

Premas ✓
Mailed:
Jan. 31, 1963

Monthly
Encumenical
Letters from
Laboratories
Of
N - M - R
No. 52

Lit. nicht
durchgesehen!

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DEADLINE FOR NEXT ISSUE
February 25, 1963

Eine monatliche Sammlung informativer Privatbriefe aus den Kernresonanz-Laboratorien.

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A. CAREFULLY !!!



UNION CARBIDE CHEMICALS COMPANY

DIVISION OF UNION CARBIDE CORPORATION

P.O. BOX 8361, SOUTH CHARLESTON 3, W. VA.

RESEARCH AND DEVELOPMENT

January 25, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 5th Avenue
Pittsburgh, Pennsylvania

Dear Barry:

Enclosed is a preview for your MellonNMR readers of the titles and authors of the papers proposed for presentation at 4th OCEANS. The detailed time scheduling of all sessions has not been included because, frankly, it has not at this time been resolved. Although it was once intended that the program for 4th OCEANS should consist merely of 12 ninety minute sessions, certain of the 12 sessions are bulging badly; it appears at moments of despondency that 4th OCEANS will have to begin its sessions on Eastern Daylight Time each morning and conclude them on Pacific Standard Time each evening, if there is to be a reasonable time for general discussion. Recommendations from your ingenious readers about ways to cope with this problem are invited.

In addition to the formal program, there may be one or more informal and impromptu evening sessions, depending on the whims of the attendees as well as on the availability of talent to lead the discussions of interest. Numerous suggestions have already been received that such extra sessions should include: (1) Spectrometer Troubleshooting (With Emphasis on the A-60), and (2) Review of Optimum Operational Techniques (Including

Dr. B. L. Shapiro

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January 25, 1963

Sample Preparation, Referencing, Calibration, Particularly for the A-60). Prospective attendees should be certain to express their feelings about such Evening Bull Sessions either to me or to other members of the 4th OCEANS Committee (Paul Lauterbur, Tom Page, Jim Shoolery, or Louis Allred).

Sincerely,

Charlie.

Chas. W. Wilson, III
Chairman, 4th OCEANS Committee

CWW/dtf

P.S. Any NMR spectroscopist who has not yet received an individual notice of 4th OCEANS, and who desires to be included on the mailing list for this and/or future OCEANS, is urged to send me his name and address at once. The final mailing, discussing scheduling and local arrangements for 4th OCEANS, will be made in about two weeks.

P.P.S. ^{wasting} Knowing of your basic resentment of ^{of} this golden space, Barry, let me try to fill it in this manner:

Q. How do PORCUPINES MAKE LOVE ???

A. (See top of page 1)

Tentative

4th OCEANS Program

Mellon Institute, Pittsburgh, Pa.
February 28 through March 2, 1963

(The following papers will be presented at 4th OCEANS. The order of presentation of papers within each session may, however, be varied; in a few cases, transfer of papers from one session to another may occur in an effort to better utilize the available time. Final program scheduling and arrangements will be announced later.....No distinction is made herein between "invited" and "contributed" papers. Anticipated maximum lengths of papers — in minutes — are indicated in the left margin. Discussion cut short in any session may be resumed at the end of the last session each day.)

Thursday, February 28 (Morning)

Session A-1: "New Broadline Techniques and Applications"

Chairman: D. I. Bolef (Westinghouse Electric Corp.)

- 25 I. "Effect of Electric Fields on NMR and NQR"
R. W. Dixon (Harvard University)
- 25 II. "Single Crystal Techniques in NMR"
P. L. Sagalyn (U. S. Army Materials Research Laboratory)
- 25 III. "Techniques of NMR in Ferromagnetic Materials"
L. H. Bennett (National Bureau of Standards)

Session A-2: "NMR in Solids Other than Polymers"

Chairman: T. J. Rowland (University of Illinois)

- 30 I. "NMR Saturation Effects in Solids"
W. I. Goldberg (Pennsylvania State University)
- 25 II. "Applications of NMR to Transition Metals and Their Alloys"
D. O. Van Ostenburg (Argonne National Laboratory)
- 30 III. "Magnetic Anisotropy and Broadline PMR Studies on Sandwich Compounds"
L. N. Mulay (University of Cincinnati)

Thursday (Afternoon)

Session A-3: "NMR in Polymers (General)"

Chairman: D. W. McCall (Bell Telephone Laboratories)

- 15 I. "NMR Fiber Studies in Polymers"
D. Hyndman (Lear Siegler, Inc.)
- 15 II. "Fiber Samples and Parameters for Broadline NMR Studies"
W. O. Statton (E. I. duPont de Nemours & Co.)

- 15 III. "Modification of a Pulsed NMR Spectrometer for Solids"
D. C. Douglas and D. W. McCall (Bell Telephone Laboratories)
- 10 IV. "NMR Investigation of Poly- α -olefin Fibers"
A. Peterlin and H. G. Olf (Research Triangle Institute)
- 10 V. "Sub-Molecular Motion in Solid Polyvinylbiphenyl"
E. E. Genser (Jet Propulsion Laboratory)

Session A-4: "New NMR Applications"

Chairman: R. S. Codrington (Varian Associates)

- 30 I. "NMR Lineshift and Enhancement in Organic Free Radicals"
J. H. Burgess (Washington University)
- 30 II. "Electron Nuclear Double Resonance (ENDOR)"
P. M. Llewellyn (Varian Associates)
- 10 III. "RF Bridge for Pulsed NMR"
I. J. Lowe and D. Barnaal (University of Pittsburgh)
- 10 IV. "Effects of RF Pulse Length on Free Induction Decays"
D. Barnaal and I. J. Lowe (University of Pittsburgh)
- 10 V. "Determination of Low Frequency Motional Spectra Using Measurements of T_1 in the Rotating Reference System"
D. C. Look and I. J. Lowe (University of Pittsburgh)

Friday, March 1 (Morning)

Session B-1: "NMR Instrumentation: Shortcomings and Maintenance"

Chairman: T. J. Flautt (The Proctor & Gamble Co.)

- 30 I. "The Care and Feeding of Spectrometers"
J. D. Ramsay (Varian Associates)
- 30 II. "What to Do Until the Doctor Arrives"
P. Bender (University of Wisconsin)
- 10 III. "HR-60 Performance with Varian V-K3529 High Sensitivity Probe Modification"
R. H. Elsken (U. S. Department of Agriculture)

Session B-2: "New Developments in NMR Instrumentation"

Chairman: E. B. Baker (The Dow Chemical Company)

- 20 I. "High Resolution NMR by Modulation Through the Spin Coupling"
W. A. Anderson (Varian Associates)

- 20 II. "Results with NMR at Room Temperature with a Superconducting Magnet"
H. E. Weaver (Varian Associates)
- 20 III. "Pulsed NMR in Rapidly Rotating Solids"
H. Kessemeler (Washington University)
- 20 IV. "Proton Stabilized NMR Spectrometer for all Magnetic Nuclei, Using a Frequency Synthesizer; Double Resonance and INDOR"
E. B. Baker (The Dow Chemical Company)

Friday (Afternoon)

Session B-3: "High Resolution NMR in Polymers"

Chairman: F. A. Bovey (Bell Telephone Laboratories)

