

Premas
Mailed: August 29, 1962

Monthly
Editorial
Letters from
Laboratories
of
N - M - R
No. 47

A.A.B. and B. L. S.	Policies and Practical Considerations Concerning MELLONMR	1
Koster, Lundergan, Poradek, Danti	Miscellaneous A-60 Items	2
Stewart	Percent Hydrogen by Integration	8
Whipple	Proton Spectra of 2,5-Dimethylpyrrole in Acid Solutions	9
Freeman, Bhacca	Proton Couplings Through Five Bonds	11
Chamberlain, Saunders	Calibration of A-60 Charts	14
Heffernan, Black	Proton Spectra of Benzimidazole and Benzotriazole	16
Bumgardner	Fluorine Spectra of Benzotrifluorides	17
✓ Zürcher	Anisotropy of the Magnetic Susceptibility of the C-C Bond	19
Reeves	Conformational Study of 2,6-Tetradeutero- cyclohexanol Esters; Methyl Nitrite- Temperature Dependence of Free Induction Decay	20
! Jardetzky	Improving the HR-60 Sensitivity and Application to DPN/protein Binding	21
Allen	Experimental Tips on the A.E.I. RS2 Spectrometer; Proton Resonances in Cyclic Phosphonitrilic Methyls and their Protonated Cations	23
Lauterbur	On Brevity	24
Hollis, Pier	Quantitative Analysis of Small Samples on the A-60	25
Davis	B ¹¹ Chemical Shifts, particularly in Symmetrical Tetrahedral Ions	26
Crutchfield	Observations of Weak Signals on the A-60	27

DEADLINE FOR NEXT ISSUE
September 26, 1962

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

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

27 August 1962

Policies and Practical Considerations Concerning MELLONMR

The following is a reworking in one place of all the scattered statements about policies and practical considerations which we have put in various issues. They are gathered here in an up-dated version for your convenience.

1. Policy: MELLONMR is first and foremost a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything.". (This is usually followed by the mental reservation "that won't land us in jail".)

As suitable subjects for contributions, we have suggested the following:

1. Reproductions of spectra or parts of spectra.
2. Measurements and calculations of same.
3. Theoretical considerations and interpretations.
4. Novel experimental methods and techniques.
5. Complete or partial mysteries.
6. Comments on material appearing in earlier letters.
7. Requests for help in locating odd or rare compounds.
8. Announcements of forthcoming meetings, colloquia, symposia, books, etc. Also "Preprints Available".
9. Notices of "Positions Available" or "Situations Wanted".
10. Wild theories (this category added at the request of Dr. Ray Freeman).
11. Anything else which you feel your co-workers in the field might find interesting -- even mild polemics.

Foreign participants should not feel obliged to render their contributions in English.

2. Bibliography: The titles and references appearing in the "Bibliography" section are merely those which the NMR people here at Mellon come across in their perusal of the literature. No claims for completeness are made and we once again invite all participants to send in references and titles which we have missed for inclusion in a subsequent issue.

3. Subscriptions: We still feel able to continue our policy of covering all the cost of concocting and distributing this Newsletter ourselves. We would, however, be grateful for the cooperation of all participants as outlined in the section below on "Practical Considerations".

MELLON INSTITUTE

-2-

27 August 1962

Participation was and is the prime requisite for receiving MELLONMR. We feel that we have to be ruthless in this connection and the following schedule is in effect: Seven months after your last contribution, you will receive a "reminder letter". If no contribution is then forthcoming nine months after your last contribution, you will receive the "ultimatum letter", and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending in a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of 9 per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these.

4. Brevity: Brevity is good -- see the section on Practical Considerations.

5. Public Quotation: Public quotation is not good, and reference to MELLONMR in the scientific literature is never permissible. We remind you that in order to quote results or use material from MELLONMR, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

6. Practical Considerations:

(i) Until further notice, all contributions to MELLONMR should be sent to the attention of B. L. Shapiro, since A. A. Bothner-By is about to depart for a sabbatical year abroad. (Address for period 1 September 1962 to 1 June 1963, Institut der Organischen Chemie, Universität München, West Zone, Germany.)

(ii) Participants who are able to send in copies of their contribution are reminded that, due to our increased circulation, they are requested to send at least 200 copies of all pages of their contribution (Copies of some of the pages of a contribution are of no use, since this makes the collation costs much higher.). All pages should be 8-1/2 x 11" and should have 1/2" margin on the left hand side. All contributions of more than one page should be sent both unstapled and uncollated. Those contributors who find sending 200 copies either impossible or inconvenient should not worry, as this is in no way a necessary condition for receiving the Newsletter.

(iii) Since photocopies of various kinds do not reproduce too well, contributors are urged to submit their originals to us and we will be happy to return these if requested.

(iv) Brevity is getting more and more golden as our mailing list increases. Single spacing is almost as good as brevity, and in general, you will help us keep our costs down to a reasonable level by sending in as much material as you wish, but by planning it to fill the minimum number of pages. This will help cut the costs of both reproduction and mailing.

7. Suggestions: We welcome them.

A. A. B. and B. L. S.

AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS

CHEMICAL THERMODYNAMIC PROPERTIES CENTER

Department of Chemistry

COLLEGE STATION, TEXAS



AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 44
MANUFACTURING CHEMISTS ASSOCIATION RESEARCH PROJECT

July 18, 1962

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

We wish to contribute some items that may be useful to operators of the A-60 Spectrometer.

We have experimented with various ways of preparing and running samples of ethanol that are useful for optimizing the settings of the instrument. We wish to describe only one procedure for preparing a good sample. This procedure involves a combination of good points that we obtained through correspondence with George Slomp, Jim Shoolery, and Nugent Chamberlain. The absolute ethanol that we used was of a good grade, fresh, and apparently quite dry. We tried drying one portion with CaH_2 but feel that this is probably not necessary. We found that it was all right to use the ethanol directly from our stock. George Slomp recommended that the ethanol be distilled off of KOH pellets in vacuum and the vacuum broken with dry nitrogen gas. (This distillation should be carried out reasonably soon after the KOH pellets are added.) The pure ethanol was put into a dry NMR tube and the triplet arising from the OH recorded. Dry HCl vapor, as free of air as possible, was added slowly until the triplet collapsed to a sharp singlet. This sample was then transferred to a dry NMR tube attached to a standard taper and sealed under good vacuum. The HCl gas was obtained by using a rubber squeeze bulb and pulling the vapor over concentrated hydrochloric acid through a small tube of P_2O_5 . With a little practice, the amount of HCl gas bubbled into the ethanol through a long capillary can be made such that three or four additions are required before the sharp singlet appears. For thorough degassing, we normally melt and resolidify about three or four times, if it is not possible to have the sample spread out over a large area. The sample of ethanol in CCl_4 , for which we show the quartet in Figure 1, was prepared in the same way. It would appear that the resolution is slightly better for this case. We have only slight evidence to indicate that the sample prepared

from ethanol that was distilled over KOH is a bit better than that prepared directly from the stock.

We have used George Slomp's method of adjusting the field (M.E.L.L.O.N-M-R- No. 41). As our instrument contrived to improve in performance, the method became more applicable. We found, however, that without peak performance the method does not work too well.

Of late, we have been using a well degassed sample of pure ortho dichlorobenzene and acetaldehyde to check the resolution. Figures 2 and 3 give an indication of the resolution that has been achieved. Figure 3 was scanned from high to low field and helps to clarify effects due to ringing. To calibrate the frequency scale we use the peak due to trace amounts of CHCl_3 in CDCl_3 and also peaks of para anisaldehyde for which we received measurements from Nugent Chamberlain. Jim Shoolery informed us that the chloroform peak is at 435.5 cps from TMS. It should be possible for careful workers to measure to within ± 0.3 cps.

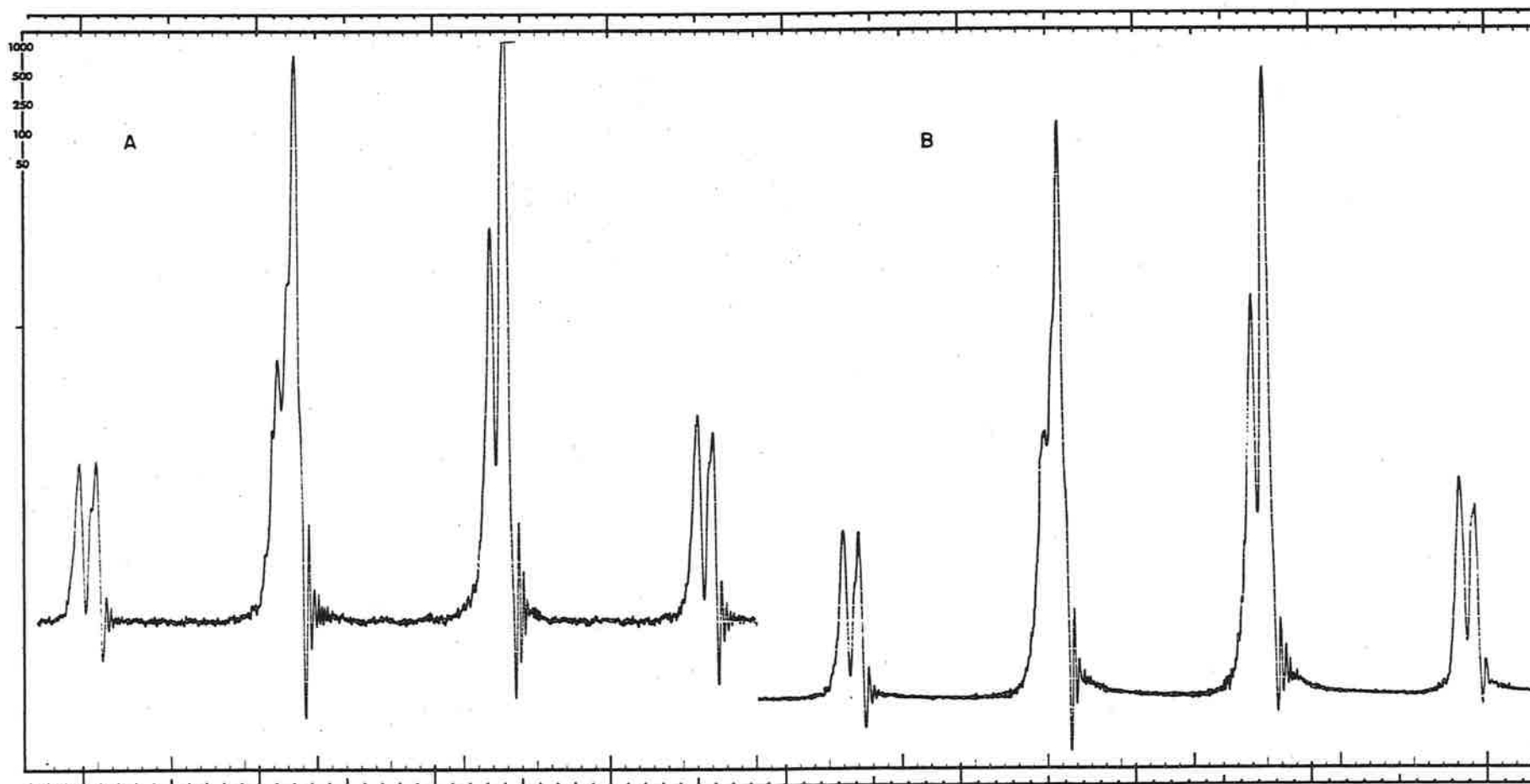
We have gone a period of almost four months without recycling and we turn the instrument off only when forced to do so by the utilities department.

