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Newsletter

No. 142
JULY, 1970

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O V E R

Deadline Dates: No. 143: 3 August 1970
No. 144: 7 September 1970

All Newsletter correspondence, etc., should be addressed to:

Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

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PLEASE ADDRESS REPLY TO
RESEARCH LABORATORIESTELEPHONE
AREA CODE 716 458-1000

May 25, 1970

Professor B. L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas 77843

Dear Barry:

SELECTION OF SPECTRAL REGIONS IN FOURIER TRANSFORM NMR.

In the past few months since we have been doing NMR by Fourier transform methods we have found two particular drawbacks to using the Varian C-1024 as our digitizer. One is its limited memory and the other the lack of vertical range (1 part in 512). The first limitation reduces the resolution we can obtain for a given spectral width. The second drawback limits our ability to distinguish weak resonances when there is a strong line in the spectrum. This is quite often the case when trying to observe spectra of solutes at concentrations below $10^{-3}M$. Even in aprotic solvents where concentrations are below $10^{-3}M$, the lock line contributes enough signal to cause small resonances to be masked by digitizing noise.

The resolution obtained from Fourier transformation of the FID can be expressed as the number of points in the spectrum divided by the highest frequency. If C equals the number of channels in the digitizer, then

$$C/2 = \text{number of points } \underline{\text{unique}} \text{ in frequency information (1)}$$

$$C/2T = \text{highest frequency (2)}$$

$$\therefore 1/T = \text{resolution (Hz/point) (3)}$$

Therefore, to increase resolution we must look for longer periods of time. At the same time in order to satisfy equation (2) we must insure that there are no frequencies higher than $C/2T$, otherwise these would be downconverted into the region we are interested in.

Professor B. L. Shapiro

-2-

May 25, 1970

The solution to both problems has been to use a very sharp low-pass filter on the free induction decay (FID) before digitization. The type of filter that can be used should have as sharp a cutoff as possible. A KROHNHITE model 3342 filter which has an attenuation rate of 96 dB/octave when the two sections are ganged is most suitable. We use either a KROHNHITE filter or a homemade unit with a fixed cutoff frequency of 100 Hz. The latter unit allows us to accumulate 5.0 seconds of the FID giving a resolution of 0.2 Hz per point.

In order to make full use of this filter one needs a way of offsetting the zero frequency point in the spectrum from lock. This can be accomplished by phase locking a second reference oscillator to the lock oscillator. In actual practice, all that must be done is to insure that the r.f. pulse is triggered at the point when both oscillators are at the same phase angle. This can be accomplished very simply as shown in Figure 1. The pulse trigger circuit described in our previous communication is used. (1) The circuit is also shown in Figure 1 since a modification has been added that increases the life of the thyatron. The underlined component values indicate the changes. The circuit is good for offsets from lock of 50-1000 Hz.

The aromatic region of the nmr spectrum of $10^{-3}M$ 1,1'-diethyl-2,2' cyanine chloride in D_2O is shown in Figure 2. The lower trace is obtained by Fourier transformation of the filtered FID. The other trace is the slow sweep spectrum. The large peak from residual HDO would have normally caused the aromatic proton signals to be masked by digitizing noise.

Please credit this contribution to the account of
Dr. P. I. Rose.

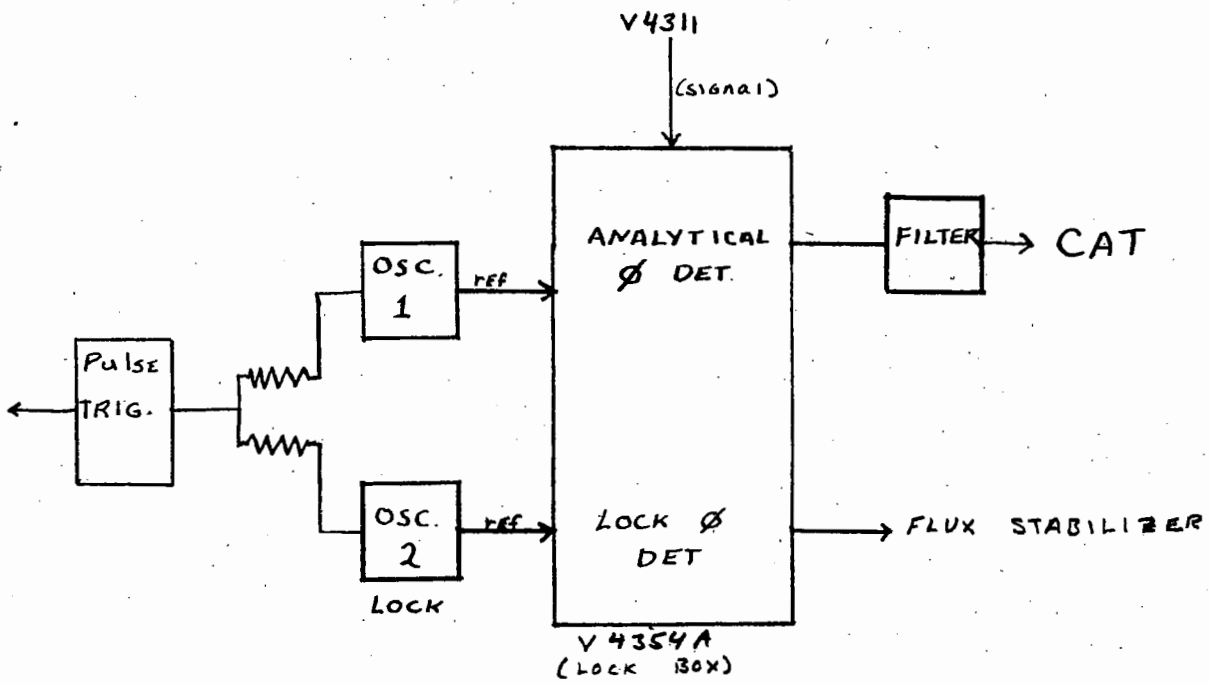
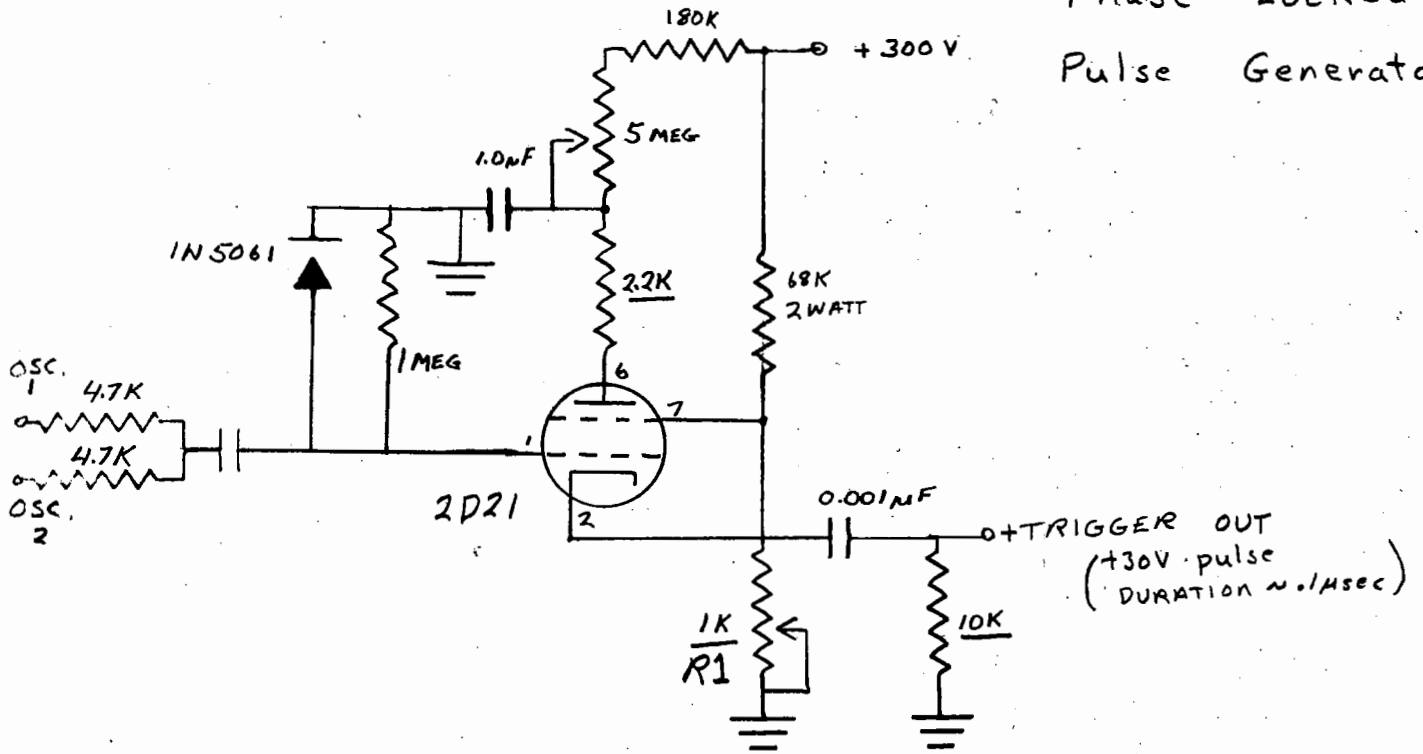
Richard E. Graves

Research Laboratories

REGraves:mw

(1) S. Gross, R. E. Graves, P. I. Rose, *Tamunmr* 131, 4 (1969)

Phase Locked
Pulse Generator



June 25, 1970.

