

Primer

7

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 5

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 5

Starting on page 11 is a bibliography of recent publications on NMR. The listing is a chronological record of papers, abstracts, etc. of NMR interest which have been received in the Mellon Institute Library during the period 28 January 1959 to 27 February 1959, inclusive.

M.E.L.L.O.N.M.R. recipients are invited to send us the names, authors and references of any publications which have appeared but which we have missed, and we will be happy to put these in the next issue.

Contributors to M.E.L.L.O.N.M.R. are reminded that they should leave at least a one inch, left-hand margin on all sheets of their contributions.

Beginning with the next issue of M.E.L.L.O.N.M.R. we will include a section on "Preprints available". If you have a preprint which you are willing to circulate on request, you are invited (nay, urged) to submit title of same, and name and address of person to whom requests for copies should be sent.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

STERLING CHEMISTRY LABORATORY
225 PROSPECT STREET

27 January 1959

Drs. Bothner-By and Shapiro
Mellon Institute
Pittsburgh, Pennsylvania

Dear Aksel and Barry:

I was very pleased to receive your fine newsletter. I am enclosing the solution of a practical problem which arose at Yale in the hope that it might be of use to your readers.

Quite often, I find that n.m.r. lines fall so close together that they cannot be prevented from overlapping even with the best of fields. When this occurs, the observed peak positions no longer correspond to the true positions, since the peaks pull one another together. In order to correct this error, without knowing the answer to begin with, one has to observe something related to the amount of overlap. The simplest quantity of this kind to measure is the ratio of the minimum height between the peaks to the maximum height. Now, if we really are down to the natural line width, each peak should have been Lorentzian and the sum curve can be written out as a function of the distance between the true peaks. At this point, in order to avoid work, I trained the IBM 650 to calculate the positions and heights of the maxima and minima and the correction factors for the case where the peaks are of equal intensity. The enclosed curve gives the results.

As can be seen, the correction can be applied usefully over but a limited range. If the minimum height is half the maximum or less, then the correction is 1% or smaller and probably negligible. If the minimum is 9/10 of the maximum or more, it is probably difficult to measure it well enough to correct accurately, since the curve is becoming steep. In any case, one can very readily see where one stands.

