

Illinois  
Institute of  
Technology  
N-M-R  
Newsletter

No. 75  
DECEMBER, 1964

*Prima*



Kaiser	1
Negative Electronic Intermolecular Nuclear Overhauser Effect. Part II: Solution of the Mystery	
Feeney, Sutcliffe, Walker	6
Long Range F-F Coupling in a Saturated Compound	
Tiers	9
A Plug for AM; Non-Varian Recorder Pens; Concerning the New A-60 Sweep Kit	
Gutowsky	10
Spin-Echo Studies of Chemical Exchange	
Greenhalgh, Weinberger	12
Methyl Proton Resonance of Substituted Isopropyl N,N-dimethylphosphoramidates	
Retcofsky	14
Identification of the 4- and 7-Indenol Isomers	
Voevodskii, Molin, Sagdeev	15
Spin Density Transfer in Charge-Transfer Complexes; Concerning the Contribution of R. U. Lemieux in IIT NMR Newsletter No. 66	
Ciecuch	16
Aqueous Solutions of Formaldehyde and Trimethylamine Hydrochloride	
Foster, Jäger	18
NMR Studies in the Chlorine Series	
Orrell	22
Variable Temperature Studies of Some Oxazetidines	
Maciel	26
$C^{13}$ Chemical Shifts of Vinyl Carbons	
Maciel	28
Solvent Effects on the $C^{13}$ Chemical Shifts of the Carbonyl Group	
Maciel	30
$C^{13}$ Chemical Shifts in 1-Substituted-1-hexynes	
Thorpe	32
P.m.r. Studies of Purine and Substituted Purines	
Smith, G. W.	34
H-C-X Couplings in $(CH_3)_mX$ Compounds; Wide Line Studies of Solid $X(CH_3)_4$ Compounds	
Fliteroft, Rest, Stone	38
Stereochemistry of Square-Planar Platinum Complexes	
Burdett, Burger	43
$P^{31}$ - $H^1$ Couplings in Organophosphorus-Uranyl Complexes	
McIntyre, Quinn	46
Silver Tetrafluoroborate - Olefin Complexes	
Béné	48
Relative Signs of the P-H Coupling Constants in Tri-n-propyl Phosphate	
Benson, Lustig	51
NMR Spectra of Carbamates; A-60 Cooling Water System	
de Kowalewski, Kowalewski	52
Double Long Range Coupling in Benzaldehydes: Splittings of Combination Lines	
Szymanski	55
Two NMR Programs	
Manatt, Elleman	56
Spectra of Cyclopentadiene and Cyclohexadiene	

Deadline dates: No. 76: 22 January 1965  
No. 77: 19 February 1965

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".

## HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street  
Cambridge 38, Massachusetts, U.S.A.

October 22, 1964

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

Dear Prof. Shapiro:

Negative Electronic Intermolecular Nuclear Overhauser Effect

## Part II: Solution of the Mystery

Last month's IIT NMR Newsletter reported in Part I of this investigation that in a variety of 3-component solutions with simple 3-line nmr spectra a large negative intermolecular Overhauser effect had apparently been observed. The experimental procedure was to lock the field/frequency ratio of the spectrometer to one of the 3 spectrum lines, to irradiate a second line, and to simultaneously observe the third. This was accomplished by modulating the magnetic field with 3 audio frequencies and by using lock-in detection at two of these frequencies to extract the control and observation signals from the output of the rf receiver. The peak height of the observed line had been found to decrease by a considerable amount when the irradiation was centered on the resonance line of another component of the solution and, although the decrease showed some characteristics expected for a genuine intermolecular Overhauser effect (dilution dependence, no effect in  $\text{CHCl}_3 + \text{CHBr}_3$ ) we had been unable to understand the sign and magnitude of the effect. Especially perturbing was the conclusion that the observed effect required the transverse relaxation time  $T_2$  of the resonances in the solutions to be considerably shorter than the spin-lattice relaxation times  $T_1$ , and that this should probably also apply to the neat liquids where it is definitely contradicted by the facts.

We felt that useful information might be provided by a study of the transient characteristics of the effect. The first such experiment did indeed provide the key for the solution of the mystery. Fig. 2 shows a continuous recorder trace obtained in the following manner with a degassed and sealed sample of benzene + acetone + TMS:

(a) The irradiation frequency was adjusted to equal the benzene resonance frequency but the amplitude of the irradiation field was attenuated to  $\gamma H_2/2\pi \sim 10^{-3}$  cps. The observation frequency was adjusted to the center of the acetone resonance so that the recorder trace monitors the peak height of the acetone line. No change in the observation channel was subsequently made until step (f) when the observation field  $H_1$  was turned off so that the recorder traces the base line.

At (b) the attenuation of the irradiation field was suddenly reduced so that  $\gamma H_2/2\pi \sim 0.5$  cps, and the ensuing reduction in the acetone peak height illustrates the effect with this sample.

At (c) the attenuation of the irradiation field was suddenly further reduced so that  $\gamma H_2/2\pi \sim 5$  cps, At (d) the irradiation amplitude was suddenly returned to its previous value  $\gamma H_2/2\pi \sim 0.5$  cps, and at (e) the irradiation amplitude was suddenly further reduced to the first value  $\gamma H_2/2\pi \sim 10^{-3}$  cps. The acetone peak height after this step does not quite reach the value it had after (a) because the homogeneity of the magnet had deteriorated slightly in the meanwhile.

The important features of this recording are the following:

(i) The decrease at (b) occurs too fast to have anything to do with the saturation of the benzene resonance. In fact, the incipient saturation occurs with the time constant of the slight recovery of the signal after step (b).

(ii) The increase in the irradiation intensity at step (c) leads to considerable saturation of the benzene resonance with a time constant of order  $T_1$  indicated by the trace. But instead of further decreasing as would be expected for an Overhauser effect, the peak height of the acetone line recovers from 30% to 70% of its original magnitude.

- 3 -

(iii) After the irradiation intensity is suddenly reduced at step (d) the benzene line is still saturated and recovers only in a time of order  $T_1$  so that a considerable decrease of the acetone peak height should prevail if it was caused by the Overhauser effect. Instead, the peak height jumps immediately to its maximum value and then decreases in time  $T_1$  to the same level as after step (b).

It is apparent that the decrease of the observed (acetone) line height is not caused by the saturation of the irradiated (benzene) line as it should be in an Overhauser effect. Instead it seems that the decrease is a monotonic function of the signal produced by the irradiated resonance. Monitoring this signal with the oscilloscope at the signal channel amplifier output (position 6 in our circuit<sup>1</sup>) showed that there was indeed a strong component at the irradiation audio frequency immediately after step (b). This component decreased somewhat and slowly after step (c) due to saturation, it was zero immediately after step (d) because of the previous saturation, and afterwards recovered slowly to its previous magnitude.

At no time could any distortion or non-linearity in the amplifiers be observed, but since it had now been established that the decrease was related to the signal from the irradiated line, it was desirable to ascertain that such a signal would not upset the electronics in any way. For this purpose the experiment that led to Fig. 1 of Part I was repeated, but the signal from the irradiated resonance was simulated by connecting the audio generator for the irradiation sideband not to the sweep coils but into the cable leading from the output of the rf receiver (J314 of the Varian V4311) to the input of the lock-in detectors. When the amplitude of this simulated signal matched the value previously generated by the irradiated resonance line, the same decrease of the observed resonance peak height occurred. The effect was thus produced in the electronics of the lock-in detectors, and its absence with diluted samples or with  $\text{CHCl}_3 + \text{CHBr}_3$  must be explained by the smaller density of protons giving a smaller signal upon irradiation.

The responsible electronic components are not the amplifiers or transformers but the diode ring demodulator in the signal channel lock-in detector. It is easy to see (by hindsight) that for the double rings used in our circuit<sup>1</sup> the peak amplitude of the signal input voltage to the diode rings must be less than half the reference voltage amplitude. Since the signal channel lock-in detector was designed to be used for frequency-sweep experiments it does not contain a filter, and the superposition of the strong signal from the irradiated resonance leads to a violation of the above condition. A filter to reject the irradiation frequency should be used in the signal and control channel amplifiers whenever possible in double resonance experiments!

MORAL<sup>2</sup>: It is sometimes difficult to distinguish between molecule and spectrometer.

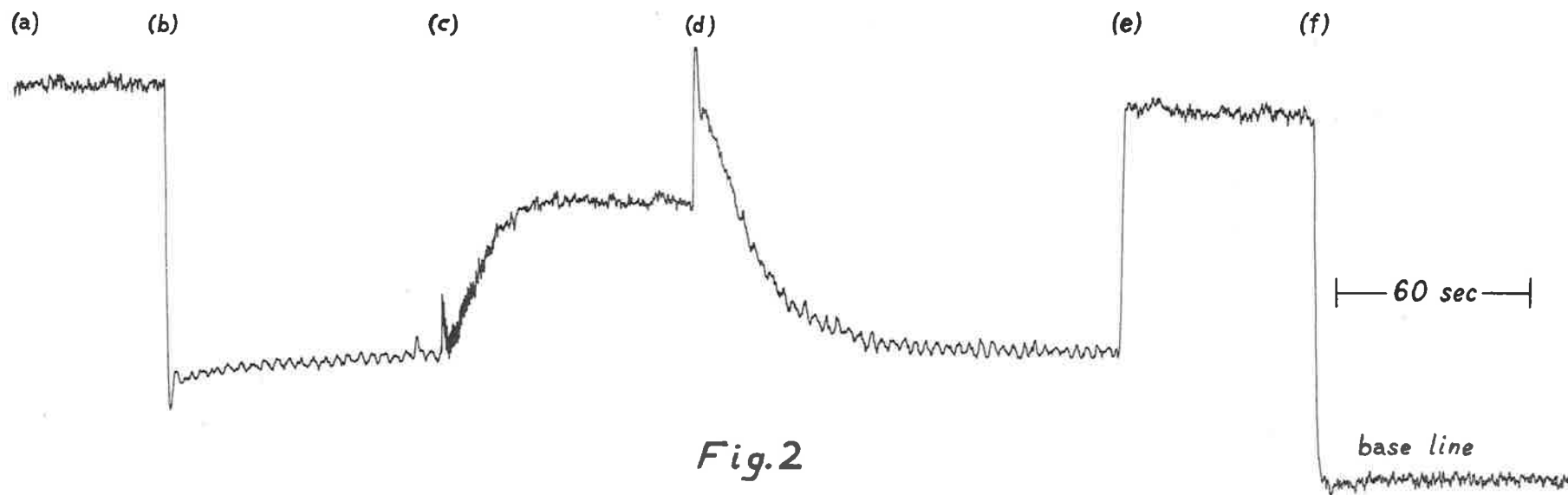
Sincerely yours,



R. Kaiser

#### REFERENCES

1. J. H. Noggle, Rev. Sci. Instr. 35, 1166 (1964).
2. by J. D. Baldeschwieler.



**Fig.2**

Fig. 2: Continuous recorder trace of the peak height of the acetone resonance of a degassed sample of acetone + benzene + TMS with the benzene resonance irradiated with amplitude  $\gamma H_2/2\pi$  (a)  $10^{-3}$  cps, (b) 0.5 cps, (c) 5 cps, (d) 0.5 cps, (e)  $10^{-3}$  cps. The amplitude changes were switched suddenly to study transient effects.

## THE UNIVERSITY OF LIVERPOOL

TELEPHONE: ROYAL 6022  
Extension 356



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

Long Range F-F Coupling in a Saturated Compound.

J. Feeney, L.H. Sutcliffe and S.M. Walker.

The stereospecificity of long range F-F spin-spin interactions in saturated molecules can only be characterised if a full knowledge of the conformational situation is available. The conformational problem is at its simplest in fluoroalicyclic compounds where it is often possible to have molecules in fixed conformations. For example, in perfluoromethylcyclohexane the conformation with the  $\text{CF}_3$  group in the equatorial position is thought to be highly populated. The 40 Mc/s  $^{19}\text{F}$  spectrum of the  $\text{CF}_3$  group of this compound is shown in the figure. The main splittings consist of a quintet ( $J(\text{CF}_3)(\text{CF}_2)_{2,6} = 13.6$  c/s) of doublets ( $J(\text{CF}_3)\text{F}_1 = 6.1$  c/s): the further small triplet splittings (0.94 c/s) are only observed when the compound is examined as a dilute solution in  $\text{CFCl}_3$  <sup>(1)</sup>. Spin decoupling and variation of temperature experiments are being undertaken to determine the origin of the long range 0.9 c/s coupling constant. This coupling involves ring fluorine nuclei and must take place through either 5 or 6 bonds. If the  $\text{CF}_3$  group really is in the equatorial position then the interacting fluorine nuclei are separated by at least 4.4 Å. However if the  $\text{CF}_3$  group spends an appreciable fraction of its time in the axial position the separation between the  $\text{CF}_3$  fluorine nuclei and the axial fluorines at positions 3 and 5 is 1.8 Å, that is, less than the van der Waal's distance of 2.73 Å <sup>(2)</sup>. In this situation, if a spatial coupling mechanism does operate it should make a relatively large contribution to the observed coupling constant.

THE UNIVERSITY OF LIVERPOOL

TELEPHONE: ROYAL 6022  
Extension 356

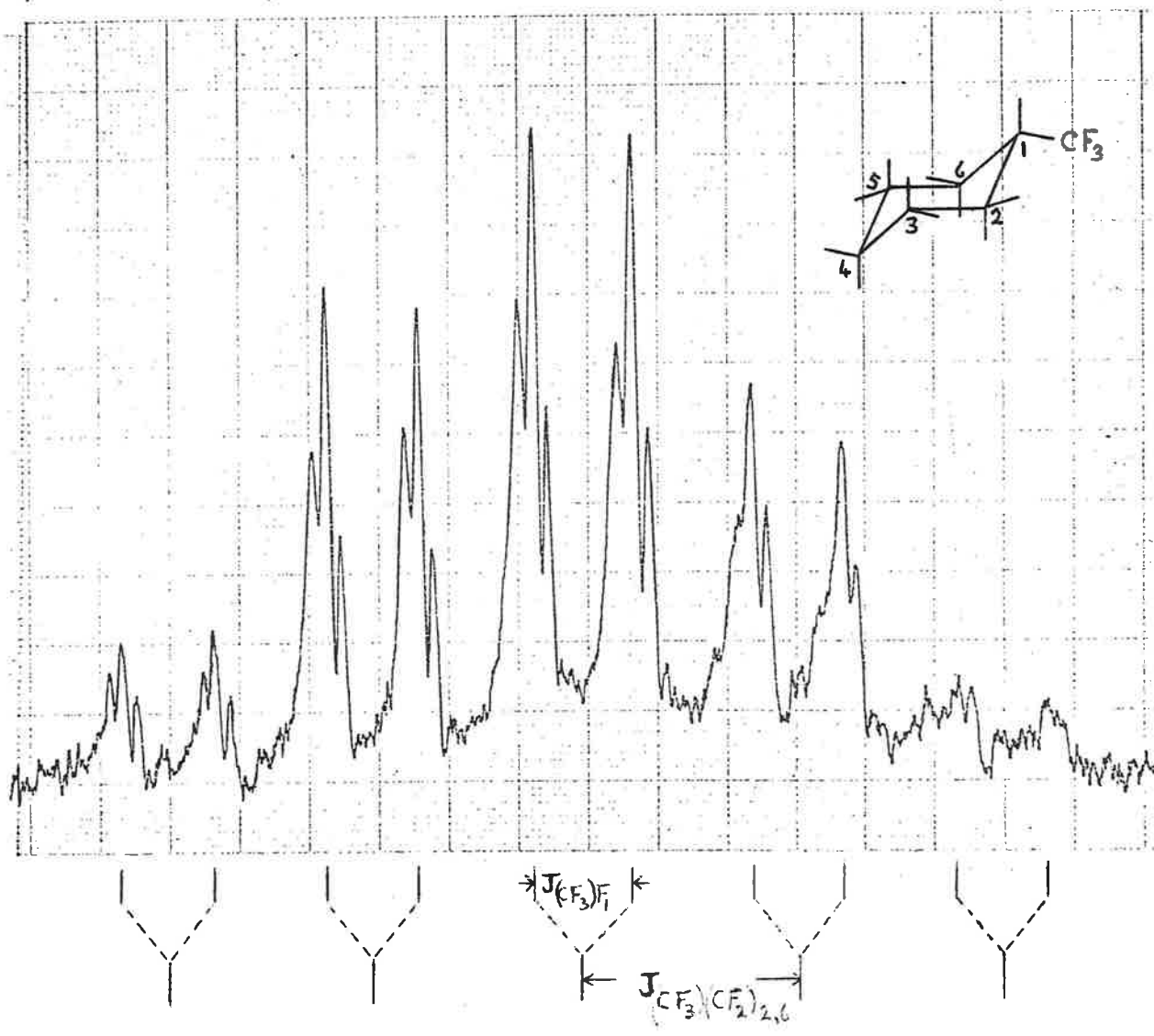


DEPARTMENT OF  
INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY  
THE DONNAN LABORATORIES  
VINE STREET, LIVERPOOL, 7

A compound which would be of great assistance in establishing the feasibility of a correlation between F-F coupling constants and internuclear separations is perfluoro-cis-1,4-dimethylcyclohexane. If anyone will supply us with a small sample we should be most grateful.

1. A. Malera, Private Communication.
2. L. Petrakis and C.H. Sederholm, J. Chem. Phys., 35, 1243, (1961).







GENERAL OFFICES • 2501 HUDSON ROAD • ST. PAUL, MINNESOTA 55119 • TEL. 733-1110

**Central Research Laboratories**

PLEASE REPLY TO: 2301 HUDSON ROAD • SAINT PAUL, MINN 55119

November 23, 1964

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

Dear Barry:

It would seem that comparatively few NMR workers have installed amplitude modulation circuitry in their HR spectrometers. This, despite its substantial advantages over frequency modulation for fluorine (phosphorus, carbon-13, etc.) sidebanding. I have tried to call attention to the convenience of AM in F-F spin decoupling - J. Phys. Chem., 67, 928 (1963) - but doubt if anyone except Stan Manatt noticed it! However, the paper describing the extremely simple modifications required, and the numerous advantages of AM, has been in print well over a year - L.G. Alexakos, and C.D. Cornwell, Rev. Sci. Instr., 34, 790 (1963) - so it may be that some have overlooked it.

We very strongly recommend this technique for all fluorine work (save that at lowest frequencies for which field modulation, as commonly practised in proton work, is satisfactory) and know of no disadvantages, since we have had no problems with it.

Presumably others have been annoyed by the Varian pens on the G-10 and G-14 recorders. We have gone over to the K and E "Leroy" Reservoir Pens, No. 61-0050-"", cost \$3.50 each, which we find very satisfactory. These come in a variety of pen widths; the width code, from "00" for .013 in. to "5" for .055 in. being inserted in the pen number. We prefer "0", .017 in. It is necessary to make an adapter, which should allow for eventual wear of the point. With proper design the pen can also rest tilted, so that it is off the paper. A particular feature (in addition to choice of widths) is the self-cleaning feature - a tiny weighted needle in the tube which unclogs the pen by shaking. We haven't yet tried it on the A-60, but will soon.

