16.Nov.65

Primas (handwritten signature)

Illinois
Institute of
Technology
N – M – R
Newsletter

No. 85
OCTOBER, 1965

Deadline Dates: No. 86 - 18 November 1965
                 No. 87 - 18 December 1965

Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9

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

Your Ref:

Our Ref: PL/PHY-5
Research Department.

21st September, 1965.

Dear Professor Shapiro,

SWEEP MODE DIAGRAM FOR VARIAN HA SYSTEMS

The proton stabilised modes of operation in Varian HA spectrometers employ modulation side-bands generated by two independently variable audio frequency oscillators.   The stabilisation system locks the field to a sideband of the internal reference peak, generated by oscillator No.1.   The spectrum of the sample is then recorded by detecting the side-bands generated by oscillator No.2.   One oscillator has its linear frequency sweep locked to the x-travel of the recorder.   If this oscillator acts as No.1 above a field sweep is produced; if acting as No.2 the frequency sweep mode results. The other oscillator frequency is set by a manual control.

Calculating the manual oscillator setting needed to bring a particular region of the spectrum on to the recorder chart does not always come easily.   The Varian handbook shows a slide-rule that can be used for calculating sweep ranges.   Recently we have done some heteronuclear (N^{14}) spin decoupling experiments using the locked modes, and the calculation of N^{14} chemical shifts from the measured decoupling frequencies required us to think most carefully about the principles involved.   We therefore devised a chart which has the threefold purpose of

(a)   helping us to think clearly about what we are doing when we use HA modes,

(b)   illustrating the principle of operation to new operators or to anyone else interested,

(c)   replacing the slide-rule method, if the chart is accurately drawn.

The diagram is a two-dimensional representation, with magnetic field plotted on the X-axis and frequency on the Y-axis.   The resonance conditions for a nucleus with a particular screening constant are represented by a straight sloping line.   We have shown a family of such lines corresponding to different δ-values; these lines are as near parallel as makes no difference for our purpose, (in fact, if extrapolated, they converge to an origin about 2 miles away).

The HR mode of operation is represented in the centre of the diagram by the horizontal line through O on the Y-axis, indicating the fixed nominal 100 Mc/s operating frequency. The ± 2000 c/s side-band frequencies used in HR mode decoupling experiments are also shown. Sweeping the appropriate field region then gives the spectrum. In the two HA modes, the point to remember when using the diagram is that the control loop automatically fixes the field to the resonance condition of the chosen locking peak at the side-band frequency corresponding to the control channel.

In the Frequency Sweep Mode (top right of diagram) the control channel detects the manual oscillator frequency. The value of this frequency and the choice of locking peak (e.g. TMS) determine the fixed value of the magnetic field. The swept oscillator now generates the spectrum as shown by the vertical black arrow.

In the Field Sweep Mode (bottom left of diagram) the control channel detects the swept oscillator frequency. Depending upon the sweep width and the locking peak chemical shift, a portion of the magnetic field will be swept therefore. The diagram shows TMS as the locking peak with a 1000 c/s swept oscillator scan and the 45° white arrow defines the swept field region (vertical dotted lines). The spectrum channel detects the manual oscillator frequency and the value of this frequency governs the chemical shift range of the observed spectrum (black arrow).

In order to replace the slide-rule method of calculating sweep ranges, two additional charts can be drawn accurately on a larger scale covering the field sweep and frequency sweep regions respectively.

Yours sincerely,

A.Mathias.   P.Hampson.   J.K.Becconsall.

AM/PH/JKB/AYK.

SWEEP MODE CHART FOR HA-100 NMR SPECTROMETER

normal frequency sweep range

+3500

swept oscillator
(spectrum channel)

left

FREQUENCY
SWEEP
MODE

spectrum channel

manual oscillator
(control channel)

+2500

right

+2000

+1500

−10.0 ppm
−7.5 ppm
−5.0 ppm
−2.5 ppm
0.0 ppm (TMS)
+2.5 ppm

frequency
(c/s relative to centreband)

0

centreband resonance

recorder
X-travel

manual
setting

frequencies used for
HR mode operation
(field sweep)

−1500

−1000

−2500

spectrum channel

control channel

FIELD SWEEP
MODE

manual oscillator
(spectrum channel)

right

swept oscillator
(control channel)

−3500

left

normal field
sweep range

field

Calculation of coupling constants.

P.G. Perkins,
Department of Inorganic Chemistry,
University of Newcastle upon Tyne,
England.

Pople and Santry's equation [1] for the reduced coupling constant between atoms A and B, K_{AB} is,

$$K_{AB} = -\frac{256}{9}\pi^2\beta^2[s_A|\delta_{r_A}|s_A][s_B|\delta_{r_B}|s_B]$$
$$\times \sum_L \sum_j \frac{c_{L s_A} c_{j s_A} c_{L s_B} c_{j s_B}}{{}^3\Delta E_{L\to j}}$$

where $S(0)^2_i$ is the electron density at nucleus i and $= [s_L|\delta_{r_L}|s_L]$

$$K_{AB} = \frac{2\pi}{\hbar\gamma_A\gamma_B} J_{AB}$$

Since s-electron density only is important $S_A(0)^2$ and $S_B(0)^2$ may be substituted by the corresponding expressions from the Fermi-Segre equation [2] then,

$$K_{AB} = -\frac{256}{9}\pi^2\beta^2\left[\frac{Z^0_A Z^{*2}_A\left(1-\frac{d\Delta n_A}{dn_A}\right) Z^0_B Z^{*2}_B\left(1-\frac{d\Delta n_B}{dn_B}\right)}{\pi^2 a_0^6 Y^3_{n_A} Y^3_{n_B}}\right]$$

$$\times \sum_L \sum_j \frac{c_{L s_A} c_{j s_A} c_{L s_B} c_{j s_B}}{{}^3\Delta E_{L\to j}}$$

Further since Z_A^* and Z_B^* are the charges of the ions in the potential field of which the electrons move then,

$$z_i^* = z_i^{*0} - \alpha (P_{ii} - 1)$$

$$P_{ii} = \sum_\lambda^i P_{\lambda\lambda} \quad \text{and} \quad P_{\lambda\lambda} = \sum_j n_j c_{j\lambda}^2$$

Z_i^{*0} is the effective nuclear charge taking into account only internal (non-bonding) orbitals. α is the usual Slater shielding constant for electrons in the same shell (0.35 or 0.30).
Thus,

$$K_{AB} = -\frac{256}{9} \beta^2 \left[\frac{Z_A^0 \left(Z_A^{*0} - \alpha (P_{AA} - 1) \right)^2 \left(1 - \frac{d\Delta n_A}{dn_A} \right)}{a_0^3 \gamma_{n_A}^3} \right.$$

$$\times \frac{Z_B^6 \left(Z_B^{*0} - \alpha (P_{BB} - 1) \right)^2 \left(1 - \frac{d\Delta n_B}{dn_B} \right)}{d_0^3 \gamma_{n_B}^3}$$

$$\times \sum_i \sum_j \frac{c_{is_A} c_{js_A} c_{is_B} c_{js_B}}{{}^3\Delta E_{i \to j}}$$

[1] Pople and Santry, Mol. Phys. 8, 1, (1964).
[2] Fermi and Segre, Z. Phys. 82, 729, (1933).

DIVISION OF PHYSICAL CHEMISTRY

THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70
SWEDEN

September 21, 1965

Cable address: Technology

EF/MH

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

Professor Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center

CHICAGO 60616

USA

Dear Dr. Shapiro:

Thank you for your kind reminder of the subscription dues.

In the course of an NMR study of water fixation in cellulose I and II we have found reason to reconsider some of the questions related to the configuration of the poly-saccharide chains and the intrachain hydrogen bonding. Attempting to satisfy the IR demands for full intramolecular hydrogen bonding in the Meyer and Misch[1] straight chain model by means of the very reasonable coupling of the C6 and C2' hydroxyls suggested by Mann and Marrinan[2] we found that an intramolecular strain would preclude the appearance of the bond. To remedy this we decoupled the bridge oxygen between the pyranose rings, relaxing the straight chain condition until the proper C6/C2' hydroxyl distance and bond directions were obtained while retaining the proper valence bond angles and directions of the oxygen and the 4 and 1' carbons. To our surprise and great satisfaction we then found that the C3 hydroxyl had arrived at the proper position for a second intramolecular hydrogen bond with the adjacent ring oxygen as suggested many years ago by Hermans[3] and recently advocated by Liang and Marchessault[4], who try to refute the C6OHOC2' bond on the basis of IR data. For reasons that cannot be elaborated in this letter we believe that both types of bonding are correct, and if by any good fortune these lines should find a reader of a different opinion I would be delighted at the opportunity to present our case and have a peaceful private argument pending the completion of the investigation.

-2-

Starting from our modified chain structure and the associated proton lattice we have made use of the theory of O'Reilly and Tsang[5] to compute the second moment of the cellulose I proton broad band. The theoretical value obtained by R.P. Gupta of our Group for the waterfree lattice amounts to 24.6 $(gauss)^2$ while the preliminary mean of the experimental second moment value at 1.5 % regain is 25.2 $(gauss)^2$. No corrections for thermal motion and random interchain water bridges have so far been made.

Higher moment computations are in progress and any information on O'Reilly-Tsang coupling coefficients for the monoclinic lattice is gratefully received. Lattice coordinates for the model are available on request.

Yours truly,

E. Forslind

References

1. Meyer, K.H.   Helv. Chim. Acta 20, 232, 1937
    Misch, Lore

2. Mann, I.   J. Polymer Sci. 21, 301, 1956
    Marrinan, H.I.

3. Hermans, P.H.   Kolloid Z. 102, 169, 1943

4. Liang, C.Y.   J. Polymer Sci. 37, 385, 1959
    Marchessault, R.H.   43, 71, 1960

5. O'Reilly, D.E.   Phys. Rev. 128, 2639, 1962
    Tsang, Tung

UNIVERSITY OF EXETER

Tel. 77911

Dr. K. G. Orrell

Department of Chemistry,
Stocker Road,
Exeter

8th September, 1965.

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

Dear Professor Shapiro,

I would like to present some results I obtained while at Manchester of some perfluoro (monomethyl piperidine) compounds, which I feel will be of interest to I.I.T.N.M.R. readers. The spectra of the 2-, 3-, and 4-substituted compounds were investigated at 60 Mc/sec at ambient temperature, that of the 2-substituted compound being depicted in the Figure. All three spectra were found to consist of a large number of lines which can only be interpreted as a series of overlapping AB type patterns due to the non-equivalent axial and equatorial fluorines of the $-CF_2-$ groups. This assumes, however, that, unlike perfluoropiperidine[1], these molecules are not rapidly interconverting between their two chair conformations. Furthermore, although there are two possible isomeric forms for each of these compounds, the spectra are compatible with only a single rigid structure in each case. The spectra were essentially unchanged in the temperature range 100 to -90 ^{o}C, thus supporting the suggestion of conformationally rigid structures. The full assignment of the spectral bands is given in Table 1.

It will be observed from the table that the geminal coupling constant values, J_{ae}, are smallest for $-CF_2-$ groups adjacent to the heterocyclic atom. The values for the 3-, 4-, and 5- positions in the ring agree with corresponding values obtained by Homer and Thomas[2] for substituted perfluorocyclohexanes. Whereas the geminal couplings remain virtually constant within the series of compounds, the internal geminal chemical shifts, $(\nu o\delta)_{ae}$, are dependent on the presence and location of the CF_3- substituent. In perfluoropiperidine, $(\nu o\delta)_{ae}$ for the α-fluorines is considerably smaller than for the β- and γ- fluorines. In the substituted compounds, this relative order still holds but the CF_3- group deshields the ortho fluorines in such a way that $(\nu o\delta)_{ae}$ is reduced by 6-8 p.p.m. from its value in perfluoropiperidine (see Table 2).

This table indicates that the effect of substituting a CF_3- group for a fluorine atom is to deshield the adjacent equatorial fluorine by ca. 10 p.p.m. and the adjacent axial fluorine by ca. 4 p.p.m. (with the exception of the 2-substituted compound). The anomalous values associated with perfluoro (2-methyl piperidine) can possibly be explained as follows. The CF_3- group can be attached either as an axial or an equatorial substituent. From steric considerations it is more likely for this bulky group to be equatorially oriented. This reasoning is supported by the nature of the multiplet structure

Professor B. L. Shapiro.   -2-   8th September, 1965.

of the CF_3- group in the 3- and 4- substituted compounds being a quintet of doublets. This implies equal coupling to the four fluorine nuclei in the adjacent ring positions and this would be most probable if the CF_3- group were equatorially oriented and thus symmetrically disposed towards the -CF_2- groups. In the 2-substituted compound, however, the multiplet structure of the CF_3- group indicates non-equivalent coupling to the adjacent -CF_2- fluorines. This observation is therefore suggestive of either a departure by the perfluoro- piperidine ring from its normal chair form or possibly of the CF_3- group being axially oriented with respect to the ring. Either of these possibilities would, of course, explain the anomalous deshielding effect of the substituent in the 2-position (Table 2).

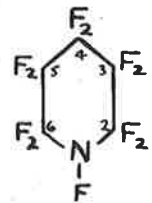Yours sincerely,

K. G. Orrell
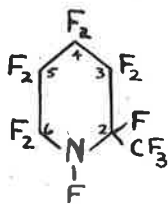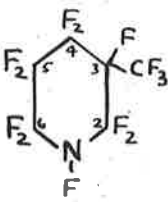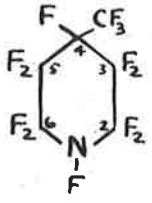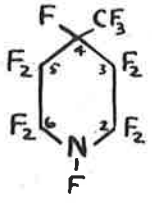
K.G.Orrell

References

1.   L. W. Reeves, E. J. Wells, Disc. Far. Soc., 1962, **34**, 177.

2.   J. Homer, L. F. Thomas, Trans. Far. Soc., 1963, **59**, 2431.

Title

Conformational Studies of Some Perfluoropiperidine Compounds.

KGO/LL

Table 1

Compound	Band No.	p.p.m.[a]	Assignment	$(\nu_{o\delta})_{ae}$ (p.p.m.)	J_{ae} (c/sec)
	1, 2, 3, 5	109.5[b]	2, 6-	6.5	185
	6, 8, 10, 12	131.7	3, 5-	19.2	282
	7, 9, 11, 13	133.9	4-	17.6	285
	4	113.5	-N-F		
	1	72.8	CF_3-		
	2, 4, 5, 6	107.0	6-	8.8	199
	7, 9, 11, 12	126.5	3-	11.2	293
	8, 10, 13, 14	132.1	4, 5-	18.4	289
	3	102.6	-N-F		
	15	158.2	$\geq$C-F		
	1	70.1	CF_3-		
	2	102.0	2-	Ca 0	?
	3, 4, 5, 7	109.7	6-	6.2	198
	8, 9, 10, 11	126.7	4-	11.1	289
	8, 9, 12, 13	129.9	5-	17.6	284
	6	113.0	-N-F		
	14	184.0	$\geq$C-F		
	1	70.4	CF_3-		
	2, 3, 4, 6	108.0	2, 6-	6.6	196
	7, 8, 9, 10	124.2	3, 5-	13.3	286
	5	112.4	-N-F		
	11	188.6	$\geq$C-F		

a. Relative to 20% $CFCl_3$ (int)

b. Values for perfluoropiperidine obtained at -74 °C.

