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Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
N - M - R  
No. 19

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McMASTER UNIVERSITY  
HAMILTON COLLEGE  
HAMILTON, ONTARIO

April 13, 1960

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

Dear Dr. Bothner-By:

We thought that the following experimental points might be of interest to readers of "M.E.L.L.O.N.M.R."

We have recently had occasion to prepare 5mm O.D. sample tubes of very hygroscopic liquids that must be handled in a dry box. We have found small Teflon caps to be very useful for sealing the tubes. They were made by drilling a 5mm diameter hole in a 15mm length of 7mm diameter Teflon rod. With a little care these caps can be made to fit quite tightly. They are adequate to close the tube for immediate examination of the sample, or temporarily until it can be sealed with a flame.

A further useful device is obtained by drilling a smaller diameter hole through the top of such a cap. A second concentric tube may be inserted through this hole. A 0.5mm hole may be used for a reference capillary. A 2mm hole may be used to hold a sealed sample tube, the outer annular space then being used for the reference liquid.

We have been studying certain mixtures in which some volatile products are formed and it was desirable to retain as much as possible of these products in solution in order to identify them by their n.m.r. spectra. This can be conveniently done by placing the two components (two liquids or one liquid and one solid) in the two arms of the apparatus sketched. The tubes can be temporarily sealed for weighing with the Teflon caps. They may then be sealed with a flame and the components mixed by tipping the liquid from one side to the other. Finally the sample is run into the long arm, cooled in liquid air and sealed off as indicated.

The need to use a minimum volume of sample is always recurring (see M.E.L.L.O.N.M.R. No. 12). We have adopted a solution to the problem which seems simpler than the others proposed from time to time. 5mm O.D. sample tubes have been constructed with the bottom 14mm consisting of 5mm rod. Only 2mm depth (or perhaps less) of liquid is then required. The tubes do not require any other special fitment at all and are used in exactly the same manner as ordinary sample tubes. There is probably some loss of resolution due to the proximity of the solid glass to the receiver coil and the very short axis of the liquid cylinder.

..... 2.

Dr. Aksel A. Bothner-By

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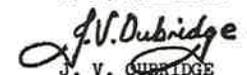
April 13, 1960

We have found it desirable to run the electromagnet continuously to maintain it at constant temperature. However, a necessary precaution is to monitor the coil temperature. An immediate solution to this problem was provided by the presence in the same room of a Leeds Northrup recording potentiometer. The thermocouple already embedded in the electromagnet coil was connected to this, using the 2.5mV full scale deflection range. Two pieces of Paxoline about 2 1/2" x 1" were clamped to the scale of the potentiometer by bolts through each end and carried one contact. The moving pointer was made the second contact. This requires no permanent modification of the instrument and we frequently dismantle it to use the potentiometer for other purposes during the day. When the contacts meet they close the sensing circuit of a standard electronic relay. This relay supplies the 110v to both the magnet power supply and the recording potentiometer itself. Thus overheating switches the electromagnet off. Since it also switches the potentiometer off the magnet would not be switched on again when it had cooled down, thus it is a 'fail safe' mechanism. The thermocouple cold junction was conveniently made by binding it to the cold water supply to the magnet.

Yours sincerely,



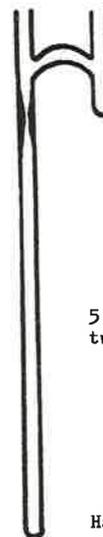
R. J. GILLESPIE



J. V. CURBRIDGE

RJG:gmc

Seal off point,  
width sufficient  
to admit dropper



Curved to  
prevent  
premature  
mixing

5 mm O.D.  
tube throughout

Half actual size



# VARIAN associates

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

April 22, 1960

Dr. Aksel Bothner-by  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Dear Aksel:

The problem of standardization of spectra has been preying on our minds of late and we have felt compelled to bring this unpleasant subject up once again in an effort to introduce some order where chaos still appears to be developing. The efforts of the ASTM committee E-13 do not seem destined to bear mature fruit in the near future because agreement must be reached by such a large number of parties concerning details of a system which is not actually in use by an appreciable number of workers, if any. It seems to us that what is needed at the present time is a proposal which would be palatable enough to a large enough number of workers so that they would publish their results in conformity with it, thus establishing sufficient precedent in the literature to justify future adoption on a formal basis by E-13 or a similar group. We would like to suggest a standardization scheme with this hope in mind, realizing however, that it must meet with majority approval if it is to become sufficiently incorporated in the literature to survive\*.

Nearly complete agreement seems to have been reached on only a few points. These are:

- 1) Spectra shall be swept from low to high applied magnetic field.
- 2) Whenever possible, tetramethylsilane shall be used as internal standard<sup>(1)</sup>.
- 3) A field-independent scale in ppm (parts per million) is desirable, at least for proton work.

Considerable adavance seems to exist on some other conventions, the general adoption of which, however, we feel would lead to serious difficulties. These possible trouble spots include the following:

- a) The desire to have chemical shifts in ppm all be positive and to increase from low to high applied field. This has lead to adoption in some quarters of the  $\tau$  scale ( $\text{Si Me}_4 = 10.00$ ).