- 20 I. "Structure Elucidation of Polymers and Hydrocarbons by NMR"
K. W. Bartz (Humble Oil Company)
- 20 II. "Saturation Effects in Solutions of Polymethyl Methacrylate"
R. D. Bakula and D. L. Glusker (Rohm and Haas Company)
- 20 III. "The Use of Spin Decoupling in the Elucidation of Polymer Structure"
F. A. Bovey, E. W. Anderson, and D. C. Douglass (Bell Telephone Laboratories)
- 15 IV. "NMR Spectra of Some Fluorine-Containing Polymers"
C. W. Wilson, III and E. R. Santoe, Jr. (Union Carbide Chemicals Company)
- 10 V. "Sequence-Distribution Studies in Copolymers by NMR"
J. Harwood (University of Akron), W. M. Ritchey (SOHIO), and J. V. Postinger (Monsanto)

Session B-4: "NMR Relaxation Phenomena"

Chairman: S. Meiboom (Bell Telephone Laboratories)

- 25 I. "The Study of Ion Binding to Macromolecules by Proton Relaxation Techniques"
J. Eisinger (Bell Telephone Laboratories)
- 25 II. "Measurement of the Rates of Inversion of Amines"
M. Saunders (Yale University)

- 40 III. "Spectral Assignment Using a General Nuclear Overhauser Effect"
K. Kuhlmann (Harvard University)
- 10 IV. "Nuclear Spin Relaxation in Water Adsorbed on Cellulose"
E. D. Stejskal (University of Wisconsin)

Saturday, March 2, 1963 (Morning)

Session C-1: "Double Resonance"

Chairman: J. D. Baldeschwieler (Harvard University)

- 10 I. "Interpretation of Field-Sweep-Decoupled Spectra"
S. L. Manatt and D. D. Elleman (Jet Propulsion Laboratory)
- 10 II. "Remarks on Signs of Various Spin-Spin Coupling Constants"
G. V. D. Tiers (Minnesota Mining and Manufacturing Co.)
- 10 III. "Relative Signs of Some H-H, H-F, and F-F Coupling Constants"
M. Barfield (Harvard University)
- 10 IV. "Multiple Decoupling of Spins"
F. A. Nelson (Varian Associates)
- 10 V. "An RF Oscillator for Heteronuclear Double Resonance"
R. C. Hopkins (Harvard University)
- 10 VI. "Adaptation of a Varian Variable-Frequency R-F Unit to Spin-Decoupling"
D. D. Elleman and S. L. Manatt (Jet Propulsion Laboratory)
- 10 VII. "Determination of the Spectra of Hydrogen Bonded to Nitrogen by Spin-Decoupling Technique"
M. Sheinblatt (National Institutes of Health)

Session C-2: "Non H^1 NMR Spectra and Special Techniques"

Chairman: P. C. Lauterbur (State University of New York)

- 20 I. "Deuterium NMR Spectroscopy"
P. Diehl (University of Basel)
- 10 II. "The Effect of Paramagnetic S-State Ions on the B^{11} NMR Spectra of Boron Hydrides"
J. D. Baldeschwieler (Harvard University)
- 10 III. "Use of Metal Ions as an Aid in Spectral Interpretation"
N. C. Li and R. Mathur (Duquesne University)

- 10 IV. "Theory and Practice of Averaging as Applied to NMR Spectroscopy"
J. B. Krauss (Mnemotron Corporation)
- 10 V. "¹¹B, ¹⁹F, ¹H, and ³¹P NMR Studies of Boron Complexes of Polycyclic Phosphites"
J. G. Verkade, C. W. Heitsch, and R. W. King (Iowa State Univ.)
- 10 VI. "Determination of ¹³C Chemical Shifts by Proton Decoupling"
D. M. Grant (University of Utah)
- 10 VII. "Determination of Relative Signs of the Couplings in A₂B₂ NMR Spectra of 1,2-Disubstituted Ethanes"
R. C. Hirst and D. M. Grant (University of Utah)

Saturday (Afternoon)

Session C-3: "A-60 Type Instruments and Quantitative NMR Measurements"
Chairman: B. L. Shapiro (Mellon Institute)

- 20 I. "A Survey of A-60 Practices, Performance Characteristics, Opinions, Hopes, and Desires"
B. L. Shapiro (Mellon Institute)
- 10 II. "Use of a Hybrid A-60/HR-60 System"
E. D. Becker and R. B. Bradley (National Institutes of Health)
- 15 III. "Recent A-60 Work at Varian on Microcell Techniques, High and Low Temperature Spectra, and Quantitative Measurements"
D. P. Hollis (Varian Associates)
- 15 IV. "Signal-to-Noise Ratio Improvement by CAT Method"
P. Laszlo, L. C. Allen, P. V. R. Schleyer and R. M. Erdahl (Princeton University)
- 15 V. "Souping up Your A-60"
T. J. Flautt (Proctor and Gamble)
- 10 VI. "Quantitative Measurement of Hydrogen Types by Integrated NMR Intensities"
J. L. Jungnickel and J. W. Forbes (Shell Development Co.)
- 10 VII. "Long-Term Drift Control for the A-60"
J. P. Heeschen (The Dow Chemical Company)
- 10 VIII. "Increased Sensitivity for the A-60"
M. M. Crutchfield (Monsanto Chemical Company)

Session C-4: "NMR Spectral Analysis"

Chairman: C. A. Reilly (Shell Development Company)

- 20 I. "Deceptively Simple Spectra"
H. J. Bernstein (National Research Council, Canada)
- 20 II. "Direct Analysis of NMR Spectra"
D. R. Whitman (Case Institute of Technology)
- 20 III. "Assignment of Energy Levels by Double Resonance Techniques"
W. A. Anderson (Varian Associates)
- 10 IV. "Computer Analysis of NMR Spectra: Symmetry Factoring"
R. C. Ferguson (E. I. duPont de Nemours & Co.)
- 10 V. "Protonation of Methyl Pyrazine N-Oxides for Structure Determinations by NMR"
T. E. Beukelman (E. I. duPont de Nemours & Co.)
- 10 VI. "NMR Spectral Parameters for 1,1-Dichloro-2-Phenyl-Cyclopropane"
C. A. Reilly (Shell Development Company)

Supplementary Programme*

- 10 I. "Determination of Oil in Wax by Wide-line NMR"
R. C. Barras, J. F. Boyle, and C. F. Grainger (The Atlantic Refining Company)
- 10 II. "Higher Accuracy in Low-Frequency Measurement by Period Gating"
W. B. Moniz (Naval Research Laboratory)
- 10 III. "Substituent Effects on NMR Coupling Constants and Chemical Shifts in a Saturated System: Hexachlorobicyclo 2.2.1 heptenes"
K. L. Williamson (Mount Holyoke College)

*Papers arrived after deadline, or have been presented previously elsewhere, or both. These will be read only if, in the opinion of the Session Chairman, time is available at the conclusion of the regular program for Session C-4. Abstracts of these papers will, in any case, be included along with the papers constituting the regular program.

December 29, 1962.
THE OHIO STATE UNIVERSITY
 DEPARTMENT OF CHEMISTRY
 88 WEST 18TH AVENUE
 COLUMBUS 10, OHIO

Dr. E. L. Shapiro
 Mellon Institute
 4400 Fifth Avenue
 Pittsburgh, Pa.

