Premier

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 2

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 2

For issue No. 2 of M.E.L.L.O.N.M.R., we are pleased to include contributions from Messrs. Brownstein, Reilly, Sheppard, Tiers and Zimmerman, as well as some local data and thoughts.

As is seen, Messrs. Reilly and Sheppard have separately joined battle with us over the issues of standardization and scales. Dr. Sheppard suggests that this Newsletter might well serve as a forum for discussing standardization and we agree that this would be a very good idea. With this in mind, we feel impelled to present some defense of our scheme for standardization as set forth in issue No. 1 of M.E.L.L.O.N.M.R.

With respect to the functions of the internal reference and the external reference, we would like to point out that the internal reference corrects for more than just the classical $\frac{2\pi\kappa}{3}$ bulk susceptibility effect. In general, the use of a spherical sample will not result in line positions independent of solvent composition. From previous measurements on mixtures of dioxane and toluene, one can deduce that in a spherical cell the lines from these substances will shift over a range of one-half a part-per-million as the proportions of the mixture are varied. On the other hand, the lines will stay at relatively constant separation from each other (cf. Bothner-By and Glick, J. Chem. Phys. 26, 1651 (1957). As far as spherical cells them-

selves go, we are aware of no design for such a cell which gives the necessary almost perfect sphericity.

Incidentally, even with " well-behaved " mixtures, absolute line positions are shifted by anywhere from 0.0 to 0.9 $\Delta\kappa$ in spherical samples, depending on specific molecular interactions (see Bothner-By and Glick, J. Chem. Phys. 26, 1647 (1957) ; cf. Evans, Proc. Chem. Soc., 115 (1958)), Schneider, Bernstein and Pople, J. Chem. Phys., 28, 601 (1958).

In view of these considerations, we still think that a scale running from the internal reference is more practical, if less absolute, than one running from the external reference. The additional inclusion of the latter will allow such now practical data to be converted to absolute data when the theory of solvent shifts catches up with experiment.

There is also a problem which we are not sure is generally recognized in connection with the automatic referencing by means of the Baker system. In order that the static field at the reference sample and at the unknown sample should vary in as parallel a manner as possible, it is desirable that these be placed as close to one another as is convenient. If, however, an unknown sample of volume V and susceptibly κ is introduced into the field at a distance of r cm. from the reference, it will cause a shift in the field at the reference of $2V\kappa/r^3$ (This assumes that the radius vector joining the two samples is parallel to the static field.) Introducing some typical numbers illustrates that this could result in shifts of the zero of the scale of up to 0.1 ppm.

AAB BLS

Proton Resonance Spectrum of Gallium Triethyl

Line	Intensity
0.0	1.5
4.1	6.0
5.0	1.5
10.4	48
13.2	15
14.0	8.0
21.2	150
22.2	38
26.8	72
28.5	68
33.4	163
34.7	72
35.4	16
40.5	178
44.4	12
47.5	19
49.6	17
51.1	4.0
55.5	3.0

Cornell University
Chemistry Department

SAMPLE: Pure Gallium Triethyl, vacuum distilled into sample tube.

FREQUENCY: 40 megacycles/second

SCAN RATE 0.09 milligauss/second

$\frac{J}{\delta} = 0.391$

Cornell University
Chemistry Department

SD 438 MIMEO REV. 6-53 PRINTED IN U.S.A.

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA
TELEPHONE OLYMPIC 3-2100

19 November 1958

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

Dear Aksel:

Thank you for including me on your mailing list for M.E.L.L.O.N. I would like to suggest that you consider adding John Zimmerman from Magnolia to the distribution. I have several comments to make concerning standardization of NMR spectra and shall try to present them in at least a semi-organized fashion.

First of all, with respect to the added capillary vs. precision cell method for external referencing, Zimmerman has recently shown quite conclusively that the added capillary method is not reliable If you get in touch with him directly, he might be willing to contribute the results of his experiments to your publication.

With respect to your choice of referencing procedure, I am pleased to note that you plan to adopt the suggestion made at the Gordon Conference of using both an internal and an external reference. I am somewhat disturbed, however, that you plan to tie all measurements to the internal reference, $SiMe_4$. My most recent thoughts concerning the referencing problem are as follows. I regard the use of cylindrical samples and consequently of an internal reference with its attendant uncertainties as strictly a temporary expedient until better instrumentation and techniques become generally available. With a feedback system of the Baker (or related) type spectra will be automatically referenced to the control sample, i.e. to an external reference. The need for eliminating bulk susceptibility effects via an internal reference can then be avoided by using spherical samples. Thus, the use of an external reference as the primary one seems more consistent with developments that are likely to occur in the not too distant future.

