

July 63

Mailed:  
28 June 1963

Premier ✓

Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
N-M-R

No. 57

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chem. shift



DEADLINE FOR NEXT ISSUE  
25 July 1963

Ilgakuine eraviisiliste kiriade kogu NMR laboratooriumeiar. Kogus leiduv informatsioon on mõeldud ainult lugeja tarbeks. Tsiteerimine ei ole lubatud; ehk kui ainult otseselt kokkuleppel kirja autoriga ja siis peab tsitaadile lisama viite "Eraviisiline teade".

UNIVERSITY OF ILLINOIS

Department of  
CHEMISTRY AND CHEMICAL ENGINEERING  
URBANA

The William Albert Noyes Laboratory

May 14, 1963

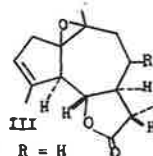
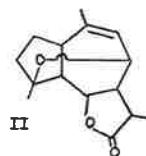
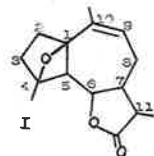
Dr. B. L. Shapiro  
Mellon Institute  
1400 Fifth Avenue  
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

We think that a compilation of NMR spectra of terpenoids would be valuable to those who encounter terpenoids and related substances in their research, and are making such a compilation. The spectra are being obtained in the same manner as were those in the Varian Spectra Catalogs, and will eventually be published in similar form. We have been concentrating on mono- and sesquiterpenoids, and currently have about 200 spectra.

If any of your readers would be interested in spectra of any particular terpenoids, we would be glad to furnish them if we have them. If anyone wants to donate samples, we would be delighted to supply them with the list of compounds which we have to avoid duplication.

NMR spectra, of course, reveal a good deal about the structural features of most terpenoids, particularly the lower terpenoids. Some recent examples from our laboratory include arborescin IIIa and globicin IIIb (samples provided by Drs. Čekan, Procházka, and Herout, Prague, Czechoslovakia). Previously proposed structures for arborescin are I and II; for globicin the location of the double bond and ether oxygen and the stereochemistry were not known at the time the NMR spectrum was run. The NMR and NMRD spectra of these substances coupled with previous chemical studies led to formulas IIIa and b (except for absolute configurations, which are proposed on biogenetic grounds). The relative configurations shown are derived from observed coupling constants through the use of Karplus (and modified Karplus) equations and Dreiding molecular models. Structure IIIa for arborescin has recently been confirmed by synthesis.



a R = H  
b R = OAc

Dr. B. L. Shapiro

- 2 -

May 14, 1963

A more striking example of the power of NMR with certain terpenoids (and an illustration of the value of a compilation of spectra of known substances) is the case of IV (sample provided by Dr. S. Dev, Poona, India), the sesquiterpenoid isoprenolog of  $\alpha$ -pinene. With the NMR spectrum, the molecular formula, the pre-NMR idea that the compound was tricyclic, and the spectrum of  $\alpha$ -pinene, it was possible to derive the structural formula and stereochemistry (except for the absolute configuration) in a matter of minutes. The methyl group attached to  $sp^3$  carbon is clearly shielded by the ring double bond, necessitating the relative stereochemistry shown.



Very truly yours,

*Robert B. Bates*

Robert B. Bates  
Assistant Professor

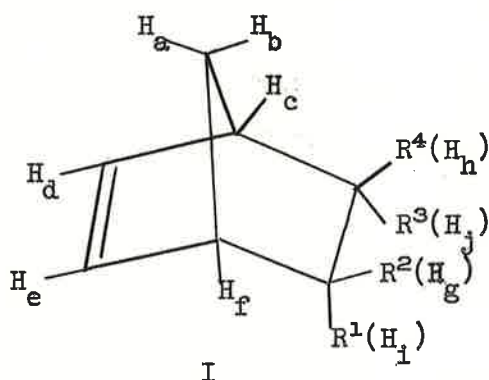
REB:ltg

PRINCETON UNIVERSITY  
Department of Chemistry  
Princeton, New Jersey

May 23, 1963

Dear Barry:

Because of their known and fixed geometry, bicyclo[2.2.1]heptane ring systems - norbornene and norbornane derivatives - are of continuing interest to n.m.r. spectroscopists. Complete analysis of the proton spectra of these systems is difficult since "virtual coupling" can decrease the amount of useful information obtainable from the regular spectra alone. By the use of  $^{13}\text{C}$  satellites and of selective solvent shifts we have been able to assign all proton resonances and to measure all proton chemical shifts and non-zero H-H coupling constants for several norbornene derivatives (I).



$J_{de}$	5.1-5.8	$ J_{aj} $	2.0-3.1
$J_{cd,ef}$	2.4-3.0	$J_{ch,fg}$	3.2-4.0
$J_{ce,df}$	0.5-1.0	$J_{gh}$	7.5-9.2
$ J_{ab} $	8.5-9.4	$J_{gj}$	2.1-3.4
$J_{ac,af}$	1.5-2.0	$J_{cj,fi}$	0
$J_{bc,bf}$	< 1.3-1.5	$ J_{hj} $	10.4-13.2

Ranges for H-H coupling constants in cps. are given above; noteworthy is the long-range coupling  $J_{aj}$ , and absence of such coupling  $J_{cf} = 0$  (which parallels Muller and Rose observation for  $\beta,\beta$ -dimethyl trimethylene oxide, Mellonmr 55-9). The allylic J's are of the same sign as  $J_{de}$ , the olefinic-olefinic coupling constant; their magnitude is consistent with the observations of Sternhell (Mellonmr 54-6).

The magnitudes of some of the vicinal coupling constants are found not to depend exclusively upon the respective dihedral angles: for example,  $J_{ac} \neq J_{bc}$  and  $J_{de} \neq J_{gh}$  - substituent electronegativities and other factors also are important. For monosubstituted norbornenes of the type  $R^1 = X$  the vicinal coupling constants  $J_{gh}$ ,  $\Sigma J_{fg} + J_{gj}$  as well as the internal chemical shifts  $H_g-H_h$  and  $H_g-H_f$ , vary in an approximately linear way with the electronegativity  $E_x$  of the substituent X, (Cavanaugh and Dailey, J. Chem. Phys., 34, 1099 (1961)).

Sincerely yours,

Gene Caruth

Pierre Laszlo

Paul Schleyer

Paul Schleyer



## ESSO RESEARCH AND ENGINEERING COMPANY

ANALYTICAL RESEARCH DIVISION

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

May 28, 1963

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

Dear Dr. Shapiro:

This letter reports certain modifications to the Varian V-4365 Field Homogeneity Control that increase the ease and rapidity with which optimum field homogeneity adjustments can be made and maintained. More in the nature of "human engineering" than fundamental improvement, the three modifications described are individually optional. Collectively, the modifications should prove operationally advantageous in laboratories that employ the HR-60, DP-60, or other spectrometer assembly embodying the V-4013A twelve-inch magnet and V-4365 control unit, particularly if the usage schedule requires frequent removal and reinsertion of probes.

### I. X- and Y- Axis Switches

Installation of three-position switches in the X- and Y-axis shim coil circuits makes it possible to execute the manipulations required to position the probe on geometric center without using the X- and Y-axis control potentiometers. Consequently, over-all manipulations are considerably simplified, and the operator may "check for center" at any time without disturbing the carefully optimized settings of X- and Y-axis homogeneity controls.

Grayhill three-position rotary switches, with spring-return to center (#24102, two-deck, X-axis; #24101, single-deck, Y-axis), are mounted on the front of the V-4365 control unit in the space between the X-axis control and the battery test posts. Leads that originally connected to the center tabs (wipers) of the X- (dual) and Y- (single) potentiometers are shifted to the moving arms of the corresponding switches and decks. The center-position tab of each switch is connected to the center tab (wiper) of the corresponding potentiometer. Clockwise and counterclockwise tabs of the switch decks are connected to the respective tabs of corresponding potentiometers.

When thus connected, operation of the X- or Y-axis switch is electrically equivalent to turning the corresponding control to an extreme position. Releasing the switch, in effect, restores the control to its original setting.

## II. Curvature Control

Magnets that are difficult to overcycle characteristically require a "dishing" correction, i.e., a curvature control setting in the region of 85 to 95. In this region the original control is quite nonlinear with respect to current through the shim coils and is difficult to optimize. With the wiring changes described below, the full rotation of a single potentiometer applies the dishing correction, with "0" the neutral setting.

Leads connected to the center tab (wiper) of one (either) section of the dual 500-ohm curvature potentiometer are shifted to the counterclockwise tab, and then that section of the potentiometer is entirely disconnected from the circuit. The remaining section is replaced with a single 200-ohm wire-wound potentiometer (2 watts). Adjustment of the curvature control becomes less critical than in the original circuit by a factor of roughly five.

## III. Y-Axis Control

The original 1-turn potentiometer (single) is replaced with a three-turn potentiometer of the same resistance (1000 ohms). A multi-turn dial may be used but is scarcely necessary.

The writer wishes to acknowledge the kindness of Dr. Eugene I. Snyder who has for some time shared his personal subscription to Mellon-M-R with interested colleagues.

Very truly yours,



B. E. Hudson, Jr.

BEH:par



Department of Chemistry  
University of Utah  
Salt Lake City 12, Utah  
June 7, 1963

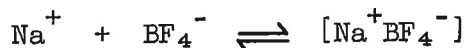
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Re: The BF Coupling Constant in  $\text{BF}_4^-$

Dear Barry,

The  $\text{B}^{11}\text{-F}^{19}$  coupling constant in the  $\text{BF}_4^-$  ion has been reported<sup>1</sup> to be 4.8 cps. We have found that the splitting in the fluorine and boron-11 NMR spectra of  $\text{MBF}_4$  solutions is not constant, but depends on the concentration, cation, type of anion accompanying extra cations, and the solvent. The observed splitting, which we call  $J_e$ , is apparently an average coupling for two or more labile species in equilibrium. The  $\text{B}^{11}$  spectra of these solutions consist of a sharp 1:4:6:4:1 quintet and three adjacent broad peaks with peak height ratio very nearly 1:3:3. It is presumed that these latter are components of the quartet due to  $\text{BF}_3\text{OH}^-$  with the fourth peak falling under the  $\text{BF}_4^-$  quintet. The presence of  $\text{BF}_3\text{OH}^-$  from hydrolysis of  $\text{BF}_4^-$  in these solutions is quite well established on chemical grounds. That it is long lived enough to give a separate NMR spectrum from  $\text{BF}_4^-$  is confirmed by the kinetic data of Anbar and Guttmann.<sup>2</sup>

The changes in  $J_e$  must therefore be due to ion-ion and ion-solvent interactions. With a simple ion-pair model we have fit the data for  $\text{NaBF}_4$  in aqueous solution. Ignoring solvation we may write,



with

$$K = \frac{1-a}{a^2c}$$

1. R. C. Chambers, H. C. Clark, L. W. Reeves, and C. J. Willis, Can. J. Chem. 39, 258 (1961)
2. M. Anbar and S. Guttmann, J. Phys. Chem. 64, 1896 (1960)

then with

$$J(\text{BF}_4^-) = J_0 \text{ and } J(\text{Na}^+\text{BF}_4^-) = J_p, \quad J_e = J_0 a + J_p(1 - a)$$

using  $J_0$ ,  $J_p$ , and  $K$  as parameters, the criterion for fit was that a value for  $K$  be selected which gave a minimum variance for a linear regression on  $J_0$  and  $J_p$ . The activity coefficients of  $\text{NaClO}_4$  were used to approximate those for  $\text{NaBF}_4$  because of the unavailability of the latter. The values for  $\text{NaClO}_4$  were selected because of the similarities in the  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  ions. The parameters obtained in this manner are  $K = 0.22 \pm 0.07 \text{ l. mole}^{-1}$ ,  $J_0 = 1.13 \pm 0.07 \text{ cps}$ ,  $J_p = 11 \pm 2 \text{ cps}$ .

The data for aqueous  $\text{NaBF}_4$  and  $\text{NH}_4\text{BF}_4$  are shown in Fig. 1 along with the theoretical curve. The two agree well over both the concentration range for which the "approximate" activity coefficients are known, and over the extrapolated region (dashed line) for the remaining data.

Unlike the splittings in  $\text{NaBF}_4$ , the values of  $J_e$  for  $\text{NH}_4\text{BF}_4$  show essentially no concentration dependence. A linear extrapolation of these data to infinite dilution gives  $J_0 = 1.15 \text{ cps}$ , in good agreement with the value predicted for  $\text{NaBF}_4$  ( $J_0 = 1.13 \text{ cps}$ ).

In Fig. 2, we have shown for a 0.501 M solution of  $\text{NaBF}_4$  the dependence of  $J_e$  on the concentration of various nitrates. For comparison the data on pure  $\text{NaBF}_4$  are shown for the concentration in excess of 0.501 M. In agreement with the ion-pair model proposed, there is a definite common ion effect, and very different behavior is noted for different cations.

The difference between the sodium nitrate curves and the pure fluoroborate curve is probably due to a competition between the nitrate and the fluoroborate anions for the available Na. This also would explain the slight decrease in coupling for the increasing  $\text{NH}_4\text{NO}_3$  concentration.

Sincerely yours,

*David M. Grant*

David M. Grant

*Karl F. Kuhlmann*

Karl F. Kuhlmann

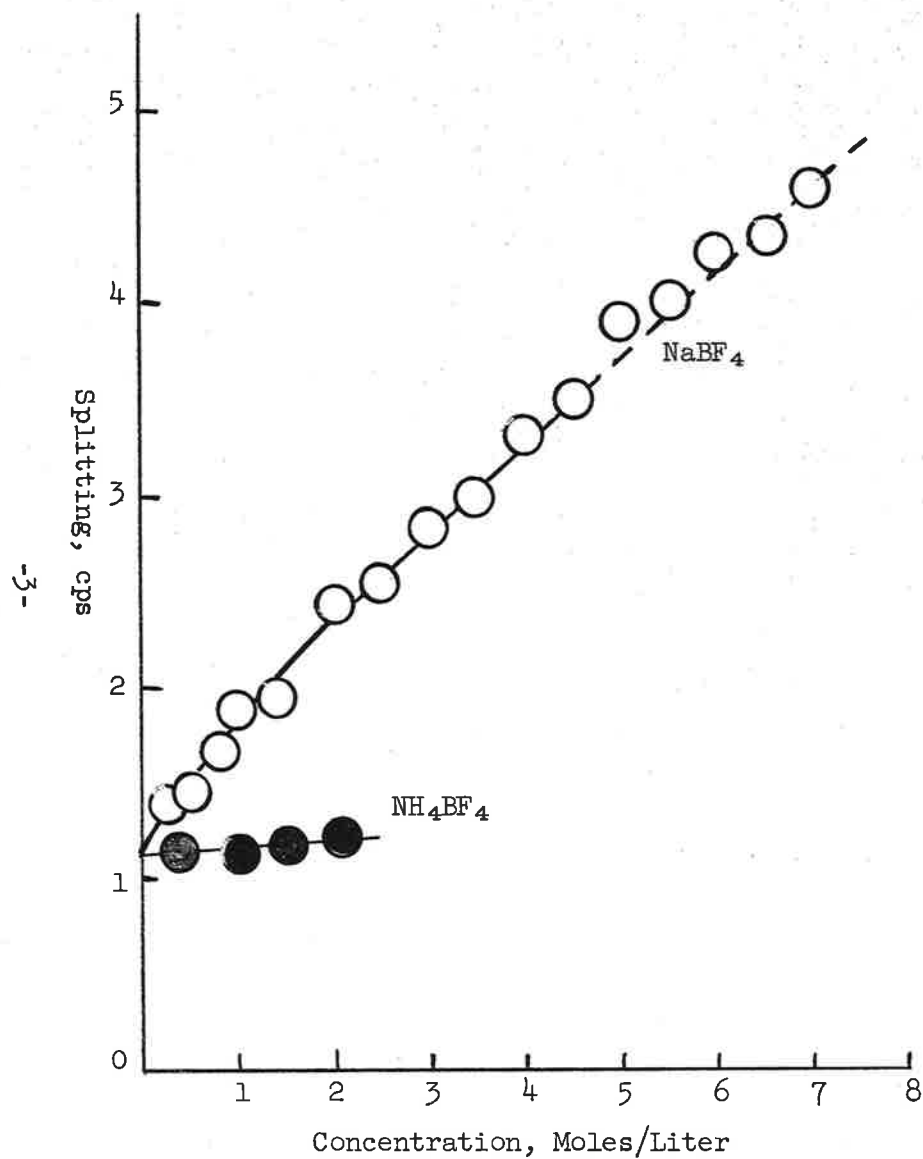
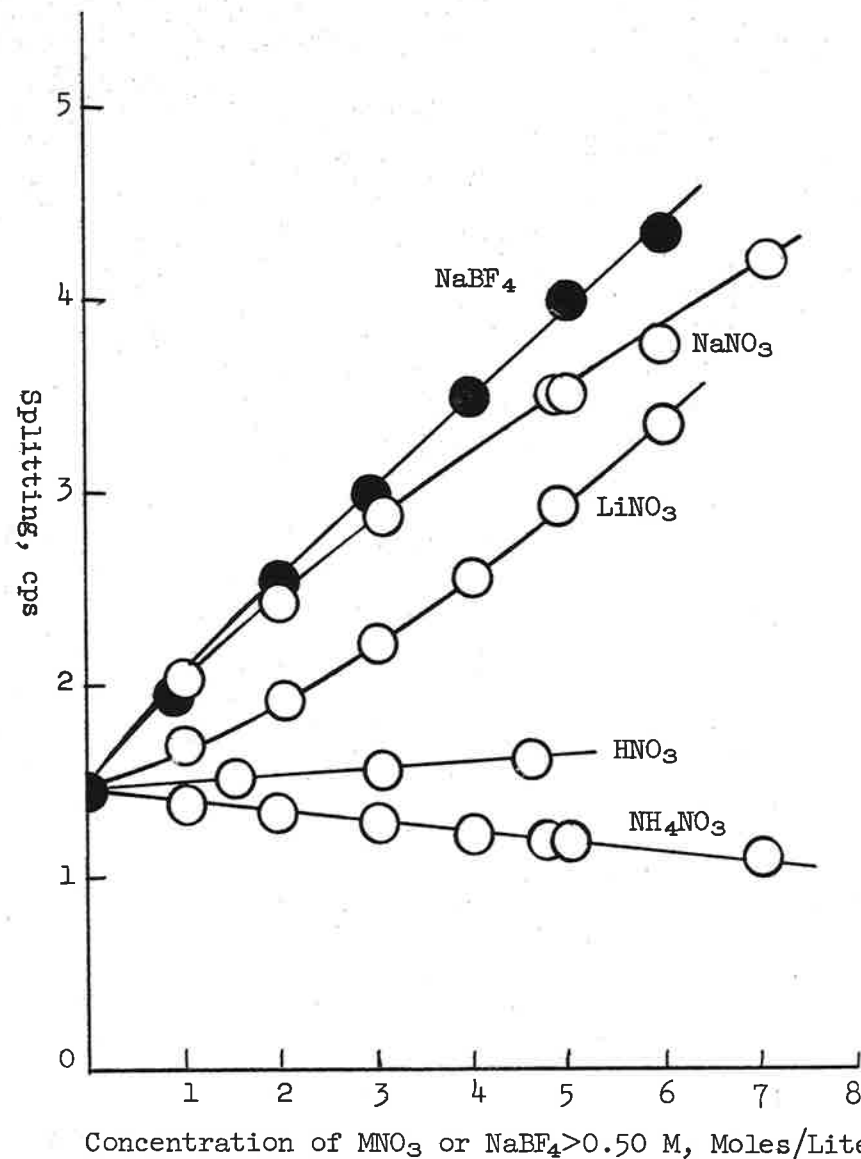


Fig. 1. Concentration dependence of  $\text{BF}_4^-$  splitting in aqueous  $\text{NaBF}_4$  and  $\text{NH}_4\text{BF}_4$  solutions.



Concentration of  $\text{MNO}_3$  or  $\text{NaBF}_4 > 0.50$  M, Moles/Liter

Fig. 2. Dependence of  $\text{BF}_4^-$  splitting on concentration of nitrates in 0.501 M  $\text{NaBF}_4$  solutions.



We have found that we could obtain a spectrum of chlorophyll a in carbon disulfide and carbon tetrachloride from the Varian A60 spectrometer only by using the slow scanning speeds (0.4 cps/sec). The spectrum only barely showed resonances from the  $\alpha$ ,  $\beta$ , and  $\delta$  protons and more clearly the resonances from the phytol protons, but the other resonances present were broad and could not be correlated with the chemical shifts for the porphyrins. In order to surmount these difficulties we have used the much discussed C.A.T. method to obtain distinct spectra of saturated solutions of chlorophyll a in acetone  $d_6$  and carbon disulfide.

Experimental Procedure

Using the C.A.T. without an external memory channel advance meant that the longest input time for the data was 32 sec. So that a final composite spectrum would not have to be made of too many pieces, a 5 cps/sec sweep rate on the 500 cps sweep width was used. On this basis 160 cps of the spectrum could be taken at a time. The first 15 to 25 cps of the stored spectrum were not useful since the ringing decay from the trigger signal was contained in these channels. The calibration for the spectrum was obtained by taking the position of the first channel as that of the TMS side band trigger signal. In general, about 120 cps of useful spectrum were obtained at a time. The composite spectrum in Fig. 2 is from five such portions of the NMR spectrum.

The spectrum of chlorophyll a in acetone is shown in Fig. 1 and we can readily assign most of the chemical shifts present in the spectrum by considering the effect of the induced molecular

magnetic fields arising from the circulating  $\pi$  electrons, and reported assignments on porphyrins (1). The assignments are shown

---

1. W.S. Caughey and W.S. Koski, Biochemistry 1 932 (1963), and references reported therein.

---

at the particular lines in Fig. 1. Unfortunately, the protons on ring IV are obscured by the large number of transitions originating from the protons on the phytol chain. We point out that a very similar spectrum of chlorophyll a in acetone  $d_6$  was obtained using the Varian A60, which could also be fairly easily interpreted, but the resonances from single protons and especially those from the vinyl group are more distinct in the C.A.T. spectrum.

