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Illinois
Institute of
Technology
N-M-R
Newsletter

No. 76
JANUARY, 1965

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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".



Department of Scientific and Industrial Research
NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

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BASIC PHYSICS DIVISION

Please address any reply to
THE DIRECTOR
and quote: BP.5/7/01
Your reference:

22nd December, 1964.

Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago 16,
Illinois, U.S.A.

Dear Barry,

Since chemical shifts may be related to anisotropies of bond susceptibilities¹, readers of IITNMRN may be interested in the result of a recent measurement of the magnetic birefringence (Cotton-Mouton effect) of gaseous ethane by A. D. Buckingham, W. H. Prichard and myself. Using known optical polarizabilities and neglecting temperature independent term the molecular magnetic susceptibility had an anisotropy given by $(\chi_{||} - \chi_{\perp})_{C_2H_6} = -4.9 \times 10^{-6} \text{ cm}^3/\text{Mole} =$

$(\chi_{||} - \chi_{\perp})_{C-C} - 2(\chi_{||} - \chi_{\perp})_{C-H}$. The last form in terms of bond anisotropies assumes additivity and regular tetrahedral angles.

Yours sincerely,

D. H. Whiffen.

1. J. A. Pople, Disc. Far. Soc., 1962, 34, 68.

TELEPHONE : MW 0522.



The University of Sydney
Dept. of Organic Chem.
SYDNEY, N.S.W.

14.12.1964

IN REPLY PLEASE QUOTE :

Prof. B.L. Shapiro
Illinois Institute of Technology

Ring proton shifts in anilines and acetanilides- a large specific ortho effect.

Dear Barry,

In connection with another project, R.F.C. Brown and I.D. Rae (Australian National University, Canberra) and myself have examined the p.m.r. spectra of some simple anilines and their derivatives. The figures against the ring positions are the chemical shift changes (in c/s at 60 MC in the downfield direction) of the relevant protons on converting the amines to their acetyl derivatives (i.e. from R-H to R- -COCH_3).

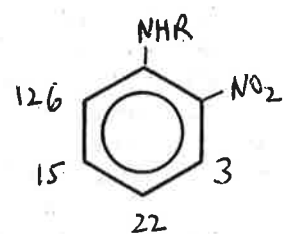
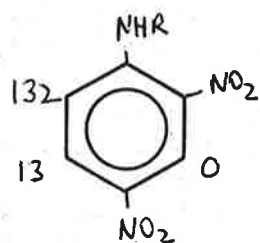
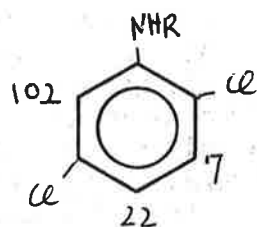
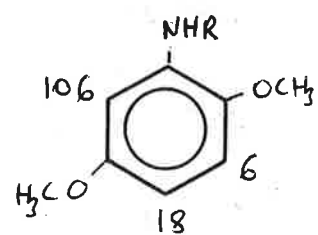
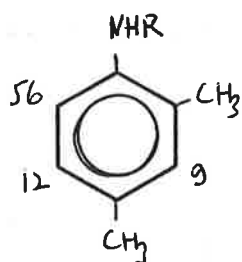
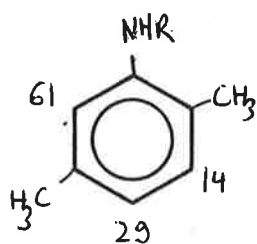
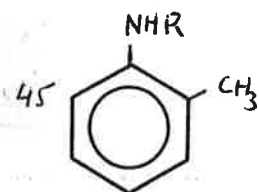
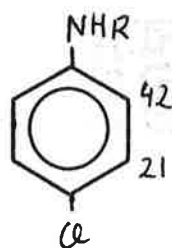
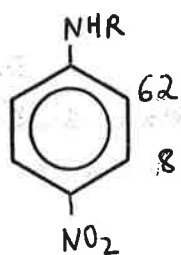
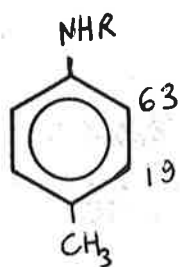
Very large paramagnetic shifts of the ortho protons are apparently associated with the presence of an ortho substituent capable of forming a hydrogen bond with the amide proton. This presumably orients the carbonyl group so that its anisotropy and/or electric dipole effects bear strongly on the remaining ortho proton. Further, in the same group of compounds, the two meta positions are shifted unequally, apparently also due to long-range deshielding, although unequal charge distribution should also be considered.

Other substituents have also been investigated: it appears that benzylation has an effect similar to acetylation (only more so) while conversion to dimethylanilino derivative causes only moderate upfield shifts, as expected. Further work in progress. All spectra are for dilute (1 - 3%) solutions in CDCl_3 .

The seasons greetings to the editor and
all readers of IITNMRN

yours sincerely


(S. Sternhell)



BASF

Dr. W. Brügel i.Fa.

*Badische Anilin- & Soda-Fabrik AG*LUDWIGSHAFEN AM RHEIN
HAUPTLABORATORIUM**Luftpost**

Dr. B. L. Shapiro

Department of Chemistry
Illinois Institute of
TechnologyChicago, Illinois 60616

U S A

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IHRE NACHRICHT VOM

UNSERE NACHRICHT VOM

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TAG

Dr. Brü/Fa

17. Dez. 1964

BETREFF

Long range coupling in tetralone and indanone

Dear Dr. Shapiro,

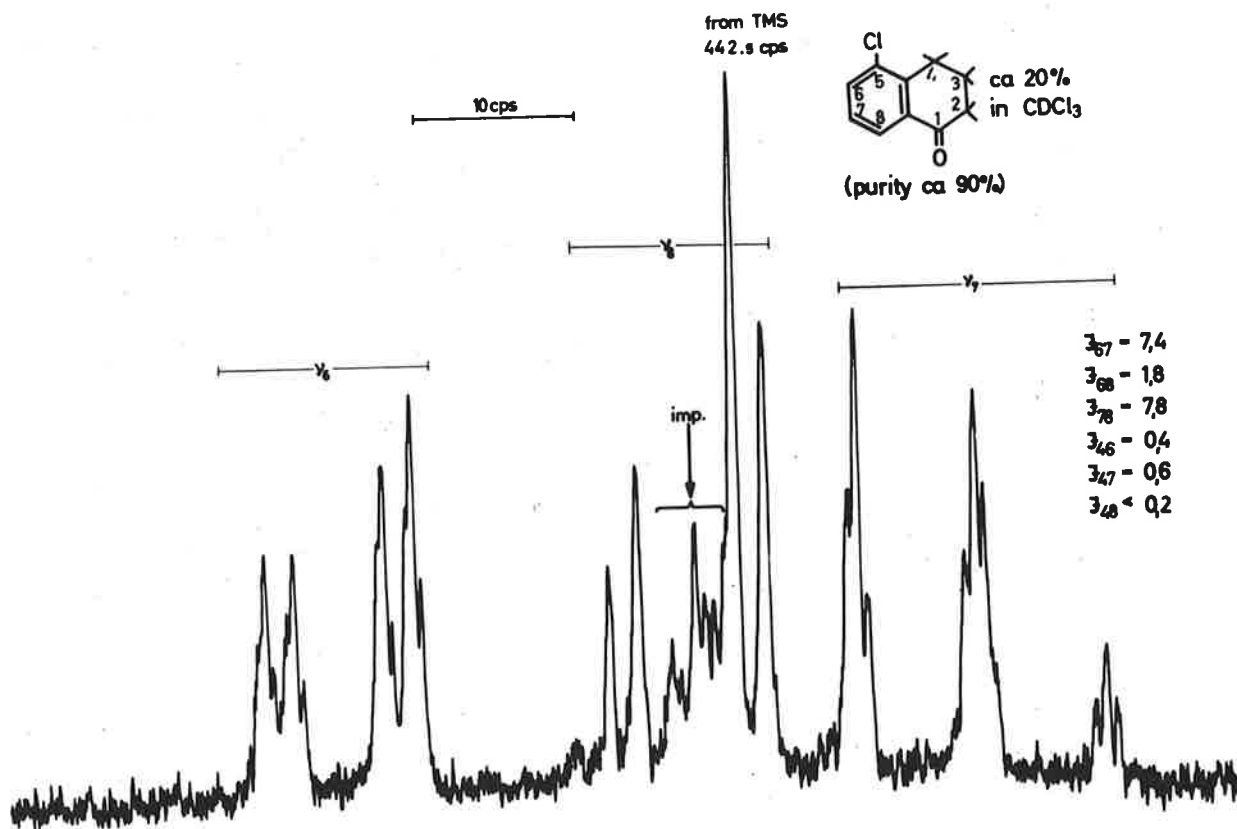
To find new long range couplings is a sport for NMR-spectroscopists. I feel it is a matter of a good instrument as well as a certain amount of fortune. Investigating the spectra of benzo-compounds with methylene groups attached to the benzene ring I found an unusual and - to my knowledge - unknown long range coupling. I enclose the low field part of the spectrum of 5-chloro-1-tetralone (the substance had a purity of about 90% only). The four lines of the proton in 7-position clearly show a splitting in tripletts. The same is the case with the lines of the 6-proton in contrast to the 8-proton. May be, the assignment of ν_6 and ν_8 has to be exchanged but this does not alter the conclusions for the 7-proton. Obviously the triplett splitting results from a long range coupling between the 7-proton and the methylene group in 4-position over six bonds with $J_{47} = 0,6$ cps. If my assignment of ν_6 and ν_8 is right, there is also a long range coupling between the methylene group in 4-position and the 6-proton but not with the 8-proton. This would agree with the statement of KOKKO and GOLDSTEIN (Spectrochim. Acta 19, 1119, (1963) that $J_{4,CH_2} = 0,0$ in acridane. If the assignment is incorrect, there is a long range coupling between the methylene group in 4-position and the 8-proton with a coupling constant smaller than J_{47} .

- 2 -

Parallel results are obtained for other compounds of similar structure, for example indanones and chromanes. If, however, there is no substitution in the benzene ring the spectra are too complicated for an exact analysis. Of course, I investigated also the signal of the methylene group in 4-position. The lines are broadened by multiple splitting as expected, but no coupling constant can be derived.

Yours sincerely,

W. Breyer





SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY

EMERYVILLE, CALIFORNIA

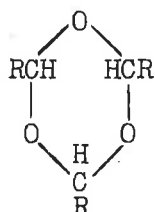
December 17, 1964

Professor B. L. Shapiro
 Editor, IIT NMR Newsletter
 Illinois Institute of Technology
 Technology Center
 Chicago, Illinois 60616

Dear Barry,

Comments on the following spectral interpretation are invited from the readers of this Newsletter.

In a recent paper [Rec. Trav. Chim. 83, 391 (1964)], Barón and Hollis have analyzed the spectra of several symmetrically substituted trioxanes:



For $R = -CCl_2CHClCH_3$ two isomers were prepared. In one of these the three ring protons are equivalent and in the other one no two ring protons are equivalent.

These results were explained on the basis of restricted rotation about the bond connecting the R group to the ring. We do not find the arguments in favor of this explanation very convincing and propose an alternative one.