Table 2

Deshielding of α-fluorines by CF_3- group

Compound	Ring Position	$\Delta(\nu_0\delta)^a_{ae}$	Δ^b_a	Δ^b_e
	3	8.0	1.2	9.3
	2	6.5	4.2	10.7
	4	6.5	4.0	10.5
	3, 5	5.9	4.6	10.6

a. Defined as the change in the geminal internal chemical shift of
    -CF_2- fluorines on replacing an α-fluorine by an α-CF_3- group.

b. Defined as the change in the axial or equatorial fluorine chemical
    shifts on replacing an α-fluorine by an α-CF_3- group.

Figure. Spectrum of Perfluoro(2-methylpiperidine)

72.8   158.2 ppm
                                        from $CFCl_3$
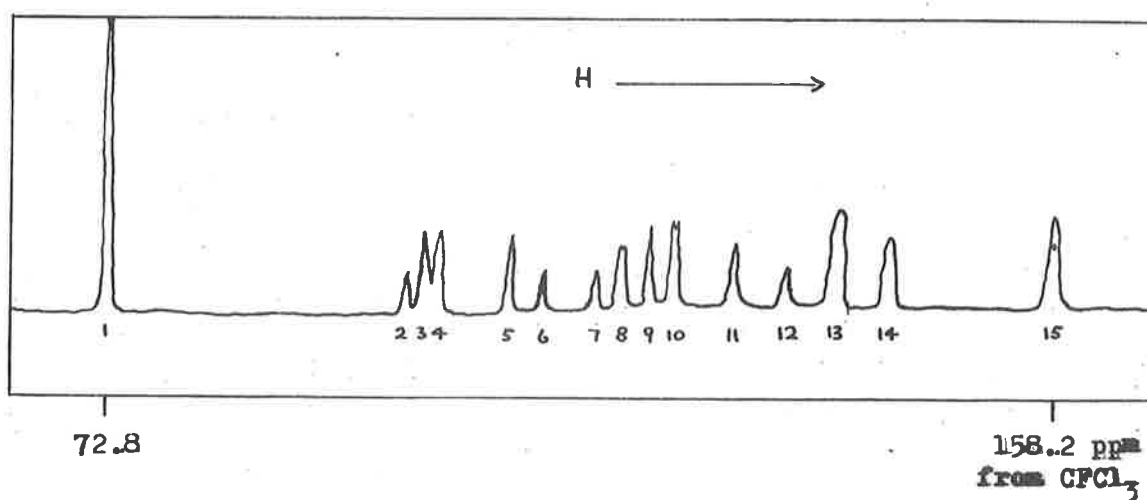
Gulf Research & Development Company

N. D. Coggeshall
DIVISION DIRECTOR
PHYSICAL SCIENCES

September 22, 1965

Reference: 625-2TE00

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

Dear Professor Shapiro:

We wish to make a contribution towards receiving again the IIT NMR Newsletter.

We have been interested for some time in wide line Al^{27} NMR measurements of organo-aluminum compounds and complexes. Recently we have completed a study of the $NaF \cdot 2AlR_3$ complexes and have found the following.

1. The line widths of the Al^{27} NMR spectra of the $NaF \cdot 2AlR_3$ complexes were found to increase as the size of the R group increased at a given temperature. This increase has been attributed in part to an increase of the effective molecular radius and also to an increase in the viscosity as the size of the alkyl group increases.

2. The increase in the activation energy for nuclear relaxation as the size of the R group increases in these complexes has been attributed to an increase in the energy required for molecular reorientation.

3. By using Al^{27} NMR it has been shown that the alkyl groups will not interchange when $NaF \cdot 2TEA$ (TEA = triethylaluminum) is mixed with $NaF \cdot 2TNBA$ (TNBA = tri-n-butylaluminum) at 150°C. However, a $NaF \cdot 2AlR_3$ complex prepared from a mixture of two different aluminum alkyls exhibited a line width intermediate to the line widths obtained from the $NaF \cdot 2AlR_3$

complexes prepared from the individual alkyls. This also is evidence that an alkyl interchange takes place when two different aluminum alkyls are mixed.

4. It has been demonstrated that Al^{27} NMR can be used at room temperature to study the reaction between donor molecules and the $MF \cdot 2AlR_3$ complexes.

5. And finally, the Al^{27} NMR spectra of the $NaF \cdot 2AlR_3$ complexes show a single line ($\sim$ 3-30 gauss) suggesting that the aluminum nuclei are equivalent. We feel this observation supports a proposed structure with an aluminum-fluorine-aluminum collinear bond instead of a proposed structure where two different types of aluminum nuclei exist.

Our measurements were made on a Varian V-4200-A wide line NMR spectrometer with 12 inch magnet equipped with a Varian V-FR2100 Fieldial to regulate and scan the magnetic field. A BC-221-D Bendix Corp. frequency meter and the Fieldial were used to calibrate and measure the peak to peak line widths of the first derivative absorption curve. Most of the measurements were made at 10.0 Mc/s radio-frequency and a corresponding magnetic field near 9000 gauss.

The aluminum alkyls, being pyrophoric, must be handled in a nitrogen-controlled atmosphere.

To obtain more information in an effort to nail down the structure of these complexes, we intend carrying out high resolution studies of the F^{19} resonance since the F^{19} lines are much narrower and saturate at the high r-f field used for the Al^{27} study.

Sincerely yours,

Harold E. Swift.

Harold E. Swift

J. F. Itzel

J. F. Itzel

WDC
MRB/ABK
HES/JFI:vb

Eidg. Technische Hochschule

Laboratorium
für Physikalische Chemie

Zürich

ZÜRICH 6, 27.9.1965.
Universitätstrasse 22
Tel. (051) 32 73 30

Prof. H. Primas
Hi

Professor Dr. B.L. Shapiro
Editor ITT-NMR Newsletter
Chemistry Department
Illinois Institute of Technology
CHICAGO, Illinois
U.S.A.

"Any simple theory of chemical shift must be wrong", (A moral lesson)

I am referring to the interesting letter of Norbert Muller in
ITT-NMR-Newsletter No. 83, especially to his statement:"... any
simple theory of the origin of chemical shifts must be wrong".
I doubt whether the situation is so rosy. The best thing I can do
is to quote Karl R. Popper ["Conjectures and Refutations", p. 36
(Routledge and Kegan Paul, London, 1936)] on the criteria of the
scientific status of a theory:

" (1) It is easy to obtain confirmations, or verifications, for
  nearly every theory – if we look for confirmations.
 (2) Confirmations should count only if they are the result of
  <u>risky predictions</u>; that is to say, if, unenlightened by the
  theory in question, we should have expected an event which
  was incompatible with the theory – an event which would have
  refuted the theory.
 (3) Every "good" scientific theory is a prohibition: it forbids
  certain things to happen. The more a theory forbids, the
  better it is.
 (4) A theory which is not refutable by any conceivable event is
  nonscientific. Irrefutability is not a virtue of a theory
  (as people often think) but a vice.
 (5) Every genuine <u>test</u> of a theory is an attempt to falsify it,
  or to refute it. Testability is falsifiability; but there
  are degrees of testability: some theories are more testable,
  more exposed to refutation, than others; they take, as it
  were, greater risks.
 (6) Confirming evidence should not count <u>except</u> <u>when</u> <u>it</u> <u>is</u> <u>the</u>
  <u>result</u> <u>of</u> <u>a</u> <u>genuine</u> <u>test</u> <u>of</u> <u>the</u> <u>theory</u>; and this means that
  it can be presented as a serious but unsuccessful attempt to
  falsify the theory.
 (7) Some genuinely testable theories, when found to be false, are
  still upheld by their admirers – for example by introducing
  <u>ad</u> <u>hoc</u> some auxiliary assumptions, or by re-interpreting the
  theory <u>ad</u> <u>hoc</u> in such a way that it escapes refutation. Such
  a procedure is always possible, but it rescues the theory
  from refutation only at the price of destroying, or at least
  lowering its scientific status."

-2-

Accepting these propositions of one of the foremost philosophers of science, it is, according to my opinion, misleading to speak of a genuine "theory of chemical shift". We have the rigorously derived Ramsey-formula which we cannot evaluate for molecules and therefore not test; we have hopes, vague and half-baked ideas, a lot of exciting models; but we do not have a quantum mechanical theory of molecular shielding, distinguished by mathematical rigor and honest appraisal of the validity of assumptions. That makes a great difference. I should like to plead for modesty, and propose to use the term "theory" if and only if we can stand up most conscientiously for its scientific status. To question the scientific status of a method is, of course, not at all equivalent to asking whether these methods are desirable or useful. My issue is not polemic but deep sorrow.

With best regards

yours sincerely

Hans Primas

NUCLEAR MAGNETIC

NMR Specialties

RESONANCE SPECIALTIES

I N C O R P O R A T E D

1410 Greensburg Road

New Kensington, Pa.

Area Code 412
337-7727

SEPTEMBER 22, 1965

PROFESSOR B. L. SHAPIRO
DEPARTMENT OF CHEMISTRY
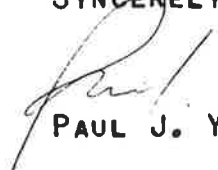ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS 60616

DEAR BARRY:

WE ARE INTERESTED IN PURCHASING A USED ELECTROMAGNET SYSTEM, INCLUDING POWER SUPPLY, FOR GENERAL LABORATORY USE. ANY VARIAN TYPE 6 TO 12 INCH SYSTEM WOULD BE DESIRABLE; IT NEED NOT BE A HIGH-RESOLUTION MAGNET.

PERHAPS SOMEONE IN THE NMR COMMUNITY HAS A SPARE MAGNET, OR WOULD LIKE TO SELL THEIR SYSTEM FOR THE PURPOSE OF MODERNIZING OR UPDATING THEIR FACILITY BY PURCHASING A NEW ONE.

IT WOULD BE APPRECIATED IF YOU COULD MENTION THIS MATTER IN THE NEXT ISSUE OF IIT NMR NEWSLETTER.

SINCERELY,

PAUL J. YAJKO

PJY/CK

SCIENTIFIC APPARATUS — *ELECTRONIC INSTRUMENTATION* — *RESEARCH AND DEVELOPMENT*

BATTELLE-NORTHWEST

PACIFIC NORTHWEST LABORATORIES a division of BATTELLE MEMORIAL INSTITUTE

September 28, 1965

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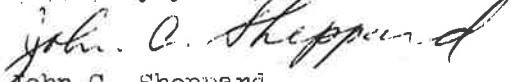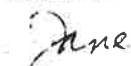Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

For our contribution to the IIT NMR Newsletter, we would
like to give results of a study involving methanol exchange
in dilute solutions of neptunium(V) ions.

The relaxation of the methyl and hydroxyl
protons of methanol by neptunium(V) has been ex-
amined over the temperature range of -80° to +50°.
The results indicate that the rate of methanol
exchange between the coordination sphere of
neptunium(V) and the bulk solvent is measurable
and has a rate constant of $9.0 \times 10^4 \text{sec}^{-1}$ at 0°.
ΔH^* and ΔS^* for this reaction are 7.5 kcal/mole
and -8 e.u. respectively.

Preprints will be available.

Sincerely yours,

John C. Sheppard

Jane L. Burdett

JLB:bt

Monsanto
C O M P A N Y

_____ _INORGANIC CHEMICALS DIVISION_

800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
(314) WYdown 3-1000

October 1, 1965

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

Dear Barry:

Since Ray Freeman expressly invited it, I cannot help proposing an alternative acronym for his new NMR technique C U S P I D O R (Carbon-13 Unravelling by Slowly Pulsed Internuclear DOuble Resonance), described in the August Newsletter.

I suggest the name E X P E C T O R A T E (EXperimental Procedure for Enhancing Carbon-13 To Observe Relative Arrangement of Transition Energies). Although less flashy, it fits appropriately within his original concept.

F A C E T I O U S L Y (Frantic Application to a Commendable Editor in The Interest of Obtaining an Uninterrupted Subscription to these Letters of Yours),

Maw

M. M. Crutchfield
Scientist

cm

Dr. Lee's Professor of Chemistry:
R. E. Richards F.R.S.

Tel: Oxford 57757
STD Code OOX2

PHYSICAL CHEMISTRY LABORATORY,
SOUTH PARKS ROAD,
OXFORD.

28 September 1965

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

Dear Barry,

During the past year we have devoted a good deal of effort on the improvement of the quantitative accuracy and reliability of our nuclear electron double resonance apparatus, working at 9 KMc/s and at 35 KMc/s. We have used the machines to test various physical models for the behaviour of solutions of certain free radicals in organic solvents, and to find information about molecular motion. One striking result we have obtained is that solutions of radicals in fluorinated solvents often show <u>scalar</u> coupling between radical electrons and fluorine nuclei. The models for the interaction have been considered, and with the help of a theory developed by Paul Hubbard, we have shown that a model of diffusing spheres is reasonably satisfactory, in which the scalar coupling varies exponentially with distance between radical and solvent molecule. Triple resonance experiments have shown that the "3-spin effect" (Disc. Faraday Soc. <u>34</u>, 96; Phys. Letters <u>2</u>, 53) is usually unimportant in relation to the scalar coupling. An estimate of the magnitude of the scalar coupling constant can be obtained and for hexafluorobenzene this would imply a scalar shift of the fluorine resonance in the solution used of about 5×10^{-9}. A shift has indeed been observed of about 1 in 10^7 but it is only just within experimental error. The shift is partially nullified when the electron resonance is irradicated. Details of this work are in a paper to be published in Proc. Roy. Soc. A.

Yours sincerely,

Rex

Short title: Intermolecular Scalar Coupling.

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45239

September 24, 1965

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

Title: C-1024 Adjustments and
HA-100 Decoupling

Dear Barry:

I would like to pass on a few comments about the HA-100-C-1024 combination. It was interesting to read last month (IIT NMR-83) that Connor reports calibration difficulties with the readout of the C-1024 because we have been plagued with the same problem for a long time. We had a hard time finding out how to change the readout time. Perhaps some of the other readers would like to know the procedure.

Calibration can be accomplished with the frequency counter and the oscilloscope on the spectrometer. The scope and counter are connected to card #14 (the first 2-Binary card). There is a lug at the top of the card from which a square wave is derived when the C-1024 is reading out the analog signal. This square wave causes the 1024 channels to be read out successively. The frequency of the signal determines the rate at which the channels will be scanned. In order to measure the frequency accurately, the period function of the counter is used. For the various readout settings the appropriate period is given by the equation: Period (msec.) = Setting (in sec.) X 1.9532. Adjustment of the readout frequency is accomplished on card #36. There are six trimpots for the six readout times.

Dropping counts from the core memory can be a problem. This can be minimized by adjustment of the power supply voltage. The voltage is monitored at the "Add" current jack. Go to "Display" on the function selector and adjust the Rollover switch to "Add." Then adjust the trimpot on #39 in one direction until points are dropped. Record the voltage where this happens. Then adjust the trimpot in the opposite direction until points are erratic again. Record this second voltage. The proper voltage is halfway between the two recorded voltages. It is important to make this adjustment when the instrument has warmed up, since the set point is temperature dependent. We have gone to the trouble to drill a hole in the cover above the trimpot so that the adjustment can be made with the interior enclosed.

