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Institute of
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N - M - R
Newsletter

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APRIL, 1964

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Deadline Date for Next Issue: May 20, 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".

Department of Chemistry,
Imperial College,
London, S.W.7.

18th March, 1964.

Dear Dr. Shapiro,

For my belated contribution to the Newsletter, may I mention some measurements Dr. Taddei and I made to try to find the ionisation sequences of amino-acids? In a monobasic acid $R_2CH-X-H$, the observed (weighted average) shift of the CH proton appears to be related linearly to the degree of dissociation of the acid group $X-H$. In lysine, whose structure (after the ionisation of the carboxyl proton) is $^+H_3N-(CH_2)_4-CH(COO^-)NH_3^+$, the two ammonium groups are separated by five aliphatic carbon atoms, and we assumed that the shifts of the α and the ϵ CH protons are related linearly to the degrees of ionisation of the α and ϵ ammonium groups, respectively. These ionisations overlap, but by following the changes with pH of the separate CH shifts, we estimated the microscopic dissociation constant of the α ammonium group to be about 5 times greater than that of the ϵ ammonium group, which agrees with estimates based on comparisons of pK values. We could not do the same with the more interesting acids like cysteine, $HS-CH_2-CH(COOH)NH_3^+$, since the shift of any one CH proton is affected by the ionisation of all three acid groups, although the coupling constants indicate the preferred conformations of these acids, as shown already by Pachler [Spectrochimica Acta, 19, 205 (1963)].

In valine $(CH_3)_2CH-CH(COOH)NH_3^+$ and iso-leucine $CH_3CH_2-(CH_3)CH-CH(COOH)NH_3^+$ the small values of the vicinal coupling constants (3.5 - 5 cps.) suggest that the preferred conformations are those in which the two CH are gauche; on steric grounds, ignoring the effect of the solvent water, one might expect them to be trans. Freeman (MellonMR, 55, p. 15) found a similar small J (3.0 cps.) in 1,1,2,2-tetrabromoethane, and I wondered if anyone knows whether the usual correlation between vicinal J and dihedral angle doesn't work with this type of molecule?

Yours sincerely,

L. Pratt
L. Pratt

Glaxo Research Limited

Greenford · Middlesex

TELEPHONE: BYRON 3434 TELEGRAMS: Glaxotha, London, Telex CODE: New Standard, Bentleys

12th March, 1964.

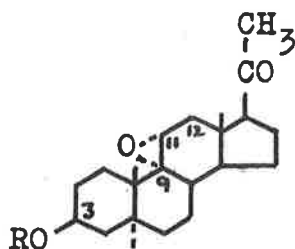
~~Please address reply to:~~

Professor B.L. Shapiro,
 Department of Chemistry,
 Illinois Institute of Technology,
 Technology Centre,
 Chicago,
 Illinois 60616,
 U.S.A.

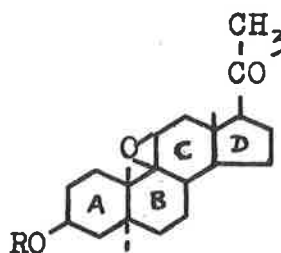
Dear Professor Shapiro,

Stereochemistry of Steroidal 9,11-epoxides

Following the work of Cross¹ and of Collins, Hobbs and Sternhell² on steroidal 5,6-epoxides and 4,5-epoxides, respectively, we have shown that p.m.r. spectroscopy can be used to distinguish between, and to identify, 9 α ,11 α - and 9 β ,11 β -epoxides. The steroidal 9,11-epoxides, which had been prepared by colleagues in these laboratories, were examined in deuteriochloroform solution on a Varian A-60 spectrometer; the chemical shifts were measured against tetramethylsilane (SiMe₄ = 10 τ) used as an internal standard.



(I)



(II)

The 11-proton of 3 β -hydroxy- and 3 β -acetoxy-9 α ,11 α -epoxy-5 α -pregnan-20-ones (I, R = H or Ac) gave a pair of broad doublets (J, 4.5 c./sec.; J', 1.5 c./sec.) centred at 6.81-6.82 τ , whereas the 11-proton for the corresponding 9 β ,11 β -epoxides (II, R = H or Ac) gave a broad singlet (half height

width, 5 c./sec.) at 6.54-6.55 τ . By measuring on Dreiding models of the isomeric epoxides, the angles (θ) subtended by the C-H bond at C₁₁ with the C-H bonds at C₁₂ and applying the Karplus relationship,³ we calculated that for the 9 α ,11 α -epoxide, the coupling constants between the 11 β - and 12 α -protons (θ , $96 \pm 30^\circ$) and between the 11 β - and 12 β -protons (θ , $23 \pm 30^\circ$) are 0.2 ± 0.2 and 6.9 ± 0.4 c./sec., respectively; for the 9 β ,11 β -epoxide, the coupling constants between the 11 α - and 12 α -protons (θ , $70 \pm 30^\circ$) and between the 11 α - and 12 β -protons (θ , $55 \pm 30^\circ$) are 0.7 ± 0.3 and 2.5 ± 0.4 c./sec., respectively.

It is noteworthy that whereas the observed coupling constants for the 9 β ,11 β -epoxides are in rough agreement with the calculated values, the observed constants for the 9 α ,11 α -epoxides agree less well, one coupling constant being higher and the other lower than the calculated values. Cross¹ found that the observed coupling constants for the 6-proton of 5,6-epoxides were lower than the calculated values.

The introduction of carbonyl groups or double-bonds into rings-A, -B or -D causes, as might be expected, big changes in the position of the 11-proton peaks, but has a smaller effect on the coupling constants. We therefore believe that stereochemical assignments for 9,11-epoxides based on coupling constant differences are likely to be more reliable than those based on chemical shift differences.

Yours sincerely,



J.E. Page



G.F.H. Green



S.E. Staniforth

- 1.) A.D. Cross, J. Amer. Chem. Soc., 1962, 84, 3206.
- 2.) D.J. Collins, J.J. Hobbs, and S. Sternhell, Tetrahedron Letters, 1963, 623.
- 3.) M. Karplus, J. Chem. Phys., 1959, 30, 11.

Lincoln College,
Oxford,
England.

March 18th, 1964.

Professor Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
CHICAGO,
Illinois,
U. S. A.

Dear Barry,

I am writing to send you my subscription to the IIT Newsletter and would like to tell you about two experiments which have been done recently in Oxford.

The first experiment is concerned with nuclear electron double resonance. If a solution of a free radical is arranged so that its nuclear and electron resonance spectra can be excited simultaneously, an Overhauser effect can be observed. If the coupling between the unpaired electrons and the nuclei is dipolar and in a normal mobile liquid, the effect of strongly exciting the electron resonance is to cause the nuclear resonance to be inverted and increased in intensity. This effect is purely a relaxation effect caused by simultaneous flips of the electrons and nuclei and is best observed when the nuclear relaxation time is dominated by the paramagnetic radicals in a solution. In order to demonstrate this, Dr. White and I have done an experiment on a solution of a free radical in benzene at a proton resonance frequency of 53 Mc/s and an electron resonance near 35,000 Mc/s. The results of one such experiment are shown in the Figure. On the left of the Figure a large nuclear resonance field was applied so as to saturate the nuclear resonance, and this was then turned down to a low value and the instrument set to make frequent repetitions of the benzene proton resonance. The nuclear resonance grows (in the Figure downwards) with a time constant equal to the nuclear spin lattice relaxation time. When the nuclear resonance signal had reached its equilibrium value, we turned on the microwave power when the nuclear resonance becomes inverted and the time constant for the inversion is exactly equal to the time constant for the regrowth of the nuclear resonance, i.e. to the nuclear spin lattice relaxation time. When the inverted signal had reached an equilibrium value, the microwave power was turned off when the nuclear resonance returned exponentially to its normal value, once again with exactly the same time constant. This experiment fully confirms that this effect is a simple relaxation process. Incidentally, we have found that this provides an extremely convenient method for measuring spin lattice relaxation times quickly and roughly. Quite a weak nuclear resonance can be strongly enhanced and inverted by applying a large microwave power and this allows the decay of the resonance to be plotted on an oscilloscope with considerable ease. At Q-band we have been able to obtain enhancements up to about 40 times, but at X-band enhancements of 3 or 4 times this can often be obtained.

....2/

- 2 -

The nitrogen resonance chemical shifts have been studied in a series of metal thiocyanate complexes in collaboration with Mr. O.W. Howarth and Dr. L.M. Venanzi. In five complexes which are known to be S-bonded, the nitrogen resonance is shifted slightly down the field from the free thiocyanate ion, by a few parts per million. For seven known N-bonded complexes the resonance is shifted up field by about 100 parts per million. This establishes a very reliable means of structural differentiation between these two types of complexes. The nitrogen resonance shift in sodium tetrathiocyanate cadmium are independent of concentration in any one solvent but show a strong solvent effect. It seems likely therefore that this substance exists in solution with both N- and S-bonded species in kinetic equilibrium. The more polarisable N-bonded form is favoured by the less polar solvents. Experiments on solutions containing thiocyanic acid show that the main tautomer present is HNCS. In an N-bonded platinum complex the spin spin coupling constant between nitrogen and platinum is 430 c/s.

With very best wishes,

Yours sincerely,



R.E. Richards.

Enc.

67-6

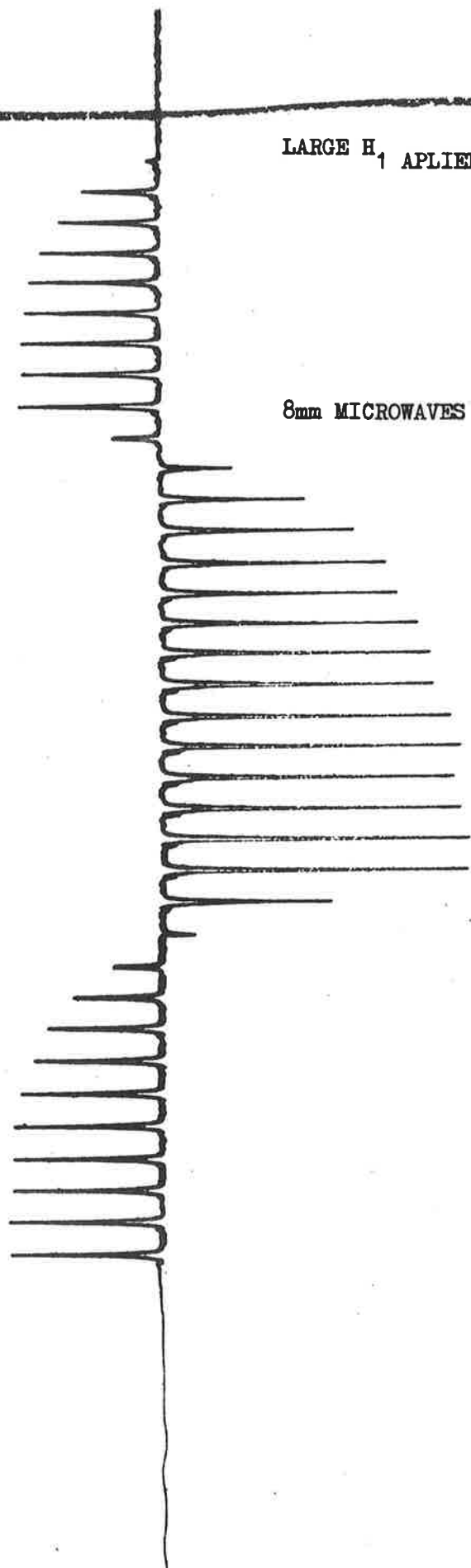
NORMAL N.M.R.

LARGE H_1 APLIED

8mm MICROWAVES APLIED

INVERTED N.M.R.

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JET PROPULSION LABORATORY California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California

16 March 1964

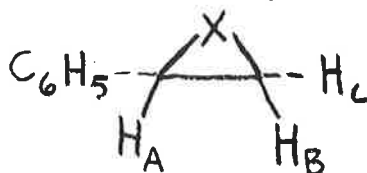
Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Barry:

Some time ago we determined by double resonance that the relative signs of proton-proton spin couplings between the three protons of the oxirane ring of styrene oxide(1) are all the same. This rather striking contrast in the signs of geminal couplings constants in nearly sp^3 hybridized systems (where the sign of the geminal coupling is different from the sign of the vicinal coupling) and in 1 suggested to us that a study of the proton NMR spectra of the nitrogen and sulfur analogs of 1 should provide some additional information concerning the factors which dictate the signs and magnitudes of the geminal coupling.

The enclosed figures show results on styrene imine(2) (20% in benzene with added hydrogen chloride gas) and styrene sulfide(3) (neat liquid) which demonstrate that J_{gem} is positive in the former and negative in the latter. These results were obtained with our field-lock spectrometer. The following table shows the observed coupling constants for these compounds along with those previously reported for two related molecules.

