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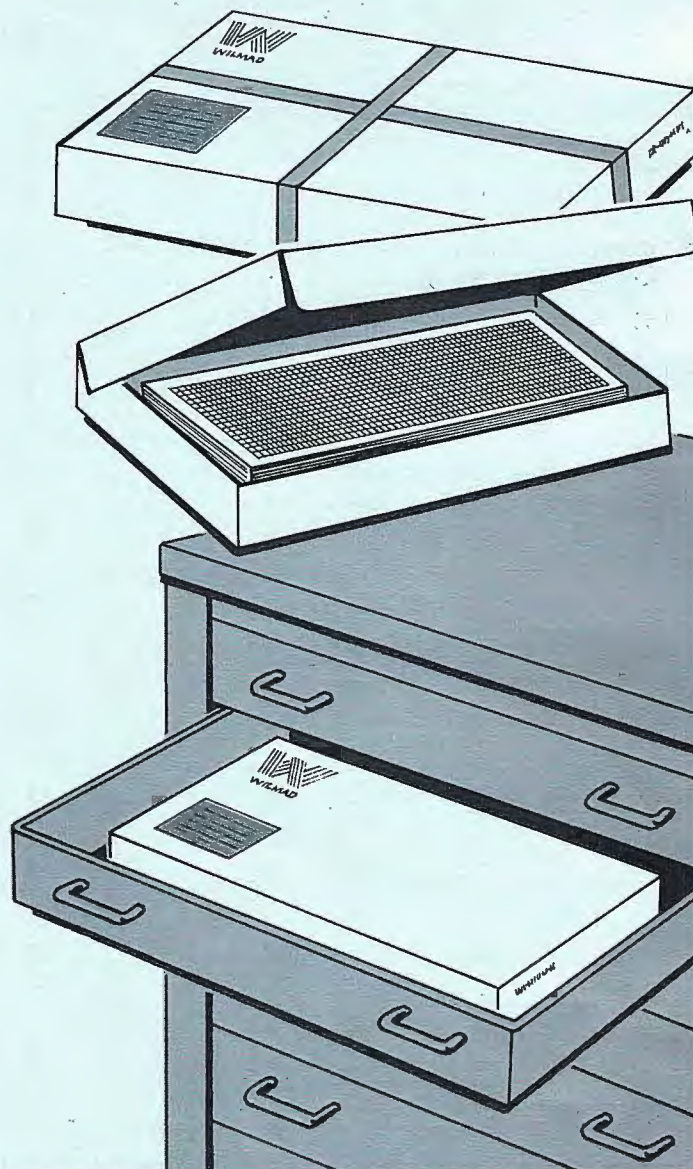
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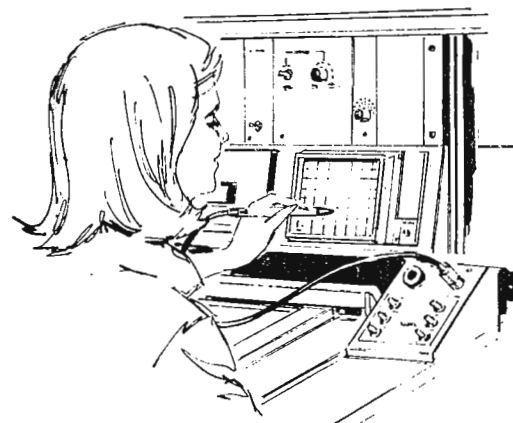
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Dr. Bernard L. Shapiro  
 Department of Chemistry  
 Texas A&M University  
 College Station, TX 77843 U.S.A.

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4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

July 15, 1977

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

Title:  $^{13}\text{C}$  Chemical Shifts of Exocyclic Methylene Carbons.

Dear Professor Shapiro:

For various reasons (dependent on funding agency approached) we have been looking at a series of substituted bicyclic dimethylene compounds. Their  $^{13}\text{C}$  spectra raise some points in connection with a recent paper by H.U. Pfeffer (Org. Mag. Res. 9, 121 (1977)). In that paper it is proposed that the steric compression in these compounds can be estimated from the relative shielding of the exomethylene carbons. One exception is noted for the norbornane-norbornene pair. We also find this discrepancy along with several others. Some typical compounds are listed below in the order of increasing exomethylene shielding and hence alleged decreasing structural flexibility. We have numbered the compounds so that they overlap with the relevant tabulation in the quoted paper. Thus we see the 4a, 4b discrepancy noted above and a similar discrepancy for our 9a, 9b pair. Even the relative shifts of 4a, 9a and 4b, 9b pairs are not in agreement with a steric compression argument. In addition, the substituted derivatives 4d and 5d should be somewhere between their respective a, b partners in order to conform; 5c is in the right position but 5e and 5f clearly are not.

In some bridgehead substituted derivatives (with groups such as methyl and t-butyl) an upfield shift of the closest exomethylene can be seen, consistent

with the introduction of a second compression shift, but shifts in both directions can be seen for the furthest exomethylene. Thus quite subtle structural changes are occurring and the situation which obtains is clearly not amenable to a one parameter interpretation. We are most doubtful that the exomethylene shift is a reliable indication of steric hindrance. Relative Diels Alder rates, which might reasonably be expected to reflect the degree of interaction between the exomethylenes, also show no decipherable correlation with the  $^{13}\text{C}$  shifts.

The only thing we can do now is hope that these compounds turn out to be biologically relevant!

Yours sincerely,

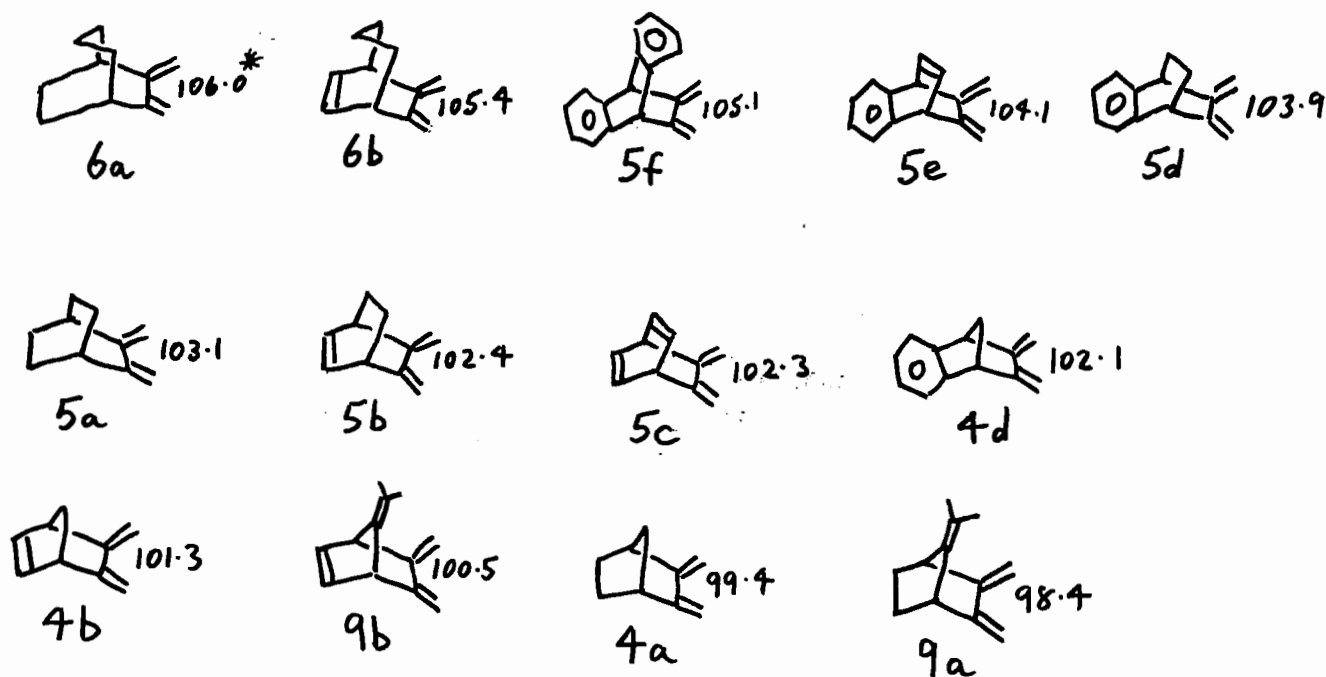
*Clive E. Holloway*

C.E. Holloway  
Associate Professor  
Chemistry

CEH/kap

With special acknowledgements to Professor D.N. Butler and Dr. R.A. Snow who made the derivatives.

FIGURE 1.



\* exomethylene  $^{13}\text{C}$  shift in ppm from TMS. Ordered in increasing shielding top left to bottom right.

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№ 43

June 28, 1977

Prof. Bernhard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College of Science  
College Station, Texas 77843

U S A

Solid state high resolution NMR of  $^{29}\text{Si}$ ; AMPERE Congress in Tallinn

Dear Professor Shapiro,

Thank you very much for your multicolored reminders. We have recently been as active as ever in the solid state high resolution NMR field, spinning nuclei heavier than carbon (mostly tin and silicon), and using the three nice new techniques,<sup>1</sup> as contrived and ably described by Stejskal et al.<sup>2</sup> Many tin and silicon compounds show complicated isomerization, condensation and association equilibria in solutions and solid state NMR provides the only means available for structure determination of amorphous solids. The  $^{29}\text{Si}$  chemical shifts are close to those in liquids in the absence of isomerization-association phenomena and we have used the low field (M) signal of the cubic  $\text{M}_8\text{Q}_8$  molecule as a solid state chemical shift secondary standard. The spectrum of this compound contains two sharp lines at  $\delta(\text{M}) = 12.6$  ppm,  $\Delta\nu_{\frac{1}{2}} = 10$  Hz and  $\delta(\text{Q}) = -108.4$  ppm,  $\Delta\nu_{\frac{1}{2}} = 16$  Hz, respectively [both shifts are given from liquid TMS on the  $\delta$ -scale;  $\text{M} = (\text{CH}_3)_3\text{SiO}_{0.5}$  and  $\text{Q} = \text{Si}(\text{O}_{0.5})_4$ ]. The central silicon (Q) provides the more anisotropic line with  $|\delta_{\perp} - \delta_{\parallel}| \approx 40$  ppm. A  $7.8^\circ$  deviation from the magic angle of rapid sample spinning was used for this determination.

Various pure silicates that give quite complicated pH- and concentration-dependent spectra in water solutions have only one sharp line in the solid state high resolution spectrum (at  $-89.1$  ppm in the cyclotetrasilicate  $\text{K}_4\text{H}_4\text{Si}_4\text{O}_{12}$ , for example).

We also want to point out that we are going to organize the XXth Congress AMPERE in Tallinn, Estonian SSR in the next year, from August 21 to 26, 1978. The Congress is going to cover all new aspects of NMR and EPR, spin relaxation and the related phenomena in optics and radiation physics, but novel applications in biochemistry and technology are going to be given serious consideration in addition to pure physics and chemical physics. Those interested in receiving the second circular are invited to contact us (T.Saluvare) before October 15, 1977.

*E. Lippmaa*  
/E.Lippmaa/

*M. Alla*  
/M.Alla/

*G. Engelhardt*  
/G.Engelhardt\*/

*T. Saluvare*  
/T.Saluvare/

1. E.Lippmaa, M.Alla and T.Tuherm, in Magnetic Resonance and Related Phenomena, Proceedings of the XIXth Congress AMPERE, Eds. H.Brunner, K.H.Hausser and D.Schweitzer, Heidelberg-Geneva, 1976, p. 113.
2. E.O.Stejskal, J.Schaefer and R.A.McKay, J. Magn. Res. 25, 569 (1977).

\* On leave from the Zentralinstitut für physikalische Chemie der AdW der DDR, Berlin-Adlershof.

XXth Congress Ampere  
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June 30, 1977

Professor B. L. Shapiro  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Dear Professor Shapiro,

RE: V2 708 Power Supply - Voltage Regulator  
TAMU NMR Newsletter April 1977 No. 233, Page 29

The advantage of the SG3501 regulator is that it is a  $\pm 15$  TRACKING regulator - i.e. positive and negative voltages are not independent as with an LM320/LM341 combination.

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2. Silicon general 3501A (3501AJ, 3501AD, etc.) - this chip is identical except that it is rated at 200 Ma output. In addition, this chip version has thermal shutdown protection.

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College Station, TX 77843

Attn: Dr. Barry L. Shapiro

Dear Barry,

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We would also appreciate recommendations from scientists who have knowledge of a potential candidate for this position.

Yours faithfully,

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Donald R. Ware  
Corporate Secretary

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Villeurbanne, le 1er Juillet 1977

Cher Docteur Shapiro,

Détermination de  $J_{35\text{Cl}-1\text{H}}$  à partir d'une mesure de  $T_{1\rho}$  du proton de  $\text{CH}_2\text{Cl}_2$ .

Il est bien connu que dans les halogénométhanés, la contribution prépondérante au temps de relaxation spin-spin du proton provient du mécanisme de couplage scalaire entre l'halogène et le proton. L'importance du phénomène dépend à la fois du temps de relaxation de l'halogène et de la constante de couplage  $J_{\text{X-H}}$  [1].

Habituellement les mesures de  $T_{1\rho}$  utilisant un faible  $H_1$  conduisent à  $T_{1\rho} = T_2$  en milieu liquide.

