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Illinois
Institute of
Technology
N-M-R
Newsletter

No. 68
MAY, 1964

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Deadline Date for Next Issue: 19 June 1964

Měsíční vydání soukromých dopisů z NMR laboratoří. Veškeré informace jsou určeny pouze pro potřebu čtenáře. Citace nejsou dovoleny, výjimkou je přímá domluva s autorem dopisu, a materiál musí být citován jako "Soukromé sdělení".

**ESSO RESEARCH AND ENGINEERING COMPANY**

ANALYTICAL RESEARCH DIVISION

P. O. BOX 121, LINDEN, N. J. 07036

April 10, 1964

NMR Instrumentation

File 4970

Dr. B. L. Shapiro, Editor IIT-NMR
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr. Shapiro:

Thank you for the reminder of contributions due the newly renamed and very worthwhile NMR newsletter.

Vertical Positioning of the A-60 Probe

The simple system of reference marks provided for locating the probe in the magnetic field of the Varian A-60 has doubtlessly been of great aid to users of this instrument. However, we have for some time employed a secondary scheme for more precisely positioning the probe in the vertical (Y-axis) direction. The net result is that positive interaction of "Curvature" and "Y-gradient" controls is rather completely eliminated, and optimum adjustment of these controls can thereafter be reached more quickly. The procedure follows.

1. Adjust homogeneity controls in the normal manner.
2. With the water sample spinning, (a) turn "Curvature" to counterclockwise extreme, and (b) re-optimize "Y-coarse".
3. Turn "Curvature" to clockwise extreme.
4. Re-optimize "Y-coarse", noting amount and direction of readjustment. If none is required, leave probe in present position.
5. Change probe elevation by two turns of the adjusting screw. Repeat steps 1-4, and note if readjustment (4) increased, decreased, or changed direction.
6. Guided by the result of (5), alter the vertical position of the probe in the direction required and in successively smaller increments until no net readjustment is required in (4).

Optimum position along the Y-axis can in this way be determined to $\pm 1/2$ turn of the elevation screw, i.e., $\pm 1/64$ ".

Very truly yours,

B. E. Hudson, Jr.

B. E. Hudson, Jr.

BEH:par



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

21 April 1964

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

Dear Barry:

Recently we reported that the relative signs of the H-C-P-H, H-C-P and H-P couplings in dimethylphosphine were all the same and we surmised that they are probably all positive¹. We used H¹-[P³¹]

-
- (1) S. L. Manatt, G. L. Juvinall and D. D. Elleman, J. Am. Chem. Soc. 85, 2664 (1963).
-

decoupling to secure this information at the frequencies 40 and 16.2 Mc., respectively. Sometime ago we received a V-4311 unit at 24.3 Mc. and so we decided to look at the P³¹ spectra of some of our ^{methyl} phosphine samples. From analysis of the H¹ spectrum² and our H¹-[H¹] decoupling experiments

-
- (2) See G. W. Whitesides, J. L. Beauchamp and J. D. Roberts ibid. 85, 2665 (1963).
-

it has been determined that the H-P and H-C-P couplings are the same sign. In fig. 1 is shown the P³¹ spectrum of methylphosphine along with two calculated spectra for the two assignments of the H-C-P-H coupling; the same and different from the H-P and H-C-P coupling; it should be obvious that the former assignment is correct. We are starting the analysis of the P³¹ spectrum of triethylphosphine now.

In fig. 2 is shown a P³¹ spectrum for trimethylphosphine which we would like to enter in the contest (if you will start one) for best resolution for a P³¹ spectrum. All ten lines are visible. At higher gain and power we saw C¹³ satellite lines which lead us to believe that the C¹³-P³¹ coupling is at most only a few cycles! We intend to investigate this point further using weak perturbing fields at the C¹³ and P³¹ frequencies while looking at the H¹ spectrum.

With best regards,

Stan

Stan L. Manatt

Stanley L. Manatt
Gordon L. Juvinall

SIM/GLJ: jas
Air Mail

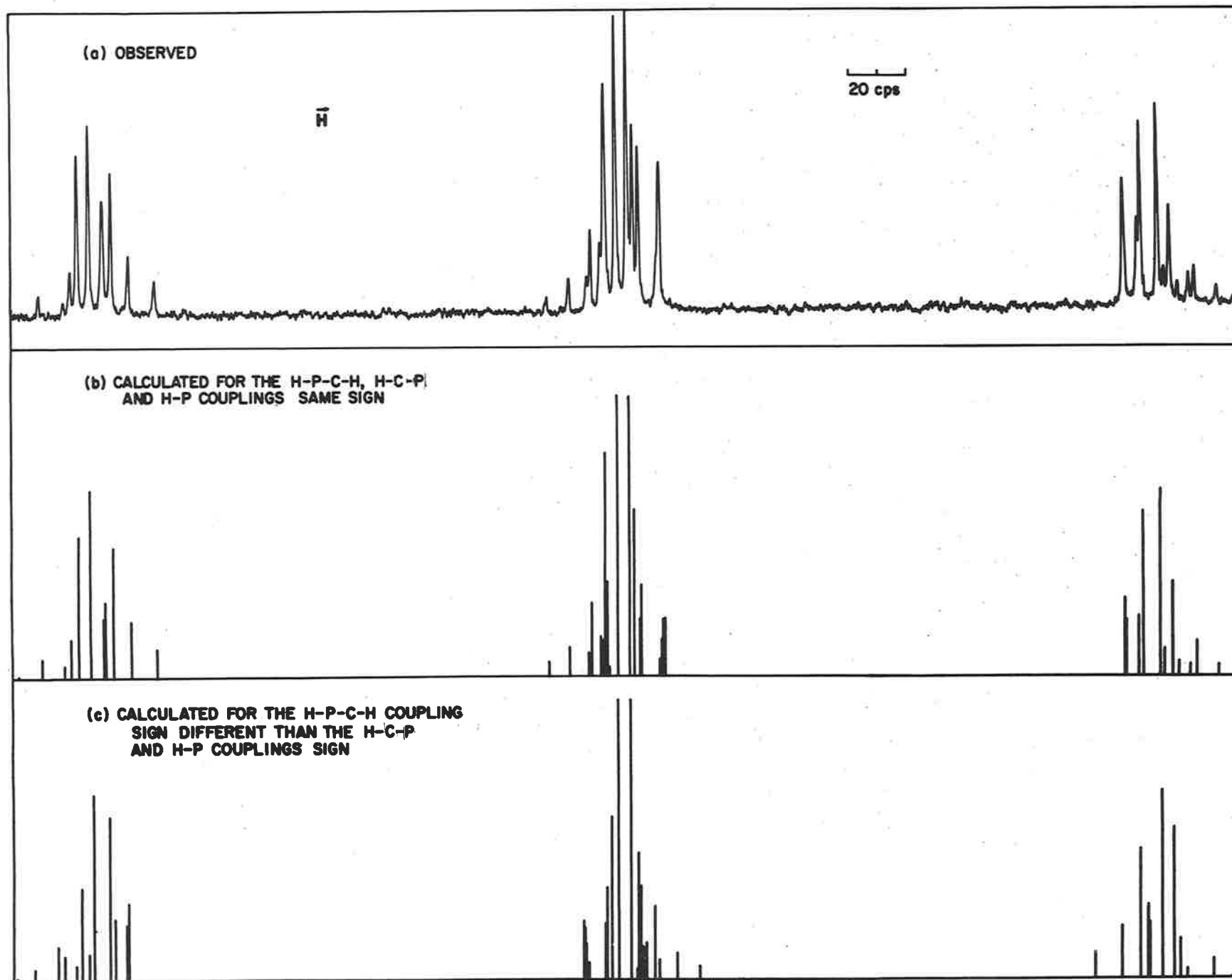


FIGURE 1

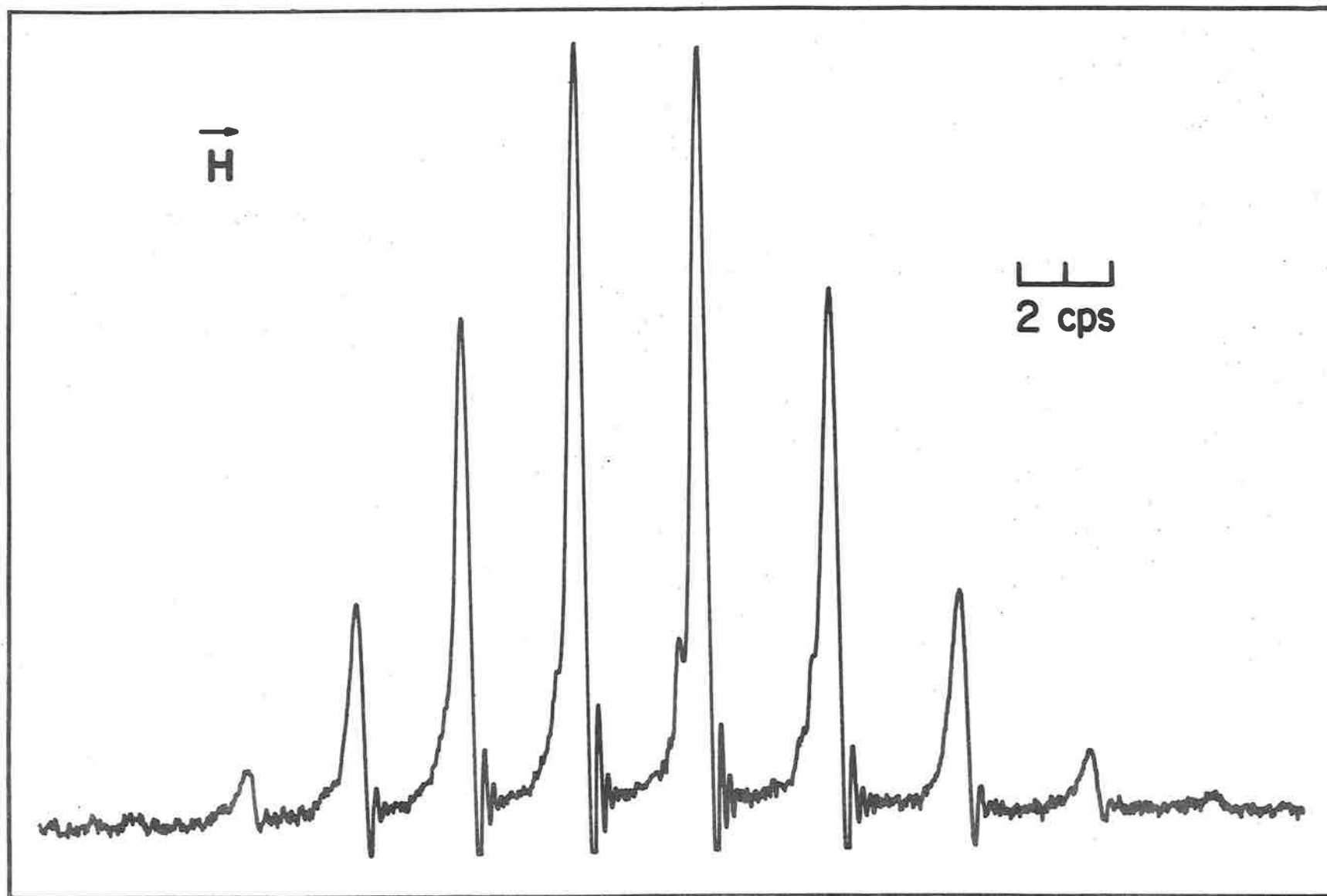


FIGURE 2

THE SQUIBB INSTITUTE

FOR MEDICAL RESEARCH

NEW BRUNSWICK, N.J.

May 6, 1964

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

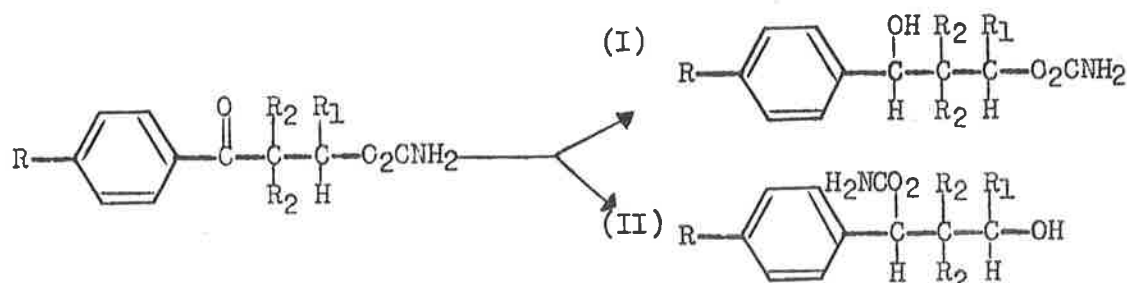
Dear Doctor Shapiro:

Thank you for the reminder.

Before discussing my contribution, I would like to ask for some assistance. Recently, we published a correlation of substituent effects on the C-18 and C-19 methyl resonances by computer regression¹. We are collecting additional data for another "computer run" and would appreciate C-18 and C-19 methyl resonance data collected in other laboratories. No compounds please!

With dimethylsulfoxide (DMSO) making medical news, I would like to emphasize its usefulness in NMR spectroscopy. Chapman and King² have recently published a note on the use of the solvent in the classification of alcohols. I have had the same experience in the use of the solvent for alcohols.

Slomp et al³ recently published the quantitative determination of primary and secondary carbamates. I was asked to settle the assignment of the carbamates, I and II, formed during the reduction of the ketone. Because of the solubility of the compounds, DMSO was found to be an extremely useful solvent.



The chemical shift data is shown in the accompanying Table. Several samples were shown to be mixtures of primary and secondary carbamates. The spectra were obtained in both pyridine and DMSO (TMS as an internal reference).

Because DMSO is a mild proton acceptor, aliphatic hydroxyl proton resonances appear between 3 and 4 τ . Along with the other criteria for assignment, the coupling pattern of hydroxyl proton show it to be primary or secondary. Deuterium exchange is performed by adding D₂O to make a 5% solution. Precipitation of sample on addition of D₂O infrequently occurs.

Yours truly,

Allen I. Cohen

Allen I. Cohen

- (1) A. I. Cohen and S. Rock, Jr., *Steroids*, **3**, 243 (1964).
- (2) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).
- (3) G. Slomp, R. H. Baker, Jr., and F. A. MacKellar, *Anal. Chem.*, **36**, 375 (1964).

ISOMER FORMULA	R	R ₁	R ₂	SOLVENT	CHEMICAL SHIFTS, TAU ^a				
					H(R ₁)CO- ^b	H(Ph)CO-	-OH	-NH ₂	CH ₃
I	H	H	Cl	DMSO	5.62(d,12.5) ^c 5.98(d,12.5)	4.92(d,5)	3.48(d,5)	3.22 ^d	
				DMSO-D ₂ O	5.50(d,12) ^c 5.62(d,12)	4.91(s)	e	3.23 ^d	
II ^f	H	H	Cl	DMSO-D ₂ O	g	3.88(s)	e	3.22 ^d	
I	Cl	H	Cl	DMSO	5.48(d,12) ^c 5.58(d,12)	4.89(d,5.5)	3.32(d,5.5)	3.18 ^d	
				DMSO-D ₂ O	5.43(d,11.5) ^c 5.59(d,11.5)	4.87(s)	e	3.20 ^d	
				Pyridine	4.76(d,11.5) ^c 5.04(d,11.5)	4.46(s)	e	e	
II	Cl	H	Cl	DMSO	g	3.91(s)	3.75(t,6)	3.13 ^d	
				DMSO-D ₂ O	g	3.91(s)	e	3.13 ^d	
				Pyridine	5.55(d,12) ^c 5.85(d,12)	g	e	e	
I	H	CH ₃	Cl	DMSO	4.67(q,6.5)	4.90(d,5)	3.68(d,5)	3.31 ^d	g
				DMSO-D ₂ O	4.73(q,6.5)	4.92(s)	e	e	g
				Pyridine	3.84(q,6.3)	4.40(s)	e	e	8.22(d,6.3)
II	H	CH ₃	Cl	DMSO	g	3.70(s)	4.12(d,5)	3.22 ^d	g
				DMSO-D ₂ O	g	3.68(s)	e	e	g
				Pyridine	5.93(q,6)	g	e	e	8.39(d,6)

					CHEMICAL SHIFTS, TAU ^a				
ISOMER FORMULA	R	R ₁	R ₂	SOLVENT	H(R ₁)CO- ^b	H(Ph)CO-	-OH	-NH ₂	CH ₃
I	H	H	Et	DMSO DMSO-D ₂ O	g g	5.37(d,5) 5.33(s)	4.95(d,5) e	3.65 ^d e	
I ^h	H	H	Me	DMSO DMSO-D ₂ O	g g	5.48(m) 5.46(s)	4.78(m) e	3.58 e	
II ^h	H	H	Me	DMSO DMSO-D ₂ O	g g	4.48(s) 4.50(s)	--	--	

^a Chemical shifts in tau: in parentheses no. of peaks; s - singlet, d - doublet, q - quartet, m - multiplet; J in cps.

^b If R₁ is H, the chemical shifts to the methylene signals.

^c Methylene protons coupled to each other.

^d Broad

^e Ionizable and exchangeable with solvent.

^f Only 30% secondary carbamate (II).

^g Under proton signals of solvent.

^h Mixture 70% primary carbamate (I), 30% secondary carbamate (II).