We leave the instrument on operate and the spinner air is also left running. The air is dried and filtered by an "Aqua-jet" and a "Whirlflow" manufactured by the Wilkerson Corporation of Englewood, Colorado. The Johnson Cover Company, P. O. Box 331, Houston, Texas is a good supplier of binders made especially for A-60 charts.

Respectfully Submitted,

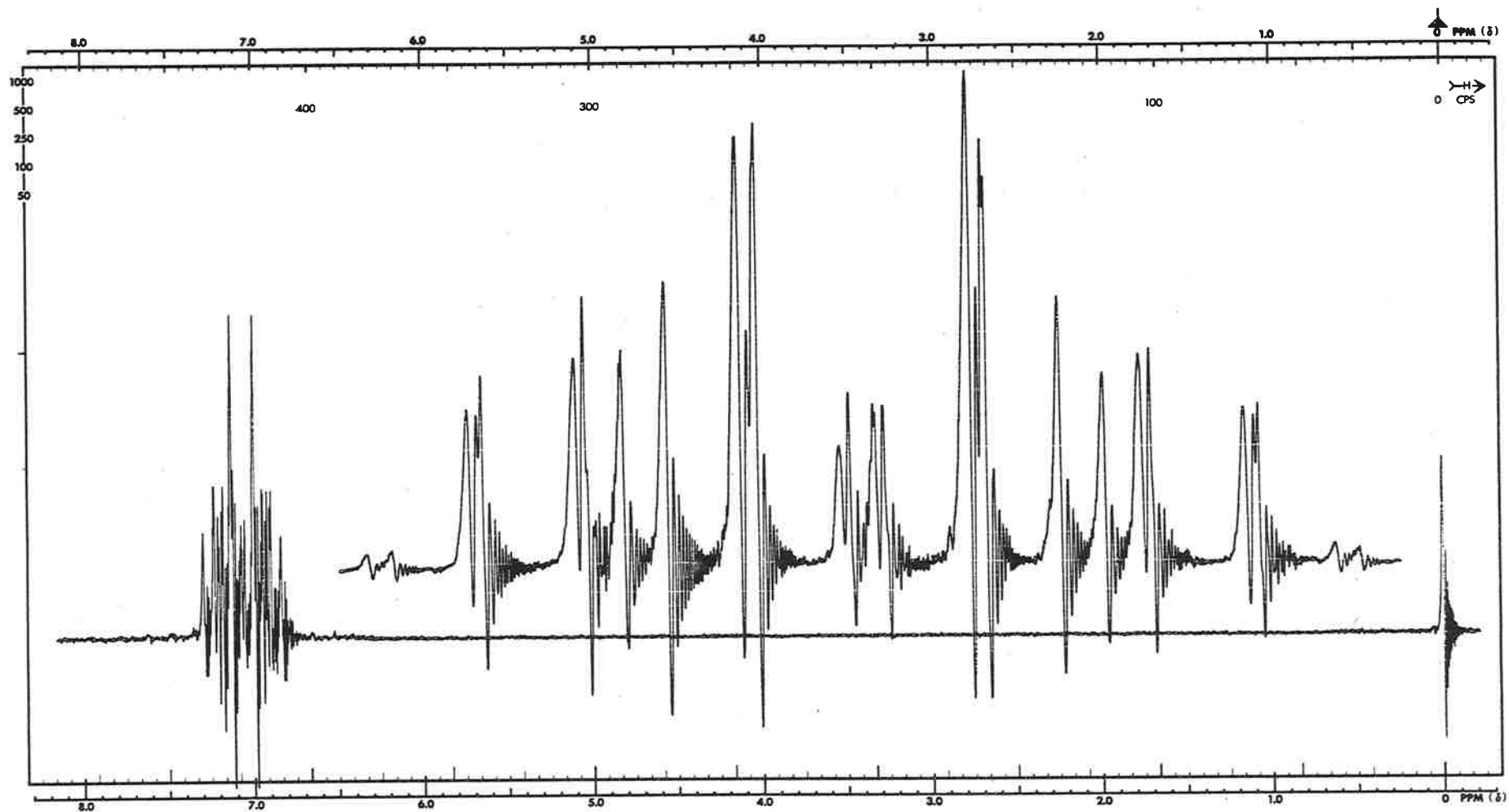
David F. Koster
Jerry C. Poradek

Regina Lundergan
Alfred Danti



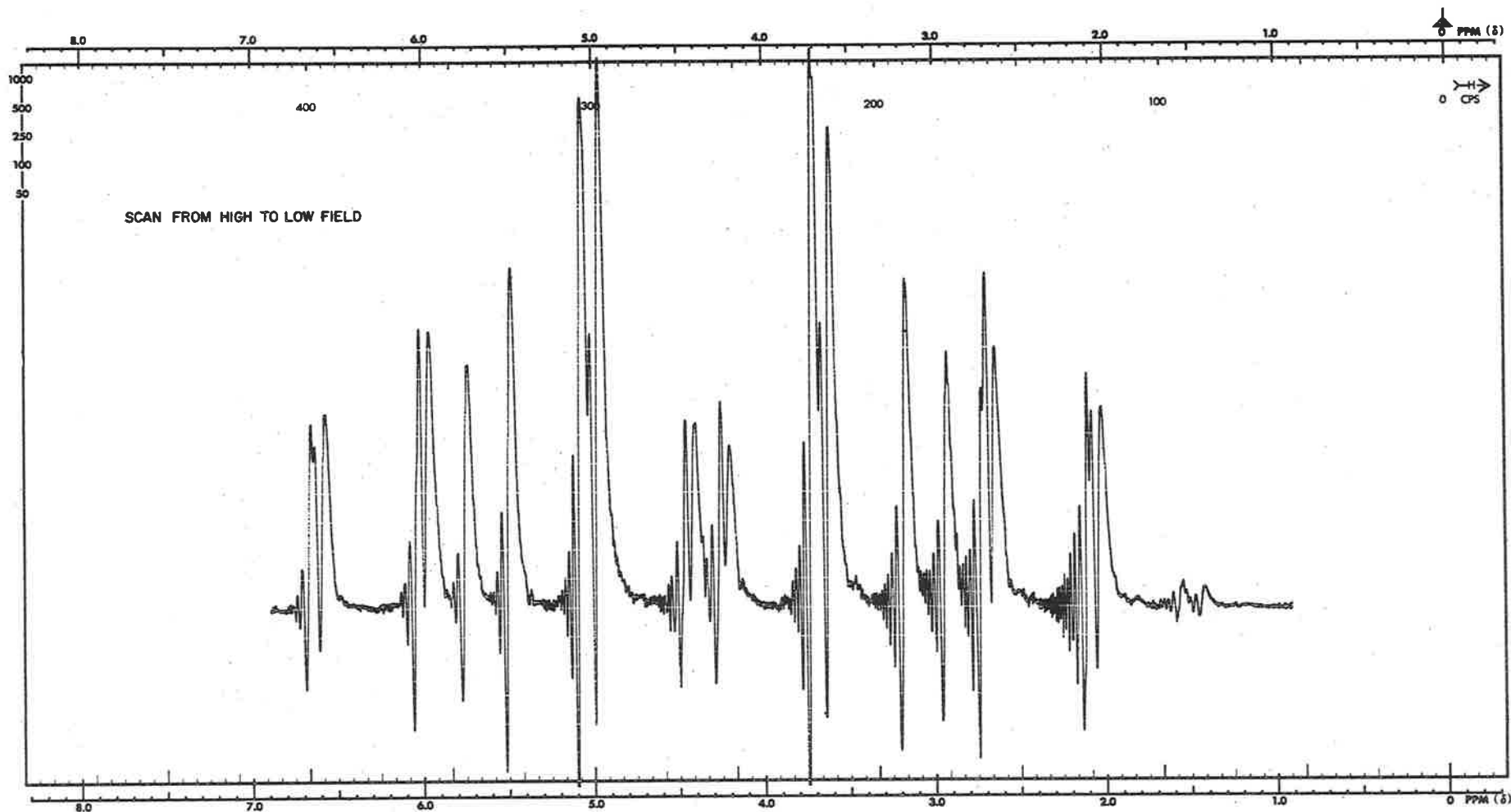
COMPOUND		INSTRUMENT AND CONDITIONS	
Name: Ethanol <chem>C2H6O</chem> CH ₃ - CH ₂ OH	State: Liquid and Liquid Solution Solvent: CCl ₄ Concentration: Spectrum A: ~30 Percent Spectrum B: 100 Percent Temperature: ~35°C Cell: Varian Precision Tube, 5 mm OD	Instrument: Varian Associates Spectrometer, Model A-60 Frequency: 60 Mcps Scanning Rates: Standard (Spectrum A): 0.1 cps/second Other (Spectrum B): 0.1 cps/ second External Reference: Precision of Measurement:	RF Field Intensity (H ₁): A: 0.02 milligauss B: 0.03 milligauss Spectrum Amplitude: A: 1.25 B: 0.4 Internal Reference: Concentration: Resonance Position:
Purity: Absolute			
LABORATORY: Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas			