We have also analyzed the spectra of several symmetrically substituted trioxanes and reach much the same conclusions regarding their structure as do Barón and Hollis (with the above exception). When $R = -CH-CH_2$ we obtain results similar to the above for the

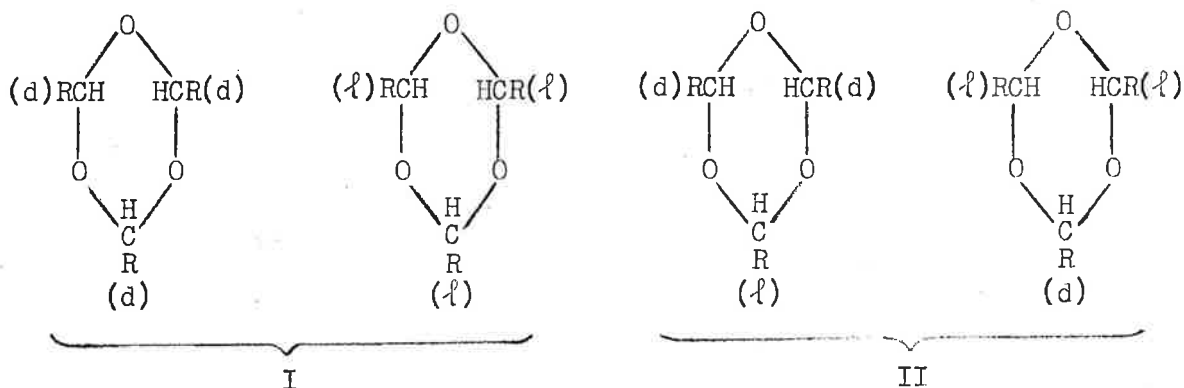
chemical shifts of the ring protons. The individual shifts depend upon the solvent but seem to be largely independent of temperature in any one solvent.

Professor B. L. Shapiro

-2-

December 17, 1964

We note that in each of the above exceptional cases the R group contains an asymmetric carbon atom. This leads to the formation of two possible racemic pairs of isomers (I and II).



In racemate I the C_3 axis of symmetry through the center of the ring makes all three ring protons equivalent. In II, which has no symmetry at all, the three ring protons can have three different chemical shifts, and in fact they do in chloroform solution.

Sincerely yours,

Charlie

C. A. Reilly

*and**for* J. L. Jungnickel

School of Chemistry
The University,
Leeds, 2,
England.

JASS/SAH

19th December, 1964.

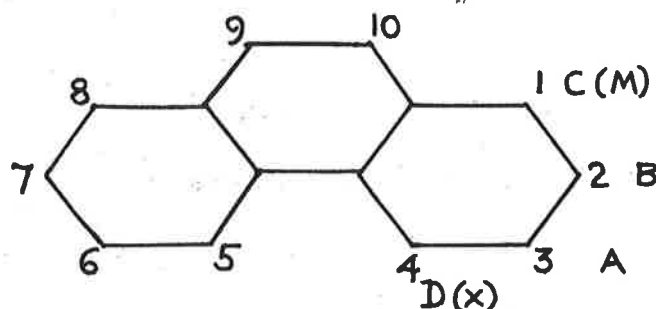
Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
CHICAGO 16, Illinois, U.S.A.

Dear Professor Shapiro,

Our apologies for the lateness of this contribution; we hope it will re-establish our "subscription".

Since our last letter, we have been studying in a systematic way the spectra of some substituted phenanthrenes, in particular the direction and approximate magnitude of the substitution shifts of the ring protons. This has already proved useful in that we have been able to identify the position of substitution (hitherto unknown) of an ethyl 9,10-dimethyl phenanthrene; this work was done in collaboration with Dr. P. M. G. Bevin of Smith Kline and French Laboratories Ltd., Welwyn.

The basis of the method is the solution of the n.m.r. spectrum of phenanthrene given by Batterham, Tsai and Ziffer (Austral. J. Chem., 1964, 17, 163). They assumed, as in previous work, (Jonathan, Gordon and Dailey, J. Chem. Phys., 1962, 36, 2443), that there are significant low-field steric shifts for the 1,4 protons, and so derived starting parameters by treating the system as



ABMX (as in the diagram): these were then refined in a symmetrical ABCD system (viz. $J_{12} = J_{34}$, $J_{13} = J_{24}$) by an iterative computer technique. We have also studied the spectrum of 9,10-dimethyl phenanthrene in a similar way; the signals from H_1 and H_8 now appear almost midway between those of H_2 , H_3 (and H_6 , H_7) and H_4 , H_5 (as in figure 1), instead of close to H_2 , H_3 as in phenanthrene.⁷ With these assignments, the parameters can be refined both as ABMX and symmetrical ABCD (in which we acknowledge the assistance of Dr. T.J. Batterham). The two sets of data compare sufficiently well with respect to the line positions (not the intensities) to suggest that the more approximate ABMX parameters can be used in making positional assignments. The effect of alkyl substituents at other positions has also been studied and the analyses are summarized in table 1. The spectrum of 3,6-dimethyl phenanthrene (figure 2) is solved by an ABX treatment

- 2 -

($H_1 = A$, $H_2 = B$, $H_4 = X$) almost exactly, since $\nu_X - \nu_B / J_{BX}$ is about 30. With 3-methyl and 3-ethyl phenanthrene (figures 3 and 4), the spectra of the substituted ring can be separated from those of the unsubstituted ring, since H_2 and H_4 in the former are shifted to slightly higher field than those of H_7 and H_8 respectively in the latter; in addition, H_4 gives a broad singlet, presumably because of weak and unresolved coupling to H_1 and H_2 .

The ethyl 9,10-dimethyl phenanthrene, in which the position of substitution of the ethyl group was unknown, gave the spectrum reproduced in figure 5. By analogy with 9,10-dimethyl phenanthrene, the lines of the ABMX pattern of H_5 , H_6 , H_7 , and H_8 can be readily picked out, since the separation of the outermost and strongest lines of the AB, M, and X groups will be very nearly the same. As for the rest, the broad singlet 0.2 ppm to the high-field side of H_5 (X, at the lowest field) has an intensity equivalent to one proton, and is in the predicted position for H_4 with small meta and para couplings. On the high-field side of this, H_8 is superimposed on two slightly broadened lines separated by 8.4 c/s, which we attribute to H_1 coupled to another proton with $J = 8.4$ c/s. The magnitude of this coupling suggests that the latter must be an ortho proton; in confirmation, we find in the highest-field group two doublets, whose centres are 8.4 c/s apart, which we assign to H_2 . The spectrum is therefore explained by 3-ethyl-9,10-dimethyl phenanthrene.

This assignment is confirmed by an analysis of the spectrum of the acetyl compound (figures 6) from which the ethyl derivative was prepared by reduction. Again, the ABMX pattern of H_5 , H_6 , H_7 , and H_8 can be picked out, but in the substituted ring H_4 (still a broad singlet) moves to the low-field side of H_5 , and H_2 also moves down field to a position near H_1 (and H_3). The chemical shifts and coupling constants derived from the spectra of both the 3-ethyl and 3-acetyl compounds are given in Table 1.

Other positions for the ethyl substituent are not consistent with the n.m.r. spectra. For example, in 2-ethyl-9,10-dimethyl phenanthrene, we expect a reasonably sharp doublet for H_4 , as in the spectrum of 2,6-dimethyl phenanthrene, rather than the broad singlet observed. Similarly, substitution at the 4 position would give a signal at $\tau < 1.8$ corresponding to only one proton, and at position 1 we expect a signal near $\tau = 2.1$ again corresponding to only one proton.

Yours sincerely,

K. D. Bartle (pp.)



K. D. Bartle

J. A. S. Smith

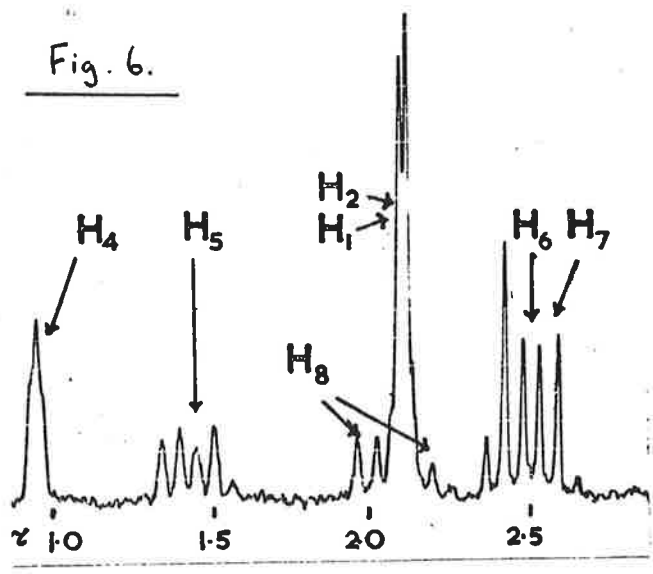
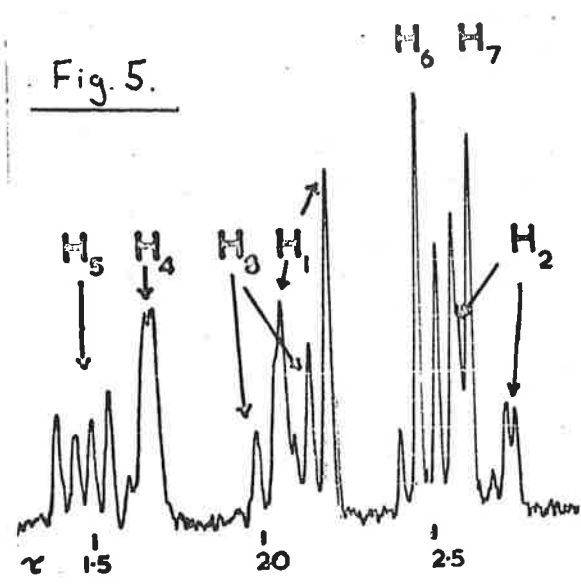
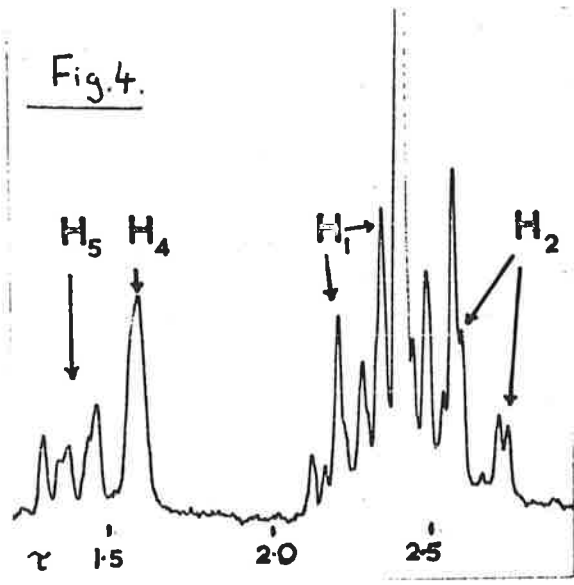
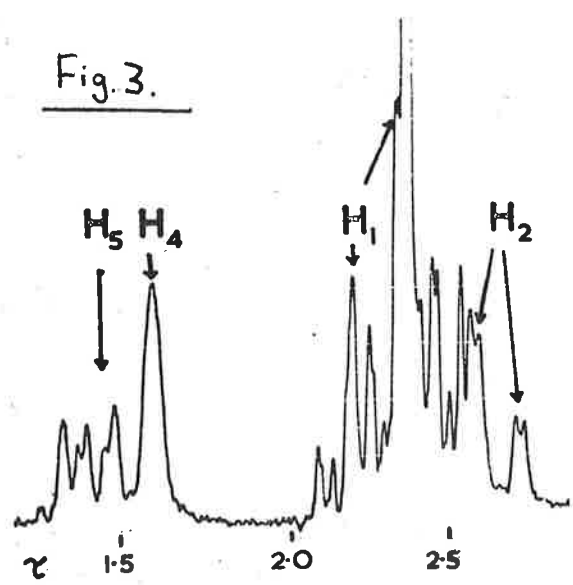
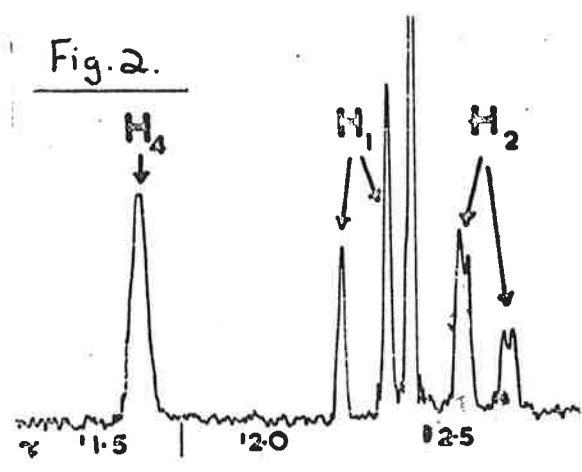
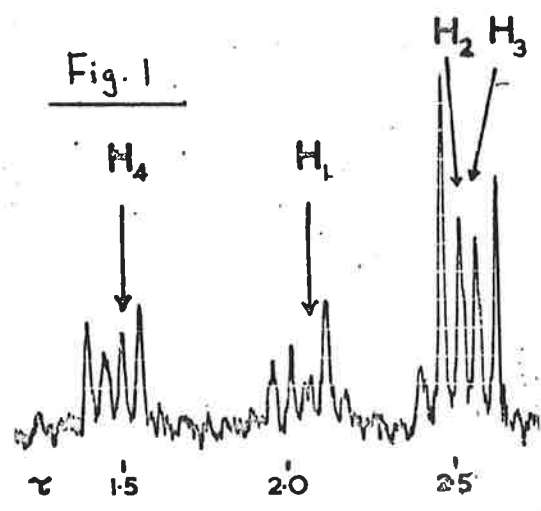


