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Mailed: March 2, 1962

Monthly
Ecumenical
Letters from
Laboratories
of
N - M - R
No. 41

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DEADLINE FOR NEXT ISSUE

MARCH 27, 1962

A monthly collection of informal private letters from laboratories of nmr.
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February 24, 1962

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

Dear Barry:

In a recent issue of MELLONMR (No. 35) you welcomed communications regarding A-60 techniques. We have found it rapid and convenient to tune in our A-60 spectrometer on ethanol, a sample which no laboratory should be without.

After the usual optimizing procedure (on the broad water resonance) the y-adjustment was optimized and the curvature controls were set using the OH line of acidified ethanol. On the assumption that this line is a singlet (as a result of rapid exchange) it should be observed at proper tuning as a symmetrical line. By sweeping in both directions over this line, one could evaluate its symmetry in respect to both line shape and ringing. The ringing, evaluated from the peak-to-peak amplitude of the first beat, appeared to be a much more sensitive criterion of the field than was the line shape (see Figure 1). Thus, undercycled conditions gave a larger ringing on the low-field side while overcycling gave larger ringing on the high-field side of the resonance line.

The method quickly indicates which way to change the curvature control for optimum resolution and has the advantage of comparing two present situations instead of comparing present line shapes with something you remember or recorded earlier. When the curvature has been adjusted to give nearly symmetrical ringing the ethanol quartet comes out fairly good (see Figure 2).

It may be worth mentioning that a clinical thermometer is convenient for temperature measurement in the A-60 probe. Ours was 103.6° F. and sample storage in the magnet case, in front of the probe (suggested by Bob Williams of Varian), saved time ordinarily required to warm samples from room to probe temperature.

Very truly yours,



George Slomp
Physical and Analytical
Chemistry

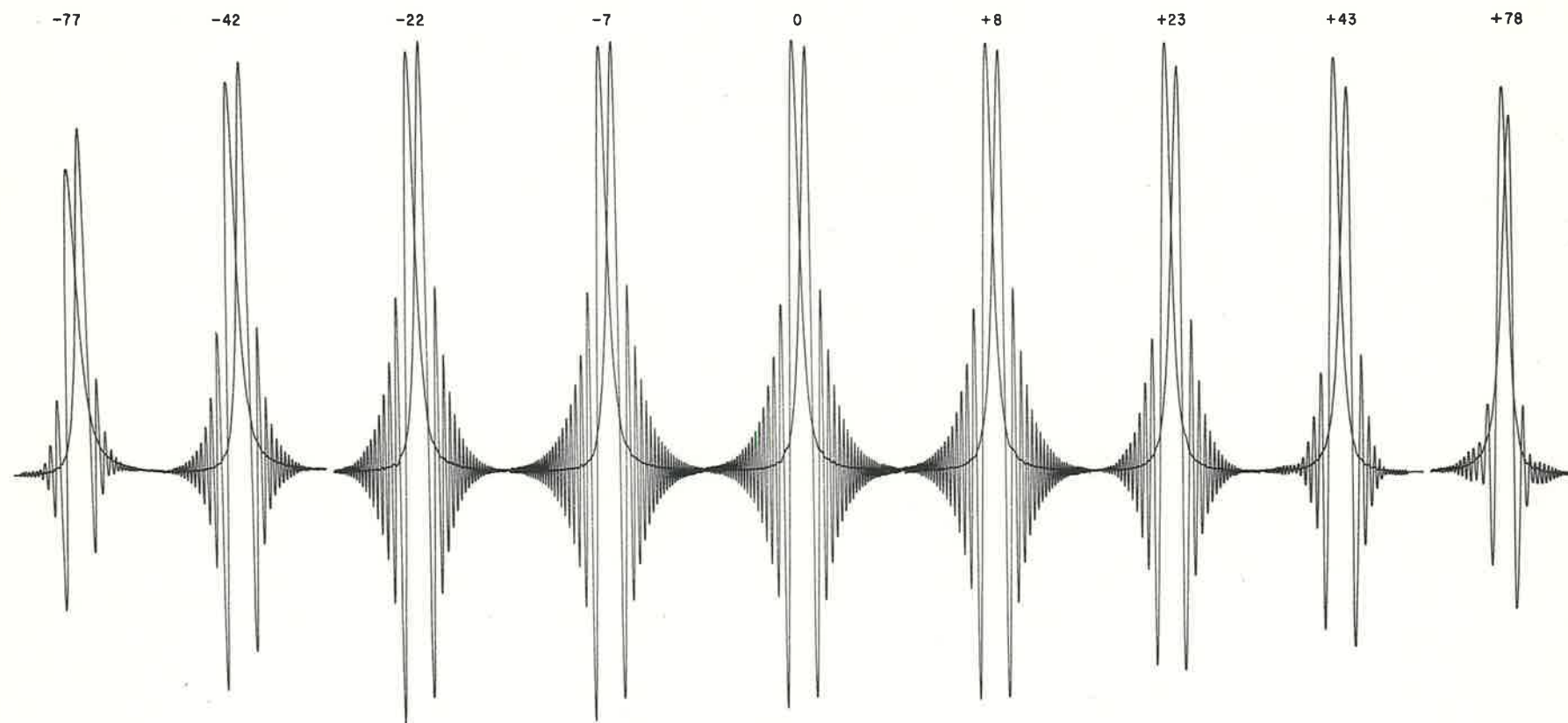


Figure 1

Traces of the OH resonance from acidified ethanol at varying curvature settings. Numbers indicate curvature settings, in hundredths of a turn, on a ten-turn pot. The y setting was optimized each time

