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30 January 1964

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 64

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REMINDER: Contributions to the Newsletter should now be sent to:

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

DEADLINE FOR NEXT ISSUE:
24 February 1964

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

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

LAFAYETTE, INDIANA

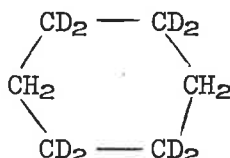
January 14, 1964

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

Dear Barry,

Here is a contribution for the readers of MELLONMR on the subject "Long-range deuterium isotope effect in proton NMR."

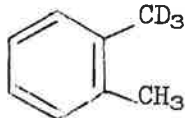
In order to obtain some more reliable values for the axial and equatorial hydrogen chemical shifts in cyclohexane, Mr. Peter Schultz has prepared the octadeutero compound.



We expect soon to report on its low-temperature NMR spectrum. A surprising observation is that at room temperature the hydrogen resonance is 1.4 ± 0.5 cps upfield (at 60 Mcps) from the resonance of ordinary cyclohexane. This difference was measured directly using a sample in which both cyclohexane species were present together. The low precision is due to some (we hope) temporary instability trouble in our equipment.

I know of two or three reports of D-C-H isotope shifts but I believe this is the first example of a "remote" deuterium shift, which may be either D-C-C-H or even D-C-C-C-H. The latter possibility is raised because the axial proton on C_1 and the axial deuteron on C_3 are very near one another and hence may be interacting.

We propose to hunt for other examples of "long-range" isotope effects, perhaps in molecules like



Best wishes for a productive career at IIT. Perhaps we shall now meet less infrequently. And as always, thanks for the newsletter, whatever its name.

Sincerely,

Norbert Muller

NM:bs

THE UNIVERSITY OF ROCHESTER

COLLEGE OF ARTS AND SCIENCE

RIVER CAMPUS STATION

ROCHESTER 27, NEW YORK

DEPARTMENT OF CHEMISTRY

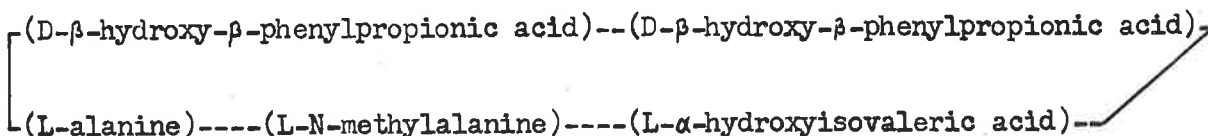
December 20, 1963

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

Dear Dr. Shapiro,

In the course of some work carried out in co-operation with Prof. L. H. Briggs, Dr. B. R. Davis, and Mr. P. W. Le Quesne of the University of Auckland, New Zealand, on the structure of pithomycin we have found the spin decoupling technique to be very useful in untangling a complicated spectrum and helping with structural assignments.

We now know that pithomycin, a depsipeptide isolated from the fungus *Pithomyces chartarum*, has a cyclic structure composed of amino-acid and hydroxy-acid residues in the order shown. There is an amide linkage between the alanine and the hydroxyphenylpropionic acid residues.



An initial difficulty in deciding from the analytical figures between the formulae $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_8$ and $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_8$ was resolved in favour of the latter when the integral indicated a proton count of 36.

Apart from readily identified aromatic (2.66 and 2.70 τ) and N-methyl (7.14 τ) lines the 60 mc/s, CDCl_3 spectrum (see Fig.) contains a number of complex, overlapping multiplets which at first proved difficult to sort out, especially as all the residues had not been identified at that stage. This problem was overcome by some decoupling experiments, as follows:

(a) When the transitions near 377 c/s (two protons) were irradiated the group of lines near 178 c/s (four protons) collapsed to two lines (partly masked by the N-Me line). No other couplings involving these six protons could be detected. These two groups of lines must arise from the overlapping spectra of the two hydroxyphenylpropionic acid residues (the 377 c/s lines from the CH groups; the 178 c/s lines from the CH_2 groups). The chemical shifts are in accord with this assignment.

(b) The single 475 c/s proton (assigned to NH of the alanine residue) was found to be coupled ($J = 9.0$ c/s) to one of the three protons absorbing near 284 c/s.

(c) The six proton doublet at 88.2 c/s ($J = 7.4$ c/s) collapsed to a singlet when the 284 c/s transitions were irradiated. Evidently there are two methyl groups with identical chemical shifts and coupling constants, each coupled to

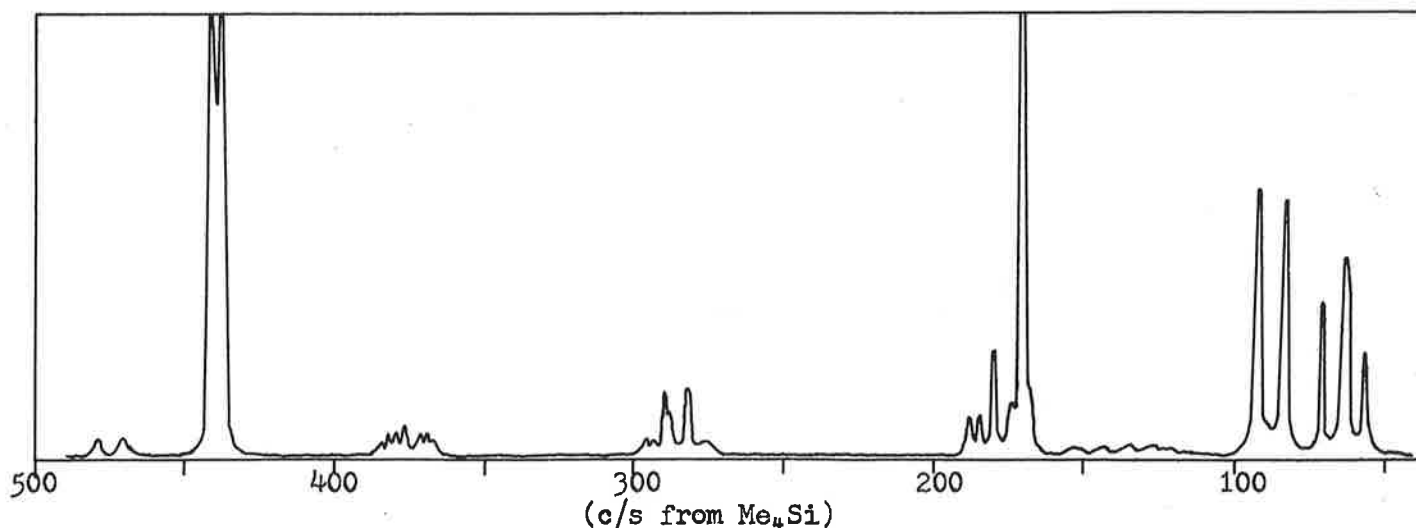
a single proton absorbing near 284 c/s. The chemical shifts of the single protons rule out the possibility of an isopropyl group, so the 88.2 c/s doublet is assigned to the methyl protons of alanine and N-methylalanine, the α -protons of which might be expected to absorb near 284 c/s. One of the three 284 c/s protons remains unaccounted for at this stage.

(d) The middle member of the group of three lines (due to six protons) at 63 c/s has a broadened appearance, suggesting that it consists of two unresolved lines. When the transitions near 131 c/s (due to a single proton) were irradiated these three lines collapsed to two lines. In addition, the 131 c/s proton was shown to be coupled to a 284 c/s proton (presumably the remaining unassigned proton of this group). From a consideration of this information, the chemical shifts, and the coupling constant involved (about 7 c/s), the 63 c/s lines were assigned to the methyls and the 131 c/s lines to the methine proton of an isopropyl group. The chemical shift between the methyls of the isopropyl group is about 0.12 p.p.m. As it was known from degradation experiments that the remaining (C_5) fragment of pithomycin included a further hydroxy-acid residue, and as the presence of the grouping $-CH-CH(CH_3)_2$ was indicated it was concluded that an α -hydroxyisovaleric acid residue must be present. This has now been confirmed.