Figure 1



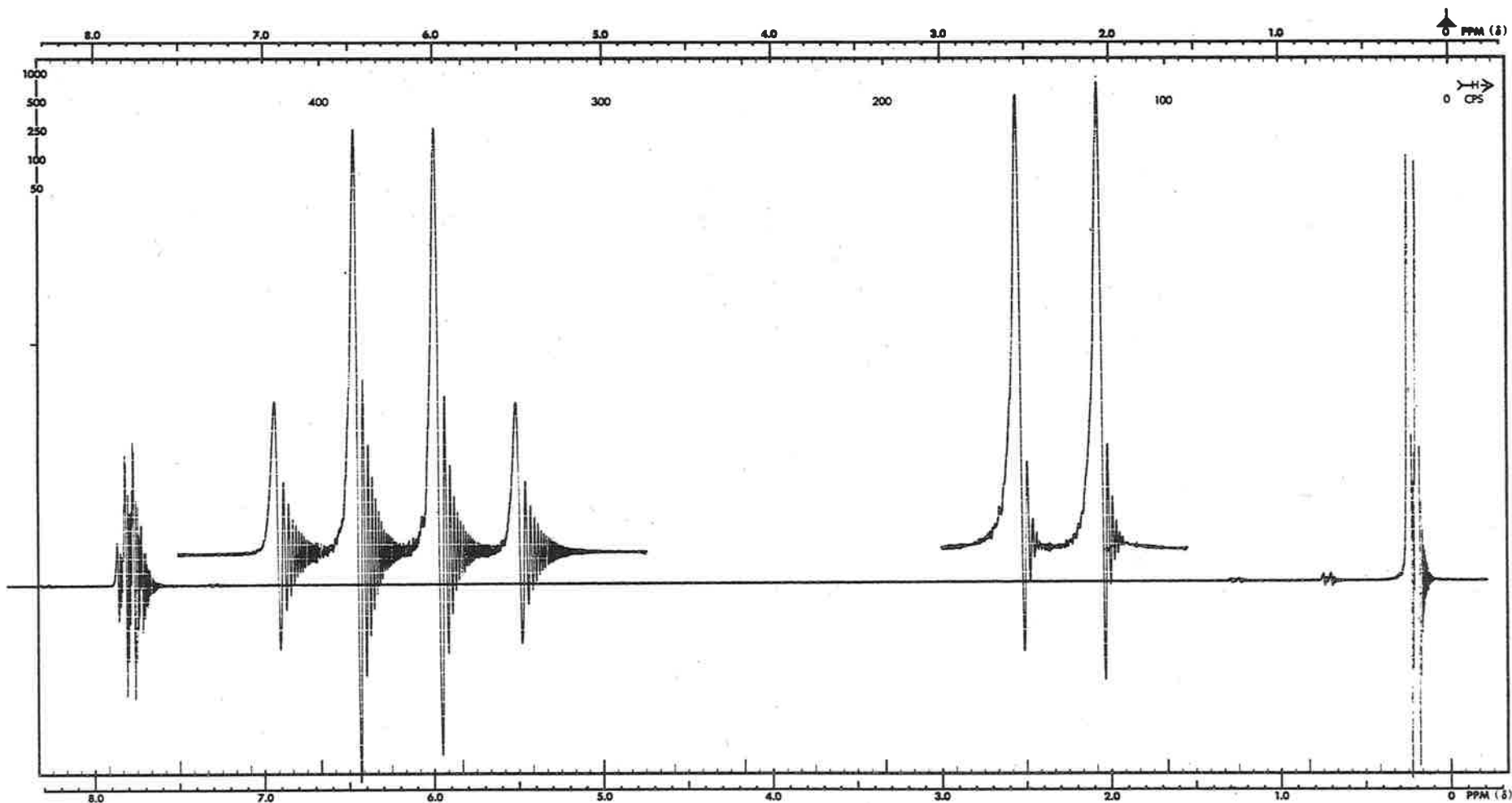
COMPOUND		INSTRUMENT AND CONDITIONS	
Name: o-Dichlorobenzene C ₆ H ₄ Cl ₂	State: Liquid	Instrument: Varian Associates Spectrometer, Model A-60	Frequency: 60 Mcps
			RF Field Intensity (H ₁): A:0.03 milligauss B:0.04 milligauss
		Scanning Rates: Standard (Spectrum A): 1.0 cps/second Other (Offset): 0.1 cps/second	Spectrum Amplified:A: 0.63 B: 0.5
Source:	Temperature: ~ 35°C	External Reference:	Internal Reference: Tetramethylsilane Concentration:
	Cell:Varian Precision Tube, 5 mm OD		Resonance Position:
Purity:		Precision of Measurement: One cycle/second or better	
LABORATORY: Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas			

Figure 2



COMPOUND		INSTRUMENT AND CONDITIONS	
Name: <i>o</i> -Dichlorobenzene	State: Liquid	Instrument: Varian Associates Spectrometer, Model A-60	
<chem>C6H4Cl2</chem>		Frequency: 60 Mcps	RF Field Intensity (H_1): 0.4 milligauss
		Scanning Rates: Standard (Spectrum A): 0.1 cps/second	Spectrum Amplitude: 0.63
		Other (Spectrum B):	
Source:	Temperature: $\sim 35^\circ\text{C}$	External Reference:	Internal Reference:
	Cell: Varian Precision Tube, 5 mm OD		Concentration:
Purity:		Precision of Measurement:	Resonance Position:
LABORATORY: Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas			

Figure 3



COMPOUND		INSTRUMENT AND CONDITIONS	
Name: Ethanal (Acetaldehyde)	State: Liquid	Instrument: Varian Associates Spectrometer, Model A-60	
$\begin{array}{c} \text{C}_2\text{H}_4\text{O} \\ \text{CH}_3 - \text{C} = \text{O} - \text{H} \end{array}$		Frequency: 60 Mcps	RF Field Intensity (H_1): 0.04 milligauss
Source: Varian Associates	Temperature: $\sim 35^\circ\text{C}$	Scanning Rates: Standard (Spectrum A): 1.0 cps/second	
Purity:	Cell: Varian Precision Tube, 5 mm OD	Other (Offset): 6.7 cps/second	Spectrum Amplitude: 0.16
		External Reference:	Internal Reference:
		Precision of Measurement: One cycle/second or better	Concentration:
			Resonance Position:
LABORATORY: Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas			

Figure 4



Corporation

GENERAL CHEMICAL DIVISION

RESEARCH LABORATORY • P. O. BOX 405 • MORRISTOWN, NEW JERSEY

JEFFERSON 8-8000

August 15, 1962

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

Dear Dr. Shapiro:

We are interested in Dr. Smith's report (MELLONMR 46) on the determination of percent hydrogen by integration of absorption signals. We have been employing a form of Williams' equation but using a different procedure for obtaining the percentages. We use a known amount of a convenient standard mixed with the unknown compound and separately integrate the peaks given by standard and unknown. The following relationship holds,

$$H_1 = H_2 (A_1/A_2) (P_2/P_1)$$

where H_1 and H_2 represent total percentages of hydrogen for unknown and known; A_1 and A_2 represent peak areas for unknown and known; and P_1 and P_2 represent weight percents for unknown and known.

This procedure is also capable of giving accurate results. The method essentially cancels out any random variations contained in the proportionality constant. Also this method allows the determination of a group equivalent weight, which is often useful. A convenient expression for this quantity is the following,

$$M_1/N_1 = (M_2/N_2) (P_1/P_2) (A'_2/A'_1)$$

where M_1 and M_2 represent the molecular weights of unknown and standard, N_1 and N_2 represent the number of unknown and standard protons being integrated, and A'_1 and A'_2 represent the group areas of unknown and standard. In some cases the molecular weights can also be deduced.

Sincerely yours,

Burch B. Stewart
Research Chemist



UNION CARBIDE CORPORATION

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

UNION CARBIDE
RESEARCH INSTITUTE

August 16, 1962

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

Dear Barry:

I'm sorry you had to prompt me again. Too many of us probably depend on you to keep our schedules in order for us.

I have attached a copy of the proton resonance spectrum of 2,5-dimethylpyrrole in 12M sulfuric acid and indicated our assignments on the basis of mixed α - and β -protonation in a 2:1 ratio. The notation refers to the ring position and group (H or R=methyl), with the protonation site in parentheses. A 3.1 c.p.s. splitting in 2R(5) is due to the 5-proton, thereby necessitating a reassignment of the spectra described by Abraham, Bullock, and Mitra (Canad. J. Chem. 37, 1859 (1959)). Mutual consistency among some dozen examples leads us to confirm their structures, however, our only modification being to permute their assignments of 2R(5) and 4R(5) in the bases considered.

On diluting the solvent-acid, a time averaging of the methyl lines in β -protonated 2,5-dimethylpyrrole occurs, while the α -protonated spectrum is not affected. This incidentally permits clear observation of the fine structure in 2R(5). The rate and equilibrium measurements together require of any sample proton transfer process that the rate of β -protonation exceed that of α -protonation by at least a factor of five. N-methylpyrrole also appears to undergo β -protonation faster in strong acids (observed by isotope exchange), although not in weaker acids where the free base predominates.

