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Mailed: April 30, 1963

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Monthly

Ecumenical

Letters from

\_aboratories

N - M - R

No. 55

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Reeves
Low Temperature Equipment for the HR-60

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Unusual NMR Dilution Shift for Acetic Acid in Acetic Anhydride; C<sup>13</sup>H Splitting in a 4-membered Ring Compound

Paterson

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Kowalewski, de Kowalewski Long-range H-H Couplings in Formates; Ethyl Maleate as High Temperature Resolution Standard

Fraenkel, Adams, Kim
Proton NMR and UV Studies of Organometallic Compounds and Aromatic Heterocyclic Amines

Smith, W. B. Concerning A-60 Magnet Cooling Systems

Freeman Sign of J(C<sup>13</sup>CH)

Baldeschwieler, Barfield Concerning the Absolute Sign of J<sub>HF</sub> (gém); A Table of Relative Signs of H-F, H-H, C<sup>13</sup>-H, and C<sup>13</sup>-F Couplings

Control Loop for HR-60, with Examples; Relative Signs of H-H Couplings in Propylene Oxide; Rig for H<sup>I</sup>-[F<sup>19</sup>] and F<sup>19</sup>-[H<sup>1</sup>] Decoupling; Relative Signs of H-F and F-F Couplings; Concerning McLauchlan and Buckingham's Negative J<sub>HF</sub> (gem)

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Lancaster, Neglia Olefin-Iron Tetracarbonyl and  $\pi$ -Allyl Iron Tetracarbonyl Halide Complexes

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Raccolta mensile di lettere private ed informali da laboratori di N.M.R. Le informazioni qui contenute servono per l'uso esclusivo del lettore. Non è permessa alcuna quotazione delle notizie riportate senza previa e diretta autorizzazione da parte dell'autore della lettera; in quest'ultimo caso la notizia deve veire quotata come "Comunicazione Privata".

### HUMBLE OIL & REFINING COMPANY

BAYTOWN, TEXAS

RESEARCH AND DEVELOPMENT

P. O. BOX 4255

J. F. MATHIS MANAGER

March 25, 1963

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

Dear Barry:

My responsibilities here were recently changed to problems involving the physical properties of polymers so this will probably be my last contribution to your excellent newsletter.

We have obtained the NMR spectra of about sixty hydrocarbon mono-olefins and have summarized the chemical shifts and coupling constants in the attached charts. Spectra were obtained on our A-60. Great care was taken to insure the accuracy of the chemical shift scale by daily calibration. Solvent shifts (relative to TMS internal standard) were investigated for nine compounds by comparing the chemical shifts obtained from the neat liquids and from solutions containing five per cent solute in CCl4. Solvent effects were less than 0.01 ppm for all the non-olefinic hydrogen resonances except for tertiary hydrogens alpha to an olefinic carbon atom. In two instances the latter exhibited solvent shifts from 0.05 to 0.10 ppm - the neat liquid resonance was downfield relative to the resonance obtained in very dilute solution. With this single reservation, all the data given in Figure 1 may be used with confidence either for diluent solutions in CCl4, for neat liquids, or for mixtures of olefins. Olefinic hydrogen resonances were found to be solvent dependent; chemical shifts in the neat liquids were 0.04 ± 0.02 ppm downfield from those found in 10% solutions in CClh. Data in Figure 2 apply to the neat liquid state. Table I summarizes the coupling constants we found.

The utility of the chemical shift charts is evident from the almost astonishingly narrow ranges found for most of the hydrogen types. Geometrical isomers of di- and tri-substituted ethylenes can often be identified from the chemical shifts of  $\beta \text{CH}_3$ 's or  $\alpha\text{-CH}^<$ 's. This is generally easier than trying to ascertain the cis or trans nature of a di-substituted ethylene from the magnitude of the coupling constant between the olefinic hydrogens.

We hope to rationalize some of the chemical shifts and to illustrate the use of the data in determining the structures of oligomers of mono-olefins and polymers of di-olefins in a future paper. In the meantime additional copies of the charts can be obtained on request.

Sincerely yours,

Terdinand C. Stelling
Ferdinand C. Stehling

FCS:ms

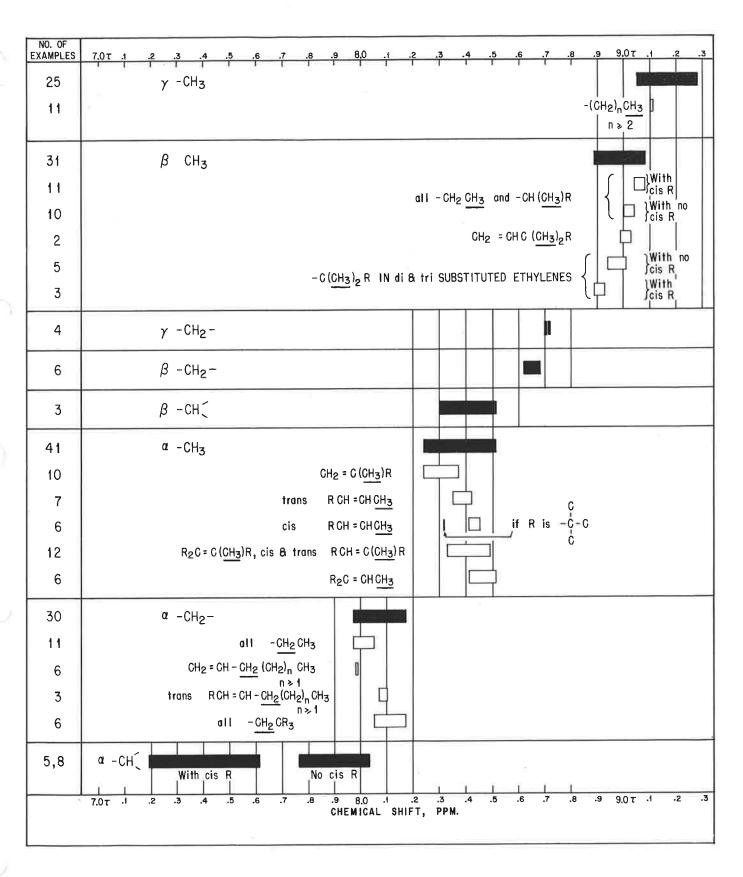


Fig. 1. Chemical Shifts of Non-olefinic Hydrogens in Mono-olefin Hydrocarbons.

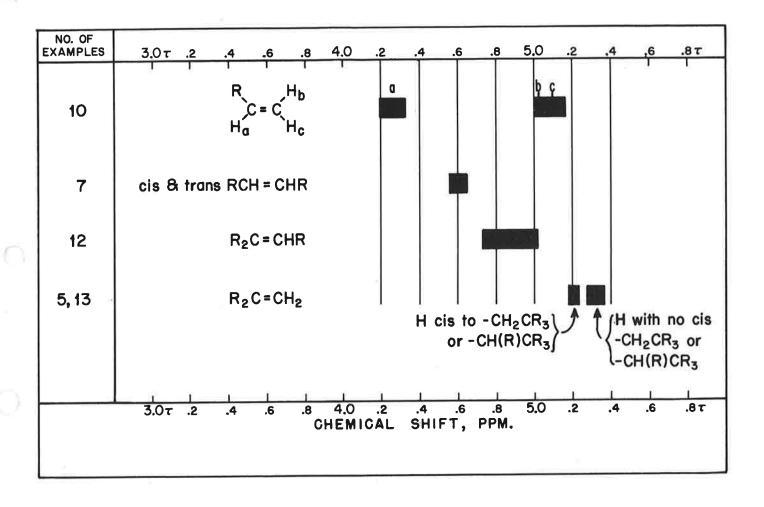


Fig. 2. Chemical Shifts of Olefinic Hydrogens in Mono-olefin Hydrocarbons.

No. OF EXAMPLES	STRUCTURE	COUPLING CONSTANT, J, OR OBSERVED SEPARATION, A.		
	R C = C H	$J_{trans}$ H-H = 16.6 - 17.4 cps a $J_{cis}$ H-H = 9.6 - 11.1 a $J_{gem}$ H-H = 0.1 - 2.1		
3	H	J <sub>trans</sub> H-H = 15.5-15.7		
4	H R C = C R	J <sub>cis H-H</sub> = 11.0-12.3		
3,6,1	$=C \xrightarrow{CH_3} = C \xrightarrow{CH_2R} = C \xrightarrow{CHR_2}$	J = 6.1-7.1		
4	cis or trans $RCH_a = C H_b$	J <sub>Ha-CH3</sub> + J <sub>Hb-CH3</sub> = 4.7-5.6		
8	CH <sub>3</sub> C = C H	$J_{\text{trans H-CH}_3}$ = 1.2-1.5, negative		
8	CH3 H C=C.	$J_{cis}$ H-CH <sub>3</sub> = 0.8-1.4, negative		
6	cis or trans RCH <sub>2</sub> -C=CH	JH-CH <sub>2</sub> = 0.8-1.4, negative		
8	CH(CH <sub>3</sub> )R C = C	A <sub>H-CH<sub>3</sub></sub> = 6.7 ± 0.2		
7	C = C CH <sub>2</sub> - CH <sub>3</sub>	$A_{CH_2-CH_3} = 6.8 \pm 0.2, 7.8 \pm 0.2^{c}$		
5	C = CC-CH <sub>2</sub> CH <sub>3</sub>	$A_{CH_2-CH_3} = 6.2 \pm 0.2, 7.6 \pm 0.1^{c}$		

Table I, Coupling Constants in Mono-olefin Hydrocarbons.

Data taken from Brügel, W., Elektrochem 64, 1121 (1960).

Separation between perturbed CH<sub>3</sub> doublet.
Separation between central and low field bands, and central
band and high field band, respectively, in perturbed CH<sub>3</sub>
triplet. Separations were measured between the most intense
lines (at resolution of <u>ca</u> 0.4 cps) in three portions of CH<sub>3</sub> spectrum.

#### THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY INDIANAPOLIS 6, IND., U. S. A.

April 15, 1963

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

Dear Dr. Shapiro:

Since the major portion of our work involves running spectra on a large variety of organic compounds with the Varian HR-60 spectrometer, we have found it desirable to display the curves on a standard 500 cps sweep. Following is a description of a few modifications which have made this convenient.

As the time base on the recorder (Mosley Model 2S) was not sufficiently reproducible, an external X axis drive was installed. This was provided with a span adjust to compensate for sweep variations between spectra. A fixed sweep rate resistor was installed on the slow sweep unit to give a standard sweep rate of about 3.5 cps/sec.

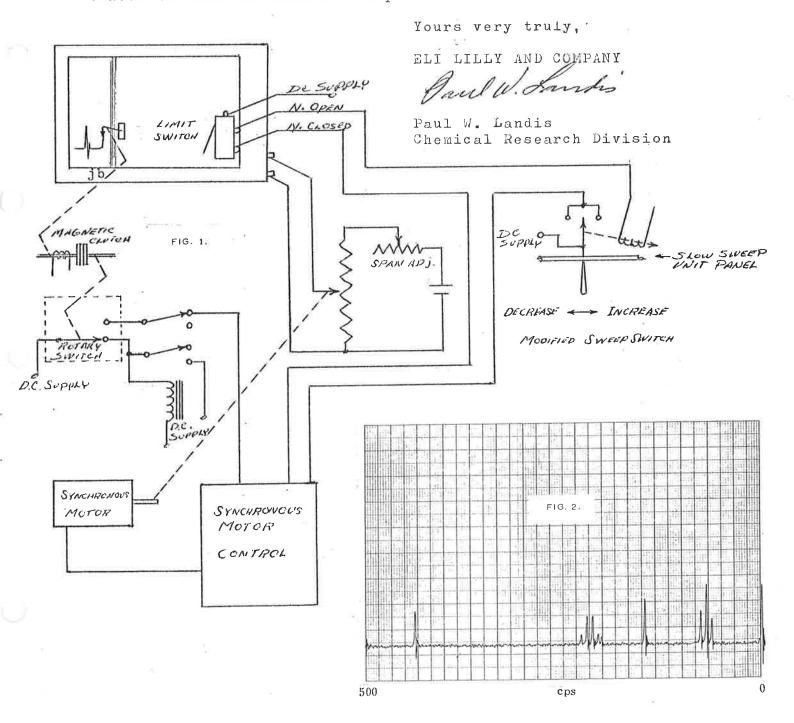
For a standard curve, an audio generator is used to produce the 500 cps side band of TMS. With the field on the low side of the side band, the slow sweep switch is turned on and when the recorder pen reaches the top of the TMS side band the recorder external sweep is turned on.