Yours sincerely,

L. D. Colebrook.

L. D. Colebrook.



60 Mc/s spectrum of pithomycin ($CDCl_3$ solution)

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT

69 HEIDELBERG, January 10, 1964
Tiergartenstraße
Tel. 271 21 (über Chirurg. Klinik)

Dr. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Bothner-By:

In the last issue of MELLONMR W.B. Miller and P. Haake ¹⁾ reported on the unusually large $^{13}\text{C-H}(2)$ coupling constants in thiazoles and oxazoles, and they shortly mentioned preliminary results on rates of exchange of the 2-hydrogen of these compounds. With regard to this letter we would like to give you some further details we obtained in an independent study continuing our previous work on H/D exchange in the azole series ²⁾.

Half lives for the H/D exchange of some azoles and azolium ions in CH_3OD are given in the attached table. It is seen that the rates of exchange of the 2-hydrogens in oxazolium and imidazolium compounds are extremely high even at 37° . Parallel to this unusually high C-H acidity we find the τ_2 values of those azolium ions abnormally low in a range down to approximately -1.30. The H(2) shifts strongly depend on the solvent and we hope to do some further work on them.

As with imidazoles and benzimidazoles ^{2,3)} we studied protonation of oxazoles in conc. H_2SO_4 . The N-H proton exchanges slowly enough to be coupled to H(2), J_{23} ranging from 1.2 to 1.8 cps.

With kindest regards,

Yours sincerely,

Heinz A. Staab Mou-Thai Wu
Heinz A. Staab Mou-Thai Wu

Albrecht Mannschreck
Albrecht Mannschreck

	Solvent	τ_2	$t_{0.5}$ [min]	T [°C]	64-5
Oxazole	CCl ₄	2.16			
	CH ₃ OD	1.92	600	~ 60	
Benzoxazole	C ₂ Cl ₄	1.90			
	CH ₃ OD	1.56	7000	~ 60	
4.5-Di-n-propyl-oxazole	CCl ₄	2.46			
	CH ₃ OD	2.07	600	60	
4.5-Diphenyl-oxazole	CCl ₄	2.24			
	CH ₃ OD	1.78	1100	69	
1-Benzyl-imidazole	THF	2.51			
	CH ₃ OD	2.30	110	60	
3-Methyl-4.5-di-n-propyl-oxazolium	CDCl ₃	-0.82			
	CH ₃ OD	+0.30 ^{a)}	<3	37	
3-Methyl-4.5-di-phenyl-oxazolium	CDCl ₃	-1.28			
	CH ₃ OD	-0.26 ^{a)}	<3	37	
1.3-Dibenzyl-imidazolium ^{b)}	CDCl ₃	-0.6			
	CH ₃ OD	+0.7 ^{a)}	<3	37	

Half lifes of the H/D exchange in the
2-position of azoles and azolium salts

[a) Measured in CH₃OH; b) Prepared by G.Schwalbach]

- 1) W.B.Miller and P.Haake, MELLONMR 60, 38 (1963).
- 2) cf. A.Mannschreck, W.Seitz and H.A.Staab, Ber.Bunsenges. physik.Chem. 67, 470 (1963).
- 3) H.A.Staab and A.Mannschreck, Tetrahedron Letters 1962, 913.

64-6PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 - TEL. 430422
VORSTEHER: PROF. DR. P. HUBER

January 14, 1964.

PD Dr. P. Diehl

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

Dear Barry,

Here is a short MELLONMR contribution on a subject we discussed at the 4th OCEANS. As J.D. Baldeschwieler pointed out, preferential relaxation of nuclei can be used to decouple H^1 or F^{19} from B^{11} , C^{13} or N^{14} .

An even more effective decoupling should be observed in the D-resonance of partially deuterated molecules. As an example (fig.) I used partially deuterated acetone. The singlet corresponds to $-CD_3$, the doublet to $-CHD_2$. With increasing concentration of Mn^{++} the proton of the $-CHD_2$ group is relaxed more effectively than are the deuterons. This is due to the much larger γ_H^2 , ($\gamma_H^2 \sim 42,5 \gamma_D^2$). At a certain concentration of paramagnetic ions the J_{HD} coupling disappears without appreciable broadening of the $-CD_3$ signal.

This very simple type of decoupling experiment can be a valuable aid in the analysis of more complex D-spectra.

Yours sincerely,

Diehl

PD Dr. P. Diehl

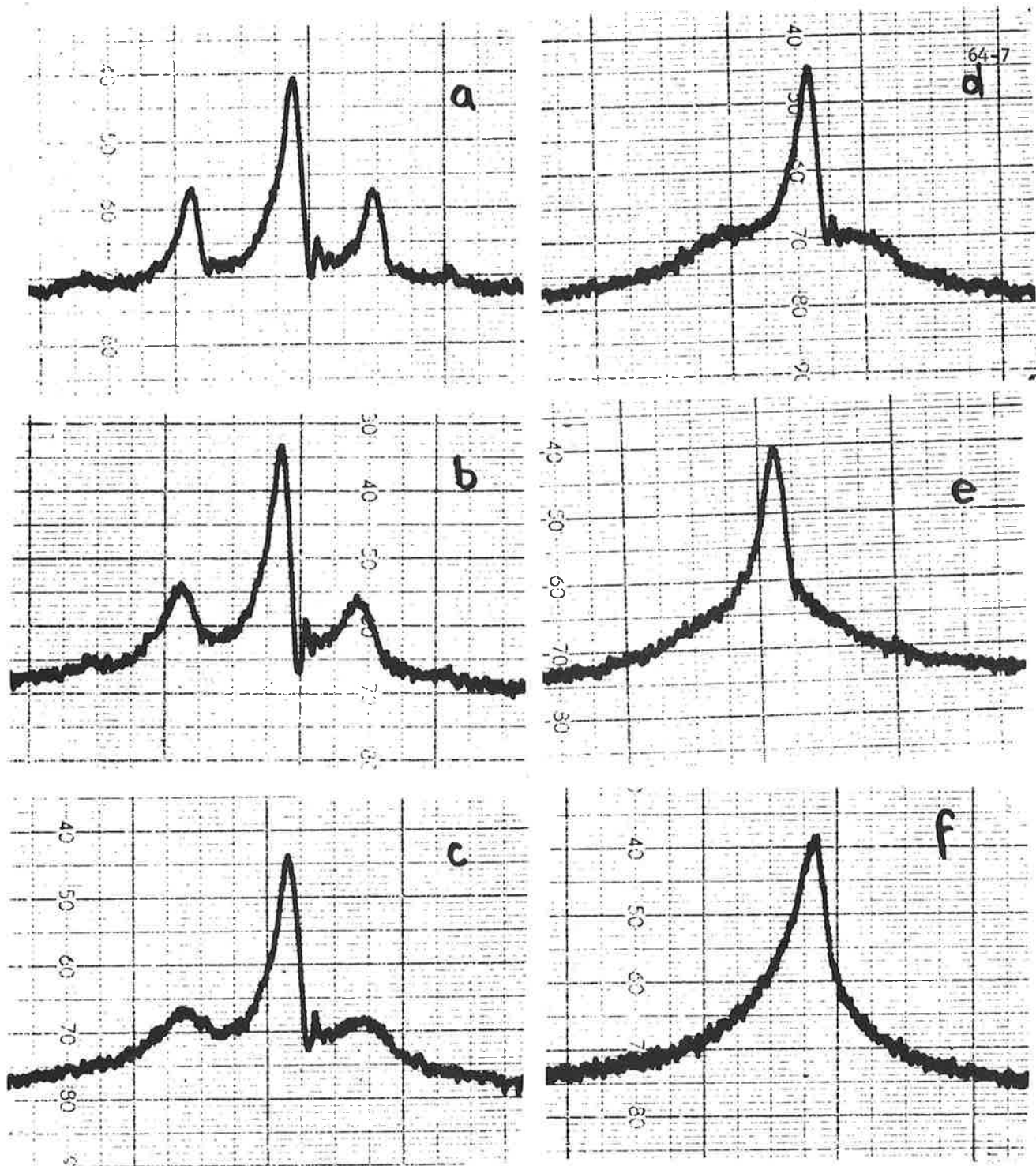


Fig. Proton-deuteron spin decoupling by preferential relaxation of protons in partially deuterated acetone. (D-spectrum)

singlet: $-\text{CD}_3$

doublet: $-\text{CHD}_2$; $J_{\text{HD}} = 2.18$ cps

concentration of ions: $[\text{Mn}(\text{C}_4\text{O}_4)_2]$

a. 0

b. $6.6 \cdot 10^{17} \text{ Mn}^{++}/\text{cc}$

c. $1.65 \cdot 10^{18} \text{ "}$

d. $3.3 \cdot 10^{18} \text{ Mn}^{++}/\text{cc}$

e. $6 \cdot \text{ "}$

f. $1.2 \cdot 10^{19} \text{ "}$

MONSANTO CHEMICAL COMPANY

ORGANIC CHEMICALS DIVISION
JOHN F. QUEENY PLANT
ST. LOUIS 77, MISSOURI

January 7, 1964

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

Dear Dr. Shapiro:

Measurement of NMR Signals with Digital Integrator

We would like to summarize results obtained by integrating NMR signals with a voltage to frequency type integrator. This type of integrator has a potential advantage in time savings over a continuous-type analog integrator such as the Varian V-3521 Integrator since it allows simultaneous recording of the spectrum and integral, and presents the data in digital form suitable for area calculations. An improvement in precision might also result because of the larger dynamic range of this instrument.