Approximate values of other coupling constants we observe in various 5-protonated methylpyrroles are:

$$\begin{array}{ll} J_{3H,4H} = 6 \text{ c.p.s.} & J_{2R,1H} = 1.0 \text{ c.p.s.} \\ J_{3H,4R} = 1.5 \text{ c.p.s.} & J_{2H,3H} < 2 \text{ c.p.s.} \\ J_{1H,2H} = 4.8 \text{ c.p.s.} & \end{array}$$

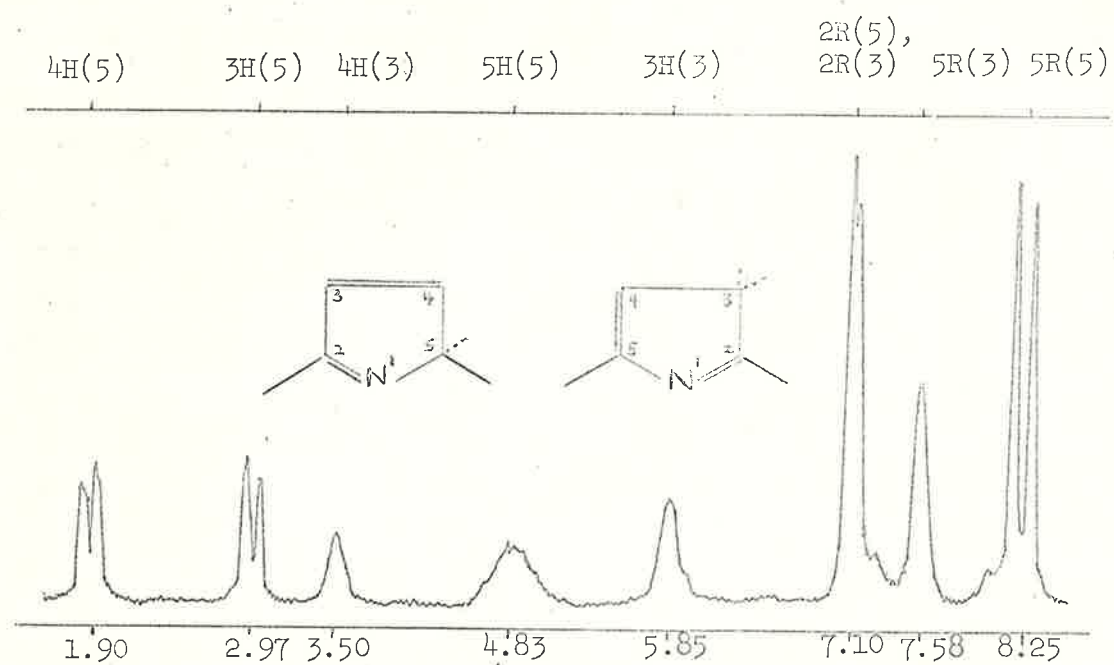
Shortly we hope to be able to demonstrate some of their relative signs.

If anyone is interested in doing any more work on the free bases I would be glad to exchange samples for results. We have about twelve, and will make three or four more of the twenty possible methylpyrroles.

Sincerely yours,

E. B. Whipple

EBW:pma
Enclosure (1)



T



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

Dear Dr. Shapiro:

PROTON COUPLINGS THROUGH FIVE BONDS

In the last editorial harangue you suggested a list of seven possible subjects for Mellon letters; there was no heading "Wild theories" and we cannot help feeling that this was a mistake. May we present No. 1 of this series? Criticism is welcomed; polite criticism positively encouraged.

We had hoped that our letter about methyl salicylate (Mellon No. 42) would incite someone to suggest a theory of long-range proton couplings over five chemical bonds. The only response was from Dr. Sheppard who mentioned that he thought it had something to do with the approximate straight line relation of the intervening bonds. In some ways our proposal is an extension of this.

The theory must attempt to explain three things:

- (a) The finite magnitude of several observed five-bond couplings in aldehydes, and in a few hydroxyl, thiol and methyl compounds.
- (b) The fact that in certain instances they are only observed when there are substituents ortho to the side chain.
- (c) Why other protons in these molecules do not show long-range couplings although separated by five or even four bonds from the aldehyde or hydroxyl proton.

The suggestion is that for all these compounds, at least one canonical form can be drawn in which the two coupled protons are connected by a planar diene-like fragment:



with the protons pointing away from each other, which, for want of a better expression, we shall call "trans". If we assume that this form makes only a small contribution to the actual structure, then the conjugated diene itself would need to have a rather large coupling to satisfy condition (a). The only experimental evidence we have found so far is disappointing in that the molecule (cis-cis-dimethyl muconate*) may not be planar and the measured coupling is only 1.3 cps.

Requirement (b) would ensure a "trans" arrangement of protons (possibly through formation of an intramolecular hydrogen bond**) and at the same time stabilize the particular resonance structure proposed.*** The specific effect (c) would arise because other protons are not related by a diene-like configuration, or if they are, they are "cis" instead of "trans". Ted Schaefer's work on vinyl formate⁹ throws some light on this last point, for he finds the "trans" coupling twice as large as the "cis". Most five bond couplings are already so small that halving them would be enough to render them unresolvable.

Nine examples are shown in the diagram. Thiophene has been taken to illustrate the rather similar results for furan and pyrrole derivatives. In each case one of the possible diene-like resonance forms has been indicated; there may be others.

We would appreciate comments. Even if this suggestion is quite wrong it may perhaps stimulate someone to look into this rather puzzling problem and find the answer.

Yours sincerely,

R. Freeman *N.S. Bhacca*
R. Freeman and N.S. Bhacca
Instrument Division

*Elvidge and Jackman - Proc. Chem. Soc. 89 (1959).

**In some cases this could have the opposite effect, which may explain why 4-bromo-3-thiophenealdehyde does not show the expected coupling². An intramolecular hydrogen bond would orient the aldehyde proton the wrong way ("cis").

***See Pauling- The Nature of the Chemical Bond, 3rd Edition, p 278.

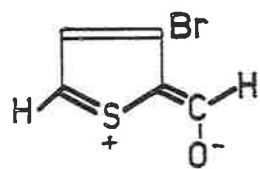
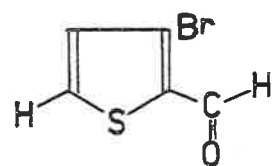
EXAMPLE #

REFERENCES

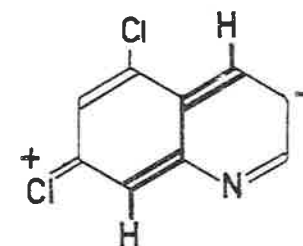
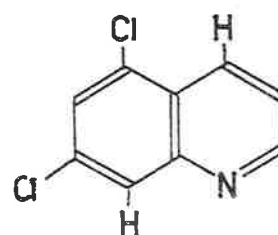
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|-----|---|
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| 3 | Bhacca and Freeman - Mellon No. 42. |
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Mellon No. 42. J. Chem. Phys. to be published. |
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| 6 | Goldstein and Kokko, Mellon No. 46. |

R.FREEMAN AND N.S.BHACCA

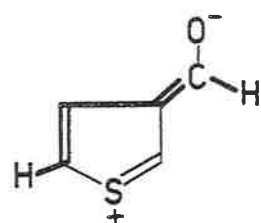
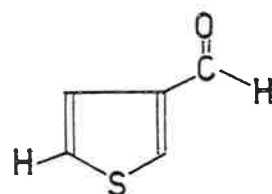
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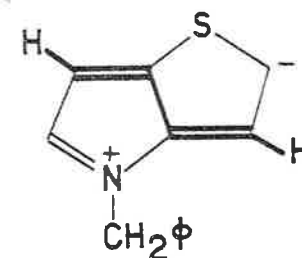
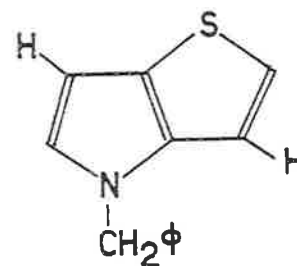
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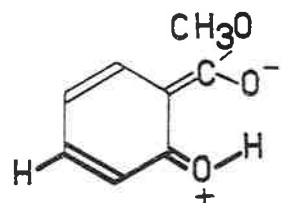
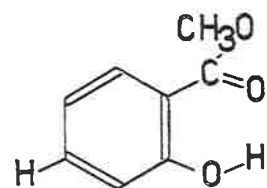
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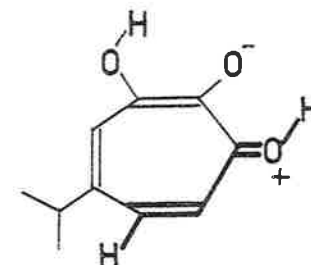
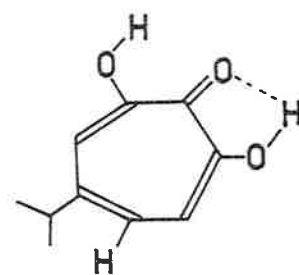
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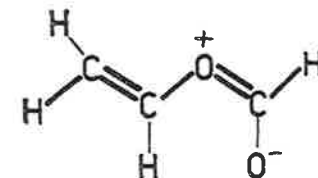
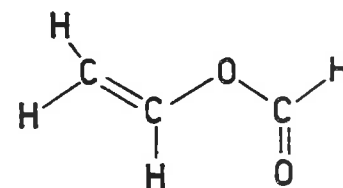
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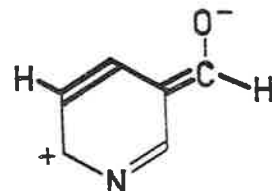
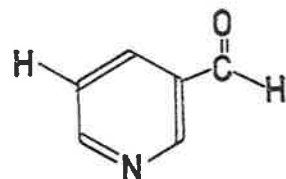
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9



5



HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT

August 24, 1962

Calibration of
A-60 Spectrometer

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

Dear Barry:

The availability of high stability in an NMR spectrometer makes it worthwhile to make chemical shift and spin coupling measurements directly from precalibrated chart scales rather than by the time-consuming sideband method. Once the scales have been precisely calibrated by the sideband method, it is convenient to make periodic checks of the calibration with a sample which provides a variety of peaks throughout the spectral range being observed. We have found p-anisaldehyde containing tetramethylsilane to be quite satisfactory for checking the A-60 spectrometer. A commercial sample of the aldehyde, containing the desired amount of TMS, and sealed into an A-60 sample tube, can be used to check all five scan widths.

The exact positions of the anisaldehyde resonances vary with gross changes in concentration. It is therefore necessary to establish the initial calibration by the sideband method (benzene provides a convenient signal for this) and then to run a set of reference spectra of the aldehyde. Thereafter, the aldehyde spectra can be compared with these reference spectra to determine calibration errors. Once sealed, the aldehyde sample retains its calibration for several months, at least, even though some chemical deterioration may take place.

Using this technique, we have found that our A-60 spectrometer retained its calibration at the 1000 cps sweep width with a standard deviation of $\pm 0.13\%$ over a period of 2-1/2 months. At the 250 cps sweep width the standard deviation was $\pm 0.19\%$. Under unusual conditions, such as component deterioration, the calibration has been found in error by 3 to 4%. Periodic use of the anisaldehyde sample, with infrequent adjustments to the instrument, makes it easy to maintain calibration to better than 0.5%.