Dear Barry:

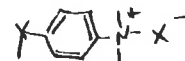
We acquired our A60 Spectrometer last summer. The instrument performed fabulously for three months and we have been trying ever since to repeat the original 0.1 cps resolution. It would be helpful if the manufacturer provided a list of standard adjustments for routine service on the A60. We have equipped both spectrometers with styrofoam magnet insulation based on the J.P.L. design of Manatt. Not all magnets are of the same shape and it is important to check all measurements before cutting the styrofoam. The tap water in our buildings is warm even during the winter and this requires that the heat exchanger operate sometimes through a 2 degree C temperature differential. We have used a Chevrolet car radiator but are switching over to the Dunham Busch Inc. Water converter 8" x 6" with bronze head and copper coils, four pass.

Our work on the NMR spectra of anilinium salts in solution has been sent off for publication and preprints are available. Briefly the results are as follows: The ring proton line shapes we obtain for solutions of anilinium salts in solvents of widely different polarity are remarkably dependent on the nature of the accompanying anions. The effect is not present when the nitrogen is heavily substituted and when the accompanying anion is large. In that case spectra of anilinium cations unperturbed by anions are obtained and as expected from the inductive effect of N^+ the ortho hydrogens are less shielded than the meta and para hydrogens. From the NMR data we find that all our salts are not dissociated into the parent acids and bases to any measurable extent, that under our conditions the rate of NH exchange for a particular salt varies widely whilst the ring hydrogen line shape changes not at all and that the rate of exchange of anions between cations is very fast. If we compare the shifts for the ring hydrogens in N,N,N -trimethyl-*p*-chloroanilinium chloride (2.17 and 2.53 tau units for hydrogens *ortho* and *meta* to nitrogen, respectively) and in *p*-chloroanilinium chloride (2.55 tau units for all hydrogens) determined with dimethyl sulfoxide solutions it would appear that in the unsubstituted salt the N^+ substituent had no effect on the shifts of the ring hydrogens as the hydrogens in chlorobenzene all appear at 2.51 tau units. Thus

contd.

THE OHIO STATE UNIVERSITY
 DEPARTMENT OF CHEMISTRY
 88 WEST 18TH AVENUE
 COLUMBUS 10, OHIO

the effect of the anion is to counteract the inductive effect of N^+ on the charge distribution around the ring. The effect of charge on shift has been treated by Musher, Buckingham and ourselves. The only configuration in which the anion will counteract the effect of the cation is one in which the two centers of charge are next to one another, within four angstroms. Such a species would be called an intimate ion pair and is not to be confused with the one described by Winstein. A suitable model for such an ion pair is the BF_3 adduct of *p*-chloroaniline where we know that the centers of charge are juxtaposed. The NMR spectrum for this species is very similar to that of the hydrochloride of *p*-chloroaniline. Then we can claim that the hydrochlorides and trifluoroacetates of primary anilines all exist in our solutions as intimately associated ion pairs of this structure, I. These are the extreme cases involving closest approach for the two centers of charge. As these two centers move further apart the accompanying anion will exert less effect and in the limit we have the unperturbed anilinium cation.



We have recently analysed the ABX multiplet obtained from benz-bromocyclobutene. The parameters of interest are:

δ_A	6.521	tau units	$J_{AB} = 8.3$
δ_B	6.243	" "	
δ_X	5.310	" "	$J_{AX} = 2.7$
			$J_{BX} = 1.2$

We looked at the spectrum under conditions of high power, Whiffen's method and I suspect that the geminal coupling is of opposite sign to the other two.

Best wishes.

Gideon Fraenkel

3 January 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13 Penn.
USA

Dear Dr. Shapiro,

I would appreciate it very much if you could put me on the mailing list for Mellonir. As a contribution to this publication I would like to describe some of our recent work:

We have been measuring relaxation times (by the saturation methods) of ^{14}N in CH_3CN dissolved in various solvents. We used a pulsed type (at 5Kc) spectrometer constructed in Rehovot by M. Sasson and A. Szoke. The frequency was 2.3Mc corresponding to a permanent magnet of 7 KO. T_1 measurements were much less accurate than T_2 measurements, the reason being partly attributed to difficulties in the calibration of the RF field. In most cases, however, T_1 values were within 20 percent of the T_2 values.

Some of the results are given in the following Table:

Concentration of CH_3CN (per- cent by Volume)	$T_2 \times 10^3$ (sec)		
	in H_2O	in C_6H_6	in CH_3OH
50	2.8 ± 0.1	2.7 ± 0.1	3.4 ± 0.2
33	2.8 ± 0.1	2.7 ± 0.1	3.4 ± 0.2
20	3.0 ± 0.1	2.7 ± 0.1	3.3 ± 0.2

When the results are "corrected" for bulk viscosity the differences between the T_2 values for the solutions become even smaller. The presumed H bond formation in CH_3OH or H_2O solutions, does not seem to have any marked effect on the T_2 values.

Further work on ^{14}N nmr spectroscopy, conducted with a Varian Spectrometer, is being continued at present.

Yours sincerely,

A. Loewenstein
A. Loewenstein

Alrab



התחנה לכימיה
DEPARTMENT OF CHEMISTRY

UNIVERSITY OF MARYLAND
COLLEGE PARK

DEPARTMENT OF CHEMISTRY

January 10, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

Recently considerable attention has been given to the problem of interpreting chemical shifts in terms of intra- and intermolecular electrostatic fields. Buckingham in an important paper (Can. J. Chem. 38, 300 (1960)) showed that the proton screening constant in an X-H bond is modified in a manner which can be represented by

$$\sigma_e = -A \langle E_x \rangle - B \langle E^2 \rangle$$

where E_x is the electric field along the X-H bond, E^2 is the square of the field, and A and B are bond parameters that depend on X. This model has been applied with considerable success to the interpretation of chemical shifts due to medium effects, and more recently extended by Musher to the calculation of shifts due to "inductive effects" within a molecule.

At this time I would like to report a number of A's and B's for bonding situations involving fluorine. I am also including for comparison some other values involving protons. Values for which there is no literature reference given have been determined as part of a wider program on medium effects at the NRC laboratory of Dr. H. J. Bernstein.

Bond	$A \times 10^{12}$ esu	$B \times 10^{18}$ esu
$\text{SiF}(\text{SiF}_4)$		43.5 ± 5.1
$\text{SF}(\text{SF}_6)$		29.5 ± 2.4
$\text{CF}(\text{CHF}_3)$	-9.9 ± 3.6	15.1 ± 3.0
$\text{CF}(\text{CF}_4)$		16.4 ± 2.1
$\text{CH}(\text{CHF}_3)$	2.9 ± 0.8^a	0.84 ± 0.3^a
CH (nonpolar hydrocarbons)		1.0 ± 0.3^b
HCl	40.4 ± 2.0^b	0.38 ± 0.1^b

^aL. Petrakis and H. J. Bernstein, J. Chem. Phys., 37, 2732 (1962)
^bW. T. Raynes, A. D. Buckingham, and H. J. Bernstein ibid 36, 3481 (1962)

It should be noted that the experimental values listed here were obtained from the pressure dependence of the chemical shift of the indicated gases. It is significant that not only can the values of A and B change appreciably, but A can also change in sign. A detailed discussion of these parameters is to be given in a forthcoming publication in J. Chem. Phys. that Dr. Bernstein and I are preparing.