As long as we are concerned with relatively simple spectra which can be analyzed into δ and J contributions, either an internal or an external reference would appear to be equally satisfactory as the primary one. However, as we find it more and more advantageous to use "fingerprinting" techniques for the identification of unknowns, the external reference (and a shielding number scale) seems to me to have the edge as the primary one.

I am enclosing two copies of "Publication of NMR Spectra by API Research Project 44" which was revised following the Gordon Conference discussions. The most recent recommendations to the Advisory Committee included the requirement for use of a precision cell plus a slight revision to Table 1 as below. The proposal for publication of spectra (including the above recommendations) was accepted by the Advisory Committee. It is anticipated that the API will begin issuing standard NMR spectra in the near future. Since the recommendations made for the publication of standard NMR spectra represent what appears to be the best compromise among many different points of view, it would seem to make the task of intercomparison of spectra much easier if everyone could see his way clear to adopt the standard presentation.

Table 1. NMR Reference Separations at 40 Mcps

Compound	$\Delta\nu$ at 25°C	$\frac{d(\Delta\nu)}{dt}$ in cps/°C
Benzaldehyde		
Aldehyde H	- 107.1	< 0.01
Ring H	multiplet	
Chloroform	- 33.9	- 0.079
Benzene (undegassed)	0	0
Toluene		
Ring H	3.1	+ 0.010
1,4-Dioxane	125.4	+ 0.039
Dimethyl Sulfoxide	161.4	+ 0.040
Toluene		
Methyl H	199.4	< 0.01
Acetone	202.3	+ 0.042
Cyclohexane	212.2	+ 0.029
Tetramethyl Silane	277.1	+ 0.055

The $\Delta\nu$ separations given in the Table represent a reconciliation of the measurements made here, at Magnolia and at Humble and are accurate to ± 0.5 cps. The temperature coefficients were determined only at this laboratory. I would appreciate receiving any data either in agreement or in disagreement with the above numbers so that a revised table with more accurate numbers can eventually be established and made available to all NMR spectroscopists.

Please feel free to quote from this letter for your monthly publication. With best wishes for success with M.E.L.L.O.N.

Sincerely yours,

Charlie

C. A. Reilly

UNIVERSITY CHEMICAL LABORATORY
LENSFIELD ROAD
CAMBRIDGE
TELEPHONE: 56491

NS/VMW.

31st October, 1958.

Drs. A.A. Bothner-By and B.L. Shapiro,
The Editors,
N-M-R News Sheet,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pa.,
U.S.A.

Gentlemen,

May I say how pleased I was to receive the first number of your N-M-R monthly letter which will, I am sure, fill a much needed gap in communications. I am inspired to write to you at once as if I don't do it now I won't do it tomorrow!

My feeling is that one of the most important functions that your 'letter' can fulfil is to provide a forum of opinion on the vexed problem of how to standardise NMR spectra. This should have been done years ago as we all know. May I as a beginner in this field - but at least a person who has many organic and inorganic chemist's NMR spectra to look at - presume to make some comments on your suggested systems?

Suggestion (A) This is a brilliant one as no-one can complain that it doesn't incorporate their own recommendations! Here in Cambridge we prefer the internal standard when possible, but it is very true that a satisfactorily well-behaved internal standard is not always available.

cont'd -

Suggestion (B) Our choice of reference has been cyclohexane which shares with $(CH_3)_4Si$ many desirable properties as an internal reference - in particular it is likely to have little specific interaction with its molecular neighbours in solution. However I feel quite happy to change over once I have located a cheap and reliable source of the silicon compound. Of course what we really need is a short list of acceptable 'well-behaved' internal reference compounds so that if one of them has its peak on top of that of the substance whose NMR spectrum is being determined another can be used.

Suggestion (C) This is the only point where I would seriously put in a plea for an alternative, i.e., the definition of 'zero'. Our own procedure to date has been to refer all our values to cyclohexane defined as =+3.9 in p.p.m. By this means we go back to Gutowsky's classical paper on chemical shifts where (in slightly different units!) he measured this value of cyclohexane as an external reference again water and took the latter as 'zero'. Because of temperature dependence the water reference is a less satisfactory real zero and anyway it is not easy to measure C_6H_{12} as an internal reference in H_2O! Hence our value is really an arbitrarily defined one as is your value of +10.0 for $(CH_3)_4Si$. However, in so far as any system has been adopted in the literature, one based roughly on Gutowsky's scale has been used (with differences here and there only of sign and powers of ten!). As one who has to teach N-M-R correlation rules the 'water zero' has the overwhelming advantage of being essentially the unit chosen in Wertz's extremely useful review article.