Eastern Laboratory
E.I. du Pont de Nemours & Company
Gibbstown, New Jersey

Dr. B. L. Shapiro

~~Mellon Institute~~

~~4400 Fifth Ave~~

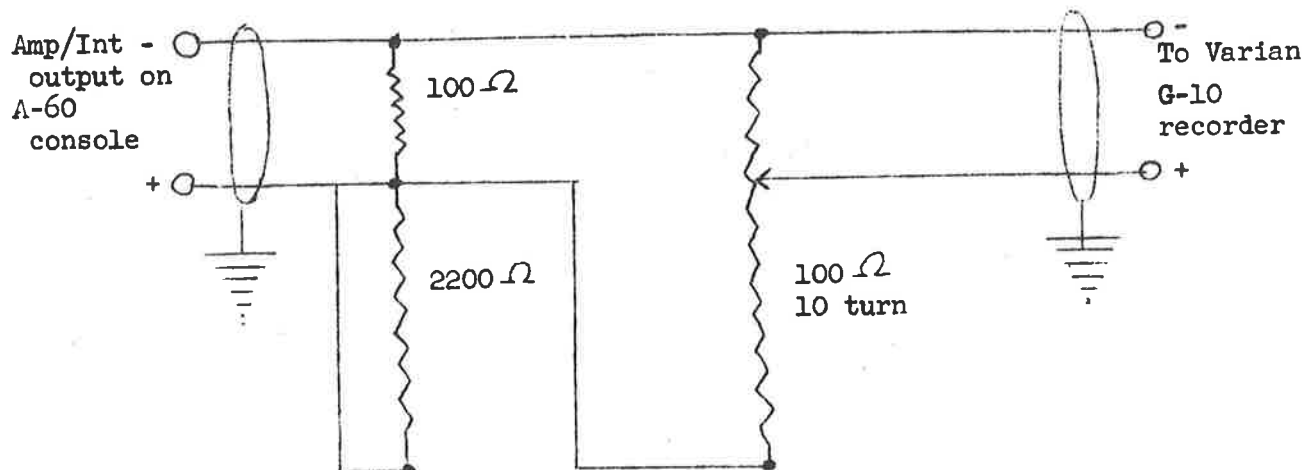
~~Pittsburgh, Pa~~

Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Ill.

Dear Dr. Shapiro:

We ~~from~~ very sorry for the delay in sending ~~my~~ ^{our} contribution to MELLON-M-R. Recently we have obtained an A-60 with a variable temperature probe. This is in addition to the DP-60 we have had for about four years. Currently we are using the DP-60 exclusively for P^{31} and F^{19} , but we are planning to do some C^{13} and thallium resonance studies. Most of our recent work on P^{31} and F^{19} will be published shortly.

Since we use our A-60 for analytical service as well as research we needed a slave recorder to enable us to duplicate the spectra on a Xerox machine. For our old Varian G-10 (100 mv) recorder we designed an attenuator which permits us to have this recorder directly hooked to the A-60 amplifier output. The circuit diagram is shown below. There is no interference between this recorder and the A-60 recorder and the amplitude of the slave spectrum can be easily adjusted.



- 2 -

Since both copies are recorded at the same time, calibration of the slave spectra is no problem; we simply copy the numbers from the A-60 spectra. This is a very satisfactory system which eliminates the need to go into the amplifier for modification.

Sincerely yours,

G. S. Reddy
P. F. Koehler

G. S. Reddy
P. F. Koehler

University of East Anglia

UNIVERSITY OF EAST ANGLIA

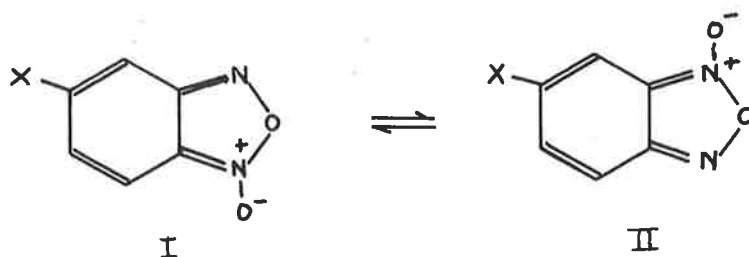
School of Chemical Sciences
 Wilberforce Road, Norwich NOR 54H
 Telephone Norwich 52651

28th April, 1964.

Dear Dr. Shapiro,

We are pleased to report that our Perkin Elmer 40 Mc instrument (ex Cambridge) is now working well, and we hope that by the time this letter is printed so will our A.E.I. 60 Mc instrument (ex Oxford). Although the NMR side of our research activities will be immeasurably strengthened next October when Professor Norman Sheppard and also Dr. Robin Harris take up their posts here, research is already proceeding apace. Mr. M. J. Sewell is using NMR to study the conformational analysis of benzo-dioxans; Mr. F. J. Swinbourne is looking at the effect of mutual interaction between the substituents on J_{trans} for disubstituted ethylenes. Mr. R. E. Reavill has elucidated the A₂B₂ spectrum of biphenylene. Mr. B. Ternai is studying the position of protonation in polyaza-heteroaromatic compounds with Dr. R.A.Y. Jones, and Dr. B. J. Ridgewell is using NMR to follow H-D exchange in heterocyclic compounds.

We are also following up our earlier work on the molecular rearrangement of benzofuroxans. We have measured the spectra at a series of



temperatures for 5-methyl-, 5-methoxy- and 5-chloro-benzofuroxans (I, X = Me, MeO, Cl), and thus determined the energy differences between the 5- (I) and the 6- isomers (II) and the energy of activation for their interconversion.

The results are as follows:-

Substituent	OMe	Me	Cl
Excess energy of 6-isomer	590	<100	160 cals
Energy of interconversion	14.6	?	13.9 Kcals

These results will later be published in full together with the results of other substituted benzofuroxans.

Yours sincerely,

A. J. Boulton

A. R. Katritzky

B. Wallis

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

THE OHIO STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY
88 WEST 18TH AVENUE
COLUMBUS 10, OHIO

May 4, 1964

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

Dear Barry,

Here is a miscellaneous collection of recent results. NMR tubes (with apologies to Varian et. al): we now obtain precision NMR tubes by having ordinary 5 mm O.D. pyrex tubing centerless ground to $0.196 \pm 0.0005''$. The work is done by Yorde Machine Products Co., 1200 Chesapeake Ave., Columbus 12, Ohio, at a cost of 40¢ per tube. We have even found that standard 5 mm O.D. soft glass tubing is excellent for the A60 Room temperature probe.

Cis diene NMR parameters: In connection with another problem we have obtained the NMR parameters for spiro-cyclopentadiene-cyclopropane. The coupling constants should be typical for a cis diene^a. We obtain $\delta_5 = 8.60$, $\delta_1 = 4.030$, $\delta_3 = 3.578$ ppm respectively, $J_{1,2} = 2.03$, $J_{3,4} = 1.92$, $J_{1,3} = 5.25$, $J_{1,4} = 1.58$ cps respectively, from a 5% solution in CCl_4 . The signs of the coupling constants are all the same. We would like to check this point with a 20 Mc spectrum.

Deuterium exchange, ammonium ion: Dr. Yutaka Asahi and I have measured the rate of exchange of trimethyl ammonium ion in D_2SO_4 . A mixture of $(\text{CH}_3)_3\text{NH}^+$ and $(\text{CH}_3)_3\text{ND}^+$ in strong acid gives the pattern below^b, where $J_{\text{CH}_3, \text{NH}} = 5.4$ and $J_{\text{CH}_3, \text{ND}} = 0.7$ cps, respectively. In strong acid the exchange rate is so slow that it can be measured by integrating the CH_3 multiplets. Over the range 0° to 103° , 20% to 100% D_2SO_4 we find the exchange rate constants to be linear with H^+ (Arnett). We think the slow step is $\text{BH}^+ \rightarrow \text{B} + \text{H}^+$ where the base which carries off the proton is probably D_2SO_4 ; ΔE^\ddagger is about 22 k cal. We did less extensive experiments with other amines. In ammonium ion there is an isotope effect on the chemical shift of hydrogen with increasing deuterium substitution NH_4^+ , 0; NDH_3^+ , -0.015; ND_2H_2^+ , -0.030; ND_3H^+ , -0.045 all ppm.

Finally, let me say how glad I am that you are carrying on this invaluable newsletter.

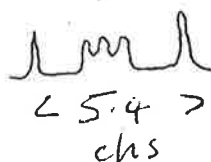
Yours sincerely,

Gideon

Gideon Fraenkel



b.



UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY 4, CALIFORNIA

May 5, 1964

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

Dear Barry;

Congratulations on your new position, and best wishes for a successful continuation of the Newsletter. Thank you, as well, for the reminder about renewing our subscription. For a change of pace, we submit a brief resume of a paper based upon P^{31} NMR data.

The Structure of "Ethylmetaphosphate" (Langheld Ester)

The product of the reaction of ether and phosphorus pentoxide¹⁾ which is usually called "ethylmetaphosphate" recently was used for the synthesis of polynucleotides, polypeptides and polysaccharides²⁾. Further studies of this synthesis are necessary, since inconsistent results were obtained by several groups^{2,3)}. Even the structure of the "ethylmetaphosphate", which is used as the condensation reagent, is not known for certain. The resolution of its composition was determined by use of phosphorus NMR measurements.

Until now, the proposal of Rätz and Thilo⁴⁾ that "ethylmetaphosphate" is a mixture of tetraethyl-cyclotetraphosphate (Fig. 1, structure III) and of tetraethyl-isocyclotetraphosphate (Fig. 1, structure IV) was accepted. This mixture should show a phosphorus NMR spectrum with a large peak of middle bonded phosphorus (P_m) and two smaller but equal peaks of branched bonded (P_b) and terminal bonded phosphorus (P_t). The NMR spectrum with 3% P_b and 25% P_t obtained by Van Wazer et al⁵⁾ does not conform to that assumption. However, while in this laboratory⁶⁾, a similar result with 6% P_b and 32% P_t was obtained from one preparation, and from another sample a ratio of 13% P_b and 15% P_t was obtained. The possibility of partial hydrolysis as the cause of the discrepancy in the sizes of the peaks of P_b and P_t , as it was thought first⁶⁾, could now be eliminated.

In a new series of experiments, different products were obtained by heating ether and phosphorus pentoxide in chloroform, depending on the time of heating, and the amount of ether which was used. They differed not only in the phosphorus NMR spectrum, but also in their colligative properties.

-continued-


We obtained a solid plastic-like material (A) with 1 equivalent of ether, a material ranging from a rubberlike substance (B) to a highly viscous oil (C) with 1 to 2 equivalents of ether, and an oil of intermediate viscosity (D) with more than 2 equivalents of ether, all soluble in chloroform. Refluxing with ether transformed the materials A, B, and C into D. Refluxing for a long period (65 hours) with ether converted all the materials into an oil of low viscosity (E). In the phosphorus NMR spectrum, the peak of the branched bonded phosphorus (P_b) decreased from 22.9% to 4.0%; the peak of the terminal bonded phosphorus (P_t) increased from 5.2% to 26.2%; and the peak of the middle bonded phosphorus increased first from 71.9% (A) to 78.7% (B), and decreased then to 69.8% (E) in the series from (A) to (E). If we look on the structures in Fig. 1, substance II should show 50% P_b and 50% P_m ; substance III, 100% P_m ; substance IV, 50% P_m , 25% P_b , and 25% P_t ; and substance V, 50% P_m , and 50% P_t .

From the preparative and the phosphorus NMR results it can therefore be concluded: P_4O_{10} (I) reacts with a little ether to form II. Substance II reacts partially further with ether to form III and IV. Material A consists of II, III, and IV. With more ether, compound II is completely transformed into III and IV, and then partially into V (material B, C, and D). After a long period of refluxing, mainly III and V are obtained (E).

The so-called "ethylmetaphosphate (materials C and D) consists of III, (50% to 45%, depending on the conditions of its preparation); IV, (36% to 25%); and V, (14% to 30%). The content of the compounds II, III, IV or V in the mixtures, as given in parenthesis, can easily be calculated from the NMR results. The correct composition of "ethylmetaphosphate" can be obtained from the phosphorus NMR spectrum in each preparation. It is profitably prepared in a two-step procedure from P_4O_{10} with material A as an intermediate.

-
- 1) K. Langheld, Chem. Ber., 43, 1857 (1910); 44, 2076 (1911).
 - 2) G. Schramm, H. Groetsch, and W. Pollman, Angew. Chem., 74, 53 (1962).
 - 3) G. Weill, UCRL/10934, 7/29/63, p.79.
 - 4) R. Raetz and E. Thilo, Liebigs Ann. Chem., 572, 173 (1951).
 - 5) I.R. Van Wazer, C.F. Callis, J.N. Shoolery, and R.C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
 - 6) G. Weill, M. Klein, and M. Calvin, Nature, 200, 1005 (1963).

Sincerely yours,


Gottfried Burkhardt*
Melvin P. Klein

GB,MPK:ep

* Postdoctoral fellow of the Deutscher Akademischer Austauschdienst (Germany).

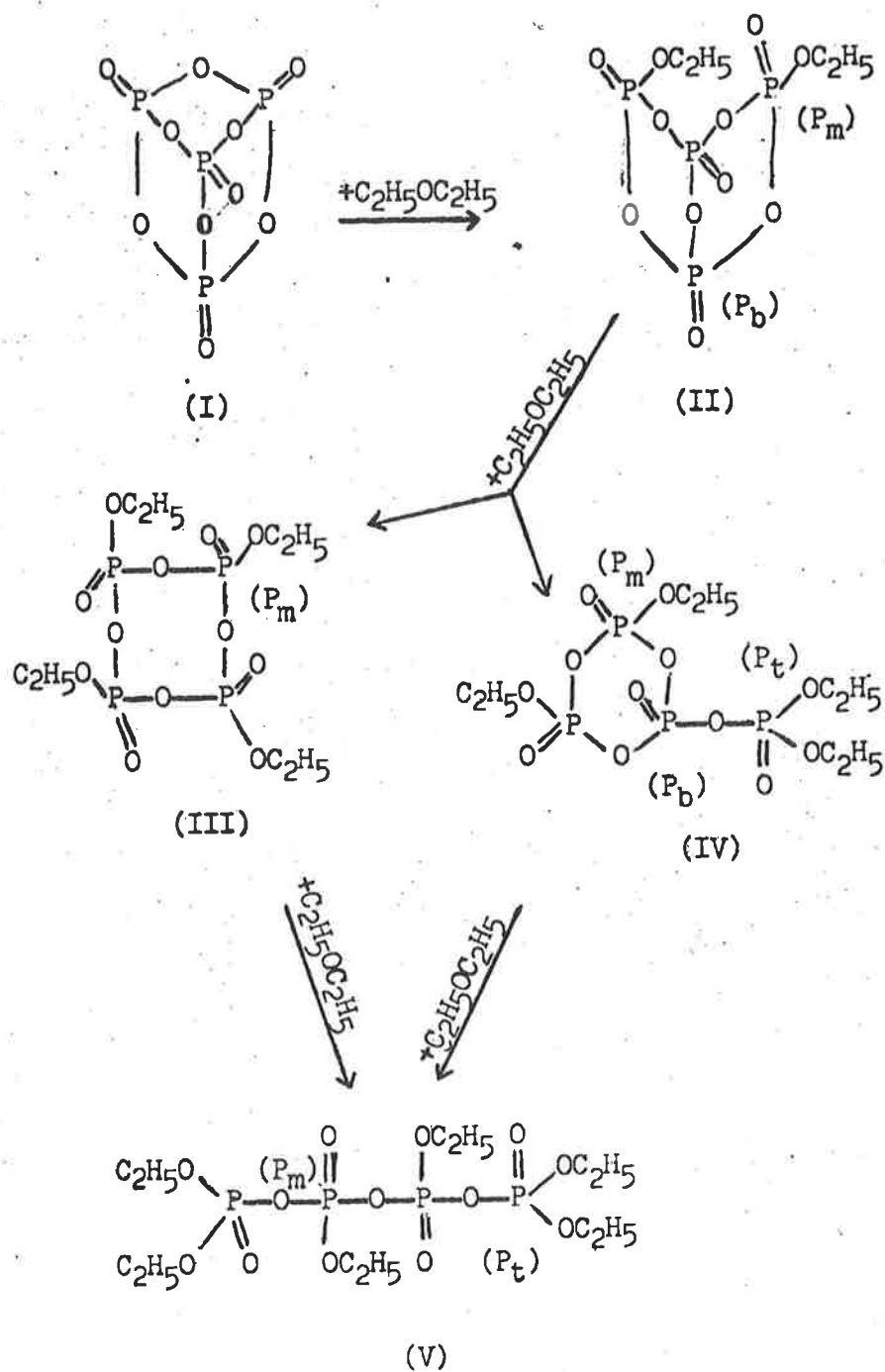
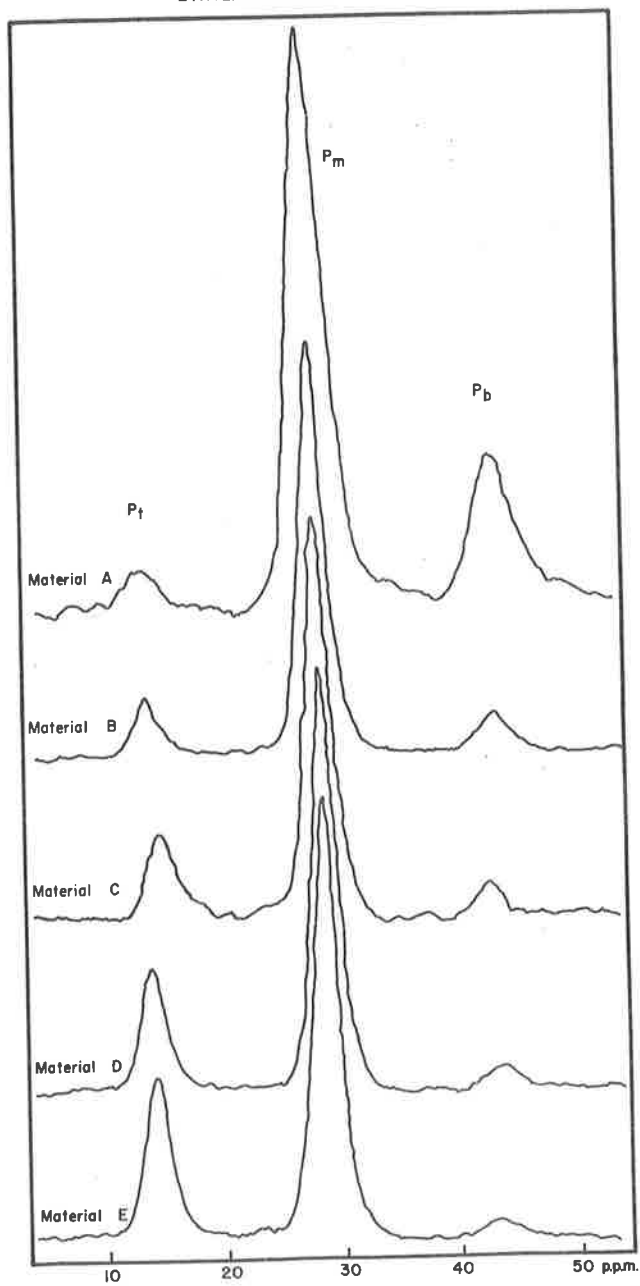


Fig. 1. Reaction of P_4O_{10} with ether.