	X	J_{AB}	J_{AC}	J_{BC}
1	O	4.06	2.52	5.66
2	N	6.03 ± 0.05	3.19 ± 0.03	0.97 ± 0.02
3	S	6.54 ± 0.05	5.60 ± 0.03	-1.38 ± 0.02
4	CCl_2	10.5	8.6	-7.3

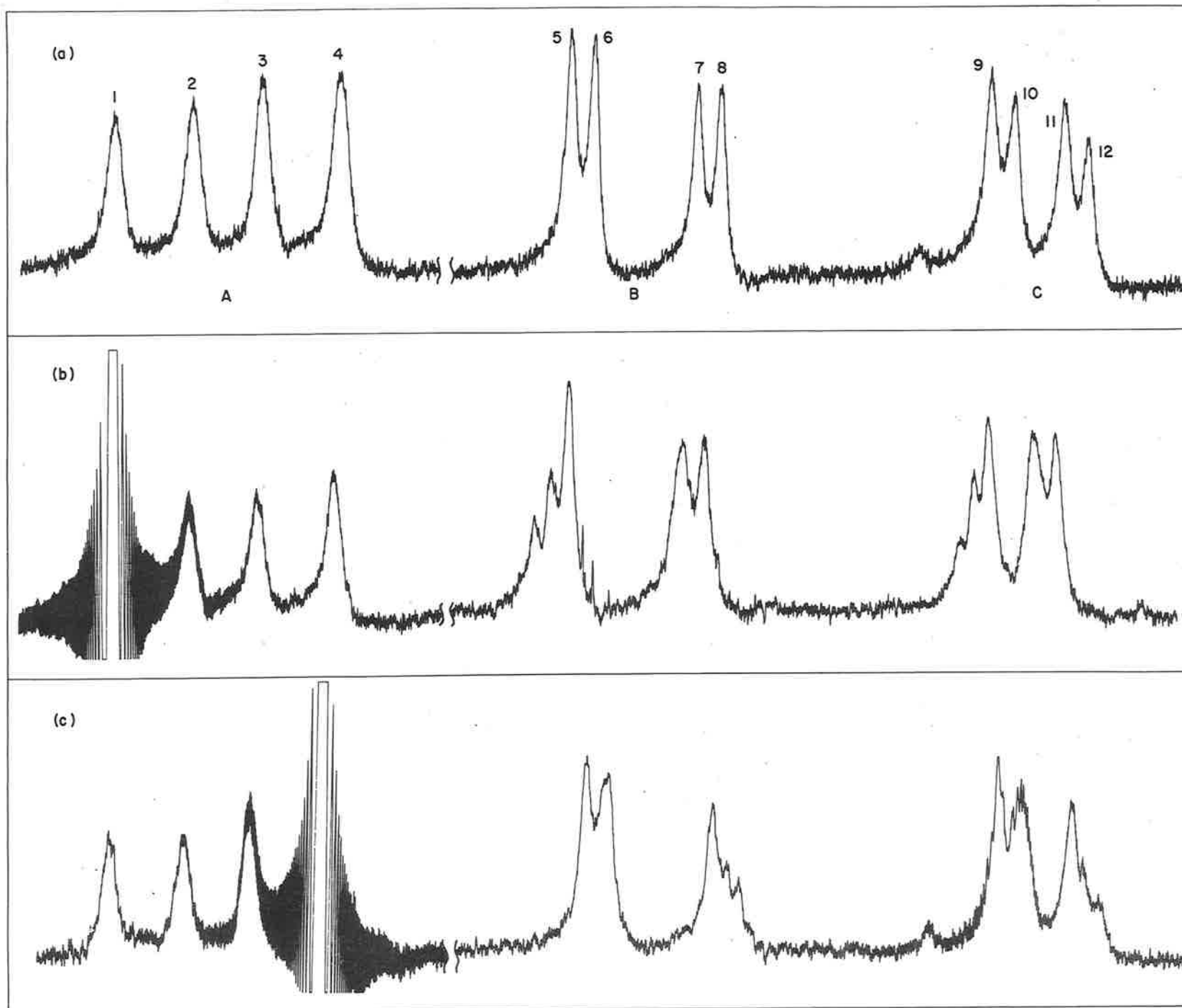


With best regards,

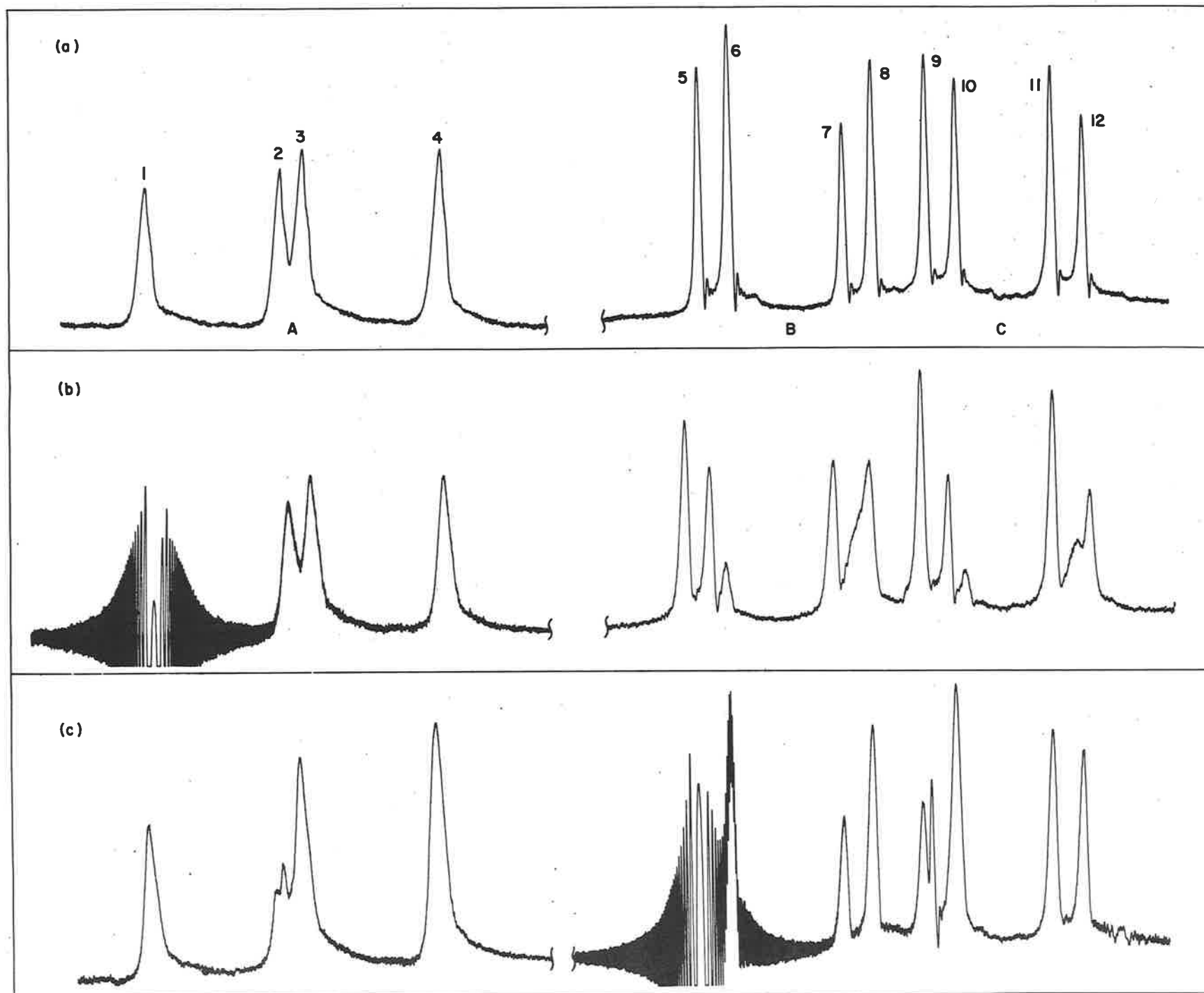
Stan Dan Stan Brois
S. L. Manatt, D. D. Elleman and S. J. Brois*

SLM/DDE/SJB:jas
Air Mail

* Esso Research and Engineering Co., Linden, New Jersey



STYRENE IMINE



STYRENE SULFIDE

RÉPUBLIQUE FRANÇAISE
PREMIER MINISTRE

COMMISSARIAT A L'ÉNERGIE ATOMIQUE

CENTRE D'ÉTUDES NUCLÉAIRES DE GRENOBLE

CHEMIN DES MARTYRS - GRENOBLE (ISÈRE)

ADRESSER LA CORRESPONDANCE :
BOITE POSTALE 269 - GRENOBLE

TÉL. 87-59-11

Associate Pr B.L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
Technology Center

CHICAGO - Illinois 60616

RÉFÉRENCE A RAPPELER :
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GRENOBLE, LE 19 Mars 1964

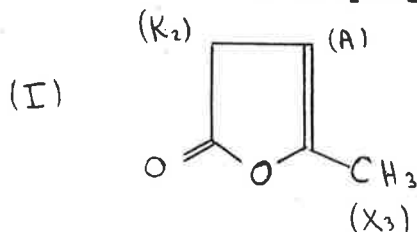
VOTRE LETTRE DU

- SIGNES DE COUPLAGES ALLYLIQUES ET HOMOALLYLIQUES -

Cher Docteur SHAPIRO,

Nous avons déterminé les signes relatifs de couplages dans deux dérivés furanniques dont les spectres ont été précédemment décrits (1).

1° - Dans 1° α -angelica-lactone (I), en supposant positif le couplage vicinal AK, on trouve (2) :

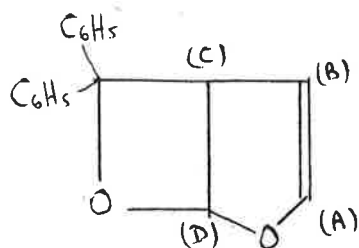


$$\begin{aligned} J_{AK} &= + 2,5 \text{ cps (couplage } {}^3J, \text{ vicinal)} \\ J_{AX} &= - 1,6 \text{ cps (couplage } {}^4J, \text{ allylique)} \\ J_{KX} &= + 2,7 \text{ cps (couplage } {}^5J, \text{ homoallylique)} \end{aligned}$$

Ces résultats confirment les résultats théoriques de Karplus (3) sur les couplages par l'intermédiaire des électrons σ et π .

2° - Dans le produit de photosynthèse (II), la détermination des signes relatifs J_{AC} et J_{CD} nous a amené à pousser à la limite les possibilités de double irradiation sélective quand on enregistre le spectre en balayant le champ magnétique H_0 .

(II)



signes relatifs $J_{AC} - J_{CD}$: irradiation de raies de D, observation de A

$$\delta_{AD} \approx 0,11 \text{ p.p.m.}$$

$$\text{Résultat : } J_{AC} \cdot J_{CD} < 0$$

On irradie deux raies de D, et on observe le regroupement de deux des huit raies de A (fig. 1).

Le tableau I montre les prévisions et le résultat dans les deux hypothèses possibles pour les signes relatifs des couplages. (f_1 fréquence de champ d'observation H_1 , f_2 fréquence du champ d'irradiation H_2).

TABLEAU I

Raies regroupées	$ f_1 - f_2 $		
	$J_{AC} \cdot J_{CD} > 0$	$J_{AC} \cdot J_{CD} < 0$	Mesuré
1 - 2	6,5 cps	10,8 cps	10,8
3 - 4	9,7 cps	5,2 cps	5,6
5 - 6	3,6 cps	8,1 cps	8,2
7 - 8	6,7 cps	2,3 cps	2,3

Le regroupement des raies 3 et 4 correspond à l'irradiation des raies 9 et 10 qui sont à moins de 6 cps des premières. Ceci n'est possible que parce que le champ H_2 nécessaire est très faible ($\frac{\gamma H_2}{2\pi} < 2 \text{ cps}$).

.../...

Par contre il a été impossible de regrouper les raies 7 et 8 par irradiation des raies 9 et 10, qui sont à moins de 3 cps de distance !

Cet exemple donne un nouvel exemple de couplage allylique négatif (en supposant le couplage vicinal positif).

D'autre part, dans le même exemple, J_{AD} a été trouvé de même signe que J_{DC} , soit $J_{AD} > 0$ (couplage à longue distance $^4J_{H-C-O-C-H}$).



D. GAGNAIRE



E. PAYO SUBIZA



A. ROUSSEAU

Laboratoires de Chimie Organique Physique et de Résonance Magnétique.

- BIBLIOGRAPHIE -

- (1) - D. GAGNAIRE et E. PAYO SUBIZA - Bull. Soc. Chim. France, 1963 p. 2623 -
- (2) - D. GAGNAIRE, P. SERVOZ GAVIN et A. ROUSSEAU - J. Chim. Phys. à paraître.
- (3) - M. KARPLUS et S. STERNHELL, J. Chem. Phys. 1960, 33, 1842 -

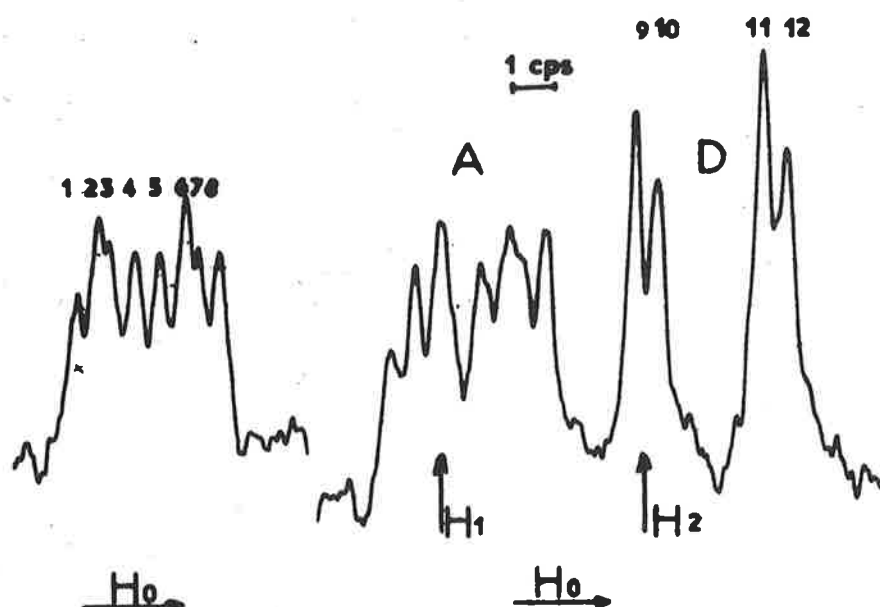


Figure 1: -à gauche: Spectre haute résolution du proton A
 - à droite: Les raies 3 et 4 de A se regroupent quand on irradie les raies 9 et 10 dans le spectre de D.

NOTATION

----- Nous avons adopté pour la classification des spectres découplés la notation suivante:

$$\{A\} D (C)$$

On irradie dans le spectre du noyau A les raies qui correspondent à une orientation donnée du spin de D. On observe les modifications apportées au spectre du noyau C.