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station Texas 77843 U.S.A.

A new description for a familiar phenomenon.

Dear Barry,

When polar molecules are dissolved in aromatic solvents, their pmr signals incur large shifts from their position in "inert" solvents such as cyclohexane or carbon tetrachloride. Considerable attention has been focussed upon the assumption of a discrete solute-solvent complex as an explanation for these solvent shifts, a model commendable for its intuitive simplicity, and which has gained widespread acceptance.

Consideration of various inadequacies of this model for weak interactions - i.e those characterized by apparent equilibrium constants smaller than ca.0.5 l/mole - has led us to seek an alternative. We have selected the camphor molecule as a polar solute whose various protons have well-defined positions relative to one another and to the carbonyl group.

The observed solvent shifts are obviously due to some kind of ordering of the aromatic solvent

molecules about the polar solute. The single most important feature of our model is the straightforward notion that, because of the slow time-scale of nuclear magnetic resonance, the interactions between the camphor solute and its aromatic solvents will be time-averaged. According to the notion of a clustering of solvent molecules around the polar sites of the solute, because of this time-averaging, the solvent shift can be decomposed into a site factor and a solvent parameter. The former depends only on the geometry of the solute, while the latter reflects the size of solvent molecules - in fact their concentration - together with the truly intrinsic part of the solute-solvent interaction. The factors to be discerned are primarily dipolar and magnetic susceptibility contributions from within the solvent molecule.

It is impossible in such a brief letter to summarize all of our arguments and experiments. The Figure is a graph of the solvent shift for the C-9 methyl in camphor versus those for the C-8 methyl for something like 50 aromatic solvents of all sorts, polar and non-polar. The slope is simply the ratio of the site factors for the 8- and the 9-methyl group with respect to the solvated carbonyl group, which we approximate by the McConnell dipolar term.

We have elaborated a general and quantitative treatment, which is very satisfactorily in accounting for and predicting the experimental data. It will be described in the full paper, which we are preparing.

Best regards,

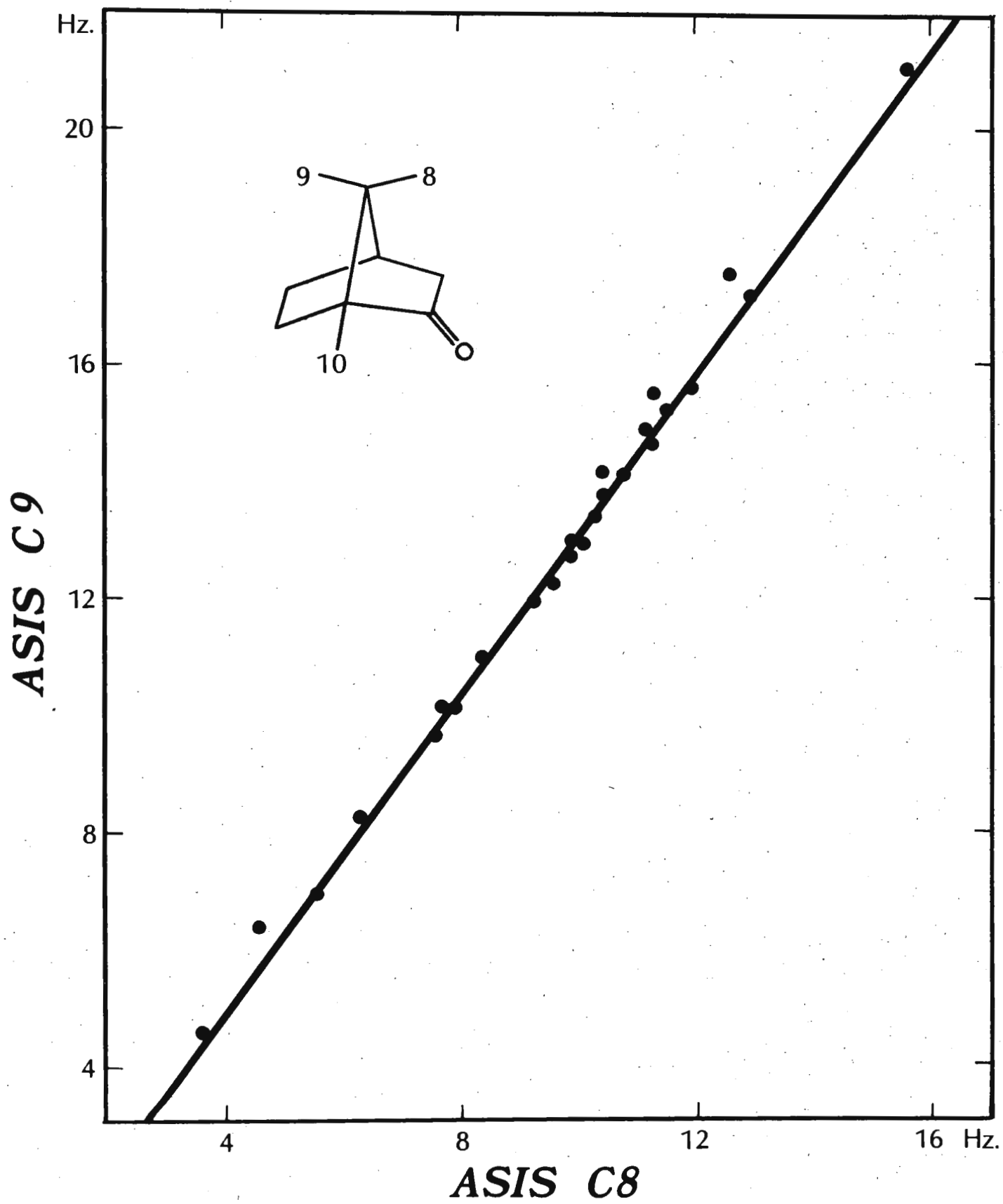


Edward M. Engler



Pierre Laszlo

Encl.



Dr. W. Brügel, Dr. M. Patsch c/o
Badische Anilin- & Soda-Fabrik AG

BASF

Telefon (06 21) 601 (Vermittlung)
Telex 464 811 basf d (Zentrale)
Telegramme: BASF Ludwigshafenrhein
Bankverbindung: Landeszentralbank
6700 Ludwigshafen, Girokonto 51/82

BASF · 6700 Ludwigshafen

Prof. Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University

College Station, Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Telex	6700 Ludwigshafen
		Brü/Pat/Fa	(06 21) 60-	464	18. Juni 1970

Betreff Dependence of aromatic proton chemical shift in phenol solutions on pH

Sehr geehrter Herr Dr. Shapiro!

In den vergangenen Jahren wurde eine Anzahl von Untersuchungen über NMR-Spektren von Säuren und Basen veröffentlicht. Meist handelte es sich um Amin/Ammoniumsalzgemische in wässrigen Lösungen [1]. Uns sind keine Untersuchungen bekannt, wo ähnliche Messungen an Phenol/Phenolat-Gemischen durchgeführt wurden.

Wir haben in den letzten Wochen eine Reihe von Phenolen und Phenolaten mit unserem 220-MHz-Gerät untersucht. Erwartungsgemäß absorbieren die aromatischen Protonen der Phenolate im Vergleich zu den entsprechenden Phenolen bei höherem Feld (relativ zu TMS). Die Lage der Aromatensignale in Mischungen hängt vom Verhältnis der beiden Komponenten ab, d.h. vom pH-Wert der Lösung. Da die Phenole bei tieferem Feld absorbieren als die Phenolate, verschieben sich die Aromatensignale mit zunehmender Basizität der Lösung nach höherem Feld.