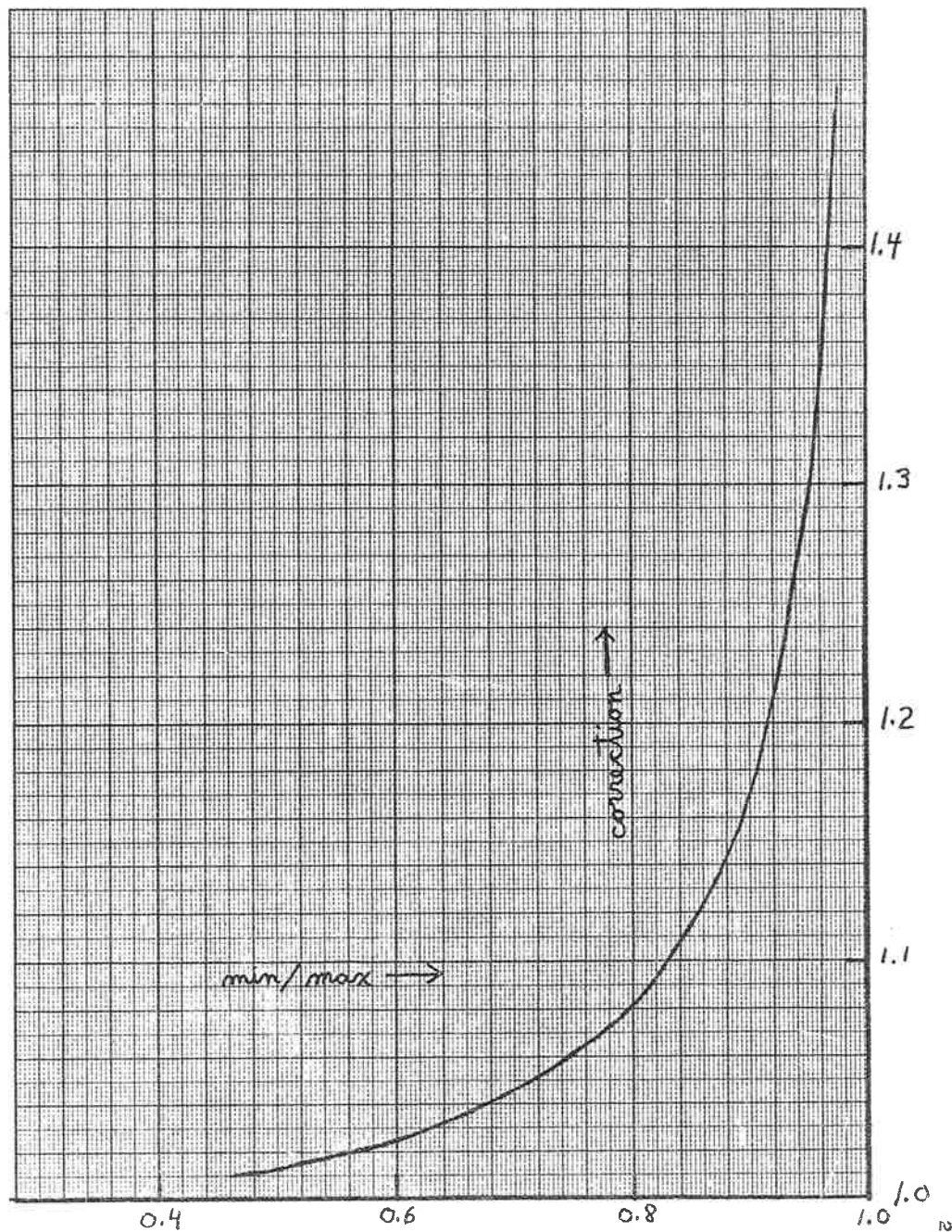
Yours truly,

Martin

Martin Saunders

MS:jsp

Enclosure





MINNESOTA MINING AND MANUFACTURING COMPANY

GENERAL OFFICES • 500 BUSH AVENUE • SAINT PAUL 5, MINNESOTA • TELEPHONE PR. 6-3311

CENTRAL RESEARCH DEPARTMENT

2301 HUDSON ROAD
ST. PAUL 9, MINNESOTA

Dr. A. A. Bothner-By

-2-

February 12, 1959

February 12, 1959

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

Dear Dr. Bothner-By:

As I indicated in earlier correspondence, I am sending you in this letter some preliminary data on the spin-lattice relaxation of organic liquids. This work is being carried out in part for general information, but also more specifically in connection with the use of T_1 measurements for calculating the rates of reorientation of various segments of polymer chains in solution. (F. A. Bovey and G. V. D. Tiers, paper to be presented at Symposium on Stereoregulated Polymers, April, 1959, A.C.S. Meeting.)

The calculation of spin-lattice relaxation arising from intermolecular magnetic dipole interaction is rather awkward; to us, for example, the Bloembergen-Purcell-Pound calculation (Phys. Rev. **73** 679 (1948)) of the intermolecular contribution to the T_1 of water is not entirely convincing, and we feel that a better calculation can be based on a more specific consideration of the actual proton neighbors. Admittedly, in highly associated liquids such as water, one has more reason to expect intermolecular effects, and we are continuing the study of these liquids both experimentally and theoretically. In non-associated organic liquids, we felt that intermolecular relaxation might prove to be negligible because of the $1/r^6$ factor in the interaction of two dipoles. If this were true, it would greatly simplify the treatment of the relaxation of protons in polymers.