41-2

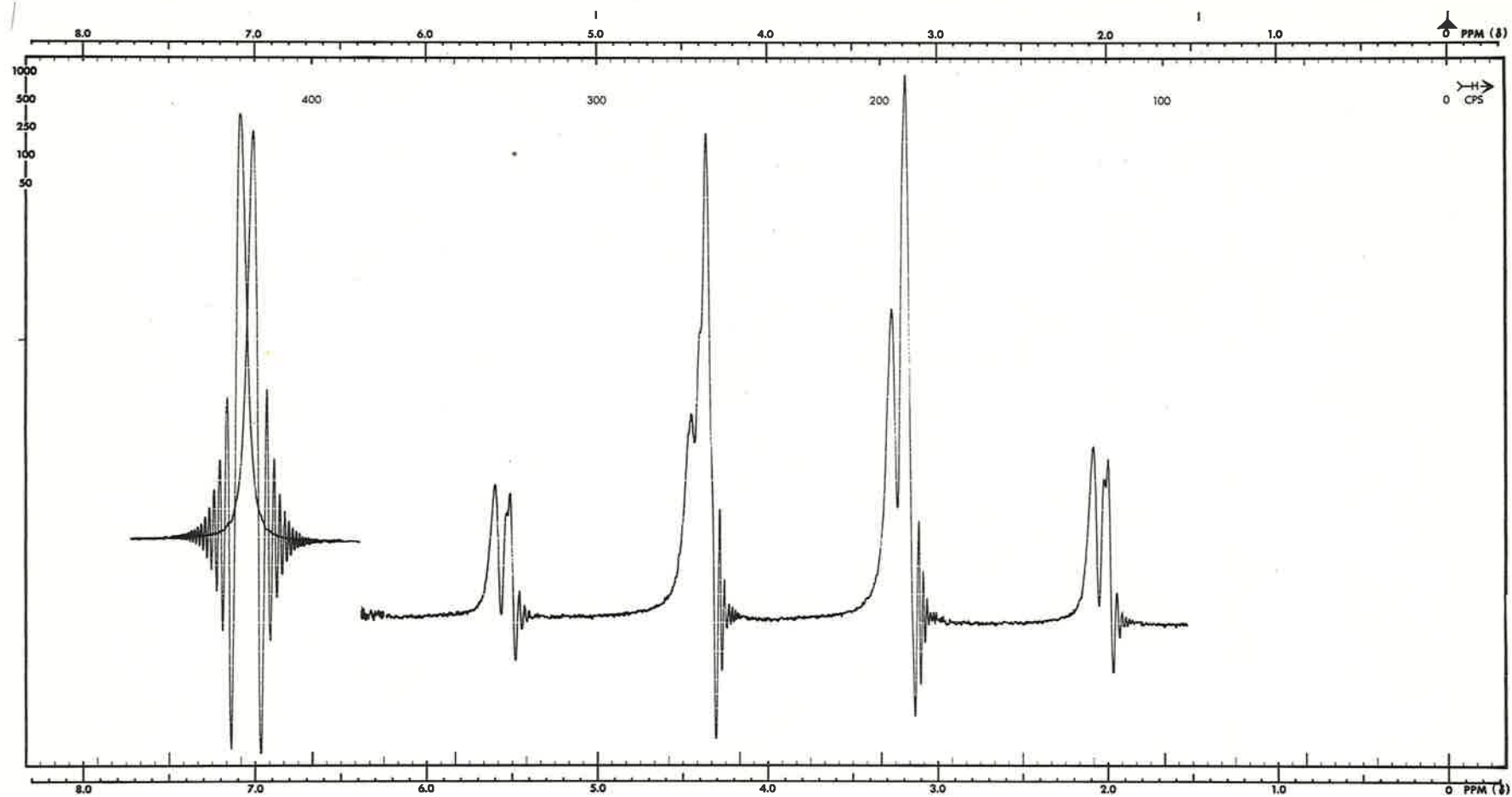


Figure 2
Partial A-60 NMR spectrum of acidified ethanol

2-17

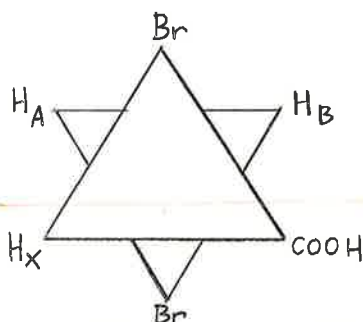
Professor A. A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Professor Bothner-By:

GEMINAL AND VICINAL PROTON COUPLINGS

Recent work by Kaplan and Roberts on diethyl sulphite (J.A.C.S. 83, 4666 (1961)), Fraser, Lemieux and Stevens on dioxolanes (J.A.C.S. 83, 3901 (1961)), and Reilly and Swalen on epichlorhydrin (J.C.P. 35, 1522 (1961)) indicates that in certain special circumstances geminal and vicinal proton couplings can be demonstrated to have opposite signs. The consequences of these results are disturbing in view of the theoretical predictions of Gutowsky, Karplus and Grant (J.C.P. 31, 1278 (1959)) and Karplus (J.C.P. 30, 11 (1959)) for the magnitude and sign of these coupling constants.

In the three examples cited above the interpretations were based on the fact that if the geminal and vicinal couplings were taken to have like sign, an iterative computer program was unable to produce a solution which gave a reasonable fit to the observed spectra. An entirely different approach is now available in the spin decoupling method (Mol. Phys., 4, 321 (1961)) and we report here results which demonstrate that in 2:3 dibromopropionic acid the geminal coupling has opposite sign to the two vicinal couplings. This compound may exist in three possible rotational conformers, the form which predominates is most probably:



(and its mirror image)

K. Pachler has studied solvent effects on this molecule in great detail and has demonstrated that J_{AX} and J_{BX} vary with solvent because the statistical weights of the three rotational isomers change, but J_{AB} remains constant and can therefore be assigned with confidence to the geminal coupling. His work also indicated strong preferential solvent shifts and this led us to choose benzene as solvent for the spin decoupling work so that the spectrum was well spread out. At 60 Mc/s an ABX analysis gives

$$\begin{array}{ll}
 \nu_A = 0 & \text{c/s} \\
 \nu_B = 22.7 & \text{c/s} \\
 \nu_X = 58.5 & \text{c/s}
 \end{array}
 \qquad
 \begin{array}{l}
 |J_{AB}| = 9.7 \text{ c/s} \\
 \left. \begin{array}{l} J_{AX} = 4.5 \text{ c/s} \\ J_{BX} = 10.8 \text{ c/s} \end{array} \right\} \text{ Like sign}
 \end{array}$$

Two modulation frequencies ν_1 and ν_2 were used in the double irradiation experiments at 60 Mc/s. The signal was recorded in a synchronous detector at ν_1 , using the 'field sweep' method. With ν_2 at (a) of Figure 1 the high field A doublet coalesces to give line (b) in the middle trace, and with ν_2 at (c) the low field A doublet gives line (d) in the bottom trace. Hence J_{AB} and J_{BX} have opposite signs. A similar experiment confirms that J_{AX} and J_{BX} have like signs. We have confirmed these results by ABC analysis of a 15 Mc/s spectrum.

The facts then are clear. A large geminal coupling has opposite sign to two vicinal couplings one of which is also large. The implications are somewhat disconcerting. Geminal and vicinal couplings have been shown to have like signs in most vinyl compounds if the geminal coupling is large. The same appears to be true for the few epoxides where signs have been checked, and we have shown by a spin decoupling experiment similar to that described above that the three couplings in styrene oxide (epoxyethyl benzene) are of like sign.

One may simplify the discussion by arbitrarily taking the large trans coupling of ethylene to be positive. Then the evidence of crotonaldehyde and crotonic acid (Mol. Phys. 4, 385, (1961)) suggests that the vicinal coupling in ethane undergoing free rotation (~ 7 c/s) is also positive. Only small variations of this average value are observed in substituted ethanes (Glick and Bothner-By, J.C.P. 25, 362, (1956)) so that it seems unlikely that substituent effects would cause both the trans and the gauche couplings to go negative in 2:3 dibromopropionic acid. The second possibility is that the geminal coupling (9.7 c/s) is negative, which, if it is to be reconciled with the theory of Gutowsky, Karplus and Grant, would require either that substituent effects produce enormous deviations from the theory or that the HCH bond angle is very much larger than normal.

It seems that the question of proton coupling constants is still rather open and that we should draw structural inferences from measured couplings with extreme caution.