The integrator used was the Infotronics Corporation Model CRS-1 Digital Chromatograph Readout System which has been found to give excellent results in our Gas Chromatography laboratory. This integrator provides manual and automatic integrating modes. The data is printed on paper tape and a manual "total" button is provided, allowing the total area of any given number of peaks to be recorded. Only minor modifications are required to connect this instrument to the recorder output of a HR-60 spectrometer.

Resolution of this integrator was found to be at least one peak every two seconds (mainly limited by the mechanical printer used). Precision and accuracy were determined by measuring the relative areas of peaks in synthetic mixtures chosen to give spectra containing only well resolved singlets. S/N was varied by adjusting H_1 .

Satisfactory results were obtained in the automatic integrating mode when all peaks in the spectrum had large S/N ratios. The accuracy of the results obtained, progressively decreased as S/N decreased, a bias against the weakest peak being introduced. Representative data are given below:

Dr. B. L. Shapiro

- 2 -

January 7, 1964

SAMPLE COMPOSITION

S/N of PEAK C	ACTUAL			CRS-1*			PLANIMETER		
	A	B	C	A	B	C	A	B	C
25:1	61.1	30.0	8.9	62.2 \pm 1.3	29.7 \pm 0.7	8.1 \pm 0.8	64.9	25.1	10.0
15:1				62.8 \pm 1.2	30.2 \pm 0.8	6.8 \pm 0.6	60.0	29.7	10.3
9:1				63.4 \pm 0.6	30.4 \pm 0.8	6.4 \pm 0.5	60.7	30.8	8.4
3:1				67.1 \pm 0.4	29.7 \pm 0.4	3.3 \pm 0.2	63.7	26.6	9.7

* Results represent averages for 5 or more figures.

This bias against weak signals apparently results from peak sensing limitations, since in the manual integrating mode accuracy is considerably improved. Despite this drawback, this instrument is useful in certain applications involving large numbers of samples and peaks having high S/N ratios.

The Infotronics Corp. (1401 South Post Oak Road, Houston 7, Texas) has reviewed our application of the Model CRS-1 System to NMR. As a result of this study, a Model NRS-1 system has been proposed by Infotronics which should correct the limitations of the Model CRS-1 when applied to NMR work.

Sincerely yours,

M.W. Dietrich R.E. Keller.

M. W. Dietrich and R. E. Keller

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

M.W D. and R.E.K.

UNIVERSITÉ D'OTTAWA
FACULTÉ DES SCIENCES PURES ET APPLIQUÉES



OTTAWA 2, CANADA

UNIVERSITY OF OTTAWA
FACULTY OF PURE AND APPLIED SCIENCE

DÉPARTEMENT DE CHIMIE
365, RUE NICHOLAS

DEPARTMENT OF CHEMISTRY
365 NICHOLAS ST.

January 17, 1964.

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

Dear Barry,

Thank you for your reminder that my subscription is due. I find MELLON-M-R very useful and I am sure that ILT NMR N will be as good, although the new title could be more attractive (my suggestion: ILT NMR Letters).

One comment I have concerns the bibliography, which I used to find most useful, but which is rapidly reaching the stage of having an infinite number of references in infinitely small type. Since practically all organic chemistry reported nowadays involves n.m.r., I suggest that these papers be left out when the n.m.r. aspects are purely routine. I realise that this involves work on the part of the Editor, but I think it would be well worthwhile.

Frequency-stabilization of VFO of decouplers

Owners of NMR Specialties heteronuclear decouplers may be interested in our attempts to overcome the frequency drift of the ca 5.3 Mc/sec. variable frequency oscillator (VFO) of the decoupler. We have tried three approaches:

(a) The VFO is replaced by a crystal-controlled oscillator (furnished by NMR Specialties) and amplitude modulation is carried out at the power output stage. However, with the voltage available from the usual audio oscillators, the modulation index is small, so this method is most suitable for carrying out "tickling" experiments (i.e. weak r.f. field double irradiation)

- 2 -

Dr. B.L. Shapiro

January 17, 1964.

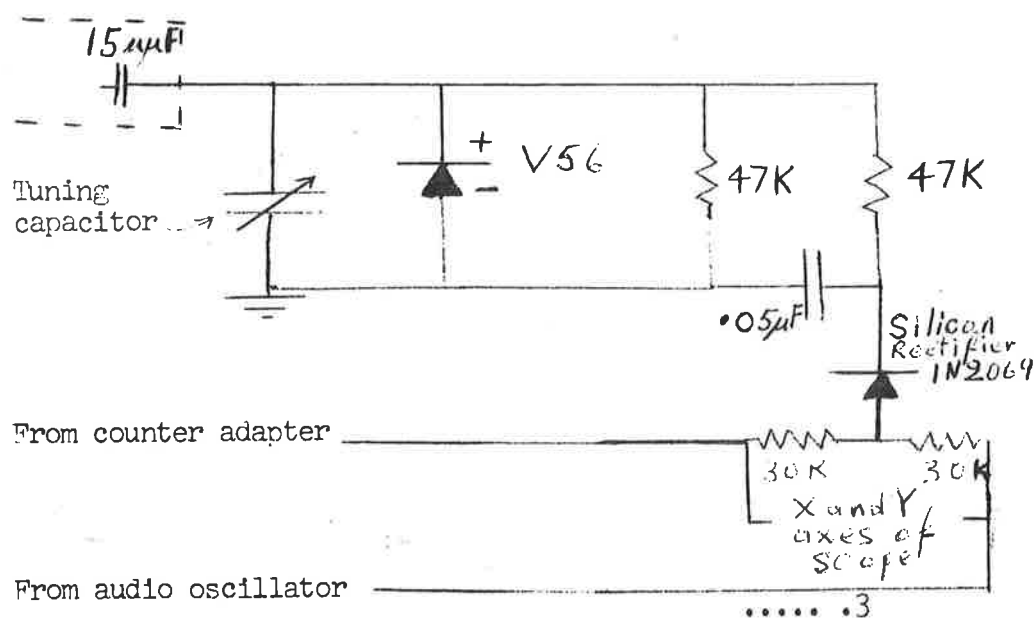
(b) The frequency of the crystal-controlled oscillator above may be varied by placing a variable capacitor across the crystal (c.f. MELLON-M.R 60 - 45), but the range of frequency, at any rate with our instrument, is rather small.

(c) Stabilization of VFO frequency

There is an easy way of doing this, provided that the NMR Specialties "counter adapter" is available (also needed are an audio oscillator and an oscilloscope, equipment generally available in an NMR lab.).

The difference frequency of the VFO and a 5.3 Mc/sec. crystal-controlled oscillator is given by the counter adapter. This is mixed with the frequency of an audio oscillator and the rectified output is applied to a voltage variable capacitor (I used a spare V 56 type, obtained from Varian, as is present in the modulation circuit of our 60 Mc/sec. r f unit) in parallel with the tuning capacitor of the VFO unit (see diagram)

V F O Module



Dr. B.L. Shapiro

January 17, 1964.

This frequency-control method, applied to r.f. frequencies, has been described by J. Jeener (Rev. Sci. Inst. 32, 27 (1961)) and has been used by Benedek et al. (J. Chem. Phys. 39, 3349 (1963)). It is worthwhile to increase the range of the tuning capacitor, normally about 5,000 c.p.s. This can easily be done by increasing the value of the capacitor in series with it (this capacitor is inside the VFO module and is normally 2.5 μ F) as shown in the diagram. The tuning capacitor will then have a range of about 50,000 c.p.s.