We recently successfully installed the Varian A-60 sweep replacement kit, and it has given no trouble since then. (This work was actually done by Dave Johnson, our A-60 technician and electronics expert.) Anyone contemplating this step should be warned that there were some errors in the instructions (write us if interested), and also that some of the wires furnished were too short! About par.

I hope these miscellaneous comments may prove helpful to at least a few NMR workers.

Sincerely,

Dr. George V.D. Tiers

/mfv

UNIVERSITY OF ILLINOIS URBANA 61803

## DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

THE WILLIAM ALBERT NOYES LABORATORY

November 23, 1964

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

Dear Barry:

Thanks for your reminder that our subscription to the NMR Newsletter requires renewal. Perhaps the enclosed abstract of some just completed spin-echo work will suffice.

To it I should add that a good part of our current effort is being devoted to the development and use of spin-echo methods for studying fast chemical exchange reactions. The methods evolved in I [J. Chem. Phys. 41, 2115 (1964)] and II [see the abstract] have been applied to the conformational isomerization of  $d_{11}$ -cyclohexane and cyclohexane itself. The former is particularly suitable for spin-echo study and Adam Allerhand and Fu-ming Chen have measured the exchange rate in it over 5 orders of magnitude. The value found for  $\Delta H^\ddagger$  is  $9.1 \pm 0.1$  kcal/mole in both compounds; the main "new feature" of the results is that nmr-determined rates are still very susceptible to systematic errors. Because of this, little or no significance can be attached to the entropies of activation, in spite of what's already in the literature to the contrary.

As an example of chemical exchange in a coupled AB system, we have studied the fluorine resonance in 1,1-difluoro cyclohexane. This involves a theoretical analysis of the echo decay in the Carr-Purcell train, as a function of pulse separation, and a comparison with experiment. Some spectacular echo patterns occur at exchange rates too slow to average out  $J_{AB}$ . This work, as well as that on  $d_{11}$ -cyclohexane and cyclohexane is now being written up.

So far, we have not worked through an unequal population case experimentally; however, bullvalene seems to be a good candidate of this type and we've started experiments on it.

With best regards,

  
H. S. Gutowsky

HSG:jml  
Enc.

II. CLOSED FORMULAE FOR THE  $T_2$  OF TWO SITES\*

Adam Allerhand and H. S. Gutowsky

Noyes Chemical Laboratory, University of Illinois,  
Urbana, Illinois

Closed expressions are derived for the decay in amplitude of successive echoes in nuclear magnetic resonance experiments for systems with two exchanging sites having different resonance frequencies but equal transverse relaxation times "in the absence of exchange." The decay is found to be the sum of two exponential terms and two "pseudo-exponential" terms; the absolute values of the latter decay exponentially but the sign alternates from one echo to the next. For the case of two equally populated sites the decay simplifies to the sum of just one exponential and one "pseudo-exponential" term. In most cases of experimental importance a single exponential term is much larger than the rest and adequately describes the decay in echo amplitude.

An iterative computer procedure is described which uses the expressions to extract information about the system from measurements of the apparent decay time constant ( $1/T_2$ ) as a function of  $180^\circ$  pulse separation ( $t_{cp}$ ). In favorable cases the method yields values not only of the lifetime between exchanges ( $1/\tau$ ) but also of the chemical shift ( $\delta\omega$ ) and the relaxation time in the absence of exchange ( $1/T_2^0$ ). Moreover, it is applicable to both slow and fast exchange whereas use of the approximate equation derived by Luz and Meiboom leads to inaccurate values for relatively slow rates with large chemical shifts between the sites. Our experience shows that the spin-echo technique can be very useful for the study of fast exchange processes, but even when closed expressions of appropriate accuracy are used the nature of these expressions is such that a high speed computer is required for fitting the experimental data, unless some "outside" information is available about  $\delta\omega$  and  $1/T_2^0$ .

DEFENCE RESEARCH BOARD



CONSEIL DE RECHERCHES POUR LA DÉFENSE

 DEPARTMENT OF NATIONAL DEFENCE  
 MINISTÈRE DE LA DÉFENSE NATIONALE  
 CANADA

 DEFENCE CHEMICAL, BIOLOGICAL AND  
 RADIATION LABORATORIES

OTTAWA, ONTARIO

 LABORATOIRES CHIMIQUES, BIOLOGIQUES ET  
 RADIOLOGIQUES DE LA DÉFENSE

OTTAWA, ONTARIO

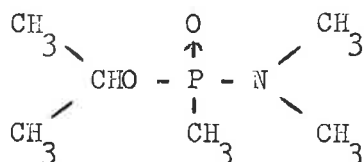
November 24, 1964

 Associate Prof. B.L. Shapiro,  
 Dept. of Chemistry,  
 Illinois Institute of Technology,  
 Technology Centre,  
 Chicago, Illinois,  
 U.S.A.

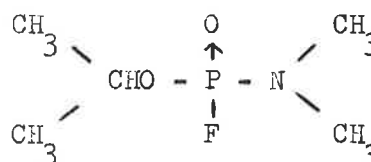
 Re: Methyl Proton Resonance of Substituted Isopropyl  
N,N-dimethylphosphoramidates

Dear Dr. Shapiro:

Currently we are looking at some asymmetric and dissymmetric isopropyl esters of organophosphorus acids to see if we can get more information on factors determining the non-equivalence of the two methyl groups. The compounds to date which exhibit the largest non-equivalence are the amidates. In  $C_6H_6$ , the  $\Delta\delta$  of the methyl protons of the isopropyl group of isopropyl N,N,P-trimethylphosphonamidate (I) at 60 mc/s is 10.6 cps, whilst in  $CCl_4$  or  $CHCl_3$  it is about 3 cps. The non-equivalence is temperature dependent ranging, in xylene, from 5.8 cps at  $102^\circ C$  to 12.0 cps at  $-28^\circ C$ .



I



II

Equally interesting has been the N-methyl resonance of the amidates; here the methyl groups are usually equivalent at 60 mc/s. Compound I\* shows a doublet ( $J_{\text{P-NCH}_3} = 9.4$  cps) in  $C_6H_6$ ,  $CHCl_3$  and  $CCl_4$  at 60 mc/s. At 100 mc/s, a further splitting of the spectrum is observed in benzene solution only, indicative of possible non-equivalence.

\* We wish to thank Dr. S. Brownstein for running spectra at 100 mc/s.

- 2 -

DCBRL 904-1

The N-methyl resonance of isopropyl N,N-dimethylphosphoramidofluoridate (II), with  $J_{P-NCH_3} = 10.4$  cps was, however, doubled by a further split of 1.8 cps in  $C_6H_6$ ,  $CHCl_3$  and  $CCl_4$  at 60 mc/s. This splitting was temperature independent over the range  $30 - 180^\circ C$  in nitrobenzene. The invariant nature of this doubling with respect to solvent and temperature changes discounts the possibility of it originating from non-equivalent methyl groups due to restricted rotation about the N - P bond and suggests that the  $NCH_3$  protons are coupled to the fluorine nucleus. Examination of the fluorine resonance at 56.4 mc/s revealed two broad peaks  $J_{P-F} = 957$  cps, with a width at  $1/2$  peak height of 6.0 cps. This is even larger than the calculated value of about 5 cps assuming that  $J_{CH_3-F} = 1.8$  cps and that the peak width is the same as that observed in the same field for isopropyl methylphosphonofluoridate (1.5 cps). The fluorine spectrum, therefore, provides additional evidence that the fluorine couples with the  $NCH_3$  protons in II.

No coupling was observed between fluorine and the isopropyl methine proton of II, even when the isopropyl methyl protons, which in this case are equivalent, were decoupled. Thus although the methine proton and the N methyl protons are both separated from the fluorine by 4 bonds, only the latter protons are split. This can be explained by the difference in bond order of the N - P and O - P bonds. It is well established that they can both have a bond order greater than one and that it will be greater in N - P than O - P. We visualize then the F -  $NCH_3$  coupling as being transmitted via the  $\pi$ -electron system. It is of interest that, despite the multiple bond character, the  $NCH_3$  protons are found to be equivalent in contrast to the classical case of N,N dimethylformamide.

Sincerely,

R. Greenhalgh

M.A. Weinberger



PITTSBURGH  
COAL RESEARCH CENTER

UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES

4800 FORBES AVENUE  
PITTSBURGH, PENNSYLVANIA 15213

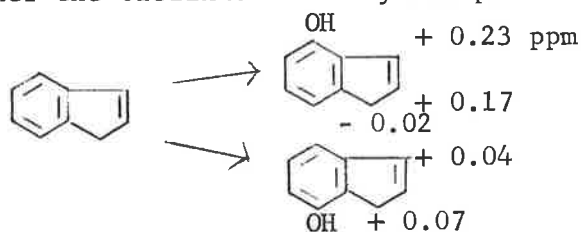
November 24, 1964

Dear Barry:

As R. A. Friedel is spending the year in Australia at C.S.I.R.O., I am submitting the following for inclusion in IIT Newsletter to keep our subscription up-to-date.

Identification of the 4- and 7-indenol isomers

Friedman et al.<sup>1/</sup> of this laboratory have recently dehydrogenated 4-indanol and produced a substance that gave two GC peaks. Mass spectra gave the molecular weight of each as 132; the IR spectrum suggested 1,2,3- aromatic ring substitution. An ultra-violet study indicated conjugation of an olefinic bond and an aromatic ring. Differences in the wavelength of UV absorption for the two suggested the unsaturated group to be adjacent to OH in one fraction and meta in the other. Proton NMR spectra of the two were in accord with the indenol structures. NMR differentiation between the two isomers came as a result of studying chemical shift differences between the signals exhibited by the GC fractions and those of indene, and by a comparison of the concentration dependences of certain resonances of the materials. The first, summarized below, indicated perturbations in chemical shifts due to the oxygen being in close proximity to either the olefinic or methylene protons:



A comparison of NMR spectra of GC peaks 1 and 2 with those of the 4- and 5-indanols run at various concentrations in  $\text{CCl}_4$  reveals a marked concentration dependence of the methylene proton shifts for peak 1 and for one of the methylene multiplets in 4-indanol, but only slight changes for the remaining two compounds. This also indicates a difference due to the position of the oxygen on the aromatic ring, and the subsequent weakening of intermolecular hydrogen bonding by solvent dilution. This study also suggested that the shift differences indicated in the above diagram would be greatly enhanced at higher concentrations. In addition to these facts, the methylene resonance in peak 1 was better resolved than that of either peak 2 or indenol, indicating the lack of 1,7 coupling just as was found for 7-methylindene.<sup>2/</sup>

We conclude that spectral studies on these GC fractions not only confirm that they are both indenols, but also that peak 1 is the 7-indenol and is the first to be eluted from the chromatography column.

<sup>1/</sup> Tetrahedron, in press

<sup>2/</sup> J. Chem. Soc., pp. 590-592, 1963

*H. L. Retcofsky*  
H. L. Retcofsky

Prof. V.V. Voevodskii  
 Institute of Chemical Kinetics  
 and Combustion  
 Siberian Department of the  
 USSR Academy of Sciences  
 Novosibirsk-72

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

November 9, 1964

Dear Professor Shapiro,

1. H.S. Gutowsky and Julia Chow Tai have shown recently (J.Chem.Phys. 39, 208, 1963) the occurrence of spin density transfer from DPPH and DTBN radicals to fluorine aromatic compounds, as following from an anomalous  $T_1/T_2$  ratio for the relaxation of fluorine nuclei. However, they failed in attempting to detect this phenomenon from proton relaxation times for hydrocarbon solvents. It seems that the conditions for recording of the spin delocalization would be considerably more advantageous with systems involving good electron donors or acceptors. Molecules of this kind would seem to form relatively stable charge-transfer complexes with radicals, as the ionization potential of free radicals is low, and the electron affinity high. Our observations seem to be consistent with this prognosis. The maximum deviation of  $T_1/T_2$  from unity was found for systems of DPPH- $\text{CCl}_4$ -naphthalene, DPPH- $\text{CCl}_4$  - diphenyl, DPPH - nitromethane, DPPH - nitrobenzene.

We attempt to record the NMR signals shifts in these systems in order to obtain independent evaluation of the hyperfine interaction constant  $A$  and the complex lifetime  $\tau$ .

2. We avail ourselves of the opportunity for drawing the attention of Dr. R.V. Lemieux et al (IIT NMR No. 660) to that their results are very well described by the anamorphose

$$\frac{1}{\Delta} = \frac{1}{\Delta_0} + \frac{1}{K\Delta_0} \frac{1}{[\text{Et}_4\text{NCl}]}$$

giving the same  $\Delta_0$  and  $K$  values, but in a more simple way. The anamorphose expression will be easily obtained, under certain conditions, from an exact formula (see, for example M.W. Hanna, A.L. Asbaugh, J. Phys. Chem. 68, 811 (1964)).

Sincerely yours

*V. Voevodskiy*  
*Moruly*  
*Chavich*

V.V. Voevodskii  
 Yu.N. Molin  
 R.Z. Sagdeev





# POLAROID CORPORATION

RESEARCH LABORATORIES  
CAMBRIDGE 39, MASSACHUSETTS

December 1, 1964

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

Dear Barry:

Aqueous Solutions of Formaldehyde and Trimethylamine Hydrochloride

In a definitive paper on the species and equilibria in deuterium oxide solutions of formaldehyde, Skell and Suhr<sup>1</sup> clearly identified three methylene proton resonance peaks, separated by 0.07 ppm. These they attributed, in order of decreasing field, to: a) monomeric methylene glycol, b) methylene groups in dimeric species ( $\text{HOCH}_2\text{OCH}_2\text{OH}$ ) as well as the end group methylenes in higher polymeric species, and, c) the internal methylene groups in trimeric and longer species. We were interested in the absolute positions of these three bands, relative to a trace of dioxane as internal standard in deuterium oxide. On our A-60 Spectrometer, we find that in neutral or weakly acidic solutions the three "formaldehyde" bands fall at 4.80, 4.87 and 4.93 ppm. relative to dioxane at 3.70 ppm. In concentrated NaOD in deuterium oxide a single "formaldehyde"-methylene peak was observed, which showed some concentration dependence, falling about 4.85-4.90 ppm.

Our particular interest was in the detection of possible adducts between trimethylamine hydrochloride and formaldehyde. Only mono- and dialkylamines have thus far been shown to give methylolamine products ( $\text{RR}'\text{NCH}_2\text{OH}$ ) when reacted with formaldehyde.<sup>2</sup> Musser<sup>3</sup> prepared alkoxymethylene quaternary ammonium derivatives from the hydrochlorides of tertiary amines with a lower aliphatic alcohol and paraformaldehyde.

---

<sup>1</sup> P. Skell and H. Suhr, Chem. Ber., **94**, 3317 (1961).

<sup>2</sup> J. Frederic Walker, "Formaldehyde", Reinhold Publishing Corp., New York, (1964), p. 359 ff.

<sup>3</sup> D. M. Musser, U. S. Patent 2,681,342 (1954).

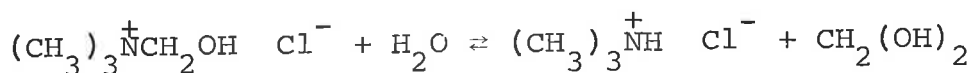
Page 2

Dr. B. L. Shapiro, Illinois Inst. of Technology

December 1, 1964

We found that in the spectrum of a roughly 2M solution of trimethylamine hydrochloride in deuterium oxide, into which about 1.5 equivalents of formaldehyde vapor was passed, two singlet peaks appeared in addition to the three "formaldehyde"-methylene peaks, the methyl absorption of the amine hydrochloride itself (2.88 ppm), and the broad HOD peak (4.72 ppm). The areas of these two new peaks at 3.00 and 4.62 ppm. were in the ratio of 9 to 2, and the 3.00-ppm. peak had about 1.7 times the area of the 2.88-ppm. peak. These latter two peaks, attributed to two types of methyl groups, became roughly equal in area with the sample heated to 80°C., the 9 to 2 ratio persisting for the former pair. The only significant position shift with temperature was that of the HOD band, which appeared at about 4.32 ppm. at 80°C.

We conclude that under our conditions substantial amounts of a 1:1 formaldehyde-trimethylamine hydrochloride adduct are present in aqueous solution, in equilibrium with the starting materials, and that increasing temperature favors hydrolysis of the adduct.



Thanks for your subscription reminder, and best regards.

Sincerely,

*Ron Cieciuch*

Ronald F. W. Cieciuch

RFWC/br

## INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. H. H. INHOFFEN

33 BRAUNSCHWEIG  
SCHLEINITZSTRASSETelephon Hochschule 47 81  
Durchwahl Institut 47 82 25  
Vorwahl 0531

December 1st, 64

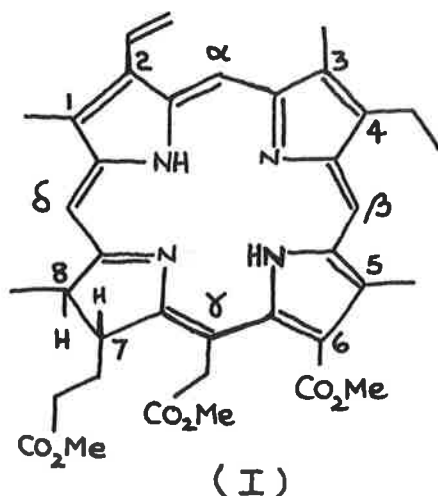
Assoc. Prof. B.L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Center,

Chicago / Illinois 60616  
=====

U. S. A.

Dear Professor Shapiro,

Thank you for your "subscription" reminder. We hope the following will bring us up to date again with our contributions.



We recently had cause to identify specifically the six methyl group resonances to be found between  $\tau = 5$  and  $\tau = 7$  in the spectrum of Chlorine  $e_6$  trimethyl ester (I) (Fig. 1). This process was eased considerably by Prof. Strain's recent work on the pheophorbides (J. Amer. Chem. Soc., 1963, 3809). The main problem was to identify the  $C_1$  and  $C_5$  methyl resonances since the other methyl resonances

can be identified by the study of known compounds in which the respective methyl groups have been replaced by suitable substituents. We proposed to use the long-range de-shielding effect of the carbonyl group to aid us in identifying the two resonances in question.

2-Acetyl chlorine  $e_6$  trimethyl ester was prepared by the addition of water to the  $C_2$  vinyl group of (I) and subsequent oxidation of the alcohol so produced. The spectra of Chlorine  $e_6$  trimethyl ester, the alcohol and the ketone were essentially identi-

- 2 -

cal in the 5 - 7 $\tau$  region except that the peak at 6.63 $\tau$  in the Chlorine  $e_6$  ester had moved upfield to 7.05 $\tau$  in the spectrum of the alcohol, and downfield to 6.46 $\tau$  in the ketone spectrum. We thus feel reasonably confident in identifying the 6.63 $\tau$  peak in the Chlorine  $e_6$  ester spectrum with the  $C_1$  methyl group.