Spin decoupling is another special feature of the HA-100 which is still somewhat more of an art than a science. We have found that the choice of an audio oscillator is perhaps the most crucial feature of this experiment. We have tried several units: a Hewlett Packard 200AB, an HP 204B oscillator coupled to a 467A power amplifier, and an HP 200CD matched

THE PROCTER & GAMBLE COMPANY

Dr. B. L. Shapiro   Page 2   September 24, 1965
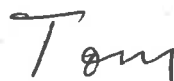
into the modulation coils with a Stancor universal output transformer (A8103) with the 16 Ω tap attached to the oscillator and 4 Ω attached to the sweep coils and floating. Of the three, the last combination seems to work best. It is very important to have a smooth spinning of the sample tubes. This means that they should be straight--a check can be made by rolling one on a plate of smooth glass. The Varian tubes are generally satisfactory. Spinning rate is equally important. We find that a rate just barely fast enough to give high resolution is best.

We have incorporated a couple of modifications suggested by Roy Johnson to help with decoupling. The first is the addition of an attenuator (20 DB max. is enough) between the receiver and the lock box. This is used when the decoupling energy excites a signal so large that the lock box amplifier becomes non-linear. The attenuator decreases the amplitude of the signal, but there is usually enough audio gain to reach instrument noise. The second "fix" is the addition of a switch to turn the receiver detector diode in and out. Removal of the diode seems to decrease a certain amount of the beat notes between the various modulation frequencies which are present (sweep frequency, lock frequency, spinning frequency, and 60 cps.).

Finally to show some results of both spin decoupling and using the C-1024, I am enclosing a picture of the C^{13} satellites from the vinyl region of methyl oleate. The blow-up shows the vinyl region (A), fifty sums of the lower C^{13} satellite (B), and twenty-five sums of the lower C^{13} satellite decoupled from the allyl protons.
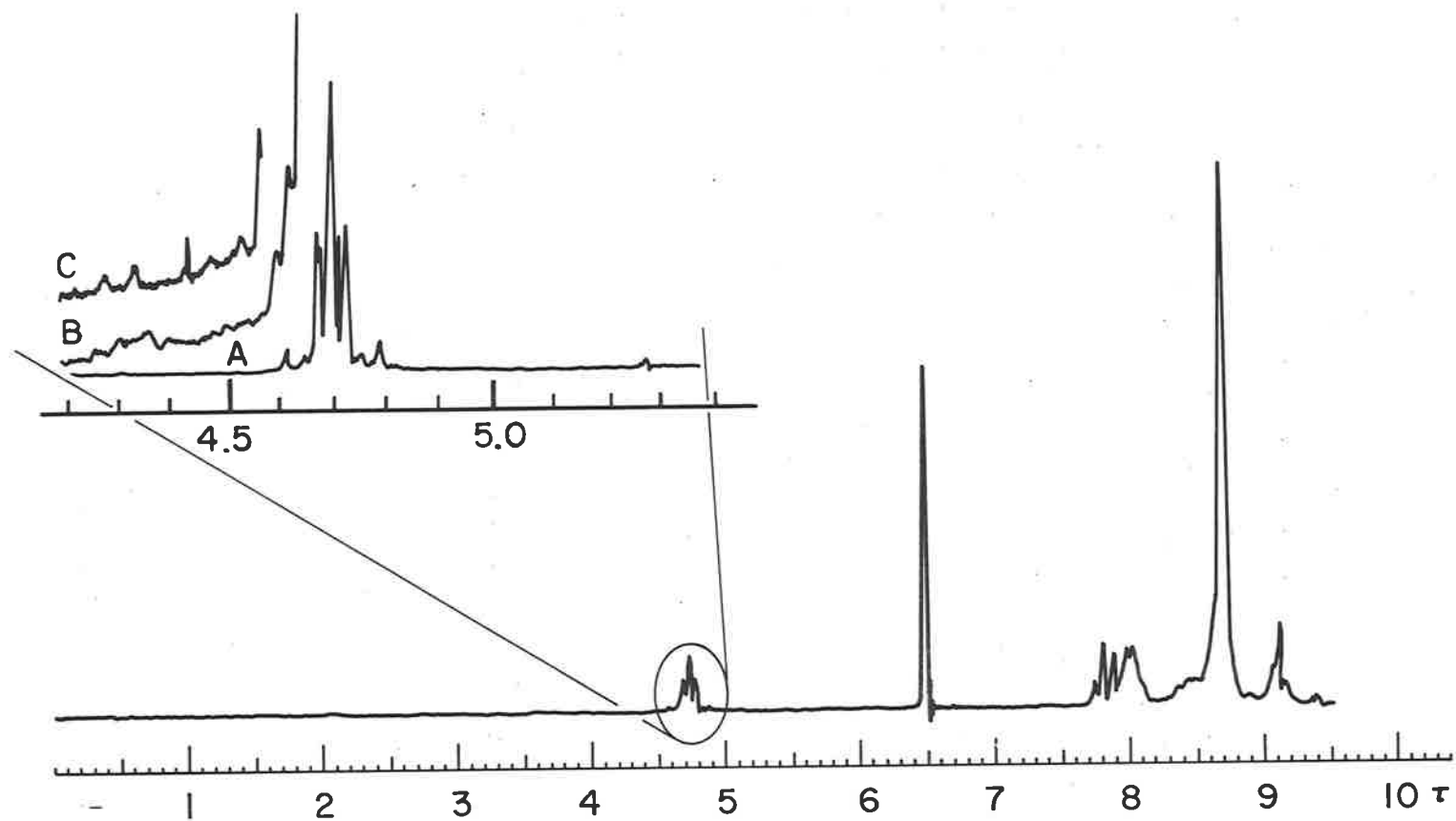
Sincerely,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

T. J. Flautt
Research Division

cw

Enc.

Université Libre de Bruxelles

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

Organic Chemistry
Dir.:Prof.R.H.MARTIN.

(A rappeler dans la réponse)

SOLVENT EFFECT ($CDCl_3$-BENZENE d_6) ON THE
SPECTRA OF UNSUBSTITUTED POLYCYCLIC AROMA-
TIC HYDROCARBONS BELONGING TO THE "PHENE"
SERIES.

Associate Professor B.L.SHAPIRO,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago 16, Illinois 60616

Dear Dr.Shapiro,

    We have compared the NMR spectra taken in $CDCl_3$ and in benzene d_6 of six polycyclic aromatic hydrocarbons (I - VI) which have different types of angular hydrogens : H-α3, H-α4 and H-α5.
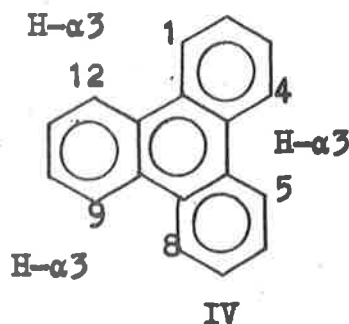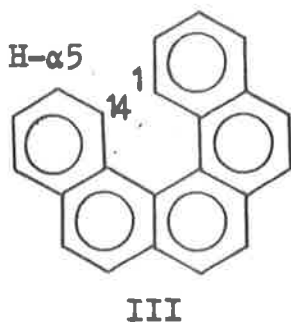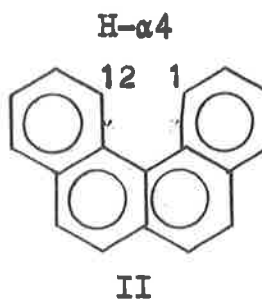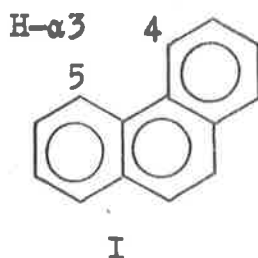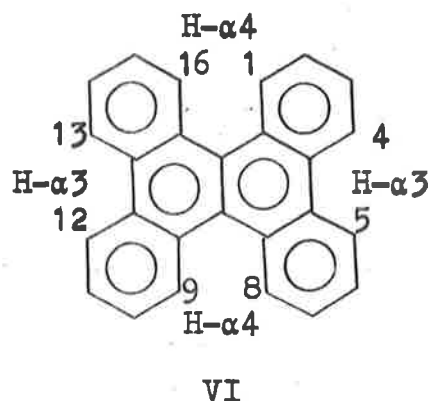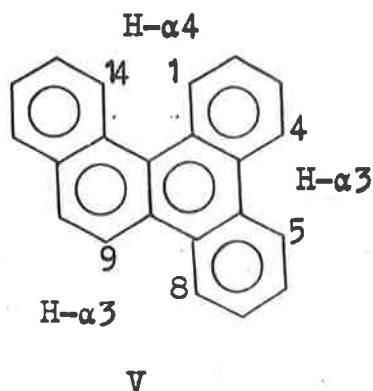
As a rule, the spectra of <u>unsubstituted aromatic hydrocarbons</u> recorded in $CDCl_3$, CCl_4, $Cl_2CH-CHCl_2$, CS_2, dioxanne and C_6D_6 are very similar; one essentially observes a general shielding or deshielding of the spectra, without a specifically marked effect on particular protons.

For example, in the case of phenanthrene, the entire spectrum undergoes a shielding of 12 c/s in passing from $CDCl_3$ to benzene d_6, without variation of the spacing between the multiplet of the strongly deshielded protons (H4 and H5) and those of the other protons of the molecule.

On the contrary, in the more hindered hydrocarbons of the "phene" series, such as benzo[c]phenanthrene (II) and dibenzo[c,g] phenanthrene (III), we have observed a specific effect of benzene on the angular hydrogens.

Although, in these two hydrocarbons, the non-angular hydrogens are normally shielded from 10 to 12 c/s in benzene (with respect to $CDCl_3$), the angular hydrogens (H1 and H12) of benzo[c]phenanthrene (II) are essentially not displaced and those (H1 and H14) of diben-zo[c,g]phenanthrene (III) are deshielded.

Thus, with an increase of steric hindrance, one observes an in-crease of spacing ($\Delta C_6D_6 - \Delta CDCl_3$ in the table below) between the multiplet of angular hydrogens and those of other hydrogens (0 c/s for I, 9 c/s for II and 18 c/s for III).

This phenomena is also observed in hydrocarbons which possess angular hydrogens of different types (V and VI).

	$*\delta_1$		$**\delta_2$		Angular Type H	$***$ $\triangle C_6D_6 - CDCl_3$
	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6		
I	464	453	520	508	2H-α3	1
II	467	455	549	546	2H-α4	9
III	452	440	510	516	2H-α5	18
IV	456	445	516	506	6H-α3	-1
V	463	452	513	502	4H-α3	0
			533	531	2H-α4	9
VI	454	442	518	507 $\simeq$	4H-α3	1 $\simeq$
			518	518 $\simeq$	4H-α4	12 $\simeq$

$* \delta_1$ = center of principal multiplet in c/s at 60 Mc. (TMS = 0);

$** \delta_2$ = center of multiplet of angular hydrogens;

$*** \triangle = \delta_2 - \delta_1$

These preliminary results encourage us to continue our research in this area.

With kind regards,

Yours sincerely,

D.BOGAERT-VERHOOGEN.   N.DEFAY.   R.H.MARTIN.

Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry

October 7, 1965

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

^{19}F **Line Widths in NaBF₄ Solutions**

We have been using our DA-60-I (a DP-60 with V4354 Internal
Lock Unit) for frequency sweep ^{19}F spectra. It is fairly
inconvenient for this, because of the fairly limited sweep
range and the fixed base frequency on the swept oscillator
(ca. 2.5 KC). However the chemical shift of BF₄⁻ ions in
water relative to external CF₃COOH are such that we can get
respectable spectra by locking on the high field sideband
of CF₃COOH and observing the low field sideband of BF₄⁻
solutions. One gets bona fide frequency sweep spectra from
this setup, i.e. reversed from bona fide field sweep spectra.
The accompanying figure is a spectrum obtained in this way of
a solution of NaBF₄ in water, degassed by flushing with nitrogen.
The spectrum consists of a ^{11}BF quartet and a ^{10}BF septet.
The centers of these features are shifted by 2.9 cps (56.4 mc),
the ^{10}BF's being less shielded. The ^{11}BF coupling is 3.07 cps,
indicating a concentration of ca. 3.5 M NaBF₄. The integrated
intensities of the two ^{11}BF peaks uncomplicated by ^{10}BF peaks
are equal as would be expected. However, their peak heights,
and thus line widths are definitely not equal. If the ^{19}F line

Professor B. L. Shapiro   2
October 7, 1965

were being broadened by ^{11}B quadrupole relaxation, one would
expect equal widths for all four lines. My guess is that the
^{19}F lines are being broadened by ^{11}B relaxation, but the ^{11}B
relaxation is dominated by a mechanism which produces
$\Delta m(^{11}B) = \pm 1$ transitions with equal (or nearly equal)
transition probabilities. In the case $W \pm 3/2 \leftrightarrow \pm 1/2$
$= W \pm 1/2 \leftrightarrow -1/2 = W$, the contribution of the ^{11}B relaxation
to the width of fluorine lines would be W for lines originating
in $m(^{11}B) = \pm 3/2$ states, and 2W for lines originating in
$m(^{11}B) = \pm 1/2$ states. The most likely candidates for the
^{11}B relaxation mechanism are ^{11}BF dipole-dipole interactions
and spin-rotation interaction.

I plan to investigate the concentration dependence (if any)
of this effect, and possibly to try some Overhauser effect
experiments. This work will in general parallel efforts to
better understand the concentration and solvent dependence
of the ^{11}BF coupling.