The power of the C.A.T. method is even better demonstrated by the spectrum from chlorophyll a in carbon disulfide (Fig. 2) which is markedly different from the spectrum of chlorophyll a in acetone. The resonances due to the ( $\alpha$ ,  $\beta$ , and  $\delta$ ) methine protons and those from the phytol chain are still distinct. Associated with the methine protons there is what seems to be another similar group of three ( $\alpha'$ ,  $\beta'$ , and  $\delta'$ ) resonances and between them and the phytol resonances there are several resonances which must be associated with the remaining peripheral hydrogens of the porphyrin ring (Me, Et, V, etc.). We also scanned downfield 1000 cps from TMS with 50 scans stored by the C.A.T. looking for a possible enol proton, but did not find any resonances below 554 cps.

We make the suggestion, based on other spectroscopic evidence, that the chlorophyll a is associating in carbon disulfide, through

the chlorin rings, thus shifting and broadening the groups on the chlorin rings but allowing the phytol resonances to remain unaltered.

We intend to study the concentration dependence of chlorophyll a in carbon disulfide with the C.A.T. technique and perhaps learn something about chlorophyll a aggregation from NMR.

Sincerely yours,

A.F.H. Anderson  
I.D. Kuntz, Jr.  
Bio-Organic Chemistry Group  
Lawrence Radiation Laboratory  
University of California  
Berkeley 4, Calif.

D.P. Hollis  
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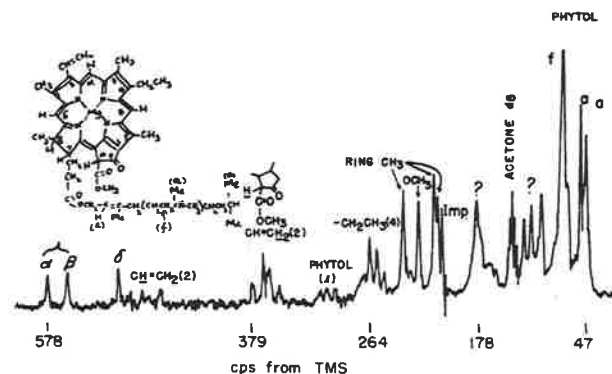


FIG. 1. Chl. a saturated soln. in acetone  $d_6$ . Signal/noise improvement using C.A.T. 60 mc

MU-30536

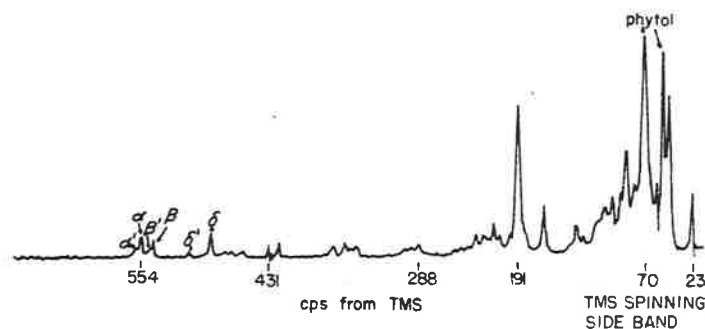


FIG. 2. Chl. a saturated soln. in  $CS_2$ . Signal/noise improvement using C.A.T. 230 repeats

MU 30537

# MONSANTO CHEMICAL COMPANY

AGRICULTURAL CHEMICALS DIVISION

AGRICULTURAL RESEARCH LABORATORY  
800 NORTH LINDBERGH BOULEVARD  
ST. LOUIS 66, MISSOURI

May 28, 1963

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

Dear Dr. Shapiro:

We would like to report our recent work concerning n.m.r. spectra of *cis*- and *trans*-epoxyamides (Tables I and II) which may be of interest to readers of MELLO-N-M-R.

The coupling constant for  $\alpha$ - $\beta$  hydrogen ( $J_{H_\alpha H_\beta}$ ) in the *cis*-epoxyamides is 5.0 c.p.s. and for the *trans*-isomer ( $J_{H_\alpha H_\beta}$ ) 2.0 c.p.s. These are in agreement with published data for simple epoxides.

(1) C. A. Rely and J. D. Swalen, J. Chem. Phys., **32**, 1378 (1960).

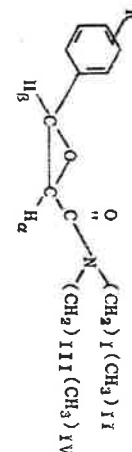
The n.m.r. spectra for the *cis*-isomers showed two non-equivalent methyl and methylene groups with a difference of chemical shift ranging from 16.2 c.p.s. to 21.6 c.p.s. for methyl and 9.6 c.p.s. to 19.2 c.p.s. for the methylene group. The non-equivalency of the ethyl groups are clearly due to the restricted rotation about the CN bond at room temperature.<sup>2</sup> Consequently their environments,

(2) The n.m.r. spectra of *cis*-N,N-diethyl 3-phenylglycidamide at 85° exhibited only one triplet for two methyl groups and one quartet for two methylene groups.

particularly with respect to the 3-aryl group are different. Although rotation about CN bond is still restricted in the corresponding *trans*-isomer, the non-equivalency of these groups with respect to the 3-aryl group is reduced due to the greater distance. The difference in chemical shift is therefore diminished. The assignment of (CH<sub>2</sub>)<sub>I</sub> and (CH<sub>2</sub>)<sub>II</sub> at higher field than (CH<sub>2</sub>)<sub>III</sub> and (CH<sub>2</sub>)<sub>IV</sub>

TABLE I  
CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS  
OF *CIS*-N,N-DIETHYL GLYCIDAMIDES FROM DARZENS CONDENSATION

Compound R	Chemical Shifts $\tau$						Coupling Constants c.p.s.			
	(CH <sub>3</sub> ) <sub>I</sub> Triplet	(CH <sub>3</sub> ) <sub>IV</sub> Triplet	$\Delta\delta$ c.p.s.	(CH <sub>2</sub> ) <sub>I</sub> Quartet	(CH <sub>2</sub> ) <sub>III</sub> Quartet	$\Delta\delta$ c.p.s.	H <sub>a</sub> Doublet	H <sub>b</sub> Doublet	J <sub>CH<sub>2</sub></sub> c.p.s.	J <sub>CH<sub>2</sub></sub> c.p.s.
H	9.24	8.97	16.2	6.88	6.72	9.6	6.13	5.75	7.2	7.2
2,6-Dichloro-	9.03	8.70	19.8	6.80	6.34	12.0	5.97	5.76	7.2	7.2
2,4-Dichloro	9.22	8.86	21.6	7.00	6.68	19.2	6.13	5.64	7.2	7.2
m-nitro	9.20	8.84	21.6	6.80	6.60	12.0	5.95	5.55	7.2	7.2
N,N-diethyl 3-phenyl glycidamide							6.10	5.72		5.0



Dr. Bernard L. Shapiro

-4-

May 28, 1963

is based on the assumption that the average environment of the former is nearer the 3-aryl group. Hence the shielding effect of the phenyl ring should be greater.

The reliability of n.m.r. spectra in quantitative determination of *cis-trans*-epoxy amides is demonstrated as follows. An authentic mixture of 49.1% of *cis*-N,N-diethyl 3-phenyl glycidamide and 50.9% of the corresponding *trans*-glycidamide showed 51% of *cis* and 49% of *trans* respectively by measuring the area of one doublet,  $J_{H_a H_b} = 5.0$  c.p.s., ( $H_b$ ) for *cis* and another doublet,  $J_{H_a H_b} = 2.0$  c.p.s. ( $H_b$ ) for *trans*-isomer. Also, the *cis-trans* mixture of N,N-diethyl 3-phenyl glycidamide before chromatographic separation from Darzens condensation (m.p. 43-47°) was found to consist of 50% *cis* and 50% *trans* by the same method of n.m.r. analysis. The isolated yields were 52.7% *cis* and 47.3% *trans*. Thus, n.m.r. spectra serve as a very convenient means to determine the percentage of *cis*- and *trans*-epoxyamides from Darzens condensation without involving the tedious process of separation.

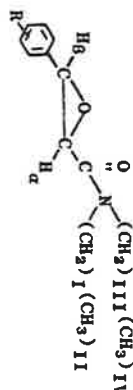
Sincerely,

C. C. Tung

P.S. To help keep your mailing list down, we share a single copy of MELLON-M-R among the four Monsanto Divisions doing NMR work in St. Louis. Please credit this "contribution" from our Agricultural Research Lab. to our account and continue to send our subscription to Dr. M. M. Crutchfield.

C.C.T.

TABLE II  
CHEMICAL SHIFTS\* AND SPIN-SPIN COUPLING CONSTANTS  
OF TRANS-N,N-DIETHYL GLYCIDAMIDES FROM DARZENS CONDENSATION



Compound R	Chemical Shifts $\tau$					Coupling Constants c.p.s.			
	(CH <sub>3</sub> ) I Triplet	(CH <sub>3</sub> ) IV Triplet	$\Delta\delta$ c.p.s.	(CH <sub>3</sub> ) I Quartet	(CH <sub>3</sub> ) II Quartet	$\Delta\delta$ c.p.s.	$H_a$ Doublet	$H_b$ Doublet	$J_{CH_3 CH_3}$ Doublet
H	8.84	8.80	2.4	6.55		0	6.43	5.94	7.2
2,6-dichloro	8.88	8.76	7.2	6.66		0	6.34	5.92	7.2
2,4-dichloro	8.93	8.82	6.6	6.71		0	6.60	5.93	7.2
m-nitro	8.80	8.73	4.2	6.58		4.8	6.35	5.76	7.2
N,N-diethyl 3-phenyl glycidate							6.40	6.03	2.0

\* NMR spectra were measured at 60 mc sec. on a modified Varian model A-60 spectrometer. The samples contained tetramethylsilane (TMS) as internal reference.

Quadrupole Relaxation for Spin  $I = 3/2$ :

The  $F^{19}$  N.M.R. Spectra of  $BF_3$  and  $CF_3F$

Pople (1) has developed the general theory for the effect of quadrupole relaxation of high spin nuclei ( $I > 1/2$ ) on nuclear magnetic resonance multiplets. On the basis of this theory he derived an expression for the line shape of the n.m.r. spectrum of a spin  $1/2$  nucleus coupled to a nucleus having  $I = 1$ . Since a number of interesting inorganic molecules contain nuclei with  $I = 3/2$  we have extended Pople's treatment to this case.

The lifetime of each of the spin states  $m = 3/2, 1/2, -1/2$  and  $-3/2$  is given by the expression

$$\tau_q = \frac{1}{10} \left( \frac{e^2 q Q}{h} \right)^2 \tau_c$$

where  $\tau_c$  is the correlation time for molecular reorientation and  $\frac{e^2 q Q}{h}$  is the quadrupole coupling constant.

It may then be shown that the line shape is given by the following expression

$$I(\eta, x) \propto \tau f(\eta, x) \quad \dots \quad (1)$$

$$\text{Where } f(\eta, x) = \frac{320 + 16\eta^2(25x^2 + 17) + \eta^4(80x^4 + 56x^2 + 45)}{1024x^8 + 64\eta^2(36x^6 - 20x^4 + 25) + 16\eta^4(96x^6 - 160x^4 + 110x^2 + 45) + \eta^6(256x^6 - 1280x^4 + 1888x^2 - 720x^2 + 81)}$$

$$\eta = \frac{2\pi J\tau}{1} \quad x = \frac{\omega_0 - \omega}{2\pi J} \quad \omega_0 \text{ being the centre of the unperturbed multiplet.}$$

Line shapes calculated from this expression as a function of  $\eta^2$  are shown in Figure 1. As  $\eta$  decreases (that is, as the rate of quadrupole relaxation increases), the outer lines of the quartet move inward while the inner lines move outward, resulting in a broad doublet-like structure at values of  $\eta^2$  near 2. Finally the "doublet" collapses to a single line.

We have used the above expression to interpret the collapse of the quartet in the  $F^{19}$  spectra of  $BF_3$  and  $CF_3F$ . As the temperature is lowered, the correlation time  $\tau$  increases, and quadrupole relaxation increases, resulting in the collapse of the 1:1:1:1 quartet due to coupling with  $B^{11}$  or chlorine.

We find for  $BF_3$  that  $J = 18.5 \pm 0.2$  c/sec. and that the variation of transition probability with temperature corresponds to a thermally activated molecular reorientation process described by the equation

$$\tau_q = \tau_q^0 \exp \left( \frac{E}{RT} \right) \quad \text{where } E = 1.4 \text{ kcal/mole}$$

Moniz and Gutowsky (2) have found that the  $N^{14}$  relaxation process may be described in a similar manner.

Figure 2 shows the collapse of the perchloryl fluoride ( $ClO_4F$ ) spectrum as the temperature decreases. By taking the experimental spectrum as the sum of two spectra, one due to the  $Cl^{35}O_4F$  molecule and the other to the  $Cl^{37}O_4F$  molecule (both isotopes have  $I = 3/2$ ), and making allowance for the different magnetogyric ratios and quadrupole moments of the two isotopes, we were able to fit a calculated spectrum to each experimental spectrum.  $JCl^{35}F$  is  $278 \pm 5$  c/sec. The straight line plot of  $\log \tau$  vs  $\frac{1}{T}$  gave an activation

energy of 0.95 kcal/mole. This is less than the corresponding activation energy for any of the twelve nitrogen compounds studied by Moniz and Gutowsky (2). This is presumably due to the small size and high symmetry of the molecule.

A more complete report on this work is being submitted for formal publication.

Department of Chemistry,  
McMaster University,  
Hamilton, Ontario.

J. Bacon  
R. J. Gillespie  
J. W. Quail

#### References

1. J. A. Pople, Mol. Phys., **1**, 168 (1958).
2. W. B. Moniz and H.S. Gutowsky, J. Chem. Phys. **38**, 1155 (1963).

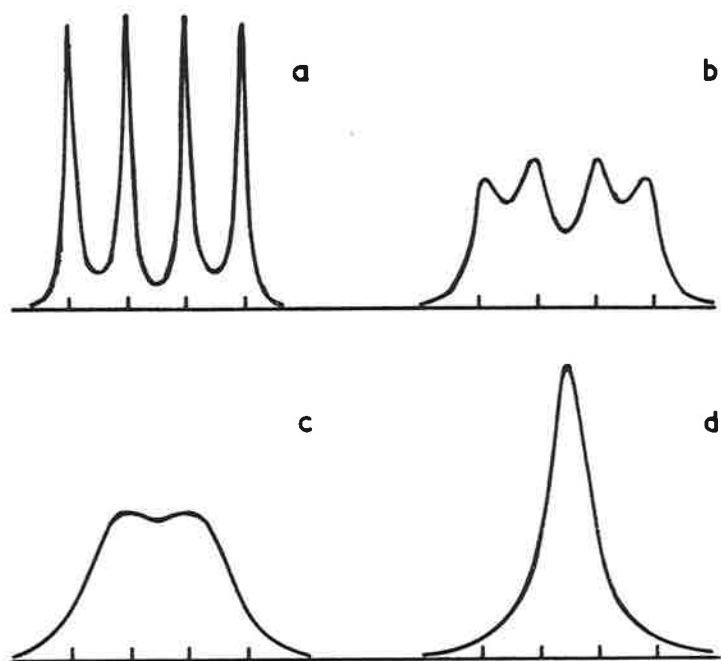


Fig. 1

Theoretical line shapes for the spectra of nuclei of spin  $1/2$  coupled to a nucleus of spin  $3/2$  according to equation (1). (a)  $\eta^2 = 100$ , (b)  $\eta^2 = 10$ , (c)  $\eta^2 = 1$ , (d)  $\eta^2 = 0.1$ . The vertical lines indicate the positions of the components of the quartet in the absence of quadrupole relaxation.

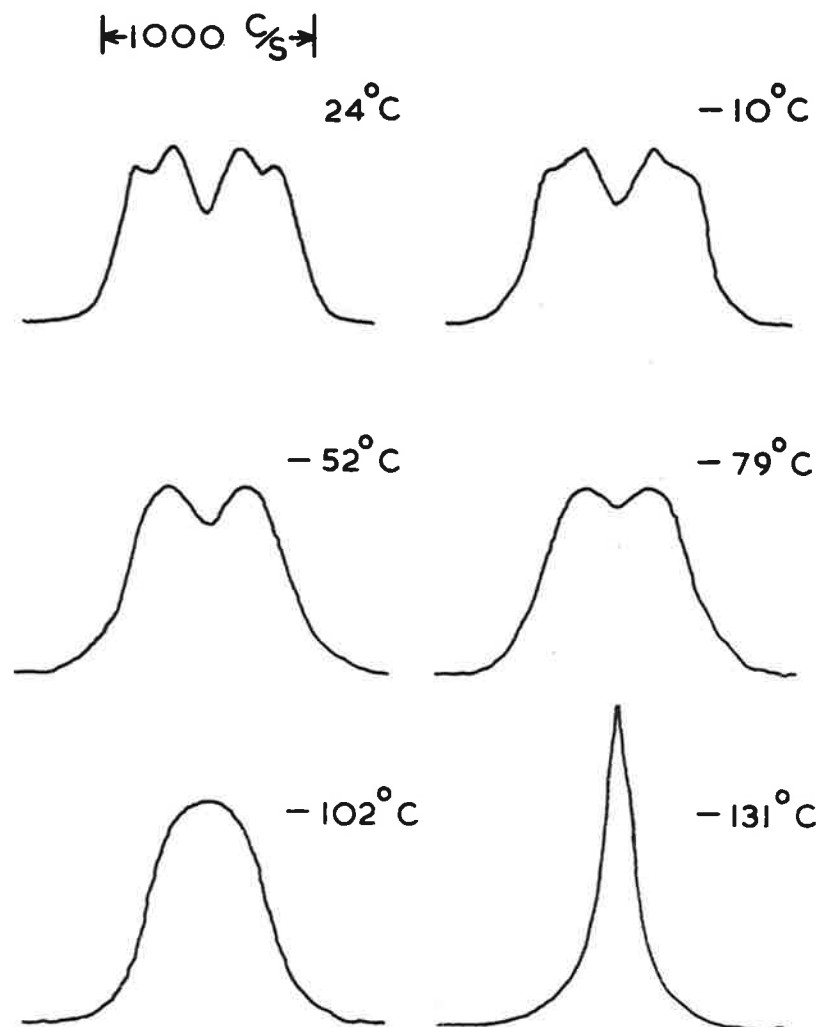


Fig. 2

The observed  $F^{19}$  n.m.r. spectrum of  $ClO_3F$  at various temperatures



AN NMR STUDY OF THE ALKALI HEXAFLUOROPHOSPHATES' DYNAMIC STRUCTURE\*

Gerald R. Miller<sup>1</sup> and H. S. Gutowsky

Noyes Chemical Laboratory, University of Illinois,  
Urbana, Illinois

The fluorine nuclear magnetic resonance spectra of the sodium, potassium, rubidium and cesium hexafluorophosphates were studied between 77°K and 400°K. It was found that in each of the salts the  $\text{PF}_6^-$  ions are reorienting about the octahedral axes at random or nearly so for temperatures of 200°K and above. The broadening of the fluorine resonance in these solids at lower temperatures indicates that the ease with which the  $\text{PF}_6^-$  groups reorient increases with increasing size of the alkali metal cation, so that for  $\text{CsPF}_6$  the fluorine resonance is still narrow at 77°K. A quantitative study of the potential barriers to  $\text{PF}_6^-$  group reorientation was discouraged by the discovery that the fluorine line shapes and widths are remarkably sensitive to the physical state and in the case of  $\text{KbPF}_6$  the thermal history of the sample. These effects are attributed to crystal imperfections which lower the potential barriers to  $\text{PF}_6^-$  group reorientations and decrease the size of domains in which there is a cooperative "freezing out" of the reorientations. Thus, in the region of changing line width, we postulate domains with frozen out  $\text{PF}_6^-$  groups and others with reorienting groups. In samples which should have relatively low imperfection concentrations and where such domains should be large, we find distinguishable broad and narrow components in the fluorine resonance, with one grown

the expense of the other as the temperature is changed. This two-phase behavior disappears in finely powdered samples, in which high concentrations of imperfections were probably introduced by the mechanical grinding. Fluorine line shape studies reported previously for solid  $\text{CF}_4$  are reinterpreted in terms of a similar two-phase, cooperative process for the freezing out of the  $\text{CF}_4$  reorientations.

Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
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 not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".



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

22nd May, 1963

Dear Dr. Shapiro,

As my nine months grace is rapidly drawing to a close, here is my contribution to Mellon.

Dr. Pachler<sup>1</sup> and I have just completed an investigation into the proton resonance spectra of some 1,2 disubstituted ethanes, i.e.  $XCH_2CH_2Y$ .<sup>2</sup> In this work we were concerned only with compounds which gave the "full" (i.e. 20 line for these systems)  $A_2B_2$  spectrum. From these spectra we can obtain values for M, N, L (and  $\delta_{AB}$ ) but not for K. The spectra are consistent with a wide variation in K. Hoffman and Gronowitz (Mellon No.51) recently emphasised this point which was made in the original  $A_2B_2$  analysis, but seems to have been neglected of late. Many 1,2 disubstituted ethanes give much simpler spectra, (14 line, 10 line or merely the "first order" two triplet spectrum). These we excluded from our investigation as they are examples of deceptively simple spectra. They can be analysed on the basis of  $L=0$  but also fit exactly with a spectrum calculated for non zero values of L.

