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Newsletter

No. 72  
SEPTEMBER, 1964

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Deadline for Next Issue: 20 October 1964

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

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August 19, 1964

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Thank you for your subscription reminder. The complicated proton spectra from phenyl phosphorus compounds (Hendrickson, et.al, Tetrahedron 20, 449) has been a deterrent to the determination of PH couplings in aromatic rings. We have had occasion recently to look at a few para-substituted phenyl phosphorus compounds. Here, since the para proton is absent, and the cross-ring couplings are small, the spectra appear as only slightly perturbed ABX spectra, where X is the  $P^{31}$  nucleus, and A and B correspond to the ortho and meta protons, respectively. From these spectra, values of  $J_{PH}(\text{ortho})$  ( $J_{AX}$ ) and  $J_{PH}(\text{meta})$  ( $J_{BX}$ ) can be read off directly.

It has come to our attention that Prof. C. E. Griffin of the University of Pittsburgh has been conducting a parallel and more extensive investigation of para-substituted phenyl phosphorus compounds, and his results will appear shortly in Tetrahedron. Summarizing data from both Prof. Griffin's work and ours, it appears that  $J_{PH}(\text{ortho})$  ranges from 10.4 to 11.5 cps. in primary phosphine oxides and phosphonium salts, increases slightly (12.7 to 13.2 cps.) in secondary phosphine oxides, but decreases slightly (6.5 to 7.1 cps.) in phosphines.  $J_{PH}(\text{meta})$  ranges from 0.8 to 3.4 cps., with the values from 0.8 to 1.1 cps. applying to phosphines.

In this letter we wish to add the results of double-quantum experiments which determined the relative sign of  $J_{PH}(\text{ortho})$  and  $J_{PH}(\text{meta})$ . Following Whiffen's procedure (Proc. Chem. Soc. April, 1962, p. 144) two double-quantum lines were observed in the center of the AB part of the spectrum at sufficiently high r.f. levels to saturate the normal spectrum. Only a slight broadening was observed due to the presence of the cross-ring couplings. We examined one each of the four types: phosphine, phosphine oxide, secondary phosphine oxide, and phosphonium salt. In all cases, the separation of the double-quantum lines was within 0.5 cps. of one-half of the sum of the  $J_{PH}(\text{ortho})$  and  $J_{PH}(\text{meta})$  values, and thus one can conclude that they have the same sign.

We would like to thank Dr. Griffin for sending us a preprint of his work.

Very truly yours,

*John E. Lancaster*  
J. E. Lancaster  
*Manuateresallegria*  
M. T. Neglia  
Magnetic Resonance Group  
Research Service Department

THE UNIVERSITY OF LIVERPOOL  
DEPARTMENT OF ORGANIC CHEMISTRY

TELEPHONE: ROYAL 6022



THE ROBERT ROBINSON LABORATORIES,  
OXFORD STREET,  
LIVERPOOL 7.

Dr. B.L. Shapiro,  
Editor, IIT.NMR,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago,  
Illinois 60616.  
U.S.A.

18th August, 1964.

CH.CF and CF.CF Coupling Constants.

Dear Dr. Shapiro,

As my subscription to your news letter is due for renewal shortly, I trust this will keep me "in the news" for the next nine months.

Dr. Cavalli and I have just completed an investigation into CF.CH and CF.CF couplings in substituted ethanes.<sup>1</sup> Our results can be summarised as follows. The average coupling constants, (defined as the coupling constant for equal populations of the rotational isomers) in CH.CF and CF.CF fragments obey a similar electronegativity relationship to the CH.CH coupling. These are, from a collection of the unambiguous values of these couplings (see Table),

$$J_{AV}^{HF} = 53.03 - 3.38 \sum E$$

and

$$J_{AV}^{FF} = 91.4 - 6.15 \sum E$$

where  $\sum E$  is the sum of the electronegativities of the first atom of the four remaining substituents. The mean deviation of the  $J_{AV}^{HF}$  points is 1.3 c.p.s. over a range of 22 c.p.s. The agreement of the F-F couplings is by no means as good, although most of the exceptional cases can be removed by taking the electronegativity of the CF<sub>3</sub> group equal to that of Cl (3.15).

/ cont.

Consideration of these equations with the corresponding one for  $J_{AV}^{HH}$ , vis

$$J_{AV}^{HH} = 14.5 - 0.80 \angle E$$

shows that for a large number of highly electronegative substituents all the couplings decrease to zero. (e.g. In the case where  $\angle E$  equals that for  $CF_3.CF_2.CO_2H$ ,  $J_{AV}^{HH}$  equals 0.0 c.p.s.,  $J_{AV}^{HF}$  1.5 c.p.s. and  $J_{AV}^{FF}$  2.3 c.p.s. (calculated) and 1.5 c.p.s. (observed)). This limit cannot be reached in practice for those couplings involving hydrogen due to its low electronegativity. However, the point here is that the "peculiarly small" F-F couplings are no more than a consequence of the high electronegativity of fluorine combined with the relative ease of obtaining perfluoroethanes. Also, the similarity between these couplings, coupled with the theoretical predictions that  $H-F$  couplings are always positive, suggests that both  $J_{FF}^{FF}$  and  $J_{FF}^{HF}$  approach zero for highly electronegative substituents,  $\angle$  and do not change sign and thus accidentally cancel.

The values of  $J_{AV}$  can be used as a base to investigate the temperature dependence of the coupling in an unsymmetric ethane, as  $J_{AV}$  will represent one limit (an upper or lower one depending on whether the coupling is increasing or decreasing with temperature) to the  $J$  v temperature curve, the other theoretical limit being the coupling in the most stable rotamer. It is of interest to consider F-F couplings in this light as it is known that in some compounds  $J_{AV}^{FF}$  changes with temperature.<sup>2</sup> The molecule  $CF_2Br.CFBrCl$  is an ideal case for this, as both  $J_{FF}^{FF}$  couplings in the individual isomers and the high temperature couplings are known.<sup>3</sup> The mean of the two  $CF.CF$  couplings in the rotamers are 13.3, 14.0 and 20.8 c.p.s., and the rotamer with the smallest coupling is the most stable. Thus the high temperature averaged coupling should increase from 13.3 c.p.s. to, at infinite temperatures,  $J_{AV}$  (16.0 c.p.s.). In fact the observed coupling (in  $CFCl_3$  solution) decreases from 13.95 c.p.s. at 242°K to 13.70 c.p.s. at 371°K and in the pure liquid the coupling again decreases from 14.11 c.p.s. to 13.36 c.p.s. at 466°K.<sup>4</sup>

We attempted to fit these results by using different signs of the coupling constants of the individual rotamers. This, however, gave no reasonable answer. Thus we are left with the conclusion that the observed temperature dependence cannot be accounted for by the change in the percentage of the rotamers with temperature.

/ cont.

An even more striking example is  $\text{CF}_2\text{Br.CFBr}_2$  in which, from the known coupling constants of the individual rotamers, the observed high temperature coupling will only change from 17.4 c.p.s. at (zero) temperatures to 17.9 c.p.s. at infinite temperatures. i.e. Over any practical range of temperature the variation in the coupling due to the changing populations of the rotational isomers will be less than the experimental error of measurement (ca. 0.1 c.p.s.).

Thus it is clear that in CF.CF couplings, the relatively small differences between the couplings in the individual isomers and the relatively large changes in these couplings with temperature may combine to produce a situation in which the temperature dependence of the observed coupling in an unsymmetric ethane is not primarily due to the changing populations of the rotational isomers.

The situation with CH.CH couplings is the reverse of this. Here  $J_{\text{AV}}^{\text{HH}}$  does not change appreciably with temperature and the differences between the couplings of the individual isomers are much greater. We suggest that CH.CF couplings resemble CH.CH rather than CF.CF, though here the lack of experimental evidence (e.g. in the temperature dependence of  $J_{\text{AV}}^{\text{HF}}$ ) precludes any certainty on this.

- 1 R.J. Abraham and L. Cavalli, submitted to Mol.Phys., (1964).
- 2 W.S. Brey and R.C. Ramey, J.C.P., 39, 844 (1963)
- 3 R.A. Newmark and C.H. Sederholm, J.C.P., 39, 3131 (1963).
- 4 H.S. Gutowsky, G.G. Belford and P.E. McMahon, J.C.P., 36, 3353 (1962).
- 5 S.L. Manatt and D.D. Elleman, J.A.C.S., 84, 1305 (1962).

Yours sincerely,



R. J. Abraham.

CH.CF and CF.CF Coupling Constants in Various Compounds

Compound	$J_{AV}^{HF}$	Compound	$J_{AV}^{FF}$
$CH_3 \cdot CH_2 F$	25.2	$(CF_3 CFH)_2 Hg$	17
$CH_3 \cdot CHF_2$	20.8	$CF_3 CFH_2$	15.3
$CH_3 \cdot CFCl \cdot CH_2 Cl$	18.4	$(CF_3)_2 \cdot CF I$	12.4
$CH_3 \cdot CF_2 \cdot CH_2 Cl$	17.7	$CF_3 \cdot CF I \cdot CF_2 Cl$	11.8
$CH_3 \cdot CF_2 Br$	15.9	$(CF_3)_2 : CF \cdot CF : (CF_3)_2$	9.0
$CH_3 \cdot CF_2 Cl$	15.0	$(CF_3)_2 \cdot CF Br$	8.7
$(CF_3 \cdot CH_2)_2 Hg$	15	$CF_3 CFCl Br$	7.8
$CF_3 \cdot CH_3$	12.7	$(CF_3)_2 CF \cdot CH : CHF$	7.6
$CF_3 \cdot CH_2 \cdot CH_3$	10.5	$(CF_3)_2 CF Cl$	6.4
$[CF_3 \cdot (CH_2)_3]_2$	10.4	$CF_3 \cdot CF Cl_2$	5.5
$CF_3 \cdot CH_2 \cdot CF_3$	9.17	$CF_3 \cdot CF_2 I$	4.6
$CF_3 \cdot CH_2 Br$	8.92	$(CF_3)_3 CF$	4.0
$CF_3 \cdot CH_2 Cl$	8.41	$CF_3 \cdot CF_2 H$	2.8
$CF_3 \cdot CFH_2$	7.98	$CF_3 \cdot CF_2 Cl$	1.6
$CF_3 \cdot CHCl \cdot CF_3$	5.93	$CF_3 \cdot CF_2 \cdot CO_2 H$	1.48
$CF_3 \cdot CF_2 H$	2.60	$CF_3 \cdot CF_2 \cdot CF_2 I$	0.8
$CF_2 Cl \cdot CH_2 Cl$	9.5	$CF_3 \cdot CF_2 \cdot CF_3$	0.7
$CF_2 Br \cdot CH_2 Br$	10.6	$CF_2 Br \cdot CF_2 Br$	7.25
$CF_3 \cdot CF_2 \cdot CF_2 \cdot CH_2 I$	13.5	$CF_2 Cl \cdot CF_2 Cl$	4.63
$CH_2 Cl CH_2 F$	17.5	$CF_2 I \cdot CF_2 Cl$	8.2
$CH_2 Br \cdot CH_2 F$	19.3	$CF_3 \cdot CFH \cdot CF_3$	11
$CF_3 \cdot (CF_2)_5 \cdot CF_2 H$	3		
$CF_3 \cdot CFH \cdot CF_3$	5.5		
$(CF_3)_3 CH$	7		



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ISOTOPE DEPARTMENT

August 20, 1964

חלקת האיזוטופים

Prof. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago 60616

Dear Barry:

$O^{17}$  NMR Spectrum of Methanol

In connection with a study of hydrogen bonding we have examined the spectra of dilute solutions of  $O^{17}$ -labelled methanol in a variety of solvents. Methanol containing 8.6 atom %  $O^{17}$  was prepared by the partial hydrolysis of trimethyl phosphate in  $O^{17}$ -enriched water. The NMR spectra were obtained at room temperature ( $23^{\circ}C$ ) on a Varian D.P. 60 spectrometer operating at 8.13 Mc. As is usual, the derivative of the absorption mode was recorded. A 20 cps modulation frequency was used, the modulation field being kept small to avoid modulation broadening as far as possible. A small capillary tube containing  $O^{17}$ -enriched water was used as an external standard. The  $O^{17}$ -spectrum of methanol appeared as doublet of equal intensity (with some overlap) due to  $O^{17}$ -proton spin-spin coupling. This partial overlap is due to the relatively small ratio  $J/\Delta$  (see Christ and Diehl, Helv. Phys. Acta **36**, 170 (1963)). On the other hand the spectrum of  $CH_3O^{17}D$  (prepared from  $D_2O^{17}$ ) consists of a single line (with about the same line width). The  $O^{17}$ -D coupling is expected to be smaller than  $O^{17}$ -H one by a factor of 6.5, so that the  $J/\Delta$  ratio is smaller by the same factor.

Preliminary  $O^{17}$  NMR parameters for methanol are given in the following table:



<u>Solvent</u>	<u>% conc. mole CH<sub>3</sub>OH mole solv.</u>	<u><math>\delta</math> (1) (ppm)</u>	<u>Splitting (2) (cps)</u>	<u><math>\Delta</math> (3) (cps)</u>
CH <sub>3</sub> OH	neat	37.0	76.0	60
CH <sub>3</sub> OD	neat	38.8	-	68
Acetone	6.05	39.1	76.6	55
Benzene	7.2	34.9	83.0	47
CHCl <sub>3</sub>	1.3	33.3	79.0	42
CCl <sub>4</sub>	8.0	33.3	76.4	54

(1) Chemical shifts are accurate to within  $\pm 1$  ppm.

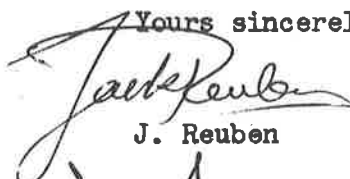
(2) Splittings are accurate to within  $\pm 2$  cps.

(3)  $\Delta$  is the peak to peak line width.

It is apparent from this table that the chemical shift varies from solvent to solvent and also that there is an isotope effect on the chemical shift. A similar effect was found for water (H<sub>2</sub>O<sup>17</sup> and D<sub>2</sub>O<sup>17</sup>) by Christ et al [Helv. Chim. Acta 44, 865 (1961)].

The observed splittings and line widths also vary from solvent to solvent. We are now engaged in a more systematic study of the nature of these effects.

Yours sincerely,



J. Reuben



D. Samuel

## NUCLEAR MAGNETIC



## RESONANCE SPECIALTIES

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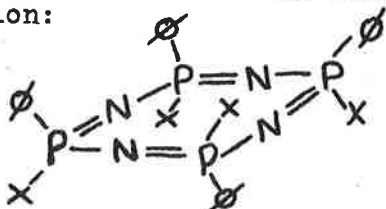
August 26, 1964

Dr. Bernard L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago, Illinois 60616

Dear Barry:

In continuation of our studies on phosphonitrile ring systems with Dr. I. I. Bezman and Mr. C. T. Ford of Mellon Institute (see Mellonmr 63, 31), we have had occasion to obtain N.M.R. spectra of three isomers of  $P_4N_4(C_6H_5)_4[N(CH_3)_2]_4$ , phenyl-N-dimethylaminotetraphosphonitrile. This compound, of course, can exist in three cis-trans isomeric forms. The position of the N-dimethyl and phenyl groups had been previously established by chemical methods.

The N.M.R. spectrum (which was obtained on our A-60 as a 20% solution in  $CDCl_3$ ) of one of the isomers proves to be most interesting (see Figure 1) in that it appeared that three methyl protonic environments were indicated by three doublets in the spectrum, each doublet corresponding to a  $J_{PH}$  of 10.5 cps. The fact that these doublets did indeed represent three distinct protonic environments could not be adequately proven until a phosphorus decoupling experiment was performed and revealed three sharp singlets (see Figure 2). The intensity of these singlets was in the expected 1:2:1 ratio revealing that the isomer could only have the following configuration:



X =  $N(CH_3)_2$

⊙ = Phenyl

Further explanation of the chemical shifts of these lines, as well as the complete story on this problem, will appear in Inorganic Chemistry this fall. I do feel, however, this is a rather pretty "textbook" example of decoupling.

Thank you for your recent reminder concerning our contribution to the IITN-M-R Newsletter. I trust this will keep us in good standing for a while.

Sincerely,

*Frank E. Dickson*  
 Frank E. Dickson  
 Executive Vice President

FED/ck

Enc.