On our spectrometer we have provided a semi-automatic operation for starting the recorder on the 500 cps side band. A rotary SPDT switch is attached to the Y axis drive of the recorder through a magnetic clutch. When the clutch is energized a relay is connected to the normally open contact of the rotary switch. As the pen goes up with the side band, the relay is latched. This puts the normally closed contacts in series with the X drive starting circuit and as soon as the pen starts down, the circuit is energized. The audio generator and rotary switch are disconnected by a two second time delay relay. A limit switch on the recorder stops the external recorder sweep and turns off the slow sweep unit through a solonoid acting on a modified lever switch.

By using a calibrated span adjust on the recorder sweep we can routinely keep the TMS band within ± 5 cps of the reference line on our paper (see Fig. 2). This, of course, is dependent on the magnet stability and we have often obtained several consecutive spectra within ± 2 cps.

A slave recorder coupled to the Mosley 2S through a control transformer and DC servo system reproduces the sweep scale of the main recording.

One further convenience permits us to switch spectrometer operation from scope to spectrum to integral by using the one function switch of the integrator. A printed circuit mounted externally on the integrator panel becomes a SPDT switch with the contacts mounted on the function switch knob. This energizes a relay in the spectrum and integral positions to turn off the linear sweep generator and energized the recorder servos. In the scope position the relay is released to turn the linear sweep on and the recorder off.



#### ROHM & HAAS COMPANY

REDSTONE ARSENAL



RESEARCH DIVISION

March 12, 1963

Dr. Barry Shapiro The Mellon Institute Pittsburgh 19, Pennsylvania

Dear Dr. Shapiro:

We have recently observed some interesting shielding effects which may be of interest to readers of Mello-N-M-R. In examining the spectra of some phenylcyclopropane derivatives, we noticed that a methyl group (and presumably other groups) cis to the phenyl ring appeared at higher fields than in cyclopropanes without the phenyl group and at lower fields when trans to the phenyl group. Closs and co-workers have also suggested a similar correlation. We have used authentic samples of cis- and trans-l\_phenyl-2-methylcyclopropanes, l-methylcyclopropyl acetate, and 1,2,2-trimethylcyclopropyl acetate as our standards for the compounds listed in the table.

In addition another shielding effect was noted with regard to the methyl group of the acetate function in compounds A-D in the table. The acetate methyl groups in those isomers in which the phenyl and acetate groups are  $\underline{\operatorname{cis}}$  appear at higher fields than when they are  $\underline{\operatorname{trans}}$ . This shift makes analysis of a  $\underline{\operatorname{cis}}$ -trans cyclopropyl acetate mixture very easy since the areas of the two peaks gives the ratio of the two isomers.

This same effect seems to hold for the <u>cis</u>- and <u>trans</u>-ethyl 2-phenylcyclopropanecarboxylates. In the <u>cis</u> isomer both the methyl and methylene groups appear at higher fields than those groups in the <u>trans</u> isomer.

In connection with this work we have found that the 1-phenyl-2-methyl-3,3-dichlorocyclopropane reported by Graham and Rogers [J. Am. Chem. Soc. 84, 2249 (1962)] is the trans isomer and not the cis as reported. This reassignment has no particular effect on the conclusions reached in their paper since the vicinal proton coupling constant of the authentic cis isomer (11 c/s) is larger than that of the trans isomer (8 c/s) as would be predicted from their paper.

Dr. Barry Shapiro

-2.-

March 12, 1963

#### Proton NMR Spectra of Cyclopropyl Acetates

Compound	Group Chemical Shift $(\tau)^a$		
	1-CH <sub>3</sub>	2-CH <sub>3</sub>	CH <sub>3</sub> CO <sub>2</sub> -
1,2,2-Trimethyl	8.52	8.95, 8.88	8.08
l-Methyl <sup>b</sup>	8.53	<del>3</del> .)	8.12
cis-2-Phenyl (A)	9.1	<del>-2</del> 0	8.30
trans-2-Phenyl (B)	e.	<b>3</b> /2	8.12
l-Phenyl-2,2-dimethyl	25	9.20, 8.70	8.10
cis -2-Phenyl-1-methyl (C)	8.35	30	8.35
trans -2-Phenyl-1-methyl (D)	8.80	:20	8.03
cis -1,2-Diphenyl			8.13
1,2-Diethyl-2-methyl <sup>c</sup>	200	8.98, 8.95	8.12
l-Phenyl	<b>20</b>	390	8.12
cis-1-Phenyl-2-methyl	*	9.19	8.16
trans -1 -Phenyl -2 -methyl	Sec. 1	8.75	8.04
cis -1-Phenyl-2-methylcyclopropane	40	9.18	244
trans -1-Phenyl-2-methylcyclopropane	4	8.88	12

a Spectra were measured on Varian Associates V-4300 B 40 mc. and A-60 spectrometers of dilute (5-10%) solutions in CCi<sub>4</sub>, TMS internal std.

Sincerely yours.

Lemma ( ) Lucian

Jeremiah P. Freeman

JPF:bac

 $<sup>^{*</sup>b}$  We are indebted to Dr. C. H. DePuy for the spectrum of this material.

C Mixture of cis-trans isomers. In the other cases the use of the terms cis and trans refers to the orientation of the group at Carbon 2 and the acetate group except with the cis-1, 2-diphenyl case in which the two phenyl groups are cis.

#### THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

March 23, 1963.

Dr. Shapiro, dellon Institute, 4400 Fifth Avenue, Pittsburgh 13, Pa., U. S. A.

Dear Dr. Shapiro:

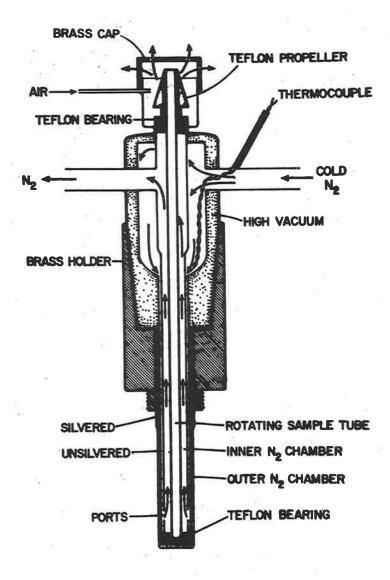
I include a diagram of our home built low temperature equipment for the NR. 60. It is satisfactory to at least -120°C. The apparatus has the advanture of interchangeable samples at low temperature with an isolation of receiver coil from the cooled region. The critical dimensions are the lim. ... insert clearance from the dewared vessel which should be as small as possible and the height of the dewar since samples must be short enough to clear the magnet voke insulation on removal. The credit for this design should be shared with Mr. Jansen and Mr. Krakower of this department, and the excellence of our glasshlowers. We can supply further details on demand.

Yours sincerely,

Leonard W Rieves

Leonard W. Reeves,

LWR:kg



'SPINNING SAMPLE' DEWAR INSERT

#### PURDUE UNIVERSITY

LAFAYETTE, INDIANA
April 1, 1963

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

Dear Barry:

We must applicate to you and the readers of MELLONMR for including in our letter in issue  $\pi^0$ 32 some conclusions which have turned out to be wrong.

After correcting some unfortunate errors, we find that the dilution shift for acetic acid in acetic anhydride is <u>unlike</u> any previously reported curve for a carboxylic acid in a donor solvent. We enclose for your information a preprint of a communication to JACS which precents our results, and we leave it to your judgment whether to reproduce it in NELLOMAR or let the readers wait (we hope not long) to see it in print.

To change the subject entirely: We have wondered whether the long-range coupling reported by Meinwald (JACS 83, 2769 (1961)) for a 2,1,1 bicyclohemane derivative would have a counterpart in the spectrum of a four-membered ring compound not in a fused-ring situation. To test this, Dick Reiter has prepared 3,3 dimethyl trimethylene oxide,

C(H<sub>2</sub>)<sub>2</sub> and we have looked for fine structure on the C<sup>13</sup> sidebands from the methylene groups. We found that the sidebands are sharp simplets, indicating absence of cross ring coupling. The value of  $J_{\rm CH'}$  140.5 one is a little surprising when compared with other reported values for cyclic C-CH<sub>2</sub>-C groups. (Sheppard and Turner, Proc. Roy. Soc. A252, 506 (1959). Thus for

Where is the expected uniform variation with ring-size?

With best regards,

norbed miller Phil Rose (N.m)

Unusual NMR Dilution Shift for Acetic Acid in

Acetic Anhydride. 1

Sir:

NMR studies of carboxylic acids in electron-donating solvents have revaaled a marked concentration-dependence of the chemical shift of the acidic hydrogen. 2,3 This "dilution shift" is believed to result from a rapid equilibrium between dimeric acid molecules and a monomeric species, probably hydrogen-bonded to a solvent molecule. A difficulty with this interpretation is that the data appear to imply that at moderate concentrations (10 to 20 mole percent) considerably more than half of the solute is dimerized. This conflicts with the earlier view, 4 that in such solvents "carboxylic acids associate with the solvent molecules rather than with their own species. Thus they give normal molecular weights in ethers, esters and ketones." Another alarming symptom is the poor quantitative agreement between two independently determined curves of chemical shift versus concentration for acetic acid (AcOH) in acetone. 2,3

If AcoH is dissolved in acetone contaminated with water, rapid proton exchange between water and acid should occur and the observed hydroxyl chemical shift should be the weighted average of the true value for the acid and that for water. Although each of these varies with concentration, it is safe to say that the proton resonance for water in dilute solution<sup>5</sup> is several parts per million upfield from the averaged hydroxyl resonances of the acid species present. A very large spurious "dilution shift" for the acid will result even if the solvent contains as little as 0.2 weight percent of water. Quite elaborate procedures are often necessary to prepare solvents free of such traces of water. However, in reference 2 "analytical or reagent grade" solvents were used, and it has been reported that Baker C. P. acetone, for exemple, contained 0.39% water by weight. Then perhaps the discrepancy between the results of references 2 and 3 is due to a difference in dryness of the solvents used. Moreover, there is some likelihood

-3-

that neither study was made with solvent sufficiently anhydrous to reveal the true AcOH dilution shift from which reliable conclusions about the dimerization equilibrium might be drawn.

In order to determine the dilution shift in rigorously anhydrous samples we examined NMR spectra of solutions of AcOH in acetic anhydride (Ac<sub>2</sub>O). Our purified Ac<sub>2</sub>O contained 0.8±0.1 mole percent of AcOH, found by comparing the intensity of the methyl NMR peak of the AcOH with that of the C<sup>13</sup> sideband from Ac<sub>2</sub>O. A series of samples was prepared volumetrically by adding known amounts of water to Ac<sub>2</sub>O. The reaction

could be followed by studying the NMR spectrum as a function of time. A sharp, time-independent hydroxyl signal was not obtained until hydrolysis was complete and all water, from whatever source, had been decomposed.

Figure 1 shows a plot of the hydroxyl chemical shift against the total AcOH concentration. The Varian high-resolution spectrometer was operated at 56.4 Mcps. The zero of the chemical shift scale is the Ac<sub>2</sub>O resonance, which is 2.28 p.p.m. down-field from tetramethylsilane. The sample temperature was 30±2°C. The dashed curve was calculated for a <u>hypothetical</u> situation where the true dilution shift coincides with our measured curve but the "observed" value is shifted because the solvent is wet. For this calculation the chemical shift for dissolved water was taken as -2.3 p.p.m. from tetramethylsilane\* and the mole fraction of water as 0.01 times the mole fraction

\*This is approximately where we found the water peak for dilute solutions of water in acetone.

of solvent. In a real situation this might represent 0.2 to 0.4 weight percent water, depending on the molecular weight of the solvent. The uppermost curve in the figure represents the data of Reeves<sup>3</sup> for AcOH in acetone.