Considering the values of the coupling constants obtained from the 20 line spectra. We can express the parameters N and L in terms of the coupling constants in the individual rotational isomers as follows:

$$N = \frac{1}{2} J_t + 3J_g + n_t(J_t - J_g) \quad 1.$$

$$L = \frac{1}{2}(1 - 3n_t)(J_t - J_g) \quad 2.$$

Hence, 
$$\frac{1}{2}N + \frac{1}{2}L = J_t + 2J_g \quad 3.$$

Thus the quantity  $\frac{1}{2}N + \frac{1}{2}L$  should be a constant for a given compound and independent of the proportions of the rotational isomers. From the analysis of the spectrum only the magnitudes of N and L can be found. N can be assumed positive thus by measuring one compound in conditions which give different proportions of the rotational isomers (i.e. at different temperatures or in different solvents), equation 3 can be used to determine the sign of L and thus to obtain uniquely  $J_t + J_g$ . Also the sign of L gives directly the relative stability of the rotational isomers. (This follows from equation 2). Table I gives our results, together with the values of  $J_t + 2J_g$ . These results lead to several interesting conclusions. To mention briefly two of them:

The value of  $\frac{1}{2}N + \frac{1}{2}L$  is not precisely constant for a given compound but always seems to increase as the percentage of the trans isomer increases. This we have explained on the basis that the X.C.C.Y dihedral angle in the gauche isomer is not exactly  $60^\circ$ . Also, the proportions of the rotational isomers obtained are most odd, e.g. The proportions of the rotational isomers in 2 chloroethanol and 2 chloroethyl acetate are virtually the same and in both compounds the gauche form is more stable. This disproves the idea that the greater stability of the gauche form of 2 chloroethanol in solution is due to intramolecular hydrogen bonding.

We also used the values of  $J_t + 2J_g$  obtained in this way to check the dependence of vicinal coupling constants on the electronegativity of the substituents. In Table II we have collected most of the available data on this "average" coupling constant, i.e.  $\frac{1}{2}(J_t + 2J_g)$ , which also includes some values for  $CH_3CHXY$  compounds measured in this investigation.

Assuming a linear relationship between the average coupling constant and the sum of the Huggins electronegativities of the six substituents on the C-C fragment, a least mean squares treatment gives

$$J_{av} = 15.0 - 0.80 \sum E$$

with a mean square deviation of 0.3 c.p.s. The line and some of the experimental points are shown in the figure. Another useful form of this equation is

$$J_{av} = 7.7 - 0.80 \sum \Delta E$$

where  $\Delta E$  is the difference between the electronegativity of the

substituent and that of hydrogen. This latter equation is almost identical to the one obtained by Sheppard who considered only ethyl compounds.

Having obtained this relationship we can begin to consider the reasons for the deviations from it in any instance. One generality does appear to exist, i.e. that in  $XCH_2CH_2Y$  compounds the deviation from the line increases as the percentage of the trans isomer increases. Obviously this is consistent with the increase in  $J_{AV}$  with increasing percentage of the trans isomer mentioned previously. Thus it appears that in some compounds at any rate,  $J_{AV}$  will be considerably different for the two rotational isomers and it is possibly only the average of this quantity over an equal statistical distribution of the isomers (i.e. two-thirds gauche, one-third trans) which obeys the electronegativity relationship.

We also discussed the geminal coupling constants  $M$ , but I think I have said enough for one subscription!

Best wishes,

Yours sincerely,

*Roy Abraham*

R. J. Abraham.

Present address: The Chemical Physics Group, South African Council for Scientific and Industrial Research, Pretoria, South Africa.

Submitted Mol. Phys.

J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", Ch. 6.

C. N. Banwell and N. Sheppard, Disc. Far. Soc., (1962).

Table I. Proton Coupling Constants and Chemical Shifts in 1,2 disubstituted Ethanes.

Compound	M	N	L	$\frac{3}{2}N + \frac{1}{2}L$	$J_t + 2J_g$
<u>1-chloro-2-bromoethane</u>					
liquid	12.60	0.95	15.00	3.07	24.0(21.0)
1:1 in Acetonitrile	20.21	1.02	14.00	1.58	21.8(20.2)
<u>2-chloroethanol</u>					
liquid	11.24	0.81	11.18	1.90	17.7(15.8)
1:2 in $CCl_4$	13.20	0.76	10.82	2.15	17.3(15.2)
1:1 in Acetone	10.83	0.80	11.43	1.22	17.8(16.5)
<u>2-bromoethanol</u>					
liquid	22.8	1.94	11.72	1.20	18.2(17.0)
1:1 in $CHCl_3$	25.0	1.71	11.30	1.48	17.7(16.2)
1:1 in $CS_2$	25.65	1.77	11.64	1.05	18.0(16.9)
1:1 in Acetone	21.8	-	12.09	0	18.1(18.1)
<u>2-methoxyethanol</u>					
liquid	11.70	1.53	9.61	2.24	15.5(13.3)
1:2 in $CCl_4$	12.20	1.87	9.73	2.80	16.0(13.2)
1:1 in $D_2O$	8.98	1.24	9.66	2.82	15.9(13.1)
1:1 in Acetone	11.52	1.52	10.02	2.08	16.1(14.0)
<u>2-chloroethyl acetate</u>					
liquid	34.8	0	11.06	2.10	17.6(15.5)
1:1 in $CCl_4$	35.4	0	11.52	1.76	18.1(16.4)
<u>2-methoxyethyl acetate</u>					
liquid	36.3	0.83	9.68	2.83	15.9(13.1)
1:1 in $CCl_4$	35.8	0.89	9.80	2.79	16.1(13.1)
1:1 in Acetone	35.9	0.85	9.73	2.88	16.0(13.2)
<u>Laevulinic Acid</u>					
1:1 in $CHCl_3$	10.72	1.10	13.17	1.35	20.4(19.1)
1:1 in $D_2O$	15.36	1.18	12.90	1.91	20.3(18.4)
<u>Ethyl laevulate</u>					
liquid	14.40	1.15	13.07	1.54	20.4(18.8)
1:1 in $CHCl_3$	13.87	1.08	12.96	1.38	20.1(18.8)
1:1 in MeOH	15.39	1.26	13.12	1.88	20.6(18.7)
2:3 in $CF_3CO_2H$	15.4	1.73	12.78	1.93	20.1(18.2)
<u>4-Cyano-2,2-dimethyl butyraldehyde</u>					
liquid	29.3	2.82	15.89	3.94	25.8(21.9)

Table II. Proton-Proton Coupling Constants for Various Fragments.

1.  $(CH_2-CH_2)_nX$

X	$J_{av}$ [c.p.s.]
H	8.0 $\pm$ 0.1
CH <sub>3</sub>	7.26 $\pm$ 0.1
OH	6.97 $\pm$ 0.1
O <sub>2</sub> CH	6.93 $\pm$ 0.1
F	6.9 $\pm$ 0.1
Cl	7.07 $\pm$ 0.1
Br	7.25 $\pm$ 0.1
J	7.16 $\pm$ 0.1
SH	7.27 $\pm$ 0.1
CN	7.24 $\pm$ 0.1
$\phi$	7.37 $\pm$ 0.1
CO <sub>2</sub> H	7.41 $\pm$ 0.1
N- $\phi$	6.96 $\pm$ 0.1
O	6.96 $\pm$ 0.1
Li	8.4
S	7.42 $\pm$ 0.05
CO	7.5 $\pm$ 0.1
Hg	7.0
N	6.9
P <sup>III</sup>	7.6
Sn <sup>IV</sup>	8.2
Pb <sup>IV</sup>	8.2
Si <sup>IV</sup>	7.9 $\pm$ 0.02
CH <sub>2</sub> CN	7.7
CH <sub>2</sub> Cl	7.4
CH <sub>2</sub> Br	7.3
CH <sub>2</sub> J	7.2
O-CO	6.96 $\pm$ 0.1

2.  $XCH_2-CH_2Y$

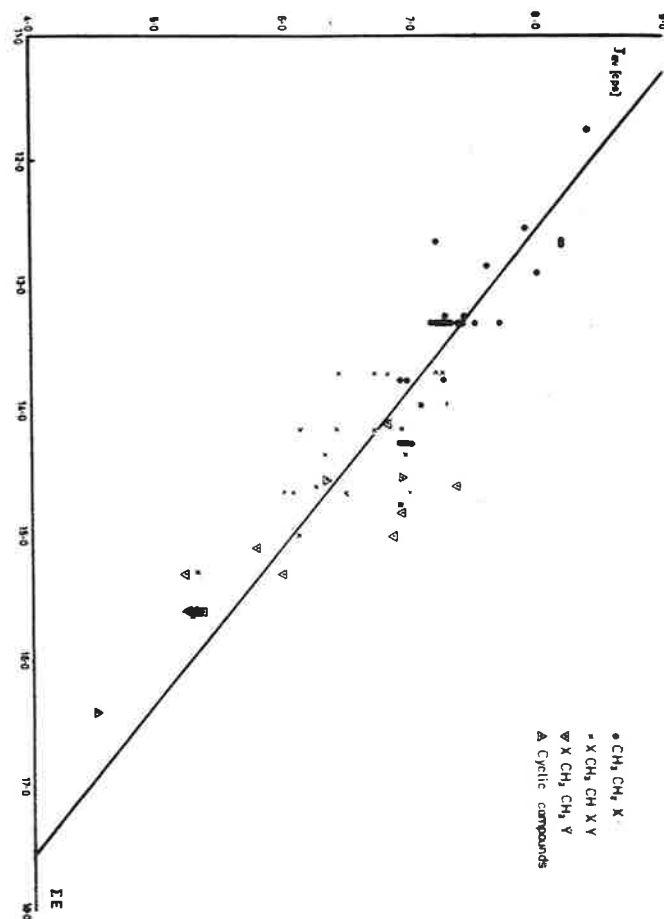
X	Y	$J_{av}$ [c.p.s.]
Cl	Cl	6.83 $\pm$ 0.1
Br	Cl	6.87 $\pm$ 0.1
Br	Br	7.37 $\pm$ 0.1
Br	OH	6.00 $\pm$ 0.1
Cl	OH	5.83 $\pm$ 0.1
MeO	OH	5.33 $\pm$ 0.1
CH <sub>3</sub> CO	CO <sub>2</sub> H	6.80 $\pm$ 0.1
CH <sub>3</sub> CO	CO <sub>2</sub> Me	6.80 $\pm$ 0.1
MeO	O <sub>2</sub> C-CH <sub>3</sub>	5.33 $\pm$ 0.1
Cl	O <sub>2</sub> C-CH <sub>3</sub>	5.97 $\pm$ 0.1
HO	OH	5.27
MeO	OMe	5.3

3.  $CH_3-CHXY$

X	Y	$J_{av}$ [c.p.s.]
Me	Me	6.8 $\pm$ 0.2
Me	CO	6.49 $\pm$ 0.1
Me	J	6.42 $\pm$ 0.1
Me	Br	6.40 $\pm$ 0.1
Me	Cl	6.31 $\pm$ 0.1
Me	NH <sub>2</sub>	6.11 $\pm$ 0.1
Me	OH	6.05 $\pm$ 0.1
CO <sub>2</sub> H	CO <sub>2</sub> H	7.22 $\pm$ 0.2
Br	Br	6.24 $\pm$ 0.4
Cl	Cl	6.1 $\pm$ 0.15
OH	OH	5.26 $\pm$ 0.07
Cl	CO <sub>2</sub> H	6.94 $\pm$ 0.03
Br	CO <sub>2</sub> H	6.92 $\pm$ 0.01
OH	CO <sub>2</sub> H	6.97 $\pm$ 0.02
OH	$\phi$	6.47 $\pm$ 0.05
Cl	OE <sub>t</sub>	5.28 $\pm$ 0.1
CH <sub>3</sub>	CO <sub>2</sub> H	7.2 $\pm$ 0.1
CH <sub>3</sub>	O	5.98 $\pm$ 0.1
Br	CHBrCO <sub>2</sub> H	6.70 $\pm$ 0.1

4. Cyclic Compounds

	$J_{av}$ [c.p.s.]
-NH <sub>2</sub> <sup>+</sup> - CH(CO <sub>2</sub> <sup>-</sup> ) - CH <sub>2</sub> - C	6.32 $\pm$ 0.1
-CO - CHBr - CH <sub>2</sub> - C	6.9
-O - CH(OAc) - CH(OAc) - C	4.5



• CH<sub>2</sub>-CH<sub>2</sub>-X  
 × X-CH<sub>2</sub>-CH<sub>2</sub>-Y  
 △ X-CH<sub>2</sub>-CH<sub>2</sub>-Y  
 ▽ Cyclic compounds

# KARL-MARX-UNIVERSITÄT

PHYSIKALISCHES INSTITUT

Herrn  
Dr. Barry Shapiro  
Mellon-Institut

LEIPZIG C 1, LINNÉSTR. 5 · TEL. 6 51 50, 6 53 42, 6 53 56

am 28.5.1963 An: Dr. Kl/Gae.

Pittsburgh / Pennsylvania

USA

Sehr geehrter Herr Dr. Shapiro!

Jackman [1] wies auf den Zusammenhang zwischen der inneren chemischen Verschiebung der Exomethylenprotonen von  $\alpha$ -Methylen-cycloketonen und dem s-cis-Charakter der Keto-Methylen-Gruppe hin. Er stützte sich dabei auf die experimentellen Ergebnisse, die an Ringverbindungen mit maximal 7 Ring-C-Atomen erhalten wurden.

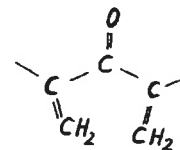
Wir untersuchten  $\alpha$ -Methylen-cycloketone  $O=C-(CH_2)_{n-2}-CH_2$

bis zu maximal 16 Ring-C-Atomen ( $n = 16$ ). Die erhaltenen chemischen Verschiebungen (auf unendliche Verdünnung in Tetrachlorkohlenstoff extrapoliert) der Exomethylenprotonen sind im Bild in Abhängigkeit von der Ringgröße dargestellt. Für Verbindungen mit  $n = 5$  bis 8 bleibt die Differenz der  $\tau$ -Werte entsprechend der s-cis-Konformation der Keto-Exomethylen-Gruppe annähernd gleich und beträgt ungefähr 0,60 ppm. Dagegen ergibt sich für die untersuchten Verbindungen mit  $n = 9$  und 10 gleich Null und für  $\alpha$ -Methylen-cyclohexadecanon eine Differenz von  $\approx 0,28$  ppm. Wie aus theoretischen Betrachtungen geschlossen werden kann, liegt die Keto-Exomethylen-Gruppe bei den Verbindungen mit  $n = 9$  und 10 in einer s-trans-Konformation vor, und bei  $\alpha$ -Methylen-cyclohexadecanon findet (bei Zimmertemperatur) eine teilweise freie Rotation statt.

Bei dem untersuchten  $\alpha\alpha$ -Dimethylen-cyclodecanon ist die Differenz der  $\tau$ -Werte Null; die Keto-Dimethylen-Gruppe liegt

- 2 -

also wie die Keto-Methylen-Gruppe von  $\alpha$ -Methylen-cyclodecanon in der s-trans-Konformation



vor.

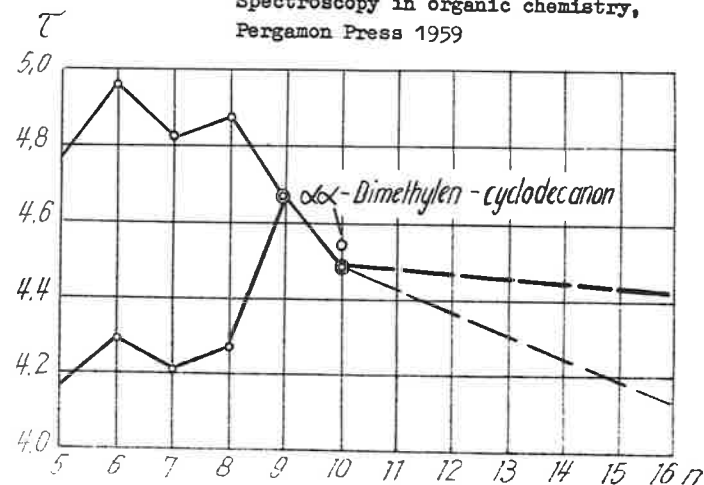
Die Arbeit wird ausführlich in der Zeitschrift "Molecular Physics" veröffentlicht.

Hochachtungsvoll

Ihr ergebener

*Gerhard Klöse*  
(Dr. G. Klöse)

[1] L.M.Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in organic chemistry, Pergamon Press 1959



ORGANISCH-CHEMISCHES INSTITUT  
DER UNIVERSITÄT BONN  
Dr.G.Snatzke, H.Lander

53 Bonn, den 3.6.1963  
Meckenheimer Allee 168  
Telefon 31961

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

Dear Dr.Shapiro,

Herewith I send you our first contribution for MELLONMR and hope, that this will keep me on your mailing list for this most valuable letter collection.

In our department we have a KIS-25 spectrometer (Trüb, Täuber a.Co), which is equiped with a Primas proton stabilizer. This uses the single sideband method and should therefore make possible proton spin decoupling experiments by double irradiation (cf e.g. D.W.Turner, J.chem.Soc. 1962, 847). Under usual operation conditions the transmitter output is too small, but simply bridging the last voltage divider in the signal channel of the transmitter raises this by about 20 db, which is sufficient for our purposes.

In running the spectra the SSB generator is tuned to the decoupling frequency. That one of the two sidebands is selected, which during sweeping runs "behind" the main band to avoid unwanted relaxation phenomena. The sweeping is achieved by linear field variation, just as it is done by running the KIS-25 without the proton stabilizer.

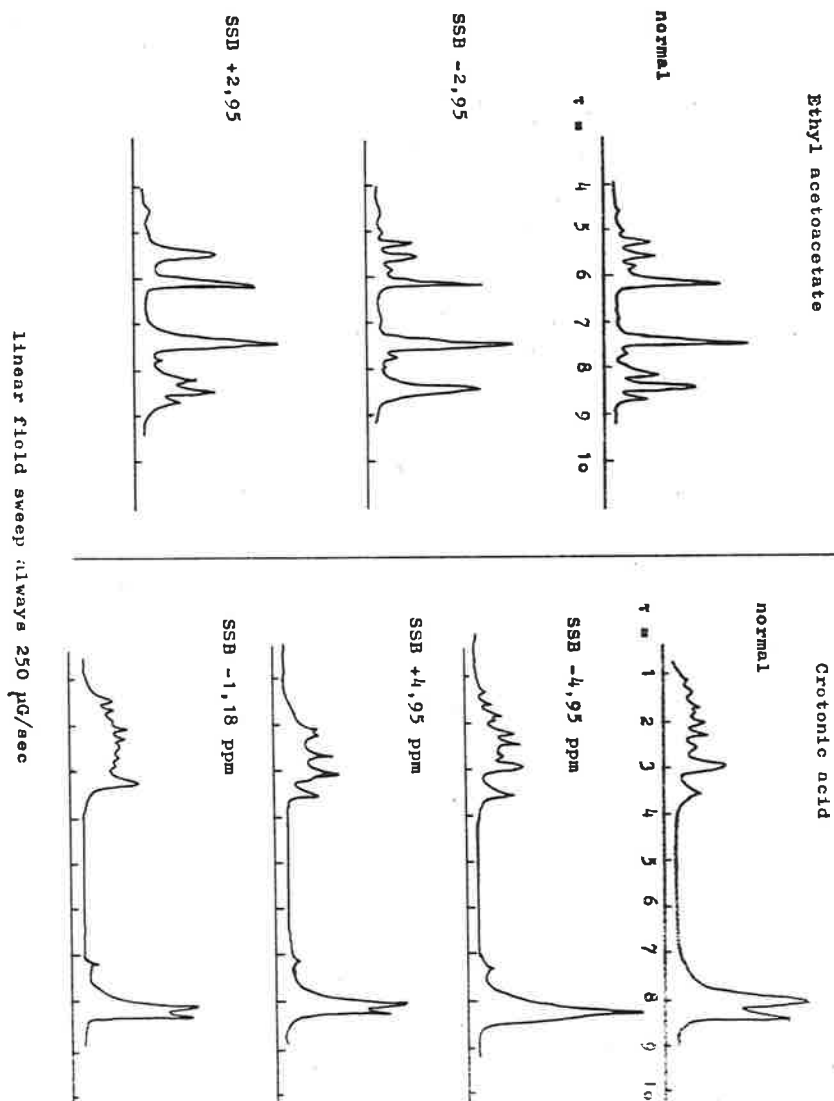
This simple modification surely will not satisfy ingrained NMR-theorists, but helped us organic chemists to simplify complex spectra and to find correlations, where it is rather difficult at 25 Mc. To avoid leakage from the signal (= irradiation) to the reference (= transmitting and amplification) channel the distance of the two signals to be decoupled must be more than 1 ppm.

In this way we were able to decouple, e.g., the  $\alpha$ - and  $\beta$ -protons of tetrahydro furan, the septet and the doublet of i-propanol, the triplet and quadruplet of ethanol and several ethyl esters (acetate, acetoacetate,  $\alpha$ -fluoro- $\alpha$ -isopentenyl acetoacetate) and the  $\beta$ -H from the methyl protons and the  $\alpha$ -H in crotonic acid (in the last mentioned case the 60 Mc spectrum is easier to explain than the 25 Mc spectrum, cf the VARIAN catalog and the contribution of Yajko and Kurland in MELLONMR 49, p.5).

With kindest regards

Yours sincerely

*G. Snatzke*  
(Günter Snatzke)





Department of Chemistry  
Kobe University  
Kobe, Japan

June 4, 1963

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

Dear Dr. Shapiro:

The work described below has been done together with Prof. H. Narumi.

At first interested in the isotope effect on nuclear magnetic shielding<sup>1)</sup>, and now as an aid to obtain better values of the absolute proton shielding and proton magnetic moment, we have calculated the proton shieldings in the H<sub>2</sub> and HD molecules averaged over the appropriate vibrational and rotational states.

The method is essentially the same as that of Ramsey<sup>2)</sup> except a few refinements.

Our calculated value of  $\langle (R/R_e)^3 \rangle$  is (fortuitously,<sup>3)</sup> in better agreement with experiment than Cooley's value<sup>3)</sup> obtained with a digital computer, and our values and Cooley's for  $\langle (R/R_e)^m \rangle$  agree well where Cooley's duplicate ours. In view of this, our values of  $\langle (R/R_e)^n \rangle$  may be trusted to an accuracy of 1 part in 10<sup>3</sup>.