The approach of Reilly and Strombotne (J. Chem. Phys. **26** 1338 (1957)), in which the relaxation of solute protons is measured as a function of dilution in CS_2 (which contains no magnetic nuclei), seemed to be sound, and so we applied it to several liquids, including mesitylene, which they reported on. When the molecular reorientation rate $1/\tau_c$ is much greater than the observing r.f. frequency, we have the following for the intramolecular relaxation rate, employing the Stokes-Einstein approximation for τ_c :

$$\frac{1}{T_1} = \frac{3h^2 \gamma^4}{10\pi kT} \cdot \frac{a^3}{b^6} \cdot \eta \quad (1)$$

a being the molecular radius, calculated from the molar volume, b the distance apart of proton neighbors (if there are more than one, there will be complications, which we consider below), γ the proton gyromagnetic ratio, and η the viscosity of the liquid. For a given compound, diluted in a solvent having a different viscosity, we may expect the quantity $1/\eta T_1$, which we call β for convenience, to be a constant if intermolecular relaxation is negligible. If intermolecular relaxation is important, a plot of β vs. vol. per cent of solute will have a positive slope, as Reilly et al. point out. It appears to us to be very important, however, to plot β and not $1/T_1$. We have done this in Fig. 1 for mesitylene ring and methyl protons, tetramethylsilane, cyclohexane, and benzene, and have also included points for pure toluene and benzotrifluoride. All T_1 measurements were made at 25° by the direct method, using a Brush recorder and a Varian V-4300-2 40.00 Mc/sec. spectrometer. Some of the curves show an upward bow in the middle, which suggests that for solutions of some compounds (or groups) in another liquid of differing viscosity, the Stokes-Einstein relationship does not give quite the correct value of τ_c . In all cases, however, the pure liquid and its 10% solution in CS_2 show about same value of β ; for aromatic ring protons, the value is the same at all concentrations. These results appear to us to indicate that for non-associated organic liquids, at least, intermolecular relaxation is unimportant.

We then turned to a further consideration of the relaxation rates in pure organic liquids containing one, two, and three hydrogen atoms on a carbon atom, and also several fluorine-containing compounds. The results are shown in Table 1, the second column of which gives the molar volumes, while the third and fourth give T_1 and β for the various types of H and F. The two columns headed τ_c show the correlation time τ_c^i calculated from the BPP equation:

$$\tau_c^i = \frac{1}{T_1} \frac{40\pi^2}{9h^2} \cdot \frac{b^6}{\gamma^4} \quad (2)$$

and the quantity τ_c^e , calculated from the Stokes-Einstein equation:

$$\tau_c^e = \frac{4\pi \eta a^3}{3kT} \quad (3)$$

The last column gives the ratio τ_c^i/τ_c^e , and provides a test of the BPP equation. Discrepancies are observed in both directions: $\tau_c^i/\tau_c^e < 1$ (i.e. calculated relaxation rates too fast) and $\tau_c^i/\tau_c^e > 1$ (calculated relaxation rates too slow). Most compounds

Dr. A. A. Bothner-By

-3-

February 12, 1959

fall into the first class. For methyl groups, $\tau_c'/\tau_c'' = 0.195 \pm 0.055$; benzene ring protons show a smaller deviation: $\tau_c'/\tau_c'' = 0.58 \pm 0.08$. The discrepancies observed for methyl groups may be due to (a) failure of additivity of relaxation processes to hold where two protons relax a third (see P. S. Hubbard, Phys. Rev. 109 1153 (1958)); in methyl groups, τ_c' is calculated by dividing equation (2) by 2, but this is probably not strictly correct; or (b) to failure of the Stokes-Einstein τ_c'' to represent the true correlation time for methyl groups, which may spin considerably faster than the molecule as a whole. Neither of these explanations, however, can hold for CH_2Cl_2 and CH_2Br_2 . We do not feel that inaccuracies in nuclear moments or internuclear distances could account for these deviations.

Chloroform and CCl_2F are cases of large deviations in the other direction. The calculated proton relaxation expected to arise from the three chlorines is less than 2% of the expected effect of one neighboring proton; the chloroform proton relaxes about 3 times faster than expected. In CCl_2F , the fluorine relaxation is very much faster than expected (see Gutowsky and Woessner, Phys. Rev. 104 843 (1956)). We suggest that the chlorine nucleus, possibly because it is being flipped over through interaction of its quadrupole moment with the electric field of the molecule, is actually more effective in causing relaxation than one would expect from γ^2/b^6 .