Sincerely yours,

Leon Petrakis
Leon Petrakis

LP:sjb

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA

January 9, 1963

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Your reminder that a contribution to M.E.L.L.O.N.M.R. is due surprised me - until I looked at the calendar and found Justice to be on your side.

Of the various fruits maturing on the local vine, the one which seems to have reached just the right degree of ripeness is a study of the concentration dependence of the chemical shift in the system acetic acid-acetic anhydride.

I have long been disturbed by the following situation: G. Allen and E. F. Caldin in Quart. Revs. 7, 278 (1953) make the statement, which seems to be widely accepted, "In solvents which are capable of forming hydrogen-bonded complexes, carboxylic acids associate with the solvent molecules rather than with their own species. Thus they give normal molecular weights in ethers, esters and ketones." On the other hand, NMR results on solutions of carboxylic acids in donor solvents, such as some by Reeves, have been interpreted on the basis of a monomer-dimer equilibrium. Indeed, if the statement of Allen and Caldin were correct, no concentration dependence of the OH shift should be found in such systems. Instead, a marked concentration dependence is always observed.

It seemed that one must conclude either that the citation from Allen and Caldin is in error or that the observed concentration dependence is somehow spurious. The most likely source of a nongenuine concentration dependence would be contamination with water. Thus in a solution containing 1 mole percent acid, 0.1 mole percent water and 98.9% solvent, the OH resonance would be a long way from its position in the anhydrous sample. As the acid concentration rises, with constant water concentration, the error would gradually become less important. Overall, a quite incorrect curvature would be obtained for a chemical shift vs. concentration plot.

It is very difficult to assert with confidence that a sample is completely free of water, but the acetic acid-acetic anhydride system is exceptional in this respect. Traces of water soon react with the solvent (a process which can be followed by NMR) to produce a slight increment of solute, and after a suitable reaction time one is assured that the only

-2-

molecules containing OH groups are indeed acetic acid.

The observed concentration dependence is very similar to those found previously for other carboxylic acids in electron-donor solvents. We feel that this is the first experimental indication that the samples used were sufficiently dry to exclude the possibility that the concentration dependence was fictitious. Of course it is still possible that traces of water influenced the detailed shapes of the reported shift-concentration curves. At any rate, it then seems likely that the carboxylic acids do dimerize in these solvents. Perhaps many of your readers will say that they knew this all along, but the majority of chemists with whom I've talked have voted with Allen and Caldin. It is noteworthy that molecular-weight data for this kind of system are extremely sparingly available. Some of the people here will be taking a vacation from the practice of NMR spectroscopy to do some work that will help to remedy this lack.

With best regards,

Nobley
Norbert Miller

Phil Rose
Philip I. Rose.

NM/FIR:bs

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of
Chemistry and Chemical Engineering

January 11, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

In a previous report we have shown that the nuclear magnetic resonance spectrum of the α -methylene protons in 1-dodecyl disulphide dioxide supports the unsymmetrical thiol-sulphonate structure, $\text{RSO}_2\text{-SR}$, (I), rather than the symmetrical disulphoxide structure, RSO-SOR , (II). The fact that two triplets were observed in the spectrum (see figures in reference (1)) was cited as evidence favoring the unsymmetrical structure, whereas a single triplet was expected for the symmetrical structure.

However, in dialkyl sulphites², RO-SO-OR , cyclic sulphites³ and sulphinic esters⁴, RSO-OR , the two protons of the same α -methylene group are not equivalent. This non-equivalence has been interpreted⁴ as the result of asymmetry of the non-planar sulphur atoms in these compounds even though the methylene groups are free to rotate about the C-S bonds. Consequently, if 1-dodecyl disulphide dioxide has the symmetrical structure, (II), the NMR spectrum of the α -methylene protons could have the form of an ABX_2 system⁵. From an examination of the spectrum shown in the Figure¹, one cannot rule out such a possibility since an ABX_2 system could result in a complexity of lines similar to this spectrum⁶. Therefore, our earlier conclusion¹ that the dioxide is unsymmetrical may be somewhat questionable⁷.

To overcome this objection we have examined the NMR spectra of the methylene protons of dibenzyl disulphide, its monoxide and dioxide. In contrast to 1-dodecyl disulphide and its oxygen derivatives, interpretations of these spectra are much more straightforward because there are no protons on the neighboring atoms to cause additional couplings.

1. Allen, Jr., P., Berner, P. J. and Malinowski, E. R., *Chem. & Ind.*, 1961, 1164.
2. Finegold, H., *Proc. Chem. Soc.*, 1960, 283.
3. Pritchard, J. G. and Lauterbur, P. C., *J. Am. Chem. Soc.*, 1961, **83**, 2105.
4. Waugh, J. S. and Cotton, F. A., *J. Phys. Chem.*, 1961, **65**, 562.
5. The notation used here is taken from Pople, J. A., Schneider, W. G. and Bernstein, H., "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., N. Y., 1959.
6. Mortimer, F. S., *J. Mol. Spec.*, 1959, **3**, 335.
7. We wish to thank Dr. J. van der Veen for bringing our attention to this point.

Dr. B. L. Shapiro

-2-

January 11, 1963

Dibenzyl disulphide is symmetrical and does not contain an asymmetric sulphur atom; as expected, the methylene hydrogens give a single line ($\tau = 6.41$ p.p.m.). Dibenzyl disulphide monoxide is unsymmetrical and contains an asymmetric sulphur atom. According to the arguments presented above the proton spectrum of the two different methylene groups could exhibit the characteristic of two different AB systems. The spectrum obtained consists of only two sharp lines ($\tau = 5.73$ p.p.m. and $\tau = 5.77$ p.p.m.) indicating that the protons common to a methylene group in this molecule have identical chemical shifts in spite of the asymmetric sulphur atom. The presence of two lines, corresponding to two different methylene groups, rules out the possibility of any symmetrical structure, RS-O-SR , and is in complete agreement with the unsymmetrical structure, RSO-SR .

If dibenzyl disulphide dioxide is symmetrical the two methylene groups would be identical. Furthermore, the protons of the same methylene group could be non-equivalent due to the asymmetry of the two sulphur atoms, resulting in a four line spectrum typical of an AB system. However, the protons of the same methylene group could be equivalent in spite of the asymmetric centers (as in the case of the monoxide), resulting in a single line. If, on the other hand, the dioxide is unsymmetrical, having no asymmetric center, then the proton spectrum would show two lines corresponding to the two different methylene groups. Indeed, the NMR spectrum exhibits two distinct lines ($\tau = 5.81$ p.p.m. and $\tau = 5.98$ p.p.m.), thus proving the unsymmetrical structure of thiol-sulphonates.

Upon studying ditolyl disulphide and its oxygen derivatives we reach the same conclusions. The protons of a methyl group, unlike those of a methylene group, are equivalent if the group freely rotates, even though the molecule has an asymmetric center. This is true for the tolyl derivatives and complications due to mutual coupling between protons of the same methyl group do not arise. Each methyl group produces only one line in the proton spectra.