Fig. 2. PHOSPHORUS NMR SPECTRA OF DIFFERENT SAMPLES OF
"ETHYLMETAPHOSPHATE"



MUB-2702

UNIVERSITY OF ILLINOIS URBANA 61803

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

THE WILLIAM ALBERT NOYES LABORATORY

May 5, 1964

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

Dear Barry:

Thank you very much for your reminder. I must admit that I have no convenient excuse for my delay, particularly, working in such an excellent place as Noyes Lab.

Recently, Professor H. S. Gutowsky and I have studied the temperature dependences of F-F coupling constants in 6-X substituted 2-fluorobenzotrifluorides.

The temperature dependence of the coupling constant between the 2-fluorine and the fluorines of the CF_3 group can be interpreted in terms of thermally excited motion of the molecule in the potential well. The direction of the change of $J(2\text{-F-CF}_3)$ with temperature, i.e., either a decrease or an increase, is governed by the size of the substituent at the 6 position. This can be seen in Table I, which gives the $J(2\text{-F-CF}_3)$ constants at various temperatures for some compounds studied.

Prof. Shapiro

-2-

May 5, 1964

Table I

Temperature Dependence of the $J(2-F-CF_3)$ Coupling Constants
in Substituted Benzotrifluorides

Substituent	$J(2-F-CF_3)$, cps		
	-35°C	25°C	100°C
2-F	11.52	12.68	13.79
2,3,5-F	12.11	13.33	14.42
6-Cl-2,3,4,5-F	32.82	32.23	31.53
6-I-2,3,4,5-F	35.02	34.15	33.31
2,4,6-F-3-NO ₂	22.12	22.59	22.85

The direction of the temperature dependences in individual compounds can be explained by assuming different equilibrium conformations of the CF_3 group which is dependent on the size of the substituent at the 6 position. The temperature change produces a change in the average conformation of the CF_3 group. It is worth while to mention that rotational averaging occurs.

One of the additional features is the finding that the CF_3 group is "long-range" coupled to hydrogens and/or fluorines at meta and para positions. The fine structure of the CF_3 group spectra is well resolved in all compounds. I would like to mention some facts about the CF_3 group spectrum in 2-fluorobenzotrifluoride, which may be of some interest to IITNMRN readers.

The CF_3 group spectrum in 2-fluorobenzotrifluoride appears as a doublet (splitting due to $J(2-F-CF_3)$) and each band of the doublet is a symmetric quintuplet with the splitting of 0.6 ± 0.1 cps. This finding was, at first, a little surprising to us. However, the occurrence of the quintuplet is due to the fact

Prof. Shapiro

-3-

May 5, 1964

that the hydrogen atoms are strongly coupled to each other and shifted, of course, far away from the resonance of the CF_3 group, and so exhibit an effect similar to the so called effect of "virtual coupling". All hydrogen behave as a single particle of total spin angular momentum $2\hbar$.

A detailed discussion of this topic will be submitted to J. Chem. Phys.

Best regards.

Yours sincerely,

J. Jonáš
J. Jonáš

JJ:jh

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UNIVERSITY OF COLORADO

BOULDER, COLORADO 80304

DEPARTMENT OF CHEMISTRY

May 8, 1964

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

Dear Barry:

The following is the abstract from our latest paper on NMR studies of Hydrogen Bonding. It discusses the theory and significance of the hydrogen bond shift. Preprints are available.

NMR Studies of Hydrogen Bonding:
II. Calculation of the Shift Upon Complex Formation.

Abstract

The shift upon hydrogen bond formation for the weak hydrogen bonds formed between chloroform and nitrogen bases was assumed to arise from two contributions: a) the Buckingham electric field effect and b) the neighbor anisotropy effect. The magnitudes of these two effects were obtained as functions of the various parameters entering into the calculation. The electric fields were found by integrating over approximate nitrogen lone pair electron distributions. The Pople-McConnell dipolar approximation was used to estimate effect (b). The results proved to be insensitive to all parameters except the hydrogen bond length. Experimental values of the shifts were used to find these lengths, which proved to be in accord with X-ray crystallographic data, and to increase as the hybridization of the lone pair went from sp^3 to sp . It was concluded that, for these weak hydrogen bonds, the above two effects are an adequate explanation for the shift upon hydrogen bond formation, and that this shift is a good criterion of "basicity" for weak hydrogen bonds if magnetic anisotropy effects are small, or if they are approximately constant for a series of electron donors.

Sincerely yours,

Peter J. Berkeley, Jr.
Peter J. Berkeley, Jr.

msel
Melvin W. Hanna



The University of Sydney

Professor B.L.Shapiro SYDNEY, N.S.W.
 Illinois Institute of Technology

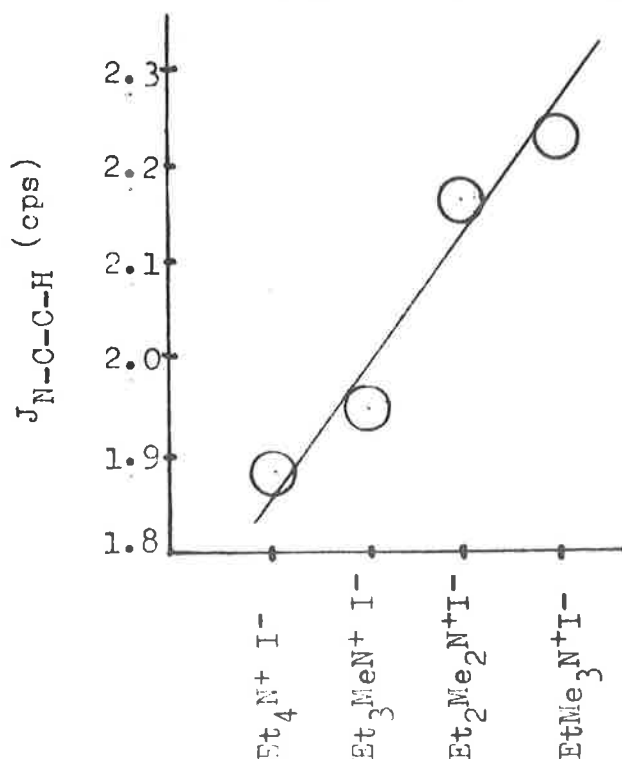
5th May 1964

IN REPLY PLEASE QUOTE :

Dear Barry,

N^{14} -C-C-H coupling and long-range coupling in indoles.

Spin-spin coupling between nitrogen and the protons on the β -carbon (i.e. $J_{N-C-C-H}$) has been observed in alkylammonium salts^{1,2,3} although coupling between nitrogen and the protons on the α -carbon (i.e. J_{N-C-H}) is negligible. This behaviour is similar to other heteronuclear interactions^{4,5} and has been related^{1,2} to the quadrupole moment of N^{14} . We have observed a remarkable dependence of this interaction on substitution in a series of ethylammonium iodides. It is difficult to decide what is the precise significance of the phenomenon, but the variation observed does not support the hypothesis that the interaction depends upon a highly symmetrical environment - in



fact the gradual replacement of the ethyl group by methyls appears to increase the absolute magnitude of the coupling constant suggesting a hyperconjugation linked phenomenon. We have also observed some dependence of $J_{N-C-C-H}$ on the anion and will look into the influence of the dihedral angle.

We have commented before upon long-range coupling⁶ in indoles. Changing solvents and labile proton exchange etc allows us to make the following first order estimate of spin-

spin interactions: (approximate deviation is 0.05 c/s)

$J_{2,3}$: 3.18 cps

$J_{1,3}$: 2.05 cps

$J_{3,7}$: 0.80 cps

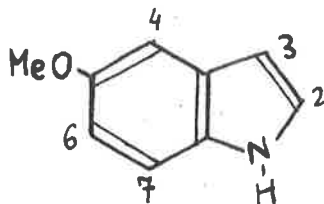
$J_{6,7}$: 8.65 cps

$J_{6,4}$: 2.45 cps

$J_{2,4}$: 0.4 cps

$J_{2,6}$: 0.4 cps

$J_{4,7}$: 0.8 cps



Particularly revealing is the signal (405 cps ex TMS in concentrated acetone solution) attributed to H_6 which is a well resolved doublet of doublets of doublets with the smallest splitting of 0.4 cps. The H_3, H_7 coupling is not of a novel type⁷ but the H_2, H_6 and the, less clear, H_2, H_4 interactions appear to have no close analogy. Interestingly the path between H_2 and H_6 conforms well with Sheppard's zig-zag hypothesis⁸.

With best regards

Sev
(S. Sternhell)

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8. Banwell and Shappard-Disc.Farad.Soc. No 34 115 (1962) and refs therein.

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE.
TELEPHONE: 56491.

4th May, 1964.

Professor B. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
CHICAGO,
Illinois, U.S.A.

Dear Barry,

We apologise for our late contribution to the NMR newsletter. May we also belatedly congratulate you on your new appointment and say how much we appreciate your willingness to keep the Newsletter going at I.I.T. At the same time we should like to thank Aksel Bothner-By for his past efforts for MELLON-M-R.

Long-range (H,H) coupling constants

Some while ago Banwell and N.S. (Disc. Faraday Soc., 1962, 34, 115) pointed out that the majority of the long-range (H,H) couplings observed through 4 or 5 bonds (4J and 5J) occurred when these intervening bonds formed a planar zig-zag (or 'straight') set. We suggested that this stereochemical feature might be significant and gave reasons for considering that these might be σ -bond transmitted couplings. Most of the long-range couplings measured since follow the planar zig-zag pattern (a notable example is the 1:3 equatorial-equatorial coupling in six-membered sugar rings as reported by Hall and Hough, Proc.Chem.Soc., 1962, 382) although some measureable values have been found when the path is not strictly planar. In this latter connection we should expect some type of $\cos^2\theta$ dependence to be present as occurs for the well-known 3-bond (vicinal) coupling constants.

2.

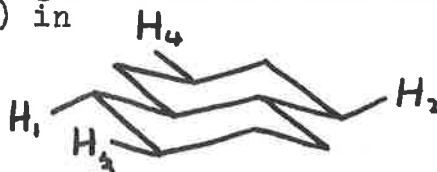
A particularly clear-cut and long-standing exception to the planar zig-zag rule which we still do not understand is the long-range coupling constants found by Bothner-By and Naar-Colin in the spectra of the 2:3 dihalogen butanes (J.Amer.Chem.Soc., 84, 743 (1962)).

Because of the limited availability of suitable molecules it is true that most of the appreciable 5J 's are observed in unsaturated systems where, as suggested by Freeman and Bhacca (MellonMR, No. 47, 11), either ground or excited 'diene' electronic states of the type

$\text{H}-\text{C}=\text{C}-\text{C}=\text{C}-\text{H}$ might be expected to play a part. Most of the observed 4J 's on the other hand are in saturated

systems $\text{H}-\text{C}-\text{C}-\text{C}-\text{H}$ and these, as Dr. Sternhell has pointed out to us, might alternatively be brought about by overlapping of the 'tails' of the coplanar CH orbitals (cf. Meinwald and Lewis, J.Amer.Chem.Soc., 1961, 83, 2769). This latter explanation would not be applicable to the 5J examples.

A test between the two hypotheses (planar zig-zag σ -orbital versus π -orbital coupling) for 5J could best be made by observation of the magnitude of 5J couplings in saturated molecules. Suitably rigid systems are not easy to come by, but can be found in bicyclic molecules. We should therefore like to put forward the suggestion that readers of the Newsletter might be on the look-out for measureable 5J 's for (H_1, H_2) in



with suitable substituents. 6J (H_3, H_4) coupling would also occur by a planar zig-zag path, and it would be very interesting to know if this is observable experimentally.

Correlation of NMR and ESR coupling data

Fessenden and Schuler (J.Chem.Phys., 39, 2147 (1963)) and Cochran, Adrian and Bowers (J.Chem.Phys., 40, 213 (1964))

have measured the isotropic part of the hyperfine couplings of many hydrocarbon free radicals in the liquid state or in matrices. We have noticed that there is a close correlation with some of the NMR (H,H) coupling constants of the corresponding parent molecules as shown in the table.

If the geometry and hybridisation of a molecule is unaltered by the removal of a hydrogen atom the NMR and ESR coupling would be expected to be proportional, assuming that the couplings are transmitted by similar mechanisms of spin polarisation through the bonds. The proportionality observed for the vinyl, methyl-vinyl, and formyl radicals is therefore of interest, and confirms the conclusions, previously deduced from the ESR data above, that the uncoupled electron remains in an orbital in the plane of the double bond and does not transfer appreciably to a π -orbital. The parallelism between the abnormally high hyperfine splitting of the formyl radical and the equally abnormal geminal coupling constant of formaldehyde (Shapiro et al, J.Chem.Phys., 1963, 39, 3154) is particularly striking. Contributions to (H,H) coupling caused by exchange integrals between the $1s$ orbital of the first H atom and orbitals in other bonds than the C-H e.g. direct geminal $H(1s)-H(1s)$ exchange for a CH_2 group, could provide spin-polarisation paths for which there would be no equivalent in the analogous radical. Such a contribution may be responsible for the abnormal geminal a/J ratio of the small couplings of the vinyl radical.

Finally (a/J) for the ethynyl radical and acetylene does not have the value observed in the other unsaturated systems although it seems likely that the geometry is not dissimilar. Possibly in this case the uncoupled electron resides appreciably in π -orbitals, or additional spin-polarisation paths are available in acetylene.

Yours sincerely,

Ruth Lynden-Bell
Norman Sheppard
Ruth M. Lynden-Bell
Norman Sheppard

4.

Radical	a (gauss) from ESR*	Molecule	J (c/s) from NMR	a/J
$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \cdot \quad \text{H} \end{array}$	α (13.4) (16.0) β $\begin{cases} +65 & +68 \text{ (trans)} \\ +37 & +34 \text{ (cis)} \end{cases}$	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	α +2.5 (gem) β $\begin{cases} +19.1 \text{ (trans)} \\ +11.6 \text{ (cis)} \end{cases}$	5.9 3.5 3.1
$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \cdot \quad \text{H} \end{array}$	β $\begin{cases} (19.5) \text{ (CH}_3\text{)} \\ +57.9 \text{ (trans)} \\ +32.9 \text{ (cis)} \end{cases}$	$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	β $\begin{cases} +6.4 \text{ (CH}_3\text{)} \\ +16.8 \text{ (trans)} \\ +10.0 \text{ (cis)} \end{cases}$	3.0 3.3 3.3
$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ / \\ \cdot \end{array}$	+137	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ / \\ \text{H} \end{array}$	(~41.1)	3.3
$\cdot \text{C}\equiv\text{C}-\text{H}$	(16.1)	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	(9.5)	1.7

* Numbers in brackets are of uncertain sign. For the first 2 free radicals it is assumed that the largest β hyperfine splitting is positive.

BASF

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Chicago/Illinois 60616
 USA



Dr. Werner Brügel in Fa.

Badische Anilin- & Soda-Fabrik AG

LUDWIGSHAFEN AM RHEIN
 Hauptlaboratorium

Luftpost

IHRE ZEICHEN

IHRE NACHRICHT VOM

UNSERE NACHRICHT VOM

UNSERE ZEICHEN

TAG

Dr. Brü/Ih

11. Mai 1964

BETREFF

Dear Dr. Shapiro,

First, congratulation to your moving to Chicago, good luck and success in your work and thank for continuing as the editor of the NMR-Newsletter!