These studies are continuing because we feel they may provide new information concerning organic molecules, and because they appear to point to the need for a more satisfactory theory of thermal relaxation. We invite comment from others who have made similar observations or who have any thoughts concerning this work.

Very truly yours,

F. A. Bovey

F. A. Bovey
Research Associate

FAB:js

Enc. 2

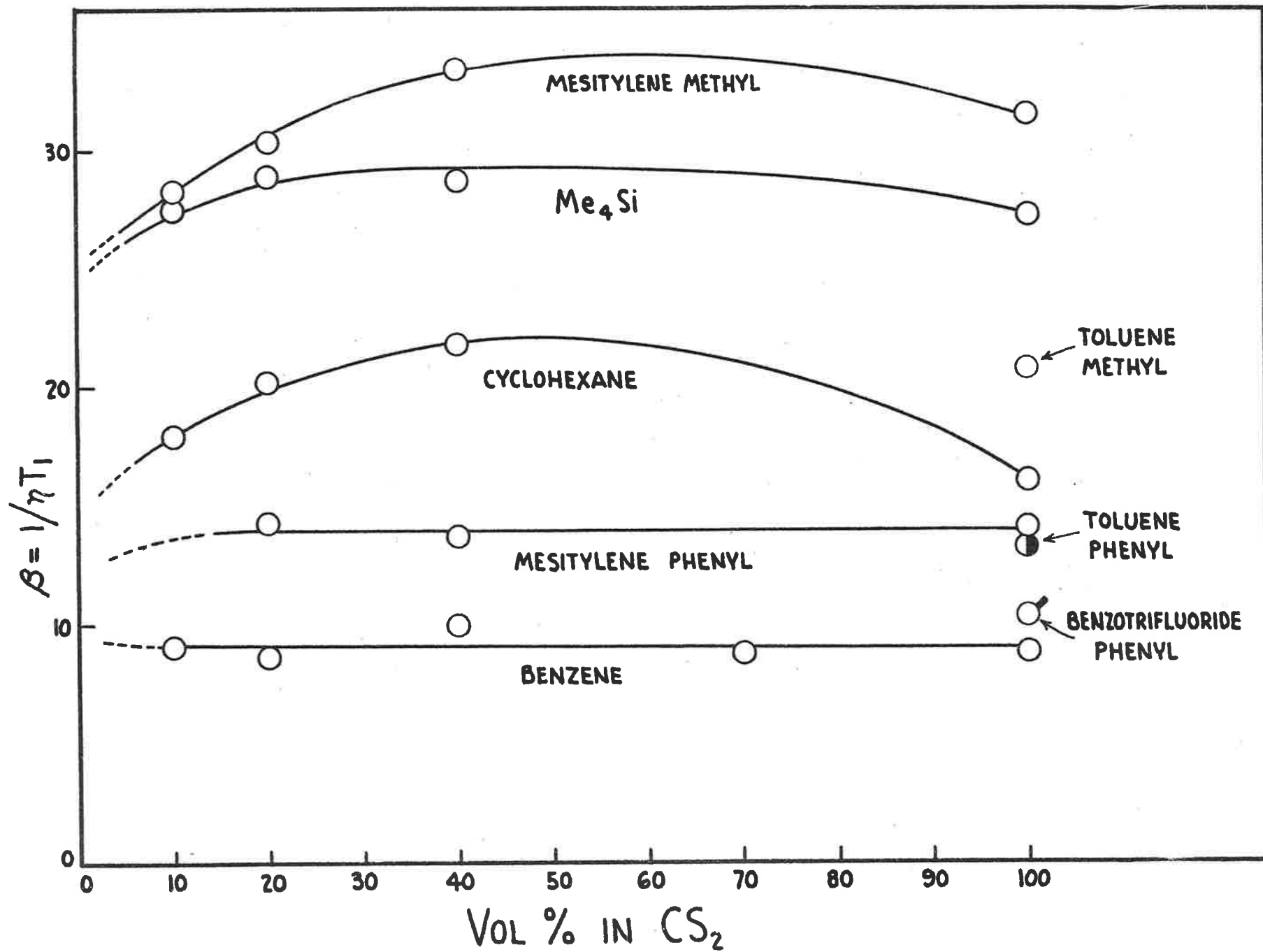
Table 1

Spin-Lattice Relaxation of Protons and Fluorine Nuclei
in Pure Organic Compounds (25°)