The proton shift between H<sub>2</sub> and HD by use of these average values turns out to be in p.p.m.

$$\text{HD}_\sigma - \text{H}_2_\sigma = 26.118 - 26.010 = 0.108.$$

The above shift value is based on Ramsey's choice of  $m = +1.7$  in  $\sigma^{\text{hf}} \sim (R/R_e)^m$ , while the alternative choice of  $m = -1.9$  gives

$$\text{HD}_\sigma - \text{H}_2_\sigma = 26.600 - 26.565 = 0.035.$$

If we use Marshall's result<sup>4)</sup> in combination with our values of  $\langle (R/R_e)^n \rangle$ , we get

$$\text{HD}_\sigma - \text{H}_2_\sigma = 0.049$$

and use of Ishiguro's result<sup>5)</sup>, which is at present the best theoretical calculation of the H<sub>2</sub> shielding, yields

$$\text{HD}_\sigma - \text{H}_2_\sigma = 27.548 - 27.507 = 0.041$$

The experimental value available for  $(\text{HD}_\sigma - \text{H}_2_\sigma)$  due to Wilmott<sup>6)</sup> is 0.017, though with considerable uncertainties. Thus the choice of  $m = -1.9$ , which was not favored by Ramsey on rather shaky grounds, appears to agree better with other values.

To settle upon the choice of  $m$  and hence the shielding in H<sub>2</sub>, a more precise measurement of  $(\text{HD}_\sigma - \text{H}_2_\sigma)$  is desired, although the experiment may be difficult on account of the short relaxation time of H<sub>2</sub>.

Yours sincerely,

A. Saika

A. Saika

- 
- 1) A. Saika and H. Narumi, Progress Report (Japan) No.9, 16(1959).
  - 2) N.F. Ramsey, Phys. Rev. 87, 1075(1952); W.E. Quinn, et al., ibid. 112, 1929(1958).
  - 3) J.P. Auffray and J.W. Cooley, Phys. Rev. 122, 1203(1961); J.W. Cooley, AEC Res. & Development Report (1961).
  - 4) T.W. Marshall and J.A. Pople, Mol. Phys. 3, 339(1960); T.W. Marshall, ibid. 4, 61 (1961).
  - 5) E. Ishiguro and S. Koide, Phys. Rev. 94, 350 (1954).
  - 6) T.F. Wilmott, Phys. Rev. 91, 476 (1953).



RESEARCH LABORATORIES  
GENERAL MOTORS CORPORATION

June 7, 1963

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

Dear Barry:

Here is my contribution to MELLONMR. In the September, 1962, issue (No. 48), I tabulated substituent constants,  $S_o$  and  $S_m$ , which give the effect of a substituent on the chemical shift of benzene ring protons ortho and meta to it. This work extended the earlier measurements of Diehl [Helv. Chim. Acta 44, 829 (1961)], who studied 11 substituents.

The Diehl additivity theory states that for a compound of the type  $X-\text{C}_6\text{H}_4-\text{Y}$ , the chemical shift of a proton ortho to X is given by  $\delta_{o,X} = S_{o,X} + S_{m,Y}$ . For monosubstituted benzenes,  $\delta_{o,X} = S_{o,X}$ ;  $\delta_{m,X} = S_{m,X}$ ;  $\delta_{p,X} = S_{p,X}$ .

Our work was based on paradisubstituted benzenes and has since been revised and expanded. The attached table lists the revised S-values for 69 substituents.

The number of spectra used in deriving the S-value listed in the first occupied column for each substituent is given in parentheses following the formula for that substituent. No number is listed if only one spectrum was used or if one compound was run in several polar solvents. In the body of the table the average S-value is given, followed by the average deviation (a rough measure of precision but not accuracy), and, in brackets, the absolute value of the maximum

Dr. B. L. Shapiro  
June 6, 1963  
Page 2.

deviation of any single determination from the average S-value. Results for both  $\text{CCl}_4$  and polar solvents are given as well as the original results of Diehl. The line positions for monosubstituted benzenes (which give directly the S-values) as found by two labs are also given. Spiesecke and Schneider [J. Chem. Phys. 35, 731 (1961)] used 5 mole % solutions in cyclohexane and an internal standard. Corio and Dailey [J. Am. Chem. Soc. 78, 3043 (1956)] used 50% solution in cyclohexane with an internal reference (except for COOH for which acetone was the solvent). S-values found from data taken from Tiers (Characteristic NMR Shielding Values, 3M Co., March 28, 1958) or from the Varian NMR catalog (Varian Associates, 1962) are indicated by a superscript T or V.

The attached figures are self-explanatory. A few preprints of this work are available. A few copies of our Diamagnetic Susceptibility Compilation and Supplement are also available.

Yours truly,

*George*

George W. Smith  
Physics Department









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TABLE VI


NMR Substituent Constants

Substituents	$S_o$ (pphm)					$S_m$ (pphm)				
				Line Positions of Monosub Benzenes					Line Positions of Monosub Benzenes	
	Present Work		Diehl	SpS	CD	Present Work		Diehl	SpS	CD
	CCl <sub>4</sub>	Polar Solvent				CCl <sub>4</sub>	Polar Solvent			
F (6)	23±3 [7]	25±1	25	31	40	3±3 [7]	3±6	1	2	13
Cl (11)	- 6±1 [3]	- 4±2	-5	-2	0	6±2 [4]	5±4	6	3	0
Br (11)	-20±2 [4]	-16±1	-22	-22	0	12±2 [3]	11±2	11	9	0
I (6)	-38±1 [2]	-41	-41	-40	-30	23±1 [3]	14	22	25	17
NO <sub>2</sub> (5)	-99±3 [4]	-92	-98	-95	-97	-21±3 [8]	-18	-21	-21	-30
NO	-48					11				
NH <sub>2</sub> (2)	71±7	70±8	68	76	77	21±3	24±8	22	20	13
NHMe	71				80	20				30
NMe <sub>2</sub>	79 <sup>T</sup>	75±1		60	50	20 <sup>T</sup>	15±3		10	20
NEt <sub>2</sub> (2)	56±4					10±7				
NH $\phi$		-6					-11			
NHNH <sub>2</sub>		48±9					35±5			
NHCSNH-( $\phi$ )-Me		-31					-13			
NHN=C (CF <sub>2</sub> H) CH <sub>2</sub> COOEt		-56 <sup>V</sup>					-15 <sup>V</sup>			
NHCOMe (3)		-28±2 [4]					- 3±3 [5]			
-N=N $\phi$	-75					-12				
-N=NBF <sub>4</sub>		-136±20					-58±20			
NH <sub>2</sub> .HCl (2)		- 39±12					-18±13			
NH <sub>2</sub> .2HCl		- 80					-29			
NCO	10					7				
OH (7)		48±5 [9]	50		37		13±5 [7]	16		37
OMe (6)	45±2 [6]	37±4	42	43	23	14±1 [2]	6±3	10	4	23
OEt (4)	44±2 [3]	41				14±2 [3]	18			
O $\phi$ , O-( $\phi$ )-Br (2)	26±0					3±2				
OCH <sub>2</sub> $\phi$		30					-5			
OCOMe	21 <sup>T</sup>					2 <sup>T</sup>				
OSO <sub>2</sub> -( $\phi$ )-Me	26					5				
ONa		109					36			
SH	-1					10				
SMe	3					0				
SEt	-7					2				
SO <sub>2</sub> F	-76 <sup>T</sup>					-32 <sup>T</sup>				
SO <sub>2</sub> Cl (3)	-83±2 [3]					-26±5 [8]				
SO <sub>2</sub> NH <sub>2</sub> (2)		-60±1					-22±3			
SO <sub>2</sub> -N( $\phi$ )-NSO <sub>2</sub> -( $\phi$ )-Me		-51 <sup>V</sup>					-21 <sup>V</sup>			
SO <sub>2</sub> Na.2H <sub>2</sub> O		-37					-14			
SO <sub>2</sub> -( $\phi$ )-Me		-71					-21			
SO <sub>3</sub> Na		-45±5					11±9			
SO <sub>3</sub> H.H <sub>2</sub> O		-55±4					- 21±4			
SO <sub>3</sub> C <sub>n</sub> H <sub>2n+1</sub> (4)	-62±1 [1]					-27±1 [1]				
SO <sub>3</sub> -( $\phi$ )-Cl	-58					-25				
COOH		-83±8		-63*			- 15±3			-10*
COOMe	-81 <sup>T</sup>	-79	-74	-93		- 7 <sup>T</sup>	- 5	-10		-20

TABLE VI - NMR Substituent Constants-(Cont'd.)

Substituents	$S_o$ (pphm)					$S_m$ (pphm)				
	Present Work		Diehl	Line Positions of Monosub Benzenes		Present Work		Diehl	Line Positions of Monosub Benzenes	
	CCl <sub>4</sub>	Polar Solvent		SpS	CD	CCl <sub>4</sub>	Polar Solvent		SpS	CD
COOBu	-83					-15				
COOCH <sub>2</sub> CH <sub>2</sub> NEt <sub>2</sub>		-78 <sup>V</sup>					-8 <sup>V</sup>			
CHO (3)	-60±1 [1]	-63±4		-58	-73	-20±0 [1]	-22±3		-21	-23
COMe (4)	-68±3 [4]	-72±2			-63	-11±2 [3]	-11±2			-27
COCH <sub>2</sub> Br		-70 <sup>V</sup>					-18 <sup>V</sup>			
CO- 	-57					-15				
CO-  -NMe <sub>2</sub>		-72					-23			
COC1	-86	-84			-90	-19	-6			-23
CN	-36	-45	-35		-30	-18	-27	-13		-30
Me (12)	17±4 [7]	9±2	17		10	14±3 [5]	5±2	13		10
Et	10				7	7				7
CHMe <sub>2</sub> (5)	10±1 [2]	4				7±1 [2]	1			
CMe <sub>3</sub>	-8					5				
CMe <sub>2</sub> CH <sub>2</sub> CMe <sub>3</sub>		-7 <sup>V</sup>					3 <sup>V</sup>			
CH <sub>2</sub> Cl (4)	-10±3 [3]				0	-3±4 [7]				0
CH <sub>2</sub> CN		-11					-4			
CF <sub>3</sub>		-36 <sup>V</sup>					-16 <sup>V</sup>			
CHMeOH		1 <sup>V</sup>					5 <sup>V</sup>			
CH <sub>2</sub> OCH <sub>2</sub> O-  -Me	1 <sup>T</sup>					-2 <sup>T</sup>				
CMe <sub>2</sub> -  -OH		4					-2			
CH(  -NMe <sub>2</sub> ) <sub>2</sub>		11 <sup>V</sup>					-17 <sup>V</sup>			
 ,  -X (4)	-26±1 [2]					-11±2 [2]				
CH=CHMe		-11 <sup>V</sup>					1 <sup>V</sup>			
CH=CHCOEt		36 <sup>V</sup>					16 <sup>V</sup>			
										
Ferrocene		7 <sup>V</sup>					-15 <sup>V</sup>			
Si(φ-OMe) <sub>2</sub> C <sub>2</sub> H <sub>4</sub> OH	-36					-14				
AsO <sub>3</sub> H <sub>2</sub>		-41					-22			

\*Acetone solvent used

NOTE: Me = CH<sub>3</sub>, Et = C<sub>2</sub>H<sub>5</sub>, Bu = n-C<sub>4</sub>H<sub>9</sub>, and φ =   
 T = Tiers<sup>10)</sup> data used. V = Varian<sup>11)</sup> data used.

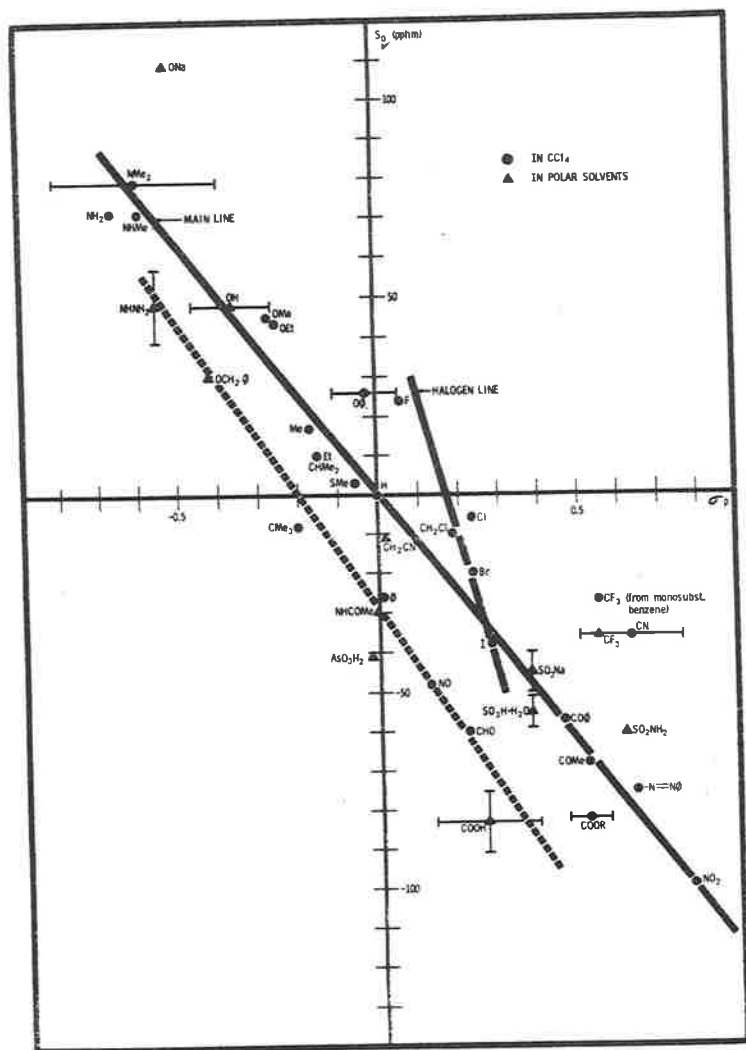


FIG. 1 Ortho NMR substituent constant ( $S_o$ ) vs. para Hammett substituent constant ( $\sigma_p$ ). Symbols are explained in the tables.

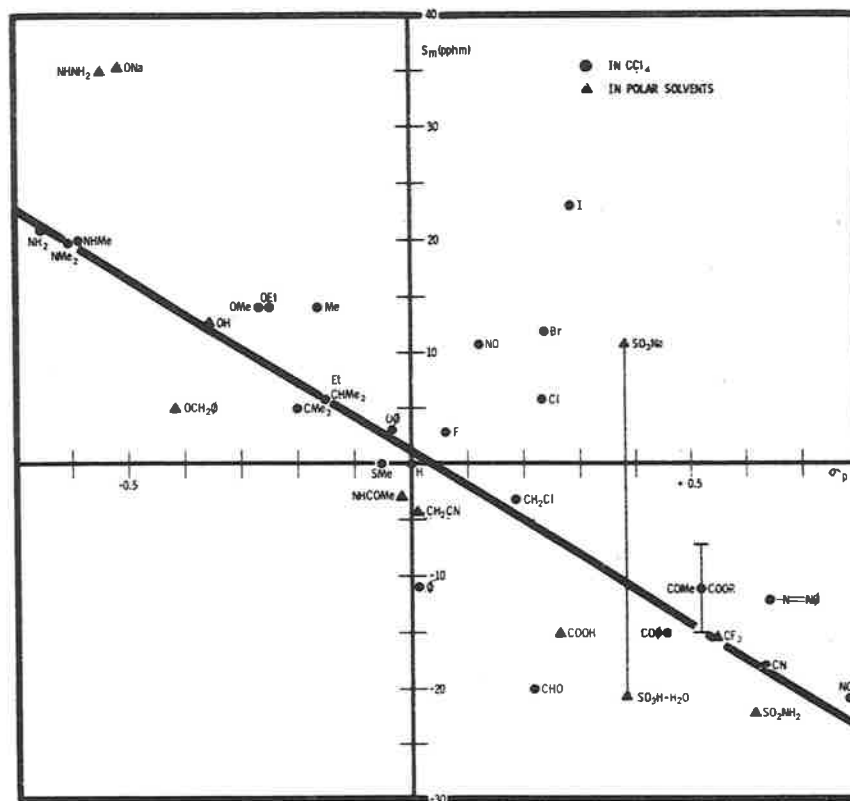
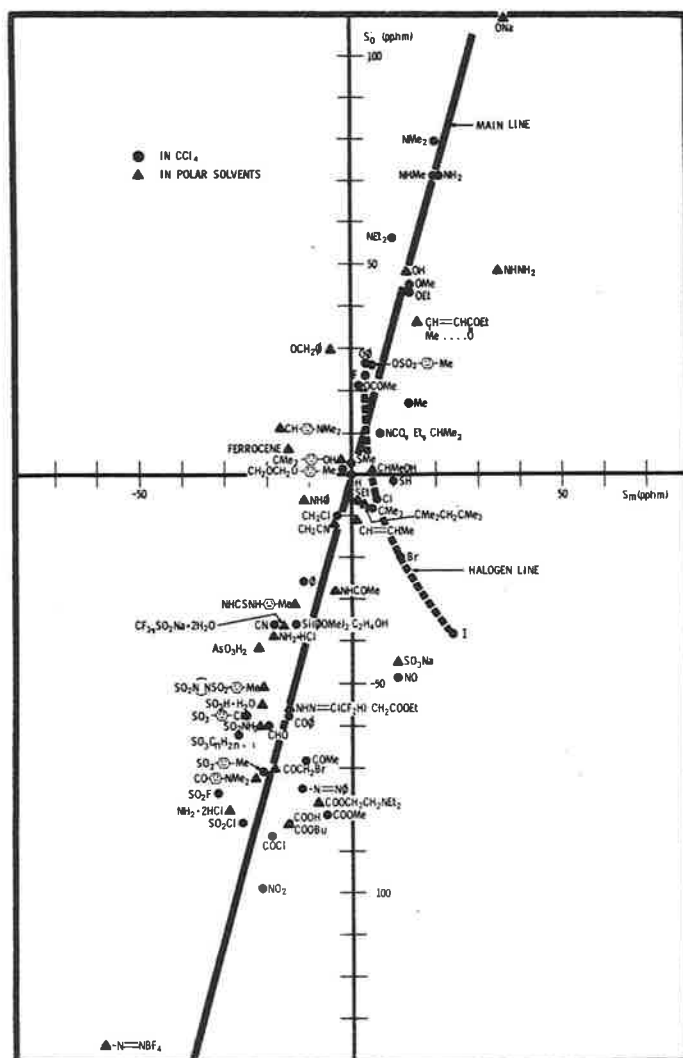
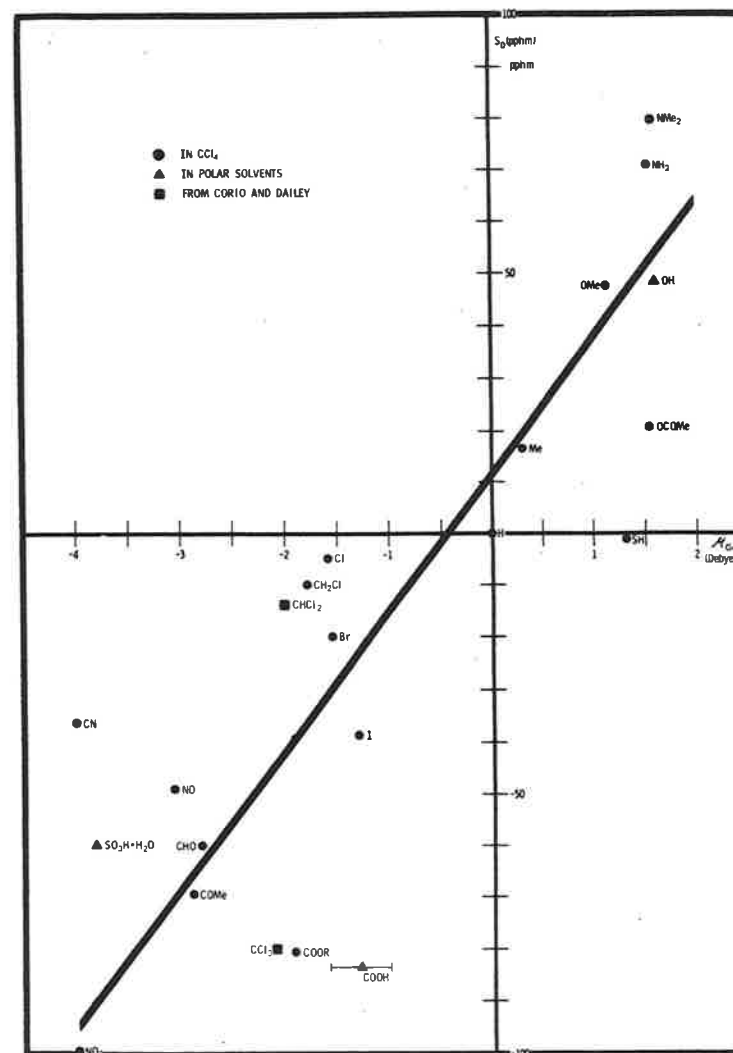


FIG. 2 Meta NMR substituent constant ( $S_m$ ) vs. para Hammett substituent constant ( $\sigma_p$ ).



**FIG. 3** Ortho NMR substituent constant ( $S_o$ ) vs. meta Hammett substituent constant ( $S_m$ ).



**FIG. 4** Ortho NMR substituent constant ( $S_o$ ) vs. group electric dipole moment ( $\mu_{Gr}$ ).



7th. June, 1963.

Lincoln College, Oxford, England.

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

Dear Dr. Shapiro,

I am enclosing my subscription to the excellent Mellon Newsletter. Long may it continue.