Ditolyl disulphide is symmetrical and the methyl protons yield only a single line ($\tau = 7.72$ p.p.m.) as expected. Ditolyl disulphide monoxide possesses two non-equivalent methyl groups because two lines corresponding to the methyl protons are found in the spectrum ($\tau = 7.60$ p.p.m. and $\tau = 7.64$ p.p.m.); therefore the disulphide monoxide is unsymmetrical. Ditolyl disulphide dioxide also contains two non-equivalent methyl groups ($\tau = 7.60$ p.p.m. and $\tau = 7.65$ p.p.m.), thus again establishing the unsymmetrical structure of thiol-sulphonates⁸.

In view of these findings our earlier assignments and conclusions concerning dodecyl sulphides, disulphides and related oxygen-containing compounds¹ are correct.

8. A note in added proof. - Recently, R. R. Crenshaw and T. C. Owen (*Proc. Chem. Soc. (London)*, 1961, 250) have shown, by means of radioactive

³⁵S techniques, that thiol-sulphonates have the unsymmetrical structure, (I).

Sincerely yours,

Edmund R. Malinowski

E. R. Malinowski, P. Allen, Jr. and P. J. Berner



DEPARTMENT OF NATIONAL DEFENCE
DEFENCE RESEARCH BOARD
DEFENCE RESEARCH CHEMICAL LABORATORIES
SHIRLEY BAY, OTTAWA, ONTARIO

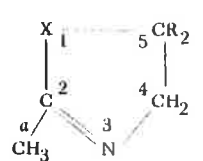
10 January, 1963.

Dr. B. L. Shapiro,
Mellon Institute,
4400 Fifth Ave.,
Pittsburgh 13,
Pennsylvania, U.S.A.

Dear Dr. Shapiro:

Long Range Coupling

In 2-methyl- Δ^2 -oxazoline, 2-methyl- Δ^2 -thiazoline and their methyl derivatives we have found some more examples of 5 bond couplings. The following coupling constants were observed between the protons of the 2-methyl group and those of one pair of the ring methylenes:

	X	R	J (cps)
	O	H	1.38
II	S	H	1.6.
III	O	CH ₃	1.45
IV	S	CH ₃	1.65

In all four compounds the 2-methyl proton spectra are slightly skewed (1:2:1) triplets. The spectra of the ring methylenes in I and II are A_2B_2 systems ($J_{AB} = J'_{AB}$, one side further split by methyl protons) whilst in the substituted derivatives III and IV they are (1:3:3:1) quartets.

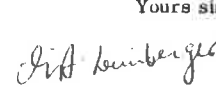
When the 4-position instead of 5-position hydrogens are replaced by methyl groups the 2-methyl proton peaks are singlets, so that it is the 4-position protons which couple with the 2-methyl protons.

- 2 -

Like Randall¹ we could not visualize the "wild" diene structures of Freeman and Bhacca² which would be necessary for our compounds. Now Hoffman and Gronowitz³ have clarified the situation it is clear that the present long range couplings belong to the methyl group category for which hyperconjugation is the favored explanation.

2-Methyl- Δ^2 -oxazoline (I) is a very similar case to 2-methyl-4,5-dihydrofuran in which an even larger 1,5 coupling is observed (2 cps)⁴. The reduction in coupling constant observed when the C₃ carbon is replaced by the more electronegative nitrogen indicates that the latter produces an increased localisation of the π electron system. In this connection it is interesting to note that when the nitrogen is protonated, as it is in aqueous solution below pH 4, the coupling constant in I drops to 1.0 cps.

Yours sincerely,


M. A. Weinberger


R. Greenhalgh

1. Randall, Mellonmr 49, 22
2. Freeman and Bhacca, *ibid* 47, 11
3. Hoffman and Gronowitz, *ibid* 51, 11
4. Gagnaire and Csakvary, *ibid* 45, 9

UNIVERSITY OF COLORADO
BOULDER, COLORADO

January 14, 1963

DEPARTMENT OF CHEMISTRY

Dr. B. L. Shapiro
The Mellon Institute
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Recent experimental work by Snyder and Roberts (J. Am. Chem. Soc. 84, 1582 (1962)) has shown that in a large number of allenes and acetylenes the spin-spin splittings between protons separated by four carbons (J_{14}) are between 2 and 3 cps. These experimental results can be nicely correlated by Karplus' (J. Chem. Phys. 33, 1846 (1960)) theory of π -electron coupling of nuclear spins. In this theory the π -electron contribution to the spin-spin splitting, $A_{HH'}$ (π) is given approximately by

$$A_{HH'}(\pi) = 2.1 \times 10^{-15} \sum_T \frac{a_H(T)a_{H'}(T)}{\Delta E(T)} \quad (1)$$

where a_H and $a_{H'}$ are the hyperfine coupling constants of protons H and H' respectively and $\Delta E(T)$ is the π -electron singlet-triplet transition energy. For the methyl-substituted allenes studied by Snyder and Roberts Eq. 1 predicts $J_{14} = 2.9$ cps.

4-Vinylidenecyclopentene (I) has recently been isolated in these laboratories, and its NMR spectrum is of interest in checking a more general application of Eq. 1. The proton resonance peaks of interest are a triplet due to the four allylic protons at 6.87 τ and a quintet due to the vinylic protons at 5.40 τ . The spin-spin splitting is 4.58 ± 0.08 cps., substantially larger than the long range splitting in the methyl allenes. This larger splitting is of interest because of the basic structural difference between allene I and the allenes studied by Snyder and Roberts. In the latter case the methyl groups are freely rotating and the average value of $a_{H_1} = 75 \times 10^6$ cps was used in Eq. 1 to calculate $A_{HH'}$. In allene I the methylene protons have a fixed spatial orientation with respect to the 2-p orbital on the adjacent carbon. This allows a test of the more general equation for the hyperfine coupling of an H - C - C fragment. In this case

$$a_{H_1} = (+155 \cos^2 \Theta) \times 10^6 \text{ cps} \quad (2)$$

where Θ is the angle between the H - C - C plane and the $C\pi$ -orbital axis. Assuming an HCH bond angle of 109° , a_{H_1} is 99.4×10^6 cps. Using this value in Eq. 1 gives $A_{HH'}(\pi) = +5.4$ cps in good agreement with the observed value of 4.6 cps. The important thing is that a larger splitting is predicted for allene I than for methyl allene.

Melvin W. Hanna
Melvin W. Hanna

Sincerely yours,

J. K. Harrington
J. K. Harrington



Varian Associates

100 BARKHAY WAY • PALO ALTO, CALIFORNIA • DAVENPORT 8-4000

January 17, 1963

Dr. Barry Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Barry,

Following a suggestion in MELLONMR #47, I would like to contribute under the heading "Positions Available".

The activities of the applications laboratories of Varian Associates in High Resolution NMR, Wide-line NMR, and EPR are well-known to many readers of MELLONMR. We are contemplating an increase in this type of activity particularly in the eastern part of the United States. If people with suitable experience and interests will forward their resumes to me promptly, it may be possible to arrange interviews at the Pittsburgh Spectroscopy Conference and 4th OCEANS meeting between February 28 and March 6.

Opportunities also exist in Field Sales of magnetic resonance spectrometers and magnets. A strong background in chemistry with some experience in magnetic resonance is desired. Applicants interested in this type of activity should contact Mr. Wayne Lockhart in care of the Instrument Division.

By way of clarification it might be noted in passing that we Californians tend to designate as "Eastern" anything on the other side of the Rocky Mountains.