Compound	V, c.c.	T_1		τ_c , sec. x 10 ¹¹		τ_c'/τ_c''	
		$\beta=1/\eta T_1$	τ_c' , from T_1	τ_c'' from Stokes-Einstein	τ_c'' from		
benzene	89	18.9	8.9	1.20	2.14	0.56	
toluene	107	ring: 13.6	13.5	1.66	2.33	0.71	
		CH ₃ : 8.9	20.8	0.38		0.16	
α -D-toluene	107	ring: 13.5	13.6	1.67	2.33	0.72	
		CH ₂ D: 11.8	15.6	0.58		0.25	
mesitylene	140	ring: 10.7	14.2	—	3.71	—	
		CH ₃ : 4.8	31.6	0.71		0.19	
phenylacetylene	110	ring: 10.1	11.1	2.3	4.00	0.56	
		acetylenic H: 17.9	6.2	—		—	
benzotrifluoride	103	ring: 18.1	10.1	1.25	2.26	0.55	
		CF ₃ : 2.76	65.2	3.18		1.40	
benzene sulfonyl fluoride	122	ring: 6.40	7.9	3.50	9.66	0.36	
		F: 6.04	8.4	—		—	
acetonitrile	53	13.8	21.4	0.24	0.72	0.33	
nitromethane	54.5	13.0	12.6	0.26	1.34	0.19	
dimethyl disulfide	89.5	11.3	15.2	0.30	2.11	0.14	
CH ₂ CCl ₃	101	8.6	13.5	0.39	3.14	0.12	
acetylene dicarbox. acid di-Me ester	122	1.96	15.5	1.7	16.1	0.11	
(CH ₃) ₄ Si	140	16.7	27.3	0.20	1.10	0.18	
cyclohexane	109	7.1	16.1	—	3.83	—	
methyl formate	62.6	CH ₃ : 13.2	25.2	0.21	0.76	0.28	
		H: 22.0	15.1	—	—	—	
ethanol	59	(CH ₃ CH ₂ -)	2.32	40.4	1.45*	2.38	0.61
CH ₂ Cl ₂	64.6	18.4	12.9	0.30	1.09	0.28	
CHCl ₃	81.6	38.4	4.8	5.8	1.78	3.2	
CH ₂ Br ₂	69.5	11.1	9.2	0.43	2.74	0.16	
CHBr ₃	88.2	14.6	3.6	3.5	6.60	0.53	
CF ₃ CCl ₃	119	7.0	20.4	1.25	3.35	0.37	
CCl ₃ F	93.5	2.94	83.6	184	1.53	120	

*Calculated for CH₃ assuming no interaction with CH₂.

Fig. 1



UNIVERSITY OF WASHINGTON
DEPARTMENT OF CHEMISTRY
SEATTLE 5

6.

KENNETH B. WIBERG

February 18, 1959

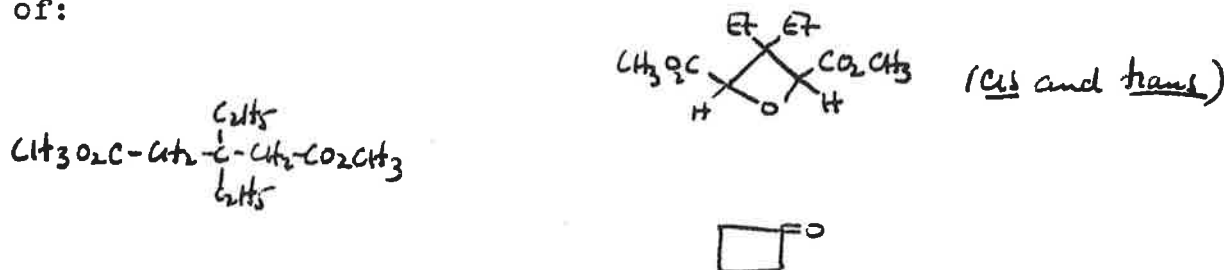
Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Thank you for including my name on the mailing list for M.E.L.L.O.N-M-R. The note attached to issue no. 4 has finally catalysed my slow letter-answering processes, and so I am now writing to request that my name remain on the mailing list. I think it will prove to be a very useful publication (it has been quite useful to me already) and you and Aksel are to be congratulated for starting it.

