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Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R

Primas
Mailed:
September 28, 1962

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October 25, 1962

Collectio per mensem sine nimio apparatu privatarum epistolarum ex officinis NMR missa. Commentarii hic scripti solum ad legendum mittuntur. Aliis locis scribendo proferre prohibitum est nisi solum is qui primum commentarios scripsit ipse sua manu consentit, et commentarii sic prolati necesse est ut privati indicentur.



RESEARCH LABORATORIES


GENERAL MOTORS CORPORATION

August 7, 1962

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

Dear Dr. Shapiro:

Since the appearance of the article by Diehl (Helv. Chim Acta 44, 829 (1961)) there has been considerable interest in the additivity of substituent effects in the high resolution PMR of substituted benzenes. Diehl's work is also described in MELLONMR 29. Brey and Lawson have presented results on substituted benzenes in MELLONMR 36.

Diehl shows that the effect of a substituent on ring proton resonances can be described in terms of constants characteristic of the substituent. These constants - S_o , S_m , and S_p - represent the effect of the substituent on the chemical shift of the protons ortho, meta, or para to it. For monosubstituted benzenes the S 's are just the shifts of the ring protons with respect to that of pure benzene. In para disubstituted benzene , the chemical

shift (wrt benzene) of the proton ortho to X is the sum of the S_o of X and the S_m of Y, thus:

$$\delta_{o,X} = S_{o,X} + S_{m,Y}. \quad (1)$$

Similar relations for other types of substitution can readily be seen. Diehl has shown that in ortho substituted benzenes a different substituent effect exists. The results of Brey and Lawson differ from those of Diehl in several ways which they point out.

This present letter describes work at General Motors Research on para disubstituted benzenes which has been in progress for over two years (off and on). Para disubstituted benzenes were chosen because of the ease of spectral analysis. (The spectrum is a good approximation of that of an AB compound).

The samples were usually run in CCl_4 (5 - 10%) with internal TMS as standard. Good agreement with the line positions of Diehl was found - except that a small correction of five parts per hundred million (pphm) was needed due to differences in experimental methods. Because of the good agreement, it was possible to use Diehl's S values as a basis from which additional values of S_o and S_m could be found using my corrected results and equation (1).

GENERAL MOTORS TECHNICAL CENTER

12 MILE AND MOUND ROADS

WARREN, MICHIGAN

The enclosed table (which is from a private internal report) summarizes S_0 and S_m values (in pphm) as found by Diehl, Brey and Lawson (B & L), and the present work. In some cases, it was necessary in the present work to use polar solvents. S values found using data taken using polar solvents are followed by an (*). In parentheses is given the number of compounds used to derive each set of S_0 and S_m values. It can be seen that good agreement is obtained between the present work and that of Diehl. The biggest deviation occurs for OH (6 pphm) for which polar solvents were used.

Also included in the table are S values derived from the monosubstituted benzene data (50% in cyclohexane) of Corio and Dailey (C & D) (JACS, 78, 3043 (1956)), and that of Page and Jakobsen (MELLONMR 39 in $CDCl_3$ wrt TMS). Using the present work as a basis it was also possible to derive further S values from the τ -Table of Tiers (Minn. Mining and Mfg. Co., St. Paul, Minn, 1958) in (CCl_4 wrt TMS) and from the Varian catalog (Varian Associates, Palo Alto, Calif., 1962) in $CDCl_3$ wrt TMS). These derived values are also included in the table for comparison. It can be seen that the largest deviations occur for the work using polar solvents and for that on monosubstituted benzenes at high concentrations in cyclohexane. Actually, however, the polar solvent data are quite acceptable for estimates of line positions.

The present work has continued beyond the stage reported here. We hope to publish in the near future more detailed results, including S values for an additional twenty substituents.

Yours very truly,

George W. Smith

George W. Smith
Physics Department

f

Encs. (2 sheets)

TABLE VI

 S_o and S_m From Various Workers

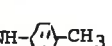
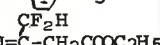


















Subst.	S _o (pphm)							S _m (pphm)						
	Present Work	Diehl	from Tiers	from Varian*	B&L	from P&Ja*	C&D ^a	Present Work	Diehl	from Tiers	from Varian*	B&L	C&D ^a	
F	23 (5)	25	18 (1)	30 (2)			40	4	1	1	9		13	
cℓ	- 7 (9)	- 5	-7 (3), -3 ^a	0 (4)	-5		0	6	6	6	11	6	0	
Br	-18 (8)	-22	-24 (2), -4 ^a	-10 (2)	-11		0	13	11	8	17	8	0	
I	-38 (5)	-41	-39 (1)	-33 (1)	-22		-30	23	22	20	21	19	17	
NO ₂	-96 (6)	-98	-96 (2)	-91 (1)	-93		-97	-18	-21	-23	-13	-25	-30	
NH ₂ .Hcℓ	-10 (2) *							-17 *						
-N=NBF ₄	-145 * or -125 *							-47 * or -67 *						
NH ₂	72 (4)	68		69 (1)	78		77	24	22		34	17	13	
NHCH ₃							80						30	
N(CH ₃) ₂	80 (1) *		80 (1)	82 (2)			50	21 *		20	22		20	
	-16 (1) *							2 *						
				-53 (1)							-12			
NHCOCH ₃				-22 (2)							4			
OH	56 (4) *	50			58		37	12 *	16			14	37	
OCH ₃	44 (5)	42		46 (4)	50		23	12	10		9	3	23	
OC ₂ H ₅	45 (3)		43 (1)	46 (1)				15		13	23			
OCOCH ₃			21 (1)							2				
OSO ₂ -  -CH ₃	25 (1)							6						
SO ₂ F			-76 (1)							-32				
SO ₂ cℓ	-80 (1)		-85 (1)					-33		-27				
SO ₂ -  -CH ₃	-65 (1) *							-15 *						
SO ₂ NH ₂	-60 (1) *					-69		-17 *						
SO ₂ NHCH ₃						-63								
SO ₂ -N  -NSO ₂ -  -CH ₃				-45 (1)							-15			
SO ₃ C _n H _{2n+1}	-62 (4)							-27						
SO ₃ -  -cℓ	-58 (1)							-24						
SO ₃ Na	-27 * to -55 (2) *							5 * to -31 *						
SH				~13 (1)							~1			
COOH	-75 (1) *			-88 (1)			-63	-20 *			-10		-10	
COOCH ₃	-73 (1) *	-74	-80 (1)				-93	- 9 *	-10	- 6			-20	
COOC ₄ H ₉	-79 (1)							-21						
COOC ₂ H ₄ N(C ₂ H ₅) ₂				-75 (1)							- 3			
CHO	-61 (2)		-62 (4)	-57 (3)	-52		-73	-21		-18	-14	-32	-23	
COCH ₃	-70 (3)		-68 (1)	-67 (2), -59 ^a			-63	-10		-17	- 5		-20	
COCH ₂ Br				-65 (1)							-11			
CO-  -N(CH ₃) ₂	-67 (1)							-18						
COCℓ	-88 (2)						-90	-15					-23	
CONH ₂						-56								
CONHCH ₃						-51								
CON(CH ₃) ₂						-13								
CN	-35 (2)	-35	-32 ^a		-24		-30	-17	-13			-17	-30	
CH ₃	17 (9)	17	15 (3), 12 ^a	15 (3)	23		10	14	13	11	11	9	10	
CH ₂ CH ₃			10 ^a		20		7					5	7	
CH(CH ₃) ₂	11 (4)		10 (1), 10 ^a	10 (1), 7 ^a	13			8		7	9	3		
C(CH ₃) ₃			3 ^a											
C(CH ₃) ₂ CH ₂ C(CH ₃) ₃				0 (1)							1			
CH ₂ cℓ			-6 ^a				0			-5 (1)			0	
CH ₂ Br			-5 ^a							-6 (1)				
CHBrCH ₂ CCℓ ₃			-14 ^a											
CHcℓ ₂							-13						-13	
CCℓ ₃							-80						-17	
CF ₃			-38 (1), -29 ^a	-30 (1)						-18	-10			

TABLE VI - (Cont'd.)