Yours sincerely,

Karl F. Kuhlmann
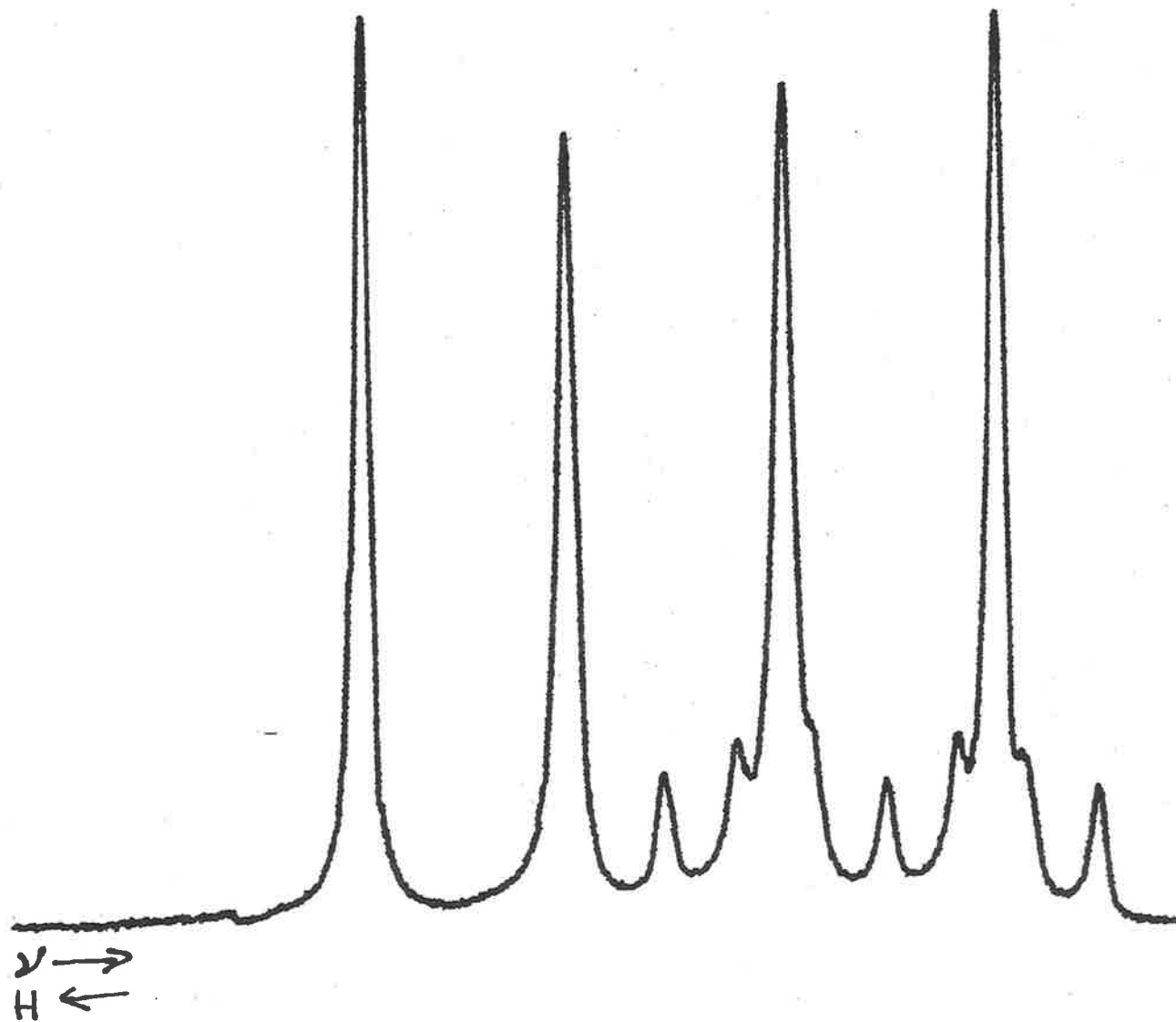Assistant Professor of Chemistry

KFK:lc

Enclosure

$J_{B^{11}F} = 3.07$ cps

$F(^{11}B) = 73.74$ ppm

Ref. CF_3COOH

$F(^{11}B) - F(^{10}B) =$

.051 ppm

$\nu \rightarrow$

$H \leftarrow$

Frequency sweep spectrum of ca. 3.5M NaBF₄ in water

Universidad de Buenos Aires

Facultad de Ciencias Exactas

y Naturales

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Buenos Aires, october 4,1965.

Dr. Bernard Shapiro

Associate Professor
Illinois Institute of Technology
Chicago,60616.
U.S.A.

Ref: H.R. freq. sweep
with the DP-60.

Dear Dr. Shapiro:

Through the kindness of Dr. W.Proctor I spent
last year a month working at the Varian Research Lab. in
Zurich (Switzerland).There I got acquainted with their ex-
cellent A 56/60 and HA-100 instruments.Back home I introduced
some of the HA-100 ideas into my primitive frequency swept
DP-60.It works splendid now.Besides the advantages of repro-
ducibility of the spectra the internal lock method of prof.
H.Primas compensates for the short term frequency fluctua-
tions of the crystal oscillator and sweeps as slow as 20 mm/cps
are readily made.The continuous monitoring of the homogene-
ity makes it possible to have always a resolution of 0.2 cps.
I include a copy of the signal of the OCH proton of 2,4 di-
nitrobenzaldehyde.

The system we use is basically the one described
elsewere by Ray Freeman and Weston Anderson,with the follo-
wing variations:The Internal Reference Stabilizer Controller
was built here and is similar to the one of J.H.Noggle (R.S.I.
35,1166,(1964).The several modulation frequencies are intro-
duced into the V-4250 A Sweep Unit through the Ext.Osc. input,
with all amplitude controls at maximum.From this it goes to the
Sweep Mod. input of the V-4352 Linear Sweep.This gives enough
power for the production of the necessary sidebands and chan-
ging from field to frequency sweep is readilly accomplished.
Besides the input capacitors of the V-4352 unit improve some-
what the phase characteristic of the system.The V-4311 R.F.
Unit is usually used with only 30 db of attenuation and with
the receiver in position 4.

We use several audio oscilators,all fed from
a constant voltage transformer,but the heart of our equip-
ment is a Muirhead-Wigan D-890-A Decade Oscillator.This has
an excellent stability,better than 0.1 cps per hour and is
mainly used for calibration.It also has an internal 2000 cps
crystal standard and a monitoring 1" scope.We use this 2 Kc.
oscillator for field locking,usually with H.M.D.S. (hexame-
thyldisiloxane) or any other peak,the locking signal being
fed directly to the pick-up coils of the Superstabilizer.

Universidad de Buenos Aires

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y Naturales

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The spectrum is swept from about 1400 to
2000 cps with a H.P. 200-AB oscillator.This has also a
remarkable stability and is fairly linear at this particuar
range.It is driven through a 1:40 reduction gear (surplus
dial) plus the reducing gears set and reversible motors of
the V-4280 Precession Field Scanning Unit.The sweep is
perfectly continuous and a precision of 0.1 cps can be
easily obtained.The spectra are calibrated with the Wigan
Decade oscillator (by Lissajous figures) and the events
marker of the G-11 recorder.We are now building (follo-
wing Varian's) an L-R oscillator (linear) though we still
intend (unlike Varian) to lock always at 2000 cps.

We found that double and triple resonance
experiments can be easily done with this setup and we have
been able,for instance,to determine the relative signs of
the long range couplings of the sample spectrum:

$$(J_{OCH-5} = + 0.62 \text{ cps} ; J_{OCH-3} = + 0.18 \text{ cps})$$

Some troubles were found with the decoupling
of strongly coupled spectra.The locking system used to
jump off.This was solved with the aid of a narrow band
selective amplifier tuned to the locking frequency (T.J.Seed,
R.S.I. 35,473,(1964).Now the stability is excellent and
the field stays locked except for very severe line tran-
sients.Nevertheless,with this system,which is equivalent
to frequency modulation,strong sidebands for decoupling
cannot be obtained,since the power goes into just more
number of sidebands of multiples of the modulating fre-
quency and our limit for decoupling seems to be,as an
example,the pyridine,which can be reduced to a nearly per-
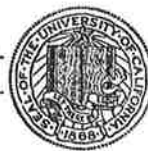fect AB_2 spectrum with the R.F. unit at only 10 db of at-
tenuation.

Yours sincerily,

V.J.Kowalewski.

OCH signal of 2-4 dinitro-benzaldehyde.
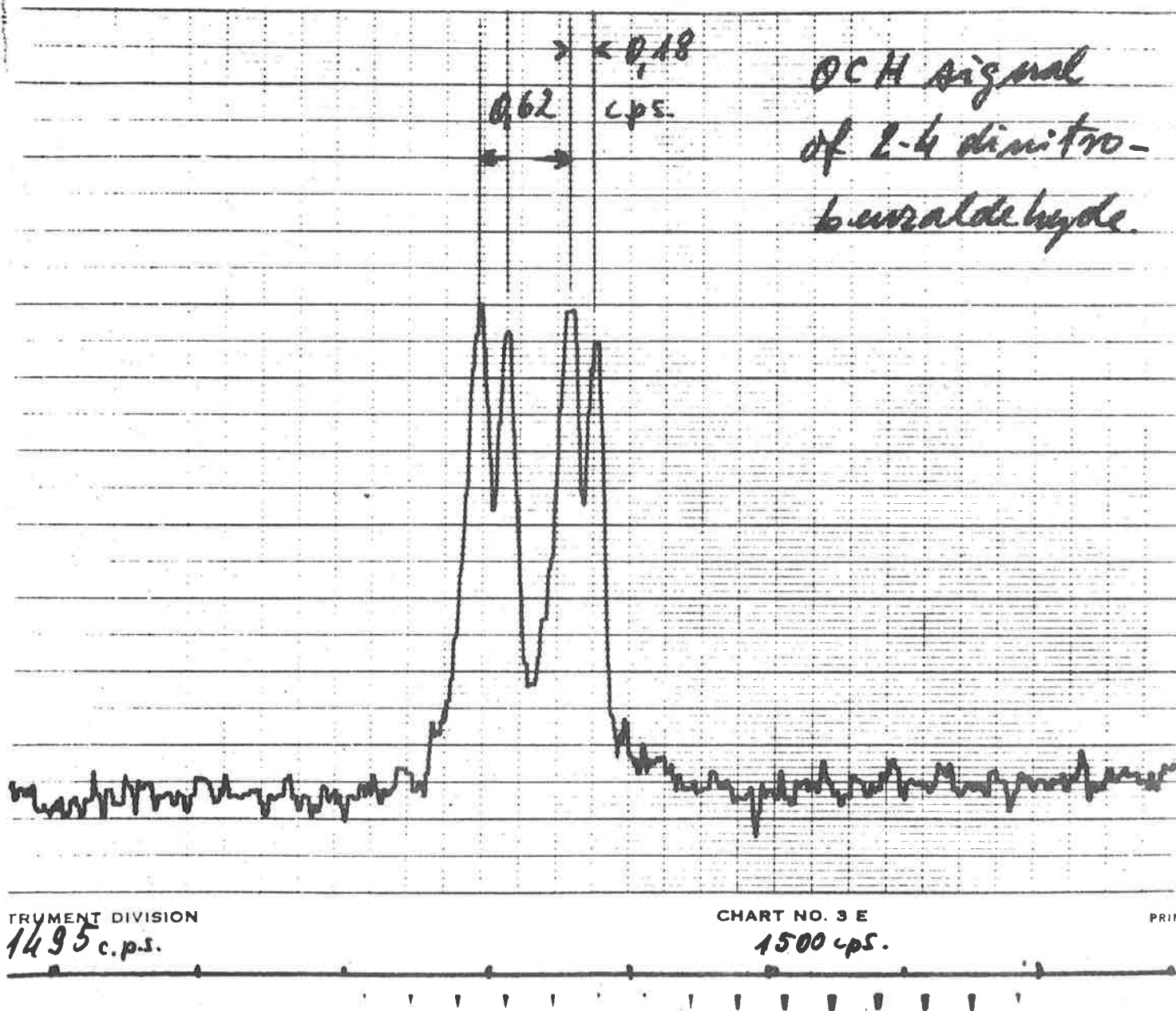
UNIVERSITY OF CALIFORNIA, IRVINE

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY   IRVINE, CALIFORNIA   92650

October 8, 1965

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

Dear Dr. Shapiro:

As our first contribution to the IITNMR Newsletter, I would like to describe
our recent work relating to the n.m.r. spectra of some vinyl sulfides and
vinylsulfonium salts. These compounds were of interest to us in that we hoped
to obtain some information from the n.m.r. spectra concerning the nature of
the sulfur-carbon bonding in the grouping $-CH=CH-S^{\oplus}(CH_3)_2$.

To date, we have only had a close look at three methyl vinyl sulfides and their
corresponding dimethylsulfonium salts. The chemical shift data of interest
for these compounds are tabulated below.

Compound		Chemical Shift, ppm[a]			J_{HH}, cps
		H_α[b]	H_β	$S-CH_3$	
I		5.98	6.30	2.01	11
II		6.68	6.20	2.04	16

Dr. B. L. Shapiro   -2-   October 8, 1965

Compound	Chemical Shift, ppm[a]			J_{HH}, cps
	H_α[b]	H_β	S–CH$_3$	

III

p CH$_3$O–C$_6$H$_4$, S–CH$_3$ on C=C, with H_β and H_α

| | 6.47 | 6.20 | 2.25 | 16 |

IV

C$_6$H$_5$, $\overset{\oplus}{S}$(CH$_3$)$_2$ on C=C, with H_β and H_α

| | 6.45 | 7.63 | 3.00 | 9.5 |

V

C$_6$H$_5$, H_α on C=C, with H_β and $\underset{\oplus}{S(CH_3)_2}$

| | 6.95 | 7.64 | 3.02 | 15 |

VI

p–CH$_3$O–C$_6$H$_4$, H_α on C=C, with H_β and $\underset{\oplus}{S(CH_3)_2}$

| | 6.97 | 7.64 | 3.04 | 16 |

The interesting feature about these results is the pronounced deshielding effect the dimethylsulfonium group has on the β-vinyl proton (i.e., beta to sulfur) in each of the three sulfonium salts studied. The chemical shifts of the β-vinyl protons of the salts IV, V and VI are respectively 1.33, 1.44 and 1.44 ppm to lower fields than the shifts of the β-vinyl protons of the sulfides, I, II and III.

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a. Relative to TMS

b. Identification of the resonance lines with the α- and β-vinyl protons was established by deuterium substitution.

In comparison, the deshielding effect of positive sulfur on the α-vinyl protons is less pronounced. The α-vinyl protons of the sulfonium salts IV, V and VI are shifted respectively only 0.47, 0.27 and 0.50 ppm to lower fields than the α-vinyl protons of the corresponding sulfides I, II and III.

These results are indicative of a conjugative effect in the vinylsulfonium salts involving overlap between the 2p orbitals on carbon and a vacant sulfur orbital. The positive charge on sulfur is, therefore, delocalized to some extent and effectively deshields the β-protons.

$$Ar\ CH=CH-\overset{\oplus}{S}(CH_3)_2 \longleftrightarrow Ar\ \overset{\oplus}{C}H-CH=S\ (CH_3)_2$$

The nature of the acceptor orbital on sulfur (as 3p or 3d) is an interesting question in itself. We are engaged in trying to answer this question by studying the temperature dependence of the n.m.r. spectra of vinylsulfonium salts. Assuming that satisfactory 2p - 3p π-overlap requires a planar configuration whereas 2p - 3d overlap does not, we anticipated non-equivalent methyl resonances to become evident at low temperatures if the bonding were of the 2p - 3p π-variety.

(planar framework)
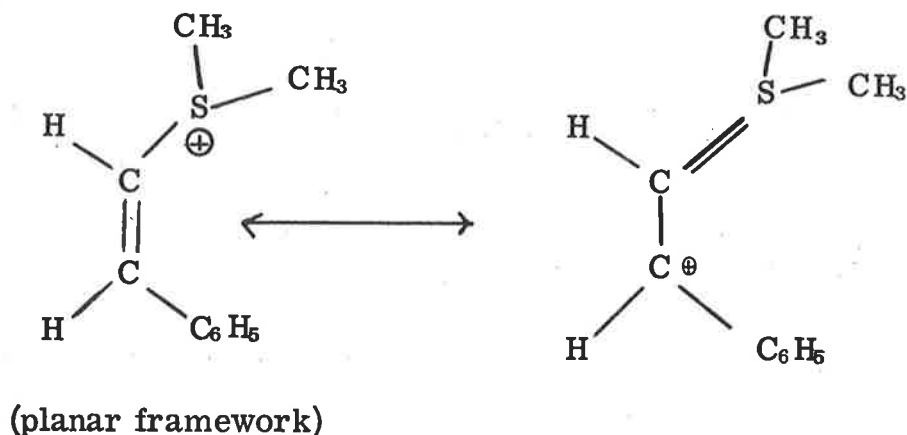
However, there was no perceptible broadening of the methyl resonance of IV from 30° to -60°. We have not as yet recorded the spectra at temperatures lower than -60°.