We are still in the process of preparing the appropriate compounds required to identify the  $C_5$  methyl group by the same method.

The spectrum of the above mentioned alcohol appears to show a remarkable long-range coupling effect. In the low-field portion of the HR-100 spectrum measured in  $CDCl_3$  (Fig. ii) a doublet and a quintet can be observed. When the spectrum of the same compound is measured in deuterio-acetone containing a few drops of  $D_2O$  these two multiplets degenerate to a singlet and a quartet, respectively. According to our assignment of the peaks it seems that the -OH proton in the side chain at  $C_2$  is coupling with the  $\alpha$  meso-proton!

This letter should appear at just about the right time to wish you and all co-contributors a Merry Christmas and a Happy New Year.

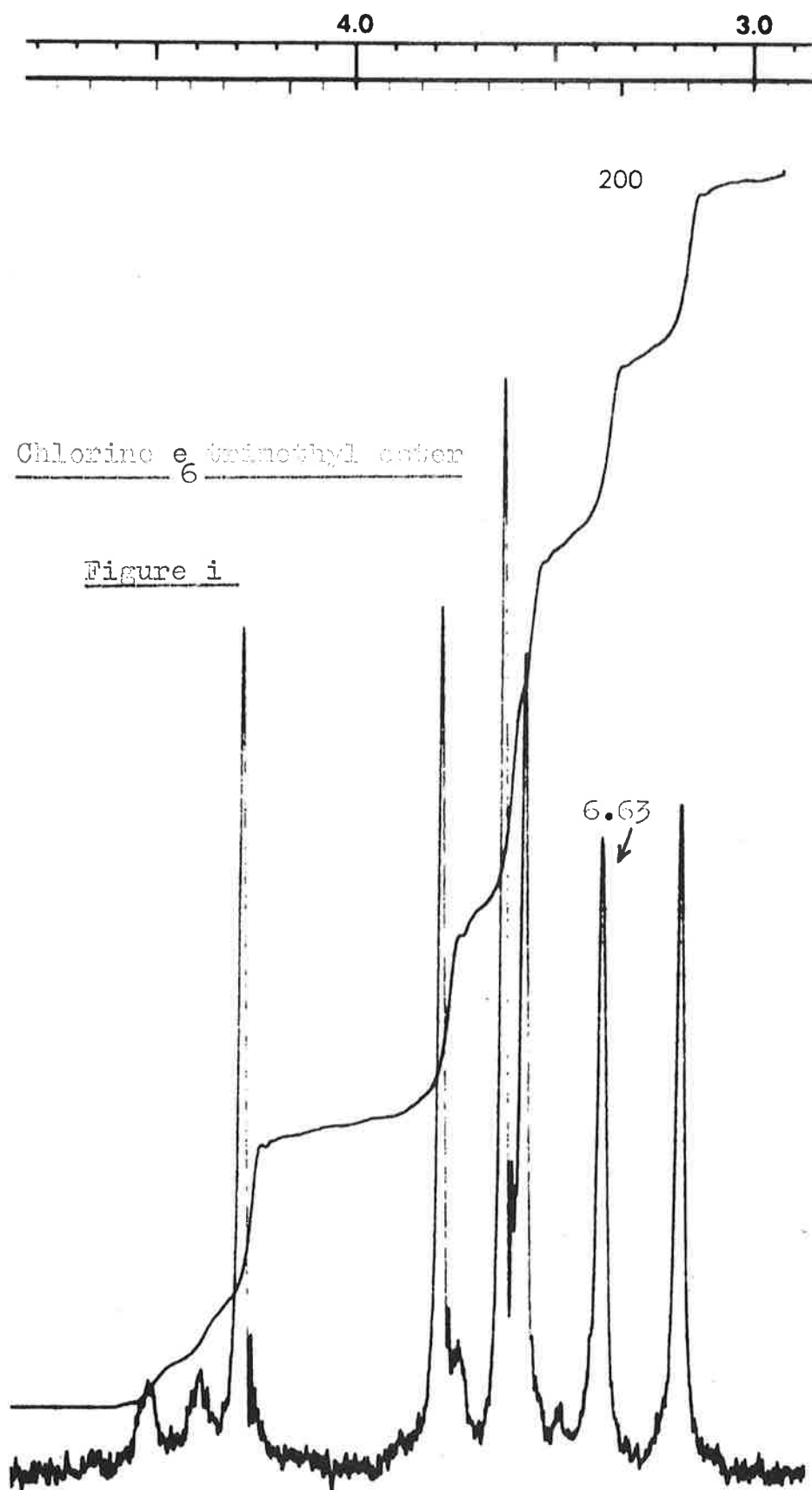
Yours sincerely,

R.G. Foster.

(R.G. Foster)

P. Jäger

(P. Jäger)

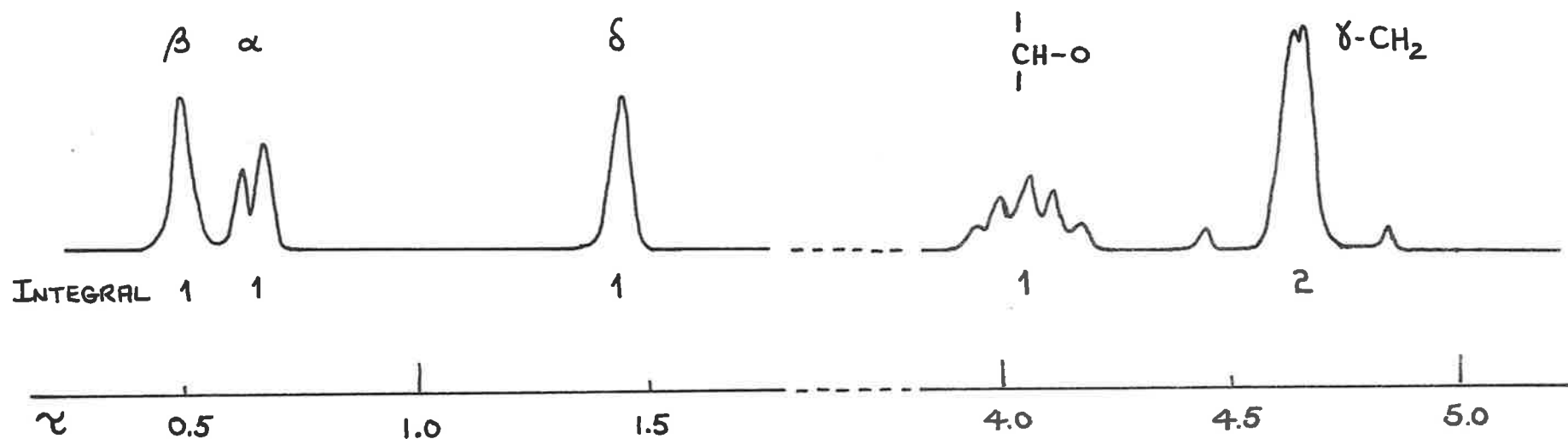


6.63



LOW-FIELD PORTION OF HR-100 SPECTRUM OF ALCOHOL (I WITH  $\text{CH}_3\text{CH}_2\text{OH}$  AT  $\text{C}_2$ )

FIGURE ii



## UNIVERSITY OF EXETER

Dr. K.G. Orrell

Department of Chemistry

Tel. 77911



The Washington Singer Laboratories,  
Prince of Wales Road,  
Exeter

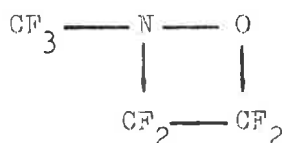
Dr. B.L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago,  
Illinois 60616.

10 November 1964

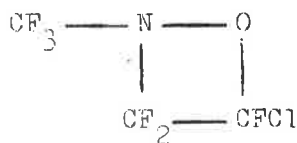
Dear Dr. Shapiro,

For the last three years I have been an avid reader of the NELLONMR and, of late, IPTNMR newsletters copies of which were obtained through Dr. J. Lee of the Manchester College of Science and Technology under whom I was carrying out research in N.M.R. spectroscopy. Recently, I have moved from Manchester to the University of Exeter where I am continuing research in N.M.R. As I believe the N.M.R. newsletter provides a most valuable information service for N.M.R. spectroscopists I would very much appreciate being placed on your mailing list.

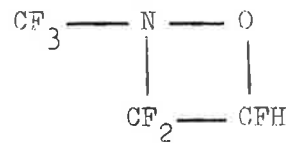
As a first contribution to the newsletter I would like to present some results I obtained while I was at Manchester concerning some studies at variable temperatures of a number of oxazetidine compounds. The compounds investigated were as follows:



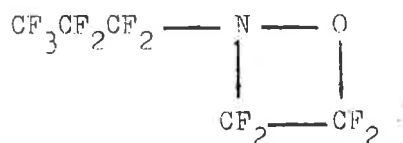
I



II



III



IV

Spectra were recorded in the temperature range - 100 to +100 °C, using an

Dr. B.L. Shapiro,

- 2 -

10 November 1964

A.E.I. R.S. 2 spectrometer operating at 60 Mc/s. In the room temperature spectra of these compounds the  $-CF_2-N-$  absorption was invariably broad and structureless. This was explained as being the result of a partial chemical shift averaging of the two fluorines due to an intermediate rate of nitrogen inversion vibration. On cooling such compounds to ca.  $-70^\circ C$  the inversion process was retarded sufficiently for the chemically inequivalent fluorines of the  $-CF_2-N-$  group to be distinguished. In the case of compounds I and IV only one isomer is expected at low temperatures whereas with compounds II and III two isomers are expected and were in fact observed in the abundance ratio of ca. 60:40%. At temperatures within the slow inversion limit the  $-CF_2-N-$  absorption consisted of an AB pattern the individual bands of which exhibited further multiplet structure. As an example, the ambient and low temperature spectra of compound II are shown in the Figure. The geminal coupling constant for the  $-CF_2-N-$  group was found to be in the range 130 - 150 c./s for the series of compounds studied.

The change in nitrogen inversion rate on lowering the sample temperature was also reflected in the change of the spin interaction of the  $CF_3-N-$  group fluorines with the  $-CF_2-N-$  fluorines. At ambient temperatures, the former group interacts with both fluorines of the  $-CF_2-N-$  group with a time-averaged value of ca. 7 c/s. whereas, at low temperatures, only one of the fluorines of this group participates in an observable interaction (ca. 14 c/s.) with the  $CF_3-N-$  group. Above the coalescence temperature (ca.  $-30^\circ C$ ) of the  $-CF_2-N-$  absorption in these oxazetidine compounds, it is estimated that the rate of nitrogen inversion must exceed  $2000 \text{ sec}^{-1}$ . The spectral parameters obtained from the spectra of compound II at the various temperatures are shown in the Table.

Further details of this work are to be published shortly.

Yours faithfully,

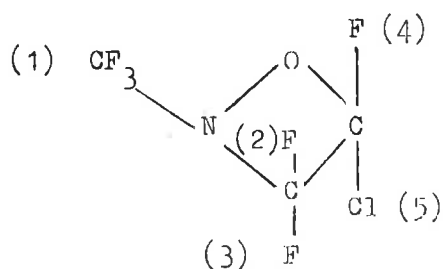
K.G. Orrell

(K.G. ORRELL)

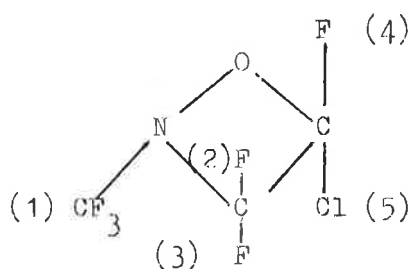


TABLE

Spectral Parameters of 4 - Chlorotrifluoro - 2 - trifluoromethyl  
- 1 : 2 - oxazetidine



Isomer I



Isomer II

## a) Chemical Shifts

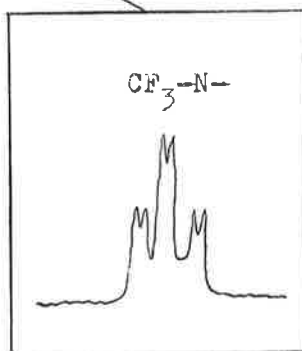
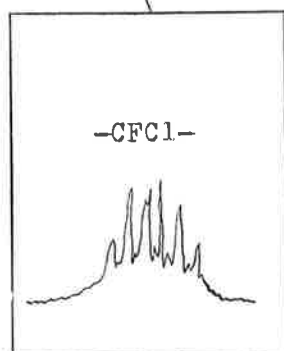
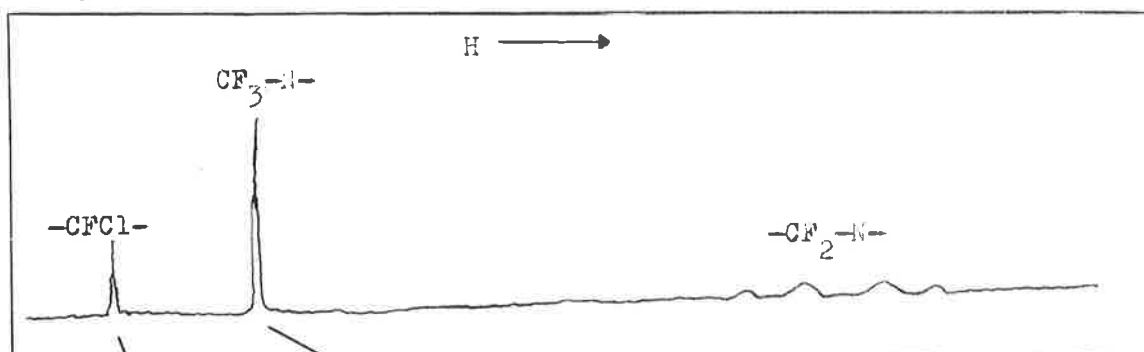
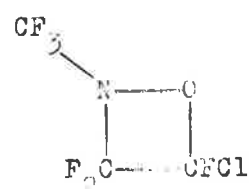
Temp (°C)	Isomer	p.p.m. from CFCl <sub>3</sub>			
		(1)	(2)*	(3)*	(4)
66	I + II	70.3	95.1	90.4	64.6
26	I + II	70.2	95.3	90.7	64.4
-79	I	69.7	97.1	86.9	63.6
-79	II	70.0	69.8	116.2	64.4

## b) Spin Coupling Constants

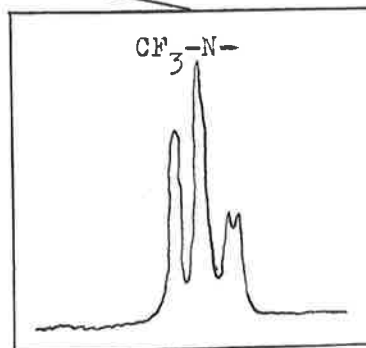
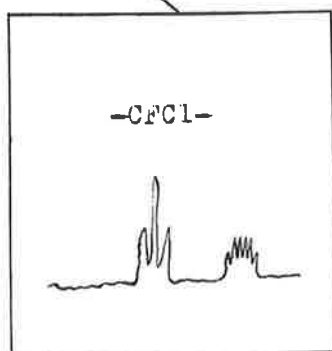
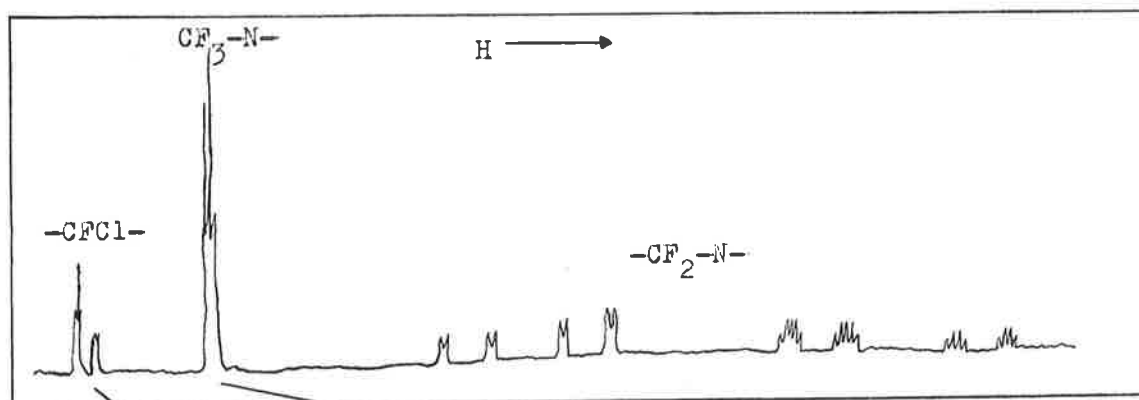
Temp.	Isomer	Coupling Constants					
		J <sub>12</sub>	J <sub>13</sub>	J <sub>14</sub>	J <sub>23</sub>	J <sub>24</sub>	J <sub>34</sub>
66	I + II	7.3	7.3	2.4	129	7.5	?
26	I + II	7.4	7.4	2.7	134	?	?
- 79	I	13.0	1	1	133	8.3	8.2
- 79	II	1	14.1	3.7	132	11.8	3.5

\* Distinction between these nuclei is based on the assumption that the absorption to higher field which exhibits spin coupling to the CF<sub>3</sub> - group fluorines is due to the nucleus CIS - oriented to the CF<sub>3</sub> - group.

Spectrum at 20° C.

Compound

Spectrum at -79° C.



## UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

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

Dear Dr. Shapiro:

The purpose of this letter is to communicate the  $C^{13}$  chemical shift data we have accumulated for a series of 18 vinyl compounds  $C_\beta H_2 = C_\alpha H-X$ , with a variety of substituents X. These results are of interest with regard to the data previously reported for the effect of substituents on the  $C^{13}$  shifts of  $SP^2$ -hybridized carbons.<sup>1,2</sup> Only fragmentary data on olefins have been available.<sup>3-5</sup>

The  $C^{13}$  n.m.r. spectra were obtained in natural abundance, using dispersion mode and rapid-passage conditions and a concentric-sphere sample container with a variety of appropriate references. In most cases the separate triplet ( $C_\beta$ ) signals and doublet signals ( $C_\alpha$ ) could be discerned. When overlap occurred reasonable and consistent assignments could be made on the basis of peak intensities and the assumption of  $C^{13}$ -H splittings of roughly 150 c.p.s.<sup>3,4</sup> The following data were thus obtained.