These results for AcOH-Ac<sub>2</sub>O solutions are quite different from any previously reported for a carboxylic acid in a donor solvent. For the first time the dilution shift can be extrapolated to zero concentration yielding an averaged shift of -9.04±.06 p.p.m. from tetramethylsilane for the solute species (presumably free AcOH in equilibrium with an AcOH·Ac<sub>2</sub>O complex) at infinite dilution at 30°C. This value represents an upper bound for the hydroxyl chemical shift of AcOH·Ac<sub>2</sub>O, in sharp contrast to the shift near -3 p.p.m. estimated<sup>2</sup> for the AcOH-acetone complex. Since in either case the acid proton is strongly hydrogen bonded, a value near -9 p.p.m. seems more in accord with other observations on hydrogen-bonded species.

The difference between our dilution curve and that<sup>2,3</sup> for AcOH- acetone, together with the similarity between the latter and our "hypothetical wet solvent curve" may indicate that indeed the solvents used in the earlier work were not adequately dried. However, it may be instead that this difference reflects the ability of AcOH and Ac<sub>2</sub>O to form a complex with structure I, perhaps more stable than the AcOH-acetone complex. II.

$$AcoH$$
 $O=C$ 
 $CH_3$ 
 $AcoH$ 
 $O=C$ 
 $CH_3$ 
 $T$ 

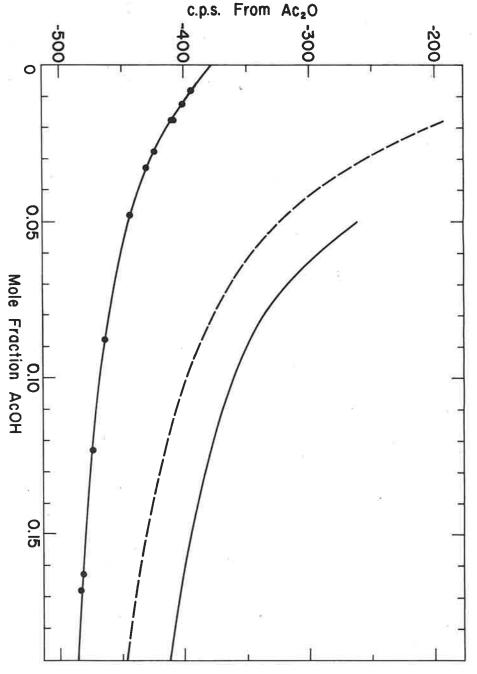
We hope that experiments in progress here will soon provide a basis for a choice between these interpretations.

> Norbert Muller Philip I. Rose

Department of Chemistry
Purdue University
Lafayette, Indiana

- 1. Supported by research grant NSF G-17421 from the National Science Foundation.
- 2. C. M. Huggins, G. C. Pimentel and J. N. Shoolery, J. Phys. Chem. <u>60</u>, 1311 (1956).
- 3. L. W. Reeves, Trans. Far. Soc. <u>55</u>, 1684 (1959).
- 4. G. Allen and E. F. Caldin, Quart. Revs. 7, 278 (1953).
- 5. J. R. Holmes, D. Kivelson and W. C. Drinkard, J. Am. Chem. Soc., <u>84</u>, 4677 (1962).
- 6. W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, Ibid. 62, 3504 (1940).

Figure I. Chemical shift (in cps from Ac20 at 56.4 Mcps.) of the hydroxyl proton as a function of AcOH concentration. Lower curve: Results of this study for AcOH in Ac20. Middle curve: Calculated shifts for AcOH in "hypothetical wet solvent" (see text). Upper curve: Results of reference 3 for AcOH in acetone.



55-11

#### DEPARTMENT OF CHEMISTRY



#### EDMONTON, ALBERTA CANADA

April 2, 1963

Dr. B.L. Shapiro Mellon Institute 4400 Fifth Avenue PITTSBURGH 13, Pa U.S.A.

Dear Barry:

In reply to your letter of March 28, here is my MELLONMR contribution.

We have continued our work on proton exchange in neutral alcohol-water systems. For the reaction ROH +  $IIOH^* \stackrel{\sim}{\leftarrow} ROH^* + HOH$ , we find the following rate constants at  $42^\circ$ :

The data were obtained from measurements of the line width of the  $\rm H_2O$  signal and the -OH multiplet spacing of the alcohol

Signal. The method is summarized in Can. J. Chem. 41, 714 (1963). Work is in progress on the butanols. We use pyrex sample tubes for the measurements, and find that an extremely thorough cleaning is necessary to obtain reproducible results. Before each measurement of a butanol-water sample, the tube is cleaned by the following substances in the order written, with multiple water rinsings between each treatment: cone. HNO3, not detergent, dilute HC1,

dilute ammonia. Then the tubes are baked for several hours at  $120-150^{\circ}$ .

2..

B.L. Shapiro

April 2, 1963

Using the spin decoupler accessory for the Varian integrator, we have shown that the coupling constants in the heter ocyclic ring of quinoline are all of the same sign. The spectrum is close to first order at 100 Mc/s, so that the method of Ray Freeman, Mol. Phys.  $\frac{\mu}{4}$ , 385 (1961) was applicable.

My collaborators in these projects have been Dr. Harold Spedding and Mr. Glen  ${\tt Bigam.}$ 

Yours sincerely,

Bill

W. G. Paterson

WGP/mf

Monthly

Ecumenical

Letters from

Laboratories

**O**f

N-M-R

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

Universidad de Rumas Auss

## Facultad de Ciencias Exactas

y Naturalis

Buenos Aires, march 29,1963.

Dr. Bernard L. Shapiro. Mellon Institute. 4400 Fifth Avenue. Pittsburgh 13, Pa. U.S.A.

Dear Dr. Shapiro:

while certain results of research made on alkyl esters by sound absorption methods (1)(2) point to the presence of two isomeric forms for these substances, others (electron diffraction (3), dipole moment (4), infra red (5) and microwave spectroscopy (6)) insist on the sole cis configuration:

$$\frac{0}{R_3}$$
c - 0  $\frac{R_1 - R_2}{R_3}$ 

It was decided in this laboratory to tackle the problem with the NMR technique which gave so good results in the case of the alkyl nitrites (7). For this purpose 60 Mc spectra were taken of several commercially available esters at temperatures between its freezing and its boiling points. The results were completely negative. The spectra remained unchanged and no trace of signals was found which could be attributed to eventual isomers.

It is perhaps interesting to observe the existence, in the <u>formiates</u>, of a long range J-couplimng across the C - O bond which is only slightly (if) dependent on the other radicals:

#### Universidad de Banes Aus

### Facultad de Ciencias Exactas y Naturales

	R <sub>1</sub> - R <sub>2</sub>	$^{\mathrm{J}}$ och-or $^{\mathrm{1}}$	JOCH-OR <sub>2</sub>	
	och <sub>3</sub>	0.85		cps.
	с <sub>2</sub> н <sub>5</sub>	0.85	0.57	п
	nC <sub>3</sub> H <sub>7</sub>	0.88	0.62	11
isc	C <sub>3</sub> H <sub>7</sub>	0.93	0.56	
	с <sub>3</sub> н <sub>7</sub> сн <sub>6</sub> ∙Ф	0.98		11

We would like to point to the users of high temperature equipment that we found <a href="ethyl">ethyl</a> maleate a convenient sample for high temperature resolution adjustement, since the first peak of the ethyl quartet is quite similar to the corresponding ethanol peak (0.45 cps doublet) while the substance boils at 2252 C, slightly above the upper temperature limit of the Varian probe.

Yours, sincerily.

Worsel M. V.J.Kowalewski.

Dora G. de Kowalewski.

- 1) J.Karpovich, J.Chem. Ph. 22, 1767, (1954).
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#### THE OHIO STATE UNIVERSITY

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

March 29, 1963

Dr. B. L. Shapiro Mellon Institute 4400 5th Avenue Pittsburgh 13, Pennsylvania

Dear Barry:

We would like to describe some work concerning paramagnetic shifts in organometallic compounds and aromatic heterocyclic amines.

The hydrogens  $\propto$  to nitrogen in pyridine, pyrimidine, pyrazine, pyridazine and related molecules are greatly deschielded with respect to the hydrogens in benzene. These shifts move to higher field with hydrogen bonding at nitrogen, the limit of the upfield shift being represented by the N-protonated bases.

Ordinarily  $\Delta E_{n \to \pi} *$  increases with hydrogen bonding. We have found that for a variety of inert and hydrogen bonding media  $\int_{\infty} H$  is inversely proportional to  $\Delta E_{n \to \pi} *$  the proportionality constant being different for each solute. This behavior is precisely that predicted by Pople for a paramagnetic shift. The surprising thing is that the other contributions to the chemical shifts should remain constant during the transition through hydrogen bonding to protonation.

Phenyl carbanion is isoelectronic with pyridine. It is generally believed that there is a high degree of ionic character to the carbon metal bonds in phenylmagnesium bromide and phenyllithium. The spectral characteristics of these species are parallel to those for pyridine. The chemical shifts of the hydrogens ortho to the O'--M'+ bond occur below that for the hydrogens in benzene, vary among different solvents and also from lithium to magnesium. In contrast the chemical shifts for the other hydrogens change very little. The UV spectrum of phenylmagnesium bromide is very similar to that of pyridine. (\$\epsilon = 200\$) There is a tail around 2900 AO to which we assign the n-7\* transition only by analogy to pyridine.

We conclude that the paramagnetic shift due to magnetic mixing of the ground and nearest excited electronic states of the organometallic reagents is important only for the ortho hydrogens. Its magnitude should be inversely proportional to  $\overline{AE}_{n\to\pi\pi}$  which in turn is a simple measure of the ionic character of the carbon metal bond.

Dr. B. L. Shapiro Page 2 March 29, 1963

Typical data are listed below.

 $4-D-\phi MgBr$   $\delta_0$ , 2.363;  $\delta_{m}$ , 2.992;  $J_0=7.23$ ;  $J_2$ , 6=2.06;  $J_3$ , 5=2.53;  $J_p=0.74$ , ether solution.

 $4-D-\phi I \le \delta_0$ , 1980;  $\delta_m$ , 2.980;  $J_{2,6}=1.96$ ;  $J_{3,5}=2.43$ ;  $J_p=0.80$ , ether solution.

4-MgBr-oMgBr &=2.30, tetrahydrofuran. Sis in tau units, J in cps.

Best regards,

Gidan

Gideon Fraenkel
Assistant Professor of Chemistry

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DELATO WORTH

8

GF/ebh



DEPARTMENT OF CHEMISTRY

April 5, 1963

Dr. B. L. Shaprio Mellon Institute hh00 Fifth Avenue Pittsburgh 13. Pennsylvania

Dear Dr. Shapiro:

It is evident from the many MEILOMNR letters on the subject that A-60 magnet cooling systems are still items of interest. On looking over the results of your 4th O.C.E.A.N.S. survey on A-60 operations, I was surprised to note that only one person indicated using the Varian magnet cooling system. It was apparent from the time we ordered our A-60 that Fort Worth water could not be used to cool the magnet directly. After consultation with several local firms, it became even more apparent that home-designed, custom built equipment offered dubious operational characteristics and uncertain reliability. Consequently, we went whole hog and ordered the Varian model V-3520 Coolant Control System.

On installation it was found that over a period of several days the temperature of the recirculating water built up to the point where the magnet cut itself off. A day's cooling off period was then required before things could be put back into operation at which point the whole process repeated itself.

The cause of the difficulty and its solution was quickly achieved by Cappy Joller and associates as follows. The V-3520 simply supplies more water than the A-60 can use, and the excess is returned to the recirculating tank through a by-pass which is in front of the heat exchanger. Consequently, the temperature in the tank slowly mounts beyond the critical point for the heat exchanger. The solution was to replumb the system with the by-pass to the tank coming after the pass through the heat exchanger. This involved a new valve and hose supplied by Varian and thirty minutes of time for the school plumber. The result was a very fine magnet cooling system which has now operated for almost a year with no down time.