We are continuing to explore quadrupole relaxation processes in various systems, following up some work on bromine relaxations which has just been published. Donald Herbison-Evans has been studying quadrupole dominated line-widths in nitrogen resonances in a number of different systems. One set of compounds he has studied are the alkyl nitrates. The quadrupole coupling constant at the nitrogen in these compounds is moderately well-known and is fairly constant with changing alkyl group at about 3.6 Mc/s. The nitrogen relaxation times in these compounds have been measured as a function of the viscosity of the medium and linear plots with viscosity are obtained. The slopes of the lines give a measure of the quadrupole coupling constant and of the correlation time of the molecule. If we take the quadrupole coupling constant as 3.6, it is possible to obtain an estimate of the correlation time in the various solutions. This correlation time can be calculated from the molecular parameters using the simple Stokes theory, the theory of Hill or the empirical modifications suggested by Wertz. We have found that in these compounds the correlation times obtained agree well with the formula suggested by Wertz, namely that they are one sixth of the value calculated from the simple Stokes theory. R.A. Craig has measured the spin lattice relaxation times of lithium nuclei in lithium salt solutions by the method of fast passage. For a given solvent,  $T_1 \propto$  the viscosity is always a constant so that quadrupole coupling cannot arise in these solutions from ion-ion interaction. The slope of the plot of  $1/T_1$  against viscosity gives a measure of the quadrupole coupling constant and it is found that this remains approximately constant in solutions of water, methanol and formic acid. In dimethyl formamide, however, the quadrupole coupling constant is much greater and this can be interpreted in terms of the less symmetrical arrangement of the dimethyl formamide molecules about the lithium ion than is possible in the case of water. Similar measurements by R. Thompson on aluminium relaxation times in solutions of aluminium salts give quite different results. If one takes a strong solution of aluminium chloride in water and adds organic solvents to it, the aluminium relaxation time multiplied by the viscosity remains virtually constant. Evidently, in all the solvents we have been able to use so far, the aluminium retains its sphere of water molecules about it regardless of the composition of the bulk of the liquid. This is in quite marked contrast with the behaviour of sodium and bromine resonances where the environment of these ions clearly takes on the bulk property of the liquid medium. No doubt the different behaviour in the case of aluminium is due to its small size and high charge.

During the past nine months we have been rebuilding our nuclear electron double resonance apparatus and Dr. J.W. White has constructed a double resonance apparatus working at 8 millimetres microwaves, and Mr. J. Kenworthy has just completed a new X-band apparatus. Both of these machines are capable of observing proton resonances under moderately high resolution conditions, and at the moment we are working with line widths of about 5 c/a.

p.t.o.

In the 8 millimetre apparatus we have been able to observe multiple resonances due to chemically distinguishable protons in an organic solution of a free radical, and when the microwave pumping is started up, the different resonances are enhanced or reversed to different extents depending on the mechanism of their coupling to the radical. We have observed some recordings in which some resonances are quite strongly inverted whilst others are strongly enhanced. This work is only just beginning and I am afraid I do not have any detailed results to report, but it is clear that there is a considerable amount of information locked up in spectra of this kind.

Mr. Alan Pidcock has observed the platinum resonances in a considerable number of platinum complexes. We had hoped to correlate the chemical shifts with electronic transitions observable in these substances, but the situation appears to be much more complicated than in the case of cobalt complexes. We have not, so far, been able to assign the visible and ultra-violet spectra in a way which is consistent with the chemical shifts of the nuclear resonances.

The results I have mentioned are all concerned with work which is not yet quite complete and we hope to publish papers on these topics during the next 6 months or so.

With best regards,

Yours sincerely,

*R. E. Richards*  
R. E. Richards.

NEW YORK UNIVERSITY  
UNIVERSITY HEIGHTS, NEW YORK 53, N.Y.

DEPARTMENT OF CHEMISTRY

TELEPHONE: LUDLOW 4-0700

June 9, 1963

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

Dear Dr. Shapiro:

We have had occasion to examine the n.m.r. spectra of numerous compounds containing methylene protons which are magnetically non-equivalent by virtue of molecular dissymmetry. This letter reports some salient results.

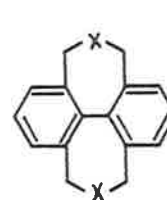
We begin by pointing out that geminal protons in  $\text{XCH}_2\text{Cabc}$  are strictly speaking diastereomeric protons. This definition can be legitimately applied to geminal protons in non-dissymmetric molecules, such as diethyl acetal and propene, and it may be extended to include the non-equivalent methyl protons of diisopropyl acetal. We would like to propose this term<sup>1</sup> for general usage, to replace less specific terms like "intrinsic asymmetry". The proposed designation (a) applies rigorously to all of the cases which have been described so far (it can be extended to other nuclei where pertinent), and (b) it does not commit the user to a specification of the source of the magnetic non-equivalence<sup>2,3</sup>.

We have measured the n.m.r. spectra (in  $\text{CDCl}_3$ ) of a series of p-tolyl alkyl sulfoxides  $\text{CH}_3\text{C}_6\text{H}_4\text{SOR}$ , where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$  and  $t\text{-Bu}$ . These compounds contain asymmetric sulfur and may be prepared in optically active form. In the aliphatic region the methyl compound displays a singlet at  $\tau$  7.31, the ethyl sulfoxide shows a complex

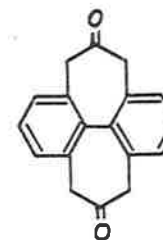
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methylene multiplet centered at  $\tau$  7.19 and a methyl triplet at  $\tau$  8.83, the isopropyl sulfoxide shows a multiplet centered at  $\tau$  7.19 and two methyl doublets at  $\tau$  8.80 and 8.86, and the t-butyl sulfoxide shows a methyl singlet at  $\tau$  8.84. Obviously the spectra of the ethyl and isopropyl sulfoxides reflect the asymmetry of the sulfur. This result has special significance since in a recent letter to MELLONMR it was remarked<sup>4</sup> that the two protons in either one of the two methylene groups of dibenzyl disulfide monoxide "have identical chemical shifts in spite of the asymmetric sulfur atom". The remainder of our letter will be concerned with the very serious problem of the apparent identity of diastereomeric and therefore magnetically non-equivalent protons, at least at 60 Mc.

We ran into this very problem in connection with our work on doubly bridged biphenyls: while compounds Ia and Ib showed the anticipated AB quartet<sup>5</sup>, compound II showed a sharp singlet in  $\text{CDCl}_3$ , and this despite its conformational stability



Ia, X = O  
Ib, X = S

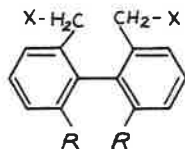


II

under the conditions of measurement<sup>6</sup>. We were puzzled by this and related anomalies. Finally, following a suggestion by J. D. Roberts, we started to vary the solvent: the results were dramatic enough and a sampling is given in the accompanying Table I and (by way of illustration) in Fig. 1. We intend to discuss the results in detail elsewhere; in this letter we would only stress that every one of the compounds with apparent methylene  $A_2$  is conformationally stable and must therefore be of the AB type. It was only through knowledge of this fact

(i. e. optical stability) that we were forced to question the "singlet" nature of the absorption. The implications are obvious. In particular, caution should be attached to the interpretation of a methylene singlet as  $A_2$  when the possibility of an AB system is given (this is the old problem of negative evidence).

We observed the same anomaly elsewhere. Compounds IIIa and IIIb have diastereomeric methylene protons absorbing at  $\tau$  5.85, 6.02 ( $J_{AB}$  11.6 c/s) and at  $\tau$  5.83, 6.00 ( $J_{AB}$  11.8 c/s) respectively. The bromides IIIc and IIId on the other hand have sharp singlets at  $\tau$  5.85. We have not yet done a solvent study and we reserve comments for another letter.



IIIa, X = OH, R = CH<sub>3</sub>  
 b, X = OH, R = CD<sub>3</sub>  
 c, X = Br, R = CH<sub>3</sub>  
 d, X = Br, R = CD<sub>3</sub>

Sincerely yours,

*Kurt Mislou*  
 Kurt Mislou  
*George H. Wahl, Jr.*  
 George H. Wahl, Jr.

# Footnotes

- (1) This should also answer the question posed by D. W. Moore in MELLONMR No. 43.
- (2) H. S. Gutowsky, J. Chem. Phys., **37**, 2196 (1962).
- (3) The idea of steric non-equivalence of identical substituents "a" in a symmetric molecule Caabc has been discussed in another connection by P. Schwartz and H. E. Carter, Proc. Natl. Acad. Sci., **40**, 499 (1954). In line with our proposal, the protons in (for example) CH<sub>2</sub>ClBr may be referred to as enantiomeric.
- (4) E. R. Malinowski, P. Allen, Jr. and P. J. Berner, MELLONMR, No. 52.
- (5) K. Mislou and M. A. W. Glass, J. Am. Chem. Soc., **83**, 2780 (1961). For correction of the n.m.r. data, see J. Am. Chem. Soc., **84**, 4999 (1962).
- (6) K. Mislou, E. Simon and H. B. Hopps, Tetrahedron Letters, No. 22, 1011 (1962).

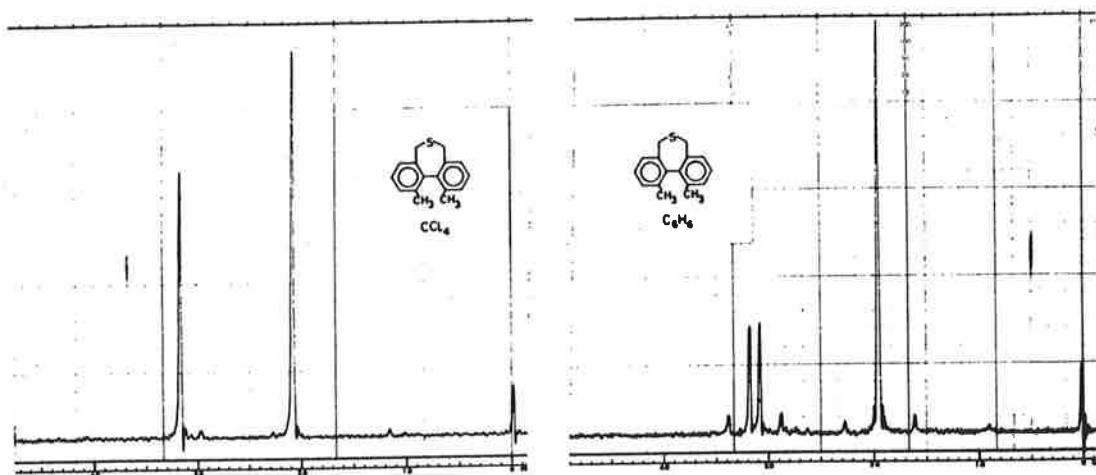
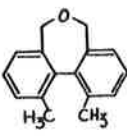
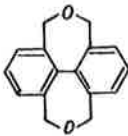
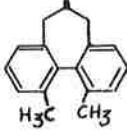
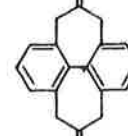
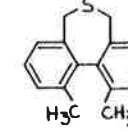
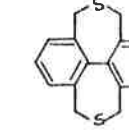


fig. 1.

Table 1.

Methylene p. m. r. absorption, Varian A-60 spectrometer, ~10% sol., internal TMS, chemical shifts in p. p. m. on the  $\tau$  scale.  $J_{AB}$  in c. p. s. indicated in parentheses.

						
<u>SOLVENT</u>						
$\text{CCl}_4$	5.73 6.10 (11.1)	5.53 5.89 (11.5)	6.57 6.78 (14.8)	6.48	6.81	too insol.
$\text{C}_6\text{H}_6$	5.61 5.90 (11.1)	5.51 5.81 (11.4)	6.74	6.69 6.81 (15.5)	6.75 7.00 (12.4)	6.73 7.06 (12.7)
$\text{CDCl}_3$	5.61 6.00 (11.0)	5.45 5.82 (11.5)	6.47 6.68 (15.2)	6.43	6.75	6.62 6.71 (12.7)
$\text{C}_5\text{H}_5\text{N}$	5.48 5.88 (11.0)	5.30 5.73 (11.1)	6.44 6.56 (15.5)	6.37	6.70	6.58

'Nuclear Spin-Spin  
Coupling Constants Involving the Group IV Elements'

L. W. Reeves and E. J. Wells  
Chemistry Department  
University of British Columbia  
Vancouver 8, B. C.

Consideration of correlations involving coupling constants between different nuclei has been mostly confined to those involving  $C^{13}$  and hydrogen (1, 2, 3, 4). The interest has centred around the following topics; dependence of  $J_{C^{13}-H}$  on s character (1, 2, 3, 4), the variation of  $J_{C^{13}-H}$  in molecules of the type  $CHXYZ$ , (5, 6, 7, 8) and the use of  $J_{C^{13}-H}$  in conjunction with chemical shift data to indicate diamagnetic anisotropy (9).  $J_{Si^{29}-H}$  coupling constants have been measured (16) but these are influenced by polar effects besides being dependent on hybridization (6). Long range  $J_{C^{13}-C-H}$  and  $J_{C^{13}-C-C-H}$  coupling constants have been measured both in enriched compounds (10, 11) and in natural abundance (12). The unfavourable magnetic properties of  $Ce^{73}$  makes it unlikely that parameters will be available for Germanium (17). Recent reports of coupling constants for  $Sn^{119}$ ,  $Sb^{121}$  and  $Pb^{207}$  (13, 18, 19, 20) are available for comparison with some measured recently by us (21). As a minor point we find coupling constants measured in reference (13) to be 3% lower than ours in dimethyltin-dihydride.

In the accompanying table are listed coupling constants involving Group IV elements in situations where hybridization is near  $sp^3$  for the group IV elements. The neighbouring atoms are also chosen so as to eliminate the possibility of back donation of charge into the unfilled d orbitals of a group IV atom.

In order to eliminate the contribution to  $J_{MN}$  arising from nuclear constants it is necessary to divide by the dissimilar magnetogyric ratios. In the series,  $C^{13}$ ,  $Si^{29}$ ,  $Sn^{119}$  and  $Pb^{207}$  all have spin 1/2 properties so division by the nuclear moment in nuclear magnetons is sufficient. It is to be noted that  $J_{C^{13}}$  and  $J_{Pb^{207}}$  are positive and  $J_{Si^{29}}$  and  $J_{Sn^{119}}$  are negative.

The underlying prerequisite of the present discussion is a knowledge of the electronic contribution to  $J_{X-H}$  and this is represented in column 5 of the table. We will presume that  $J_{C^{13}-H}$  and  $J_{Pb^{207}}$  have opposite sign to  $J_{Si^{29}-H}$  and  $J_{Sn^{119}-H}$  merely because of a change in the sign of the gyromagnetic ratio of the group IV nucleus. This assumption has yet to be tested. Since we assume the electronic contribution to  $J_{X-H}$  has the same sign down the group we shall use for our purpose  $|J/\mu|$ . Discussions regarding absolute magnitudes of coupling constants should compensate for nuclear dependence.

We have found a most satisfactory linear correlation of

$$\sqrt{\frac{J_{X-H}}{\mu_X}}$$

with the atomic number  $Z_X$  for group IV element X, with the conditions specified earlier. This is shown in figure 1. The same relationship

$$\sqrt{J_{X-C-H} / \mu_X}$$

versus  $Z_X$  also holds and is shown in figure 1. Data for long range couplings  $J_{X-C-C-H}$  is too sparse but the data for  $J_{X-F}$  (14, 15, 16) is partially available and some values of  $J_{X-C-F}$  (14, 21). The square root law can be tested in this case by taking values of

$$\sqrt{\frac{J_{X...F} \times J_{C^{13}}}{J_{C^{13}...F} \times \mu_X}}$$
 versus atomic number.

Three available points give good linear relationship. This is shown in figure 2.

The above correlations may be represented analytically:-

$$\sqrt{\frac{J_{X-H}}{\mu_X}} = 0.676 Zx + 8.0 \quad - (1)$$

$$\sqrt{\frac{J_{X-C-H}}{\mu_X}} = 0.107 Zx + 1.95 \quad - (2)$$

$$\sqrt{\frac{J_{X...F} \mu_{Cl^3}}{J_{Cl^3...F} \mu_X}} = 0.0245 Zx + 0.84 \quad - (3)$$

In a recent paper using the valence bond approach, Gutowsky and Juan (6) have formulated the contact contribution to  $J_{X-H}$  ( $X = C^{13}$  or  $Si^{29}$ ) in  $sp^3$  molecules of the type we are considering. Their expression can be generalised, in their notation, as:

$$J_{X-H} = \frac{\gamma_H \gamma_X}{h \Delta E_X} \left( \frac{16\pi\beta\hbar}{3} \right)^2 \rho_X^2 \alpha_H^2 |n S_X(0)|^2 |S_H(0)|^2 \quad - (4)$$

The assumptions are that the contact term is the dominant one as has already been shown for  $C^{13}$  (22), that the perfect pairing approximation may be used for all the ground state wave functions down the group, and that the product of the contact matrix elements over all excited triplet states may be replaced by the diagonal element over the ground state, coupled with a mean triplet excitation energy,  $\Delta E_X$ . The terms which depend on the group IV atoms X are  $\Delta E_X$ , the normalisation term  $\rho_X^2$  and the atomic s electron charge density at the nucleus  $|n S_X(0)|^2$ . An estimate of the dependence of this latter on Z may be obtained from the hyperfine splitting of the  $^2S$  ground states of the atomic alkali metals, where the only I.S interaction mechanism is through the scalar contact term. The most accurate hyperfine splitting energies are from atomic microwave measurements and have been tabulated by Ramsey (23). The hyperfine structure separation for a single s electron ( $L = 0$ ) is (24)

$$\Delta E = \frac{8\pi\beta}{3} \mu_X |n S_X(0)|^2 \frac{(2I_X+1)}{I_X} \quad - (5)$$

Thus the contact charge density of the alkali metals may be obtained from knowledge of the splittings  $\Delta E$ , the nuclear magnetic moments and the nuclear spins  $I_X$ . Figure 3 shows the correlation of the square root of the contact charge against the atomic number.

Although this correlation fails for small Z values, it is sufficient to allow a qualitative explanation of the  $J_{X-F}$  dependence in terms of equation (4). In moving from Group I of the alkalis to Group IV b without increasing the principal quantum number, we should tend to increase the slope of figure 3, and also to iron out the Li - Na irregularity. The conclusion is that most of the Z dependence noted in  $J_{X-F}$  is contained in  $|n S_X(0)|^2$ . Were the atomic wave functions hydrogenic, this dependence would be as  $Z^3$ , but is reduced to approximately  $Z^2$  by the inner filled shells. It appears reasonable that the screening by the increasing number of core electrons should leave  $\Delta E_X$  roughly independent of Z. Thus any Z dependence in  $\rho_X^2$  caused by the changing ionicity of the X-H bond must be slight.

#### Acknowledgements

We wish to thank Dr. J. A. R. Coope for several enlightening discussions. This work was generously supported by the National Research Council of Canada and the Petroleum Research Fund of the American Chemical Society.

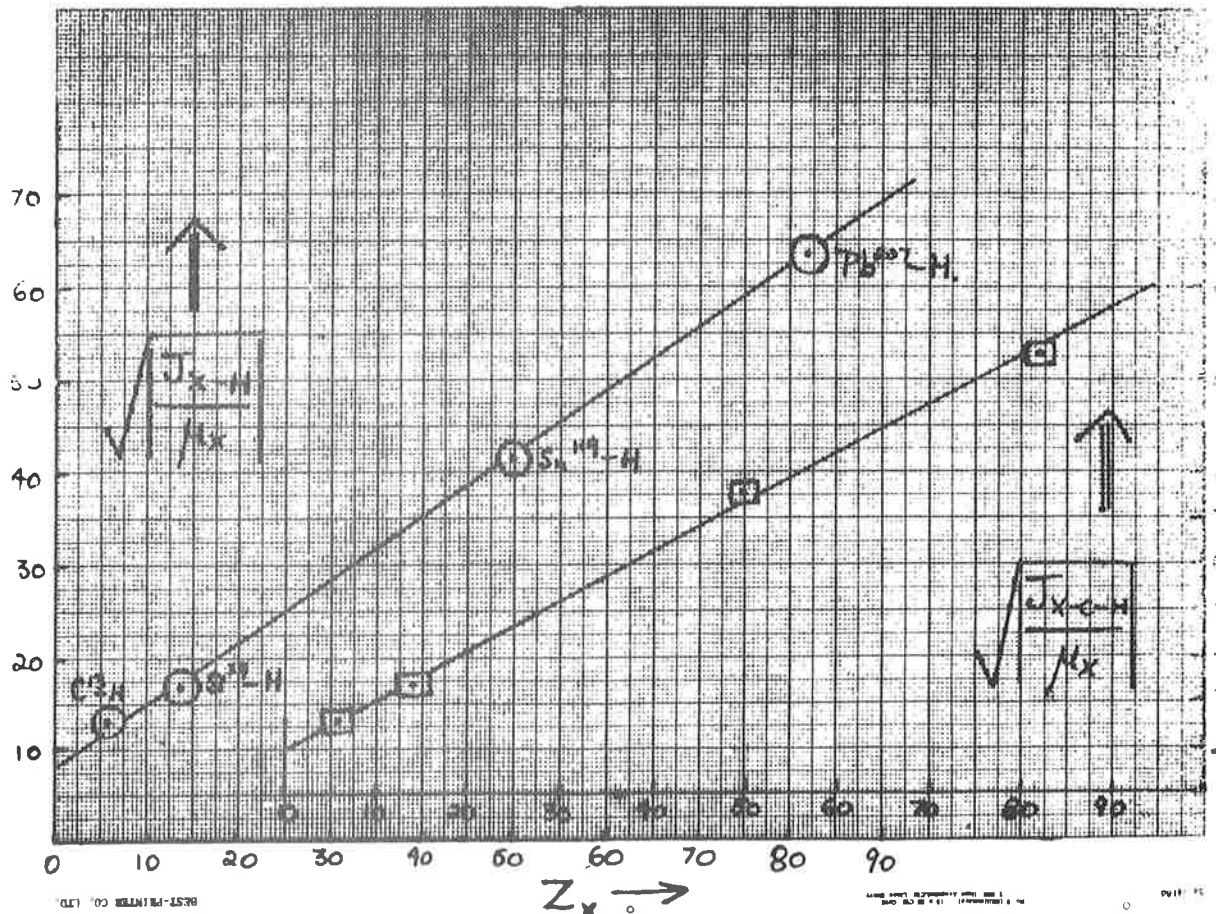
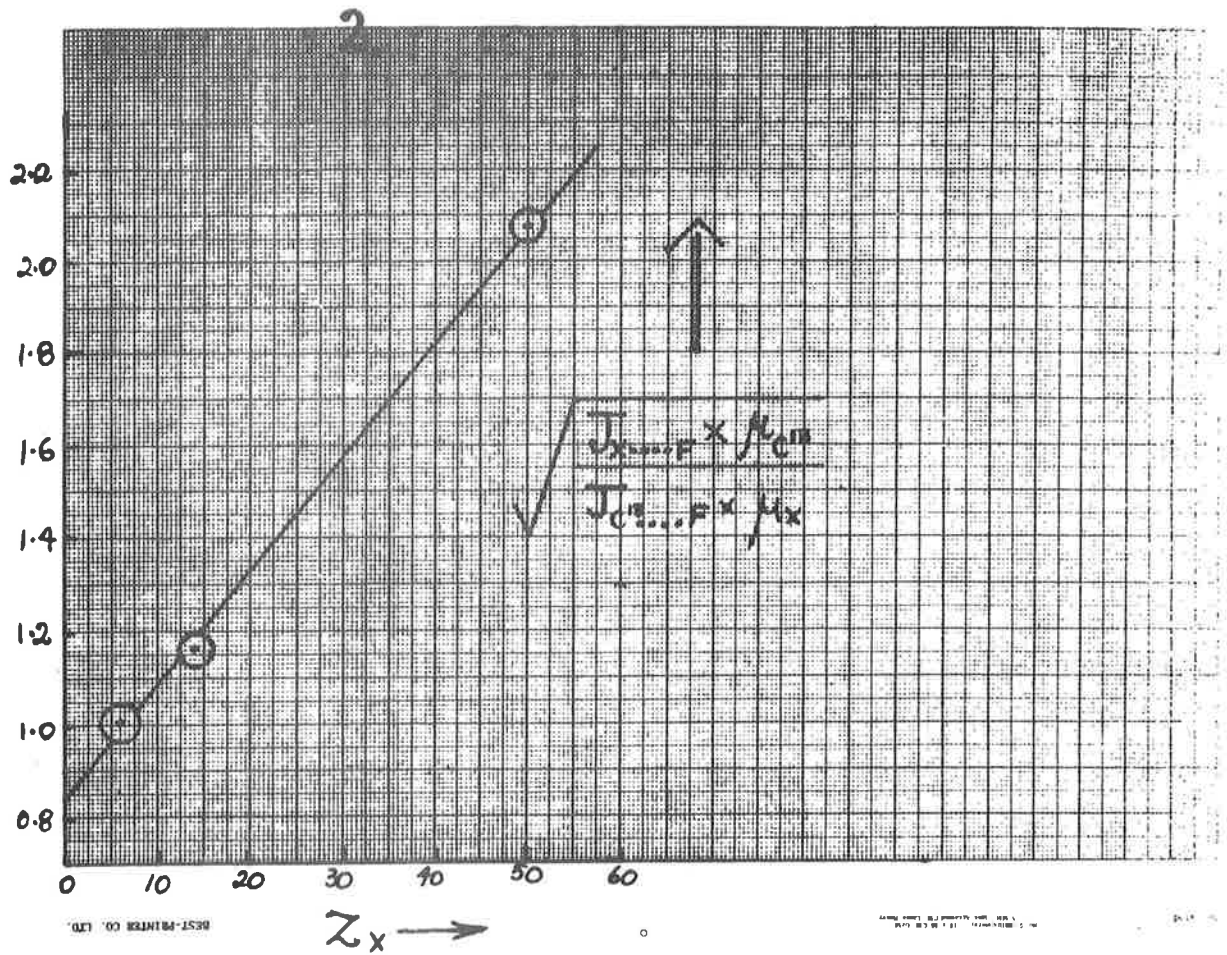