Yours truly,

N. F. Chamberlain

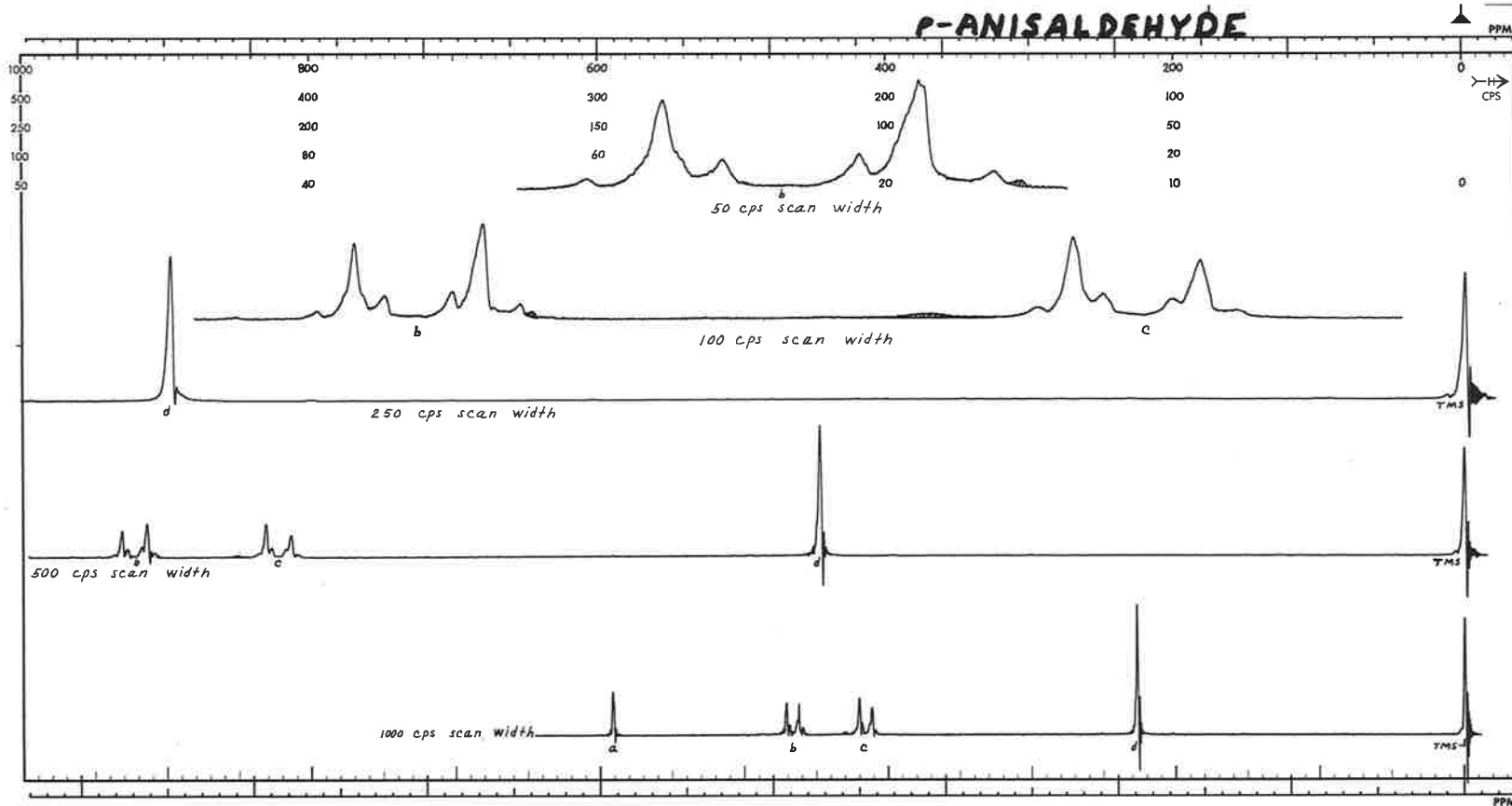
N. F. Chamberlain

R. K. Saunders

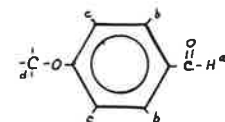
R. K. Saunders

NFC:vt
RKS

P-ANISALDEHYDE



60 MC NMR
SPECTRUM NO. 100
OPERATOR: JPR DATE: 2-20-62
SAMPLE: P-ANISALDEHYDE
+ TETRAMETHYL SILANE



SOLVENT: ~10% CCl₄
FILTER BANDWIDTH: 4 cps
R. F. FIELD: 0.10 mG
SWEEP TIME: 500 sec
SWEEP WIDTH: All Volts cps
SWEEP OFFSET: 0 cps
SPECTRUM AMP: 0.25
INTEGRAL AMP:
REMARKS: A-60 CALIBRATION



CHART 5-60B

PRINTED IN U.S.A.

MONASH UNIVERSITY

DEPARTMENT OF CHEMISTRY

Telephone 544 0481

Head of Department
Professor R. D. Brown

P.O. Box 92
Clayton, Victoria,
Australia

1st August, 1962.

Dr. Aksel A. Bothner-By,
Director of Research,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13
Pennsylvania, U. S. A.

Dear Dr. Bothner-By,

We have recently had a Varian DP-60 spectrometer installed and have been using it for both wide-line and high resolution studies. The wide-line studies have been on low abundance Hg^{199} and Cr^{53} as well as on Be^{9} compounds. In connection with some proton high resolution studies on heterocyclic compounds, we recently had cause to analyse the A_2B_2 systems arising from the aromatic protons in benzimidazole (I) and benzotriazole (III).

These systems are of A_2B_2 type because of the rapid proton exchange that takes place in an organic solvent.

Initially we used the method given by Pople, Schneider and Bernstein¹ but then noted some recent work by Dischler and his co-workers^{2,3}. We found that this latter method was more convenient to use in practice and furthermore it gave a non-zero value for the para coupling constant, J_{17} , directly. Since there is inevitably some error in the experimental line positions, we found that the line spacing rules used as internal checks on the validity of our parameters were not obeyed exactly. However, by assuming small deviations in the observed line positions (ca 0.1 cps) it was possible to obtain unambiguous values for the parameters.

The parameters obtained for these two systems together with those obtained by Dischler and Englert² for the related compound benzofurazan (III) are shown below. Our spectra were run as saturated solutions (ca 5%) in acetone at a frequency of 56.4 Mcps. The spectra are shown below.

The H_2 peak in benzimidazole is a singlet in organic solvents owing to the rapid proton exchange as shown recently in MELLON-M-R by Mannschreck and Staab (No. 44, p. 19). This brings me to a final comment. NMR research in Australia is just getting under way and as we are sometimes just a little slower in receiving overseas journals, it is obvious that your Newsletter is a great boon to us.

-2-

	$J_{15} = J_{6,7}$ cps	$J_{2,6}$ cps	$J_{4,6} = J_{5,7}$ cps	$J_{3,7}$ cps	τ_4	τ_5	δ ppm.
Benzimidazole	8.2	7.1	1.4	0.7	2.30	2.74	0.44
Benzotriazole	8.6	7.2	0.8	1.0	2.03	2.55	0.52
Benzofurazan	9.3	6.5	0.9	1.2	2.05	2.44	0.39

Sincerely Yours,

Michael L. Heffernan
Michael L. Heffernan

Peter J. Black
Peter J. Black

1. Pople, Schneider and Bernstein, Can. J. Chem., 35, 1060 (1957)
2. Dischler and Englert, Z. Naturforsch., 16a, 1180, (1961)
3. Dischler and Maier, Z. Naturforsch., 16a, 318, (1961).

ROHM & HAAS COMPANY

REDSTONE ARSENAL



RESEARCH DIVISION

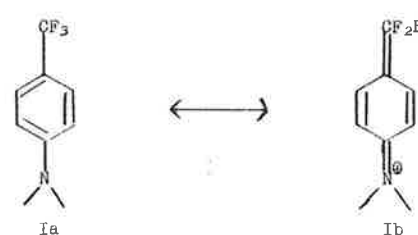
HUNTSVILLE, ALABAMA

July 25, 1962

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By,

The electronic effect of the trifluoromethyl group attached to an aromatic ring and the dipole moment of p-dimethylaminobenzotrifluoride have been discussed in terms of resonance forms I a-b. [Roberts, Webb and McElhill, *J. Am. Chem. Soc.*, **72**, 408(1950).]



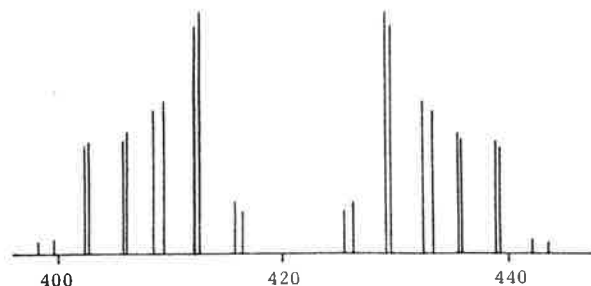
In view of this work and that of Tart et al. [*J. Am. Chem. Soc.*, **82**, 756(1960)] who interpreted the F^{19} chemical shifts in various substituted fluorobenzenes as evidence for contributing forms II a-b,



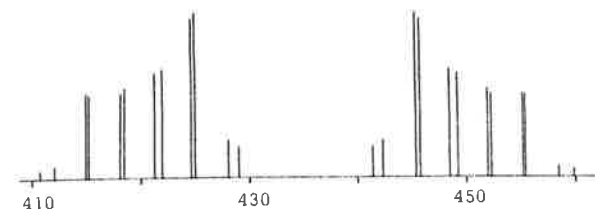
we examined several benzotrifluorides to see if their n.m.r. spectra reflect contributions from form Ib. Table I summarizes our observations.

• CHEMICALS FOR INDUSTRY •

(a)



(b)



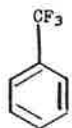
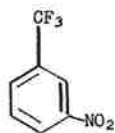
cps from tetramethylsilane

Experimental and calculated spectra of

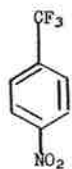
(a) benzimidazole (b) benzotriazole

July 25, 1962

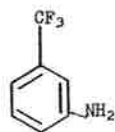
TABLE I

CYCLOHEXANE^a METHANOL^a2565 c.p.s.^b 2507

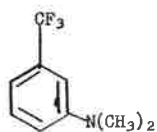
2570 2523



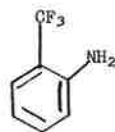
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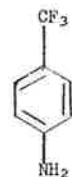


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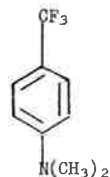


2552 2503

July 25, 1962



2490 2447



2480 2431

a. Approximately 5% solutions by volume.

b. Relative to internal CCl₃F. Measurements made at 25° using 40 mc. probe.