In order to avoid the reminder letter I send you this contribution. By courtesy of Prof. WELKER, Dr. IWANTSCHIEFF and Dr. DÖTZER (Forschungslaboratorium of SIEMENS-SCHUCKERT-Werke AG., Erlangen) I had the possibility to investigate the high resolution proton resonance spectra of a lot of metal alkyls especially derivatives of Ga, Al, In and Sb. The chemistry and properties of the In-alkyls are described by TODT and DÖTTER (Z.anorg.allg.Chem. 321, 120, 1963), the IR spectra of the Ga-, In- and Sb-alkyls by OSWALD (Z.anal.Chem. 197, 309, 1963). The results of re-measurements of some compounds already described in literature are added. The spectra are taken at a VARIAN A-60 using the pure liquids with a drop of tetramethylsilane as an internal standard. The table gives the chemical shifts of the different alkyl groups (δ -values in ppm from TMS, the positive sign downfield) and the coupling constants as far as measured in cps. The accuracy is estimated few units of the last decimal.

At this moment I do not like to discuss the results, but perhaps they are valuable for colleagues interested in metal alkyls too and for considerations about the DAILEY-SHOOLERY-equation and similar subject.

Yours sincerely

W. Brügel

NMR parameters of metal alkyls

Compound		δ_α	δ_β	δ_γ	δ_δ	δ_ϵ	δ_z	$J_{\alpha\beta}$	$J_{\beta\gamma}$
Ga (CH ₂ CH ₃) ₃		0.677	1.172					8.0	
Ga Cl(CH ₂ CH ₃) ₂		0.868	1.193					8.1	
Ga F(CH ₂ CH ₃) ₂		0.611	1.166					8.0	
Ga (CH ₂ CH ₃) ₃ : O(CH ₂ CH ₃) ₂	Ga	0.450	1.125					8.1	
	O	3.725	1.175					7.0	
Ga (CH ₂ CH ₃) ₃ : N(CH ₃) ₃	Ga	0.273	1.070					8.0	
	N	2.390							
GaBr(CH ₂ CH ₃) ₃ : N(CH ₃) ₃	Ga	0.390	1.088					8.0	
	N	2.520							
Ga (CH ₂ CH ₂ CH ₂ CH ₃) ₃		ca. 0.75	ca. 1.23	ca. 1.43	ca. 0.88				
Ga Cl(CH ₂ CH ₂ CH ₂ CH ₃) ₂		ca. 0.92	ca. 1.43	ca. 1.43	ca. 0.92				
Ga (CH ₂ CH[CH ₃] ₂) ₃		0.810	2.080	0.939				6.1	6.1
Ga Cl(CH ₂ CH[CH ₃] ₂) ₂		0.992	2.075	0.992				6.5	6.5
Ga (CH ₂ CH ₂ CH ₂ CH ₂ CH ₃) ₃		ca. 0.73	ca. 1.27	ca. 1.38	ca. 1.38	ca. 0.88			
Ga (CH ₂ CH[CH ₃] ₂ CH ₂ CH ₃) ₃		ca. 0.92	ca. 1.60	ca. 1.22	ca. 0.92				
Ga (CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃) ₃		ca. 0.75	ca. 1.27	ca. 1.33	ca. 1.33	ca. 1.33	ca. 0.88		
Sb (CH ₂ CH ₃) ₃		1.318	1.210					7.8	
Sb (CH[CH ₃] ₂) ₃		ca. 1.62	ca. 1.30						
Sb (CH ₂ CH ₂ CH ₂ CH ₃) ₃		ca. 1.44	ca. 1.44	ca. 1.44	0.893				
Sb (CH ₂ CH[CH ₃] ₂) ₃		1.396	1.873	0.977					6.1
Sb (CH[CH ₃] ₂ CH ₂ CH ₃) ₃		ca. 1.58	ca. 1.58/1.276	0.982					6.8

Compound		δ_α	δ_β	δ_γ	δ_δ	δ_ϵ	δ_z	$f_{\alpha\beta}$	$f_{\beta\gamma}$
Sb $(\text{CH}_2\text{CH}_3)_3$: Ga $(\text{CH}_2\text{CH}_3)_3$	Sb	1.480	1.258					7.8	
	Ga	0.457	1.133					8.0	
(Sb = O) $(\text{CH}_2\text{CH}_3)_3$		1.817	1.363					6.5	
In $(\text{CH}_2\text{CH}_3)_3$		0.650	1.317					8.4	
In $(\text{CH}_2\text{CH}[\text{CH}_3]_2)_3$		0.963	2.340	0.963				6.4	6.4
In $(\text{CH}_3)_3$: N $(\text{CH}_3)_3$	In	- 0.313							
	N	1.837							
$[(\text{C}_2\text{H}_5)\text{InIn}(\text{C}_2\text{H}_5)] \cdot [\text{N}(\text{CH}_3)_4]$ • 2 Toluene	In	0.358	1.358					8.1	
	N	2.608	(toluene: ph 7.180, CH_3 2.192)						
Al $(\text{CH}_2\text{CH}_3)_3$		0.375	1.095					8.0	
Al Cl $(\text{CH}_2\text{CH}_3)_2$		0.262	1.080					8.0	
Al Cl $_2(\text{CH}_2\text{CH}_3)$		0.514	1.114					8.1	
Al $(\text{CH}_2\text{CH}_3)_3$: N $(\text{CH}_2\text{CH}_3)_3$	Al	- 0.145	1.023					7.9	
	N	2.760	1.138					7.2	
Al $(\text{CH}_2\text{CH}_3)_3$: N $(\text{CH}_3)_2(\text{C}_6\text{H}_5)$	Al	- 0.157	0.992					7.8	
	N	2.775	(ph: 7.155)						
Al Cl $(\text{CH}_2\text{CH}_3)_2$: O $(\text{CH}_2\text{CH}_3)_2$	Al	- 0.070	1.000					8.0	
	O	4.193	1.391					7.0	
$[\text{AlCl}(\text{CH}_2\text{CH}_3)_3] \cdot [\text{N}(\text{CH}_3)_3 \text{benzyl}]$	Al	- 0.184	1.108					7.0	
	N	3.130	(benzyl: ph 7.530, CH_2 4.620)						
Al $(\text{CH}_2\text{CH}_2\text{CH}_3)_3$		0.342	1.425	0.977				7.7	6.8
Al $(\text{CH}_2\text{CH}[\text{CH}_3]_2)_3$		0.350	1.850	0.965				6.8	6.2

Compound		δ_α	δ_β	δ_γ	δ_δ	δ_ϵ	δ_ζ	$J_{\alpha\beta}$	$J_{\beta\gamma}$
Al $\text{H}(\text{CH}_2\text{CH}[\text{CH}_3]_2)_2$	Al 0	0.325	ca. 1.90	0.950	(H: 3.48)			6.8	6.0
Al $(\text{CH}_3)_3 : \text{O}(\text{CH}_2\text{CH}_3)_2$		- 0.923							
		4.000	1.293					7.0	
B $(\text{CH}_2\text{CH}_3)_3$		ca. 1.02	ca. 0.95						
B $(\text{CH}_2\text{CH}_2\text{CH}_3)_3$		ca. 1.29	ca. 1.35	0.924					6.0
B $(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$		ca. 1.31	ca. 1.31	ca. 1.31	0.897				
B $(\text{CH}_2\text{CH}[\text{CH}_3]_2)_3$		1.198	2.067	0.887				7.0	6.2
Si $(\text{CH}_2\text{CH}_3)_4$		0.532	0.950					7.8	
Si $\text{H}(\text{CH}_2\text{CH}_3)_3$		0.594	0.985	(H: 3.682, $J_{\text{Si,H}} = 3$)				7.9	
Si $\text{Cl}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$		ca. 1.43	ca. 1.43	1.055					7.3
Sn $(\text{CH}_2\text{CH}[\text{CH}_3]_2)_4$		0.877	1.918	0.944				6.8	6.1
Sn $\text{Cl}(\text{CH}=\text{CH}_2)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$		ca. 1.33	ca. 1.55	ca. 1.55	0.917			7	6.6
Zn $(\text{CH}_2\text{CH}_3)_2$		0.312	1.153					8.5	
MgBr $(\text{CH}_2\text{CH}_3)_3$		- 0.710	1.168					8.1	

Dr. H. Fritz
c/o J.R. Geigy S.A.
Basle 21 (Switzerland)

28th April, 1964

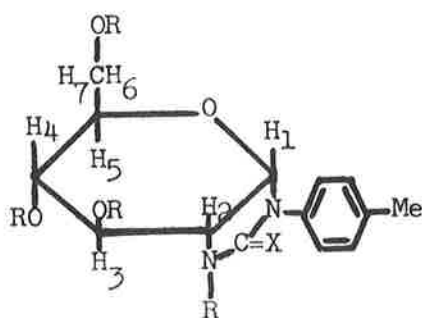
Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616.

Dear Professor Shapiro:

I am sorry you had to remind me that a contribution to IITNMRN is due from our laboratory.

" Stereochemistry in bicyclic derivatives of D-glucoseamine "

The compounds discussed in this letter have been synthesized by Dr. Ch. J. Morel of our company. Synthesis and chemistry of Ia and IIa are already described in the literature 1.). The compounds are examples of fused bicyclic systems consisting of a sixmembered and a five-membered ring. The rings in such systems can be either cis- or trans-fused. While for the sixmembered ring in a trans-fused system only a chair conformation can be envisaged, two possibilities have been suggested for cis-fused compounds 2.): either the sixmembered ring is a chair (presumably slightly deformed), or the sixmembered ring is a boat with the five-membered ring fused to the eclipsed bonds at the side of the boat.



Ia : X = S R = H

Ib : X = S R = COCH₃

IIa : X = O R = H

IIb : X = O R = COCH₃

For compounds Ib and IIb the stereochemistry of ring fusion and the conformation of the glucopyranose-ring can be determined from their NMR-spectra a.). This determination assumes, of course, validity (or approximate validity) of the Karplus-equation 3.) for the dihedral angle dependence of vicinal coupling constants.

The protons of the pyranosering in Ib and IIb give simple first order spectra, in which the absolute values of all coupling constants correspond to line separations and can easily be determined.

τ - and $|J|$ -values for the two compounds are given in Table I. Also shown are the two possible sets A and B of dihedral angles, that can be calculated by the Karplus-equation, and that are compatible with the stereochemistry of glucopyranose b.).

- Spectra were run on an A 60 as 20 % solutions (weight by volume) in CDCl₃. TMS was added as internal standard.
- From consideration of the Karplus equation alone, also values of $\varphi_{34} = 55^\circ$ and $\varphi_{45} = 0^\circ$ would be possible. However, as can be demonstrated with models, $\varphi_{45} = 0^\circ$ can be excluded, because H₄ and H₅ are trans in glucopyranose and cannot be eclipsed in any conceivable conformation. If only $\varphi_{45} = 180^\circ$ is permitted, $\varphi_{34} = 55^\circ$ can also be excluded, because H₃ and H₄ are trans to each other and cannot be made to assume an angle of 55° without undue strain.

- 2 -

Table I

chem. shift τ -units	Ib	IIb	coupling constant cps	Ib	IIb	Dihedral angles from Karplus-equation		
							A	B
$\tau(H_1)$	4.07	4.13	J_{12}	6.6	6.3	γ_{12}	25°	145°
$\tau(H_2)$	5.08	5.45	J_{23}	0	0	γ_{23}	90°	90°
$\tau(H_3)$	4.24	4.36	J_{34}	3.0	3.0	γ_{34}	125°	125°
$\tau(H_4)$	5.72	5.82	J_{45}	9.4	9.0	γ_{45}	180°	180°
$\tau(H_5)$	4.77	4.85	J_{56}	2.3	2.3			
$\tau(H_6)$	5.41	5.55	J_{57}	4.2	4.5			
$\tau(H_7)$	5.90	5.95	J_{67}	12.0	12.0			

Set A corresponds to cis-fusion, set B to trans-fusion of the two rings; neither of the two sets is compatible with a chair conformation for the pyranose-ring. Consideration of this fact permits exclusion of set B, because in a trans-fused system the glucopyranose-ring cannot be in any other conformation but the C 1 chair ^{4.}), since all other conformations are energetically very unfavorable.

As can be shown with Dreiding models, the C 1 chair in a cis-fused system can quite easily be deformed by moving carbonatom 3 towards the plane of the other four carbonatoms. If this is done, until an angle γ_{23} of 90° is reached, all other dihedral angles correspond to those of set A.

Summarizing, we conclude that the rings in compounds I and II are cis-fused. The conformation of the pyranose-ring can be described as an intermediate between a C 1 chair and a B 3 boat, closer to the boat than to the chair form. Probably this conformation is favored because of the tendency of the fivemembered ring to be planar.

Yours sincerely,

Heinrich Fritz

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MELLON INSTITUTE

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PITTSBURGH, PA. 15213

12 May 1964

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

Dear Barry:

I have been following up the work on diphosphine derivatives I reported in MelloN-M-R 62 by attempting to obtain the relative signs of coupling constants in several instances. Since this is still one of the popular sports in the N.M.R. field, I feel the results may be of some interest to readers. Spectral analysis shows that the two (H,P) coupling constants for tetramethyldiphosphine have the same sign, in contrast to the case for tetramethyldiphosphine disulphide. Double resonance experiments at low irradiating power on tetramethyldiphosphine monosulphide have now been successful. Figure 1 shows the proton spectrum during irradiation of each of the four phosphorus resonance bands (of the broadened AB type of spectrum), in order of decreasing field-strength for spectra (a) to (d). Thus irradiation is occurring at P^{III} resonance frequencies for (a) and (b) but at P^V resonance frequencies for (c) and (d). Trace (e) shows the "normal" spectrum. These experiments remove the ambiguity in the assignment of the coupling constants (see MelloN-M-R 62). They also show that the two (H, P^{III}) coupling constants are opposite in sign to J_{PP} , whereas one of the (H, P^V) coupling constants has the same sign as J_{PP} . These double resonance experiments were carried out using the A60 spectrometer and the decoupling apparatus recently developed by Nuclear Magnetic Resonance Specialties Inc. I am grateful to N.M.R. Specialties for allowing me to do this work at their New Kensington, Pa., laboratory.

Table 1 compares the relative signs for these compounds with similar published values. This table has been arranged as far as is possible so that the upper sign of any pair is related to a positive sign for a 3J in the same molecule. I feel that the upper signs are therefore most likely (but are, of course, by no means proved). If this is so, then it is implied that $^1J_{PP}$ is negative, which was tentatively suggested by Ruth Lynden-Bell¹ for P^{III} diphosphine. I hope to relate these signs more positively to the "standard" $J_{^{13}C-H}$ in the near future.

With best wishes,

Robin Harris

R. K. Harris

(References - next page)

MELLON INSTITUTE

Assoc. Prof. B. L. Shapiro

-2-

12 May 1964

References: -

1. R. M. Lynden-Bell, Trans. Faraday Soc., 57, 888 (1961).
2. W. A. Anderson, R. Freeman and C. A. Reilly, J. Chem. Phys., 39, 1518 (1963).
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4. G. M. Whitesides, J. L. Beauchamp and J. D. Roberts, J. Amer. Chem. Soc., 85, 2665 (1963).
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6. P. T. Narasimhan and M. T. Rogers, J. Chem. Phys., 34, 1049 (1961).

Table 1
RELATIVE SIGNS OF J_{PP} AND J_{HP}

Compound	Reference	$^1J_{PP}$		$^1J_{HP}$		$^2J_{HXP}$		$^3J_{HXYP}$		Notes
		Type	Value ^d	Type	Value ^d	Type	Value ^d	Type	Value ^d	
$(CH_2 = CH)_3P$	2					$P^{III}, X=C$	± 11.74	$P^{III}, X=Y=C(sp^2)$	$\left\{ \begin{array}{l} \pm 13.62(cis) \\ \pm 30.21(trans) \end{array} \right.$	a
CH_3PH_2	3, 4			P^{III}	± 186.4	$P^{III}, X=C$	± 4.1			
$(CH_3)_2PH$	3, 4			P^{III}	± 191.6	$P^{III}, X=C$	± 3.6			b
$(CH_3CH_2)_3P$	6					$P^{III}, X=C$	∓ 0.5	$P^{III}, X=Y=C$	± 13.7	
$(CH_3)_2CHP(:O)Cl_2$	5					$P^V, X=C$	$\mp (h)$	$P^V, X=Y=C$	$\pm (h)$	
$(CH_3)_2CHP(:S)Cl_2$	5					$P^V, X=C$	$\mp (h)$	$P^V, X=Y=C$	$\pm (h)$	
$[O_3P \cdot PHO_2]^{3-}$	1			P^V	± 444	$P^V, X=P^V$	± 94			
$H_2P \cdot PH_2^e$	(i) 1	P^{III}, P^{III}	∓ 108.2							c
	(ii) 1			P^{III}	± 186.5	$P^{III}, X=P^{III}$	± 11.9			
$(CH_3)_2PP(CH_3)_2$						$P^{III}, X=C$	± 6.9	$P^{III}, X=C, Y=P^{III}$	± 7.3	f
$(CH_3)_2P(:S)P(CH_3)_2$		P^{III}, P^V	∓ 220			$P^{III}, X=C$	± 4.09	$P^{III}, X=C, Y=P^V$	± 5.84	
						$P^V, X=C$	∓ 12.02	$P^V, X=C, Y=P^{III}$	± 17.61	
$(CH_3)_2P(:S)P(:S)(CH_3)_2^g$						$P^V, X=C$	∓ 12.74	$P^V, X=C, Y=P^V$	± 7.26	f

a $^2J_{HCH} = \pm 2.02$, $^3J_{HC=CH}^{cis} = \pm 11.76$, $^3J_{HC=CH}^{trans} = \pm 18.37$.

b $^3J_{HCPH} = \pm 7.61$.

c $^2J_{HPH} = \mp 12$, $^3J_{HPPH} = \pm 10.5$, ± 6.8 (trans and cis).

d All coupling constants are in c/sec.

e It is not possible to determine the relative signs between groups (i) and (ii).

f The magnitudes may be interchanged

g Assuming the accepted structure.

h Magnitudes not listed.