Yours sincerely,

Marjorie C. Caserio

Marjorie C. Caserio
Assistant Professor of Chemistry

MCC/mp

ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, 60616

DEPARTMENT OF CHEMISTRY

Tetramethylsilane Source Needed

Until now, we have been buying TMS from Anderson Chemical Co.,
now a division of Stauffer Chemical Co. The quality of the TMS has
been excellent and the price - until recently - has been reasonable.
When we wished to replenish our supply a few weeks ago, we found
that the price had gone up - since we had last ordered, ca. 15
months ago - from $14.00 per 1/4 lb to $25.00 and from $192.00 per
gallon to $516.80. (They will offer a substantial discount - if
you'll buy 100 lb.) I find these new prices rather steep and the
amount of the increase (for a chemical whose use must still be
expanding rapidly! cf. The price of $CDCl_3$ which has plummetted as
use has increased during the last few years) unreasonable, and I
would therefore appreciate hearing from anyone who has another
high-quality TMS source which is still reasonable in its price
schedule.

Annoyedly,

Bernard L. Shapiro
Associate Professor of Chemistry

BLS:afc

THE ROCKEFELLER INSTITUTE

A Graduate University and Research Center

NEW YORK, N.Y. 10021

October 11, 1965

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

Dear Barry:

Isotope effect in H_2-HD-D_2

The letter of Anders, Balschwieler and Lauterbur on isotope effects prompts three comments.

(1) Their gas phase result of $0.038 \pm 0.008 \times 10^{-6}$ for HD-H_2 agrees quite well with the liquid phase - in CCl_4 solution - result of D. F. Evans, Chem. and Ind. p. 1960 (1961), of $0.036 \pm 0.002 \times 10^{-6}$.

(2) Using my non-symmetrical zeroth-order wave function for the hydrogen molecule [J. Chem. Phys. 42, 2633 (1965)] I obtain the zeroth-order shielding as

$$\sigma_0 = \frac{e^2 \alpha}{3mc^2} \left[1 + (1+\rho)e^{-\rho} \right]$$

where $\rho = 2\alpha R$. If we wished to evaluate this as an average over vibrational levels for each rotational level then we would use for each molecule (H_2, HD and D_2)

$$\langle \sigma_0 \rangle = \sigma_0(\rho_e) + \frac{e^2 \alpha}{3mc^2} e^{-\rho_e} \left\langle -\rho(\rho-\rho_e) + \tfrac{1}{2}(1+\rho)(\rho-\rho_e)^2 - \cdots \right\rangle$$

where $\rho_e = 2\alpha R_e$ for the equilibrium internuclear distance R_e. Since

2--Prof. B. L. Shapiro

there is no simple way to evaluate the term in brackets $\langle \rangle$ using readily available data, we have taken the easy way out of determining $\langle \sigma_0 \rangle$ by merely substituting the values for ρ_e of the three isotopes into the expression $\sigma_0(\rho_e)$ and neglecting the second term. Herzberg gives $R_e = 1.4245$, 1.4217 and 1.4184a_0 for H_2, HD and D_2 respectively. We obtain for two values of $\alpha(\times 10^{-6})$

	$\alpha = 1$	$\alpha = 1-2$	expt.
$\Delta\sigma$ (HD - H_2)	0.020	0.018	0.036, 0.038
$\Delta\sigma$ (D_2 - HD)	0.016	0.016	0.048 ± 0.032
$\sigma(H_2)$	21.7	24.4	26.5

where for completion we have included the total chemical shift for H_2 and considered the best experimental value that of Saika and Narumi [Canad. J. Phys. 42, 1481 (1964)] since its isotope shifts agree best with the NMR shifts. (They give for m = -1.9(-), 0.036 and 0.043 for the respective shifts.) In fact the remarkable point of their paper is that based on the isotope shifts one is able to choose, somewhat at least, between the possible experimental values. Therefore, at least until we have better evidence, we must assume that this value supercedes Ramsey's value of 26.2 ± 0.3 and likewise σ^{HF} from the spin-rotational constant should be -5.5 rather than -5.9.

We feel the agreement of our simple calculation with experiment to be quite good as first, a factor of two, in and of itself is not bad, and second the average over vibrations should increase the $\Delta\sigma$'s. Incidentally, using what I called the Covalent Approximation [Ann. Phys. N. Y. 24, 188 (1963)] a somewhat different expression for σ was obtained which gave 0.018 and 0.024 for the two $\Delta\sigma$'s.

(3) Note that all but a very few calculations of chemical shifts etc. do not consider the average over vibrations and rotations, and in fact choose differing values of R for the static picture, e.g. $R_e = 1.42a_0$ or $R_0 = 1.40a_0$. Thus the error in calculation is also at least a few per cent assuming everything else is done correctly, while that of experiment is 1%.

Best regards,

Jeremy I. Musher

JIM/kss

DOW CHEMICAL OF CANADA, LIMITED

SARNIA, ONTARIO

September 21, 1965

Prof. B.L. Shapiro
Illinois Institute of Technology
Technological Center
Chicago, Illinois 60616
U.S.A.

Dear Barry:

Tube Cleaning Apparatus

A technique that may be of interest to IITNMR readers is a rapid method to clean NMR tubes. A simple tube cleaner and drier has been described previously (IITNMR No. 73-6) in which solvent is pulled through the tube. We have found the following method more adaptable for cleaning a large number of tubes in one operation with little time expenditure.

The apparatus shown in the diagram uses an intermittent extraction technique. Fifty to seventy tubes are inverted in a wire basket and placed in the extractor. Both heaters are turned on until the solvent in both the round flask and the extractor is boiling. Fresh solvent distils into the extractor, the inverted tubes expel solvent and the excess overflows into the round flask. When heating is stopped, the tubes fill completely with hot solvent. The cycle is repeated and the tube contamination concentrates in the round flask. At the end of one day of operation the tubes are quite clean.
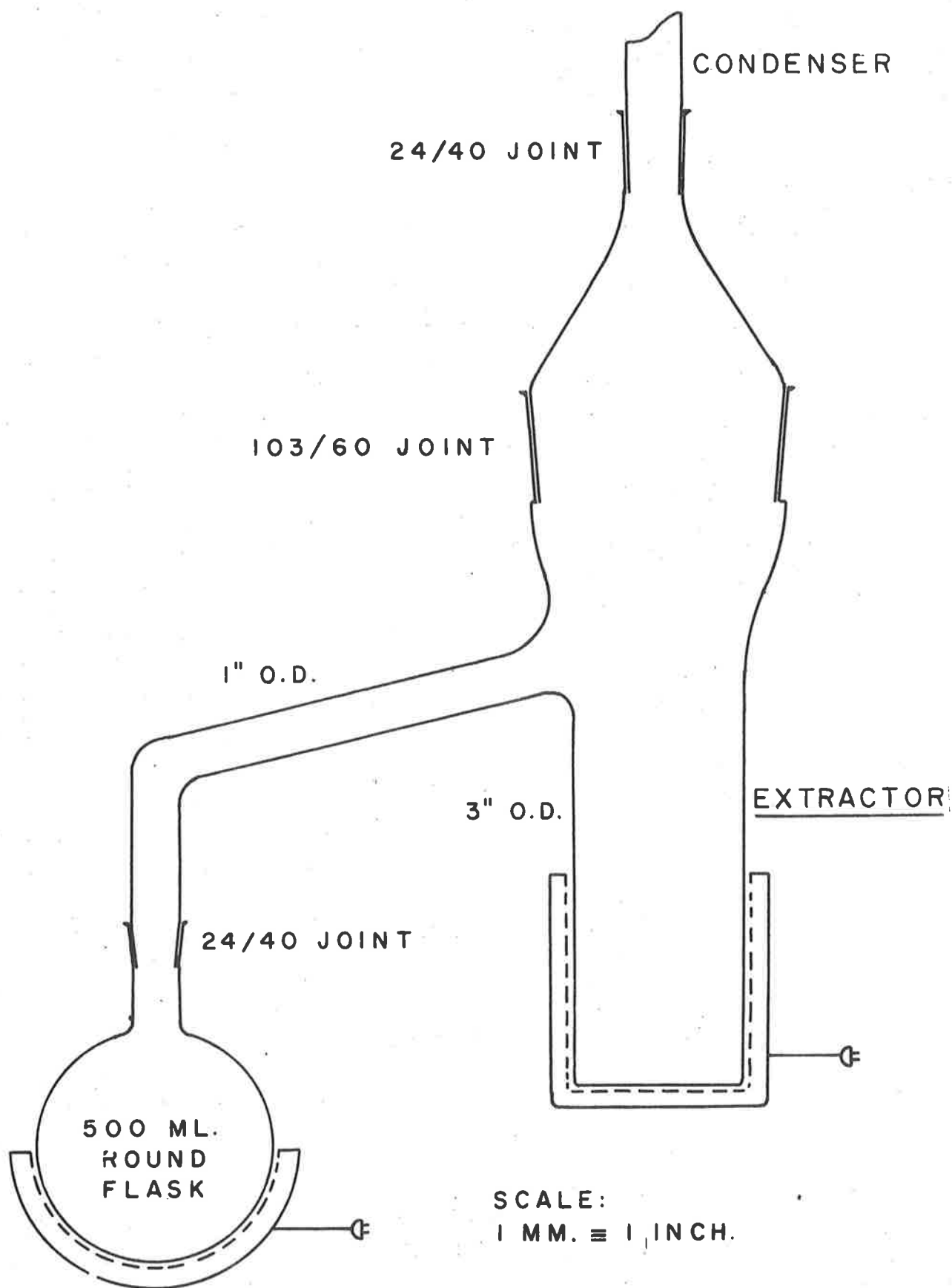
On-off switching is provided by a repeat cycle timer (Flexopulse HG 96) which is connected through two separate Variacs to the heaters. For acetone, a 12 min. on and 12 min. off cycle was found sufficient.

Yours sincerely,

H. Mak

J. S. MacIntyre

/em

CONDENSER

24/40 JOINT

103/60 JOINT

1" O.D.

EXTRACTOR

3" O.D.

24/40 JOINT

500 ML.
ROUND
FLASK

SCALE:
1 MM. ≡ 1 INCH.

NMR TUBE CLEANER

**ORGANISCH-CHEMISCHES
INSTITUT
DER UNIVERSITÄT ZÜRICH**

8001 Zürich, Rämistrasse 76
Telephon 242450

Direktion Prof. Dr. H. Schmid

Dr. W. v. Philipsborn   October 12, 1965

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

Dear Barry:

In this letter I take advantage of the possibility to submit
a very short communication only ("brevity is golden").

1. Included you will find in a printed form a summary of some
   of our work on the proton spectra of complex C_{40} indole
   alkaloids and of catalposide and fulvoplumierine. The
   second part of this brochure contains spectra of derivatives
   of Δ^2-furenidone-(4) (="β-hydroxyfuran")and the determin-
   ation of the proton-proton coupling constants in p-cyclo-
   hexadienones. Altogether 37 mostly unpublished spectra
   are shown.
   A few copies are still available for those subscribers of
   the IIT-NMR Newsletters who are interested in these topics.

2. A request: Who is able to obtain ^{79,81}Br spectra of a
   very interesting tricyclic tetrabromide, the proton spectra
   of which we are studying at present. A helpful advice or
   cooperation in this matter would be most gratefully accepted.

With best wishes,

Yours sincerely

Wolf

W. v. Philipsborn

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITAT

69 HEIDELBERG, October 13, 1965
Tiergartenstraße
Tel. 27121 (über Chirurg. Klinik)

Albrecht Mannschreck

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

Concerning the Separation of Rotational Isomers
(Thioamides and Nitrosamines)[1]

Dear Dr.Shapiro:

Thioamides[2] and nitrosamines[3] are known to exist as rotational isomers in equilibrium, but their separation did not attract chemists' attention, although the activation energies[2,4] might be high enough for the isolation of such isomers. The only exception until now was N-benzyl-N-methyl-thioformamide, one isomer of which was obtained in pure form[5], whereas no nitrosamine at all seems to have been enriched hitherto.

1) Results reported at the "Hauptversammlung der Gesellschaft Deutscher Chemiker", Bonn, September 16, 1965.

2) A.Loewenstein, A.Melera, P.Rigny and W.Walter, J.Physic.Chem. 68, 1597 (1964); R.C.Neuman,Jr. and L.B.Young, J.Physic.Chem. 69, 2570 (1965).

3) H.W.Brown and D.P.Hollis, J.Mol.Spectry. 13, 305 (1964); G.J.Karabatsos and R.A.Taller, J.Amer.Chem.Soc. 86, 4373 (1964).

4) C.E.Looney, W.D.Phillips and E.L.Reilly, J.Amer.Chem.Soc. 79, 6136 (1957); W.D.Phillips, C.E.Looney and C.P.Spaeth, J.Mol. Spectry. 1, 35 (1957).

5) W.Walter and G.Maerten, Liebigs Ann.Chem. 669, 66 (1963).

For the separation of _thioamides_ those of mesitoic acid have been chosen, since the mesityl group proved to be especially suitable for the enrichment of the corresponding oxygen compounds[6,7]. Miss A. Mattheus and Mr. W. Seitz prepared and separated A and B (Fig. 1). Both compounds are stable in the crystalline state; in solution, however, they equilibrate (68% A $\rightleftharpoons$ 32% B) according to a first order process with a half-life value of (24.7 ± 2.8) h in $CDCl_3$ at 50°, evaluated by integration[6]. From this we obtained the free energies of activation $\Delta F_A^{\ddagger} = 27.3$ and $\Delta F_B^{\ddagger} = 26.8$ kcal mole^{-1}. For the corresponding oxygen derivatives we measured 22.9 and 22.3 kcal mole^{-1} respectively[6], i.e. they isomerised much faster than the sulfur compounds. The dipolar formula II
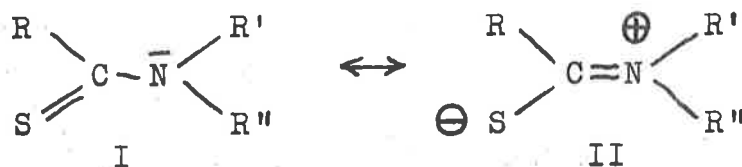
is more important in the case of S, as compared to O, because of hindered π-overlap between the S and the C atom in structure I. This view is supported by some other thioamides which we have not yet separated completely.