Par suite de la présence de différents isotopes de l'halogène, l'évolution de l'aimantation transversale du proton, s'écrit dans les conditions de spin locking sous forme d'une somme de termes exponentiels. Et plus spécialement pour  $\text{CH}_2\text{Cl}_2$  du fait de la présence des 3 types de molécules

$\text{CH}_2^{35}\text{Cl}_2$ ,  $\text{CH}_2^{37}\text{Cl}^{35}\text{Cl}$  et  $\text{CH}_2^{37}\text{Cl}_2$  nous aurons :

$$\frac{M(t)}{M_0} = \left[ \frac{9}{16} \exp - \frac{t}{T_{\text{scal } 55}} + \frac{6}{16} \exp - \frac{t}{T_{\text{scal } 57}} + \frac{1}{16} \exp - \frac{t}{T_{\text{scal } 77}} \right] \exp - \frac{t}{T_1}$$

avec

$$T_{\text{scal } 55}^{-1} = 10 \pi^2 J_{35}^2 T_{1 \text{ } ^{35}\text{Cl}}$$

$$T_{\text{scal } 57}^{-1} = 5 \pi^2 \left[ J_{35}^2 T_{1 \text{ } ^{35}\text{Cl}} + J_{37}^2 T_{1 \text{ } ^{37}\text{Cl}} \right]$$

$$T_{\text{scal } 77}^{-1} = 10 \pi^2 J_{37}^2 T_{1 \text{ } ^{37}\text{Cl}}$$

On peut admettre que  $\frac{J_{35}}{J_{37}} = 1,2$  et  $\frac{T_{1\ 37\text{Cl}}}{T_{1\ 35\text{Cl}}} = 1,64$  [2] et exprimer les

différentes contributions scalaires en fonction de  $J_{35}$  et  $T_{1\ 35\text{Cl}}$  :

$$T_{\text{scal } 57}^{-1} = 10,69 \pi^2 J_{35}^2 T_{1\ 35\text{Cl}}$$

$$T_{\text{scal } 77}^{-1} = 11,39 \pi^2 J_{35}^2 T_{1\ 35\text{Cl}}$$

Or l'expérience montre que l'évolution de l'aimantation est pratiquement exponentielle si bien que l'on admettra que l'on observe un  $T_{1\rho}$  apparent :

$$T_{1\rho}^{-1} \text{ apparent} = T_1^{-1} + T_{\text{scal}}^{-1} \text{ apparent}$$

$$\text{avec } T_{\text{scal}}^{-1} \text{ apparent} = \frac{9}{16} T_{\text{scal } 55} + \frac{6}{16} T_{\text{scal } 57} + \frac{1}{16} T_{\text{scal } 77}$$

$$\text{soit } T_{\text{scal}}^{-1} \text{ apparent} = 1,035 T_{\text{scal } 55}$$

Le spectre du chlore 35 observé en bande large à 22°C conduit à une séparation pic à pic de la dérivée du signal d'absorption, égale à 11,3 Gauss. On en déduit  $T_{2\ 35\text{Cl}} \approx 39 \mu\text{s}$ . L'incertitude est de l'ordre de 5 %

Les valeurs de  $T_1$  ( $29,4 \pm 0,8$  s) et  $T_2$  ( $11,38 \pm 0,15$ ) du proton, obtenues par impulsions audiofréquence [3] à 30°C conduisent à  $T_{\text{scal}} = 18,6 \pm 0,7$  s. On obtient ainsi une valeur de  $J_{35\text{Cl}-1\text{H}} = 3,67 \pm 0,15$  Hz.

Recevez, cher Docteur Shapiro l'expression de nos sentiments les meilleurs.



A. BRIGUET



J. DELMAU



J.C. DUPLAN



G. TETU

[1] A. ABRAGAM "Les Principes du Magnétisme Nucléaire" PUF 1961

[2] J.H. STRANGE et R.C. MORGAN J. Phys. C (Solid State Physics) 3 1999 (1970)

[3] R. FREEMAN et S. WITTEKOEK J. Magn. Res. 1 238 (1969)



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THE UNIVERSITY OF ALBERTA  
EDMONTON, ALBERTA, CANADA  
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June 30, 1977

Dr. Barry L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas  
U.S.A. 77893

Re: Pinching the FID

Dear Barry:

We recently installed a new  $^{13}\text{C}$  pulse unit (B-LV80) on our HFX-90 and noticed "lumps" about the  $^{13}\text{C}$  resonances which were not due to sidebands nor to apodization. They only appeared with the new pulser but not with our old BSV-2 unit.

These lumps could be correlated with a pinch in the FID shown below, at about 5m sec. into the FID. Solvents with strong lock signals, e.g. acetone- $\text{d}_6$  or  $\text{MeOD}-\text{d}_4$  would produce excellent  $^{13}\text{C}$  spectra, but  $\text{CDCl}_3$  as a  $^1\text{H}$  lock would result in the lumps. We finally found the problem in the Stabilizer Feedback Amplifier, part of which is shown in Fig. 1. The large  $^{13}\text{C}$  RF pulse was getting into the amplifier (via the  $^2\text{D}$  lock circuitry), consequently causing the stabilizer and the magnetic field to do a dance (the one step) near the beginning of data collection. As a short term cure we increased the time constant of the feedback circuit shown in Fig. 1 by adding the components indicated with the dashed line. The best solution, of course, is to eliminate the  $^{13}\text{C}$  pulse from the  $^2\text{D}$  lock channel with an appropriate filter.

Sincerely,

*Tom Nakashima*

Tom Nakashima

TN/ss

P.S. Making the time constant too long results in a sluggish lock response.

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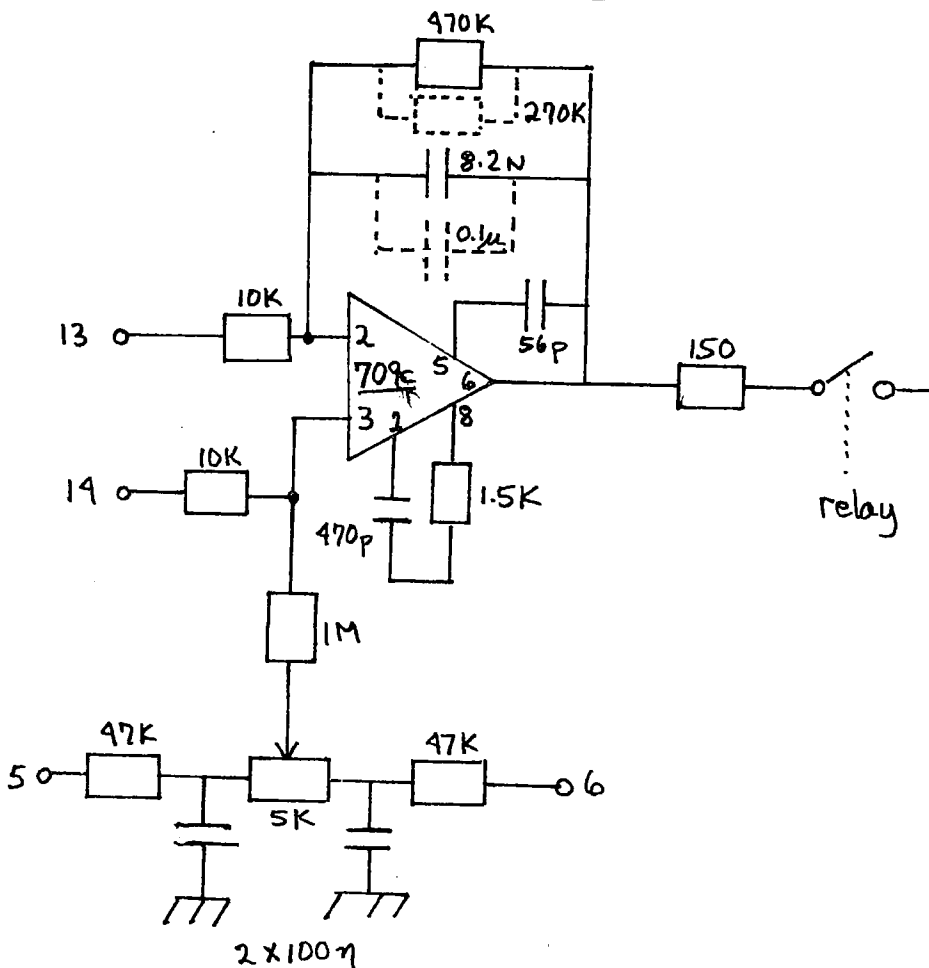
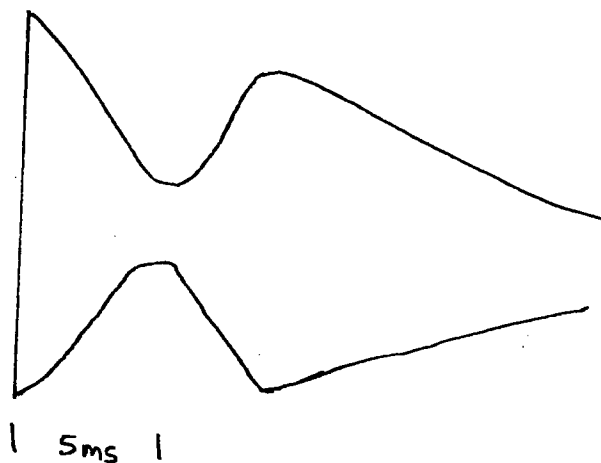
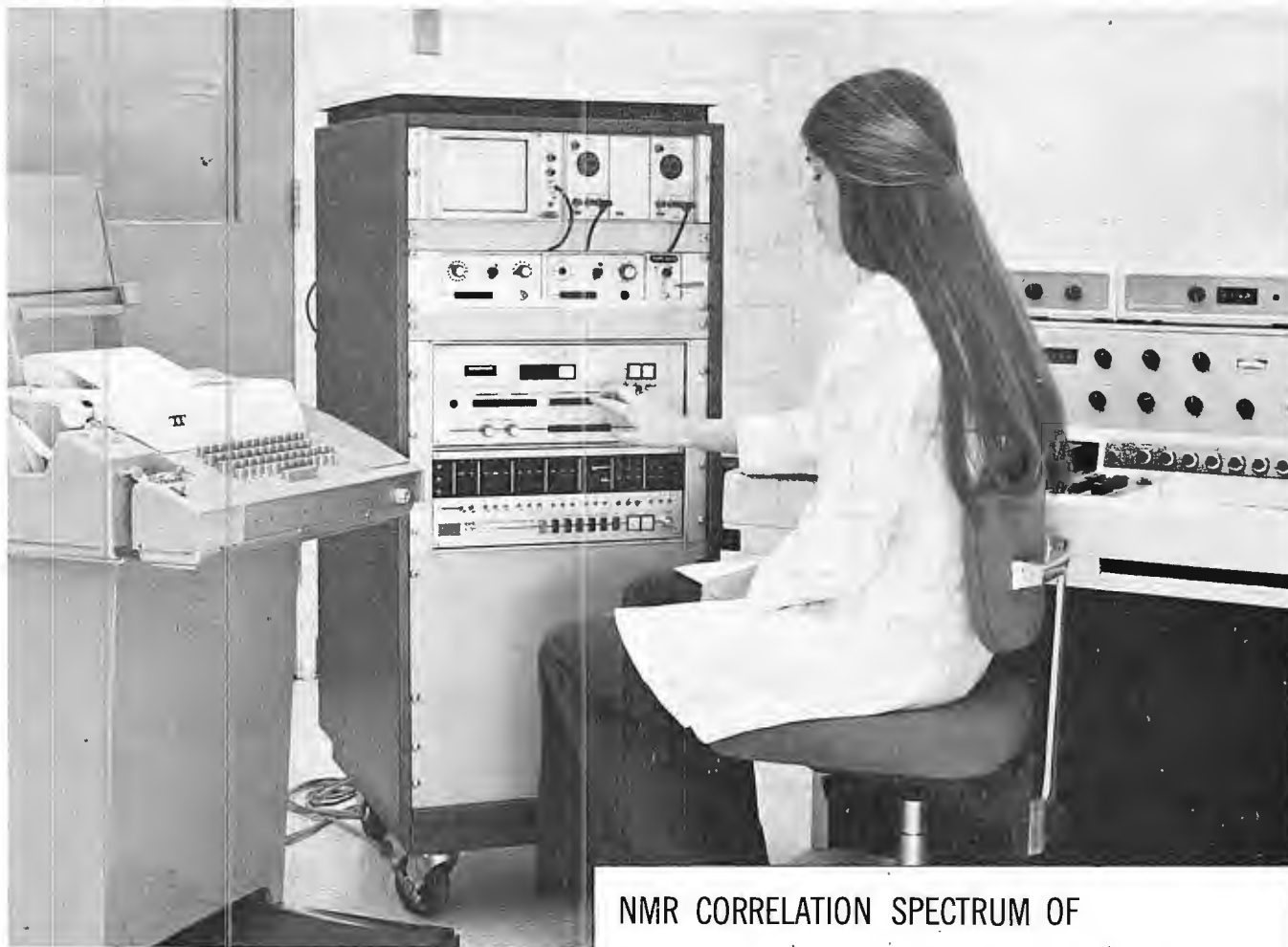


Fig 1. Stabilization Feed back Amplifier



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FID

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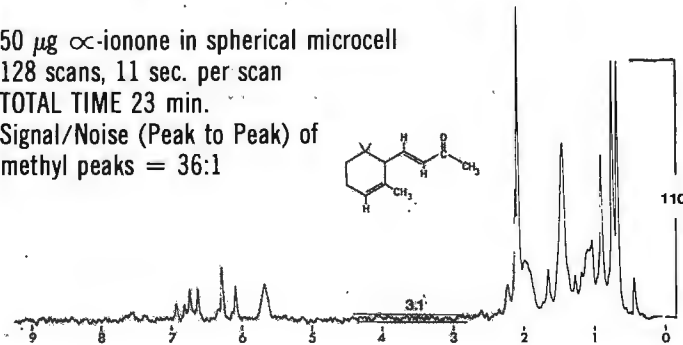
## NMR CORRELATION SPECTRUM OF

50  $\mu$ g  $\alpha$ -ionone in spherical microcell

128 scans, 11 sec. per scan

TOTAL TIME 23 min.

Signal/Noise (Peak to Peak) of methyl peaks = 36:1



This spectrum of 50 micrograms of  $\alpha$ -ionone was obtained by correlation NMR in 23 minutes. Normal CW averaging techniques would require over 4 hours.

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## University of East Anglia

From Dr. R. K. Harris

School of Chemical Sciences  
The University of East Anglia  
Norwich NR4 7TJ  
Telephone Norwich (0603) 56161  
Telegraphic Address UEANOR NORWICH  
**ENGLAND**

1st July, 1977

Dear Barry,

NMR COMPUTER PROGRAM LIBRARY - POSITION AVAILABLE

A few months ago it looked as though finance for the Library, which now contains 34 working NMR programs and has a mailing list of about 300 institutions, would cease. Indeed it did cease on 31 March, but I have now heard that renewed support is available for the period 1977-79. Consequently I am looking for suitable candidates for appointment to a Senior Research Associate position for two years commencing (for preference) 1 October 1977. The work is to co-ordinate, develop and manage the Library. Contact with NMR spectroscopists at other U.K. universities and with the Science Research Council laboratory at Daresbury is involved, and the person appointed would also, of course, be part of the lively NMR scene here at East Anglia. Obviously some experience in computing (particularly FORTRAN programming) as well as NMR is essential. In the past the post has helped chemists obtain permanent jobs in the computing field! The starting salary will be up to £3761 per annum, depending on qualifications. There are automatic increments each August. Applications, giving a full curriculum vitae, should be sent to me as soon as possible. Further details of the post are, of course, available on request.

NMR spectroscopists on our mailing list can take this as an early indication that I hope we will be resuming the Library service on 1 October. Anyone not on our mailing list who wishes to receive manuals, bulletins etc after that date should write to me before then.