With a suitable output (e.g. 20 v.) from the counter adapter and the audio oscillator, the difference frequency stays locked to that of the audio oscillator over a range of 3 to 10 kc/sec. This locking can easily be seen by observing the simple Lissajou pattern (slightly distorted because the output of the counter adapter is not a good sine wave) on the scope. Turning the tuning capacitor knob does not change the frequency of the VFO (it does change its phase) in the locking range. When the system unlocks, a very complex pattern is obtained on the scope, although locking may also occur at frequencies which are in certain fixed ratios. This can also be clearly seen on the scope. The extent of locking is rather small in these cases.

The frequency stability of the decoupler then depends on the stability of the crystal-controlled oscillators in the decoupler and in the counter adapter, and on the stability of the audio oscillator. Even at 20 kc/sec., the HF* oscillator, which is switched on permanently, has a short term stability of about 0.1 c.p.s., so that even tickling experiments ought to be feasible. We have been using this set-up for deuterium decoupling for a couple of months with very satisfactory results.

Ring inversion of cyclohexane-d₁₁

Drs. L.D. Hall and M. Ahmad and I have been studying the inversion rate of cyclohexane-d₁₁. The proton spectrum (at -103°) with and without deuterium decoupling is shown in the Figure. From a study of the change of the spectrum with temperature, we have found $\Delta H^\ddagger = 10.9$ kcal/mole and $\Delta S^\ddagger = 2.9$ e.u. (for the chair-boat process). Dr. Evey has informed us that his group has carried out similar studies, and their results are in excellent agreement with ours.

* Hewlett Packard, model 200CD

Dr. B.L. Shapiro

January 17, 1964

The results are also in good agreement with the unpublished work of Meiboom, but not with those of Harris and Sheppard, as originally published. However, Dr. Harris has informed us that a reconsideration of the data in the light of the above work gives new values for the activation parameters in good agreement with those above.

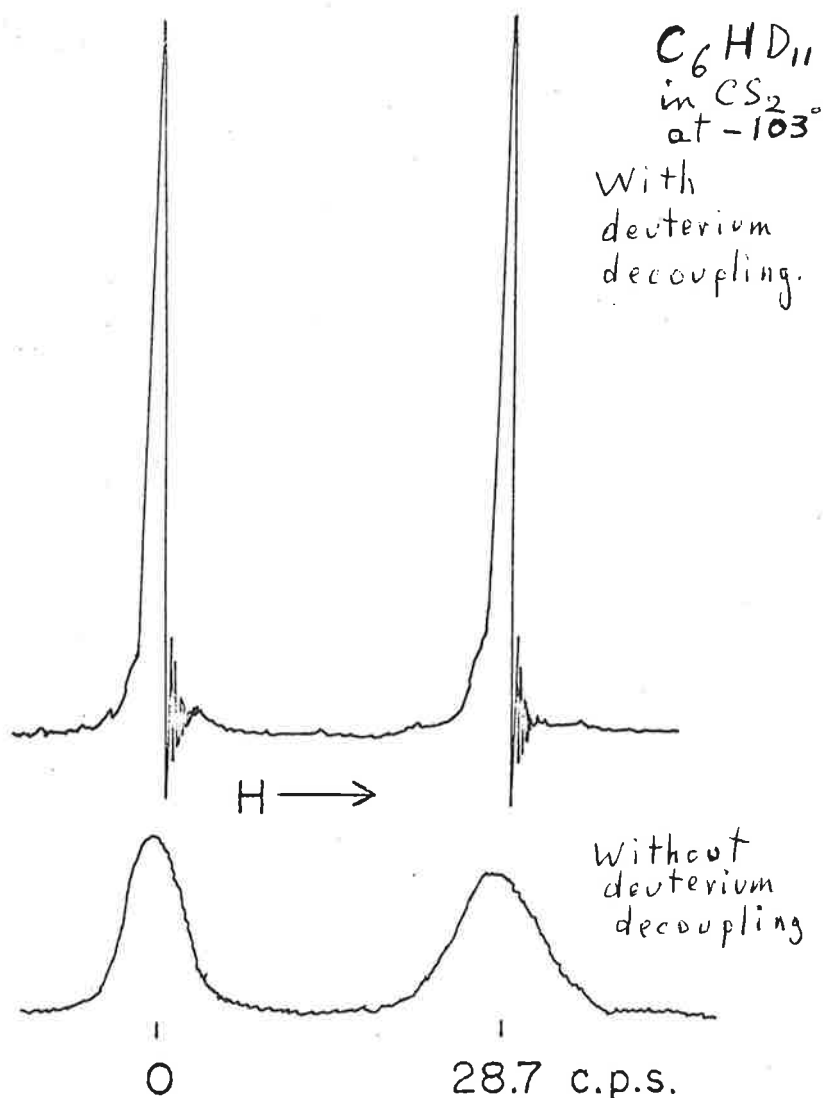
With best regards,

Yours sincerely,

Frank

FALA/ vb

F.A.L. Anet.



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RESEARCH & DEVELOPMENT DEPARTMENT
RESEARCH DIVISION500 SOUTH RIDGEWAY AVENUE
P. O. BOX 85
GLENOLDEN, PA.

January 20, 1964

File: 207-4

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa. F^{19} Spectra of two $(CF_3)_2$ -cyclo C_4F_6 Isomers

Dear Barry:

The analysis, or I should say attempted analysis, of two samples which are believed to be $(CF_3)_2$ -cyclo C_4F_6 isomers may be of interest to some of the readers.

The high resolution F^{19} spectra, 94.1 mc./sec., of the two samples are shown in Fig. 1. Some fine structure is observable as shown in Figs. 2 and 3. The resolution is relatively poor in both cases, however this is characteristic of most fluorinated cyclo-butanes and is probably due to the number and the magnitude of spin-spin interactions.

The assignment of sample B to isomer IV (Fig.3) is straightforward and is based on the postulated spectra for the four isomers as shown in Fig. 3. Unfortunately, the assignment of Sample A is not straightforward. The spectra seems to indicate that the material may be either isomer I or II, however there are a number of uncertainties in this assignment.

The predicted spectra are based in part upon the results of two dichloro-hexafluorocyclobutanes(1) and a number of other substituted fluoro-butanes. A search of the literature yielded one reference(2) which reports the physical properties and the NMR spectra(3) for three of the four possible isomers (Fig.3). The reported NMR spectra for these samples are consistent with the predicted spectrum of isomer IV, only.

The assignment of Sample A to isomer III is ruled out on the basis of symmetry and the observed unequal coupling the b fluorines with the CF_3 groups as shown in Fig. 2.

We are in dire need of a small sample of $n-C_6F_{14}$ to complete a series on the NMR parameters of some saturated fluorocarbons. Any information concerning a small sample or a possible source will be kindly appreciated.

Sincerely yours,


Kermit C. Ramey

KCR:LH

- (1) R. Freeman and W.A. Anderson, J.C.P., 37, 2053 (1962).
- (2) M. Hauptschein, H. Fainberg, and M. Braid, J. Am. Chem. Soc., 80, 842 (1958).
- (3) NMR spectra were interpreted by Dr. Gutowsky.