It would seem that those who are experiencing difficulties with their present systems or who are contemplating the purchase of an A-60 might well profit from our experience.

Yours sincerely,

William B. Smith

William B. Smith Professor of Chemistry



Please address any reply to THE DIRECTOR

#### Department of Scientific and Industrial Research NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex Telegrams: Physics, Teddington Telephone: TEDdington Lock 3222, ext. 601/199 Basic Physics Division

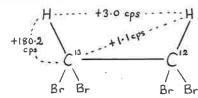
22nd Larch, 1963

Your reference: Dear Barry.

and quote:

#### Sign of J(c13cH

Wes Anderson and I have been tickling 1,1,2,2tetrabromoethane:



taking  $J(0^{13}H)$  to be positive (Gee Mellon Newsletter No. 54). Confidence shaken, we went back and remeasured the sign of  $J(C^{13}CH)$  after reading Dreeskamp and Sackmann  $\mathbb{Z}_{\bullet}$  phys. Chem. 34 261 (1962) 7 who show by a rather ingenious method that J(C13CH) and J(C13H) have opposite signs in ethyl iodide. Ours was still positive. So  $J(C^{13}CH)$ , like J(HCH), can have either sign.

Yours sincerely,

Ray Freeman R. Freeman, Basic Physics Division.

Dr. B. L. Shapiro. Mellon Institute. 4400, Fifth Avenue, Fittsburgh 13, Fa.

U.S.A.

entgegengesetztes Vorzeichen

#### HARVARD UNIVERSITY

#### DEPARTMENT OF CHEMISTRY

12 Oxford Street

Cambridge 38, Massachusetts, U.S.

April 10, 1963

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

Dear Barry:

We noted with interest the recent contribution to the MELLON-M-R by Keith McLauchlan regarding his work with David Buckingham on the determination of the absolute signs of  $J_{\rm HH}$ , and  $J_{\rm HF}$ . A negative sign for  $J_{\rm HF}$  is puzzling to us in view of the relative sign determinations of Tiers, as well as some of our own results, which relate the signs of  $J_{\rm HF}$  to  $J_{\rm HH}$  in fluoroethane and l,l-difluoroethane. We have included a table which gives a variety of H-F, H-H,  $C^{13}$ -H and  $C^{13}$ -F coupling constants. The relative signs given in this table were obtained by double resonance or complete spectral analyses.

A positive absolute sign for  $J_{\rm HH}$ , in p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me implies a positive absolute sign for  $J_{\rm Cl3_{-H}}$  in this compound. A positive absolute sign for  $J_{\rm Cl3_{-H}}$  further implies that  $J_{\rm HF}({\rm gem})$  is positive through the relative sign determinations with CHFCl<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>F. However, the absolute sign of  $J_{\rm HF}({\rm gem})$  reported by McLauchlan for CHF<sub>3</sub> is negative. Since  $J_{\rm HF}({\rm gem})$  in CHF<sub>2</sub>X molecules has been found to increase in magnitude with increasing electronegativity of X (B. H. Arison, et al, J. Chem. Soc. 1962, 3828), a reversal in the sign of  $J_{\rm HF}({\rm gem})$  in going from CHFCl<sub>2</sub> to CHF<sub>3</sub> seems improbable. We feel that this inconsistency raises some doubts about the absolute  $J_{\rm HF}({\rm gem})$  sign reported by McLauchlan.

Sincerely, John Baldeschwieler Michael Barfield

Compound	J <sub>HF</sub> (gem)	J <sub>HF</sub> (vic)	J <sub>HH</sub> ,(vic)	J <sub>C</sub> 13_H	J <sub>C</sub> 13_F
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Me CHCl=CHCl			8.2 <sup>a</sup> cps	ъ	
CH2C1CH2C1	77		+ 6.8°	+ 154°	
FC <sub>6</sub> H <sub>5</sub>		+ 9.4 <sup>d</sup>	+ 8.9 <sup>d</sup>		
CH2FCH3	+ 46.7 <sup>e</sup>	+ 25.2 <sup>e</sup>	+ 6.9 <sup>e</sup>		
CH <sub>3</sub> F	46.5 <sup>I</sup>			149 <sup>g</sup>	158 <sup><b>f</b></sup>
CCÍ_HF	+ 53.6 <sup>h</sup>			+ 220 <sup>h</sup>	-294 <sup>h</sup>
CHF <sub>2</sub> CH <sub>3</sub>	+ 57.3 <sup>e,1</sup>	+ 20.9 <sup>e,i</sup>	+ 4.5 <sup>e</sup>		
CH <sub>2</sub> F <sub>2</sub>	50.4 <sup>1</sup>			185 <sup>j</sup>	232 <sup>£</sup>
(CHF <sub>2</sub> -C) <sub>Avg</sub>	54.5 <sup>k</sup>				
(CHF <sub>2</sub> -N) <sub>Avg</sub>	59 <b>.2</b> k				
(CHF <sub>2</sub> -0) <sub>A▼g</sub>	74.0 <sup>k</sup>				
CHF3	79.0 <sup>f</sup>				272 <b>£</b>

R. E. Richards and T. P. Schaefer, Trans. Faraday Soc. <u>54</u>, 1280 (1958).

P. C. Lauterbur and R. J. Kurland, J. Am. Chem. Soc. <u>84</u>, 3405. (1962).

P. C. Lauterbur, private communication.

B. Bak, J. N. Shoolery and G. A. Williams, J. Mol. Spect. 2, 525 (1958).

M. Barfield and J. D. Baldeschwieler, J. Mol. Spect., in press. S. L. Stafford and J. D. Baldeschwieler, J. Am. Chem. Soc. 83, 4473 (1961).

N. Muller and D. T. Carr, J. Phys. Chem. <u>67</u>, 112 (1963).

N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 1471 (1959).

h G. V. D. Tiers, J. Am. Chem. Soc. 84, 3972 (1962). G. V. D. Tiers, J. Am. Chem. Soc., in press.

D. F. Evans, S. L. Manatt and D. D. Elleman, J. Am. Chem. Soc. 85, 238 (1963).

N. Muller, J. Chem. Phys. 36, 359 (1962).

B. H. Arison, T. Y. Shen and N. R. Trenner, J. Chem. Soc. 1962, 3828. These are average values from a number of compounds.



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

11 April 1963

Dr. B. L. Shapiro Mellon Institute Pittsburgh, Pennsylvania

Dear Barry:

5) Ivan 0-6811

We have built a control loop for our HR-60 similar to that described by Anderson and Freeman. For protons we have been using a 1000 cps. field

a. W. A. Anderson and R. Freeman, <u>J. Chem. Phys.</u>, <u>37</u>, 85 (1962),
 b. R. Freeman and W. A. Anderson, <u>ibid.</u> <u>37</u>, (1962).

modulation, tetramethylsilane as an internal reference, and a phase detector similar to that described by us previously.<sup>2</sup> We monitor the signals two places.

(2) D. D. Elleman and S. L. Manatt, <u>ibid.</u>, <u>37</u>, 2346 (1962).

First we look at the output of the V-431l before it enters the phase detector and then monitor the phase detector output. By observing the former signal continuously it is possible to detect rather small changes of homogenity i.e. of the order of 1 to 2 parts in  $10^{10}$ ! We have experimentally determined that the actual resolution which we can obtain and maintain for several minutes to tens of minutes is of the order of 1-2 parts in  $10^{10}$ . This is somewhat better than is usually needed. With this system it is possible to combat slight degradation of the resolution by an appropriate change of the ten-turn pot of the y-gradient control. We have a more detailed description in the mill. Because our process of building this system was somewhat irrational, we haven't got all the details in any sort of order.

Enclosed are some examples of the system's performance at 56.4 Mc. The spectrum of propylene oxide has a lot of lines and we think rather shows off the performance. We have included a good A-60 spectrum of propylene oxide for comparison.3

(3) The spectra of propylene sulfide and propylene imine are also shown. The spectrum of the former is rather more resolved than that reported by Musher sometime ago. We hope to do some tickleing experiments on both these compounds. JET PROPULSION LABORATORY California Institute of Technology . 4800 Oak Grove Drive, Pasadena, California

Dr. B. L. Shapiro 4/11/63 Page 2

The double resonance spectra of propylene oxide show that the relative signs of the coupling constants are:

It is rather interesting that the  $J_{\rm BD}$  and  $J_{\rm CD}$  are of different signs. We think this stereochemical dependence of this long-range coupling is a general thing in all epoxides and rigid alliphatic systems. We will have more to say about this point in a future communication.

Enclosed is one further example of the use of our system for F<sup>19</sup> spectra. Shown is the F<sup>19</sup> spectrum of the -CF<sub>2</sub>H group in the molecule HCF<sub>2</sub>CF<sub>2</sub>CF=CF<sub>2</sub>. Here we used a 4600 cps. locking frequency and octafluorocyclobutane as the internal reference.

We also have a rig for doing  $H^1$   $F^{19}$  and  $F^{19}$   $H^1$  decoupling. It consists of two M Mc. crystals multiplied up to 56.4 and 60.0 Mc. From there it goes to a power amplifier which gives us 1 watt of output (real power, J. Baldeschwieler). We are able to swing the center band  $\pm$  40Kc. and over most of the range we get stability of fractions of a cycle. So far we have been able to relate the various  $H^1$   $F^{19}$  and  $F^{19}$  relative signs we reported a short time ago  $H^1$ 

(4) D. F. Evans, S. L. Manatt and D. D. Elleman, J. Am. Chem. Soc., 85, 238 (1963); in this paper we added a Note in Proof which apparently got garbled up by the type setter. The relative signs given for

C1 C = C F(2) should be 
$$J_{12}^{\mp}$$
,  $J_{34}^{\mp}$ ,  $J_{23}^{\mp}$ ,  $J_{13}^{\pm}$ ,  $J_{14}^{\pm}$  and  $J_{24}^{\pm}$ .

(3) (4)

to the various  $H^1$ - $H^1$  couplings. The various coupling constants then have the following absolute signs:

$$F = C - C - C$$

$$F = C - C - C$$

$$F = C - C - C$$

### Dr. B. L. Shapiro 4/11/63 Page 3

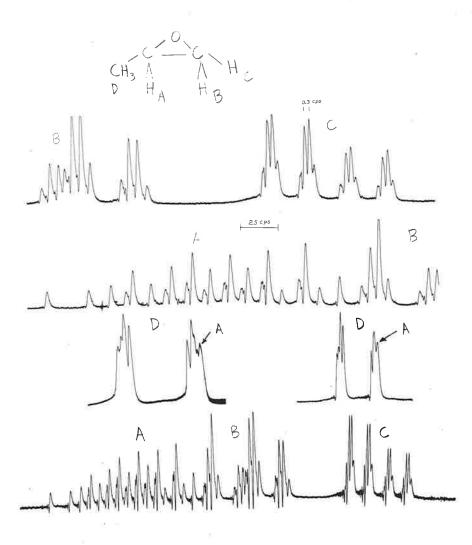
John Baldeschwieler and co-worker and George Van Dyke Tiers have previously reported and/or informed us of similar experiments which establish the same relationships.

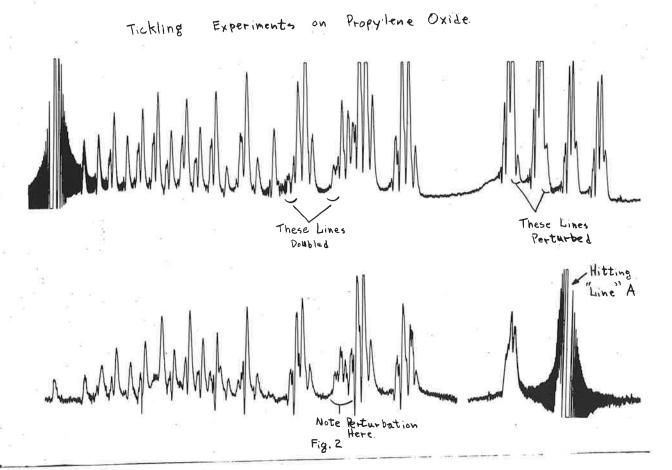
Very truly, Stan

Daniel D. Elleman Stanley L. Manatt Claude D. Pearce Elande & Rank

DDE/SLM/CDP:jas Air Mail

P. S. - McLauchlan and Buchinghan's recent absolute sign determination results (MELLO-N-M-R 54) predict a negative H CF coupling. This does not fit with our relative sign work. Somebody is wrong!