I am not sure whether or not this contribution qualifies me for an extension of my MELLONMR subscription. I submit this to your judgment.

Sincerely yours,

James N. Shoolery
James N. Shoolery
Instrument Division

JNS:jl

Dr. B. L. Shapiro
Nelson Institute
4400 Fifth Ave.,
Pittsburgh 13, Penna. U.S.A.

Dear Barry:

Sum rules for NMR spectra are fascinating things, and even prove useful in interpreting spectra sometimes. Several of them have been noted at various times, for example, intensity sum rules for transitions between the various sub-matrices with different F_1 (Gionousis and Eyalen), frequency sum rules (Castellano and Waugh), moment sum rules for the whole spectrum (McConnell and Anderson) and first-moment sum rules for transitions between the sub-matrices (Kummer in HELVETICA 49 and 50). I thought it might be interesting to make a table showing the sums for various cases, and a copy of it is appended hereto. I believe the sum rules for $\sum \nu_i^2$ and for $\sum \nu_i^2 I_i$ for the various sub-matrices have not been given before, nor the fact that the $\sum \nu_i I_i$ of Kummer has the value shown in the table, though this is probably implied in the paper of Anderson and McConnell. The sum rule for $\sum \nu_i^3$ can be derived simply from the invariance of the trace and the invariance of the quadratic form of the matrices under the similarity transformation. I have not deduced the expressions beyond 3 nuclei, as the job is rather tedious, and the expressions are complicated enough that they do not look very useful. The expressions for the sums of the first and second moments for the transitions between the sub-matrices were not derived at all, but simply noted from a number of machine-calculated spectra, chosen more or less at random. The probability that the exact agreement with these expressions is fortuitous appears to me to be vanishingly small.

Examination of the table reveals several interesting things, for example the frequent recurrence of the binomial coefficients. Thus the intensity sums are just $N \times C_1$, where N is the number of nuclei, and the C_1 are the binomial coefficients for $(N-1)$. The coefficients of $\sum \nu_A$ and $\sum (\nu_A^2)$ in the first and second moment sums are likewise just the binomial coefficients C_1 . The coefficients of $\sum \nu_A$ in the expressions for $\sum \nu_j$ are given by $C_1 C_2 / N$, when C_1 and C_2 are the orders of the two matrices connected by the transitions. So far, I do not see an expression for the coefficients of $\sum \Delta$ in these sums.

Best wishes,

ABW

Abul

Table of Sums

Nuclei	Matrices	I_1	$\sum \nu_i$	$\sum \nu_i^2$	$\sum \nu_i^3$	$\sum (\nu_i^2)$
1	$\begin{array}{c} 1 \\ \diagup \\ 1 \end{array}$	1	ν_A	ν_A^2	ν_A^3	ν_A^2
2	$\begin{array}{c} 1 \\ \diagup \\ 2 \\ \diagup \\ 1 \end{array}$	2	$\sum \nu_A + \sum \Delta$	$\sum (\nu_A^2) + \sum (\Delta^2) + \sum \nu \Delta$	$\sum \nu_A$	$\sum (\nu_A^2)$
		2	$\sum \nu_A - \sum \Delta$	$\sum (\nu_A^2) + \sum (\Delta^2) - \sum \nu \Delta$	$\sum \nu_A$	$\sum (\nu_A^2)$
3	$\begin{array}{c} 1 \\ \diagup \\ 3 \\ \diagup \\ 3 \\ \diagup \\ 1 \end{array}$	3	$\sum \nu_A + \sum \Delta$	see below	$\sum \nu_A$	$\sum (\nu_A^2)$
		6	$\sum \nu_A$		$2 \sum \nu_A$	$2 \sum (\nu_A^2)$
		3	$\sum \nu_A - \sum \Delta$		$\sum \nu_A$	$\sum (\nu_A^2)$
4	$\begin{array}{c} 1 \\ \diagup \\ 4 \\ \diagup \\ 6 \\ \diagup \\ 4 \\ \diagup \\ 1 \end{array}$	4	$\sum \nu_A + \sum \Delta$	-	$\sum \nu_A$	$\sum (\nu_A^2)$
		12	$6 \sum \nu_A + 2 \sum \Delta$		$3 \sum \nu_A$	$3 \sum (\nu_A^2)$
		12	$6 \sum \nu_A - 2 \sum \Delta$		$3 \sum \nu_A$	$3 \sum (\nu_A^2)$
		4	$\sum \nu_A - \sum \Delta$		$\sum \nu_A$	$\sum (\nu_A^2)$
5	$\begin{array}{c} 1 \\ \diagup \\ 5 \\ \diagup \\ 10 \\ \diagup \\ 10 \\ \diagup \\ 5 \\ \diagup \\ 1 \end{array}$	5	$\sum \nu_A + \sum \Delta$	-	$\sum \nu_A$	$\sum (\nu_A^2)$
		20	$10 \sum \nu_A + 5 \sum \Delta$		$4 \sum \nu_A$	$4 \sum (\nu_A^2)$
		30	$20 \sum \nu_A$		$6 \sum \nu_A$	$6 \sum (\nu_A^2)$
		20	$10 \sum \nu_A - 5 \sum \Delta$		$4 \sum \nu_A$	$4 \sum (\nu_A^2)$
		5	$\sum \nu_A - \sum \Delta$		$\sum \nu_A$	$\sum (\nu_A^2)$
6	$\begin{array}{c} 1 \\ \diagup \\ 6 \\ \diagup \\ 15 \\ \diagup \\ 20 \\ \diagup \\ 15 \\ \diagup \\ 6 \\ \diagup \\ 1 \end{array}$	6	$\sum \nu_A + \sum \Delta$	-	$\sum \nu_A$	$\sum (\nu_A^2)$
		30	$15 \sum \nu_A + 5 \sum \Delta$		$5 \sum \nu_A$	$5 \sum (\nu_A^2)$
		60	$30 \sum \nu_A + 10 \sum \Delta$		$10 \sum \nu_A$	$10 \sum (\nu_A^2)$
		60	$30 \sum \nu_A - 10 \sum \Delta$		$10 \sum \nu_A$	$10 \sum (\nu_A^2)$
		30	$15 \sum \nu_A - 5 \sum \Delta$		$5 \sum \nu_A$	$5 \sum (\nu_A^2)$
		6	$\sum \nu_A - \sum \Delta$		$\sum \nu_A$	$\sum (\nu_A^2)$
7	$\begin{array}{c} 1 \\ \diagup \\ 7 \\ \diagup \\ 21 \\ \diagup \\ 35 \\ \diagup \\ 35 \\ \diagup \\ 21 \\ \diagup \\ 7 \\ \diagup \\ 1 \end{array}$	7	$\sum \nu_A + \sum \Delta$	$\begin{aligned} & \sum (\nu_A^2) + \sum (\Delta^2) + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta \\ & 5 \sum (\nu_A^2) - 2 \sum \nu_A \Delta + 4 \sum (\Delta^2) - 2 \sum \nu \Delta \\ & \sum (\nu_A^2) + \sum (\Delta^2) + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta + \sum \nu \Delta \end{aligned}$		

the coupling constants

$$\sum \nu_i = \nu_A + \nu_B + \nu_C + \nu_D + \nu_E + \nu_F + \nu_G + \nu_H + \nu_I + \nu_J + \nu_K + \nu_L + \nu_M + \nu_N + \nu_O + \nu_P + \nu_Q + \nu_R + \nu_S + \nu_T + \nu_U + \nu_V + \nu_W + \nu_X + \nu_Y + \nu_Z$$