5000

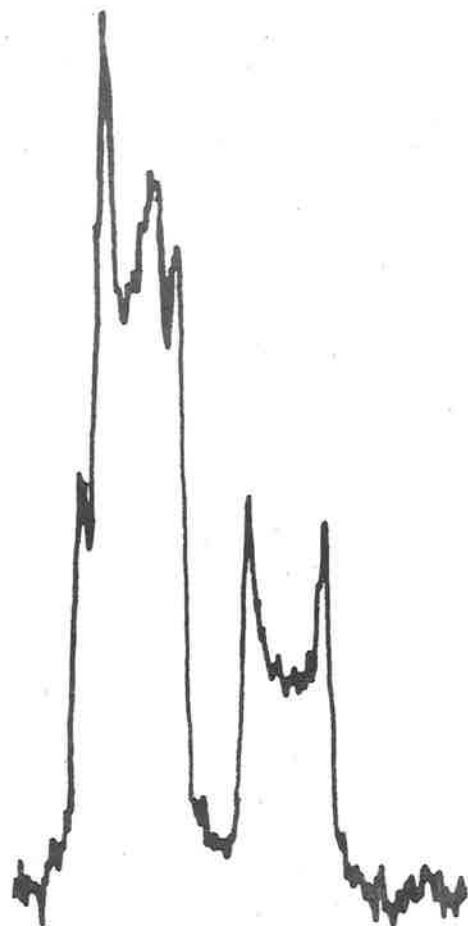


Fig 1

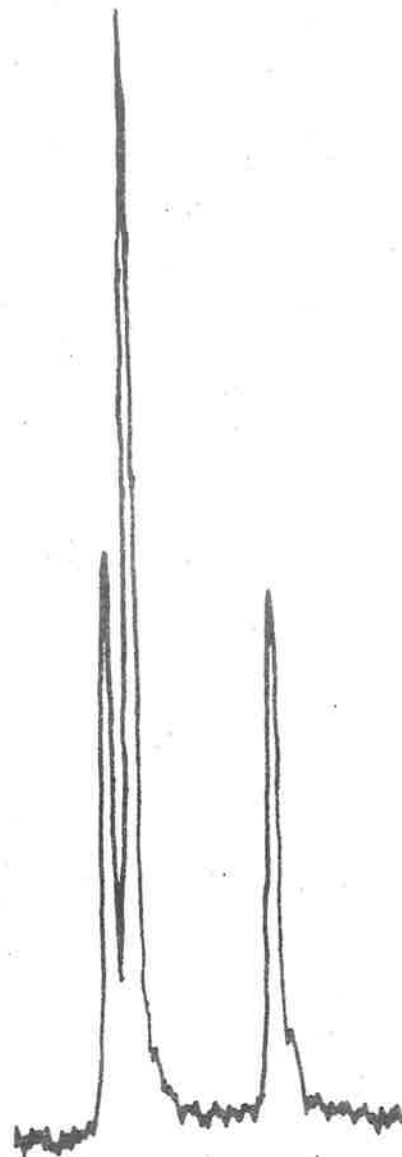


Fig 2

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## BELL TELEPHONE LABORATORIES

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August 28, 1964

DR. BERNARD L. SHAPIRO  
 Department of Chemistry  
 Illinois Institute of Technology  
 Technology Center  
 Chicago, Illinois 60616

Dear Barry:

I have induced Dean Douglass to contribute one of his useful ideas to save our IIT NMR subscription. Other work in progress involves new equipment design and construction for our "relaxation in the rotating frame" experiments. Additional self-diffusion work is being written up. Further relaxation studies in the n-alkanes are under way.

The Bloch decay following a  $90^\circ$  pulse is a useful method of observing a nuclear resonance. It is the Fourier transform of the steady state resonance shape. When the steady state spectrum consists of two chemically shifted lines (A & B) whose widths are small compared with their separation the Bloch decay is an oscillating function that oscillates at the frequency characteristic of the resonance separation. The envelope decays with a time proportional to the reciprocal of the individual line widths.

Let the lines A & B have different  $T_1$ 's,  $T_{1A}$  &  $T_{1B}$ . We apply a  $180^\circ$  pulse at times  $\tau$  before the  $90^\circ$  pulse and observe the Bloch decay. (We assume  $T_{1A}$  &  $T_{1B} \gg$  Bloch decay. This is usually so in liquids as the Bloch decay is usually magnet controlled,  $\sim 10^{-2}$  sec.). If  $\tau = T_{1A}/\ln 2$ , then the A magnetization is zero when the  $90^\circ$  pulse is applied (and substantially zero during the Bloch decay period to follow) and no oscillation is observed in the decay. Similarly when  $\tau = T_{1B}/\ln 2$  there will be no oscillation.

The procedure for a resonance composed of two lines is to vary  $\tau$  and look for the Bloch decays without oscillation.  $\tau$ 's thus determined lead directly to the individual  $T_1$ 's.

The advantage of the method is that  $T_1$ 's that lie quite close to one another can be distinguished and measured accurately. For example, in acetic acid at  $23^\circ\text{C}$   $T_1(\text{methyl}) = 1.125$  sec and  $T_1(\text{acid}) = 1.412$  sec.

Dr. Bernard L. Shapiro - 2

When the A and B lines differ in intensity the  $T_1$ 's can be unambiguously assigned from the Bloch decay  $T_1$  intensities.

The method can be generalized to a larger number of spins but the analysis becomes more involved. A wave analyzer has obvious applications here.

Spin coupling can complicate the analysis.

Sincerely yours,



DAVID W. McCALL

MH-1123-DWM-MC



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
PUBLIC HEALTH SERVICE

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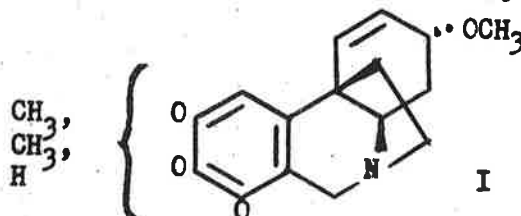
NATIONAL INSTITUTES OF HEALTH  
Tel: 656-4000

August 24, 1964

Professor B.L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois

Dear Dr. Shapiro:

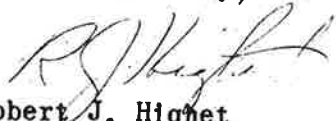
Recently our laboratory faced the problem of determining which of the oxygen atoms on the aromatic ring of Amaryllisine (I)



is that of the free phenolic group. This question was settled when it was found that the aromatic proton resonance frequencies of a phenol are affected in a characteristic manner by conversion to the anion. The spectra of ten alkyl- and alkoxy-substituted phenols and their corresponding sodium salts in dimethyl sulfoxide solution were measured (no need to use the deuterated solvent). The upfield shifts resulting from conversion to the anion fell within discrete ranges for the different protons: ortho, 0.42-0.59; meta, 0.10-0.38; and para, 0.71 to 0.79 p.p.m. Amaryllisine proved to possess an ortho proton.

More variously substituted phenols do not conform to this generalization. However, eight p-hydroxyacetophenones and vinylogues showed the following characteristic shifts: ortho, 0.60-0.84 and meta, 0.22-0.47 p.p.m. Evidently the method can be used to identify the protons remaining on the ring of many poly-substituted phenols if suitable models can be studied.

Yours very truly,

  
Robert J. Highet  
Section on Chemistry  
National Heart Institute

Dr. B. L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Technology Center  
 Chicago, Illinois 60616

Dear Sir:

We would like to receive the I.I.T. - N - M - R - Newsletter. We present some data for substituted crotonolactones which demonstrates the electronic effect of electronegative substituents on allylic and vincinal coupling.

The two  $\gamma$ -protons in both crotonolactone and  $\beta$ -bromocrotonolactone have C-H bonds of essentially equal and fixed orientation with respect to the plane of the double bond. Therefore, the smaller allylic coupling constant in  $\beta$ -bromocrotonolactone results from a disturbance in the  $\pi$ -electron system by the bromine atom. The vincinal protons of  $\alpha$ -bromocrotonolactone couple more effectively than the corresponding protons of crotonolactone.

The chemical shifts for the  $\alpha$ ,  $\beta$  and  $\gamma$  protons are given in  $\delta$ -values in p.p.m. from tetramethylsilane and the coupling constants (J) are in c.p.s. (1) Crotonolactone (from Dr. Danny L. Stephenson):  $\alpha$ , 6.05;  $\beta$ , 7.65;  $\gamma$ , 4.88;  $J_{\alpha\beta}$  5.9;  $J_{\alpha\gamma}$  2.25;  $J_{\beta\gamma}$  1.7. (2)  $\alpha$ -Bromocrotonolactone (from Dr. Yoshiteru Hata):  $\beta$ , 7.65;  $\gamma$ , 4.87;  $J_{\beta\gamma}$  2.0. (3)  $\beta$ -Bromocrotonolactone:  $\alpha$ , 6.35;  $\gamma$ , 4.88;  $J_{\alpha\gamma}$  1.9.

Dr. M. G. Ettlinger's suggestions and discussions were helpful.

Sincerely yours,

*Tom J. Mabry*

Tom J. Mabry  
 Assistant Professor  
 Department of Botany  
 University of Texas  
 Austin, Texas 78712

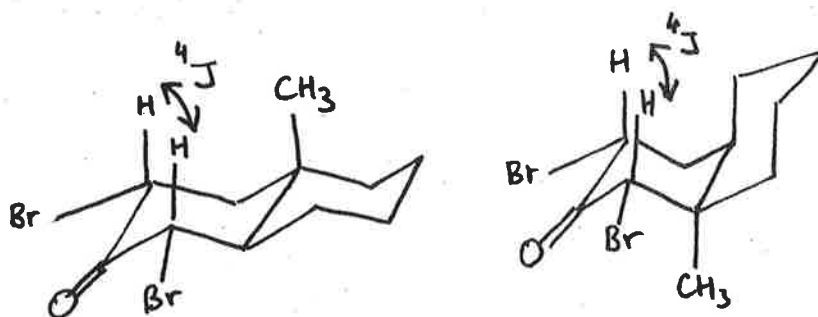
INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES  
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TÉL. 928 46-76

1<sup>er</sup> septembre 1964

Cher Barry,

Nous avons mesuré les couplages  $^4J$  indiqués, dans des bromodécalones  
obligeamment fournies par les Prs. Bordwell et Fétizon :



$$^4J = 1,0-1,3 \text{ cps}$$

Un Mémoire détaillé paraîtra au Bulletin de la Société Chimique.  
Veuillez créditer cette contribution à J.I.M.

Cordialement,

*Pierre Laszlo*  
Pierre Laszlo

*Jeremy I. Musher*  
Jeremy I. Musher



THE UNIVERSITY OF WESTERN ONTARIO  
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DEPARTMENT OF CHEMISTRY

LONDON, CANADA

September 3, 1964.

Dr. B. L. Shapiro,  
Dept. of Chemistry,  
Illinois Institute of Technology,  
Technology Center,  
Chicago, Ill., 60616, U.S.A.

Dear Barry,

Vinyl C<sup>13</sup> Shieldings of Some Substituted Styrenes

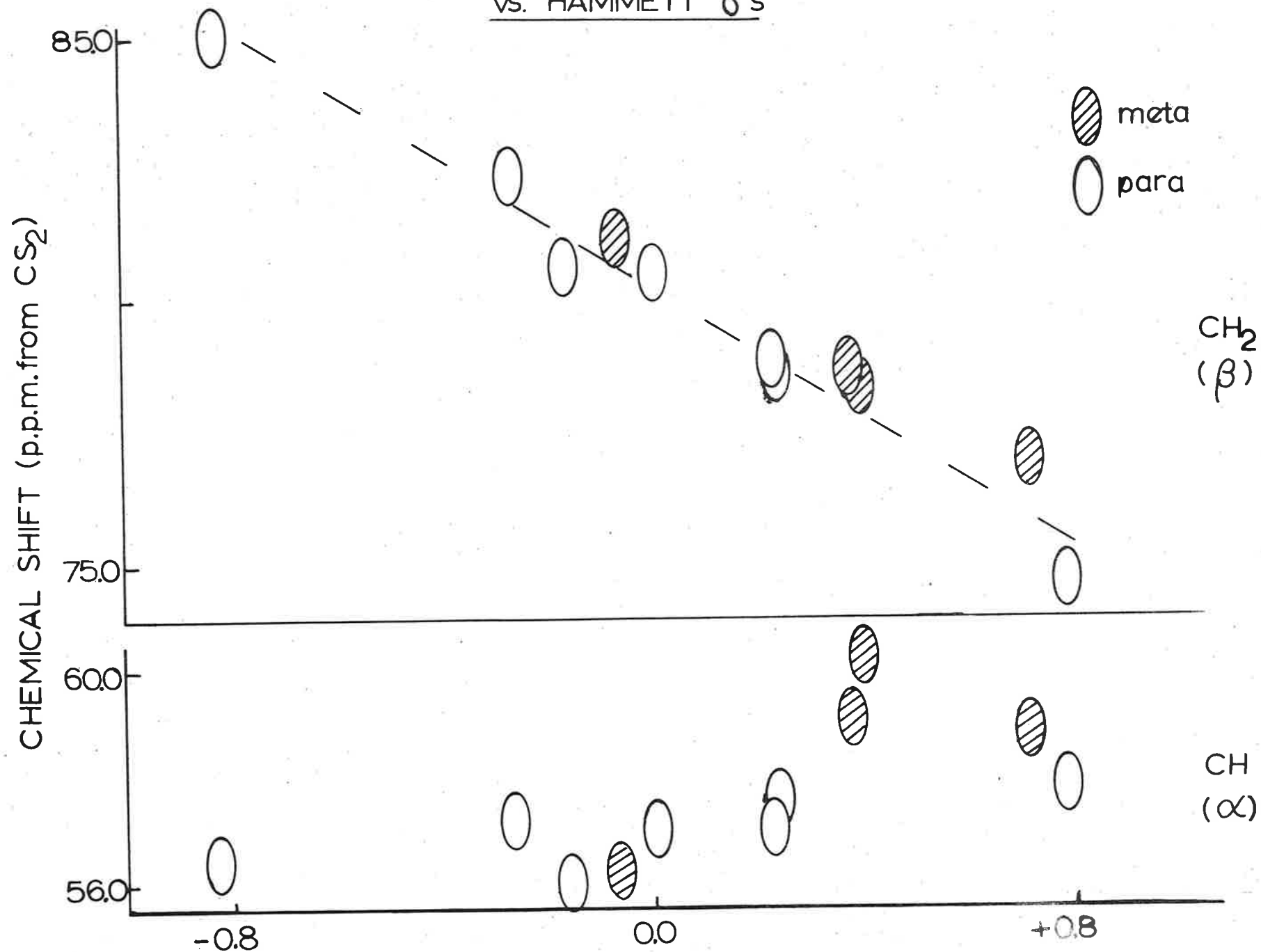
Judging from the number of comments in the No. 71 Newsletter, I am only one of several who are unable to keep track of time and so require your reminder for payment of my subscription to I.I.T. N.M.R.