Table

Coupling Constant J	Value c. p. s.	Compound Measured	References	
$C^{13}\text{-H}$	125	many $sp^3$ type	(1, 3)	178
$Si^{29}\text{-H}$	202.5	$SiH_4$	(16)	289
$Sn^{119}\text{-H}$	1800	$(CH_3)_2SnH_2$	(21)	1730
$Pb^{207}\text{-H}$	2380	$(CH_3)_3PbH$	(13)	4075
$C^{13}\text{-C-H}$	3.8	$(C_2H_5)_3COH$	(11)	5.4
$Si^{29}\text{-C-H}$	6.57	$(CH_3)_4Si$	(15)	11.8
$Si^{119}\text{-C-H}$	60.2	$(CH_3)_2SnH_2$	(21)	57
$Pb^{207}\text{-C-H}$	66.7	$(CH_3)_3PbH$	(13)	114
$C^{13}\text{-F}$	257	$CF_4$	(14)	366
$Si^{29}\text{-F}$	274.8	$SiHF_3$	(16)	495
$C^{13}\text{-C-F}$	38.5	$CF_3CH_2Br$	(14)	54.8
$Sn^{119}\text{-C-F}$	251	$(CH_3)_2Sn(C_2F_4H)_2$	(21)	239

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# The Standard Oil Company

(An Ohio Corporation)

Research Department

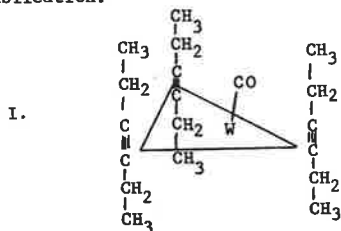
4440 Warrensville Center Road

Cleveland 28, Ohio

June 12, 1963

Dear Barry,

Recently we have been looking at some organo metal carbonyl complexes with NMR. We have chosen one system (hexyne-3 tungsten carbonyl) to illustrate how dramatic the NMR results can be. Spectrum B is of the solution of hexyne-3 in acetone- $d_6$ . The typical ethyl group ( $A_2B_3$ ) splitting is observed with the solvent line falling in the lowest field peak of the methylene quartet. Spectrum A is that of the complex and it is readily seen that there are non-equivalent groups present in approximately equal quantities. Also there is no evidence for non-equivalence of protons within a methylene or methyl group. Both elemental analysis and the molecular weight indicate that the compound's empirical formula is (hexyne-3) $_3$ WCO. One can infer from the spectra that the hexyne molecules are bound to the W via  $\pi$ -complexing through the triple bond. Secondly, the common formation of the benzene type structure from the three triple bonds apparently does not take place in this case. The non-equivalence of the ethyl groups suggest that half of them are in the environment of the carbonyl while the others are not. Furthermore, consider the ethyl group assumed to be in the environment of the carbonyl - here the methylene group appears to be more deshielded than the methyl group. Thus I is easily deduced. Supporting arguments were also obtained from infrared, but will not be given here. This and some similar systems are currently being written up for publication.



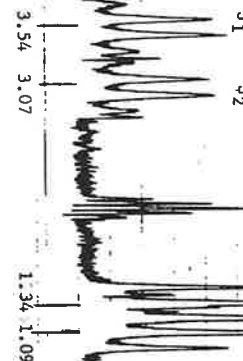
Sincerely,

*Bill*  
W. M. Ritchey

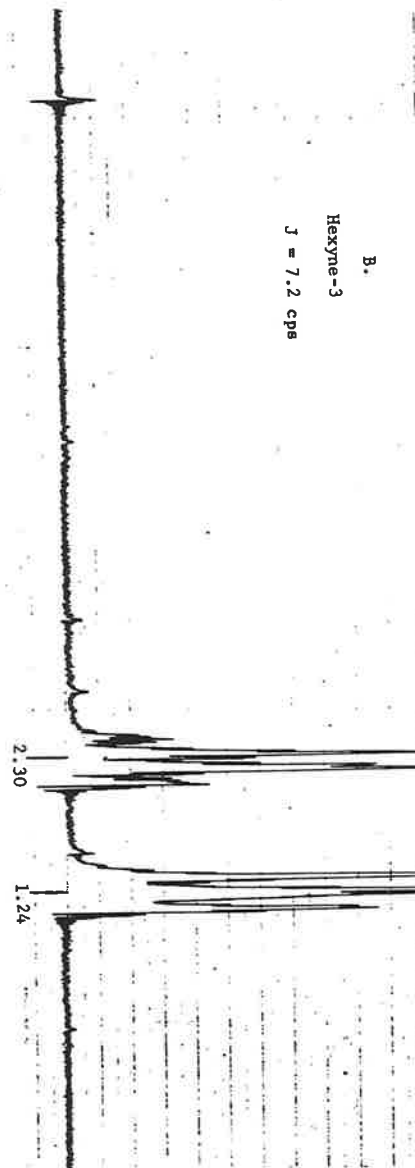
WMR:cnp  
Att.

A.  
Title Hexyne-3 Tungsten Carbonyl

$J_1 = 6.6$  cps  
 $J_2 = 7.8$  cps



B.  
Hexyne-3  
 $J = 7.2$  cps



# MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

June 4, 1963

## Phosphorus-phosphorus Coupling in Derivatives of Tetramethylbiphosphine

As a first contribution to MELLONMR, I would like to report some observations we have made on the proton N.M.R. spectra of some metal carbonyl complexes of  $(CH_3)_2P-P(CH_3)_2$ .

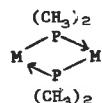
The methyl resonance in  $P_2(CH_3)_4$  itself (neat liquid) is a well-defined 1:2:1 triplet at  $\tau = 8.94$  with a splitting of 7.0 cps (G. W. Parshall, J. Inorg. Nucl. Chem., 14, 291 (1960)). In the nickel tricarbonyl and molybdenum pentacarbonyl complexes, however, the strong central peak of the triplet becomes weaker and broader, as shown on the right.

The change of pattern on formation of the complex is probably due to an increase in the ratio  $\frac{J_{CH_3-P}}{J_{P-P'}}$ , i.e., to a decrease in  $J_{P-P'}$ . It is possible

to speculate on the origin of this effect, assuming that spin-spin coupling between the nuclei of atoms directly bonded together occurs through the bonding electrons.

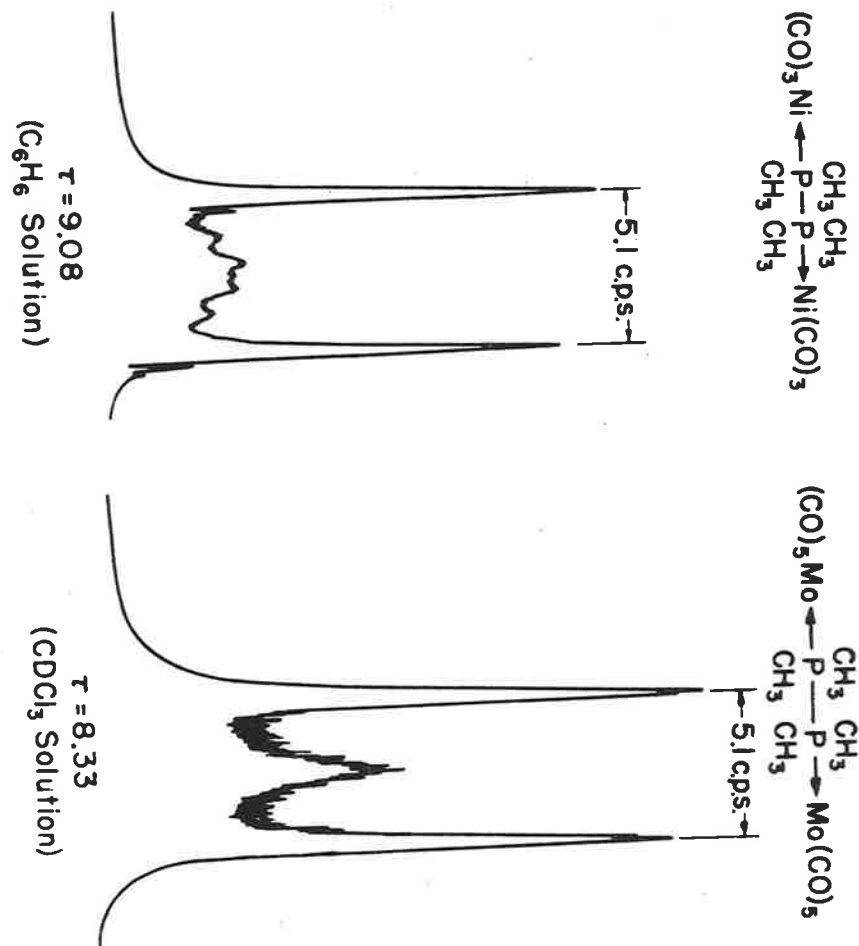
In  $P_2(CH_3)_4$ , the single bond between the two phosphorus atoms is augmented by partial double bonding due to overlap of the orbital containing the free electron pair of a trivalent phosphorus atom with the empty 3d orbitals of the adjacent phosphorus atom. On complex formation, the availability of the electron pair for such overlap will be greatly reduced, thus reducing the phosphorus-phosphorus interaction. This in turn may reduce  $J_{P-P'}$ .

In heterocyclic rings of the type



(M = Ni, Fe, Mn, Mo, and W), we have found that the methyl resonance is a 1:2:1 triplet (splittings range from 4.3 to 6.6 cps). In this case, strong phosphorus-phosphorus coupling is presumably transmitted through the metal atom and may be aided by the pseudo-aromatic character of the ring. It would be interesting to learn whether similar effects are observed in analogous compounds of the non-transition metals (e.g., where M = B, Al, Be, etc.).

*R. G. Hayler*  
R. G. Hayler



# THE SCHOOL OF PHARMACY

UNIVERSITY OF LONDON



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

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

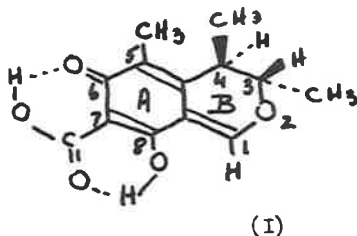
WBW/JT

12 June, 1963.

Dear Dr. Shapiro,

We very much appreciate receiving your excellent newsletter, MELLONMR, and have pleasure in submitting our first contribution.

From an examination of the N.M.R. spectrum of the fungal metabolite citrinin<sup>1</sup> (I) we have been able to assign the most likely conformation of this molecule. The proton signals observed and their assignments are as follows:



	$\tau$	H	J	Assignments
Two doublets with centre line of each superimposed	8.75	3	6.5	CH <sub>3</sub> at C <sub>4</sub> coupled geminally to H
	8.62	3	6.5	CH <sub>3</sub> at C <sub>3</sub> " " " "
Single peak	7.97	3	-	CH <sub>3</sub> at C <sub>5</sub>
Quartet centred at	6.96	1	6.5	H at C <sub>4</sub> coupled geminally to CH <sub>3</sub>
Quartet centred at	5.16	1	6.5	H at C <sub>3</sub> " " " "
Single peak at	1.7	1	-	H at C <sub>1</sub>
Single peak at	-3.7	1	-	{ H of OH at C <sub>8</sub> H of carboxyl group } signals disappear on deuteration
Single peak at	-5.2	1	-	

- 2 -

Whilst ring A is a rigid structure, ring B is relatively mobile about positions 2, 3 and 4. Since the methyl groups are trans to each other<sup>2</sup>, this means that two conformations are possible.

Along the line of the C<sub>3</sub> - C<sub>4</sub> axis these are as follows:-

(a) where the dihedral angle  $\theta$  between the protons is  $\approx 60^\circ$  and (b) where the dihedral angle is  $\approx 180^\circ$ .

From the data of Conroy<sup>3</sup> the vicinal coupling constant for  $\theta \approx 180^\circ$  is of the order 10 - 11 c/sec. and would be expected to lead to further splitting of the quartets centred about 6.96 and 5.16. For  $\theta \approx 60^\circ$  the coupling constant is 1 - 2 c/sec. and in fact fine splitting of this order can be observed in the lines of the two quartets concerned.

In (b) moreover the methyl groups at C<sub>3</sub> and C<sub>4</sub> are more nearly co-planar with the methyl group on C<sub>5</sub> and of the two conformers this is obviously that which shows the greater degree of steric hindrance.

We conclude that the spectrum is consistent with the conformation (a).

Yours sincerely,

*David W. Mathieson*

D.W. Mathieson

*W.B. Whalley*  
W.B. Whalley.

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Dr. B.L. Shapiro,  
Mellon Institute,  
4400 Fifth Avenue,  
Pittsburg, 13,  
Pennsylvania,  
U.S.A.

June 18, 1963

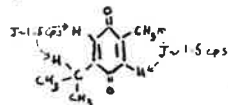
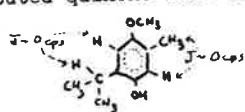
DEPARTMENT OF CHEMISTRY

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

Dear Dr. Shapiro:

We wish to report another case of long range coupling which seems to be a subject of considerable interest in recent issues of MELLONMR. We have studied the NMR spectra of several substituted phthalans and isochromans (Fig. I) as part of their structure elucidation, which has also been established on the basis of chemical evidence, infra red measurements and elemental analyses.<sup>1</sup>

1-phenylphthalan gave a typical ABX spectrum with equal  $J_{AX}$ ,  $J_{BX}$  coupling constants. An analysis of the spectrum gave  $J_{AX} = J_{BX} = 2.2$  cps. and  $J_{AB} = 12.5$  cps. This long range coupling is not to be found in 3,3-diphenylisochroman. Sheppard and Lynden-Bell reported coupling in similar positions in eleutherin and isoeleutherin.<sup>2</sup> However, the presence of the benzenoid ring rather than the quinone ring fused to the pyran system may account for the absence of coupling here. This argument is similar to that used to explain coupling in a substituted quinone that subsequently disappears in the hydroquinone.<sup>3</sup>



This would also suggest that the probable route for coupling would be predominantly through the saturated four-bond ether linkage in 1-phenylphthalan.

This work is being continued with other substituted isochromans.

Our apologies for the lateness of this contribution.

Sincerely yours,

James C. Randall

James C. Randall

James J. McLeskey, III

James J. McLeskey, III

John E. Baxter

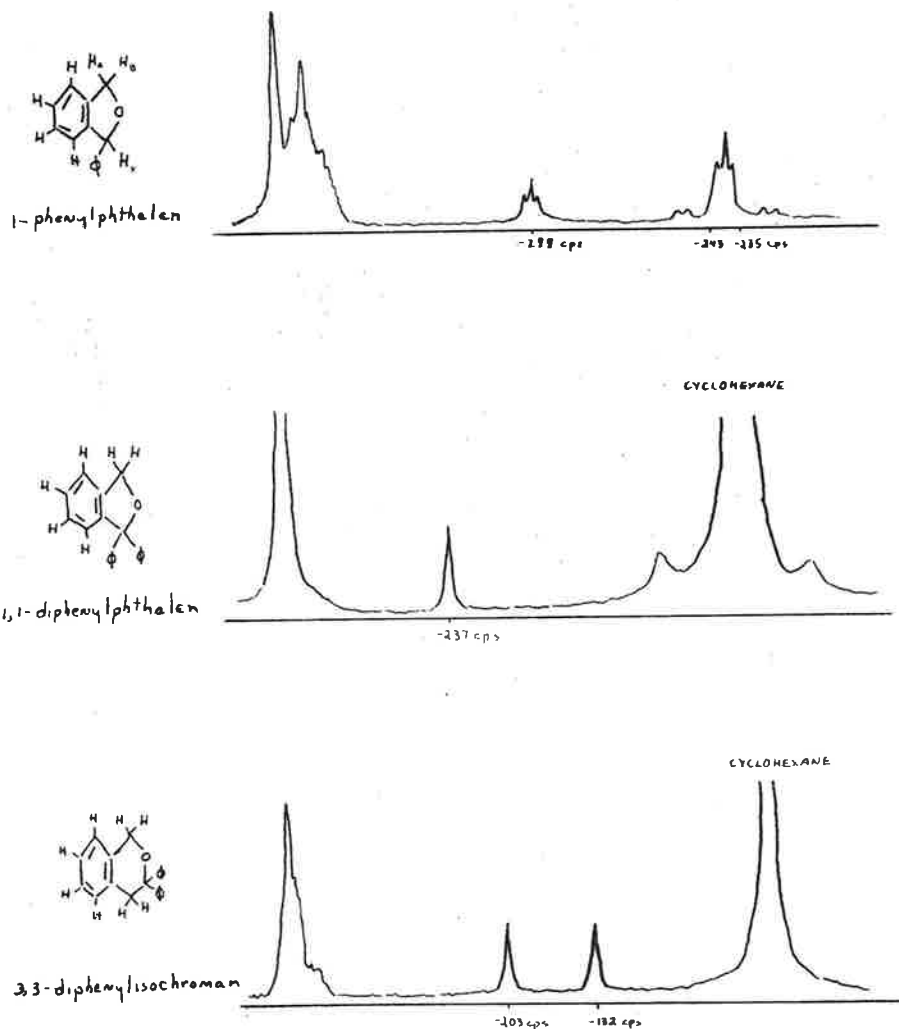
John E. Baxter

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Figure I



Chemical shifts are with respect to an external cyclohexane reference and are extrapolated to infinite dilution in carbon tetrachloride.



Stockholm, June 16, 1963

Cable address: Technology  
SF/MU

Dr. Bernard L. Shapiro  
Mellon Institute  
4400 Fifth Avenue

PITTSBURGH, Pa.  
U.S.A.

Dear Dr. Shapiro,

Moderately rapid chemical exchange rates by nuclear magnetic double resonance.

Nuclear magnetic resonance has successfully been applied in a number of studies on chemical exchange rates and the general principles of the method, which is based on the analysis of the line shapes in high resolution spectra, are well known. The upper limit imposed on the lifetime at any one site depends ultimately on the resolution of the spectrometer and on the line separations in the spectrum; longer lifetimes requiring smaller line separations.

\*) Evidently NMR can also be used as an analytical tool for measuring the relative amounts of the reacting species in slow reactions. Applied in this way the NMR method is not principally different from other physical and chemical methods and we shall not consider this type of application.

However, the time constants intrinsic in the NMR method are the inverse of the natural line widths ( $T_1$ ) rather than the inverse of the apparent line widths. With the innovation of the homo-nuclear double resonance method a technique that does not depend on the widths and the separations in the single resonance spectra has become feasible.

To be specific, let us consider a simple two component system in which a nucleus X is rapidly transferred back and forth between two nonequivalent sites A and B. Then it is intuitively evident that an enduring retrenchment of the magnetization in site B should, because of the exchange processes, lead to a reduction of the magnetization in site A. For example, a complete saturation of the signal B should reduce the intensity of the signal A. The new equilibrium value of the z-magnetization will depend on the lifetime of X in site A ( $\tau_A$ ), and on the spin lattice relaxation time ( $T_{1A}$ ) in site A.