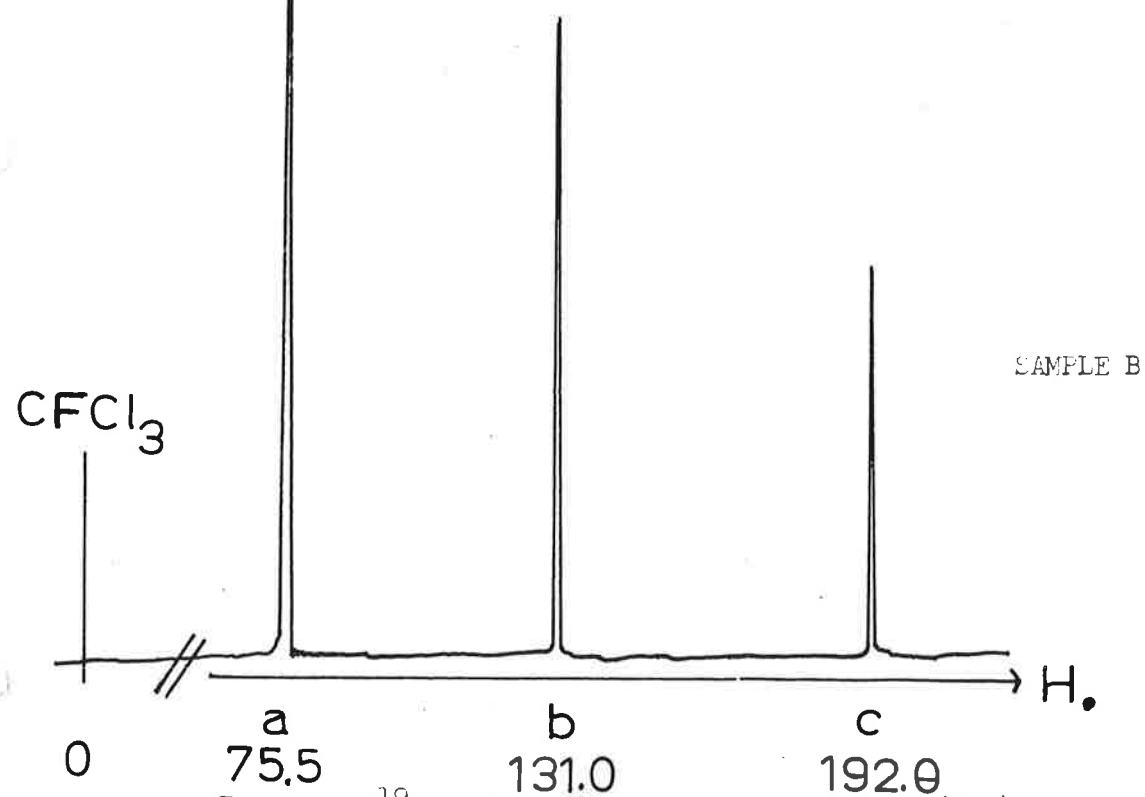
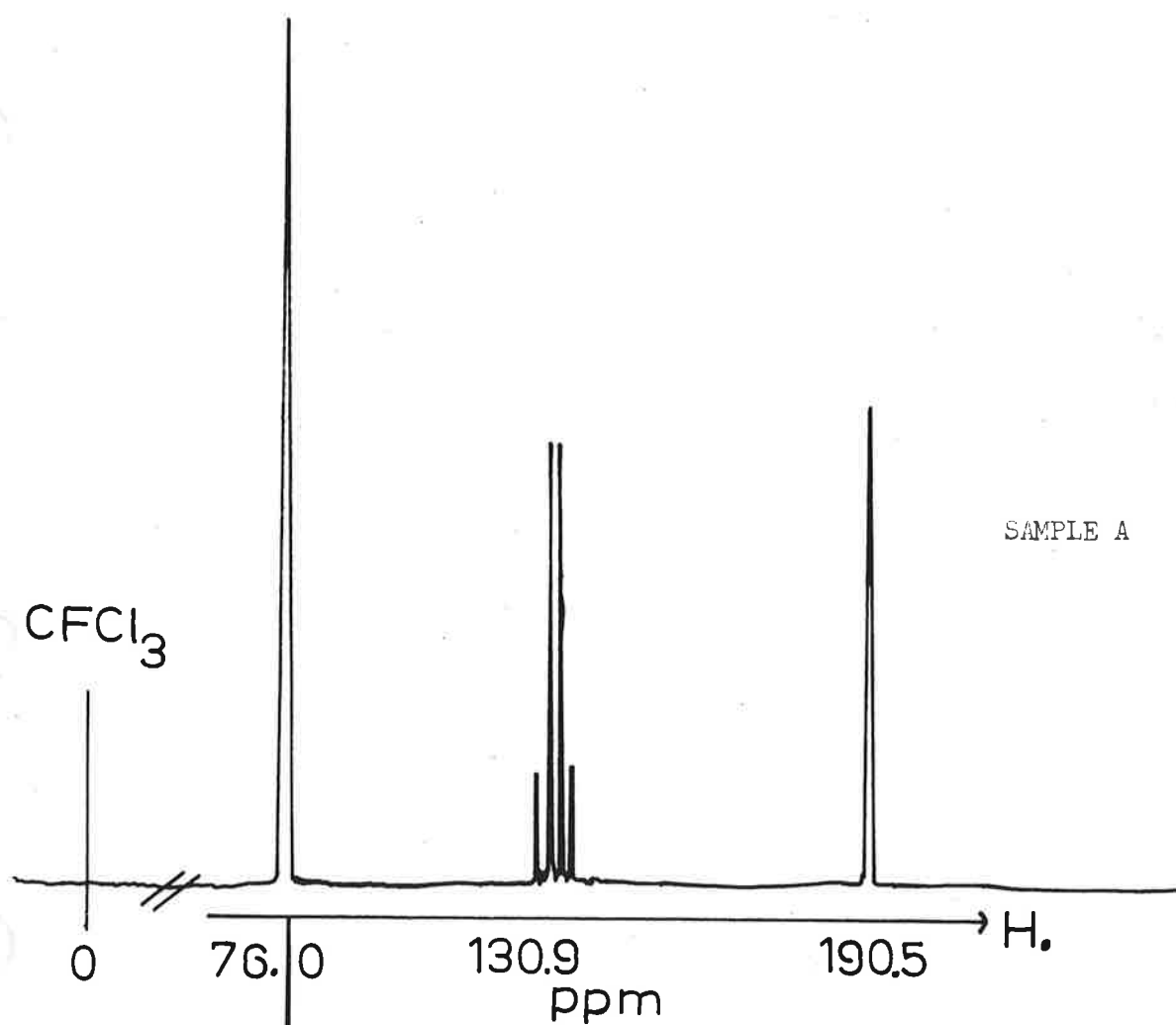


Fig. 1. F^{19} spectra, 24.1 mc./sec., of two $(CF_3)_2C_4F_6$ isomers.

