistry. XV. A Survey of Long-Range Proton-Fluorine Coupling in Fluorosteroids"
A. D. Cross and P. W. Landis
J. Am. Chem. Soc. 86, 4005 (1964)

"Steroids. CCLXII. Spectra and Stereochemistry. XVI. A Study of the Mechanism of Long-Range 19-Proton-6 β -Fluorine Coupling in 6 β -Fluorosteroids"
A. D. Cross
J. Am. Chem. Soc. 86, 4011 (1964)

"Substituent Effects on Nuclear Magnetic Resonance Chemical Shifts in *para*-Substituted Phenylhexachlorobicyclo[2.2.1]heptenes and Ethylbenzenes"
K. L. Williamson, N. C. Jacobus and K. T. Soucy
J. Am. Chem. Soc. 86, 4021 (1964)

"Nuclear Magnetic Resonance Spectra of Substituted Ethanes. II. *meso*- and *dl*-2,5-Diphenylhexanediol-2,5"
D. Jung and A. A. Bothner-By
J. Am. Chem. Soc. 86, 4025 (1964)

"Mechanistic and Exploratory Organic Photochemistry. IX. Phenyl Migration in the Irradiation of 4,4-Diphenylcyclohexenone"
H. E. Zimmerman and J. W. Wilson
J. Am. Chem. Soc. 86, 4036 (1964)

"Carbenoid Formation of Arylcyclopropanes from Olefins, Benzal Bromides, and Organolithium Compounds and from Photolysis of Aryldiazomethanes"
G. L. Closs and R. A. Moss
J. Am. Chem. Soc. 86, 4042 (1964)

"The Photochemical Properties of a 2-Methyl-1,4-dien-3-one"
P. J. Kropp
J. Am. Chem. Soc. 86, 4053 (1964)

"The Addition of Nitrosyl Halides to Olefins. Dependence of Steric Course on Olefin Structure"
J. Meinwald, Y. C. Meinwald and T. N. Baker, III.
J. Am. Chem. Soc. 86, 4074 (1964)

" α -Halosulfones. I. Conformational Requirements of α -Sulfonyl Carbanions in the Synthesis of Phenanthrenes from 2-Chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-Dioxides"
L. A. Paquette
J. Am. Chem. Soc. 86, 4085 (1964)

"Unsaturated Heterocyclic Systems. IX. Derivatives of 3H-Azepine"
L. A. Paquette
J. Am. Chem. Soc. 86, 4096 (1964)

"Cumulative Influence of Dimethylamino Groups on the π -System Properties of Aromatic Hydrocarbons"
A. Zweig, J. E. Lancaster, M. T. Neglia and W. H. Jura
J. Am. Chem. Soc. 86, 4130 (1964)

"1-Arylisoindoles"
D. F. Veber and W. Lwowski
J. Am. Chem. Soc. 86, 4152 (1964)

"The Reaction of Methyl 2,3-Anhydro-D-ribofuranosides with Thiocyanate Ion"
L. Goodman
J. Am. Chem. Soc. 86, 4167 (1964)

"Interaction and Association of Bases and Nucleosides in Aqueous Solutions. III. A Nuclear Magnetic Resonance Study of the Self-Association of Purine and 6-Methylpurine"
S. I. Chan, M. P. Schweizer, P. O. P. Ts'o and G. K. Helmkamp
J. Am. Chem. Soc. 86, 4182 (1964)

"Stable Carbonium Ions. VIII. The 1-Adamantyl Cation"
P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. E. Comisarow and G. A. Olah
J. Am. Chem. Soc. 86, 4195 (1964)

"A Quantitative Scale of Acceptor Strengths from Fluorine Nuclear Magnetic Resonance Shielding"
R. W. Taft and J. W. Carten
J. Am. Chem. Soc. 86, 4199 (1964)