Table 1: Chemical Shifts and Coupling Constants in Phenanthrene and Substituted Phenanthrenes

Compound	Phenan- threne	9,10-dimethyl phenanthrene	9,10-dimethyl phenanthrene	3,6-dimethyl phenanthrene	3-methyl phenanthrene	3-ethyl phenanthrene	3-ethyl- 9,10-dimethyl phenanthrene	3-acetyl- 9,10-dimethyl phenanthrene
Spin System	Symmetri- cal ABCD	ABMX	Symmetrical ABCD	ABX	ABX	ABX	ABX ¹ A ¹ B ¹ MX ¹	ABMX
Solution and conc.	10% in CDCl ₃	I.D. in CS ₂	I.D. in CS ₂	I.D. in CS ₂	I.D. in CCl ₄	I.D. in CCl ₄	I.D. in CS ₂	I.D. in CS ₂
ν_1	1.875	2.025	2.035	2.38	2.32	2.275	2.11	N.M.
ν_2	2.175	2.535	2.525	2.715	2.675	2.645	2.65	N.M.
ν_3	2.12	2.55	2.54	-	-	-	-	-
ν_4	1.07	1.45	1.455	1.685	1.61	1.58	1.665	0.91
ν_5	1.07	1.45	1.455	1.685	1.40	1.36	1.455	1.415
ν_6	2.12	2.55	2.54	-	N.M.	N.M.	2.54	2.49
ν_7	2.175	2.535	2.525	2.715	N.M.	N.M.	2.54	2.49
ν_8	1.875	2.025	2.035	2.38	N.M.	N.M.	2.04	2.02
J ₁₂	8.4	9.0	8.5	8.2	8.2	8.0	8.4	N.M.
J ₁₃	1.6	0.9	1.4	-	-	-	-	-
J ₁₄	0.5	0.5	0.5	0.3	0.4	0.4	0.3	N.M.
J ₂₃	7.3	6.9	6.9	-	-	-	-	-
J ₂₄	1.6	1.7	1.4	1.8	1.6	1.6	1.8	N.M.
J ₃₄	8.4	8.0	8.5	-	-	-	-	-
J ₅₆	8.4	8.0	8.5	-	N.M.	N.M.	8.5	8.3
J ₅₇	1.6	1.7	1.4	1.8	N.M.	N.M.	1.2	1.5
J ₅₈	0.5	0.5	0.5	0.3	N.M.	N.M.	0.4	0.4
J ₆₇	7.3	6.9	6.9	-	N.M.	N.M.	6.9	7.0
J ₆₈	1.6	0.9	1.4	-	N.M.	N.M.	1.3	1.4
J ₇₈	8.4	9.0	8.5	8.2	N.M.	N.M.	8.6	8.3

Chemical Shifts (ν) in p.p.m. on τ -scale. Coupling constants (J) in c/s. I.D. = Infinite dilution. N.M. = Not measured.

AEROSPACE CORPORATION

*Post Office Box 95085, Los Angeles, California 90045*

December 28, 1964

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

Dear Professor Shapiro:

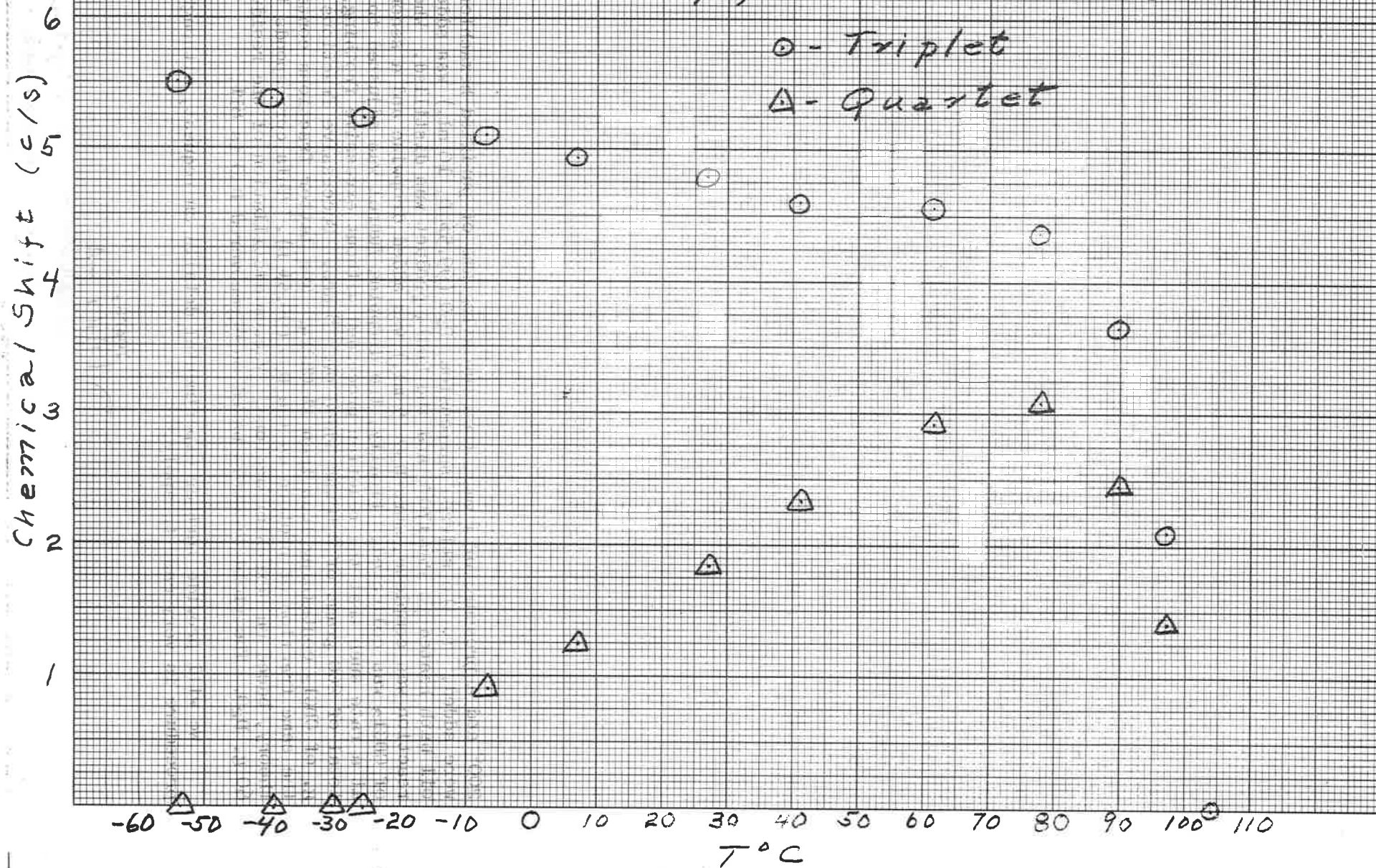
We continued our study of the chemical shifts due to hindered rotation in N substituted amides, and we continue to find rather unusual results. One of the most outstanding curiosities is shown in Fig. 1 which gives the chemical shift as a function of temperature for an 11% solution of diethylformamide in CFCl_3 . These results show two features worthy of note. 1) The chemical shift for the triplet does not approach a limiting value at low temperature as it should according to the usual theoretical considerations. 2) The chemical shift of the quartet not only does not approach a limiting value, but it goes through a maximum and then reaches a low temperature coalescence. These phenomena have us rather confused at the moment. Presumably, the amide has some strong interaction with the solvent, but it is not clear why the quartet should be a great deal more perturbed than the triplet. We will welcome any discussion that anyone would like to contribute on this subject.

Sincerely yours,

A. Greenville Whittaker

AGW/ba

Chemical Shift vs Temperature (56.4 mc)
for
11% Diethylformamide - CFCl_3



UNIVERSITY OF ILLINOIS

Department of
CHEMISTRY AND CHEMICAL ENGINEERING

URBANA

61803

The William Albert Noyes Laboratory

January 5, 1965

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

Dear Barry:

The large amounts of CDCl_3 used in n.m.r. spectroscopy make a convenient low-cost synthesis of the material very desirable. We have found the route involving hydrolysis of hexachloro-2-propanone (hexachloroacetone, Eastman Practical Grade, \$4.85 per kg.) to be very satisfactory if the starting material is suitably purified. The crude ketone contains an amount of hydrogen which gives an objectionable CHCl_3 peak in the product CDCl_3 if used without treatment. This suggests that the hydrogen is exchangeable. In fact, it is possible to reduce the amount of proton contamination greatly by a preliminary exchange with D_2O .

Two kilograms of hexachloroacetone (Eastman Kodak, Practical) were mixed with 5 ml. of pyridine and 10 ml. of heavy water. The mixture was stirred for three days. The pyridine layer was removed and the hexachloroacetone was distilled through a packed column under vacuum. Approximately the first 200 ml. of distillate were discarded. The portion which was collected boiled from $74-78^\circ$ at approximately 8 mm.

Deuteriochloroform was prepared in a 5 l. flask fitted with stirrer, addition funnel and a 60 cm. Vigreux column topped by a condenser and head designed to collect CDCl_3 and return D_2O to the reaction vessel.

Potassium carbonate (275 g.) was dried in the flask for a half hour at 200° and a pressure of 1 mm., then two kilograms of purified hexachloroacetone were added. To the stirred suspension, D_2O (99.5% D, 10 ml.) was added, the oil bath heated to $150-170^\circ$, and the CDCl_3 product was distilled. When reaction was complete, more D_2O (5 ml.) was added dropwise and a second fraction of CDCl_3 was collected. Finally, the dropping funnel was adjusted to add D_2O at a rate such that the reaction proceeded without excessive frothing. A total of 200 grams of D_2O was added over 8 hrs. Successive fractions gave 1370 g. of CDCl_3 containing less than 1% CHCl_3 . The latter fractions contained about the same fraction of protons as the D_2O (99.5% D). This corresponds to 75% of theory, based on hexachloroacetone. Vacuum distillation of the residue gave 60 g. D_2O . The yield of CDCl_3 based on unrecovered D_2O is 81%.

We will provide further experimental details on request, although the procedure is very easy to apply.

Yours,

J. C. Martin, J. H. Englemann

PD Dr. W. v. Philipsborn
Organisch-chemisches
Institut der Universität
Zürich

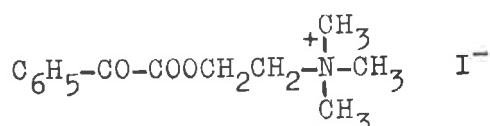
Jan. 6, 1965

Prof. B.L. Shapiro
Illinois Institute of Technology
Chicago, Illinois 60616

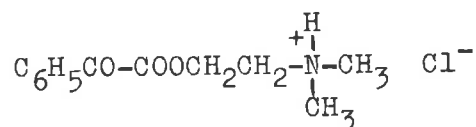
Dear Barry:

Despite your efforts to "catalyse" another contribution from our laboratory I did not make the deadline of Dec. 18, sorry. Here now is a still incomplete story or the semi-quantitative picture of an observation we recently made.