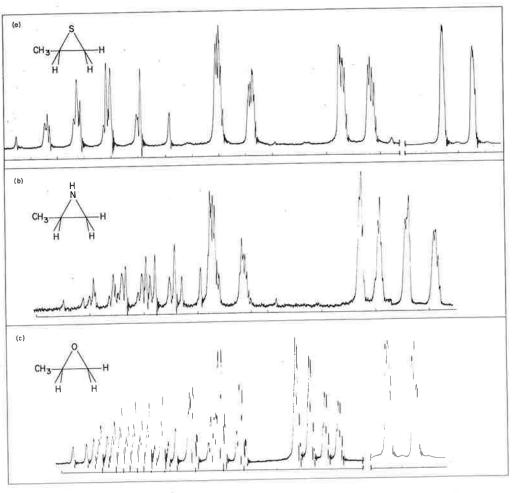
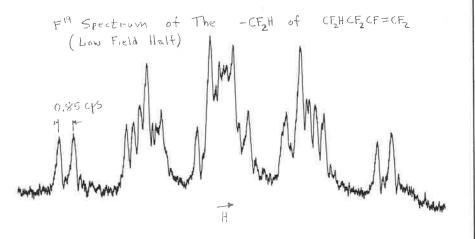


Fig. 3 A-60 50 CP Sweep Width



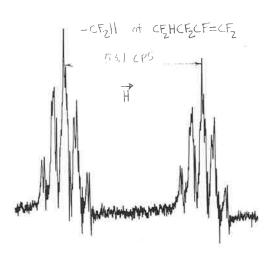


Fig. 4

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

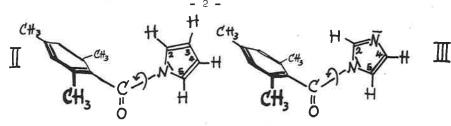
Dear Dr. Shapiro:

Please excuse the delay in sending you the overdue contribution to MELLCNMR. We hope our letter will reach you just at the eleventh hour to prevent you from eliminating our address from your mailing list!

Rotational isomerism of amides has been extensively studied by several NMR groups. We would like to add to this problem some observations we made on N-acyl-azoles (I; "azolides"). These compounds are expected to have an especially

I 
$$\Re \left( \frac{1}{\sqrt{2}} \right) = \frac{1}{\sqrt{2}}$$
 H-N = imidazole pyrrole

low C-N bond order 1) and accordingly, there are no indications in NMR spectra supporting hindered rotation around the C-N bond for amides of this type. The only exceptions are the azolides of mesitoic acid. Whereas in other N-acyl-pyrroles the azole protons show two triplets of equal intensity corresponding to the equivalent H-2, H-5 and H-3, H-4 respectively (cf. table below), N-mesitoyl-pyrrole (II) at 37° C in CCl<sub>4</sub> gives three rather broad signals of relative intensities 1:1:2. Obviously, the two-proton signal at = 3.8 rises from the approximately equivalent 3- and 4-protons. The other two signals which are shifted remarkably downfield ( = 2.4) and upfield ( = 3.5) suggest hindered rotation which causes one proton to be shielded by the aromatic ring-current and the other proton to be deshielded by the neighboring carbonyl group.



Similarly, NMR spectra of N-mesitoyl-imidazole (III) in  ${\rm CCl}_4$  and  ${\rm C}_4{\rm Cl}_6$  at  $37^{\circ}$  C show strongly broadened H-2 and H-5 signals, whereas H-4 absorption is nearly uninfluenced. With rising temperature  $^{2)}$ H-2 and H-5 signals sharpen and at  $65^{\circ}$  C the ABX system appears which is known from the spectra of all other N-acyl-imidazoles at room temperature  $^{3)}$ . There seems to be a surprisingly strong dependance of the rotational barrier from solvent polarity which will be further investigated.

Proton resonance of N-mesitoyl-2-methylimidazole shows two sharp dublets with  $\ell=3.28$  and  $\widehat{\ell}=3.32$  (in CCl<sub>4</sub>) for the azole protons in 4- and 5-position; apparently, at room temperature this molecule is fixed in the less crowded form where the methyl group is turned away from the aromatic ring. No hindered rotation has been observed with N-(2',6'-dimethoxyben-zoyl)-imidazole at room temperature. This and some other facts connected with the problem under discussion may be seen from the table below.

Some weeks ago, we very much enjoyed the visit of Dr. A.Bothner-By who kindly helped us to disentangle some of our more tricky NMR problems. By the way, many thanks for sending us Frequint IV.

With kindest regards,

Sincerely yours.

h.a. franc

A. Maunobreck

D. Wumub- gerlick

Heinz A.Staab

Albrecht Mannschreck

Doris Wurmb-Gerlich

- For a review on the chemistry of azolides see H.A.Staab, Angew.Chem. 74, 407 (1962).
- We are grateful to Dr. A.Melera of Varian AG, Zürich for measuring the N-mesitoyl-imidazole spectra at higher temperatures.
- B) Proton resonance of azoles and azolium ions: A.Mannschreck, W.Seitz and H.A.Staab, Ber.Bunsenges.physik.Chem.(in the press).

	Solvent	Azole-CH
N-mesitoyl-pyrrole	CC1 <sub>4</sub>	$\tau_{5}=2.4(b)$ $\tau_{2}=3.5(b)$ $\tau_{3}=3.8(b)$
N-acetyl-pyrrole	CDC13	$\tau_2 = \tau_5 = 2.72(t)$ $\tau_3 = \tau_4 = 3.73(t)$
N-mesitoyl-imidazole	CC14	$\tau_{2}$ =2.4(b) $\tau_{5}$ =2.7(b) $\tau_{4}$ =3.01(m)
Ħ	C <sub>4</sub> Ci <sub>6</sub>	$\tau_2 = 2.3(b)$ $\tau_5 = 2.7(b)$ $\tau_4 = 2.98(m)$
<b>n</b>	C <sub>4</sub> Cl <sub>6</sub> , 65°	$\tau_2 = 2.3 \text{(m)}  \tau_5 = 2.8 \text{(m)}  \tau_4 = 3.0 \text{(m)}$
N-(2',6'-dimethoxy- benzoyl)-imidazole	CC1 <sub>4</sub>	$T_2 = 2.37 \text{ (m)}  T_5 = 2.64 \text{ (m)}  T_4 = 3.05 \text{ (m)}$
N-acetyl-imidazole	CDC13	$\tau_{2}=1.82(m)$ $\tau_{5}=2.49(m)$ $\tau_{4}=2.86(m)$
N-benzoyl-imidazoles (p-substitued)	THE	$\tau_2$ =1.82(m) $\tau_5$ =2.49(m) $\tau_4$ =2.86(m) $\tau_2$ =1.92(m) $\tau_5$ =2.40-3(m) $\tau_4$ =2.89-93 (m)
N-mesitoyl-2- methylimidazole	CC1 <sub>4</sub>	$\tilde{\mathcal{L}} = 3.28(d)$ $\tilde{\mathcal{L}} = 3.32(d)$
N-(p-nitrobenzoyl)-2- methylimidazole	THF	T=2.89(d) T=3.16(d)

b = broad

t = triplet

m = multiplet, portion of ABX

d = dublet, portion of AB

#### BELL TELEPHONE LABORATORIES

INCORPORATED

MURRAY HILL NEW JERSEY
TELEPHONE
AREA CODE 201
Local 582-3000 April 17, 1963

DR. BERNARD L. SHAPIRO Mellon Institute 4400 Fifth Avenue Pittsburgh, Pennsylvania

Dear Barry:

It seems as though subscription time for your news letter comes around very often indeed. I am enclosing a preprint of a paper that we hope to publish in the journal Polymer. Preprints are available, if anyone should be interested. I cannot recall whether I have sent this to you before or not.

As a matter of minor interest there has recently been some question as to whether the nuclear magnetic resonance and tracer techniques for studying self-diffusion yield equivalent results. We have looked at this problem closely and we find that there are no significant or systematic outstanding cases of disagreement. It is interesting that the NMR and tracer methods agree better with one another than the various workers in the tracer field agree among themselves.

For example, self-diffusion in water has been measured by many workers over a period of a number of years and values from about 2.1 to 2.7 x  $10^{-5}$  cm<sup>2</sup>/secs have been reported. Robinson and thokes made a careful selection of the data and came up with the value 2.44 x  $10^{-5}$  at  $25^{\circ}\mathrm{C}$ .

We have been studying water recently by the NMR technique and our average over about 30 determinations is 2.45 x 10-5 at 23°C. The spadient calibration was made by an NMR technique in our methods. Thus, ours is an absolute determination. I believe that the gradient calibration may be reasonable for a part of the discrepancy between the results of Rice and Waugh and Gavin for liquid  $\mathrm{CH}_h$ .

Finally, a word may be in order concerning our subscription. Our NMM group in the Chemical Department at BTL is geographically centered around Ernie Anderson's High Resolution Laboratory. Thus, a copy of the 'Mellonmr' that is sent to me is used by Ernie Anderson, Dean Douglass, Bill Slichter, Frank Bovey, Tony Fratiello, and me. I will send you preprints covering some of the work of these other readers as they become available.

Sincerely yours,

Dane

DAVID W. McCALL

MOLECULAR MOTION IN POLYETHYLENE, IV

bу

David W. McCall and Dean C. Douglass Bell Telephone Laboratories, Incorporated Murray Hill, New Jersey

#### ABSTRACT

The proton magnetic resonance spin-lattice and spin-spin relaxation times,  $T_1$  and  $T_2$ , have been measured for various polyethylenes as a function of temperature. Transient methods were employed. The data are discussed in terms of methyl group rotations, corresponding to  $T_1$ -minima below -100°C, and liquid-like molecular motions, associated with  $T_1$  minima near -30°C. The importance of spin diffusion is emphasized.

(PREPRINTS AVAILABLE)

Done Perry,

I cutaning find Melicome industrial and energys for being truly in any "subscription"

The attacked not to be published not as protops not original, but I think at

Across Comment on Valence Bond Theory and the Dirac Vector Model\*

#### J. I. Musher

Department of Chemistry, Harvard University Cambridge 38, Massachusetts

We wish to demonstrate by a simple argument the gross inadequacy of the single structure valence bond (VB or HSLP) and by implication the Dirac vector model (DVM) methods for semi-quantitative molecular or crystal calculations.