Suggestion (D) I agree in preferring your choice of p.p.m. and the sign to other alternatives. The alternative of parts in 10^5 (although quite acceptable for fluorine work) involves - to my mind - too much unnecessary writing of 0 point, i.e., 0.39 etc., for hydrogen work. If large numbers of spectroscopists are in favour of parts in 10^7 rather than 10^6 I would be happy to change, but I prefer the reasonably time-honoured p.p.m. The sign convention I like because of the correlation with shielding.

I had intended to write a few words and have ended up by writing many! I hope that everyone doesn't write to you this month on the same theme or No 1 of your news letter might be the last one for financial reasons! I certainly hope not!

Yours sincerely,

Norman Sheppard

N. Sheppard.

VARIAN NUCLEAR RESONANCE WORKSHOP (1958) IDEA EXCHANGE

We suggest that participants bring lists of titles of current NSR work from their labs. (especially those not yet in the literature!) Short abstracts of each should be included, as illustrated below.

PROTON NSR SPECTROSCOPY I.
RELIABLE SHIELDING VALUES BY "INTERNAL REFERENCING" WITH TETRAMETHYLSILANE. George V.D. Tiers, J. Phys. Chem., 62, 1151 (1958). (Reprints available soon).

This technique is shown to be reproducible, precise, convenient, and applicable to all organic media. Results are fully equivalent to those obtained by external referencing when the latter are extrapolated to infinite dilution. A new and particularly convenient method of reporting spectral position (the τ -scale) is defined.

PROTON NSR SPECTROSCOPY II.
A DEUTERIUM ISOTOPE EFFECT. G. V.D. Tiers, J. Chem. Phys. (1958) (accepted) (Some preprints).

The methyl peak for $C_6H_5CH_2D$ is split (by D) into an equal-intensity triplet ($J = 2.38 \pm 0.02$ cps), and is displaced 0.015 $\pm$ 0.002 ppm. to higher field than that of $C_6H_5CH_3$.

PROTON NSR SPECTROSCOPY III.
ANNIHILATION OF NITROGEN QUADRUPOLE BROADENING BY MEANS OF STRONG MOLECULAR ELECTRIC FIELD GRADIENTS.
G. V.D. Tiers and F. A. Bovey, J. Phys. Chem. (1959) (accepted) (Some preprints).

Sharp NH peaks (having the expected multiplet structure due to their proton neighbors, a fact which rules out chemical-exchange narrowing) are observed for peptides and related molecules in CF_3CO_2H solvent. Examples include N-acetyl-valine, glycyl-methionine and glycocyamine.

PROTON NSR SPECTROSCOPY IV.
CHARACTERISTIC SHIELDING VALUES, τ , FOR ORGANIC STRUCTURES: CORRELATION WITH CHEMICAL PARAMETERS. G. V.D. Tiers, J.A.C.S.,(?) (1959) (No preprints)

A table of more than 1000 τ-values for "all" types of organic compounds is presented. Various examples are given of correlations of peak displacements by means of physical-organic parameters. The highly precise measurement technique makes possible the quantitative study of small displacements, e.g., the methyl peak in o, m, and p - substituted toluenes, and in other aromatic systems, and similar studies on benzaldehydes, anisoles, and dimethylanilines.

PROTON NSR SPECTROSCOPY V.
STUDIES OF AMINO ACIDS AND PEPTIDES IN TRIFLUOROACETIC ACID.
F. A. Bovey and G. V.D. Tiers, J. Am. Chem. Soc., (1959)
(A few preprints)

Tables of τ-values are presented; multiplet structure and J-values or else line widths are also reported. All the common and several less common amino acids are included, as are many of their glycyl peptides and N-acetyl derivatives; tetramethylsilane is used as the internal reference. Conclusions are drawn concerning charge distribution, inductive effects of polar groups and of positive charges, rates of proton exchange with the CF_3CO_2H solvent, base strength, and (in one case) molecular conformation.

PROTON NSR SPECTROSCOPY VI.
STUDIES OF PROTEINS IN TRIFLUOROACETIC ACID. F. A. Bovey, S. S. Yanari and G. V.D. Tiers, J. Am. Chem. Soc. (1959)
(Some preprints)

CF_3CO_2H dissolves nearly all proteins in a manner permitting their NSR spectra to be observed. The data from Part V is used to interpret features of these spectra. Optical rotation studies indicate that proteins are "uncoiled" in CF_3CO_2H solution.

PROTON NSR SPECTROSCOPY VII.
SHIELDING VALUES FOR FERROCENES AND RELATED COMPOUNDS,
G. V.D. Tiers and Peter L. Pauson, J.A.C.S. (1959)
(Preprints soon)

A compilation of characteristic τ-values is presented. The effect of substituents upon τ-values for the cyclopentadienyl ring is shown to be very similar to that for benzene. In ferrocenes, the transmission of effects from one ring to the other is slight. Monocyclopenta-dienyliron compounds are readily distinguished from ferrocenes. NSR is shown to be a very powerful tool for structure determination in these (and related) classes of organoiron compounds.