- "Structural Identification of a Geometric Isomer of Tetrameric Phenylphosphonitric Chloride"
B. Grushkin, J. L. McClanahan, and R. G. Rice
J. Am. Chem. Soc. 86, 4204 (1964)
- " α -Elimination in 2-Phenyltetrachloropropene. Synthesis of Phenylhydroxycyclopropenone"
D. G. Farnum and P. E. Thurston
J. Am. Chem. Soc. 86, 4206 (1964)
- "The Solvolysis of 7-anti-Bromo-2-exo-benzenesulfonamido-bicyclo[2.2.1]heptane. An Example of Solvolytic Ring Opening."
L. H. Zalkow and A. C. Oehlschlager
J. Am. Chem. Soc. 86, 4208 (1964)
- "2,3-Dimethyl-7,7-dimethoxyquadricyclo-[2.2.1.0^{2,6}.0^{3,5}]heptane"
P. G. Gassman, D. H. Aue and D. S. Patterson
J. Am. Chem. Soc. 86, 4211 (1964)
- "Chemical Studies on Lincomycin. I. The Structure of Lincomycin"
H. Hoeksema, B. Bannister, R. D. Birkenmeyer, F. Kagan, B. J. Magerlein, F. A. Mackellar, W. Schroeder, G. Slomp and R. R. Herr
J. Am. Chem. Soc. 86, 4223 (1964)
- "Celesticetin. IV. The Structure of Celesticetin"
H. Hoeksema
J. Am. Chem. Soc. 86, 4224 (1964)
- "Nuclear Magnetic Resonance and Optical Spectroscopy of $[Co(MeOH)_5Cl]^{+}$ in Methanol and the Kinetics of Methanol Exchange of the Solvation Shell"
Z. Luz
J. Chem. Phys. 41, 1748 (1964)
- "Nuclear Magnetic Resonance Study of Cobalt-Chlorine Complexes in Methanol"
Z. Luz
J. Chem. Phys. 41, 1756 (1964)
- "NMR Studies of Asymmetric Ethnic Rotators: 1,2-Disubstituted Propanes"
H. Finegold
J. Chem. Phys. 41, 1808 (1964)
- "Nuclear Magnetic Relaxation in Camphor"
J. E. Anderson and W. P. Slichter
J. Chem. Phys. 41, 1922 (1964)
- "NMR Study of Rotational Barriers and Conformational Preferences. II. d_{11} -Cyclohexane"
F. A. Bovey, F. P. Hood III, E. W. Anderson and R. L. Kornegay
J. Chem. Phys. 41, 2041 (1964)
- "Anisotropic Proton Hyperfine Interaction in the CH Bond"
J. Higuchi
J. Chem. Phys. 41, 2084 (1964)
- "Computer Analysis of NMR Spectra: Magnetic Equivalence Factoring"
R. C. Ferguson and D. W. Marquardt
J. Chem. Phys. 41, 2087 (1964)
- "NMR Spectra of ClF_3 and ClF : Gaseous Spectra and Gas-to-Liquid Shifts"
L. G. Alexakos and C. D. Cornwell
J. Chem. Phys. 41, 2098 (1964)
- "Remarks on the Determination of Electric Dipole Moments from Rotational Magnetic Moments. The Dipole Moment of Hydrogen Fluoride"
S. I. Chan and D. Ikenberry and T. P. Das
J. Chem. Phys. 41, 2107 (1964)
- "Spin-Echo NMR Studies of Chemical Exchange. I. Some General Aspects"