 S_0 and S_m From Various Workers

Subst.	S_0 (pphm)				S_m (pphm)			
	Present Work	from Tiers	from Varian*	C+D ^a	Present Work	from Tiers	from Varian*	C+D ^a
n-C ₃ F ₇		-31 ^a						
C ₃ H ₆ Br			10 ^a					
CH ₂ (CH ₃) ₂ Cl			5 ^a					
CH ₂ OH		5 ^a	4 ^a	7	-6(1) ^b			7
CH(CH ₃)OH			6(1)				11	
CH ₂ OCH ₂ - 		-2 ^a						
CH ₂ OCH ₂ -  -CH ₃		1(1)				-2		
 -CH-CH ₂			4 ^a					
C ₂ H ₄ OCOCH ₃			3 ^a					
CH ₂ NH ₂				3				3
CH ₂ N(CH ₃) ₂		2 ^a						
CH(CH ₃)NH ₂			2 ^a					
CH ₂ N(CH ₂ CN) ₂			7 ^a					
CH ₂ N  NSO ₂ φ			9 ^a					
CH ₂ -N(CH ₂ φ)CH ₂ N(CH ₂ φ) ₂			7 ^a					
C ₂ H ₄ NHCOCH ₃			7 ^a					
CH ₂ - 		8 ^a						
CH ₂ -  -CONH ₂			11 ^a					
CH(φ)COCH ₃			7 ^a					
C(CH ₃) ₂ -  -OH	6(1)				-9			
CH(-  -N(CH ₃) ₂) ₂			16(1)				-12	
CH(φ)NCCr(CO) ₅	-12 ^a							
C ₂ H ₄ - 		11 ^a						
C(CH ₃) ₂ COOH		-10 ^a						
C ₂ H ₄ COCH ₃		11 ^a						
 , X- 	-27(4)	-26(2)			-10	-12		
-CH=CHCH ₃			-3(1)				8	
CCH ₃ =CH ₂		-8 ^a						
CH=CH-CH=CHφ	-1 ^a							
CH=CHCHO		-24 ^a						
CH=CHCOCH ₃		-14 ^a						
φ=CH ₂		-2 ^a						
CH=CHBr		-1 ^a						
CH=CH-CH=CH φ	4 ^a							
Fe(CO) ₃								
 -C(=O)-C(=O)C ₂ H ₅			-78(1)				-9	
Ferrocene			-12(1)				10	
C ≡ CH		-11 ^a						
SiH ₃		-15 ^a						

[Figures in () are number of spectra averaged]

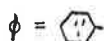
* - Data taken in polar solvents only

^a From monosubstituted benzenes

B & L: Brey and Lawson

P & J: Page and Jakobsen

C & D: Corio and Dailey

^b Derived using Tiers value of S_0 

Department of Chemistry
University of Utah
Salt Lake City 12, Utah
August 30, 1962

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

Dear Barry:

In view of the recent work of Anet¹ and of Lauterbur and Kurland,² negative geminal H-H coupling constants seem to be well substantiated experimentally. The direct contradiction of these results with theory, suggests a re-examination of the valence-bond calculations of geminal coupling constants by Karplus and co-workers.³ It is to be noted that these calculations are extremely sensitive to one of the exchange integrals, $K(C_2, H_1)$ between a carbon hybrid orbital and a non-bonded hydrogen orbital, and which is determined from the differences of crude empirical exchange integrals of the form described by Van Vleck.⁴ We have estimated that an error of only ten percent in the values of these integrals could give an error as large as ± 30 cps in the geminal coupling constant. It appears, therefore, that even semi-quantitative VB calculations of geminal coupling constants will not be feasible until a better method of independently estimating $K(C_2, H_1)$ is available.

The pi electron effect on the geminal coupling constant⁵ can be treated theoretically, either by the valence-bond method⁶, or in a manner analogous to that used by Holmes and Kivelson⁷ for the indirect pi electron effect on the long range H-H coupling constant in acetone. The latter treatment is based on the approximate theory of Karplus⁸ for long range pi electron coupling constants in unsaturated molecules, and has the advantage that σ - π exchange terms are estimated from experimental e.s.r. hyperfine constants. Since the geminal protons in a molecular fragment of the type $CH_3-\dot{C}=X$ are coupled to the same pi electron, the geminal protons are expected to have parallel spin orientations, and the pi contribution to the geminal coupling constant is the negative of the one reported by Karplus,⁸

$$J_{HH'}^{gem}(\pi) = - 2.1 \times 10^{-15} \frac{(a_H a_{H'})}{\Delta\pi} \quad (1)$$

where $\Delta\pi$ is the triplet state energy and a_H is the hyperfine constant for an $H_3C-\dot{C}$ radical, which was shown by McLachlan⁹ to be proportional to the sigma-pi exchange term in the VB perturbation calculation of the hyperfine interaction. With the value of $+150 \times 10^6 \cos^2 \varphi$ cps reported by Karplus⁸ for this quantity, Equation (1) can be written

$$J_{HH'}^{gem}(\pi) = - k \cos^2 \varphi \cos^2(\varphi + 120^\circ) \quad (2)$$

Equation (2) emphasizes several features of the pi electron contribution to the geminal coupling constant. First, it is negative in agreement with experiment, and second, it explains the enhancement of the π contribution to the geminal coupling constants for methylene groups in "planar" ring systems such as pro-piolactone,³ malic anhydride,¹⁰ and cyclopentenedione.³ The geminal coupling

constant, estimated from Equation (2), due to "free" rotation of a methylene group adjacent to a double bond is approximately -1.5 cps. This result is in agreement with the six electron VB calculations based on the above approximate form for the sigma-pi exchange integral.

With the acquisition of more geminal coupling constant data, an interesting trend has become apparent. In Figure 1 experimental coupling constants of compounds having adjacent π bonds are plotted as a function of the number of adjacent pi bonds. An examination of the slope of the straight line drawn through the experimental circles in this figure, indicates that the contribution is additive within the experimental error of the measurements, and that the contribution is about -1.9 cps. per adjacent pi electron bond. This value is only slightly larger in magnitude than that calculated.

1. F. A. L. Anet, Symposium on High Resolution Nuclear Magnetic Resonance Spectroscopy, University of Colorado, Boulder, Colorado, July 2-4, 1962.
2. P. C. Lauterbur and R. J. Kurland, J. Am. Chem. Soc., in press.
3. M. Karplus and D. H. Anderson, J. Chem. Phys., 30, 6 (1959).
H. S. Gutowsky, M. Karplus, and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).
4. J. H. Van Vleck, J. Chem. Phys., 2, 20 (1934).
5. M. Barfield and D. M. Grant, J. Am. Chem. Soc., 83, 4726 (1961).
6. M. Barfield and D. M. Grant, J. Chem. Phys., 36, 2054 (1962). M. Barfield, Ph. D. Thesis, University of Utah, 1962.
7. J. R. Holmes and D. Kivelson, J. Am. Chem. Soc., 83, 2959 (1961).
8. M. Karplus, J. Chem. Phys., 33, 1842 (1960).
9. A. D. McLachlan, Mol. Phys., 1, 233 (1958).
10. L. E. Erickson, Ph. D. Thesis, University of Wisconsin, 1959.

Sincerely,

Michael Barfield
David M. Grant

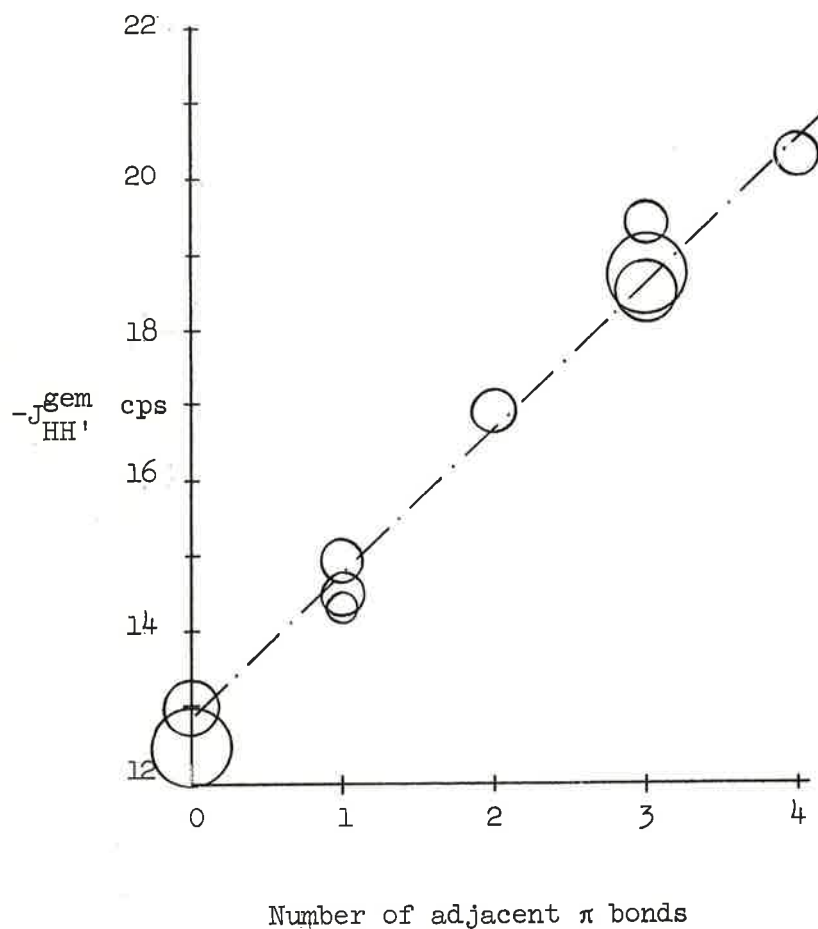


Figure 1. Geminal H-H coupling constants plotted as a function of the number of adjacent π bonds. The corresponding compounds, listed in ascending order, are methane, 1,1,1-trichloroethane, 2,5-hexanedione, acetic acid, acetone, acetonitrile, phenylacetonitrile, ethyl cyanoacetate, vinylacetonitrile, and malononitrile. Circles indicate experimental error in coupling constant measurements. Some coupling constant data was reported in Ref. 3 and 6. Data for 1,1,1-trichloroethane from the unpublished work of H. J. Bernstein.



CONTINENTAL OIL COMPANY

P. O. DRAWER 1267
PONCA CITY, OKLAHOMA

September 20, 1962

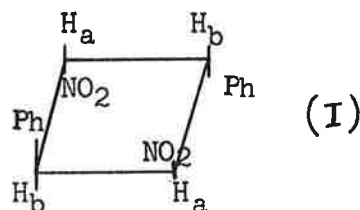
Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

We have studied the 60 mc ^1H spectrum of 1,trans-3-dinitro-cis-2,trans-4-diphenylcyclobutane⁽¹⁾(I) as a 5 per cent solution in 10 per cent acetic acid/acetone. The A_2B_2 spectrum was analyzed using the programs NMRIT and NMREN of J. D. Swalen.