- 2 -

Empfänger

Unsere Zeichen

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Blatt

Prof. Dr. B.L. Shapiro

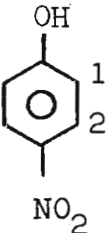
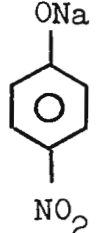
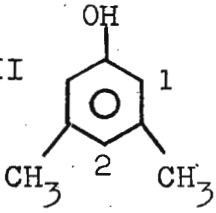
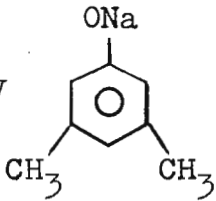
Brü/Pat/Fa

18. Juni 1970

2

Betreff

Wir benutzten für unsere Messungen d_6 -Dimethylsulfoxid und d_4 -Methanol; Temperatur im Meßraum war 17°C .

	Lösungsmittel	H 1 (Hz)	H 2 (Hz)
I		d_6 -DMSO	1528 1542 1785 1796
II		"	1337 1345 1711 1722
I/II = 2:1	"	1483 1494	1764 1777
I/II = 1:2	"	1456 1465	1757 1766
III		d_4 -Methanol	1404 1420
IV		"	1375 1337

Badische Anilin- & Soda-Fabrik AG

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Prof. Dr. B.L. Shapiro

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18. Juni 1970

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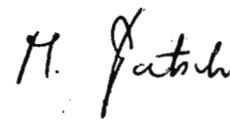
Betreff

Zum Schluß möchten wir Ihnen noch mitteilen, daß die spektroskopische Gruppe in unserem Hauptlaboratorium vergrößert wurde um die Herren Dr. Friebolin und Dr. Patsch. Wir bitten, in Zukunft auch die Beiträge dieser neuen Kollegen für die BASF gutzuschreiben.

Mit freundlichen Grüßen



(Dr. W. Brügel)



(Dr. M. Patsch)

- [1] H. Suhr, Anwendung der NMR-Spektroskopie in der Organischen Chemie, Springer Verlag 1965, S. 332

Koninklijke / Shell - Laboratorium, Amsterdam

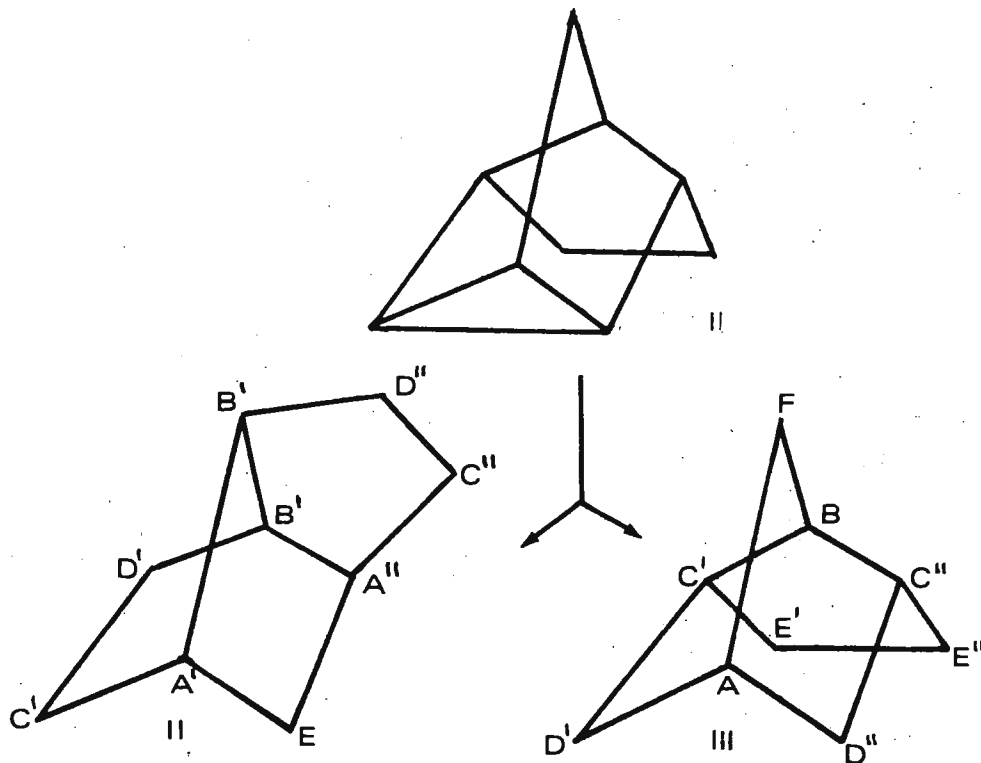
BADHUISWEG 3, AMSTERDAM - N.

TELEFOON (0 20) - 36 11 11

Dear Professor Shapiro,

Structure elucidation of a tricyclononane by means of ^{13}C NMR

The catalytic hydrogenation of tetracyclo [4.3.0.0³,7.0²,9] nonane (I) results in a compound C_9H_{14} the structure of which has been investigated with 220 MHz PMR and 25.1 MHz ^{13}C NMR. It is evident from both the proton and ^{13}C spectrum that no CH_3 groups or cyclopropyl rings are present. This reduces the number of possibilities to two, viz. II and III.



In order to distinguish between these two possibilities, we ran three ^{13}C spectra of the undiluted liquid sample and obtained the following evidence:

The noise-decoupled spectrum (A) showed five signals at 146.3, 151.4, 160.3, 160.6, and 169.5 ppm (with respect to CS_2) with relative intensities 2 : 2 : 1 : 2 : 2.

In the partially decoupled spectrum (B) the two low-field signals at 146.3 and 151.4 ppm were split into doublets, while those at 160.6 and 169.5 ppm became triplets. The observed multiplicities clearly indicated that the low-field signals originated from two sets of two equivalent CH groups, and the two high-field signals from two sets of two equivalent

- 2 -

CH₂ groups. The one carbon signal at 160.3 ppm could not be assigned by the procedure, because of overlap by the triplet at 160.9 ppm.

In the proton-coupled ¹³C spectrum the 160.3 ppm signal was also split into a triplet and hence the molecule contained four CH and five CH₂ groups.

The numbers of equivalent carbon atoms correspond to structure II, viz. the CH groups A' = A'' and B' = B'' and the CH₂ groups C' = C'', D' = D'' and E, but not to III, which contains three types of CH, viz. A, B and C' = C''.

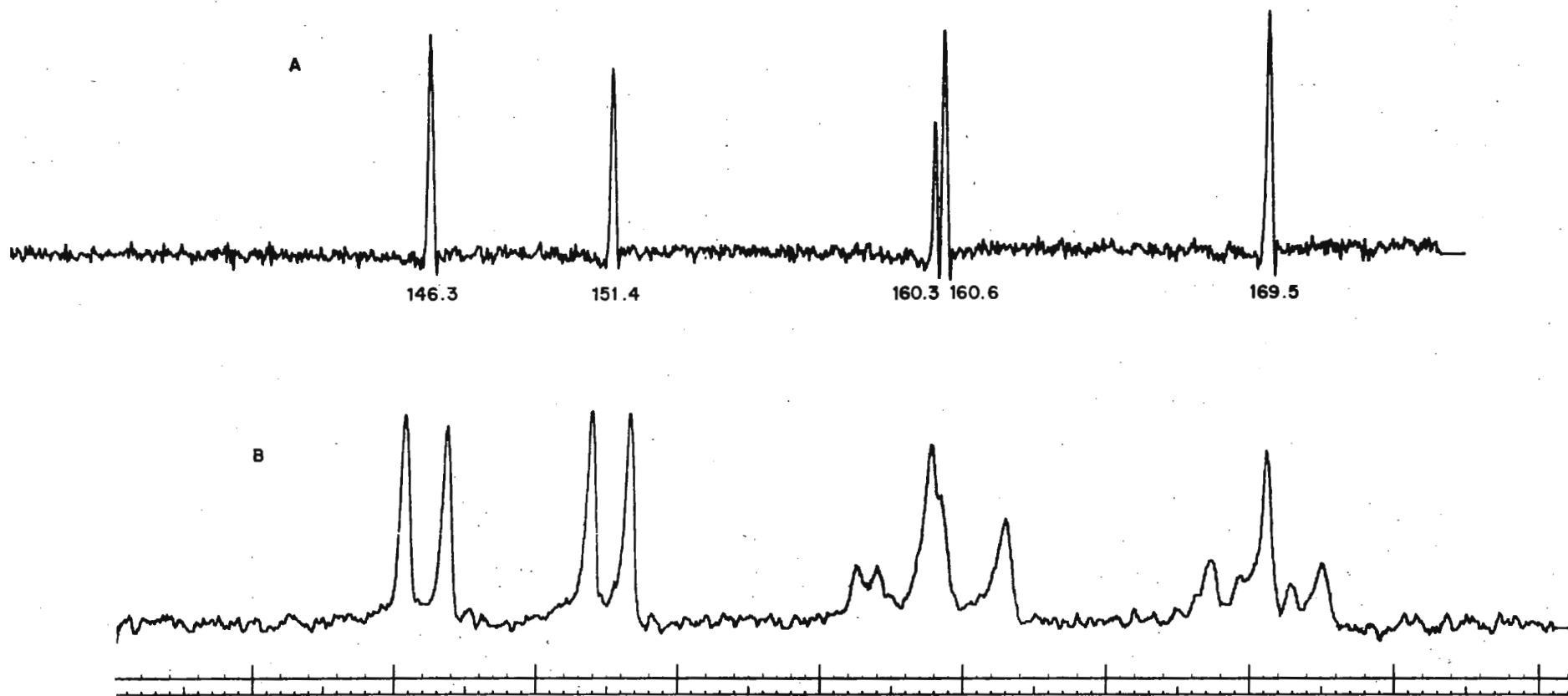
We have not attempted to assign the signals to individual CH and CH₂ groups (except E). Taking the origin of the product and its empirical formula into account, however, the conclusion seems warranted that the reaction product is an equimolar mixture of structure II and its mirror image.