A. Allerhand and H. S. Gutowsky
J. Chem. Phys. 41, 2115 (1964)
- "Isotropic Proton Resonance Shifts of Some Bis-(triaryl-phosphine) Complexes of Cobalt(II) and Nickel(II) Dihalides"
G. N. La Mar, W. DeW. Horrocks, Jr. and L. C. Allen
J. Chem. Phys. 41, 2126 (1964)
- "NMR Study of Iodine Complexes"
A. Fratiello
J. Chem. Phys. 41, 2204 (1964)
- "Aspects of Stereochemistry. Part XVII. Behavior of 1,2:5,6-Di-O-isopropylidene-3,4-di-O-toluene-p-sulphonyl-D-mannitol on Benzoate Exchange"
M. A. Bukhari, A. B. Foster and J. M. Webber
J. Chem. Soc. 2514 (1964)
- "Photochemical Transformations. Part XV. Synthetic Studies on Geigerin and its Derivatives"
D. H. R. Barton, J. T. Pinhey and R. J. Wells
J. Chem. Soc. 2518 (1964)
- "Studies on Sesquiterpenoids. Part VI. Synthesis of 3,5,8-Trimethylazuleno[6,5-b]furan (Linderazulene)"
K. Takeda, H. Minato and M. Ishakawa
J. Chem. Soc. 2591 (1964)
- "Syntheses of Heterocyclic Compounds. Part VIII. Cyclisation of N-2-Acylaminophenyl Heterocycles with Polyphosphoric Acid"
O. Meth-Cohn and H. Suschitzky
J. Chem. Soc. 2609 (1964)
- "The Structure of Pyoluteorin"
A. J. Birch, P. Hodge, R. W. Rickards, R. Takeda and T. R. Watson
J. Chem. Soc. 2641 (1964)
- "Transition-metal Fluorocarbon Complexes. Part V. Tetrakis-(trifluoromethyl)cyclopentadienone and Some Related Fluorocarbon Complexes of Rhodium"
R. S. Dickson and G. Wilkinson
J. Chem. Soc. 2699 (1964)
- "The Constitution of Gmelinol. Part IV. Stereochemistry and Relationships to Other Lignans"
A. J. Birch and M. Smith
J. Chem. Soc. 2705 (1964)
- "The Conversion of Gmelinol into Neogmelinol"
A. J. Birch, B. Moore, E. Smith and M. Smith
J. Chem. Soc. 2709 (1964)
- "Dinuclear Phosphorus and Arsenic Bridged Carbonyl Compounds. Part II."
J. Chatt and D. T. Thompson
J. Chem. Soc. 2713 (1964)
- "Proton Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Transition-metal Hydrides: Octahedral Complexes"
A. D. Buckingham and P. J. Stephens
J. Chem. Soc. 2747 (1964)
- "Alkaloid Studies. Part XLV. Mass Spectroscopy in Structural and Stereochemical Problems. Part XLIII. Some Aspects of the Chemistry and Mass Spectrometry of Uleine"
J. A. Joule and C. Djerassi
J. Chem. Soc. 2777 (1964)
- "2-Hydroxy-3-methyl- and 3-Hydroxy-2-methyl-1,4,6-triazanaphthalene: A Correction"
J. W. Clark-Lewis and R. P. Singh
J. Chem. Soc. 2825 (1964)