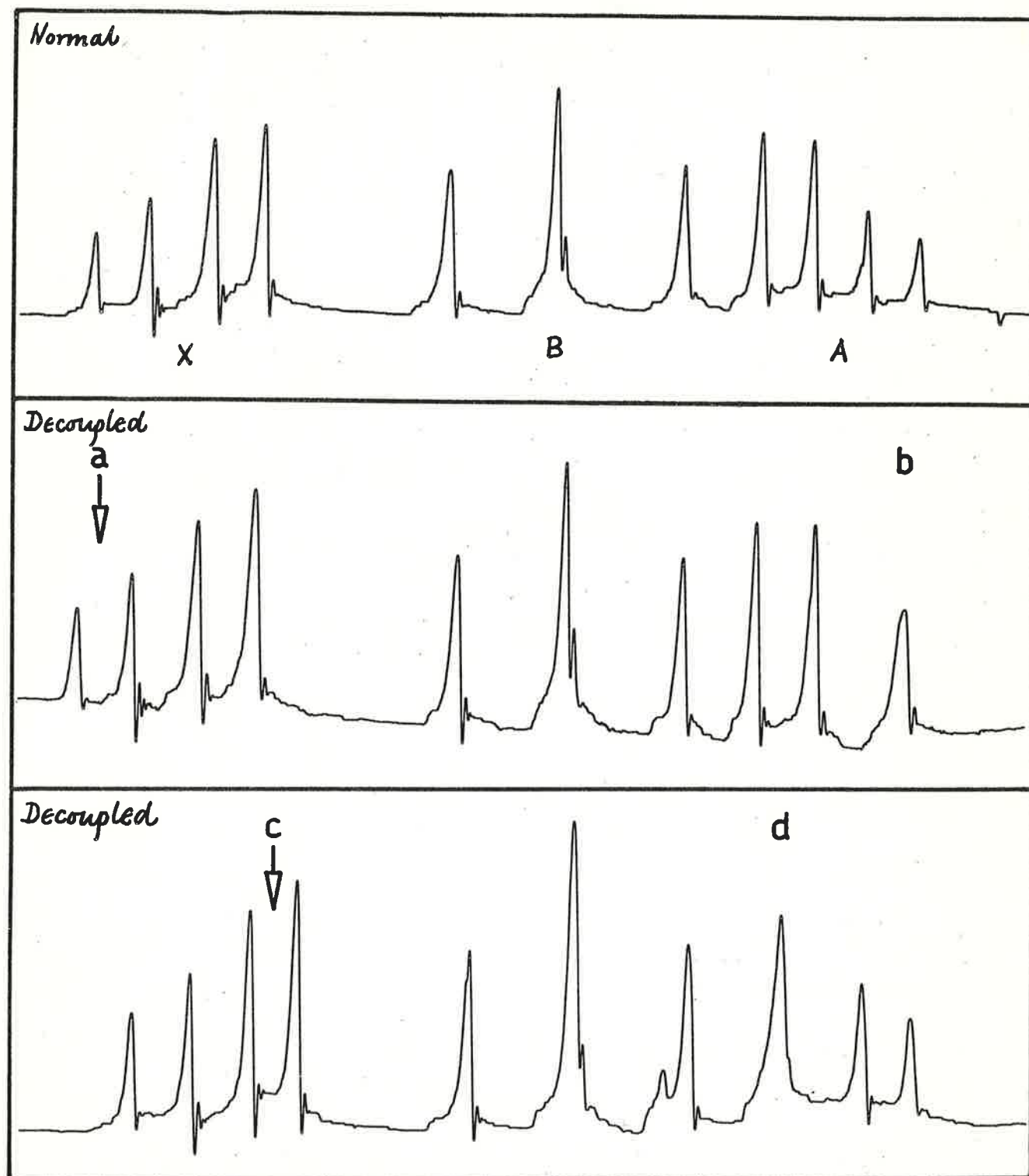
This work was a joint effort with Keith McLauchlan and Klaus Pachler of the National Physical Laboratory in England and Jeremy Musher of the Lyman Laboratory at Harvard, and is being submitted in greater detail to Molecular Physics.

Yours sincerely,

Ray Freeman

Ray Freeman
Instrument Division
Varian Associates
Palo Alto, California

Geminal and Vicinal Couplings - Figure 1



Freeman et al.

Basle, January 28, 1962

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

Dear Dr. Shapiro,

In Mellon-letter No. 23 I told you about the deuteration of phosphorous and hypophosphorous acids and mentioned some isotope effects to be published elsewhere. The fact is, I forgot about these results and only lately came across them again. Because I still think it is a very instructive case of isotope-effects, affecting not only the chemical shifts but also the spincoupling constants, I will give you the full details.

In a mixture of hypophosphorous acid and heavy water three species of molecules can be observed:

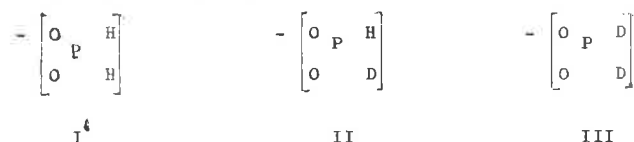
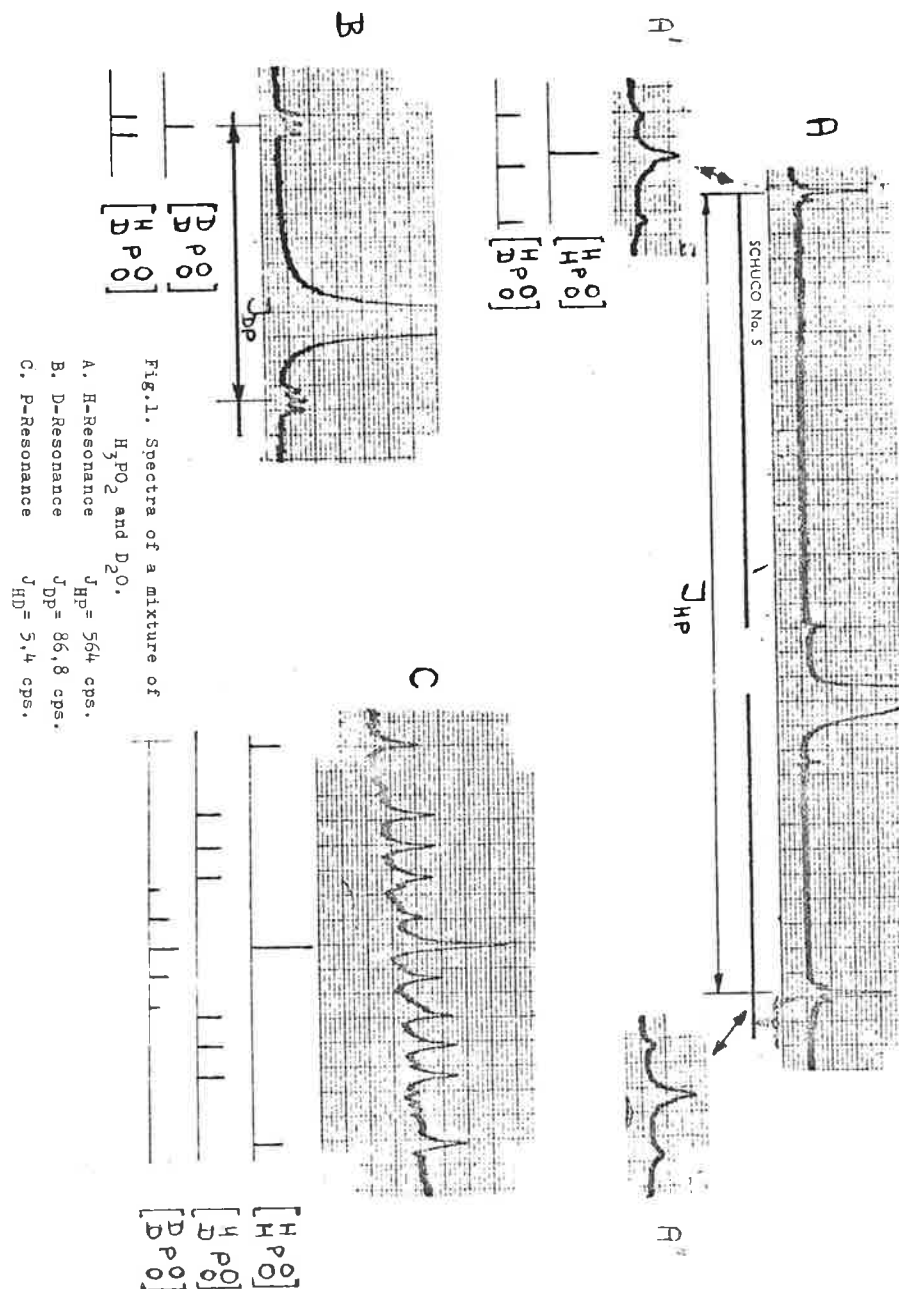


Fig. 1 shows the proton-, deuteron- and phosphorus-spectra of forms I, II and III. The proton spectrum (A) is a superposition of a doublet due to the large J_{HP} (form I) and of two triplets due to the coupling of the deuteron with the proton (form II). On careful inspection of this superposition (see A' and A'') it can easily be seen, first that the two triplets are not exactly on the top of the doublet lines and second that the amount of this shift is not the same for the two halves of the J_{HP} doublet. There seems to be only one explanation for this: The chemical shifts of the protons and the spincoupling constants J_{HP} are not the same in forms I and II. Substitution of the deuteron causes a high-field shift of the proton and at the same time diminishes the coupling constant J_{HP} .