Yours sincerely,



A.D.H. Clague

Amsterdam, 18th June 1970



^{13}C SPECTRA OF TRICYCLONONANE

A PROTON - DECOUPLED

B PARTIALLY DECOUPLED

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT

69 HEIDELBERG 1, June 18, 1970
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Tel. 56/2411
bei Durchwahl 56.....

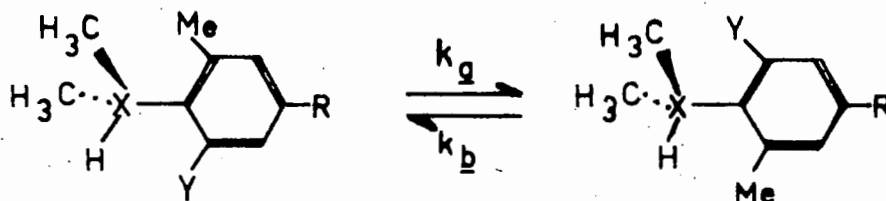
Albrecht Mannschreck, Ludger Ernst, Elmar Keck

Professor B.L.Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas

Rotamers with Respect to the sp^3 - sp^2 Bonds
in Toluenes and Anilinium Ions

Dear Professor Shapiro,

we have studied rotamers of toluenes, e.g. 1a/1b and 2a/2b, and of anilinium ions, such as 4a/4b and 5a/5b, in order to investigate nonbonded interactions between ortho substituents and groups at the sp^3 center. In the stable conformations (see formulae) the hydrogen at the sp^3 center eclipses an ortho substituent, evidence



		<u>a</u>	<u>b</u>	$\overline{\Delta G^\ddagger}$ kcal/mole
Toluenes, X = C	<u>1</u> , Y = Cl	33%	67%	13.6 (-28°)
	<u>2</u> , Y = Br	54%	46%	14.4 (-9°)
	<u>3</u> , Y = Me	-	-	12.8 (-35°) ¹⁾
Anilinium Ions, X = N [⊕]	<u>4</u> , Y = Cl	45%	55%	17.3 (+49°)
	<u>5</u> , Y = Br	65%	35%	17.7 (+54°)
	<u>6</u> , Y = Me	-	-	15.9 (+26°) ¹⁾

for this being derived from the literature^{1,2,3)} and from a Westheimer-Hendrickson-Wiberg (WHW) calculation for 3. We have found two sets of $^1\text{H-NMR}$ signals for toluenes 1 and 2 in CS_2 at -55° and for anilinium ions 4 and 5 in CF_3COOH at $+27^\circ$. For instance, α -H, ortho methyl, and α -methyl groups in 1a resonate at $\tau = 6.18$, 7.63, and 8.74, respectively; the values for 1b are 6.69, 7.72, and 8.65. All rotamers a and b were correlated with the sets of signals by comparison of chemical shifts with those of the corresponding 2,6-dimethyl derivatives 3 and 6.

The populations of rotamers a and b depend upon nonbonded interactions in the favoured conformations. An ortho substituent interacts either with one eclipsed hydrogen or with two gauche CH_3 groups at the sp^3 center. According to the above mentioned WHW calculation for 3, the sum of these two gauche interactions is more repulsive than the single eclipsed one. If this result is presumed to be generally valid, the percentages of a and b (see table) can be qualitatively interpreted by steric requirements in the order $\text{Br-C} > \text{Me-C} > \text{Cl-C}$.

The barriers to rotation are given in the table for the sake of simplicity as mean values $\overline{\Delta G^\ddagger}$, derived from $\bar{k} \equiv 0.5 (k_a + k_b)$. Coalescence⁴⁾ of ortho methyl signals resulted in k_a and k_b . Barriers for the halogen-containing toluenes 1 and 2 as well as for α,α -dichloro-2,4,6-trimethyltoluene (14.0 kcal/mole, -12°) can be compared with $\Delta G^\ddagger = 12.8$ kcal/mole for α,α -2,4,6-pentamethyltoluene (3). A similar barrier decrease is found when halogen atoms in the anilinium ions⁵⁾ 4 and 5 are replaced by methyl groups: Only 15.9 kcal/mole were found for N,N,2,6-tetramethylanilinium ion (6). These kinetic results apparently do not fit

into the above order of steric requirements derived from rotamer populations. We hope to explain this unexpected behavior by WHW calculations for la and lb. We should be grateful for any comments concerning this problem.

Sincerely yours,

Albrecht Mannschreck *Ludger Ernst*

Albrecht Mannschreck

Ludger Ernst

Elmar Keck

Elmar Keck

-
- 1) A.Mannschreck and L.Ernst, Tetrahedron Letters 1968, 5939.
 - 2) T.Schaefer, R.Schwenk, C.J.Mcdonald, and W.F.Reynolds, Canad. J.Chem. 46, 2187 (1968); cf. T.Schaefer, TAMUNN 130, 19 (1969).
 - 3) A.Mannschreck and H.Muensch, Tetrahedron Letters 1968, 3227; R.D.Chambers, J.A.Jackson, W.K.R.Musgrave, L.H.Sutcliffe, and G.J.T.Tiddy, Tetrahedron 26, 71 (1970); see however F.W.van Deursen and G.Breman, TAMUNN 139, 4 (1970).
 - 4) Cf. A.Jaeschke, H.Muensch, H.G.Schmid, H.Friebolin, and A.Mannschreck, J.Molec.Spectry. 31, 14 (1969).
 - 5) The interconversions $\underline{a} \rightleftharpoons \underline{b}$ of anilinium ions might also occur via deprotonation, inversion, and reprotonation. We suppose the barriers in the table to be due to rotation in the ions because CH-NH coupling is preserved in CF_3COOH (0.3 m) above the coalescence temperatures.

UNIVERSITY OF ILLINOIS

Department of
CHEMISTRY AND CHEMICAL ENGINEERING

URBANA

61801

The William Albert Noyes Laboratory

June 5, 1970

Dr. Barry L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77843

Dear Barry:

Density Dependence of ^{129}Xe Chemical Shifts in Gaseous Mixtures
(A. K. Jameson, C. J. Jameson, and H. S. Gutowsky)

Keith (Loyola University) and Cynthia Jameson (University of Illinois at Chicago Circle) have recently completed a paper on xenon chemical shifts as a function of density in mixtures with other gases. The experiments were done here at Urbana by Keith, so perhaps you'll permit me to use their results to pay my subscription to the TAMU NMR Newsletter.

In any event, unlike other chemical shifts in gaseous systems which have been found to have strictly linear dependence on density, we have found the ^{129}Xe chemical shift in pure xenon gas to have a quadratic and cubic dependence in addition to the dominant linear dependence on density. This implies the importance of three or more body interactions in xenon. In mixtures of xenon with another gas (Ar, Kr, CO_2 , HCl, CH_4 , CH_3F , CH_2F_2 , CHF_3 , CF_4), the dependence of the ^{129}Xe chemical shift on the density of the other gas is found to be linear within experimental error, and varying from 2300 to 11,700 ppm/mole cc^{-1} . These shifts are orders of magnitude greater than the reported H and F shifts in gases. Analysis of the results show that the density dependence can not adequately be reproduced by the contributions

$$\sigma_1 = \sigma_b - B\langle \epsilon^2 \rangle - B\langle F^2 \rangle$$

which had been adequate for H and F shifts.