Rotational isomers of _nitrosamines_ may be enriched very nicely by a procedure which will be described for A and B (Fig. 2): The crystals, m.p. 20-22°, obtained by routine synthesis, consist of 94% A and 6% B, approximately. I measured this composition by dissolving the crystals and running the spectrum immediately (Fig. 2, top). The equilibrium 81% A $\rightleftharpoons$ 19% B was estab-

6) A. Mannschreck, Tetrahedron Letters _1965_, 1341.
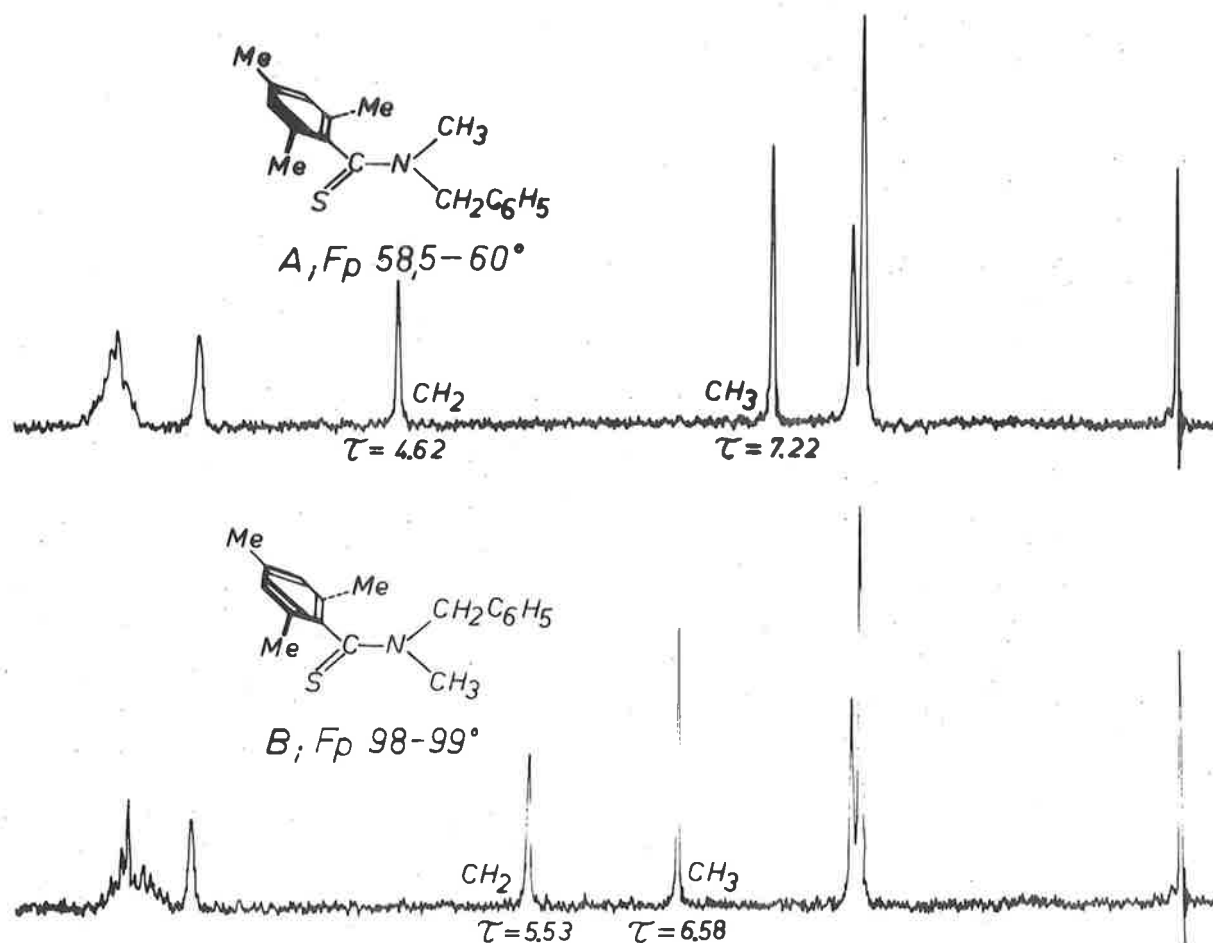
7) A. Mannschreck, IITNN _68_, 44 (1964).

Fig.1: Isomers of N-benzyl-N-methyl-mesitylenecarboxamide in CCl$_4$
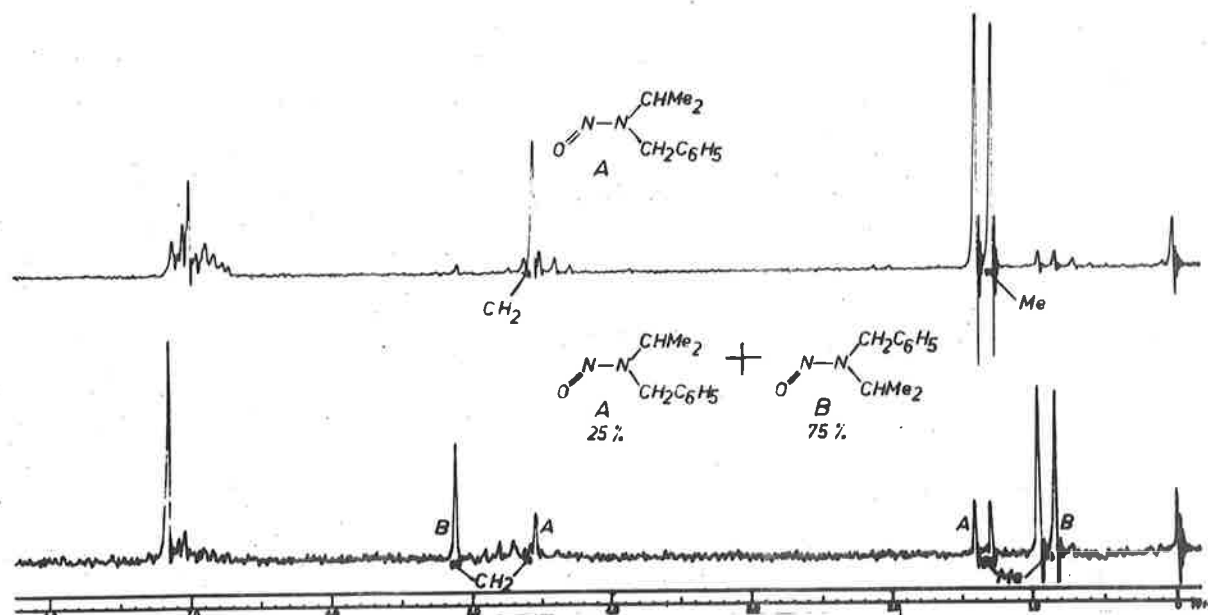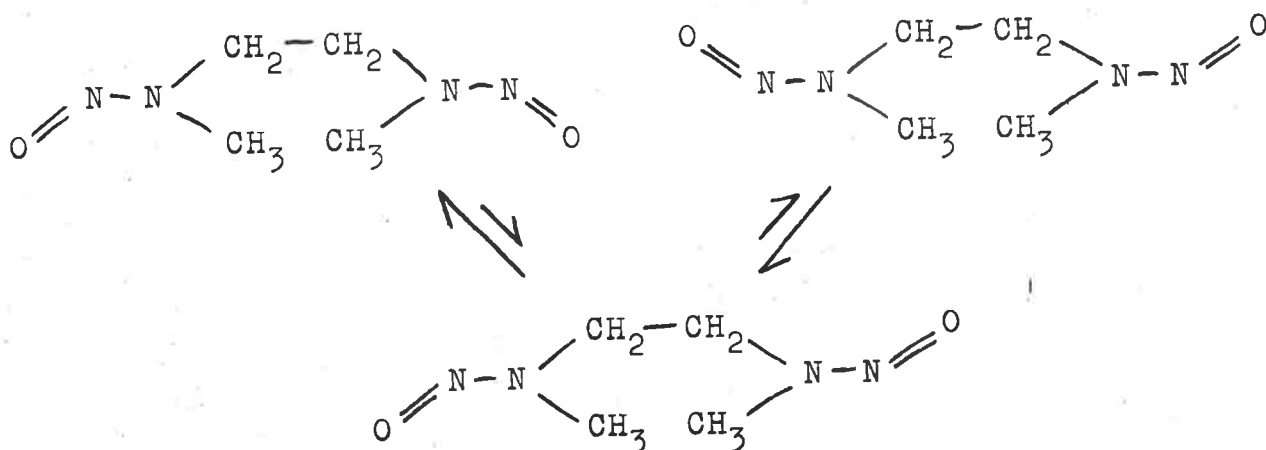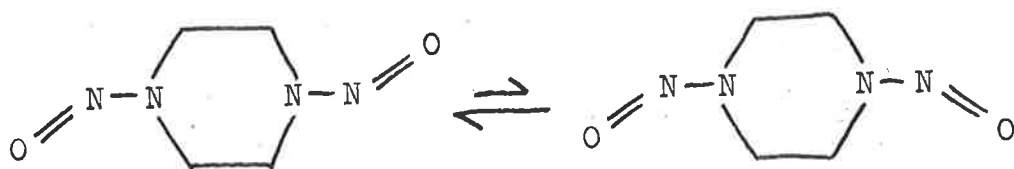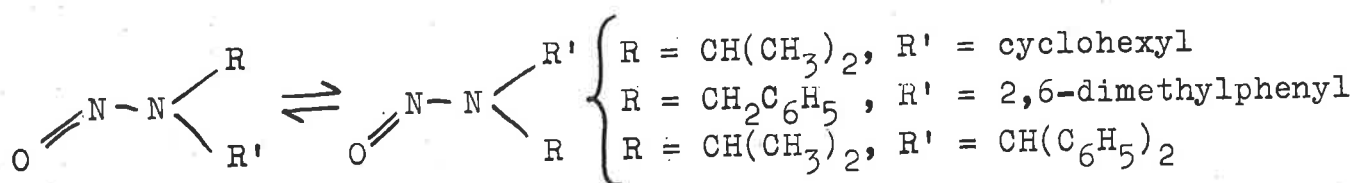

Fig.2: Isomers of benzyl-isopropyl-nitrosamine in CS$_2$ at 37°.

Top: 2 min after dissolving the crystals.

Bottom: Filtrate of a crystallization at -60°, see text.

Spectrum taken 2 min after filtering.

lished with a half-life value of $(8,2 \pm 2.0)$ min in CCl_4 at 36°, corresponding to $\Delta F_A^{\ddagger} = 23.2$ and $\Delta F_B^{\ddagger} = 22.3$ kcal mole^{-1}. From an equilibrium mixture in CS_2 at -60° the crystallization of A is favored. The filtrate contains up to 75% B (Fig.2, bottom), because B isomerises very slowly at this temperature. The chemical shifts were correlated to the structures A and B according to the literature[3]; surprisingly, the phenyl proton absorptions of the isomers (Fig.2) are quite different. I have been able to observe the equilibrations of several other crystalline nitrosamines, prepared by Mr. G.Albert, and to enrich both isomers of them in some cases:

$R = CH(CH_3)_2$, $R' = $ cyclohexyl
$R = CH_2C_6H_5$, $R' = $ 2,6-dimethylphenyl
$R = CH(CH_3)_2$, $R' = CH(C_6H_5)_2$

From <u>symmetrically N,N-disubstituted compounds</u> I obtained the following $\Delta F^{\ddagger}$ values by means of the coalescence temperatures of the methyl signals:

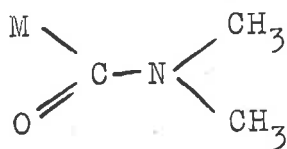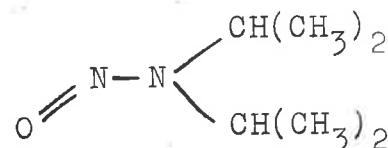$$\underset{\text{S}}{\overset{\text{M}}{\diagdown}} C-N \underset{\text{CH}_3}{\overset{\text{CH}_3}{\diagup}}$$
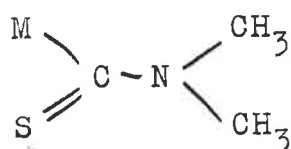
$\gt 23$ kcal mole^{-1}

$(\gt 175°, C_4Cl_6)$

$$\underset{\text{O}}{\overset{\text{M}}{\diagdown}} C-N \underset{\text{CH}_3}{\overset{\text{CH}_3}{\diagup}}$$

$22._5$ kcal mole^{-1}

$(160°, C_4Cl_6)^{6)}$

$$O = N-N \underset{\text{CH(CH}_3)_2}{\overset{\text{CH(CH}_3)_2}{\diagup}}$$

$22._6$ kcal mole^{-1}

$(166°, C_6H_5OC_6H_5)$

(M = 2,4,6-trimethylphenyl; C_4Cl_6 = hexachlorobutadiene)

These energies are similar to the $\Delta F_A^{\ddagger}$ values measured by the above mentioned equilibration technique:

$$\underset{\text{S}}{\overset{\text{M}}{\diagdown}} C-N \underset{\text{CH}_2C_6H_5}{\overset{\text{CH}_3}{\diagup}}$$
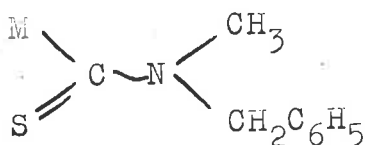
27.3 kcal mole^{-1}

$(50°, CDCl_3)$

$$\underset{\text{O}}{\overset{\text{M}}{\diagdown}} C-N \underset{\text{CH}_2C_6H_5}{\overset{\text{CH}_3}{\diagup}}$$
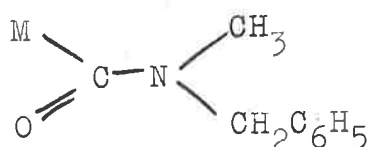
22.9 kcal mole^{-1}

$(38°, CCl_4)^{6)}$

$$O = N-N \underset{\text{CH}_2C_6H_5}{\overset{\text{CH(CH}_3)_2}{\diagup}}$$
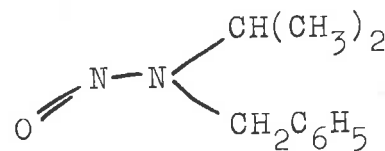
23.2 kcal mole^{-1}

$(36°, CCl_4)$

The results obtained by the line broadening technique and similar results in the literature were the starting point for the attempts to separate rotational isomers. Sometimes it is advisable to take such energy values seriously!

Sincerely yours,

Albrecht Mannschreck

Albrecht Mannschreck

Department of Chemistry,

The University,

GLASGOW, W.2.

Scotland.

12th October, 1965.

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

The ABCD spectra of a) the aryl resonance of p-nitroso-N,N-dimethylaniline in trifluoracetic acid and b) the aryl resonance of salicylaldehyde.   The relative signs of the aromatic coupling constants in these compounds.   A lower limit to the free energy of activation, $\Delta G^{\pm}$, for rotation about the C=N bond in an oxime.

