13.7.64

Preuss.

Illinois Institute of Technology N-M-R Newsletter

No. 69
JUNE, 1964

Deadline Date for Next Issue: 22 July 1964

Mėnesinis rinkinys neformaliu, privačiu laišku iš NMR laboratorijų. Visos čia randamos informacijos yra skirtos tik skaitytojo naudojimui. Citavimas nėra leistinas be tiesioginio susitarimo su laiško autorium. Cituojama medžiaga turi būti pavadinta "Privačia komunikacija."

Argonne National Laboratory

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TELEGRAM WUX LB ARGONNE, ILL. CLEARWATER 7-7711 TELETYPE TWX ARGONNE, ILL. 312-257-2409

May 21, 1964

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

Dear Barry:

We would like to report the following study: Conformation and Internal Rotation of Nitroaromatic Amines in Solution as Detected by Proton Magnetic Resonance by Joachim Heidberg, John A. Weil, Gaile A. Janusonis, and Judith K. Anderson.

The 60 Mc/sec proton magnetic resonance spectra of N-methyl-2,4,6-trinitroaniline (I) and of N-methyl-2,6-dinitroaniline (II), as well as of the analogous N-diphenylamino compounds, show that the 3- and 5-phenyl protons are inequivalent at low temperatures in solution, but act as equivalent at sufficiently high temperatures. The N-unsubstituted anilines and N,N-dimethyl-anilines corresponding to I and II show no such inequivalence. The coalescence with temperature of the AB quartet of the picryl protons in the picrylaniline (I) and diphenylpicrylhydrazine in dichloromethane solution could be described quantitatively by the lineshape equations for two coupled protons exchanging with each other. The analysis yielded the lifetimes of the ground state configurations of these molecules, with Arrhenius activation energies of 14.5 ± 0.3 and 12.5 ± 0.2 kcal/mole and frequency factors of 1.4×10^{15} and 6×10^{10} sec^{-1}, respectively, for the intramolecular exchange process. A model for these observations, including Hückel MO calculations, has been formulated in terms of the barrier to rotation about the amino nitrogen-ring carbon bond, the orientation of the nitro groups ortho to the amino group, and hydrogen bonding between the amino group and these nitro groups.

The chemical shift and spin-spin coupling parameters for these compounds and for the 2,4-dinitro analogues were tabulated and compared. The chemical shift values exhibit regularities in excellent agreement with the model introduced.

To appear in J. Chem. Phys.; preprints available.

Sincerely yours,

John A. Weil

John A. Weil
Chemistry Division

JAW:mje

Dr. H. Spiesecke
C C R - Ispra
Italy

May 19, 1964

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

Dear Barry,

After the trouble of getting reasonable C^{13} spectra first of all, the proper assignment of the individual peaks poses the next problem. Besides the well known techniques of using selectively methyl- or deuterium-substituted compounds I found fluorine substitution in aromatic systems to be quite useful too.

In para-substituted fluorobenzenes, for example, one finds a long range coupling between fluorine and the carbon atoms ortho to it. This J_{C-C-F} is of the order of 20 cps. Since J_{CF} is about 240 cps and J_{CH} in benzene is 159 cps it is no problem to assign the remaining lines once the distinction between the ortho and meta position relative to fluorine is made.

In the case of meta-substituted fluorobenzenes the two ortho positions are no longer equal by symmetry. One has to make use now of the fact that the shifts of disubstituted benzenes are to a first approximation the sums of the corresponding shifts in the individual monosubstituted benzene derivatives. The difference of the shifts in the 2 and 6 positions is almost always large enough to make an unambiguous assignment even taking into account that the "calculated" shifts are only accurate to $\pm$ 1 ppm.

In principle there should be a dependance of J_{CCF} on the nature of the substituents but using rapid passage and dispersion mode the accuracy of the measurements is a little bit shaky, especially, if one uses CH_4 as reference which is 137 ppm up field from benzene.

In a recent publication (Mol.Phys.7, 301 (1963-64) Pople has calculated the C^{13} chemical shifts of some simple hydrocarbons. Here are the experimental values for ethylene and allene:

ethylene: + 5.4 ppm fr. C_6H_6 J_{CH} = 158 cps
+70.4 ppm fr. CS_2 (why not about 170?)

allene C: -84 ppm fr. C_6H_6 CH_2: + 54 ppm fr. C_6H_6 J_{CH} = 169 cps
-19 ppm fr. CS_2 +119 ppm fr. CS_2

PARA SUBSTITUTED FLUOROBENZENES

X	C_1 exp.	C_1 calc.	J_{CF} (cps)	C_2 exp.	C_2 calc.	J_{C_2CF} (cps)	C_3 exp	C_3 calc	C_4 exp	C_4 calc	C_5 exp	C_5 calc	C_6 exp	C_6 calc
F	-24.6	-30.7	243	18.3	13.4	20								
Cl	-33.5	-33.1	247	11.1	13.3	22	-2.2	-1.1	-1.6	-2.0				
I	-34.9	-34.7	246	9.5	11.7	19	-11.6	-10.8	39.4	36.7				
OCH_3	-29.6	-27.0	237	11.9	13.4	21	12.6	13.8	-28.4	-25.8				
NH_2	-28.6	-25.6	233	11.8	13.0	20	12.5	11.5	-15.9	-14.8				
CHO	-37.9	-41.1	255	11.8	13.1	22	-4.0	-2.1	-5.1	-4.6				
NO_2	-38.5	-41.1	258	12.0	13.5	24	1.8	4.4	-16.2	-15.2				

META SUBSTITUTED FLUOROBENZENES

F	-35.3	-36.0	250	24.2	28.6		-35.3	-36.0	16.9	18.7	-2.5	-1.8		
Cl	-34.8	-36.1	246	11.5	14.1		- 7.9	- 7.4	3.2	4.2	-2.6	-1.9	13.8	16.3
I	-34.1	-37.7	248	1.8	4.4		33.4	29.7	-6.0	-5.5	-4.1	-3.5	12.6	14.7
OCH_3	-35.6	-36.0	245	26.8	29.0		-33.1	-31.1	17.7	19.1	-2.0	-1.8	20.9	22.4
NH_2	-36.2	-36.4	243	24.9	26.7		-21.0	-20.1	16.3	16.8	-2.9	-2.2	24.9	23.8
CHO	-35.0	-36.3	249	12.6	13.1		-10.7	- 9.9	1.6	3.2	-3.4	-2.1	6.7	8.3
NO_2	-34.3	-35.9	249	17.3	19.6		-21.1	-20.5	8.2	9.7	-3.2	-1.7	7.3	8.3

The spectra were taken at low temperature in the liquid state using ethyl ether and cyclopentane as internal references respectively.

Sincerely yours,

69-4

Duke University
DURHAM
NORTH CAROLINA

DEPARTMENT OF CHEMISTRY

POSTAL CODE 27706
TELEPHONE 919-681-0111

May 20, 1964

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

Dear Dr. Shapiro:

We have recently observed a long-range effect of an asymmetric group on methylene non-equivalence in some ortho and meta substituted N,N dimethylbenzyl amines and one benzyl alcohol. This work, including some spectra, is scheduled to appear in the August J.A.C.S. The spectra of compounds included here were not submitted.

Eighteen compounds were investigated. In every case in which the molecule did not have a plane of symmetry, including some meta substituted compounds reported in the referenced paper, the benzylamine protons gave an AB quartet ($J \sim 12.5$c/s). Otherwise the normal A_2 singlet appeared as expected. Spectra I-VI illustrate the results obtained.

Spectra were run on a Varian A-60 equipped with a variable temperature probe. CCl_4 was the solvent for all but V ($CHCl_2CHCl_2$). Concentrations were in the range 0.5-1 M. TMS was used as internal reference. The probe temperature was ca. 32°C, except as noted in figures.

A preliminary temperature study on several compounds exhibiting the AB system indicates that the benzyl amine protons remain non-equivalent, though δ_{AB} is less at elevated temperatures than at room temperature.

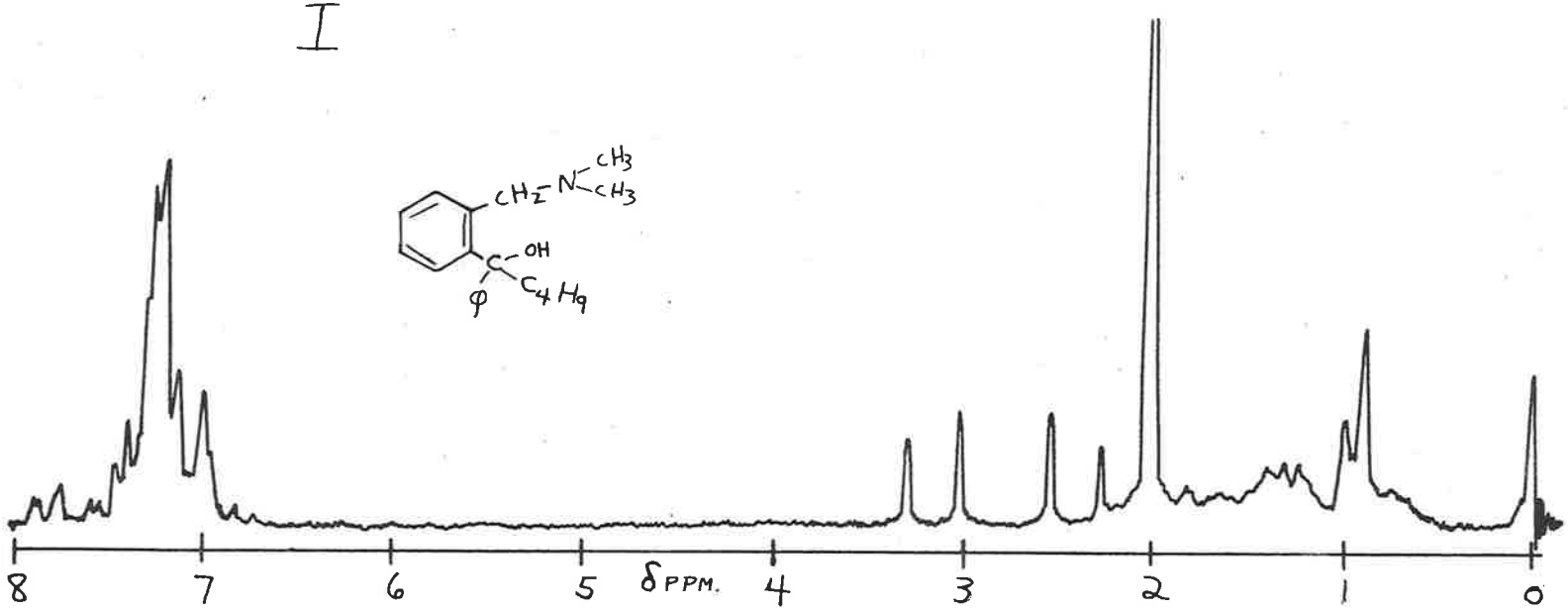
The benzyl amines were made available by the research group working here with Prof. C. R. Hauser. We wish to thank Dr. R. L. Vaulx and Mr. K. P. Klein for purified samples of the compounds reported herein.