\*In other words, this "mutation" must be evolutionarily favorable if it is to withstand the forces of natural selection.



Dr. Aksel Bothner-by  
Mellon Institute

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- b) The desire to have a frequency scale which also increases from low applied field to high (left to right).
- c) The desire to include all possible peak positions in a "standard" spectrogram. This lead to the API recommendation that a 12.5 ppm sweep range be employed, although there are still resonances which fall outside the recommended range at either end.

We feel that our proposed scheme should embrace the points upon which there is already wide spread agreement. Hence we accept and recommend items 1, 2, and 3, thereby fixing the reference at the right hand, high-field end of the spectrum<sup>(2)</sup>. Uncritical acceptance of conventions a and b, however, then leads to some serious difficulties in the everyday use of the spectra, at least in our experience. The problem is basically this: The directly measured "working units" of peak position are frequency units, namely cps (or c/s), and this is likely to continue to be the case as long as accuracy of 1 cps or better in peak position is desired, for it is difficult to achieve and maintain this accuracy without recourse to the "audio sideband" methods. With such methods, the data obtained inevitably are referred to the reference substance at zero. Even if this choice were not dictated by the method of measurement, it would appear to be the least arbitrary one. By defining the reference position as zero cps, however, we are in conflict with convention b unless we attach a negative sign to all peaks which occur at lower applied field than  $\text{Si Me}_4$ . This would not appear to be a desirable procedure since the vast majority of resonances fall on the low field side of  $\text{Si Me}_4$ . If the negative sign is accidentally omitted the results are then in error, but if we attach a positive sign to low field peaks we can avoid the use of either a positive or negative sign in practically all data.

In consequence of the direct measurement of so many of his spectra in cps, the NMR spectrographer tends to think in these units. Unfortunately, however, since there are instruments operating at various field strengths, we need a "universal language" for reporting the data in field-independent units. One of the prime requisites of this "language," it seems to us, is that it be readily translatable into the "native tongues" of the various users. Consequently, we propose a direct correspondence between the frequency and ppm scales, thus allowing the observed frequency to be converted mentally be simple division to ppm and the reverse by simple multiplication. Of course, we must pay for this convenience by abandoning convention a), which however, arbitrarily defines the reference position as other than zero, and we are will rid of this weakness.

We have to have a name for the field-independent unit and we can think of no better one (nor do we wish to confuse the issue by frequent and continuous invention of new symbols) than our old friend  $\mathcal{J}$ , fixed up with a new definition<sup>(3)</sup>:

$$\mathcal{J} = 10^6 \left( \nu - \nu_{\text{Si Me}_4} \right) / \nu_{\text{Si Me}_4}$$



Dr. Aksel Bothner-by  
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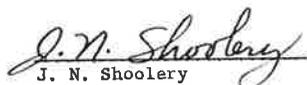
April 22, 1960

in which the numerator simply turns out to be the oscillator reading and the denominator is the operating frequency of the instrument. More information can be conveyed with a compound  $\delta$  symbol such as  $\delta^{\text{int.}}$  ( $\text{C}_6\text{H}_6$ ) which gives the method of referencing, the peak referenced, and the reference substance, but there are other ways of accomplishing this and at present the most urgent need for agreement and usage is just in the basic symbol and definition.

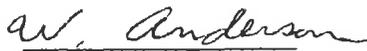
One objection which might be anticipated is that the scale of  $\delta$  proposed here decreases with increased shielding. This is most easily reconciled by observing that increased shielding corresponds to decreased unshielding. If we must have  $\delta$  parallel to some molecular parameter, let it be unshielding<sup>(4)</sup>, corresponding to the various molecular sources of paramagnetic contributions to the chemical shift.

The main point at which we feel that our proposal will encounter resistance is the esthetic one of having the scales start at zero at the right hand end and increase toward the left. But all proposals are destined to run into one difficulty or another, and we think that this is the smallest price to pay for having a consistent pair of scales with a logical origin which will be of value both in daily work and for reporting in the literature. We intend to publish our own work in accord with this scheme until such time as another one appears which seems more logical to us or until it is evident that another apparently less logical scheme has nevertheless achieved sufficiently wide acceptance to merit our support.

Sincerely yours,

  
J. N. Shoolery

  
L. F. Johnson

  
W. A. Anderson



Dr. Aksel Bothner-by  
Mellon Institute

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April 22, 1960

- 1) It is fairly simple to "dope" all organic solvents with 1/4 to 1/2 percent of  $\text{Si Me}_4$  for this purpose.
- 2) A few classes of compounds such as metal hydrides and porphyrins will then have to be considered separately. We think that a total sweep of 8.33 ppm on the low field side of  $\text{Si Me}_4$  (500 cps at 60 mc) is sufficient to handle a very large majority of compounds without needlessly cramming their spectra into a small portion of the spectrum. Peaks falling outside this region can be handled in a special section on the standard spectrogram card, as are expanded scale sections of the spectra. We concur with the existing recommendations of sweep rate (1 cps/sec) and scale factor (1 cps/mm).
- 3) In any published NMR work, it seems desirable to us to define  $\delta$  specifically.
- 4) If the term "unshielding" is unpalatable, it should be possible to agree on another term, for example, "augmentation", or some similar word that implies an increased field at the nucleus due to its surroundings.