Here are the exact figures:

$$\sigma_H (HDPO_2) - \sigma_H (H_2PO_2) = 1,33 \pm 0,12 \cdot 10^{-8}$$

$$J_{HP} (H_2PO_2) - J_{HP} (HDPO_2) = 0,54 \pm 0,07 \text{ cps.}$$

The deuteron spectrum (B) is a superposition of a doublet due to J_{PD} (form III) and of two doublets due to the coupling of the deuteron with the proton (form II). Again isotope-effects can be measured:

$$\sigma_D (D_2PO_2) - \sigma_D (HDPO_2) = 2,5 \pm 0,5 \cdot 10^{-8}$$

$$J_{DP} (HDPO_2) - J_{DP} (D_2PO_2) = 0,12 \pm 0,03 \text{ cps.}$$

This means, substitution of a second deuteron causes a high field shift of the first deuteron and again a reduction of a spincoupling constant (J_{DP}). In order to compare the magnitude of the spincoupling isotope effects one must of course multiply the deuteron effect by a factor of $\gamma_H/\gamma_D = 6,52$. We then see, that it is not possible to determine which is the larger.

The isotope shifts obviously are different from each other, the deuteron isotope effect being about twice as large as the proton isotope effect. So far I do not see how this factor could be quantitatively explained.

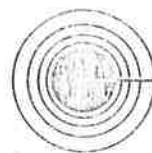
The P-spectrum (C) shows a superposition of the spectra of all three forms (I, II, III). The slight asymmetry is due to a (PO_4) impurity.

I measured the isotope-effects mentioned above as a function of pH and did not find any changes.

Sincerely yours

P. Diehl

Encl.
Fig. 1



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February 12, 1962

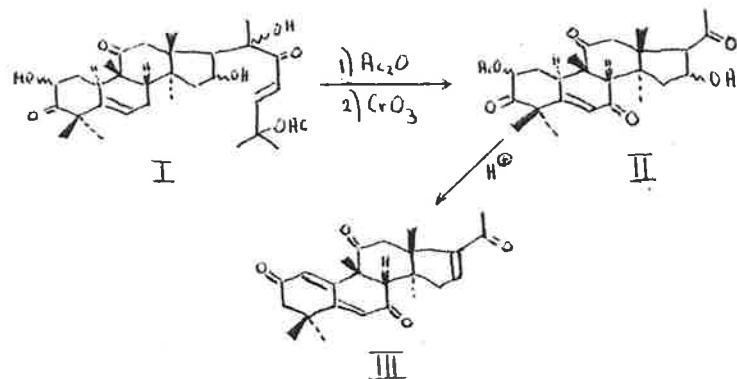
Dr. A.A.Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

USA

Dear Editor,

The last sentence in Ye Editors Corner (39th issue of thy wonderful Mellon Letters) has induced a very long range coupling in thy reader's mind. I would thus like to submit to you and to those of your readers that might be interested in, an NMR spectrum of a degradation product from Cucurbitacin B, which has played a capital role in the formulation of Structure (I) for the latter.*

Compound (III) was obtained simply by acid treatment of Cucurbitone A (II)!



* a more detailed communication will appear elsewhere.





BP RESEARCH CENTRE

PETROLEUM DIVISION

SUNBURY-ON-THAMES

ENGLAND

75 Mcps HIGH RESOLUTION SPECTROMETER

(Conversion of 40 Mcps Commercial Instrument)

It is particularly important in the petroleum field to have the maximum possible resolution in the 7.5 - 9.5 τ region and indeed a resolution greater than that obtainable at 60 Mcps is desirable. Consequently we have modified our Varian 40 Mcps high resolution spectrometer with the object of providing a high resolution system capable of operating at field strengths of 20,000 gauss.

The magnet has been modified by replacing the Varian pole caps by conical Permendur pole caps which we have designed. These have a face diameter of 7.9" and the gap width has been reduced from 1.75" to 1". The Super Stabiliser coils are now carried on triangular sectioned plastic annuli which are held in position by the pole cap retaining bolts.

Most of the 'x' and 'y' gradients have been eliminated by careful adjustment of the pole piece retaining bolts. Residual gradients along these axes and also the 'z' gradient are controlled by a set of Golay type shim coils. Curvature control is effected by a set of coil pairs as described by Zurcher in Mellonur No. 25. A plot of field strength against magnet current, obtained with the aid of a marginal oscillator type of field strength meter modified as recommended by Buss and Bogart (Rev. Sci. Inst., 1960, 31, 204), showed that with a 2.0 amp energising current the field strength was 22,400 gauss.



- 2 -

At present the instrument is being operated at a field strength of 17,600 gauss (75 Mcps) which is obtained with a magnet current of only 1.05 amperes. Because of the reduced gap width it was necessary to construct a new probe unit and this we have done using an Anderson "twin T" type bridge circuit. The 75 Mcps radio frequency is generated by a conventional quartz crystal oscillator, while the receiver consists of a normal cascode input superhet. Considerable care had to be taken to decouple the receiver from the transmitter. We have also constructed a 1.4 Kcps field modulation system which is basically the circuit suggested by Varian except that we have found it necessary to put a narrow band 1.4 Kcps filter before the synchronous detector. We use the D.C. amplifier for signal amplification as well as integration.

Using the above radio frequency system we find that it is possible, using a 3mm i/d sample tube, to obtain spectra with a resolution of 1 in 10^8 . Figure 1 shows the acetaldehyde quartet with this order of resolution. Figures 2 and 3 show the spectra of the ethyl group of ethyl benzene at 40 Mcps and 75 Mcps respectively and Figures 4 and 5 show the 40 Mcps and 75 Mcps spectra of 3:4-dimethylhexane. These spectra illustrate the improvement in chemical shift obtained by operating at 75 Mcps.

S.A. Knight

S.A. Knight

R.L. Erskine

R.L. Erskine

15th February, 1962

41-10

BP

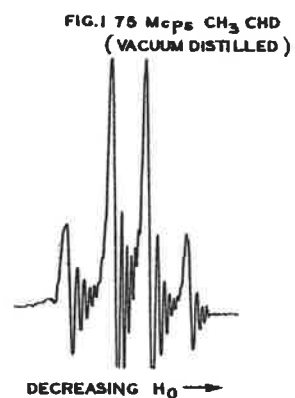
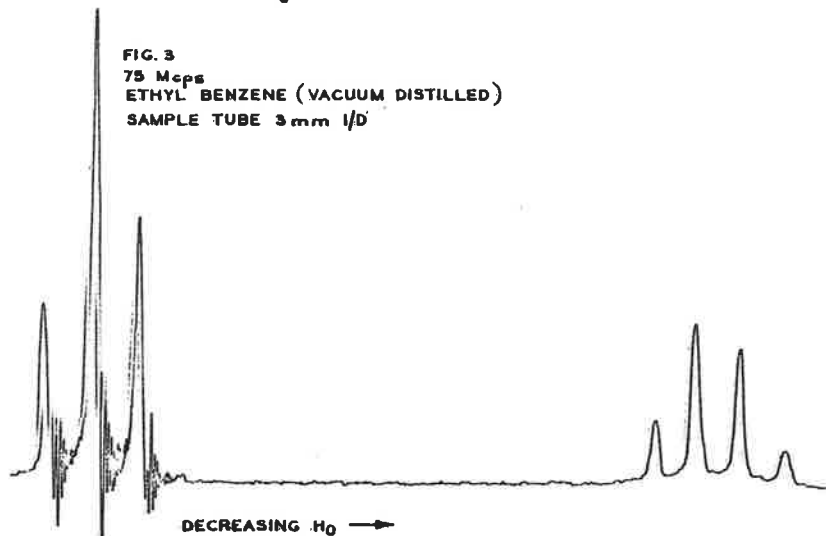
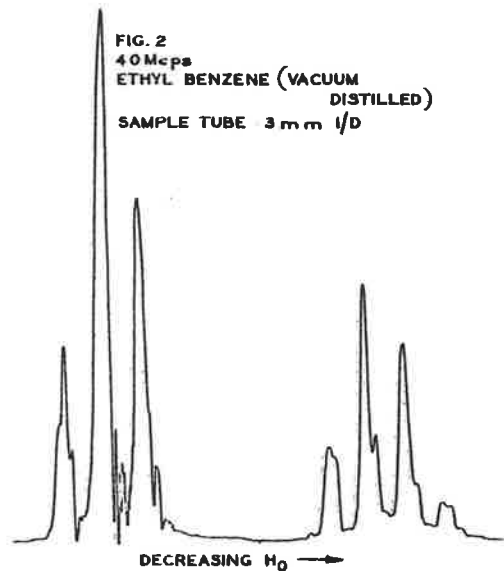