Dear Barry,

Recently we have had cause to analyse the two complex ABCD systems, a) the aryl resonance of p-nitroso-N,N-dimethylaniline (I) dissolved in trifluoracetic acid, and (b) the aryl resonance of salicylaldehyde (II).
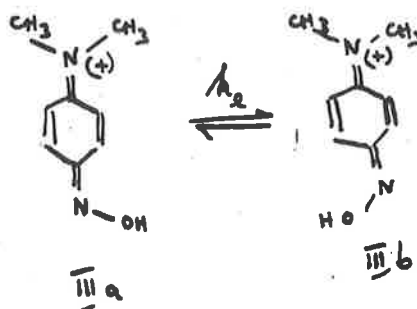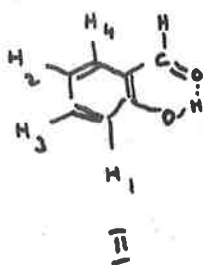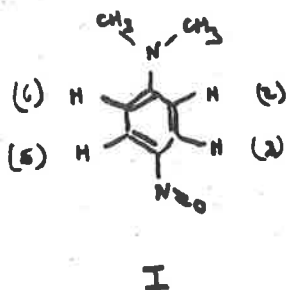
These spectra have been fully analysed and in both cases the four protons involved are tightly coupled so that the relative signs of the <u>ortho</u>, <u>meta</u> and <u>para</u> coupling constants can be obtained from the spectra; these are ++- in both compounds.

The actual chemical shifts and coupling constants extracted from the spectra are as follows.

I. <u>Chemical Shifts</u> (τ units)

$H(2) = 2 \cdot 51$; $H(3) = 1 \cdot 83$; $H(2) = 2 \cdot 19$; $H(6) = 2 \cdot 58$

<u>Coupling constants</u> (c/s)

$J(2,3) = 11 \cdot 18$; $J(2,5) = -0 \cdot 5_1$; $J(2,6) = 2 \cdot 2_7$;

$J(3,5) = 1 \cdot 9_9$; $J(3,6) = -0 \cdot 4_9$; $J(5,6) = 10 \cdot 7_7$.

II. <u>Chemical Shifts</u> (τ units)

$H(1) = 2 \cdot 92$; $H(2) = 2 \cdot 90$; $H(3) = 2 \cdot 38$; $H(4) = 2.36$

<u>Coupling constants</u> (c/s)

$J(1,2) = 1 \cdot 4_7$; $J(1,3) = 8 \cdot 4_8$; $J(1,4) = -0 \cdot 36$; $|J(1,C\underline{H}O)|$ * $= 0 \cdot 6$;

$J(2,3) = 7 \cdot 1_6$; $J(2,4) = 7 \cdot 8_4$; $J(3,4) = 2 \cdot 1_2$

* The relative sign of this coupling constant can not be deduced from the spectrum.

The ABCD spectrum obtained from I and the magnitudes of the coupling constants show that in trifluoroacetic acid solution this compound exists in the form of the oxime cation III. The proton absorption peaks observed at about room temperature are rather broader than should be expected, and if the broadening can be ascribed to the interconversion of IIIa and IIIb then the lifetimes of these species may be estimated. Magnetic coupling to ^{14}N nuclei, incompletely collapsed by quadrupole relaxing mechanism, and hindered rotation about the C(1)-N bond may account for some of this broadening but if the

broadening is assumed to be entirely due to slow rotation about the C(4)-N bond then a lower limit can be placed on the rate constant k_e. This turns out to be $6 \cdot 3 \text{ sec}^{-1}$. The lower limit to the free energy of activation, $\Delta G^{\pm}$, for rotation about this bond at $303 \cdot 5 °K$. can therefore be set at $16 \cdot 9 \text{ k.cal. mole}^{-1}$.

With best wishes,

D.D. MacNicol,
A.L. Porte,
R. Wallace.

"Favorsky Rearrangements. III. Syntheses of cis-3-Halogeno-
  acrylic Acids from 1,1,3-Trihalogenoacetones"
C. Rappe
Acta Chem. Scand. 19, 31 (1965)

"NMR Chemical Shift of the Hydroxyl Ion"
R. Grahn
Acta Chem. Scand. 19, 153 (1965)

"Favorsky Rearrangements. VII. Attemps to Rearrange 2,2,5-
  Tribromocyclopentanone; the Preparation of 3-Bromocyclo-
  pentane-1,2-dione"
C. Rappe
Acta Chem. Scand. 19, 270 (1965)

"Proton Mobility of α-Haloketones"
C. Rappe
Acta Chem. Scand. 19, 276 (1965)

"Synthese von 5-Chlormethyl-2.2-dinitrotetrahydrofuran"
E. Steininger
Angew. Chem. 77, 427 (1965)

"Untersuchungen and Hochsubstituierten Äthylenen und Glykolen,
  II. Synthese des 3,4-Bis-[4-Oxo-Cyclohexyl]-Hexens-(3) mit
  Hilfe der Kuhn-Winterstein-Reaktion"
H. H. Inhoffen, K. Radscheit, U. Stache, und V. Koppe
Ann. Chem. 684, 24 (1965)

"Verbindungen mit drei Ringen über einer C-C-Bindung, I.
  Tricyclo[4.4.3.0]Tridecanon-(11), Tricyclo[4.4.4.0]
  Tetradecanon-(2) und -Dion-(2.3)"
G. Snatzke und G. Zanati
Ann. Chem. 684, 62 (1965)

"Reaktionen der 1-Aryl-1.2.3.4-Tetrahydro-β-Carboline in
  Saurer Lösung"
K. Freter, H. H. Hübner, H. Merz, H. D. Schroeder und K. Zeile
Ann. Chem. 684, 159 (1965)

"Nuclear Magnetic Resonance Spectra and Structures of Some
  C-Glycosylflavonoids"
W. E. Hillis and D. H. S. Horn
Australian J. Chem. 18, 531 (1965)

"(+)-Hygroline, the Major Alkaloid of Carallia Brachiata
  (Rhizophoraceae)"
J. S. Fitzgerald
Australian J. Chem. 18, 589 (1965)

"The Synthesis of [18]Annulen Trioxide and of [18]Annulene
  Oxide Disulphide"
G. M. Badger, J. A. Elix, G. E. Lewis, U. P. Singh, and
T. M. Spotswood
Chem. Comm. 269 (1965)

"1,3-Diphenylisoindoles"
J. C. Emmett, D. F. Veber, and W. Lwowski
Chem. Comm. 272 (1965)

"Oxidation of Veratrole by Quinones"
I. M. Matheson, O. C. Musgrave, and C. J. Webster
Chem. Comm. 278 (1965)

"Reactions of Phosphoryl Azides with Norbornene. Formation of
  a Novel Phosphorylated Triazoline"
K. Darrell Berlin and L. A. Wilson
Chem. Comm. 280 (1965)

"Some Labile cis-Dialkoxybis(acetylacetonato)titanium Compounds"
D. C. Bradley and C. E. Holloway
Chem. Comm. 284 (1965)

"The Two 1,4:3,6-Dianhydro-D-hexopyranoses"
G. R. Bedford, and D. Gardiner
Chem. Comm. 287 (1965)

"Résonance Magnétique Nucléaire. — Étude par résonance
  magnétique nucléaire du temps de relaxation de l'hydrogéne,
  perturbé par des molécules étrangères"
E. Dayan et G. Widenlocher
Compt. Rend. 260, 4495 (1965)

"Chimi Organique. — Étude de la configuration de l'hydroxy-
  galégine naturelle et synthèse de son stéréoisomère"
M. Olomucki, G. Desvages, N-V. Thoai et J. Roche
Compt. Rend. 260, 4519 (1965)

"Zur Kenntnis der Hexaalkylbenzole. 5. Mitteilung. Über die
  Struktur der Dienaddukte des Hexaäthylidencyclohexans"
H. Hopff und G. Kormany
Helv. Chim. Acta 48, 437 (1965)

De la chimie des ptérines. 11e communication [1]. Sur une
  nouvelle synthèse de ptérines 7,8-dihydrogénées et sur l'
  obtention inattendue de l'hydroxyméthyl-6-ptérine isoméri-
  quement pure"
M. Viscontini et G. Nasini
Helv. Chim. Acta 48, 452 (1965)

"Struktur von Coleon A"
D. Karanatsios und C. H. Eugster
Helv. Chim. Acta 48, 471 (1965)

"Zur Kenntnis der Hexaalkylbenzole. 6. Mitteilung [1]. Hexa-n-
  propyl-benzol und Hexaisopropylbenzol"
H. Hopff, und A. Gati
Helv. Chim. Acta 48, 509 (1965)

"Spektren und Basizität der reinen trans-Konfigurationen von
  substituierten 4-Dimethylaminostilbenen"
M. Syz und H. Zollinger
Helv. Chim. Acta 48, 517 (1965)

"Zur Methylierung von 1-Phenyl-5-sulfanilamido-pyrazol"
K. Eichenberger, R. F. Zurcher, A. Rossi, M. Wilheim und P.
  Schmidt
Helv. Chim. Acta 48, 524 (1965)

"Welkstoffe und Antibiotika. 34. Mitteilung [1]. Synthese von
  Isojavanicin und vereinfachte Synthese von Javanicin"
E. Widmer, J. W. Meyer, A. Walser und E. Hardegger
Helv. Chim. Acta 48, 538 (1965)

"NMR.-Spektren von Zwischenprodukten elektrophiler aromatischer
  Substitutionen und Elektronen-Donator-Acceptor-Komplexen"
W. Koch und H. Zollinger
Helv. Chim. Acta 48, 554 (1965)

"Uber eine Vereinfachung der Beschreibung und Analyse von
  komplizierten kermagnetischen Resonanzspektren mit Hilfe
  von Teilspektren"
P. Diehl
Helv. Chim. Acta 48, 567 (1965)

"Uber die Bindung der Wassermolekel in den Verbindungen Me^{II}
  SO$_4$, 1 H$_2$O und Me^{II}SeO$_4$, 1 H$_2$O: II. Infrarotspektrograph-
  ische und kernmagnetische Resonanz-Untersuchungen. (Me^{II} =
  Mg, Ni, Cu, Co, Fe, Zn, Mn)"
H. R. Oswald
Helv. Chim. Acta 48, 600 (1965)

"Dielectric and Nuclear Magnetic Resonance Studies of the
  Synthetic Polypeptides in the β-Form in the Solid State"
K. Kamashima
Jap. J. Appl. Phys. 4, 259 (1965)

"The Preparation and Oxygen-17 Nuclear Magnetic Resonance
  Spectrum of XeO^{17}F$_4$"
J. Shamir, H. Selig, D. Samuel, and J. Reuben
J. Am. Chem. Soc. 87, 2359 (1965)

"Exchange of Parts between Molecules at Equilibrium. VII.
Scrambling of Sulfur with Halogens on Dimethylgermanium"
K. Moedritzer and J. R. Van Wazer
J. Am. Chem. Soc. 87, 2360 (1965)

"Reaction of $B_{10}H_{10}^{-2}$ with Aryldiazonium Salts"
M. F. Hawthorne and F. P. Olsen
J. Am. Chem. Soc. 87, 2366 (1965)

"Trends in Transition Metal Ion-Ligand Covalency from Nuclear
Magnetic Resonance Contact Shifts"
B. B. Wayland and R. S. Drago
J. Am. Chem. Soc. 87, 2372 (1965)

"Reaction of Diphenyldichlorosilane with Lithium"
H. Gilman and D. J. Peterson
J. Am. Chem. Soc. 87, 2389 (1965)

"The Electronic Properties of Fluoroalkyl Groups. Fluorine
p—π Interaction"
W. A. Sheppard
J. Am. Chem. Soc. 87, 2410 (1965)

"Extraordinary Dipositive Carbonium Ions. A Re-examination
of the Evidence for Their Formation in Sulfuric Acid"
R. J. Gillespie and E. A. Robinson
J. Am. Chem. Soc. 87, 2428 (1965)

"The Proton Magnetic Resonance Spectra of Olefins. IV.
3-Fluoropropenes"
A. A. Bothner-By, S. Castellano, and H. Günther
J. Am. Chem. Soc. 87, 2439 (1965)

"Concerning Linear Fluorine Nuclear Magnetic Resonance
Shielding--Stabilization Energy (Ionization Potential)
Relationships. The para-Substituted Triphenylmethyl
Cations"
R. W. Taft and L. D. McKeever
J. Am. Chem. Soc. 87, 2489 (1965)

"Monocarbahexaborane(7)"
T. Onak, R. Drake and G. Dunks
J. Am. Chem. Soc. 87, 2505 (1965)

"Application of Taft's Fluorine-19 Chemical Shift Correla-
tions to the Study of Secondary Deuterium Isotope Effects"
G. E. Maciel and D. D. Traficante
J. Am. Chem. Soc. 87, 2508 (1965)

"Diene Complexes from the Reaction of Activated Vinylcyclo-
propanes with Iron Pentacarbonyl"
S. Sarel, R. Ben-Shoshan and B. Kirson
J. Am. Chem. Soc. 87, 2517 (1965)

"A New Synthetic Approach to the Penicillins"
E. J. Corey and A. M. Felix
J. Am. Chem. Soc. 87, 2518 (1965)

"Fluorine NMR Spectra and Conformational Isomerization of 1,1-
Difluorocyclohexane"
J. Jonas, A. Allerhand, and H. S. Gutowsky
J. Chem. Phys. 42, 3396 (1965)

"On the Use of Overhauser Effects to Study Nuclear Magnetic
Relaxation by Spin-Rotational Interactions"
P. S. Hubbard
J. Chem. Phys. 42, 3546 (1965)

"Effect of External Magnetic Field on the Rate of Exchange
of Magnetic Dipoles"
H. Shimizu
J. Chem. Phys. 42, 3599 (1965)

"Spin Relaxation and Differential Saturation of ESR Multiple
Lines"
H. Shimizu
J. Chem. Phys. 42, 3603 (1965)

"Relations between Raman Spectroscopy and Nuclear Spin
Relaxation"
R. G. Gordon
J. Chem. Phys. 42, 3658 (1965)

"Deuterium Isotope Effect in Proton-^{13}C Coupling Constants"
G. Fraenkel, and W. Burlant
J. Chem. Phys. 42, 3724 (1965)

"Geminal Spin-Spin Coupling Constants in Disubstituted
Methanes"
R. A. Niedrich, D. M. Grant, and M. Barfield
J. Chem. Phys. 42, 3733 (1965)

"Nuclear Magnetic Resonance in RbMnF3"
R. E. Payne, R. A. Forman, and A. H. Kahn
J. Chem. Phys. 42, 3806 (1965)

"Deuteron Magnetic Resonance in Deuterated Polycrystalline
Ammonium Chloride and Sulfate"
S. W. Rabideau and P. Waldstein
J. Chem. Phys. 42, 3822 (1965)

"Polymer NMR Spectroscopy. XI. Polystyrene and Polystyrene
Model Compounds"
F. A. Bovey, F. P. Hood III, E. W. Anderson, and L. C. Snyder
J. Chem. Phys. 42, 3900 (1965)

"Theoretical Study of C-H Nuclear Spin-Spin Coupling Using a
Constrained SCF Model"
D. S. Bartow and J. W. Richardson
J. Chem. Phys. 42, 4018 (1965)

"Motion of the H_2O Molecule in Barium Bromate Monohydrate"
J. W. McGrath
J. Chem. Phys. 42, 4111 (1965)

"Quadrupole Splitting of the Magnetic Resonance Spectrum of
^9Be in Chrysoberyl"
H. L. Reaves and T. E. Gilmer, Jr.
J. Chem. Phys. 42, 4138 (1965)