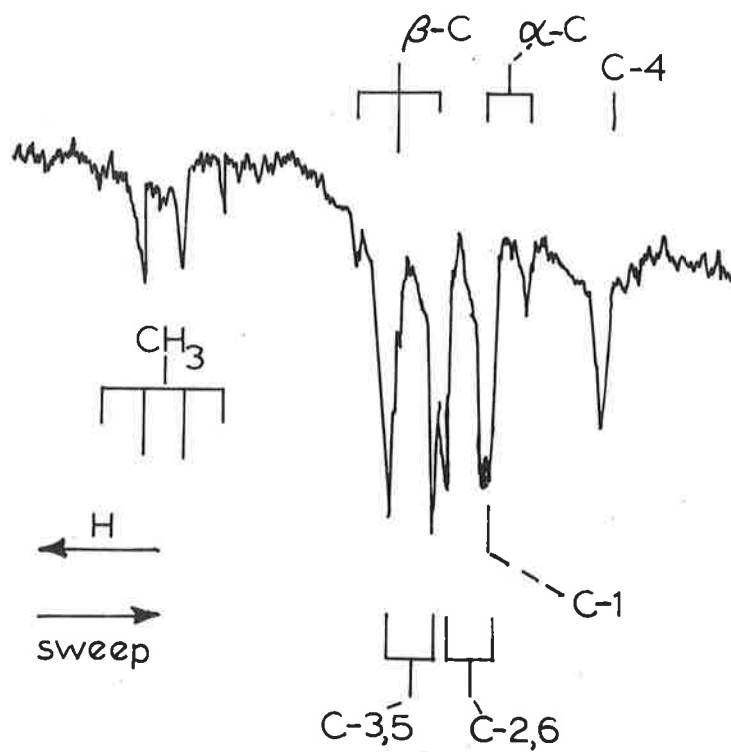
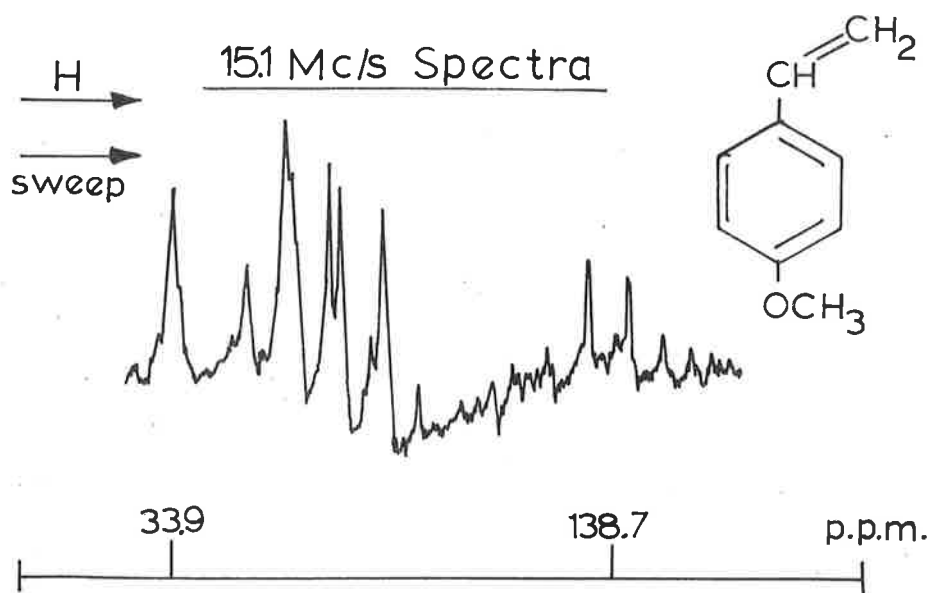
One feature observed in our survey of carbonyl compounds (reference to which has been made in No.'s 63 and 67) is the apparent lack of sensitivity of carbonyl carbon shieldings to meta- and para-substituents in, for example, acetophenones, benzoates and benzaldehydes. This result may be due to the fact that the carbonyl carbon nucleus is not at a terminal position in the resonance system so that there are no pronounced electron density changes with different polar substituents. As one possible test of this naive interpretation, a series of substituted styrenes has been examined to determine the effects of polar substituents at the vinyl carbons. One would expect the resonance position of the  $\beta$ -carbon nucleus to be dependent on the nature of a meta- or para-substituent if our present view is not totally incorrect. The series included the following substituents: meta- methyl, chloro, bromo and nitro; para- methyl, methoxyl, N,N-dimethyl-amino, chloro, bromo, and nitro. The observed shieldings for the vinyl carbon nuclei are plotted vs. the Hammett sigma parameter in one of the figures enclosed. It is clear that the  $\beta$ -C shielding is dependent on the polarity of the substituent and in the expected direction while the shielding of the  $\alpha$ -C nucleus exhibits approximately the same behavior as the carbonyl carbon in substituted acetophenones. It is interesting that the scatter is greater for the meta-derivatives in the latter cases. To determine the chemical shifts with any certainty for most of these cases we found it necessary to make extensive use of proton spin-decoupling since the vinyl absorption appears in the same region as that of the aromatic nuclei. One example of the sort of spectrum obtained is shown in the other figure enclosed and the assignments are indicated. The lower spectrum is run after first determining the appropriate decoupler frequency for each multiplet separately and then changing the decoupling frequency while sweeping through the C<sup>13</sup> spectrum. The NMR Specialties, Inc. SD-60 decoupling unit was used for these experiments. (The sweep rates are slightly different for the two spectra illustrated.)

Sincerely,

*Jake*  
J. B. Stothers  
Associate Professor

VINYL  $C^{13}$  SHIELDINGS of m- and p-SUBSTITUTED STYRENES  
vs. HAMMETT  $\sigma$ 's





Perkin-Elmer NMR; <sup>u</sup>Aqueous referencing; Plea for compounds

I have been operating a Perkin-Elmer 60 Mcs. proton MR instrument for 10 months now. This has a built-in 200/400 cps. calibrating oscillator controlled by a 4 Kcs. crystal. We could not understand why we were getting chemical shifts some  $\frac{1}{2}\%$  in error although the crystal was spot on, until the P-E service engineer found the oscillator circuit to be free running and its nominal 400 cps. was really 398 cps.

I have investigated the system resorcinol-water and was therefore interested in the letter of E.S.Hand<sup>1</sup> describing his similar system. We too experimented with dioxan as internal standard, and find that with increasing resorcinol concentration the dioxan line does indeed move upfield. But Hand apparently made no allowance for bulk diamagnetic susceptibility effects and we have<sup>2,3</sup>. We then find that the dioxan moves upfield and the "water" peak downfield. The results are shown in the accompanying figure<sup>4</sup>.

In connection with our high-resolution work, we have a compound which we believe may be

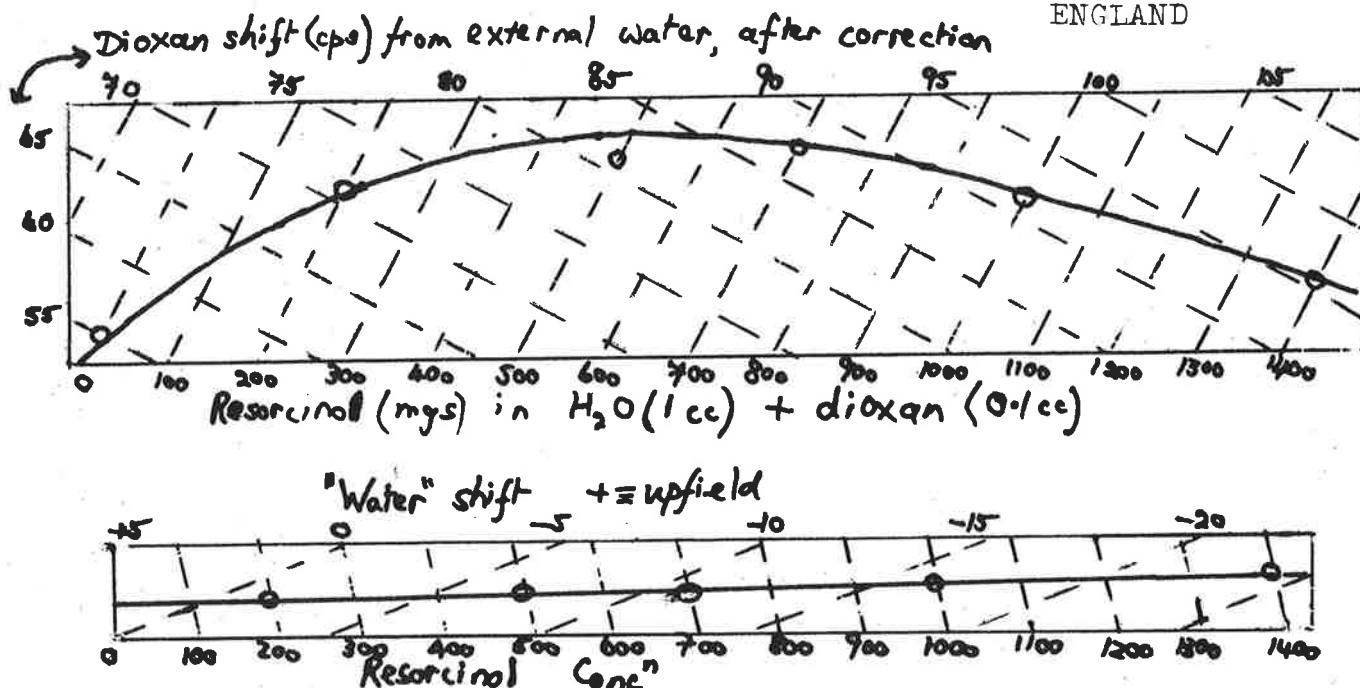


has anybody any spectra or compounds they would be willing to let us have, to help in identifying the proposed 1-acyl oxytetrahydrofuran end?

1. HAND Newsletter No.69
2. ZIMMERMAN and FOSTER J.Phys.Chem., 61 282(1957)
3. FREI and BERNSTEIN J.Chem.Phys., 37 1891(1962)
4. LAUTERBUR Newsletter No.47

*Jordan Hall*

Colworth House  
SHARNBROOK  
BEDFORD  
ENGLAND



**THE OHIO STATE UNIVERSITY**

DEPARTMENT OF CHEMISTRY  
88 WEST 18TH AVENUE  
COLUMBUS, OHIO 43210

September 1, 1964

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

HR-60 Sources of Instability and Multiple R. F. Unit Switching

Dear Barry:

We have had instability problems in the HR-60. We hope that this communication will be of use to other people with similar problems. Although each of the following deficiencies could have caused the instability alone, instability generally comes from several sources acting in concert in a complicated way.

Magnet Power Supply (V-2100B)

- (1) The cathode-filament buss bars were corroded. We removed all connections and cleaned them with steel wool.
- (2) Three of the grid caps on the 304 TL's were internally broken.
- (3) On one of the 872 A's, the plate stud was pulled loose from the glass envelope.
- (4) The plate lead connection to the cooling fins of the 304 TL's were badly corroded.
- (5) The 304 TL's were old and were conducting unequally. - Replaced the whole set.
- (6) The Power Supply was generally dirty. We cleaned it up.

Super Stabilizer (V-3506)

- (1) Balance Operate switch was taken apart and cleaned with emery paper.
- (2) All coper-to-copper contacts in the 5 ohm insert were also cleaned the same way, including the leads to the stabilizer coils.
- (3) The leads into the socket of the light bulb were making bad connection. The wires were restripped, doubled and then replaced in the socket.
- (4) Completely realigned the optical system.

Slow Sweep Unit (V-3507)

- (1) A very common trouble here was unsoldered connections on the resistor board. We soldered the rivets to the lugs on the battery holders.
- (2) The switches were all cleaned.
- (3) Removed the Jones plug and soldered the leads to each other directly.

Dr. B. L. Shapiro  
September 1, 1964  
Page 2

- (4) Soldered the crimped lugs on the 2.7 volt battery.

Probe (V-4331A)

- (1) Took the probe apart and cleaned each piece with  $\text{CCl}_4$ .  
(2) Insured the transmitter coil was firmly attached to the Faraday Shield.  
(3) Glued all components into position with Duco cement so there would be no movement.  
(4) Checked insert for cracks.

The final considerations for instability are the temperature control of air and magnet water. We use a diffused air system to hold the room temperature to  $1^\circ\text{C}$ . and the water system should hold the magnet temperature to  $1^\circ\text{C}$ . above room temp. and control to  $1^\circ\text{C}$ . with distilled water.

We have both Hydrogen (60 mc.) and Boron (19.3 mc.) R. F. Units. We found it time consuming and troublesome to switch all the cabling and to turn the system on and off whenever we wanted to change frequencies. Therefore, we have a switching system which will work with any number of R. F. Units although we only have two.

Our system was a DP-60 but it was decided that we were not going to run Wide Line spectra so all of these components were removed. We also removed all the cabling in the console and recabled using a different Selector Panel. We mounted the Boron R. F. Unit in the console in the right hand table top. A Probe holder was built and attached to the right of the console and holds the Probe (already connected to the R. F. Unit) not in use. We removed the Selector Panel that was originally used.

We do all the change over between frequencies by just putting the new Probe in the field changing to the correct sweep cable, and by switching the knobs on the Selector Panel to their correct positions, see enclosed schematic, *see diagram*.

To those interested in this system, be sure you have non-short-  
ing switches able to handle the respective currents.

For any further questions please contact us directly.

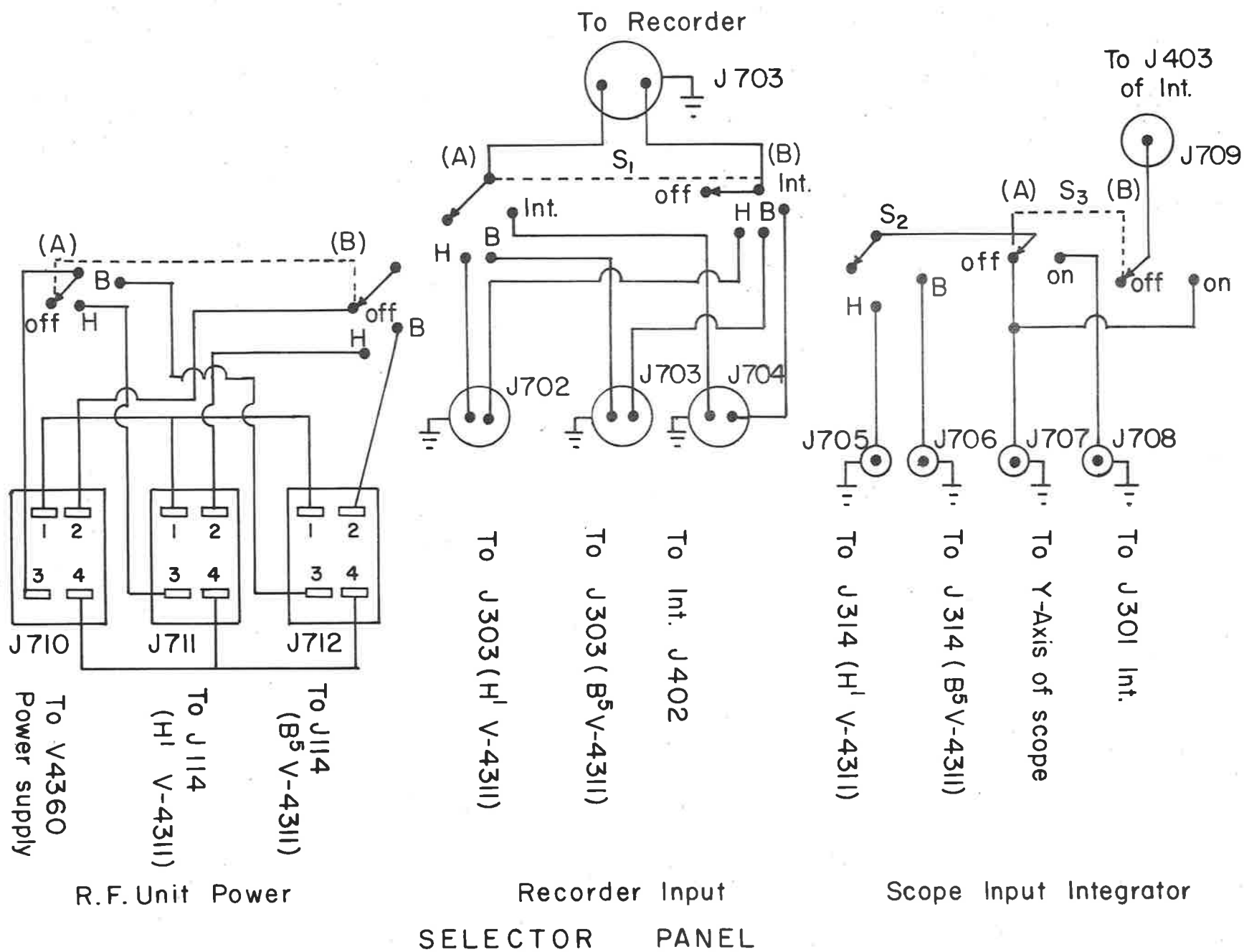
$\text{P}^{31}$  and  $\text{Li}^7$ : We now obtain NMR spectra for both of these isotopes using the  $\text{B}^{11}$  probe, 19.3 mc.;  $\text{Li}^7$  comes at 11.66,  $\text{P}^{31}$  at 11.2 K.G. respectively.

Yours sincerely,

*Howard C. Meyer*  
Howard C. Meyer

*Gideon*

Gideon Fraenkel  
Assistant Professor of Chemistry





LABORATORIUM  
VOOR  
ORGANISCHE CHEMIE

Dir.: Prof. Dr. F. GOVAERT

GENT, September 9th 1964.

J. Plateaustraat, 22

Tel. 25.28.02

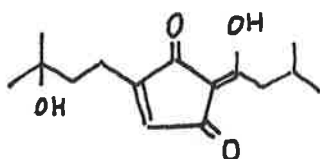
Dr. B. L. SHAPIRO,  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Center,

CHICAGO, Illinois 60616.

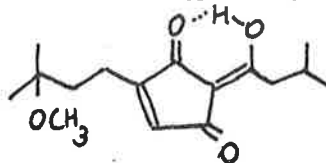
Concerning : Differentiation of proton signals by (enolic) tautomerism.