The following NMR parameters were found:

- a) Chemical shifts:
 $(\text{H}_a) = 6.15 \text{ ppm (or } 5.21 \text{ ppm)}$
 $(\text{H}_b) = 5.21 \text{ ppm (or } 6.15 \text{ ppm)}$
- b) Coupling constants
 $J_{ab} = \pm 10.0 \text{ cps}$
 $J_{ab'} = \pm 6.2 \text{ cps}$
 $J_a \approx J_b = \mp 1.0 \text{ cps}$



The average deviation of calculated and observed line positions was 0.13 cps. The line positions were equally well reproduced when all coupling constants were taken with the same sign; however, the calculated intensities were unacceptable.

In this investigation, it was not possible to determine whether J_{cis} or J_{trans} is larger; but they are definitely of the same sign. The rather large difference between these constants and those determined by Lustig⁽²⁾ may indicate that the geometry of the cyclobutane ring is highly dependent on the nature and position of substituents.

- (1) The structure of this compound is known. Donald B. Miller, Ph.D. Dissertation, Ohio State University, 1957. Dr. Miller kindly supplied the sample.
- (2) Ernest Lustig, Mellon NMR 45, 6.

Yours very truly,

Paul F. Cox
Paul F. Cox

Central Research Division

Pat W. Flanagan
Pat W. Flanagan
Analytical Research Section

Copies to:

KARL-MARX-UNIVERSITÄT

PHYSIKALISCHES INSTITUT

LEIPZIG C4, LINNÉSTR. 5 - TEL. 65150, 65342, 65356

Herrn
Dr. Barry Shapiro
Mellon-Institute

am 4.9.1962 An: Dr. Kl/Gae.

Pittsburgh / Pennsylvania

Sehr geehrter Herr Dr. Shapiro!

In den vergangenen zweieinhalb Jahren befaßten wir uns sowohl experimentell als auch theoretisch mit der indirekten Spin-Spin-Kopplung zwischen Protonen und schweren Isotopen über zwei und drei Bindungen (s.z.B.[1]). Von den experimentell untersuchten Verbindungen möchten wir hier die Ergebnisse mitteilen, die wir für die n-Propylverbindungen von Cd, Sn, Hg und Pb mit einem Trüb-Täuber-Spektrometer bei 25 MHz erhielten.

Die Spektren dieser Propylverbindungen entstehen durch die Überlagerung eines $A_3B_2C_2$ - (an die Metallisotope mit dem Spin Null gebundene Propylgruppen) und eines $A_3B_2C_2X$ -Spektraltyps (an die Metallisotope mit dem Spin 1/2 gebundene Propylgruppen). Die exakte Analyse eines $A_2B_2C_2$ -Spektrums ist sehr schwierig.

Das $A_3B_2C_2X$ -Spektrum kann durch Einführung von vier effektiven chemischen Verschiebungen (s.Beziehung (1)) auf zwei $A_3B_2C_2$ -Spektren zurückgeführt werden. Es wird besonders einfach, wenn die Bedingungen

$$J_{BC} \ll \left| J_{BC} \pm \frac{1}{2}(J_{BA} - J_{CA}) \right| \quad (1)$$

$$J_{AB} \ll \left| J_{AB} \pm \frac{1}{2}(J_{BA} - J_{CA}) \right|$$

erfüllt sind. Die α -Methylen- und die Methylprotonen ergeben

1 G. Klose, Inauguraldissertation, KMU, Mai 1962

- 2 -

dann bei $J_{AC} = 0$ je zwei Triplets symmetrisch zu ν_C bzw. ν_A und die β -Methylenprotonen zwei Sechstetts symmetrisch zu ν_B .

Die Analyse des Spektrums von n-Dipropylquecksilber aus dem Satellitenspektrum ist relativ einfach. Dagegen ist die Auswertung der übrigen Spektren wesentlich schwieriger, weil ein Teil der schwachen Satellitenlinien von den intensiven Linien des Hauptspektrums überdeckt wird.

Die erhaltenen Ergebnisse sind in der Tabelle zusammengestellt.

	Cd	Sn	Hg	Pb
J_{X-C-H}	51,6	49,1	95,0	40,5
$J_{X-C-C-H}$	60,2	67,2	110,3	102,4
Vorzeichen-Verhältnis	entg.-ges.	entg.-ges.	entg.-ges.	entg.-ges.
$J_{(CH_3)-(\beta-CH_2)}$	~ 7,4	~ 7,8	~ 7,2	~ 7,3
$J_{(\beta-CH_2)-(\alpha-CH_2)}$	7,4	7,5	7,2	7,5
$\delta_{(CH_3)-(\beta-CH_2)}$	16,9	18,8	22,2	13,8
$\delta_{(\beta-CH_2)-(\alpha-CH_2)}$	-24,2	-13,4	-19,1	- 8,5

Sämtliche Werte in Hz

Die Kopplungskonstanten J_{X-C-H} und $J_{X-C-C-H}$ besitzen entgegengesetzte Vorzeichen und die gleiche Größenordnung wie die der entsprechenden Äthylverbindungen

Die angegebenen Zahlen für die H-H-Kopplungskonstanten, insbesondere für $J_{(CH_3)-(\beta-CH_2)}$ sind nur grobe Näherungswerte. Um die erhaltenen Werte für die chemischen Verschiebungen zu überprüfen, und genauere Werte für die H-H-Kopplungskonstanten zu erhalten, wird die exakte Analyse der Hauptspektren vom Typ $A_3B_2C_2$ vorbereitet.

Hochachtungsvoll

Ihr ergebener *G. Klose*

(Dr. G. Klose)

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of
Chemistry and Chemical Engineering

August 27, 1962

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

Dear Dr. Shapiro:

This note is in reference to the recent letter of Forslind and Bergqvist concerning aqueous salt solutions (MELLONMR, 42, 21 (1962)). We would like to report some of our findings using an internal standard technique.

To test the effects of internal standards on chemical shifts, three internal standards were used to study proton chemical shifts of H_2O in $NaCl$ solutions. The least square slopes of chemical shift versus molal concentration are as follows: acetone 0.074 ± 0.005 ppm, ethyl alcohol 0.069 ± 0.005 ppm, and acetonitrile 0.078 ± 0.005 ppm. These values are identical within experimental error and consequently we cannot be certain that the internal standards have significantly different effects on the proton chemical shift of water.

To avoid an excess of acetone in the salt solutions, the following procedure was employed. A small beaker was rinsed with acetone and dried with a hot air blower for one minute. The sample under investigation was introduced into this beaker and then transferred to an N.M.R. tube. A minute trace of acetone (less than 1%) could be detected in the N.M.R. spectra and its signal was used as the reference.

In Table I we compare our results with those of Forslind and Bergqvist who employed an external standard technique. Noticeably our results are consistently lower than those reported by Forslind and Bergqvist. In fact, the following approximate relationship could be formed: $\delta(\text{acetone}) \text{ internal} = 0.83 \delta(H_2O) \text{ external}$. We wonder whether the difference observed is due to an effect of the internal reference standard on the water molecules, or a failure of the Lorentz cavity model which would alter the coefficient $2\pi/3$ in the formula

$$\left[\frac{H - H_{\text{ref}}}{H_{\text{ref}}} - \frac{2\pi}{3} (K - K_{\text{ref}}) \right] \cdot 10^6$$

for external standards.

Even though the least-square slopes for the three internal standards do agree within experimental error, it would be interesting to see whether alcohol would give proportionately lower least-square slopes and acetonitrile proportionately higher least-square slopes for the various salts.

Scientific curiosity prompted us to measure the chemical shift of an aqueous solution containing a mixture of potassium iodide and sodium chloride. For a solution containing two molals of each salt we found the shift of the water

Dr. B. L. Shapiro
Mellon Institute

-2-

August 27, 1962

protons to be 0.42 ± 0.01 ppm. If the effects of both salts upon the water molecules are independent then, from the data shown in Table I, we would predict a value of 0.040 ± 0.02 ppm. Within experimental error this value is in agreement with the observed value.

Table I

Proton Chemical Shift (ppm) per Molal Concentration

Salt	Internal Standard	External Standard
	(Present Work)	(Forslind and Bergqvist)
KCl	0.061 ± 0.005	0.099 ± 0.003
KBr	0.099	0.123
KI	0.128	0.150
$LiCl$	0.022	0.017
$RbCl$	0.065	0.075
$CsCl$	0.048	0.059
$NaBr$	0.102	0.119
NaF	-0.034	-0.036
$NaCl$	0.074	0.086

Respectfully yours,

E. R. Malinowski + P. Weiner

E. R. Malinowski and P. Weiner

KARL-MARX-UNIVERSITÄT

PHYSIKALISCHES INSTITUT

Herrn
Dr. B.L. Shapiro
Mellon-Institute

Pittsburgh/Pennsylvania
4400 Fifth Avenue

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

am 4.9.1962 An: Dr.Ra/Gae.

Sehr geehrter Herr Dr. Shapiro!