Sincerely,

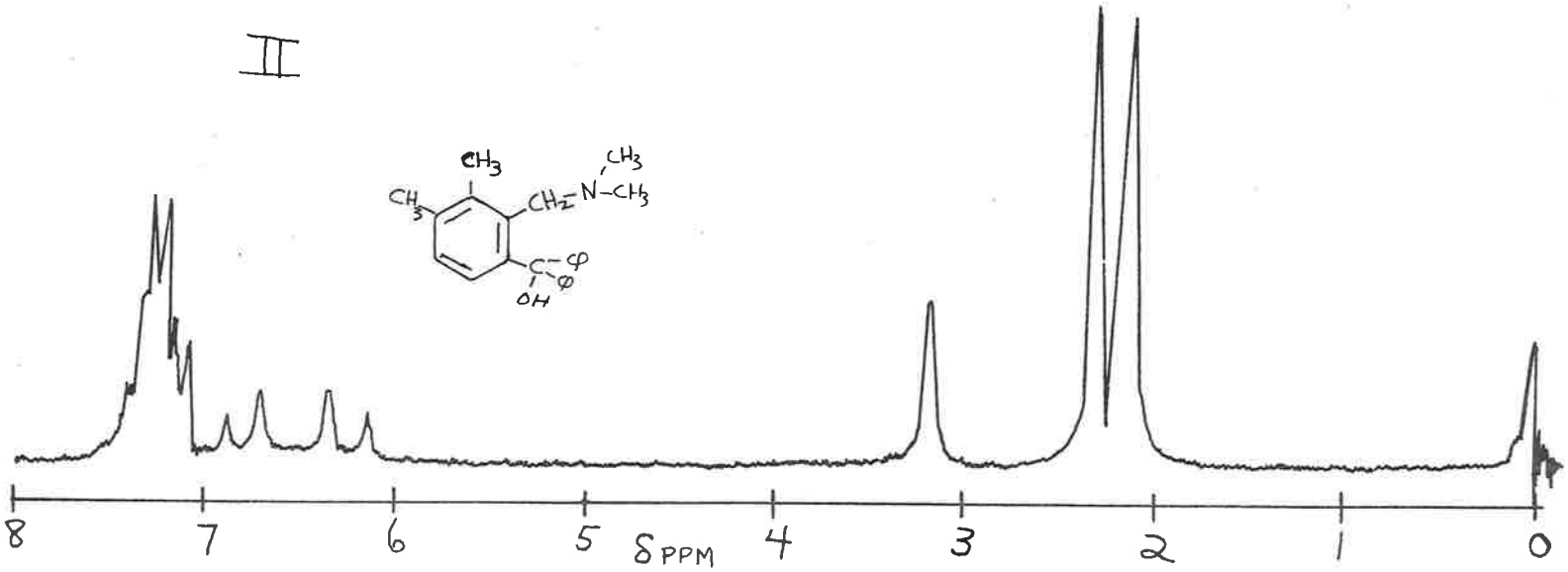
James C. Randall James J. McLeskey, III John E. Baxter

James C. Randall James J. McLeskey, III John E. Baxter

I



II



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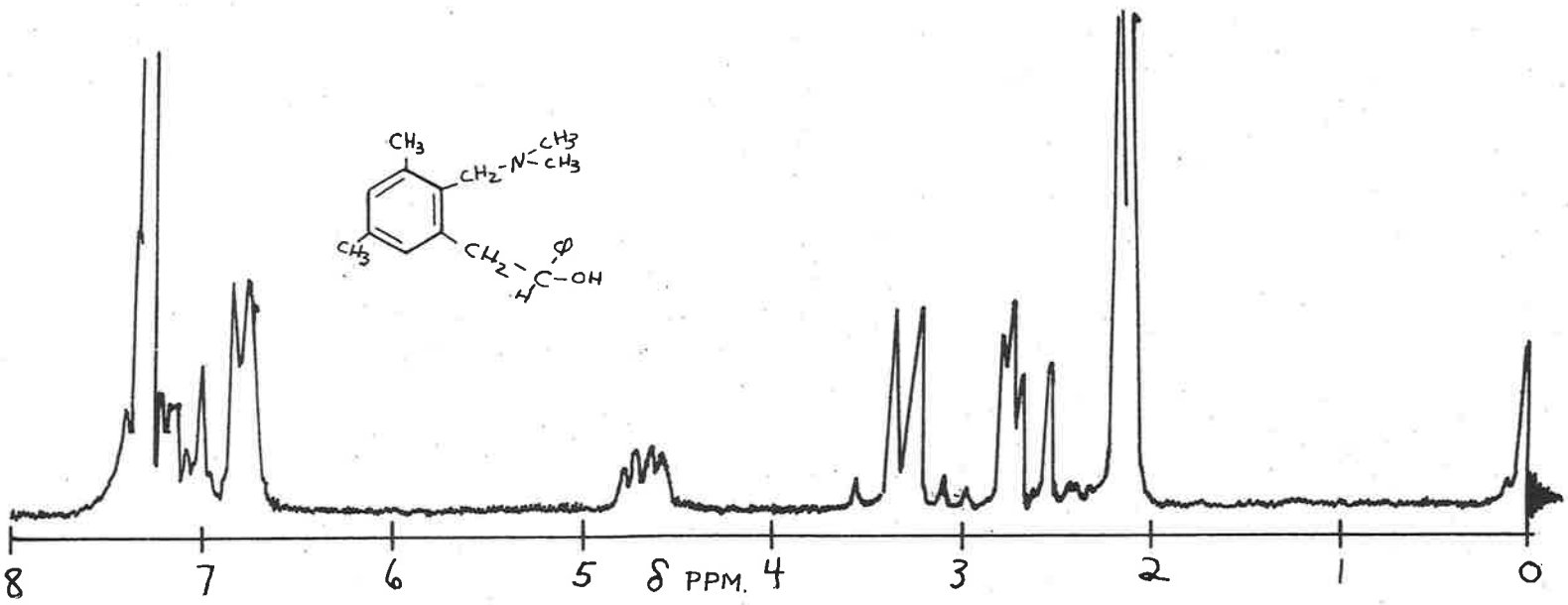
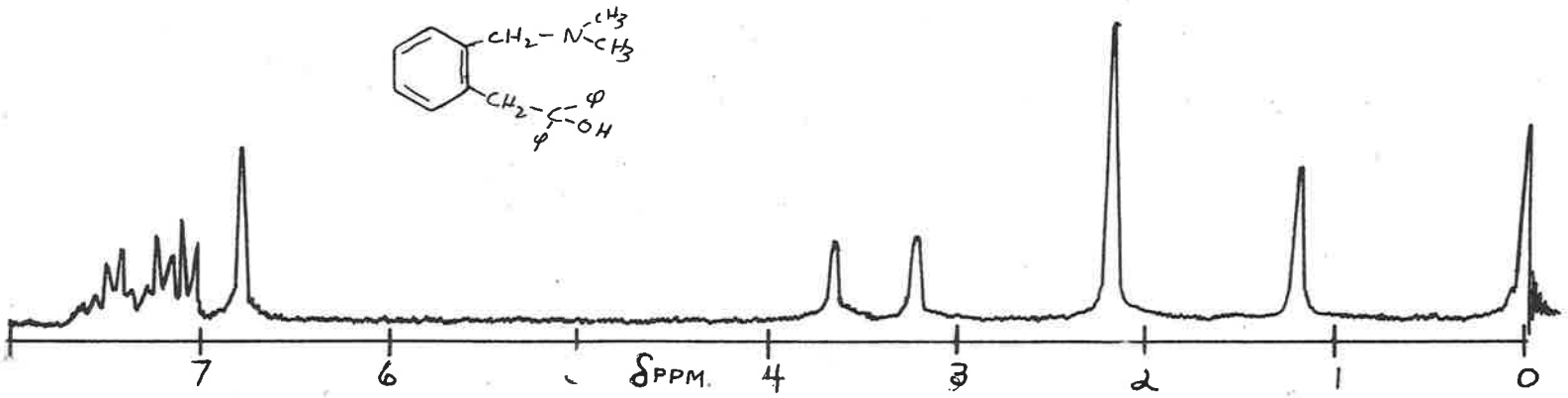
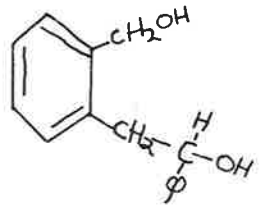


IV



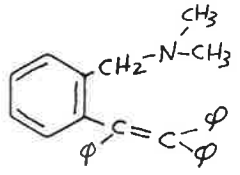
V


CH_2OH
CH_2
H
C
OH
φ

T = 67 °C

8
7
6
5
δ PPM.
4
3
2
1
0

VI


CH_3
CH_2–N–CH_3
φ
C = C
φ
φ

8
7
6
5
δ PPM.
4
3
2
1
0

69-8

KARL-MARX-UNIVERSITÄT

PHYSIKALISCHES INSTITUT

LEIPZIG C1, LINNÉSTR. 5 · TEL. 64511, 65342, 65150

am 24. 5. 64 Az.: Deut/her

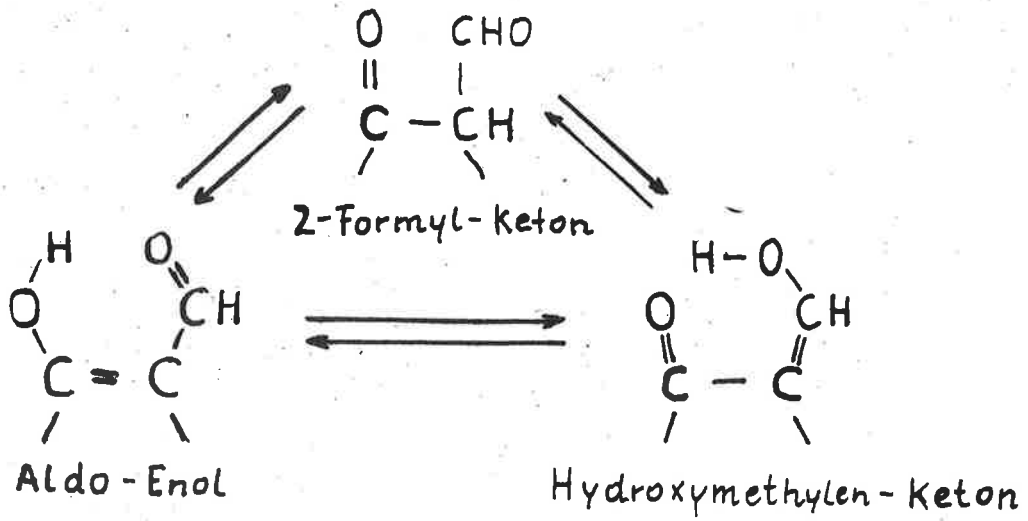
Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Hydroxymethylen - Aldo Enol Gleichgewicht von 2 - Formylcycloketonen

Sehr geehrter Herr Professor Shapiro!

Mit einem Trüb-Täuber-Spektrometer (25 MHz) untersuchten wir bei Zimmertemperatur das Hydroxymethylen- Aldo Enol Gleichgewicht an einer Reihe 2 - Formylcycloketonen. Die Ergebnisse werden für Sie vielleicht von Interesse sein.

Für diese Substanzen sind folgende Tautomere möglich:



	τ_{CH} [ppm]	Hydroxymethylen Keton		%
Hydroxymethylen-cyclopentanon	2,66	75 %	78 %	[1]
2-Formylcyclo-hexanon	1,39	24 %	24 %	[1]
Hydroxymethylen-suberon	2,35	63 %	66 %	[1]
Hydroxymethylen- - indanon	2,44	66 %		
2 - Formyltetralon	1,84	42 %		
Hydroxymethylen-benzsuberon	2,o5	5o %		

In der Tabelle sind nur die τ -Werte für die CH-Linien angegeben.
In Übereinstimmung mit der Arbeit von Edgar W. Garbisch [1] haben wir gefunden, daß zwischen der Aldo Enol - und der Hydroxymethylen - Ketonform ein sehr schneller Austausch stattfindet, so daß für die CH und OH keine getrennten Linien auftreten.
Verwendet man die gleichen Bezugsstoffe wie [1], so erhält man für die Konzentration der Hydroxymethylen-Ketonform die in der Tabelle angegebenen Werte.
Die 2 - Formylketonform tritt nur bei Hydroxymethylencyclopentanon auf. Aus den Intensitäten der entsprechen Linien ergibt sich 1o,6 %.