An abstracted lecture on the hydration of pyruvic acid ^{*)} prompts us to report first results of our studies on a similar system. We came across the hydration of α -ketocarboxylic acid esters while examining the NMR spectra of phenylglyoxylcholine iodide (I) and N,N-dimethyl-2-phenylglyoxyloxy-ethylamine hydrochloride (II).



(I)



(II)

Since II is soluble in CDCl_3 and D_2O one can conveniently study the effect of hydration from the NMR spectra. Furthermore the very pronounced temperature dependence of the D_2O spectra facilitates equilibrium and kinetic studies.

The 60 Mc/s spectrum ^{**) of II in CDCl_3 and the assignment of peaks are shown in fig. 1. The spectrum in D_2O (fig. 2) shows a doubling of the N-methyl, $\text{N-CH}_2\text{-}$ and $\text{O-CH}_2\text{-}$ signals and a characteristic change in the aromatic pattern. The relative integrals of the above mentioned signal pairs correspond to the expected values. However, the ratio of the integrals of the low field aromatic quartet and the main aromatic absorption is now about 1 : 2.7 compared with the value of 1 : 1.5 in the spectrum in CDCl_3 indicating that in D_2O in about one third of the material the keto group is masked. The presence of two species in aqueous solution in equilibrium is demonstrated by the reversible changes in the}

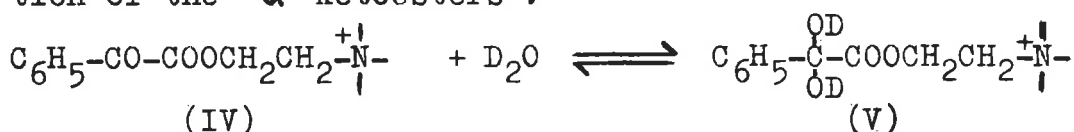
W.v.Philipsborn page 2

in the intensities and the relative chemical shifts of all signal pairs when the solution is heated or cooled. Fig. 2 gives the results obtained for the N-methyl peaks.

Compound I in D_2O (fig. 3) shows the same features but at $31^\circ C$ the ratio of the two species is about 1:1.

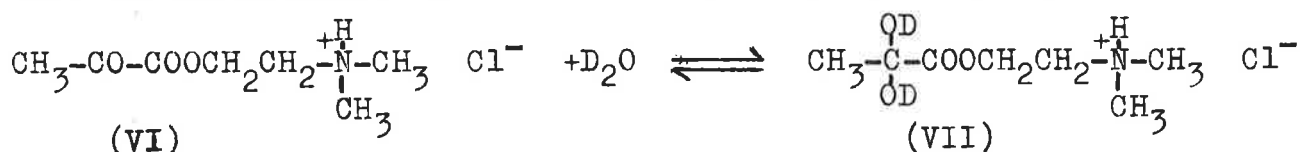
The benzoylcholine cation $C_6H_5-COOCH_2-\overset{+}{N}(CH_3)_3 I^-$ (III) however gives a normal spectrum both in CF_3COOH and D_2O . For the quaternary methiodides CF_3COOH was chosen instead of $CDCl_3$ for solubility reasons. The spectrum of I in CF_3COOH also arises from a single form and is very similar to those of II in $CDCl_3$ (fig. 1) and of III in CF_3COOH (fig. 4).

The observed abnormal spectra can be interpreted in terms of hydration of the α -ketoesters:



The possibility that V reacts with a second molecule of ketoester to form a hemiketal dimer cannot be excluded at this time.

The pyruvic acid ester VI in D_2O also shows the presence of a mixture of the ketoester and the corresponding hydrated form VII:



The higher multiplicity of the $O-CH_2-$ compared with the $N-CH_2$ - proton signals in I and III (fig. 3 and 4) may belong to the wellknown phenomenon of β -CH protons coupled to a quaternary nitrogen atom.

The relatively large chemical shift ($\Delta\delta$) of the terminal N-methyl protons in the ketoesters and hydrated ketoesters (~ 0.3 ppm) seems remarkable and calls for further studies.

The work was carried out in collaboration with Dr. K. Banholzer and we wish to thank Dr. K.N. Nagarajan for stimulating discussions.

With best wishes for a prosperous New Year to the very efficient staff of the IIT NMR Newsletter

Yours sincerely,



(W. v. Philipsborn)

W. v. Philipsborn page 3

- *) M. Becker, Deutsche Bunsengesellschaft für Phys.Chem. eV., Frankfurt/Main, Abstracts of the 63. meeting, Berlin, May 7, 1964, page 122.
- **) Chemical shifts for CDCl_3 and CF_3COOH solutions are relative to TMS as internal standard. For $^3\text{D}_2\text{O}$ solutions a 5% solution of TMS in CCl_4 was used in a separate tube (DHO signal at 285 c/s from ^4TMS at 31°C).