Two main features strike us:

- (1) In the same solvent, there is little difference in the spectrum of the compounds examined except for the p-amino and p-dimethylanilino-benzotrifluorides.
- (2) In these two compounds, the fluorines are deshielded, contrary to expectations based on form Ib which suggests the fluorines should be highly shielded.

We have no satisfactory explanation for these results. The behavior of the p-amino compounds, however, may be related to other examples of abnormal deshielding. [Tiers, *J. Am. Chem. Soc.*, **78**, 2914(1956); Muller, Lanterbur and Svatos, *ibid.*, **79**, 1807(1957).]

If any of your readers have suggestions or comments, I would appreciate hearing of them. I hope this note will continue our Mello nmr subscription which is sent to Dr. C. B. Colburn of this laboratory.

Sincerely yours,

Carl L. Bumgardner
Carl L. Bumgardner

CLB:bac

R.F.Zürcher c/o
CIBA Limited, Basle, Switzerland

August 3, 1962

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

Dear Dr.Shapiro:

I feel that I have come a step nearer to understanding why the anisotropy of the magnetic susceptibility of the aliphatic C-C bond, $\Delta\chi^{CC} = \chi_{||}^{CC} - \chi_{\perp}^{CC}$, is positive. All workers in this field agree about the sign of $\Delta\chi^{CC}$, if not about the magnitude. The fact that $\Delta\chi^{CC}$ is positive is rather surprising at first glance, for if the C-C bond is assumed to be axially symmetrical then $\chi_{||}^{CC}$, the magnetic susceptibility along the bond, must be negative, i.e. diamagnetic, whereas χ_{\perp}^{CC} , the magnetic susceptibility across the bond, consists of a diamagnetic (negative) and a second-order paramagnetic (positive) term. This latter term is the result of the loss of axial symmetry across the bond and partially counteracts the diamagnetic part of χ_{\perp}^{CC} . Yet, χ_{\perp}^{CC} must be more diamagnetic (negative) than $\chi_{||}^{CC}$ in order to make $\Delta\chi^{CC}$ positive. The question arises why the diamagnetic part of χ_{\perp}^{CC} should be much bigger than $\chi_{||}^{CC}$. Can this phenomenon be related with another, possibly more familiar one? I believe so.

In 1932 Kirkwood (Physik.Z. 33, 57) and Vinti (Physic.Rev. 41, 813) showed the close connection between diamagnetic susceptibility χ and electron polarizability α . In 1935 Gans and Mrowka (Schr.Königsberger Gel.Ges.Nat.Kl. 12, 1) were able to generalize their findings by including the second-order paramagnetic part (Van Vleck). The Gans-Mrowka equations:

- 2 -

$$\chi_x = - \frac{e^2 N}{8mc^2} \cdot \sqrt{a_0} n \left[\underbrace{\sqrt{\alpha_y} + \sqrt{\alpha_z}}_{\text{diamagnetic}} - \underbrace{\frac{(\sqrt{\alpha_y} - \sqrt{\alpha_z})^2}{\sqrt{\alpha_y} + \sqrt{\alpha_z}}}_{\text{"paramagnetic"}} \right]$$

etc.

e = electronic charge N = Avogadro number
 m = rest mass of electron c = velocity of light in vacuo
 a_0 = radius of the first Bohr orbit of the hydrogen atom
 n = number of participating electrons

show χ_x , the principal magnetic susceptibility along the x-axis, to be a function of the two principal electron polarizabilities perpendicular to it. In the case of axial symmetry $\alpha_y \equiv \alpha_z$, and the second-order paramagnetic term vanishes.

It has been well known for a long time that the longitudinal polarizability of the C-C bond, $\alpha_{||}^{CC}$, is much bigger than α_{\perp}^{CC} , that perpendicular to the bond. In view of the Gans-Mrowka equations it is therefore immediately clear why χ_{\perp}^{CC} is more diamagnetic than $\chi_{||}^{CC}$. This can also be made intuitively evident by saying that the rotation of the electrons around the C-C axis, and hence $\chi_{||}^{CC}$, must be small because α_{\perp}^{CC} , the polarizability or in other words the mobility of the electrons perpendicular to this axis is small. Just the opposite argument holds for the diamagnetic term of χ_{\perp}^{CC} which is slightly diminished by the second-order paramagnetic part. This line of reasoning may, of course, be applied to all sorts of bonds.

I have used the Gans-Mrowka equations together with a handful of others to determine the longitudinal and transverse electron polarizabilities and magnetic susceptibilities of the aliphatic C-C and C-H bonds. This work includes a discussion of the most probable value for $\Delta\chi^{CC}$, the anisotropy of the magnetic susceptibility of the C-C bond. It will appear in JCP.

Sincerely yours,

R. Zürcher

R.F.Zürcher

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

August 8, 1962.

Dr. Aksel A. Bothner-By,
Staff Fellow,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.,
U. S. A.

Dear Aksel:

We have been doing a little more on conformational studies, in particular, the esters of 2,6 tetradeutero cyclohexanol. The small axial to equatorial chemical shift of the adjacent proton which is not distinguishable at low temperature in the undeuterated esters is well resolved in the deuterated compounds in CS₂ solution. The conformational equilibrium constants, which are accurate to about $\pm 2\%$ on the figure quoted for the % equatorial group, are given in the enclosed table. The figure for the acetate agrees well with that by Anet (J. Am. Chem. Soc. 84 p. 1053 1962).

We have also constructed a first model 'Spin Echo' spectrometer using a Varian 6" magnet with a 1" gap and a radio frequency of 40 Mc. The figure enclosed shows nicely the behaviour of free induction tails following a $\pi/2$ pulse in a simple exchanging system, methyl nitrate. The induction tails are exponential at room temperature and on cooling the decay is strongly damped and becomes non-exponential as the coalescence temperature of the static spectrum is approached. Below the coalescence temperature the induction tails become long once again and have the 43 cps. chemical shift modulation. The behaviour follows exactly the predictions of Woessner (J. Chem. Phys. 35 p. 41 (1961)).

Wishing you an enjoyable year in Europe.

Yours sincerely,

Len
Leonard W. Reeves.

LWR:kg

Enclosure

Compound	Temp °C	δ_a c.p.s.	δ_e c.p.s.	$\delta_{eq,ax}$ c.p.s.	% Equatorial Ester Group	Coalescence Temp °C	$(\delta_a - \delta_e)$ c.p.s.
Acetate	-96	-179.4	-191.7	-182.4	76	-72.5	12.3
Formate	-65 \rightarrow +25	-184.0	-198.9	-189.9	61	-77.5	14.9
Trifluoroacetate	-100	-189.6	-203.9	-193	76	-74.5	14.3
Nitrate	-50 \rightarrow +25	-188.7	-203.0	-192.6	73	-82.5	14.3
	+25						

August 21, 1962

METHYL NITRITE

Temperature dependence of free induction decay

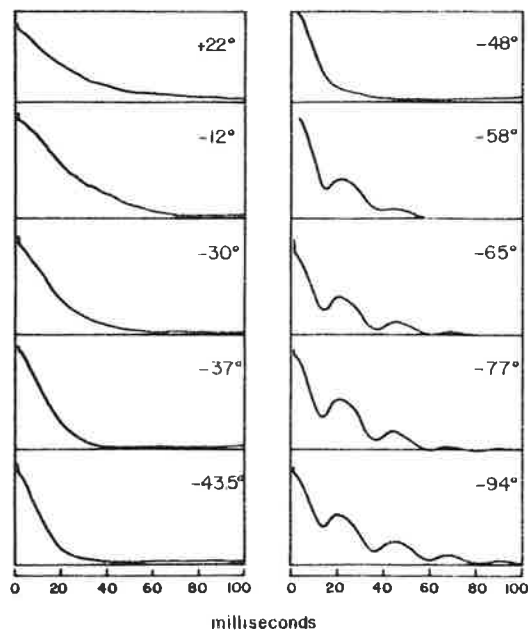


Fig. 2.

Dr. Barry Shapiro
The Mellon Institute
Pittsburgh, 13, Pa.

Dear Barry,

The possibility of improving the sensitivity of NMR has been discussed at some length this summer and it became apparent that several laboratories are interested in the use of computer techniques for this purpose. I would like to give a brief account of our experiences along these lines, and you will undoubtedly hear from others.

Using the Mnemotron Model 400 Computer of Average Transients (the CAT) we have been able to improve the effective sensitivity of our HR-60 spectrometer by a factor of fifty. That is, we can obtain interpretable high resolution spectra from compounds containing single hydrogen peaks at concentrations of $10^{-3}M$, as compared to the best performance of our spectrometer, or $5 \times 10^{-2}M$, signal to noise ratio ~ 2 . It appears that another factor of 2 can be added with some additional effort, but further significant improvement is clearly going to be limited by the requirement for excessively long sweep times (6 months, or so).

For the most part we have encountered very few of the initially anticipated difficulties. To ensure the reproducibility of successive sweeps we have attempted to trigger the CAT from a marker. This proved impossible because the rise time of an NMR signal was too slow, but the problem was temporarily solved by triggering a Tektronix 535A oscilloscope from the marker and letting the scope trigger the CAT. A more permanent solution was found in a modified Schmitt trigger.

Either the Varian Linear Sweep Unit or the sawtooth output of the Tektronix scope, equipped with a home-made attenuator, can be used to sweep the field. We have found it quite satisfactory for our purposes to use sweep rates

August 21, 1962

up to 10 cps/sec over a region of 300 cps. The sweep of the CAT can then be centered by an appropriate choice of delay time to cover the 100 cps of the spectrum which fall in the linear portion of the linear sweep. This gives us about 4 CAT channels (total 400 channels) per cps. As can be ascertained from the attached CAT NMR spectra, this will be adequate for many purposes. Slower sweeps and 10 CAT channels per cps will give somewhat better resolution when needed, but thus far we have not found them necessary.