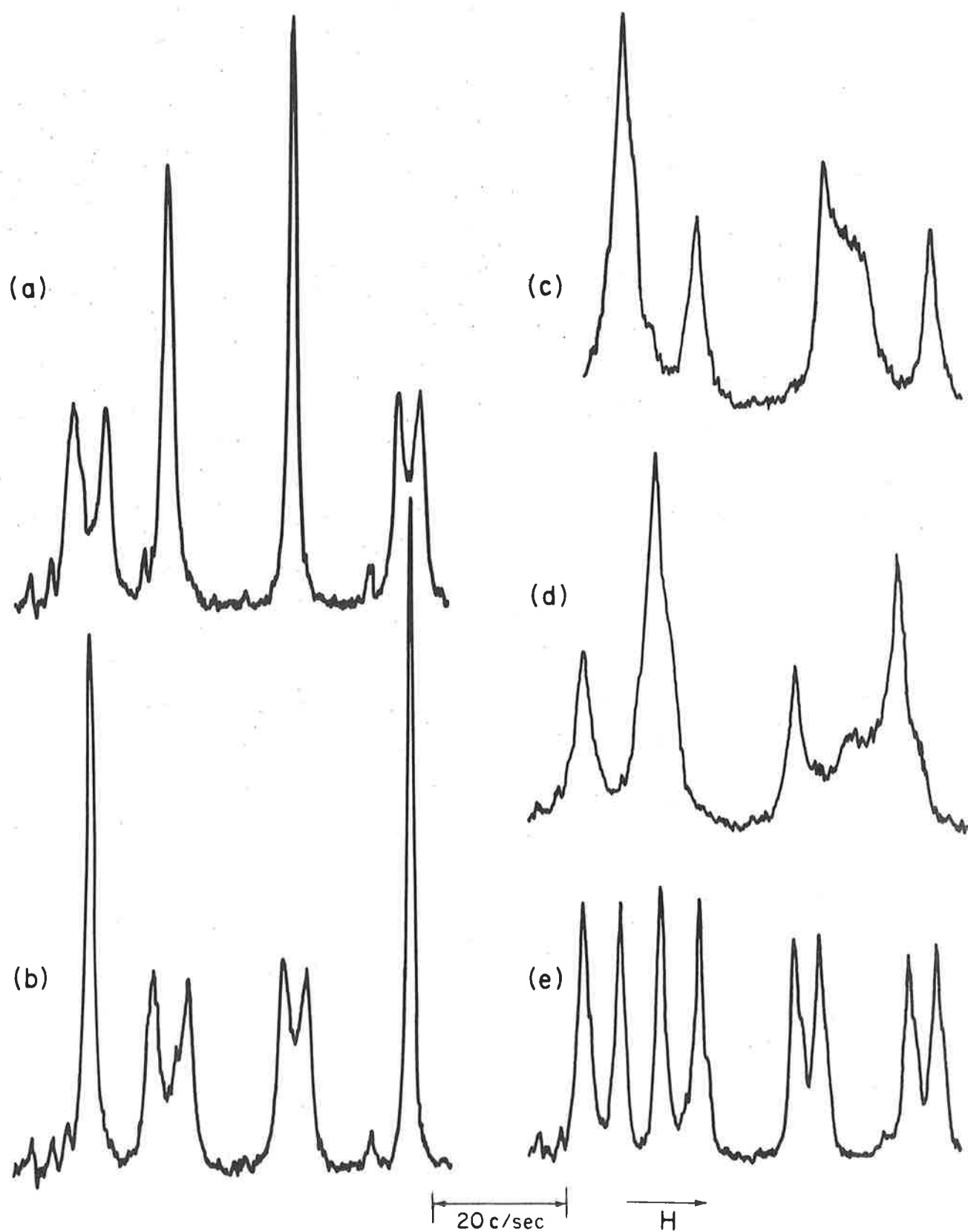


FIGURE 1
 $^1\text{H} - \{^{31}\text{P}\}$ SPECTRA OF TETRAMETHYLDIPHOSPHINE SULPHIDE

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY

Frick Chemical Laboratory

May 13, 1964

Dear Barry,

Numerous proposals for raising the Karplus curve have appeared recently [*inter alia*, R.U. Lemieux, J.D. Stevens, and R.D. Fraser, Can. J. Chem., 40, 1955(1962); R.U. Lemieux and J.W. Lown, Can. J. Chem., 42, 893(1964); and O. Jardetzky, MELLONMR, 57, 46(1963)]. We are concerned about these proposals in view of results we have obtained for coupling constants in the adamantane system.

Karplus [J. Am. Chem. Soc., 85, 2870(1963)] has warned that vicinal coupling does not depend upon dihedral angle only, and cited among possible factors also influencing J, the other valence angles of the fragment under consideration, bond lengths, and the electronegativity of substituents. There are a number of recent practical demonstrations of the effects of factors other than dihedral angle upon vicinal J's, of which the following are but a few: P. Laszlo and P. Schleyer, J. Am. Chem. Soc., 85, 2017; 2079(1963); P. Laszlo and P. Schleyer, Bull. Soc. Chim. France, 87(1964); K.L. Williamson, J. Am. Chem. Soc., 85, 516(1963); O.L. Chapman, J. Am. Chem. Soc., 85, 2014(1963); and G.V. Smith and H. Kriloff, J. Am. Chem. Soc., 85, 2016(1963).

In adamantane, all bond lengths are normal, all bond angles tetrahedral, and the rigid architecture permits no deviation from 60° dihedral angles between vicinal protons. Furthermore, the relatively large separation (at least three bonds) of the substituents from the protons under consideration minimizes the effect of electronegativity upon J.

Although the NMR spectra of adamantane derivatives generally show little splitting, presumably because long range and/or virtual coupling "washes out" the ordinary vicinal coupling, in a few instances, Table I, J_{vic} is measurable.

Table I
COUPLING CONSTANTS IN ADAMANTANE DERIVATIVES

Compound	$J_{\beta\gamma} = J_{\gamma\delta}$, cps ± 0.1
1-fluoroadamantane	2.7
1-bromoadamantane	2.5
1-iodoadamantane	2.5
1-aminoadamantane	2.7
1-hydroxymethyladamantane	2.5
1-methyladamantane	2.6
1-phenyladamantane	2.5
Average	2.6 ± 0.1

We have also examined the ^{13}C satellites of the methylene groups of adamantane itself [P. Laszlo, *Sciences*, 26, 58(1963)] with the aid of a CAT. The satellites are unresolved multiplets, with the appearance of a broad single line, $W_H = 5.30$ cps. Thus J must be 2.65 cps. or less, a value in excellent agreement with the average value for the substituted adamantanes. This value is also in reasonable agreement with the prediction of the Karplus equation, 1.8 cps. Our J_{vic} gives a dihedral angle of about 54° .

We note with some confusion that our value, $J = 2.5 \pm 0.1$ cps for 1-bromoadamantane is significantly different from the 3.0 cps reported by Jardetzky in his letter. It seems also that the electronegativity correction of 0.4 cps applied by Jardetzky to this J is rather large, since none of the protons involved in the coupling is geminal to the bromine.

In consideration of our results in a system having only minimal perturbing influences, we would like to suggest some caution in proposals for large upward displacements of the Karplus curve. We feel also that attempts to generate a single curve, applicable to all systems, are probably foredoomed.

Sincerely,

Cienc

Pierre Laszlo

Paul

Paul Schleyer

Ray

Ray Fort

HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT

P. O. BOX 4255

May 6, 1964

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

Dear Dr. Shapiro:

In compliance with the participation requirement for subscription to IIT NMR Newsletter, please accept the following contribution on behalf of the NMR group at Humble.

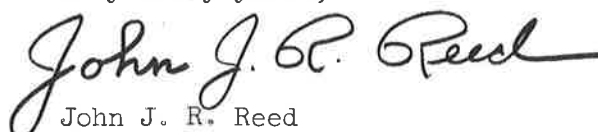
EFFECT OF ETHYL SILICATE ON EXCHANGE OF ALCOHOLIC PROTONS

Recently, while studying chemical shifts of some alkyl silicates, we stumbled on a rather curious effect of these compounds on the proton exchange rate of alcohol. An example of this effect is depicted in Figure 1. The "absolute" ethanol shown here was used as purchased, without purification. Clearly, it contained sufficient catalyst as impurity to promote rapid exchange of the alcoholic protons as evidenced by the singlet OH resonance and simple quartet methylene resonance. Ethyl silicate, run as ten volume per cent solution in carbon tetrachloride, gives a methyl triplet at 8.83 τ and a methylene quartet at 6.28 τ . These are both slightly downfield, respectively, from the resonances of ethanol: CH_3 , 8.87 τ and CH_2 , 6.49 τ .

The addition of ethyl silicate to ethyl alcohol does more than simply overlay the two spectra. Immediately evident in Figure 1 is the increased multiplicity of the OH resonance, suggesting coupling between methylene hydrogens and the alcohol hydrogen. Figure 2 shows detailed structure of the resonances and a first order interpretation thereof. The OH- CH_2 coupling constant is of the order of 5 cps and the CH_2 - CH_3 constant, about 7 cps. The ethyl silicate resonances are also clearly in evidence, slightly downfield from the corresponding ethanol resonances.

According to our experiments, ethyl silicate has no effect on the exchange rate of amine protons. This suggested to us that alcohol protons exchange via a different mechanism than do amine protons. Perhaps ethyl silicate removes the catalyst or initiators in the case of the alcohols, and has no effect on the amines because the amine hydrogens are labile enough to exchange without catalyst.

Very truly yours,



John J. R. Reed

JJRR:osa
Attachment

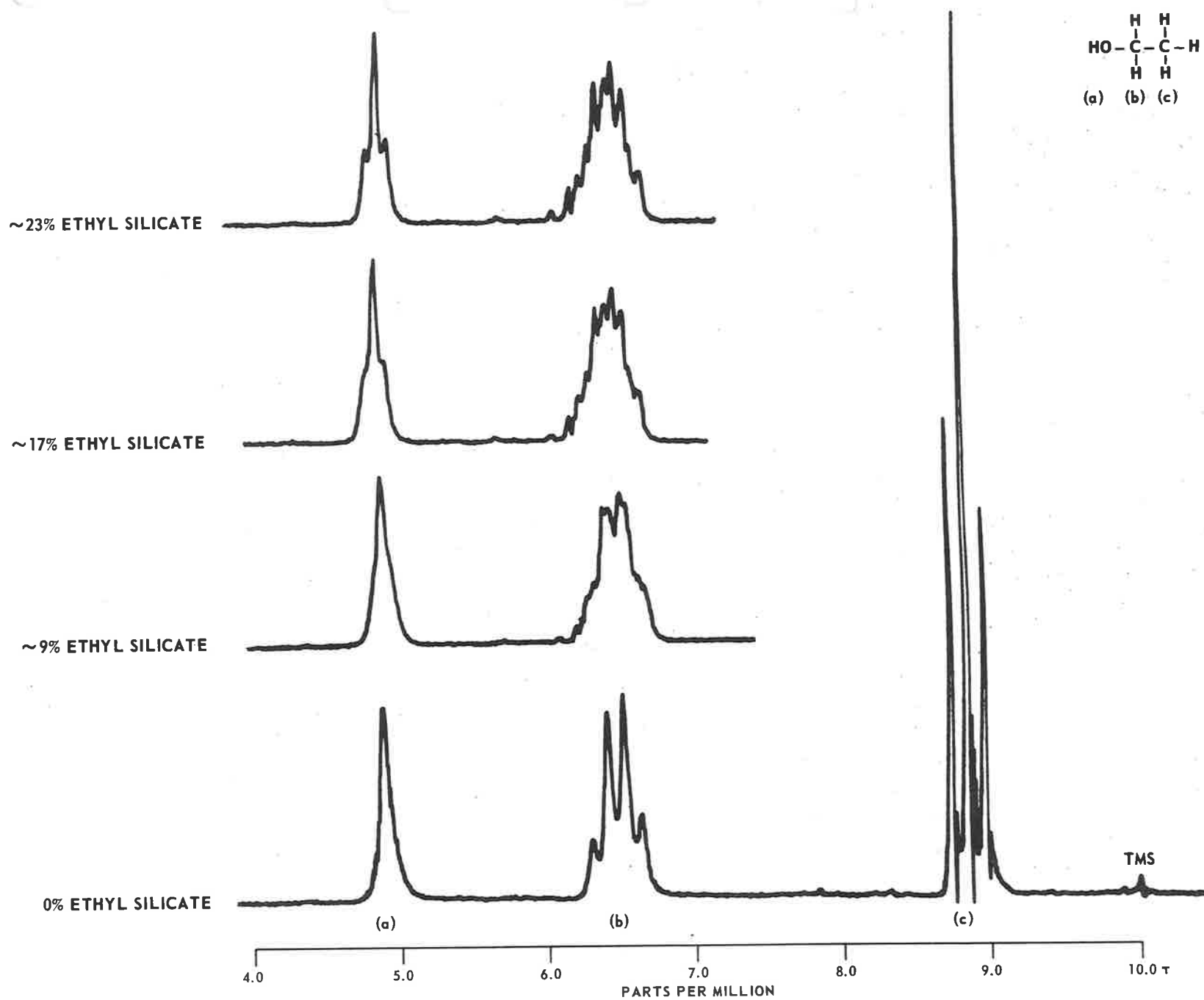


Fig. 1. Proton Magnetic Resonance Spectrum of Absolute Ethanol Showing Effect of Addition of Ethyl Silicate.

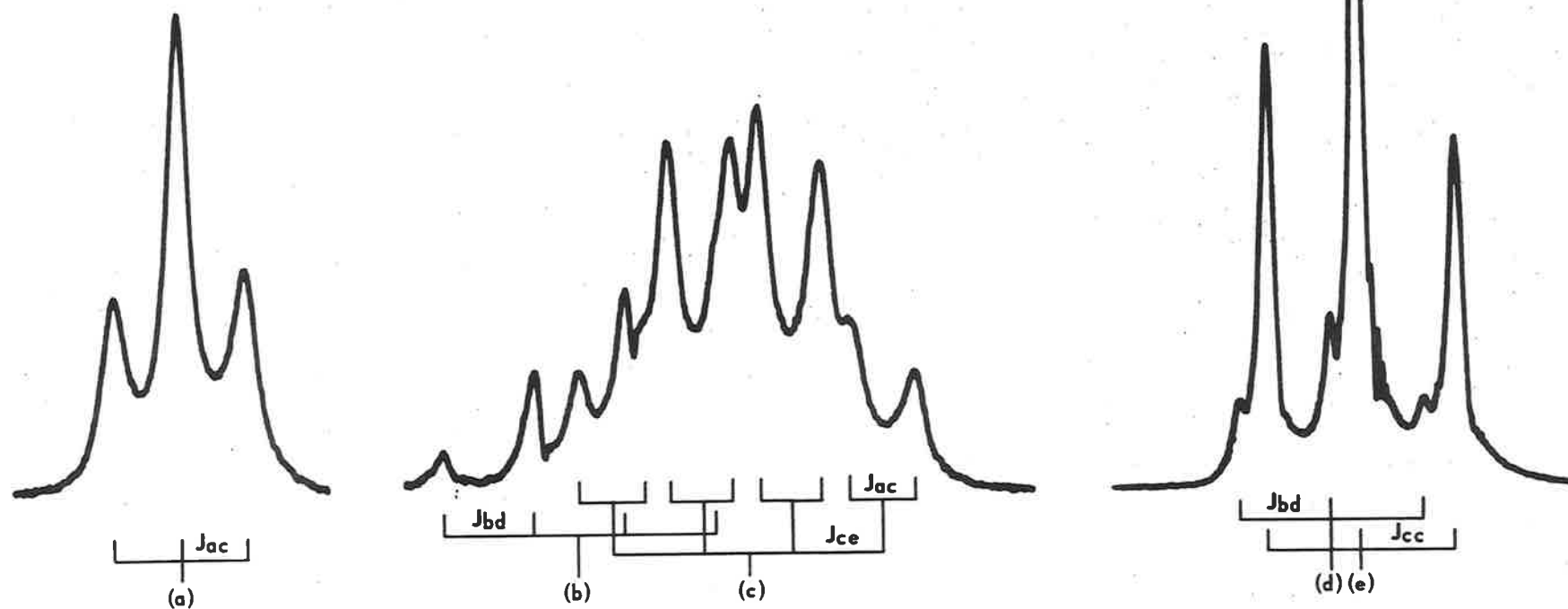
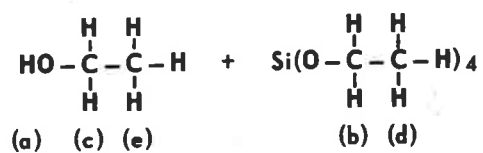


Fig. 2. Detailed Structure of Resonance Signals from Mixture of Absolute Ethanol and Ethyl Silicate.



Fysiska Institutionen, Uppsala, April 21st, 1964.

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

Dear Professor Shapiro,

We have lately been working on the analysis of spectra from symmetrical molecules by perturbation methods, and our first contribution to the new IITNMRN will be a report on some results for A_2B_2X systems.