Cette notation permet de préciser des cas
 - tels que II- où les noyaux A et C peuvent entrer dans deux triangles (ABC et ADC)

Department of Chemistry,
The University,
Glasgow, W.2., Scotland.

19th March, 1964.

Assoc. Prof. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago 16,
ILLINOIS, U.S.A.

Dear Barry,

Inquiry for ALGOL Programs

The advent of an English Electric KDF 9 computer has raised the need for programs to perform the usual high resolution n.m.r. computations in ALGOL, so we wondered if you would allow us to repeat the plea made in the letter sent by Drs. Sekuur and Kaptein to MELLONMR 57. We would be indeed grateful to hear from IITNMRN readers who know of any such programs which may be already in existence, or alternatively of a translator program which will convert one of the numerous n.m.r. programs in FORTRAN etc. into ALGOL language.

Yours sincerely,

Andrew Porte.

A.L. Porte

D.A. Morton-Blake.

D.A. Morton-Blake

ORGANISCH CHEMISCH LABORATORIUM, RIJKSUNIVERSITEIT LEIDEN

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Prof. dr L. J. Oosterhoff

nr.:

onderwerp:

MELLONMR (IITNMRN)
Associate Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago, Illinois 60616,
U.S.A.

Leiden, April 8, 1964

Dear Dr Shapiro,

There seem to be very few NMR computer programs written in Algol, although there are a lot of computers, including the X-1 (Electrologica) computer of the Leiden University, for which Algol is the most convenient interpolative language.

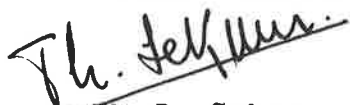
For this reason we started some months ago the translation of Fortran programs into Algol. We have translated now Dr. Bothner-By's program FREQINT IV. There are some differences between the Algol version of the program and the original one:

- 1) Because of storage limitations of our computer the program is applicable to problems of less than six nuclei only.
- 2) We made a new plot (based on the old one).
- 3) The in- and output procedures are different.

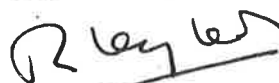
We will be happy, to supply a listing of this program to anyone interested. We are now translating Reilly and Swalen's programs NMRIT and NMREN.

If anyone knows about the existence of these or other NMR programs in Algol or has any other information concerning the subject, please let us know.

Yours sincerely,



Th. J. Sekuur



R. Kaptein.



The University of Sydney

SYDNEY, N.S.W.

IN REPLY PLEASE QUOTE : Department of Organic Chemistry

19.3.64.

A-60 SENSITIVITY: MOUSE by CAT out of DOG

Greatly enhanced sensitivity can be obtained by buying a CAT (1). Not having \$11,500 up our sleeve (and when we do it will go on a down payment for a mass spectrometer) we looked for a cheaper alternative. Crutchfield(2) described a simple manual technique for increasing A-60 sensitivity and pointed out that it would not be difficult to automate. Our Electronics Technical Officer, Carl Dehlsen, devised such a gadget and constructed it in an afternoon from standard parts worth \$11.50. We christen it MOUSE. MOUSE is a real two-timer: one called the "Travel" timer operates the slow speed sweep motor for a set time so that the carriage movement is quantized; another called the "Stationary" timer sets the interval for which the carriage is stationary between movements. Both timers are variable for flexible operation. Of various timing circuits available, the one chosen was dictated more by the components that happened to be in our Store than anything else. Figure 1 shows the circuit and Figure 2 indicates the simple modifications needed to attach it to the A-60. Three pairs of cables go into the A-60 from MOUSE and if shielded cables are not used, care must be taken to position them in the console so as to avoid transient inductive interference to the sample signal from the relay actions. The circuit shown gives a Stationary time variation of from 4 to 110 sec, and a Travel time variation from about 0.1 to 10 sec. For a Sweep Width setting of 500 cps, these Travel times correspond to carriage movements of 0.1 to 10 cps. For a Stationary time longer than 110 sec, the resistance of R_1 would need to be increased. Depending on the matching of the tubes, the timer sequence may or may not initiate automatically when MOUSE is switched on. A starter button is provided if the timers do not start by themselves.

MOUSE permits two types of spectral presentation, both of which have DOG characteristics (3). Now the maximum sensitivity for normal A-60 operation is obtained using the longest Sweep Time (500 sec) and optimized Filter Bandwidth and RF settings. For the sake of a reference from which to discuss the performance of MOUSE

we call such a spectrum a "standard scan" (Figure 3).

MOUSE-A

This is Crutchfield's presentation. In this mode the integral of the sample signal at any point accumulates for the period set by the Stationary timer. Then the Travel timer moves the carriage a set distance and during this period the integrator is returned to and held at zero. Switch S3 (Figure 2) is closed for this automatic reset operation. The cycle repeats automatically, building up the picture in Figure 4. Theoretically, MOUSE-A operation improves signal to noise (S/N) over that in the "standard scan" by the square root of the integrating time in seconds at each point. In practice, the gain is a little less than theory but nevertheless strikingly valuable for such a simple and cheap accessory. The spectrum Amplitude is reduced from that of the "standard scan" so that the tallest peaks stay on the paper. For our A-60, an Integral Amplitude setting in the range 12.5 to 40 produces least drift. For the best appearance of MOUSE-A spectra, extremely delicate adjustment of the Detector Zero is necessary to minimize integrator drift. Presumably such drift will not change the real S/N but if present it generates a broader baseline and gives one a false impression of a performance lower than it actually is. A minor irritant for MOUSE-A is that a freely running pen can make nasty blots for small Travel timer settings where the successive carriage movements are less than the thickness of the pen line.

MOUSE-B

This is a stepwise DOG presentation which produces the histogram in Figure 5 rather than the normal continuous curve. Compared with a "standard scan" DOG operation requires that the filter bandwidth be reduced and the sweep time increased by the same factor. The theoretical S/N gain is the square root of this factor. For MOUSE-B, the carriage is moved by the Travel timer as before, and the Stationary timer is fixed at the interval required for the spectrum signal to seep completely through the reduced filter setting (A-60 integrator OFF). The Spectrum Amplitude is increased to produce a suitable peak height on the paper, taking care not to saturate the amplifier with noise. The Signal Level meter deflection is kept just below full scale. The sensitivity gain for MOUSE-B is limited by the smallest setting on the A-60 Bandwidth control (0.02 cps). Compared with a "standard scan" taken using a Bandwidth setting of, say, 1 cps, the maximum reduction possible is by a factor of 50. Thus the Stationary timer is set at 50 sec, and then the theoretical improvement is approx. 7. Further gain is not possible without alterations to the A-60 Bandwidth control and we are not proposing to do this. For "standard scans" where the Bandwidth setting was not 1 cps, the theoretical gain would be correspondingly different. In practice the performance again falls a little short of

theory but is still quite good. For MOUSE-B we open switch S3 to eliminate transients from the integrator reset relay. MOUSE-B is easier to set up than MOUSE-A since there is no fiddling with the Detector Zero, and the appearance of the spectrum is cleaner with less likelihood of blots.

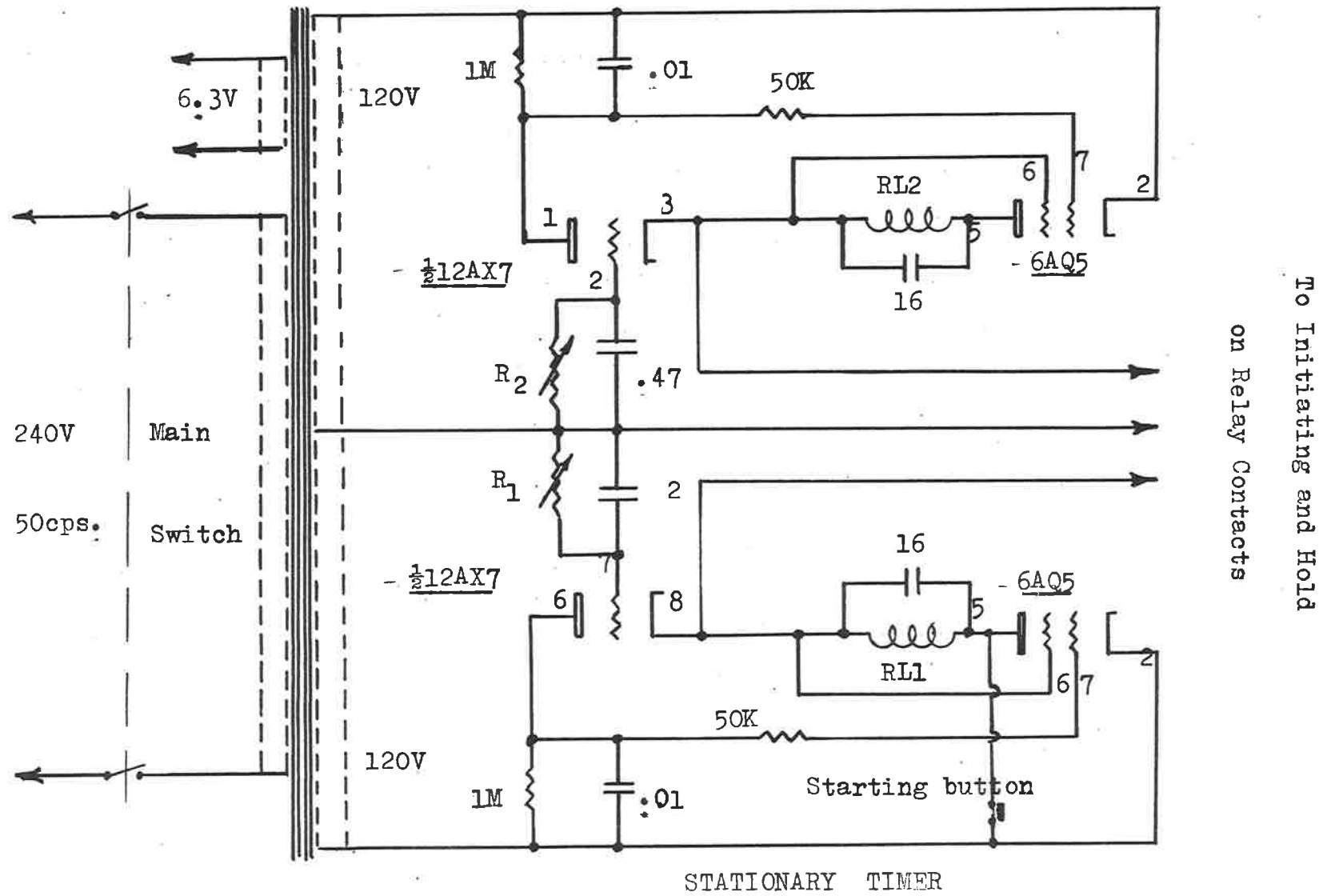
MOUSE has already been used to obtain spectra on compounds whose solubility was so low that S/N in a "standard scan" was about 1. Here we scanned across 500 cycles using MOUSE-B with a Travel time corresponding to carriage jumps of 2 cps in order to locate the signals from the sample. Then MOUSE-A was used with the longest Stationary time and reduced Travel time settings to display the maximum information in the signals. The A-60 clearly has sufficient stability to achieve sensitivity gains approaching 10 with our MOUSE circuit, and more may be feasible. Actually the best operational stability is obtained by leaving the instrument room once MOUSE is working automatically! We have not yet studied in any detail the optimum R.F. settings for MOUSE operation, but obviously saturation effects must be kept in mind.

- (1) Allen and Johnson, J.A.C.S., 85, 2668 (1963).
- (2) Crutchfield, MELLONMR, 47-27.
- (3) Ernst and Primas, MELLONMR, 48-21.

Alex. Robertson

A.V. ROBERTSON.

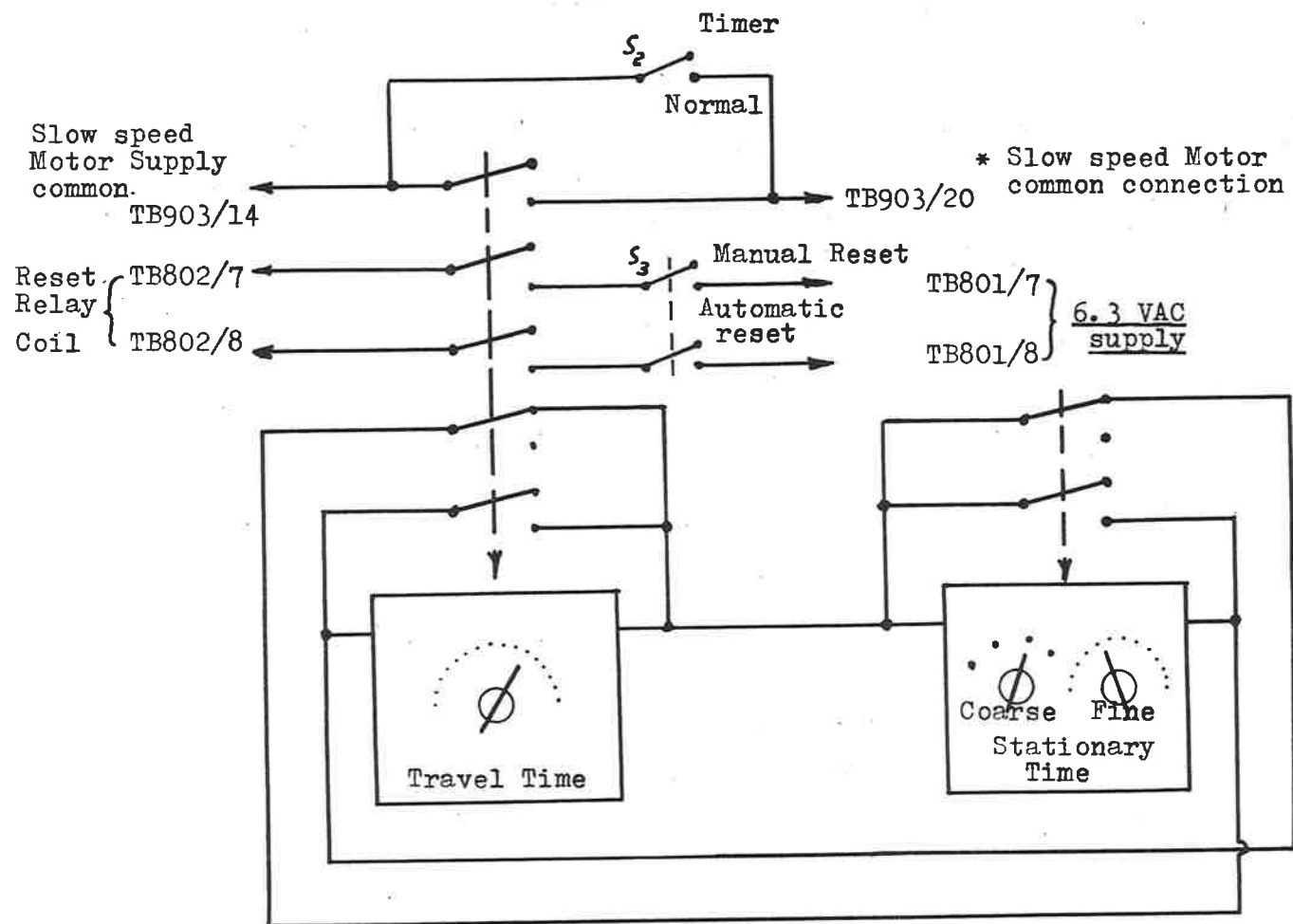
TRAVEL TIMER



R_1 = Variable from 0.5 to 15M.