JNS:ras

# MELLON INSTITUTE

4400 FIFTH AVENUE

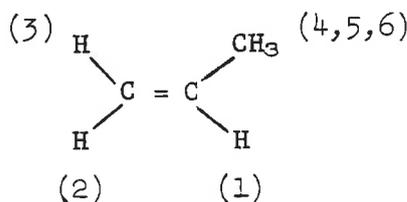
PITTSBURGH 13, PA.

April 29, 1960

In Figure 1 is shown the spectrum of the olefinic hydrogens in propylene measured with the 60 mc. Varian instrument on a sample consisting of approximately 50-50 propylene-tetramethylsilane. Immediately below is the calculated spectrum using the IBM 704 program mentioned previously (see M.E.L.L.O.N.M.R. No.11). The parameters used were as follows:

$$\begin{array}{l}
 W(1) = 255.97 \\
 W(2) = 307.46 \\
 W(3) = 302.20 \\
 W(4) = 500.50 \\
 W(5) = 500.50 \\
 W(6) = 500.50
 \end{array}
 \quad
 W(\text{SiMe}_4) = 600$$

$$\begin{array}{l}
 A(1,2) = +10.02 \\
 A(1,3) = +16.81 \\
 A(1,4) = + 6.40 \\
 A(1,5) = + 6.40 \\
 A(1,6) = + 6.40 \\
 A(2,3) = + 2.08 \\
 A(2,4) = - 1.33 \\
 A(2,5) = - 1.33 \\
 A(2,6) = - 1.33 \\
 A(3,4) = - 1.75 \\
 A(3,5) = - 1.75 \\
 A(3,6) = - 1.75 \\
 A(4,5) = +12.00 \\
 A(4,6) = +12.00 \\
 A(5,6) = +12.00
 \end{array}$$

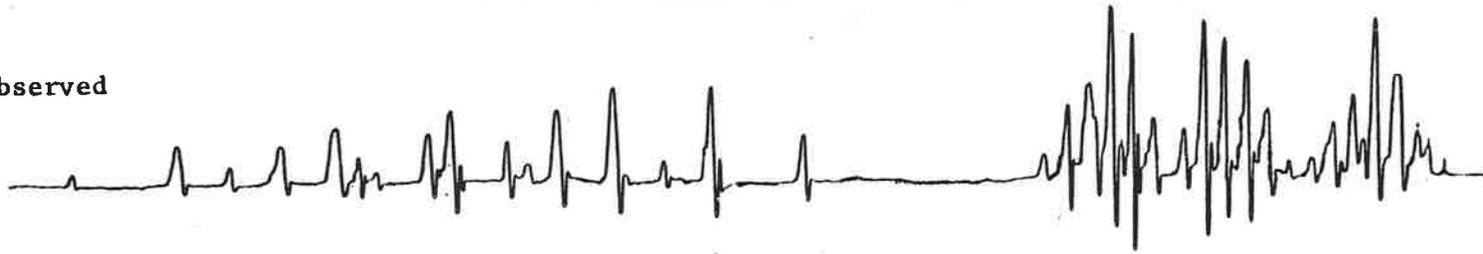


Similar calculations are at present underway for propylene in carbon tetrachloride solution and for butene-1 both neat and in carbon tetrachloride solution.

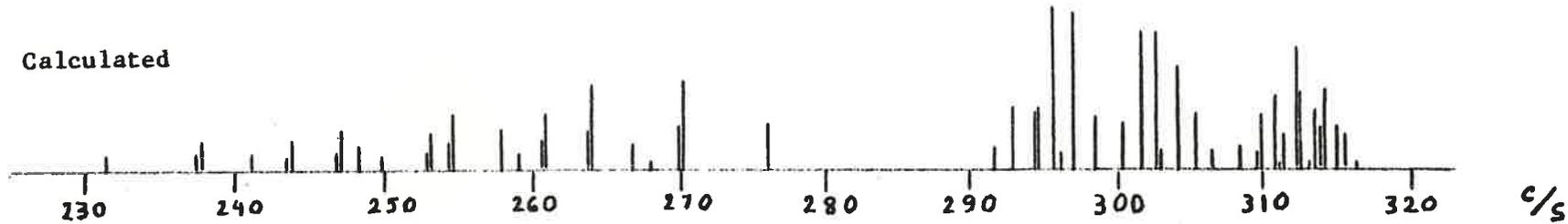
The methyl signals from the propylene (not shown) consist of a doublet of triplets. The doublet spacing is about 6.1 cycles. The triplet spacing is about 1.55 cps. The intensities of the six lines are in the ratio 1:2:1:1:2:1. (C. Naar-Colin and A. A. Bothner-By)

60 Mc. Proton Magnetic Resonance Spectrum of Propylene, Neat

Observed



Calculated



(Tetramethylsilane Internal Reference = 600 c/s)

Figure 1