Inge Deutsch
(Inge Deutsch)

Literatur:

[1] Edgar W. Garbisch J. Am. Chem. Soc. 85 1696 (1963)

69-10

THE SCHOOL OF PHARMACY

UNIVERSITY OF LONDON

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

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

WBW/CLS

3rd June, 1964

Dear Dr. Shapiro,

I must apologise for having fallen behind with our contribution to the IIT NMR Newsletter but I plead as an excuse a relatively protracted absence from the Department occasioned by my visit to the Third International Symposium on the Chemistry of Natural Products in Japan.

Since we presently do not have another contribution concerning NMR itself, you may be interested in the following information about a Summer School in NMR Spectroscopy for organic chemists which is being run from 6th - 12th September at the School of Pharmacy. This is part of the Summer Schools programme of the Royal Institute of Chemistry: it has been designated a NATO Advanced Study Institute. The emphasis throughout is on the interpretation of spectra in terms of an organic structure. Morning lectures will cover the main aspects of theory, whilst afternoon sessions will be organized for small groups of ten participants each in the charge of a tutor. During these sessions, actual spectra will be discussed and analyzed qualitatively, although no mathematics other than simple algebra are required - the course is specifically designed for organic chemists!

Instrumentation for such a course is a problem but in addition to our own A60, the manufacturers have been extremely co-operative and we are keeping our fingers crossed and hope that the utility of spin decoupling and 100 Mc runs can be demonstrated.

As a measure of the interest in this venture, applications from Europe and America have topped the 170 mark. We can offer 100 places!

I hope this contribution makes some reparation for our past omission and that we will continue to receive your most useful Newsletter.

Yours sincerely,

W. Basil Whalley

W. B. Whalley

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

CONOCO

CONTINENTAL OIL COMPANY

P. O. DRAWER 1267
PONCA CITY, OKLAHOMA
Research and Development Department

June 4, 1964

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

Dear Barry:

Parameters for Diethylaluminum Hydride

We would like to add one more compound to the fine list submitted by Brügel (IITNMR 68, 26). For $(CH_3CH_2)_2AlH$, δ_{CH_2} = 0.23 ppm, δ_{CH_3} = 1.11 ppm, $\delta_H \approx$ 2.9 ppm and J = 8.3 cps. Our results for $(CH_3CH_2)_3Al$ duplicate those of Brügel.

Sample Boiling

The Varian V-4340 Variable Temperature Probe Accessory requires a sample tube at least 6" long. Only the lower 2½" of this tube is heated; thus when a sample is heated above the boiling point, refluxing occurs. To stop this we have been inserting a glass rod, just smaller than the I.D. of the sample tube, into the sample tube before sealing. The bottom of the glass rod should project slightly into the heated zone. Using this device we have examined water solutions at 175° C. Care must be taken that the tube is not liquid-full at temperature. The device prevents refluxing, not explosions!

P. W. Flanagan

P. W. Flanagan

C. E. Godsey

C. E. Godsey

PWF-CEG/CC

A BROAD-LINE PROTON MAGNETIC RESONANCE STUDY OF A POLYCRYSTALLINE URANIUM OXIDE HYDRATE

David Scott Olson, Jeff C. Davis, Jr., and James E. Boggs
Dept. of Chemistry, The University of Texas

The broad-line nuclear magnetic resonance spectrum of polycrystalline $UO_3 2H_2O$ has been studied at 56.4 Mc from 107°K to 300°K and the low temperature spectrum analyzed to determine the structure of the solid. The second-moment at 107°K of 23.9± 0.2 $gauss^2$ and the shape of the experimental curve indicate that this compound is not a simple hydrate. The best fit is obtained with parameters corresponding to the empirical formula $U_2O_5(OH)_2 \cdot 3H_2O$. The second moment calculated with these parameters is 24.2 $gauss^2$.

P.S. A NOTE ON CLOGGED A-60 MAGNET SYSTEMS

Sometimes the terrible mismatch that arises between administration, research people, plumbers, and the like can have disastrous results. We here at Texas have just pulled through such a disaster - a completely clogged cooling system in the A-60. With little help from Varian Associates (but lots of guesses on their part regarding the details of the magnet construction) we have managed to completely clear the system and we thought it might be of interest to others just how one cleans out 100+ feet of small diameter copper tubing rather tightly coiled inside a magnet. The unlikely solution (and I still can't help shuddering at the thought) turned out to be a mixture of fluoroboric acid and HF. This was forced into one end of each coil using a completely closed water-hammer vacuum system. After numerous washings the mess on the inside was eaten out and as far as we can tell no damage was done to the coils or any of the rest of the cooling system. Valves and the like were bypassed in this operation and each coil treated separately. We may never recover from this traumatic experience but hope that this information (the last of several things we tried) may save the day for anyone else who encounters similar troubles.

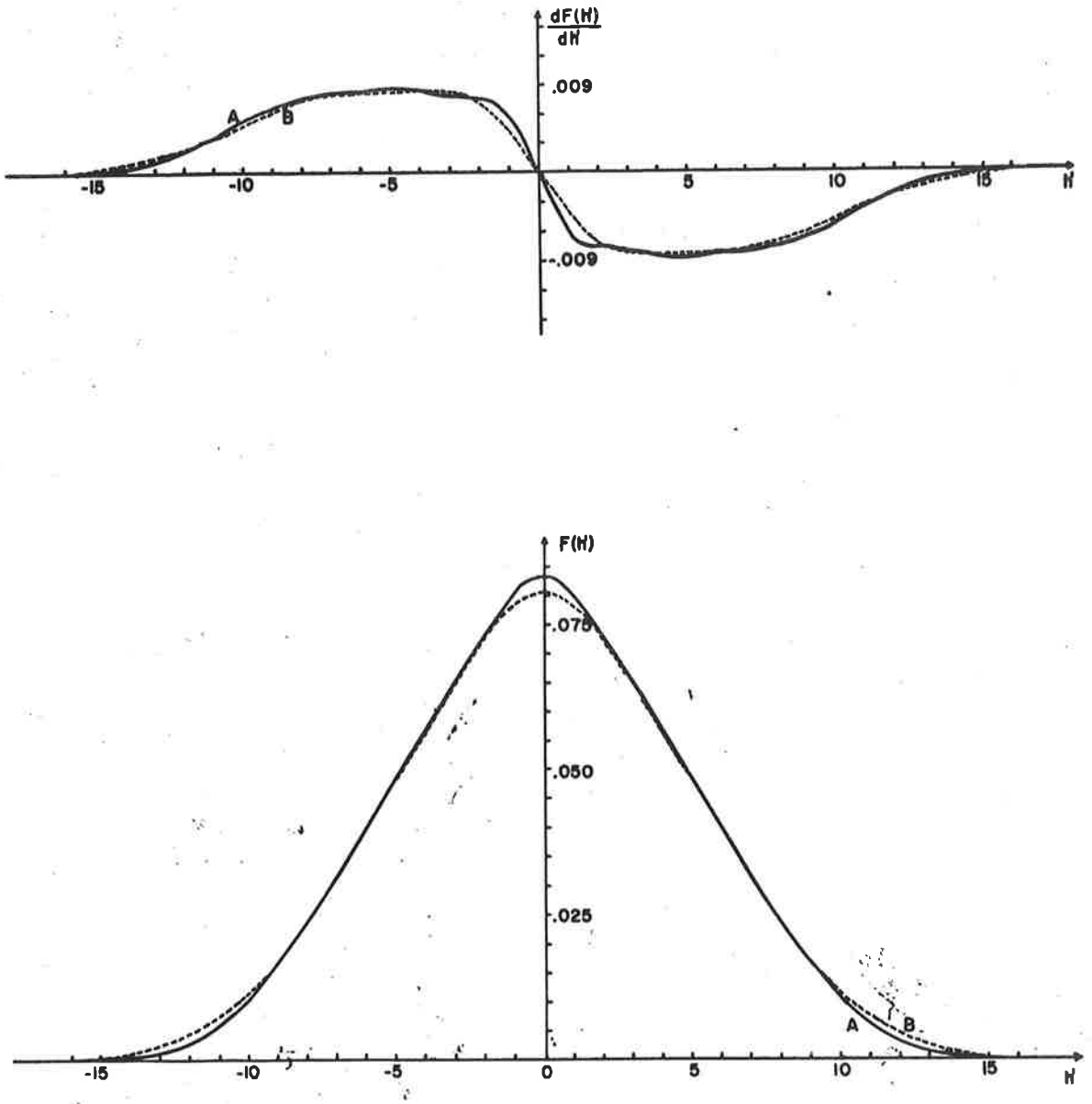


Figure ■. Observed and Theoretical Curves. Curves A (——) were observed for α-$UO_3 \cdot 2H_2O$ at 107°K. Curves B (---) were obtained from equation (22) with α_1 = 5.4 gauss, β_1 = 2.8 gauss, α_2 = 1.1 gauss, and β_2 = 2.4 gauss.