Die Abhängigkeit der direkten und entfernten C^{13} -H-Kopplungskonstanten von den Substituenten ist wesentlich komplizierter als bei den H-H-Kopplungskonstanten. Nach einfachen VB-Berechnungen ergibt sich bekanntlich für die C^{13} -H-Kopplungskonstanten ebenso wie für die H-H-Kopplungskonstanten eine Abnahme mit steigender Polarität der Bindung, d.h. mit zunehmender Elektronegativität der Substituenten. Bei den H-H-Kopplungskonstanten läßt sich diese Abnahme mit zunehmender Elektronegativität auch experimentell sehr schön beobachten. Bei den direkten C^{13} -H-Kopplungskonstanten wurde schon in der Arbeit von Muller und Pritchard [1] ein völlig davon abweichendes Verhalten beobachtet. Bei den C^{13} -C-H-Kopplungskonstanten stellten Karabatos, Graham und Vane [2] fest, daß keine Proportionalität zu den entsprechenden H-C-C-H-Kopplungskonstanten vorhanden ist. Sie nehmen deshalb an, daß zur Erklärung der entfernten C^{13} -H-Kopplungskonstanten auch die anderen Nicht-Kontakt-Beiträge im Ramsey'schen Ausdruck mit zur Erklärung dieser Kopplungskonstanten herangezogen werden müssen.

Man kann aber in vielen Fällen zeigen, daß die direkten und entfernten C^{13} -H-Kopplungskonstanten völlig gleichartig durch die Substituenten beeinflusst werden. In Tabelle 1 wird das an einigen Beispielen gezeigt. Durch die Substituenten O bzw. Cl am C^{13} -Atom erhöhen sich die C^{13} -C-H und C^{13} -C-C-H-Kopplungskonstanten ebenso wie die C^{13} -H-Kopplungskonstanten.

Dieses Verhalten ist in Übereinstimmung mit der Erwartung. Unter Berücksichtigung des Kontaktterms ergeben sich alle diese Kopp-

- 2 -

Tabelle 1 (entfernte C^{13} -H-Kopplungskonstanten nach [2])

Substanz	$J_{C^{13}-H}$	Substanz	$J_{C^{13}-C-H}$	$J_{C^{13}-C-C-H}$
CH_3CHO	173	$(CH_3CH_2)_2C^{13}O$	$5,7 \pm 0,1$	$4,7 \pm 0,1$
$HOCHO$	222	$CH_3CH_2C^{13}O \begin{smallmatrix} H \\ \\ CH_3 \end{smallmatrix}$	$6,4-6,5 \pm 0,3$	$5,3-5,5 \pm 0,2$
		$((CH_3)_2CH)_2C^{13}O$	4,1	$5,1 \pm 0,1$
		$(CH_3)_2CHC^{13}O \begin{smallmatrix} H \\ \\ CH_3 \end{smallmatrix}$	$5,2-5,6 \pm 0,1$	$5,4 - 5,8$
CH_4	124	$C^{13}H_3-\overset{\alpha}{C}H_2-\overset{\beta}{C}(Cl)CH_2CH_3$		$\alpha: 3,2 \pm 0,2$ $\beta: 3,0 \pm 0,2$
CH_3OH	141	$C^{13}H_3-\overset{\alpha}{C}H_2-\overset{\beta}{C}(OH)CH_2CH_3$		$\alpha: 4,2 \pm 0,2$ $\beta: 3,2 \pm 0,2$
CH_3Cl	150,5	$(CH_3CH_2)_n C^{13}(OH)D_{3-n}$		$4,5-6,4 \pm 0,2$
		$(CH_3CH_2)C^{13}(Cl)(CH_3)_2$		$5,7 \pm 0,1$

lungskonstanten proportional zum 2s-Charakter der Kohlenstoffbindungseigenfunktionen

$$J_{C^{13}-H} \sim \alpha^2 \phi_{C^{13}}^2(\psi); (\psi = a \phi_{C^{13}} + b \phi_{C^{13}-H})$$

Durch den Substituenten wird die Hybridisierung der Kohlenstoffeigenfunktionen und damit der 2s-Charakter geändert. Es müssen sich also alle C^{13} -H-Kopplungen völlig gleichartig ändern. Das meiste experimentelle Material liegt für die direkten C^{13} -H-Kopplungskonstanten vor. Die von uns früher angegebene empirische Formel [3]

$$J_{C^{13}-H} = 64 + 15,4 \cdot \sqrt{(C-X) \cdot E_X}$$

gibt z.B. die C^{13} -H-Kopplungskonstanten von monosubstituierten Methanen sehr gut wieder. Man kann zeigen, daß die 2s-Charaktere, die sich aus diesen C^{13} -H-Kopplungskonstanten (unter Zugrundelegung der Theorie von Gutowsky und Juan [4]), ergeben, in sehr guter Übereinstimmung mit den Regeln von Bent [5] für die

Änderung der Hybridisierung durch die Substituenten sind. Ausführlicher werden wir über dieses Problem in den Annalen der Physik schreiben.

Hochachtungsvoll

(Dr.J.Ranft)

- 1 N. Muller, D.E. Pritchard, J.Chem.Phys. 31, 1471, 1959
- 2 G.J. Karabatsos, J.D. Graham, F. Vane,
J.Am.Chem.Soc. 83, 1230, 1961; 84, 37, 1962; 83, 2778, 1961
J.Phys.Chem. 65, 1657, 1961
- 3 J. Ranft, Tagungsband Hochfrequenzspektroskopie, Berlin 1961,
S. 18
- 4 H.S. Gutowsky, C.S. Juan, J.Am.Chem.Soc. 84, 307, 1962
- 5 H.A. Bent, Chem.Revs. 61, 275, 1961

Nuclear Spin Relaxation in Liquid CHFC1_2

R.J.C. Brown, H. S. Gutowsky and K. Shimomura

Noyes Chemical Laboratory, University of Illinois

Urbana, Illinois

Nuclear spin relaxation times have been measured for liquid CHFC1_2 , the values of T_{1H} and T_{1F} between 132° and 298°K at 27, 20 and 17 Mc, and T_{2H} and T_{2F} over the same temperature range at 20 Mc. The results of these measurements are discussed, and the following relaxation mechanisms are shown to be important: (a) intermolecular dipole-dipole interactions, including their effect upon the electronic, scalar coupling of the proton and fluorine nucleus, (b) the quadrupolar relaxation of the chlorine nuclei, which are coupled to the proton and the fluorine nucleus by scalar couplings, and (c) the spin-rotation interaction between the fluorine nucleus and the reorientation of the molecule.

The statistical assumptions of rotational Brownian motion of the molecule, in the liquid, when applied to the spin-rotation interaction, are found to predict the wrong temperature dependence of T_{1F} at high temperatures. A model is proposed in which the molecules "jump" from one orientation to another at random times, the spin-rotation interaction is assumed to operate during these "jumps" when the molecule is actually rotating. The statistical properties of such a model are calculated, and it is shown that T_{1F} is predicted to have the correct temperature dependence. The dipole-dipole and quadrupole interactions are discussed in detail, and a treatment of intermolecular dipole-dipole relaxation by Redfields' method is given, with results indicating that the electronic, scalar coupling of nuclei contributes to the inequality $T_2 < T_1$ often found in liquids.

September 5th, 1962.

Lincoln College,
Oxford,
England.

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

Dear Dr. Shapiro,

This is my subscription to the excellent Newsletter.

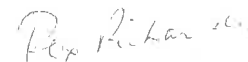
We have a Varian variable frequency wide line spectrometer which we have been using for chemical shift measurements and various other n-m-r- problems. We found that the measurement of chemical shifts was severely limited by the accuracy with which we could measure the magnetic field during the scan of a spectrum using the scanning unit provided. We have therefore made certain changes which enable us to work with a fixed magnetic field taking advantage of the super stabilizer, and to scan the spectrum by varying the frequency. Three large holes were punched on the left hand side of the radio frequency unit in each of the main three compartments. Three small variable air condensers were mounted on a stout piece of aluminum angle and connected by gear and worm drive to a single shaft which was connected through a multispeed gear box to a clock motor. This assembly is bolted on to the side of the radio frequency unit so that the three variable condensers poke through the large holes in each compartment. The condensers are connected in parallel with the three main sections of the tuning condenser. It was found to be necessary to provide a screening can for the trimmer in the radio frequency amplifier section at the back. These trimmers scan the radio frequency unit at any predetermined rate and they provide a scan of as much as 2% when the main condenser is fully in and a greater range when the condenser is out. The frequency of the radio frequency unit is measured by taking a signal from the crystal locking connector and mixing it with a standard reference frequency from a frequency synthesiser. The beat is applied to a counter which then displays at regular intervals a number giving the exact value of the frequency at any moment. As the spectrum is scanned marks are put on the recorder manually and the reading of the counter is written against them. These calibrations can be put on as frequently as seems necessary. With the magnet and super stabiliser working we are able to scan extremely slowly and have found no difficulty in measuring chemical shifts to better than 5 c/s when the line width permits. The spectrometer is much simpler to use and one knows the calibration with confidence at any time. The radio frequency unit itself is remarkably stable when it has been on for some days and we have not encountered any difficulties from drift.

Mr. B.A. Yorke has been measuring line widths of bromine and sodium resonances in solutions of bromides in water and non-aqueous solvents. He finds for sodium and calcium bromide solutions that the line width is a linear function of the viscosity. The slopes of the lines are in the ratio of the squares of the quadrupole moments for the two bromine isotopes, thus indicating that the slope of the line is a good measure of the quadrupole coupling constant of the bromine nucleus in accordance with the theory of Abragam and Pound. The linear plots show that the quadrupole coupling constant is independent of concentration in these solutions and must therefore arise from interactions between the bromine ion and the solvent molecules and not between the bromine ion and the positive ion.