Fig. 1

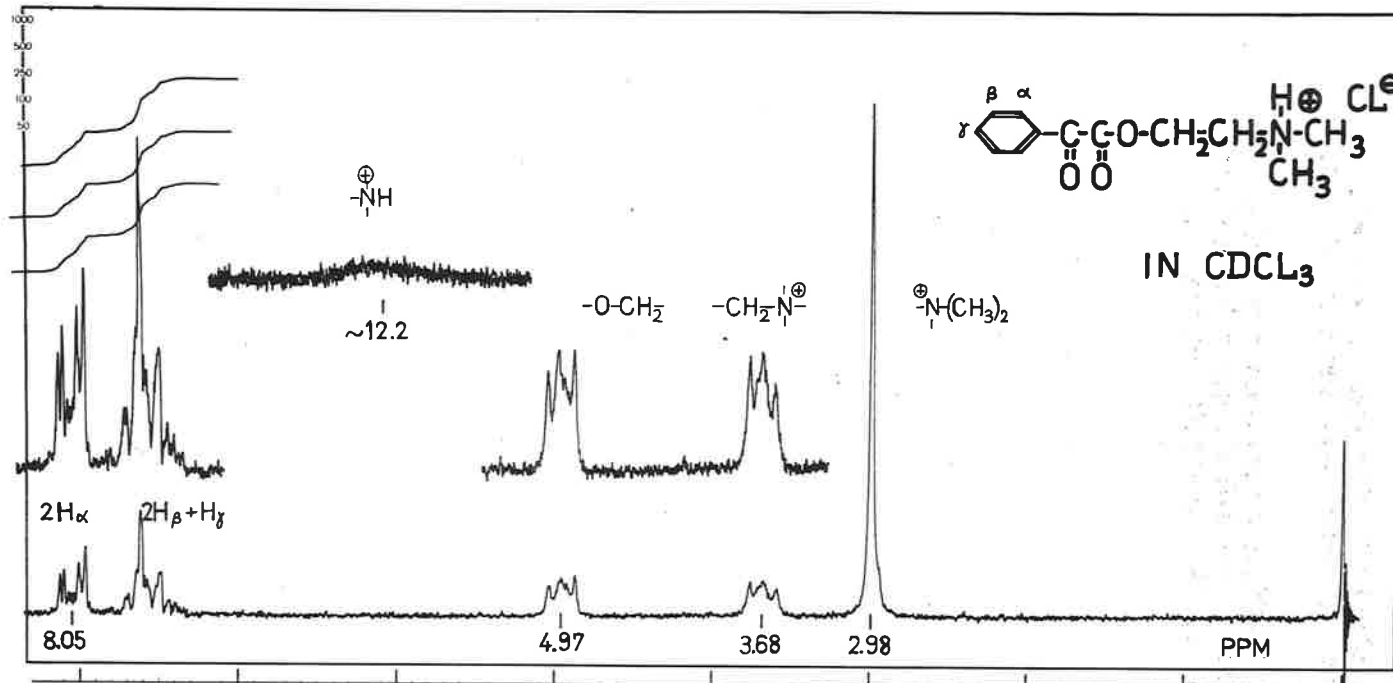


Fig. 2

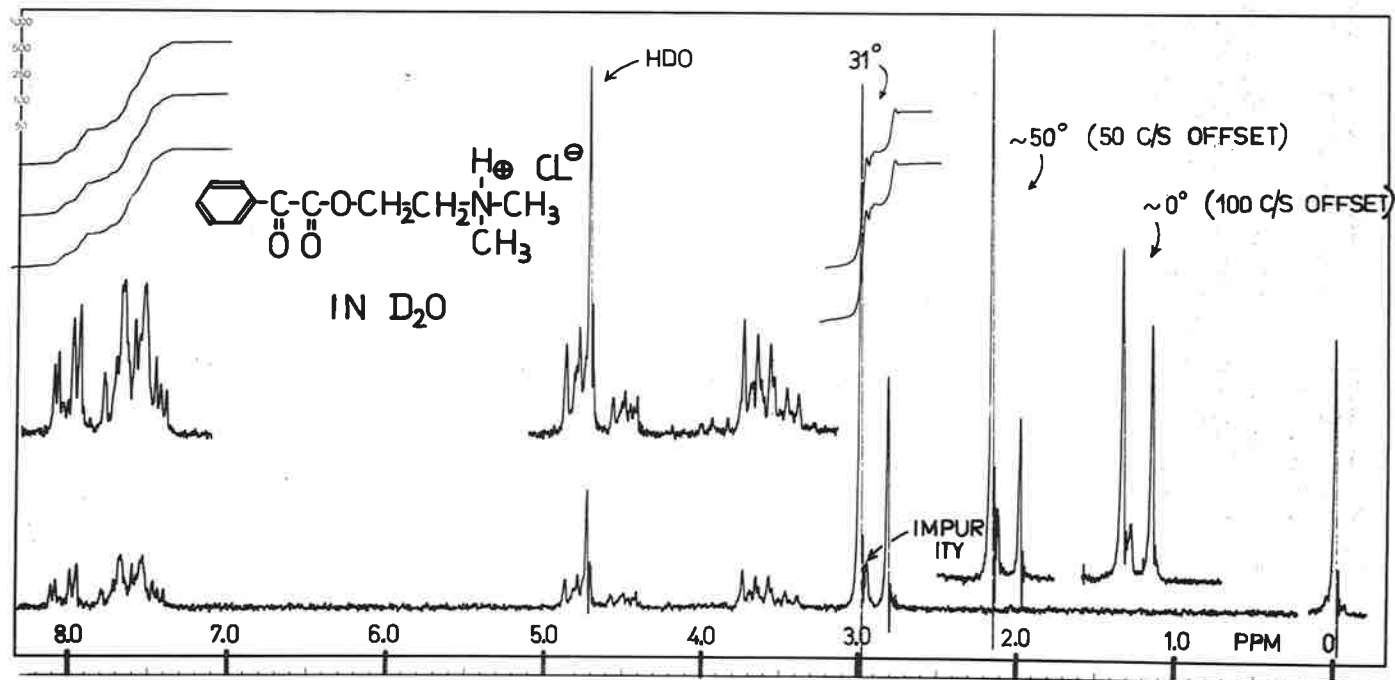


Fig 4

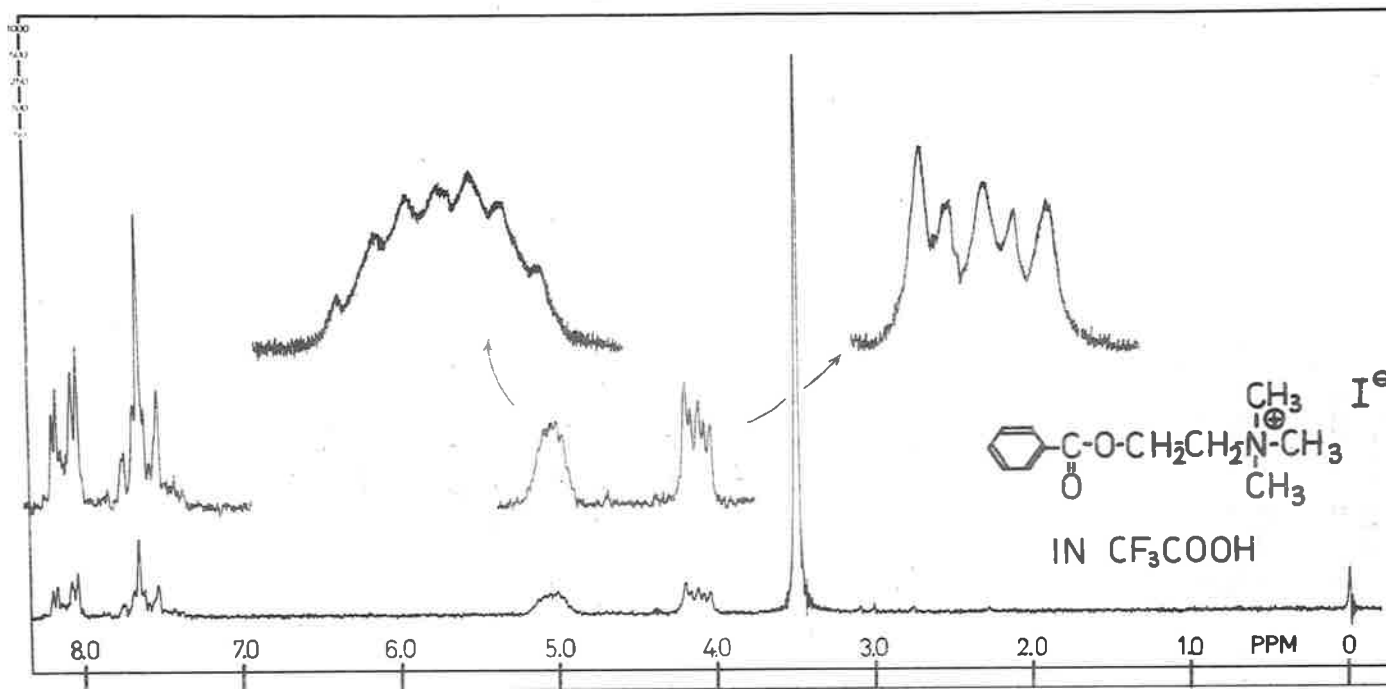
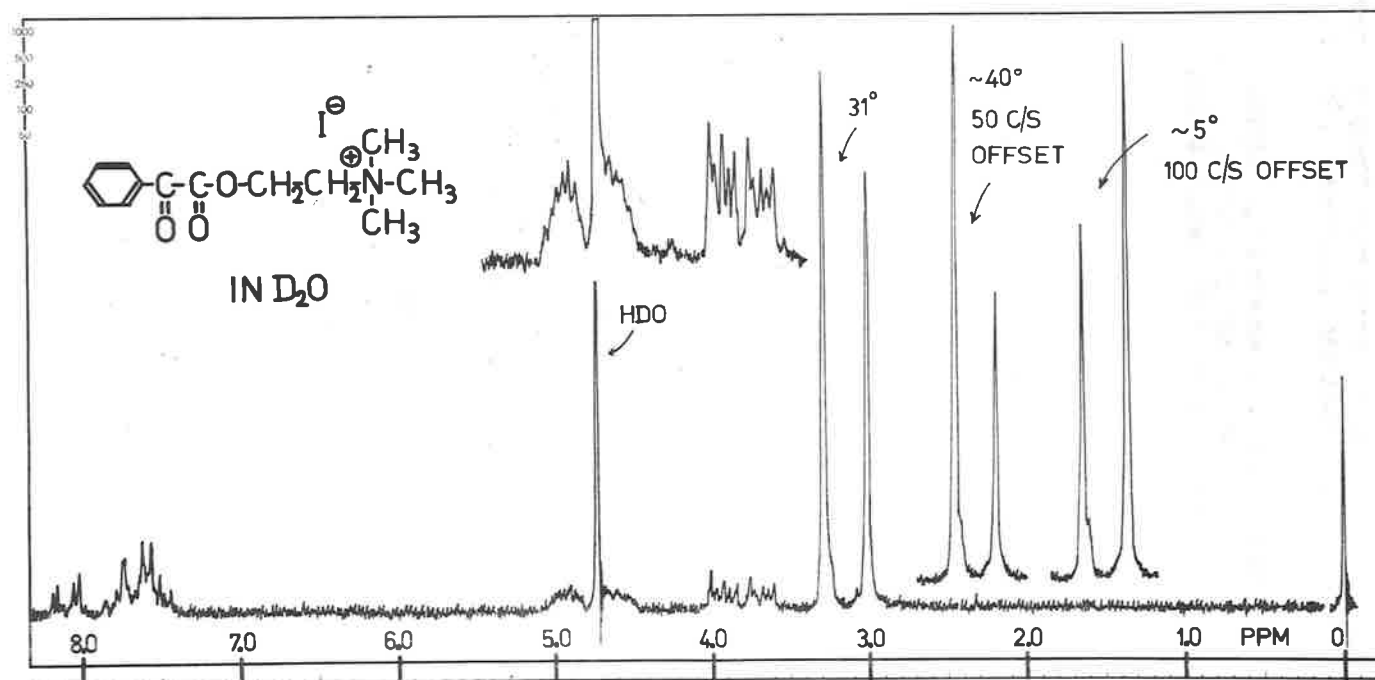


Fig 3



INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Dr. H. Günther

KÖLN, January 9, 1965
ZÖLPICHER STRASSE 47
TELEFON: 2024 239

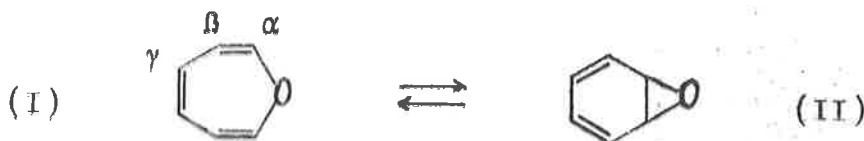
Associate Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois
U S A

Oxepin NMR-spectra

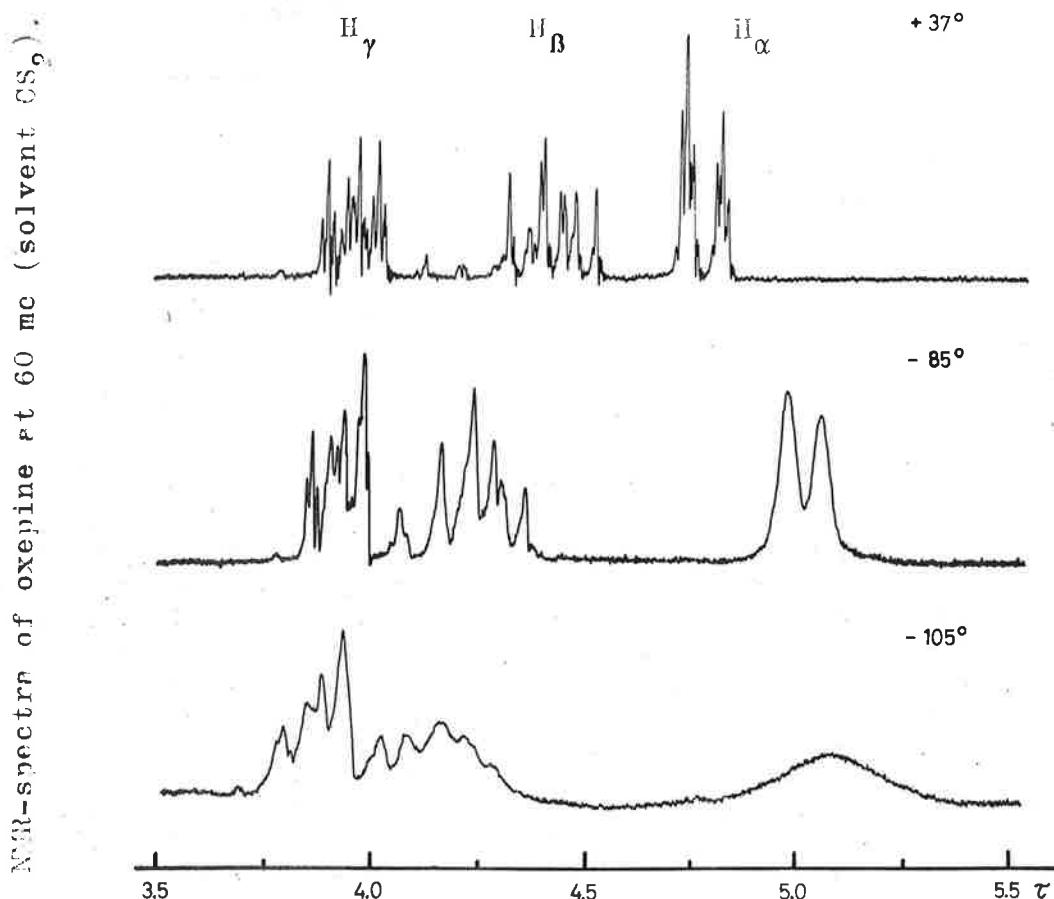
Dear Barry,

The NMR-spectrum of the recently synthesized oxepin (I) (E. Vogel, R. Schubert u. W.A. Bill, Angew. Chem. 76, 535 (1964).) shows three multiplets between 3.8 and 4.9 τ (intensity ratio 1:1:1), whose relative chemical shifts are large enough to allow assignment by first order considerations. The α -protons of I give rise to the doublet at 4.76 τ , further split by β - and γ -protons, which by themselves constitute an A_2X_2 -system, again of higher multiplicity due to additional coupling. Formally, the spectrum is of the $A_2X_2Y_2$ - or even $A_2B_2C_2$ -type and I am at present working on its analysis.

The surprising feature of the spectrum is the appearance of the α -protons at highest field. This led to the idea of a possible equilibrium between oxepin and its valence tautomer benzene oxide (II):



By comparison with model compounds one would expect the α -protons in I to absorb around 3.8 τ (values from various cyclic enolethers), whereas those of II are believed to appear between 6.5 and 7.0 τ (values from vinyl-substituted epoxides). In the rapid exchange limit all shifts (as well as the couplings) are averaged according to $\nu = \gamma_I \nu_I + \gamma_{II} \nu_{II}$ (Pople, Schneider, Bernstein, High-resolution NMR, page 218 ff.). From the above considerations and the observed chemical shift the composition of the equilibrium mixture may be estimated as close to I : II \sim 0.5 (at 37° C, 10 vol% in CS_2).



Low-temperature spectra, which were kindly recorded by Dr. H. Friebohn of Freiburg's Institut für Elektrowerkstoffe, support the original assumption (see figure above). The fine structure of the spectrum gradually disappears. The α -proton doublet finally coalesces at $-105 \pm 3^\circ C$. Lack of suitable solvents prevented so far measurements at still lower temperatures, which eventually should yield the superposition of the individual spectra of I and II.

Besides the line broadening the signal shifts with variation in temperature provide further evidence for the equilibrium $I \rightleftharpoons II$. I have found for a number of compounds, that in sevenmembered cyclic olefins of the cycloheptatriene-type the γ - and β -protons constitute an A_2X_2 -system, whereas cyclohexadienes show A_2B_2 spectra for the olefinic protons. This seems to be mainly due to the anisotropy of the double bonds, whose number and steric relationship in both systems are different. The changes in the oxepin spectra confirm these observations and indicate an equilibrium shift to benzene oxide at lower temperatures. The α -protons move to higher field, whereas the chemical shift between the γ - and β -protons gradually decreases. This behaviour is reversible and high-temperature spectra show shifts in the opposite directions. This seems reasonable with regard to the higher conformational flexibility of I as compared with the rigid II.

The observations are in accord with the olefinic character of oxepin as predicted by Hückel's rule.

Sincerely yours,

H. H. H.

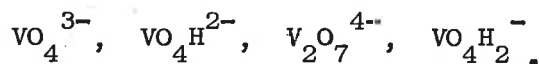
Physical Chemistry Laboratory,
South Parks Road,
Oxford.