FIG. 4
40 Mcps
3,4 - DIMETHYLHEXANE
(NEAT, UNDEGASSED)
SAMPLE TUBE 3 mm I/D

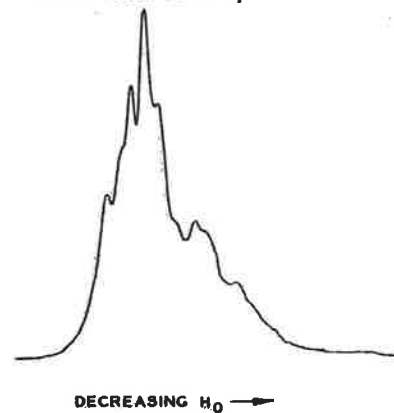
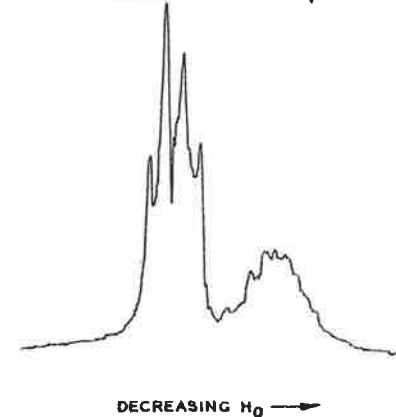


FIG. 5
75 Mcps
3,4 - DIMETHYLHEXANE
(NEAT, UNDEGASSED)
SAMPLE TUBE 3 mm I/D



41-11

ECOLE NATIONALE SUPERIEURE
DE CHIMIE

8, RUE DE L'ECOLE-NORMALE

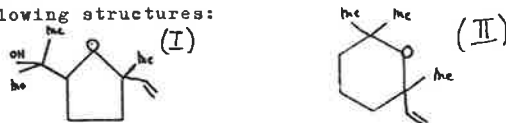
TELEPHONE 72.49.19

Prof. Max Mousseron,
Director.Dr. A.A. Bothner-By,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, 13,
Penn.,
U.S.A.

Dear Dr. Bothner-By,

First of all, may I apologize for the fact that my subscription is very much overdue.

I have a question to put to your readers concerning a rather tricky structure problem. Miss Levallois, who is preparing a "Thèse d'Etat" under Mme. Mousseron's direction in this laboratory has been investigating the properties of "linalol oxide" and a certain number of related compounds. The initial problem was to see if N.M.R. could tell us whether the compound had one of the two following structures:



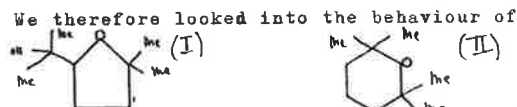
Here are the facts as we find them:

1. The two geometrical isomers of linalol oxide give only slightly different N.M.R. spectra, the noticeable difference in chemical shift being the position of the vinyl band.

2. The proton adjacent to the OH group shows an unusually complicated group of lines.

3. The spectra in CCl_4 solution at different dilutions show the expected concentration shift of the alcohol proton, but further, some methyl groups positions are sensitive to dilution.

The same features show up with compounds possessing an ethyl or an isopropyl group in the place of the vinyl.



which has the advantage of being symmetrical and having no geometrical isomers.

We noticed here:

1. The -CH- proton is no longer as complicated, but gives rise to a triplet centered at $\tau = 6.30 \pm 0.01$

ECOLE NATIONALE SUPERIEURE
DE CHIMIE

8, RUE DE L'ECOLE-NORMALE

TELEPHONE 72.49.19

-2-

independent of concentration

2. The $\text{CH}_2\text{-CH}_2$ band is centered at $\tau = 8.30 \pm 0.02$ and is also concentration independent.

3. The hydroxyl proton dilution shift, as shown in the figure I may well be consistent with intramolecular hydrogen bonding.

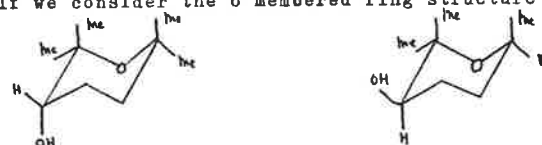
(The infra red evidence is as follows)

Mole fraction	OH bands in cm^{-1}			
1	main peak	3450	3575	small inflexion
0.7		3450	3575	inflexion
0.3	resolved	3450	3575	well resolved
0.15		3460	3575	
0.02	very small	3475	3575	
0.003 Molar		nil	3575	

4. One of the gem dimethyls is split in dilute solution, less so in concentrated solution, and almost coalescent in the pure liquid. The other gem dimethyl is unaffected by concentration. (see Fig. II)

It appears that either of the two possible structures can explain this behaviour. In structure I the two methyls on the side chain will not be quite equivalent, as the carbon in the ring is asymmetric. Even if internal rotation were rapid, one might expect the methyls to have slightly different shifts; further, if internal rotation is hindered by some factor, the shifts should become larger. As there is more intramolecular H bonding in dilute solution than in concentrated, one would expect rotation to be more hindered in dilute solution, hence the methyls more resolved. This is what we find. Furthermore, the rigid 5 membered ring structure accounts for the concentration independence of the other bands.

If we consider the 6 membered ring structure II



we may take it that the two chair forms are in equilibrium, but that the position of the equilibrium may change with concentration (intramolecular H bonding favoring axial -OH). This would explain