Best wishes,

Yours sincerely,

*Robin*

R. K. Harris

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

RKH/KJS



**EIDG. TECHNISCHE HOCHSCHULE  
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**Laboratorium  
für Physikalische Chemie**

Prof. Dr. R. R. Ernst

CH-8006 Zürich, 3 July 1977  
Universitätstrasse 22  
Tel. (01) 32 62 11

Prof. B. L. Shapiro  
Department of Chemistry  
Texas A+M University  
College Station, Texas 77843

EFFECTS OF MAGNETIC FIELD INHOMOGENEITY ON MULTIPLE  
QUANTUM TRANSITIONS

Dear Barry,

It is an old dream of NMR spectroscopists to record high resolution spectra without having to shim in advance the magnet for hours. We would like to show here that by selecting the proper transitions it is possible to obtain high resolution spectra in rather inhomogeneous magnetic fields. These magic transitions are the zero quantum transitions (ZQT) with  $\Delta M = 0$ . These transitions are normally forbidden but can easily be observed by means of two-dimensional spectroscopy (1).

Zero quantum transitions involve simultaneous absorption and emission of one quantum, both being affected in the same manner by the magnetic field such that their difference remains unaffected by field inhomogeneity. In a two-spin  $1/2$  system, there is only one such transition, namely  $\alpha\beta \rightleftharpoons \beta\alpha$  for weak coupling. It is indicated in the following figure, and it can be seen that it is much narrower than the four single quantum transitions (1QT).

Zero quantum transitions are special examples of multiple quantum transitions. One can easily show that the susceptibility of a p-quantum transition to magnetic field inhomogeneity is just proportional to p. Therefore, double quantum transitions (2QT) should be twice as broad as 1QT's. In the two-spin  $1/2$  system, there is again a single 2QT, the transition  $\alpha\alpha \rightleftharpoons \beta\beta$ . The figure confirms the expected additional broadening of the 2QT.

For larger systems, the number of ZQT's rapidly increases, e.g. for 3 spins  $1/2$  there are 6 ZQT's, for 4 spins  $1/2$  27 ZQT's. In many cases, these transitions contain sufficient information to determine the relevant parameters of the system although it must be emphasized that only frequency differences within a coupled spin system can be measured this way and that, for example, no chemical shifts relative to a standard like TMS can be obtained.

The figure shows a 2D spectrum of a two-spin system in an inhomogeneous magnetic field. The spin system has initially been prepared by means of two non-selective  $90^\circ$  pulses separated by 250 ms. A  $90^\circ$  mixing pulse has been applied between evolution and detection periods (1). A one-dimensional zero or multiple quantum transition spectrum could easily be obtained by projecting the 2D spectrum onto the horizontal  $\omega_1$ -axis.

(1) W.P.Aue, E.Bartholdi and R.R.Ernst, J.Chem.Phys.64, 2229 (1976)

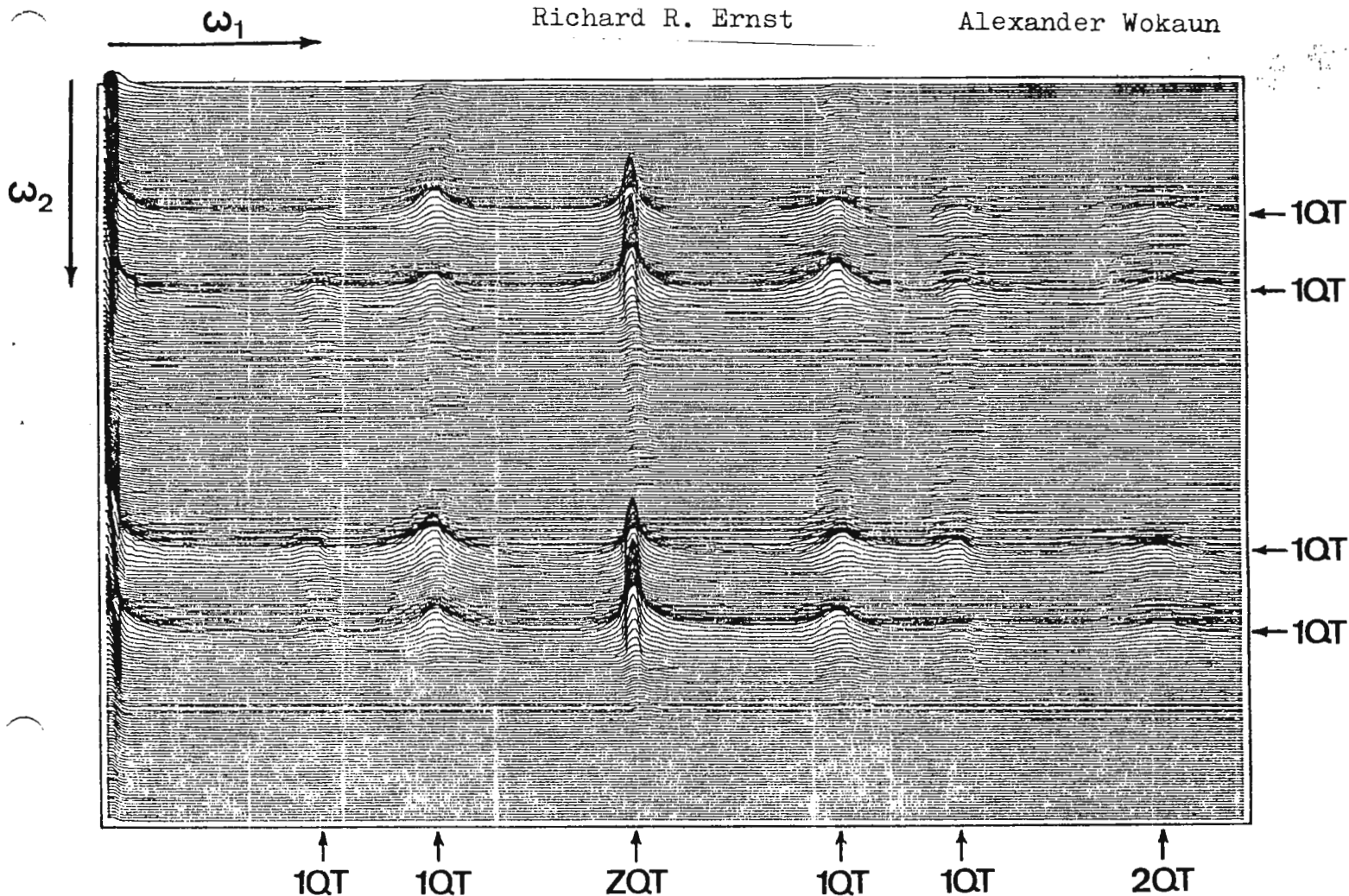
Sincerely yours

*Richard*

Richard R. Ernst

*Alexander Wokaun*

Alexander Wokaun





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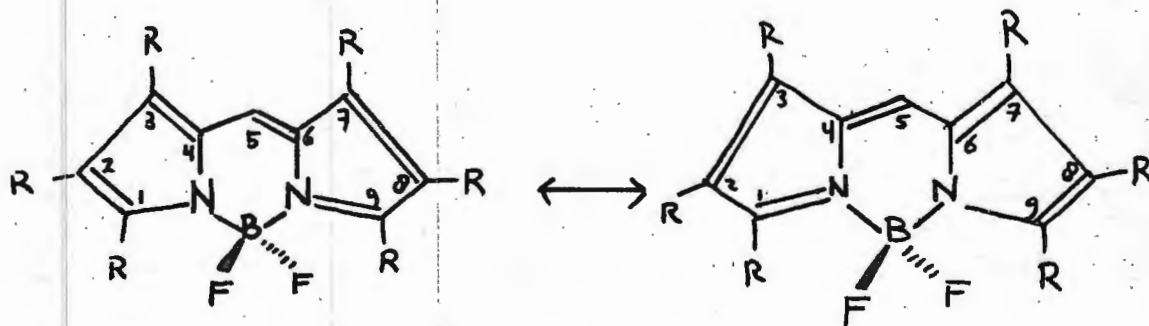
Onderwerp: Dear Professor Shapiro,

LEIDEN, 4-7-1977

Pyrromethene  $\text{BF}_2$ -complexes (4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes).

Pyrromethenes can be considered as half porphyrin systems. Metalloporphyrins play a fundamental role in life. The study of metallopyrromethenes could give useful information relevant to the biological systems. Pyrromethene  $\text{BF}_2$ -complexes can easily be prepared by reacting the corresponding pyrromethene with  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  under basic conditions. Some of the compounds we made are listed below:

- |     |                               |   |
|-----|-------------------------------|---|
| I   | R 1,3,7 and 9 = $\text{CH}_3$ | R 2,5 and 8 = H                                   |
| II  | R 2,3,7 and 8 = $\text{CH}_3$ | R 1,5 and 9 = H                                   |
| III | R 1 and 3 = $\text{CH}_3$     | R 5,7,8 and 9 = H    R 2 = $\text{C}_2\text{H}_5$ |
| IV  | R 1 and 9 = $\text{CH}_3$     | R 2,3,5,7 and 8 = H                               |



Pyrromethene  $\text{BF}_2$ -complexes

The  $\text{BF}_2$ -group in these compounds can be regarded as a pseudo-mono-valent metal ion. To our knowledge only one highly alkylated  $\text{BF}_2$ -pyrromethene complex is reported in the literature<sup>1)</sup>. The compounds are stable and easily soluble in organic solvents, and show mass-spectral fragmentation patterns that compare well with those of metal-porphyrins.

The 100 MHz  $^1\text{H}$  NMR spectra are consistent with the structures. The chemical shift values (Table 1) of the different hydrogens can be assigned fairly confidently. As expected, diatropic shift effects (such as occur in porphyrins) are absent. The  $^{10}\text{B}$ ,  $^{11}\text{B}$ ,  $^{14}\text{N}$ , and  $^{19}\text{F}$  nuclei do not cause visible coupling effects in the  $^1\text{H}$  NMR spectra.

Table I  
Chemical shift  $\delta$  in ppm. Solvent  $\text{CDCl}_3$ .

	H							$\text{CH}_3$					$\text{C}_2\text{H}_5$	
	1	2	3	5	7	8	9	1	2	3	7	8	9	2
I	-	6.00	-	7.00	-	6.00	-	2.54	-	2.24	2.24	-	2.54	-
II	7.54	-	-	7.18	-	-	7.54	-	1.98	2.16	2.16	1.98	-	-
III	-	-	-	6.96	6.70	6.24	7.42	2.52	-	2.10	-	-	-	2.36/1.04
IV	-	6.27	6.95	7.07	6.95	6.27	-	2.63	-	-	-	-	2.63	-

$$J_{\text{C}_2\text{H}_5}(\text{III}) = 7.1 \text{ Hz. } J_{2-3} = J_{7-8}(\text{IV}) = 4.1 \text{ Hz.}$$

In table II the 25 Mc/s  $^{13}\text{C}$  chemical shift values of three  $\text{BF}_2$  complexes are tabulated.

Table II  
Chemical shift  $\delta$  in ppm. Solvent  $\text{CDCl}_3$ . Jeol PFT 100.

	C								
	1	2	3	4	5	6	7	8	9
I	141.2	118.9	133.6	156.6	120.0	156.6	133.6	118.9	141.2
II	143.4	126.6	133.9	153.4	123.0	153.4	133.9	126.6	143.4
III	141.1	132.0	134.7	163.1	132.4	136.0	125.1	115.5	137.5
	$\text{CH}_3$						$\text{C}_2\text{H}_5$		
	1	2	3	7	8	9	2		
I	14.6	-	11.2	11.2	-	14.6	-		
II	-	9.6	9.8	9.8	9.6	-	-		
III	14.2	-	13.2	-	-	-	17.2/9.4		

The noise decoupled spectra only show singlets. The signals of carbons attached to hydrogens could be correlated with the  $^1\text{H}$  N.M.R. signals by selective decoupling. The assignment of quaternary carbons is much less certain, especially of carbons 3 and 4 (also 6 and 7) could be reversed.

The values found for the pyrromethene complexes compare favorable with those of corresponding atoms in porphyrins.

Sincerely,

C. Erkelens, J.A. van Koevinge, J. Lugtenburg.

Cees

Johan

Johan

Dr. A. Steigel  
Institut für Organische Chemie  
der Universität Düsseldorf

Direktor: Professor Dr. L. Birkofer

4 Düsseldorf, den 7. 7. 1977  
Universitätsstraße 1  
Fernsprecher 311-2298/99

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

NMR of a  $\beta$ -amidoalcohol

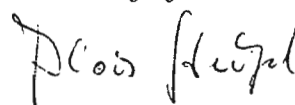
Dear Professor Shapiro:

In this communication I want to describe some preliminary NMR observations on a  $\beta$ -amidoalcohol, which indicate the simultaneous occurrence of a conformational equilibrium between a folded and a stretched species and of association equilibria. The compound studied,  $\alpha$ -Phenyl- $\beta$ -(N-methylformamido)-ethanol, has been synthesized by Mr. A. Kopp using a method developed in this institute some time ago (L. Birkofer and H. Dickopp, Chem. Ber. 102, 14 (1969)).

As expected for a N,N-dialkylated amide, the two rotational isomers are found in similar quantities. In dimethylsulfoxide however, one rotamer is favored, which is easily shown to be the E-isomer by means of  $^{13}\text{C}$ -NMR. This fact allows an unambiguous assignment of the  $^1\text{H}$ -NMR signals in  $\text{CDCl}_3$  as solvent by adding small quantities of  $d_6$ -DMSO.