69-14

UNIVERSITY OF PITTSBURGH

PITTSBURGH 13, PENNSYLVANIA

DEPARTMENT OF CHEMISTRY

June 1, 1964

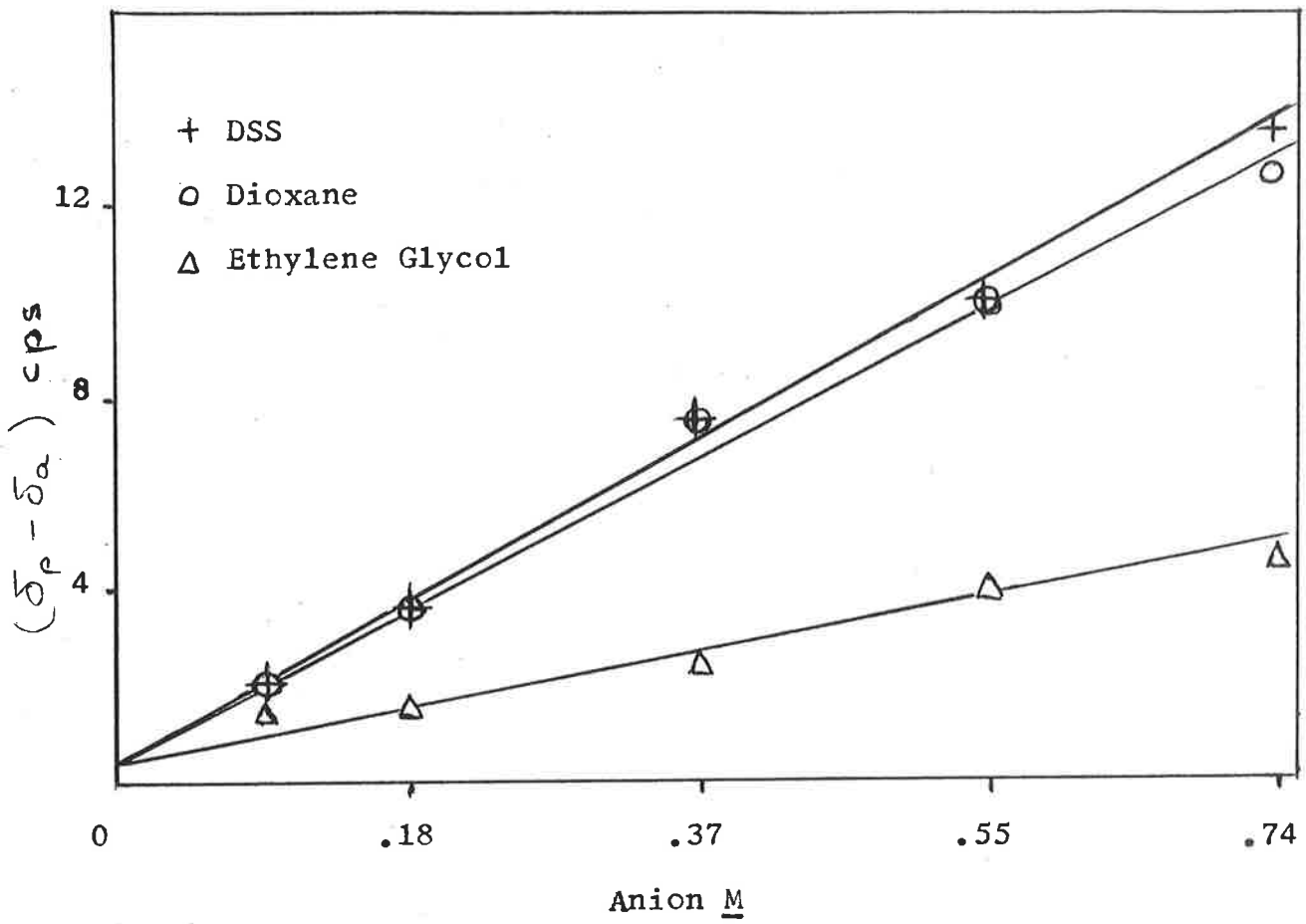
Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois, 60616

Large medium effects on the chemical shift of DSS and other "standards"

Dear Barry:

During the course of some n.m.r. studies on aqueous solutions of 1,3-naphthalenediol we observed that the absorption of various internal "standards" was shifted upfield and that this shift depended on the concentration of the naphthalene. Since the methyl absorption of sodium trimethylsilylpropane sulfonate (DSS), in particular, is generally believed to be independent of the presence of solute in dilute solution we are submitting some preliminary results as a word of warning.

The water absorption was at δ = 4.74 p.p.m. at 27°, when external TMS = 0, and shifted only slightly (to 4.72) when internal DSS = 0. In the presence of 1,3-naphthalenediol (supersaturated, approximately 1 M) the water peak had the same chemical shift (to within 1-2 cps, relative to external TMS) but the DSS absorption was now shifted upfield by ca. 35 cps! The acetonitrile and dioxane peaks were upfield by ca. 16 cps, while the methylene absorption of ethylene glycol was shifted upfield by only 2 cps. Consecutive approximate 1:1 dilutions with water showed that these shifts decreased linearly with decreasing naphthalenediol concentration. In the presence of naphthalenediol monoanion the DSS, dioxane and ethylene glycol absorption peaks were also shifted upfield (acetonitrile was not tested). The pertinent chemical shifts of a solution 0.74M in the K salt of naphthalenediol, 0.067 M in DSS, 0.25 M in dioxane, and 0.29 M in ethylene glycol were measured. This solution was then diluted for subsequent measurements. After the final dilution (0.09 M in K salt) the concentrations of DSS, dioxane and ethylene glycol were increased to about their original molarity. No change in their chemical shifts was observed. The dependence of the chemical shifts of these compounds on the anion concentration is depicted below. The ordinate is the shift of DSS, etc. from the water peak in the presence of the anion (δ_p) minus the shift of the corresponding compound from the water peak in the absence of naphthalenediol (δ_a). The effect



of the anion is appreciably less than the effect of the neutral naphthalenediol on the DSS absorption; about the same on the dioxane absorption; and somewhat greater on the ethylene glycol absorption. Since the slopes of $[\delta_p - \delta_a]$ (or δ_p) vs. the concentration of the anion (or the neutral species) are not the same it cannot be primarily the absorption of the water that is affected by the naphthalene derivative. Thus, in this instance the solvent water absorption appears to be a much more reliable standard than other added materials.

Please add my name to your mailing list.

Best regards,

Elli

Elli Smakula Hand

69-16

THE UNIVERSITY OF MANCHESTER,

DEPARTMENT OF CHEMISTRY,

MANCHESTER, 13.

TELEPHONE: ARDWICK 3333

8th June, 1964.

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

Dear Professor Shapiro,

Our contribution to I.I.T.N.M.R. gives some preliminary results on internal rotation and proton exchange phenomena. We used a Mercury programme first devised by Joe Lee[1] which has now been modified for the Atlas computer.

Internal Rotation: Dimethyl nitrosamine has been studied by Looney et al[2] who reported a coalescence of the methyl doublet at ~180°C and an activation energy of 23 k.cal.mole^{-1}. We observe two clearly resolved lines up to 190°C and coalescence began above this temperature near the upper limit of our probe. The approximate activation energy calculated from the ratio of maximum to minimum intensities in the V-mode is 24±5 k.cal.mole^{-1}, but a value of 10±3 k.cal. is obtained from the temperature dependence of the separation of the lines. We hope to resolve this difference by extending the range of our A60 probe to give a more reliable result.

Proton Exchange: The CH_3 doublet arising from coupling to the NH proton in N-methylformamide has a coalescence temperature of 130°C so we have been able to study the rate process over a much wider range of temperature. Activation energies were calculated by four different methods with the results:

Before Coalescence		After Coalescence	
Ratio of $\frac{\text{max.}^m}{\text{min.}^m}$ in V-mode	Peak Separation	Half Band Width	Peak Height.
Ea k.cal.mole^{-1}	Ea k.cal.mole^{-1}	Ea.k.cal.mole^{-1}	Ea k.cal.mole^{-1}
9.5	14.4	12.6	16.5

Since it is difficult to decide whether these differences are real we have investigated Ea in a range of solvents. For a given method of calculation, consistent values of Ea were obtained in a range of solvents at various concentrations. However, comparing the different methods of calculation for a given solution, again showed a spread in activation energy.

Yours sincerely,

G. Allen.

G. Allen

D. J. Blears.

D.J. Blears.

1. J. Lee Private communication.

2. Looney, Phillips and Reilley. J. Amer. Chem. Soc. 72, 522 (1957).

69-18

Hubert Schmidbaur, Walter Siebert
INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MARBURG
DIREKTOR: PROF. DR. MAX SCHMIDT

355 MARBURG, Gutenbergstraße 18
Fernruf 731, Nebenstelle 3614
bei Durchwahl 733614

8. Juni 1964

Prof. Dr. B. L. Shapiro
Illinois Institute of Technology
Department of Chemistry, Technology Center
Chikago 60616, USA

Coupling Constants and isotopic effects in hydrogen sulfide, selenide and telluride

Dear Dr. Shapiro

In this contribution to IIT NMR Newsletters we wish report some results of our NMR studies on hydrogen sulfide, selenide and telluride H_2X (where X= S, Se, Te).

In order to determine the proton-proton coupling constants $J_{gem}(\underline{H}X\underline{H})$ we undertook the preparation of the partially deuterated species HXD from the reaction of the appropriate aluminium chalcogenide Al_2X_3 with mixtures of hydrogen and deuterium oxide in various relative concentrations, ranging from H_2O/D_2O = 50/50 up to 1/99 (in which, of course, HOD is present as well):

$$Al_2X_3 \xrightarrow{HOH/HOD/DOD} H_2X \;/\; HXD \;/\; D_2X \;.$$

The gaseous mixtures obtained from these reactions were bubbled into pure carbon disulfide at low temperatures and the saturated solutions subjected to PMR investigations in a Varian A 60 at room Temperature (sealed tubes.)

The products isolated from Al_2S_3 and H_2O / D_2O = 75 / 25 proved to consist of nearly aequimolar amounts of H_2S and HSD by the appearence of a singulett at -43 c/s (internal reference TMS) and a 1:1:1 triplett at -41 c/s. The low-field triplett signal obviously was in coincidence with the singulett. (D_2S, of course, did not show up at all in PMR.) On reduction of the percentage in H_2O down to 5% v/v the H_2S could be eliminated and a clear 1:1:1 triplett was observed for HSD : J_{gem}(HSD) = 2.0 c/s ($\mp$ 0.1 c/s). The isotopic shift HSH / HSD, leading to the coincidence of the low field in stead of the

central triplett signal and the singulett signal, is of rather unusual magnitude and is incidentally equal to J(HSD) at 60 Mc (2.0 c/s). Hydrolysis of Al_2Se_3 with H_2O / D_2O mixtures required a H / D ratio of 5 / 95 in order to obtain reasonable amounts of HSeD along with H_2Se and an excess of D_2Se. The spectrum of this mixture showed the same general features with a H_2Se singulett at + 63.7 c/s and a 1:1:1 triplett for HSeD at + 65.8. Again the low field triplett signal overlapped with the singulett and a J_{gem}(HSeD) and an isotopic shift HSeH / HSeD of 2.1 $\mp$ 0.1 c/s could be determined.

In the hydrolysis of Al_2Te_3 a tremendous isotopic effect was observed for this reaction. Even when treated with H_2O / D_2O mixtures of the ratio 1.5/98.5 almost only H_2Te and D_2Te were formed in company with very small amounts of HTeD, showing up as a triplett of an intensity being nearly in the signal to noise limit of the experiment. Surprisingly, coupling constant J_{gem}(HTeD) and isotopic shift were again of the same order and direction, namley 2.1 c/s. δ_{H_2Te} = + 323.5 and δ_{HTeD} = + 325.6 c/s at 60 Mc.
(Negative δ-values are supplied for the low field side of TMS)
The constants J(HXD) now may easily be converted by multiplication with the factor 6.5144 to obtain the desired J(HXH) values.

At present no satellite signals, arising from spin-spin coupling of the protons with the isotopes ^{77}Se and ^{125}Te could be detected. This may be due to the small intensity of these satellites or to the relatively small recording range of the A 60 (-2000 to + 1000). We therefore are trying now to extend this range by the well known auxiliary apparatus.

Finally we want to thank You for the reliable delivery of the Newsletters, which were always quite interesting and helpful for both of our NMR laboratories here in Marburg.

Yours sincerely

(Walter Siebert) (Hubert Schmidbaur)

W. Siebert. H. Schmidbaur

69-20

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA 90024

June 11, 1964

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

Dear Barry:

^{1}H and ^{31}P Magnetic Resonance Spectra for $CH_2=CHP(CH_3)_2$

We are continuing our investigations of vinyl tin and phosphorus derivatives from the stock of compounds presently available to us (of which a sample of trivinylphosphine was shared with W. A. Anderson and R. Freeman at Varian Associates who used it to illustrate the technique of double-quantum transitions, double resonance "tickling").[1]

We can present some preliminary results on the derivative dimethyl-(vinyl)phosphine, see Fig. 1 and Table I. The parameters may be compared with those reported previously for trimethylphosphine[2] and trivinylphosphine.[1] The second order vinyl pattern was analyzed with the aid of the self-iterating program of Swalen and Reilly;[3] the calculated spectrum thus obtained is compared to the observed spectrum, on Fig. 2.

With the above mentioned parameters we intend to calculate a ^{31}P spectrum to compare with the observed (upper trace, Fig. 1). We do not at this time wish to submit that spectrum in Manatt and Juvinall's ^{31}P-resolution contest[4] (we plead insufficient notice).