The general formulation for calculation of the A and B parameters, the coefficients of the linear and quadratic electric field terms in the theory of chemical shift in gases, is developed. An approximate calculation of B for atoms is given, and the repulsive and anisotropic contributions are estimated. The sensitivity of the chemical shift to the form of the intermolecular potential is suggested in the case of Xe and the fluoromethanes where the results are consistent with a non-central field potential but not with a central field potential like the Lennard-Jones.

Preprints are available.

With best regards,


H. S. Gutowsky

HSG/amw

cc: A. K. Jameson
C. J. Jameson

PHYSIQUE EXPÉRIMENTALE MOLÉCULAIRE

FACULTÉ DES SCIENCES

9, Quai Saint-Bernard - 75 - PARIS (5^e)Tour 32 - 2^e étage

Tél. : 336-25-25 - Poste 40-53

Paris, le 29 Janvier 1970

Professor Bernard L. SHAPIRO
 Department of Chemistry
 Texas A and M. University
 College Station

TEXAS 77843 (U.S.A.)

70.206/MS/MC

Cher Docteur Shapiro,

Tautomérie de composés hétérocycliques

Nous avons étendu nos recherches sur la tautomérie des composés hétérocycliques (1 et 2) à l'étude de la tautomérie thiol-thione et ol-one en -2 du phényl-4 et du p-chlorophényl-4-thiazole.

Nous avons pour cela été amenés à synthétiser les modèles moléculaires correspondants aux formes thiazole (1, 2, 3) et thiazoline type (4, 5, 6, 7,), c'est-à-dire, dans le cas envisagé, ceux des dérivés S-méthylé et O-méthylés en -2 et N-méthylés en -3 correspondants.

Les résultats que nous avons obtenus en R.M.N. nous ont montré que le seul examen des signaux du groupement phényle ou p-chlorophényle en -4 permet une diagnose sûre de la structure thiazole ou thiazoline. Dans le cas de la structure thiazole, le phényle en -4 présente la structure à 2 multiplets d'un système AB_2C_2 ou la structure d'un système A_2B_2 dans le cas de la substitution en para par un chlore, mais c'est un singulet dans le cas d'une structure thiazoline. Nous avons ainsi pu mettre en évidence l'influence des solvants sur la forme tautomère prépondérante. Le diméthylsulfoxyde deutérié favorise l'énol ou l'énethiol ; le méthanol stabilise la forme carbonylée ou la thione ; l'acétone favorise la forme carbonylée ou le thiol. D'une manière générale, comme on pouvait le prévoir, l'équilibre est d'autant plus décalé vers la forme énolique que le solvant est plus basique, plus apte à s'associer par liaison hydrogène comme attracteur de proton.

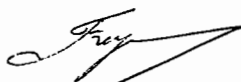
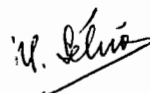
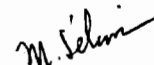
Nous présentons nos résultats sous forme de tableaux indiquant les déplacements chimiques en ppm (TMS en référence interne, concentration molaire de l'ordre de 1% - 60 MHz, A 60).

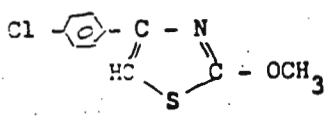
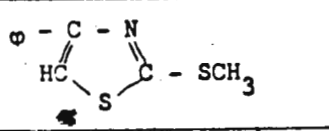
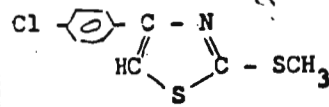
Avec nos sentiments cordiaux.

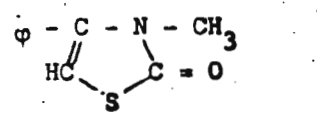
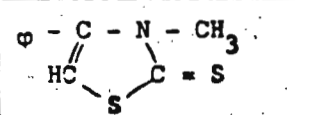
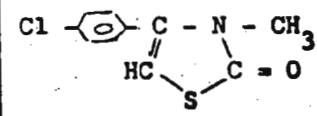
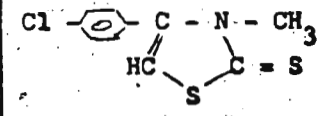
R. FREYMANN

M. SELIM

M. SELIM

Thiazole	Groupement phényle ou p-Cl phényle en -4 δ en ppm			H en -5	Solvant
	δ ortho	δ méta, para ou δ méta	δ ortho- δ méta, para ou δ ortho- δ méta, para		
	7,89	7,42	0,47	7,46	CD ₃ -SO-CD ₃
	7,80	7,26	0,54	7,13	CCl ₄
	7,88	7,38	0,50	7,31	CDCl ₃
	8,01	7,47	0,51	7,95	CD ₃ -SO-CD ₃
	7,95	7,45	0,50	8,01	CD ₃ -SO-CD ₃

Thiazoline	Groupement phényle ou p-Cl phényle en -4 Singulet. δ en ppm	H en -5	Solvant
	7,38	5,90	CCl ₄
	7,47	6,01	CDCl ₃
	7,50	6,63	CH ₃ -CO-CH ₃
	7,51	6,83	CD ₃ -SO-CD ₃
	7,48	7,41	CCl ₄
	7,46	7,46	CDCl ₃
	7,45	7,71	CD ₃ -SO-CD ₃
	7,53	6,45	CD ₃ -SO-CD ₃
	7,55	7,07	CD ₃ -SO-CD ₃

Thiazole ou thiazoline Forme prépondérante	Groupement phényle ou p-Cl phényle en -4. 1 ou 2 multiplets suivant le solvant			H en -5	Solvant
	δ ortho	δ méta, para ou δ méta	δ ortho - δ méta, para ou δ méta		
$\begin{array}{c} \text{C} - \text{C} - \text{NH} \\ \text{HC} \quad \text{S} \quad \text{C} = \text{O} \end{array}$		7,53		6,58	CH ₃ OH
$\begin{array}{c} \phi - \text{C} - \text{N} \\ \text{HC} \quad \text{S} \quad \text{C} - \text{OH} \end{array}$	7,68	7,45	0,23	6,81	CD ₃ -SO-CD ₃
$\begin{array}{c} \text{Cl} - \phi - \text{C} - \text{NH} \\ \text{HC} \quad \text{S} \quad \text{C} = \text{O} \end{array}$		7,51		6,62	CH ₃ -CO-CH ₃
$\begin{array}{c} \text{Cl} - \phi - \text{C} - \text{N} \\ \text{HC} \quad \text{S} \quad \text{C} - \text{OH} \end{array}$	7,68	7,46 7,39	0,29	6,55 6,76	CH ₃ -OH CD ₃ -SO-CD ₃
$\begin{array}{c} \phi - \text{C} - \text{NH} \\ \text{HC} \quad \text{S} \quad \text{C} = \text{S} \end{array}$		7,47		6,70	CDCl ₃
$\begin{array}{c} \phi - \text{C} - \text{NH} \\ \text{HC} \quad \text{S} \quad \text{C} = \text{S} \end{array}$		7,67		6,98	CH ₃ OH
$\begin{array}{c} \phi - \text{C} - \text{N} \\ \text{HC} \quad \text{S} \quad \text{C} - \text{SH} \end{array}$	7,76	7,49	0,27	7,35	CD ₃ -SO-CD ₃
$\begin{array}{c} \text{Cl} - \phi - \text{C} - \text{N} \\ \text{HC} \quad \text{S} \quad \text{C} - \text{SH} \end{array}$	7,75	7,42	0,33	7,05	CH ₃ -CO-CH ₃
$\begin{array}{c} \text{Cl} - \phi - \text{C} - \text{NH} \\ \text{HC} \quad \text{S} \quad \text{C} = \text{S} \end{array}$		7,52		7,02	CH ₃ OH
$\begin{array}{c} \text{Cl} - \phi - \text{C} - \text{N} \\ \text{HC} \quad \text{S} \quad \text{C} - \text{SH} \end{array}$	7,79	7,48	0,31	7,30	CD ₃ -SO-CD ₃



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GENEVE

GJB/sb

Genève, le 16 juin 1970

Professeur Bernard L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science

College Station, Texas 77843
U.S.A.

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 2 juin 1970.

1. XVIth COLLOQUE AMPERE
"MAGNETIC RESONANCES AND RELATED PHENOMENA"
Bucharest - Romania, September 1-5, 1970.

The XVIth Colloque AMPERE will be held in the building of the Congress Hall of the Republic's Palace (Sala Palatului Republicii) in the centre of Bucharest.