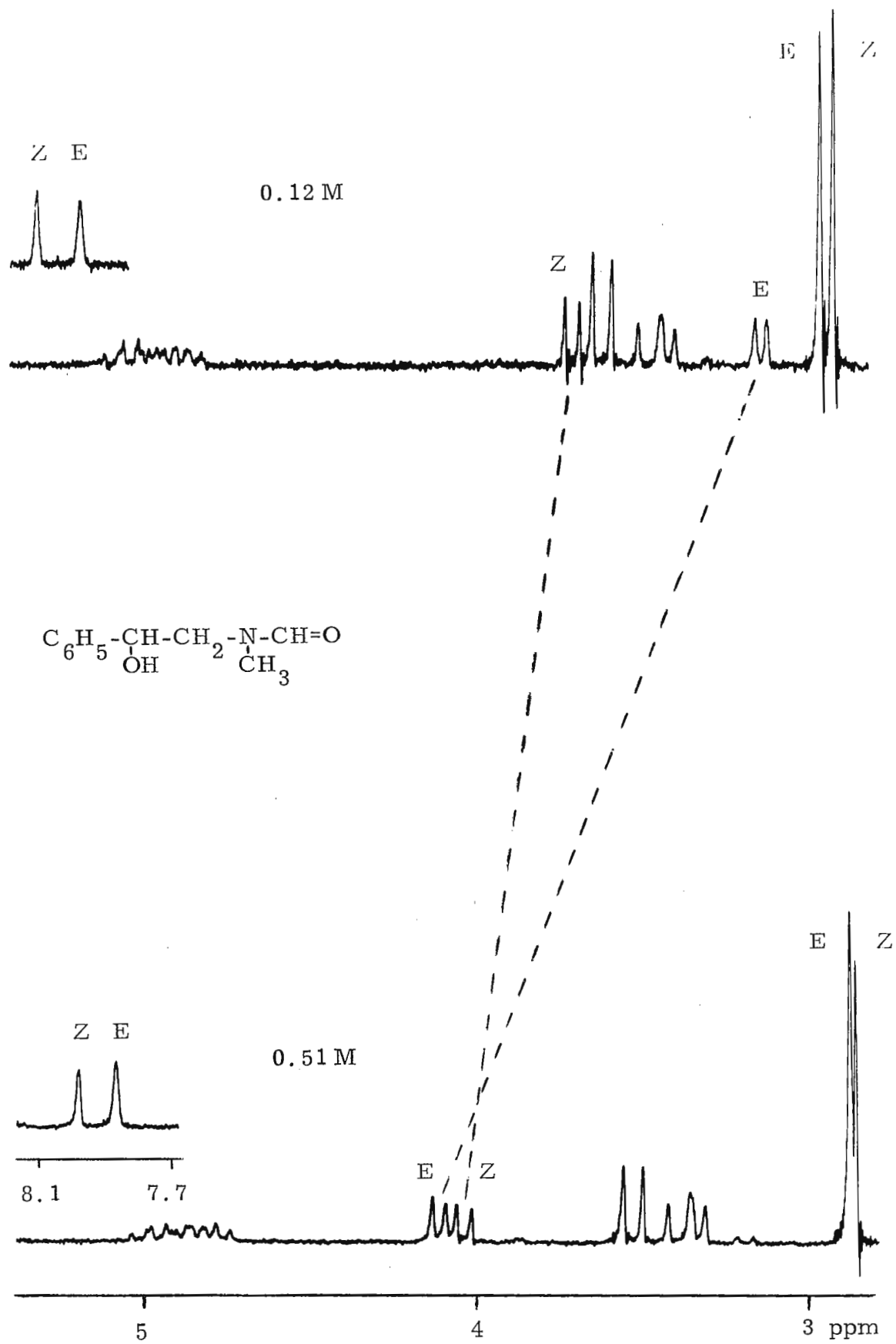
The  $^1\text{H}$ -NMR spectra in  $\text{CDCl}_3$  taken at different concentrations (cp. figures) can shed some light on the hydrogen bonding situation for the two amide rotamers. The hydroxyl protons of both rotamers give rise to doublets showing the absence of proton exchange via  $\text{OH} \cdots \text{OH}$  association. Apparently,  $\text{OH} \cdots$  amide carbonyl H-bonding is preferred. In the case of the Z-rotamer, this hydrogen bond can be achieved even at small concentrations by formation of a seven-membered chelate ring. The low-field position of the hydroxyl doublet relative to that of the E-rotamer may be taken as evidence for the intramolecular H-bond. On the other hand, intermolecular hydrogen bonding of the E-rotamer is clearly implied by the shift to low field of the E-hydroxyl resonance, when concentration is enhanced. Since the hydroxyl doublet of the Z-rotamer is shifted in the same direction, at first to a much smaller extent than the E-rotamer, but at higher concentrations to a more distinct degree, it is tempting to explain this behavior by an equilibrium between the folded and the stretched conformation of the Z-rotamer. Thus in this case it appears that the seven-membered H-bond chelate is not strong enough to prevent its cleavage by neighboring molecules.

Sincerely yours,



Alois Steigel





THE UNIVERSITY OF UTAH

SALT LAKE CITY, UTAH 84112

DEPARTMENT OF CHEMISTRY  
CHEMISTRY BUILDING

July 11, 1977

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

Dear Barry:

At the 18th Experimental NMR Conference we gave a paper demonstrating some of our preliminary results on a 22 mm sample tube probe for the XL-100-15 magnet. Since then we have made several improvements which have increased the sensitivity considerably. Enclosed is a single transient spectrum of 80% dioxane run in a coupled mode (decoupler off) which has a signal to noise ratio of 274/1. This signal to noise ratio represents state of the art sensitivity for large diameter sample tube probes and is comparable to the WH-180, the only other instrument to our knowledge that is capable of exceeding 200/1 on 80% dioxane.

Best regards,

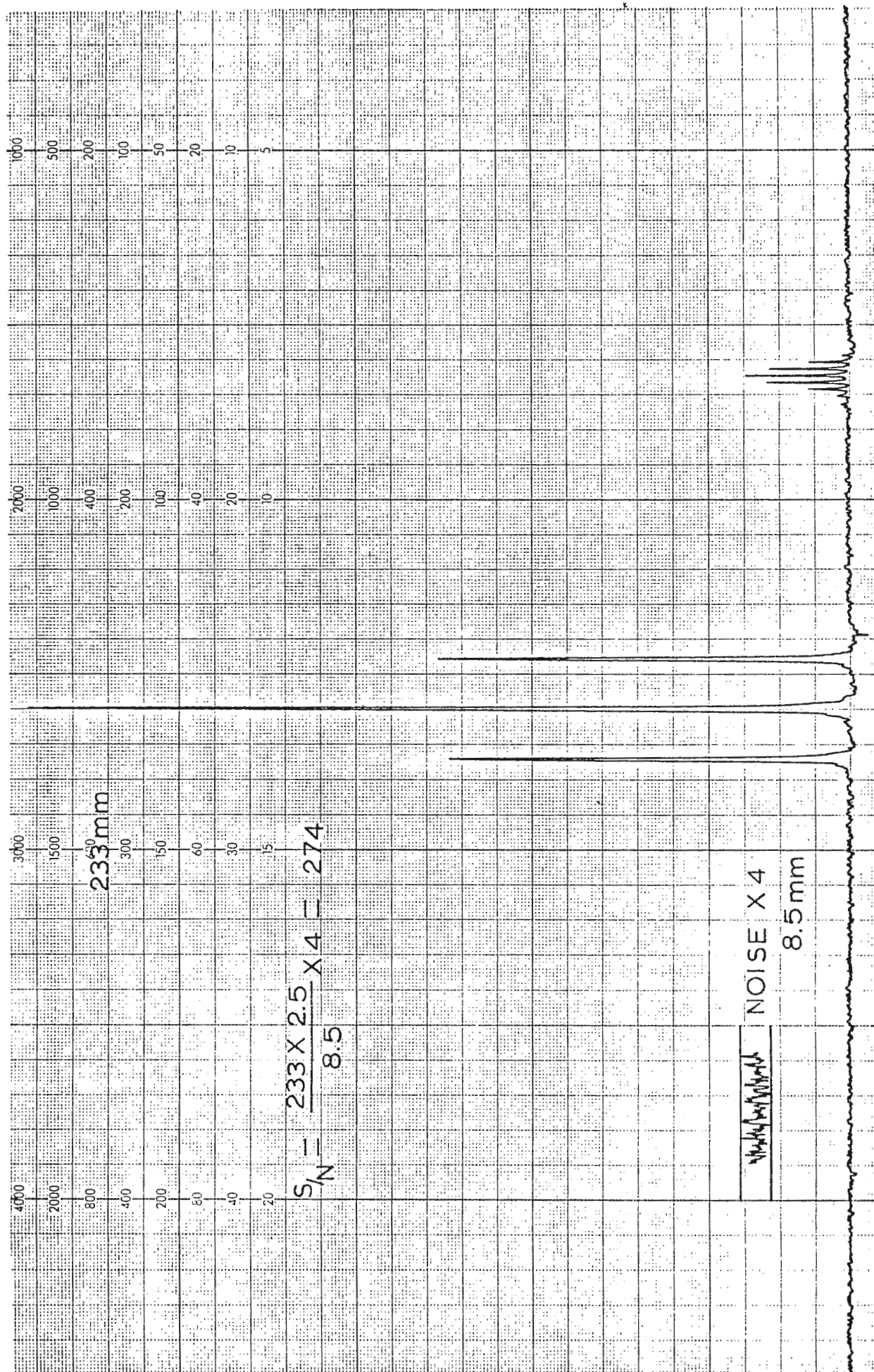
Toby Zens

*Toby Zens*

David M. Grant

*David M. Grant*

Encl.



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## Départements:

Instrumentation Scientifique  
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Professor B. L. SHAPIRO  
 Department of Chemistry  
 Texas A & M University

COLLEGE STATION Tex. 77843 USA

N/Réf. 77 07 531 CB/MCH

Wissembourg, le July 5<sup>th</sup> 1977

V/Réf.

Dear Prof. Shapiro,

Very often, Deuterium NMR is used on highly enriched materials ; I would like to show here how natural abundance Deuterium NMR can give valuable results which could not have been obtained via  $^{13}\text{C}$  or  $^1\text{H}$  NMR.

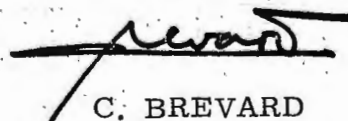
Although the Deuterium nucleus suffers from its low sensitivity and isotopic abundance, FT multinuclear systems readily allow access to Deuterium NMR without too great a sensitivity loss as one can judge from the following spectrum recorded with a WH 90/DS and multi-nuclear accessory. Spectrum 1 shows the proton spectrum of 2 butanol. If one focuses on the methylene resonance, no clear evidence of  $\text{H}_\text{A}$ ,  $\text{H}_\text{B}$  diastereotopy due to the  $\text{C}_2$  asymmetric center can be seen.

Switching to natural abundance  $^2\text{D}$  NMR, spectrum 2, recorded under proton broad band decoupling clearly shows one distinct resonance for each deuteron, allowing the experimenter to determine accurately each proton chemical shifts.

This method could be of interest in setting starting parameters for highly coupled proton spectra simulations or for studying subtle conformational changes when  $^1\text{H}$  or  $^{13}\text{C}$  NMR cannot be used.

Hoping to see you sometimes in Wissembourg.

Sincerely yours,

  
 C. BREVARD



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Fig. 1 -  $^1\text{H}$  spectrum of butanol

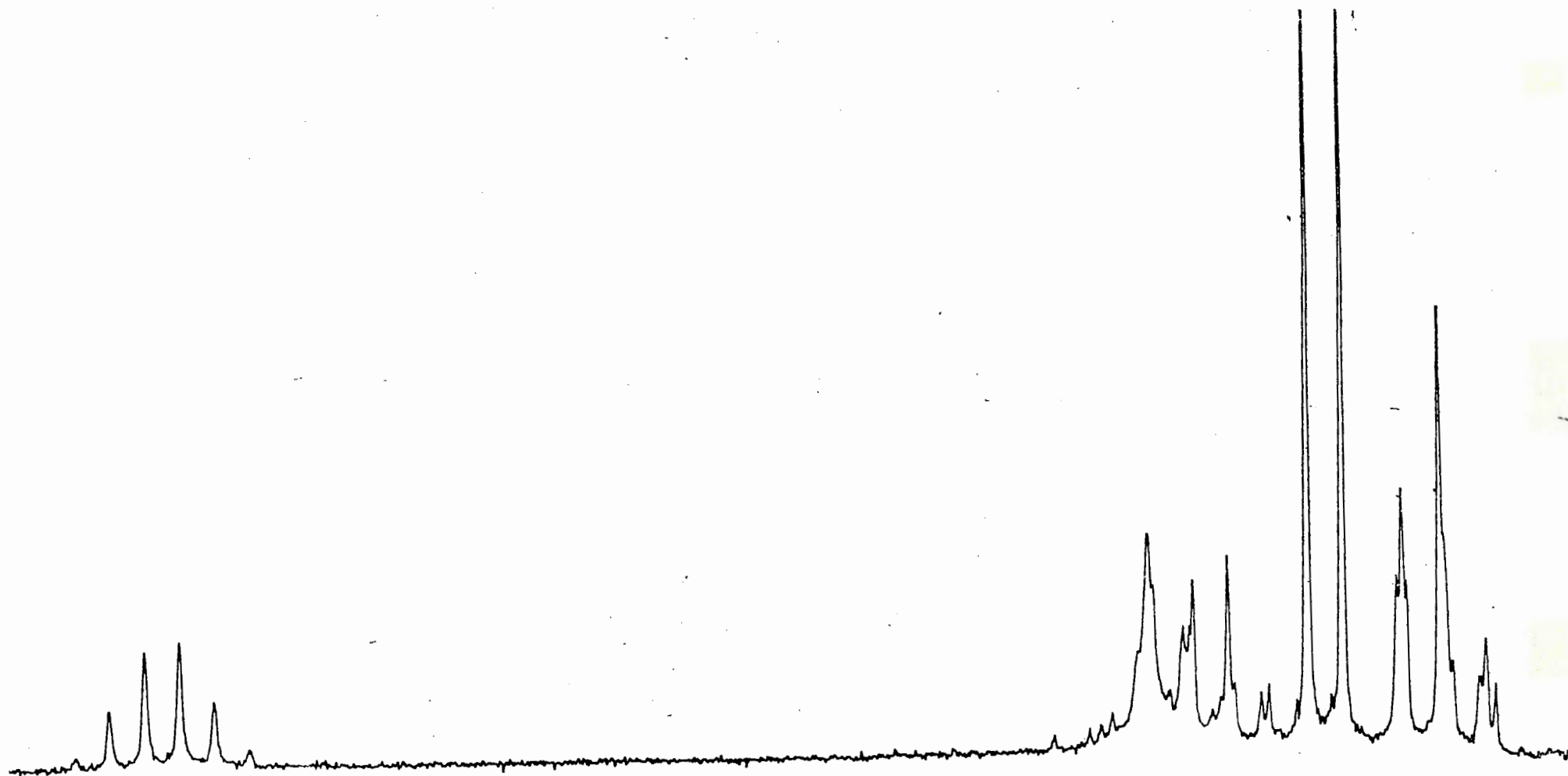
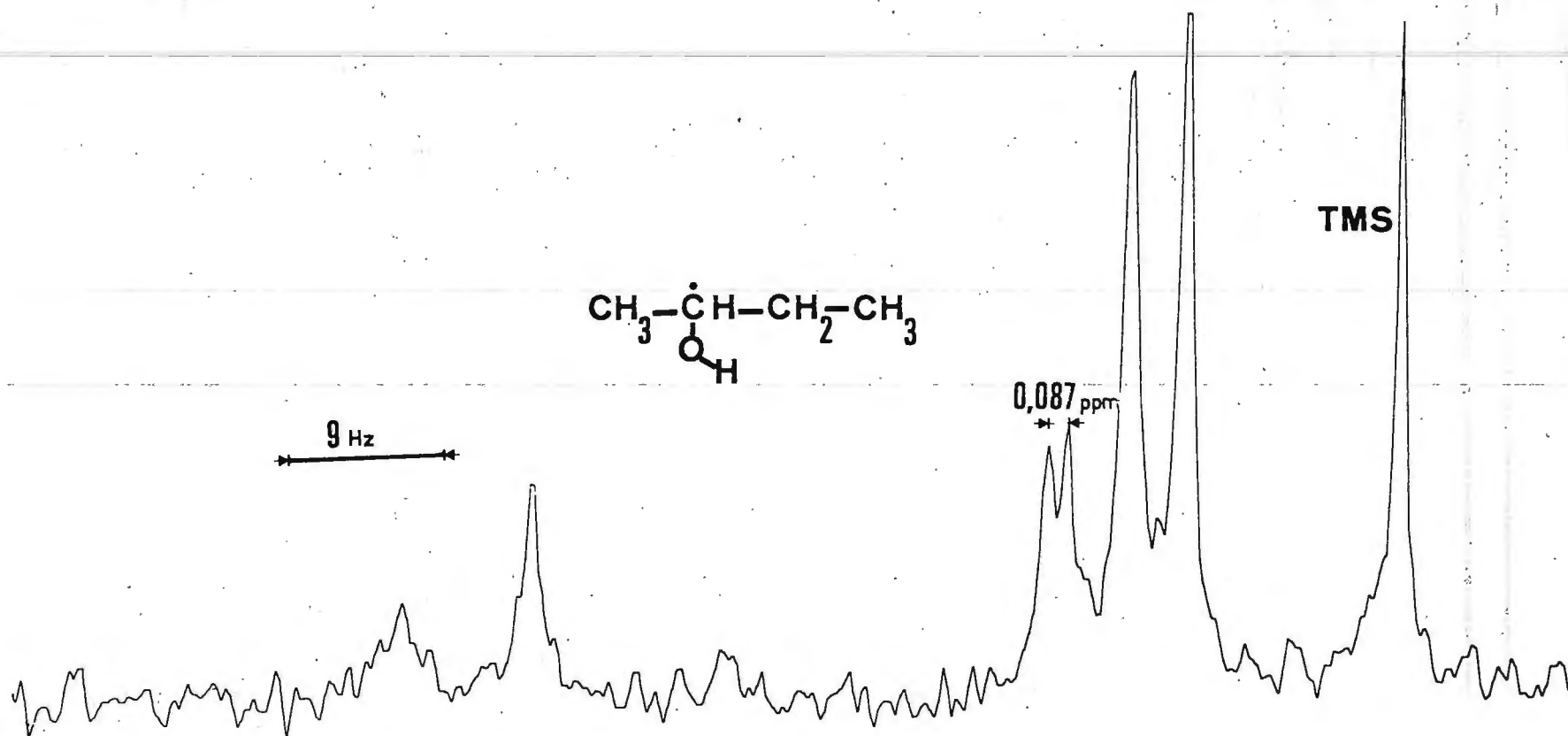