 $C^{13}$  Chemical Shifts for  $C_\beta H_2 = C_\alpha H-X$ 

X	$\delta C_\alpha$	$\delta C_\beta$	X	$\delta C_\alpha$	$\delta C_\beta$
I	43.3	-1.8	$SnCl_2CH=CH_2$	-6.5	-11.9
Br	13.1	6.6	$CH_2OC_2H_5$	-7.1	14.0
Cl	2.6	11.3	$CH_2OCH_2CH=CH_2$	-7.1	12.6
$CO_2C_2H_5$	-1.1	-1.8	$Sn(CH=CH_2)_3$	-7.5	-7.9
$NCO(CH_2)_3$	-1.3	34.4	$SO_2CH=CH_2$	-9.1	-2.7
$SiCl_3$	-3.1	-10.0	$OCOCH_3$	-13.0	32.3
$CH_2Br$	-4.5	11.0	$Pb(CH=CH_2)_3$	-16.7	-6.4
$CH_2Cl$	-5.0	11.2	$O-n-C_4H_9$	-22.9	45.6
$Si(CH=CH_2)_3$	-5.8	-6.8	$OCH_3$	-24.2	44.1

No simple relationships could be found between these  $C^{13}$  shifts and the corresponding proton shifts reported by Brügel, Ankel and Krückeberg.<sup>6</sup> However, rough linear relationships were demonstrated between  $\delta C_\alpha$  and the corresponding  $C^{13}$  shifts of the substituted carbon atoms in phenyl compounds,<sup>2</sup> and between  $\delta C_\beta$  and the ortho carbon shifts in phenyl compounds.<sup>2</sup>

-2-

Dr. Bernard L. Shapiro  
Pittsburgh 13, Pennsylvania

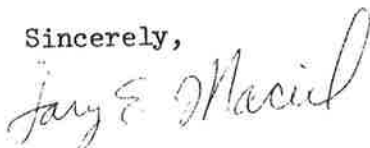
These correlations are interpreted as due to similar inductive, resonance, and neighbor effects in both sets of compounds as a result of similar electronic structures and molecular geometries.

A linear correlation was not found between  $\delta C$  and the carbon -13 shifts in corresponding acetyl compounds; presumably reflecting the different properties such as polarizability of C=O compared to C=C.

References:

1. J. B. Stothers and P. C. Lauterbur, Can. J. Chem., 42, 1563 (1964).
2. H. Spiessacke and W. G. Schneider, J. Chem. Phys., 35, 731 (1961).
3. R. A. Friedel and H. L. Retcofsky, J. Am. Chem. Soc., 85, 1300 (1963).
4. P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Chapt. 7, Edited by F. C. Nachod and W. D. Phillips, Academic Press, 1962.
5. G. B. Savitsky and K. Namikawa, J. Phys. Chem., 67, 2754 (1963).
6. W. Brügge, T. Ankel and F. Krückeberg, Zeitschrift für Elektrochemie, 64, 1211 (1960).

Sincerely,



Gary E. Maciel  
Assistant Professor

GEM:vh

## UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

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

Dear Dr. Shapiro:

Last year we communicated the first systematic investigation of solvent effects in  $C^{13}$  magnetic resonance spectroscopy, a study of the carbonyl shift of acetone.<sup>1</sup> We have now extended that study to include other ketones and esters to learn the influence of the structure of a carbonyl compound on its sensitivity to solvent effects.

The  $C^{13}$  chemical shifts were obtained at 15.085 Mc/sec in natural abundance, using dispersion mode and rapid passage conditions and a concentric sphere sample container with an external reference of saturated aqueous  $NaO_2C^{13}CH_3$ . Solutions with 1:5 mole ratio of solute to solvent were employed. As previously found for acetone, the  $C^{13}O$  chemical shifts of unhalogenated ketones were found to be quite sensitive to an environment consisting of proton donors and relatively insensitive to environment if proton donors were not present. The sensitivity of carbonyl  $C^{13}$  shifts to changes in solvent was decreased by substitution of the alkyl groups of ketones by  $CCl_3$ ,  $OCH_3$  or  $OC_2H_5$  groups. When the  $C^{13}$  shifts of the ketones and esters in various solvents were plotted vs. the  $C^{13}$  shifts of pinacolone in the same solvents, approximate linear correlations were obtained, yielding the relative solvent sensitivities: acetone 1.05, pinacolone 1.00, fenchone 0.90, di-t-butyl ketone 0.81, ethyl acetate 0.51, methyl formate 0.37, dimethyl carbonate 0.15, hexachloroacetone 0.03. This trend is interpreted as probably reflecting the effect of a reduction in carbonyl basicity by the electron-withdrawing substituents  $OCH_3$ ,  $OC_2H_5$  and  $CCl_3$ .

The solvent effects seem to be primarily determined by hydrogen bonding in those solvents capable of providing an acidic hydrogen, and can be rationalized in terms of solvent effects on the polarity of the  $CO$   $\pi$  bond. Solvent effects in non-hydrogen bonding solvents appear to correlate with solvent shifts in the  $CO$  stretching frequencies, indicating the importance of electrostatic and van der Waals influences.<sup>2</sup>

-2-

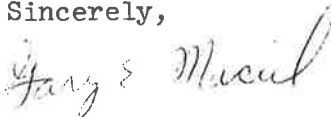
Dr. Bernard L. Shapiro  
Pittsburgh 13, Pennsylvania

The very low sensitivity of the  $C^{13}O$  chemical shift of dimethyl carbonate to environment in 1:1 solutions in eleven representative solvents suggests its use as an internal reference in cases where other methods may be less convenient. Thus, the separation of  $102.7 \pm 0.4$  p.p.m. between the CO and  $CH_3$  signals may provide a useful means of chart calibration, and the shift of  $-28.0 \pm 0.2$  p.p.m. for CO w.r.t. benzene provides a convenient and reliable reference point for the spectra.

References:

1. G. E. Maciel and G. C. Ruben, J. Am. Chem. Soc., 85, 3903 (1963).
2. A. D. Buckingham, T. Schaefer and W. G. Schneider, J. Chem. Phys., 32, 1227 (1960).

Sincerely,



Gary E. Maciel  
Assistant Professor

GEM:vh

## UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

December 15, 1964

Dear Dr. Shapiro:

In this letter I wish to communicate our data on the  $C^{13}$  chemical shifts of a series of 1-substituted-1-hexynes  $n-C_4H_9-C \equiv C-X$  with a variety of substituents X. In spite of the rapidly growing volume of  $C^{13}$  data of the past few years, a systematic study of acetylenic compounds has been conspicuously absent from the literature. Only few data have been available.<sup>1,2</sup>

The  $C^{13}$  n.m.r. spectra were obtained in natural abundance at 15.0<sup>0</sup>5 Mc/sec using dispersion mode and rapid-passage techniques.<sup>3</sup> The sample container was of the concentric-sphere type<sup>4</sup> with an external reference of a 1:1:1 (weight ratio) of  $NaO_2C^{13}CH_3$ ,  $Na_2C^{13}O_3$  and water. The eight compounds studied correspond to X=H, Cl, Br, I,  $C_6H_5$ ,  $COCH_3$ ,  $CH_3$  and  $C \equiv C-n-C_4H_9$ . In each case, except for X=H (where the expected splitting<sup>1,2</sup> due to the acetylenic proton was observed), two acetylenic peaks were found. These resonance lines seemed to fall into a recognizable pattern: the peak corresponding to the less shielded carbon was somewhat broader and shorter than that of the more shielded carbon. We interpret the broadness of the less-shielded resonance to be due to the presence of an adjacent alkyl group, probably a result of appreciable splitting by the methylene hydrogens, in agreement with the proton- $C^{13}$  splitting data for methyl acetylene.<sup>5</sup> Thus, the lower-field, broader peaks are assigned to  $C_\beta$ , and the sharper, higher-field peaks to  $C_\alpha$ , resulting in the following shifts.

 $C^{13}$  Chemical Shifts for  $n-C_4H_9-C \equiv C-X$ 

X	$\delta C_\alpha$	$\delta C_\beta$
H	58.7	43.0
$CH_3$	(50.4)*	(47.0)*
Cl	72.0	59.9
Br	90.3	48.9
I	132.0	31.9
$COCH_3$	41.7	31.3
$C_6H_5$	45.6	36.7
$n-C_4H_9-C \equiv C$	60.7	50.0

\* May be reversed

-2-

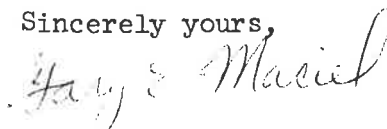
The assignment for  $X=H$  is unequivocal from splitting data, and seems on firm grounds for  $X=COCH_3$  and  $X=C_6H_5$  on the basis of arguments based on the approximate additivity of substituent effects on the  $C^{13}$  shift of acetylene.

We have found no obvious correlation between these shifts and the substituent constants  $\sigma_I$  or  $\sigma_R$  due to Taft or the  $C^{13}$  shifts of other series of compounds, except that similar trends at  $C_\alpha$  and  $C_\beta$  are observed for the halogen substituents in substituted ethanes, benzenes, ethylenes and acetylenes (1-substituted-1-hexynes). This situation is not to be explained in terms of an overwhelming influence of anisotropy effects in these pseudo-linear systems. The opposite signs of the trends of  $\delta C_\alpha$  and  $\delta C_\beta$  with changes in halogen substituents in the 1-substituted-1-hexynes cannot be explained on the basis of the rather flexible anisotropy model.

References:

1. P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Chapt. 7, Edited F. C. Nachod and W. D. Phillips, Academic Press, 1962.
2. R. A. Friedel and H. L. Retcofsky, J. Am. Chem. Soc., 85, 1300 (1963).
3. P. C. Lauterbur, *ibid.*, 83, 1838 (1961).
4. H. Spiesscke and W. G. Schneider, J. Chem. Phys. 35, 722 (1961).
5. G. J. Karakatsos, J. D. Graham and F. M. Vane, *ibid.*, 84, 37 (1962).
6. H. Spiesscke and W. G. Schneider, J. Chem. Phys., 35, 722 (1961).

Sincerely yours,



Gary E. Maciel  
Assistant Professor

GEM:vh



## Southern Research Institute

2000 NINTH AVENUE SOUTH  
BIRMINGHAM 5, ALABAMA

December 8, 1964

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

Subject: P.m.r. Studies of Purine and Substituted Purines

Dear Dr. Shapiro:

We have recently submitted for publication the results of work which we have done on purine and on 6-monosubstituted and 2, 6-disubstituted purines.

Despite the many times that the p.m.r. spectrum of purine has been discussed in the literature, no one has yet commented on the spin-spin coupling observable between  $H_2$  and  $H_6$  and  $H_6$  and  $H_8$  in acid solutions. This coupling is not observed in neutral  $D_2O$  where the predominant species is the neutral molecule. In water solution acidified with HCl to pH 2.4, about half the purine molecules should be protonated, and splitting begins to be observed. Below pH 0.5 the predominant species is the cation and splitting is clearly observed, as shown in the accompanying figure.  $J_{2,6} = (1.05 \pm 0.05)$  c.p.s.  $J_{6,8} \cong 0.3$  c.p.s. The assignments of  $J_{2,6}$  and  $J_{6,8}$  were confirmed from the spectra of purine-6-d and purine-8-d, determined under identical conditions. All solutions were 0.416 M in purine. Spin-spin coupling between  $H_2$  and  $H_6$  was also observed in a solution of purine in trifluoroacetic acid, with the same value for  $J_{2,6}$ .

Our results on 2- and 6-monosubstituted and 2, 6-disubstituted purines indicate that substituents in the 2 and 6 positions exert approximately equal effects on the chemical shift of the 8 proton, and that this effect is best measured by Brown's  $\sigma_p^+$  substituent constants. In dimethylsulfoxide solution, sixteen 2, 6-di-, eight 6-, and two 2-substituted purines give a linear correlation of the chemical shift of the 8-proton with  $\sigma_p^+$ :

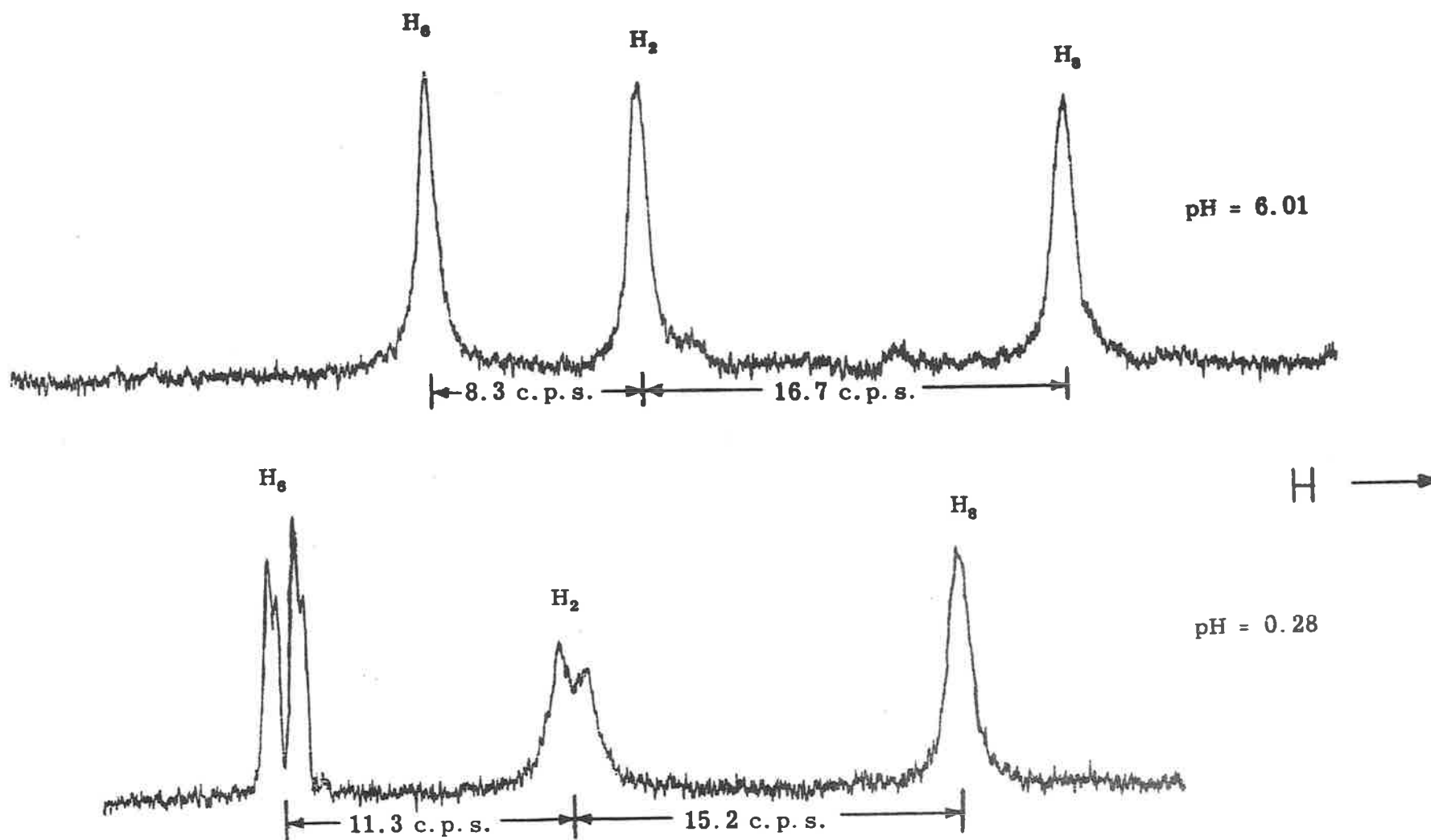
$$\delta H_8 = (8.655 \pm 0.013) + (0.347 \pm 0.013) \sum_{2,6} \sigma_p^+,$$

where  $\delta H_8$  is in p.p.m. downfield from internal TMS. The correlation coefficient is 0.984, and the standard deviation in  $\delta H_8$  is  $\pm 0.064$  p.p.m.

We are enjoying the newsletter, and trust that this will pay up our subscription on time.

Sincerely yours,

Martha C. Thorpe  
Associate Chemist



P.m.r. spectra of purine in water at 38°C. Top: neutral molecule; bottom: cation.  
 Solute concn. = 0.42 M in each case. (Not referenced).



RESEARCH LABORATORIES  
GENERAL MOTORS CORPORATION

December 9, 1964

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

Dear Barry:

Thanks for your reminder notice of October 21. Once again my contribution consists of a high resolution and a wide line part.

My high resolution comments deal with coupling of the type  $J_{XCH}$  in  $X(CH_3)_m$  compounds [see also 1) J. Chem. Phys. 39, 2031 (1963), 2) J. Chem. Phys. 40, 2037 (1964), and 3) IITNMRL No. 65]. One way of estimating NMR J-coupling constants is from hyperfine coupling constants since these are related to electron densities at the nucleus. A recent project has been to calculate and compile hyperfine coupling constants  $a(s)$  for outer s electrons from beam experiment results, optical hfs experiments, Goudsmit's equation, and Hartree-Fock wave functions. We have determined  $a(s)$  values for more than 70 atoms. Some of these data were then used to estimate  $J_{XCH}$  for  $X(CH_3)_m$  compounds using the average excitation energy ( $\Delta E$ ) approximation under two assumptions: (1)  $\Delta E$  is a constant, (2)  $\Delta E$  decreases with atomic number of X and can be estimated from a bond energy sum à la Karplus. We are aware that the average energy approximation has come into question [see papers at 3rd National SAS meeting, Cleveland, September 28, 1964]; however, for the similar compounds  $X(CH_3)_m$ , there may still be some value in our considerations. In effect, they are along the same lines as those of Dreeskamp for  $J_{X-Y}$  coupling [4) Z. Naturforsch 19, 139 (1964)]. Our calculations give somewhat better agreement with experiment under assumption (1) above. A communication concerning this work will appear shortly in J. Chem. Phys.

Dr. B. L. Shapiro

Page two

December 9, 1964

The assumption that  $\Delta E = \text{constant}$  and the inclusion of the Goudsmit relativistic factor  $K$  in the H-like wave function necessitates the modification of the  $Z^*$  vs  $Z$  plot of Ref. 2) above. Interestingly, the two effects offset one another to a certain extent. Equation (1) of Ref. 2) becomes:

$$J_{XCH} = \alpha_X^2 \frac{g_X}{g_H} \left( \frac{Z_X^*}{n} \right)^3 K_X J_{HCH} \quad (1)$$

where  $\alpha_X^2$  is the s-character of the outer s-electrons of the X atom,  $Z_X^*$  the effective nuclear charge in the squared H-like relativistic wave function  $Z_X^{*3} K_X / (\gamma a_0^3 n^3)$ , the g's are nuclear g-factors,  $n$  is the principal quantum number of the outer s-electrons,  $a_0$  is the Bohr radius, and  $K_X$  is the Goudsmit relativistic factor [5] Phys. Rev. 43, 636 (1933)]. The revised plot of  $Z_X^*$  vs  $Z$  is given in the attached figure.

This  $Z^*$  vs  $Z$  correlation can still be used in the manner of Ref. 2) to estimate  $\alpha_X^2$  values for  $X(\text{CH}_3)_m$  compounds from their  $J_{XCH}$  values. For example, Klose [6] Ann. Phys. 8, 220 (1961)] gives  $J_{77\text{Se}-\text{C}-\text{H}} = 11.2$  cps for  $\text{Se}(\text{CH}_3)_2$ . Using this value in Eq. (1), we get  $\alpha_{\text{Se}}^2 = 0.16$ . From bond angle and bond energy calculations à la Pauling [The Nature of the Chemical Bond, Cornell U., 1960, p 122] give  $\alpha_{\text{Se}} = 0.14$  and  $0.02$  respectively.