Dear Dr. Shapiro,

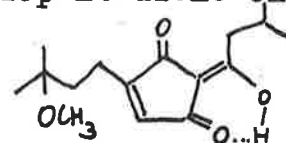
We have elucidated at these laboratories the structure of some isomeric humulinic acids (isomers A, B<sup>1</sup>, C, D<sup>2</sup>) which are derived from the degradation of "humulone", one of the main constituents of hops (*humulus lupulus*). One of these, HAD (I), is especially interesting with respect to its P.M.R. spectrum. As it is extremely difficult to isolate it as such, the most data were obtained through its methyl derivative which has structure II. Its enolization should be rather exocyclic as illustrated, since it is known that cyclopentadiene-one



I



IIa



IIb

systems are in general very unstable. We observe in the P.M.R. structure two olefinic triplets ( $\delta = 6,39$  and  $6,48$ ) with a total surface corresponding to one proton, the allylic coupling being  $J^3 = 1,5 \pm 0,1$  c/s (Fig. 1a). This must be attributed to two different tautomeric structures as illustrated (IIa and IIb). With an upfield irradiation at  $+ 231$  c/s the triplets become singlets.

The enolic resonance peak at  $\delta = 11,73$  points to a rather strong hydrogen bridge. Yet we should not expect any resonance-stabilization, the latter demanding the enolic double bond to become endocyclically. Furthermore this peak, although possessing a broad line width, is single in contrast to the doublets of triplets. From this we can conclude that the rate of proton exchange is faster than the rate of rotation around the exocyclic (double) bond.

We have added two drops of trifluoro acetic acid to the 10 %  $\text{CCl}_4$  solution. Some broadening of the two triplets is observed, and only by adding more trifluoroacetic acid the peaks collapse into one singlet (fig. 1b).

We hoped also to obtain some more information in running the spectrum in DMSO (dimethylsulfoxide) for which it is known that protonic exchange for alcohols is more difficult<sup>3</sup>. To our surprise how-

.../...





UNIVERSITY OF SOUTH FLORIDA  
TAMPA, FLORIDA 33620

AREA CODE 813: 988-4131

September 9, 1964

Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

The factor of  $3/16$  in the expression for  ${}^4I_{HH'}$ , which I reported in IIT NMR Letter No. 71, p. 20, should be replaced by  $3/8$ . The treatment is, however, semi-empirical in that similar eqns. were used to estimate the exchange integral parameters,  $K(C_i, \gamma_j)$  from other types of coupling constant data. The recalculated results, in which the minima in Fig. 1 and the maxima in Fig. 2 are increased by about 0.2 cps, will be reported in J. Chem. Phys.

For what it may be worth, use of the same equation and exchange integral parameters, yields  ${}^5I_{HH'} = 0$  to  $+0.4$  cps for proton coupling over five saturated bonds. The maximum value corresponds to the completely staggered conformation.

Sincerely yours,



Michael Barfield  
Assistant Professor, Chemistry

MB:af

## U.S. DEPARTMENT OF COMMERCE

## NATIONAL BUREAU OF STANDARDS

ADDRESS REPLY TO

NATIONAL BUREAU OF STANDARDS

WASHINGTON, D.C. 20234

9 September 1964

IN YOUR REPLY  
REFER TO FILE NO.  
313.01

Professor B. L. Shapiro  
Department of Chemistry  
\* Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60616

$^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{11}\text{B}$  Spectra of  $\text{HBF}_2$

Dear Professor Shapiro:

We submit the following, and request that Dr. Farrar's name be added to the mailing list to receive the ITT NMR Newsletter.

We have obtained high resolution boron, fluorine, and proton n.m.r. spectra, over a  $90^\circ$  temperature range, for the recently reported<sup>1</sup> compound difluoroborane ( $\text{HBF}_2$ ). The n.m.r. parameters for this compound are of considerable interest, inasmuch as it is a member of a very small class of compounds containing hydrogen bonded to a three-coordinate boron atom, and the only such derivative containing both hydrogen and fluorine.

The spectra were recorded at 60.0 ( $^1\text{H}$ ), and 56.4 ( $^{19}\text{F}$ ), and 19.25 ( $^{11}\text{B}$ ) MHz with a Varian HR-60 Spectrometer modified for low-temperature work. Measurements were made over the temperature range  $140^\circ$  to  $230^\circ\text{K}$  for four different samples containing difluoroborane and varying amounts of boron trifluoride and diborane. Representative spectra are shown in the figures. Sample compositions and chemical shifts are given in Table I.

Table I

Sample Composition and Chemical Shifts						
Sample	% $\text{HBF}_2$	% $\text{BF}_3$	% $\text{B}_2\text{H}_6$	$\delta \text{H}^a$	$\delta \text{F}^b$	$\delta \text{B}^b$
1	75	20	5	-0.12	-61.5	
2	50	50	1	-	-62.3	11.7
3	95	5	1	-	-59.6	12.0
4	10	90	-	-	-62.8 <sup>c</sup>	

<sup>a</sup>Shift in p.p.m. from center of terminal hydrogen quartet in diborane.

<sup>b</sup>Shift in p.p.m. from  $\text{BF}_3$ . The  $\text{BF}_3$  resonance was a single line in all samples.

<sup>c</sup>In this sample the  $\text{BF}_3$  resonance spectrum was a 4-line multiplet. The  $\text{BF}_3$  and  $\text{HBF}_2$  concentrations were estimated from the heights of the  $^{19}\text{F}$  resonance.

The proton chemical shift is only slightly different from that of the terminal protons in diborane. The fluorine chemical shift, though somewhat dependent upon sample composition, is in the region of shifts observed in halo-<sup>2</sup> and alkylboron difluorides<sup>3</sup>.

Professor B. L. Shapiro

- 2 -

9 September 1964

As indicated in the figures, the spectra obtained at the higher temperatures are clearly consistent with the monomeric structure of the compound<sup>1</sup>. The following values were obtained for the spin coupling constants:  $J_{\text{HF}} = 108 \pm 1$ ,  $J_{\text{11BH}} = 211 \pm 1$ ,  $J_{\text{11BF}} = 84 \pm 1$  Hz. All coupling constants are averages taken from at least fifteen spectra.  $J_{\text{HF}}$  is constant within experimental error throughout the entire temperature range.  $J_{\text{11BH}}$  and  $J_{\text{11BF}}$  have the values given above in the temperature range 230°K to about 165°K. Below 165°K the multiplet structure arising from the  $\text{11BH}$  of  $\text{11BF}$  coupling begins to collapse, owing to the interaction of rapidly fluctuating electric field gradients with the electric quadrupole moment of boron<sup>4</sup>. The spin coupling constants were all independent of sample composition.

The value of 211 Hz for  $J_{\text{11BH}}$  --the largest yet observed for a boron-hydrogen coupling constant--is of some interest in connection with the possibility that  $J_{\text{11BH}}$  may be related to the boron hybridization. The  $J_{\text{11BH}}$  values for many four-coordinate boron compounds range from 80 Hz in  $\text{BH}_4^-$  up to 100 Hz in some borane complexes. For compounds containing hydrogen bonded to three-coordinate boron, typical values are ca. 135 Hz (in borazoles) to 141 Hz (in  $\text{HB}[\text{OCH}_3]_2$ ). It is interesting to note that the analogous C-H coupling constant in the isoelectronic  $\text{FCHO}$  is also "high" as are CH coupling constants in a number of fluorinated derivatives.

Preprints of an article prepared for publication are available.

#### References

1. T. D. Coyle, J. J. Ritter, and T. C. Farrar, Proc.Chem.Soc., 25 (1964).
2. T. D. Coyle and F. G. A. Stone, J.Chem.Phys., 32 1892 (1960).
3. T. D. Coyle, S. L. Stafford, and F. G. A. Stone, J.Chem.Soc. 83, 3103 (1961).
4. J. Bacon, R. J. Gillespie, and J. W. Quail, Can.J.Chem., 41, 3063 (1963).

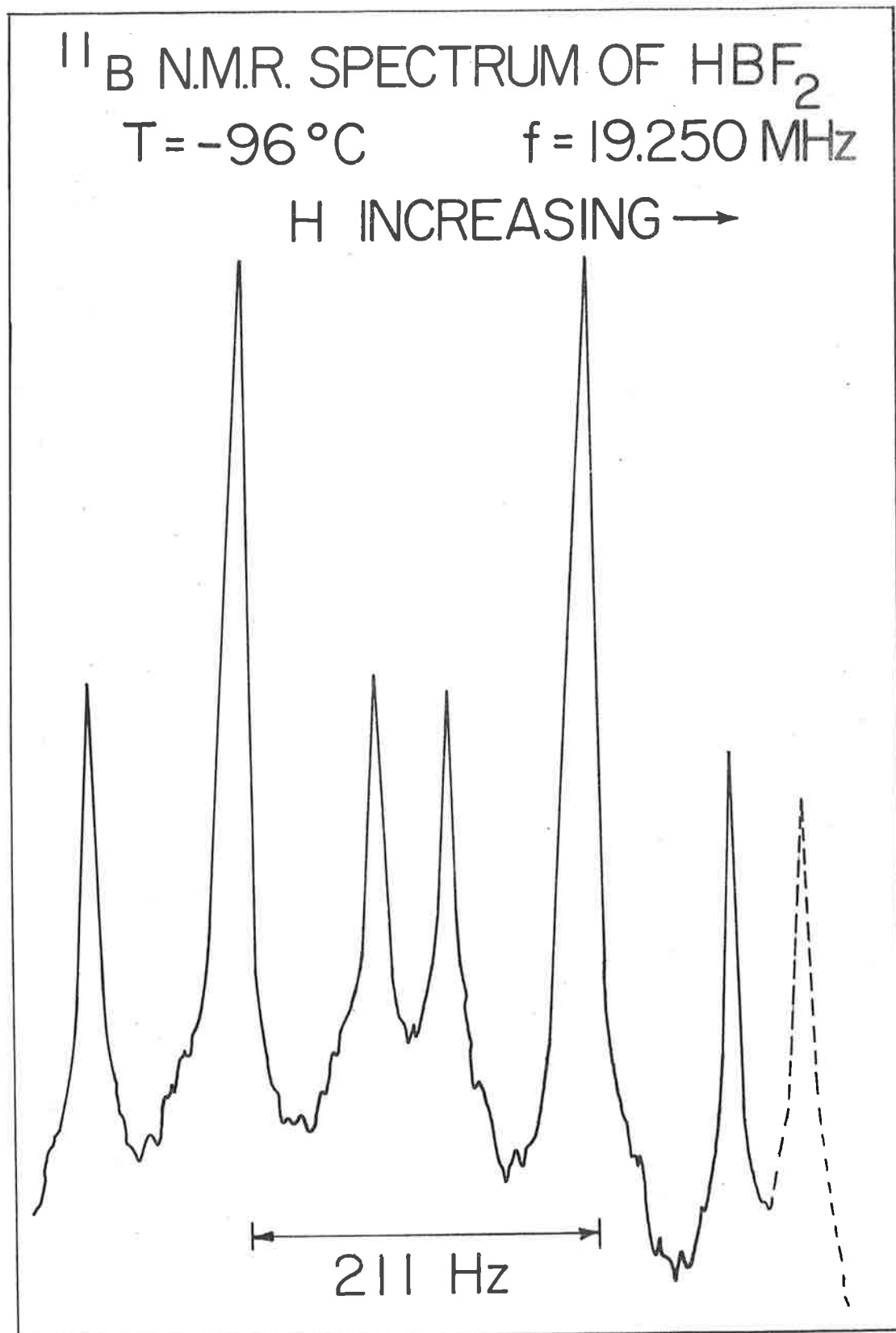
Sincerely yours,

*Thomas C. Farrar*

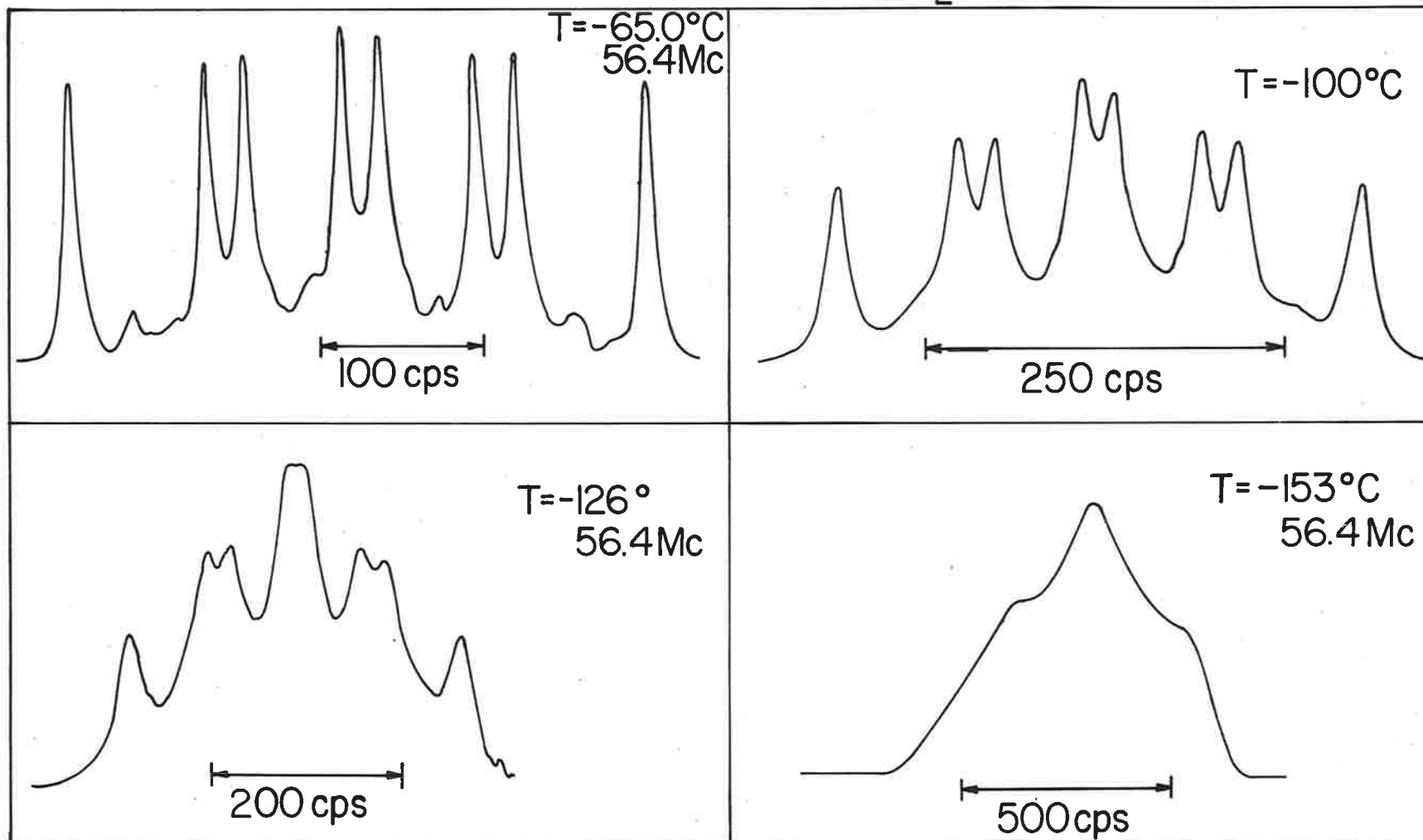
Thomas C. Farrar  
Inorganic Chemistry Section