The major conclusion of single structure VB theory from the point of view of its applicability to molecules is that the two-electron singlet and triplet interaction energies are given by  $C + K(1,2)/(1+S^2)$  and  $C - K(1,2)/(1-S^2)$  respectively. In the molecular prototype, the  $H_2$  molecule,  $C(r_H)$  the Coulomb energy is about 10% of the effective exchange energy  $K(r_{HH})$ , and the overlap  $S(r_{HH})$ , is significant only for  $r_{HH} \lesssim 4a_0$ . Thus the calculated singlet and triplet energies at a given  $r_{HH}$  are roughly  $\pm K(1,2)$  respectively relative to two H atoms at infinite separation. Therefore, since  $\frac{1}{2}(1+4s_1\cdot s_2)$  has eigenvalues of  $\pm 1$  for singlet and triplet states respectively, the interaction Hamiltonian can be expressed as  $-K(1,2)\frac{1}{2}(1+4s_1\cdot s_2)$  which is known as the DVM. When this is generalized to many electron systems, each VB diagram has an energy of  $\pm 1$ 0 for each pair of singlet electrons,  $\pm 1$ 1,2 for each pair of triplet electrons and  $\pm 1$ 2,3 for each pair of

uncorrelated electrons, the sum being over all electron pairs. The VB and DVM procedures have been used for semi-empirical calculations over the years<sup>2</sup> and a recent critique of the errors involved other than (explicitly) the problem raised here is given by Coulson.<sup>3</sup>

The simple VB and DVM procedure could be justified by a favorable comparison with data 4 on the  $1\Sigma$  and  $3\Sigma$  states of the hydrogen molecule: apparently such a comparison has not been made previously. [Note that the spatial parts of the singlet and triplet VB wave-functions differ only by their symmetry properties, and it is therefore not legitimate in the strict sense to choose different orbital exponents in order to minimize separately the energies of the two states. It is thus possible that the VB  $^{1}\psi$  and  $^{3}\psi$  are not equally good approximations to the true  $^{1}\psi$  and  $3_{\psi}$ , e.g. the  $1_{\psi}$  might be very good while the  $3_{\psi}$  is very poor. An indication of the lack of equal "goodness" for the two states is shown by the following in which the reasonably good Wang-VB function is used for  $^{1}\psi$ , the same screening  $(Z = 1.166)^{5}$  is used for  $3_{\psi}$ , and yet the triplet energy is decidedly poor.] According to VB theory at any value of  $\rm r_{HH}$  , (1-S^2)E(triplet)  $\equiv ^3 \! K$  should roughly equal the negative of  $(1+S^2)E(singlet)\equiv {}^1K$  or neglecting the Coulomb term,  $-({}^{1}K/{}^{3}K)=1$ . If one tries to determine  ${}^{1}K$  and  $^{3}$ K emprically from the 'most probable' potential curves  $^{4}$  of  $\rm{H}_{2}(^{1}\Sigma)$ and  $H_2(^3\Sigma)$  one gets for  $r_{HH}/a_0=1.4$  (equilibrium separation), 2.0, 2.5, 3.5, 4.0, and 5.0 respectively,  ${}^{1}K/(1+S^{2})={}^{1}E=-4.7$ ,

<sup>\*</sup>This research was supported in part by a fellowship from the Division of General Medical Sciences, U.S. Public Health Service and by support extended Harvard University by the Office of Naval Research.

-3-

-3.8, -2.6, -0.87, -0.43 and -0.08 eV;  ${}^3K/(1-S^2) = {}^3E = 5.5$ , 2.9, 1:3, 0.37, 0.19 and 0.04 eV; and  ${}^{-1}K/{}^3K = 2.5$ , 2.2, 2.6, 2.5, 2.3 and 2.0. Inclusion (arbitrary but near maximum<sup>1</sup>) of  $C(r_{HH})=10\%$  of the binding energy gives  ${}^{-1}K/{}^3K = 2.0$ , 1.7, 1.9, 1.8, 1.7 and 1.5. Thus, contrary to expectation, the singlet-triplet ratio does not always equal one for  $H_2$ , and in the absence of studies on other molecules, this discrepancy must, by implication, be considered general. The only conclusion therefore is that the VB and DVM methods have little valid applicability without modification to include at least three 'exchange integrals': singlet, triplet and 'uncorrelated'. The Dirac identity, of course, holds; it is only the expression for the interaction Hamiltonian which does not.

It is not certain why the VB picture fails despite the fact that  $^1\psi$  gives a reasonably good energy. Clearly the triplet state must be represented in some different way that would serve to depress its energy. One way to do this would be to use a different orbital exponent for  $^3\psi$ , from which one would obtain a  $^3K$  to give  $^{-1}K/^3K\sim 2$  in agreement with experiment.  $^8$ 

In order to illustrate the danger of using simple VB theory as long as the singlet-triplet ambiguity obtains, we take the very sensitive, and therefore perhaps unfair, example of the NMR proton-proton coupling constant in methane. Calculations of this have been performed by VB $^9$  and DVM $^{10}$  methods. Perturbation theory in VB-DVM gives for the Fermi term  $J_{\rm HH} = v_{\rm O}(\beta + \% - 2\delta)$  4 where

 $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are the unique VB exchange integrals. The VB atomic C-C integral, Y = 1.01 eV, is calculated explicitly, while the VB bonding and non-bonding C-H integrals,  $\delta$  = 0.233 eV and  $\alpha = -3.8$  eV are evaluated empierically. The H-H exchange integral, B, is evaluated empirically from the Ho potential curves<sup>5</sup> at  $r_{HH} = 1.77$  A as either  ${}^{1}K = -1.07$  eV $^{9}$  or  ${}^{-3}K = -0.47$  eV. The expression for  $\mathbf{J}_{\text{HH}}$  and all the integrals used should, in the sense of this note, be modified to distinguish between the  $^{1}$ K,  $^{-3}$ K and OK, where OK indicates the exchange integral for uncorrelated spins. Although we have not done this we feel that it is nevertheless instructive, to substitute into the VB-derived equations for  $\boldsymbol{J}_{HH}$  the two possible empirical values of  $\beta$  keeping the remaining integrals constant. (This is done merely as a demonstration of the non-quantitative nature of VB theory. It is not to be taken as a calculation.) For  $\beta = {}^{1}K(H,H)$  and  ${}^{-3}K(H,H)$  one finds  $J_{HH}$  =+38 cps and -4.7 cps respectively. 12,13 Such diverse results imply that a procedure which does not distinguish between the different types of K's at all necessary stages cannot be meaningful. Although the present is a highly sensitive example with an extreme ambiguity in the result, one expects that simple VB theory is also rather suspect for any non-trivial semi-empriical calculation.

We believe that the problem of calculating the Ferm-contact coupling constants between non-bonded nuclei should be treated by considering the random orientation of non-bonded spins to be principally perturbed by the effect of Hund's rule, disregarding the VB results and the above choice integrals. <sup>14</sup> In this case  $^{\rm n}J_{\rm HH}^{15}$  is negative and positive for neven and odds respectively. <sup>16</sup> This is so, e.g. on a fragment  ${\rm H_1C_1H_2}$  since excess spin  $\alpha$  on  ${\rm H_1}$  implies excess spin  $\beta$  on  ${\rm C_1}$  in all of its unfilled orbitals, which implies excess spin  $\alpha$  on  ${\rm H_2}$  giving a megative  $^2J$  by the expression  $^{17}$ ,  $^{12}J_{\rm H_1H_2}=-{\rm C}({\rm F}_{12}^{\alpha\beta}-{\rm F}_{12}^{\alpha\alpha})$ . This is believed to be correct experimentally  $^{18}$  for saturated  $^2J$ 's,  $^3J$ 's and  $^4J$ 's. The interaction with the  $\pi$ -electron could oppose Hund's rule  $^{19}$  and lead to the negative  $^2J$  in ethyleneand ethylene oxide. The success of the VB calculations on the  $^3J$ 's in ethane and ethylene  $^{20}$  might be due to the angular dependence not being critically affected by the magnitude of the K's taken separately, since the J's depend on the square of a sum of integrals.  $^{10}$ 

#### REFERENCES

- 1. This is so only for  $\rm H_2$  and the surprising results for  $\rm LI_2$  make simple VB theory all the more questionable. See S. Fraga and R. S. Mullikan, Revs. Mod. Phys. 32, 254 (1960). Their  $\eta$  is equal to our K which in other notation =  $\rm H_{12}$   $\rm S^2H_{11}$ .
- 2. The classic article of J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 167 (1935) remains the principal review of these methods. See also H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry, John Wiley and Sons, New York (1957), Ch. 12.
- 3. C. A. Coulson, Valence, Oxford University Press (1960) Ch. 7.7
- 4. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Mccular Theory of Gases and Liquids, John Wiley and Sons, New York (1954) Ch. 14 and references cited therein.
- J.C. Slater's opinion of the theory is well shown by the figures on pp. 55-57 of his new book. The Quantum Theory of Molecules and Solids, Vol.I (No-Graw-Hill, New York, 1963).

- 5. Since this only enters into the calculation of S, the results only change by a few percent if the pure Heitler-London (Z=1) function is used.
- 6. It is perhaps unfair to single out these theories for criticism since many of the more refined theories involving either only a single configuration or the neglect of overlap reduce to an expression similar to that of simple VB theory. e.g. R. McWeeny, Rev. Mod. Phys. 32, 335 (1960).
- 7. A similar problem in atomic spectroscopy was pointed out by G. W. King and J. H. Van Vleck, Phys. Rev. 56, 464 (1939).
- 8. In any case this procedure destroys the simplicity of the VB method.
- 9. M. Karplus and D. H. Anderson, J. Chem. Phys. 30, 6 (1959).
- 10. S. Alexander, J. Chem. Phys. 34, 106 (1961).
- 11. H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys. 31, 1278 (1959).
- 12. Accepting the experimental result of K. A. McLauchlan (personal communication) for the sign of  $\rm J_{C-H}$
- 13. Using/this perturbation calculation the energy denominator of 9 eV from ref. 9 give +15 and -2 cps. These calcuations neglect the Coulomb energy, and so e.g. differ from ref. 9.
- 14. This could be done by third-order perturbation theory with the Fermi-contact Hamiltonians and the electron-correlation operators as the coupled perturbations.
- 15. n is the number of bonds between the protons.
  16. See also S. Alexander, thesis, Hebrew University (Jerusalem, 1958). This thesis Contains the first and only reference to the alternation of the sign of J's. It will break down for very small J's across many bonds because of competing interactions of similar magnitude:
- 17. H. M. McConnell, J. Chem. Phys. 24, 460 (1956).
- 18. P. C. Lauterbur and R. J. Kurland, J. Am. Chem. Soc. 84, 3405 (1962); F. A.L. Anet, J. Am. Chem. Soc. 84, 3767 (1962); R. Freeman, J. Musher, K. A. McLauchlan and K. G. R. Pachler, Mol. Phys. 5, 321 (1962) and others.
- 19. The H- $\pi$ -carbon exchange integral seems likely to be negative whether it be  ${}^1K$  or  $-{}^3K$ .
- 29. M. Karplus, J. Chem. Phys. <u>30</u>, 11 (1959).

Theory of Carbon NMR Chemical Shifts in Conjugated Molecules

M. Karplus and J. A. Pople

#### ABSTRACT

A molecular orbital theory for carbon 13 chemical shifts in conjugated molecules is formulated. Consideration of the various possible contributions to the shift shows that the local paramagnetic term  $\sigma_p^{AA}$  is expected to dominate. By a detailed LCAO analysis of  $\sigma_p^{AA}$ , its variation with the salient features of the electron environment is determined. A significant dependence on the local charge  $\rho_A$  is found that agrees in sign and order of magnitude with the empirical relationship. Also, it is demonstrated that the shielding should be a function of the free valence  $F_A$  of the atom under consideration and of the polarity of its sigma-bonds. Linearizing the equation for the  $C^{13}$  chemical shift (with respect to benzene), one finds

$$\Delta \sigma_{A} \text{ (ppm)} = 10^{6} (\sigma_{A} - \sigma_{benzene})$$
  

$$\approx (86.7 + 46.0 \lambda_{H}) (\rho_{A} - 1) + 46.0 (F_{A} - 0.399)$$

where  $\boldsymbol{\lambda}_H$  represents the polarity of the C-H bond for a non-bridge carbon. Some results are given in Table I.