If the signal B is saturated instantaneously the time dependence of the z-magnetization in site A ( $M_z^A$ ) may be calculated from the appropriate Bloch equation modified to include chemical exchange

$$\frac{dM_z^A}{dt} = \frac{M_0^A}{T_{1A}} - \frac{M_z^A}{\tau_{1A}} \quad (1)$$

where  $M_0^A$  is the initial z-magnetization of X in site A and

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A} \quad (2)$$

The solution of equation (1) reads

$$M_z^A = M_0^A \left( \frac{\tau_{1A}}{\tau_A} \cdot e^{-\frac{t}{\tau_{1A}}} + \frac{\tau_{1A}}{T_{1A}} \right) \quad (3)$$

From a logarithmic plot of the decay curve the time constant  $\tau_{1A}$  may be evaluated and the ratio  $\tau_{1A}/T_{1A}$  is given by the asymptotic value of  $M_z^A(t \rightarrow \infty)/M_0^A$ .

When a weak rf field is used to observe the NMR signal A the signal intensity is proportional to the value of  $M_z^A$ . If the inhomogeneity line widths are made large enough, one may - in a time which is short compared with  $\tau_{1A}$  - make several recordings of the signal A undisturbed by "wiggles", and thus by repeatedly studying the signal intensity one may follow the decay of  $M_z^A$ .

To illustrate the present method we have studied the exchange of the hydroxyl protons in an approximately equimolar mixture of *tert*-butylalcohol (A) and 2-hydroxyacetophenone (B) in a 50 % carbon disulphide solution. Two representative decay curves are displayed in Figs 1a and 1b.

From the mean values of  $\tau_{1A}$ ,  $\tau_{1B}$ , and the quotients  $\tau_{1A}/T_{1A}$  and  $\tau_{1B}/T_{1B}$  the values of  $\tau_A$ ,  $T_{1A}$ ,  $\tau_B$  and  $T_{1B}$  are obtained from equation (1) and are found to be

$$\begin{aligned} \tau_A &= 2.1 \text{ sec.} & \tau_B &= 2.3 \text{ sec.} \\ T_{1A} &= 3.7 \text{ sec.} & T_{1B} &= 4.2 \text{ sec.} \end{aligned}$$

The ratio  $\tau_A/\tau_B = 0.9$  compares favourable with the ratio 1.1 of the signal intensities  $A/B$  as obtained from the integration of the single resonance spectrum.

It should be noted, that the present method provides not only the lifetimes at the two sites but also the two spin-lattice relaxation times. This is interesting



since the recovery after saturation of signals from exchangeable nuclei depends in general on more than one time constant none of which equals the relaxation time at any one site. A more detailed discussion of the time dependence of the recoveries will be given later.

The present method may readily be generalized to cases when a nuclear spin is exchanged between several nonequivalent sites. We are presently engaged in such studies and from our preliminary results it appears that some interesting information on the mechanism of exchange may be obtained with this method.

We understand that this letter will for the coming century make us the exclusive claim-holders of this method and its conceivable applications!

Yours sincerely

*Sture Forsén*

Sture Forsén

*Ragnar A. Hoffman*

Ragnar A. Hoffman

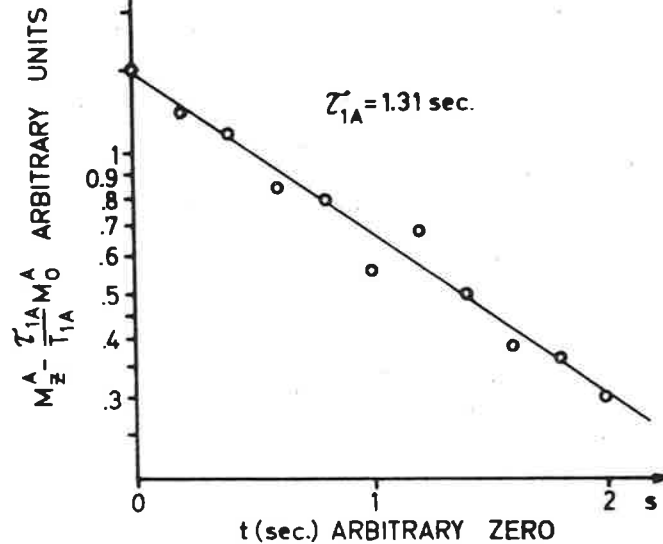


Fig 1a

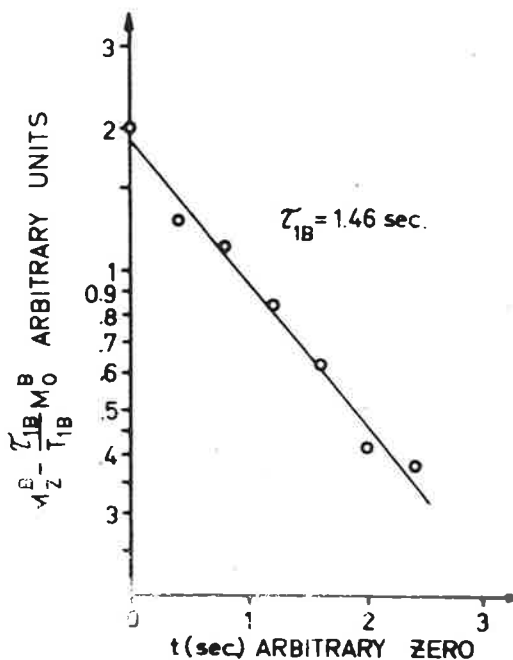


Fig 1b



Fysiska Institutionen, Uppsala, Sweden. 8 June 1963

FYSISKA INSTITUTIONEN  
UPSALA

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

Dear Dr. Shapiro,  
The story of 3-bromo-2-thiophenealdehyde once again, or:

"The case for TSI-ing thrice."

In a letter submitted to the preceding issue of these newsletters we described a new method for tracing the level arrangements in high-resolution NMR-spectra. The general idea of this method is to produce transitory changes in the level populations through transitory selective irradiation (TSI) of selected lines. These changes are then detected by the intensity changes in those spectral lines which have an energy level in common with the irradiated ones.

A nice feature of this method is that it may readily be applied to systems with degenerate transitions, and as an example we considered the case of a three-spin system in which one coupling constant is negligibly small, where the successive application of three TSI:s could be used to determine the relative signs of the two remaining coupling constants. In our initial experiment we applied this technique to the side-chain spectrum of trans-cinnamic aldehyde, where the largeness of the two observable coupling constants ( 7,3 cps and 16,0 cps ) give us a favourable latitude in the choice of the experimental parameters. The difficulty in this type of experiment is to choose the frequency pre-settings of the irradiating fields large enough not to produce tickling and small enough to prevent the time elapsed between the TSI:s and their detection to surmount too large a fraction of the relaxation times.

However the technique was developed to attack less trivial problems, such as the signs of the long-range aldehyde couplings, and if samples with sufficiently long relaxation times can be prepared, the technique may readily be applied to such systems with much smaller couplings. Thus we have performed this type of experiment on the same compound ( 3-bromo-2-thiophenealdehyde ) as that investigated with the ingenious double-tickling technique by the British NPL-group. We think that it might be of interest to MELLON readers to see how these two alternative methods work on the same problem.

Our sample was prepared as a 20 % solution in  $CS_2$  and dissolved oxygen was removed by bubbling argon through the sample before sealing. The relaxation times for the ring protons in our sample were of the order of 20 seconds and for the aldehyde proton of about 50 seconds.

The single resonance spectrum of the 3-bromo-2-thiophenealdehyde is shown in Fig.1. In the terminology of our earlier letter the lines are labelled (from low to high fields) A1,A2 in the aldehyde doublet; B1,B2,B3,B4 in the 5-hydrogen quartet and C1,C2 in the 4-hydrogen doublet. In our experiment the lines B1,A2 and C2 are irradiated immediately before the recording of line B4.

Fig.2a shows the effect of a TSI at A2, Fig.2b the effect of TSI at C2 and Fig 2c the combined effect of TSI at A2 and C2 (only the quartet of the central, B-hydrogen band is displayed in Fig.2)

The crucial evidence for equal signs of the two couplings is that the negative peak for line B4 in fig.2d, which shows the combined effect of TSI at B1,A2 and C2, goes deeper than in Fig.2c, where only A2 and C2 were subjected to TSI. As is evident from Fig.2 of our earlier letter, this result is consistent only with the energy level arrangement corresponding to equal signs of the couplings.

Since the timing of the successive irradiations is of importance in the present type of experiments, we have shown schematically in Fig.3 the time-relations of the irradiations and peak height observations. Irradiation of the lines A1 and C1 was avoided by turning on the modulation fields only after these lines had passed the resonance region pertaining to the modulation frequencies used. We produced the TSI through "fast adiabatic" passage by a field-sweep method, but owing to relaxation losses (and possibly insufficient strength of the irradiation field so as not to produce tickling) the intensity reductions in figs 2a-d do not reach the theoretically possible values (intensities 0,0,-1 and -2 respectively). The fact that the line B2 is irradiated while the line B4 is still on resonance, does not affect the result, since by then there is no connection between the lines B1 and B4.

The present study is one in a series of sign determinations for long-range couplings that we have been engaged in for some time. We have earlier obtained the signs of the long-range aldehyde couplings  $J_{CHO-4}$  and  $J_{CHO-5}$  in the 2- and 3-furanaldehydes. Only  $J_{CHO-4}$  in 3-furanaldehyde was found to be negative (on the reasonable assumption that  $J_{45}$  is positive; cf MELLONMR 54-3). A limited supply of preprints <sup>45</sup> of this work is available on request to the undersigned R.A.H. An earlier work of this series confirmed the opposite signs of the couplings in the fragments  $CH_3-C=CH$  and  $CH_3-C=C-CH_3$

in tiglaldehyde. This was done by means of a TSI experiment and the full report on this work will be submitted for publication in Acta Chem.Scand.

Yours sincerely

*Bo Gestblom Solo Gronowitz Ragnar A. Hoffman*

Sture Forsgren Bo Gestblom Solo Gronowitz Ragnar A. Hoffman

ORGANISCH CHEMISCH LABORATORIUM, RIJKSUNIVERSITEIT LEIDEN

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Afdeling voor  
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Telefoon 31106  
Prof. dr L. J. Oosterhoff

nr.:

onderwerp:

Dr. M.L. Shapiro,  
Bellon Institute,  
4400 Fifth Avenue,  
PITTSBURGH 13, Pennsylvania  
U.S.A.

Leiden, June 12, 1963

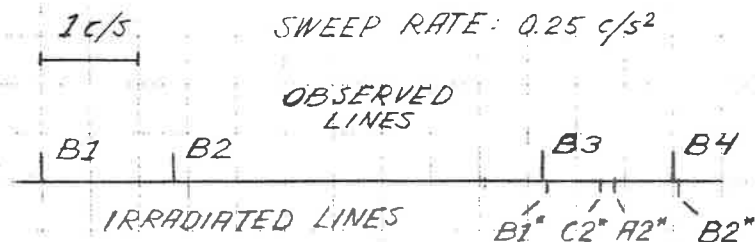
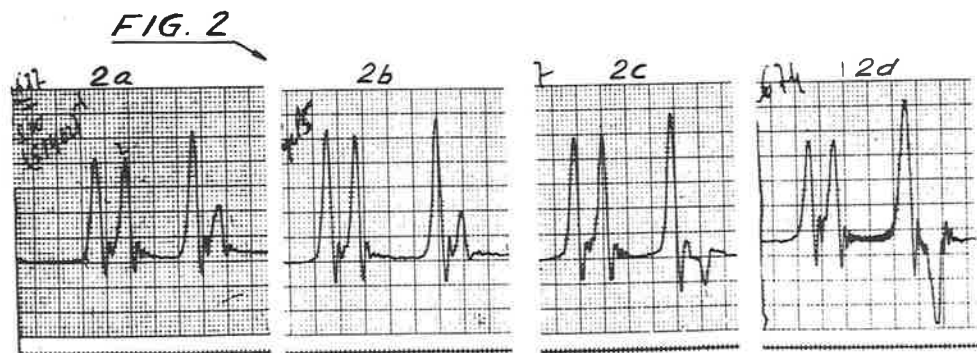
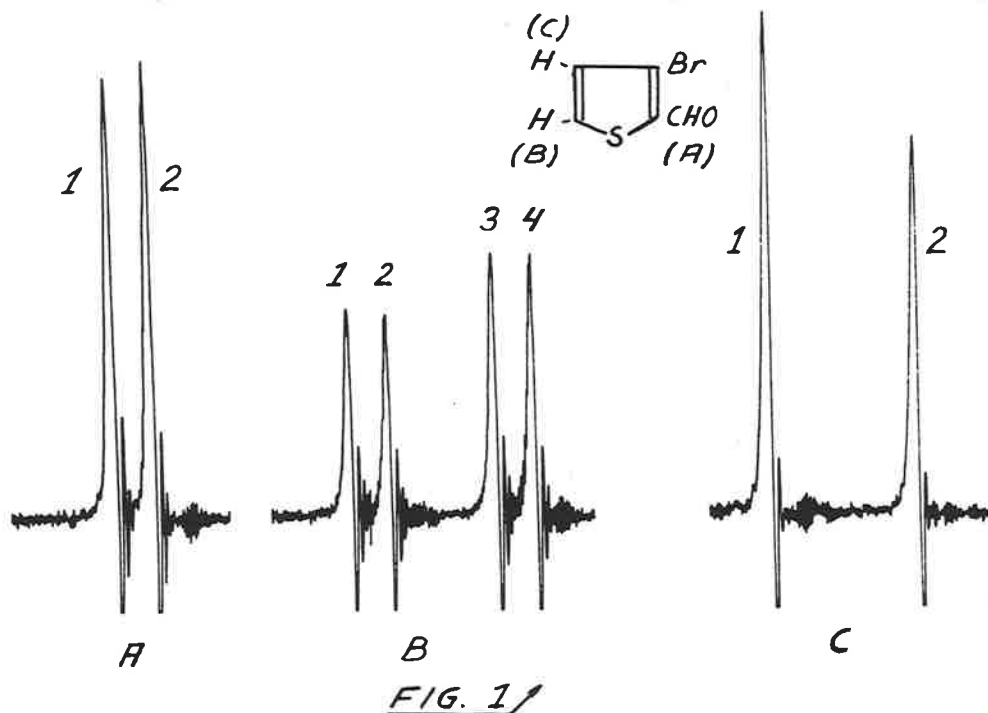


FIG. 3

Dear Dr. Shapiro,

In our NMR-work it becomes increasingly necessary to analyze rather complicated spectra. Leiden University has an electronic computer, the X-1, of the Electrologica Cy., The Hague. Programs can be written in the computer language ALGOL. The programs that NMR-workers frequently place at the disposal of colleagues in this field are of no use for us since they use a different code not suitable for our machine.

Before writing a series of NMR-programs in ALGOL we would like to know whether others have already programs in ALGOL, or FORTRAN which can also be applied to the X-1, or experience in writing these programs and if it would be possible to place their experience or these programs at our disposal.

Especially in Germany ALGOL and FORTRAN seem to be widely used. Therefore an exchange of programs might be feasible and could be quite profitable.

Could it be possible to inquire about possibilities in this field via BELLOM?

Thanking you in advance,

Yours faithfully,

*Th. J. Skuur*  
(Th. J. Skuur)

*R. Kaptein*  
(R. Kaptein)

Dr. H. Fritz c/o  
J. R. GEIGY S. A.



Pharmaceutical Department

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue

Pittsburgh 13, Pa.  
USA

Telephone: 52 78 30  
Telegrams: Geigy Basle  
Teletype No 62 355  
Your reference:  
Our reference:

Basle 16 (Switzerland) May 15, 1963

(Please mention in your reply and on the envelope)

Dear Dr. Shapiro:

As a first contribution I would like to report a case where NMR-spectroscopy proved to be an extremely simple method to distinguish between two isomers. In the course of synthetic investigations of dibenzazepine derivatives carried out by Dr. W. Schindler of our company, two isomeric compounds of mp = 207° C and mp = 239° C were obtained, one of which should have structure I, the other structure II.

An assignment could easily be given by inspection of the NMR-spectra of the compounds (taken on an A-60 as 10 % solutions in CF<sub>3</sub>COOH, internal standard TMS).

In the spectra of both isomers (spectra a and b, only aromatic part is shown) a signal for one proton is found at low field, which has to be assigned to the proton in ortho position to the carbonyl group.

For the compound of mp = 207° C (spectrum a) this signal is a quartet at  $\tau = 2.05$  with two coupling constants  $J_1 = 8.5$  cps and  $J_2 = 2$  cps, which indicates that structure I has to be assigned to this isomer, since the proton H<sub>X</sub> is coupling with the protons ortho and meta to itself. The signals of the other protons of the ABCX system are partially overlapped by the resonances of the second benzene ring.

The isomer with mp = 239° C (spectrum b) shows a doublet for H<sub>X</sub> at  $\tau = 2.11$  with  $J = 8.5$  cps, indicating structure II for this compound. The signals for the protons H<sub>A</sub> and H<sub>B</sub> of the ABX system can also be assigned in this case:

$\tau_A = 3.10$ ,  $\tau_B = 2.82$ ,  $J_{AX} = 8.5$  cps,  $J_{AB} = 2.0$  cps,  $J_{BX} = 0$  cps

- 2 -

For comparison, the spectrum of III was taken (spectrum c); as expected it shows the same splitting for H<sub>X</sub> as the spectrum of I.

In the same manner structures could be assigned to the isomeric pairs IV, V and VI, VII.

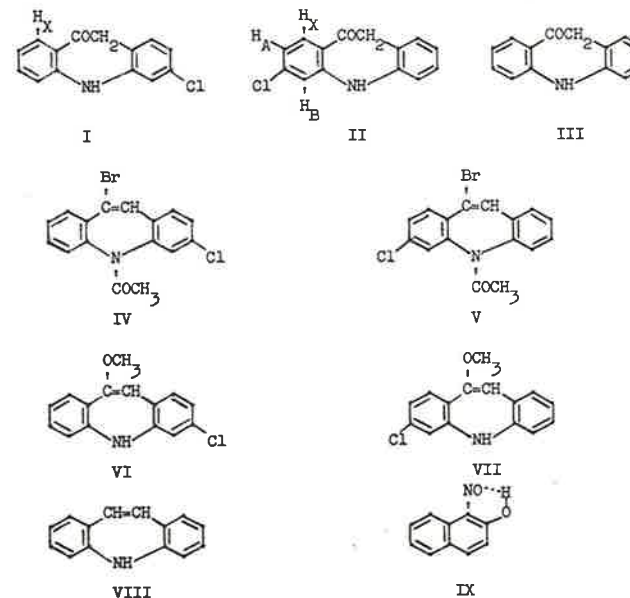
Here the groups  $\begin{matrix} \text{Br} \\ | \\ -\text{C}- \end{matrix}$  and  $\begin{matrix} \text{OCH}_3 \\ | \\ -\text{C}- \end{matrix}$  cause a low field shift of the ortho-proton, while for VIII no signal was observed at low field.

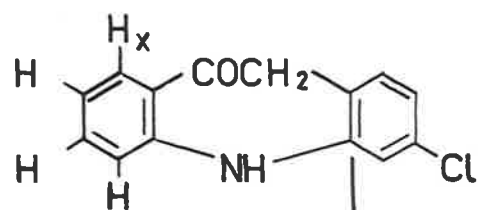
In addition I would like to report an observation of an extremely low field signal (out of the normal 1000 cps range). The resonance for the -OH proton of IX ( $\alpha$ -Nitroso- $\beta$ -hydroxynaphthalene) appears as a sharp singlet at  $\tau = -7.47$  (10 % solution in CDCl<sub>3</sub>).

Thank you very much for sending us the MELLONMR-letters, they really are very useful to us.

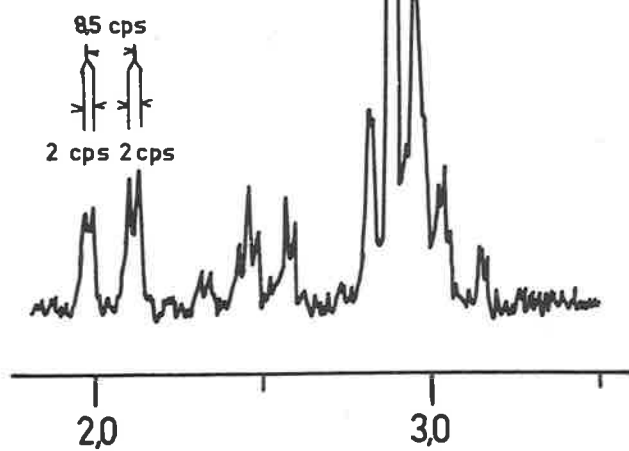
Yours sincerely,

*André Fritz*

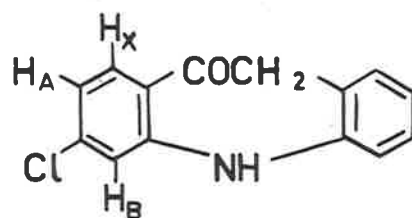




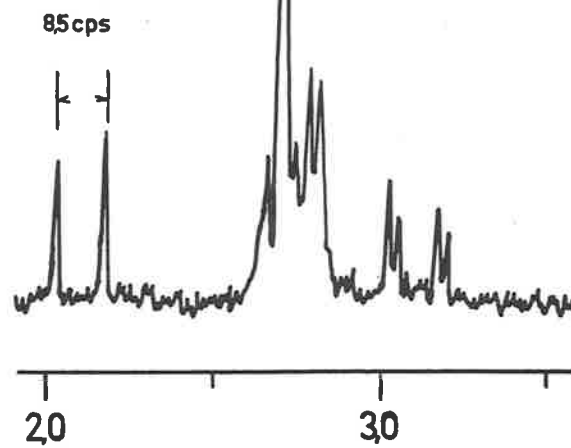
I mp. 207°C



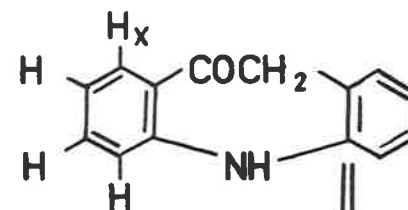
a.