With relatively rapid sweep rates the reproducibility of the individual sweeps is very good for total sweep times up to 6 hrs/spectrum. The correction of slow drifts does, however, present a problem. Since our HR-60 spectrometer is not equipped with the A-60 proton stabilization system, this had to be done by the graduate student-in-attendance method.

The technique has allowed us to carry out some experiments which could not have been done before. Thus we have examined the interaction of the coenzyme Diphosphopyridine nucleotide (DPN) with the enzyme alcohol dehydrogenase, which is known to bind 4 molecules of DPN/protein molecule. As long as one was confined to the relatively high DPN concentrations (0.1M) the excessively high protein concentrations required would have made the experiment meaningless. With the present system one can observe the disappearance of the pyridine spectrum in the presence of the enzyme, (in approximately stoichiometric proportions) with relatively little effect on the adenine spectrum, as is seen in Fig. 1 (d). This cannot be accounted for either by a shift or by a viscosity effect, since in the latter case the ratio of amplitudes of either of the two adenine peaks to any of the pyridine peaks should have remained constant. The exact interpretation of this finding in terms of binding and/or exchange is still open pending further experiments. However, a detailed study of this type of problem is now clearly in the realm of possibility.

Sincerely,



Oleg Jarutzky

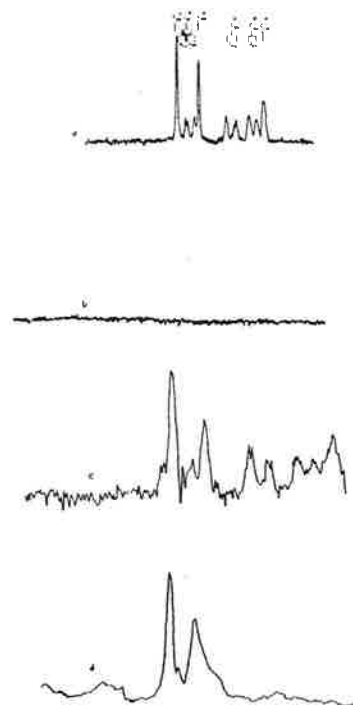
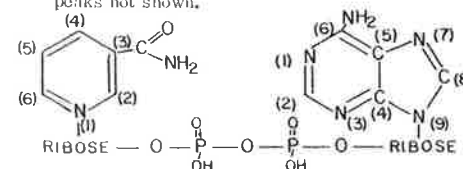


Fig. 1. (a) Conventional NMR spectrum of the aromatic region of .1 M DPN in D_2O increasing field from right to left. $C^A_{(2)}$ and $C^A_{(8)}$ adenine protons, $C^P_{(2)}$, $C^P_{(4)}$, $C^P_{(5)}$ and $C^P_{(6)}$ pyridine protons, with coupling constants as indicated.

(b) Conventional NMR spectrum of .005 M DPN in D_2O .

(c) CAT NMR spectrum of .005 M DPN in D_2O (1 hr run) (same solution as b).

(d) CAT NMR spectrum of .005 M DPN in D_2O in the presence of .0005 M alcohol dehydrogenase (3 hrs run) solvent and ribose peaks not shown.





TELEPHONE: ARDWICK 3333

THE UNIVERSITY OF MANCHESTER,

DEPARTMENT OF CHEMISTRY,

MANCHESTER, 13.

15th August, 1962.

Dr. A. A. Bothner-By,
MELLON INSTITUTE
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania.

Dear Dr. Bothner-By,

Thank you for the reminder that our first installment is due. In the past year we have begun to operate an A.E.I. RS2 spectrometer in the dual role of routine and research instrument. There are two tips on experimentation which we would like to pass on:-

- (1) A melting point tube held concentric in the normal sample tube by means of two teflon spacers is a cheap device for housing external standards when concentric tubing is not readily available.
- (2) Hard polymers such as teflon and crystalline polypropylene are useful substitutes for glass in constructing r.f. probe units, especially when space is scarce and a precision job is required.

In collaboration with Norman L. Paddock we have recently been studying the proton resonances in cyclic phosphonitrilic methyls $[-P(Me)_2N=]_n$ and their protonated cations. The results obtained at 60 and 25 Mc/s are summarised below:

Solvent	Homologue	J_{PH}	c/s	J	c/s	P^H
CCl_4	trimer	8.68 ± 0.01	13.5 ± 0.5	1.5 ± 0.5		
	tetramer	8.68	12.5	-		
	pentamer	8.68	13.0	-		
$HC10_4$	trimer, H^+	{	7.9 (int.2)	14.0	-	
			7.5 (int.1)	14.0	-	
	tetramer, H_2^+	7.6	13.0	-		
	pentamer, $H_2^+(?)$	7.7	13.5	-		

In each case the proton resonance is a doublet due to coupling with the parent P^{31} atom but whereas the doublets consist of two sharp lines in the tetramer and pentamer, each component of the trimer doublet is, in fact, a triplet. The origin of this fine structure is probably due to long range spin-spin interaction ($J=1.5$ c/s) with the remaining two ^{31}P atoms in the ring. In view of the aromatic character of these compounds long range effects are not unexpected but the fact that no fine structure has been resolved in the bigger rings may mean that they are less aromatic than the trimer.

Protonation produces an overall shift to low field and in the case of the trimer removes the long range coupling. Furthermore two doublets are observed in the protonated trimer, the intensity ratio of 1:2 suggesting that the proton is firmly located on one N atom. Only one doublet in the protonated tetramer suggests that this is either a symmetrical ion or that the protons are labile. In the pentamer only the latter explanation can apply.

As a beginner in the field I greatly appreciate Mellonmr.

Yours faithfully,

G. Allen.

(G. Allen)

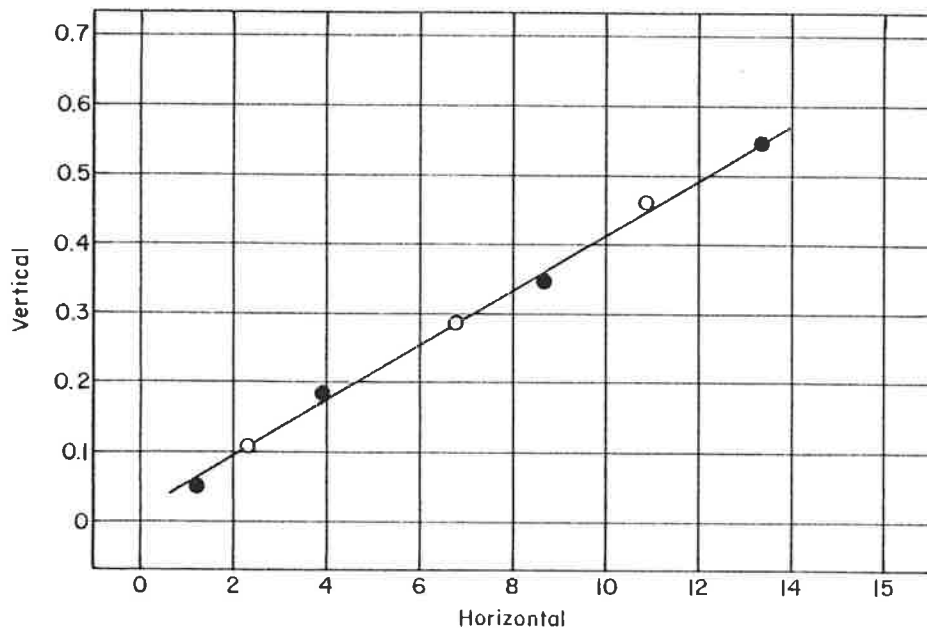
MELLON INSTITUTE

4400 FIFTH AVENUE
PITTSBURGH 13, PA.

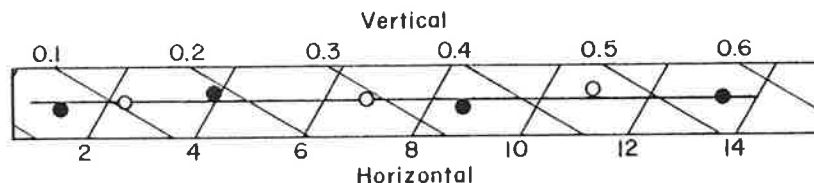
ON BREVITY

Appeals for brevity have been occupying increasing amounts of space in this organ of late, and the views of editors of most real scientific journals on this subject are well known to most of us. Prolixity and double spacing are rightly condemned, but the wisdom of the common tendency to go even further and to suppress the actual spectra which are the foundations of spectroscopic papers may be doubted. By a well-known psychological process, frustration with this state of affairs led to the formulation of the following plan to distribute excessive brevity more evenly.

Although we all recognize that the ultimate goal of most true scientific investigations is a neat linear plot, there seems to be no reason why such plots should occupy the inordinate space required by the traditional format. Consider the figure below.



In its conventional form, it takes up about six vertical inches. The same plot, without any reduction in scale but with all unnecessary area removed, may be presented as shown below.



Less than one-third the area is required, and no information has been sacrificed. Some of the space saved by this simple stratagem could be devoted to spectra, to the benefit of all concerned.

Paul C. Lauterbur
Paul C. Lauterbur

(An even greater space saver is either to fill up the pages actually used, or to prune the overflow from the previous page — however, I suspect that this is too much to ask, even from one of one's own immediate colleagues!)

BLS



VARIAN associates

611 HANSEN WAY • PALO ALTO, CALIFORNIA • DAVENPORT 6-4000

August 20, 1962

Dr. Barry Shapiro
Mellon Institute
Pittsburgh, Pennsylvania

Dear Barry:

Recently we have encountered a number of applications requiring quantitative NMR analysis on small quantities of samples. We wish to describe a technique employing the Varian Microcell in such work. The sort of results obtained is shown on the graph where the A-60 integral is plotted against the weight of a pure steroid, for identical instrumental conditions. The analytical peak used was that of a methoxyl group which appeared in a clear region of the spectrum. The points shown were obtained by averaging the results from several repeated integrals for each sample.