Table I. Chemical Shifts for Some Alternant Hydrocarbons

1 a	Free Valence	Chemical Shift b	-
Naphthalene		Calc. c	Exp. d
^ ^	$\mathbf{F}_1 = .452$	$\Delta \sigma_1 = +2.4$	Δ <sup>σ</sup> 1}= +0.8
( Y )2	F <sub>2</sub> = .404	$\Delta_{2}^{\sigma} = +0.23$	$\Delta \sigma_2$
$\sim$	F <sub>9</sub> = .104	$\Delta \sigma_9 = -13.6$	$\Delta \sigma_9 = -8.4$
	ä		
Biphenyl			lanera.
	F <sub>1</sub> = .124	$\Delta_{1}^{\sigma} = -12.7$	$\Delta q = -9.9$
	·F <sub>2</sub> = .436	$\Delta \sigma_2 = +1.7$	$\Delta \sigma_2$
	F <sub>3</sub> = .395	$\Delta \sigma_3 = -0.18$	Δ <sup>σ</sup> 3 = -0.4
*	F <sub>4</sub> = .412	$\Delta_{4}^{\sigma} = +0.60$	$\Delta \sigma_{4}$
		86	,
Phenanthrene			
	F <sub>1</sub> = .450	$\Delta^{\sigma}_{1} = +2.3$	$\Delta_{1}^{\sigma}$
<del></del>	F <sub>2</sub> = .402	$\Delta_2^{\sigma} = +0.14$	Δσ <sub>2</sub>
	F <sub>3</sub> = .407	$\Delta \sigma_3 = +0.37$	$\Delta \sigma_3 = +0.6$
	<b>F</b> <sub>4</sub> = .440	$\Delta_{4}^{\sigma} = +1.9$	$\Delta \sigma_{\!\! m{4}}^{}$
* * * * * * * * * * * * * * * * * * *	F <sub>9</sub> = .451	$\Delta \sigma_9 = +2.4$	$\Delta \sigma_9$
- s n s	F <sub>11</sub> = .108	$\Delta \sigma_{11} = -13.4$	$\Delta \sigma_{11}$
	F <sub>12</sub> = .139	$\Delta \sigma_{12} = -12.0$	Δ <sup>σ</sup> <sub>12</sub> ) ση
			- 26

#### Table I. continued

Pyrene	F <sub>1</sub> = .468	$\Delta_1^{\sigma} = +3.2$	$\Delta_{1}^{\sigma}$
	F <sub>2</sub> = .393	$\Delta \sigma_2 = -0.28$	$\Delta \sigma_{2} = +1.0$
2 .	F <sub>4</sub> = .452	$\Delta_{4}^{\sigma} = +2.4$	$\Delta \sigma_{4}$
· ·	F <sub>11</sub> = .110	$\Delta \sigma_{11}^{=-13.3}$	$\Delta \sigma_{11} = -4.4$
	F <sub>12</sub> = .148	$\Delta \sigma_{12}^{=-11.5}$	$\Delta \sigma_{12} = -8.1$



# UNITED STATES DEPARTMENT OF THE INTERIOR BUREAU OF MINES

#### REGION V

PITTSBURGH RESEARCH CENTER

4800 FORBES AVENUE PITTSBURGH 13, PENNSYLVANIA

April 18, 1963

Dear Barry:

At the recent symposium on Other Nuclei at the Pittsburgh Conference we presented a paper describing our carbon-13 work on hydroaromatics and aromatic compounds. We would like to submit a portion of this material as a contribution to MellonMR. Most of these spectra required  $\mathbf{C}^{1.3}$ -H spin decoupling; two examples are shown in figure 1. The bridgehead carbon atoms in naphthalene were found by collapsing the two aromatic doublets while the saturate region of the octahydrophenanthrene spectra yielded three methylene resonances under double resonance conditions. A chart summarizing our data plus data on 10 alkylbenzenes is shown in figure 2.

Chemical shift measurements for a few hydroaromatic compounds are shown in figure 3 along with shifts in methylbenzenes (Lauterbur) to compare the substituent effects of 6-membered saturated rings with methyl effects. The spectra in each group follow similar trends with substitution; in fact, the effects are practically identical. It should be pointed out that ethyl effects are much stronger; i.e., the ethyl substituted carbon in hexaethylbenzene has its resonance about 7 ppm below the substituted carbon in hexamethylbenzene.

The spectrum of octahydrophenanthrene (Fig. 1) intrigued us since it exhibits two  $\alpha$  methylene resonances, one of which falls at a much higher field than anticipated. We thought that this shift could be due to the spatial arrangement of the methylene carbon atoms in the 4 and 5 positions. To explore this hypothesis comparisons were made between three pairs of compounds, one member of each having a two-ring condensed structure, the other having a phenanthrene or hydrophenanthrene structure (Fig. 4). In each pair one of the resonances moved to higher field as the third ring was added; in all cases the upfield shift occurred for carbon atoms of the type present in the additional ring, whether aromatic or saturate. In at least one case (octahydrophenanthrene)  $C^{13}$  NMR is more sensitive to this type structure than proton NMR.

Figure 5 indicates that methylene bridges have their  $c^{13}$  resonances at lower field than the other methylene groups studied thus far and that methylene shifts are probably dependent on the ring system to which they are bonded. We plan to extend our studies to alkyl-substituted condensed ring systems to explore this point.

H. L. Retcofsky J Q. 4 Friell

R. A. Friedel

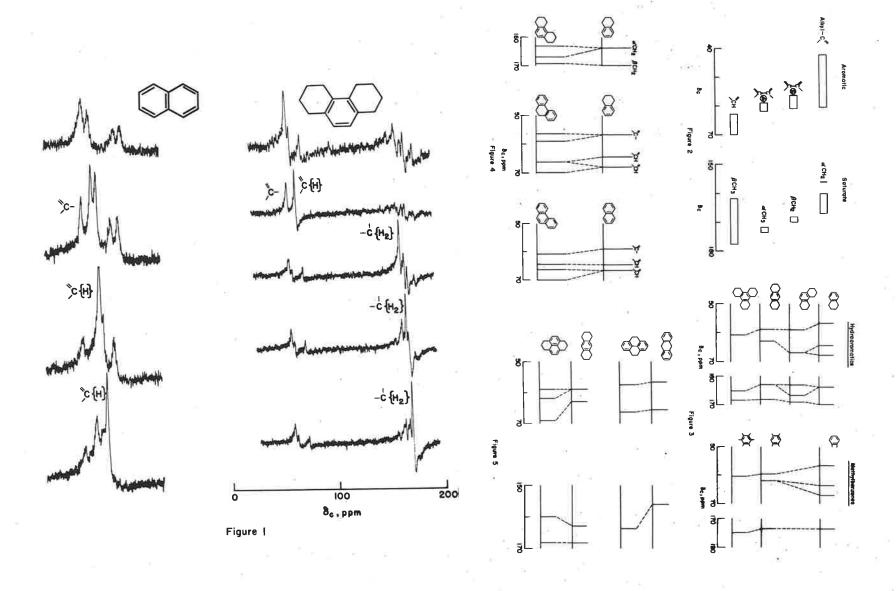
P.S. Please excuse the regrettable goof, In our January letter,
Of bond "x character" we have no proof, "s character" reads much better.

<sup>&</sup>lt;sup>a</sup>From Dictionary of Values of Molecular Constants (Vol. II), edited under the direction of the Mathematical Institute, Oxford and the Centre de Chimie Theorique de France, Paris, 1955.

bParts per million with reference to benzene.

<sup>&</sup>lt;sup>c</sup>Calculated from Eq. (19) with the assumption that ( $\rho_{\rm A}$ -1) = 0.

d<sub>From</sub> reference 2. Values bracketed together correspond to unresolved results presented in the paper. It should also be noted that some of the assignments are tentative.



#### UNIVERSITY OF FLORIDA GAINESVILLE

DEPARTMENT OF CHEMISTRY

April 19, 1963

Dr. B. L. Shapiro Mellon Institute 440 Fifth Avenue Pittsburgh, Pennsylvania

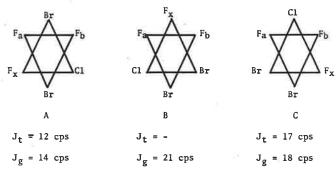
Dear Dr. Shapiro:

During my predoctoral training under Dr. W. S. Brey, Jr. at the University of Florida I have found MELLON-M-R to be very useful as well as enjoyable. I will be joining the R. & D. Dept. of Atlantic Refining Co., Philadelphia, Pa. in the near future and would very much appreciate being put on your mailing list. As an initial contribution I would like to report some results of an investigation on the temperature dependence of F-F couplings which may be classified, at least in part, as a mystery.

The fluorine spectrum of CF2Br-CFBrCl as previously discussed (1) is that of an abx type and consists of a NEQQ for the ab part, within which, a and b are unequally coupled to x. The x part of the spectrum consists of a double-doublet which overlaps to form a triplet. The chemical shifts for the a, b and x groups are -20.2, -18.4 and -10.1 ppm relative to external CF3COOH, respectively.

The temperature dependence of the ab part of the spectrum (the CF2Br group) is somewhat unusual as shown in Figures 1 and 2. At about -50°C. the peaks show a broadening and a loss of fine structure which is attributed to the slow interconversion of rotational isomers "as expected". Actually, at first, we attributed this broadening to a viscosity effect which is erroneous since a further decrease in temperature produces the original fine structure. The odd part of the temperature dependence is the unequal broadening between the a and b groups. One can think of a number of possibilities for this phenomenon, however, they are at best a guess. One would be that the quadrupole moment of the halogens may be transmitted to one of the fluorine atoms more readily than the other. A second possibility would be that the slow rotation produces different relaxation times. Actually, since this effect is observed during slow rotation, one would expect it to be a rotational effect, however, it is hard to see any difference between the environments of the two atoms as far as rotation is concerned.

At -120°C, the fluorine spectrum yields three distinguishable isomers which are shown in Figure 3. The isomers along with the observed coupling constants are listed below.



It may be noted that the observed coupling constants for the individual isomers are quite different from those calculated by Gutowsky, Belford and McMahon (1).

(1) H. S. Gutowsky, G. G. Belford and P. E. McMahon, J. Chem. Phys. 36, 3353 (1962).

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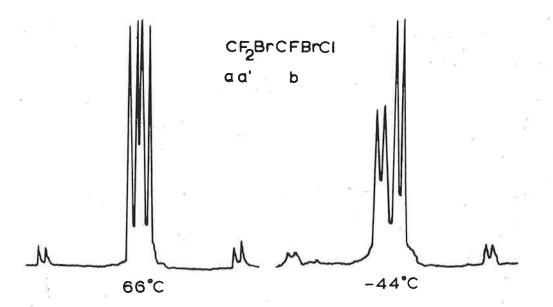


Fig. 1. The effect of temperature upon the F<sup>19</sup> spectrum of the CF<sub>2</sub>Br group in CF<sub>2</sub>BrCFBrC1 in solution in CFCl<sub>3</sub>.

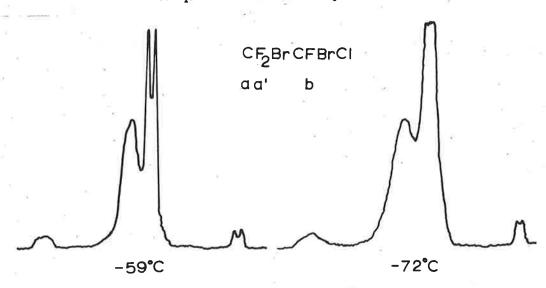


Fig. 2. The effect of temperature upon the F<sup>19</sup> spectrum of the CF<sub>2</sub>Br group in CF<sub>2</sub>BrCFBrCl in solution in CFCl<sub>3</sub>.

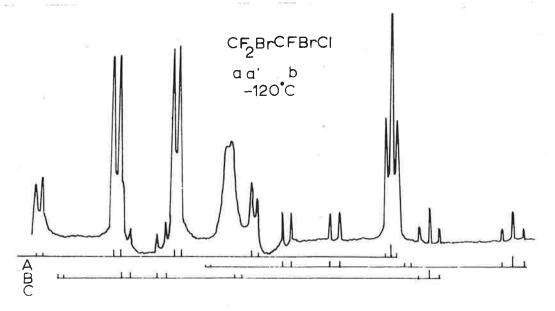


Fig. 3. The  ${\bf F}^{19}$  spectrum of CF2BrCFBrC1 in solution in CFCl3 at -120° C., where A, B, and C corresponds to the three rotational isomers.

#### 2

# UNITED STATES DEPARTMENT OF AGRICULTURE AGRICULTURAL RESEARCH SERVICE WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION 800 BUCHANAN STREET, ALBANY 10, CALIFORNIA

April 18, 1963

AIRMAIL

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

Dear Dr. Shapiro:

As a result of the paper by Mannatt et al., which was given at last year's Mellon NMR meeting (and later published in MELLONMR 50), we decided to investigate the sensitivity of various parts of our DP-60 system to a moderately strong air stream from our air turbine hose in an effort to locate the source of our deteriorating field—frequency stability. We found three sensitive points (up to several hundred cps shifts): the transmitter crystal housing and RF oscillator tube in the spectrometer and the ends of the coils on the 12" magnet. A cylindrical section of styrofoam cut to fit between the inner and outer crystal housings and a new tube completely removed the spectrometer sensitivity. Since our yoke was already enclosed, we did not build a full JFL "coffin," but simply boxed in the coils with styrofoam, filling the air pockets with pulverized poly-urethane foam. Because of the limited clearance, the inner ends of the coils were covered with 1/4" neoprene rubber. These changes gave us a marked improvement in short-term stability.