We have built the necessary apparatus and are in the process of converting a Varian HR-60 into a double quantum resonance capability with the help of Mr. Richard Gillespie of this Department and after several visits to the laboratories of Stan Manatt and Dan Elleman at J.P.L. With this we will check the above (and future) assignments and hope to contribute to the knowledge of relative signs of phosphorus-proton and proton-proton coupling constants.

Best wishes for the continued success of this newsletter at your new address.

Sincerely yours,

Michael L. Maddox

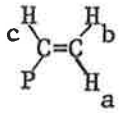
Herb

Herbert D. Kaesz

MLM/HDK:smd
Refs., Table and two figs. attached

Maddox and Kaesz p.2

TABLE I



	δ_{CH_3}*	δ_{H_a}*	δ_{H_b}*	δ_{H_c}*	J_{PCH_3}**	$J_{P\text{-}H_a}$**	$J_{P\text{-}H_b}$**	$J_{P\text{-}H_c}$**	$J_{^{13}CH_3}$**
$(CH_3)_3P$ (2)	0.89				2.7				126.7±0.2
$(CH_3)_2PCH{=}CH_2$***	0.953	6.18	5.46	5.34	2.88	14.68	25.43	11.93	127.9±0.2
$P(CH{=}CH_2)_3$ (1)		6.16	5.64	5.51		13.62	30.21	11.74	

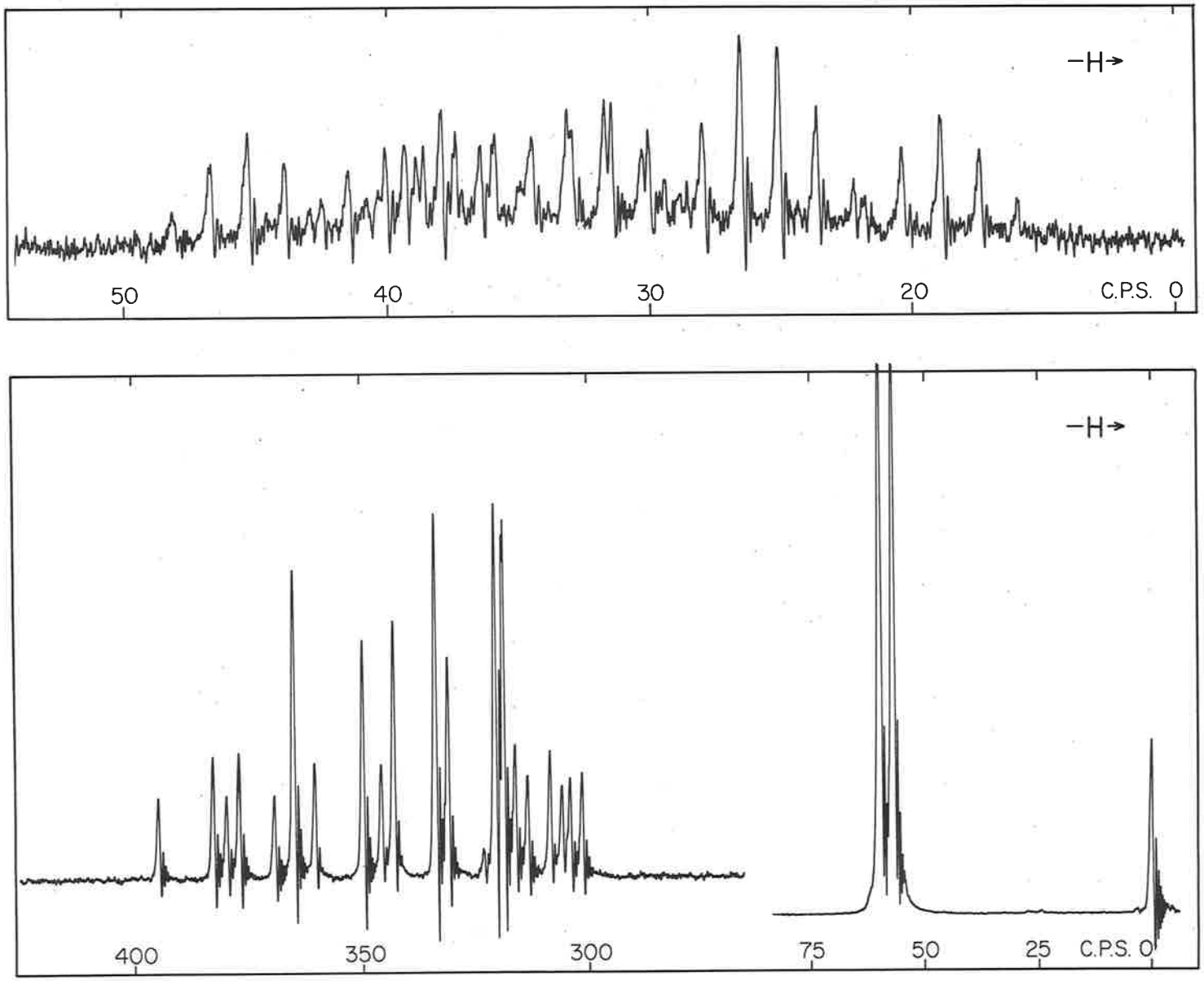
	$J_{H_b\text{-}H_c}$**	$J_{H_a\text{-}H_c}$**	$J_{H_a\text{-}H_b}$**
$(CH_3)_2PCH{=}CH_2$***	11.76	18.28	1.99
$P(CH{=}CH_2)_3$ (1)	11.76	18.37	2.02

Footnotes to Table I

(*) Chemical shift, p.p.m., downfield from hexamethyldisiloxane, internal standard.
(**) Spin coupling parameters, c.p.s.
(***) This work.

References

(1) W. A. Anderson, R. Freeman and C. A. Reilly, J. Chem. Phys., 39, 1518 (1963).
(2) Chemical shift and $^{31}P\text{-}CH_3$ coupling constant: J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, Tetrahedron, 20, 449 (1964); $^{13}CH_3$ coupling constant, this work.
(3) J. D. Swalen and C. A. Reilly, J. Chem. Phys., 37, 21 (1962).
(4) I.I.T.N.M.R. No. 68, p. 2 (1964).



$(CH_2=CH)P(CH_3)_2$
NEAT Liquid
^{31}P – 19.25 Mc/s

$(CH_2=CH)P(CH_3)_2$
NEAT Liquid
HMDS STD.
^{1}H – 60 Mc/s

Fig. 1

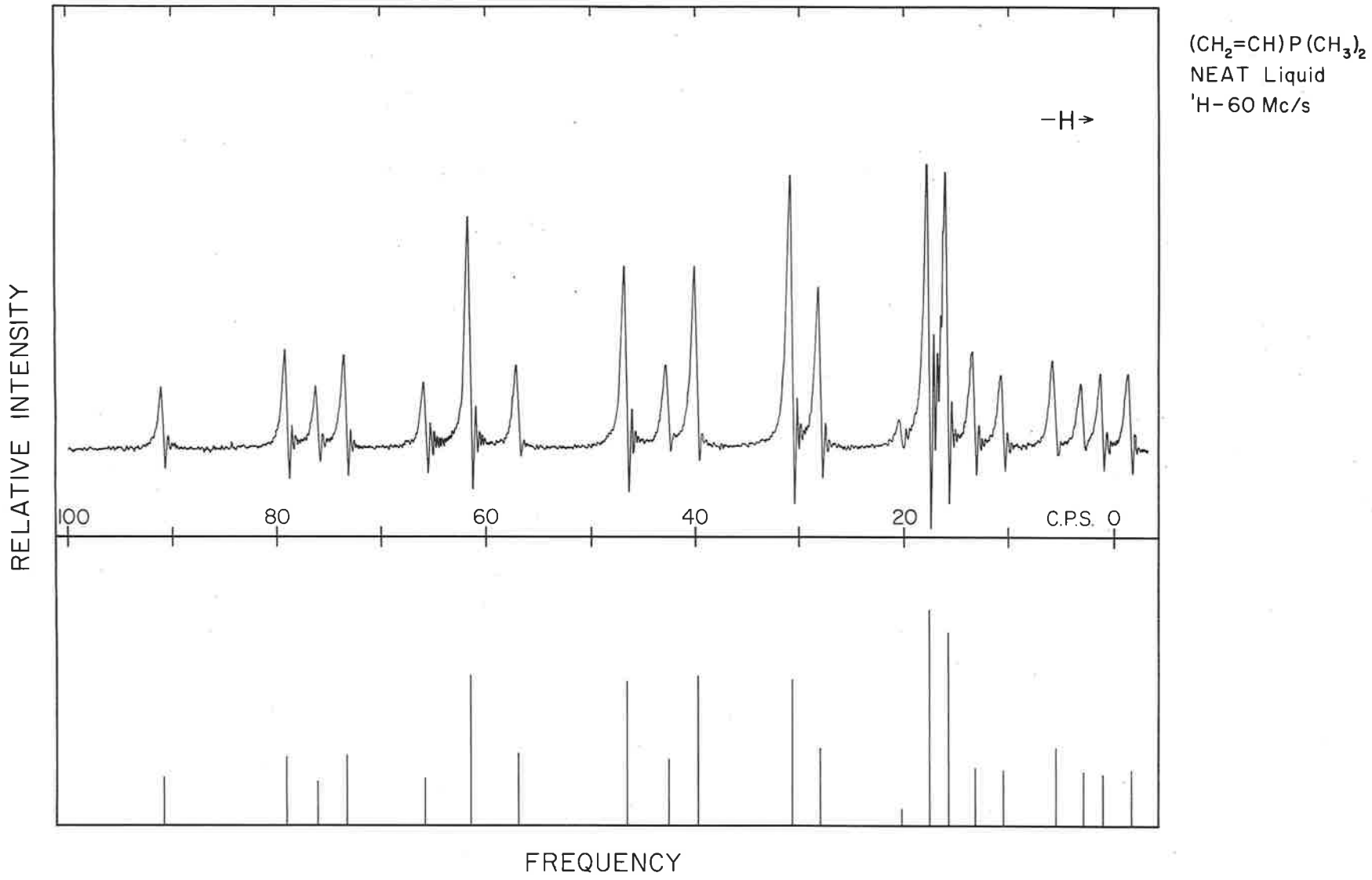

$(CH_2=CH)P(CH_3)_2$
NEAT Liquid
^1H-60 Mc/s
-H→
RELATIVE INTENSITY
100
80
60
40
20
C.P.S. 0
FREQUENCY

Fig. 2

69-24

THE UNIVERSITY OF BIRMINGHAM

TELEPHONE: SELLY OAK 1301

Chemistry Department,

BIRMINGHAM. 15.

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

26th May 1964.

Dear Professor Shapiro,

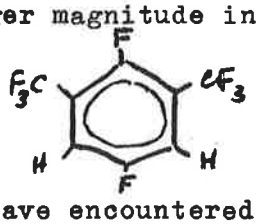
With apologies for the delay in sending this subscription to IITNMRN I shouldlike to make some observations on fluorine-fluorine coupling constants in aromatic molecules. Dr.Homer and I have looked at a series of amino- and nitro- derivatives and find the following:

J_{FF}(c/sec).	ortho	meta	para
Pentafluoroaniline	21.6, ±20	8.2, ~6, ~3	∓4
3,4,5,6-tetrafluoro-1,2-phenylene diamine	21.4, ±21.6	±6.6	6.2
2,4,5,6-tetrafluoro-1,3-phenylene diamine	21.2	0	6.6
2,3,4,5-tetrafluoro-6-nitro-aniline	19.9, 21.1, 22.5	6.4, 7.7	8.8
2,3,5,6-tetrafluoro-4-nitro-aniline	±21.5	8.8, 9.5	∓5.3
4,5,6-trifluoro-2-nitro-1,3-phenylene diamine	22.3		
2,4,5-trifluoro-6-nitro-1,3-phenylene diamine	20.8	3.7	8.2

Whilst the ortho constants are in the usual small range, those of meta and para vary quite widely. It is interesting too, that although the para couplings are of opposite sign to the ortho, as previously reported, the one meta coupling of determinable relative sign is of the same sign as the ortho.