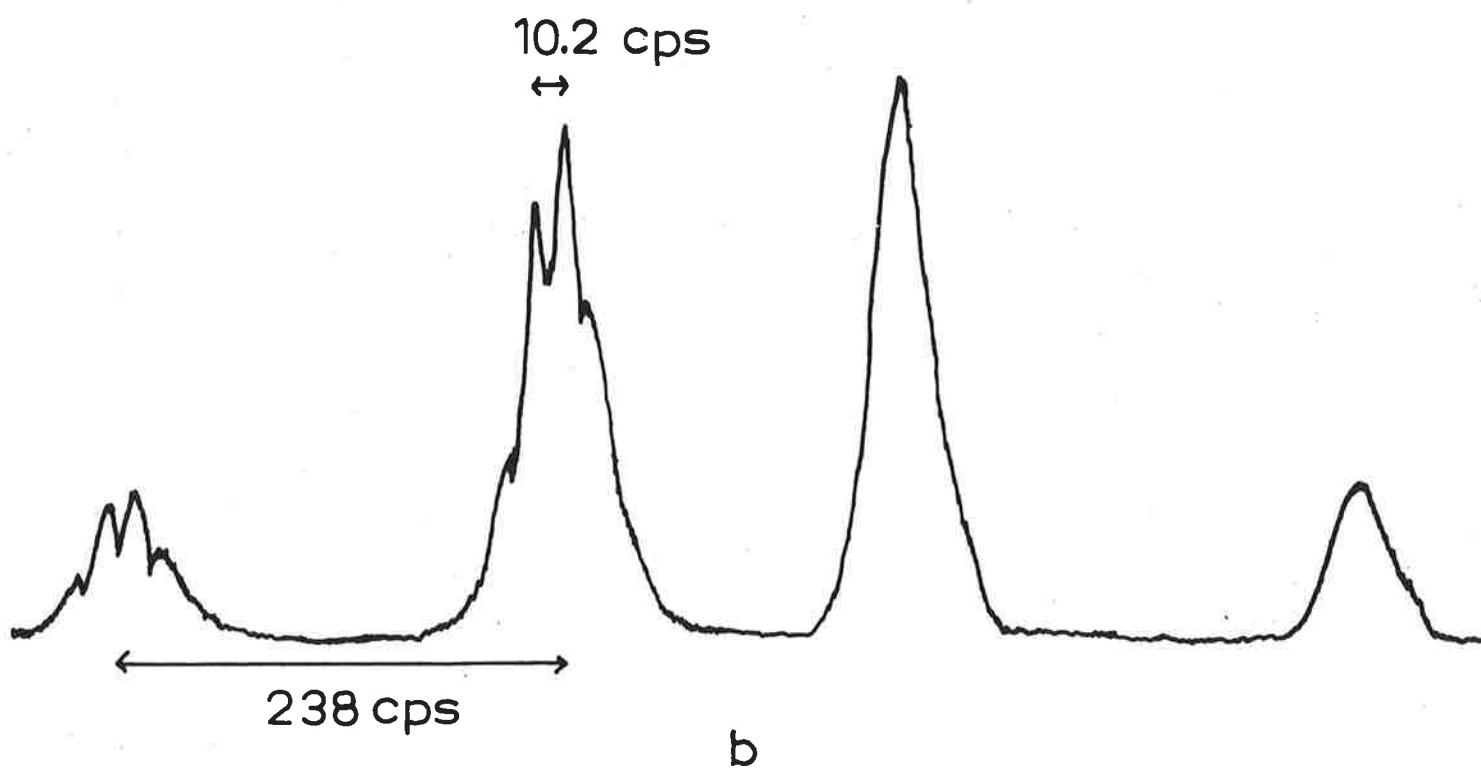
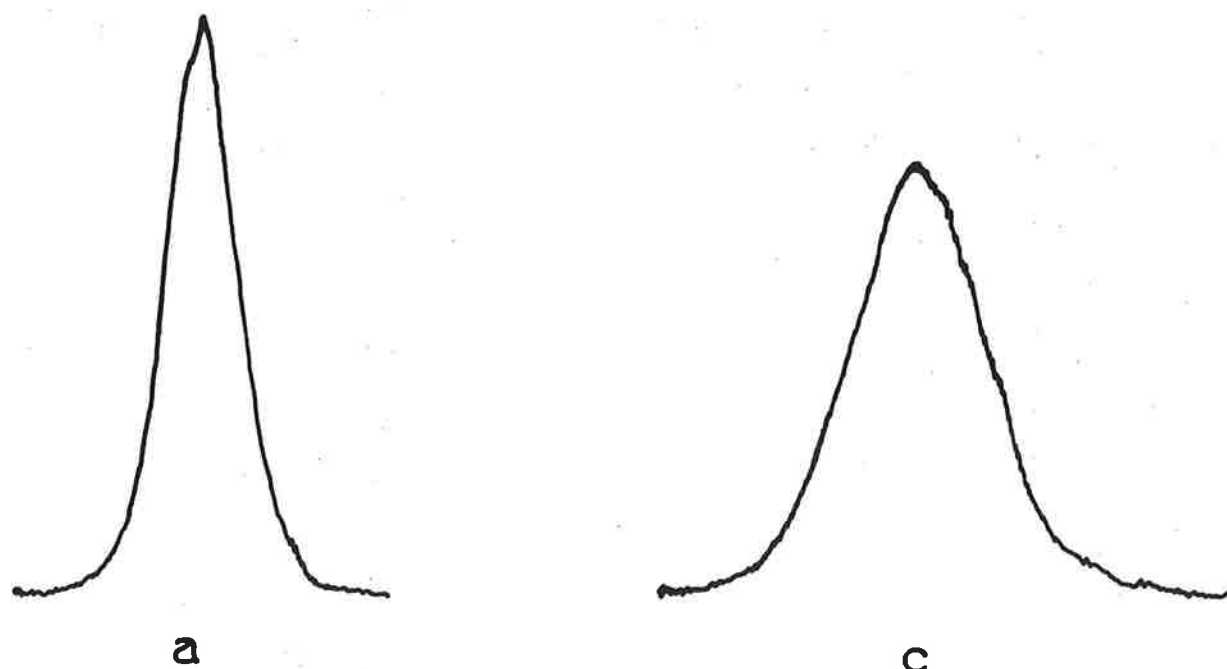


Fig. 2. Slow sweep through the spectrum of Sample A.

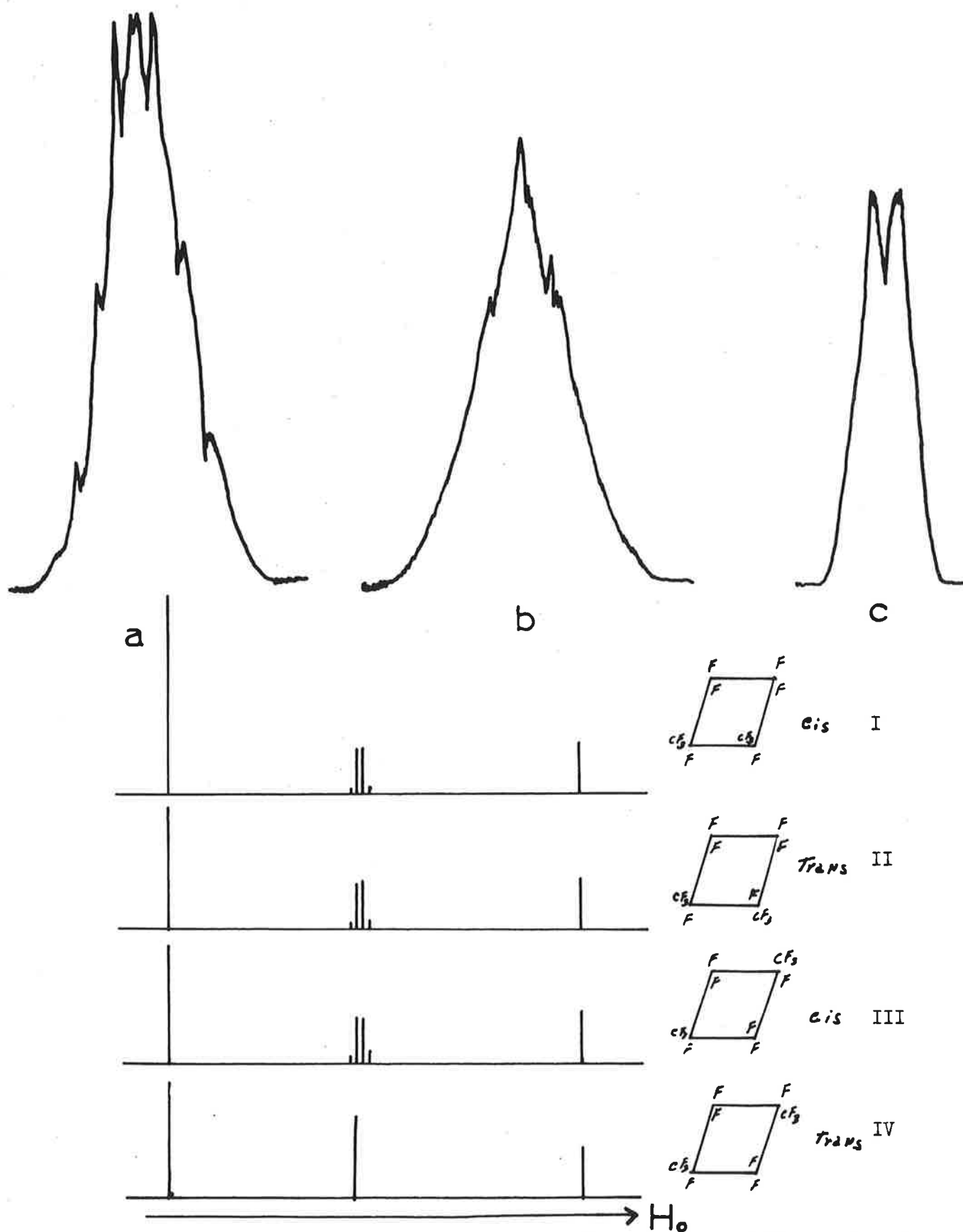


Fig. 3. Slow sweep through the spectrum of Sample B, and the predicted spectra for the four isomers.