Fig. 2. Natural abundance  $^2\text{H}$  spectrum of 2 butanol (13 000 pulses -  $^1\text{H}$  broad band decoupling).





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## Baylor College of Medicine

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July 20, 1977

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

Dear Professor Shapiro:

" $^{13}\text{C}$  NMR of Apolipoprotein-Lipid Complexes"

We are currently investigating the interaction of apolipoprotein C-III with dimyristoyl phosphatidylcholine. This work is incomplete now and will not be discussed; however, the relaxation measurements are proceeding smoothly.

" $^{13}\text{C}$  NMR of Levan"

The naturally-occurring polysaccharides dextran and levan are readily distinguished by  $^{13}\text{C}$  NMR. Comparison of natural products of known structure has led to the following assignments for a 2,6-linked  $\beta$ -D-frucofuranoside residue: 105.1, C-2; 81.2, C-5; 77.4, C-3; 76.2, C-4; 64.4, C-6; and 61.0, C-1. A more informative report has been prepared for publication.

Sincerely,

Roger D. Knapp, Ph.D.  
Instructor, Experimental Medicine  
Department of Medicine  
Division of Atherosclerosis and  
Lipoprotein Research

RDK/dm



# BP RESEARCH CENTRE

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## CYCLOPENTANES IN PETROLEUM FRACTIONS; COMMENT ON $C_A$ DETERMINATIONS

Crude oil is a very complex mixture of compounds and even fractions obtained by some distillation or chromatographic procedure are still complex. Thus it is unusual for a spectroscopic technique to show the presence of a particular compound or a group of very closely related compounds in these complex mixtures. Recently we have been examining by carbon-13 NMR some saturate fractions from petroleum boiling at temperatures between 250°C and 500°C and noticed in the chemical shift listings a group of bands which we have now identified as monosubstituted cyclopentanes. An example of this identification is shown in Figure 1. The homologous series of cyclopentanes identified by these bands do not have substituents on either the chain  $\alpha$  or  $\beta$  carbon atoms. A dilution experiment enables the concentration of these compounds to be estimated. A further refinement is to separate the petroleum fraction by urea adduction which enables monosubstituted cyclopentanes with linear chains to be differentiated from these with branched chains. Such analyses are not possible by other spectroscopic techniques eg mass spectrometry.

With the increasing availability of carbon-13 spectrometers measurement of  $C_A$  (weight per cent carbon in aromatic rings) is becoming quite popular. The instrumental pitfalls are now sufficiently well known not to need repetition here.

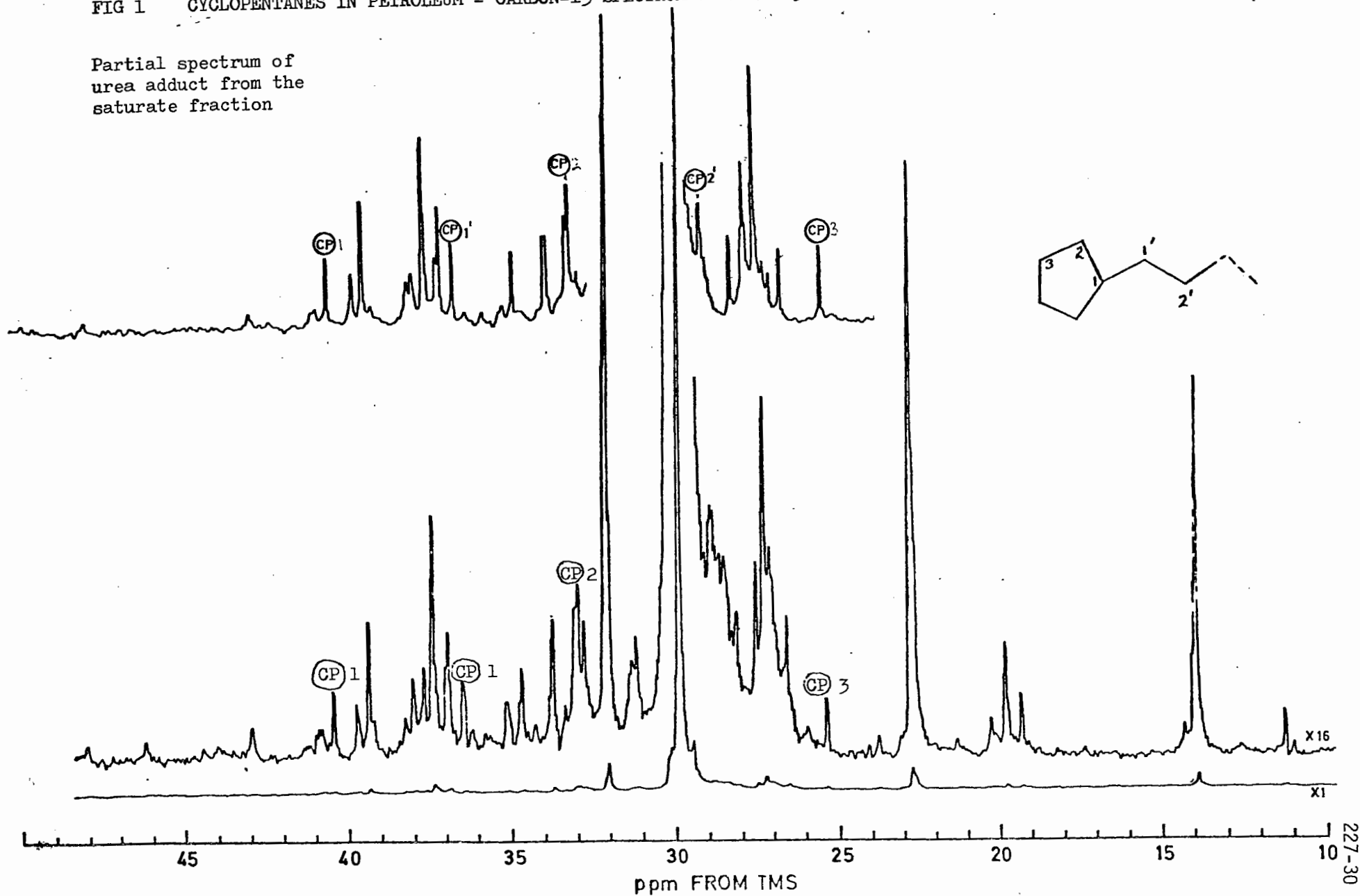
Care must be taken to ensure good base-line linearity otherwise the  $C_A$  values have a poor precision and are nearly useless for close comparisons of samples. However there are other hazards for the unwary. Many shale oils and gasolines (petrol in Europe) contain substantial amounts of olefins, thus a  $C_A$  found by carbon-13 for such samples may not be very meaningful. With the addition of increasing amounts of thermally cracked material to fuel oils this stricture will also apply to these petroleum products. The instrument, sample size and overall analysis time for carbon-13 determinations still make a formidable list of requirements. Further, to get the actual weight per cent carbon in aromatic rings requires combustion analytical results. Many authors seem unaware of a very simple proton correlation method for  $C_A$  which was developed some years ago (1). Given an approximate molecular weight (common knowledge for most petroleum fractions) only a small sample and the simplest proton cw instrument a few minutes are all that are required. The  $C_A$  values obtained for standard samples (eg monocyclic aromatic concentrates) agree very favourably with theoretical values.

S.A. Knight



FIG 1 CYCLOPENTANES IN PETROLEUM - CARBON-13 SPECTRUM OF A 400-500°C BOILING SATURATE PETROLEUM FRACTION

Partial spectrum of  
urea adduct from the  
saturate fraction



## La Trobe University

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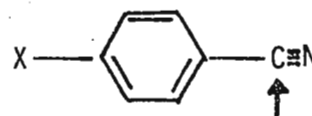
July 4, 1977.

Professor B.L. Shapiro,  
Department of Chemistry,  
Texas A & M University,  
COLLEGE STATION,  
TEXAS 77843.  
U.S.A.

Dear Barry,

We have been examining the effects of remote substituents on the C-13 shifts of carbons in aromatic side chains. One such system is the p-substituted benzo-nitriles where the chemical shift is related to Hammett substituent parameters by the DSP (Dual Substituent Parameter) equation:-

$$\delta = -2.7\sigma_I - 1.1\sigma_R^+; SD = 0.10$$



The cyanide shift data is unusual since the effect of electron donors is to shift the resonance downfield and the two negative signs in the DSP equation confirm this. It seemed to us that this system would be a good one to examine charge density/chemical shift relationships, and to examine the importance of pi and sigma electron density terms in controlling substituent chemical shifts in side chain carbons.

Gaussian-70 calculations of electron density support the proposition that  $\pi$  electron density controls the chemical shifts and show the downfield/low pi- electron density relationships with a slope of 210 ppm per electron. We and others have explained the reverse chemical shift effects in terms of a pi-polarisation mechanism of the pi-orbitals in the side chain. It is of interest that both sigma and total electron density correlations for this atom predict the wrong direction for the substituent chemical shifts with unreasonable slopes.

Please credit this contribution to Ian Rae/Mike Heffernan at Monash University who are kind enough to share the TAMU NMR Newsletter with us.

Yours sincerely,

R.T.C. Brownlee,

J. Bromilow.

Laboratorium für  
anorganische Chemie  
Eidgen. Techn. Hochschule  
CH-8092 Zürich

July 15, 1977

# $^{15}\text{N}$ Parameters in Some Palladium Complexes

Dear Prof. Shapiro,

Perhaps a few newer  $^{15}\text{N}$  results will interest your readers.

As part of our program involving Pt(II) and Pd(II) complexes we have determined the  $^{15}\text{N}$  NMR parameters for the series  $\text{trans-PdCl}_2\text{L}(^{15}\text{NH}_2(\text{CH}_2)_5\text{CH}_3)$ . As may be seen from the Table the  $^{15}\text{N}$  chemical shift is rather sensitive to the nature of the group L in a way reminiscent of the classical trans-influence. We have recently shown the same tendency for the  $^{31}\text{P}$  chemical shift in the compounds  $\text{PdCl}_2\text{L}(\text{PBu}_3)$ .<sup>1</sup> We believe that this dependence can be helpful in determining the complex geometry. Of additional interest are the values  $^2\text{J}(\text{P},\text{N})$  which are larger when the two atoms are trans than when they are cis.

Please credit this contribution to the account of Prof. L. M. Venanzi.

H. Motschi

P. S. Pregosin

*H. Motschi*

*P. S. Pregosin*

<sup>1</sup> G. Balimann and P. S. Pregosin, J. Magn. Res. 22, 235 (1976).

## $^{15}\text{N}$ Parameters for the Palladium Complexes $\text{PdCl}_2\text{L}(^{15}\text{NH}_2(\text{CH}_2)_5\text{CH}_3)$

L	$\delta^{15}\text{N}(\text{ppm from } ^{15}\text{NH}_4^+)$	L	$\delta^{15}\text{N}$	$^2\text{J}(\text{P},\text{N})\text{Hz}$
$^{15}\text{NH}_2(\text{CH}_2)_5\text{CH}_3$	- 33.2	$\text{PMePh}_2$	- 5.9	54.4
$\text{AsMePh}_2$	- 9.7	$\text{PTol}_3$	- 5.6	54.4
$\text{AsTol}_3$	- 9.2	$\text{PBu}_3^n$	+ 4.7	50.0
$\text{AsBu}_3^n$	- 7.8			

\* A negative sign indicates a shift to higher field.