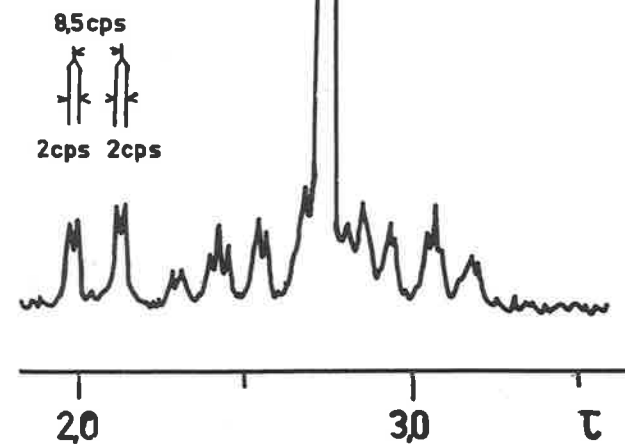
II mp. 239°C



b.



III



c.

PROFESSOR DR. F. BOHLMANN  
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Berlin-Charlottenburg 2, den 18. 6. 63  
Straße des 17. Juni Nr. 115  
Fernruf: 32 51 81/252

Dr. B. L. Shapiro  
Mellon Institute

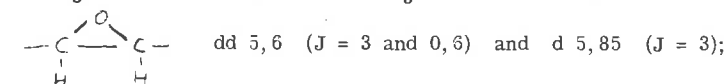
4400, Fifth Avenue  
Pittsburgh 13, Penn. USA

Dear Dr. Shapiro,

Thank you very much for the available Mellon letters.

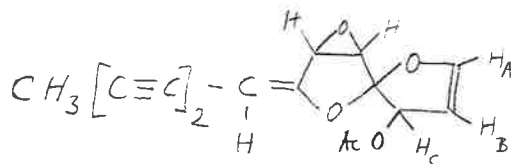
To-day I wish to represent you an example of structure determination by NMR. We have isolated a small sample of an crystalline compound from the roots of Chrysanthemum L. together with compounds from which we have already established the structures. The formula of the new compound turns out to be  $C_{15}H_{12}O_5$ . From UV a diyneene-enoether is recognizable and the IR shows the presence of an acetate-group. The NMR shows the following signals:

$-OCOCH_3$  s 7,95;  $\equiv C-CH_3$  d 8,0 ( $J = 1,3$ )



tr 4,3 ( $J = 2$ );  $-O-CH=CH-$  dd 4,75 ( $J = 3$  and 2) and dd 3,4 ( $J = 3$  and 2);  $\equiv C-CH = 4,8$ .

In connection with chemical investigations the only possible structure is:

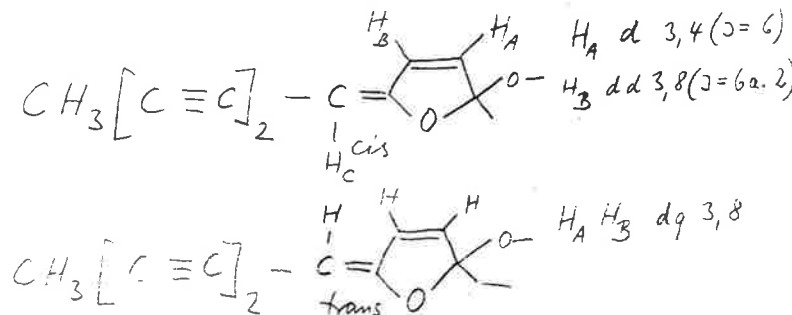


PROFESSOR DR. F. BOHLMANN  
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- 2 -

The interesting point is the chemical shift of the ethylenoxyde protons. The situation of the dihydrofuran protons is common in this field ( $J_{AC} = J_{BC} > J_{AB}$ ). The third olefinic proton gives an unsolved multiplett (coupling with the methylgroup ( $J = 1,3$ ) and the allylic proton ( $J = 0,6$ )). Furtheron I wish to represent a problem which is a partical mystery for us. We have four pairs of cis-trans isomeres of the following type:



In the trans series the protons A and B show nearly the same chemical shifts while in the cis series the proton A is shifted to lower fields. The only possible explanation I can see would be the different effect of the unsaturated electron attracting side chains in the cis and trans series, but perhaps some of the Mellon NMR readers can give a better explanation.

Sincerely yours

F. Bohlmann

June 21, 1963

An empirical alternative to the Karplus relations

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

Dear Barry,

The dependence of vicinal proton coupling constants in ethane fragments on dihedral angles (1) has been formulated by Karplus (2) in the two relations

$$\begin{aligned} J &= 8.5 \cos^2 \varphi - 0.28 & \text{for } 0^\circ \leq \varphi \leq 90^\circ \\ J &= 9.5 \cos^2 \varphi - 0.28 & \text{for } 90^\circ \leq \varphi \leq 180^\circ \end{aligned} \quad (1)$$

Although in some cases (3,4) the agreement between observed coupling constants and those calculated from Eq. (1) appeared to be reasonable, it is now generally recognized (5-8) that the magnitude of the coupling constant depends not only on the dihedral angle but also on the properties of substituents on the two carbon atoms. As a result several "Karplus type" equations have appeared in the recent literature (9-11), each applicable to a different system.

In an effort to reconcile the discrepancies which have thus arisen, we have tested a series of empirical equations relating  $J$  and  $\varphi$ , in which all coefficients were determined from coupling constants measured in rigid compounds, so that  $\varphi$  is known a priori with reasonable certainty, and, in which the dependence of  $J$  on parameters other than  $\varphi$  was explicitly taken into account. The asymmetry of  $J$  about  $\varphi = 90^\circ$  suggests that such equations are best expressed as cosine expansions of  $J$  and one might expect that deviations from this relation would arise from the variation of charge density on the two protons. However, sufficient data are not on hand to formulate a reliable and universally applicable scale of charge densities. The most readily available related parameter is the electronegativity  $\epsilon$  of neighboring substituents. Relations between  $J$  and  $\epsilon$  have been given by Glick and Bothner-By (5) for substituted ethanes and by Williamson (6) for the hexachlorobicyclo (2,2,1) heptene system. Comparison of these two relations and scrutiny of other available data reveals two

- 2 -

interesting points: (1) In compounds containing more than one electronegative substituent the effect on the coupling constant is less than the sum of the separate contributions, and (2) The effect of a given electronegative substituent is greater by a factor of roughly four in the bicycloheptene derivatives in which the protons are eclipsed, than in the substituted ethanes, where they are staggered. The first finding is not surprising and parallels the non-additivity of substituent effects on chemical shifts (12). The second indicates that the magnitude of the electronegativity contribution to the coupling constant depends on the angle of rotation about the C - C bond. A rather simple form of this angular dependence is suggested by the fact that the slopes of  $J$  vs  $\epsilon$  are approximately the same for  $\varphi = 0^\circ$  and  $\varphi = 120^\circ$  and four times the slope of  $J_{\text{average}}$  for  $\varphi = 60^\circ$  and  $\varphi = 180^\circ$  (5,6).

All of these findings can be expressed by the relation:

$$J = 1.8 - 2.5 \cos \varphi + 11.3 \cos^2 \varphi - (0.4 + 1.2 \cos^2 \frac{3}{2} \varphi) \sum_{i=1}^4 \frac{1}{k_i} \Delta \epsilon_i \quad (2)$$

where  $\Delta \epsilon_i = \epsilon_i - 2.1$ , the difference between the electronegativities of the  $i$ th substituent and that of a hydrogen atom and  $k_i$  is an integer,  $k_i = 1, 2, 3, 4$  for the four possible substituents, taken in order of decreasing electronegativity. Obviously, alternative ways of expressing the decay of the electronegativity effect with increasing number of substituents are possible, but the present is simple and seems to give a satisfactory approximation.

The coefficients can be obtained from three measured values of  $J$  for known dihedral angles:  $J_{60^\circ} = 3.0 \pm 0.1$  cps in monobromoadamantane,  $J_{90^\circ} = 9.3$  and  $J_{120^\circ} = 4.6$  for the cyano-derivative of hexachlorobicycloheptene. Electronegativity corrections are approximately + 0.4 for the bromoadamantane and + 1.3 for the bicycloheptene systems respectively, using values on the Cavanaugh-Dailey scale (13). The corrected "ethane" coupling constants are then  $J_{90^\circ} = 10.6$ ,  $J_{60^\circ} = 3.4$  and  $J_{120^\circ} = 5.9$  and the coefficients can be evaluated by solving the three simultaneous equations for  $\sum \Delta \epsilon_i = 0$ .

A comparison between coupling constants calculated from Eq. (2) and those observed in compounds with reasonably well known dihedral angles is given in Table I. Considering the crudeness of the approximation and the uncertainties inherent in the electronegativity scale the agreement can be considered satisfactory, but a considerably larger compilation of experimental data is needed to test the generality of Eq. (2).

In the absence of such information, it is of some interest to compare the predictions of Eq. (2) with those based on Karplus type

equations for non-rigid systems. A comparison of this kind is made in Table II, where  $\phi_K$  and  $\phi_2$  refer to the angles inferred from the pertinent Karplus type equation and Eq. (2) and  $J_{calc}$  to the value obtained from the latter. It is seen that the results of the two calculations differ somewhat but rarely enough to require a radical change in the postulated conformation.

The overall uncertainty in the assignment of dihedral angles from measured coupling constants can be estimated from the combined errors in  $\Delta E_i$  and the  $1/k_i$  approximation, together with the probable experimental error  $i$  of at least  $\pm 0.1$  cps and is of the order of  $5^\circ - 10^\circ$  or less. Within these limits Eq. (2) yields results consistent with those obtained from other calculations in a fairly wide range of systems.

Sincerely yours,

Oleg Jardetzky  
Oleg Jardetzky

1. R.U. Lemieux, R.K. Kullnig, H.G. Bernstein and W.G. Schneider  
J. Am. Chem. Soc. 80, 6098 (1958)
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Table I

Calculated and observed coupling constants for freely rotating and rigid compounds.

Compound	Angle	$J_{calc}$	$J_{obs}$	Ref.
Ethane	Av.	7.5	-	
Ethanol		6.98	6.97	(5)
Ethyl ether		6.98	6.96	"
Ethyl carbonate		6.98	6.96	"
Ethyl benzoate		6.98	7.00	"
Ethyl sulfate		6.98	6.94	"
Ethyl chloride		7.06	7.07	"
Ethyl bromide		7.25	7.25	"
Ethyl iodide		7.40	7.16	"
Ethyl benzene		7.40	7.37	"
Propionitrile		7.34	7.24	"
Propionic acid		7.30	7.41	"
Ethyl mercaptan		7.28	7.27	"
Isopropanol		6.73	6.05	"
Isopropyl chloride		6.81	6.31	"
Isopropyl bromide		7.00	6.40	"
Isopropyl iodide		7.15	6.42	"
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> Si		7.70	7.9	(14)
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> S		7.38	7.42	(14)
Hexachlorobicyclo [2.2.1 heptene]-R				
-COOH	0°	9.1	8.5	(6)
	120°	4.43	4.4	"
-C <sub>6</sub> H <sub>5</sub>	0°	8.9	8.9	"
	120°	4.2	4.2	"
-Cl	0°	8.09	8.0	"
	120°	3.39	3.2	"
-CH	0°	7.8	7.4	"
	120°	3.1	2.4	"
-OAC	0°	7.2	7.6	"
	120°	2.5	2.5	"
Camphanediol				(3)
2-exp-3-exo	0°	7.24	7.7	"
2-endo-3-endo	0°	7.24	8.9	"
2-exo-3-endo	120°	2.54	2.3	"
2-endo-3-exo	120°	2.54	2.2	"
	44°	4.50	4.0	"
	79°	0.31	0.4	"
		0.31	0	"



Table II

Coupling constants and dihedral angles from Eq. (2) compared to other calculations.

Compound	$\varphi$ (1)	$J_{\text{obs}}$	$\varphi$ (2)	$J_{\text{calc}}$	Ref.
Transhydroxyproline	31.25 151.25 69 51 69 51	7.66 10.44 1.41 4.31 1.22 4.09	25 145 72 48 72 48	7.41 10.25 1.30 4.38 1.20 4.28	(11)
Allo-hydroxy-L-proline	2 122 49 71 48 72	10.48 3.48 4.71 2.09 4.57 0.94	10 130 50 70 45 75	8.8 3.3 4.15 1.56 4.50 0.88	(11)
2- $\alpha$ -Acetoxycholestane-3-one	34 154	6.6 13.1	36 156	6.2 12.3	(9) "
2- $\beta$ -Acetoxycholestane-3-one	13 133	7.4 9.5	25 145	7.0 9.5	" "
4- $\alpha$ -Acetoxycholestane-3-one	148	11.6	155	11.8	"
4- $\beta$ -Acetoxycholestane-3-one	47	4.7	47	4.5	"
3- $\beta$ -Acetoxycholestane-2-one	38 158	6.2 13.0	36 156	6.2 12.3	" "
3- $\alpha$ -Acetoxycholestane-2-one	60 60	2.5 2.5	60 60	2.6 2.6	" "
2-Deoxy- $\alpha$ -glucose	48 72	3.8 0.7	50 70	4.0 1.5	(10) "
2-Deoxy- $\beta$ -glucose	181 61	9.7 2.0	140 100	9.9 1.9	" "
$\alpha$ -glucose	58	2.4	60	2.6	"
$\beta$ -glucose	151	7.5	140	7.9	"

Table II-continued

Compound	(1)	$J_{\text{obs}}$	(2)	$J_{\text{calc}}$	Ref.
glucose-borate-complex	48	3.9	50	4.0	(10)
$\alpha$ -Mannose	68(110)	1.2	70	1.5	"
$\beta$ -Mannose	76	0.5	76	0.67	"
Dibfomoethane	60 180	3.4 $\pm$ 1 15.3 $\pm$ 1	60 180	3.04 15.24	(8) "
Dichloroethane	60 180	12 $\pm$ 1.5 18 $\pm$ 4	60 180	2.98 15.18	" "
Trichloroethane	60 180	3.0 $\pm$ 1.5 10.5 $\pm$ 3	60 180	2.73 14.93	" "
Tetrachloroethane	60 180	2.5 $\pm$ 1 14 $\pm$ 7	60 180	2.66 14.86	" "

Department of  
HEALTH, EDUCATION, AND WELFARE  
Food and Drug Administration  
Washington 25, D. C.

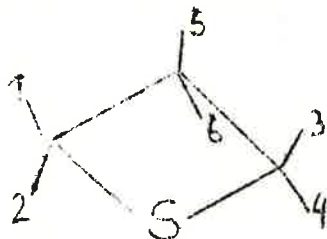
June 21, 1963

Dr. B. L. Shapiro  
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Dear Barry:

My contribution to MELLONMR seems to be about due again. Here it is. It deals with a partial analysis of the 60 mc spectrum of trimethylene sulfide (see p. 3). The analysis was made possible by the fact that trimethylene sulfide has  $C_{2v}$  symmetry; by the use of the moment method; and by the knowledge of the far less complex spectrum of trimethylene oxide.

The spectrum of a  $C_{2v}$  molecule, bicycloheptadiene, which except for the bridge protons is that of an  $A_2B_4$  system, has been analyzed by Mortimer (J. Mol. Spectr., 3, 528 (1959)), who took advantage of its symmetry properties. The coupling scheme in the present class, which includes fourmembered rings like trimethylene oxide and sulfide, cyclobutanone and 1,1-dibromocyclobutane, is different from that in bicycloheptadiene, and less simplification of the secular equations can be achieved. Another reason for this is that, to put it loosely, coupling is tighter, as it were.



$$J'_{\alpha\beta} \equiv J_{\text{cis}}, \text{ where } \alpha\beta = 15, 26, 35, 46$$

$$J'_{\text{gem}} \equiv J'_{\alpha\alpha}, \text{ where } \alpha\alpha = 12, 34$$

$$J''_{\alpha\beta} \equiv J_{\text{trans}}, \text{ where } \alpha\beta = 16, 25, 36, 45$$

$$J''_{\text{gem}} \equiv J''_{\beta\beta}, \text{ where } \beta\beta = 56$$

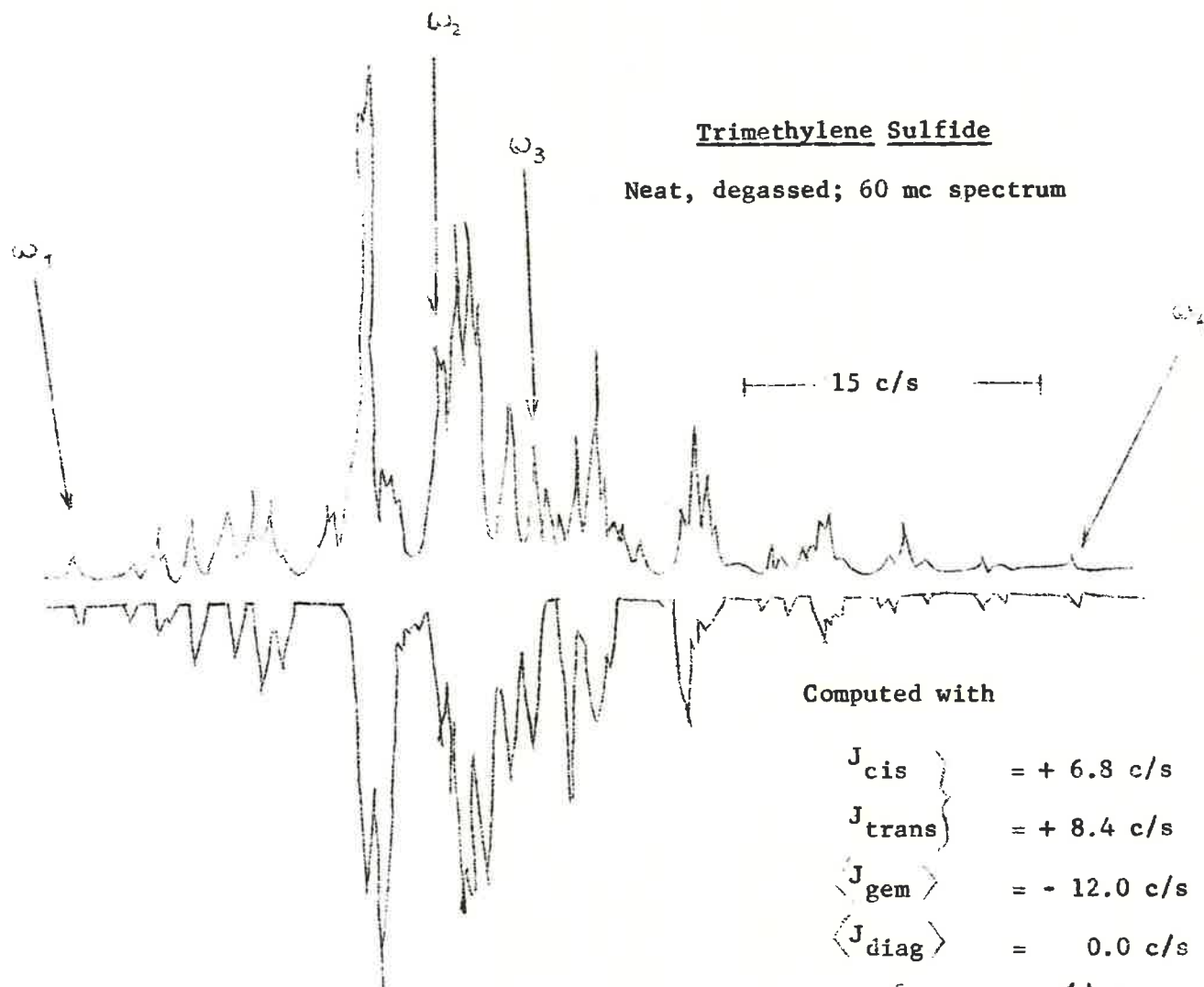
There is only one shift,  $\delta_{\alpha\beta} \equiv \delta$ .

$$J'_{\text{diag}} \equiv J''_{\alpha\alpha}, \text{ where } \alpha\alpha = 14, 23$$

$$J''_{\text{diag}} \equiv J'_{\alpha\alpha}, \text{ where } \alpha\alpha = 13, 24$$

Trimethylene Sulfide

Neat, degassed; 60 mc spectrum



Computed with

$J_{\text{cis}}$	}	= + 6.8 c/s
$J_{\text{trans}}$		
$J_{\text{gem}}$	= - 12.0 c/s	
$J_{\text{diag}}$	= 0.0 c/s	
$\delta$	= 16.2 c/s	

Fortunately the energy levels for  $F_z = \pm 3$  and  $\pm 2$  of the  $A_1$ -species can be found explicitly, and one gets for the corresponding four lines  $\omega_1, \omega_2, \omega_3$ , and  $\omega_4$ :

$$J_{\text{cis}} + J_{\text{trans}} = (\omega_2 - \omega_1) + (\omega_4 - \omega_3);$$

$$2\delta^2 = (\omega_3 - \omega_1)^2 + (\omega_4 - \omega_2)^2 - 9(J_{\text{cis}} + J_{\text{trans}})^2.$$

The second moment  $\langle \omega^2 \rangle$  is related to  $\delta$  by  $2\delta^2 = 9\langle \omega^2 \rangle$ .

For trimethylene oxide,  $J_{\text{cis}} + J_{\text{trans}} \approx 14$  c/s ( $\delta \approx 2$  ppm).

With this information and the aid of the calculable intensities of the lines  $\omega_1 \dots \omega_4$  a reasonable assignment of the latter could be made. The entire spectrum is very sensitive to  $J_{\text{cis}} + J_{\text{trans}}$  and  $\delta$ , as machine computations with Frequent III have shown. As seen in the figure, the match between computed and observed spectra is quite good, though not perfect. The values for the  $J$ 's between isochronous spins are tentative guesses. A further check on the quality of the values for  $\delta$  and  $J_{\text{cis}} + J_{\text{trans}}$  was obtained by matching a spectrum of trimethylene sulfide<sup>cis</sup> in benzene:  $\delta$  is now 23.1 c/s, but no change in  $J_{\text{cis}} + J_{\text{trans}}$  was necessary for a good fit.

I hope to refine this analysis somewhat, perhaps with the aid of better and/or other spectra of this kind and an iterative computer program.

Best regards and good wishes.

Sincerely,

*Ernest.*

Ernest Lustig