OKLAHOMA STATE UNIVERSITY • STILLWATER 74075

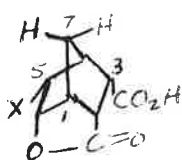
 Department of Chemistry
 Frontiers 2 6211, Ext. 7215-7218

January 10, 1964

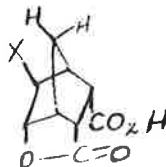
Dr. Bernard L. Shapiro
 Mellon Institute
 4400 Fifth Avenue
 Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

We have prepared over the past several years a number of compounds possessing the norbornane skeleton and having electron-withdrawing groups on carbon atoms 2,3,5 and 6. In compounds of this type the signals at highest field in the n.m.r. spectra arise from the C₇ protons and an inspection of these signals has been a useful aid in assigning stereochemistry of substituents. For example, in I, where



I



II



III



IV

X = $\text{NHSO}_2\text{C}_6\text{H}_5$, the C₇ protons give a singlet signal at δ 1.80 whereas in the isomer II the C₇ protons appear as a pair of doublets ($J=12$ cps.) centered at δ 1.84 and δ 2.18 (both spectra run in $\text{CF}_3\text{CO}_2\text{H}$). An examination of the spectra of thirty compounds of these types has thus revealed that the isomer with the exo substituent shows its C₇ protons as a pair of doublets with $J=11-13$ cps., whereas the endo isomer shows only a singlet. Some exceptions observed are III in which case $J_7=10$ cps. and compounds such as IV where $J_7=8-9$ cps.

I hope that the Oklahoma State University "debt" is paid with this communication so that we can continue to receive your valuable publication.

Yours sincerely,

Leon H. Zalkow

Leon H. Zalkow
 Associate Professor

LHZ:bbm



OUR FILE REF..... 64-19

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SHIRLEY BAY, OTTAWA, ONTARIO

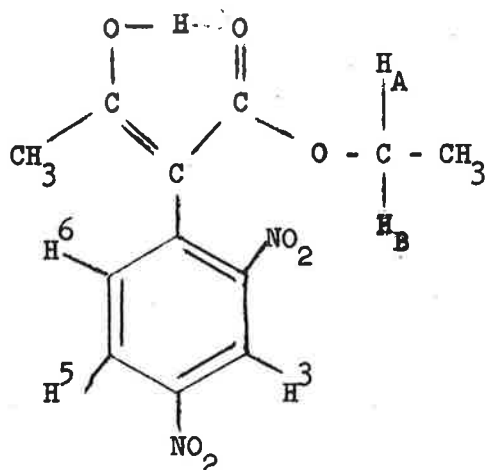
January 20, 1964

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

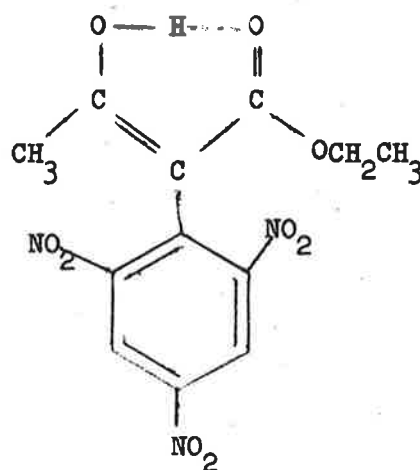
Dear Dr. Shapiro:

Some time ago we ran nmr spectra on a series of substituted 2:4-dinitrobenzenes; two of these, ethyl- α -2:4-dinitrophenylacetoacetate (I) and ethyl- α -2:4:6-trinitrophenylacetoacetate (II), show some interesting features which we will describe here. As far as can be detected by nmr both compounds are, not too surprisingly, completely in the enol form in carbon tetrachloride solution. Of particular interest is the spin coupling of the enol hydrogen to the "acetyl" methyl protons, observable in each compound. This is shown in Figs. 1 and 2 for I. Spin coupling of the enolic proton has been observed before e.g. in enolised aldehydes (1), the coupling constant being of the order of 12 cps when the proton is attached to the aldehydic oxygen for prolonged periods. The extra intervening bond is probably sufficient to reduce the $\text{CH}_3\text{-C-OH}$ coupling to 0.7 cps in I and II. The relatively large values of these 2 coupling constants are likely due to some double bond character of the C-OH bond from electron delocalisation induced by the benzene rings. The spectrum of I has been observed at 62° as well as 30° with no significant changes in this coupling constant. It is therefore believed that in I and II the hydrogen is attached to the "acetyl" oxygen for considerable periods of time.

.....2



I



II

The nmr data are given in the table. The very low field positions for the strongly intramolecularly hydrogen bonded enolic protons are not unexpected and the spectrum of II is otherwise not remarkable. In I, however, the methylene protons are not equivalent. The system was analysed as ABX_3 ($J_{AX} = J_{BX}$) and the parameters deduced from the 56.4 Mc/s spectrum used to calculate the one at 60 Mc/s. These calculated spectra and the observed ones are shown in Fig. 3. Non equivalent methylene protons in ethyl esters are usually observed in situations such as $CH_3CH_2-O-XR_1R_2R_3$ ($X = S, P, C$, etc) (2) i.e. when there is an asymmetric centre nearby. In the present examples all the relevant atoms are trigonal carbons. We are driven to the conclusion that the long range shielding effects of the o-nitro group and /or benzene ring are different for the two protons in I. This difference disappears with the introduction of the second o-nitro group in II. Molecular models have shown that such a hypothesis is not implausible.

.....3

Nmr Parameters

τ (ppm)	I	II
enol H	-3.08	-3.08
aromatic H ³	1.24	{ 1.18
H ⁵	1.60	
H ⁶	2.48	
methylene H _A	5.76	{ 5.81
H _B	5.98	
methyl (CH ₃ CO)	8.08	8.19
methyl (CH ₃ CH ₂)	8.85	8.82
J(cps)		
CH ₃ CO - H _{enol}	0.70	0.7 ₃
CH ₃ - H _A , H _B	7.0	7.1
H _A - H _B	10.7	-
H ⁵ - H ⁶	8.5	-
H ³ - H ⁵	2.3	-
H ³ - H ⁶	0.0	-

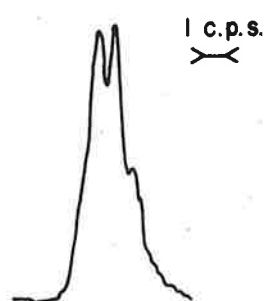
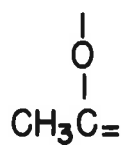
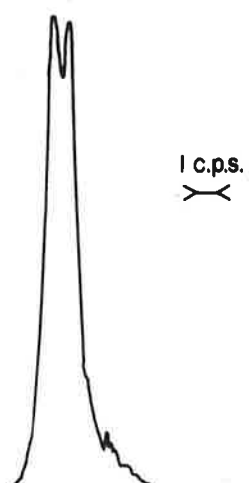
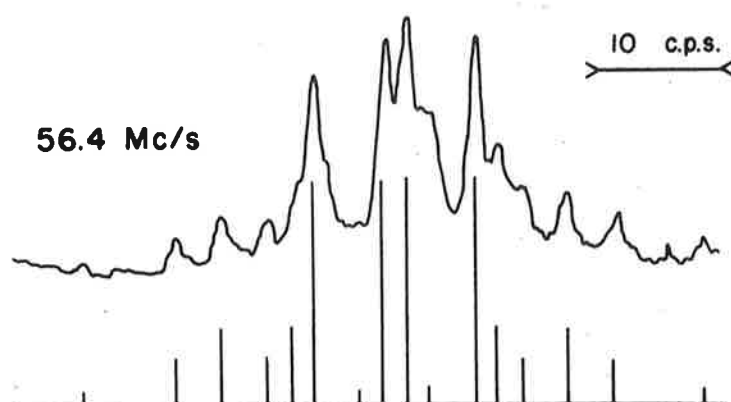
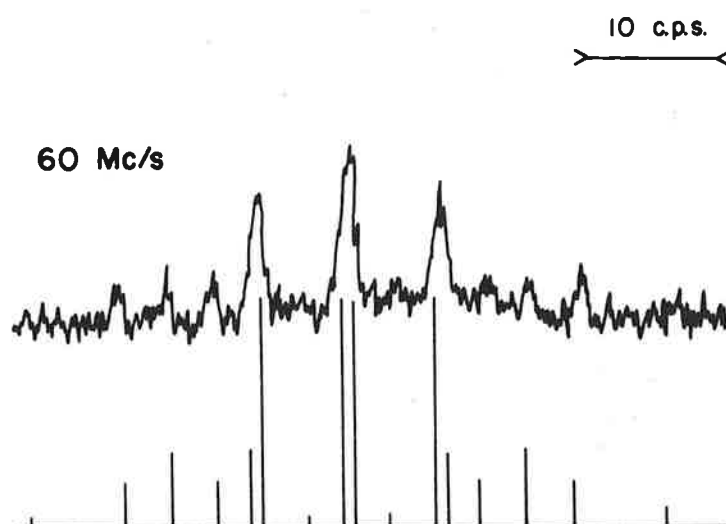
Yours sincerely,

R.A. McIvor
J.A. Weinberger

R.A. McIvor

M.A. Weinberger

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 (2) F. Kaplan and J.D. Roberts, *J. Am. Chem. Soc.* 83, 4666 (1961).