-2-

For caesium bromide solutions non-linear plots are obtained confirming the formation of ion pairs at high concentrations. In non-aqueous media the plot of line width against viscosity is once again linear provided that the nature of the solvent is kept constant. Mixtures of water with methanol, glycine, acetone, and dioxane have been used. When the composition of the solvent mixture is changed the slope of the line width versus viscosity plot changes so that clearly the quadrupole coupling constant depends on the solvent medium. There is a close relationship between the slopes of the lines and the dielectric constant of the solvent and we have interpreted the results in terms of electric field gradients at the bromine produced by charges induced in the solvent molecules. The details of this work have been submitted for publication in MOLECULAR PHYSICS.

Yours sincerely,



R.E. Richards.

UNIVERSITY OF FLORIDA
GAINESVILLE

DEPARTMENT OF CHEMISTRY

September 7, 1962

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

Dear Barry:

I should like to discuss two items which come to mind concerning proton NMR work. The first concerns the old problem of the numbers used in describing chemical shifts, and this arises in connection with the scale used in the Varian spectra catalog, where, contrary to the usual scientific and mathematical usage, the numerical scales increase from right to left. For a few years everyone seemed pretty well agreed that a number describing the chemical shift should increase with increasing field. Now, just about the time we have converted all our reference points to the tau scale, which worked pretty well, there seems to be a growing tendency to reverse the direction of things, just because TMS happens to have a high-field resonance. If everyone is going to do this, the situation is not too bad, but there is always the problem of what a minus sign means. Perhaps things could be straightened out with the frequencies themselves still having positive signs for higher fields, and the ppm scale in reverse direction but I remain sceptical. Perhaps the ACS editorial forces will one day make a decision about this, but the literature is growing so rapidly that agreement should be reached as soon as possible.

A second problem has to do with referencing. We have run some very careful shift measurements on solutions of substituted benzenes using the Wilmad precision coaxial cells with benzene as external reference. The results have been extrapolated to infinite dilution. We find a small but definite difference between the relative shifts of the ring protons in, say, benzene and toluene depending upon whether these measurements are made in carbon tetrachloride or in cyclohexane. Some of our neighbors to the north stated that if TMS were used as internal reference this difference disappeared, but we can not reproduce their result. Perhaps someone else would be interested in looking into this problem and helping to settle the question.

Having mentioned these controversial issues, I would like to describe some results we are obtaining on the temperature dependence of F-F coupling constants. Variation is observed in many compounds, apparently as the result of change in molecular conformation. If interconversion of forms is rapid, the observed J is the weighted average over the several forms. For some unsymmetrically substituted molecules one can "freeze out" several different conformers at -50 to -100°.

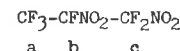
Page 2

Dr. B. L. Shapiro

September 7, 1962

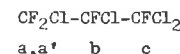
First, we have found that one must be careful in interpreting the results of temperature variation, for the J's are not always changing, as the temperature decreases, toward the value found for the predominant conformer at low temperatures. For example, in $\text{CF}_2\text{BrCFBr}_2$, the coupling constant at -40° is 17.4 and increasing with lower temperatures, but the average value for the form predominant at -110° is 17.4 (Manatt and Elleman, JACS 84, 1305 (1962)).

A possible explanation for this is suggested by the observed effect of temperature on the a-b coupling in the following molecule; The value changes from ca. 4.5 cps at 100° to 6 cps at -100°:



Since the CF_3 group is symmetrical there can not be an equilibrium between different rotational conformers in the usual sense. Nevertheless, if the coupling is angularly dependent, differences in the extent of the torsional oscillation of the CF_3 group with temperature may produce the observed result, and this effect may then be superimposed on the conformer equilibrium in unsymmetrical molecules. Incidentally, the a-c coupling in this molecule is found to decrease with decreasing temperature.

A more complicated situation occurs in:



J_{ac} increases from 18 cps at 75° to 28 cps at -100°, which is certainly one of the largest 1-3 couplings yet found and makes quite reasonable a value of 40 or 50 cps as postulated by Petrakis and Sederholm (J. Chem. Phys. 35, 1243 (1961)) for the single conformer with 1-3 contact between two given fluorines. J_{ab} and J_{bc} also increase, but to a lesser extent, with decreasing temperature, while $J_{a'b}$ and $J_{a'c}$ decrease somewhat. It would seem here that at low temperatures a conformer in which F_a and F_c are opposed is highly favored. However, freezing out was not observed at -100°.

We hope to learn a great deal more in this area. If we have not been brief, at least we have single-spaced and perhaps will be forgiven.

Cordially,

Wallace S. Brey, Jr.
Hermit C. Ramey
Kenneth D. Lawson

jm

48-14



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OTTAWA 2, 14.9.62

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

Dear Dr. Shapiro,

As sometimes it seems to be rather difficult to find accurate susceptibility data in literature, we should like to mention here a little trick to get this information from high-resolution NMR directly. The method is simple and provides an accuracy comparable to the classical methods.

Two reference tubes, a spherical and a cylindrical one, are immersed simultaneously in a spinning thin wall sample tube filled with the liquid or gas to be investigated. Two surprisingly sharp signals can be obtained, their separation being proportional to the volume magnetic susceptibility of the sample:

$$\delta_{\text{cyl}}(\text{ref}) - \delta_{\text{sph}}(\text{ref}) = [g_{\text{cyl}} - g_{\text{sph}}] [\chi_v(\text{ref}) - \chi_v(\text{sample})]$$

where δ is the chemical shift in ppm, g is a "shape factor" and χ_v is the volume magnetic susceptibility in c.g.s. units. The constant $[g_{\text{cyl}} - g_{\text{sph}}]$ equals $2\pi/3 - 0 = 2.094$ for ideal geometry but may deviate slightly in practice and has therefore to be determined by calibration.

The accuracy depends mainly on sweep and rf stability as well as on field homogeneity. However, by using the sideband/superposition method and proper adjustment of the field gradients it is possible to measure the difference of the two reference signals with an accuracy of about .2 c/s or better. The geometrical positions of sample tube, sphere and receiver coil should be kept constant during the series of experiments. As reference material - which should produce a reasonably sharp and if possible single line not interfering with the sample spectrum - water was chosen; but many other reference compounds such as tetramethylsilane, cyclopentane etc. would also be suitable.

To calibrate our present setup, fifteen compounds of well known susceptibilities were used. Using a least square treatment to fit the data of Broersma (S. Broersma, J. Chem. Phys. 17, 873 (1949)) one obtains:

$$\chi_v(\text{sample}) 10^6 [\text{in c.g.s. units}] = 0.7149 + 0.000097 \Delta\nu [\text{in c/s}]$$

with a mean deviation of $\pm 0.0012 10^{-6}$ c.g.s. units in χ_v . Table I summarizes the obtained data:

Table I: Volume susceptibilities χ_v in c.g.s. units determined by the present method, fitting the results obtained by S. Broersma.

	$\Delta\nu = \nu_{\text{cyl}} - \nu_{\text{sph}}$	$\chi_v 10^6$ [c.g.s. units] here	S. Broersma
air	- 91.90	+ .0292	+ .0294
acetone	- 31.54	- .4595	- .461
n-pentane	- 20.81	.5464	.5472
n-hexane	- 18.39	.5660	.5667
n-heptane	- 16.31	.5828	.5817
cyclohexane	- 12.61	.6129	.6115
benzene	- 12.43	.6149	.6157
toluene	- 12.13	.6167	.6179
mesitylene	- 10.09	.6332	.6333
ethylbenzene	- 10.04	.6336	.6341
o-xylene	- 8.60	.6453	.6440
carbontetrachloride	- 2.67	.6933	.691
methylenebromide	+ 27.31	.9360	.935
bromoform	+ 28.68	.9471	.948
methyleneiodide	+ 54.39	1.1553	1.156

Another application of the spherical reference tube is its use as an external standard for chemical shift measurements, reducing the bulk susceptibility correction to the order of 1 c/s. As g_{sph} can be determined empirically from the slope of the calibration line (assuming $g_{\text{cyl}} = 2\pi/3$) the "spherical" bulk susceptibility correction can be evaluated with an accuracy of better than 0.1 c/s. With other words, the true position of the external reference line can be determined with an accuracy of ± 0.1 c/s or better, even with crude susceptibility data available.

Experiments to use the spherical tube as a micro sample tube are being undertaken.

Sincerely yours

K. Frei

H.J. Bernstein

K. Frei

H.J. Bernstein

September 10, 1962

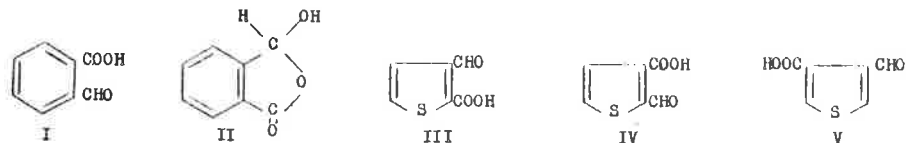
2.

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

Dear Dr. Shapiro,

It seems high time to send our "renewal subscription" on your excellent newsletter. A report on our recent studies in the furan series was, as you will remember, presented by one of us at the Boulder conference and we hope to have reprints of the full paper, to appear in Arkiv Kemi, available for distribution in the near future, so in this letter we wish to communicate some of our more recent activities.