12 January 1965

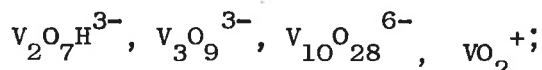
Professor Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago,
Illinois.
U.S.A.

Dear Barry,

I am writing to send you my subscription to the I.I.T. N.M.R. newsletter. I thought you might like to hear about some experiments which have been done here in Oxford by Oliver Howarth on Vanadium Resonances in Polyvanadate Solutions. The spectra were measured at 14.542 Mc/s on our wide-line spectrometer. The vanadium resonances in these solutions are often very narrow and for the narrower lines chemical shifts could be measured to ± 0.2 p.p.m. and in some cases the relative areas of lines were measured with an accuracy of about $\pm 5\%$. The reference used was VOCl_3 . This gives an extremely strong and sharp resonance. The vanadium resonance was measured in solutions of ammonium vanadate as a function of pH, of concentration, and of temperature. The ionic strength was maintained constant throughout the measurements using 6.5N sodium perchlorate. A complex series of lines was often observed in the solutions ranging over chemical shifts of about 150 p.p.m. The results confirm the existence of the ions



and also strongly support the existence of



the results broadly confirm the conclusions of Ingri and Brito (Acta Chem. Scand. 1959, 13, 1971.) The very sharp resonances obtained indicate that the basic unit in many of these structures is the VO_4 tetrahedron with its symmetrical electrical environment for the vanadium nucleus. It has been possible to observe varying exchange rates between the different species in some of the solutions.

Our double resonance work is proceeding slowly but surely. We are now able to make reasonably accurate quantitative measurements at X-band and at Q-band but progress is inevitably rather slow if the measurements are going to be accurate enough to mean anything. I hope to write more about this in my next contribution. With very best regards.

Yours sincerely,

Rex Richards

P.s. A short title would be "Vanadium resonances in vanadate solutions".

R I C H F I E L D O I L C O R P O R A T I O N

RESEARCH AND DEVELOPMENT • 1900 CRESCENT AVENUE • ANAHEIM, CALIFORNIA

January 8, 1965

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois, 60616

Dear Dr. Shapiro:

Thank you for including us on the IIT N-M-R Newsletter mailing list. We have not yet accomplished anything very sophisticated; however, we have come up with a very rapid and easy method for routine tuning of our Varian A-60 Spectrometer. This simple method is valuable to us because much personnel training and operating time is saved. The method is outlined below as we actually use it. Also described is a handy sample tube positioner.

A-60 NMR Spectrometer Tuning Procedure

I. Instrument Settings (for tuning)

<u>Control Designation</u>	<u>Setting</u>
Operate - Standby	Operate
Integral Amplitude	Off
Detector Zero	Fully Clockwise
Filter Bandwidth	4
Spectrum Amplitude	0.1
RF Field	0.08
Sweep Time	250 sec.
Sweep Width	500 cps
Sweep Zero	000 cps
Sweep Offset	Centered
Recorder Zero	Adjust pen to bottom fourth of chart.

II. Procedure

- A. Insert tuning sample (degassed solution of three parts water and one part 98% hydrazine).
- B. Place Homogeneity switch on Adjust.

- C. Adjust curvature control for maximum pen or signal meter displacement (maximum signal amplitude).
- D. Adjust γ -Gradient for maximum signal amplitude.
- E. Repeat C and D.
- F. Place Homogeneity switch on Operate.

The whole procedure takes only several minutes and results in sufficiently good resolution for most normal work. Figures 1 and 2 show "Before" and "After" tuning signals from the OH of ethanol and the acetaldehyde quartet. The "Before" OH spectrum was taken on recycling our magnet after a 1/2 day shutdown for coil flushing and the "After" spectrum was taken about three minutes later after tuning according to the above procedure. Comparison of the acetaldehyde quartet spectra of Figure 2 shows the improvement obtained on tuning with this procedure after the resolution had deteriorated under normal circumstances. Further improvements in resolution, if necessary, must be obtained by methods described by Varian.

The instrument settings shown above for tuning are quite flexible and even the critical RF field setting can be varied from 0.04 to about 0.2.

The key to this method lies in the happy compromise afforded by the water-hydrogen tuning sample between sensitivity of signal amplitude to field homogeneity changes and suitable relaxation times when locked on the signal (Homogeneity switch on Adjust). In looking for a tuning sample, proper relaxation times were most difficult to find and saturation was frequently encountered even at low RF power levels. Other tuning samples we tried were 4 and 5 to 1 solutions of water-hydrazine, water-ethylenediamine, dioxane, chloroform, formic acid, acetic acid, benzene, t-butanol-water (containing traces of Co II), acetone, and acetone-water. Of these samples the water-hydrazine solutions were best. Originally we wanted a sample that after use in tuning could also be used to check the quality of the signal by observing a ringing pattern. None of the samples gave an entirely satisfactory ringing pattern for this purpose.

Sample Tube Positioner

Since many different persons operate our A-60, we worried about probe insert breakage because of improper positioning of sample tubes in the turbine. To minimize our worries and insure proper sample tube positioning in the probe, we made a positioner by sealing one end of a piece of 9 mm O.D. (6 mm I.D.) heavy wall pyrex tubing and cutting it to the exact length (about 10.5 cm) the sample tube should extend into the probe. The result is nothing more than a narrow test tube. To position a sample tube in the turbine one simply pushes the tube into the positioner until it hits bottom with the bottom of the turbine resting on the top rim of the positioner (see Fig. 3). This positioner has been taped onto our magnet case for convenience. So far everyone has used it and no probe damage has occurred in over seven months. We're keeping our fingers crossed.