We have also had difficulty with tetramethylsilane (ours being obtained from Penninsular Chem-Research), and the impurity has been found to be diethyl ether, as you suspected. We find that the tetramethylsilane may be easily purified by passing it through a vapor phase chromatograph. We have been able to run 1 ml samples through a 1/2" column (5' long) packed with silicone, at room temperature, and have obtained a good separation.

I agree that the submission of data should be a condition for receiving your "monthly letters", and thus I am having some of our spectra photocopied and reduced to 8-1/2" x 11" size, and they will be sent to you shortly. The first spectra will be of:



In the near future, I hope to be able to send you spectra of cyclic ketones from C₅-C₁₀ (including the α, α' d₄ where necessary), cyclic olefins from C₃-C₈, and also the spectra of a number of bicyclo[2.2.1]-heptane derivatives. If this represents the kind of spectra you would like to get--fine. If these do not interest you, please let me know.

Finally, I might ask if anyone has tried to correlate J values with structure?

Sincerely yours,

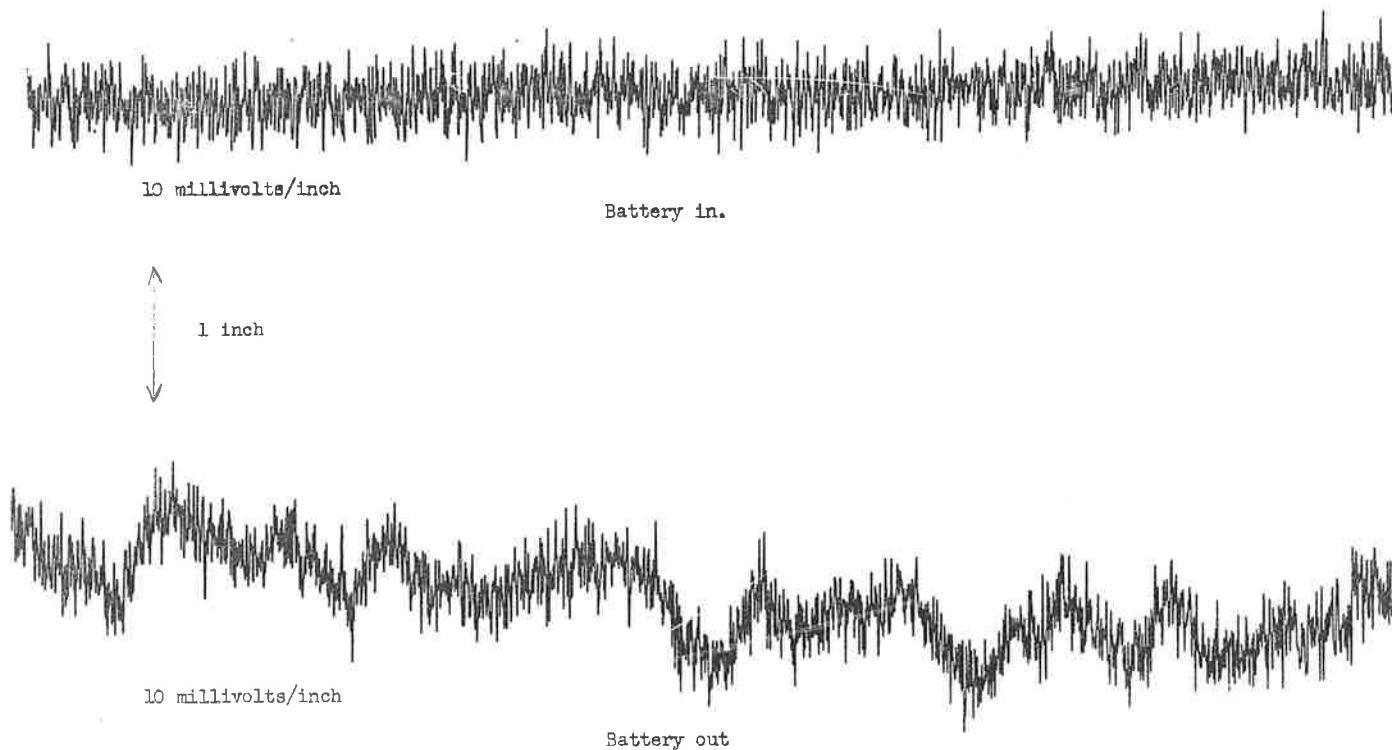


Kenneth B. Wiberg
Professor

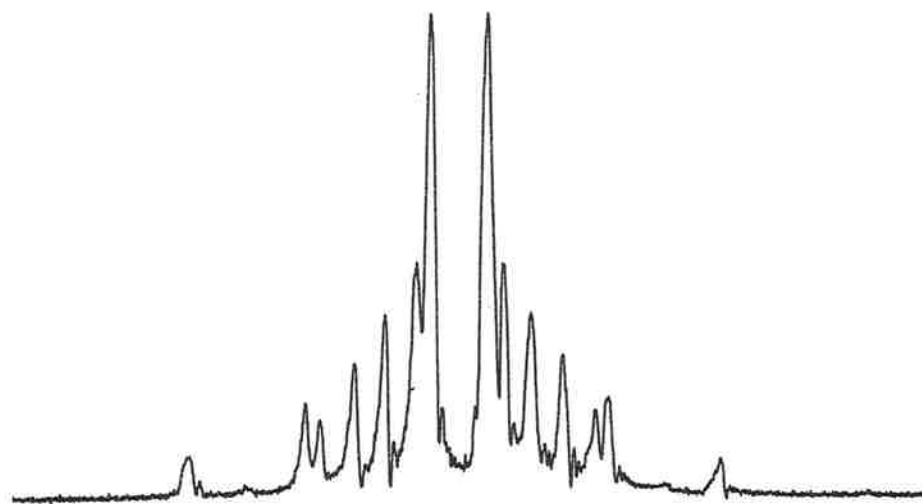
On the Stabilization of Base-lines

It is well known that the Varian Spectrometer power supply does not have adequate regulation of the filament voltage. Various workers have improved the base-line stability by use of a voltage regulator ahead of the power supply or by supplying the filament voltage from a battery. We are