Mr.Ayanbadejo has been investigating perfluorotoluene and the perfluoro-xylenes and some derivatives thereof, and ring coupling constants fall

in the range:

ortho: 17.6 to 19.9, meta: 6.0 to 14.6, para: 6.8 to 13.2 c/sec, with meta and para both of opposite sign to the ortho where determinable. Meta and para couplings are of larger magnitude in this series and, incidentally, the para coupling in  is no less than 19.0c/sec., easily the largest we have encountered so far.

Most of this data was obtained from spectra at 30.107 Mc/sec. Now that we have a Varian HR 100 spectrometer we are looking further at some of these compounds particularly with respect to relative sign determination.

Yours sincerely,

L. F. Thomas

L.F. Thomas.

69-26

SOCIETÀ EDISON

SOCIETÀ PER AZIONI CON SEDE IN MILANO
CAPITALE SOCIALE L. 375.000.000.000 - INTERAMENTE VERSATO
LABORATORIO RICERCHE DI BOLLATE

SETTORE CHIMICO

BOLLATE 25 May 1964

Località Traversagna - Telefoni 2910 - 2919
Casella Postale N. 15

Nella risposta citare il N° 2718/Cav/td

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

Subject: 2-chlorocyclohexanonoxime

Dear Professor Shapiro,

since my return from Liverpool, where I worked for a few months at the University under the direction of Dr. R.J. Abraham, I have been wondering whether I might become a recipient of your interesting and useful IIT NMR Newsletter. As a matter of fact I am working now with a new Varian A60 and I am realizing the importance of receiving the Newsletter for a profitable work in the NMR field. I know that participation is the prime requisite for receiving the IIT NMR Newsletter, so I send a short contribution on what we have begun to do in our laboratories, hoping it is of interest to some readers.

A colleague of mine and I have had some problems concerning the structure of a few oximes. We hereby enclose the 60 Mc spectrum of the 2-chlorocyclohexanonoxime (in 10% $CDCl_3$ solution). It shows two signals $\tau = 4.37$ and $\tau = 5.29$ having one intensity ratio of about 1 : 3 and corresponding on the whole to a single proton. The region where they appear in the spectrum leads us to attribute them to CHCl. According to Phillips and Lustig (1) we assign the signal at $\tau = 4.37$ to the syn isomer and the signal at $\tau = 5.29$ to the anti isomer. In addition we have noticed that the syn/anti ratio changes with time, reaching the steady value of 1 : 3 after approximately 1 hour, being all in favor of the anti isomer as the solution is prepared. The half band-width (6÷7 c.p.s.) of these two signals are typical of an equatorial proton.

On the ground of these observations we think that the compound in question is a mixture of syn- and anti- isomer with approximative ratio 1 : 3, both in the chair conformation with chloro atom in axial position. Such a conclusion seems to us substantiated by the doublet $\tau = 6.89$, whose spacing (15 cps) is independent of the strength of the applied magnetic field and of the nature of the solvent. The intensity of this doublet is to be referred to 0.75 protons. Molecular models show that in the chair conformations of the anti-2-chlorocyclohexanonoxime the C_6 equatorial proton has a H ... O distance much smaller than the

./.

corresponding distance of the (axial) geminal proton. We therefore think that the C_6 equatorial proton of the anti-isomer, deshielded by the anisotropic magnetic effect of the oxime neighbour group and coupled with the axial geminal proton, approximates the A part of an AB type system, having a coupling constant $J_{AB} \simeq 15$ c.p.s. giving rise to the doublet at $\tau = 6.89$.

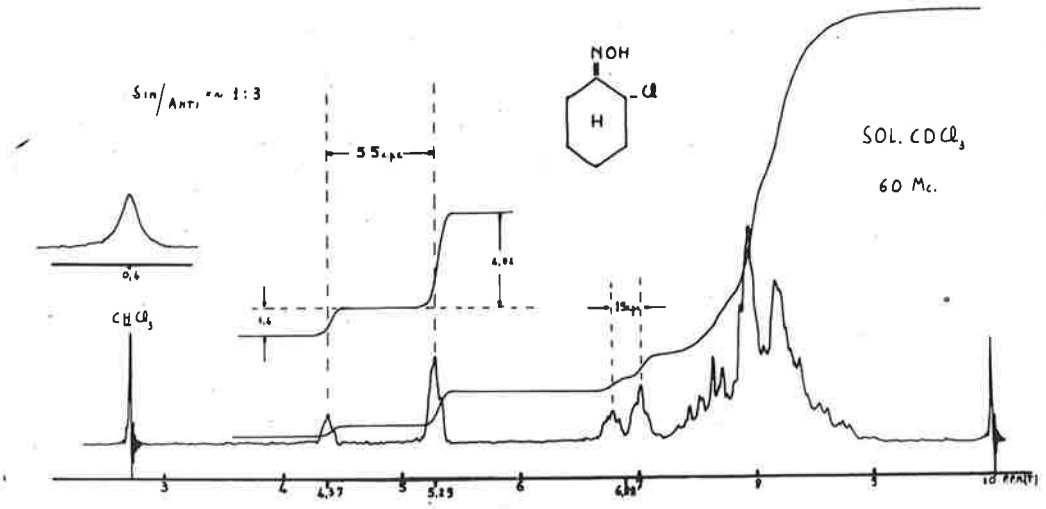
Work is in progress concerning other 2-substituted cyclohexanonoximes.

Yours faithfully

Luciano Cavalli

Luciano Cavalli

(1) W.D. Phillips, Ann. N.Y. Acad. Sci. 70, 817, 1958
E. Lustig, J. Phys. Chem. 65, 491, 1961



Illinois
Institute of
Technology
N-M-R
Newsletter

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

June 4, 1964

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

Dear Barry:

I hope this letfer beats our deadline. One of these days we are going to "pay up" our subscription in advance for five years and await your reaction.

We have just completed a study of selenophene and some of its halo-derivatives which will be submitted for publication shortly. Not surprisingly these compounds behave very much like the corresponding thiophenes, and rather unlike furan, particularly as regards the coupling constants, as the following tabulation for the parent heterocycles shows:

Cpd.	α	β	J_{23}	J_{34}	J_{25}	J_{24}
O	-437.57	-374.42	1.75	3.30	1.40	0.85
S	-430.90	-419.55	4.90	3.50	2.84	1.04
Se	-473.05	-433.57	5.40	3.74	2.34	1.46

The chemical shifts are at 60 Mc/sec, and extrapolated to infinite dilution in TMS, as solvent and internal reference.

The substituent effect at H_4 in the monohalo derivatives (C_2-X) shows the same anomolous behavior as in the corresponding thiophenes. Attempts at anisotropy corrections appear not to remedy this situation.

We also have obtained some preliminary indications of a correlation between coupling constants and mobile bond order in some of these series and hope to report this in detail later.

Sincerely,

J. H. Goldstein
J. M. Read
V. C. Thomas

JHG:lt

69-30

Delmau J
Faculté des Sciences de LYON
43 Bd de l'hippodrome
Villeurbanne (Rhône)
France

Lyon, le 12 Juin 1964

Doctor B.L.Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Cher Docteur Shapiro

L'étude des dioxannes-1,3 nous a conduits à examiner les couplages entre protons gem dans les dioxalanes. Peut-être certains de nos résultats vous interesseront-ils.

I - Méthyl-4-ethyl-4-dioxalane

- les protons en 2 ne sont pas différenciés et présentent une résonance unique.
- Par contre les protons en 5 sont différenciés et leur spectre du type AB donne directement

$$\delta = 6,3 \text{ cps}$$

$$|J_{gem5}| = 7,75 \text{ cps}$$

II - Dérivés monosubstitués en 4

Les protons en 2 sont maintenant différenciés (comme dans les dioxannes-1,3 où un substituant en 4 ou 5 fixe le composé dans la conformation chaise où le substituant est équatorial).

- Pour le chlorométhyl-4 les protons en 2 ont $\delta = 9,8$cps
- Pour l'éthyl-4-dioxalane $\delta = 8$cps

mais il est à remarquer que pour les 2 dérivés

$$J_{gem2} = 0 \text{ cps}$$

tandis que pour les dioxannes $|J_{gem2}| = 6,0$ cps

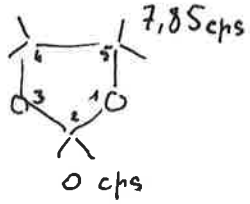
III- Dérivés monosubstitués en 2

Nous avons étudié le Méthyl-2-dioxalane. Le spectre des protons en 4 et 5 du type A_2B_2 est tout à fait analogue à celui observé par B.Mathiasson pour le cycle du dioxalane-1,3 dans le 3-Bromo-2-thiophene aldehyde ethylène acetal. L'auteur donne (1)

$$J_{gem4} = J_{gem5} = 7,00\text{cps} \pm 0,30\text{cps}$$

Nous avons trouvé sur notre premier dérivé sa valeur absolue

$$|J_{gem5}| = 7,85$$



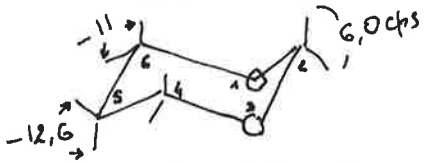
Enfin, Fraser, Lemieux et Stevens ont obtenu (2)

$$J_{gem5} = -8,3\text{cps}$$

— Rappelons que nous avons trouvé pour les dioxannes

$$J_{gem4.6} = -11,0\text{cps}$$

$$J_{gem5} = -12,6\text{cps}$$



ces valeurs étant sensiblement analogues pour les dérivés dans une conformation privilégiée (type Méthyl-4-dioxanne-1,3) et pour les dérivés donnant lieu à un échange entre deux conformations également probables (type dioxanne-1,3)

Recevez, cher Monsieur, mes sentiments les meilleurs.

C.Barbier et J.Delmau

(1) B.Mathiasson Acta Chem.Scand.17 N°7 p.2133 (1963)

(2) R.Fraser, R.U.Lemieux, J.D.Stevens J.A.C.S 83 3901 (1961)

69-32

CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK
PITTSBURGH 13, PENNSYLVANIA

June 5, 1964

DEPARTMENT OF CHEMISTRY

TELEPHONE: 621-2600
AREA CODE 412

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

Dear Barry:

A molecular orbital theory of geminal proton-proton coupling

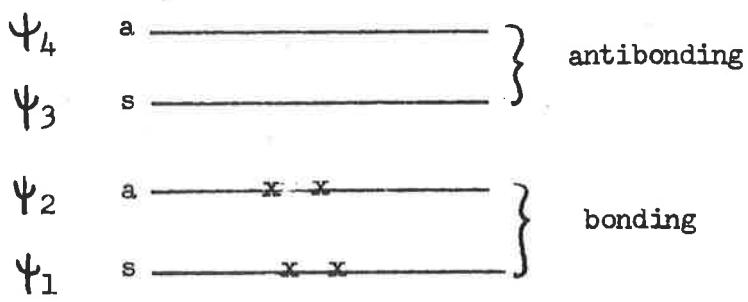
Some time ago (MELLONMR No. 60), David Santry and I wrote about a new molecular orbital theory of spin coupling and its application to directly bonded atoms. I now believe that the method leads to a simple interpretation of most observed trends in the coupling between hydrogen atoms separated by two bonds (geminal coupling).