In the A_2B_2 case closed expressions for all transitions can not be obtained, due to a 4 x 4 submatrix of the Hamiltonian belonging to the symmetrical spin zero states. In many practical cases the Hamiltonian can be treated by perturbation methods, where a suitable choice of basis functions leads to the approximate diagonalization of this troublesome 4 x 4 matrix. The large-shift A_2X_2 approximation to first order is well known. By extension of the perturbation treatment to second order, this approximation is applicable for a remarkably wide range of shifts. We have successfully applied it on a spectrum of p-bromonitrobenzene where the relative shift was only twice the ortho coupling constant.

In the $(AB)_2$ approximation one assumes that the A_2B_2 system can be treated as two almost independent AB systems. The basis functions of the matrix are then chosen as symmetrical products of the AB eigenfunctions. Then the "cross-couplings" are introduced as perturbation. This approximation is e.g. conveniently applied to the analysis of the spectra of p-substituted benzenes. The $(AX)_2$ approximation is the large shift limit of the $(AB)_2$ approximation and leads to extremely simple expressions for the transition frequencies. These approximations with pertinent illustrations are discussed in two papers to appear in Mol. Phys. and Acta Chem Scand.

These perturbation methods can be extended and applied also to somewhat more complicated systems like the A_2B_2X case. The A_2B_2 part of such a spectrum can be regarded as consisting of two overlapping A_2B_2 patterns, each of which may possibly be treated by one of these perturbation methods. Also the X part of the spectrum can be simply calculated by these approximations, quite tractable expressions are obtained.

The accompanying figure shows the spectrum of p-chlorofluorobenzene, the proton spectrum recorded at 60 Mcps and the fluorine spectrum at 40 Mcps. The theoretical spectrum was calculated by the $(AB)_2X$ approximation; the frequencies to second order and the intensities to lowest order. A root mean square deviation of 0.06 cps between calculated and theoretical frequencies is obtained. The intensities to lowest order in the A_2B_2 part, however, are not comparably good. The parameters obtained from the exact treatment (by a least squares fit procedure on a computer) are the same, although it takes more than ten times longer to get the solution.

The asymmetry in the X spectrum, which makes it possible to determine the sign of the proton-fluorine couplings relative the proton-proton couplings is well accounted for.

As a result we obtained the parameters $V_A - V_B = 0.298$ ppm, $J_{23} = 8.80$, $J_{25} = 0.30$, $J_{35} = 2.70$, $J_{26} = 3.05$, $J_{13} = 4.80$ and $J_{16} = 7.90$ cps (all ± 0.10 cps).

This $(AB)_2X$ approximation, or the simpler A_2R_2X approximation should for instance be applicable for the analysis of most p-substituted fluorobenzenes, we have successfully applied them to several other p-fluorobenzenes compounds of this kind.

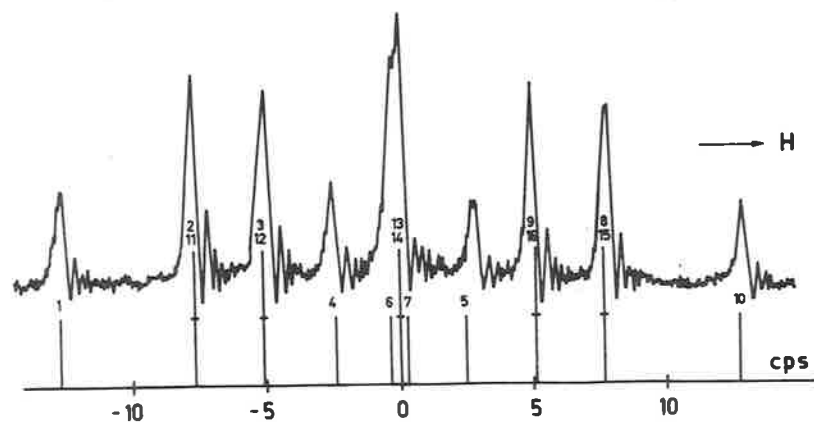
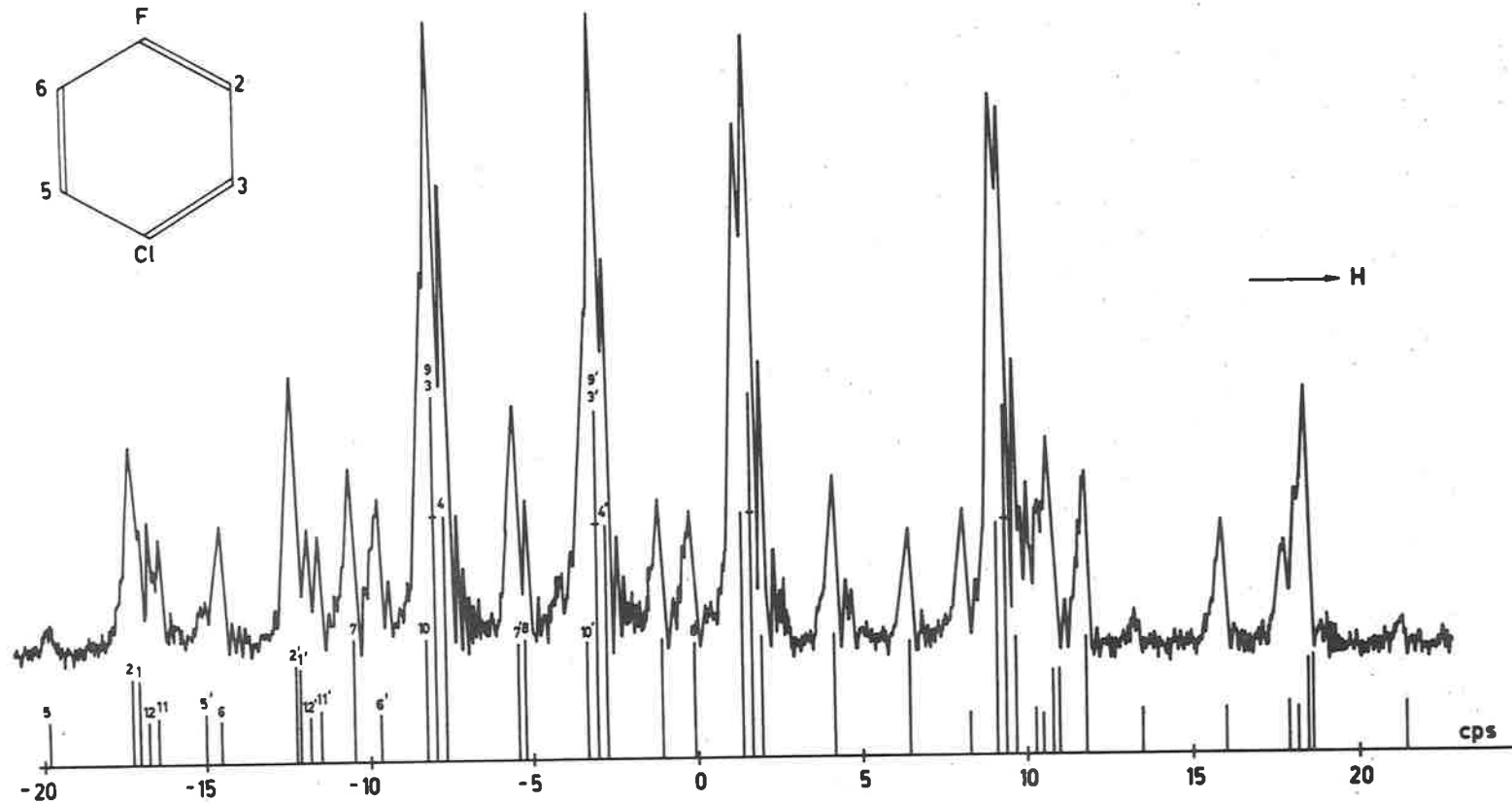
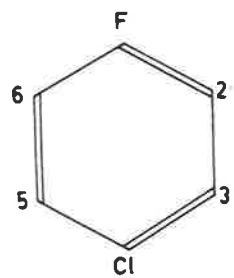
Yours sincerely

Bo Gestblom

Bo Gestblom

Sören Rodmar

Sören Rodmar



ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT

Dr. A. Mannschreck

69 HEIDELBERG, May 14, 1964
Tiergartenstraße
Tel. 27121 (über Chirurg. Klinik)

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

Direct Observation of cis-trans Isomerisation of Amides

Dear Dr. Shapiro:

We have recently investigated the internal rotation of the amides of mesitoic acid, because it is known from the corresponding azolides ¹⁾ that the mesitoyl compounds are favorable in so far as conclusive correlations of the NMR signals to the isomers are possible.

The spectrum of 1-mesitoyl-indoline at 180° (fig.1) shows a broadening of the absorption representing the methylene protons H(2) beside the N atom. At 37° this absorption is split into two groups of lines (fig.2) centered around $\tau=6.4$ and $\tau=5.8$ in the intensity ratio 66:34. Similarly, one of the six aromatic protons, namely H(7) ortho to N, consists of two resonances at $\tau=4.3$ (34%) and $\tau=1.7$ (66%). Also the two methyl signals at 180° are doubled at lower temperature. This means that rotation around the C-N bond is slow enough at 37° for the observation of two isomers. The large differences of their chemical shifts result from long range shielding by the mesityl ring current and by the carbonyl group ¹⁾. These reasonings lead to the structures I and II of fig.2 and to the isomer distributions of the table. "I" means: benzo ring is cis to the carbonyl group; "II" means: trans.

¹⁾ A. Mannschreck, H. A. Staab and D. Wurmb-Gerlich, Tetrahedron Letters 1963, 2003.

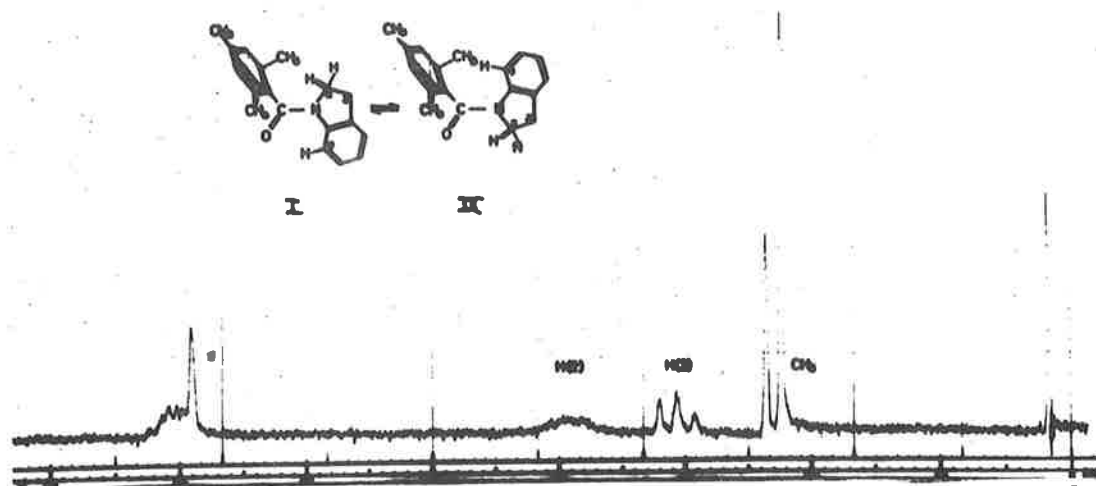


Fig.1: 1-mesityl-indoline in hexachlorobutadiene, 180°, octamethylcyclotetrasiloxane as a standard.

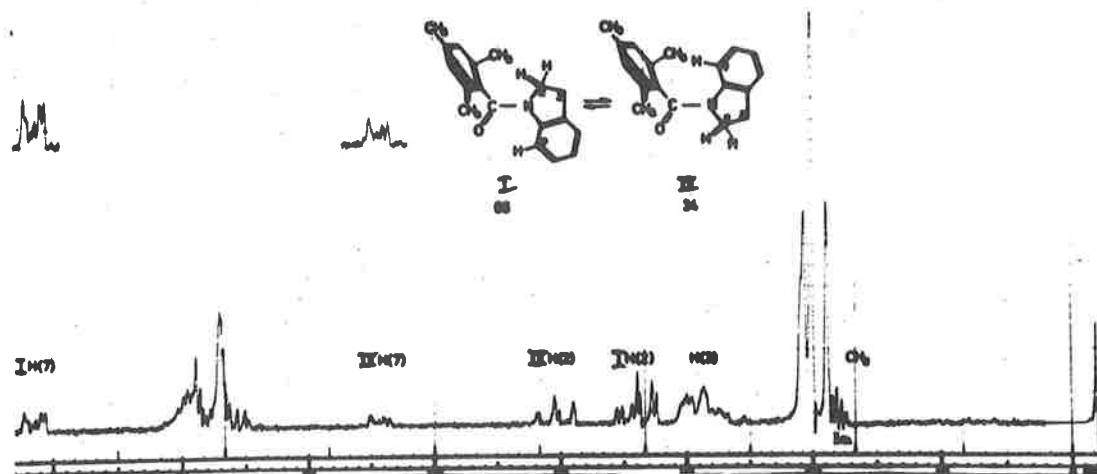


Fig.2: 1-mesityl-indoline in acetone-d₆, 37°.

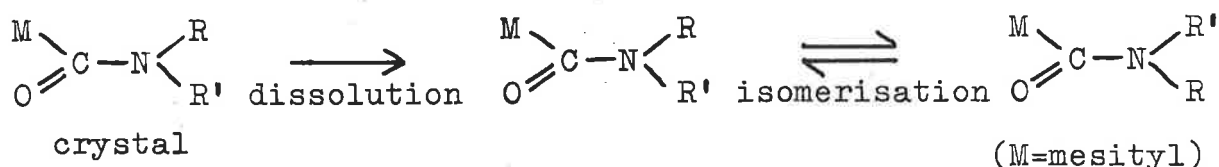
Solvent absorbs around $\tau=8.0$.

Table: Isomer distributions in acetone-d₆, 37°.

1-mesityl derivative of	I	II
indoline	66	34
2-methyl-indoline	35	65
tetrahydroquinoline	51	49
2-methyl-tetrahydroquinoline	27	73

It is seen from these data that both the substitution of the 2-position and the transition from five- to six-membered rings render the isomer II more stable.

The spectra in CF_3COOH are similar, but the equilibrium distributions are changed in favor of II, e.g. 1-mesityl-indoline I:II=45:55 (fig.3, bottom). The most surprising feature of these spectra: they are time-dependent! During the first minutes after preparing the solution from the crystalline amide, one isomer largely predominates. It isomerises slowly towards a mixture of both compounds, the half life ($t_{0.5}$) being approximately 5 to 10 min at 37° . This behavior is shown in fig.3 and 4 for mesityl-indoline, which at first exists as the isomer with the benzo ring cis to the carbonyl group. Mesityl-tetrahydroquinoline on the other hand starts with the trans configuration. In neutral solvents like acetone- d_6 and CCl_4 the rotation is faster than in acids; nevertheless we have succeeded in detecting this phenomenon in the favorable case of mesityl-indoline ($t_{0.5} \approx 1$ min):



This means that the crystal consists of one isomer which after being dissolved isomerises partly. Fig.5 gives the results for the structures of the crystalline amides. One of them is cis, the others are trans.

From this direct observation of the isomerisation we conclude that the life time of our isomers in solution is of the order of minutes. It would, therefore, seem to be possible to isolate the crystalline cis and trans forms of the same amide. We have not yet succeeded, but are optimistic, of course,

Sincerely yours

Albrecht Mannschreck
Albrecht Mannschreck

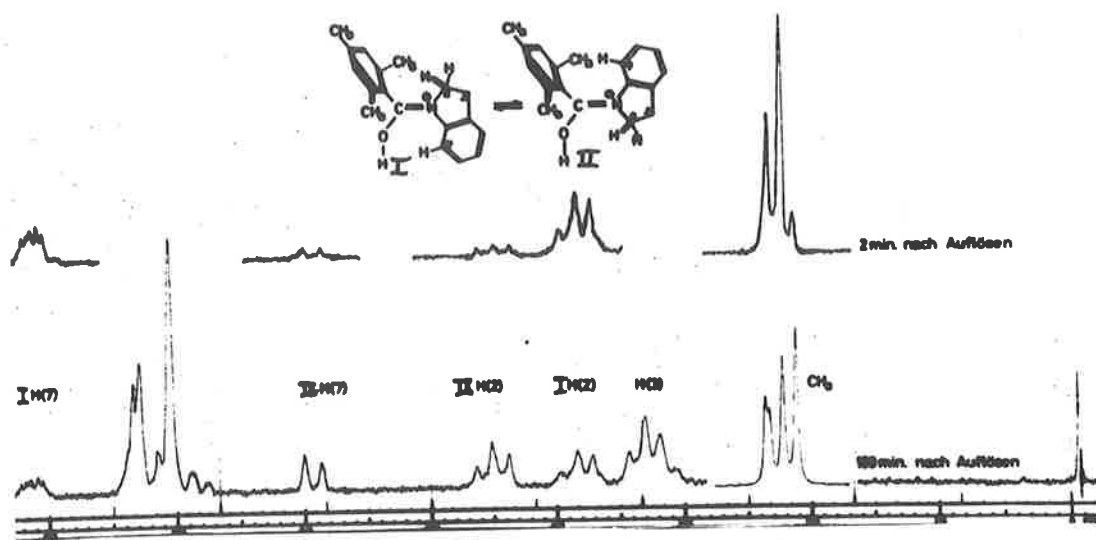


Fig.3: 1-mesityl-indoline in CF_3COOH , 37° . Gain of CH_3 signals reduced. 2 min (top) and 100 min (bottom) after dissolving the crystals.