We have for some time been studying the aldehydo-lactol type tautomerism in compounds like phthalaldehydic acid (I). NMR-spectroscopy confirmed that this compound exists as hydroxy-phthalide (II).



It showed no absorption in the aldehydic proton region around 0τ but about 3.3τ which is more like the shift for a strongly unshielded aliphatic proton. However in alkaline solution the anion is derived from I as the resonance occurs 5.2 ppm towards lower field from the water resonance, that is in the aldehydic region. In the three thiophene analogues (III-V) of phthalaldehydic acid the geometric factors and conjugation effects which could influence the stability of the open versus the cyclic form are somewhat different. However all three thiophene analogues exist in acetone or dioxane solution in the open aldehydic form as they display an aldehyde peak at -0.4 to -0.5τ . In III and IV the splitting of 1 c/s due to the well-known long-range aldehydic coupling to the 5-hydrogen could be resolved, but in V the accidental coalescence of the aromatic hydrogen peak, precluded the resolution of the expected fine-structure in the aldehyde band.

Another problem which we are studying is the connection between the NMR-parameters and the tautomeric structure of hydroxy- and aminopyrimidines, which is a quite intriguing problem. The danger of drawing erroneous conclusions regarding tautomeric structure from NMR-data has recently been pointed

out by Katritzky and Waring (Chem. & Ind. 1962, 695).

We hope that this letter is not too long and that it will entitle us to receive your valuable news-letter for another six month.

Best regards

Sincerely Yours

Salo Gronowitz

Salo Gronowitz

Ragnar A. Hoffman

Ragnar A. Hoffman

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
LOS ANGELES 24, CALIFORNIA

September 17, 1962

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

Dear Barry:

1. Relative intensity of proton resonance peaks of $(CH_3)_3SnCH_2Sn(CH_3)_3$, (I). The resonance of the methyl protons in (I) (cf. Kaesz, J. Am. Chem. Soc., 83, 1514 (1961)) are split, through the interaction $Sn-C-H$, by the principal magnetically active nuclei Sn-117 and Sn-119 (relative natural abundance ca. 7.7% and 8.7% respectively). Such resonances will appear as a main peak surrounded by satellite doublets, in the intensity ratios, 4.3:3.8:84:3.8:4.3. The methylene protons, situated on a 2° tin-substituted carbon atom, will encounter $Sn-C-H$ splitting at twice the probability of the natural abundance of the magnetically active isotopes. Such resonances will appear as peaks in the ratio 8.7:7.7:67:7.7:8.7. This is illustrated by the resonances of the methyl and methylene protons of (I) on the attached spectrum. Because of the situation explained above, the main peaks, A and B, appear in the intensity ratio $(0.84)^9 : (0.67)^1$, i.e., 11.2 : 1.

2. ^{13}C satellites in proton resonance of organotin compounds. I wish to report the following coupling constants (observed in each for the neat liquid) in the event such data might be useful to other workers:

Compound	T, °C	$J_{^{13}C-H}$ (c.p.s.)
bis(trimethylstannyl)methane, (I)	31	127.5 (observed only for CH_3 groups so far)
hexamethylditin	31	128
trimethyltin chloride	45	131*
dimethyltin dichloride	108	137*
methyltin trichloride	55	142

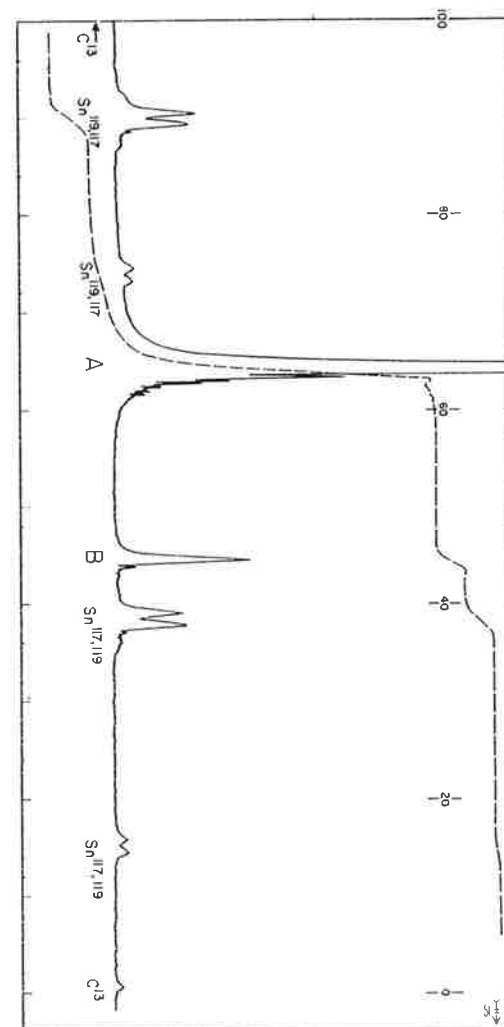
*) Comparable values for these two have been reported by Van der Kelen, Nature, 193, 1069 (1962), in an article which in other respects, is a repetition of results and conclusions previously reported by Holmes and Kaesz, J. Am. Chem. Soc., 83, 3903 (1961).

3. A forthcoming review article "Applications of N.M.R. in the Study of Organometallic Compounds" is being prepared in collaboration with J. R. Holmes and S. L. Stafford (both presently at the Allied Chemical Corporation, Morristown, New Jersey). In order to keep our article as up to date as possible, we would appreciate receiving any current preprints of reports in the above mentioned area.

Sincerely yours,

Herb
Herbert Kaesz
Assistant Professor

HDK/ar



SOLVENT: NEAT LIQUID
FILTER BANDWIDTH: 4 cps
R.F. FIELD: 0.09 mg
SWEEP TIME: 250 sec
SWEEP WIDTH: 100,000 cps
SWEEP OFFSET: 412 cps
SPECTRUM AMP: 0.9
INTEGRAL AMP: 32

$(CH_3)_3Sn-CH_2-Sn(CH_3)_3$



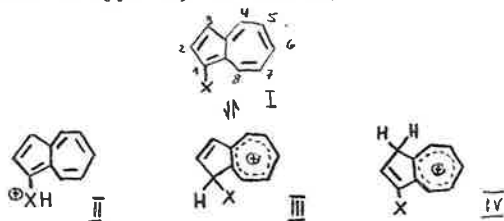
EIDG. TECHNISCHE HOCHSCHULE
ZÜRICH

Laboratorium
für Organische Chemie

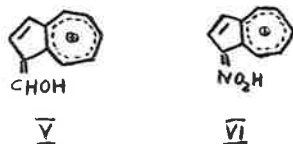
Zürich 6, 17th September 1962
Universitätstrasse 6
Tel. 32 73 30

Dear Dr. Shapiro,

We have recently investigated by n.m.r. the acid-base equilibria of azulenes of type I, which can theoretically form several isomeric conjugate acids of type II, III and IV:



The n.m.r. spectra of the conjugate acid of 1-methyl-azulene and 1,4-dimethyl-7-isopropyl-azulene (guaiazulene) are consistent only with structure type IV¹⁾ (fig. 1). This result has also been found in an earlier interpretation of the u.v. spectra, based on simple MO-calculations²⁾. For azulene-1-aldehydes³⁾ similar considerations led to structure V for the conjugate acid. The n.m.r. spectrum of the conjugate acid of 2,4,6,8-tetramethyl-azulene-1-aldehyde (fig. 2)⁴⁾ shows that protonation takes place preferentially on the carbonyl group to give the conjugate acid of type V. Fast exchange of proton resp. deuterium on C-3 (H₃, D₃) suggests that the isomeric cation of type IV also occurs in solution.



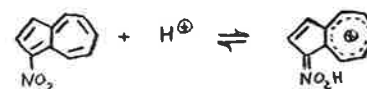
The n.m.r. spectra (fig. 3,4) of 1-nitro-azulene in strong acidic solvents show that protonation takes place predominantly on the nitro group. Also in this case, exchange of proton resp. deuterium on C-3 indicates that a small amount of the cation with structure IV is present. In solvents with higher dielectric constant than CCl₄, the polarisability

- 2 -

of 1-nitro-azulene is considerable. The signals of the different ring protons are shifted in the same direction as those of the cation with structure VI (compare table 1). Protonation on the nitro group has also been proved by following the titration of 1-nitro-azulene in F₃CCOOH with conc. H₂SO₄ by n.m.r.⁶⁾. The resulting curve (fig. 5), with a change in slope after addition of one equivalent conc. H₂SO₄ per one mole 1-nitro-azulene, fits the equation (A)

$$\delta_{\text{observed}} = \delta_{\text{base}} \cdot X_{\text{base}} + \delta_{\text{acid}} \cdot X_{\text{acid}} \quad (\text{A})$$

corresponding to the equilibrium:



(δ_{base} , δ_{acid} : chemical shift of the base, resp. of the acid;

X_{base} , X_{acid} : molarity of the base resp. of the acid;

fig. 4: $\Delta\delta$ = change in chemical shift relative to the chemical shift measurement in F₃CCOOH without H₂SO₄; v = proportion of conc. H₂SO₄ per 1-nitro-azulene at start).

In guaiazulene-3-sulfonic acid protonation occurs at the carbon atom bearing the sulfonic acid group. This behaviour may be due to release of steric strain between the sulfonic acid group and the methyl group at C-4.