The programme of this Colloque will contain communications from the field of the magnetic resonance (electron spin resonance, nuclear magnetic resonance, cyclotron resonance, ferromagnetic resonance, acoustic magnetic resonance, double resonance phenomena : ENDOR, ELDOR etc.) and of all the related phenomena (paramagnetic relaxation, nuclei polarisation, magneto-optics phenomena, some aspects of the Mössbauer effect theory or of the laser and maser theory, etc.). The sections and their programme will be fixed by the Reading Committee after the examination of the papers :

The sessions will be devoted to :

1. Invited papers
2. Short communications to be presented in formal sessions
3. Communications to be discussed in "Round Table" sessions.

The authors of the papers are requested to present especially papers dealing with problems of Physics.

The daily programme will contain in the morning plenary sessions devoted to the invited lectures, which will be followed by the formal sessions and "Round Table" sessions. There will be 4-6 concomitant sessions, depending on the number of the submitted papers and on their character.

Prof. Bernard L. SHAPIRO, College Station, Texas - 16.6.1970

Registration and Hotel Reservation

Persons wishing to participate in the XVIth Colloque AMPERE or to make hotel reservation are kindly requested to fill in the enclosed Registration Form and Reservation Card and to send them to the Secretariat of the Colloque until May 30, 1970.

Please write to the full address :

Dr. V. LUPEI
Congresul Ampere
Institutul de Fizica Atomica
C.P. 35, BUCURESTI
Romania

The organizing Committee does not take upon itself the responsibility for the strayed or late correspondence, which do not have the full address.

Participation Fee

The participation fee for each scientific member of the Congress is 30 US dollars. Its payment entails the participant to take part in the works of the Colloque and at the coctail offered to the participants and to receive the Proceeding of the Colloque.

The participation fee can be paid :

1. Either on the account of Banca de Comert Exterior - Calea Victoriei nr. 22-24 Bucuresti, cont nr. 471.2.111, with the mention "IFA - Congresul AMPERE", indicating the name of the participant for whom the payment is being effected.
2. Or at the seat of the Conference, upon the arrival in Bucharest. The participants are kindly requested to resort to this last possibility only for exceptional, well justified cases.

The scientific participants are kindly requested to indicate in the Registration Form and in the Reservation Card the number of the persons who will accompany them, and their names. The participation fee for each nonprofessional participant (except children) is 10 \$ and its payment will be effected concurrently with the payment of the scientific participant's participation fee.

The participation fee for the Banquet is of 7 US \$ and may be paid at the Secretariat of the Congress.

Prof. Bernard L. SHAPIRO, College Station, Texas - 16.6.1970

Exhibitions

For the occasion of the Colloque an exhibition of scientific instrumentation will be organised. Will be exhibited instrumentation, and the demonstrations will be made with the instrumentation from various fields as : EPR and NMR spectrometers, double resonances, various accessories, magnets, superconducting materials, magneto-optics, quantum amplifiers or generators, cryogenics etc.

Social Programme

During the Colloque a cultural, social and tourist's programme will be organised. This programme will contain tourists films, folkshow, visits to some historical and art monuments of Bucharest etc.

A Ladies Programme will be organised which will contain the city tour, visit to art Museums and historical monuments, folkshow, etc. The registration for the Ladies programme will be made at the seat of the Congress.

The scientific programme of the Congress will end on Saturday, 5th September at twelve o'clock. After the Congress several excursions will be organised.

In the hall of the Congress building an Exchange Office will be permanently open.

The following facilities will be also provided : international telephones, telex, post-office, bar, refreshment room, etc.

2. PRECESSION LIBRE DANS LES CHAMPS FAIBLES ET PARTICULIEREMENT DANS LE CHAMP MAGNETIQUE TERRESTRE

Le dispositif permettant l'observation des échos rotatoires à fréquence zéro C.R. Acad. Sc. Paris B 268, 1446-8, 1969 a été décrit en détail à la réunion de printemps de la Société suisse de Physique le 1 mai 1970

B. Borcard

"UN DISPOSITIF POUR L'OBSERVATION D'ECHOS ROTATOIRES A FREQUENCE ZERO"

On rappelle d'abord le processus de production d'échos rotatoires à fréquence zéro observés antérieurement. Les caractéristiques du

Prof. Bernard L. SHAPIRO, College Station, Texas - 16.6.1970

dispositif utilisé sont analysées. Leur influence sur la forme, l'amplitude des échos et leur amortissement est brièvement décrite. On insistera sur l'influence d'un champ statique résiduel.

L'excitation par une technique un peu différente (impulsions périodiques) a permis, dans des systèmes pour lesquels T_2 (relaxation transversale) T_1 (relaxation longitudinale) l'observation d'un phénomène nouveau, les "pseudo-échos" fournissant un moyen simple de mesure de T_1 , T_2 et de l'amplitude du champ exciteur.

B. Borcard et G. J. Béné

"RESONANCE MAGNETIQUE NUCLEAIRE"

Une méthode nouvelle de détermination rapide des temps de relaxation. Pseudo-échos en champ faible.

C.R. Acad. Sc. Paris, B 270, 634-636 (1970).

Une analyse détaillée de ces phénomènes permet de prévoir l'observation des échos à fréquence zéro sans impulsions, à l'aide d'un simple champ alternatif transversal de pulsation et d'amplitude convenables.

G. J. Béné

"ECHOS DE SPINS NON RESONNANTS"

Séance de la SPHN Genève, 21 mai 1970

Une étude d'ensemble des systèmes caractérisés par une dissymétrie de population entre sous-niveaux magnétiques dégénérés est proposée - on insiste surtout sur les méthodes de production et de détection d'une telle situation.

G. J. Béné

"DISSYMETRIE DE POPULATION ENTRE SOUS-NIVEAUX MAGNETIQUES DEGENERES"

Séance de la SPHN Genève, 21 mai 1970

(préprints disponibles).


Je signale pour terminer que nos travaux sur la haute résolution en champ faible ont fait l'objet d'un rapport d'ensemble intitulé

"SPECTRES DE HAUTE RESOLUTION DANS LE CHAMP MAGNETIQUE TERRESTRE"

G. J. Béné

qui sera publié dans le No 8 (1970) de la Revue Roumaine de Physique.

Croyez, cher Professeur Shapiro, à mes meilleurs sentiments.



Prof. G. J. Béné



NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7.

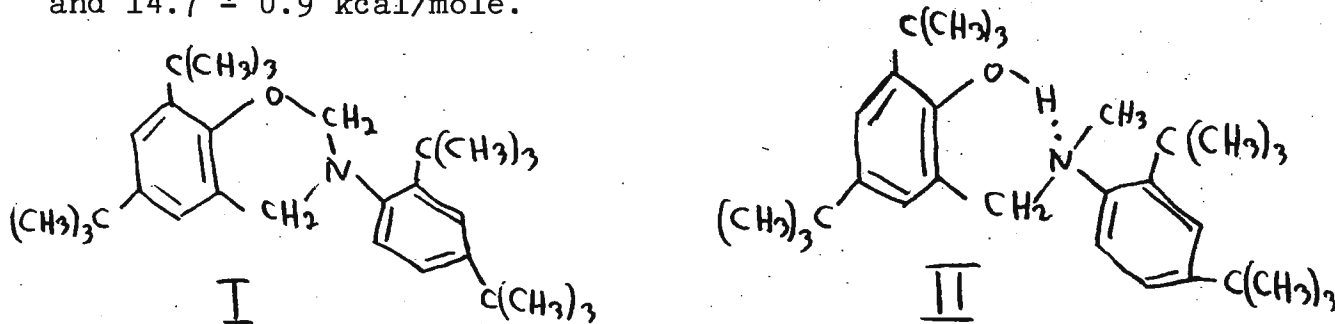
July 3, 1970

Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
College Station,
Texas 77843,
U. S. A.