The wide line portion of our work is concerned with some proton magnetic resonance (PMR) studies on solid  $X(\text{CH}_3)_4$  compounds, where  $X = \text{Si}, \text{Ge}, \text{Sn},$  and  $\text{Pb}$ . Preliminary results have been reported elsewhere [Bull. Am. Phys. Soc. II, 9, 25 (1964), and Liquids, Structure, Properties and Solid Interactions, in press, Elsevier Publishing Co.]. In this work I have been concerned with  $\text{CH}_3$  reorientations, molecular reorientations, and possible molecular self diffusion. The PMR work yields interesting results concerning the self diffusion of  $\text{Si}(\text{CH}_3)_4$  molecules in the solid metastable  $\alpha$  phase. Molecular reorientations in the solid are found to be more and more restricted as one proceeds from C to Pb. These results are found to be in qualitative agreement with the theory of Pople and Karasz [J. Phys. Chem. Sol. 18, 28 (1961) and 20, 294 (1961)]. The energy barrier restricting  $\text{CH}_3$  reorientation is found to go roughly as  $1/r^6$  where  $r = \text{methyl-methyl separation}$ .

Dr. B. L. Shapiro

Page three

December 9, 1964

In the study of the nature of the various motions, the second moment is, of course, a valuable tool. The complete report of this work, which is being submitted for publication, examines closely the methods of computation of second moments for various types of motion. Some new methods for approximating the intermolecular contribution to the rigid lattice second moment are pointed out. These methods are most useful for cases where crystal structure is unknown but the density is known.

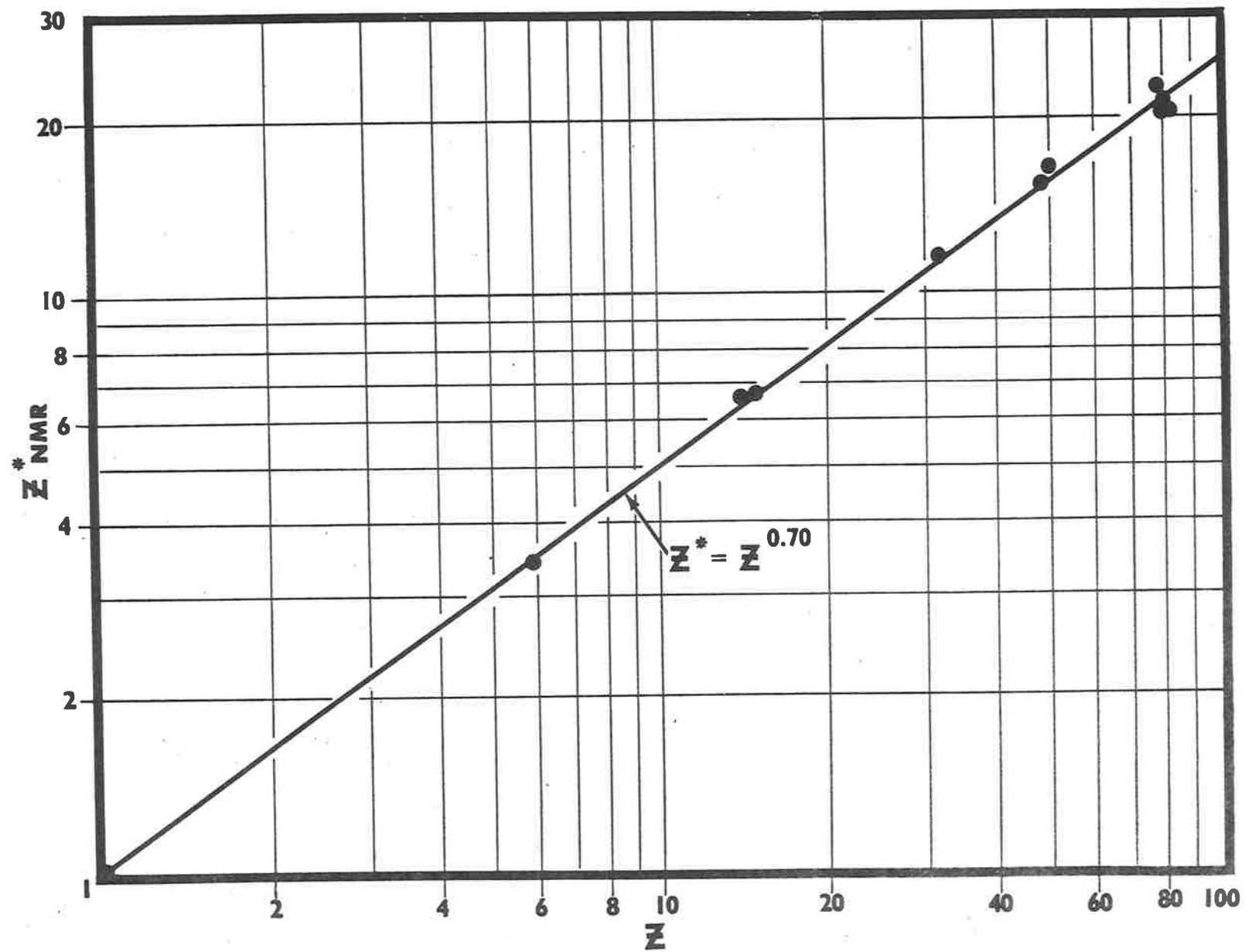
Also described in the full paper are Fortran II computer programs for calculating  $T_1$  from decay or growth curves, fitting the BPP type line narrowing equation to  $\delta H$  vs  $T$  plots, fitting the BPP  $T_1$  equation for reorientational narrowing to  $T_1$  vs  $T$  plots, determining experimental second moments from derivative curves, and calculating theoretical second moment curves. The latter two programs are based in part on programs due to W. R. Jansen.

Yours truly,



George W. Smith  
Physics Department

ks  
att



Professor F.G.A. Stone

Department of Inorganic Chemistry,  
Bristol 8  
England.

FGAS/1185

Professor Bernard L. Shapiro,  
Illinois Institute of Technology,  
Chicago 60616

Dear Barry :

Stereochemistry of Square-Planar Platinum Complexes.

In the course of other work we have prepared in this laboratory several square planar platinum complexes having triethyl phosphine groups as ligands. The stereochemistry of the majority of these was either unknown, or deducible only by comparing physical properties and the stereochemistry of the starting materials (either cis- or trans-  $(\text{PEt}_3)_2\text{PtCl}_2$ ). We are now attempting to confirm our stereochemical deductions using  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  high resolution NMR spectroscopy, and give here some preliminary details of the  $^1\text{H}$  NMR spectra [Varian A60].

Jenkins and Shaw<sup>(1)</sup> in their work on platinum and palladium complexes containing phenyl dimethyl phosphine, suggest that differences between the spectra of the cis- and trans- complexes may be explained by virtual coupling<sup>(2)</sup> between  $^{31}\text{P}$  nuclei in the trans-complexes which does not occur when the  $^{31}\text{P}$  nuclei are mutually cis-. We have prepared<sup>(3)</sup> the cis- and trans- isomers of  $(\text{Et}_3\text{P})_2\text{PtCl}_2$  and find that the proton spectrum of the cis- complex (in  $\text{CDCl}_3$  at  $50^\circ$ , fig. 1) and the trans- complex (in  $\text{CDCl}_3$  at  $35^\circ$ , fig. 2) can be explained on a first order basis using the same concepts of virtual coupling referred to above.

Although these two spectra differ only slightly from each other the differences are sufficient to permit deduction of the stereochemistry. Thus in several complexes of doubtful stereochemistry so far examined (e.g.  $(\text{PEt}_3)_2\text{Pt} \begin{smallmatrix} \text{Cl} \\ \swarrow \\ \text{C}_6\text{F}_5 \end{smallmatrix}$  fig. 3) it appears that the peak

intensity ratios in the methyl resonance, the coupling between the various spin-active nuclei and the spacing of the lines in the methylene resonance are sufficiently characteristic to distinguish between cis- and trans- isomers. Table 1 gives approximate values of the coupling

Professor B. L. Shapiro

-2-

9th December, 1964.

constants (taken directly from the spectra) assuming in all cases that (i)  $J_{\text{P-CH}_2\text{-CH}_3} = 0$  c.p.s.<sup>(4)</sup> and (ii)  $J_{\text{Pt-P-CH}_2\text{-CH}_3} = 0$  c.p.s., extrapolating from the spectrum of trans-  $(\text{Et}_2\text{S})_2\text{PtCl}_2$  in which the methyl resonance is a well-defined triplet.

Table I

Compound	$J_{\text{P-CH}_2\text{-CH}_3}$	$J_{\text{CH}_2\text{-CH}_3}$	Conclusion
cis- $(\text{PEt}_3)_2\text{PtCl}_2$	17.5	7.7	- <sup>a</sup>
trans- $(\text{PEt}_3)_2\text{PtCl}_2$	16.2	8.3	- <sup>a</sup>
? - $(\text{PEt}_3)_2\text{Pt} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{C}_6\text{F}_5 \end{array}$	16.2	8.3	trans-
? - $(\text{PEt}_3)_2\text{Pt} \begin{array}{l} \diagup \text{Br} \\ \diagdown \text{CF:CF}_2 \end{array}$	16.5	8.5	trans-
? - $(\text{PEt}_3)_2\text{Pt} \begin{array}{l} \diagup \text{Br} \\ \diagdown \text{C}_6\text{F}_5 \end{array}$	17.1	8.3	cis- <sup>b</sup>

(a) Stereochemistry well-established.

(b) Invoking the spacing of the lines in the methylene resonance; see text.

As a ligand,  $\text{Et}_3\text{P}$  is far less satisfactory than  $\text{Me}_2\text{PPh}$  for determining stereochemistry by this method, although we hope to reduce the complexity of the spectra by spin decoupling and by preparing analogous palladium complexes.

Kindest regards,

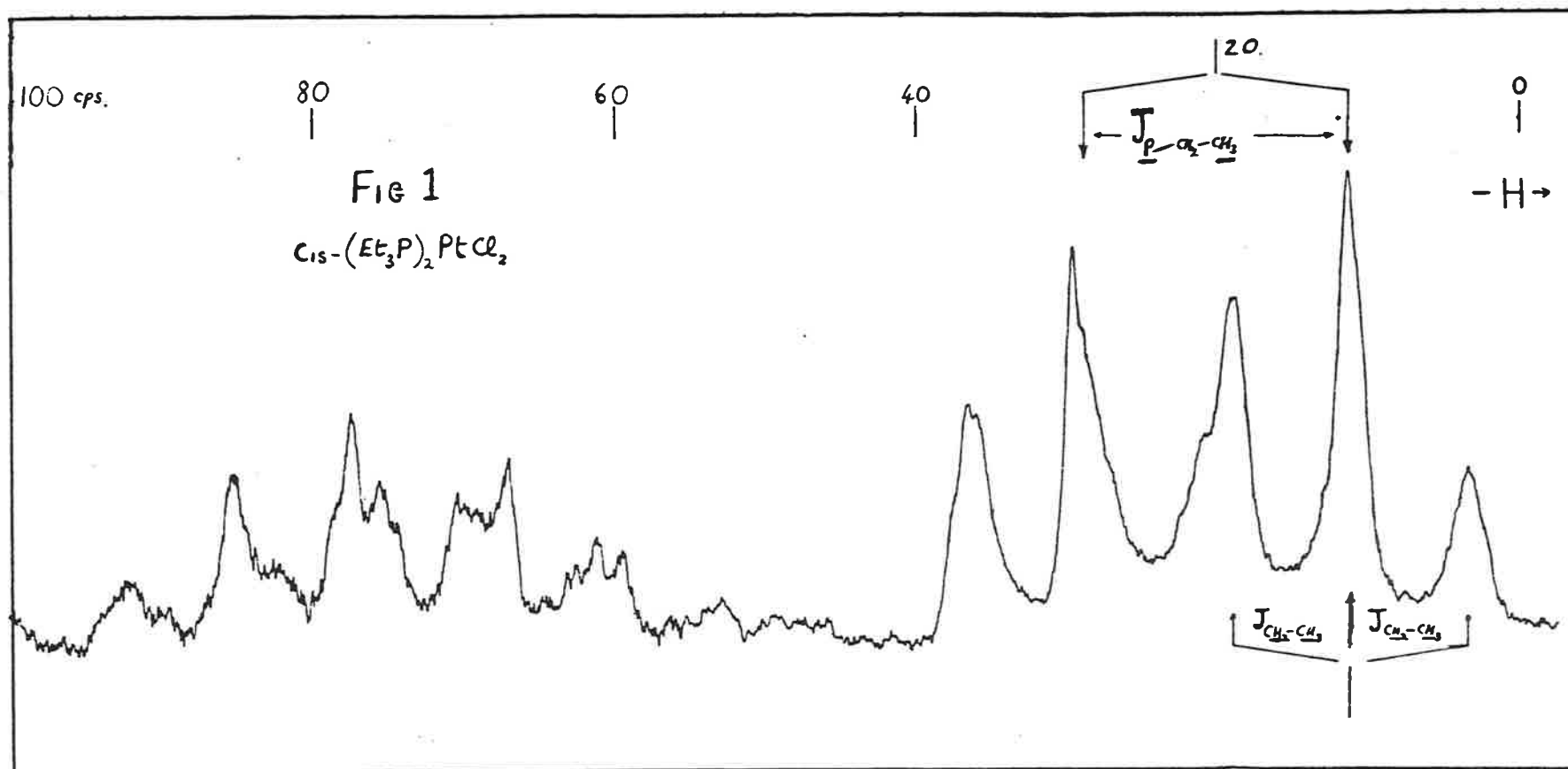
Yours sincerely,

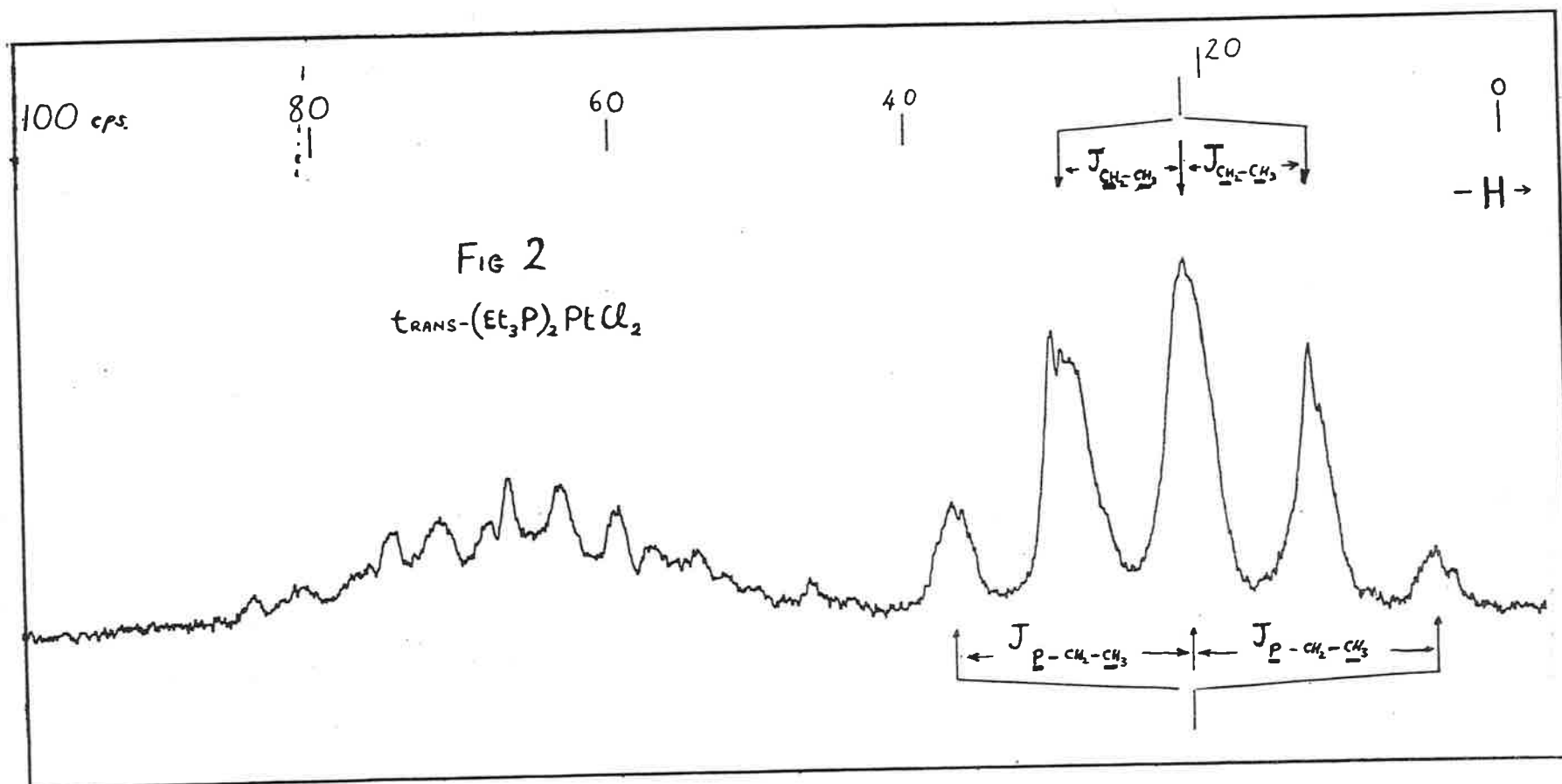
References:

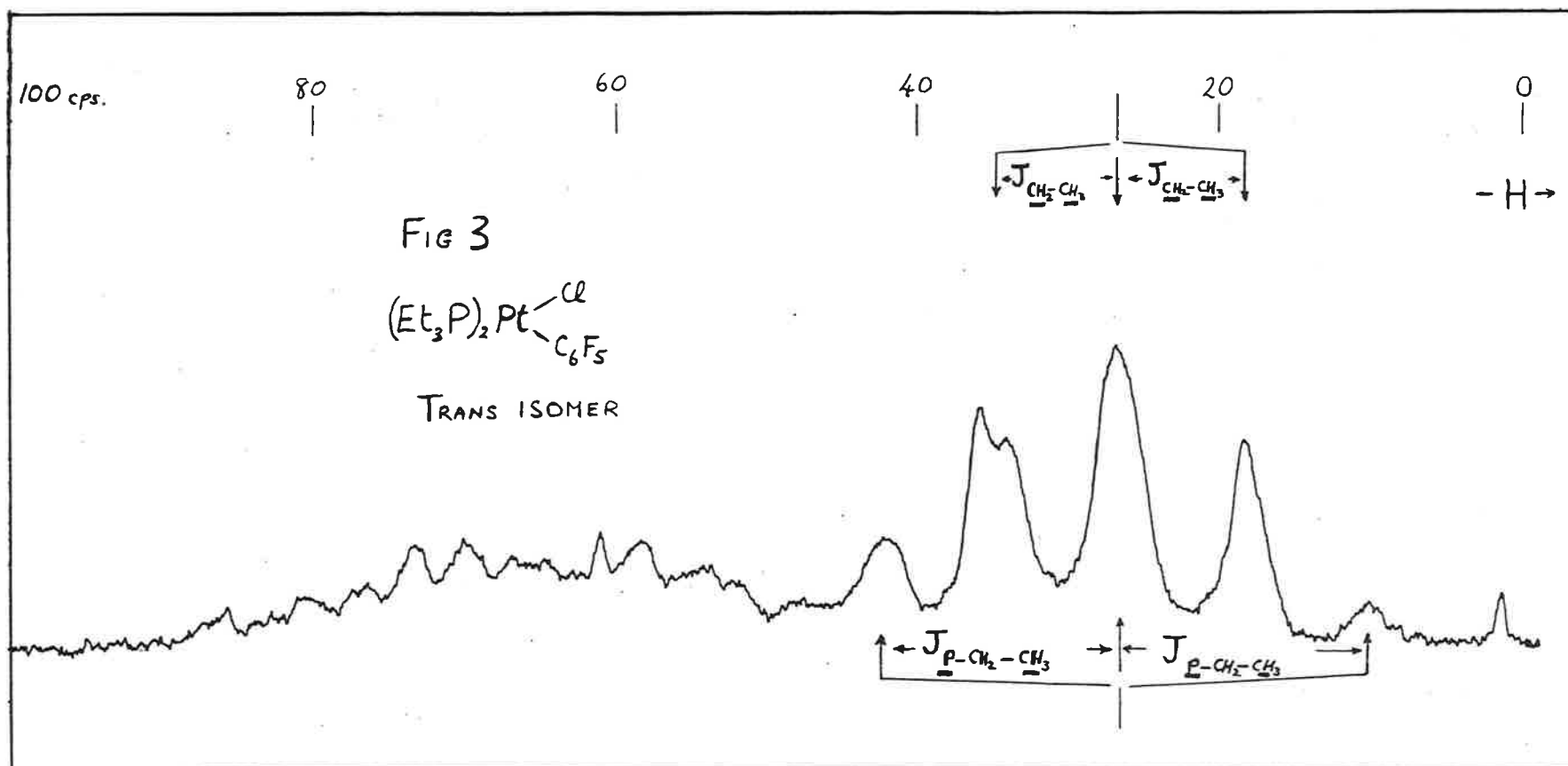
- (1) Jenkins and Shaw, Proc.Chem.Soc., 279, (1963).  
 (2) Musher and Corey, Tetrahedron, 18, 791, (1962).  
 (3) Jensen, Z.Anorg.Chem., 229, 225, (1936).  
 (4) Narasimhan and Rodgers, J.Chem.Phys., 34, 1049, (1961).