Sincerely yours,

RICHFIELD OIL CORPORATION

Fred Caserio Jr.
F. F. Caserio, Jr.
Research Associate

Fig. 1 ACETALDEHYDE QUARTET BEFORE AND AFTER TUNING

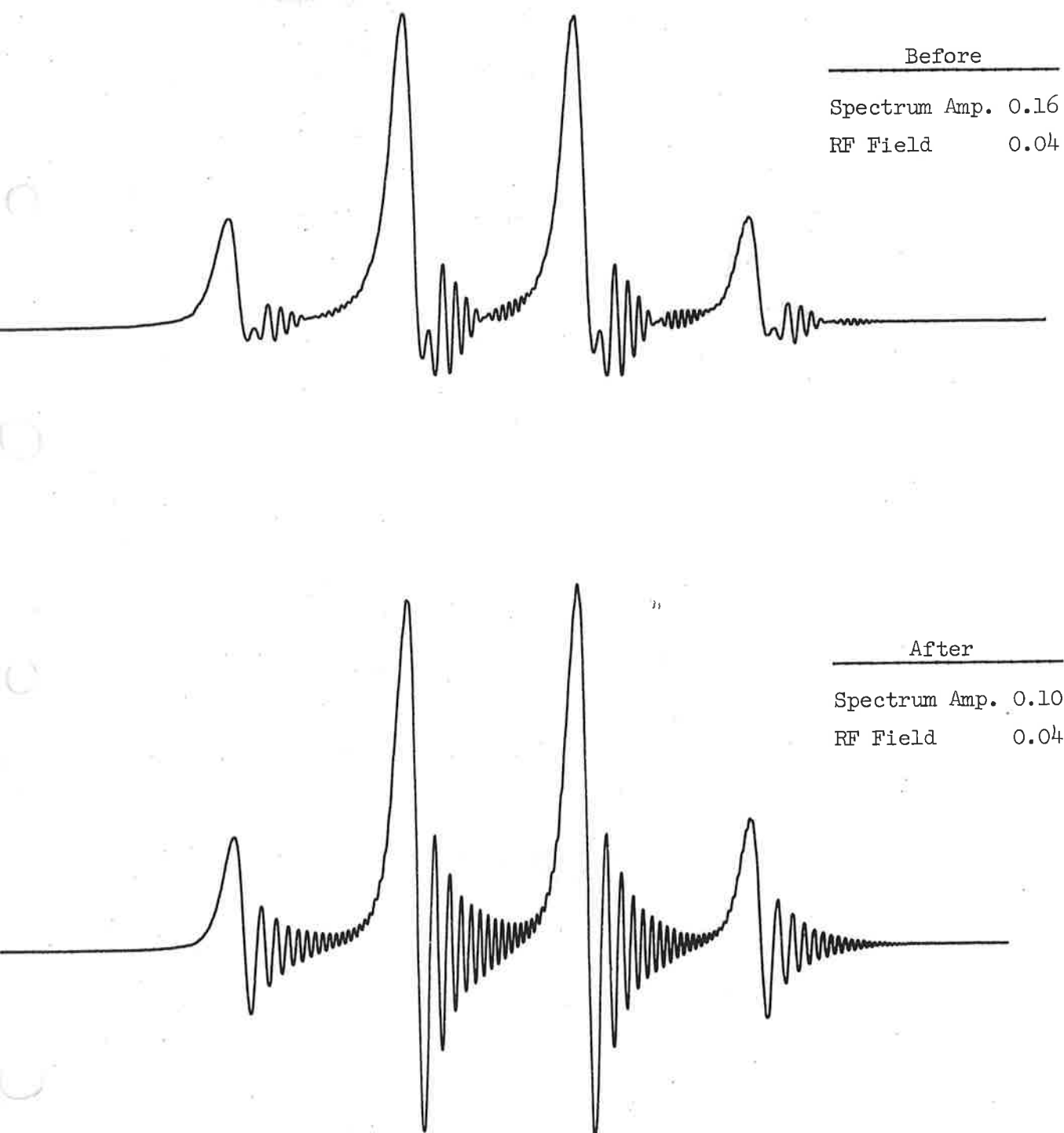


Fig. 2 ETHANOL OH ABSORPTION BEFORE AND AFTER TUNING

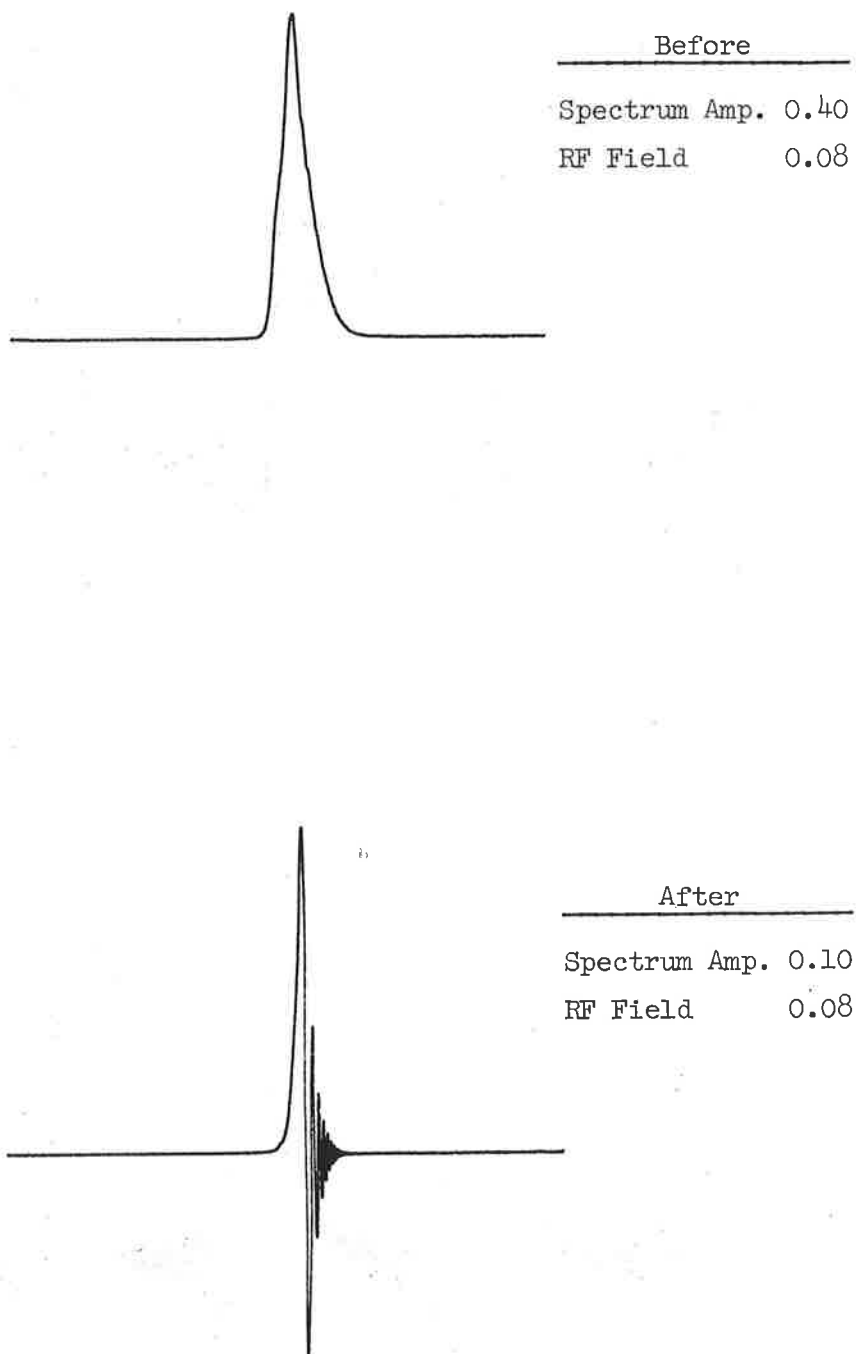
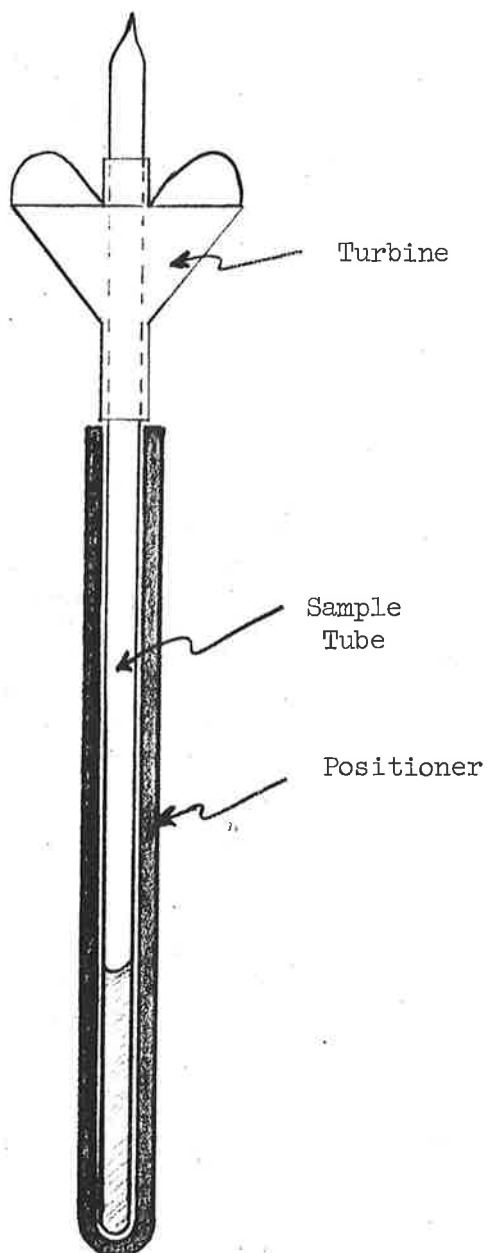


Fig. 3 SAMPLE TUBE POSITIONER



UNIVERSITY OF CALIFORNIA, LOS ANGELES

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA 90024

January 19, 1965

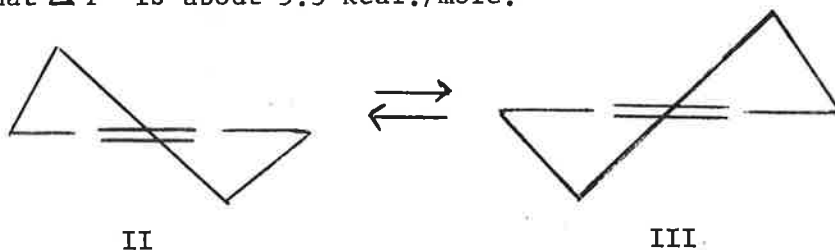
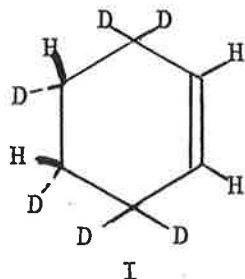
Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

We are continuing various conformational studies, which we began at the University of Ottawa, at UCLA. This involves mainly low-temperature n.m.r. measurements. One example, namely cyclohexene, which I want to mention here is of some interest because of the very low coalescence temperature, the lowest yet to be observed as far as I know. Because of the somewhat complicated spectrum of ordinary cyclohexene, we have chosen to study the deuterated cyclohexene (I), in which the protons on C4 and C5 are cis. At room temperature, H4 and H5 gave a single broad line, which became fairly sharp when strong double irradiation at the deuterium frequency was applied. Apparently, there is a small long-range coupling to the olefinic protons.

The low-temperature spectra were obtained in CF_3Br solutions. At -164° the band of H4, H5 splits into two bands. At -170° , which was the lowest temperature reached, the band separation was 19.8 c.p.s. (see Fig.) and was still increasing. The true chemical shift between axial and equatorial protons on C5 or C6 in cyclohexene is estimated to be about 24 c.p.s. Since the line width of tetramethylsilane at -170° was 6 c.p.s. it was not possible to observe any line splitting caused by the coupling of H4 and H5. Since the protons are gauche to one another the coupling constant should be small (2-4 c.p.s.).

For the ring inversion of the half-chair ($\text{II} \rightleftharpoons \text{III}$) of cyclohexene, it can be calculated from the above results that ΔF^\ddagger is about 5.3 kcal./mole.



Professor Bernard L. Shapiro

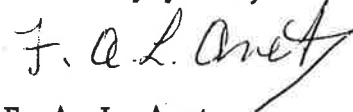
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January 19, 1965

In the last issue of IIT N-M-R Newsletter, Dr. Gutowsky mentions spin-echo work on cyclohexane and cyclohexane- d_{11} from which a value of 9.1 ± 0.1 kcal./mole was obtained for ΔH^\ddagger for ring inversion. This certainly does not agree with our results (Proc. Chem. Soc., 145(1964)) or with those of Bovey et al. If ΔH^\ddagger were 9.1 kcal./mole, it would mean that the line widths which we measured near the two extremes of the temperature range (-32° to -95°) were too small by a factor of greater than 2. As pointed out by Bovey et al. (J. Chem. Phys. 41, 2041(1964)) likely errors would tend to make the observed line-widths too large rather than too small. A value of 9.1 kcal./mole also implies a large negative entropy of activation. According to the calculation of Hendrickson, the transition state for the chair-to-boat change in cyclohexane has a cyclohexene-like geometry.

This transition state has a symmetry number of 2 and exists in mirror-image forms (previous workers have assumed a symmetry number of 1 for the transition state), so that $\Delta S^\ddagger = + 3.6$ e.u. from symmetry considerations. Of course, there may be other things contributing to ΔS^\ddagger , but these would need to amount to about -10 e.u. in order to fit the result of Gutowsky.

Sincerely yours,



F. A. L. Anet

FALA:rem

Spectrum of I at -170°

STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

DEPARTMENT OF CHEMISTRY

January 12, 1965

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

This letter is the first installment of a two-part series on carbon spectra of aromatic heterocycles for IITNMRN.

Table 1 below gives the experimental C^{13} magnetic shieldings in the six known unsubstituted azines. Theoretical shieldings have been calculated by employing a slight generalization of the Karplus and Pople treatment of aromatics to include σ charges, with the calculated wavefunctions of O. William Adams, at Abbott Laboratories, who has kindly furnished his results prior to publication. A comparison of experimental and theoretical shieldings, assuming 10% ionicity in the CN σ bonds, is shown in Fig. 1. The straight line has unit slope, and the open circles represent C - C* - C, the half-filled circles C - C* - N, and the filled circles N - C - N. It appears that the agreement in this series of compounds is quite satisfactory, even though no attempt to introduce any variation in ΔE (assumed to be 8 e.v.) was made.

A few copies of the preprint, complete with spectra and tables of line positions, are available.

Next month: five-membered rings.

Yours truly,



Paul C. Lauterbur
Associate Professor

PCL:jc

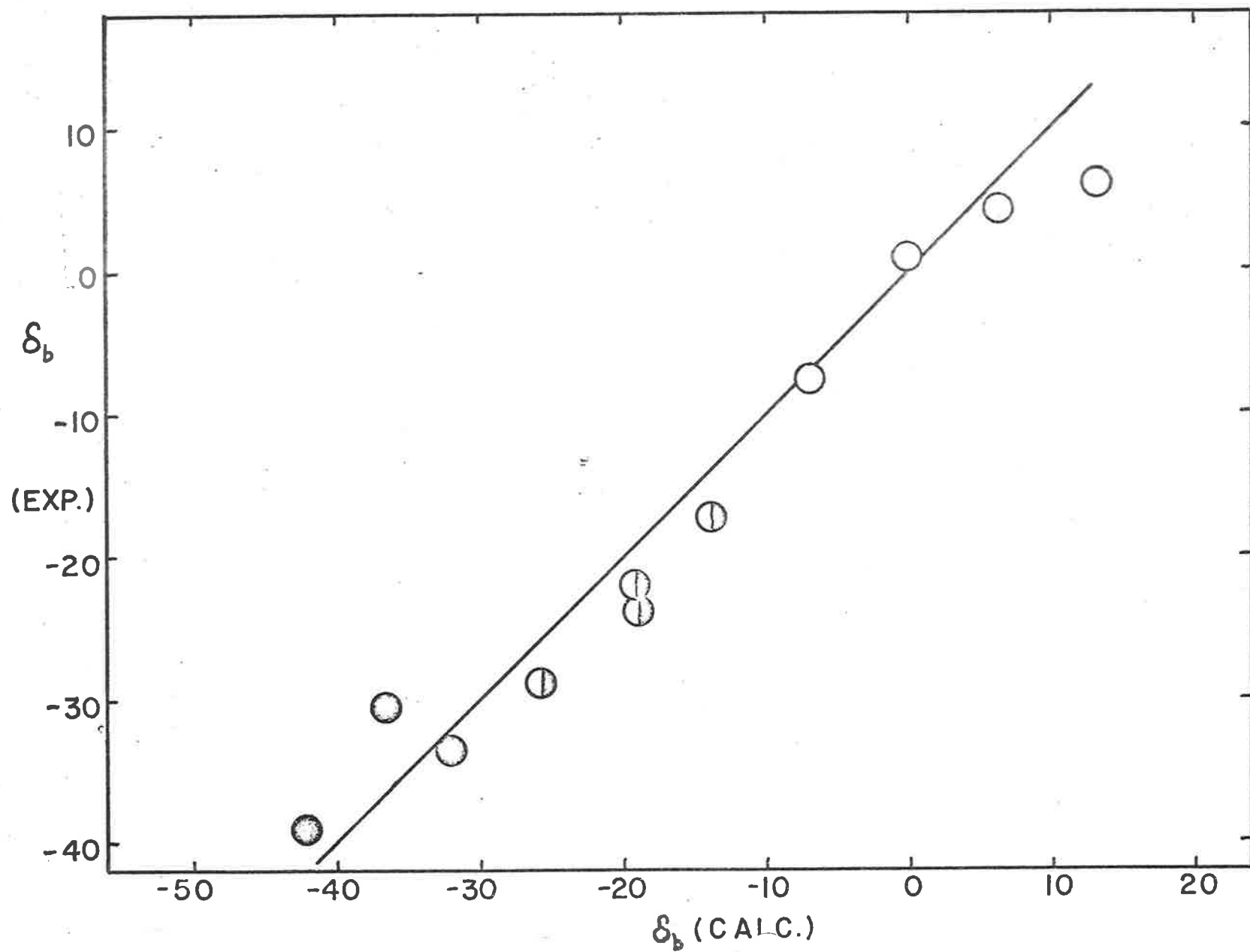
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Table I

Carbon Nuclear Magnetic Shieldings in Azines

Compound	Position	δ_c^a ppm	δ_b^b ppm	$\delta_b(\text{calc.})^c$ ppm
pyridine	2,6	43	-22	---
	3,5	69	4	---
	4	57	-8	---
pyrazine	2,3,5,6	48	-17	-18
pyrimidine	2	35	-30	-44
	4,6	36	-29	-30
	5	71	6	8
pyridazine	3,6	41	-24	-18
	4,5	66	1	-4
s-triazine	2,4,6	26	-39	-52
s-tetrazine	3,6	32	-33	-35

^aRelative to CS₂^bRelative to benzene^cCalculated from the shieldings in pyridine, assuming additivity





January 20, 1965

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

Dear Barry,

In accordance with IITNMRN policy No. 9, described most recently in Newsletter No. 66, I am writing this letter as an announcement of a Position Available.