"1-Benzyl-3-methylnaphthalene from Benzyl Methyl Ketone"
L. A. Cort, R. G. Manders and G. R. Parlett
J. Chem. Soc. 2844 (1964)

"The cis-Forms of 2-Methoxycyclohexanol and 2-Methoxy-cyclopentanol"
K. W. Buck, A. B. Foster, A. Labib and J. M. Webber
J. Chem. Soc. 2846 (1964)

"Proton Magnetic Resonance Studies of Hydrogen Bonding of 2-Propanol with N-Methylacetamide and N,N'-Dimethylacetamide"
F. Takahashi and N. C. Li
J. Phys. Chem. 68, 2136 (1964)

"Hydrogen Bonding Studies of N-Methylacetamide and Some Thiols"
R. Mathur, S. M. Wang and N. C. Li
J. Phys. Chem. 68, 2140 (1964)

"The Dipole Moment of Trifluoronitrosomethane"
J. E. Boggs, D. Coffey, Jr. and J. C. Davis, Jr.
J. Phys. Chem. 68, 2383 (1964)

"Aluminum-27 Nuclear Magnetic Resonance Studies of Triethyl-aluminum Complexes"
H. E. Swift, C. P. Poole, Jr. and J. F. Itzel, Jr.
J. Phys. Chem. 68, 2509 (1964)

"Die Polymerisation von Silicium—Stickstoffverbindungen"
E. G. Rochow
Monatsch. Chem. 95, 950 (1964)

"Nuclear Magnetic Resonance in Paraffin and Wax"
A. Carrelli and E. Ragozzino
Nuovo Cimento 33, 673 (1964)

"Study of the Hydrogen Bond by Nuclear Magnetic Resonance. II. Saturated Amines"
V. F. Bystrov and V. P. Lezina
Opt. Spectr. (USSR) (English Transl.) 16, 430 (1964)

"Investigation of H Bonds Formed by Acetylene Compounds, by Means of NMR Spectroscopy. IV. Interaction of (ene-yne) Ethers and Their Sulfur and Selenium Analogs with Solvents"
N. V. Elsakov and A. A. Petrov
Opt. Spectr. (USSR) (English Transl.) 16, 434 (1964)

"Proton Resonance Study of Antiferromagnetic $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ "
R. D. Spence, R. Au and P. A. Van Dalen
Physica 30, 1612 (1964)

"Nuclear Magnetic Resonance Line Shape of Fluorine in Apatite"
W. Van Der Lugt and W. J. Caspers
Physica 30, 1658 (1964)

"The Shape of the Proton Magnetic Resonance Lines in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Between 4.2 and 35°K "
S. Wittekoek, N. J. Poulis and G. E. Snip
Phys. Letters 11, 282 (1964)

"Magnetic-Resonance Spectra of Mn in Au and Pd"
D. Shaltiel and J. H. Wernick
Phys. Rev. 136, A245 (1964)

"Calculation of Magnetic Hyperfine Constant of P^{31} "
N. Bessis, H. Lefebvre-Brion, C. M. Moser, A. J. Freeman, R. K. Negbet and R. E. Watson
Phys. Rev. 135, A588 (1964)

"Nuclear Magnetic Resonance in Ferrimagnetic MnFe_2O_4 "
A. J. Heeger and T. W. Houston
Phys. Rev. 135, A661 (1964)

"Fast-Passage Effects in the Nuclear Magnetic Resonance of Fe^{57} in Pure Iron Metal"
D. L. Cowan and L. W. Anderson
Phys. Rev. 135, A1046 (1964)

"Bromine Nuclear Magnetic Resonance in Ferromagnetic CrBr_3 "
A. C. Gossard, V. Jaccarino, E. D. Jones, J. P. Remeika and R. Slusher
Phys. Rev. 135, A1051 (1964)

"Low-Field Relaxation and the Study of Ultraslow Atomic Motions by Magnetic Resonance"
C. P. Slichter and D. Ailion
Phys. Rev. 135, A1099 (1964)

"Nuclear Magnetic Resonance Modes in Magnetic Materials. II. Experiment"
G. L. Witt and A. M. Portis
Phys. Rev. 135, A1616 (1964)

"Colchicine"
A. R. Battersby and R. E. Herbert
Proc. Chem. Soc. 260 (1964)

"The Constitutions of Crotonosine, Linearisine, and Homolinearisine"
L. J. Haynes, K. L. Stuart, D. H. R. Barton and G. W. Kirby
Proc. Chem. Soc. 261 (1964)

" ^{19}F Nuclear Magnetic Resonance in Some Paramagnetic Fluorides"
D. Elwell
Proc. Phys. Soc. 84, 409 (1964)

"Silylcarbodiimide. IV. Sila-polycarbodiimide"
J. Pump and E. G. Rochow
Zeit. Anorg. Chem. 330, 101 (1964)