R_2 = Variable from 0.1 to 2M.

FIGURE I



Block Wiring Diagram
for connection to Varian A60

Relay contacts shown for both
timers in off position

* Motor Common connection (Blue) is
lifted from supply point TB903/14
and shifted to unused position TB903/20

FIGURE 2.

Quartet of 1% ethylbenzene in CCl_4

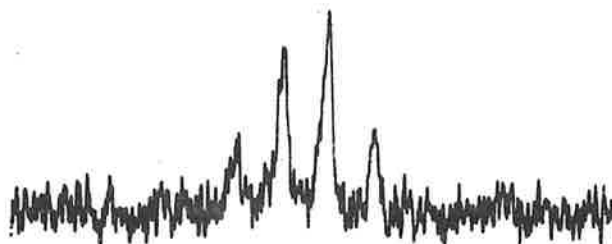
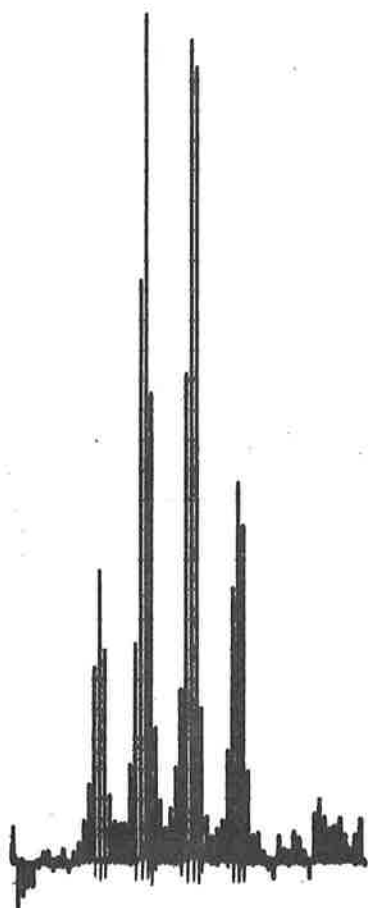


FIGURE 4: MOUSE-A

Same sample. Filter Bandwidth setting not applicable (integrating amplifier circuit by-passes filter pad).

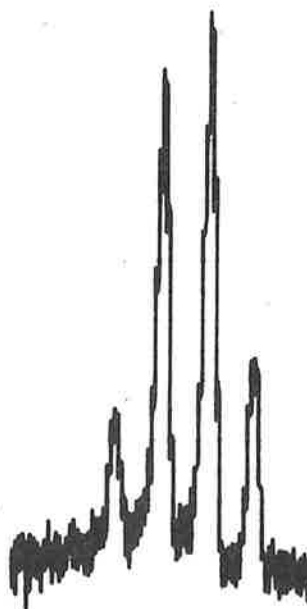
Filter Bandwidth	1.0 cps
R.F. Field	0.3 mG
Sweep Time	500 sec
Sweep Width	500 cps
Spectrum Amp.	50



R.F. Field	0.25 mG
Sweep Time	500 sec
Sweep Width	500 cps
Spectrum Amp.	4.0
Integral Amp.	40
Travel Time	1 sec
Stationary Time	110 sec

FIGURE 5: MOUSE-B

Same Sample



Filter Bandwidth	0.02 cps
R.F. Field	0.20 mG
Sweep Time	500 sec
Sweep Width	500 cps
Spectrum Amp.	200
Travel Time	0.65 sec
Stationary Time	50 sec

AEROSPACE CORPORATION

*Post Office Box 95085, Los Angeles, California 90045*

March 31, 1964

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

Dear Dr. Shapiro:

About a year and a half ago, we had reason to measure the rotational barrier in certain symmetrically substituted amides by the method developed by Gutowsky and Holm. Since then, we find that many "unusual" things happen, and the method is not really of general applicability.

In the course of this research it was found that the cis and trans resonances can interchange. It has been known for some time that the chemical shift (δ w) at room temperature of the methyl resonance due to hindered internal rotation in N,N-dimethylformamide (DMF) is significantly larger than the corresponding shift associated with the CH₂ protons in N,N-diethylformamide (DEF). However, the magnitude of the corresponding values of δ w for the CH resonance from N,N-diisopropylformamide (DIPF) are somewhat larger than those in DMF. Thus, the experimental results indicate that the values of δ w for the α protons either go through a minimum as the alkyl substituent is changed or that the cis and trans resonances change relative positions in such a manner that the CH₂ resonances in DEF just happen to occur near the "Cross-over" point.

In order to investigate the possibility of a change in the relative positions of the cis and trans resonances, the NMR spectra of methyl deuterated NN-diethylformamide-d₆ and N,N-diisopropylformamide-d₁₂ were examined. In these molecules the deuterons can be decoupled from the neighboring protons leaving only the hyperfine coupling between the α protons and the formyl protons. The latter decoupling was accomplished using a high resolution Varian 40 Mc NMR spectrometer and a Varian spin decoupling unit. The hyperfine splitting in DEF was not resolved, however, the two lines were not equally sharp. Their widths at half height were 1.7 c/s and 2.0 c/s with the low field line being broader. The spectrum of DIPF showed good resolution of the hyperfine splitting. The J values for the lines are 0.6 c/s and 0.4 c/s with the low field line showing the greater splitting. If it is assumed that the trans coupling remains greater than the cis (as found for DMF) in this series of compounds, then it follows that the resonance of the protons trans to the formyl proton occurs at the lower field in these molecules. However, in DMF, the

-2-

High field line is due to the protons trans to the formyl proton (Ref. 1). This is clear evidence that the cis and trans resonances cross over in this series of compounds rather than the chemical shift going through a minimum.

The major part of our studies on amides involves measurements of chemical shift vs temperature. In general, they indicate that even fairly simple amides can show complicated behavior. We hope we will be in a position to prepare these results for publication in the near future.

Sincerely yours,

A. Greenville Whittaker

A. Greenville Whittaker

AGW/ba

1. U. J. Kowalewski and D. G. de Kowalewski, J. Chem. Phys. 32, 1272 (1960).



UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

Department of Chemistry

March 21, 1964

Associate Professor B. L. Shappiro
Department of Chemistry
Illinois Institute of Technology
Technical Center
Chicago 16, Illinois

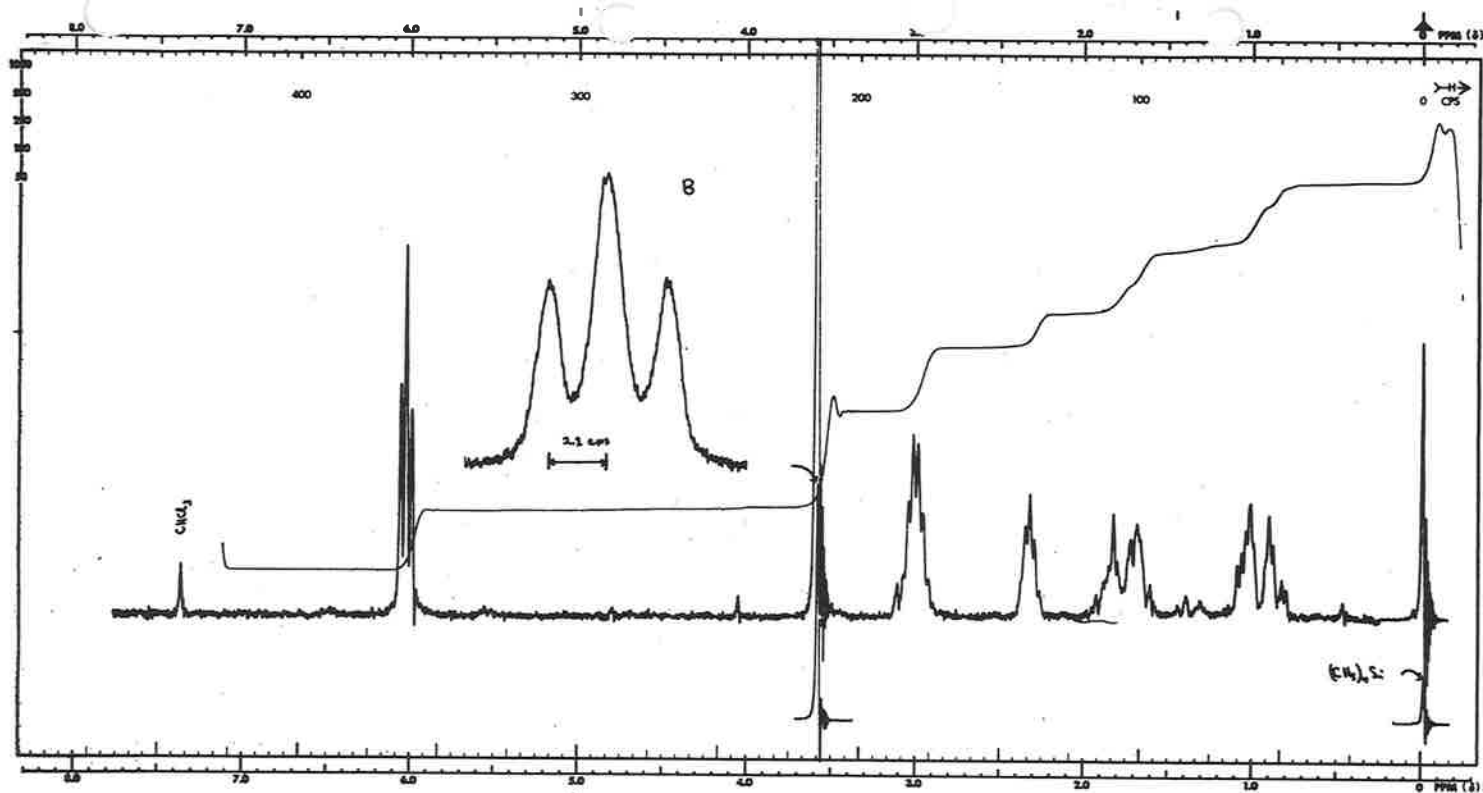
Dear Dr. Shappiro:

Over a period of the last two years, we have prepared a number of 7-monosubstituted norbornenes and examined their proton resonance spectra. We have noted that when the 7-substituent is anti to the double bond (i.e., when there was a syn-7-hydrogen), the vinyl hydrogen resonance appeared as a clean triplet, but that when the 7-substituent (other than hydrogen) was syn, the vinyl-hydrogen triplet showed some further fine splitting. We suggested that this difference in the vinyl hydrogen resonance might be used to assign the configurations of 7-monosubstituted norbornenes [J. Org. Chem., 28, 3165 (1963)]. In a recent communication [MELLONMR, No. 49, p. 42] Snyder and Franzus have also noted this phenomenon and have shown that it is due to a long range coupling, $J \sim 0.8$ cps., between the 7-anti-hydrogen and the vinyl hydrogens.

Of the 15 or so 7-monosubstituted norbornenes which have 7-anti-hydrogens whose proton resonance spectra we have observed, this long range coupling was sufficiently large in all but one to superimpose a further splitting upon the vinyl hydrogen triplet which could be easily detected with the naked eye at a sweep width (on the A-60) of 500 cps. The only exception was syn-7-carbomethoxynorbornene. Since this exception destroys the generality of this method as a means of assigning configurations, we have reexamined the proton resonance spectra of both the syn- and anti-isomers of 7-carbomethoxynorbornene. It is apparent from the spectra run at a sweep width of 50 cps. that the vinyl-hydrogen triplet of syn-7-carbomethoxynorbornene is split while the vinyl-hydrogen resonance of the anti-isomer remains a triplet. However, the splitting is now less than 0.3 cps. Thus anyone wishing to use this splitting as a basis for structural assignment is well advised to examine this triplet at a low sweep width.