PROTON NSR SPECTROSCOPY VIII.
STEREOMAGNETIC STUDIES OF THE CONFORMATION OF POLYSTYRENE CHAINS IN SOLUTION. F. A. Bovey and G. V.D. Tiers (1959) (Preprints soon)

When uninterrupted sequences of styrene units are shorter than about 12 to 15 members, (accomplished either by very low molecular weight or by copolymerization with butadiene), the aromatic resonance appears as a single peak, at τ-value similar to that of isopropyl benzene. For longer sequences, however, the peak for <u>ortho</u>-protons is shifted <u>ca</u>.0.7 ppm to higher τ, though <u>meta</u> and <u>para</u> peaks are shifted less than 0.2 ppm.

Similarly, the α-H in these long sequences is shifted 1.2 ppm. to higher τ (but the β-H only 0.1 ppm). A "stereomagnetic" interpretation of these effects requires the phenyl groups of long sequences to be clustered (or forced) together, with the α and ortho-protons very close (on the average) to the faces of nearby rings.

THE CALCULATION OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF AROMATIC HYDROCARBONS. C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys. (1958) (Reprints and tables of computations available)

Correction, improvement and extension of calculations of Waugh & Fessenden, J.A.C.S. 79 846 (1957) making use of the IBM-705 computer. Graphical plot of π -electron ring-current magnatic contribution at all points in the vicinity of a benzenoid ring.

FLUORINE NSR SPECTROSCOPY I.
RELIABLE SHIELDING VALUES BY USE OF TRICHLOROFLUOROMETHANE AS SOLVENT AND INTERNAL REFERENCE.
G. N. Filipovich and G. V.D. Tiers, J. Phys. Chem., (1959) (Preprints)

As shown by Evans, by Glick and Ehrenson, and by ourselves, fluorine spectral positions are subject to solvent effects (proportional to the polarizability of the medium), which may be eliminated by extrapolation to zero polarizability. We report an alternative and more practical procedure for tabulating reliable fluorine shielding values. Our technique consists of extrapolation of the solute peak position to infinite dilution in the excellent, (miscible with C_8F_{18}!) solvent CCl_3F. The strong, sharp peak of this solvent is used as an internal reference, its "side-bands" being used as in "Proton NSR Spectroscopy I". If dilute (5% to 10%) solutions are used, the extrapolation (ca. 0.01 to 0.02 ppm.) is usually unnecessary. A new and convenient method of reporting spectral position (the Ø -scale) is defined, based on Ø (CCl_3F) = 0.000 ppm, positive Ø-values indicating greater shielding.

OTHER NSR TABULATIONS AVAILABLE ON REQUEST:

1. The 3M Handy Pocket Guide to Characteristic Nuclear Resonance Shielding Values, τ, For Hydrogen Bonded to Carbon.

2. The 3M Handy Pocket Guide to Characteristic Nuclear Resonance Shielding Values, Ø, for Fluorine. (Available soon).

3. Table of Proton NSR τ-values for a Variety of Organic Compounds (Approx. 700 -values).

GVDT:bv

10-10-58

EXTERNAL REFERENCING

Precision Coaxial Cells vs Non-Precision (Capillary) Cells

A number of careful experiments have been made to help answer the question "Is it really necessary to use precision-type coaxial cells (e.g., Wilmad cells)?" Two samples were used for this check; one sample had two resonance lines, #1 and #2, approximately 196.4 sec^{-1} apart; the second sample had only one resonance line and was approximately 3 sec^{-1} apart from line #2 of the first sample. The objectives were to measure the line separation between #1 and #2 of the first sample and the line separation between line #1 of the first sample and the single line of the second sample. A total of 6 Wilmad precision coaxial cells and 9 capillary cell systems were used to obtain independent measurements. The results are shown on the next page in the graph entitled "Comparison of External Referencing Systems".

Each data point in this evaluation was obtained from an average of ten measurements. A criterion of instrument performance was that the average deviation of measurements for a particular data point for the separation of line #1 and line #2 always be$\leq$0.1 sec^{-1} for either the Wilmad system or for the capillary system. The results are rather obvious:

(a) The separations between lines #1 and #2 of the first sample are very closely the same for either system, as they should be.

(b) The resonance line in the film of the Wilmad precision cell varies over a total range of less than 0.1 sec^{-1} for the 6 systems tried, whereas the resonance line in the capillary of the non-precision cell system varies over a much greater range of values.