The fundamental equation for proton-proton coupling constants is

$$J_{HH} = \hbar\left(4\beta\gamma_H/3\right)^2 S_h^4(0)\; 4 \sum_i^{occ} \sum_j^{unocc} (\epsilon_i - \epsilon_j)^{-1} C_{ih} C_{ih'} C_{jh} C_{jh'} \qquad (1)$$

where β is the Bohr magneton, γ_H the magnetogyric ratio of the proton, $S_h(0)$ the magnitude of a hydrogen 1S atomic orbital at the nucleus, ϵ_i the energy of a molecular orbital ψ_i and C_{ih}, $C_{ih'}$ the coefficients of the two 1S orbitals in the LCAO expansion of ψ_i. The sums over i and j are over occupied and unoccupied molecular orbitals respectively, so that the double sum is over all singly excited configurations.

The electronic structure of a CH_2 group may be described in terms of four molecular orbitals, ψ_1, ψ_2, ψ_3, ψ_4, two of which are double occupied. The energy level diagram is as follows:



ψ_1: CH bonding, symmetrical with respect to hydrogens, i.e. $C_{1h} = C_{1h'}$

ψ_2: CH bonding, antisymmetrical with respect to hydrogens, i.e. $C_{2h} = -C_{2h'}$

ψ_3: CH antibonding, symmetrical with respect to hydrogens, i.e. $C_{3h} = C_{3h'}$

ψ_4: CH antibonding, antisymmetrical with respect to hydrogens, i.e. $C_{4h} = -C_{4h'}$

ψ_1 is below ψ_2 in energy as it has some carbon 2s character while ψ_2 only involves carbon 2p. ψ_3 is below ψ_4 for the same reason.

Of the four possible configurational excitations, $2 \rightarrow 3$ and $1 \rightarrow 4$ make positive contributions to the coupling constant, while $1 \rightarrow 3$ and $2 \rightarrow 4$ make negative contributions. Now if electrons are withdrawn from the hydrogen part of ψ_1, ψ_1 becomes less hydrogen-like and ψ_3 more hydrogen like (since the two must remain orthogonal). It follows that the product of coefficients (eqn (1)) for the $2 \rightarrow 3$ excitation becomes larger and that for the $1 \rightarrow 4$ excitation smaller. But as the energy denominator for $2 \rightarrow 3$ is considerably smaller, the net effect will be a <u>positive</u> shift of J_{HH}. A similar argument shows that electron withdrawal from the hydrogen part of ψ_2 leads to a <u>negative</u> shift of J_{HH}. We therefore formulate the following rules.

a) Withdrawal of electrons from the <u>symmetric</u> combination of hydrogen orbitals (inductive withdrawal through the σ-bond system) should lead to a <u>positive</u> change in the coupling constant.

b) Withdrawal of electrons from the <u>antisymmetric</u> (or pseudo-π) combination of hydrogen orbitals (hyperconjugative withdrawal into π-electrons systems as in toluene) should lead to a <u>negative</u> change in the coupling constant.

Most experimental substituent effects on geminal coupling constants are readily interpreted in terms of these rules and a number of predictions may be made. In particular:

1. Formaldehyde should have a large positive shift relative to ethylene. Rules (a) and (b) both give positive changes.

2. Allene and ketene should be more negative than ethylene, the principal effect being a hyperconjugative withdrawal of electrons from the CH_2 group.

69-34

3. In vinyl-X compounds, where X is electron withdrawing, molecular orbital theory predicts that withdrawal occurs from the antisymmetrical CH_2 orbital, so that a negative shift is expected (rule b).

4. In CH_3X compounds where X is an inductive electron withdrawing group (F, Cl, OH, etc.) a positive charge of the coupling constant (relative to methane) is expected (rule a).

5. In CH_3X compounds where X is a hyperconjugative electron withdrawing group (C_6H_5, C=O, C $\equiv$ N etc.) a negative charge (relative to methane) is expected (rule b).

6. For the methyl group in CH_3CH_2X compounds (β-substitution) where X is inductive electron-withdrawing, a negative charge is expected (for reasons similar to 3).

All these trends seem to show up in experimental data. The most exciting aspect of the theory is that a geminal proton coupling constant appears to make an experimental distinction between inductive and hyperconjugative electron withdrawal.

I hope to write this up for publication in more detail shortly.

Yours sincerely,

John

John A. Pople
Carnegie Professor of
Chemical Physics

JAP:kos

69-35

EL PASO NATURAL GAS PRODUCTS COMPANY
EL PASO, TEXAS

June 15, 1964

ADDRESS REPLY TO:
POST OFFICE BOX 3986
ODESSA, TEXAS

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

Dear Barry:

During the last several months I have moved the A-60 three hundred miles to a new laboratory and have also installed a new mass spectrometer. My contribution is on service on the A-60.

The original choke L 501 in the console power supply was running hot and had a 4 VDC drop on it. I installed the new heavy duty L 501 using the 0.7 ohm R 551 dropping resistor that Varian supplied. My output voltage from this setup was too low (5.9 VDC measured at TB 501-5, 6). Bob Williams sent me a 0.3 ohm resistor which I installed in place of the 0.7 ohm R 551. The output voltage was too high (7.9 VDC). I had to get from Allied Radio a Dale 0.5 ohm 1% 50 watt resistor that gave an output of 6.5 VDC. After the A-60 was moved to Odessa we put in the high Z modification and found that it was now necessary to replace the 0.5 ohm R 551 with the 0.3 ohm resistor. My suggestion to anyone changing out L 501 is to have both the 0.5 and 0.3 ohm resistors handy.

In our new laboratory the A-60 shares the room with a Hitachi-Perkin-Elmer mass spectrometer. This magnetic scanning instrument sweeps from about 400 to 6000 Gauss. We have not observed any pickup on the A-60.

Sincerely yours,

Mack C. Harvey

Mack C. Harvey
Section Leader (Analytical)

69-36

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

June 3, 1964

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

Dear Barry:

The recent letter of Laszlo, Scheyler and Fort (IIT NMR 68, 36, 1964) concerning adamantane coupling constants requires a few clarifying comments. The compounds are obviously of considerable interest for testing and modifying the Karplus relation, and for this reason we too have looked at their NMR spectra in some detail.

The problem which the cited letter brings out is: What number does one take as the measured coupling constant? With coupling constants 5 cps or larger (in well resolved spectra) there is rarely any question, but this is not so for smaller values.

First, the peak separation in the adamantane spectra varies slightly, but for the present purpose significantly, with the homogeneity of the field. The worse the resolution, the smaller the apparent "coupling constant." Taking 1-bromoadamantane as an example, we get with routine resolution measured values about 2.4 - 2.5 cps; our best value, at 0.08 cps resolution is $2.7 \pm .1$ cps.

This, of course, is still not the true coupling constant. The 1-bromoadamantane lines do not split to the baseline even with the best attainable resolution. It is easy to ascertain that in such a case the separation between the maxima of the overlapping lines is smaller than the separation between the centers of the lines. It is the latter, not the former, which reflects the coupling constant. The correction can be estimated from the degree of overlap and the line width, if one assumes a line shape. We get slightly different corrections for 1-bromoadamantane, depending on assumed T_2 (taken from a measurement of T_1 and assuming $T_1 = T_2$, or juggling the measured widths, assuming slightly different values of J), but they are all of the order of at least 10%, far from trivial. Hence our value of $2.7 \pm 0.27 = 3.0$. Still a rather rough guess, but closer

to the truth than the uncorrected peak separation.

In trying to make correlations of the type suggested by the Karplus relation, we have more and more been forced to ask: How much can we trust the small values of J's published in the literature? Most are accompanied by some respectable number specifying a range, like $\pm$ .1 cps, but this is, we fear, an index of their precision and not of their accuracy. We find little indication that the question of accuracy has been adequately considered. It would be of great help if everyone reporting small coupling constants would state explicitly whether these are derived from completely resolved or overlapping lines and whether they have been corrected for overlap. Otherwise one has to go on wondering forever, whether the Karplus equation fails to hold because of its intrinsic defects or because the measured value has not been accurately determined.

Finally, we wholeheartedly join our Princeton colleagues in calling for caution not only in correlating but also in measuring coupling constants — the urgent need for which their letter so admirably illustrates. However, we do not share their pessimism concerning the possibility of perfecting a workable approximation to a universal Karplus-type curve, and we will write more about our thoughts on this matter later. Granted, such a curve is bound to be an insult to the standards of precision and conceptual clarity fancied by the chemical physicist. But then, so are virtually all semi-theoretical relations on which so much of the so-called useful information in organic and biological chemistry is based.

Sincerely yours,

Oleg Jardetzky

Oleg Jardetzky

OJ:eg

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Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich

ZÜRICH, 15th June 1964
Universitätstrasse
Tel. (051) 32 73 30

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

Dear Professor Shapiro,

Professor Primas has asked me to subscribe on his behalf a short report on my recent work here, as a CIBA Post-doctoral Fellow, on the nmr of paramagnetic complexes in solution.

Inspired by the very successful work of Philips et al.(1) on bis (N,N-disubstituted aminotroponeiminate)Ni(II) complexes I am looking for other paramagnetic complexes likely to give similarly narrow proton resonance lines and at the same time large contact shifts. In Philip's complexes the proton relaxation time was sufficiently long for J couplings of $\simeq$ 7c/s to be reasonably well resolved as the electron relaxation was very rapid because a rapid intramolecular electron configuration equilibrium(2)

Diamagnetic $\rightleftharpoons$ Paramagnetic(2 unpaired electrons)
(Planar Complex) (Tetrahedral Complex)

provided an efficient electron relaxation mechanism. Another consequence of this equilibrium is that the measurable paramagnetic moment is intermediate between that of the two forms in equilibrium and is markedly temperature dependent. An 'anomalous' intermediate paramagnetic moment therefore suggests itself as a criterion to be used (with caution) for selecting other paramagnetic complexes likely to give narrow lined pmr spectra in solution, for instance bis (NR-salicylaldimine)Ni(II) chelates where the R group is isopropyl or sec-butyl from which I obtained reasonable spectra in $CDCl_3$ solution and which have now been studied in greater detail by Holm et al.(3)