Suggested Running Title:  $^{15}\text{N}$  NMR Parameters in Some Palladium Complexes.

varian / instrument division

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telephone (201) 822-3700

July 21, 1977

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

STATISTICAL ACCURACY OF NOE MEASUREMENTS
--

Dear Barry:

The Nuclear Overhauser Effect provides information about a variety of interesting questions: molecular conformations, correlation times, and relaxation mechanisms among others. Because of the importance of this information, the accuracy of NOE measurements has been a great concern in the literature, particularly with respect to sample preparation and adequate delay times between pulses. As far as I know, however, there has been no mention of some of the stringent requirements for precision in these measurements, and for this reason I would like to pass on some relatively trivial but nonetheless instructive calculations which I performed recently.

The NOE factor  $\eta$  is defined as  $(S-S_0)/S_0$ , where  $S_0$  is the equilibrium intensity of the peak of interest and  $S$  is the intensity of the peak in the presence of an irradiating field on some other nucleus or nuclei. Because this calculation involves a difference and a division, the relative error in  $\eta$  is found by first combining the standard errors of  $S$  and  $S_0$  and then combining the relative errors of the quantities  $(S-S_0)$  and  $S_0$ . If both  $S$  and  $S_0$  have a constant error  $x$  (assuming a constant noise level), the relative error of  $\eta$  is given by

$$\left( \frac{2x^2}{(S-S_0)^2} + \frac{x^2}{S_0^2} \right)^{1/2}$$

Normalizing  $x=1$ , we obtain the following instructive table:

RELATIVE ERROR IN NOE (%)							
$S_0$	NOE/	0.1	0.25	0.5	1	1.5	2
5		284	115	60	35	27	24
10		142	57	30	17	14	12
50		28	11	6	3	3	2
100		14	6	3	2	1	1

It is easy to see that due to the difference procedure involved in calculating the NOE, errors can be rapidly magnified, particularly for small NOEs. If we assume that the error in  $S$  and  $S_0$  is due only to noise, we can relate this calculation to the signal/noise ratio required in the  $S_0$  (non-enhanced) spectrum to obtain relative errors of 10% in the NOE:

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<u>NOE</u>	<u>S/N NEEDED FOR 10% ERROR</u>
0.1	140
0.25	60
0.5	30
1.0	18
1.5	14
2.0	12

Again, small NOEs (such as might be found for homonuclear proton NOEs or for proton-carbon NOEs of slowly rotating molecules) require a large S/N.

It should be pointed out that it is only an assumption that the error in the knowledge of peak intensity is related to the signal-to-noise ratio, although this is certainly the *limiting* factor. If, for example, one has very sharp lines, data point resolution may cause a far worse repeatability of peak heights than would be assumed from the noise. For NOE measurements on  $^{13}\text{C}$  where temperature fluctuations with decoupler on or off are common, this problem may be at its worst, since slight shifts in peak positions with temperature may cause the peak to shift from on top of one data point to in between two data points. It should be clear that if peak heights are to be used, one must either have large numbers of data points per Hz or else be able to broaden the lines sufficiently (using exponential multiplication) so that a large number of data points define the line.

The other alternative, of course, is to use integrals. In many cases, integrals will have greater S/N than peak heights and will be far less susceptible (though not impervious) to limited data point effects. The drawback to this technique, of course, is that in a complex spectrum (such as that of a protein), integrals are probably far more prone to cause *systematic* errors which would affect the accuracy of the data. If one is going to use integrals, it is good to bear in mind that "zero-filling" causes an increase in the S/N of the integral (*not* the spectrum) by 40% by essentially combining the information from the real and imaginary parts of the spectrum [D.I. Hoult, private communication]. Even in the absence of this factor, however, one would always want to use the maximum number of data points for the Fourier transformation to maximize the data point density in the spectrum.

In summary, a judicious combination of large S/N, maximum number of data points per Hz, line broadening, and integration should solve the problem of precision in NOE measurements, and return the user to the more important question of the accuracy and usefulness of those measurements!

Sincerely,

Steven L. Patt  
NMR Applications Chemist



THE UNIVERSITY OF BRITISH COLUMBIA  
2075 WESBROOK PLACE  
VANCOUVER, B.C., CANADA  
V6T 1W5

DEPARTMENT OF CHEMISTRY

July 8, 1977

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

Dear Barry,

Selective-Pulse Proton F.t. Experiments:  
A Patch for the Varian Programme 994100 - D/X2

As part of our programme to develop proton spin-lattice relaxation rates as a measure of interproton distances, my group have been evaluating a variety of highly selective, pulse-F.t. experiments. These experiments are probably best performed by the tailored excitation procedures developed in Howard Hill's group at Varian (J. Chem. Phys., 59, 1775 (1973)) and more recently in Ray Freeman's group at Oxford (J. Magn. Res., 23, 171 (1976)). Unfortunately, not everyone has access to those procedures, and we have developed an alternative approach based on the audiomodulation method originally developed by Freeman and Wittekoek. (J. Magn. Res. 1, 238 (1969)).

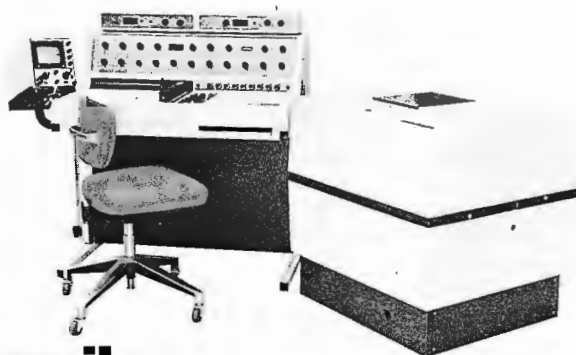
Simply, the proton decoupler of the instrument is used as the source of the long, weak perturbing pulse (or pulses) - its frequency and intensity can be trivially adjusted leaving, as the only additional requirement, a suitable gating control from the computer. The effects of the perturbing pulse(s) can then be monitored non-selectively by the usual F.t. method.

Although a suitable control line is automatically available with more recent instruments it was necessary to write a patch for the programme (994100 -D/X2) which we use with the Varian 620 L (16K) computer on the old (1972) XL-100 instrument located here. And the purpose of this letter is to inform your readers that details of that patch are now available from me.

We have used this approach for almost three years and find these selective-pulse experiments as delightful to perform as they are useful. Two recent papers (Canadian Journal of Chemistry, 54, 3526-3535 (1976): 55, 1045-1054 (1977) outline some of the experiments performed in 1975 by Roland Burton (who wrote the patch) and Dr. Klaus Bock so I shall not cite any examples here. I should comment though, that multiple, selective-pulse F.t. experiments can be readily performed by audiomodulation of the decoupler. And even if your readers are not yet interested in selective-pulse  $T_1$  determinations, they should seriously consider the pure-pulse equivalent of the c.w. INDOR experiment.

With all best wishes

1. 11/100



EM-360L

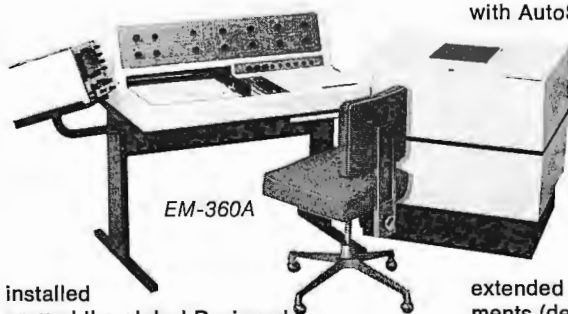
## The leading family of permanent-magnet NMR spectrometers has a new addition!

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extended to double-resonance experiments (decoupling, spin tickling, and INDOR), VT ( $-100^{\circ}\text{C}$  to  $+175^{\circ}\text{C}$ ),  $^{19}\text{F}$ ,

$^{31}\text{P}$ , and sensitivity enhancement (signal averager or rapid-scan correlation NMR).

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EM-390



C

1

C

2

3

C



1(303)491-6480

Colorado State University  
Fort Collins, Colorado  
80523

Department of Chemistry

THE MILE HIGH PENIS LABORATORY

*(almost)*

Title: Postdoctoral positions; correction to  
letterhead.

July 22, 1977

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

Dear Barry:

We have received some critical comments on the letterhead used for our last TAMU NMR Newsletter (No. 221). It has been pointed out that as the elevation of our PENIS laboratory is only about five thousand feet above sea level (not 5280 ft.), we are not justified in using the name "Mile High PENIS Laboratory." However, we wish to point out that so far the accuracy of our PENIS data are limited to two significant figures, and to that degree of accuracy our PENIS facility is 1.0 mile high. Furthermore, with a second PENIS spectrometer now under construction (Vic Bartuska is now erecting a modification of a Varian DA-60), we anticipate extending the method to ever greater heights.

Incidentally, it appears that we will have three postdoctoral openings during the coming fall and winter. The research areas are:

- 1) metal-nuclide nmr studies of metal ion interactions (including experiments on solids).
- 2) nmr studies of geochemical samples (solids and liquids).
- 3)  $^{13}\text{C}$  nmr studies of solids, with applications to plant sciences.

Sincerely,

Gary E. Maciel  
Professor

# UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

*School of Medicine G3*

DEPARTMENT OF  
BIOCHEMISTRY AND BIOPHYSICS

August 2, 1977

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

Time-Shared Lock Adaptation

Dear Professor Shapiro:

Our NV14 (DH 60) was designed with a CW lock which we run using deuterium. It has from the start been used with a single coil matched to 50 ohm cable so that the preamplifier can be some distance from the probe. Our lock sensitivity has always been limited by several troubles which are no doubt familiar to many NMR people. First, the transmitter noise appears in the lock signal so that beyond a certain increase in transmitter power, there is no improvement in signal-to-noise ratio. Second, and to me mysteriously, there is a D.C. offset occurring with larger transmitter powers (it goes away when the probe is out of the magnet gap). Third, the bridge circuit necessary to isolate the preamplifier from the transmitter (single coil system) introduces a 3dB loss in S/N.

The solution is neither clever nor original, but it is surprisingly effective and easy to implement: a time-shared (pulsed) lock. If one were designing from scratch, one would no doubt do things differently, e.g. without field modulation, but the present adaptation uses most of the already existing lock circuitry including the power amplifier, variable attenuator and audio circuits. What must be added are the passive transmit/receive (T/R) switching before the ca. 50 dB preamplifier, good gates with timing so that the transmitter and receiver are not turned on simultaneously, and a bandpass filter in the line to the probe preventing harmonics generated in the T/R circuit from getting into the observe channel (a 50 dB trap is already in the observe channel at the lock transmitter frequency).

The transmitter is on for 250 microseconds and the receiver for 750 microseconds, with about 30 microseconds delay at the start of the receive time to let the transmitter pulse completely disappear. These times are



sufficiently long that the transmitter and receiver gating are not difficult. The transmitter power amplifier is gated using two transistors each of which grounds the bias divider of a stage in the amplifier. The preamplifier output gating is through two double-balanced mixers (e.g. Mini-Circuits Lab Type SRA-1) in series. The timing is not locked to either the computer or the spectrometer master oscillator, and probably should not be because of possible coherent accumulation of disturbances in the observe channel. As the system now stands, there is no measureable interaction between the observe and lock channels, even though they use the same NMR coil (double-tuned). The bandpass filter and the trap help set the limits in this regard.

Does anyone want more details? I stand ready.

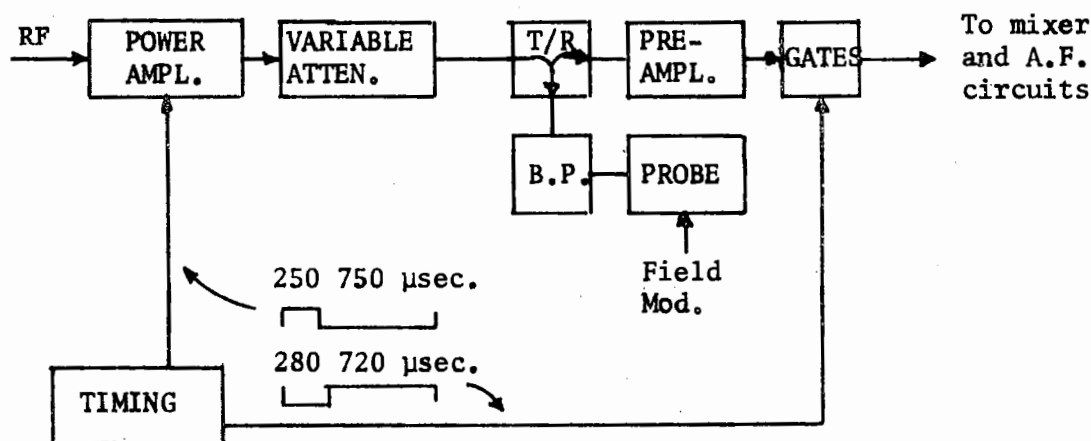
Sincerely,

*Jim Engle*

James Engle

JE/sls

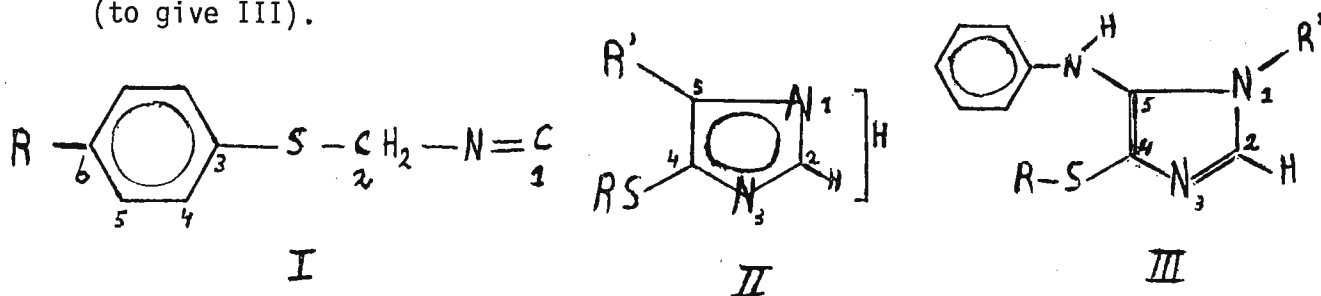
P. S. - Please credit this contribution to Dr. M. Cohn's account.



$^{13}\text{C}$  chemical shifts in  
sulphenylmethylisocyanides and sulphenylimidazoles

Dear Prof. Shapiro,

Recently we did some  $^{13}\text{C}$  n.m.r. work on sulphenylmethylisocyanides<sup>1,2</sup> (I) and 4-sulphenylimidazoles (II, III). The latter two compounds were synthesized by reaction of I with cyanides<sup>1,2</sup> (to give II) or carbodiimides<sup>2</sup> (to give III).