*Gordon*  
 N. Flitcroft,  
 A. J. Rest,  
 F. G. A. Stone.









# GENERAL ELECTRIC COMPANY

HANFORD ATOMIC  
PRODUCTS OPERATION

RICHLAND, WASHINGTON 99352 . . . AREA CODE 509, TELEPHONE 942-1111

HANFORD LABORATORIES

December 7, 1954

Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60615

Dear Barry,

## $P^{31}-H^1$ Couplings in Organophosphorus-Uranyl Complexes

Thank you for your reminder that it is time for us to send our contribution to the IIT NMR Newsletter.

We have continued our study of the effect of complexation with uranyl nitrate on certain neutral organophosphorus compounds.  $P^{31}-H^1$  couplings for several parent compounds are given in the table.

The change in coupling constants on formation of uranyl complexes is relatively small in most cases, but for  $J(P-H)$  in the dialkyl hydrogen phosphonates, the coupling is increased by as much as 61 cps. The increase in coupling for  $J(P-C-H)$  is 0.6 cps for diethyl methylphosphonate. For  $J(P-O-C-H)$  the change is significant only for a methoxy group, with an increase of 0.7 for methyl dibutylphosphinate. Only triethylphosphate showed  $P^{31}-H^1$  coupling over four bonds, and this long-range coupling is observed to increase by 0.4 cps with formation of the uranyl complex. No change in proton-proton coupling constants is observed with complexation.

There appears to be no general trend relating the change in coupling constant to complexing ability of the parent compound. However, the change



A PRIME CONTRACTOR FOR THE U.S. ATOMIC ENERGY COMMISSION

$P^{31}-H^1$  SPIN-SPIN COUPLING CONSTANTS IN ORGANOPHOSPHORUS COMPOUNDS<sup>a</sup>

Compound	Coupling Constant (cps)			
	alkyl	alkoxy		Other
	$J_{\alpha H-P}$	$J_{\alpha H-P}$	$J_{\beta H-P}$	
$(CH_3CH_2O)_3PO$	-	$\pm 8.7$	$\pm 0.9$	-
$(CH_3O)PO[O(CH_2)_3CH_3]_2$	-	$\pm 8.0^b$ $\pm 11.7^c$	-	-
$(CH_3CH_2O)_2PO(H)$	-	$\pm 9.9$	-	$\pm 690^d$
$(CH_3CH_2O)_2PO(CH_3)$	$\mp 18.1$	$\pm 8.7$	n.r.	-
$[(CH_3)_2CHO]_2PO(C_6H_5)$	-	$\pm 8.1$	-	-
$[CH_3(CH_2)_3O]_2PO(CH_2Cl)$	$\mp 11.2$	$\pm 8.2$	-	-
$(CH_3O)PO[(CH_2)_3CH_3]_2$	-	$\pm 10.9$	-	-

<sup>a</sup>Solutions are 20% v/v in carbon tetrachloride. Measurements have been made on the Varian A-60 spectrometer at  $33 \pm 2^\circ C$  and are reported to within  $\pm 0.1$  cps.

<sup>b</sup> $J_{POCH_2}$

<sup>c</sup> $J_{POCH_3}$

<sup>d</sup> $J_{PH}$  for proton attached directly to a phosphorus atom.

<sup>nr</sup>Not resolved.

**GENERAL  ELECTRIC**

Dr. Bernard L. Shapiro

-3-

December 7, 1954

in  $J(\text{P-O-C-H})$  for methyl dibutylphosphinate is considerably larger than for the phosphonates. The observed increases in coupling constant with complexation are in part a consequence of changes in the hybridization of the P-X bond orbitals. The effective withdrawal of electrons from the P=O bond is presumably accompanied by an increase in the amount of s-character in the P-X bonds.

A more complete study of these coupling constants, along with a discussion of their relative signs, may be found in a preprint which will be made available shortly to those interested.

Our thanks go to Mr. Bernard Nist for allowing us to use the Varian A-60 spectrometer at the University of Washington Department of Chemistry.

Sincerely yours,

Jane L. Burdett

  
L. L. Burger



# DOW CHEMICAL OF CANADA, LIMITED

SARNIA, ONTARIO

November 18, 1964

Professor B.L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Centre  
Chicago 16, Illinois  
U.S.A.

Dear Dr. Shapiro:

## Silver Tetrafluoroborate - Olefin Complexes

We have been studying silver-olefin complexes and are submitting some of the results obtained. These complexes are readily prepared by the reaction of  $\text{AgBF}_4$  and the gaseous olefin to form a 1:2 silver-olefin complex. A comparison of the proton spectra of the complex to that of the olefin shows that there is an increase in the downfield shift of the protons relative to tetramethyl silane (table I); the downfield shift is in the order  $\Delta\nu_1 > \Delta\nu_2 > \Delta\nu_3$  (where  $\nu$  is the chemical shift of the proton). It is apparent from the table that in the uncomplexed olefin,  $\text{H}_2$  is slightly more shielded than  $\text{H}_3$  but in the complex  $\text{H}_3$  is more shielded. The change of chemical shift of  $\text{H}_2$  relative to  $\text{H}_3$  tends to increase as the alkyl substituent becomes bulkier. The change of chemical shift with complexing is illustrated for 3,3-dimethyl-1-butane.

The study of the deshielding upon complexing of the vinyl protons in an extensive series of alkyl-substituted olefins in conjunction with infrared studies has been interpreted in terms of the positioning of the silver ion with respect to the double bond. A complete report will be published later.

Yours sincerely,

*J. M. McIntyre*  
J.S. McIntyre

*H. W. Quinn*

H.W. Quinn

/ss

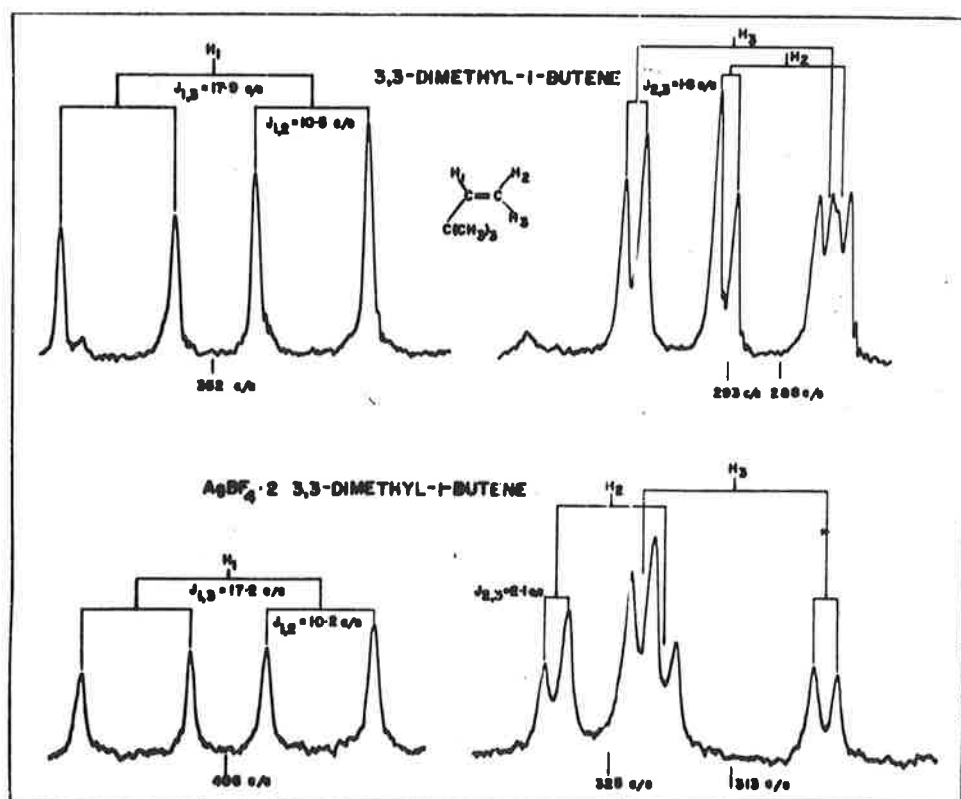
TABLE I

CHEMICAL SHIFTS FOR THE VINYL PROTONS IN 1-ALKENES  
AND THE CORRESPONDING  $\text{AgBF}_4 \cdot 2$  1-ALKENES

$$\begin{array}{c} \text{H}_1 \\ \text{R} \end{array} > \text{C} = \text{C} \begin{array}{c} \text{H}_2 \\ \text{H}_3 \end{array}$$

Olefin	$\nu_1^{\text{a)}$			$\nu_2$			$\nu_3$		
	$\nu_1^{\text{O}}$	$\nu_1^{\text{C}}$	$\Delta\nu_1$	$\nu_2^{\text{O}}$	$\nu_2^{\text{C}}$	$\Delta\nu_2$	$\nu_3^{\text{O}}$	$\nu_3^{\text{C}}$	$\Delta\nu_3$
Propene	352	400	48	295	324	29	300	319	19
1-Butene	355	407	52	296	329	33	300	322	22
1-Pentene	351	401	50	293	329	36	297	321	24
1-Dodecene	349	399	50	293	325	32	297	317	20
3-Methyl-1-butene	347	400	53	288	324	36	293	316	23
3,3-Dimethyl-1-butene	352	406	54	288	325	37	293	313	20

a) In c.p.s. downfield from T.M.S., O and C designate olefin and complex respectively.







ECOLE DE PHYSIQUE  
UNIVERSITE DE GENEVE

INSTITUT DE PHYSIQUE  
EXPERIMENTALE

BOULEVARD D'YVOY 32

TEL. (022) 25 22 10

GENEVE

Genève, le 10 décembre 1964

GJB/lmg

Prof. B.L. SHAPIRO  
Illinois Institute of Technology  
Technological Center

CHICAGO 60616

U.S.A.

Cher Professeur Shapiro,

Merci pour votre rappel de la date limite de  
notre contribution.

Après avoir déterminé les signes relatifs des  
constantes d'interaction phosphore-proton dans les triéthyl  
phosphate et phosphite 1), par R.M.N. dans le champ magnétique  
terrestre, nous pouvons maintenant annoncer les signes relatifs  
de celles-ci dans le tripropyl phosphate ( $O=P(OCH_2CH_2CH_3)_3$ )

$$|J_{P-H_\alpha}| = 7,6 \text{ c/s} \quad |J_{P-H_\beta}| \sim 0,8 \pm 0,2 \text{ c/s} \quad \text{ces deux constantes}$$

sont de même signe; quant à la valeur de  $J_{P-H_\gamma}$  elle est infé-  
rieure à 0,2 c/s. La détermination des signes relatifs a été  
faite dans ce cas par comparaison aux spectres calculés par  
l'IBM 7090 du CERN pour  $J_{PH_\alpha}$  et  $J_{PH_\beta}$  de mêmes signes ou de  
signes différents, et plusieurs valeurs de  $|J_{P-H_\beta}|$  0,6, 0,8 et  
1 c/s. L'allure du spectre change très peu entre ces valeurs.

Une interprétation théorique de l'interaction  
spin noyau spin noyau 2) nous permet d'attribuer aux constantes  
 $J_{P-H_\alpha}$  et  $J_{P-H_\beta}$  le signe positif.

- 2 -

Prof. B.L. Shapiro, Illinois Institute of Technology,  
Technological Center, Chicago 60616, U.S.A.

---

Nous vous proposons maintenant de déterminer les signes relatifs des constantes phosphore-proton dans le triéthyl thiophosphate. Nous comparerons ensuite ces constantes de couplage obtenues à la structure électronique des composés organo-phosphorés.

Avec mes meilleurs vœux pour la nouvelle  
année.



Prof. G.J. Béné

#### Références

- 1) G.J. Béné, E. Duval, A. Finaz, G. Hochstrasser,  
C.R.A.S. (Paris) 256, 2365 (1963) et  
G.J. Béné, E. Duval, A. Finaz, G. Hochstrasser, et S. Koïdé,  
Phys. Let. 7, 34 (1963)
- 2) S. Koïdé et E. Duval, J.Chem.Phys. 41, 315 (1964)  
(figure jointe )

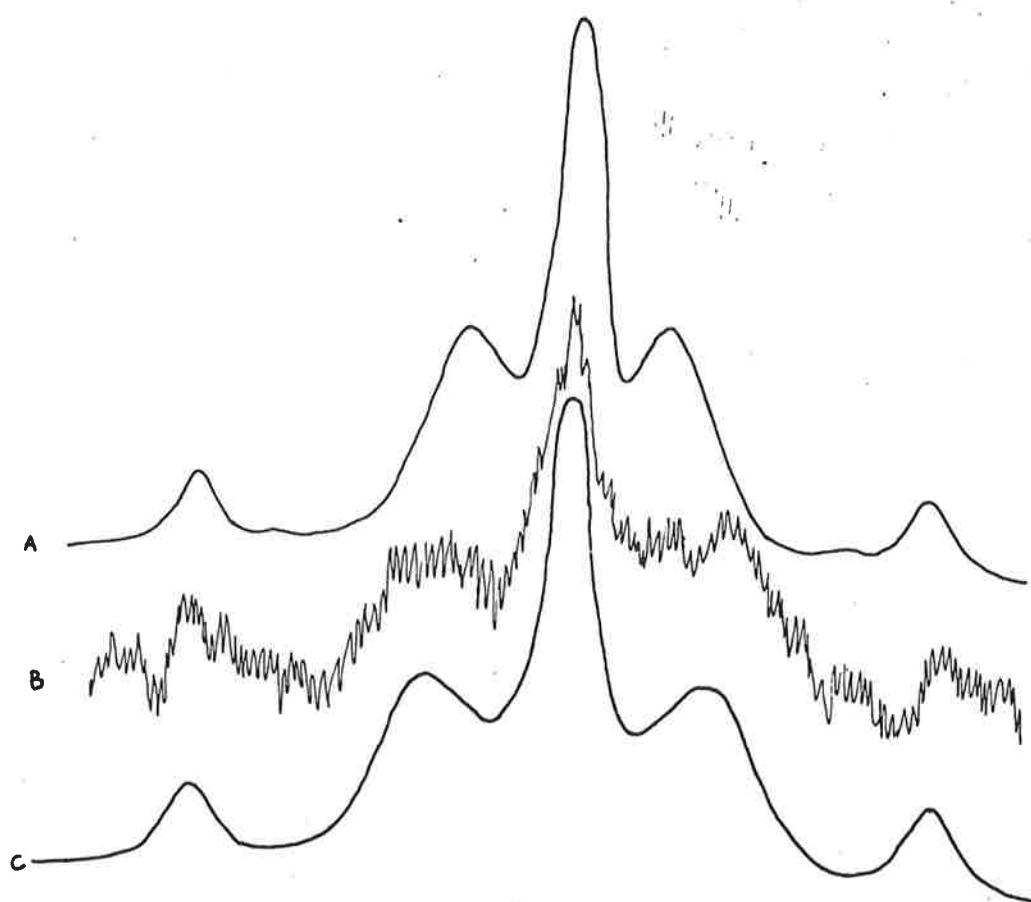


Fig. 2

Comparaison spectre expérimental spectres calculés  
pour  $J_{P-H\beta} = 0,8c/s$ .

- A - Spectre calculé :  $J_{P-H\alpha}$  et  $J_{P-H\beta}$  sont de signes différents
- B - Spectre expérimental
- C - Spectre calculé :  $J_{P-H\alpha}$  et  $J_{P-H\beta}$  sont de mêmes signes



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
FOOD AND DRUG ADMINISTRATION  
WASHINGTON, D.C. 20204

December 9, 1964

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

Dear Barry:

So, finally fate has caught up with us too, when we received your gentle reminder for a contribution to the IIT NMR Newsletter. Sorry for the delay.

We have been studying the NMR spectra of carbamates  $R_1O-C(O)-NR_2R_3$ . If in carbamates  $R_1$  is aliphatic such as methyl and ethyl, and  $R_2=R_3$ =methyl, no  $R_2R_3$ -methyl doublet due to hindered rotation about the  $C(O)-N$  bond is observed (1), in contrast to the analogous amides which have received great attention, including that with  $R_1=Cl(1)$ . Now, if  $R_1$  is aromatic, that is, if it consists of rings such as phenyl, naphthyl, imidazolyl, pyrimidyl and pyrazolyl, and if  $R_2=R_3$ =methyl, we do observe two N-methyl peaks. Their width is over 2 Hz, which can be due to incipient coalescence and/or HN coupling. At any rate, these doublets all collapse at about 60°C into a singlet. Thus, hindered rotation seems to be present at room temperature in N,N-dimethyl carbamates, provided that  $R_1$  is aromatic. We are looking further into this matter, in order to obtain activation energies and also to establish whether any steric factors or solvent effects are involved.