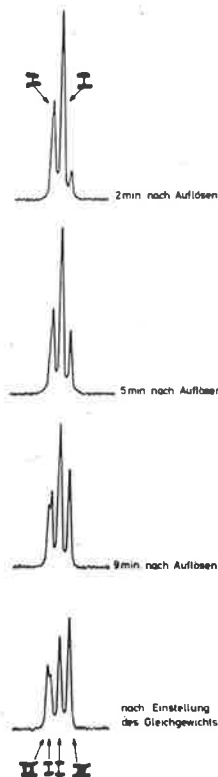


Fig.4: Same. CH_3 signals as a function of time.

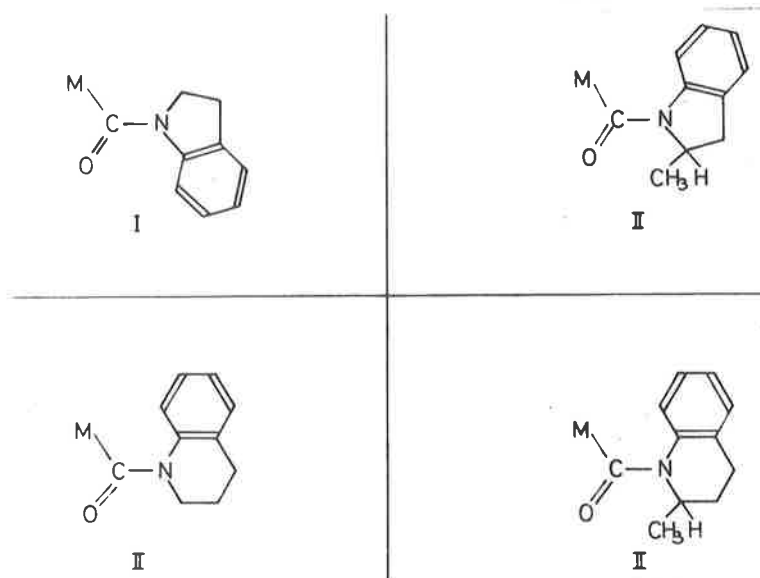


Fig.5: Suggested structures of the crystalline amides (M=mesityl)

INSTITUT NATIONAL DE RECHERCHE CHIMIQUE APPLIQUÉE

(I. R. CH. A.)

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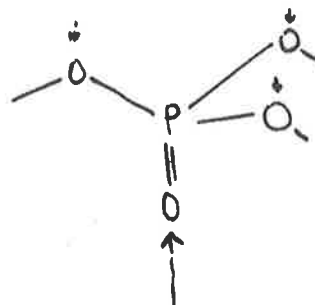
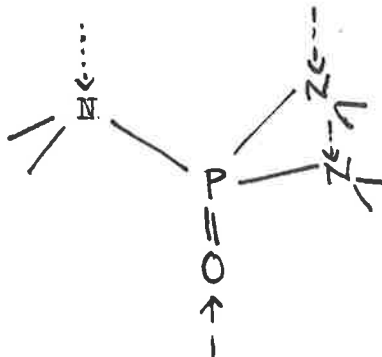
Pr. B.L. SHAPIRO
 Dpt of Chemistry
 Illinois Institute of Technology
 CHICAGO
 Illinois 60616
 U.S.A.

OBJET : INTERMOLECULAR STUDY
 OF ORGANO PHOSPHORUS
 COMPOUNDS.

Dear Barry,

I am pleased to join your NMR club and as a first contribution, I want to emphasize the interest of intermolecular study of molecular structures, when interested in compounds with different kinds of moderately polar groups. It is the case of "neutral" organo-phosphorus compounds we study with Miss G. MARTIN (Lab. Spectr. Hertz. Sorbonne). In such a case, δ effects are not simply correlated with electronic charges, due to the superposition of many different long-range effects (however, consideration of homologous series permits some conclusions) ; J effects are quite sensitive but they are observed on two, three .. bonds (except J ($C_{13}H$) the variation of which agrees quite well with theoretical considerations ; comptes rendus 257, 1703, 1963). In fact, data on δ variation of $CHCl_3$ (a few per cent) dissolved in a number of compounds - Comptes rendus 257, 2463, 1963 - permit fruitful comparisons with electronic charges calculated by Hückel method.

As shown by the following partial diagramm, with a lower charge on the phosphoryl (or thiophosphoryl), compounds with amino groups exhibit a much greater activity towards $CHCl_3$: this is probably indicative of an important participation of nitrogen atoms in inter molecular effects



.../...

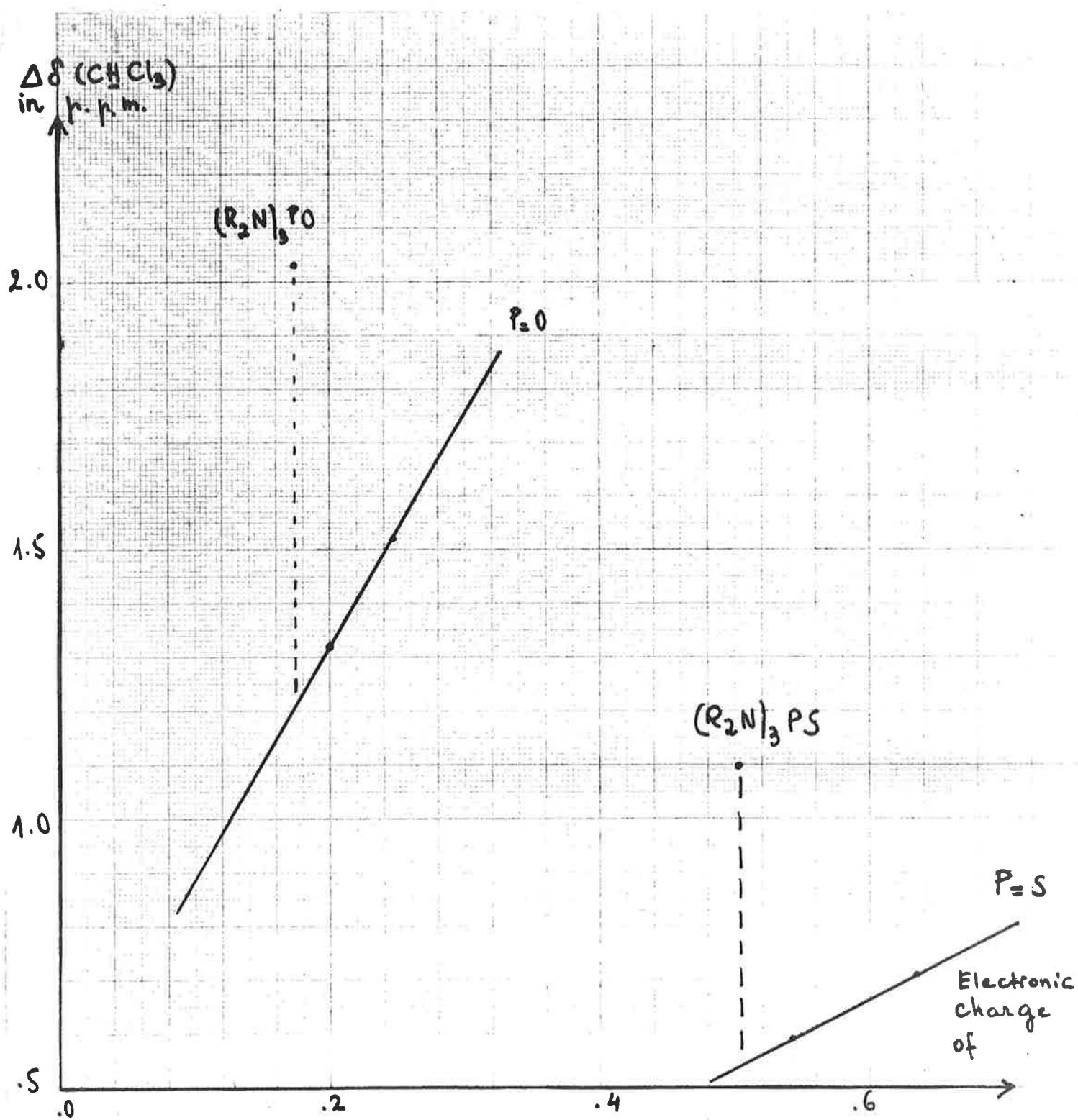
- 2 -

These effects are significantly reduced in the case of thiophosphoryl compounds ; this is not surprising. In compounds of tricoordinate phosphorus, intermolecular effects are mainly due to heteroatoms (O, N).

With the best regards of

A handwritten signature in dark ink, appearing to read 'G. Mavel', with a horizontal line underneath.

G. MAVEL



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OUR REF.

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DATE

Res/G.2050/ACC/JB.

14th May, 1964.

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

Dear Dr. Shapiro,

We have found phosphorus oxide, P_4O_6 (m.p. $23.8^\circ C$) to be an excellent standard sample for the attainment of resolution and the referencing of chemical shifts in phosphorus NMR. In both these respects it is far superior to the conventional samples. Unlike P_4O_{10} , it is not unduly hygroscopic and presents no handling problems.

For the initial location of the resonance when setting up a spectrometer for ^{31}P operation, P_4O_6 , because of its high phosphorus content and the small line width of its single-line spectrum, is unequalled.

The adjustment of resolution has always presented a problem in phosphorus resonance. Many workers, including ourselves, have used the ten-line pattern of trimethyl phosphite, but this is very slow because the spectrum has to be scanned slowly to assess the effect of each adjustment of the shim coils. In the case of P_4O_6 , the single peak may be scanned rapidly and adjustments made by observing the ringing pattern. The attainable resolution is also considerably superior; for example, a resolution of 2.2 in 10^6 was attained at 15 Mc/s. on the RS2, while the best obtained using trimethyl phosphite was 5.6 in 10^6 .

For the referencing of chemical shifts, the favourable characteristics of the P_4O_6 resonance permit the use of smaller capillaries than are necessary with 85% orthophosphoric acid; this leaves more room for sample. The relative sharpness of the P_4O_6 line also allows more accurate measurement of shifts. We therefore propose that P_4O_6 should be used as the ultimate standard for phosphorus NMR, to which all future measurements of phosphorus chemical shifts will be referred.

To this end, we have made an accurate measurement of the shift of P_4O_6 from 85% orthophosphoric acid. This is -281.2 ± 2 c/s at 25 Mc/s, i.e., -112.5 ± 0.1 p.p.m.

This company is proposing to market high purity P_4O_6 for NMR purposes. In order to provide some indication of the scale of demand for this product, it would be appreciated if those interested could write to the undersigned (A.C.C.). Further information will be sent out as soon as possible.

Yours sincerely,



A. C. Chapman.

pp. John Homer.*

* Present address:- College of Advanced Technology, Birmingham.

MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASSACHUSETTS

DEPARTMENT OF CHEMISTRY
CARR LABORATORY

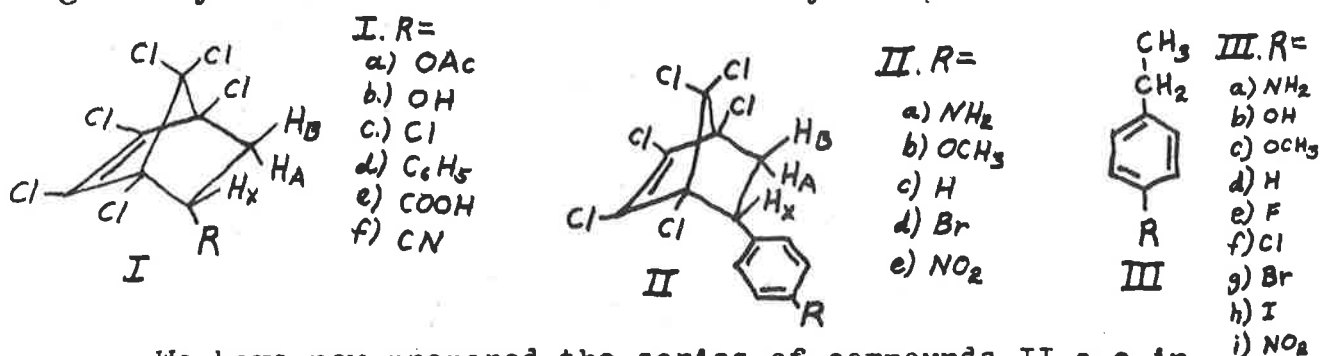
May 12, 1964

Professor Barry L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry,

SUBSTITUENT EFFECTS IN BICYCLOHEPTENES II

Some time ago (Mellon NMR 45, 7) we reported that coupling constants and internal chemical shifts ($\delta_X - \delta_A$ and $\delta_X - \delta_B$) are quite markedly influenced by changes in substituent electronegativity in the series of hexachlorobicycloheptenes I a-f.



We have now prepared the series of compounds II a-e in which the substituents are separated from the three protons on the bicyclic ring system by a phenyl group. This should reduce the effect of the substituent magnetic anisotropy on the three coupling protons while retaining, to some extent, the inductive effect of the substituent. Therefore, in contrast to the lack of correlation of chemical shifts with substituent electronegativities in the series of compounds I a-f, we find in the series of compounds II a-e with the phenyl ring interposed that the absolute values of the chemical shifts of the three protons, H_A, H_B, and H_X, can be correlated with the Hammett σ_p values for the substituents. As expected the effect of the substituent decreases as the number of intervening bonds increases so that the slope of the correlation lines for the A and B protons is different from that for the X protons. It is interesting to note that the substituents in the para position of the phenyl ring exert the same effect on both the A and B protons, in contrast to the compounds I a-e.

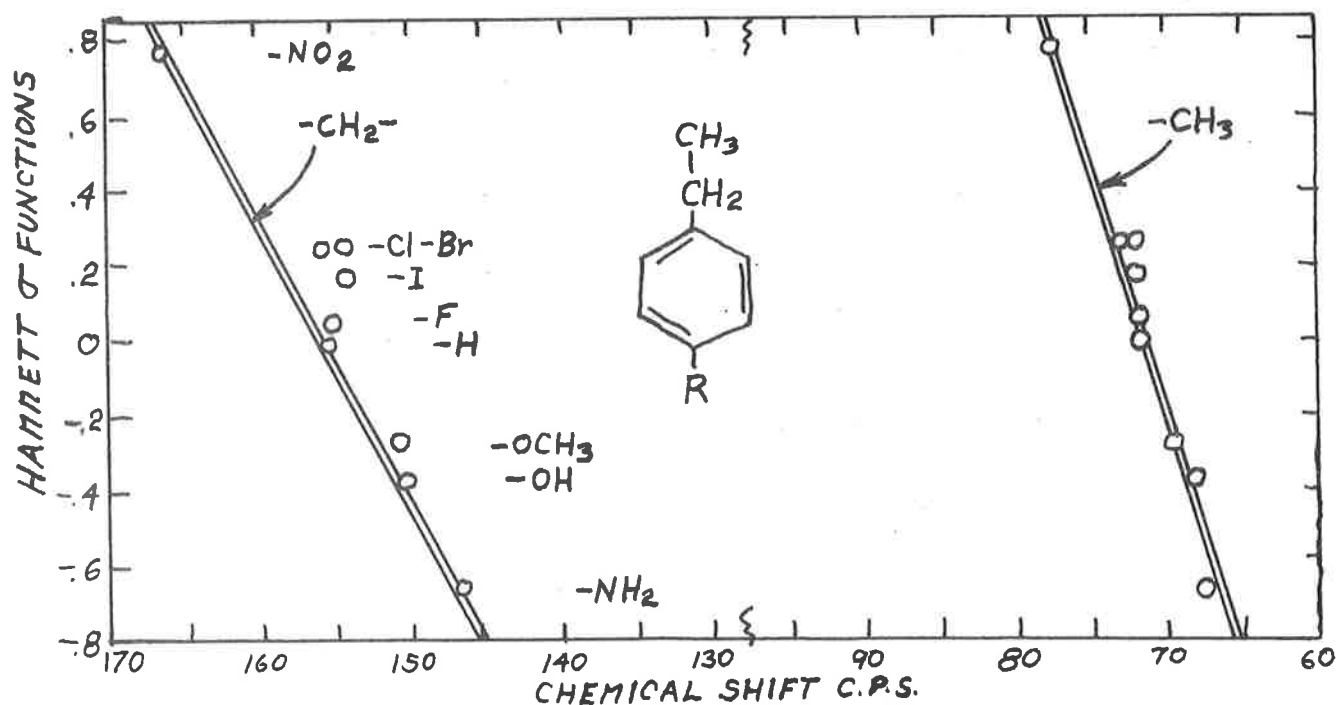
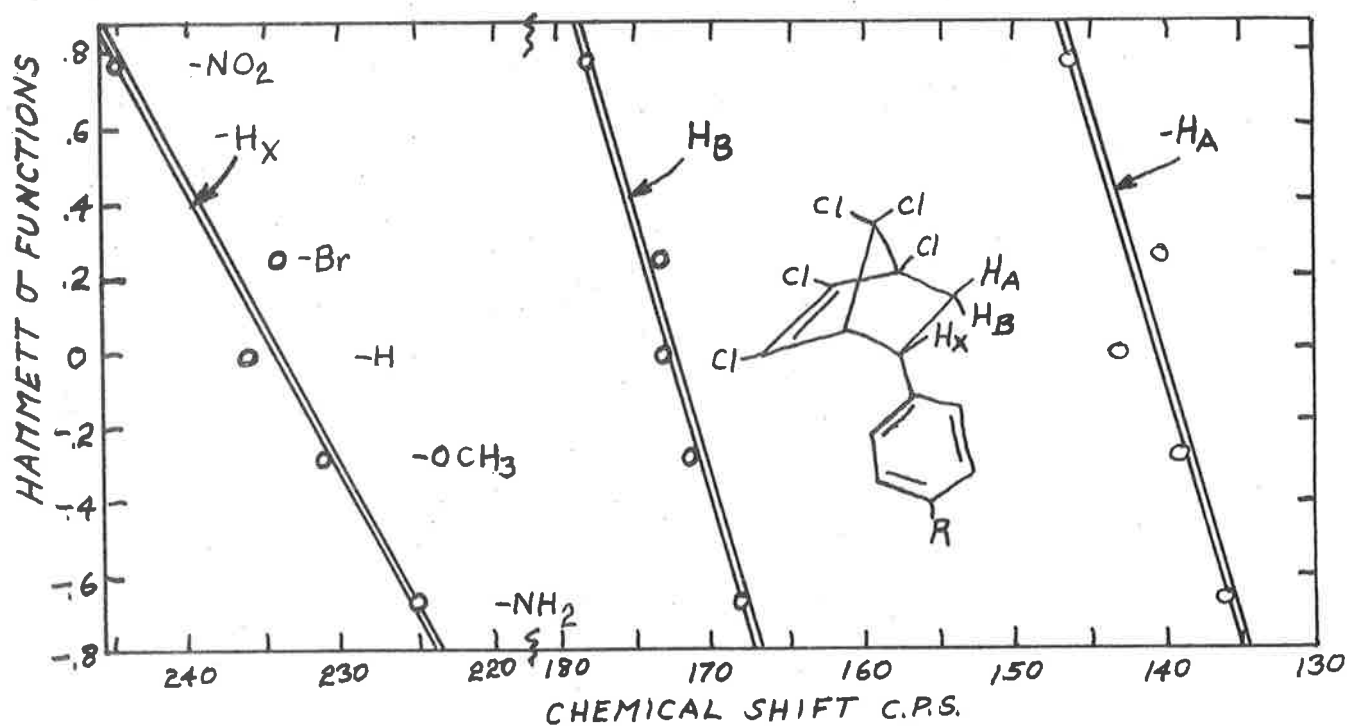
In order to determine what the effect of the rigid bicyclic ring system is on these observations, we have also examined the chemical shifts of the methyl and methylene protons in the ethyl side chain of the compounds III a-i. As indicated in the figure below, the same slope is found for the methylene group as for the A and B protons of II. Thus the fact that the A, B