One of us (Dick Elsken) reported at the recent OCEANS meeting on our experience with the close-coupled insert and neutralized preamplifier that has become available from Varian, and we thought that some of your readers who weren't at Pittsburgh might also be interested in this development. An overall improvement in signal-to-noise of approximately two is specified by Varian. As can be seen from the attached spectra of the methylene quartet from one percent ethyl benzene, the preamp and insert each improved our sensitivity by a factor of about 1.5. The RMS noise was calculated from 30 equally spaced points. Since both the new and old inserts have practically identical inductances (0.20 uh at 60 Mcps), the insert improvement arises from the net change in filling-factor and .. We calculate a filling-factor of 0.27 for the standard insert and 0.56 for the close-coupled model. The measured 4 of the standard insert at 60 Mcps is 92 and for the new insert is 83. On the basis of these values one would expect an improvement of 1.8 which agrees quite well with our results in view of the statistical uncertainty in our RMS noise value.

The enclosed "before" and "after" spectra of the acetaldehyde quartet shows that the resolution is scarcely degraded at all by the close-coupled insert. However, to obtain resolution of this quality the turbine has to be very critically positioned (not the easiest feat with the very cumbersome system that is provided for adjusting the threaded collar which holds the turbine). Also, the resolution is degraded by high spinning rates probably due to wobbling of even the best analytical tubes in the snug-fitting inner glass support for the receiver coil.

We noticed at the outset that the ratio of the major to minor peaks heights of the aldehyde quartet was 2.5 rather than the theoretical 3.0, and that this was independent of RF field intensity. In view of the close-coupling of the new insert it seemed probable that we were observing the effect of radiation damping (see Bruce et al., Phys. Rev., 104, 419 (1956) and Abragam, Nuclear Magnetism, p. 73). A calculation of the contribution from this effect on the line width of a phase-detected signal was calculated for one of the major aldehyde peaks in pure acetaldehyde using Bruce's equation. The result was 0.3 cps, which is just the observed width. The dependence of damping on spin concentration explains its larger effect on the major line. Since the damping term is proportional to the Q of the receiver coil as well as concentration, these factors were varied singly by intentionally detuning the receiver coil and using a 10% acetaldehyde in CClh solution. In both cases the theoretical intensity ratio was obtained. The result for the 10% solution is shown. In view of this result, might not such a solution be a better standard for resolution than the neat liquid?

Incidentally, we have had no success so far with Varian micro-cells in this insert with sample volumes less than  $150~\lambda$ .

Sincerely yours

R. E. Lundin

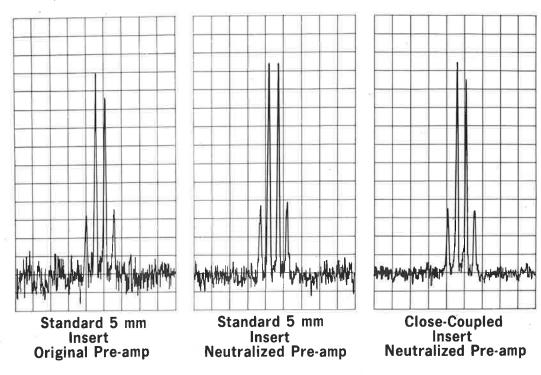
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R. H. Elsken

Fiber Physics Investigations
Wool and Mohair Laboratory

Attachment

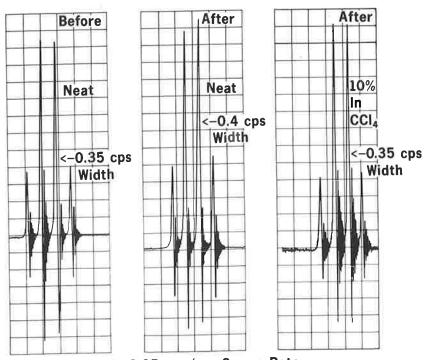
### S/N COMPARISON, METHYLENE QUARTET, 1% ETHYL BENZENE



System - DP-60 RF -  $66 \mu$  gauss

Sweep - 1 cps/sec Sample in Varian Analytical Tube Bandwidth - 1 cps

# DP-60 RESOLUTION COMPARISON WITH HIGH SENSITIVITY KIT (V-K3529)



2 cps Bandwidth, 0.25 cps/sec Sweep Rate Acetaldehyde In 4.28 mm ID Tube

April 18, 1963

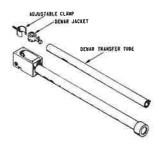
Dr. B. L. Shapiro Mellon Institute 4400 Fifth Avenue Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

E. C. HUGHES War flor Gillen

> Erratic sample spinning is obviously not desirable, but eliminating this can prove to be somewhat challenging, to say the least, when the Varian temperature apparatus is connected to the HR-60 probe.

The Dewar transfer tube exerts a pressure upon the insert that makes alignment of the insert (with respect to the spinner housing) difficult to maintain. To counteract this pressure, we use an adjustable aluminum clamp that can exert pressure from the opposite direction. The clamp should be loose fitting enough to allow shimming if a lateral adjustment should be desired.

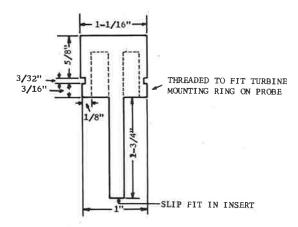


An alignment tool for the insert is another indispensable item, and the measurements are as follows:

Dr. B. L. Shapiro Mellon Institute

-2-

4-18-63



The alignment is accomplished by re-positioning the turbine mounting ring until this device can screw in and out freely. Of course, any time the insert is removed from the probe, re-alignment is necessary. This has resulted in not only more consistent sweeps on the scope, but also in some resolution improvement in the recorded spectra -- all other factors being equal.

Sincerely yours,

THE STANDARD COMPANY (OHIO)

Dr. W. M. Ritchey/ Mr. Herb Grossman

WMR/HG: cnp

### The Durham Colleges in the university of Durham

TELEPHONE DURHAM 3541-R

CHEMISTRY DEPARTMENT,
SCIENCE LABORATORIES,
SOUTH ROAD,
DURHAM CITY,

JWE/LR

22nd April, 1963.

Dear Dr. Shapiro.

Our A.E.I. R.S.2 Spectrometer was delivered here last August and since that time has been in almost continuous use. Most of the compounds studied have been highly fluorinated hydrocarbons, and my interest has been mainly in the 19F chemical shifts and coupling constants. Some of the compounds also show interesting hydrogen spectra, for example, the hydrogen spectrum of the compound

shows a peculiar long range coupling constant. The CH<sub>0</sub> resonance is split into a doublet, presumably from coupling with the nearest fluorine nucleus ( $J_{\rm HF} = 5.5 \pm 0.5$  cycles sec<sup>-1</sup>), and both components of this doublet are themselves split into two peaks ( $J = 0.62 \pm 0.05$  cycles sec<sup>-1</sup>), presumably as a result of coupling with only one of the nuclei five bonds away. The <sup>19</sup>F spectrum of the compound shows it to be a single fixed conformer at room temperature with both the H and carbonyl groups in equatorial positions, hence if there is free rotation about the C-C single bonds in the carbonyl side chain, then the methyl hydrogens have the same time-averaged spatial relationship

/with

#### Dr. Shapiro

Page 2

with each of the F and H nuclei five bonds removed. The fact that the CH<sub>B</sub> group couples strongly with only one of these nuclei suggests that re-orientation of the carbonyl group is restricted in some way, probably by internal H-bonding, so that the methyl group is in an orientation which favours coupling with only one of the F nuclei on the adjacent ring carbon atom.

The small coupling constant cannot be detected on any of the other peaks in the spectrum since the individual peaks are all at least 5 cycles sec-1 in width.

Work on the spectrum of this and similar carbonyl compounds is in progress.

Yours sincerely,

J. W. Emsley.

J.W. Emsley.

Dr. B.L. Shapiro, Mellon Institute, 4400 Fifth Avenue, Pittsburgh 13, PA., U.S.A.

### A M E R I C A N C Y A N A M I D C O M P A N Y STAMFORD RESEARCH LABORATORIES

1937 WEST MAIN STREET, STAMFORD, CONN.

FIRESIDE 8-7331

April 18, 1963

Mr. Barry Shapiro MELLON NMR News Letter Mellon Institute Pittsburgh 13, Pennsylvania

Dear Barry:

Thank you for your subscription reminder. We have recently examined the proton spectra of a number of olefin-iron tetracarbonyl and  $\pi$ -allyl iron tetracarbonyl halide complexes (I and II) which have been prepared by Drs. E. Weiss and H. Murdoch of our European Research Institute at Geneva.

The olefin complexes included the following ligands: maleic and fumaric acids and their methyl esters, maleic anhydride, cinnamic acid, cinnamaldehyde, acrylic acid, methyl acrylate, acrylamide, and acrolein. Their spectra were taken in acetone-d6, in which all were adequately soluble. The free olefin was also run in the same solvent for comparison. Some line broadening from small amounts of Fe (III) was observed, but in many cases, spectra could be sharpened considerably by the addition of a small amount of SnCl<sub>2</sub>.

All complexed olefinic protons were found to be shifted 2.5 to 3.0 ppm. to higher field from the free olefin position. This shift is usually observed with iron carbonyl complexes and is probably due to a strong anisotropy associated with the Fe (CO)4 group.

In the case of the ligands containing two or three non-equivalent hydrogens, AB, ABC or ABX spectra were obtained which yielded the H-H couplings in the complex. It was found that Jtrans and Jcis decreased from their free olefin values. For example, in free methyl scrylate, Jtrans = 17.2, Jcis = 10.2 c.p.s. (Castellano and Waugh, J. Chem Phys  $3\mu$ , 295 (61)); while in the complex  $/J_{\rm trans}/=10.8$ ,  $/J_{\rm cis}/=5.0$  c.p.s. These data for all the ligands are given in Helv. Chim. Acta, h.5, 200 (03). The  $/J_{\rm gem}/$  values are small, as in the free olefin, and although it appeared from a partial analysis that all the signs of the couplings were the same, this point is being checked with further calculations. Since the C=C bond length in acrylonitrile - Fe(CO)4 has

been observed to increase from the free olefin value of 1.34 A° to 1.40 A, (X-ray data of Luxmoore and Truter, Proc. Chem Soc. 1961, 466), it appears that the decreased couplings are in accordance with the deminished contributions to non-perfect pairing structures expected on increasing the distance between the hydrogens on different carbon atoms.

- 2 -

In the series of  $\pi$  -allyl complexes,  $\pi$ -methallyl iron tetracarbonyl chloride was found to give a very well resolved spectrum, with the aid of stannous chloride, from which the isomer configuration could be deduced. Impastato and Ihrman (JACS §3, 3726 (1961)) first reported its preparation and gave some NNR data, but they concluded, mainly from the reaction mechanism involved, that the product was the anti isomer (III).

In our spectrum, the hydrogen on the central carbon atom appears as a doubled triplet with the triplet splitting being the larger. This would indicate that the structure is the  $\underline{\text{syn}}$  isomer (IV), if we make the usual assumption that a trans coupling in this system is larger than a cis coupling. Using the numbering in (IV), the shifts (in acetone-d<sub>6</sub>) are:  $H_1$ : 7.14 $\tau$ ,  $H_2$ : 5.51 $\tau$ ,  $H_3$ : 4.65 $\tau$ ,  $H_4$ (CH<sub>3</sub>): 7.91 $\tau$ ,  $H_5$ : 5.84 $\tau$ . The couplings (absolute values) are  $J_{12}$  = 0,  $J_{23}$  = 8.1,  $J_{13}$  =  $J_{35}$  = 12.7,  $J_{16}$  = 6.3 cps.

Very truly yours.

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