The assignments of the lines of azulenes and their cations has been discussed in some earlier works⁸⁾. Some of our investigated cations show a considerable large coupling between the protons of substituents in position 1 and the ring proton or methylene protons on C-3. (e.g. 1-methyl-azulene-cation: $J_{\text{methyl-methylene}}$: 1,9 cps, $J_{\text{methyl-H}_2}$: 1,3 cps, $J_{\text{methylene-H}_2}$: 1,9 cps).

Thanks for Frequent IV and Mellon-NMR which is a most valuable help in daily laboratory work.

Sincerely yours,

Doris Meuche

Doris Meuche

Table 1. Chemical shift of the ring protons of 1-nitro-azulene and of 1-nitro-azulene-cation ⁷⁾

(δ -values in ppm relative to TMS interne)

Solvent					
CDCl ₃	7,36	8,43	8,53	9,71	(7,85)*
(CH ₃) ₂ S = 0	7,38	8,41	8,80	9,60	(8,10)*
SO ₂ , liquid	7,24	8,35	8,63	9,67	(7,98)*
F ₃ CCOOH (4,5 mol-proz. H ₂ O)	7,23	8,34	8,61	9,66	(8,07)*
F ₃ CCOOH/H ₂ SO ₄ conc. (9:1)	7,58	8,33		9,88	(8,77)*

* average δ -value of complicate not analyzed line pattern
(compare also fig. 3)

- 1) "Die Protonierung von alkylsubstituierten Azulenen", Doris Meuche, B.B.Molloy, D.H.Reid and E.Heilbronner to be published: *Helv.chim.Acta*
- 2) Pl.A.Plattner, E.Heilbronner und S.Weber, *Helv.* 32, 574 (1949)
- 3) E.Heilbronner & R.W.Schmid, *Helv.* 37, 2018 (1954)
- 4) "n.m.r. spectra of azulene-1-aldehydes and their conjugate acids". D.Dreyer, Doris Meuche, E.Heilbronner, to be published: *Helv.chim.Acta*
- 5) "Die Protonierung des 1-Nitro-azulens", Doris Meuche & E.Heilbronner, *Helv. chim.Acta*, in press
- 6) Weight samples of H₂SO₄ conc. in teflon-capillars were pressed by an injection tube into the solution of 1-nitro-azulene F₃CCOOH.
- 7) The spectra were measured on a Varian-A-60-Spectrometer in 0.25 molar non degassed solutions. (Accuracy \pm 1 cps)
- 8) S.S.Danyluk & W.G. Schneider, *J.Amer.chem.Soc.* 82, 997 (1960)

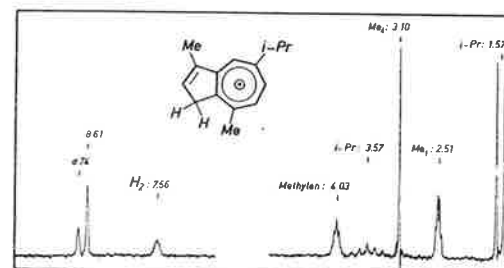
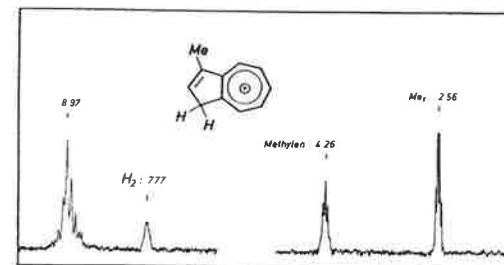


Fig. 1

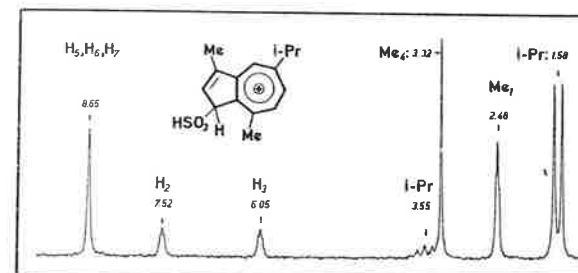
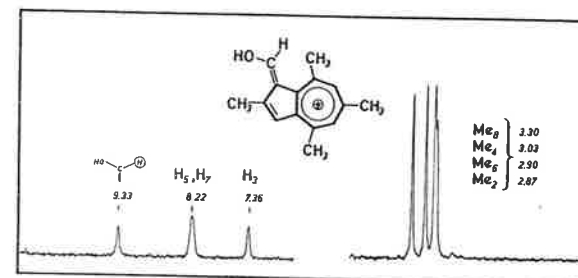


Fig. 2

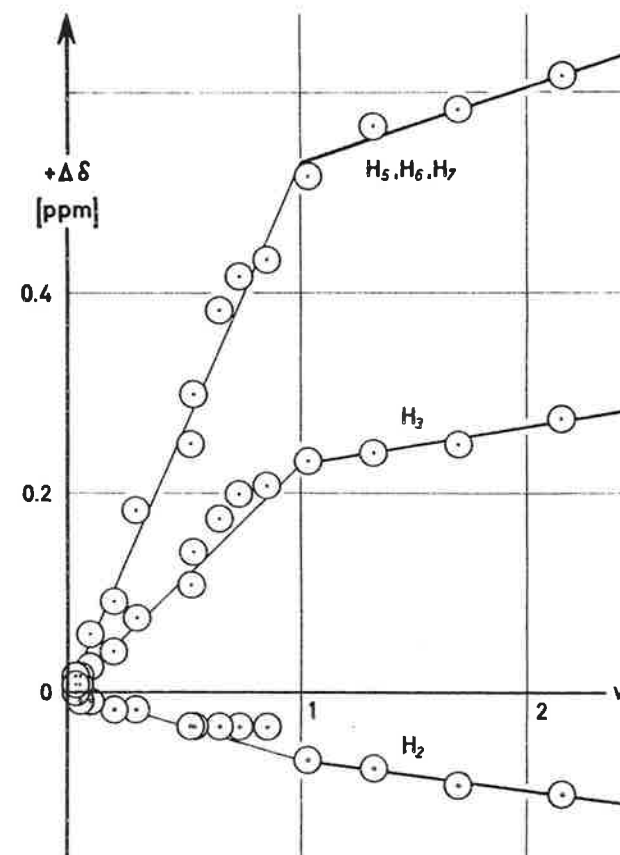
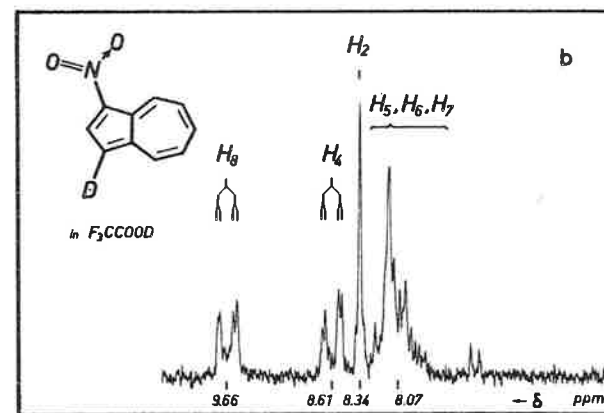
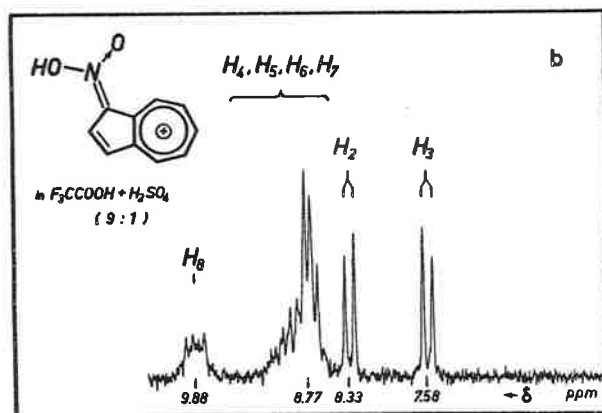
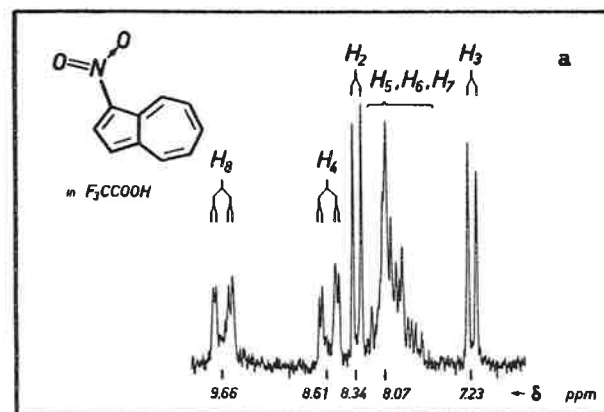
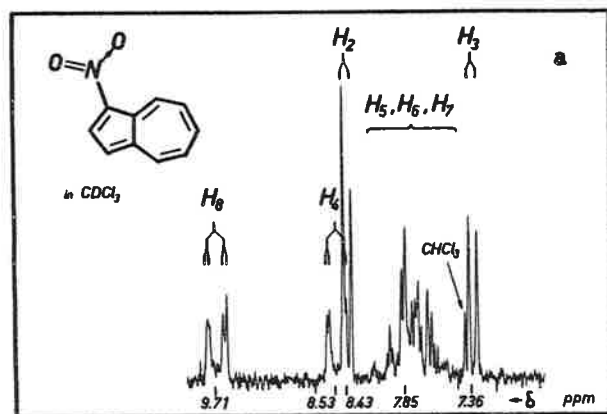


Fig. 3

Fig. 4

Fig. 5

September 20, 1962

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

Dear Dr. Shapiro:

THE STORY OF THE CAT AND THE DOG

(or: Improvement of the Sensitivity by Long-term Measurements)

Just returned from the exciting Discussion of The Faraday Society on "High Resolution Nuclear Magnetic Resonance" we would like to make a comment on the methods to improve the sensitivity of nmr-spectrometers by long-term measurements. On the occasion of discussions with several members of the conference we got the impression that there are some misunderstandings. They were partially caused by a remark of Dr. Shoolery introducing his paper on "Recent Applications of High Resolution NMR to the Determination of Molecular Structure".