and X protons are in a rigid, somewhat strained 5-membered ring and are adjacent to strongly electron withdrawing centers makes no difference in the mobility of the electrons contributing to the relative shielding of the A, B and X protons in the bicyclic system. In the series of compounds II a-e, the coupling constants are unchanged in going from one compound to another; $J_{AX} = 4.2$, $J_{BX} = 8.9$, and $J_{AB} = -12.7$ c.p.s.

Sincerely yours,

Ken Williamson

Kenneth L. Williamson



THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY • INDIANAPOLIS 6, U.S.A. • 317 MELROSE 6-2211

May 14, 1964

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

Dear Prof. Shapiro: Recovering DMF d₇; NMR Paper for a 10" x 15"
Flat Bed Recorder

We frequently encounter samples which are not soluble in CDCl₃ or D₂O. Trifluoro acetic acid has been used as have dimethyl sulfoxide, acetone and dimethyl formamide. Dimethyl formamide appears to be the most "universal" of these third choice solvents and in order to reduce the inventory of deuterated solvents, we frequently use heptadeutero dimethyl formamide (DMF d₇). Although by using the Varian micro cell, the amount per sample is only about 0.1 ml., at \$45/gm. it becomes desirable to recover the DMF d₇.

The glassware pictured in Figure 1 was fabricated in our glass shop by Mr. Robert Miller. About 5 ml. of waste solution are placed in the annular space (A) which also contains a layer of glass beads. After assembly, the pressure is reduced with a mechanical pump and the stopcock closed. The cold finger (B) is filled with acetone and small pieces of dry ice are added. The DMF d₇ first condenses on the upper part of the cold finger (B) and drops into the annular space (C). From (C) it is evaporated onto the center portion of the cold finger and collects in the cup (D). The DMF d₇ collected is relatively free of contaminants except for a small amount of water.

Although we have been able to obtain a fairly reproducible 500 c/s sweep with the HR-60 (MELLONMR 55, 5) there has been no paper available for the 10" x 15" flat bed recorder which could be divided into tens of c/s. Dr. Harold Boaz with the aid of our printing department developed the paper shown in Figure 2. The grid is made up of a series of dots spaced at intervals of 1 c/s.

We cannot make this recorder paper available in large quantity, but would be glad to send samples to anyone requesting it.

Yours truly



Paul W. Landis
Chemical Research Division

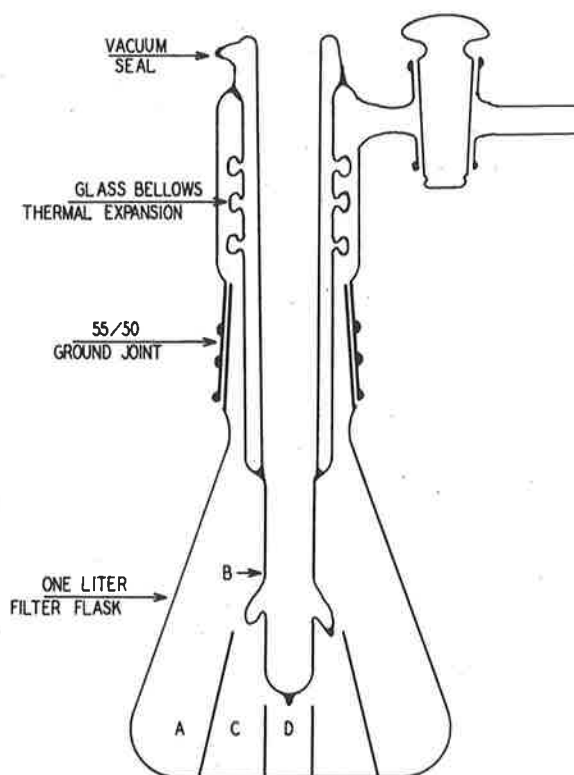


FIGURE 1

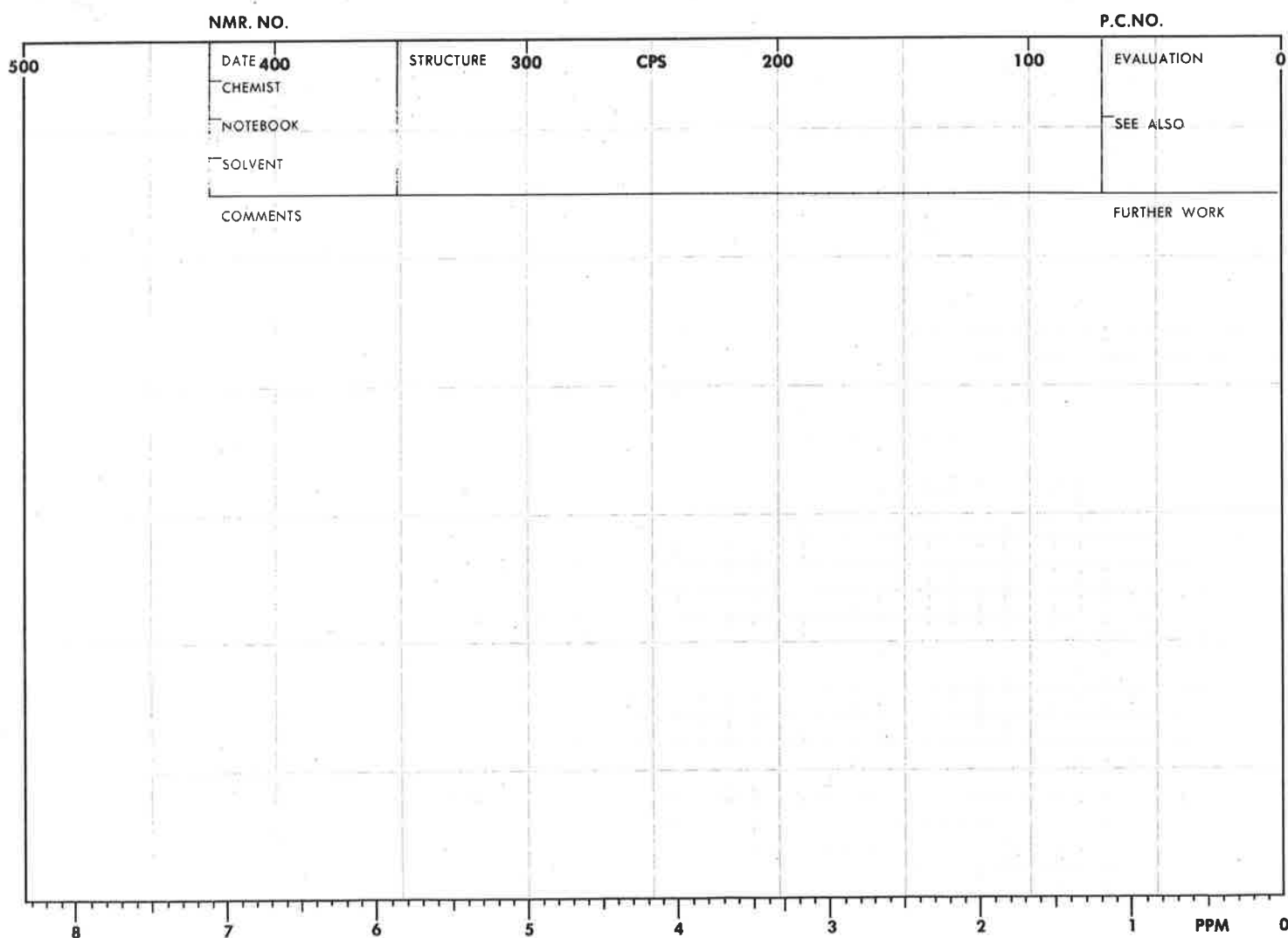
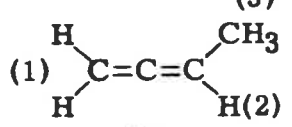
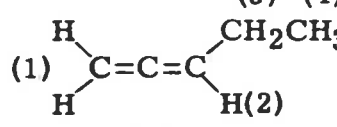
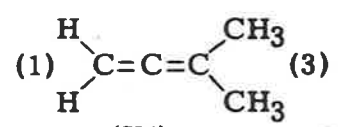
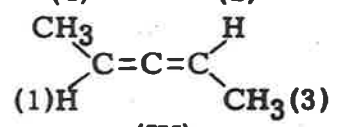


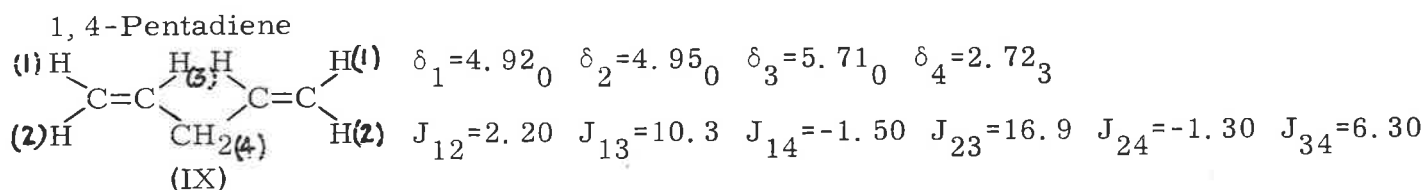
FIGURE 2

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR ALKYL ALLENES[†]

	1, 2-Butadiene (3)  (I)	1, 2-Pentadiene (3) (4)  (II)	3-Methyl-1, 2-butadiene  (III)	2, 3-Pentadiene (4) (2)  (IV)
δ (ppm)				
1	4.49 ₈	4.54 ₇	4.40 ₂	4.89 ₀
2	4.94 ₃	5.03 ₄	—	—
3	1.58 ₇	1.95 ₁	1.62 ₀	1.56 ₃
4	—	0.99 ₃	—	—
J (cps)				
12	6.67	6.77	—	6.35
13	3.45	3.50	3.15 ^(a)	3.20
23	7.10	6.23	—	6.80
34	—	7.51	—	—

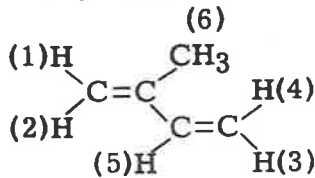
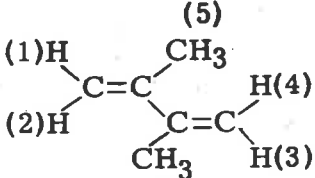
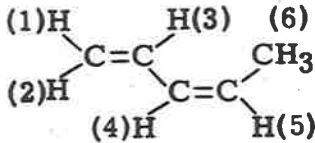
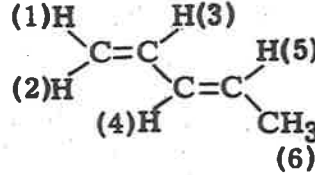
[†] Except for (III) where a first-order spectrum yields to immediate interpretation, data were obtained by calculation of the theoretical spectra. All data refer to the pure liquid. The program of Reilly and Swalen was used for the calculations.

(a) Snyder and Roberts⁵ report a value of 3.03 ± 0.06 cps.



Koster and Danti
Texas A&M University

TABLE II
CHEMICAL SHIFTS AND COUPLING CONSTANTS IN CONJUGATED DIENES[‡]

	2-Methyl-1, 3-butadiene (6)  (V)	2, 3-Dimethyl-1, 3-butadiene (5)  (VI)	1, <u>cis</u> -3-Pentadiene  (VII)	1, <u>trans</u> -3-Pentadiene  (VIII)
δ (ppm)				
1	4.87 \pm .05	4.86 \pm .05	4.99 \pm .10	4.83 \pm .10
2	4.87 \pm .05	4.96 \pm .05	5.07 \pm .10	4.92 \pm .10
3	4.94 \pm .05	—	6.58 \pm .05	?
4	5.05 \pm .05	—	5.92 \pm .05	?
5	6.35 \pm .05	—	5.41 \pm .05	?
6	1.79 \pm .03	1.86 \pm .03	1.70 \pm .03	1.72 \pm .03
J(cps)				
12		2.2		
13			10.5	
14	~0.6			
16	1.2	1.0	~0.6(?)	
23			16.6	
24	~0.6			
26	1.2			~0.6(?)
34	1.5		10.5	
35	10.5			
45	17.4		11.0	
46			1.5	
56			6.8	5.8

[‡] These data were obtained from first order interpretation of the spectra and refer to samples diluted to 50 percent by volume with CCl₄.

UNIVERSITY OF UTAH

SALT LAKE CITY, UTAH 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

May 15, 1964

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, IllinoisRe: Hyperconjugative Enhancement of the
Geminal Coupling Constant in Allenes

Dear Barry,

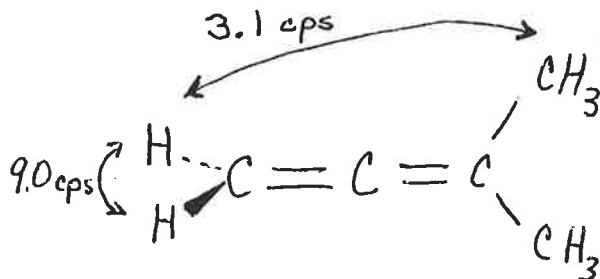
Enhanced geminal coupling constants observed by Shapiro and co-workers¹ for the sp^2 methylene group in formaldehyde and some of its derivatives would seem to argue for electron delocalization of the free pair of electrons centered on the oxygen and nitrogen atoms bonded to the methylene group. The identical symmetry of the free electron pairs and the methylene hydrogens is suggested as substantiation of this proposal. The value of the sp^2 geminal coupling in 1,1-dimethylallene has been determined in our laboratory to be $|9.0 \pm 0.3|$ cps by deuterium substitution whereas the methyl-methylene coupling over five bonds is $|3.1 \pm 0.05|$ cps. This geminal value also is considerably larger than that found in many vinyl compounds, and we believe this enhancement is due to a hyperconjugative effect of the vicinal π -bond system which is of the same symmetry as the methylene hydrogens.

The equation used by Barfield and Grant² to account for π -electron enhancements of the geminal coupling on substituted methanes is obtained from Eqs. 2 and 3 in Ref. 2 and given as follows:

$$J_{\text{gem}}^{\pi}(\text{cps}) = -8.0 \cos^2\phi \cos^2\phi' \quad (1)$$

Using this expression to approximate the value in the above allene where $\phi=0^\circ$ and $\phi'=180^\circ$, we concluded that the π -bond enhancement should be -8 cps. It is difficult, of course, to estimate the value which should be corrected with this -8 cps contribution as geminal couplings in many vinyl and ethylenic compounds vary between -1 cps to +3 cps. If the observed geminal coupling of $|9 \text{ cps}|$ in $(\text{CH}_3)_2\text{C}=\text{C}=\text{CH}_2$ is indeed negative, then the relatively large coupling has been fairly well rationalized and the hyperconjugative VB treatment upon which Eq. 1 is based is further justified. The much larger formaldehyde coupling possible may be explained in part from this type of mechanism.

For fear that the Utah subscription would elapse, we have not waited longer for the corresponding geminal value in deuterioketene which we should have shortly.



Best wishes,

Evan L. Allred

Evan L. Allred

David M. Grant

D. M. Grant

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