Symbols in the table:

ν_i = the frequencies

I_i = the corresponding intensities

ν_A = the chemical shifts

$$\sum \nu_i^2 = \nu_A^2 + \nu_B^2 + \nu_C^2 + \nu_D^2 + \nu_E^2 + \nu_F^2 + \nu_G^2 + \nu_H^2 + \nu_I^2 + \nu_J^2 + \nu_K^2 + \nu_L^2 + \nu_M^2 + \nu_N^2 + \nu_O^2 + \nu_P^2 + \nu_Q^2 + \nu_R^2 + \nu_S^2 + \nu_T^2 + \nu_U^2 + \nu_V^2 + \nu_W^2 + \nu_X^2 + \nu_Y^2 + \nu_Z^2$$

$$\sum \nu_i^3 = \nu_A^3 + \nu_B^3 + \nu_C^3 + \nu_D^3 + \nu_E^3 + \nu_F^3 + \nu_G^3 + \nu_H^3 + \nu_I^3 + \nu_J^3 + \nu_K^3 + \nu_L^3 + \nu_M^3 + \nu_N^3 + \nu_O^3 + \nu_P^3 + \nu_Q^3 + \nu_R^3 + \nu_S^3 + \nu_T^3 + \nu_U^3 + \nu_V^3 + \nu_W^3 + \nu_X^3 + \nu_Y^3 + \nu_Z^3$$



U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIFORNIA

IN REPLY REFER TO:
5058/DWM:1jb
22 Jan 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

It is possible to prepare methanol which is sufficiently dry to permit observation of proton spin-coupling structure at room temperature. We were interested in the results of Fowles and Strange (Molecular Physics 2, 329, (1962)) who studied the spin-coupling in methanol and found appreciable proton exchange effects above -20°C , and after trying a number of drying techniques were able to raise this figure to perhaps $+20^{\circ}$.

Chemical drying agents such as magnesium-iodine, calcium hydride, and phosphorus pentoxide were ineffective, so we fell back on a simple physical desiccant, calcium sulfate. Ordinary Drierite, with appropriate precautions, gave methanol which showed methyl-group splitting even at 30°C . At lower temperatures a sharp 5.0 cps doublet was seen, with the corresponding OH quartet appearing 131 cps down-field.*

The drying was done on a vacuum line fitted with separate receivers for methanol and desiccant and several NMR sample tubes. The Drierite was first dried by heating at 200°C and pumping continuously until a pressure under one micron could be maintained. It was then cooled and the methanol vacuum-distilled onto it and allowed to equilibrate overnight. In the morning it was frozen down the bone-dry product distilled at 2-3 mm into the sample tubes and sealed off.

Ten samples dried in this manner exhibit coalescence of the CH_3 doublet at temperatures from about 10° to 30°C . Quite likely improved technique could give even better material, and eventually we might reach the limit where the dissociation of pure methanol is the only significant exchange process.

Sincerely yours,

Donald W. Moore
Donald W. Moore

* 60 mc.

The Standard Oil Company
(The Ohio Corporation)

Research Department

4440 Warrensville Center Road

Cleveland 28, Ohio

E. C. HUGHES
VICE PRESIDENT

January 23, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Here are a few comments concerning the ASTM NMR Subcommittee which we would appreciate your including in the next issue of MELLONMR.

An NMR Subcommittee meeting will be held on Saturday afternoon at about 4:00 p.m. on March 2nd. The meeting will be held at Mellon Institute following the final afternoon session of the 4th OCEANS. The agenda will include nomenclature, referencing, data storage and retrieval, organizational changes, and other selected topics. Visitors are welcome, but would they please check with me so that we may arrange for adequate space for the meeting.

Secondly, the Subcommittee will be distributing a questionnaire to NMR spectroscopists surveying current opinions concerning nomenclature and referencing. If you haven't received one by the time of 4th OCEANS, it is just an oversight on our part, so please speak up.

Sincerely,

Bill

Dr. W. M. Ritchey, Chairman
Subcommittee VII of ASTM E-13

WMR:cmp



UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
REGION V

PITTSBURGH RESEARCH CENTER

4800 FORBES AVENUE
PITTSBURGH 13, PENNSYLVANIA

January 23, 1963

Dear Barry:

Our C^{13} magnetic resonance work for the past year has been confined largely to the measurement of chemical shifts in hydrocarbons. Enclosed is a chemical shift-structure correlation chart that may prove of interest to some of your subscribers.

We would like at this time to report our findings concerning substituent effects in C^{13} spectra. Below is a table summarizing alkyl substituent effects on the resonances of olefinic carbon atoms:

Structural Change		$\Delta\delta$, ppm		
		C*	C†	C‡
$-C^*=C^{\dagger}-H$ (int.)	$\rightarrow -C^*=C^{\dagger}-CH_3$	4.4 to 6.8	-3.3 to -7.3	
$-C^*=C^{\dagger}-H$ (term.)	$\rightarrow -C^*=C^{\dagger}-CH_3$	6.4 to 8.8	-9.5 to -10.4	
$-C^*=C^{\dagger}-CH$	$\rightarrow -C^*=C^{\dagger}-\dot{C}-CH_3$	0.1 to 2.2	-5.3 to -7.8	
$-C^*=C^{\dagger}-\dot{C}-CH$	$\rightarrow -C^*=C^{\dagger}-\dot{C}-\dot{C}-CH_3$	-0.1 to -2.1	0.3 to 2.8	
$C-C\ddagger=C^*=C^{\dagger}$	$\rightarrow C-C\ddagger=C^*=C^{\dagger}-C$	3.3	-11.3	-1.0
$C\ddagger=C^*=C^{\dagger}-C$	$\rightarrow C\ddagger=C^*=C^{\dagger}-C-C$	1.5	-7.3	-1.2

It can be seen that effects transmitted through a single bond to an olefinic carbon atom produce downfield shifts, whereas effects transmitted through the double bond produce upfield shifts. The downfield shifts can be compared with similar shifts in the case of singly and triply bonded carbon atoms. Using Lauterbur's data on propargyl alcohols and substituted methanes and Spiesecke and Schneider's data on ethane and propane in conjunction with our data on olefins, we find:

		$\Delta\delta$, ppm
$-C^{\dagger}-C-H$	$\rightarrow -C^{\dagger}-C-CH_3$	-7.0 to -11.5
$=C^{\dagger}-C-H$	$\rightarrow =C^{\dagger}C-CH_3$	-5.3 to -7.8
$\equiv C^{\dagger}-C-H$	$\rightarrow \equiv C^{\dagger}-C-CH_3$	-3.3

These data suggest that alkyl substituent effects transmitted through single bonds produce downfield shifts, the magnitude of which decreases as the carbon atom under study becomes more unsaturated. These results will be discussed in more detail in a forthcoming article in the Journal of the American Chemical Society.