*Thomas D. Coyle*

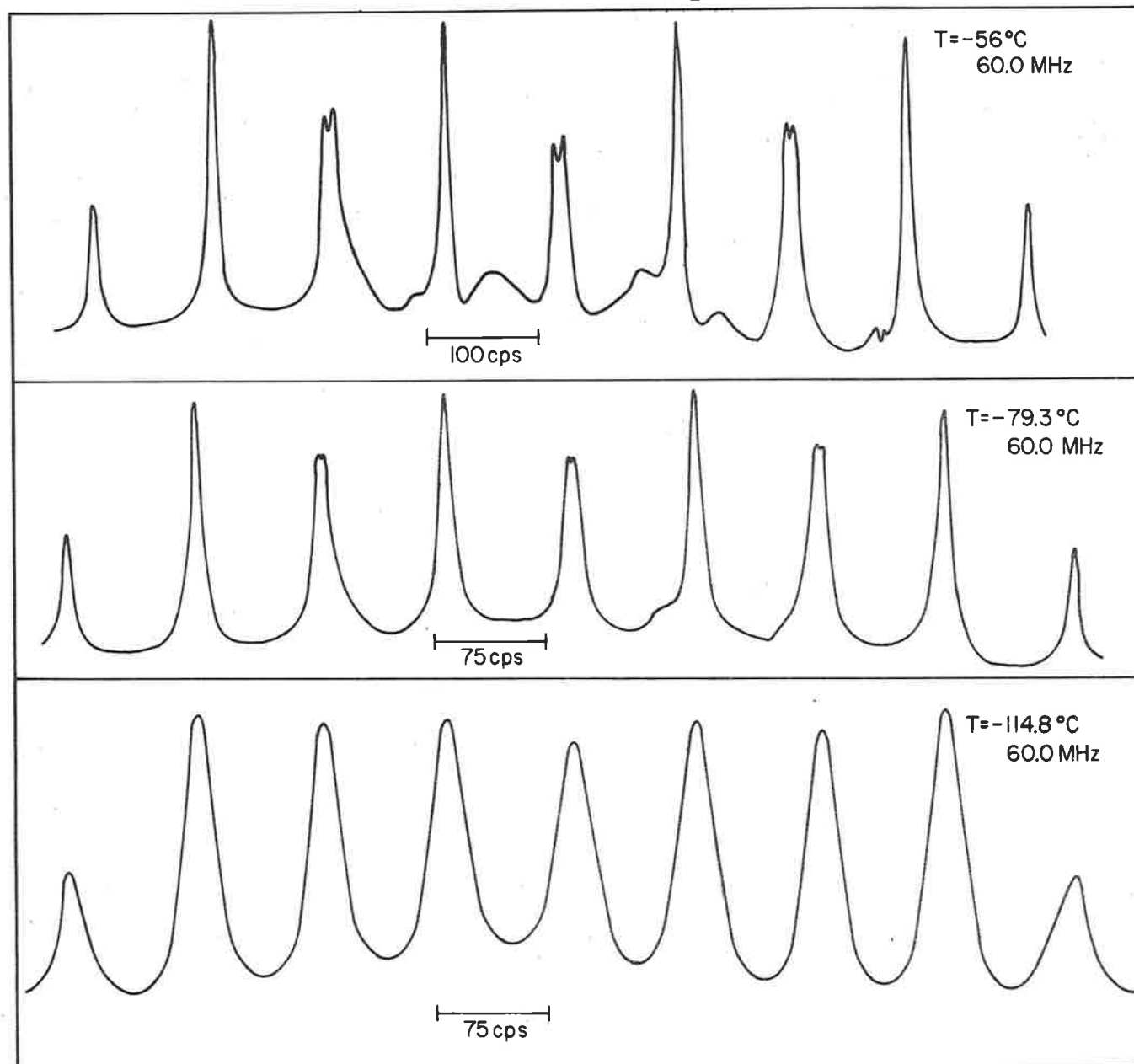
Thomas D. Coyle, Chief  
Inorganic Chemistry Section



SAMPLE COMPOSITION      95%  $\text{HBF}_2$   
                                         5%  $\text{BF}_3$   
Solid line is  $\text{HBF}_2$ ; Dotted line is  $\text{BF}_3$

$^{19}\text{F}$  N.M.R. SPECTRUM OF  $\text{HBF}_2$ 

H' SPECTRUM OF HBF<sub>2</sub>



UNIVERSITÉ DE STRASBOURG  
Faculté des Sciences

# INSTITUT DE CHIMIE

2, rue Goethe  
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Boîte postale 296

Professor G.OURISSON

STRASBOURG, le September 11<sup>th</sup>, 1964.

Dr. B.L.SHAPIRO

Department of Chemistry

Illinois Institute of Technology

CHICAGO

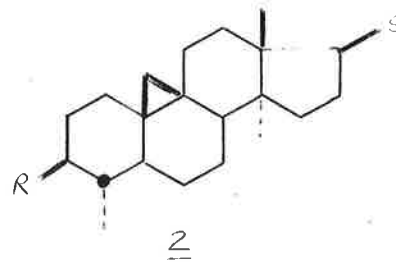
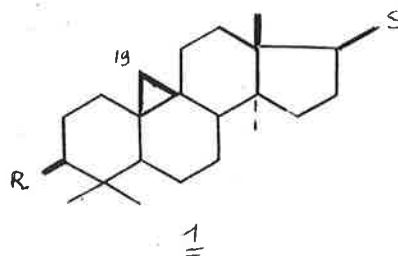
60616

## RMN de dérivés cyclolanostaniques

Cher Dr. Shapiro,

Nous poursuivons l'utilisation systématique de la RMN dans l'étude de polyterpènes. Grâce à la réduction sensible des quantités de matière nécessaires avec les micro-cellules, nous avons pu en particulier identifier une série étendue de triterpènes d'origine diverse, dont certains dans les cultures de tissus végétaux ("plant tissue cultures"). Ce dernier travail est en cours de publication dans Compt.Rend. Ac.Sc., sous forme de notes brèves.

A plusieurs occasions, nous avons ainsi comparé des dérivés du 9:19 cyclo lanostane 1, et les dérivés mono méthylés en 4 correspondants 2.



Dans tous les cas, le système AB du méthylène cyclopropanique C-19 est bien visible, comme cela est connu depuis longtemps. Nous voudrions signaler que la position de ce système AB, mais pas le couplage  $J_{AB}$ , dépend de la substitution en C-4, d'une manière très nette et qui nous a été très utile sur le plan

.../...



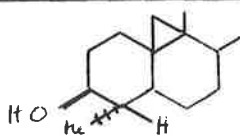
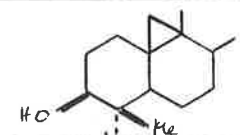
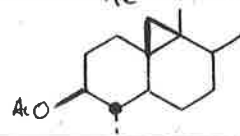
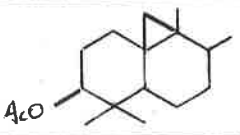
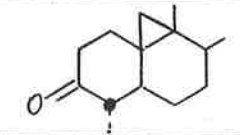
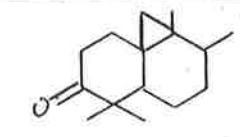
diagnostic (Tableau I). Cette remarque prend tout son sens si l'on observe que, dans la famille en question, les chaînes latérales variées, plus ou moins alcoylées, rendent difficile l'attribution sûre de tous les groupes méthyles.

J'espère que notre prochaine contribution présentera un caractère plus fondamental.

Bien cordialement

*Gouin*

Tableau I (Analyse exacte du système AB)

Cycle A	Signaux (cps à partir du: TMS, 60 Mc)	A (ppm)	B	J AB (cps)
	5, 9, 20, 24	0,11	0,36	4
	17, 21, 31, 35	0,32	0,58	4
	6, 10, 22, 26	0,13	0,40	4
	18, 22, 34, 38	0,33	0,60	4
	22, 26, 36, 40	0,44	0,63	4
	31, 35, 45, 49	0,56	0,80	4

NORTH CAROLINA STATE  
OF THE UNIVERSITY OF NORTH CAROLINA  
AT RALEIGH

SCHOOL OF PHYSICAL SCIENCES  
AND APPLIED MATHEMATICS  
DEPARTMENT OF CHEMISTRY

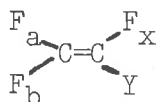
P. O. Box 5247  
RALEIGH, N. C. 27607

September 5, 1964

Dr. Bernard L. Shapiro  
Technology Center  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Dr. Shapiro,

Dr. W. S. Brey, Jr. (University of Florida) and I have looked at a number of trifluorovinyl compounds of the type  $\text{F}_a\text{F}_b\text{C}=\text{CF}_x\text{Y}$  and have found that the chemical shifts of  $\text{F}_a$  and the coupling constants,  $J_{ab}$ , depend upon the conjugating ability of the substituent, Y. The data obtained on a representative number of the compounds studied are listed below.



<u>Y</u>	<u>Chemical Shifts of <math>\text{F}_a</math> from <math>\text{CF}_3\text{COOH}</math>, ppm</u>	<u><math>J_{ab}</math>, cps</u>
Group I		
$-(\text{CH}_2)_2\text{Br}$	26.9	84.8
$-(\text{CH}_2)_4\text{CF}=\text{CF}_2$	30.4	91.4
$-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	30.1	92.5
$-\text{Cl}$	25	78
$-\text{H}$	23	87
Group II		
$-\text{OCF}_3$	40.8	87.5
$-\text{OCH}_2\text{CF}_3$	46.6	101.6
Group III		
$-\text{COF}$	0.6	6.6
$-\text{CN}$	3.2	28.4
$-\text{SCF}_3$	6.9	30.4
$-\text{Si}(\text{CH}_3)_3$	11.3	71.6
$-\text{CF}_3$	19.0	57.5

Dr. Bernard L. Shapiro

2

September 5, 1964

Each of the compounds of Group I has a substituent that would not be expected to enter into conjugation with the trifluorovinyl group. The two compounds in Group II have a substituent which could enter into conjugation by contributing electrons to the trifluorovinyl group. The chemical shift values for  $F_a$  in these compounds are 10 to 23 ppm higher than the values for the compounds in Group I. Each of the compounds of Group III has a substituent which could enter into conjugation by withdrawing electrons from the trifluorovinyl group. The chemical shift values for  $F_a$  in the compounds of Group III are 7 to 37 ppm lower than those of Group I, and 21 to 53 ppm lower than those of Group II.

The above proposal that the different substituents in Group III are capable of withdrawing electrons from the trifluorovinyl group can be rationalized as follows: (1) the ability of sulfur, iodine and silicon<sup>1</sup> to withdraw  $\pi$  electrons from an unsaturated system to which they are bonded by utilizing vacant d orbitals, (2) the ability of the highly electronegative group,  $-CF_3$  to participate in double bond-no bond resonance<sup>2</sup> and (3) 1,3 conjugation in  $CF_2=CFCOF^3$  and  $CF_2=CFCN$ .

The values for  $J_{ab}$  also follow the order Group II > Group I > Group III.

Dr. George H. Wahl, Jr., Dr. Carl L. Bumgardner and I have recently joined the Chemistry Department at North Carolina State and are looking forward to doing research on a new HA-100 spectrometer. We realize that participation is the prime requirement for receiving the IIT NMR Newsletter, so I am sending this contribution and I hope it will be of some interest to the readers.

Sincerely,

*Charles G. Moreland*

Charles G. Moreland  
Assistant Professor

CGM: jw

#### References:

- (1) R. T. Hobgood, J. H. Goldstein, and G. S. Reddy, J. Chem. Phys. 35, 2038 (1961).
- (2) J. Hine, J. Org. Chem. 85, 32 (1963).
- (3) W. S. Brey, Jr., and K. C. Ramey, J. Chem. Phys. 39, 844 (1963).

## PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY  
LAFAYETTE, INDIANA 47907

September 14, 1964

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago 16, Illinois

Dear Barry:

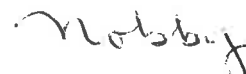
A recent article by F. Takahashi and N. Li (J. Phys. Chem. 68, 2136 (1964)) raises the question whether the change in chemical shift caused by formation of a hydrogen bond does or does not vary with the temperature.

As a matter of fact, we have had this question under investigation for some time and Mr. Richard C. Reiter has just produced a Ph. D. thesis concerned primarily with this point. We find that the proton shift in a typical, hydrogen-bonded species, represented as  $O-H\cdots O^1$ , should change with the temperature even if it is assumed that the hydrogen bond never breaks. This is a result of the variation of the chemical shift with the degree of excitation of the low-frequency, hydrogen-bond stretching, vibrational mode. This mode is almost certainly sufficiently anharmonic to lead to pronounced change in the effective  $H\cdots O^1$  distance with increasing excitation, and the chemical shift is very sensitive to such changes.

We are just submitting a preliminary communication of these results to the Journal of Chemical Physics and expect to have a few preprints for readers of the Newsletter who might want them. The title might as well serve also as a title for the epistle: "Temperature--Dependence of Chemical Shifts of Protons in Hydrogen Bonds."

With best regards.

Sincerely,



Norbert Muller

NM:jj

## Proton Magnetic Resonance Spectrum of N-Methyl Methylenimine\*

D. F. KOSTER AND A. DANTI

Department of Chemistry, Texas A&M University  
College Station, Texas

AND

J. HINZE AND R. F. CURL, JR.

Department of Chemistry, Rice University  
Houston, Texas

Pure liquid samples of the simple but rather reactive species  $\text{CH}_3\text{-N=CH}_2$  were studied at  $-55^\circ\text{C}$  to obtain the NMR constants of the molecule and to compare them with those of other more stable  $\text{CH}_2\text{=N-}$  systems previously studied<sup>1,2</sup>.

The compound was prepared with the same equipment and by the same procedure described by Sastry and Curl<sup>3</sup>. The high purity that was attained (as evidenced by the NMR spectrum) was aided by the fact that numerous preparations had been made before for the microwave studies<sup>3</sup>. Spectra were obtained with the Varian Model A-60 spectrometer equipped with a variable temperature probe. It was found that polymerization proceeds very slowly even at  $-55^\circ\text{C}$ , but it was not possible to obtain a lower probe temperature at the time of the studies. A number of spectra of a fresh sample could easily be obtained at  $-55^\circ\text{C}$  before small particles of polymer floating around in the liquid began to decrease the resolution or before polymer peaks appeared. A sudden exothermic and complete polymerization occurs at about  $-35^\circ\text{C}$ <sup>4</sup>.

Figure 1 shows the fairly good resolution that was achieved in spite of quadrupolar effects from the nitrogen nucleus. As in previous studies of related systems<sup>1,2</sup>, the resonances of the geminal proton that occur at higher field ( $\delta=6.95$ ) are especially broadened and in this case the methyl resonance is also noticeably broadened. Although the

usual constants can be obtained quite well from a first-order interpretation of an  $ABX_3$  case, the values were refined by iterating to a converged solution with the computer program of Reilly and Swalen<sup>5</sup>. Following the designation in Fig. 1 and previous assignments<sup>1,2</sup>, the chemical shifts in ppm from TMS as zero are  $X=3.20$ ,  $B=6.95$ , and  $A=7.24$ ; the coupling constants are  $J_{AB}(\text{gem})=16.32$  and  $J_{AX} \approx J_{BX}=1.57$  cps. The broader resonances of the B or trans proton would indicate that the coupling of  $^{14}\text{N}$  with B is several times greater than that with A or X.

The results obtained agree quite well with studies of similar systems. For example, the geminal couplings  $|J|_{\text{HH}}(\text{gem})$  for the neat liquids of  $\text{CH}_2=\text{N}-\text{C}(\text{CH}_3)_3$  and  $\text{CH}_2=\text{N}-\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$  were found to be 16.52 and 16.97 cps respectively<sup>1,2</sup>. The large value of the geminal coupling constant is in agreement with previous work<sup>1,2,6</sup> and with recent theoretical studies of Bothner-By and Pople<sup>7</sup>.

---

\*These studies were supported by grants to both Universities from The Robert A. Welch Foundation of Houston, Texas.

<sup>1</sup>B. L. Shapiro, S. J. Ebersole, G. J. Karabatsos, F. M. Vane, and S. L. Manatt, J. Am. Chem. Soc. 85, 4041 (1963). Attention is also called to the many references cited therein and they will not be repeated here.

<sup>2</sup>B. L. Shapiro, S. J. Ebersole, and R. M. Kopchik, J. Mol. Spec. 11, 326 (1963).

<sup>3</sup>K. V. L. N. Sastry and R. F. Curl, Jr., J. Chem. Phys. 41, 77 (1964).

<sup>4</sup>J. L. Anderson, U. S. Patent 2,729,679 (January 1956).

<sup>5</sup>C. A. Reilly and J. D. Swalen, J. Chem. Phys. 37, 21 (1962).

<sup>6</sup>B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, J. Chem. Phys. 39, 3154 (1963).

<sup>7</sup>A. A. Bothner-By and J. A. Pople, A copy of their manuscript was made available to us prior to publication.