"Spin-Echo NMR Studies of Chemical Exchange. IV. Intra-
molecular Exchange of a Coupled AB System"
A. Allerhand and H. S. Gutowsky
J. Chem. Phys. 42, 4203 (1965)

"Proton Magnetic Resonance Studies of Solid Tetramethyls
of Silicon, Germanium, Tin, and Lead"
G. W. Smith
J. Chem. Phys. 42, 4229 (1965)

"Nuclear Relaxation Processes in Systems of Two Spins"
E. L. Mackor and C. Maclean
J. Chem. Phys. 42, 4254 (1965)

"^{13}C Splittings in Proton Magnetic Resonance Spectra. IV.
Halogenated Toluenes"
N. Muller
J. Chem. Phys. 42, 4309 (1965)

"Interactions Spin-Spin Nucléaires. IV. Isomérie de
Rotations Dans des Aldéhydes α-Substitués"
J.-M. Lehn et J. Riehl
J. Chim. Phys. 62, 573 (1965)

"Cembrene, a Fourteen-Membered Ring Diterpene Hydrocarbon"
W. G. Dauben, W. E. Thiessen, and Paul R. Resnick
J. Org. Chem. 30, 1693 (1965)

"Oxidative Rearrangements of Pentacyclic Triterpenes. A
  Method for the Synthesis of Certain Naturally Occurring
  Triterpenes from α- and β-Amyrin"
I. Agata, E. J. Corey, A. G. Hortmann, J. Klein, S. Proskow,
  and J. J. Ursprung
J. Org. Chem. 30, 1698 (1965)

"Regeneration of Steroid Alcohols from their Methyl Ethers"
C. R. Narayanan and K. N. Iyer
J. Org. Chem. 30, 1734 (1965)

"Structure and Stereochemistry of Adducts of Ergosterol with
  Dihalocarbenes"
M. Z. Nazer
J. Org. Chem. 30, 1737 (1965)

"Hydroboration of α-Gurjunene. A Rational Correlation with
  Cyclocolorenone"
P. Pesnelle and G. Ourisson
J. Org. Chem. 30, 1744 (1965)

"Synthesis and Ring Opening of Fused Steroidal Aziridines"
A. Hassner and C. Heathcock
J. Org. Chem. 30, 1748 (1965)

"Synthesis of Dehydrootobain"
D. Brown and R. Stevenson
J. Org. Chem. 30, 1759 (1965)

"Characterization and Synthesis of a Monocyclic Eleven-Carbon
  Acid Isolated from a California Petroleum"
J. Cason and K.-L. Liauw
J. Org. Chem. 30, 1763 (1965)

"Constituents of Withania somnifera Dun. III. The Side Chain
  of Withaferin A"
D. Lavie, E. Glotter, and Y. Shivo
J. Org. Chem. 30, 1774 (1965)

"Studies on the Acid-Catalyzed Esterification of Substituted
  o-Benzoylbenzoic Acids in Methanol"
M. S. Newman and C. Courduvelis
J. Org. Chem. 30, 1795 (1965)

"Ring Openings of Substituted Cyclobutanes Induced by Grignard
  Reagents. II. 2,2,4,4-Tetramethyl-3-dimethylaminocyclo-
  butanone"
L. Weintraub, A. Wilson, D. L. Goldhamer, and D. P. Hollis
J. Org. Chem. 30, 1805 (1965)

"Macro Rings. XXX. Structure of Anomalous Products of
  Acylation of [2.2]Paracyclophane"
D. J. Cram and H. P. Fischer
J. Org. Chem. 30, 1815 (1965)

"2,2,4-Trimethyl-1,2-dihydroquinolines. Preparation and Nuc-
  lear Magnetic Resonance Studies"
A. Rosowsky and E. J. Modest
J. Org. Chem. 30, 1832 (1965)

"Photosensitized Cycloaddition of Haloethylenes and 1,3-
  Dienes"
N. J. Turro and P. D. Bartlett
J. Org. Chem. 30, 1849 (1965)

"Furazan"
R. A. Olofson and J. S. Michelman
J. Org. Chem. 30, 1854 (1965)

"A Free-Radical Oxidation of a Dihydropyridine"
K. A. Schellenberg and F. H. Westheimer
J. Org. Chem. 30 1859 (1965)

"Resin Acids. II. Cationic Cyclization of Isopimaric Acid
  Derivatives. Partial Synthesis of Isohibane"
W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels
J. Org. Chem. 30, 1873 (1965)

"Resin Acids. III. 9-Hydroxyabietic Acid and Its Trans-
  formation Products"
W. Herz and H. J. Wahlborg
J. Org. Chem. 30, 1881 (1965)

"Heterocyclic Studies. XIV. Some Further Rearrangements in
  the Dihydro-1,2-diazepinone Series"
J. A. Moore and W. J. Theuer
J. Org. Chem. 30, 1887 (1965)

"Heterocyclic Studies. XV. 5-Methyl-4-phenylpyrazole-1-
  acetic Acid. An Oxidation Product of 2,3-Dihydro-5-methyl-
  6-phenyl-4H-1,2-diazepin-4-one"
J. A. Moore and C. L. Habraken
J. Org. Chem. 30, 1889 (1965)

"Heterocyclic Studies. XVI. The Assignment of Isomeric and
  Tautomeric Structures of Pyrazoles by Nuclear Magnetic
  Resonance"
C. L. Habraken and J. A. Moore
J. Org. Chem. 30, 1892 (1965)

"Synthesis and Isomerization of 2,6-Dimethyl-n-butylbenzene"
F. E. Condon and A. A. Zavitsas
J. Org. Chem. 30, 1901 (1965)

"The Reduction of 1-Benzylmethylpyrazinium Salts with Sodium
  Borohydride"
R. E. Lyle and J. J. Thomas
J. Org. Chem. 30, 1907 (1965)

"Thioureas and Isothiuronium Salts. Monomeric Derivatives"
C. G. Overberger and H. A. Friedman
J. Org. Chem. 30, 1926 (1965)

"Acetylenic and Ethylenic Iodonium Salts and Their Reactions
  with a Carbanion"
F. Marshall Beringer and S. A. Galton
J. Org. Chem. 30, 1930 (1965)

"Phosphonic Acids and Esters. IX. Thermal Reactions of
  Trialkyl Phosphites with Nonactivated Acetylenes"
C. E. Griffin and T. D. Mitchell
J. Org. Chem. 30, 1935 (1965)

"3d-Orbital Resonance in Trivalent Organophosphines. I.
  Metalation of Methylphosphines"
D. J. Peterson and H. R. Hays
J. Org. Chem. 30, 1939 (1965)

"Bridged Polycyclic Compounds. XXVIII. The Proton Magnetic
  Resonance Spectra of Some Dibenzobicyclo[3.2.1]octadienes"
S. J. Cristol, J. R. Mohrig, and D. E. Plorde
J. Org. Chem. 30, 1956 (1965)

"Synthesis and Some Spectral Properties of Diphenyltriptycene"
C. F. Wilcox, Jr., and F. D. Roberts
J. Org. Chem. 30, 1959 (1965)

"Reactions of Trivalent Phosphorus Derivatives with Sterically
  Hindered 4-Bromocyclohexadienones"
B. Miller
J. Org. Chem. 30, 1964 (1965)

"Some New Tricyclic Compounds Containing the Bispidine Moiety"
S. Chiavarelli and G. Settimj
J. Org. Chem. 30, 1969 (1965)

"Chemistry of Dianions. Formation and Reactivity of Some
  Anionic Species Derived from Tetraphenylbutatriene"
R. Nahon and A. R. Day
J. Org. Chem. 30, 1973 (1965)

"The Claisen Rearrangement. III. para Claisen Rearrangement
  to Nitrogen in Allyl 3-Substituted 4-Quinolyl Ethers"
Y. Makisumi
J. Org. Chem. 30, 1986 (1965)

"The Claisen Rearrangement. IV. "Out-of-Ring" Claisen
  Rearrangement to the Active Methylene Group of a meta Side
  Chain in Allyl 4-Quinolyl Ethers"
Y. Makisumi
J. Org. Chem. 30, 1989 (1965)

"Reactions of p-Tolylsulfonylmethylmagnesium Bromide with α,β-
  Unsaturated Aldehydes and Ketones"
J. W. McFarland and D. N. Buchanan
J. Org. Chem. 30, 2003 (1965)

"The Addition of Ethanethiolic Acid to 3β-Acetoxy-5,16-
  pregnadien-20-one"
R. M. Dodson, P. B. Sollman, and J. R. Deason
J. Org. Chem. 30, 2009 (1965)

"An Assignment of threo-erythro Configurations Based on a
  Nuclear Magnetic Resonance Investigation"
J. C. Randall, R. L. Vaulx, M. E. Hobbs, and C. R. Hauser
J. Org. Chem. 30, 2035 (1965)

"Equilibration of para-Substituted Styrenes to Produce p-
  Xylylenes"
R. W. Kluiber
J. Org. Chem. 30, 2037 (1965)

"Buxus Alkaloids. VIII. The Isolation and Constitution of
  Cycloprotobuxine-D"
S. M. Kupchan and E. Kurosawa
J. Org. Chem. 30, 2046 (1965)

"Isolation and Structure of Aeneadiol"
X. A. Domínguez and V. Barragán
J. Org. Chem. 30, 2049 (1965)

"The Oxidation of Dunnione with Alkaline Hydrogen Peroxide"
M. A. Oxman, M. G. Ettlinger, and A. R. Bader
J. Org. Chem. 30, 2051 (1965)

"The 1-Azoniabicyclo[3.1.0]hexane System in a β-Benzomorphan
  Synthesis"
E. M. Fry
J. Org. Chem. 30, 2058 (1965)

"An Experimental Demonstration of the Nuclear Magnetic
  Resonance Assignments in the 6,7-Dimethylisoalloxazine
  Nucleus"
F. J. Bullock and O. Jardetzky
J. Org. Chem. 30, 2056 (1965)

"Synthesis of Analogs of δ-Aminolevulinic Acid"
C. C. Price and T. Padmanathan
J. Org. Chem. 30, 2064 (1965)

"The Structure of Secondary Amine-Sulfur Dioxide Salts"
S. T. Purrington and P. Wilder, Jr.
J. Org. Chem. 30, 2070 (1965)

"2-Hydrazino- and 2-(2,2-Dimethylhydrazino)-2-thiazoline"
T. P. Johnston, C. R. Stringfellow, Jr., and A. Gallagher
J. Org. Chem. 30, 2073 (1965)

"Free-Radical Addition of Perfluoroalkylnitriles to Propylene"
G. J. Janz, N. A. Gac, A. R. Monahan, and W. J. Leahy
J. Org. Chem. 30, 2075 (1965)

"Reactions of Phosphorus Compounds. VI. A General Synthesis
  of Cycloalkenes"
E. E. Schweizer and G. J. O'Neill
J. Org. Chem. 30, 2082 (1965)

"Ethyl Dimethylcarbamate Hydrothiocyanate. Preparation and
  Properties"
L. A. Spurlock and P. E. Newallis
J. Org. Chem. 30, 2086 (1965)

"Synthesis of 1-Methylcyclopropene"
F. Fisher and D. E. Applequist
J. Org. Chem. 30, 2089 (1965)

"Structure of Cyclization Products of Substituted 2-Amino-N-
  (2-hydroxyethyl)benzamides"
G. F. Field, W. J. Zally, and L. H. Sternbach
J. Org. Chem. 30, 2098 (1965)

"A re-examination of Ring Closure Reactions of Substituted 2-
  Aminobenzamides and Related Compounds"
A. A. Santilli and T. S. Osdene
J. Org. Chem. 30, 2100 (1965)

"The Behavior of Isopropenyl Acetate in Strong Sulfuric and
  Deuteriosulfuric Acids"
J. A. Landgrebe
J. Org. Chem. 30, 2105 (1965)

"NMR Study of Styrene-Methyl Methacrylate Copolymer Obtained
  by Radical Polymerization"
K. Ito, Y. Yamashita
J. Polymer Sci. B3, 625 (1965)

"NMR Study of Styrene-Methyl Methacrylate Copolymer Obtained
  by Anionic Polymerization"
K. Ito, Y. Yamashita
J. Polymer Sci. B3, 631 (1965)

NMR Study of Styrene-Methyl Acrylate Copolymer Obtained by
  Radical Polymerization"
K. Ito, Y. Yamashita
J. Polymer Sci. B3, 637 (1965)

"Electron Irradiation and Racemization of Isotactic Poly-
  (Methyl Methacrylate)"
E. V. Thompson
J. Polymer Sci. B3, 675 (1965)

"The Influence of Substitution on CH.CF and CF.CF Coupling
  Constants"
R. J. Abraham and L. Cavalli
Mol. Phys. 9 67 (1965)

"A Proanthocyanidin From Avocado Seed"
T. A. Geissman and H. F. K. Dittmar
Phytochem. 4, 359 (1965)

"Baptisia Flavonoids: Nuclear Magnetic Resonance Analysis"
T. J. Mabry, J. Kagan and H. Rösler
Phytochem. 4, 487 (1965)

"Studies on Conformation and Reactivity — I. The Polyphosphoric
   Acid-Catalyzed Ring Opening of 4,5-Epoxy-3-oxo Steroids—
   The Synthesis of 4-Ethylthiocholest-4-EN-3-One and its
   Analogs"
M. Tomoeda, M. Ishizaki, H. Kobayashi, S. Kanatomo, T. Koga,
   M. Inuzuka and T. Furuta
Tetrahedron 21, 733 (1965)

"The Photochemical Rearrangement of Steroidal 17-Nitrites"
C. H. Robinson, O. Gnoj, A. Mitchell and E. P. Oliveto,
   and D. H. R. Barton
Tetrahedron 21, 743 (1965)

"Studies on A-Norsteroids— IV. The C-1,2 Isomeric Ketols
   in 17β-Hydroxy-A-Nor-5β-Androstane Series"
K. Yoshida and T. Kubota
Tetrahedron 21, 759 (1965)

"Synthesis of Substituted Linear Furano[2,3-g][1]Benzopyrones
   and [3,2-b]Thianaphthenopyrones"
A. Mustafa, W. Asker, O. H. Hishmat, M. I. Ali, A.-K. E.
   Mansour, N. M. Abed, K. M. A. Khalil and S. M. Samy
Tetrahedron 21, 849 (1965)

"Tetramethoxy-Äthylen —I. Thermische Spaltung von 7,7-
   Dimethoxy-Norbornadien-Derivaten"
R. W. Hoffman und H. Häuser
Tetrahedron 21, 891 (1965)

"Studies on Plants—IX. Isolation and Structure of Ribalinium
   Salts"
R. A. Corral and O. O. Orazi
Tetrahedron 21, 909 (1965)

"Constituents of Thai Medicinal Plants—I. Aglaiol"
D. Shiengthong, A. Verasarn and P. NaNonggai-Suwanrath
Tetrahedron 21, 917 (1965)

"Diamagnetic Anisotropy and Magnetic Birefringence of Crystals
   Containing XO_3 Group in Relation to Optical Absorption"
S. P. Tandon
Z. Phys. Chem. 228, 151 (1965)