Another item may be of interest to A-60 owners. We have been using a commercial water-to-freon-to-water refrigeration type heat exchanger for the last seven months. Gone are all the too well-known problems related to magnet cooling. We are all too familiar with the frustrations associated with use of treated tap water, that is, with water pressure fluctuations, contamination of cooling coils (fortunately we never experienced clogging) and irregular flow rates, but especially with fluctuations and long-term drifts of temperature and thus field, and the resulting decay of field homogeneity. In this area, the latter used to be especially severe in midsummer when the raw water temperature rises above 25°C, and in winter, when it drops below 7°C. In the latter case temperature control of the magnet cooling water is inadequate. The distilled water in the closed loop has remained very clean; no plant growth can be detected, although no growth inhibitor was added, nor has the ion exchanger in the loop begun to change color.

We trust that this letter has put us back in good standing.

Best regards.

Sincerely,

*W. R. Benson*

*Ernest Lustig*

Walter R. Benson                      Ernest Lustig  
Bureau of Scientific Research

(1) J.C. Woodbrey and M.T. Rogers, J. Am. Chem. Soc. 84, 13 (1962).

*Universidad de Buenos Aires*  
*Facultad de Ciencias Exactas*  
*y Naturales*

Buenos Aires, December 4th, 1964.

Prof. Bernard Shapiro.  
 Department of Chemistry.  
 Illinois Institute of Technology.  
 Illinois, USA.

Double long range coupling in benzaldehydes: splittings of combination lines.

Dear Prof. Shapiro:

Since a long time ago we have been working in the problem of L.R.C. in benzaldehydes and pyridine-carboxaldehydes. We have been using two methods to detect couplings, or rather splittings, of magnitude smaller than the linewidth. The first is an analytical method, useful when a computer is available, based on the study of the combination lines. The second, which was used only for checking purposes, is based on line intensity measurements. We shall try to describe briefly both methods.

1) If in an ABC spectrum  $\delta_{AB} \sim J_{AB}$  we have an almost ABX case. Two combination lines are usually seen near the X lines. The positions of these combination lines are quite sensitive to  $\delta_{AB}$ . If we now introduce another nucleus (Y or D) which has a small coupling with, e.g., nucleus A only ( $J_{AY}$  or  $J_{AD}$ ) the combination lines are split with splittings  $S_1$  and  $S_2$ , usually alike. If we now introduce another coupling, either  $J_{BD}$  or  $J_{CD}$ , the "exact" ABCD treatment shows that  $S_1 \neq S_2$  and that, usually, though not always, the sum  $S_1$  and  $S_2$  is proportional to one of the J's while the difference is proportional to the other one. There is sometimes an uncertainty which can be usually overcome by the second method.

Universidad de Buenos Aires  
 Facultad de Ciencias Exactas  
 y Naturales

---

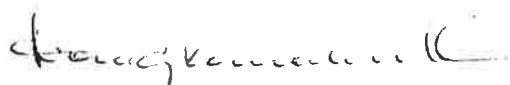
2) Assuming we have two lorentzian lines of halfwidth  $\Delta$  and height  $y_0$  which are separated by a distance  $\delta < \Delta$ , they overlap and give a line of height  $y \leq 2y_0$  which is given by the expression:

$$y = \frac{2 y_0}{1 + (\delta/\Delta)^2}$$

Thus if  $\Delta$  is known ( it can quite reasonably be taken from other lines in the same spectrum )  $\delta$  can be estimated from the differences between the experimental and the theoretical intensities. In spite of the rather low precision with which line intensities are measured in MNR spectroscopy, this method seems to work well. (A graph of the above function is included).

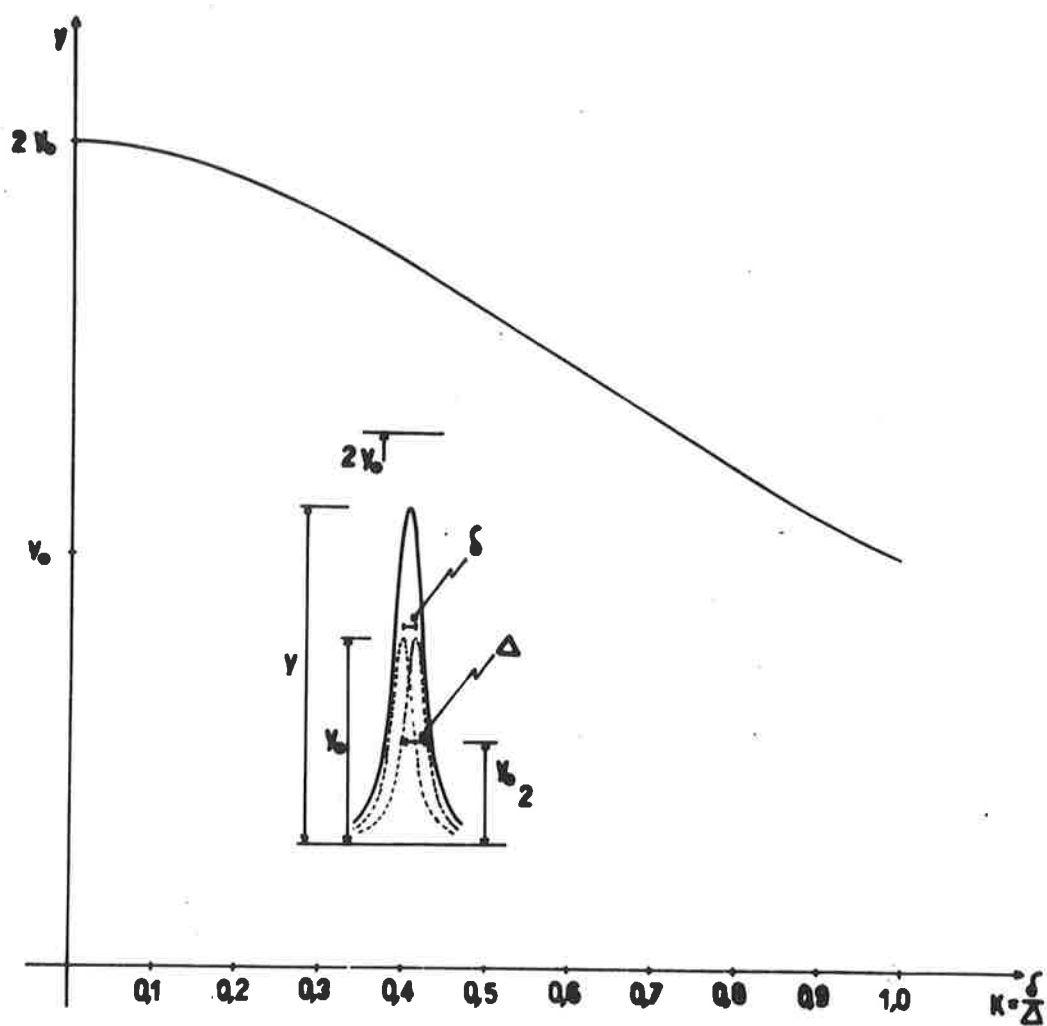
Both these methods were tried with success in some benzaldehydes in which the existence of a second L.R.C. was evident from the splittings (0.2 cps, e.g. 2,4 di nitro benzaldehyde). Then, they were applied to other substances with smaller L.R.C. and we have been able to determine the magnitudes and relative signs of several other L.R.C.'s of up to 0.1 cps. These results show that they are positive whenever the interaction is with protons 3,4 or 5 of the ring, and negative when it happens with proton 6.

Sincerely yours,



Dora G. de Kowalewski.

  
 Waldemar J. Kowalewski.





## CANISIUS COLLEGE

BUFFALO 8, NEW YORK

DEPARTMENT OF CHEMISTRY

December 14, 1964

Dr. Barry L. Shapiro  
Chemistry Department  
Illinois Institute of Technology  
10 East 35th Street  
Chicago, Illinois

Dear Dr. Shapiro:

I would like to request this letter appear in the NMR Newsletter.

I am planning two days of NMR papers for the Mid-America Symposium on Spectroscopy which will be held on June 14 through 17, 1965 at the Sheraton-Chicago Hotel, Chicago, Illinois.

One day will be devoted to papers on Organo Metallics and the second day will be papers on Polymers. I am inviting those who would like to give papers to write to me by January 30, 1965. At present I have the following authors to present papers.

Harold E. Swift - Gulf Research & Development Company, Pittsburgh, Pa. who will give a paper on  $Al^{27}$  spectra.

Claiborne E. Griffin of the University of Pittsburgh will give a paper on  $P^{31}$  NMR Spectra.

Victor Mark of Hooker Chemical Company will give a paper on H Resonance of Organo phosphorous compounds.

For the Polymer section Frank Bovey of Bell Telephone Laboratories will give the keynote paper to begin the days series of papers.

I am allowing authors from one-half to one hour time so that they may adequately present their work. I hope other authors will write me to present papers in these general areas.

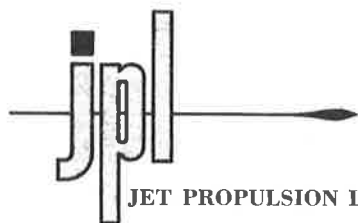
I should also like to just call attention to the NMR Spectroscopy Institute which will be held at Canisius College the week following the Mid-America Symposium, that is June 21 through the 25th and will have Leroy Johnson of Varian Associates and Nugent Chamberlain of Humble Oil give the institute lectures. Those who wish to attend this institute could write me also.

Sincerely,

*Herman A. Szymanski*  
Dr. Herman A. Szymanski  
Chairman-Dept. of Chemistry

Has/am





JET PROPULSION LABORATORY California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103

14 December 1964

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

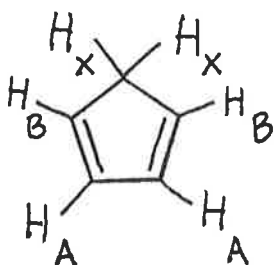
Dear Barry:

Many years ago (MELLON-M-R No. 30) we mentioned that we had field-sweep decoupled the methylene protons and vinyl proton of cyclopentadiene (I) and were attempting to analyze the resulting  $A_2B_2$  vinyl proton spectrum. We never obtained a satisfactory fit to our field-sweep decoupled spectra (one shown in fig. 1c). All these spectra, (four in number, two in each sweep direction) which we felt represented the most complete decoupling, show line 9 (see fig. 2a) significantly less intense than lines 7 and 8. Our attempts at fitting the spectrum were based on lines 7 and 8 being the two most intense symmetric transitions. The frequency sweep spectra shown in fig. 1b settled the matter; line position measurements from spectra of the quality of fig. 1b proved to be measurable to  $\pm 0.01$  cps. In figs. 2b and 2c are shown two of a number of triple irradiation experiments which were performed and which establish the energy level scheme for the  $A_2B_2$  spin system. Fig. 2c should serve to indicate that extraneous frequencies, and a shakey lock can be real problems in this kind of experiment and the results are not always as clear as in fig. 2b.

In fig. 3 are shown the results for 1,3-cyclohexadiene (II). In this case we were lucky to get what you see because the methylene protons are about 120 cps from TMS and excess modulation at the TMS position from a large modulation at the methylene position saturates the lock significantly plus causing certain extraneous beats. These effects tended to unlock the spectrometer. Line positions were only measurable to  $\pm 0.05$  cps in this  $A_2B_2$  spectrum. No triple irradiation experiments could be done on II because an additional modulation immediately unlocked the works.

The results for these molecules from NMRIIT and NMREN are given below.

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



$$\delta_{AB} = 8.079 \pm 0.004 \text{ cps (60 Mc)}$$

$$J_{AA} = +1.944 \pm 0.007$$

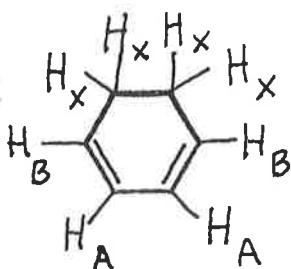
$$J'_{AB} = +1.090 \pm 0.006$$

$$J_{AB} = +5.064 \pm 0.006$$

$$J_{BB} = +1.944 \pm 0.007$$

$$J_{AX} = -1.31 \pm 0.02$$

$$J_{BX} = +1.20 \pm 0.02$$



$$\delta_{AB} = 6.394 \pm 0.013 \text{ cps (60 Mc)}$$

$$J_{AA} = +5.142 \pm 0.028$$

$$J'_{AB} = +1.064 \pm 0.027$$

$$J_{AB} = +9.417 \pm 0.033$$

$$J_{BB} = +1.944 \pm 0.028$$

We hope to obtain some values for  $J_{AX}$  and  $J_{BX}$  for II by guessing and using a computer plot routine which we have just generated. For both I and II the upfield vinyl protons are those adjacent to methylene groups; these assignments will be discussed in detail elsewhere.