In Table 1 the chemical shift data are given for the para substituted phenylsulphenylmethylisocyanides (I) (spectra were recorded using our XL100 instrument). The trend observed for the chemical shifts of  $\text{C}_2$ , going upfield from p-methoxyphenyl to p-nitrophenyl, (which is analogous to the trend in para substituted thioanisoles<sup>3</sup>) cannot be easily explained.  $^1\text{J}_{\text{C}_2\text{N}}$  has a normal value of about 6 Hz.<sup>4</sup>

R	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$
$-\text{CH}_3$	159.3	45.1	127.7	132.5	129.8	138.8
$-\text{Cl}$	159.9	44.8	129.8	133.7	129.4	135.1
$-\text{OCH}_3$	159.1	45.9	121.5	135.3	114.7	160.4
$-\text{NO}_2$	160.8	42.2	141.3	129.0	124.1	146.6

Table 1.  $^{13}\text{C}$  chemical shifts in I (solvent  $\text{CDCl}_3$ , chem. shifts in ppm, relative to TMS ( $\delta_{\text{CDCl}_3} = 77.0$  ppm)).

Because of solubility problems we had to record the spectra of most of the imidazoles II and III in the solvent mixture  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (volume ratio 2:1). We will only discuss here the signals of the carbon atoms of the imidazole ring, the chemical shifts of which are given in the Tables 2 and 3. All carbon atoms of the imidazole ring gave somewhat broadened signals, presumably due to the nitrogen quadrupole moment. The signals of  $\text{C}_2$  (in both II and III) could be found with the aid of the proton coupled spectra, which revealed a doublet with a characteristic coupling constant of about 210 Hz in all cases. The signals of  $\text{C}_4$  and  $\text{C}_5$  (in II and III) were absorptions with very low intensities, due to long relaxation times of the concerning carbon atoms.

R	R <sup>1</sup>	C <sub>2</sub>	C <sub>4</sub>	C <sub>5</sub>	J <sub>C<sub>2</sub>H<sub>2</sub></sub> (Hz)
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	135.0	121.4	135.5	208
"	C <sub>6</sub> H <sub>5</sub>	136.3	119.6	139.2	207
"	t-Bu	134.3	119.4	146.0	207
"	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	135.9	118.7	138.9	207
"	p-ClC <sub>6</sub> H <sub>4</sub>	136.6	118.8	139.1	208
p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	136.2	120.8	138.5	208
t-Bu	C <sub>6</sub> H <sub>5</sub>	135.6	118.6	141.7	205

Table 2.  $^{13}\text{C}$  nmr spectral data for II (solvent  $\text{CDCl}_3/\text{CD}_3\text{OD}$ , 2:1, chem. shifts in ppm, relative to TMS ( $\delta_{\text{CDCl}_3} = 77.0$  ppm)).

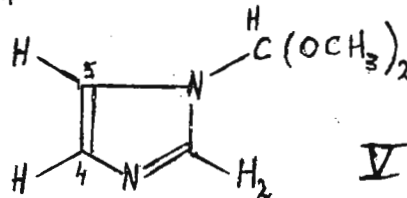
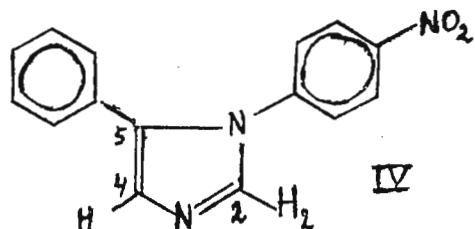
The  $\text{C}_4$  and  $\text{C}_5$  signals in II could be assigned by mutually comparing the first three compounds in Table 2. The substituent effects of a methyl, phenyl and t-butyl group on  $\text{C}_4$  and  $\text{C}_5$  in II showed the same trend as ring carbon atoms 1 and 2 in toluene, biphenyl and t-butylbenzene.

The assignment of the signals to  $\text{C}_4$  and  $\text{C}_5$  in III is based upon the long range coupling constants between  $\text{C}_4$  and  $\text{C}_5$  and  $\text{H}_2$ . For some of the imidazoles III the high field signal showed a long range coupling constant of about 10 Hz with  $\text{H}_2$ , whereas the low field signal gave a

R	R <sup>1</sup>	C <sub>2</sub>	C <sub>4</sub>	C <sub>5</sub>	J <sub>C<sub>2</sub>H<sub>2</sub></sub>	J <sub>C<sub>4</sub>H<sub>2</sub></sub>	J <sub>C<sub>5</sub>H<sub>2</sub></sub>
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	134.4	127.2	132.7	212		
t-Bu	C <sub>6</sub> H <sub>5</sub>	134.7	125.5	135.1	211		
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	135.6	123.6	134.6	210	10	<2
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	t-Bu	133.2	128.6	133.7	210	10	4.5

Table 3. <sup>13</sup>C nmr spectral data of III (solvent for the first two CDCl<sub>3</sub>, the last two CDCl<sub>3</sub>/CD<sub>3</sub>OD 2:1; coupling constants in Hz, chem. shifts in ppm, relative to TMS (δ<sub>CDCl<sub>3</sub></sub> = 77.0 ppm)).

smaller coupling constant (Table 3). In compounds IV and V J<sub>C<sub>4</sub>H<sub>2</sub></sub> was found to be about 10 Hz, whereas J<sub>C<sub>5</sub>H<sub>2</sub></sub> could not be observed.<sup>5</sup> Therefore the high field signal was assigned to C<sub>4</sub> and the low field signal to C<sub>5</sub>.



We hope that this contribution will be an aid for the interpretation of <sup>13</sup>C spectra of N-heterocycles. The complete set of nmr data will be supplied on request.

Yours sincerely,

J. Schut, H. Hiemstra and W. Mellink

*W. Mellink*

#### Notes:

1. Please credit this contribution to Dr. W.D. Weringa.
2. Our FT-16-T<sub>1</sub> program (TAMU 216) has been made available for 620-i,1 users by Dr. J. Runsink.

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
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August 2, 1977

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

Dear Professor Shapiro:

I would like to bring to the attention of the readers that NIEHS has an opening in the Environmental Biology and Chemistry Branch for a research chemist to serve as a coordinator for a bioorganic chemistry and synthesis work group.

Qualified applicants should have substantial experience and interest in the development and application of NMR to biological problems as a primary research tool and the use of modern principles and practices of synthetic organic and physical organic chemistry to the understanding of biomechanism.

In addition to independent and collaborative research program development, the incumbent would supervise the work of members of the group, including timely completion of collaborative/support requests of an organic chemical nature and otherwise providing guidance to program goals and objectives.

Interested applicants should forward, as soon as possible, their curriculum vitae and bibliography and a statement of their availability. If more detailed information is needed, I can be reached by telephone at (919)541-3253.

Sincerely,

A handwritten signature in dark ink, appearing to read "J. McKinney", is written over the typed name.

James D. McKinney, Ph.D.  
Head, Chemistry Section, EBCB


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Professor Bernard L. SHAPIRO  
Department of Chemistry  
Texas A.M. University  
College Station  
TEXAS 77843

Paris, le June 28, 1977

On newly described phosphoferrocenes

Dear Barry,

The synthesis of title compounds was recently reported (J. Am. Chem. Soc. 99, 3587 (1977) ) with some preliminary proton data. As these are rather unusual species, we present hereafter additional carbon-13 and phosphorus along with proton data (all obtained in  $CDCl_3$  sol. ; internal std. TMS for proton and carbon-13,  $P_4O_6$  for phosphorus, all chem. shifts +ve to low fields).

Proton spectra show phospholyl protons in the range of cyclopentadienyls, H-P couplings being similar to those observed in free phospholes. One especially notices a very high  $^2J(H-P)$  coupling : characteristic of phospholes (1,2) and 2-phospholenes (3).

Carbon-13 spectra present

- a sizeable deshielding of the phosphoferrocene ring compared to the ferrocene one (67.9 (4) ) ;

- a very high  $^1J(P-C)$  coupling, similar to those in phosphorines (5) and much higher than in phospholes (which are close to common phosphines). This points to a strong electron delocalization, free phospholes being only slightly aromatic (but this point is still controversial (6,7) ).

Phosphorus spectra again are of interest when the phosphorus nucleus in phospholes is significantly deshielded respect to common phosphines (1,2), it is strongly shielded in phosphoferrocenes.

Recalling that phosphorus deshielding in phospholes-previously attributed to delocalized non bonding P electrons (2)-is actually due to ring strain



227-46

according to Letcher and Van Wazer (1b), we conclude that phosphoferrocenes may present a significant delocalization of their n electrons.

With our very best regards.



G. MAVEL  
F. MATHEY  
R. MANKOWSKI-FAVELIER

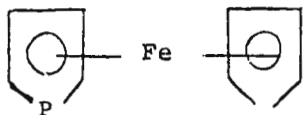
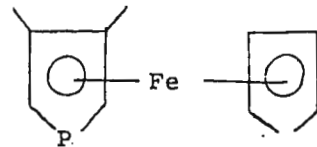
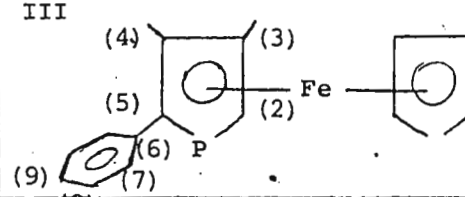
\*<sup>31</sup>P chem. shift in 1-phenyl 2,2,3,3-tetramethyl phosphetane (with a ring strain comparable to that of phospholes but with no possible delocalization) is -104 ppm (to be compared with -104.7 ppm in 1-phenyl phosphole (1b)).

#### REFERENCES

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(a) In the proton decoupled spectrum, C(2) is loss in solvent peaks (b) detected on the undecoupled spectrum.

227-47

COMPOUNDS		I 		II 		III 	
<sup>1</sup> H	Group	δ	J	δ	J	δ	J
	C <sub>5</sub> H <sub>5</sub>	4.35		4.13		4.16	
	Phospholyl CH H α	4.03	<sup>2</sup> J <sub>H P</sub> 38	3.71	<sup>2</sup> J <sub>H P</sub> 36	3.87	<sup>2</sup> J <sub>H P</sub> 36
	H β	5.25	<sup>3</sup> J <sub>H P</sub> 6				
	CH <sub>3</sub>			2.17		2.26	
	Benzenics					m. centered at 7.25	
<sup>31</sup> P		-180		-196		-185	
<sup>13</sup> C	C <sub>5</sub> H <sub>5</sub>	70.2		71.4		72.7	
	Phospholyl C α	77.2	J <sub>C P</sub> 62	78.2	<sup>1</sup> J <sub>C P</sub> 61	C(2) ≈ 77 (a)	<sup>1</sup> J <sub>C P</sub> : 60
	C β	79.8	<sup>2</sup> J <sub>C P</sub> 7	94.8	<sup>2</sup> J <sub>C P</sub> 7.2	C(3)C(4) 92 and 96	<sup>2</sup> J <sub>C P</sub> : 5.2 and 6.1
						C(5) 100.3	<sup>1</sup> J <sub>C P</sub> : 58
	CH <sub>3</sub>			16.4		15.1 et 17.2	
	Benzenics						
	C(6)					140.5	<sup>2</sup> J <sub>C P</sub> 16.8
	C(7)					130	<sup>3</sup> J <sub>C P</sub> 5.2
	C(8) (9)					127.5 et 125.7	



TEXAS CHRISTIAN UNIVERSITY  
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Department of Chemistry

July 7, 1977

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

Steroid Solution Behavior  
and Carbon  $T_1$ s.

Dear Barry:

Steroid carbon relaxation times are strongly concentration dependent and, reasonably, one might exploit this fact to measure interactions of steroids with each other and with other molecules. Recently, we have measured the  $T_1$ s and solution viscosities for cholesteryl acetate in chloroform at various concentrations. According to simple theory the reciprocal of  $T_1$  and  $\eta$  should be linear and so it is. This result contrasts with that of Allerhand, Doddrell and Komorski, J. Chem. Phys., 55, 189 (1971) who report a nonlinear plot of  $1/T_1$  vs  $\eta$  for the carbons of cholesteryl chloride. A reinvestigation of the cholesteryl chloride system showed it to be linear also. No attempt to account for the earlier report will be given.

It was further observed that plots of  $T_1$  vs  $[M]$  were linear for the various carbons in both systems. This observation stands unaided by theory as there is no general correlation of molar concentration with viscosity of which I am aware.

When one turns to hydroxyl bearing steroids the picture is quite different. Plots of carbons  $T_1$ s vs  $[M]$  for these compounds in chloroform are concave upwards and show differing slopes and degrees of curvature increasing with the number of hydroxyl groups. These results can be summarized by the average  $T_1$  values (35°, 0.5M, chloroform) for the ring methylene carbons ( $\pm 10\%$ ): methyl cholate (3 OH) groups) 0.04; methyl chenodeoxycholate (2 OH) 0.13; methyl deoxycholate (2 OH) 0.16; methyl lithocholate (1 OH) 0.39; and cholesterol (1 OH) 0.55. A completely consistent pattern emerges for this series in which hydrogen bonding between hydroxyls is evoked. The steric hindrance of the bile ester hydroxyls is evidenced and bonding to the ester function is also involved. So the initial contention is substantiated. One can use  $T_1$ s to measure steroid interactions. It remains to be seen how far it can be pushed.