4-12

Methyl peaks as function of concentration

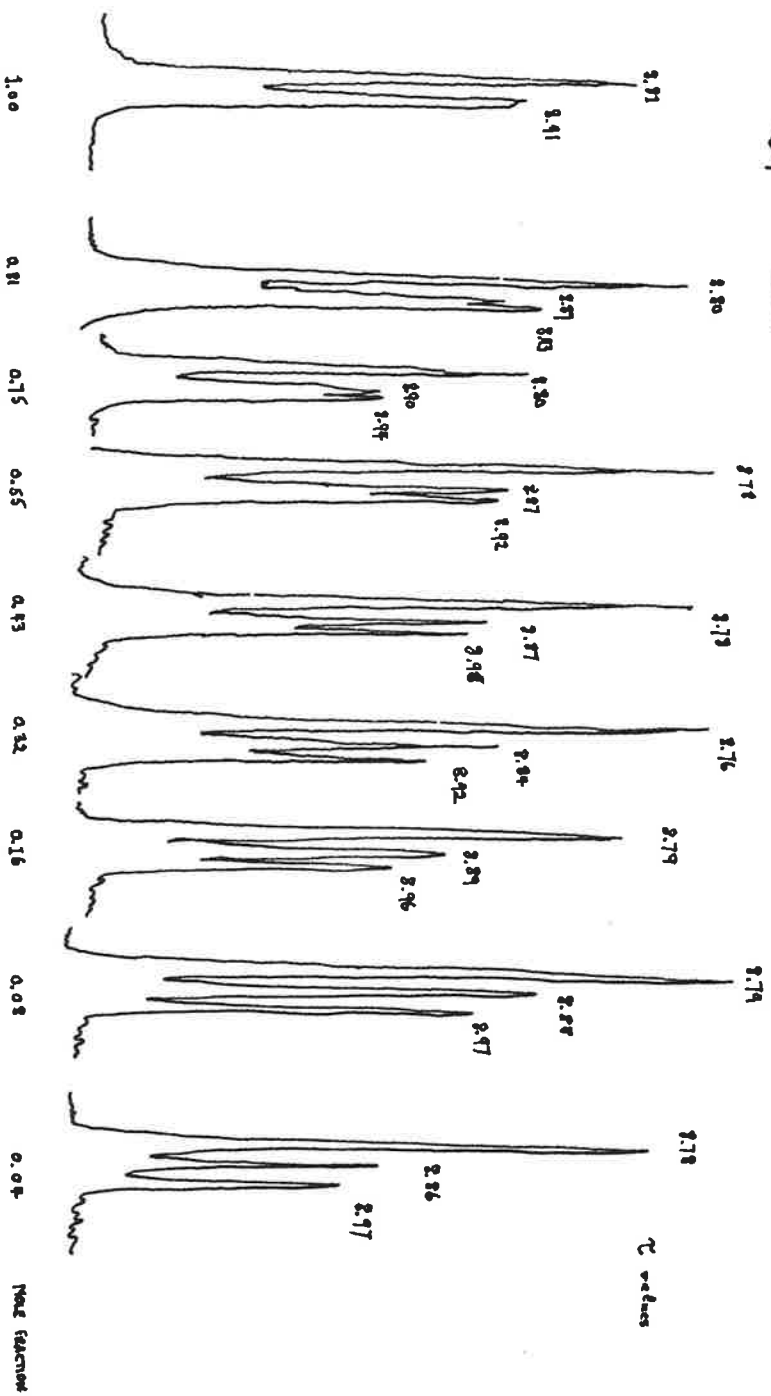
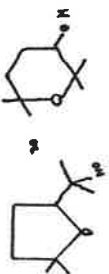
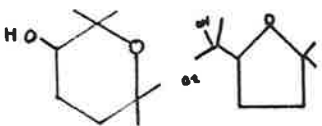
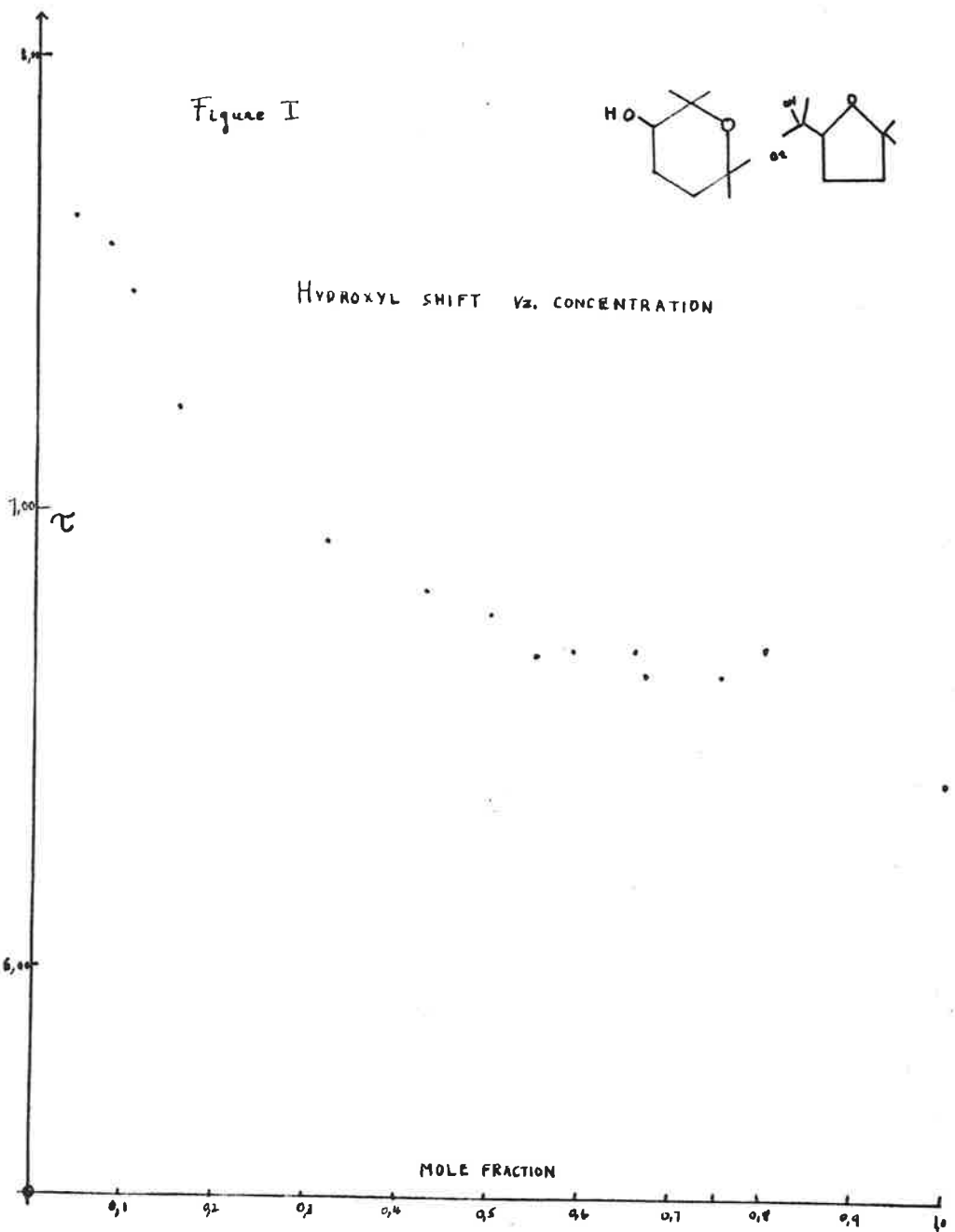


Figure II



HYDROXYL SHIFT VS. CONCENTRATION

Figure I

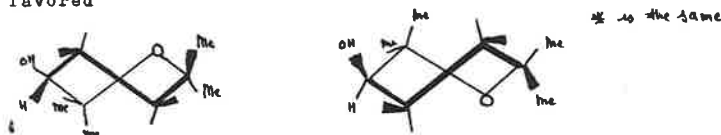


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DE CHIMIE8, RUE DE L'ÉCOLE-NORMALE
TÉLÉPHONE 72.49.19

- 3 -

the behaviour of the methyls (different non bonded interaction with OH). But the objection here is that there ought to be a dilution shift of the proton adjacent to OH if it is true that the population levels change (difference of 0.5 ppm between axial and equatorial protons).

This latter objection would be lifted if the 6 membered ring had the "twist boat" conformation, for it would explain the methyl shifts, as above, but would account for the constancy of the proton on the basis that the long range shielding of this proton due to the 2,3 and 5,6 C-C bonds whichever of the two boat forms is favored



Further evidence for the structure of these compounds may be forthcoming, but I should be very glad to have any suggestions.

Our spectrometer has settled down to working very smoothly and M. E. Arnal, Ing. Tech., C.N.R.S. is running it as a full time job.

Yours sincerely,

James Wylde.

Chargé de Recherches, C.N.R.S.

P.S. M^{me} C. Laffite
effected the J.R. spectra

February 22, 1962

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

Dear Aksel:

Readers of MELLONMR should be interested in the symposium on "High-Resolution Nuclear Magnetic Resonance Spectroscopy" sponsored by the Division of Physical Chemistry of the ACS which will be held at Boulder, Colorado, July 2-4, 1962. A program of about twenty-four invited papers is planned, and the following have accepted invitations to participate: J. D. Baldeschwieler, H. J. Bernstein, F. A. Bovey, B. P. Dailey, A. Bothner-By, Gideon Fraenkel, J. A. Goldstein, H. S. Gutowsky, O. Jardetsky, M. Karplus, S. Meiboom, J. A. Pople, L. W. Reeves, J. D. Roberts, W. G. Schneider, J. D. Swalen, N. Sheppard, and J. N. Shoolery. A complete program will be available in April. Several European scientists have also tentatively agreed to present papers if I am able to arrange for transportation through one of the government research agencies as co-sponsor; unfortunately, it will be a few weeks until I know whether or not this will be possible.

A very limited number of short papers will be accepted and authors are invited to correspond with the Chairman concerning the suitability of potential contributions.