Sincerely,

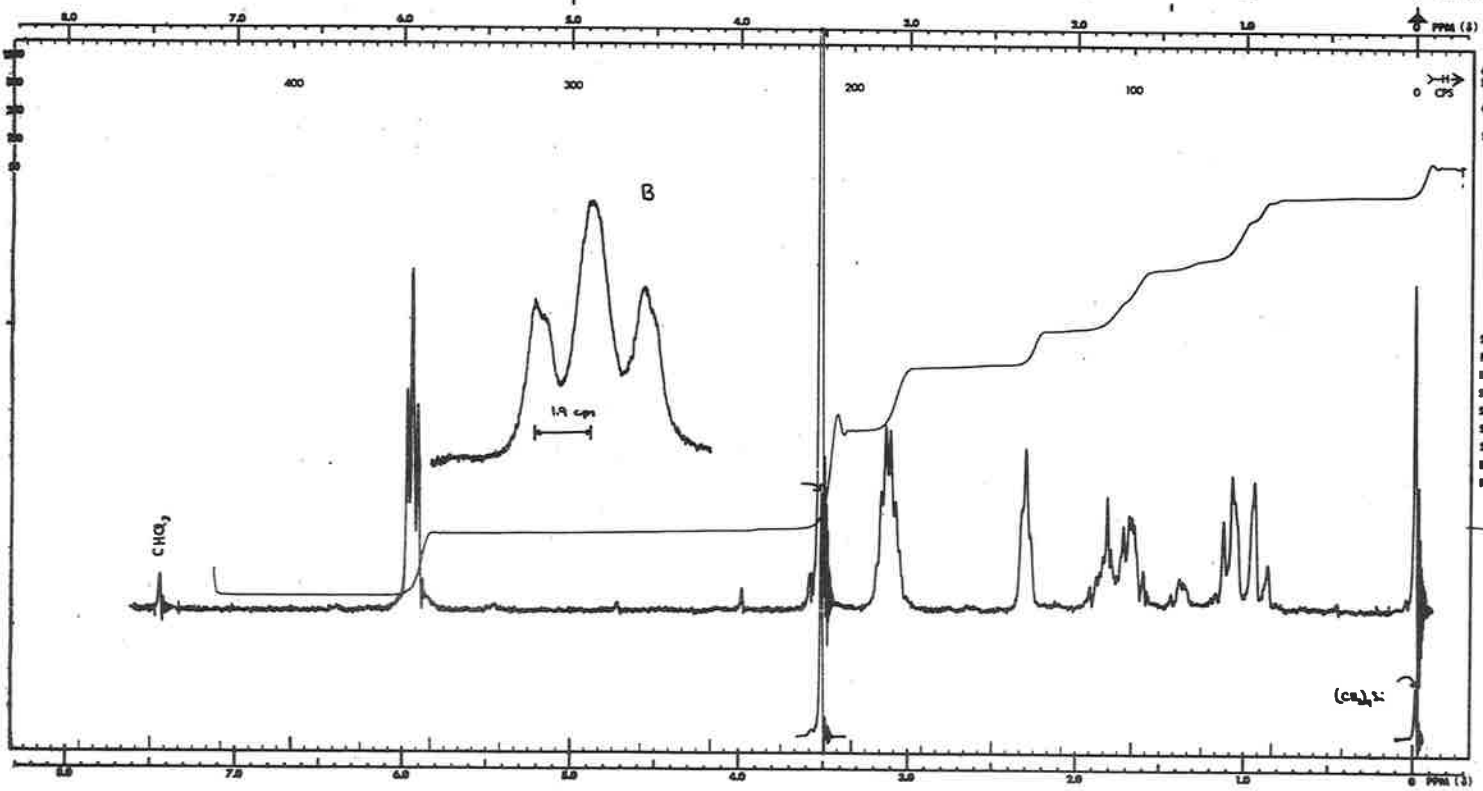
R. S. Bly
Assistant Professor
of Chemistry



VARIAN associates
PALO ALTO, CALIFORNIA
INSTRUMENT DIVISION

CHART 5-68A

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INSTRUMENT DIVISION

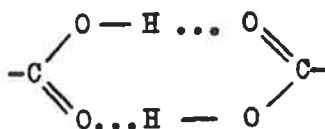
CHART 5-68A

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To Prof. B.L. Shapiro.

1) PROTON POSITIONS IN SUCCINIC ACID CRYSTALS

In order to obtain information on the positions of protons in hydrogen-bonded complexes, we have prepared deuterated succinic acid: $\text{HOOC}-(\text{CD}_2)_2-\text{COOH}$, and measured proton resonance in the solid state. The protons occur in pairs within the group:



of which two different orientations in the crystal occur. Measurements on single crystals are still in progress but we have measured the second moment of polycrystalline samples. X-ray diffraction studies [Broadley et al, Proc. Roy.Soc. A 251, 441 (1959)] roughly indicate a position of the protons outside the line joining two oxygen atoms, with an interproton distance of 2.9 \AA . With straight hydrogen bonds the interproton distance would be 2.4 \AA .

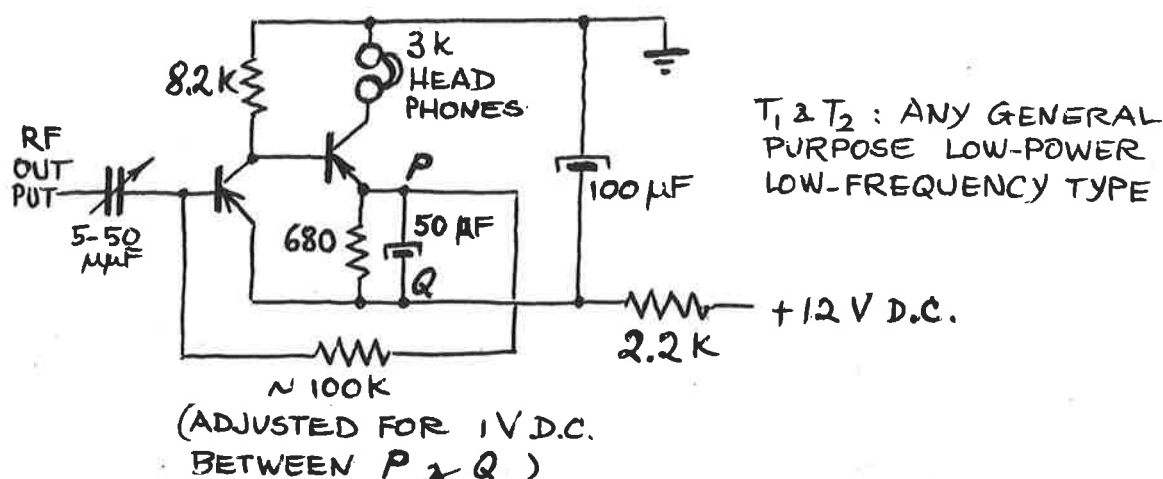
From our modulation-corrected second moment $S = 1.88 \pm 0.06 \text{ gauss}^2$ we find, after subtraction of the contribution of third and higher neighbours, an interproton distance of $2.52 \pm 0.02 \text{ \AA}$. This is considerably smaller than X-ray diffraction studies indicate. Even if we allow for a motional effect with a r.m.s. amplitude of the interproton distance of 0.3 \AA , the average interproton distance does not exceed 2.60 \AA .

These measurements lead to the conclusion that the protons are not located in the center of the X-ray electron density map, but occur closer to the line joining two oxygen atoms, probably due to the effect of hydrogen bonding.

2) A SIMPLE DEVICE FOR LOCATING WEAK RESONANCES

In order to find weak resonances of insensitive nuclei, we have found it useful to make the signal audible by a pair of headphones. By using the highest RF intensity available, many nuclei are located by rather fast scanning of the field, using a modulation amplitude of several gauss and of a frequency of 80 c/s. The device is also very useful for minimizing the leakage signal in Varian 2-16 Mc probe holders: one simply adjusts for minimum noise.

The amplifier (see diagram) is coupled permanently to the output signal of the RF unit through a variable capacitor. + 12 Volts is obtained from a Varian power supply.



H. J. C. Berendsen
(H. J. C. Berendsen)

C. Michelsen
(C. Michelsen)

STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

DEPARTMENT OF CHEMISTRY

March 31, 1964

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

Dear Barry:

As Jake Stothers mentioned in a recent communication to this newsletter, we have now completed the initial phase of our study of carbonyl carbon shieldings in organic compounds. Our survey included an examination of more than one hundred and fifty compounds selected to cover the commonly encountered functional groups such as aldehydes, ketones, carboxylic acids, esters, amides, anhydrides and acid chlorides, as well as a few bifunctional compounds. Examples were drawn from the aliphatic, alicyclic and aromatic series. A number of general features were found which apply to each class of carbonyl compound, such as the effects of alkyl substitution, of conjugation, and of hydrogen-bonding (either intra- or intermolecular).

The resonances of carbonyl carbons occur over a total range of approximately 70 ppm. at the low field end of the C^{13} spectral region. Some olefinic carbons absorb within the upper portion of this region, as do oximes, carbon disulfide, and the central carbon in allenes; otherwise, there is no interference with the C^{13} resonances of other classes of compounds for which data are available. Also, it seems likely that a distinction between carbonyl peaks and resonances of other carbons may be made on the basis of differential solvent effects.

The carbonyl group in aliphatic ketones and aldehydes absorbs in the low field region of the carbonyl range, -25 to -5 ppm. relative to CS_2 . Although the two regions are not distinct, no ambiguity arises because the aldehyde carbonyl resonances are split into doublets by

Associate Professor Shapiro

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March 31, 1964

the formyl proton. The resonances of conjugated ketones and aldehydes appear at higher field than those of the saturated compounds, usually in the range from -5 to +5 ppm. Carboxylic acid peaks appear at still higher fields, around 10 to 20 ppm., and their esters have resonances from about 20 to 30 ppm. Several acid anhydride peaks have been found in the upper portion of the ester region, around 27-30 ppm., and the few amides studied absorb slightly higher. Of the groups of compounds included in this survey, the alkyl carbonates and acetylenic esters have the most shielded carbonyl carbons. Their resonances are found at about 36-40 ppm. A number of the spectral regions are shown in Fig. 1.

The cycloalkanones, from cyclobutanone to cycloheptadecanone, show considerable variations in the carbonyl shielding, as shown in Fig. 2. Cyclopentanone has one of the lowest carbonyl carbon shieldings of any organic compound so far examined, but the fact that the shielding in cyclobutanone is even higher than that in cyclohexanone indicates that the effect is not simply related to strain in the five-membered ring. Furthermore, the carbonyl carbons in the more highly strained systems, thujone and camphor, have nearly the same shieldings as those in cyclopentanone. Also, the carbonyl resonances of cyclooctanone and cyclononanone appear at significantly lower field than do those of the six-, seven-, or ten-membered cycloalkanones, although it is generally believed that the eight- to ten-membered rings are more strained than the five-membered ones. This anomalous deshielding of the five-membered ring carbonyl carbon is also found in lactones and lactams. It is especially puzzling when compared with the carbon shieldings in the cycloalkanes, which were reported in a recent issue of this Newsletter. A similar peculiarity is found when the C₁₂ - C₁₇ cyclic ketones are compared with the cyclic hydrocarbons.

Substituent effects have been examined in some detail, but their discussion here would take up too much space. A partial summary is to be found in our Table VI, which is reproduced here. Although a number of gaps remain to be filled, it is apparent that there is considerable consistency of the effects of various substituents on the different carbonyl groups.

Intramolecular hydrogen-bonding causes a marked shift of carbonyl carbon resonances to low field. Some examples of such effects in ortho-hydroxy aromatics are to be found in Table VI. These results suggest that hydrogen-bonding solvents should also shift carbonyl resonances to low field. Examination of the spectrum of acetophenone

Associate Professor Shapiro

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March 31, 1964

in several solvents reveals that the carbonyl resonances shift more than do those of the other carbons, and in the expected direction. The largest shift was found in methanol, but chloroform is also fairly effective. Fig. 3 compares our results for acetophenone with those of Maciel and Ruben for acetone, which were published after this work had been completed. Both sets of data have been extrapolated to infinite dilution, assuming linearity with volume fraction. There is very good agreement, but the slope of the line may be slightly different from unity.

Keep up the good work with the Newsletter - and keep those Author Indexes coming!