(c) The values in the capillary system tend to be higher than those in the film of the precision cell system.

Actually, the mechanical set-up used favored the capillary system, for the capillary system employed an outer precision tube and the capillary itself was precision stock. Hence the results obtained for the capillary system should be considered better than those obtainable if non-precision tubing and capillary stock had been employed.

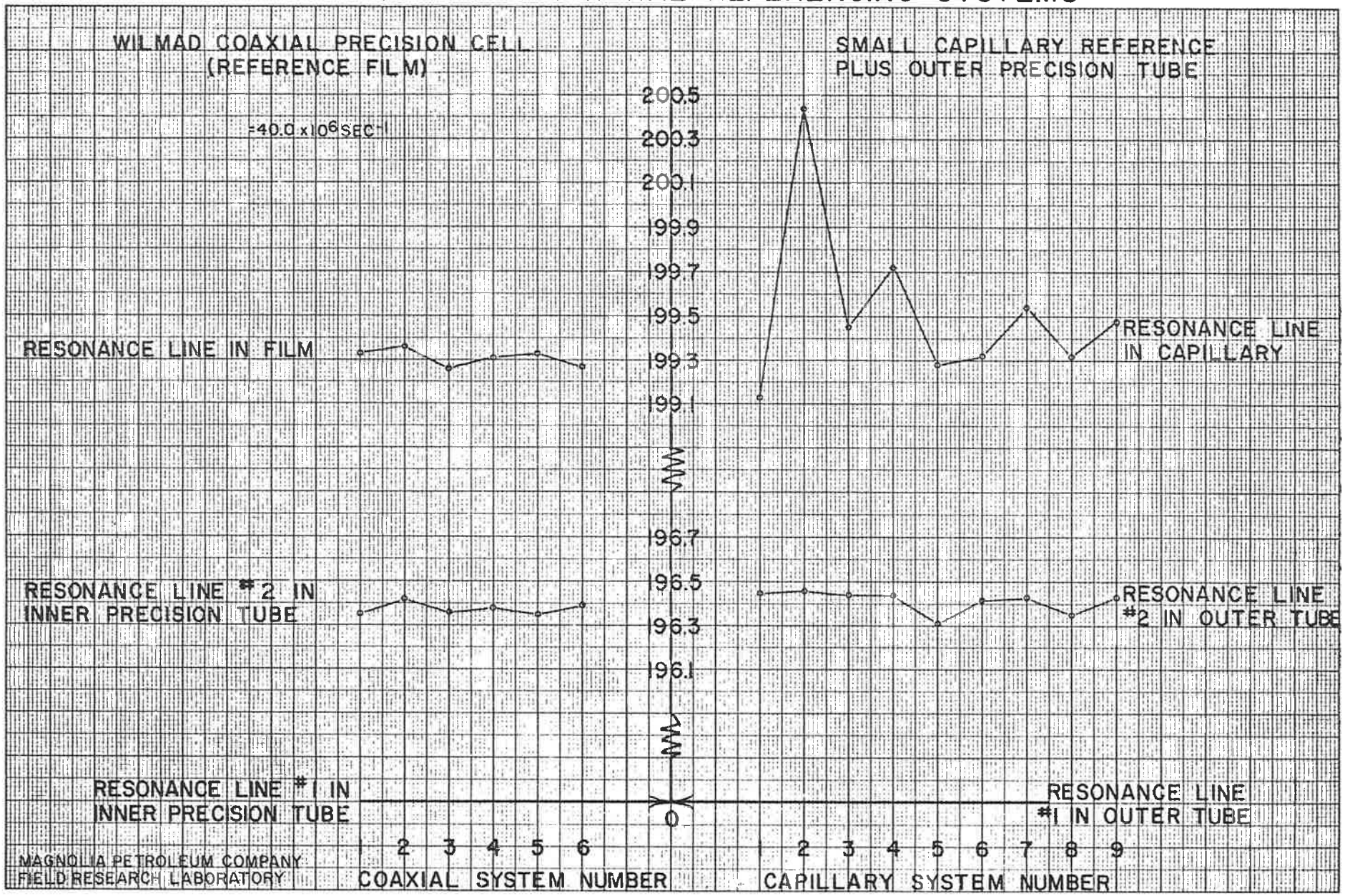
Our conclusions on external referencing are these:

(a) Although it is possible to reference externally by means of a capillary system and get <u>some</u> good values, the capillary system is definitely not a dependable system.

(b) The experimental result that the capillary technique is not reliable for accurate chemical shift measurements is in agreement with an earlier theoretical analysis of this general problem ("Standardization of NMR High Resolution Spectra" by J. R. Zimmerman and M. R. Foster, J. Phys. Chem. <u>61</u>, 282(1957)).