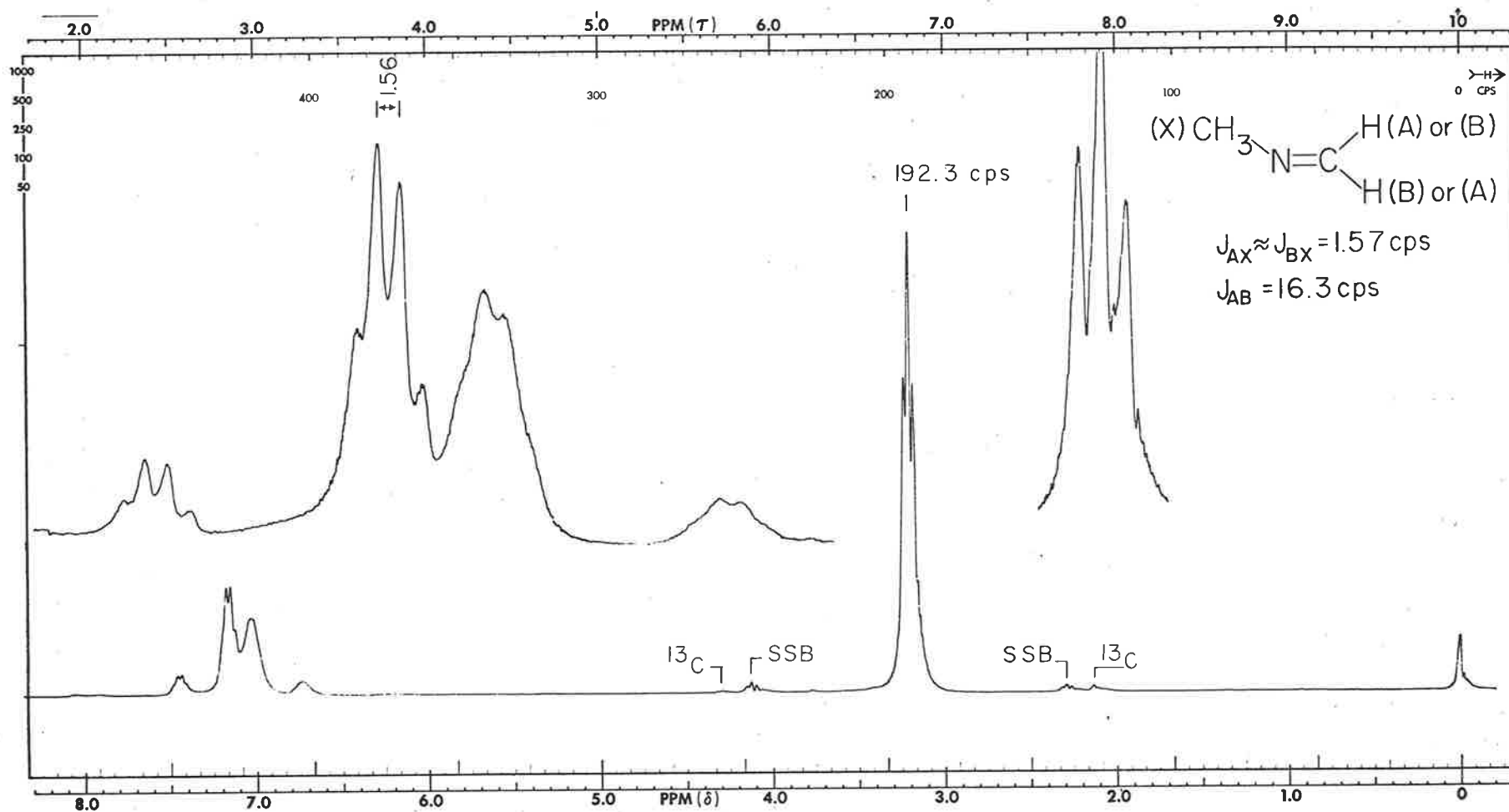


Fig. 1. The proton magnetic resonance spectrum of pure N-Methyl methylenimine liquid obtained at  $-55^\circ\text{C}$  with a Varian Model A-60 spectrometer.

CALIFORNIA STATE COLLEGE



AT LOS ANGELES

Department of Chemistry

5151 State College Drive, Los Angeles, California 90032  
(San Bernardino and Long Beach Freeways Interchange)  
Telephone 225-1631 (Area Code 213)

September 15, 1964

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60616

Dear Barry:

Recent measurements, here and elsewhere, have shown that the pH dependence of the nuclear resonance position of carbon bonded protons in amino acids can be used to indicate qualitatively the degree of protonation of these molecules. Observe the  $\delta$  - pH curves of Fig. 1 for 2M aqueous mixtures of glycine and DL-alanine. At high and low pH values, the  $\text{CH}_2$  resonance position of glycine, for example, corresponds to the species  $\text{NH}_2\text{CH}_2\text{COO}^-$  and  $^+\text{NH}_3\text{CH}_2\text{COOH}$ , respectively. The methyl signal of alanine behaved similarly but the slopes were not as sharp, presumably because this group is an extra bond removed from the protonation site. In the region over which the shifts are independent of pH ( $\sim 4-8$ ) dipolar species of the amino acids predominate.

This information proved particularly valuable in our studies of amino acid complexing with added electrolytes. Normally, one would study such solutions in basic media to provide two sites for complexing, the carboxyl group and the nitrogen lone pair. However, one must take into account possible cation hydrolysis which can produce results which are ambiguous. Thus, ions such as Zn, Cd, Mg, and to a greater extent, Be and Al, can lower the pH by several units as a result of hydrolysis at a concentration of 1M. From Fig. 1, a pH change in the range 12-9, for example, can cause shifts as large as 0.4 ppm. Thus, when investigating amino acid complexing, the pH of the solution must be closely controlled. We have conducted our measurements with the ions mentioned above, and others, in amino acid solutions of pH 4-8. We can, therefore, attribute the shifts which we observed entirely to ion-dipole interactions.

Anthony Fratiello

*Anthony Fratiello*

Calvin Buzzell

*Calvin Buzzell*

AF/ml



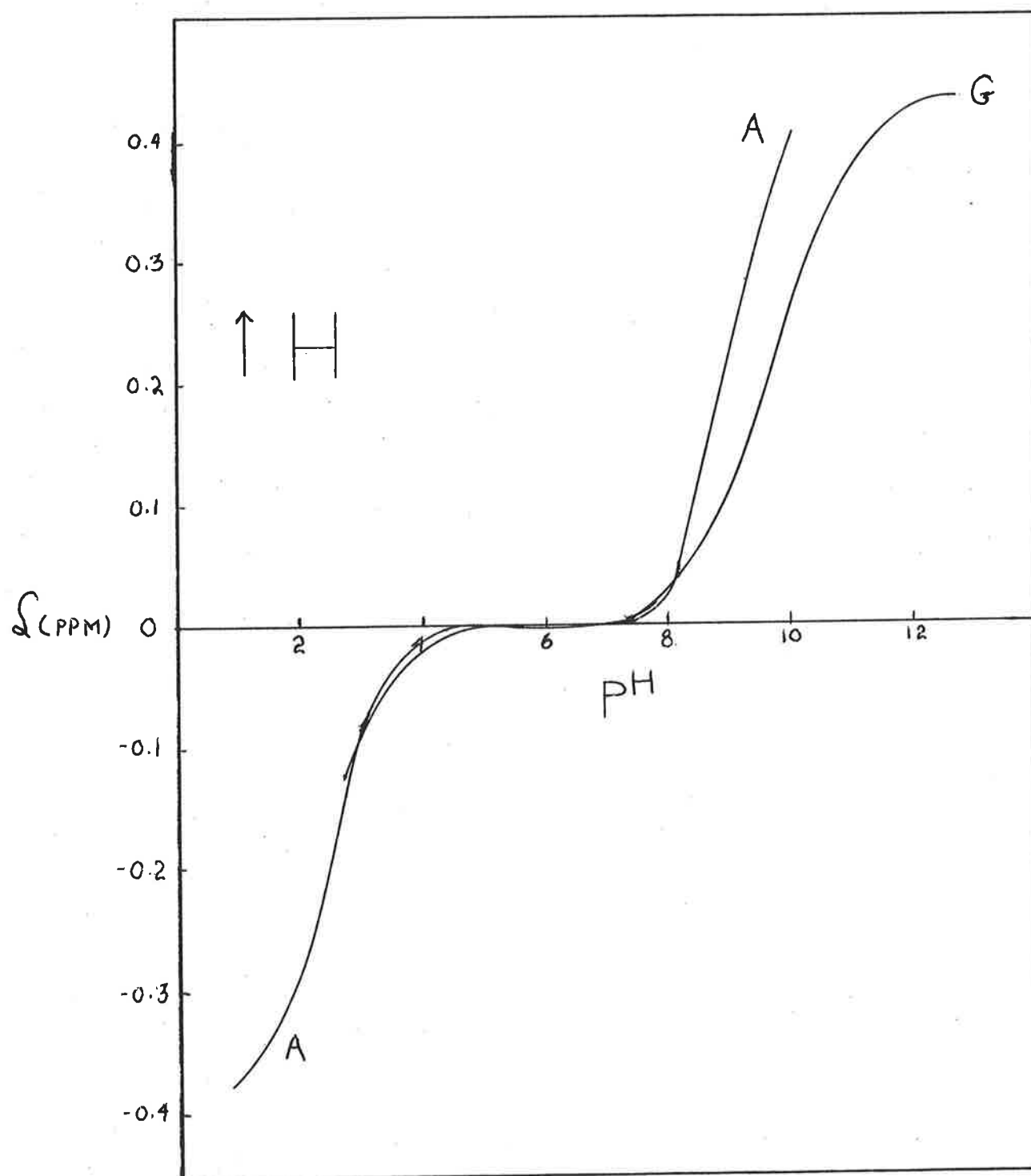


Figure 1.

Chemical shift pH dependence of the CH and CH<sub>2</sub> resonance peaks of DL-alanine and glycine, respectively, using the 2M acid solutions as standards.

## UNIVERSITY OF CALIFORNIA, SAN DIEGO

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SANTA BARBARA • SANTA CRUZ

Department of Chemistry  
SCHOOL OF SCIENCE AND ENGINEERING

P. O. BOX 109  
LA JOLLA, CALIFORNIA 92038

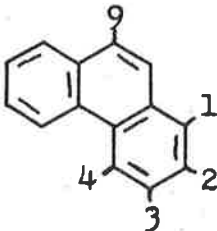
September 14, 1964

Professor Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois

Dear Dr. Shapiro:

As a first payment on a subscription to the IIT NMR Newsletter, we would like to offer the results of an analysis of the proton n.m.r. spectrum of phenanthrene.


Spectra were measured at 60 Mc. for several concentrations of phenanthrene in deuterochloroform and analyzed with the aid of the iterative computer program by Swalen and Reilly. The 9-position proton gives a single line and the remaining lines were analyzed as a four spin problem. A variety of transition assignments were tested, but only one, with all couplings positive, accurately corresponded to the observed spectra. The chemical shifts (extrapolated to infinite dilution) and coupling constants are given below:

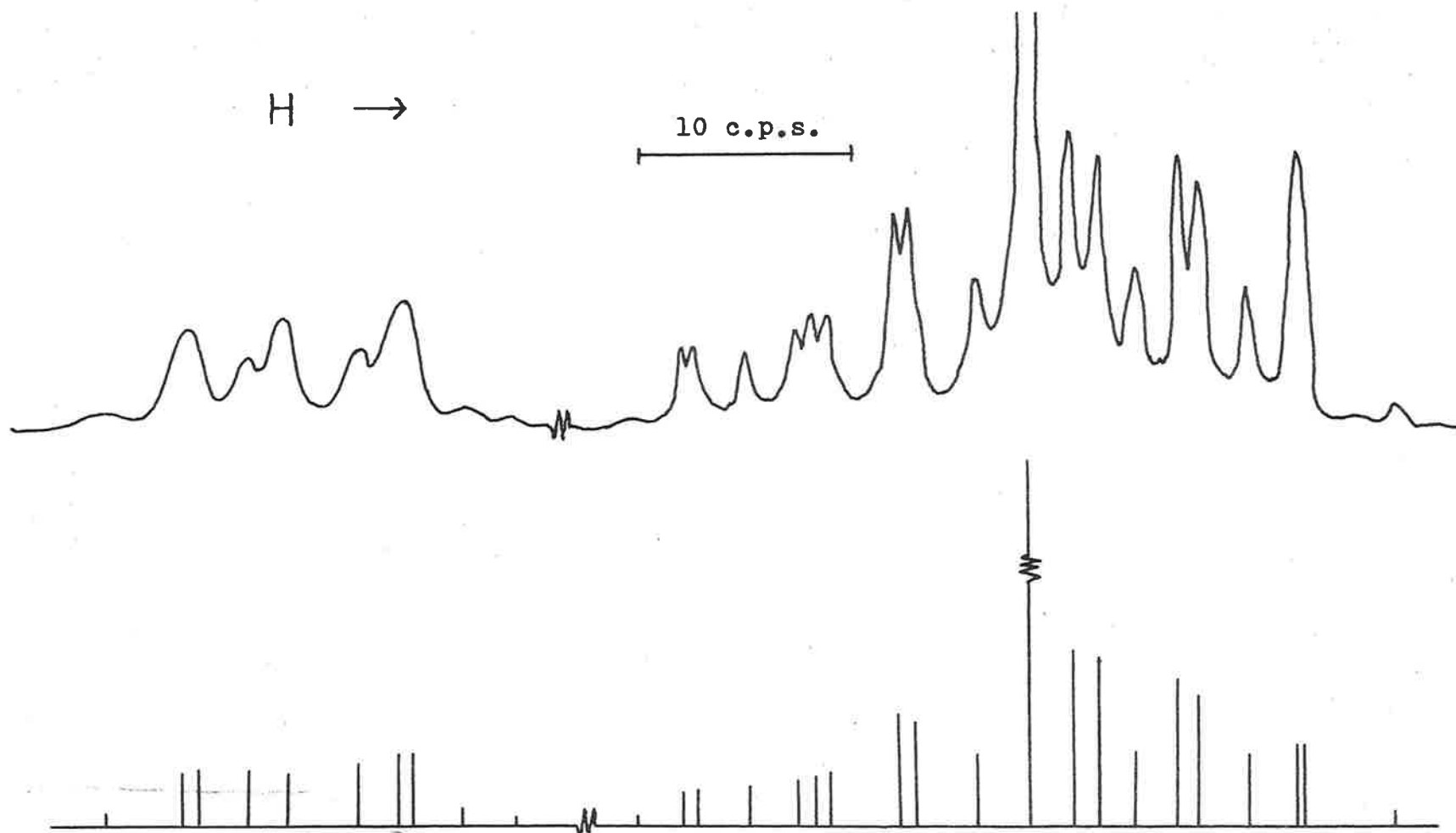
	1	$\delta_{\text{TMS}} - \delta_{\text{H}_1}$ (p.p.m.)	$1j$	$J_{1j}$ (c.p.s.)
	1	7.855	12	8.11
	2	7.570	13	1.31
	3	7.612	14	.66
	4	8.648 $\pm .005$	23	7.20 $\pm .05$
	9	7.702	24	1.24
			34	8.40

The observed and calculated 60 Mc. spectra are compared in the accompanying figure. The above parameters predict a theoretical 100 Mc. spectrum for phenanthrene which is in close agreement with the observed 100 Mc. spectrum, further justifying the assignment used.

Sincerely,

  
Robert C. Fahey

  
Gary C. Graham



Observed and calculated spectra of phenanthrene (13% in  $\text{CDCl}_3$ ) at 60 Mc.

DEPARTMENT OF ORGANIC CHEMISTRY  
THE UNIVERSITYAddress: BLOEMSINGEL 10, GRONINGEN (HOLLAND)  
Tel.: 05900-34841

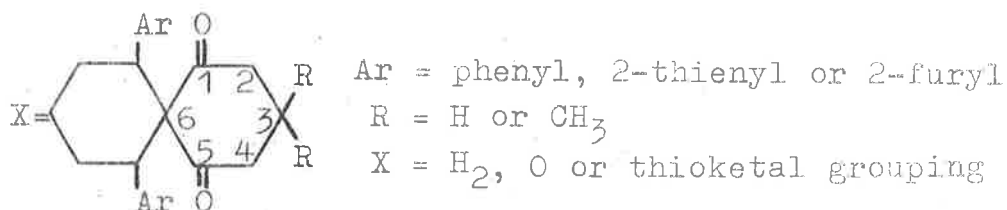
HEAD: PROF. DR. H. WYNBERG

Groningen, September 15, 1964.

Professor B.L.Shapiro.  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Center,  
CHICAGO, ILLINOIS 60616 (U.S.A.)

Dear Professor Shapiro,

The PMR spectra of several diphenyl-, dithienyl- and difuryl-spiroketones have been analysed and compared with the spectra of the analogous spiroketones without aryl groups<sup>1</sup>. The comparison reveals that the two aryl rings exert a strong shielding effect upon the protons or methyl protons at positions 2, 3 and 4 (see formula below). The upfield shift of the signal of the protons or methyl protons at the 3 position amounts to 0.95-1.45 ppm for the diphenylspiroketones and 0.58-1.07 ppm for the dithienyl- and difurylspiroketones.