Yours truly,



Paul C. Lauterbur
State University of New York
at Stony Brook



J. B. Stothers
The University of Western Ontario

PCL:jv

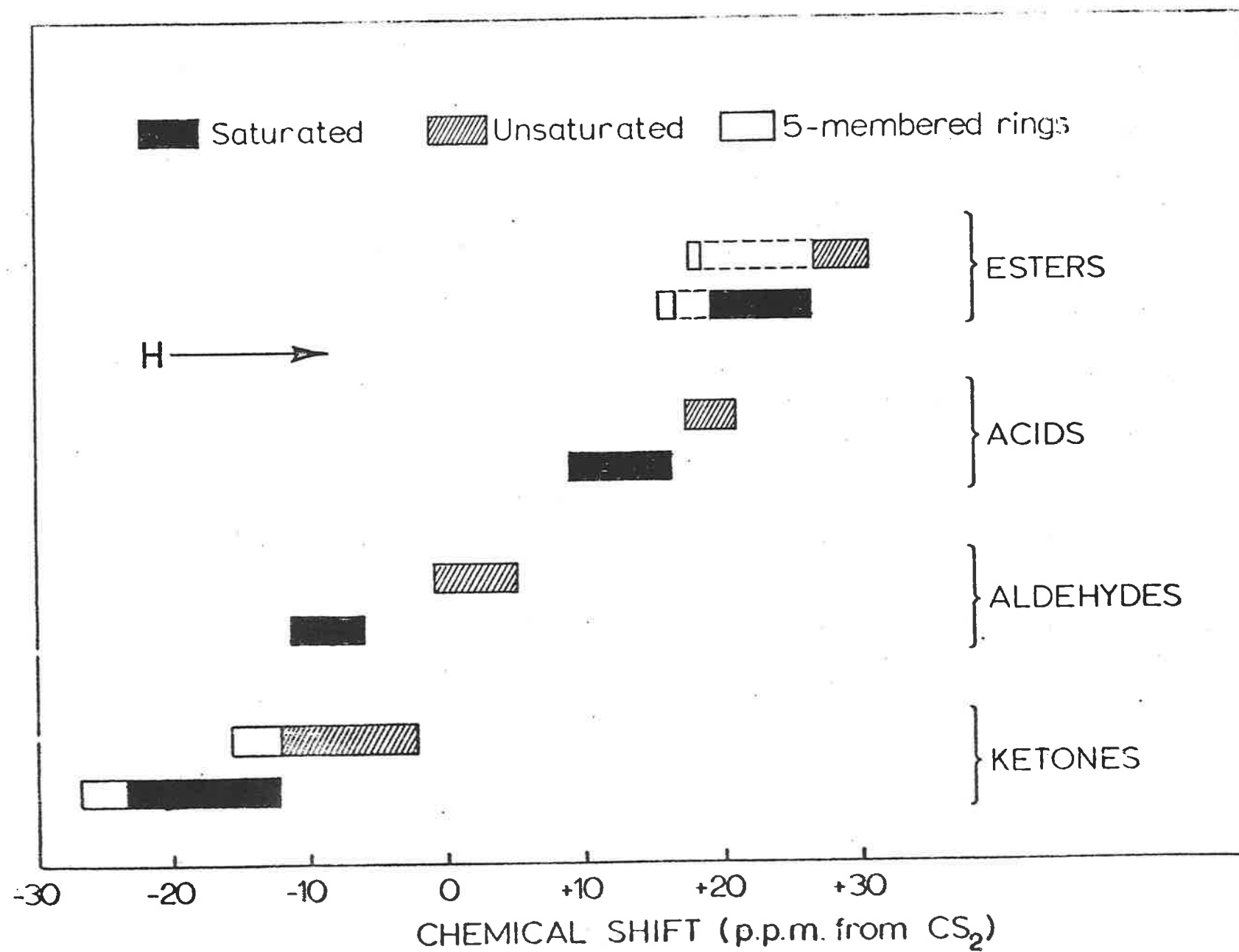
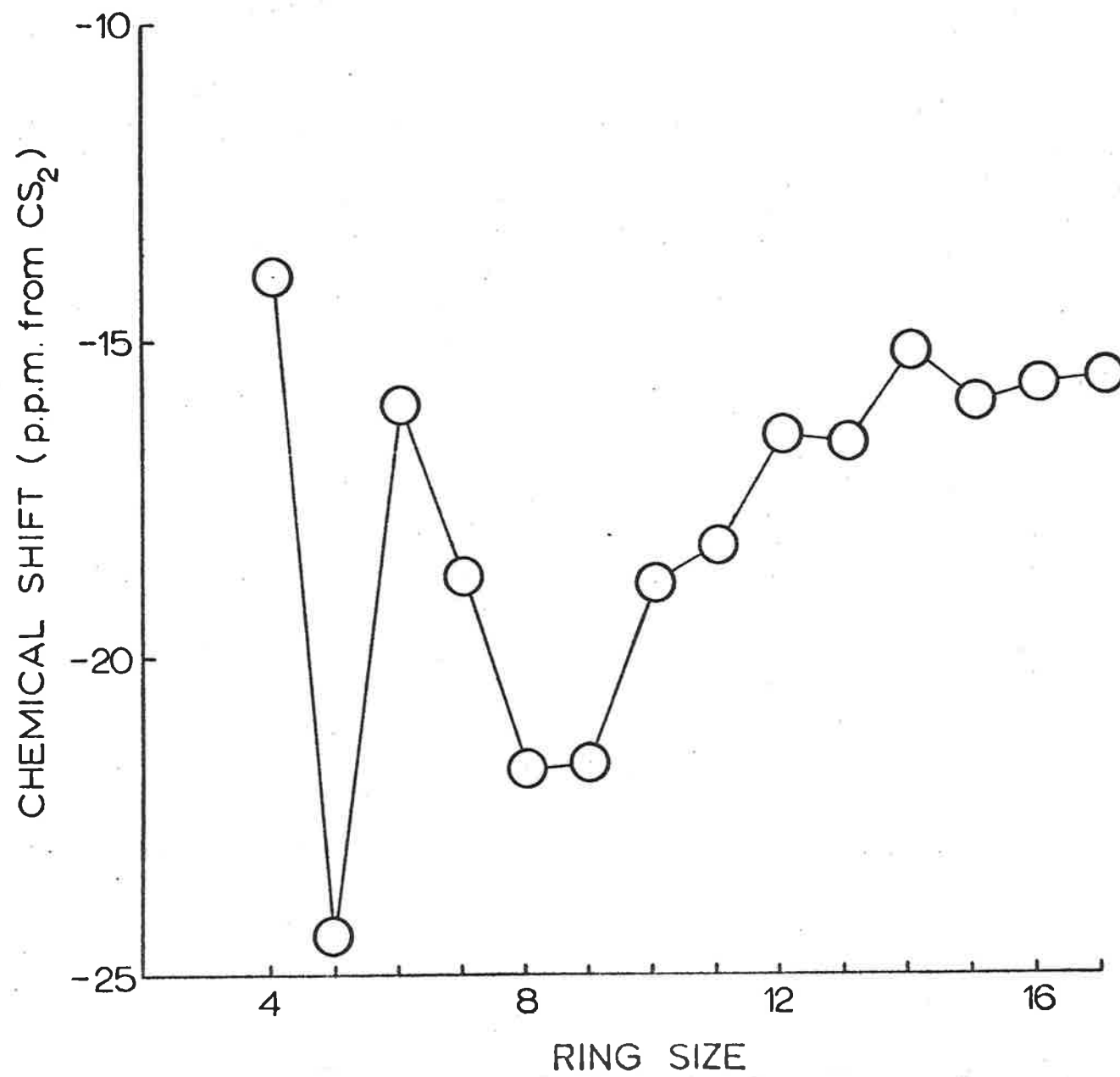


Figure 1



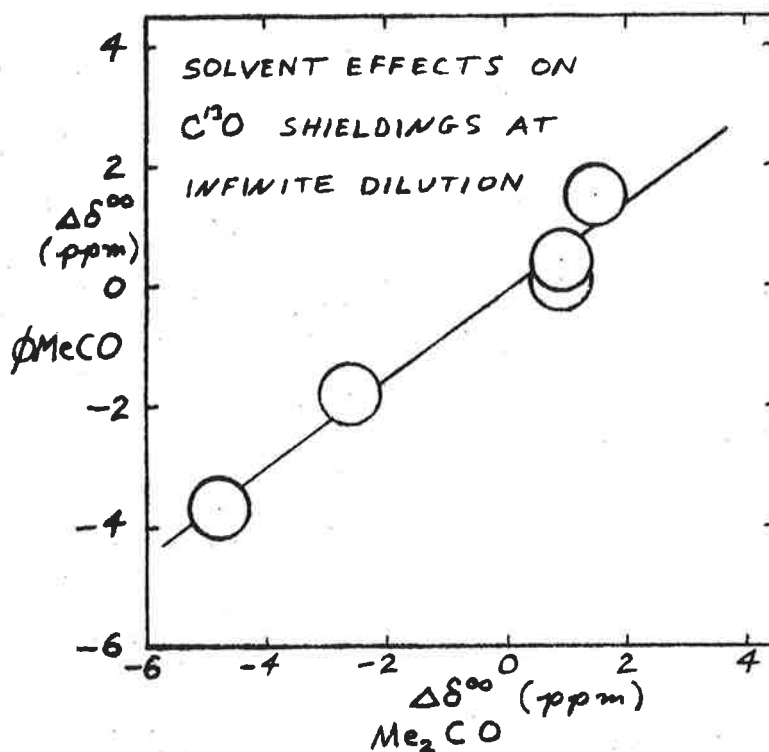


Figure 3

TABLE VI
SOME SUBSTITUENT EFFECTS ON CARBONYL CHEMICAL SHIFTS
(p.p.m. from CS₂)

R	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	$\text{R}-\text{CH}=\text{O}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	$\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$
H	-	-8.0	-	27.0	-	+1.0
H ₃ C	-6.8	-12.3	-12.3	15.6	23.8	-3.2
ClCH ₂ -	-	-7.0	-1.2	19.0*	24.0	+2.8
CH ₂ CH-	-	-	-	23.1*	27.5	7.5
Cl ₃ C-	+17.5	-	+19.0	25.7*	30.2	12.7
HO-	27.0	+15.6	-	-	-	-
H ₂ N-	27.9	-	-	-	-	-
(CH ₃) ₂ N-	30.4	-	-	-	-	-
o-HO-C ₆ H ₄ -	-3.5	-10.9	-	22.5*	-	-
p-HO-C ₆ H ₄	-	-4.6**	-	-	-	-
o-MeO-C ₆ H ₄ -	+5.3	-5.0	-	26.9*	-	-

* chloroform solution

** dioxane solution

* methyl esters

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Buenos Aires, march 31, 1964.

Dear Dr. Shapiro:

I wish to comment on the convergence of some of the iterative procedures in use for the calculation of NMR parameters.


A specially difficult ABC case called my attention, namely, the spectrum of the vinyl protons of methylvinylsilane, as studied by R. Freeman and W.A. Anderson in their very interesting paper on double resonance (J.Chem.Ph. 37, 2053, (1962)). As can be seen from their table IV, which is partially reproduced here (to three decimal places only) more than 200 iterations were necessary with the method of J.D. Swalen & C.A. Reilly (J.Chem.Phys. 37, 21, (1962)) to obtain the chemical shift and spin-spin parameters.

We tried our iterative procedure (J.Chem.Phys. 37, 2603, (1962)) programmed for a Ferranti Mercury computer, on this spectrum, using as starting parameters data obtained from a theoretical spectrum given by the computer (non iterative program) with the parameters of solution I of F. & A. paper (given with two decimal places only, what accounts for the differences in final values obtained). It should be observed that the starting parameters of this method are obtained as average values of line frequencies of the "experimental" spectrum, and these are practically equal to the values given by the iteration N° 30 of the F. & A. paper.

From the comparison of both tables it can be seen that this method is about five times faster in its convergence than the method of S. & R. Unfortunately its use is limited to completely unsymmetrical cases only (like ABC and ABCD). It is useless, for instance, in the A_2B_2 case. We are looking now for a similar procedure for this case.

We have had a lot of troubles with our programs for some time due to the use of Givens' diagonalization subroutine. We switched now to the Jacobi method. Even so, we have still sometimes troubles with the "crossing" of levels. Does some of your readers have some experience on this? We would be very glad to know.

Yours, sincerely


V.J. Kowalewski.

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Chemical shift and spin-spin coupling parameters as obtained at various stages of iterative computer analysis of a strong coupled ABC spectrum (methylvinylsilane) with two different iterative procedures.

J.D.Swalen & C.A.Reilly's method:

iter.Nº	ν_A	ν_B	ν_C	J_{AB}	J_{AC}	J_{BC}
30	-17,643	-0,488	18,132	8,860	15,680	14,150
60	-13,325	2,627	10,697	4,068	20,246	14,376
120	-13,203	2,942	10,261	3,621	20,402	14,668
240	-13,188	2,979	10,210	3,568	20,419	14,703
300	-13,188	2,979	10,209	3,567	20,419	14,704

Author's method:

iter.Nº	ν_A	ν_B	ν_C	J_{AB}	J_{AC}	J_{BC}
0	-17,645	-0,486	18,131	8,862	15,680	14,148
10	-13,326	2,611	10,715	4,409	20,293	14,348
20	-13,221	2,901	10,320	3,674	20,393	14,623
30	-13,197	2,961	10,236	3,595	20,414	14,682
40	-13,192	2,975	10,216	3,576	20,418	14,696
43	-13,191	2,977	10,214	3,574	20,419	14,697

P.S.I am sorry to tell you that I cannot make my mind to these NMR letters being called "Illinois ... letters".In someway it seems to me unfair to the Mello Institute previous work.I would rather prefer a more "neutral" name.

THE UNIVERSITY OF LIVERPOOL

TELEPHONE: ROYAL 6022
Extension 356



DEPARTMENT OF
INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY
THE DONNAN LABORATORIES
VINE STREET, LIVERPOOL, 7

Chemical Shifts of Fluorine Nuclei Ortho to
substituents in Fluorochlorobenzenes.

by N. Boden, J.W. Emsley*, J. Feeney and L.H. Sutcliffe.

Several workers have attempted to correlate ^{19}F chemical shifts in fluorinated benzene derivatives with the π -electron charge densities and the bond orders calculated using the Hückel molecular orbital method. In all cases, chemical shifts of the fluorine nuclei in meta and para positions to substituents could be predicted successfully, but large deviations were encountered for fluorine nuclei in the ortho position. We have shown that such ortho effects in the complete series of fluorochlorobenzenes can be accounted for satisfactorily in terms of intramolecular electric field contributions.

Using the equation of Prosser and Goodman¹

$$\delta = 488(\Delta E)^{-1} [0.1\Delta q(C_Z) + 11.9\Delta q(F_Z) + 3.9\Delta p(C_Z F_Z)] \times 10^{-6} \quad (1)$$

we calculated the chemical shift of the para fluorine nucleus in $\text{C}_6\text{F}_5\text{Cl}$ relative to C_6F_6 . The calculation enabled ΔE to be evaluated and hence the electronic contribution to the chemical shifts ($\delta_{\text{electronic}}$) of all the fluorine nuclei to be calculated in the fluorochlorobenzenes. The next step was to compute the chemical shift contributions (δ_{electric}) from the electric fields at the fluorine nuclei using the following equation²

$$\delta_X = -AE_Z - B(E^2 + \langle E^2 \rangle) \quad (2)$$

where A and B are constants, E_Z is the electric field component along the C-X bond direction, E^2 is the square of the electric field intensity. E_Z and E^2 were obtained as the vector sum of the fields arising from point dipoles situated at the mid-points of the C-F and the C-Cl bonds. $\langle E^2 \rangle$ is a non-zero time-average value of E^2 , being given by³

$$\langle E^2 \rangle = 3\pi I r^{-6} \quad (3)$$

in which P is the polarisability of the electron group, I is the first ionisation potential and r is the distance separating the fluorine atom from the electron group.

It was found that the term AE_Z in equation (2) could be neglected hence it was possible to set up two equations in the unknowns B and ΔE using the observed chemical shifts for the fluorine nuclei in the ortho and para positions in C_6F_5Cl - the resulting values of B and ΔE were used to calculate the chemical shift of the fluorine nucleus in the meta position, and to calculate the chemical shifts of all the remaining fluorochlorobenzenes relative to C_6F_6 . The table shows the observed and calculated values: there is no discernible pattern in the values of $\delta_{obs} - \delta_{calc}$ except that they tend to increase with increasing chlorine substitution. We cannot account for the large value of $\delta_{obs} - \delta_{calc}$ found for the symmetrical 1,3,5-trichloro compound.