The program will concentrate on current problems and recent research, and should provide an unusual opportunity for workers in the field to get together. I will send you a copy of the program when available, and we will distribute registration forms to the MELLONMR mailing list when they are available. Attendance at the meeting is not restricted.

Yours sincerely,

Max T. Rogers, Acting Head
Department of Chemistry

ct

41-14

Stockholm, 19th February 1962.

Cable address: Technology

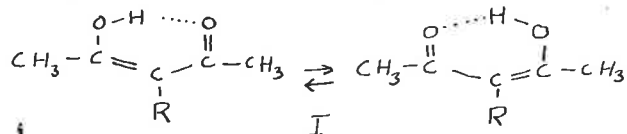
SFn/BR

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburg 13, Penn.
U.S.A.

Dear Dr. Bothner-By:

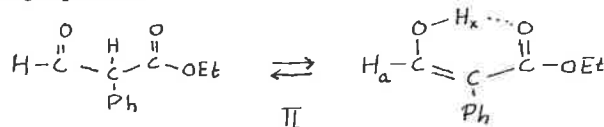
In our laboratories we have for some time been studying hydrogen bonding in enolic systems using NMR and IR spectroscopy. Most of our work has been centered on β -tricarboxyl compounds, which in general are almost completely enolised in polar and non-polar solvents. The intramolecular hydrogen bonds are very strong and for the enolic OH-protons τ -values ranging from -5 to -9 ppm have been observed. Part of this work has recently been summarised and a reprint is sent by separate mail.¹

The strengths of the hydrogen bonds are but one of the interesting aspects in the study of enolic systems. The localisation and transfer of protons may sometimes be studied. In the enolic form of acetylacetone (I, R = H) the two methyl groups are known to give only one PMR signal. This indicates a rapid interconversion of the two (identical) enol forms.²

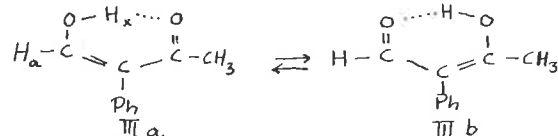


Similarly, we found that in the enol of triacetylmethane (I, R = CH₃CO-) two of the methyl groups were equivalent. In the enols of unsymmetrical β -diketones no such conclusions can be drawn.

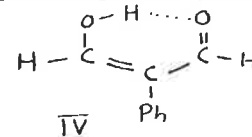
We have recently observed, however, that spin coupling effects can be observed in some enolised aldehydes ("hydroxymethylene compounds"). Thus the ethyl ester of α -formylphenylacetic acid (II) is completely enolised in carbon tetrachloride or chloroform solutions. The enolic proton (H_x) is found to couple with the "aldehydic" proton (H_a). The spin coupling constant is fairly large, J_{ax} = 12.5 \pm 0.1 c/s (field independence checked at 40 and 60 mc/s). This indicates that the enolic proton remains attached to the "aldehyde" oxygen for prolonged periods.



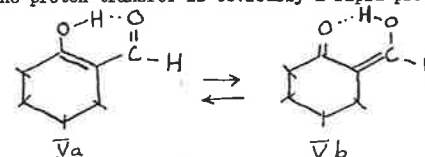
Somewhat unexpectedly, the enolic form of 1-formyl-1-phenylpropane-2-one (III) also shows spin coupling of the "aldehydic" and enolic protons. The coupling-constant is here only 6.3 \pm 0.1 c/s (at 23°C). Its value is markedly affected by the temperature of the sample. These facts indicate that the



hydroxymethylene-ketone form (IIIa) predominates over the formyl-enol form (IIIb) at room temperature and that the interconversion becomes more rapid at elevated temperatures. The compound evidently offers a possibility of examining more closely the energetics of proton transfer between the two oxygen atoms.

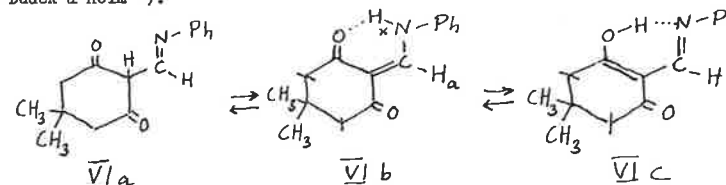


In the enol of the symmetrical phenylmalondialdehyde (IV) no spin splitting is observed and the proton transfer is obviously a rapid process.



Also 2-formylcyclohexanone (V) is completely enolised. No spin splitting can be observed which may be due to preferential formation of the formyl-enol (Va) or to rapid proton transfer.

Preliminary studies on β , β -diketoaldehydes have not yet given any additional examples of spin coupling of the type just described. Such compounds can be prepared via the corresponding anils (e.g. VI). These exist exclusively in the diketo-enamine form (here VIb), (compare recent findings on Schiff bases by Dudek & Holm³).



The spin coupling constant for H_x (τ = -6.45) and H_a is fairly large, J_{ax} = 13.4 \pm 0.2 c/s.

1. Nilsson, M., Svensk Kem.Tidskr. **73**, 447 (1961), (in English).
2. Reeves, L.W., Can.J.Chem. **35**, 65 (1957)
3. Dudek, G.O. and Holm, R.H., J.Am.Chem.Soc. **83**, 3914 (1961).

Yours sincerely

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41-15

HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT

February 8, 1962

MELLONMR Contribution

HL.179Q.62
8-4-10kl

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

Dear Dr. Bothner-By:

Although wide line NMR has been used to study stereospecific hydrocarbon polymers there have been no reported applications of high resolution NMR to polymers of this type. Bovey and Tiers have demonstrated the utility of NMR for ascertaining the stereochemical configurations in polymethylmethacrylates [J. Poly. Sci. 44, 173 (1960)]. We decided to see what information could be gained on a hydrocarbon polymer, polypropylene, although we initially thought that the chemical shift differences in the various stereochemical forms of this polymer would be exceedingly small and the spectra uninterpretable. However, nature has been kind and we have obtained some very interesting results.

The spectra of amorphous, stereoblock, and isotactic polypropylene (Figure 3) show distinct differences. These spectra could not be interpreted, however, so the spectra of the corresponding fractions of poly-(CD₃CD=CH₂) [Figure 1] and poly-(CH₃CD=CH₂) [Figure 2] were obtained. The key to the interpretations is the spectrum of the isotactic fraction of poly-(CD₃CD=CH₂) [Figure 1a]. Assuming that there is no hydrogen-deuterium exchange in polymerization, this polymer should contain hydrogen only in the methylene groups. In the isotactic fraction the methylene hydrogens are theoretically non-equivalent and if the coupling to neighboring deuterium atoms is relatively small the methylene hydrogens should give rise to a typical AB pattern. This is indeed what we have found. Dr. Leonard Reeves of the University of British Columbia was kind enough to run the sample for us at 40 mc to verify the AB interpretations. In the spectrum of the stereoblock fraction (Figure 1b) you will note a small band appearing in the center by the quadruplet. This band is much more intense in the amorphous polymer and in the unseparated polymer. We have attributed this band to methylenes in syndiotactic sequences. Methylene hydrogens in syndiotactic sequences are theoretically equivalent and should give rise to a singlet broadened slightly by the relatively small deuterium couplings. The ratio of the area of the quadruplet to that of the singlet is equal to the ratio of isotactic to syndiotactic methylenes. It is unfortunate that the accuracy with which this ratio can be determined is severely limited by extensive band

Dr. A. Bothner-By - 2
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overlap. Our conclusions are (1) in isotactic polymer the concentration of syndiotactic type methylenes is below the limit of detection; (2) assuming that the inversions in stereochemical configurations are randomly distributed along the polymer chain, the average length of sterically identical segments in stereoblock polymer is about fifteen monomer units; and (3) in amorphous polymer the ratio of isotactic to syndiotactic type sequences is approximately one.

The spectra of poly-(CH₃CD=CH₂) are entirely analogous to those of poly-(CD₃CD=CH₂) except that a broadened methyl band is superimposed. In none of the polymer samples was it possible to resolve different methyl types. A detailed account of this work will appear in the preprints of the Polymer Section of the ACS Meeting, Washington, March, 1962.