These appear to be the first examples of long range shielding effects exhibited by heterocyclic aromatic rings. The shielding values found in the diphenylspiroketones agree well with the ones calculated from the graphs of Johnson and Bovey<sup>2</sup>.

The ratio of ring currents in benzene, thiophene and furan as determined from their shielding effects amounts to 100 : 77 : 60. This agrees reasonably with the deshielding values of the aromatic protons of benzene, thiophene and furan (100 : 77 : 76) and excellently with the deshielding values of the methyl protons of toluene, methylthiophenes and methylfurans (100 : 75 : 62). These deshielding values were obtained by comparing the aromatics with related olefins in which no ring current takes place. For instance, benzene was compared with cyclohexene, thiophene with 2,3-dihydrothiophene, furan with 2,3-dihydrofuran, toluene with 1-methylcyclohexene,  $\alpha$ - and  $\beta$ -methylthiophene with propyl and isopropenylsulfides and  $\alpha$ - and  $\beta$ -methylfurans with propenyl and isopropenyl ethers. The deshielding values of thiophene and furan used in the ratio calculations above are the mean between the deshielding values of the  $\alpha$  and  $\beta$  protons, which differ appreciably. The same applies for the  $\alpha$  and  $\beta$  methylaromatics.

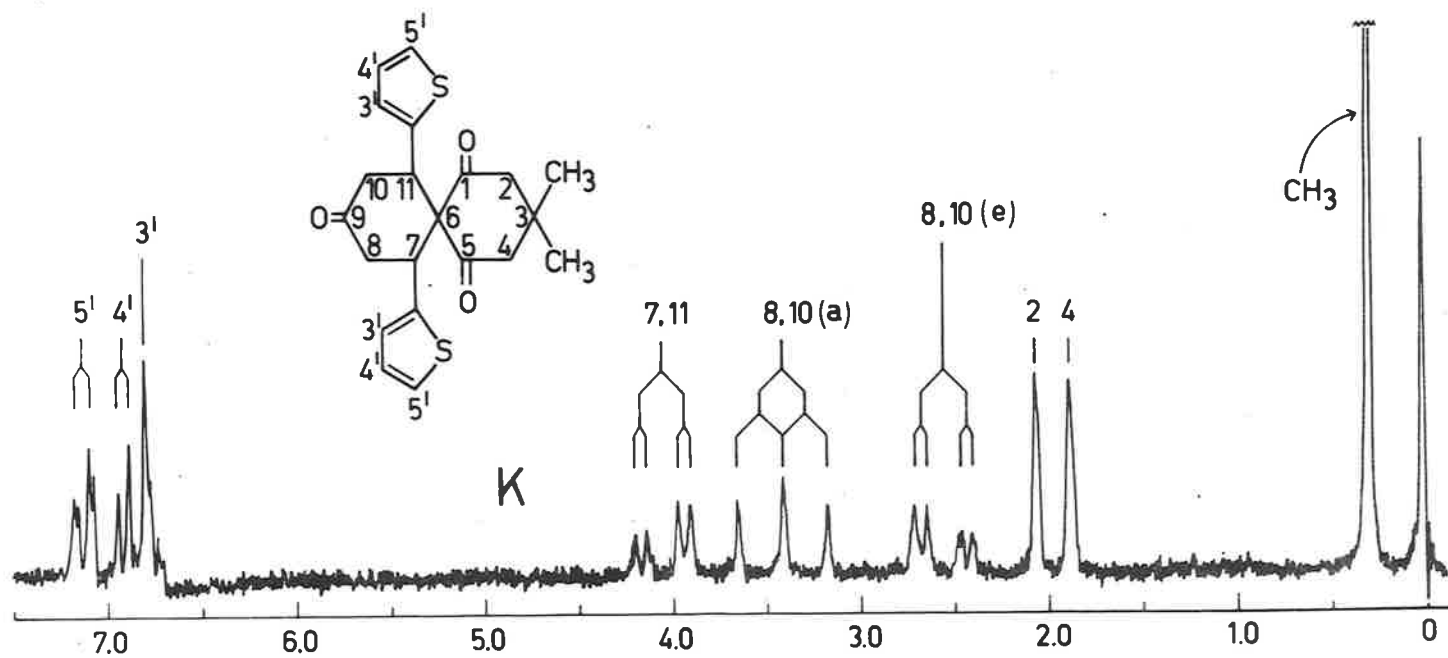
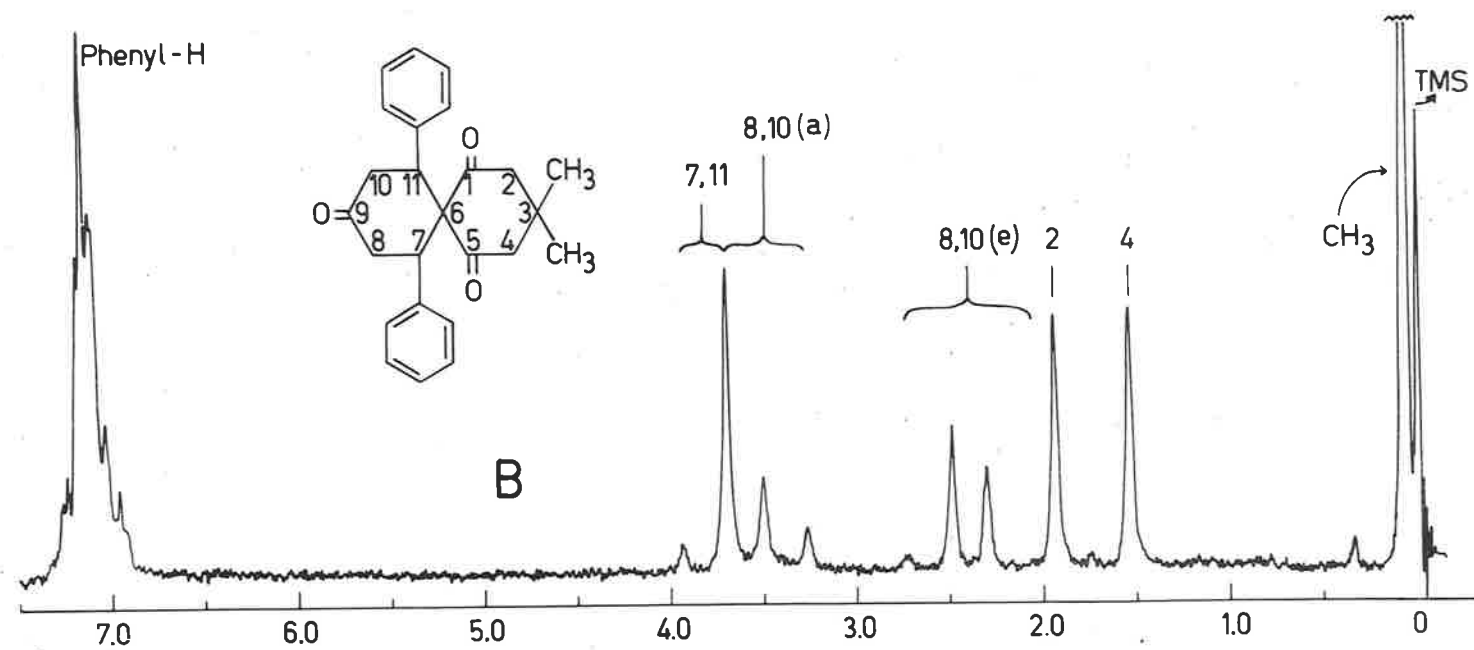
Submitted for publication to Tetrahedron.

*H.A.P. de Jongh*  
(H.A.P. de Jongh)

Sincerely,

*H. Wynberg*  
(H. Wynberg)

1. For synthesis of these compounds, see H.A.P. de Jongh and Hans Wynberg, Rec. trav. chim. Pays-Bas 82, 202 (1963).
2. C.E. Johnson Jr. and F.A. Bovey, J. Chem. Phys. 29, 1012 (1958).



## THE SCHOOL OF PHARMACY

UNIVERSITY OF LONDON

PHARMACEUTICAL CHEMISTRY  
PROFESSOR W. B. WHALLEY  
D.Sc., Ph.D., F.R.I.C.



29/39, BRUNSWICK SQUARE  
LONDON, W.C.1.  
TELEPHONE TERMINUS 7651/8

WBW/CLS

17th September, 1964

Dear Dr. Shapiro,

Anti-clogging Additive for Magnet Cooling Water System

I trust that the following comments might be acceptable as a contribution to your excellent Newsletter and also constitute a reply to the recent enquiry from Dr. Chen of the Goodyear Tire and Rubber Company.

For 18 months we have been operating a closed circuit cooling water system for our A60 spectrometer. We circulate distilled or de-ionised water. The total volume of cooling fluid is approximately 40 gallons. To this we add 1 to 2 cc. of Panacide Sodium Salt Solution every 3 to 4 months. This is marketed by the British Drug Houses Ltd., Poole, England.

Using this additive we have not been troubled by the growth of micro-organisms within the cooling water system. Since our circuit contains a Rotameter which has a glass body approximately 2' long, it is easy to observe what is happening inside the circuit. The sight-glass of this instrument has remained perfectly clear during the whole of this time.

I trust this information may be of use to other Magnetic Resonators.

Kind regards,

Yours sincerely,

W. B. Whalley

Dr. B. L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Center,  
Chicago,  
Illinois,  
U.S.A.

CHEMISCHES LABORATORIUM  
DER UNIVERSITÄT MÜNCHEN

INSTITUT FÜR ORGANISCHE CHEMIE

Prof. Dr. H. Zimmermann

8000 MÜNCHEN 2, 14. September 1964  
Karlstr. 23 - Tel. 55 79 76

Prof. Dr. B. L. S h a p i r o  
Department of Chemistry  
Illinois Institute of Technology  
C h i c a g o , Ill  
60616 USA

Sehr geehrter Herr Prof. Shapiro!

In der letzten Zeit haben wir Untersuchungen am Tetrahydrat des Bromwasserstoffs durchgeführt. Aus den Infrarotspektren geht hervor, daß der Bromwasserstoff im Kristall dissoziiert ist, die Substanz also in der Form  $\text{H}_9\text{O}_4^+\text{Br}^-$  vorliegt. Das Kation besteht dabei aus einem  $\text{OH}_3^+$ -Ion, das über sehr starke Wasserstoffbrückenbindungen durch drei Wassermoleküle solvatisiert ist <sup>1)</sup>.

Die Temperaturabhängigkeit der Leitfähigkeit der polykristallinen Substanz zeigt bei  $-93^\circ\text{C}$  einen scharfen Knickpunkt <sup>2)</sup>, der auf einen Phasensprung hinweist. Zur Verifizierung des Umwandlungspunktes wurden Breitband-Kernresonanzuntersuchungen durchgeführt. Die zweiten Momente wurden zwischen  $-195^\circ$  und  $-60^\circ\text{C}$  gemessen (Abb. 1). Erwartungsgemäß beobachtet man bei  $-93^\circ\text{C}$  in der Kurve eine Sprungstelle, die den diskutierten Umwandlungspunkt anzeigt.

Die Kernresonanzsignale der Hoch- und Tieftemperaturmodifikation unterscheiden sich in charakteristischer Weise. Die Ableitungen sind in Abb. 2 dargestellt. Die Kurvenform der Signale läßt sich qualitativ interpretieren als Überlagerung von Anteilen, die dem  $\text{OH}_3^+$ -Ion und den  $\text{H}_2\text{O}$ -Molekülen zugeordnet werden können. Die Verschärfung der Signale in der Hochtemperaturmodifikation kann auf eine Bewegung von Gitterbausteinen zurückgeführt werden.

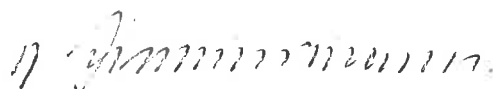
Die Bestimmung der Protonenparameter im Kristall allein aus den Kernresonanzspektren war bisher nicht möglich. Röntgenstrukturuntersuchungen wären zur Ergänzung erforderlich.

- 1) J.RUDOLPH, Dissertation Techn.Hochschule München (1964)
- 2) G.HENNING, Techn.Hochschule München, unveröffentlicht.

Mit freundlichen Grüßen



(G.Henning)



(H.Zimmermann)



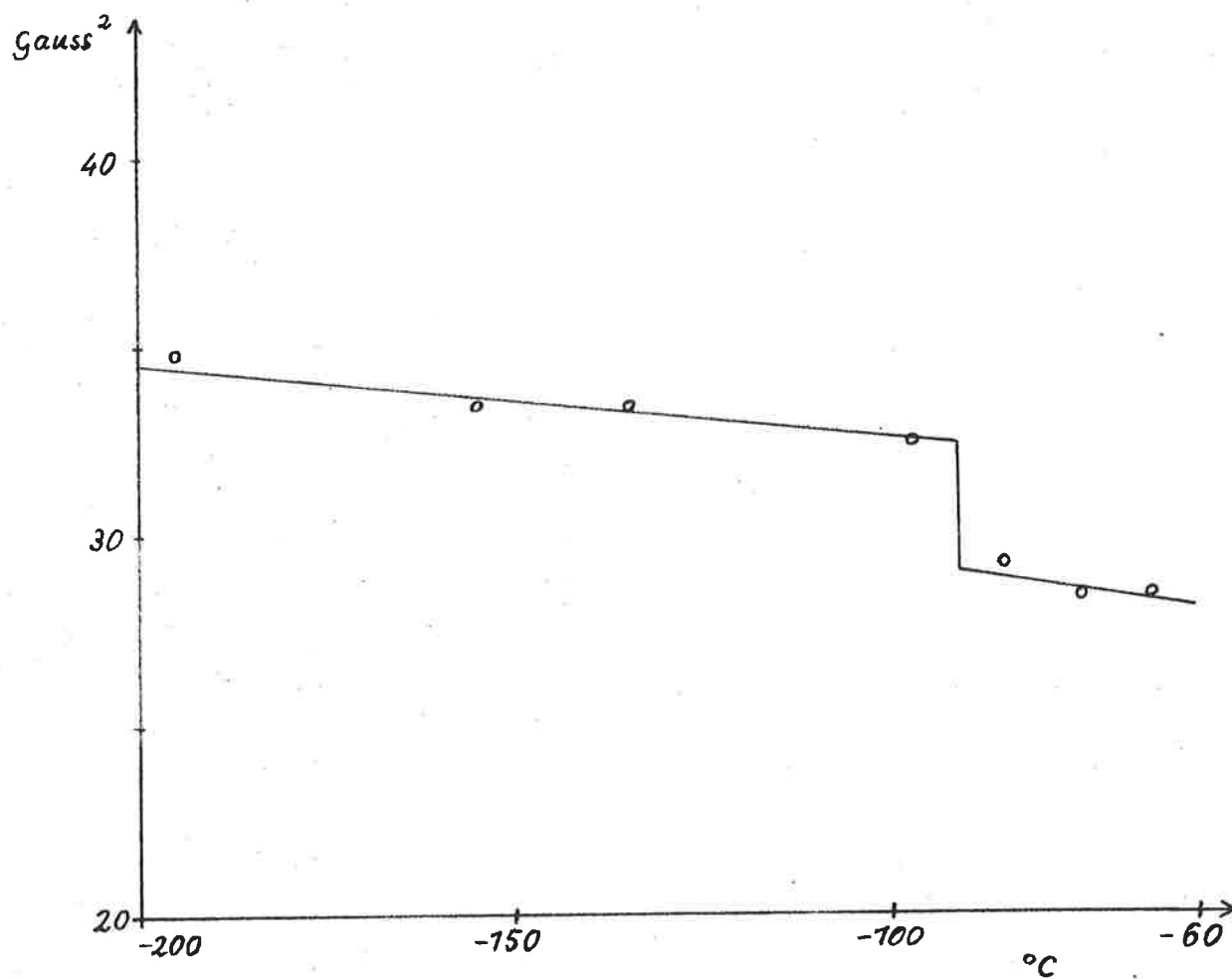


Abb. 1

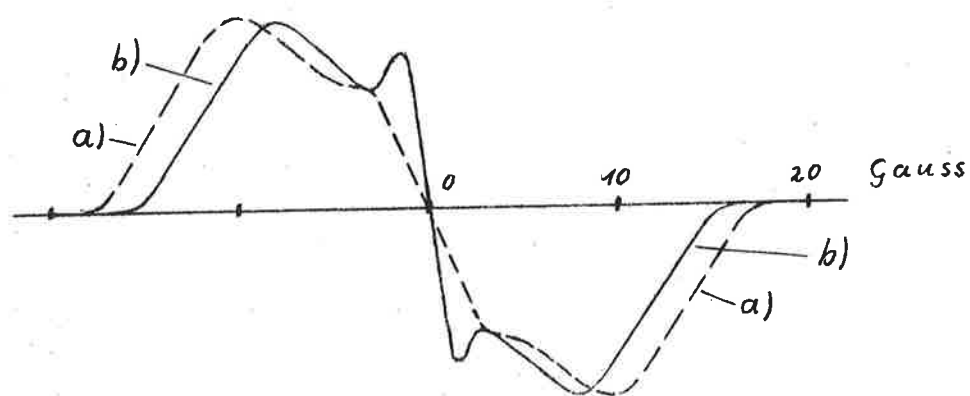


Abb. 2

- a) Tieftemperaturmodifikation ( $-195^{\circ}\text{C}$ )
- b) Hochtemperaturmodifikation ( $-65^{\circ}\text{C}$ )



# BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

## A SIMPLE LOCKED FIELD SYSTEM

Over the past few months we have developed a simple locked field system based essentially on the double audio frequency modulation systems suggested by Primas (1) and Freeman and Whiffen (2). The system used by the latter authors had the merit of simplicity but the disadvantage that the swept frequency could only be varied over a relatively small fraction of its mean frequency of operation. Larger excursions produced changes in the modulation index that made accurate band intensity measurements impossible.