Magnolia Petroleum Company
Field Research Laboratory
P. O. Box 900
Dallas 21, Texas

COMPARISON OF EXTERNAL REFERENCING SYSTEMS



The $X_3AA'X_3'$ Case

Assumptions: $J_{XX} = 0$, $J_{AX} = J_{A'X'} \neq J_{AX'} = J_{A'X}$, $\omega_X = 0$

Crude function chosen were of type	E
(1) $S_{3/2}$ $\alpha\alpha$ $S_{3/2}$	$\omega_A + J_{AA}/4 + 6\ J_{AX}/4 + 6\ J_{AX'}/4$
(2) $S_{3/2}$ $\alpha\alpha$ $S_{1/2}$	$\omega_A + J_{AA}/4 + 4\ J_{AX}/4 + 4\ J_{AX'}/4$
(3) $S_{3/2}$ $\alpha\alpha$ $A_{1/2}$	$\omega_A + J_{AA}/4 + 4\ J_{AX}/4 + 4\ J_{AX'}/4$
(4) $S_{3/2}$ $\alpha\alpha$ $A'_{1/2}$	$\omega_A + J_{AA}/4 + 4\ J_{AX}/4 + 4\ J_{AX'}/4$
(40) $S_{3/2}$ $\alpha\beta$ $A_{-1/2}$	$-J_{AA}/4 + 4\ J_{AX}/4 - 4\ J_{AX'}/4$
(41) $S_{3/2}$ $\beta\alpha$ $A_{-1/2}$	$-J_{AA}/4 - 4\ J_{AX}/4 + 4\ J_{AX'}/4$

etc., etc., where $S_{3/2} = \alpha\alpha\alpha$ $\quad S_{1/2} = \frac{1}{\sqrt{2}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$

$$A_{1/2} = \frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$

$$A'_{1/2} = \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha)$$

The only off-diagonal elements are those connecting states like (40) and (41), and they are all equal to $J_{AA}/2$. In the general case of $\psi_1 = \varphi_1\ \alpha\beta\varphi_n$ and $\psi_2 = \varphi_1\ \beta\alpha\varphi_n$, diagonalization gives two states $\mathfrak{w} = a_1\psi_1 + a_2\psi_2$ and $\mathfrak{x} = -a_2\psi_1 + a_1\psi_2$, where $a_1 = \left\{(R_i + i\delta)/R_i\right\}^{\frac{1}{2}}$, $a_2 = \left\{(R_i - i\delta)/2\right\}^{\frac{1}{2}}$. In these expressions $i = 1 - n$, $\delta = (J_{AX} - J_{AX'})/2$ and $R_i = \left\{(J_{AA}/2)^2 + i^2\ \delta^2\right\}^{\frac{1}{2}}$. The energies of $\mathfrak{w}$ and $\mathfrak{x}$ are $\left(J_{AA}/4\right) + R_i$ and $\left(J_{AA}/4\right) - R_i$, respectively. Transition energies and intensities are then obtained in the usual way and are tabulated below. In each case one-half of the symmetrical spectrum is given.

For the X-nuclei:

Position	Intensity
$(J_{AX} + J_{AX}')/2$	$192\ \mu_{oo} = 192$
$(J_{AA}/2) - R_1$	$120\ \mu_{o1}$
$(J_{AA}/2) + R_1$	$120\ \varphi_{o1}$
$R_1 - R_2$	$60\ \mu_{12}$
$R_1 + R_2$	$60\ \varphi_{12}$
$R_2 - R_3$	$12\ \mu_{23}$
$R_2 + R_3$	$12\ \varphi_{23}$

For the A-nuclei(relative to ω)

$3(J_{AX} + J_{AX}')/2$	$4\ \mu_{oo} = 4$
$(J_{AX} + J_{AX}')/2$	$36\ \mu_{oo} = 36$
$J_{AX} + J_{AX}' + (J_{AA}/2) - R_1$	$12\ \mu_{o1}$
$J_{AX} + J_{AX}' + (J_{AA}/2) + R_1$	$12\ \varphi_{o1}$
$J_{AX} + J_{AX}' - (J_{AA}/2) + R_1$	$12\ \mu_{o1}$
$J_{AX} + J_{AX}' - (J_{AA}/2) - R_1$	$12\ \varphi_{o1}$
$\left\{(J_{AX} + J_{AX}' + J_{AA})/2\right\} - R_2$	$12\ \mu_{o2}$
$\left\{(J_{AX} + J_{AX}' + J_{AA})/2\right\} + R_2$	$12\ \varphi_{o2}$
$\left\{(J_{AX} + J_{AX}' - J_{AA})/2\right\} + R_2$	$12\ \mu_{o2}$
$\left\{(J_{AX} + J_{AX}' - J_{AA})/2\right\} - R_2$	$12\ \varphi_{o2}$
$(J_{AA}/2) - R_3$	$4\ \mu_{o3}$
$(J_{AA}/2) + R_3$	$4\ \varphi_{o3}$
$(J_{AA}/2) - R_1$	$36\ \mu_{o1}$
$(J_{AA}/2) + R_1$	$36\ \varphi_{o1}$