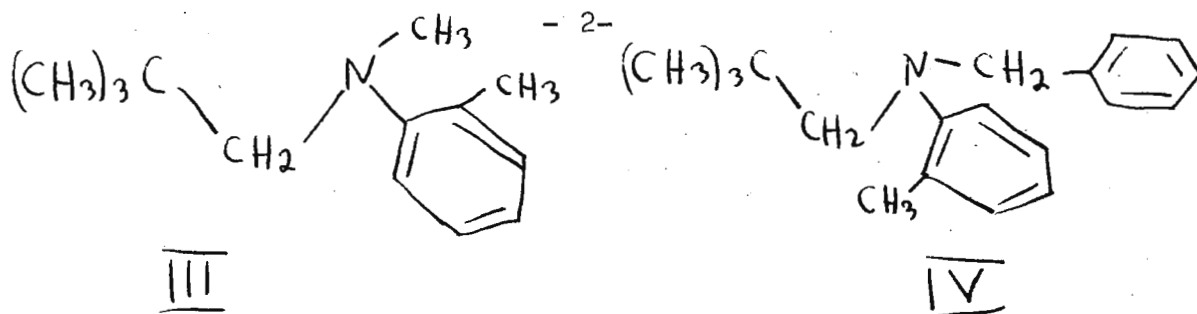
Hindered Rotation about Nitrogen-Carbon Bonds

Dear Barry,

After a fine sabbatical year I returned to Ottawa to find your blue letter awaiting me. Since we are just beginning some new investigations I can only report on some new wrinkles in one continuing study. In TAMUNMRN # 124 and 133 I wrote about structures I and II with activation enthalpies to rotation about the aromatic carbon-nitrogen bond of 16.9 ± 0.3 kcal/mole and 14.7 ± 0.9 kcal/mole.



I have now found that a ring or pseudo-ring containing the CH_2 group is not necessary for the observation of hindered rotation. In compounds III and IV the non-equivalence of the neopentyl $-\text{CH}_2$ protons is attributed to hindered rotation about the neopentyl carbon-nitrogen bond.



From an analysis of lineshape versus temperature for the AB quartet of the methylene protons activation enthalpies to rotation of 9.1 ± 0.2 kcal/mole and 8.3 ± 0.4 kcal/mole were obtained for III and IV in CS_2 as solvent. The proton resonance spectrum of IV is particularly interesting since at low temperature AB quartets are observed for both CH_2 groups. For the neopentyl methylene protons $J_{AB}=13.5$ Hz and $\delta_{AB}=0.48$ p.p.m. while for the benzylic methylene group $J_{AB}=14.5$ Hz and $\delta_{AB}=0.12$ p.p.m. The following interpretation is offered for this phenomenon.

Hindered rotation about the neopentyl carbon-nitrogen bond will cause non-equivalence of the neopentyl methylene protons and will also produce an asymmetric centre. Because of the asymmetric centre the benzylic methylene protons will be non-equivalent regardless of the rate of rotation about the benzylic carbon-nitrogen bond. However the extent of non-equivalence of the benzylic methylene protons would be expected to be less than for the neopentyl methylene protons.

Yours truly,

S. Brownstein

SB/md

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

July 1, 1970

DEPARTMENT OF CHEMISTRY

Professor Bernard L. Shapiro
Department of Chemistry
Texas A. & M. University
College Station, Texas 77843

Dear Barry:

Deuterium NMR on the XL-100-15

We wish to report obtaining deuterium spectra at 15.4 MHz on our recently acquired Varian XL-100-15. This unlocked field sweep method is very simple and appears to give spectra of reasonable quality.

In normal operation the deuterium signal is displayed on the oscilloscope by utilizing the deuterium lock preamp and observing the lock channel. It is a matter of a simple banana plug connection to feed the scope vertical signal into the external recorder outlet (J028). By operating the recorder in the external mode and simultaneously sweeping the field with the V-3508 Flux Stabilizer one can obtain a spectrum. For best results, the spectrum is recorded with the Linear Sweep Module turned off.

We have obtained the spectra of several deuterated aromatic compounds using this method. The spectrum of a deuterated iodobenzene is shown in Fig. 1. This compound was prepared by Professor G. B. Savitsky and coworkers at Clemson University. No spin-spin coupling is resolved. The full linewidth at the half height varies from about 1.6 to 2.0 Hz. The difference in the ortho and meta chemical shifts is 0.64 p.p.m. Assuming the relative order of the deuteron chemical shifts is the same as the proton chemical shifts in the protonated compound, the difference in the ortho and para chemical shifts is 0.42 p.p.m. This agrees well with Spiesscke and Schneider's values of 0.65 and 0.43, respectively, for the proton spectrum of iodobenzene [*J. Chem. Phys.*, **35**, 731 (1961)]. Our values are the average of five spectra calibrated by the sideband method with the Linear Sweep Module set at its slowest sweep. The Linear Sweep Module was left on during spectrum calibration in order to provide a convenient way of getting the audio modulation into the sweep coils.

One can of course also determine deuterium chemical shifts by locking on a deuterated compound and observing a reference peak in, say, the proton spectrum. In determining relative deuterium chemical shifts by

Professor Bernard L. Shapiro
July 1, 1970

this method one must measure the lock frequency as well as the observing frequency since a change in the frequency of the deuterium master oscillator causes a corresponding 6.5-fold change in the observing proton frequency.

Sincerely yours,

Wallace S. Brey, Jr.
Wallace S. Brey, Jr.

Ronald E. Block
Ronald E. Block



Figure 1.

LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918

69 - VILLEURBANNE

TÉL. (78) 52.07.04 et 52.12.29

Villeurbanne, le 1 Juillet 1970.

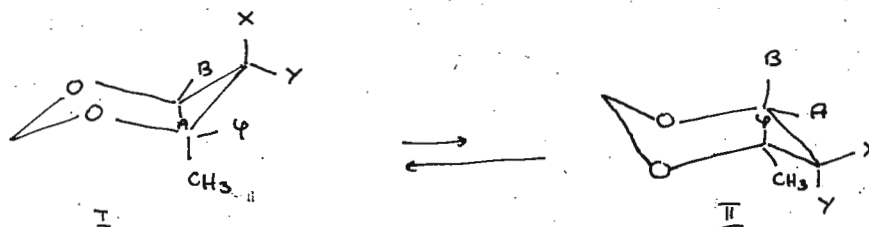
Professeur B.L. SHAPIRO
 Department of Chemistry
 Texas ASM University
 College Station, TEXAS 77843

Spectre du Phényl-4-Méthyl-4-dioxanne-1,3.

Cher Docteur SHAPIRO,

Il est intéressant de comparer, dans un dioxanne-1,3 les interactions axiales d'un phényle et d'un méthyle.

Nous avons examiné le méthyl-4-phényl-4-dioxanne-1,3.



Un programme écrit pour IBM 1130 nous a permis d'étudier le spectre ABXY. Nous avons trouvé :

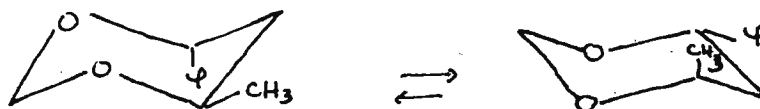
$$\begin{array}{ll}
 V_X = 0 \text{ cps} & J_{AX} = x J_{aa} + (1 - x) J_{ee} = 11,75 \text{ cps} \\
 V_Y = 12,7 \text{ cps} & J_{BY} = x J_{ee} + (1 - x) J_{aa} = 4,01 \text{ cps} \\
 V_A = 153,8 \text{ cps} & J_{AY} = x J_{ae} + (1 - x) J_{ea} = 2,81 \text{ cps} \\
 V_B = 177,8 \text{ cps} & J_{BX} = x J_{ea} + (1 - x) J_{ae} = 4,72 \text{ cps} \\
 J_{AB} = -12,11 \text{ cps} & \\
 J_{XY} = -14,62 \text{ cps} &
 \end{array}$$

La forte valeur de la constante J_{AX} montre que l'équilibre est presque complètement déplacé en faveur de l'un des conformères ; l'étude de produits analogues permet de dire qu'il s'agit du conformère I. L'énergie d'un phényle axial est donc beaucoup plus grande que celle

.../

d'un méthyle.

Ce résultat est à rapprocher de ceux obtenus par FEENEY et Coll (Bull. Soc. Chim. Belges 77, 1968, 128) qui trouvent dans le trans-méthyl-4-phényl-6-dioxanne-1,3 $\Delta G = 0,1$ kcal/mole



Ceci met en évidence une fois de plus le danger qu'il peut y avoir à déterminer l'énergie d'un conformère par additivité de valeurs associées à chacun des substituants. Dans le cas présent le phényle en position axiale semble avoir une énergie plus grande que dans le dérivé étudié par FEENEY et collaborateurs: Par suite de la présence d'un méthyle sur le même atome de carbone, il sera plus difficile, pour le phényle, de minimiser son énergie.

Recevez, Cher Docteur SHAPIRO, l'expression de nos sentiments les meilleurs.

Demilly *J.C. Duplan* *J. Delmau*

D. DEMILLY - J.C. DUPLAN - J. DELMAU

Dr. H. Dreeskamp
 MAX-PLANCK-INSTITUT
 FÜR KOHLENFORSCHUNG
 ABTEILUNG STRAHLENCHEMIE
 433 MÜLHEIM A. D. RUHR
 STIFTSTRASSE 34-36 · RUF 31073

Mülheim a. d. Ruhr,
 26. Juni 1970

Relative signs of coupling constants from NMR-Line shapes.