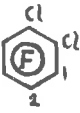









A more detailed account of this work will appear in Molecular Physics.

1. F. Prosser and L. Goodman, J. Chem. Phys., 38, 380, 1963 .
2. A.D. Buckingham, Can. J. Chem., 38, 300, 1960 .
3. A.D. Buckingham, H.J. Bernstein and W.T. Raynes, J. Chem. Phys., 36, 3481, 1963 .

* Chemistry Department, South Road, The University, Durham City.

Table

Calculated and Observed Chemical Shifts Relative to C_6F_6
in Fluorochlorobenzenes.

		δ_{electric}	$\delta_{\text{electronic}}$	total δ_{calc}	δ_{obs}^*	$\delta_{\text{obs}} - \delta_{\text{calc}}$
	1	17.589	4.107	21.693	21.693	0.000
	2	0.6254	-0.1895	0.436	0.800	0.364
	3	0.3761	5.840	6.216	6.216	0.000
	1	18.079	3.933	22.012	26.172	4.160
	2	0.8452	6.406	7.251	6.650	-0.601
	1	34.915	7.885	42.800	43.885	1.085
	2	17.673	10.565	28.238	27.739	-0.499
	3	1.255	0.1026	1.358	1.638	0.280
		18.083	4.240	22.323	22.280	-0.043
	1	18.506	10.588	29.094	31.709	2.615
	2	1.471	7.005	8.475	6.509	-1.967
	1	35.562	8.032	43.594	47.720	4.126
	2	18.307	12.031	30.338	27.714	-2.624
	3	18.717	4.657	23.374	26.120	2.746
		35.131	31.441	66.572	49.588	16.984
		18.932	12.086	31.018	31.349	0.331
		36.175	8.088	44.263	51.182	6.919
		35.760	15.299	51.059	53.271	2.212
		36.390	15.920	52.310	56.830	4.520

* Shifts were measured from $CFC1_3$ internal reference and converted to C_6F_6 reference using the relationship

$$\delta_{C_6F_6} = 162.28 + \delta_{CFC1_3}$$

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PHYSICAL CHEMISTRY LABORATORIES

Dr. K. Frei



Dr. P. Niklaus

Associate Professor B.L. Shapiro

Department of Chemistry

Illinois Institute of Technology

Technology Center

Chicago Ill. 60 616

U.S.A.

YOUR REF.

OUR REF. 30/Dr.K.F./Wu
Dr.P.N.BASLE 13. 12th February 1964
(SWITZERLAND)

Dear Dr. Shapiro,

After some experience with plastic microcells in connection with our A 60 instrument we have been investigating a simple glass construction which proved to become a convenient microcell. It consists of a glass sphere - blown at the end of a capillary - and a plastic holder. The sphere is filled with the sample, fixed in its holder and then immersed into the pure solvent inside a regular thin wall sample tube; Fig. 1.

As the sample contacts glass only, no "solvent effect" of the cell material itself is encountered (CF_3COOD Spectra!).

A good support of the sphere is essential. The holder was cut of a nylon rod and made to fit tightly the usual thin wall sample tubes of 4.0 mm i. ϕ . The lower part of the support is slotted and bears a slide ring to fix the capillary.

By means of a metal rod the insert is adjusted properly in order to obtain the optimum signal (integral); readjustment of the field homogeneity may be necessary.

Only those spheres showing reasonably good resolution (no air bubbles in the blown glass!) when checked with chloroform were selected. Filling is conveniently accomplished with a syringe; shaking or centrifuging removes any air bubbles. The capillary is supported in the slot of the holder and fixed by the slide ring. To empty the cell it is placed in a centrifuge upside down, over some cotton. Resolution does

not seem to depend much on the size of the capillary. Instability is mostly caused by vibration of the microcell. Therefore the free length of the capillary should be kept short and the sphere should fit the inner wall of the sample tube smoothly. However, any contaminations as e.g. glass dust will deteriorate the homogeneity.

With regular sample tubes, the minimum solvent amount for reasonably good resolution is 180 to 200 μ l. Whereas the volume of our microcell amounts to 25 to 40 μ l including about 10 mm of capillary length. Thus the "concentration gain factor" is somewhere between 5 and 8. The net intensity gain (measured by the ratio of the integrals), is obtained by the product of "concentration gain factor" and "filling factor" of the microcell.

To compare it with the standard sample tubes the procedure was as follows: the regular spectrum was made with a solution of 2 mg sample in 200 μ l solvent filling the ordinary sample tube. For comparison, a solution of 2 mg at a correspondingly higher concentration was filled into the microcell. Both spectra were scanned under identical conditions. The net intensity gain measured as the ratio of corresponding integrals was determined as about 3.3 (corresponding to a filling factor of about 0.66 to 0.41). The ratio of corresponding peak heights was 2.8, that is about 85 % of the integral ratio.

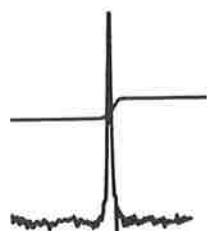
Yours sincerely

P. Niklaus
P. Niklaus

K. Frei
K. Frei

Fig. 1: Spectra, instrument settings and mechanical setup of glass microcell.

example: CH_3 signal of
2,4,6-trinitro-toluene



regular sample tube

2.0 mg $\text{C}_7\text{H}_5\text{O}_6\text{N}_3$ in
200 μl CDCl_3

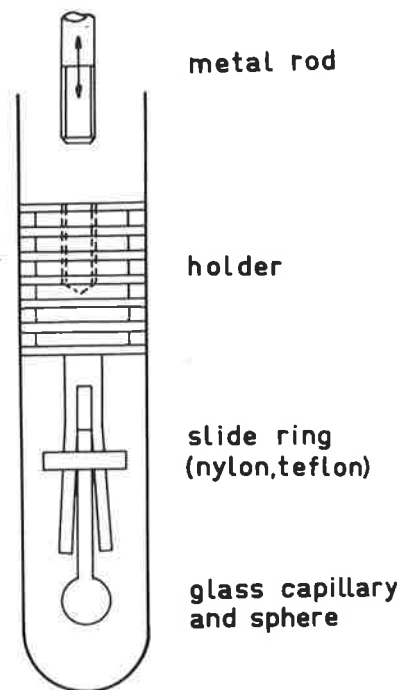


microcell

2.0 mg $\text{C}_7\text{H}_5\text{O}_6\text{N}_3$ in
25 μl CDCl_3

identical A-60 instrument settings:

frequ. response	1	
r.f. field	0.3	0.6
sweep time	500	50
sweep width	500	
spectrum amp.	40	8
integral amp.		80



ORGANISCH-CHEMISCHES INSTITUT

DER UNIVERSITÄT BONN
Dr. G. Snatzke
G. Berscheid
H. Lander

53 Bonn, den 3. 4. 1964

Meckenheimer Allee 168

Telefon 3 1961

Assoc. Prof. B. L. Shapiro
Dept. of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Ill.

-CH_x - OH - Splitting in pyridin solution.

Dear Professor Shapiro,

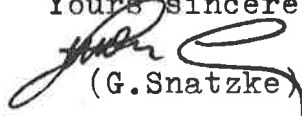
I am very sorry that you had to remind me again for sending in our contribution to IITNMRN. I hope, that the following lines will give us the pleasure of obtaining IITNMRN for the next nine months.

Spin-spin-splitting in alcohols which involve the OH-proton are only found, if the solution is completely freed of even traces of acids, which catalyze intermolecular proton-proton exchange (1). Another possibility is to use solvents, which give strong hydrogen bonds with alcohols and thus slow down this equilibration (2). Using pyridin as solvent we found with some mycarose derivatives multiplets of OH-protons (3) and are investigating now the dependance of the signals of the -CH_x-OH - grouping with concentration and the amount of added water in simple alcohols.

With methanol, isopropanol, cyclohexanol, borneol, isoborneol and menthol we always noticed the expected splitting as long as the concentration allows for a solvation cage. Methyl substituted pyridins (picolin, s-collidin) as solvents gave the same picture. If J-constants of alcohols are calculated from NMR spectra in pyridin solution (4) one must, therefore, keep in mind this complication due to extra splitting with the OH-proton. Primary, secondary and tertiary alcohols might easily be differentiated by the splitting pattern of the OH signal.

In the diagram are given some examples for methanol/water mixtures in pyridin. As in some other solvents the water line is separated from the OH-quartet (and in one case even from the OH-singulet) before it finally coalesces with it. It is interesting to note, that with higher concentrations of the alcohol some water is necessary to bring about the -CH_x-OH-splitting. Though in one example the molar ratio of water/methanol is only about 1:10 we find a well resolved quartet for the hydroxyl proton. Measurements at various temperatures are in progress.

With kindest regards,
Yours sincerely,


(G. Snatzke)

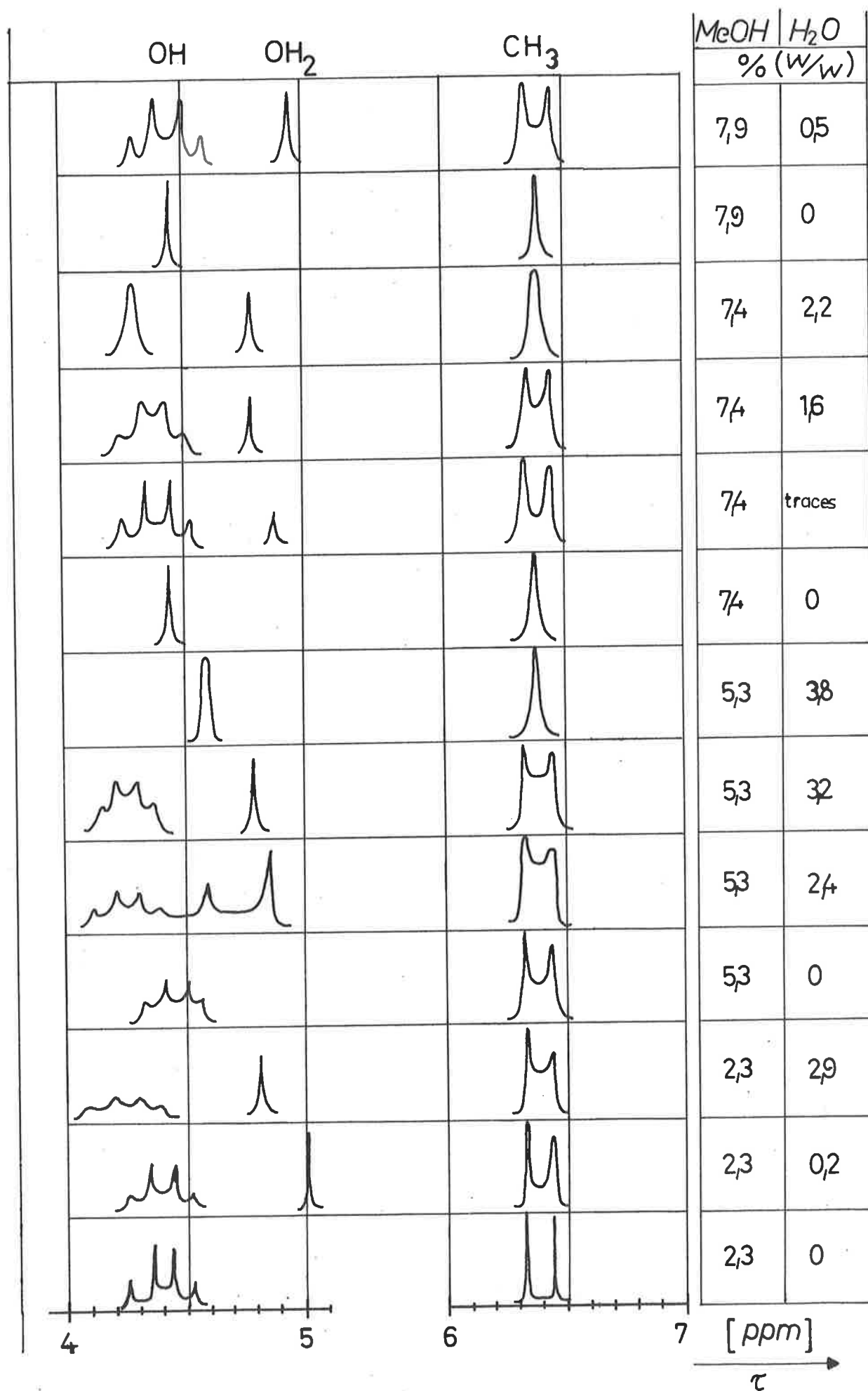
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(3) F. Korte, U. Claussen and G. Snatzke, Tetrahedron, in press

(4) cf. e.g. T. J. Flautt and W. F. Erman, J. Amer. chem. Soc. 85, 3212 (1963)



MCMASTER UNIVERSITY

HAMILTON COLLEGE

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY

April 8, 1964

Dr. Bernard L. Shapiro,
Associate Professor,
Illinois Institute of Technology,
Technology Center,
Department of Chemistry,
Chicago, Illinois 60616
U.S.A.

Dear Dr. Shapiro:

While examining the F^{19} spectra of some selenium-fluorine compounds we have observed several selenium isotope effects. The spectra consist of a main peak with a pair of satellites due to fluorine on Se^{77} ($I = 1/2$). The separation of these satellite peaks and the displacement of their centre from the main peak gave the coupling constants and isotopic shifts recorded in Table I.

Table I

	$J_{Se^{77}-F}$ (cps)	$\Delta\delta_{Se^{77}-Se^{80}}$ (ppm)
$SeOF_2$	837 ± 0.6	0.009 ± 0.005
SeO_2F_2	1584 ± 0.6	0.020 ± 0.005
$HSeO_3F$	1454 ± 0.5	0.016 ± 0.005
SeF_6	1421 ± 0.5	0.021 ± 0.004

Close examination of the main peak revealed structure due to the non-magnetic isotopes of selenium for SeF_6 , $HSeO_3F$ and SeO_2F_2 but only in the latter case was it possible to resolve the peaks well enough that accurate chemical shifts could be obtained. The expected peaks were observed for all the isotopes except Se^{74} which is only 1% abundant (Table II).