where

$$\mu_{ij} = \frac{1}{2R_iR_j}\left\{R_iR_j + ij\delta^2 + (J_{AA}^2/4)\right\} \quad \text{and} \quad \varphi_{ij} = \frac{1}{2R_iR_j}\left\{R_iR_j - ij\delta^2 - (J_{AA}^2/4)\right\}$$

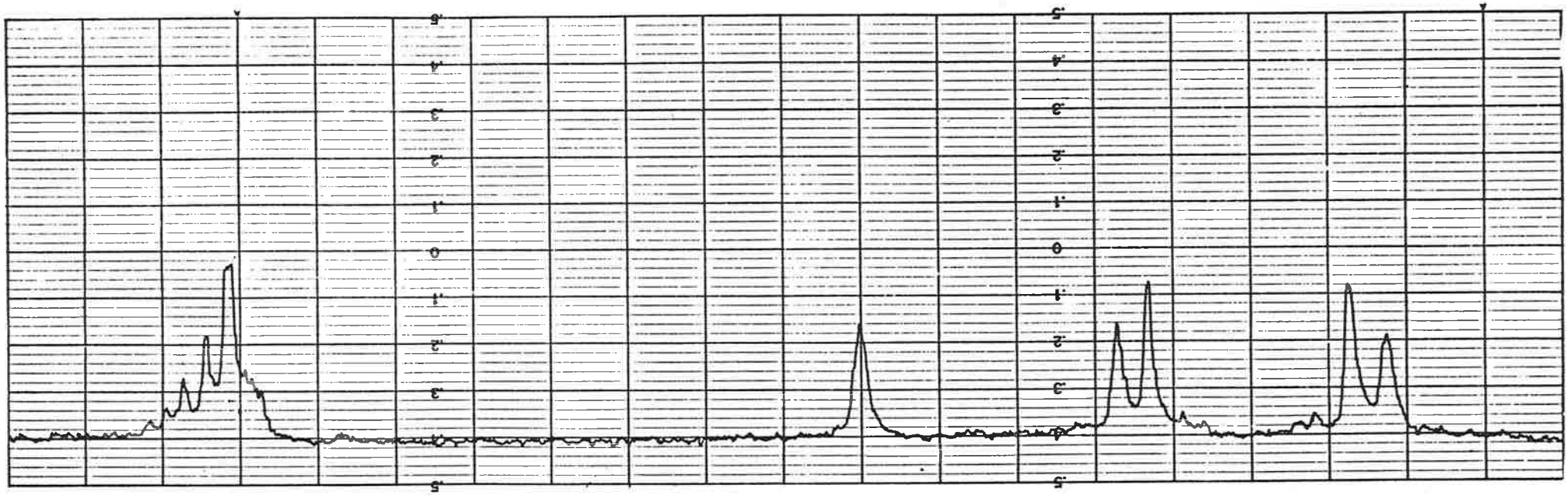
$X_2AA'X_2'$ case: Utilizing the same treatment, we get

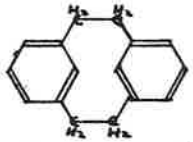
X Transitions:

$(J_{AX} + J_{AX'})/2$	30
$(J_{AA}/2) - R_1$	24 μ_{01}
$(J_{AA}/2) + R_1$	24 φ_{01}
$R_1 - R_2$	8 μ_{12}
$R_1 + R_2$	8 φ_{12}

A transitions (relative to ω):

$J_{AX} + J_{AX'}$	4
$\left\{(J_{AX} + J_{AX'} + J_{AA})/2\right\} - R_1$	8 μ_{01}
$\left\{(J_{AX} + J_{AX'} + J_{AA})/2\right\} + R_1$	8 φ_{01}
$(J_{AA}/2) - R_2$	4 μ_{02}
$(J_{AA}/2) + R_2$	4 φ_{02}
$\left\{J_{AX} + J_{AX'} - (J_{AA}/2)\right\} + R_1$	8 μ_{01}
$\left\{(J_{AX} + J_{AX'} - J_{AA})/2\right\} - R_1$	8 φ_{01}
0	8



Compound: 

Source: Prof. N. L. Allinger

Solution: 10% in CCl_4, degassed

References: Internal: $SiMe_4$ (1%)

External: $CHCl_3$ capillary; resonance found at 7.42 ppm from $SiMe_4$

R.F. 60 mc.