Change of adress.

Dear Barry :

While investigating the coupling constants in Methylfluorophosphoranes ($\text{Me}_n\text{PF}_{5-n}$, Chem. Comm. 1970, p 619 and 671) by heteronuclear INDOR - technique we came across some rather unusual line-shapes.

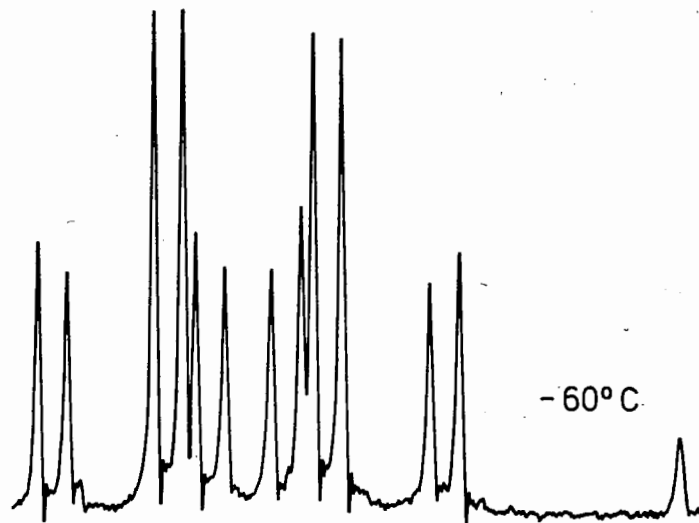
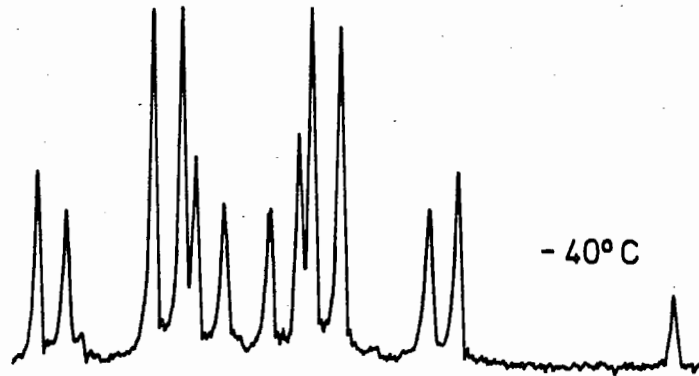
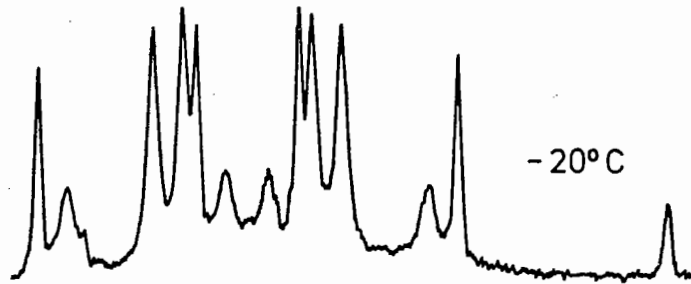
Some representative ^1H -spectra of Me_2PF_3 at rather low concentration and different temperatures are given in the attached graph. The spectrum at lowest temperature is interpreted by a coupling with one P-, two axial F- and one equatorial F-atom. The assignment of ^1H -transitions to spin states of coupling nuclei has been done in the table using the known sign of coupling constants. Assuming now an intramolecular exchange of F_a and F_e at higher temperatures to be sufficiently fast on our nmr-time-scale, only those ^1H -transitions should broaden which under exchange of F_a and F_e lead to different spin configurations e. g. line 2 ($F_a, F_a; F_e : +, +; - \longrightarrow +, -, +$) but not e. g. line 1 ($+, +, +$). This observation confirms the equal sign of the F-H-coupling constants.

Though similar spectra might be found in the literature (an early example is in W.G. Schneider et. al. Can.J.Chem. 38, 681 [1960]). This phenomenon has, to our knowledge, not yet generally been used to get information on the relative sign of \mathbf{J} . I would appreciate information on any more recent examples.

In May I have moved from Stuttgart to Mülheim where I hope to be active in both the field of luminescence and nmr.

All best wishes

H. Dreeskamp

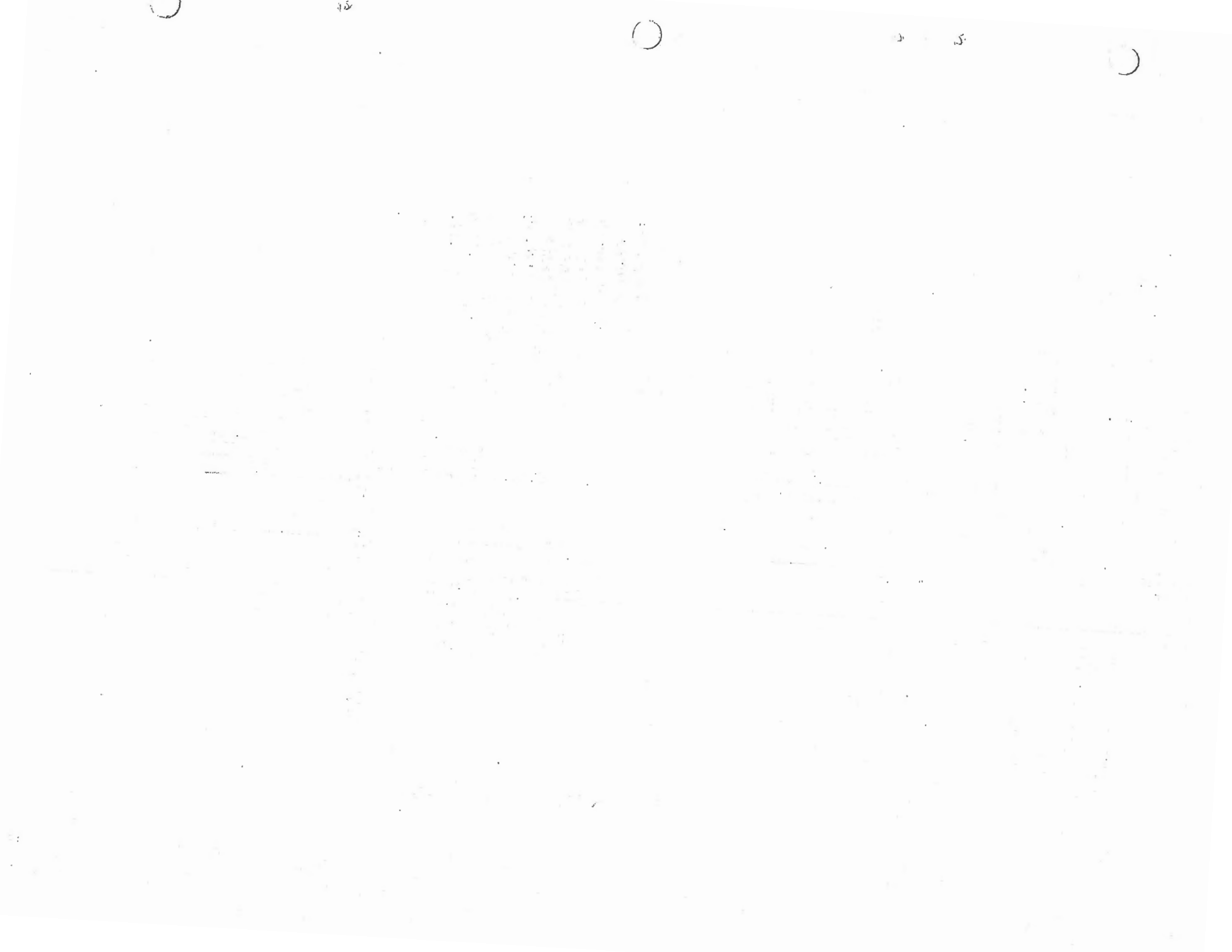
^1H -Spektrum von Me_2PF_3 

P : -- -- ++ -- ++ ++ $^2J_{\text{PH}} = -17.0 \text{ Hz}$

F_a : ++ ++++ -- ++ -- $^3J_{F_a\text{H}} = +12.6 \text{ Hz}$

F_e : +- +-+- +-+- +- $^3J_{F_e\text{H}} = +3.0 \text{ Hz}$

1 2 3 4 5 6 7 8 9 10 11 12



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