We have an opening in our Palo Alto NMR Applications Laboratory for a chemist who has had some training and/or experience in the theory, instrumentation, and applications of NMR. The position involves running samples, interpreting results, reporting results, developing promotional material, participating in workshops, shows and training programs, evaluating new instruments and accessories, developing new techniques through applied research, and a few other odd jobs (boredom is not one of our problems).

Interested people should contact me here at Palo Alto, at the 5th ENC, or through our Pittsburgh Airport office where I will intermittently be available between February 24 and March 3.

See you in Pittsburgh.

Sincerely,

LeRoy F. Johnson
Analytical Instrument Division

LFJ:jls

Department of Chemistry,
The University,
Glasgow W.2.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
CHICAGO 60616,
Illinois,
U.S.A.

21st January, 1965.

Algol program for KDF9 computer: current research interests in the
Department of Chemistry, The University of Glasgow

Dear Barry,

The facilities available for magnetic resonance studies in this department have been considerably extended since I last wrote to you.

We now have an Algol program for calculating high resolution proton magnetic resonance spectra on the KDF9 computer. Dr. Morton-Blake of this department was responsible for the program which is a modified version of Drs. Sekuur and Kaptein's Algol translation of Frequent IV. A number of British Universities will acquire KDF9 computers in the near future and we will be delighted to supply a copy of the program to any magnetic resonance spectroscopist who is interested.

We have also acquired the first Decca e.s.r. spectrometer. Since I.I.T.N.M.R. is concerned with nuclear resonance I had better not say any more about this, but I would like to say that I am pleased with its performance, and would be happy to provide more information about it to anyone who is interested.

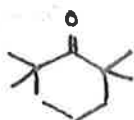
The other things that have happened here are as follows.

- a) Mr. K.W. Moore has built a spectrometer and is about to embark on a study of ^{14}N nuclear quadrupole resonances.
- b) Mr. J. McN. Barbour is studying Cl nuclear quadrupole resonances in a series of HgCl_2 complexes.

Both of these investigations are still in their infancies and so nothing is as yet available to report on them.

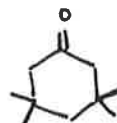
- 2 -

- c) Messrs. D.D. MacNicol and J.E. Anderson have recently been studying ring inversion and hindered rotations in several organic compounds. Among other compounds they have examined



I

and



II

Both compounds (I) and (II) show broadening of the methyl group singlets on cooling, but the individual peaks are still unresolved at $\sim -170^\circ\text{C}$., at which temperature reasonable high resolution spectra have been obtained. The solvent used was CCl_2F_2 . If it is assumed that the methyl groups are exchanging rapidly between two non-equivalent positions due to ring inversion, then it follows that the maximum value for the barrier hindering the inversion is 5 k. cal./mole. It is known that (II) exists, in the crystalline state, in a distorted chair conformation so it seems that the low barriers observed for these compounds, compared with those for other cyclohexanes, is either due to the methyl-methyl 1,3 interactions or to the introduction of the keto group, or to a combination of these effects. Mr. MacNicol is doing further work on similar compounds to try to pin down the reasons for these low barriers.

With best wishes for 1965,

Andrew

Andrew L. Porte.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

*12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.*

January 20, 1965

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60016

External Reference

Dear Dr. Shapiro:

By using a spin decoupler in conjunction with a Varian HR60 NMR Spectrometer, it is possible to perform "frequency sweep" experiments by locking the frequency-field ratio of the spectrometer to a reference signal and frequency sweeping by field modulating with an audio frequency sideband.¹ But if the material being studied is in

1. J. H. Noggle, Rev. Sci. Instr. 35, 1166 (1964).

the gas phase, it becomes rather impossible to include any material within the sample tube which will give a reasonably strong reference signal. Hence, the following procedure was adopted to obtain a reference signal:

A .075 in. OD glass capillary (KIMAX melting point capillary) was wrapped near the closed end with about 12 turns of .011 in. dia oxygen-free high conductivity wire which was insulated and held on by CIBA "Araldite" epoxy resin.² A hole of the proper diameter was drilled in

2. Paul R. Shafer, (family formula), (8-1-61).

- 2 -

the teflon backing which holds the insert in the probe such that the capillary tube is held parallel to the insert. Then the capillary was filled with tetramethylsilane (any other desired reference compound is also possible) and sealed off at the proper length. The capillary and insert were individually orientated within the probe to give minimum leakage with the coil of the capillary slightly above the receiver coil of the insert. Then the probe was balanced with the paddles as usual when both capillary and insert were connected to the RF unit. It was found that the optimum position of the capillary was in front of the insert. (Fig. 1).

The wire leads from the coil on the capillary were run up along the side of the capillary and out through the top of the probe to a coupling box containing the circuit shown in Fig. 2.³ The signal from the circuit was then fed through a 50 ohm coaxial cable to the "receiver" input of the Varian 4311 RF unit where a "tee" connector was used to permit the signal from the "preamp" on the probe to be received as well.

3. Professor R. Kaiser, (private communication).

Since the capillary is not in the center of the field the reference signal is shifted upfield or downfield by 50 to 200 cps from its normal position. Also the reference signal is broadened because of magnetic field inhomogeneity. However, since the dispersion mode signal of the sideband is used to lock, the short term stability of the lock is excellent and the long term stability better than 1 cps/hr., the drift being due to changes in the field homogeneity.

I would like to submit this note, if possible, as a down payment on a subscription to the IIT NMR Newsletter.

Yours very truly,

Leslie R. Anders

Leslie R. Anders

LRA:mo

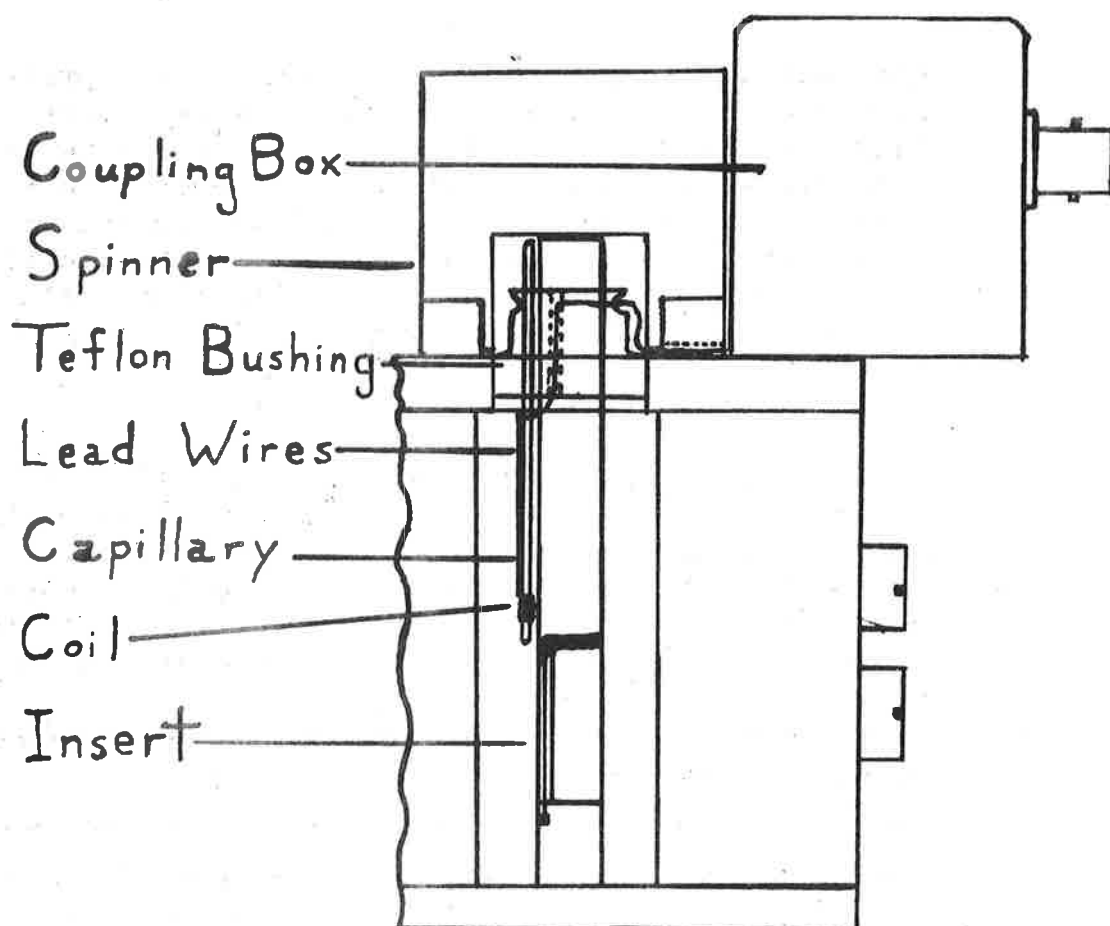


FIG. 1. Cutaway view of probe with external reference.

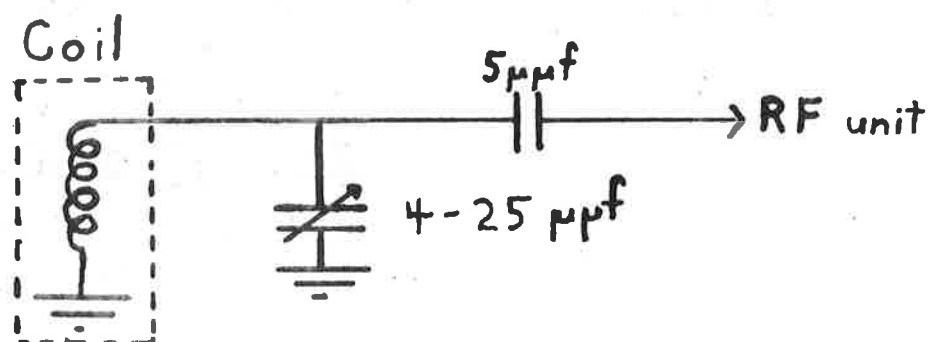


FIG. 2. Coupling circuit for tuning capillary coil to RF unit.

"Carboxylic Esters as Ligands. I. Metal Chelates of Diethyl Oxaloacetate"

R. W. Hay
Australian J. Chem. 17, 759 (1964)

"The Synthesis and Some Structural Features of 2-Methyl-1,3-Cyclobutanedione"

R. B. Johns and A. B. Krieger
Australian J. Chem. 17, 765 (1964)

"Proton Magnetic Resonance in Aromatic Nitro Compounds"

P. R. Wells
Australian J. Chem. 17, 967 (1964)

"The Synthesis and Configurational Analysis of 2,3-Diamino-cyclohexanol"

T. Suami and S. Ogawa
Bull. Chem. Soc. Japan 37, 733 (1964)

"Long-range Proton Spin-Spin Interactions in Thianaphthenes"

K. Takahashi, T. Kanda and Y. Matsuki
Bull. Chem. Soc. Japan 37, 768 (1964)

"The Cation Effect on the Polarographic Reduction of Tri-oxalatochromare(III) Ions"

N. Tanaka, E. Itabashi and R. Tamamushi
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