We have overcome this difficulty by sweeping the control frequency rather than the signal frequency. We are indebted to Dr. K. McLaughlin (National Physical Laboratory - Teddington) for this suggestion. The change in loop gain that occurs as the control frequency is swept is readily tolerated so the system can be used over the entire spectral range for routine analytical purposes. The u-mode signal obtained at the swept frequency (control channel) detector is fed to the super stabilizer. Thus linear variation of the control frequency provides an error signal to the super stabilizer which in turn produces a linear field sweep

The variable audio frequency is produced from a square wave oscillator and the requisite voltage sweep is provided by a motor driven helipot. Although some power is wasted in high harmonics in such an oscillator it can be made linear to the accuracy required (0.1 per cent), and further the modulation index used is low. The frequency is variable from 1.8 to 3.2 Kc and is fed to a power amplifier driving the sweep coils. The signal channel is our existing audio modulation and integrator unit operating at 2 Kc. The control channel detector is a similar system consisting of an audio amplifier and phase sensitive detector, diagram 1. By careful selection of the phase and amplitude of the signal to the super stabilizer the lock-in cannot be overridden with the fastest scan from our slow sweep unit (approximately 100 cps/s), using an approximately 2 per cent vol/vol TMS solution in  $\text{CCl}_4$  to provide the control signal.

A check on the lock-in is provided by a Lissajous figure displayed on a small low cost monitor oscilloscope (Cossor type 1039M). To set up the system the TMS signal is displayed on the spectrometer oscilloscope and the phase shift adjusted until a u-mode signal is obtained. The amplitude of the control frequency is adjusted to a suitable low level to avoid signal saturation and the D.C. level of the detector output (in the absence of signal) is adjusted to zero. The u-mode control signal from the detector output is then switched to the super stabilizer. Final optimization of the control frequency modulation index, magnetic field homogeneity, control channel audio amplifier gain and detector output RC network can be done visually by using the monitor scope display.

A spectrum scan is obtained by driving the helipot providing the control voltage to the variable frequency oscillator. The performance of the field lock system is good as can be seen from the constancy of the band positions in three superimposed ethyl benzene spectra, Figure 2.

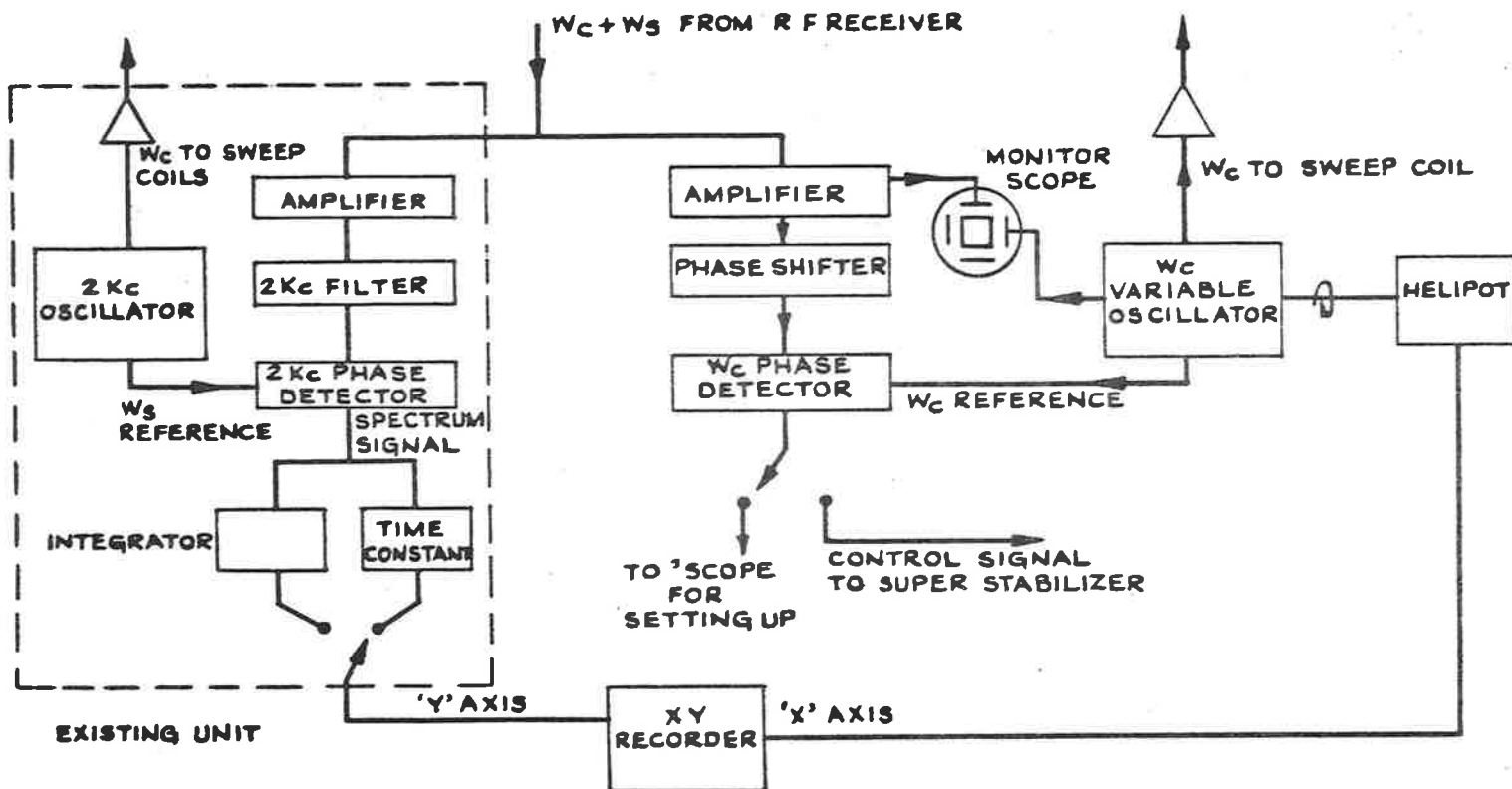
As the locked field control is in addition to the existing detection equipment, by switching off the lock and the control frequency the ordinary method of spectrum recording may be resumed.

S.A. Knight *S.A. Knight*

R.L. Erskine *R.L. Erskine*

#### Literature

- (1) R. Ernst and H. Primas, Disc. Farad. Soc., 1963, 34, 43.
  - (2) R. Freeman and D. Whiffen, Proc, Phys. Soc., 72, 794.
- + Figures 1 and 2.



SERIAL No. 64/1471/BP



72-51  
ETHYL BENZENE  $\text{CH}_3$  AND  $\text{CH}_2$  PATTERNS  
LOCKED FIELD SYSTEM

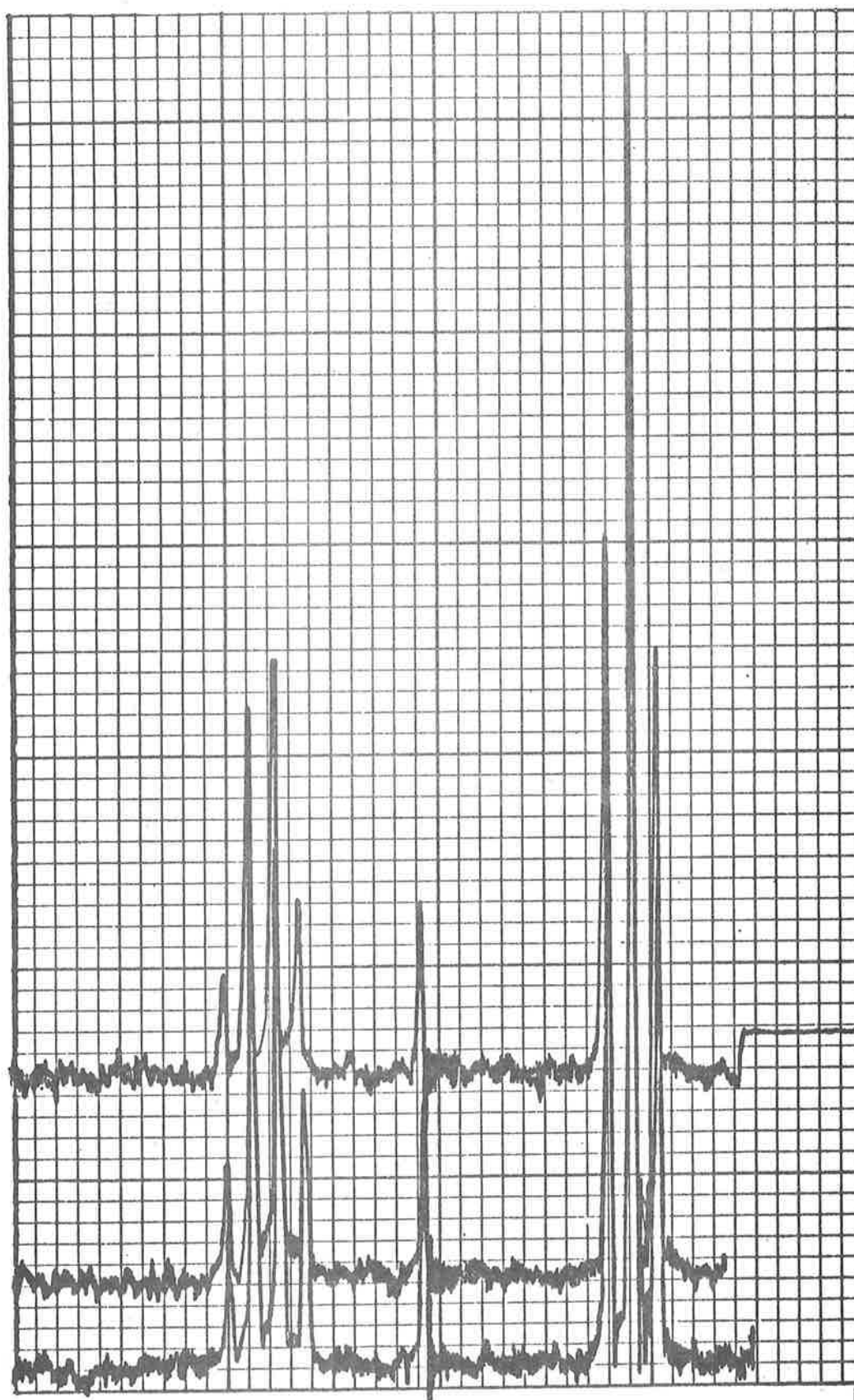


FIG 2

ILLINOIS INSTITUTE OF TECHNOLOGY  
TECHNOLOGY CENTER  
CHICAGO 16

*Department of Chemistry*

21 September 1964

I have learned recently of two NMR spectroscopists who might not be too difficult to move from their present positions. Both of these men are well-established NMR researchers of excellent personal and professional reputations. One is rather physics-oriented, the other is more chemical; both are active in experimental NMR.

Anyone knowing of positions available (or real possibilities) should let me know so that I can put one of both of these men in direct contact with the interested parties.

---

Turning to a different sphere, I am looking for one or two post-doctoral research fellows, and would appreciate hearing from or of prospects. Extensive previous NMR experience, while most desirable, is not essential. The work would involve a rather modest amount of chemical manipulation, as well as extensive high-precision small molecule NMR work. The stipend will be very competitive, and I am willing to let someone start anytime for a period of 9 months or longer. One or more publications can definitely be expected.

B. L. Shapiro

"Nuclear Magnetic Resonance Studies of Protonation of Polyamine and Aminocarboxylate Compounds in Aqueous Solution"  
J. L. Sudmeier and C. N. Reilley  
Anal. Chem. 36, 1698 (1964)

"Nuclear Magnetic Resonance Studies of Protonation of Some Polyaminocarboxylate Compounds Containing Asymmetric Carbon Atoms"  
J. L. Sudmeier and C. N. Reilley  
Anal. Chem. 36, 1707 (1964)

"Determination of Active Hydrogen by Nuclear Magnetic Resonance Spectrometry"  
P. J. Paulsen and W. D. Cooke  
Anal. Chem. 36, 1721 (1964)

"Organische Fluorverbindungen, IV. Carbonyl-Fluorolefinierungen"  
H. Machleidt und R. Wessendorf  
Ann. Chem. 674, 1 (1964)

"Untersuchungen an hochsubstituierten Äthylenen und Glykolen. Bildung eines Spiro-Cyclischen Ketons Bei Der Wasserabspaltung aus 3,4-Di(4-Oxo-Cyclohexen-(1)-YL)-Hexan-Diol-(3,4)"  
H. H. Inhoffen, D. Kampe, C. Cordes, K.-D. Müller und W. Milkowski  
Ann. Chem. 674, 36 (1964)

"über Triterpene, XIII. Zur Konstitution des Gratiogenins und über Weitere Inhaltsstoffe von Gratiola Officinalis L"  
R. Tschesche, G. Biernoth und G. Snatzke  
Ann. Chem. 674, 196 (1964)

"Quench Frequency Effects on the Nuclear Quadrupole Resonances of Some Halogen Compounds"  
M. J. Bogaard, S. Hacobian, W. Hay and E. P. A. Sullivan  
Australian J. Chem. 17, 611 (1964)

"Nuclear Magnetic Resonance Spectra, Stereochemistry, and Conformation of Flavan Derivatives"  
J. W. Clark-Lewis, L. M. Jackman and T. M. Spotswood  
Australian J. Chem. 17, 632 (1964)

"The Lability of 6-Bromo- $\Delta^4$ -3-Oxosteroids: Observations on the Conversion of 6 $\alpha$ - and 6 $\beta$ -Bromocholest-4-en-3-One to 5 $\alpha$ -Cholestane-3,6-Dione"  
D. J. Collins and J. J. Hobbs  
Australian J. Chem. 17, 661 (1964)

"Some Transformations of 6 $\alpha$ -Bromocholest-4-en-3 $\beta$ -ol and its 3-Acetate. A Convenient Synthesis of 3,6-Dialkoxysteroids"  
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Australian J. Chem. 17, 677 (1964)

"The Occurrence of 5-Hydroxy-7,4'-Dimethoxy-6-Methylflavon in *Eucalyptus* Waxes"  
J. A. Lamberton  
Australian J. Chem. 17, 692 (1964)

"<sup>199</sup>Hg Wide Line N.M.R. Spectra of Chloride Complexes of Mercury"  
P. D. Godfrey, M. L. Heffernan and D. F. Kerr  
Australian J. Chem. 17, 701 (1964)

"The 2-Desmethyl Vitamin K<sub>2</sub>'s. A New Group of Naphthoquinones Isolated from *Hemophilus parainfluenzae*"  
R. L. Lester, D. C. White and S. L. Smith  
Biochem. 3, 949 (1964)

"Ferromagnetic Resonance of Single Crystal Hexagonal Close Packed Cobalt"  
Z. Frait  
Brit. J. Appl. Phys. 15, 993 (1964)

"Acylcyclopentanones. III. The Synthesis of 2-Acetylcyclopentane-1,3-Diones"  
M. Vandewalle  
Bull. Soc. Chim. Belg. 73, 628 (1964)

"Phenylaluminum Hydrides"  
J. R. Surtees  
Chem. Ind. 1260 (1964)

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