Comments: Outer aromatic hydrogens form AB_2 multiplet with

$$\delta_A = 2.75 , \quad \delta_B = 3.03 \qquad J_{AB} = \left|0.65(\delta_A-\delta_B)\right| = 11 \text{ cps}$$

Inner aromatic hydrogens at quite high field !

$$\delta_C = 5.73$$

Methylene hydrogens give slightly perturbed non-equivalence quartet.

$$\delta_D = 6.88 , \quad \delta_E = 7.90 \qquad J_{DE} = \left|0.15(\delta_D-\delta_E)\right| = 9 \text{ cps}$$

Mellon Institute A. Bothner-By

MAILING LIST FOR M.E.L.L.O.N.M.R. No. 2

Prof. A. L. Allred
Department of Chemistry
Northwestern University
Evanston, Illinois

Dr. Weston Anderson
Varian Associates
Instrument Division
611 Hansen Way
Palo Alto, California

Dr. S. Brownstein
Department of Chemistry
Cornell University
Ithaca, New York

Prof. George Büchi
Department of Chemistry
Massachusetts Institute of Tech.
Cambridge 39, Massachusetts

Mr. N. F. Chamberlain
Research and Development Div.
Humble Oil and Refining Company
Baytown, Texas

Dr. V. M. Clark
University Chemical Laboratory
Lensfield Road
Cambridge, England

Prof. H. Conroy
Department of Chemistry
Yale University
New Haven, Connecticut

Prof. E. J. Corey
Department of Chemistry
University of Illinois
Urbana, Illinois

Dr. L. Crombie
Department of Chemistry
University of London
King's College
London, W.C. 2
England

Mr. T. J. Curphey
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge 38, Massachusetts

Dr. J. B. Dickey
Director of Research
Tennessee Eastman Company
Kingsport, Tennessee

Prof. R. E. Glick
Department of Chemistry
Whitmore Laboratory
The Pennsylvania State University
University Park, Pennsylvania

Prof. H. S. Gutowsky
Department of Chemistry
University of Illinois
Urbana, Illinois

Dr. L. M. Jackman
Department of Organic Chemistry
Imperial College of Science and Technology
London, S.W. 7, England

Dr. Charles M. Judson
Section Manager
Research Service Department
American Cyanamid Company
1937 W. Main Street
Stamford, Connecticut

Mr. P. C. Lauterbur
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Prof. L. Mandell
Department of Chemistry
Emory University
Emory University, Georgia

Dr. S. Meiboom
Department of Applied Mathematics
The Weizmann Institute of Science
Rehovot, Israel

Dr. C. Naar
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dr. W. D. Phillips
Chemical Department
Experimental Station
E. I. duPont de Nemours and Company
Wilmington, Delaware

Dr. L. Pratt
Department of Inorganic Chemistry
Imperial College of Science and Technology
London, S.W. 7, England

Herrn. H. Primas
Laboratorium für Organische Chemie
Eidgenössische Technische Hochschule
Universitätsstrasse, 6
Zürich 6, Switzerland

Dr. W. E. Putnam
Houston Research Laboratory
Shell Oil Company
P. O. Box 2527
Houston 1, Texas

Dr. C. A. Reilly
Shell Development Company
Emeryville, California

Prof. R. E. Richards
Lincoln College
Oxford, England

Prof. J. D. Roberts
Department of Chemistry
California Institute of Technology
Pasadena, California

Dr. M. Saunders
Department of Chemistry
Yale University
New Haven, Connecticut

Dr. W. G. Schneider
Division of Pure Chemistry
National Research Council
Ottawa, Ontario, Canada

Dr. N. Sheppard
University Chemical Laboratory
Lensfield Road
Cambridge, England

Dr. J. N. Shoolery
Varian Associates
611 Hansen Way
Palo Alto, California

Dr. F. Sondheimer
Daniel Sieff Research Institute
The Weizmann Institute of Science
Rehovot, Israel

Prof. G. H. Stout
Department of Chemistry
University of Washington
Seattle 5, Washington

Dr. G. V. D. Tiers
Central Research Department
Minnesota Mining and Manufacturing Co.
St. Paul 6, Minnesota

Prof. J. S. Waugh
Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Prof. K. B. Wiberg
Department of Chemistry
University of Washington
Seattle 5, Washington

Prof. R. H. Wiley
Department of Chemistry
University of Louisville
Louisville 8, Kentucky

Prof. R. B. Woodward
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge 38, Massachusetts

Dr. J. R. Zimmerman
Magnolia Petroleum Company
Field Research Laboratories
Dallas, Texas