We have also obtained some chemical shift correlations for halogenated mono-nuclear aromatic hydrocarbons (Figure 4). All samples were run at 50 ± 15 volume per cent concentration in carbon tetrachloride with TMS as an internal standard. Although data obtained on more dilute solutions would be of greater theoretical interest a high solute concentration level was chosen because many analytical samples must be run at high concentrations in order to detect and identify impurities. We have not yet attempted to rationalize the observed chemical shifts. A puzzling feature is that a methyl group shifts an ortho CH₂X group down field, whereas Nugent Chamberlain [Anal. Chem. 31, 56 (1959)] has shown that a methyl group shifts an ortho methyl group up field.

Preprints of these papers can be obtained from the writer.

Very truly yours,

Ferdinand C. Stehling
Ferdinand C. Stehling

FCS:vt

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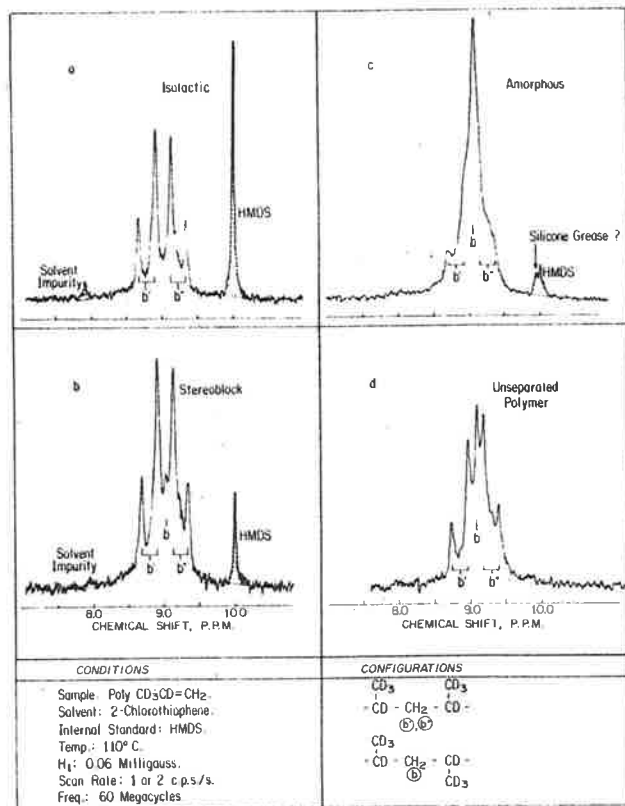


Fig. 1. NMR Spectra of Polypropene-2,3,3,3-d₄.

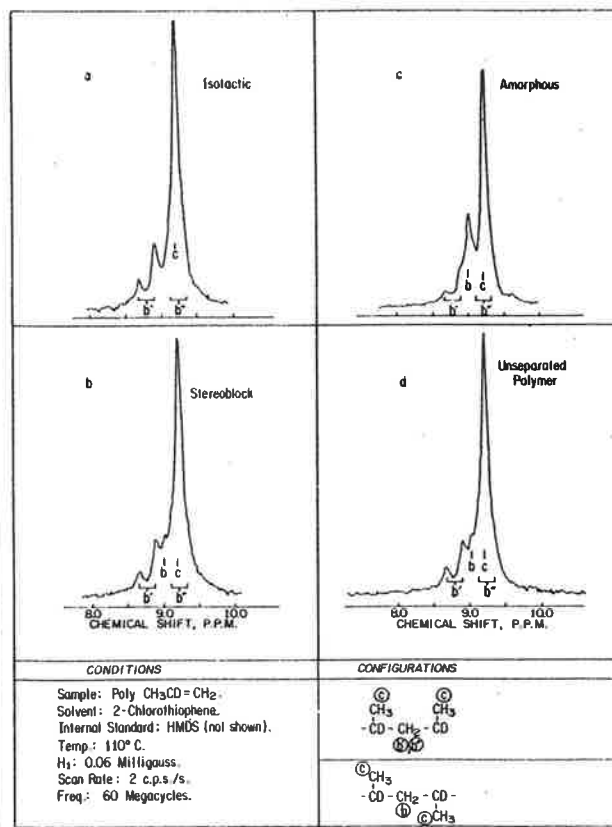


Fig. 2. NMR Spectra of Polypropene-2-d.

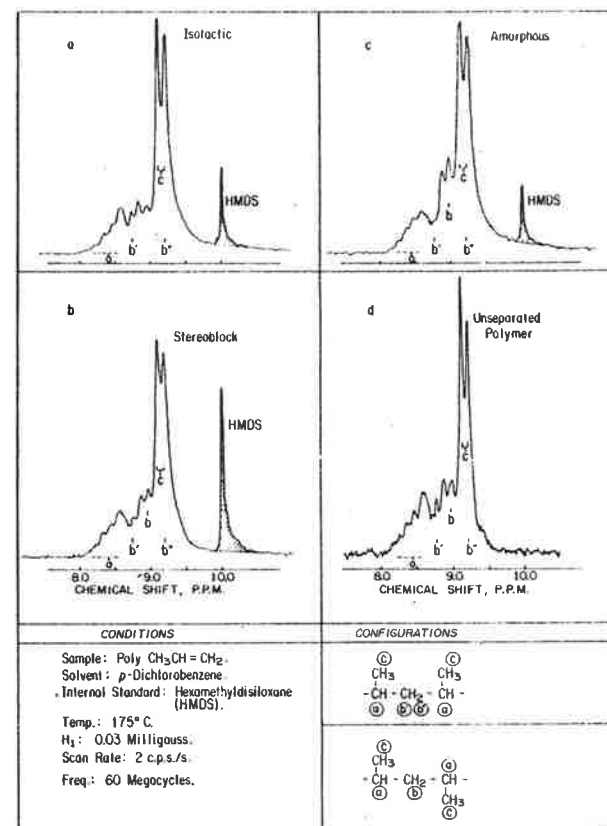


Fig. 3. NMR Spectra of Polypropene.

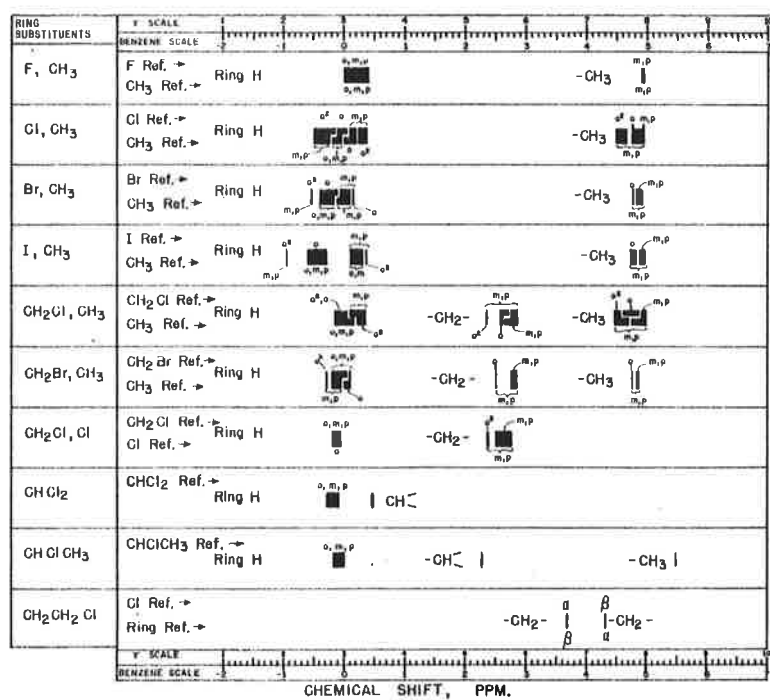


FIG. 4. HYDROGEN NUCLEAR MAGNETIC RESONANCE CHEMICAL SHIFTS IN HALOGENATED MONO-NUCLEAR AROMATIC HYDROCARBONS.