Best regards,

*Bill*

W. B. Smith,  
Chairman

## FACHBEREICH 14 DER UNIVERSITÄT DES SAARLANDES

FACHRICHTUNG 14.1 – Organische Chemie

Professor Dr. H. D ü r r

Universität des Saarlandes 66 Saarbrücken Fachr. 14.1



Herrn

Professor Dr. B. L. SHAPIRO

Department of Chemistry

Texas A and M University College Station

Texas 77843 USA

Ihr Zeichen  
Ihre Nachricht vom  
Unser Zeichen

Dü/Wi

Saarbrücken,

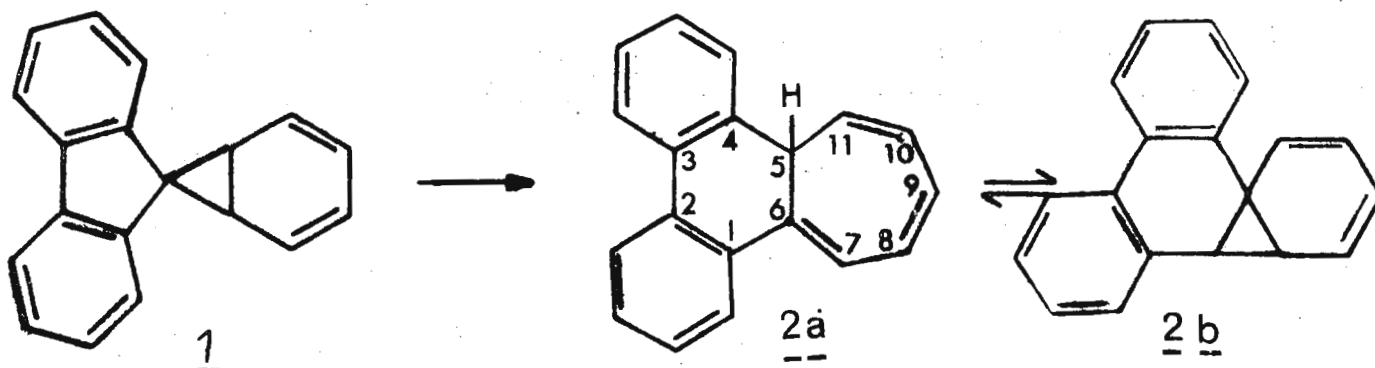
26.7.1977

Dear Professor Shapiro,

<sup>13</sup>C-NMR spectrum of a bicyclo[5.4.0]undecapentaene

The spironorcaradiene 1 was irradiated with UV-light of the wavelength  $\lambda > 300$  nm (using a K<sub>2</sub>CrO<sub>4</sub> filter). It was expected that the equilibrium system 2a  $\rightleftharpoons$  2b would be formed. The <sup>1</sup>H-NMR-spectrum recorded from the photolysate showed only one set of signals which did not change in the temperature range between 180 and 250 K<sup>1</sup>).

Because of the larger frequency difference of the signals the <sup>13</sup>C-NMR-spectrum of the photolysate was measured (see table). This spectrum did not vary between 180 and 300 K. Cooling resulted only in a broadening of the signals of the aromatic and olefinic carbons. Due to solubility problems we could not measure lower temperatures as 180 K. The obtained data are consistent only with structure 2a. The detailed assignment was made from the Off Resonance decoupled spectrum.



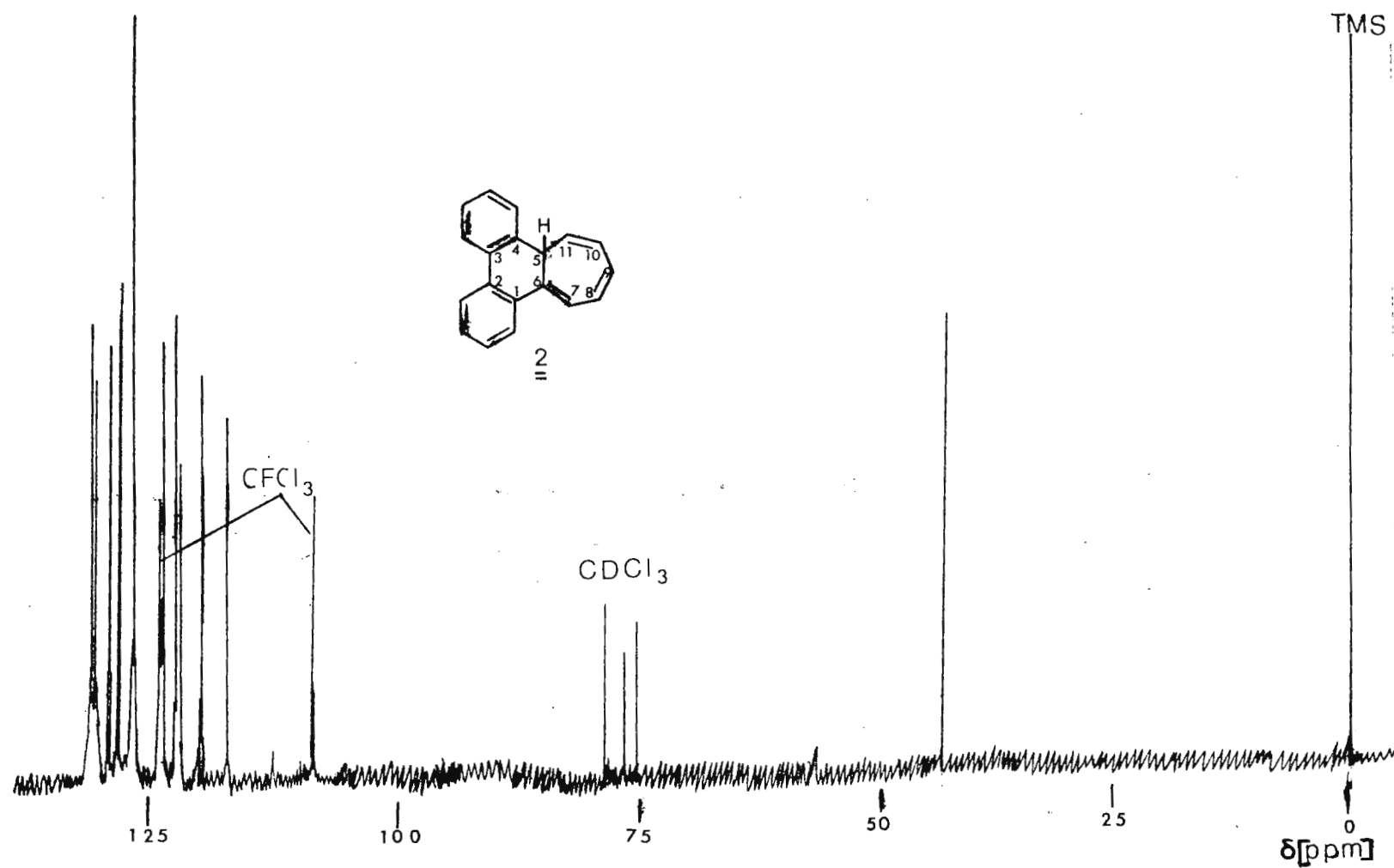


Fig.  $^{13}\text{C}$ -NMR-spectrum of **2** at 300 K.

Table:  $^{13}\text{C}$ -NMR spectrum of 2 (5% solution in  $\text{CDCl}_3/\text{CFCl}_3$  (1:1), internal standard: TMS, lock:  $\text{CFCl}_3$ )

$\delta_{\text{TMS}}$ (ppm)	multiplicity in the Off Resonance decoupled spectrum	assignment
42.8	d	C 6
118.6	s	C 5
121.0	d	C 7
123.0	d	Cl o
123.4	d	Cl l
124.5	d	C 9
127.3	s	C 1
128.1	d	C 8
128.2	s	C 2
128.4	s	C 3
130.7	s	C 4
130.9	d	} aromatic C
131.3	d	

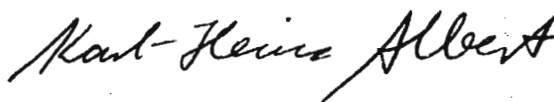
Reference:

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Yours sincerely



Professor Dr. H. Dürr

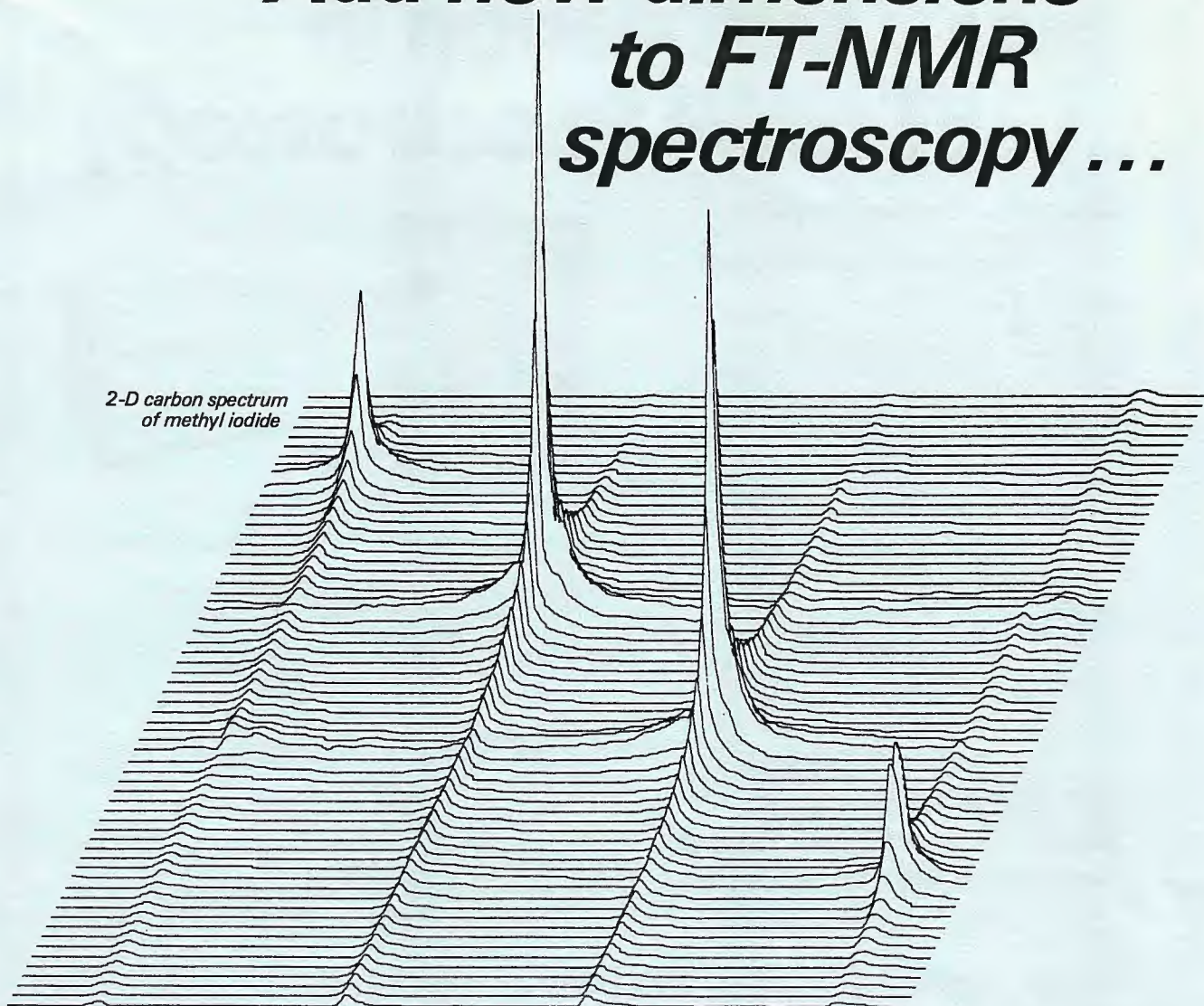


Dipl.-Chem. K.-H. Albert



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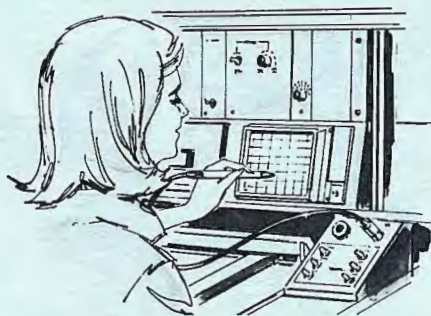


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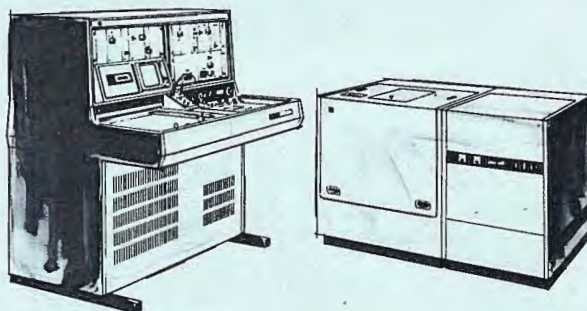
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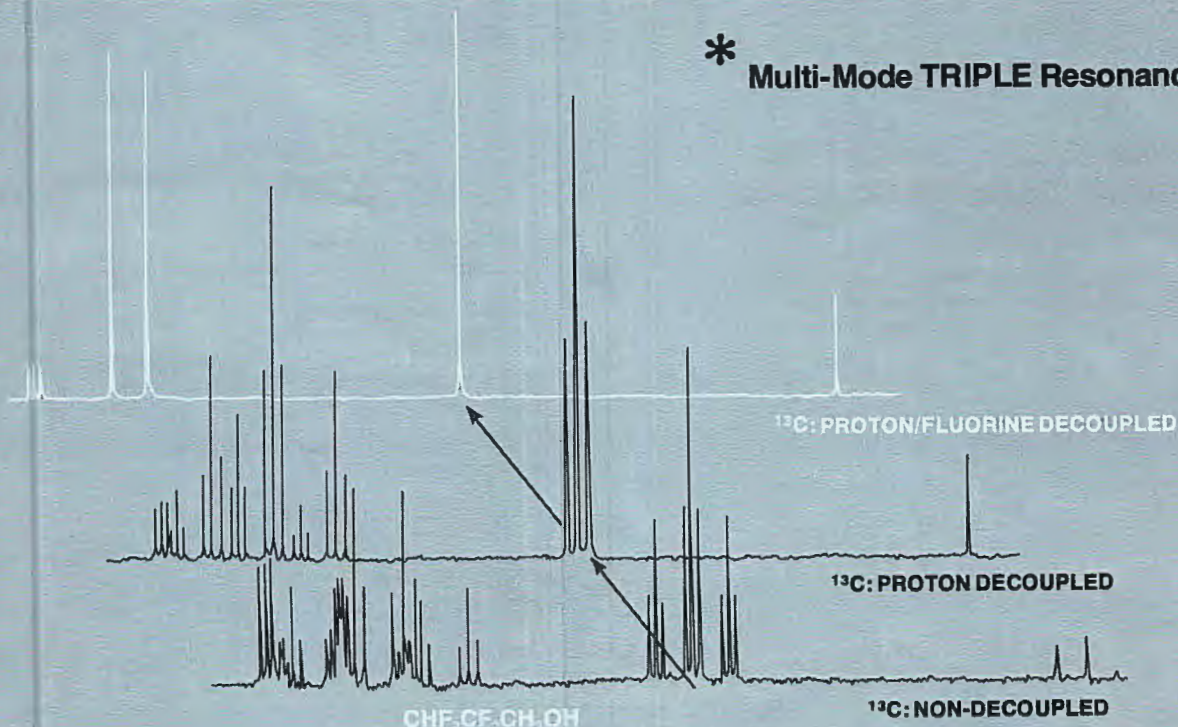
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