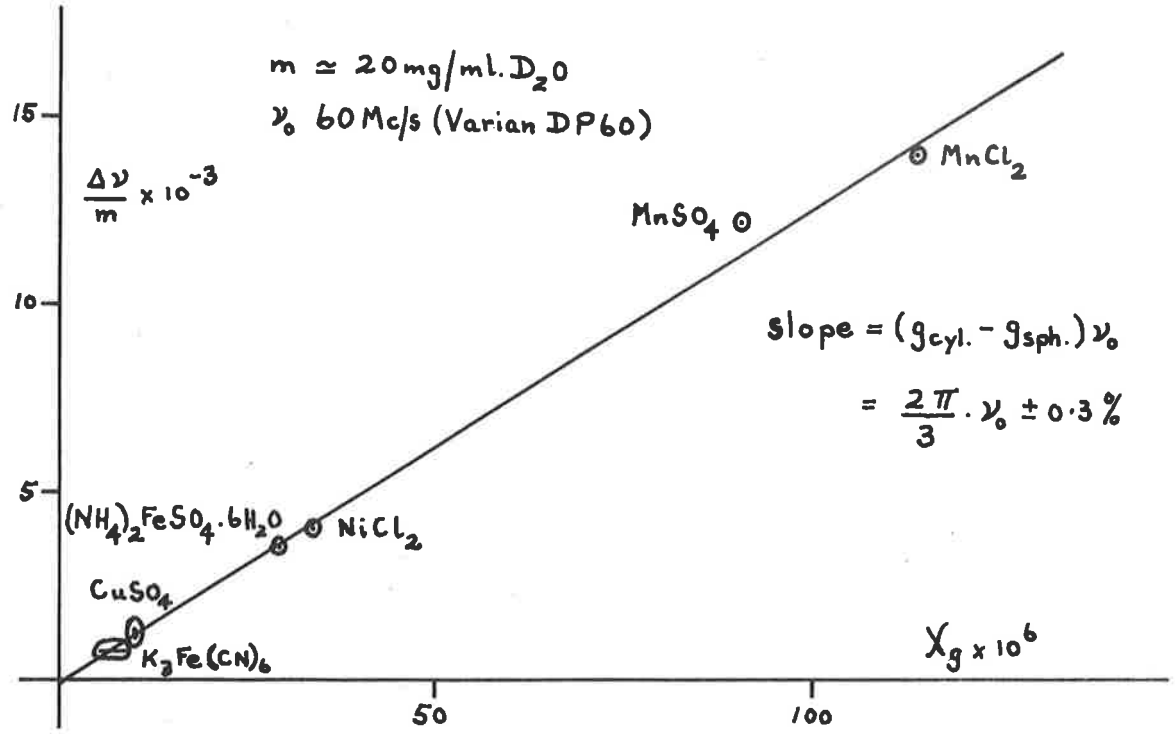
Several Co(II) chelates(4) exhibit anomalous intermediate paramagnetic moments (corresponding to about two unpaired electrons) which may be due to the following equilibrium

spin-paired $\rightleftharpoons$ spin-free
1 unpaired electron 3 unpaired electrons

both molecular configurations being approximately octahedral. If this equilibrium is fast enough it should act as an efficient electron relaxation mechanism and the pmr spectra of these complexes should show narrow lines. A particularly well defined example is bis (2,6-pyridindialdehydrazone) Co(II) iodide(5) which we are now preparing after some difficulty in obtaining the basic ligand(2,6-pyridinaldehyde) and isolating the complex.

(1) Eaton, Josey, Philips and Benson, J.Chem.Phys. 37, 347(1962).
(2) Philips, Eaton and Caldwell, J.Am.Chem.Soc. 85, 397(1963)
(3) Holm, Chakravorty and Dudek, ibid 85, 321(1963)
idem ibid 86, 379(1964)
(4) Busch in 'Cobalt' ACS Monograph No.149(1960) ca.p.132
(5) Stoufer, Hadley and Busch, J.Am.Chem.Soc. 83, 3732(1961).

We will shortly be measuring magnetic moments of these paramagnetic complexes in solution using the method of Frei and Bernstein[6] incorporating both a cylindrical and spherical external reference. This method avoids the disadvantages of very aggravating line broadening and differences in the saturation levels of the two (or more) pmr signals, experienced using the method of Evans[7], although with highly paramagnetic solutions considerable line broadening still occurs and base line stability is awkward to achieve as the rotating sample constantly varies the probe balance. The separation between water signals from the cylinder and sphere is large (30-200c/s) and can be measured to within 0.5 c/s by side band super-position (viewed on the recorder trace, exact super-position corresponding to the signal with maximum height). The following rough graph of an initial probe calibration indicates that the method is applicable with tolerable accuracy over a wide range of susceptibilities and that the form factor ($g_{cyl} - g_{sph}$) is almost exactly $2\pi/3$ after Dickinson[8].



(6) Frei and Bernstein, J.Chem.Phys., 37, 1891(1962).
(7) Evans, J.C.S., 2003 (1959).
(8) Dickinson, Phys.Rev., 81, 717(1951)

Yours sincerely

J. David Thwaites

J.David Thwaites.

69-40

UNIVERSITY OF WASHINGTON
DEPARTMENT OF CHEMISTRY
SEATTLE, WASHINGTON 98105

June 16, 1964

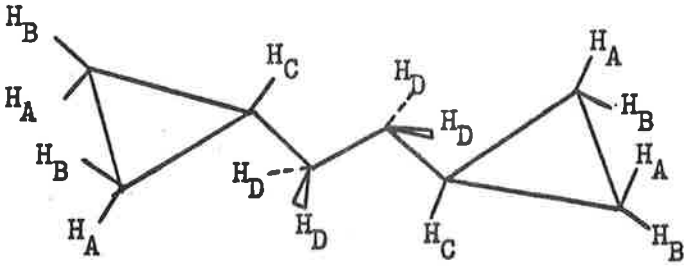
Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

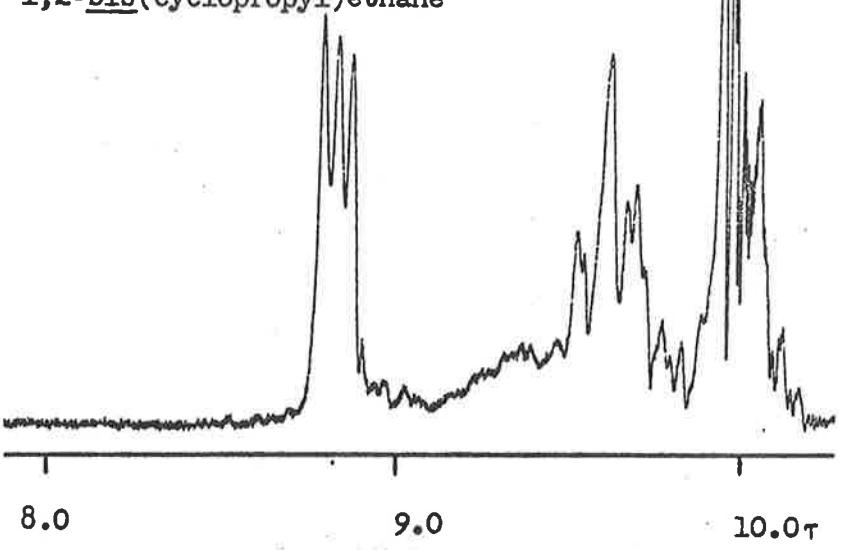
Recently I have been working on the NMR of two bicyclo systems, 1,2-bis(cyclopropyl)ethane and bis-cyclobutyl, which have been prepared by Prof. Hyp J. Dauben, Jr. and Martina L. Rathmayer of these laboratories.

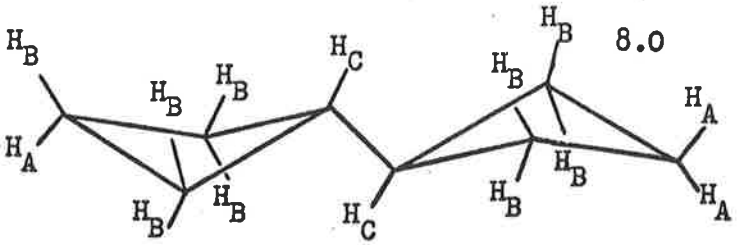
In 1,2-bis(cyclopropyl)ethane, the methylene hydrogens H_A and H_B are centered at 9.66 and 10.05$_\tau$. Although these chemical shifts are about the same in cyclopropane (9.78$_\tau$)[1], they are presumably being effected by spacial interactions or a preferred orientation between H_A or H_B on one ring with the H_D methylenes. The symmetry of the spectrum observed for these protons indicates that protons H_A and H_B spin-couple to form basic A_2B_2 or possibly two AB systems, one spin system being centered at each of the two chemical shifts. The methine hydrogens H_C appear at 9.4$_\tau$. While these hydrogens would be expected to spin-couple with the adjacent six protons, the lack of sufficient detail in this portion of the spectrum indicates a possibility of either some virtual or long-range coupling. The methylene hydrogens H_D are located at 8.77$_\tau$ and form a three-line pattern with a peak intensity ratio of approximately 1:1:1.

The chemical shifts (8.31 and 8.11$_\tau$) for the methylenes H_A and H_B in bis-cyclobutyl are up-field from the usual position for these protons in cyclobutyl systems (7.2 to 8.1$_\tau$)[1]. This was partially expected since the inductive effect of the second ring would be similar to a straight-chain hydrocarbon unless there are interactions between ring systems. The methine hydrogens H_C are at 7.90$_\tau$ which is considerably above their normal position of 5.5 to 7.0$_\tau$. As in the 1,2-bis(cyclopropyl)-ethane system, the methine hydrogens of bis-cyclobutyl are broadened but it is possible to deduce an underlining foundation of six lines. The chemical shift for H_C approximates the methine hydrogens in ethyl bicyclo(1.1.0) butane-1-carboxylate (8.03$_\tau$)[2] but what factor is governing the shielding of these protons is difficult to explain.



1,2-bis(cyclopropyl)ethane





bis-cyclobutyl

Further work on these systems using spin decoupling will make it possible to unravel some of these questions and this is planned.

Sincerely yours,

Bernard J. Nist

Bernard J. Nist

Wm J. Dauben jr.

Wm J. Dauben, Jr.

1. K. B. Wiberg and B. J. Nist, J.A.C.S. 83, 1226 (1961)
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69-42

DOW **THE DOW CHEMICAL COMPANY**

MIDLAND, MICHIGAN

June 18, 1964

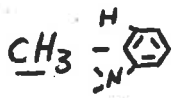
Associate Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

An item of possible interest to IIT NMR Newsletter readers is a card file functional group index of proton NMR spectra which we have started.

The index is by functional group, a la Bhacca, Johnson, and Shoolery, in the Varian High Resolution NMR Spectra Catalogs. There is a card (or cards) for each functional group notation. It gives spectrum number, solvent, and chemical shift. An example of an aromatic methyl is:

1-Vhn



R	S	SHIFT	R	S	SHIFT	R	S	SHIFT
18	1-d	-2.18						
18	16	-2.61						
18	5	-2.27						
19	5	-2.20						
19	14	-2.24						
19	16	-2.63						
20	1-d	-2.10						
32	16	-2.31						

Form C-19291 No.2

In our notation, R is compound number and S is solvent code. Our shifts are tabulated as shielding in ppm relative to TMS.

Some additions and changes to the Varian system are:

1. Greek letter phi (Φ, ϕ) for phosphorous.

2. When a miscellaneous atom is shown, its chemical symbol follows in brackets. e.g.,
   $(CH_3)_4Si$ is 1-Zaaa [Si]

We intend to enter all protons in the molecule, even when shifts cannot be assigned. In those all-too-frequent cases where spectrum complexity and/or time do not permit careful shift determination, approximate shift values are given e.g., $-2.\bar{3}$ ppm.

The fact that there is no ordering by chemical shift is not a serious problem, since one can scan the cards quickly.

When the number of entries for a given code becomes too great, we shall replace them with a single card which shows distribution by shift and solvent type. This could be done for, say, every 100-200 entries. The original cards then will be stored elsewhere.

We have found the functional group index in the Varian Catalogs invaluable for structure assignment work, especially for the less common features, and this "living" index will permit convenient and continuous addition to it.

Yours truly,

A.W. Douglas Jerry Heeschen

Alan W. Douglas Jerry P. Heeschen
Chemical Physics Research Laboratory
1603 Building

AWD:JPH:scb

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