Dr. Bernard L. Shapiro

- 2 -

April 8, 1964

Table II

Isotope	% Abundance	$\Delta\delta_{\text{Se}^x-\text{Se}^{80}}$	$\frac{\Delta\delta_{\text{Se}^x-\text{Se}^{80}}}{x-80}$
74	0.96	-	-
76	9.12	-0.026 ± 0.003	0.006 ± 0.001
77	7.50	-0.020 ± 0.005	0.007 ± 0.002
78	23.61	-0.013 ± 0.002	0.007 ± 0.001
80	49.61	-	-
82	8.84	$+0.014 \pm 0.002$	0.007 ± 0.001

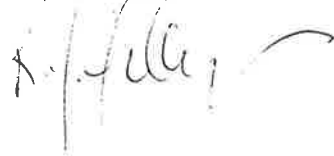
As expected the isotopic shift per unit mass difference is constant.

The isotopic shifts per unit mass difference observed in F^{19} spectra for selenium (0.003 - 0.007 ppm) are considerably smaller than those observed previously for carbon (0.07 - 0.19 ppm) and for sulphur (0.016 - 0.026 ppm) but are of the same order of magnitude as those observed for silicon (0.004 - 0.007 ppm).¹

The expected decrease of the isotopic shift with increasing mass of the atom attached to fluorine is evident in a given periodic group of elements but the differences in the isotopic shifts between different groups of elements are clearly due to some factor other than isotopic mass.

The observed isotope effect for SeOF_2 is considerably smaller than for the other compounds studied. Since the Se^{77} satellite peaks were also considerably broader than in the other cases it seems probable that fluorine exchange was occurring. This would cause the centre of the satellite peaks to move towards the main peak giving an apparent isotopic shift smaller than the actual value.

Yours sincerely,



T. Birchall
S. L. Crossley
R. J. Gillespie

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RJG/pm

HARVARD MEDICAL SCHOOL
THE DEPARTMENT OF PHARMACOLOGY
25 SHATTUCK ST., BOSTON, MASS. 02115

April 15, 1964

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

Dear Professor Shapiro:

We have been interested for some time in the use of NMR for the study of the weak, reversible interactions of small molecules with proteins. The binding of penicillin to serum albumin is a particularly convenient example because it has been extensively studied by the usual methods of equilibrium dialysis and electrophoresis, and because penicillin is quite soluble and provides a readily interpretable NMR spectrum. While the usual methods of study measure only the amount of penicillin bound, the changes in the NMR spectrum permit identification of the portion of the molecule most strongly involved in the interaction.

When albumin is added to solutions of penicillin G in D_2O , no changes in the chemical shifts of the penicillin peaks occur. However, all of the peaks broaden, the extent of the broadening varying from one peak to another. That this broadening is due to a specific penicillin-albumin interaction, rather than to the many possible non-specific causes such as increased viscosity, increased penicillin-penicillin interactions, or intermolecular effects between penicillin and the protein, is demonstrated by the following observations:

- 1) Addition of non-binding macromolecules such as gamma-globulin, methyl cellulose, or even Sephadex granules causes little or no broadening.
- 2) Studies of an array of penicillin and albumin concentrations show that the extent of broadening is roughly proportional to the ratio of the numbers of penicillin and albumin molecules. When more penicillin is added to a given penicillin-albumin solution, the penicillin peaks become narrower; showing that the effect is saturable with a single albumin molecule interacting with only a limited number of penicillin molecules.
- 3) Albumin broadens the peaks of various penicillins and penicillin breakdown products, and these mutually compete for the effect. For example, addition of a

-2-

large excess of penicillin V to a penicillin G-albumin solution will narrow the G spectral lines (the G and V spectra do not completely overlap).

Dialysis experiments, done at the high penicillin concentrations necessary for NMR work show that only a very small fraction of the penicillin is bound, less than 1%. This explains the lack of any detectable changes in chemical shifts and rules out the possibility that the broadening is due primarily to exchange. It also requires that exchange between the bound form, which presumably has a much faster relaxation rate, and the free state is rapid enough (much more rapid than the faster relaxation rate) to average the two relaxation rates. A simple kinetic model, which assumes that there is only one binding site on each albumin molecule and that the observed line widths are determined by the averaged relaxation rates of the free and bound forms, fits the observed data quite closely and also provides, by extrapolation, $1/T_2$ values for the peaks of the bound form.

When these values are compared with the appropriate $1/T_1$ values for the free form, it is seen that the ratio T_1 (free) / T_2 (bound) is much greater (about 2 1/2 times greater) for the phenyl peak than for any of the other penicillin peaks, suggesting that this group is most strongly involved in the interaction.

The results of the competition experiments mentioned above provide an independent confirmation of this conclusion. 6-Aminopenicillanic acid, the penicillin nucleus, and acetylpenicillin, a complete penicillin with a side chain that has no ring structure, do not compete for the broadening effect; while penicillin V and even phenoxacetamide and phenoxyacetic acid do so.

Studies of the effect of pH and ionic strength on the broadening suggest that the bonding is hydrophobic in nature and are thus compatible with our conclusion that the phenyl group is most strongly involved in the binding.

Please apply this contribution to the subscription of O.J.

Sincerely yours,



James J. Fischer



Oleg Jardetzky



LABORATORIUM
voor
ORGANISCHE CHEMIE

Dir.: Prof. Dr. F. GOVAERT

GENT, April 17th 1964.

J. Plateaustraat, 22

Tel. 25.26.02

Assoc. Prof. B. L. SHAPIRO,
Department of Chemistry
Illinois Institute of Technology,

Technology Center,

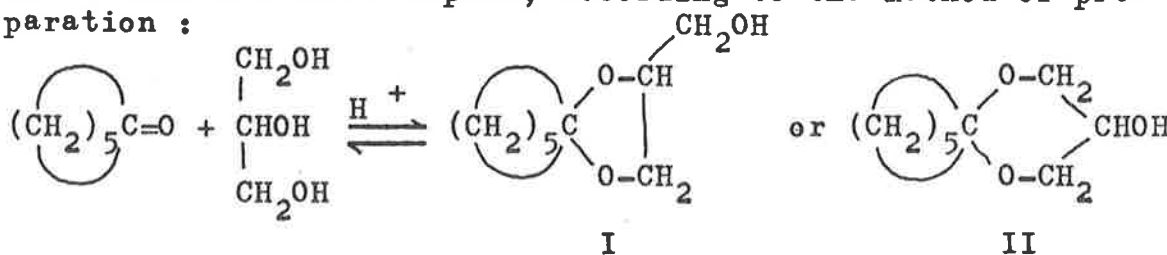
CHICAGO - ILLINOIS 60616.

U. S. A.

Concerning : structure of the ketal of glycerine with (cyclic) ketones.

Dear Dr. Shapiro,


In our present investigation on ketals, which we started at this laboratory (1), we are synthesizing a number of 1,3-dioxolanes. The 4-hydroxymethyl derivatives of some ketones form such a series in which we were interested in. For the 2,2-pentamethylene derivatives (and other cyclic ketonic derivatives) the structure elucidation is very hard, as the τ 5,8/7,5 pattern does not enable at first glance (see detail fig.) to make a choice between the two possible structures I or II that one could expect, according to the method of preparation :




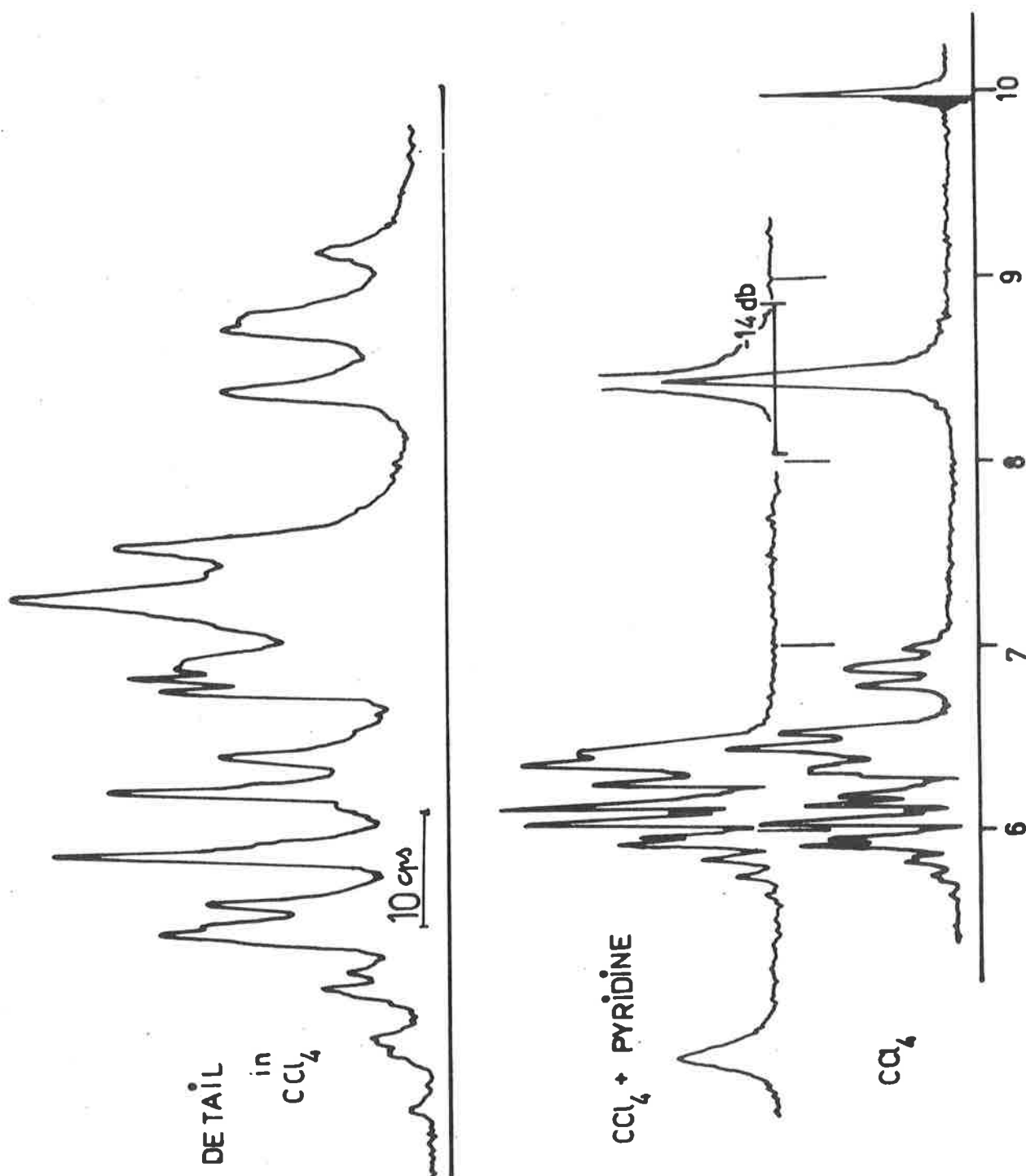
In a 10 % CCl_4 solution (lower part of figure) a triplet in the high field region is recognized, which has a relative surface of 1. This resonance is shifted by adding about 30 % pyridine or CF_3COOH . Clearly this triplet concerns the hydroxylic proton, coupling with two protons over the oxygen. This is a rather nice example of structure elucidation as it follows with certitude that only component I is formed.

With acetone as the ketone, we also have found that only the 1,3-dioxolane is formed (2) although Hibbert e.a. have mentioned (3) in this case to have obtained a mixture of the 1,3-dioxolane and the 1,3-dioxane derivative.

Yours sincerely,


Prof. F. Alderweireldt


Assoc. Prof. M. Anteunis.



67-49

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STERLING-WINTHROP RESEARCH INSTITUTE

A DIVISION OF STERLING DRUG INC.

RENSSELAER, NEW YORK

April 15, 1964

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

Dear Professor Shapiro,

Since our work has not uncovered anything of sufficient interest that I would like to offer it to my esteemed colleagues and yet the time has come for us to make a contribution to the IIT NMR Newsletters, I offer instead a suggestion concerning Varian's High Resolution NMR Spectral Catalog and an idea for NMR -- research on Grignard reagents for which I lack the equipment and which somebody might want to carry out.

I feel quite certain that most -- if not all -- IIT NMR Newsletter readers find Varian's NMR Spectral Catalog excellent and very useful and so do I. Occasionally, however, I would feel considerably happier if I could save myself going through Chem. Abst. etc. and still find the chemical evidence which led to a particular signal -- structure assignment. Just look at spectrum number 531, for instance, and there are others too. Should my interest be shared by many other readers, maybe Varian will oblige us with a supplementary list of references. --

Though the Grignard reagent has been used successfully (often, at least -- not always) by the organic chemist since the turn of the century, the nature of the "species" which are present in solutions and their equilibria are still controversial [(1) E. C. Ashby, W. E. Becker; J. Am. Chem. Soc., 85, 119 (1963). (2) R. M. Salinger: "The Structure of the Grignard Reagent and the Mechanisms of Its Reactions" in "Survey of Progress in Chemistry" by A. F. Scott; Academic Press, New York, 1963; p. 301 ff.]. One tool has been neglected so far -- at least to my knowledge -- although it should be particularly suitable for investigations of these equilibria in solutions: Mg^{25} - Magnetic Resonance Spectroscopy. The natural abundance of Mg^{25} is 10%. I do not expect that all the answers can be found that way but some questions should find unambiguous answers. For instance: How many "species" are present in a solution of a Grignard reagent? Are the same "species" present in different solvents? Is " R_2Mg " present in the Grignard solution? -- I can not foresee any opportunity to look into these questions myself. Is anyone interested in the problem?

Please credit this letter to the account of Dr. F. C. Nachod who is on your mailing list for our Institute.

Sincerely yours,

R. K. Kullnig
R. K. Kullnig

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