For the analysis the weighed samples were dissolved in a small amount (.03 cc) of CDCl_3 and were then pipetted onto the top of the microcell, the two halves of which were pushed completely together and spaced in the A-60 sample tube so that the center of the cell was about 1.5-2.0 cm from the bottom of the tube. Additional solvent was then added dropwise and drawn into the microcell by adjustment of the lower plug until a predetermined length (usually 4-10 mm, .05-.13 cc) of the solvent column was reached. The sample was then inserted into the A-60 spinner and carefully positioned so that the distance from the bottom of the spinner to the sample center corresponded accurately to the distance to the center of the RF coil, which had been determined previously as described by J. Shoolery (Mellon NMR No. 42). Because the RF field intensity is not constant along the Y-axis, it is of course necessary to employ the same sample column length in each series of runs which is to be compared. We have found that the necessary distance measurements can be made sufficiently accurate by careful use of a ruler graduated in .5 mm.

Sincerely,

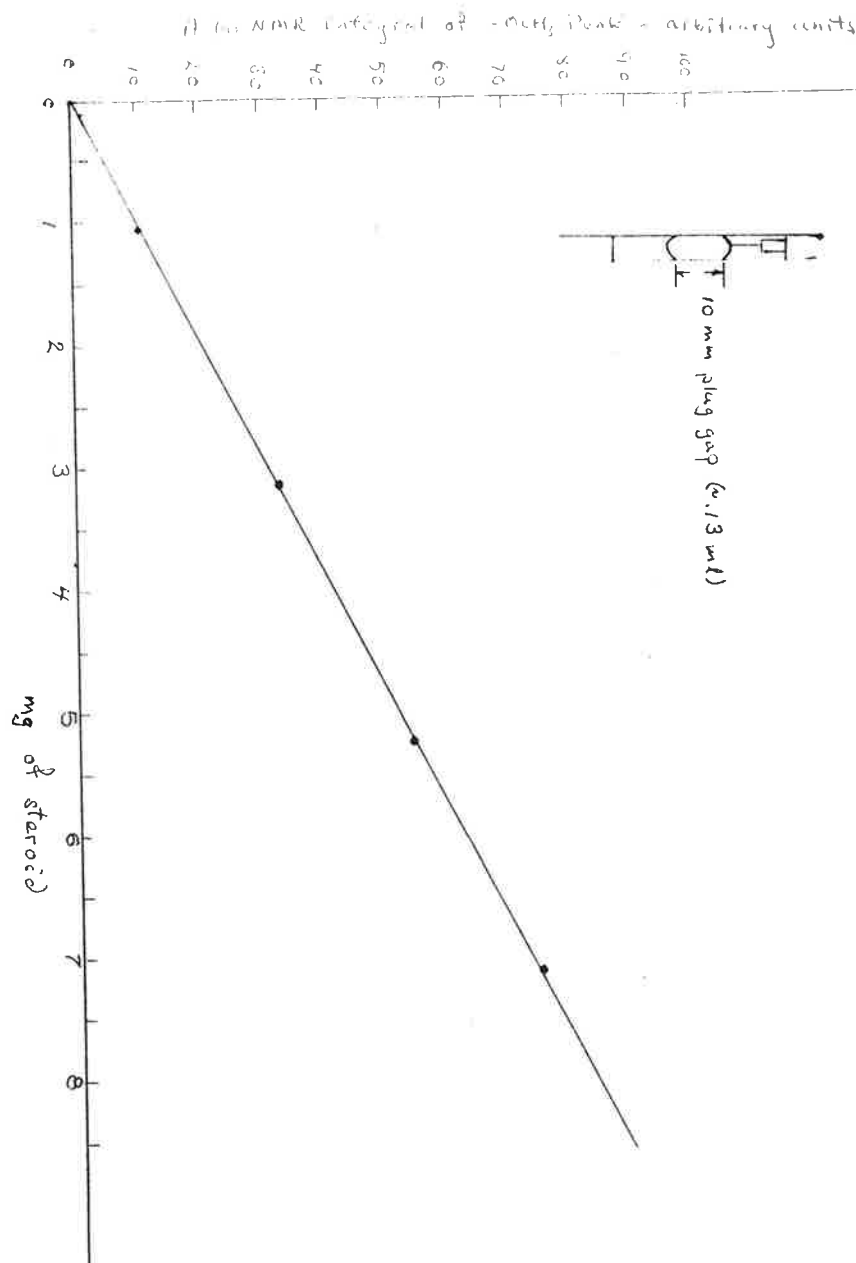
Don Hollis

Donald P. Hollis

Eugene A. Pier

Eugene A. Pier
A-60 Applications Laboratory
Instrument Field Engineering Division

DPH/EAP:pck



THE UNIVERSITY OF TEXAS
DEPARTMENT OF CHEMISTRY
AUSTIN 12

August 23, 1962

Dr. Bernard L. Shapiro
Editor, MELLONMR
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Penn.

Dear Dr. Shapiro,

For some time we have been interested in the measurement of B^{11} chemical shifts in symmetrical tetrahedral ions such as BF_4^- , $B(CH_3)_4^-$, etc.. Our original intention was to make the usual correlation between chemical shift and electronegativity with the hope of assigning useful electronegativities to such species as alkyl groups. The project has involved the synthesis of a large number of alkyl, aromatic, and unsaturated organo-boron ions with some interesting trends in chemical shift. But as usual difficulties were encountered with what should have been the simplest species, the halide ions.

The first notable anomaly is the shift measured for BF_4^- in which boron is more shielded than in ions with less electronegative halides. The unusual behavior of F has previously been noted in CF_4 and SiF_4 . But the most serious problems arose in finding a suitable solvent for the halide ions. In the course of our measurements we have used cations ranging from alkali metal ions to large substituted ammonium ions and heterocyclic ions and a large variety of solvents. In highly polar solvents such as nitrobenzene competition has been observed between the solvent and H^+ for complexing with BX_3 . The chemical shifts of BX_3 are to higher field in the solvent than in pure liquid BX_3 . The shifts are also strongly dependent on X^- concentration. The same effects are observed in CH_2Cl_2 where apparently the chlorine in the solvent is almost as suitable for addition to BCl_3 as is Cl^- ion. Similar observations have been reported in the literature.

We have also used NN-dimethylformamide and dimethylsulfoxide as solvents. In this case we observe that the BX_3 species rapidly decompose the solvent while in solutions containing BX_4^- there is no reaction indicating the absence of a $BX_3-BX_4^-$ equilibrium. The B^{11} shift of BCl_4^- is higher in DMSO than in any other solvent in which the $BCl_3-BCl_4^-$ equilibrium must be forced toward the ion by excess Cl^- . Interestingly, though, the shift for BBr_4^- in DMF is about 25 ppm lower than the highest value measured in CH_2Cl_2 even though the stability of the former solution indicates no $BBr_3-BBr_4^-$ equilibrium. Finally, we have employed liquid HX as a solvent to avoid these equilibria altogether. The only problem has been the solubility of the salts at low temperatures. The interesting effects of solvent and associated cation are now under investigation and equilibrium constants are being measured.

The following B^{11} shifts are suggested for the halide ions in the absence of solvent interference:

BCl_4^-	-6.7 ppm	from BF_3 etherate
BF_4^-	+2.1	
BBr_4^-	27.0	
BI_4^-	127.8	

Our work on tetrahedral boron has also included studies of BX_3 addition compounds. Previous chemical shift measurements have shown that substituted phosphines are apparently better electron donors to BH_3 than amines. We have done a considerable number of measurements on addition compounds of boron trihalide in which the usual trends of electron donation are found.

Some studies have also been made on compounds such as Me_2NBMe_2 . It has been found that the chemical shifts of boron in such compounds with alkyl groups on both the Nitrogen and Boron are typically of the trigonal boron configuration but when hydrogen or halogen atoms are substituted on the Boron there is apparently a diverzation leading to such higher boron shieldings in such compounds as Me_2NBH_2 . Attempts are being made to measure monomer-dimer equilibria in these systems.

A detailed report of chemical shifts in tetrahedral boron compounds will be published shortly.

Sincerely, J. C. Davis, Jr.

J. C. Davis, Jr.
Jeff C. Davis, Jr.

I am desperately in need of some 1,1,3,3-tetrafluoroacetone and have been unable to locate any. Can any of the MELLONMR readers help me?

B. L. Shapiro
Mellon Institute

MONSANTO CHEMICAL COMPANY

INORGANIC CHEMICALS DIVISION
RESEARCH DEPARTMENT
400 NORTH LINDBERGH BOULEVARD
Box 520
ST. LOUIS 60, MISSOURI

August 8, 1962

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

Dear Barry:

We have recently found a simple way to observe very weak NMR signals on the A-60 spectrometer with significantly improved signal to noise ratio. The technique may be of interest for MELLOMR.

What one does is to disengage the sweep time buttons and manually advance the recorder carriage through the resonance band, stopping to accumulate, record and cancel integral at intervals of 1 m.m. or so. The time spent in accumulation of integral is held uniform for each ordinate by timing with a stopwatch. This produces, in effect, a semi-automatic graphical differentiation of the amplified integral curve. The resulting absorption spectrum is obtained as the envelope of a series of recorded vertical lines. The growth of signal is proportional to the time spent in accumulation of the integrals, while the growth of noise is only as the square root of the time thus spent. Theoretical signal to noise ratio increases then proportional to the square root of the time spent.

Results are illustrated in the attached recordings of the quartet from 1% ethylbenzene in CCl_4 . The lower spectrum was recorded in the conventional way using instrument settings specified by Varian for an instrument sensitivity check. The upper spectrum was obtained in about an hour using the outlined procedure with a residence time of 30 seconds on each ordinate. Actual improvement in signal to noise ratio was a factor of 3 to 4 in this case.

The method is admittedly time-consuming, and the job could be done better electronically, but it has the distinct advantage of requiring neither modification of the A-60 nor additional electronics. An obvious application is in confirming the presence of peaks on the borderline of detectability. Use is limited to field-frequency controlled spectrometers with good stability during the elapsed time of the measurements.

One is left with the conclusion that the A-60 could benefit from a slower built-in sweep time.

Sincerely,

Maw

M. M. Crutchfield

Attachment
/mac

SOLVENT: 1% ETHYLBENZENE IN CCl_4
FILTER BANDWIDTH: 0.4 0.4 cps
R. F. FIELD: 0.15 0.15 mG
SWEEP TIME: 0 500 sec
SWEEP WIDTH: 500 500 cps
SWEEP OFFSET: 000 000 cps
SPECTRUM AMP: 2 50
INTEGRAL AMP: 80 —
REMARKS: A B
+ 30 SECONDS PER ORDINATE