now using another method that seems to be very satisfactory. A Standard 12 volt storage battery is connected across the spectrometer filament supply output, which has been adjusted to about 13 volts. The effect on base-line stability is shown below. It has been found necessary to keep the battery near full charge for optimum results, but it can be used continuously for at least a month before recharging becomes necessary

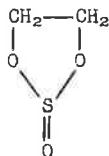
Paul C. Lauterbur
Mellon Institute



Paul C. Lauterbur
Mellon Institute



40 Mc H¹ NMR Spectrum of Ethylene Sulfite



Measurement sample: degassed

Internal reference: about 2% (CH₃)₄Si

External reference: benzene capillary-degassed

Spectrum sample: not degassed, no reference

Room temperature

The A₂B₂ type spectrum shows that the hydrogens on the two sides of the ring are not equivalent, and, therefore, that the heavy atoms are not all in one plane. Complete analyses of this spectrum and those of a number of substituted ethylene sulfites are being carried out.

Paul C. Lauterbur
Mellon Institute

40 Mc H¹ NMR Spectrum of Ethylene Sulfite

Peak	Position* (cps)
1	206.5
2	210.0
3	213.7
4	214.4
5	216.5
6	218.5
7	220.3
8	221.2
9	224.7
10	225.4
11	227.3
12	229.1
13	231.1
14	231.9
15	236.1
16	239.5

* Measured from the zero of the scale on which internal Me₄Si is at 10 ppm (400 cps at 40 Mc). The internal Me₄Si is 263.0 cps from the external benzene.

Precision: About ± 0.5 cps relative to reference and about ± 0.2 within spectrum. Measurements on three recorded spectra were averaged.