We would also like to take this opportunity to report the C^{13} chemical shifts for ethylbenzene, styrene, and phenylacetylene. Measurements on the latter two were made possible by C^{13} -H spin decoupling:

Compound	δ_{C-X}	$\delta_{CH(aro.)}$	αC	βC
Ethylbenzene	49.3	63.4 67.7	164.3	177.8
Styrene	56.4	65.5 67.3	56.4	80.4
Phenylacetylene	71.2	65.0 61.4	109.4	115.6

Definite assignments have not yet been made for the aromatic doublets. It is interesting to note that once again α substituent effects appear to be dependent upon bond order, for a plot of the C-X chemical shifts as a function of the percent s character of the bond between the two carbon atoms in the substituent group yields a straight line. We plan to extend this work by measuring the effects of alkyl, vinyl, and acetylenic substitution on singly and triply bonded carbon atoms. Preliminary work along these lines indicate that methyl groups adjacent to acetylenic groups show very strong shielding--the chemical shift is just a few ppm below the chemical shift in methane.

Thank you for continuing our subscription to this very valuable newsletter.

R. A. Friedel
R. A. Friedel

H. L. Retcofsky
H. L. Retcofsky

January 24, 1963

DEAR DR. SHAPIRO:

The two basic approaches that may be adopted are use of a single continuous measurement over the whole integration period, T , or the sum of n passes through the spectral range each of period T/n (The Dog vs. the Cat). The second requires an internal reference marker accurate to within a fraction of the line width plus an intermediate storage mechanism but no non-linear processes are introduced by segmenting the measurement. Thus if the noise background is Gaussian random and if infinite measurement precision and infinite dynamic range of the measuring instruments is maintained it is obvious that both methods are identical and give a sensitivity enhancement proportional to \sqrt{T} . A principal difficulty inherent to the first method is the essentially unavoidable noise present in all spectrometers. That part of the noise which arises from electronic sources such as "flicker noise" in vacuum tubes or solid state devices is effectively eliminated through use of synchronous or lock-in detectors but radiation leakage still remains as well as many sources arising from the thermal, mechanical, and electrical environment all of which contribute to low frequency fluctuations in the system. This implies that one should sweep through the spectral range of interest as rapidly as it is possible to do so without sacrificing resolution. Digitalizing the spectrometer output voltage is the most useful way of solving the storage and summing requirement and the full information content of a spectrum may be retained with about 4 - 6 samples per line width. Time integration is one of the few measurement processes which results in an increase in the number of significant figures in the output and here the dynamic range readily available in digital counters is an advantage over the analogue filter circuits employed in single pass time integration. (The Q of a multichannel analyzer is proportional to the number of counts per channel it can store or for a digital computer it is proportional to the word length).



1/ Partly Bureau of Mines data, contains data from:
(a) Spiessche, H., and Schneider, W.G., *J. Chem. Phys.* **35**, 722 (1961); *J. Chem. Phys.* **35**, 731 (1961);
(b) Latteburg, P.C., *Jour. Am. Chem. Soc.* **83**, 1838 (1961);
(c) Latteburg, P.C., "Determination of Organic Structures by Physical Methods," Vol. II, ed. Nachod, F. C. and Phillips, W.D., Academic Press, New York, 1962, Chap. 7, Nuclear Magnetic Resonance of Elements Other than Hydrogen and Fluorine.

Dr. B. L. Shapiro

-2-

January 24, 1963

One practical digitalizing scheme can be constructed from a digital voltmeter followed by a punch drive and high speed paper punch. The paper tape is converted to magnetic tape by standard digital computer auxiliary equipment and the traces may be added with a very simple computer program that is within the capability of any medium-sized digital computer. Some such digital computer is generally available to most institutions and the digital voltmeter, punch drive, and punch can be obtained from a variety of manufacturers for less than \$5000. The output of a digital voltmeter can also be fed directly to a high quality tape unit compatible with the digital computer tape storage units but the cost of an acceptable recording unit may be ten times that of the previous method. Another scheme is to use a multichannel analyzer. M. P. Klein and co-workers have put together commercially available units of this sort and have been quite successful with a number of physics experiments using the Varian HR-60.⁵ The CAT (Model 400 or 400A, Mnemotron Company, subsidiary of Technical Measurement Corporation) combines a voltage-to-frequency converter, 400 channel analyzer, timing circuits, and an oscilloscope display in one package. At present this latter equipment is the most convenient for typical chemical proton resonance problems. If one wants to undertake a complete search of the usual 500 cps proton range it is necessary to partition the range into approximately six sections. Many chemically interesting problems do not require such extensive search but this remains the greatest drawback. A multichannel analyzer with 4096 channels would be ideal but now costs approximately the same as the Varian A-60 proton spectrometer itself. However this price can be expected to fall rapidly. Schemes that use a multichannel analyzer enjoy perhaps a decisive advantage over all other time integration techniques because they can provide a continuous, real time, visual display of the integration process. Particularly in areas such as organic chemistry one is interested in running many, slightly different samples and for this type of operation the investigator time integrates until he achieves a subjectively satisfactory sensitivity. In our experience this generally involves a signal-to-noise increase of from 2 - 10 rather than the 40 - 50 increase obtainable in an automatic overnight run. With the CAT it is also possible to feed the result of the integration back through the spectrometer chart recorder so one can obtain a spectral trace in the standard chart format after completing the run.

The trace reference marker in the multiple sweep method must be added to the sample vial in sufficient amount to be clearly visible on each trace so that an unambiguous trigger is available for starting the channel filling timing circuitry. In general one wants to put the trigger reference line (eg. TMS or a sideband of the TMS line) as close to the line pattern to be investigated as possible but successive addition of traces can cause the tail of the trigger reference line to swamp out the adjacent region of the spectrum. This problem is avoided by use of a simple flip-flop circuit with relays that returns the output signal to zero immediately after triggering has occurred. A microswitch at each end of the desired sweep range can be easily attached to the chart recorder table and connected to the circuitry of Varian instruments to provide automatic retrace with no attention or further adjustments on the part of the investigator required.

All of our experiments to date have been done on a Varian A-60 because this instrument has proton resonance stabilization of the magnetic field. While it is possible to get some of the benefits of time integration without stabilization it is in fact the availability of nmr-stabilization that has made it worth considering extended time integration in the first place and thus it is somewhat inconsistent to purchase the accessories required for time integration without also providing nmr stabilization - certainly if one is contemplating time integration of more than an hour or two. We have found by experiment that the A-60 has a remarkably long time over all stability - much greater than the manufacturers themselves realized. For example we have made a 14 hour run on a .004% solution of ethyl benzene in CCl₄ which involved 1500 traces (a 16 second section of the standard 4 minute position was used with an 8 second flyback time). This yields an S/N increase of 50 over the .2% ethyl benzene solution that is just visible on the 4 minute trace position of the A-60. The 4 minute trace position was used because this is the fastest sweep on the A-60 which still retains the full resolution of the instrument.

The work we have described here was carried out in close collaboration with Dr. Leroy F. Johnson of the Varian Company. Mr. Robert M. Erdahl also helped and thanks are due to Dr. James N. Shouley and others of his staff for their hospitality and many useful discussions. We have been continuing this effort at Princeton with Drs. Pierre Lazlo and Paul Schleyer. Dr. Lazlo will report in more detail on our work at the forthcoming OCEANS Conference.

Finally, it may be interesting to point out that it is also possible to use filtering techniques to improve the effective resolution as well as the sensitivity of spectra. We will report on this in a later issue.

Sincerely,

Leland C. Allen

Leland C. Allen

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