With best regards,

*Stan*  
*Dan*

Stanley L. Manatt  
Daniel D. Elleman

SLM/DDE:jas  
Air Mail

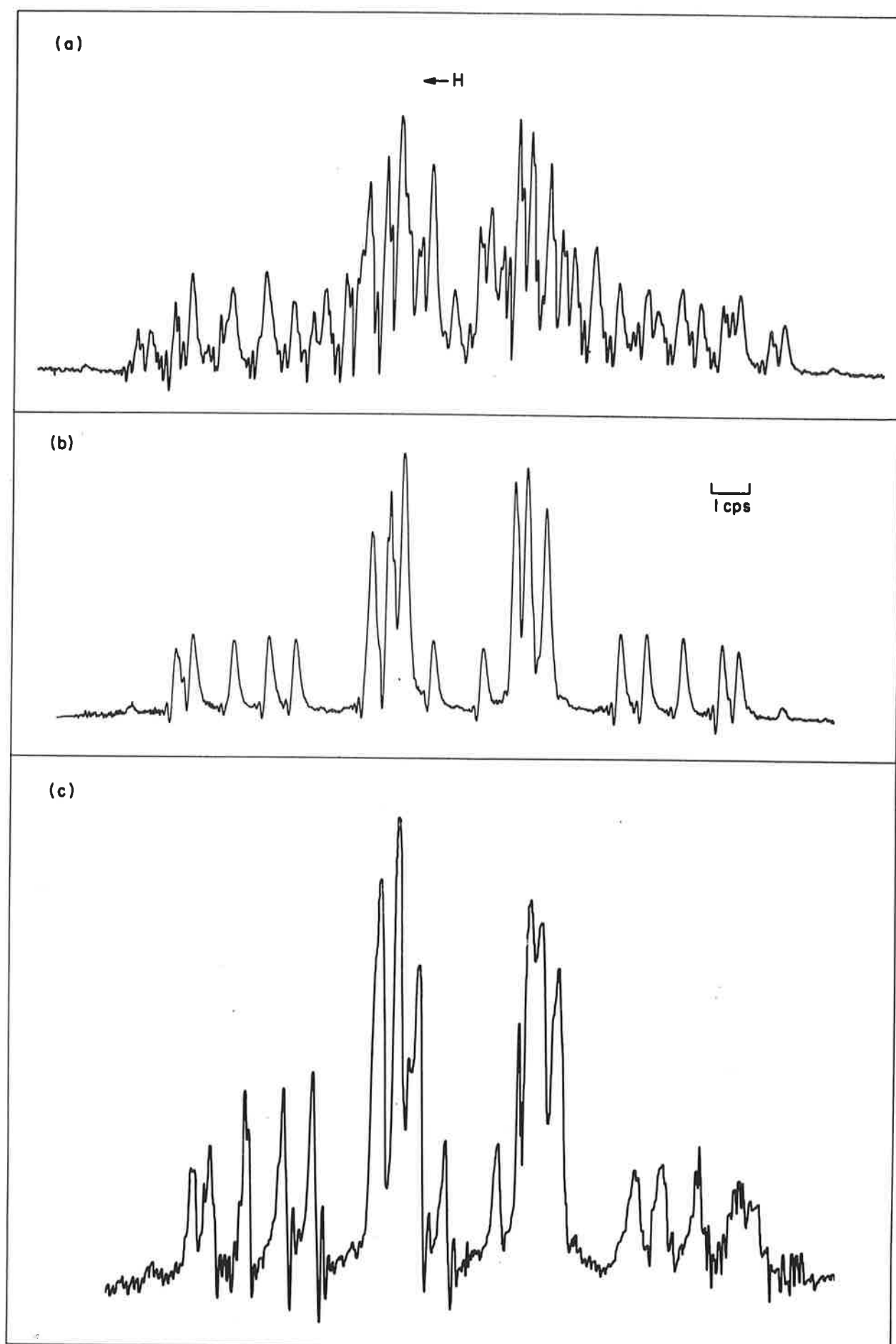


Fig. 1

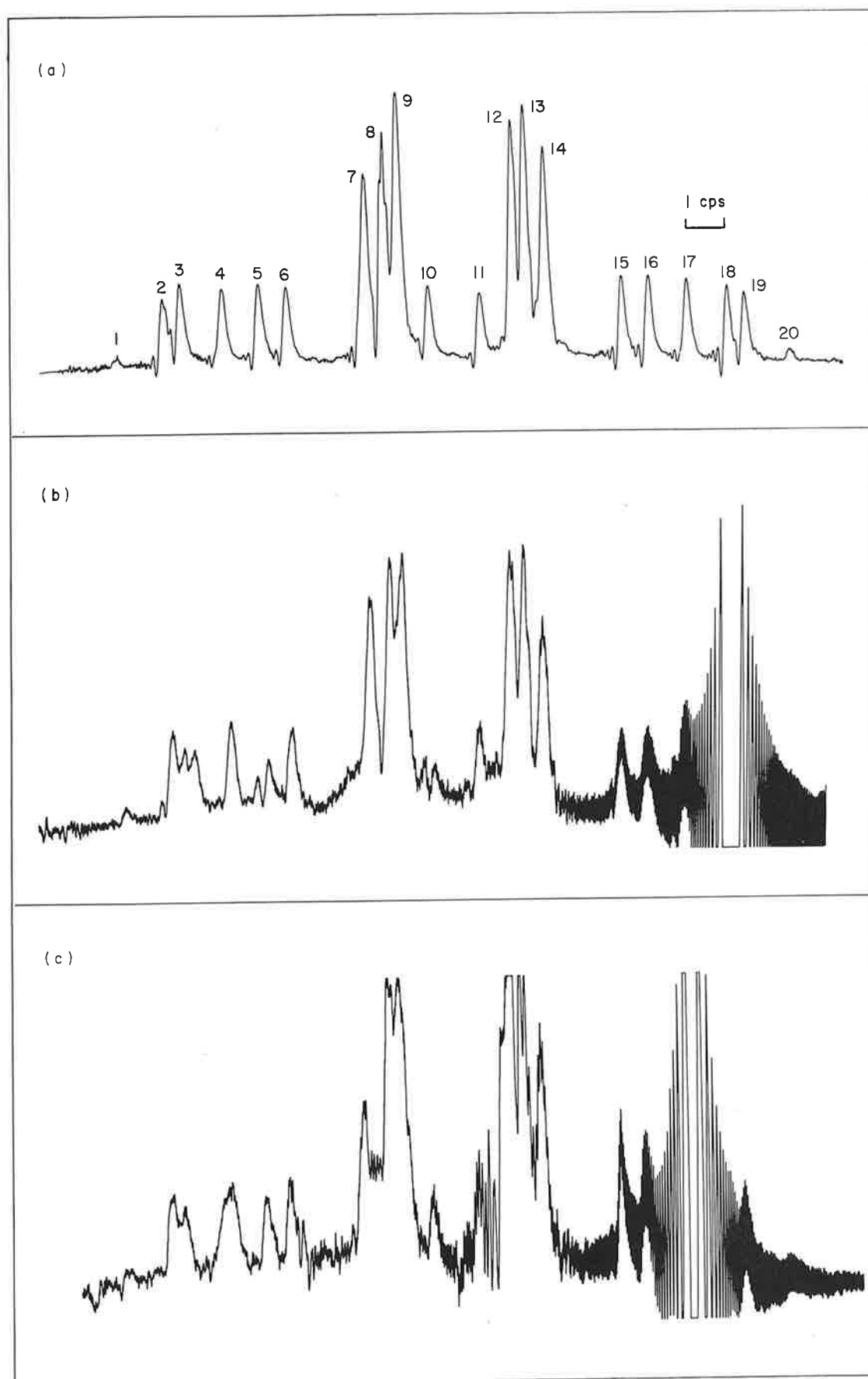


Fig. 2

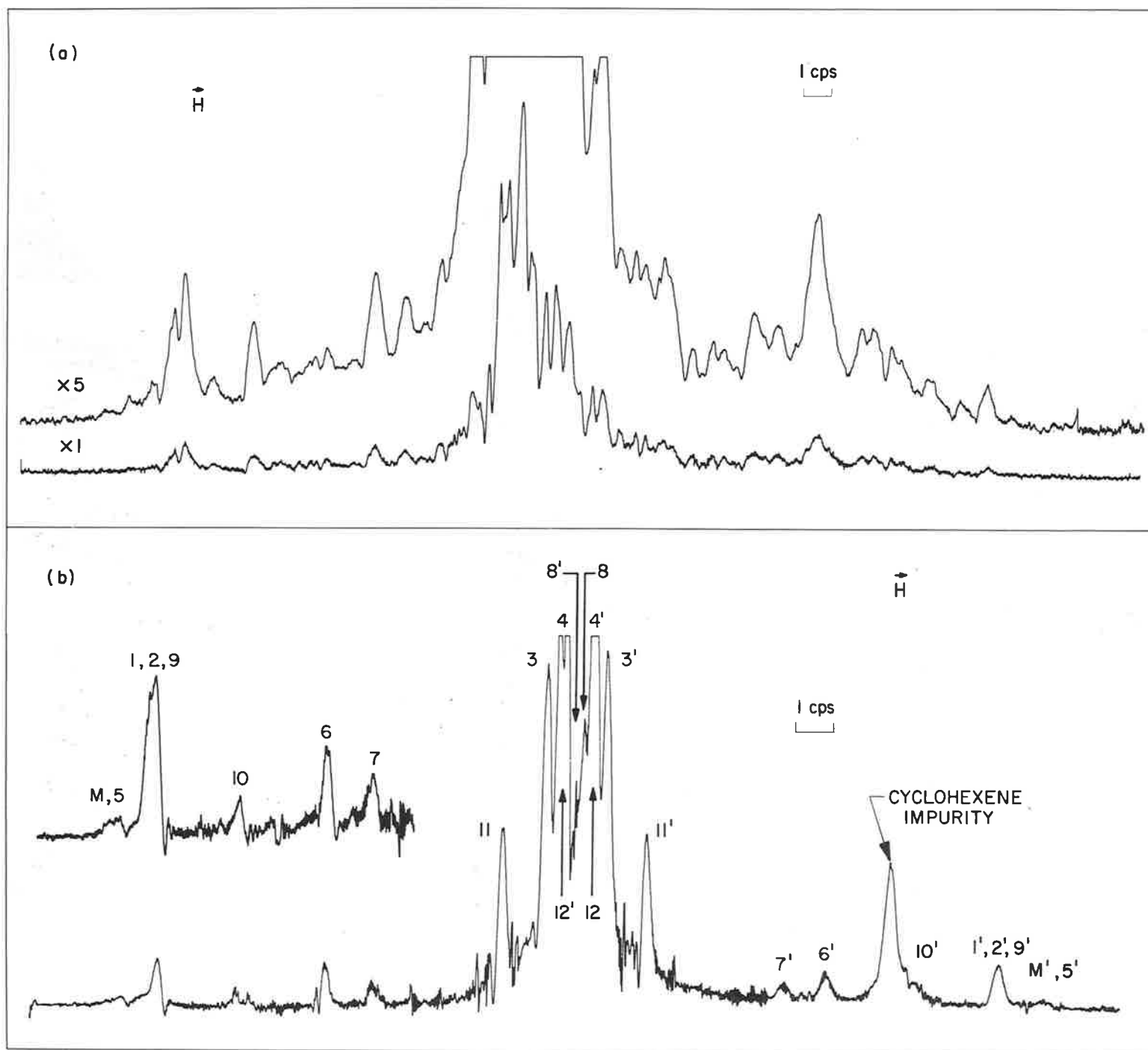


Fig.

"End-Group Analysis and Number-Average Molecular Weight Determination of Some Polyalkylene Glycols and Glycol Polyesters Using Nuclear Magnetic Resonance Spectroscopy"  
T. F. Page, Jr. and W. E. Bresler  
Anal. Chem. 36, 1981 (1964)

"Determining Structure of Paraffinic Chains by NMR"  
K. W. Bartz and N. F. Chamberlain  
Anal. Chem. 36, 2151 (1964)

"High Resolution Nuclear Magnetic Resonance Analysis of Vinyl Acetate Copolymers"  
M. W. Dietrich and R. E. Keller  
Anal. Chem. 36, 2174 (1964)

"Quinoxaline Derivatives. VIII. Betaine Structures of Dihydroquinoxaliniun and Benzimidazolium Barbiturates Formed from O-Dialkylaminoanilines and Alloxan"  
J. W. Clark-Lewis, J. A. Edgar, J. S. Shannon and M. J. Thompson  
Australian J. Chem. 17, 877 (1964)

"The Chemistry of the Euphorbiaceae. VI. A Triterpene from Beyeria Leschenaultii"  
G. V. Baddeley, A. J. Bealing, P. R. Jefferies and R. W. Retallack  
Australian J. Chem. 17, 908 (1964)

"The Chemistry of the Euphorbiaceae. VII. The Diterpenes of Ricinocarpus Stylosus Diels"  
C. A. Henrick and P. R. Jefferies  
Australian J. Chem. 17, 915 (1964)

"The Chemistry of the Euphorbiaceae. VIII. New Flavones from Ricinocarpus Stylosus"  
C. A. Henrick and P. R. Jefferies  
Australian J. Chem. 17, 934 (1964)

"Alkaloids of Desmodium Pulchellum Benth, ex Baker"  
S. Ghosal and B. Mukherjee  
Chem. Ind. 1800 (1964)

"A Novel Pyrrolo[1,2-a]indole Rearrangement"  
W. A. Remers  
J. Am. Chem. Soc. 86, 4608 (1964)

"Condensation of Formaldehyde with N-Bis(2-Haloethyl) Amines: Structure of the Products"  
G. R. Pettit and J. A. Settepani  
Chem. Ind. 1805 (1964)

"Nuclear Magnetic Resonance Studies of Diazirines. An Application to Conformational Analysis in Six-Membered Carbocyclic Rings"  
J. J. Uebel and J. C. Martin  
J. Am. Chem. Soc. 86, 4618 (1964)

"Voacamine and Voacoline"  
G. Büchi, R. E. Manning and S. A. Monti  
J. Am. Chem. Soc. 86, 4631 (1964)

"Structures of Sultones from Proton Magnetic Resonance Spectra"  
R. W. Ohline, A. L. Allred and F. G. Bordwell  
J. Am. Chem. Soc. 86, 4641 (1964)

"Kinetics of the Ring Opening of Cyclobutylmethylorganomagnesium Compounds"  
E. A. Hill and J. A. Davidson  
J. Am. Chem. Soc. 86, 4663 (1964)

"Formation of Grignard Reagents from cis- and trans- $\beta$ -Bromostyrenes"  
T. Yoshino, Y. Manabe and Y. Kikuchi  
J. Am. Chem. Soc. 86, 4670 (1964)

"Polar Radicals. I. Succinimide Radicals Generated from N-Iodosuccinimide"  
D. D. Tanner  
J. Am. Chem. Soc. 86, 4674 (1964)

"The Preparation of cis- and trans-4-H<sup>3</sup>-L-Prolines and Their Use in Studying the Mechanism of Enzymatic Hydroxylation in Chick Embryos"  
Y. Fujita, A. Gottlieb, B. Peterkofsky, S. Udenfriend and B. Witkop  
J. Am. Chem. Soc. 86, 4709 (1964)

"A Nuclear Magnetic Resonance Study of a Carbonium Ion Exchange Reaction"  
H. H. Freedman, A. E. Young and V. R. Sandel  
J. Am. Chem. Soc. 86, 4722 (1964)

"Blocked Rotation in Hexaisopropylbenzene. Evidence for Cyclobutadiene Intermediates in the Trimerization of Diisopropylacetylene by Dicobalt Octacarbonyl"  
E. M. Arnett and J. M. Bollinger  
J. Am. Chem. Soc. 86, 4729 (1964)

"Mechanism of Ultraviolet Stabilization of Polymers by Aromatic Salicylates"  
G. C. Newland and J. W. Tambllyn  
J. Appl. Polymer Sci. 8, 1949 (1964)

"Nuclear Magnetic Resonance Study of Solid Perfluorocyclohexane"  
A. Fratiello and D. C. Douglass  
J. Chem. Phys. 41, 974 (1964)

"Nuclear Magnetic Resonance Relaxation in Associated Liquids"  
A. G. Favret and R. Meister  
J. Chem. Phys. 41, 1011 (1964)

"Conformation and Internal Rotation of Nitroaromatic Amines in Solution as Detected by Proton Magnetic Resonance"  
J. Heidberg, J. A. Weil, G. A. Jamusonis and J. K. Anderson  
J. Chem. Phys. 41, 1033 (1964)

"Geminal and Vicinal Spin-Spin Coupling Constants in Substituted Metadioxanes"  
J. Delmau and C. Barbier  
J. Chem. Phys. 41, 1106 (1964)

"Temperature Dependence of the Nuclear Quadrupole Relaxation Time  $T_1$  in Para-Dichlorobenzene under Constant Pressure"  
T. Tokuhiro  
J. Chem. Phys. 41, 1147 (1964)

"Theory of Nuclear Magnetic Shielding in Diatomic Molecules"  
H. J. Kolker and M. Karplus  
J. Chem. Phys. 41, 1259 (1964)

"Deuteron Magnetic Resonance Study of Some Crystals Containing an O-D...O Bond"  
T. Chiba  
J. Chem. Phys. 41, 1352 (1964)

"Chemical Shifts, Ring Currents, and Magnetic Anisotropy in Aromatic Hydrocarbons"  
B. P. Dailey  
J. Chem. Phys. 41, 2304 (1964)

"Theory of Magnetic Multiple Resonance Spectra"  
M. Shimizu and H. Shimizu  
J. Chem. Phys. 41, 2329 (1964)

"Crystalline Field Stress Dependence"  
J. D. Stettler and W. J. Beigle  
J. Chem. Phys. 41, 2341 (1964)

"Nitrogen Electric Quadrupole and Proton Magnetic Resonances in Thiourea"

D. H. Smith and R. M. Cotts  
J. Chem. Phys. 41, 2403 (1964)

"Quasrupole Splittings in the Deuterium Magnetic Resonance Spectra of Liquid Crystals"

W. D. Phillips, J. C. Rowell and L. R. Melby  
J. Chem. Phys. 41, 2551 (1964)

ERRATUM:

"NMR-Relaxation Mechanisms of  $^{17}\text{O}$  in Aqueous Solutions of Paramagnetic Cations and the Lifetime of Water Molecules in the First Coordination Sphere"

[J. Chem. Phys. 37, 307 (1962)]  
T. J. Swift and R. E. Connick  
J. Chem. Phys. 41, 2553 (1964)

"Molecular Orbital Theory of Diamagnetism. IV. Anisotropic Properties of Benzene"

J. A. Pople  
J. Chem. Phys. 41, 2559 (1964)

"Solvent Dependence of Geminal Phosphorus-Proton Coupling Constants in Benzylphosphonium Salts"

M. Gordon and C. E. Griffin  
J. Chem. Phys. 41, 2570 (1964)

"6 $\beta$ -Acetylcholest-4-en-3-one and Some Derived 6-Substituted Steroids"

B. C. Elmes, M. P. Hartshorn and D. N. Kirk  
J. Chem. Soc. 2285 (1964)

"Dimethyltin Dinitrate"

C. C. Addison, W. B. Simpson and A. Walker  
J. Chem. Soc. 2360 (1964)

"Liquid-phase Photolysis. Part VII. Cage-dimerisation of p-Benzoquinone"

D. Bryce-Smith and A. Gilbert  
J. Chem. Soc. 2428 (1964)

"The Preparation and Properties of Trichloromethylphosphonous Acid"

J. F. Nixon  
J. Chem. Soc. 2471 (1964)

" $\pi$ -1-Methylcyclohexadienyltricarboxylmanganese"

D. Jones and G. Wilkinson  
J. Chem. Soc. 2479 (1964)

"The Hydrotetrafluorotrifluoromethylphosphate Anion:  $\text{CF}_3\text{PF}_4\text{H}^-$ "

R. G. Cavell and J. F. Nixon  
Proc. Chem. Soc. 229 (1964)

"The Structure of Zeatin, a factor Inducing Cell Division"

D. S. Lethan, J. S. Shannon, and I. R. McDonald  
Proc. Chem. Soc. 230 (1964)

"Photoisomerisations of Cyclo-octatrienes"

J. Zirner and S. Winstein  
Proc. Chem. Soc. 235 (1964)

"The Synthesis and Solution Equilibria of Bis-( $\beta$ -keto-amine) nickel(II) Complexes"

G. W. Everett, jun. and R. H. Holm  
Proc. Chem. Soc. 238 (1964)

"1,5-Hydrogen Shifts in Deamination Reactions in Steroids"

W. Nagata, T. Sugawara, Y. Hayase and K. Sasakura  
Proc. Chem. Soc. 241 (1964)

"Structure and Stereochemistry of the Monobromotigogenins"

J. P. Kutney, W. Cretney, G. R. Pettit and J. C. Knight  
Tetrahedron 20, 1999 (1964)

"Structure of Dendrobine"

Y. Inubushi, Y. Sasaki, Y. Tsuda, B. Yasui, T. Konita, J. Matsumoto, E. Katarao and J. Nakano  
Tetrahedron 20, 2007 (1964)

"Nachbargruppeneffekt Bei der Bildung von Ring-Ketten-Tautomeren O-Analogen des Echibolins. Beitrag zur Chemie des Echitamins"

H. Fritz and O. Fischer  
Tetrahedron 20, 2047 (1964)

"Reaktionen mit Phosphinalkylenen - IX. Zum Mechanismus des Hofmann-Abbaues Quartärer Triphenylphosphoniumsalze"

H. J. Bestmann, H. Häberlein und I. Pils  
Tetrahedron 20, 2079 (1964)

"The Reaction between 2,3-Dihydrofuran and Dihalocarbenes. An Attempted 2H-Pyran Synthesis"

J. C. Anderson, D. G. Lindsay and C. B. Reese  
Tetrahedron 20, 2091 (1964)

"The Vapour Phase Fluorination over Cobaltic Fluoride of the Isomeric Dichlorobenzenes. Chlorofluorocyclohexanes and their Reactions"

P. L. Coe, B. T. Croll and C. R. Patrick  
Tetrahedron 20, 2097 (1964)

"Zur Identifizierung der Cyclopropanstruktur. Nir- und NMR-Spektroskopische Untersuchungen an Cyclopropanen"

H. Weitkamp und F. Korte  
Tetrahedron 20, 2125 (1964)

"The Stereochemistry of Protopanaxadiol, a Genuine Sapogenin of Ginseng"

O. Tanaka, M. Nagai and S. Shibata  
Tetrahedron Letters 2291 (1964)

"Stereospecific Cyclization of Isoprenoids. The Cyclization of Farnesylacetone Stereoisomers and their Monocyclic Analogs"

W. A. Smit, A. V. Semenovskiy, V. P. Kucherov  
Tetrahedron Letters 2299 (1964)

"Structures of Xanthophanic and Glaucophanic Acid"

L. Crombie, D. E. Games and M. H. Knight  
Tetrahedron Letters 2313 (1964)

"Long-Range Spin-Spin Coupling Involving the Angular Methyl Groups in Steroids"

C. W. Shoppee, F. P. Johnson, Ruth Lack and S. Sternhell  
Tetrahedron Letters 2319 (1964)

"Arundoin - A Naturally-Occurring D:C-Friedo-Oleana-9(11)-Ene"  
G. Eglinton, R. J. Hamilton, M. Martin-Smith, S. J. Smith and G. Subramanian

Tetrahedron Letters, 2323 (1964)

"Photolysis of N-Nitrosoamines"

Y.-L. Chow  
Tetrahedron Letters, 2333 (1964)

"The Partial Structure of Tylosin, A Macrolide Antibiotic"

R. B. Morin and M. Gorman  
Tetrahedron Letters, 2339 (1964)

"Triterpenes of Pine Barks: Identity of Pinusenediol and Serratenediol"

J. W. Rowe  
Tetrahedron Letters, 2347 (1964)

"Chromomycinone, The Aglycone of Chromomycin A<sub>3</sub>"  
M. Miyamoto, K. Morita, Y. Kawamatsu, S. Noguchi, R. Marumoto,  
K. Tanaka, S. Tatsuoka, K. Nakanishi, Y. Nakadaira and N. S.  
Bhacca  
Tetrahedron Letters, 2355 (1964)

"The Structure of Chromomycin A<sub>3</sub>"  
M. Miyamoto, K. Morita, Y. Kawamatsu, M. Sasai, A. Nohara,  
K. Tanaka, S. Tatsuoka, K. Nakanishi, Y. Nakadaira and  
N. S. Bhacca  
Tetrahedron Letters, 2367 (1964)

"The Four Chromoses from Chromomycin A<sub>3</sub>"  
M. Miyamoto, Y. Kawamatsu, M. Shinohara, K. Nakanishi, Y.  
Nakadaira and N. S. Bhacca  
Tetrahedron Letters, 2371 (1964)

"The Solvolysis of 2,2,4,4-Tetramethylcyclobutane Derivatives"  
L. J. Dolby and C. Wilkins  
Tetrahedron Letters, 2379 (1964)

"The Rearrangement of Substituted Cyclopentadienes"  
S. McLean and P. Haynes  
Tetrahedron Letters, 2385 (1964)