Paul C. Lauterbur
Mellon Institute

C¹³ Isotope Effect on F¹⁹ Shifts

The work of Tiers on F¹⁹ and H¹ shifts caused by deuterium substitution prompted us to look for a C¹² - C¹³ isotope effect. No definite effects have been observed in comparisons of C¹²H₃ and C¹³H₃ groups, but rather large shifts have been found between C¹²F and C¹³F resonances. Those observed to date are given in the table below. In all cases the C¹³F resonance is at higher field.

Compound	J _{C¹³F} cps	Isotope shift	
		cps (at 40 Mc)	ppm
CF ₃ COOH	283.2	5.2	0.130
(CF ₃ CO) ₂ O	284.3	5.05	0.126
CF ₂ Br ₂	357.0	6.7	0.167

The measurements were made by superimposing C¹²F modulation sidebands on the C¹³F peaks and are precise to about ± 0.1 cps. The C¹²F₃C¹³OOH peaks were also measured, but no isotope effect was observed (J_{C¹³-C-F} \approx 43 cps).

Paul C. Lauterbur
Mellon Institute

HUMBLE OIL & REFINING COMPANY

MANUFACTURING DEPARTMENT

POST OFFICE BOX 3950

BAYTOWN, TEXAS

RD DEVELOPMENT DIVISION

February 13, 1959

Dr. A. A. Bothner-By - 2

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

Dear Dr. Bothner-By:

Rollie Williams and I have both found the MELLONMR to be a worthwhile means of communication in the NMR field and wish to express to you our appreciation for being included on the mailing list. We hope to be able to make contributions when our work load will permit, but for the moment I must confine myself to comments on previous issues. I will appreciate it if you will place this letter in the next MELLONMR.

Jim Shoolery has done an interesting and worthwhile job of calculating effective shielding constants (MELLONMR No. 3). This is an approach we have found quite useful even when it is not possible or convenient to eliminate all the solvent effects. Extension of this type of correlation should prove fruitful as additional precise data become available.

Those of us engaged in analytical work find NMR spectra to be extremely useful, and are grateful for their publication. Our group has just been asked to solve a difficult problem in olefin structure, and the excellent spectra of the butenes presented by Bothner-By and Naar-Colin in MELLONMR's 1 and 4 should prove very helpful.

In order to make the spectra presented in MELLONMR easier to use for rapid search work, I should like to urge strongly that H_0 always increase from left to right and that all chemical shift and coupling constant data be placed on the spectrogram near the peaks to which they apply. Our experience with sizeable collections of spectra (viz. the Humble Catalog of NMR Spectra) shows that maximum utility is achieved when the spectrograms are of uniform size and composition. A minimum requirement is that the spectra cover the same chemical shift range with reference to a suitable resonance such as benzene or tetramethylsilane, that scales or numerical data be near the spectrum, and that all scales run in the same direction. The format adopted by the API includes all these features and is recommended to all who are preparing spectra for publication.

It is not necessarily desirable, of course, to have complete uniformity in spectra presented in an informal bulletin like MELLONMR, but I believe adoption of the suggestions in the preceding paragraph, in addition to those already proposed by Bothner-By and Shapiro in MELLONMR No. 1, will materially increase the usefulness of the spectra. I am aware that some problems are encountered in presenting H_0 increasing to the right when the spectrum is scanned from low to high field and a Varian, Brown, or L & N recorder is used in the normal manner. Scanning from high to low field is one answer, although it places ringing and saturation distortions, if any, on the opposite sides of the peaks and changes the appearance of the spectrum slightly. Permanent reversal of the zero point and direction of pen travel is a good solution provided the recorder is not used for other purposes. A third solution is to turn the individual chart over and trace the spectrum on the back. This is not too tedious if a small number of spectra are to be presented, and it has the added advantage of eliminating the undesirable grid lines from some charts. Grid lines in printed spectra proved to be more of a nuisance than a help in our work, and have been eliminated from all spectra in the Humble catalog.

Yours sincerely,

N. F. Chamberlain

N. F. Chamberlain

NFC:ct