The main question is, whether it would be preferable to increase the sensitivity

- a) by taking the same spectrum many times with the usual sweep rate and computing the least square average of these spectra with a computer (the so called "CAT"-method, compare the very interesting letter of O. Jardetzky MELLONMR No.47) or
- b) by using an essentially increased sweep time (compare MELLONMR No.33 p.19). To be short we call this method the "DOG"-method.

Dr. Shoolery stated that the power spectrum of the noise of a nmr-spectrometer is increasing rapidly at very low frequencies and that therefore it would be better to use the CAT-method instead of very long sweep times as in our DOG-method.

We are of the opinion that this problem has to be discussed in some details and that several features have to be distinguished.

- 2 -

1. Proof of the Equivalence of the "CAT"- and "DOG"-Method

In the case of a white power spectrum of the noise and neglecting the fluctuations of the magnetic field the two methods are exactly equivalent in regard to the sensitivity. To get the same sensitivity the same overall time is necessary in both methods.

To prove this equivalence let us consider two experiments of the same overall duration T and with the same spectrum of the length Δ .

1. In the first experiment we sweep with a rate Δ/T only one time over the whole spectrum.
2. In the second experiment we sweep with a rate $n \cdot \Delta/T$ n times over the whole spectrum. Finally an ensemble average is made over the n spectra.

To improve the sensitivity one uses in any spectrometer an electronic low-pass filter. That means the improvement is performed by an integration averaging over the time. The optimum shape of the filter is determined by the VanVleck-Middleton criterion. This filter is in practice always approximated by a RC-filter (1) with an optimum time constant of

$$RC = 2,25 \sqrt{1 + s/a} T_2$$

with

$$\begin{aligned} T_2 &= \text{transversal relaxation time} \\ s &= (\gamma B_1)^2 T_1 T_2 = \text{saturation parameter} \\ a &= \text{sweep rate} \end{aligned}$$

The achieved sensitivity is proportional to $a^{-1/2}$.

In the first experiment the sensitivity V_1 equals therefore

$$V_1 = V_0 \sqrt{T/\Delta}$$

In the second experiment the sensitivity $V_2^{(n)}$ of a single experiment is given by

$$V_2^{(n)} = V_0 \sqrt{T/n\Delta}$$

By averaging over the n different spectra the sensitivity V_2 of the average will be by a factor \sqrt{n} higher than $V_2^{(n)}$:

$$V_2 = \sqrt{n} V_2^{(n)} = V_1$$

That means that the two achievable sensitivities are exactly the same, of course a trivial and well known result.

The argument of Dr. Shoolery that the noise power spectrum is not white but increasing at low frequencies is hardly applicable to an up to date nmr-spectrometer using a modulation method. By a sideband modulation method any additional low-frequency noise (Flicker-noise, fluctuations of the leakage etc.) will be eliminated (2). And if one uses a properly constructed phase sensitive detector this is also the experimental finding. At least we were never able to measure any increase of the noise power at low frequencies in our spectrometer.

2. Stability of the magnetic field

A very important point in this regard is the stability of the magnetic field. The fluctuations of the magnetic field and especially the fluctuations of very low frequency are strongly dependent on the sort of field stabilizer that is used. If no nmr-stabilizer is installed the drift stability will be of course not good enough to take spectra with a sweep time of several hours and even if a nmr-stabilizer with two separated probes, the control and the sample probe, is used, the maximum sweep time will be limited. In these cases the use of the CAT-method may be of advantage because the averaging over the n spectra will eliminate all fluctuations with frequencies lower than n/T . But after each run the zero point has to be adjusted by hand or automatically.

With a nmr-stabilizer with a single probe (compare MELLONMR No.33 p.19) the long-term stability is even better than the short-term stability. We have achieved a long-term stability of 0.0003 ppm over some days and this is of course by far enough for the successful use of the DOG-method.

3. Other advantages and disadvantages

An advantage of the CAT-method is that it is possible to follow up the increase of the sensitivity during the measurement and to stop when the sensitivity seems to be sufficient. This is impossible with the DOG-method. But the DOG-method has the great advantage that during the measurement no adjustments have to be made. Usually such extreme long-term spectra will be taken over night or even over the week-end. In these cases such a control is useless.

A further little advantage has the CAT-method, namely that it is possible to eliminate the fluctuations of the overall gain of the spectrometer. But these fluctuations are in general quite small and to be neglected.

A great disadvantage of the CAT-method is that the resolution will be significantly diminished by the finite number of points that will be taken into calculation. Here the information content of the spectrum will be diminished. With regard to the resolution the DOG-method is by far better.

4. Conclusion

If one has a spectrometer without a nmr-stabilizer the only alternative seems to be the CAT-method with all its advantages and disadvantages.

If one works with a spectrometer with a nmr-stabilizer with two separate probes it may be advantageous to use the CAT-method, but according to our experience even the A-60 is capable of much slower sweep rate and therefore we would prefer the much simpler DOG-method.

If one has a nmr-stabilizer with a single probe (a stabilizer of this sort is commercially available and relatively simple to construct) it is much more reasonable and simpler to use the DOG-method.

- (1) Primas, Arndt, Ernst: Z.Instrumentenkunde 68, 57 (1960)
- (2) Primas, Arndt, Ernst: Z.Instrumentenkunde 68, 59 (1960)

Yours sincerely,

R. Ernst

R. Ernst

Hans Primas

H. Primas



Eidg. Technische Hochschule

Laboratorium
für Physikalische Chemie
Zürich

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

Dear Dr. Shapiro:

The papers published till now on nmr double resonance make all some assumptions not always justified in the actually performed experiments. We therefore worked out an exact theory of double resonance in the density matrix formalism. Under certain circumstances there may be appreciable differences in the resonance frequencies and intensities (even in the number of observable lines!) between the exact and the simple theories. This work will be published soon, but here we only would like to warn against some pitfalls, especially in connection with strongly coupled systems.

E.g. in case of two coupled nuclei with spin 1/2

$$(\text{Hamiltonian } H = \Omega_A I_{AZ} + \Omega_B I_{BZ} + J \vec{I}_A \vec{I}_B + B_2 (F_x \cos \omega_2 t + F_y \sin \omega_2 t))$$

$$F_y = I_{Ay} + I_{By}$$

W. A. Anderson and R. Freeman (J. Chem. Phys. 37, 85 (1962) have given recently in the approximation of weak coupling as double resonance condition (condition for collapsing of two lines)

$$\omega_2 = \frac{\Omega_A + \Omega_B}{2} + 1/2 \sqrt{(\Omega_A - \Omega_B)^2 - 4\gamma^2 B_2^2}$$

(easily derived from their eq. 41)

But the exact result is

$$\omega_2 = \frac{\Omega_A + \Omega_B}{2} + 1/2 \sqrt{(\Omega_A - \Omega_B)^2 + J^2 - 4\gamma^2 B_2^2}$$

Because of the condition $\gamma B_2 \approx J$, this correction is important for double resonance experiments. For the case that $4\gamma^2 B_2^2 > (\Omega_A - \Omega_B)^2 + J^2$ there is a residual splitting and for $J = 2B_2$ the double resonance condition reduces to $\omega_2 = \Omega_A$ or $\omega_2 = \Omega_B$.

Yours sincerely

P. Bommer

P. Bommer

Hans Primas
H. Primas

ZÜRICH, September 20, 1962
Universitätsstrasse
Tel. (051) 327330

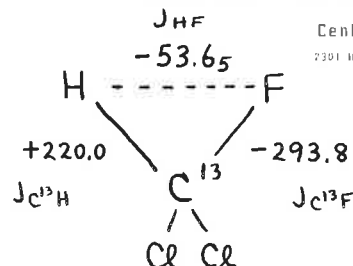


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Central Research Laboratories

2301 HUDSON ROAD • ST. PAUL 19, MINNESOTA

Sept. 24, 1962



Brevity is golden. Here are the results of $F\{H\}$ and of $F\{C^{13}\}$ spin decoupling experiments just concluded; actually I intend to repeat the work

on J_{HF} as the $F\{C^{13}\}$ modules were performing erratically (SD-60 Spin decoupler: NMR Specialties, Inc., Box 145, Greensburg Road, New Kensington, Pa.) and there is some slight possibility of error. In a separate investigation, a Kaiser-Type decoupler was used to find, for $C^{13}Cl_2F - CCl_2F$, $J_{C^{13}F} = -307.2$ c/s, and $J_{C^{13}CF} = +34.9$ c/s, the signals being taken in conformity with the above findings. Work continues apace; publications are "in press" or "in process."

George Van Dyke Tiers

Monthly

Encumencal

Letters from

Laboratories

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N - M - R

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