FIG. 1**H enol****FIG. 2****FIG. 3****CH₂ REGION**



PITTSBURGH
COAL RESEARCH CENTER

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

January 22, 1964

Dear Barry:

Much luck and success in your new position!! We'll miss you. Count on us for enthusiastic support of IITNMRN.

QUANTITATIVE H^1 and C^{13} NMR OF COMPLEX CARBONACEOUS MATERIALS

We are currently exploring the complementary use of proton and carbon-13 NMR to study the structure of coal extracts, coal derivatives, and chemically treated coal products. One example of our work is illustrated in figures 1 and 2, H^1 and C^{13} NMR spectra of a wax oil (heavy creosote from coal), before and after catalytic hydrogenation. The spectra were obtained at 60 mc/sec and 15.1 mc/sec. Intensity data from the proton spectra yielded ratios of aromatic hydrogens to hydrogens bonded to carbons located α to aromatic rings, and to hydrogens present in other non-aromatic systems. Making use of assumptions concerning aliphatic groupings, Brown and Ladner (Fuel, XXXIX, 87, 1960) have deduced information concerning the carbon skeleton of a few coal derivatives from their elemental analyses and hydrogen distributions as determined by H^1 NMR. We propose to eliminate the need for any such assumptions by obtaining reliable intensity data from C^{13} spectra. Calibration data obtained in our laboratory from the C^{13} spectra of a number of alkylaromatics and hydroaromatics indicate that aromaticities (in the classical sense) can be derived directly from C^{13} spectra. The complementary use of H^1 and C^{13} data can then be used to place limits on other structural parameters including the degree of aromatic ring substitution and the average size of the condensed ring system.

This material will be discussed in more detail in the forthcoming Pittsburgh Conference.

H. L. Retcofsky
H. L. Retcofsky

R. A. Friedel
R. A. Friedel

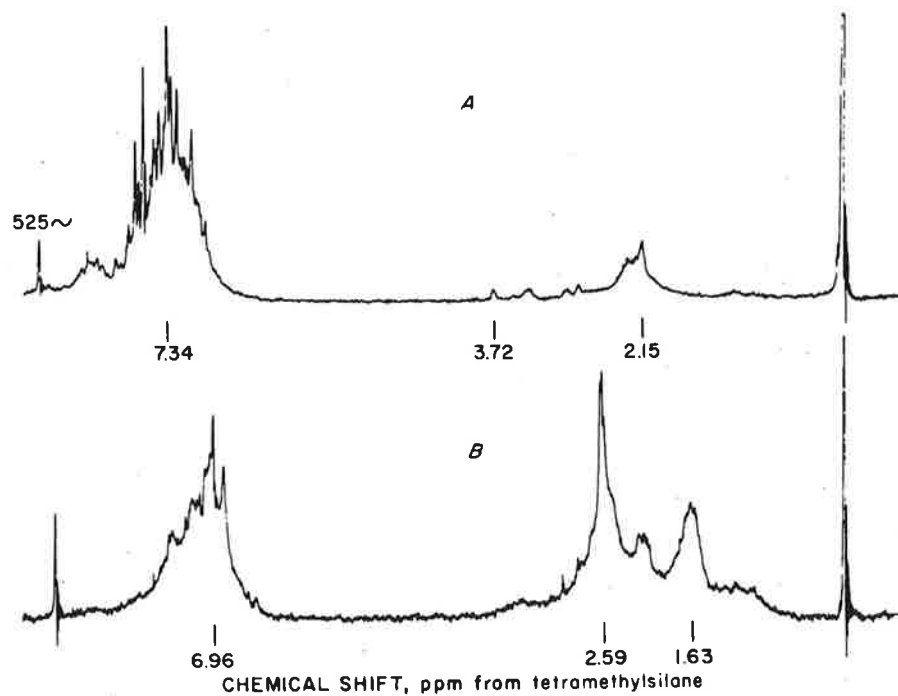


Figure 1 - Proton magnetic resonance spectra of a wax oil from coal A and its reduction product B.

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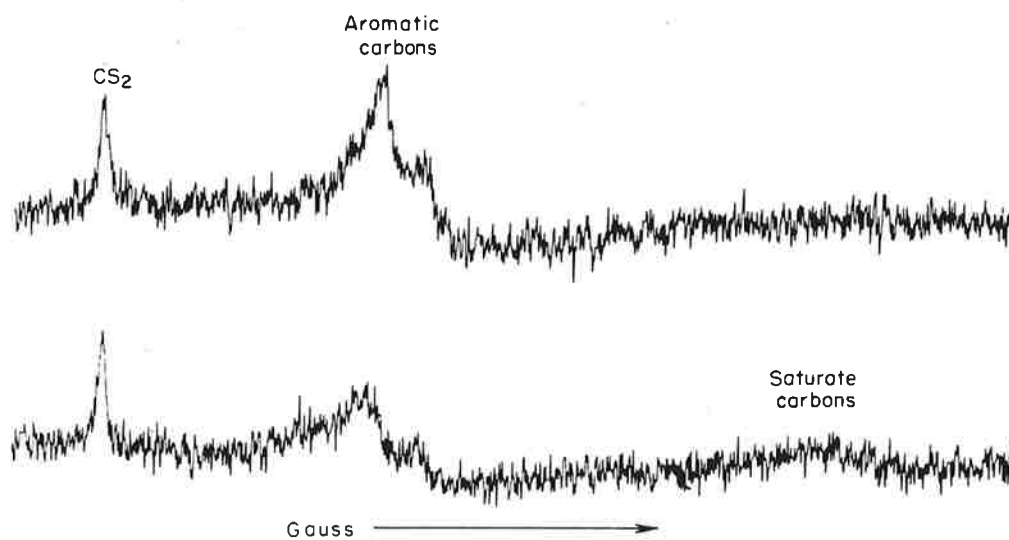


Figure 2.- ^{13}C NMR spectra of a wax oil from coal (A) and its reduction product (B).

L-8433 5-63-5

In response to the call for possible new names for MELLONMR, several of our far-flung brethren have come forward with suggestions. Some of these are rather amusing, and some may even be useful (I do not mean to imply that these two classes are mutually exclusive.). In any event, here they are for your possible entertainment and as an incentive. At the request of several of the creators, all of the suggestions are being presented anonymously..

BJS

Internationally-famous
Letters from
Laboratories
Involved in
N-M-R, with
Opportunities for
Invective and
Sarcasm

Nondescript,
Unpublished
Collection of
Letters from
Eminent but
Unscrupulous
Scientists

Nuclear
Induction
Techniques and
Writings from the
Illionis Institute of
Technology

N-M-R
Early
Warning
System

ILLinois
Institute of
Technology
Ecumenical magnetic
Resonance
And
Technique
Edition

Illinois Institute of
Technology monthly
Edition of nuclear
Magnetic resonance
Spectral knowledge.

N-M-R

Intellectually
Inspiring
Thoughts

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During the month of February 1964, this Newsletter and the undersigned will undergo the change in geography indicated in the following address, to which all Newsletter contributions and other correspondence should be sent after January 24, 1964, the deadline date for issue number 64:

Assoc. Prof. B. L. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Technology Center
 Chicago 16, Illinois.

The Newsletter (including bibliography) will continue without interruption or changes in policy as a result of this move. The Newsletter's new name will be as indicated above, in the absence of any more attractive alternatives, the call for which is hereby sounded.

B L Shapiro

Bernard L. Shapiro
 30 December 1963