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Newsletter

No. 151

APRIL, 1971

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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". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.



Calvert, I. D.; Sazavsky, C. D.  
Mars Recorder Modification, T-60 Scope Modification, and  $^{29}\text{Si}$   
NMR on the HA-100

38

Deadline Dates: No. 152: 3 May 1971  
No. 153: 7 June 1971

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

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

## CARLETON UNIVERSITY

OTTAWA 1, CANADA K1S 5B6



DEPARTMENT OF CHEMISTRY

March 3, 1971

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

Dear Barry:

Long range effects: anisotropic and shift reagents. Referees please!

So sorry for the usual delay in our contribution but we are awaiting the installation of our XL-100.

Our n.m.r. interests continue to be in the area of long-range effects both on anisotropic effects and (jumping on the band-wagon) on the use of shift reagents. Two papers should appear shortly in Can. J. Chem. examining more closely the variables involved in our earlier carbonyl group work (Tetrahedron 26, 119 (1970)) and on the shielding effects of the ethylene-ketal and -thioketal groups. Preprints of these are available. Other work in progress involves the epoxide and nitrile groups.

In the lanthanide shift area, readers may be interested to know that, as expected, N-nitrosamines complex nicely and show large shifts.

Apart from the above - nothing new.

I would however, like to use this medium to ask any of your readers who feel that they could spare some time to refereeing for the Canadian Journal of Chemistry to let me know their particular area of interest and I'll put them on my list of future 'volunteers'.

All best wishes.

Yours sincerely,

John ApSimon

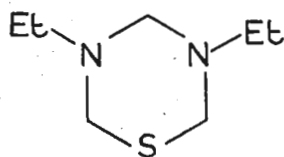
JWA/jt

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University Plain, Norwich NOR 88C  
Telephone Norwich (0603) 56161  
Telegraphic Address UEANOR

A CASE OF METHYLENE NON-EQUIVALENCE DERIVING FROM SLOW RING  
INVERSION

Dear Dr. Shapiro,

As is well-known, the protons of a methylene group are rendered non-equivalent when attached to a chiral centre. However, no case where the chirality results solely from the slow chair-chair inversion of a six-membered ring has apparently previously been reported.



At room temperature the NMR spectrum (100 MHz) of 3,5-diethyltetrahydro-1,3,5-thiadiazine (1) in  $\text{CFCl}_3/\text{CDCl}_3$  (1:1) shows sharp singlets for the 2- and 6-protons at  $\tau$  5.76 and for the 4-protons at  $\tau$  6.14 together with the  $\text{A}_2\text{X}_3$  ethyl group pattern with  $(\text{CH}_2) = 7.14$ ,  $(\text{CH}_3) = 8.96$ , and  $J = 7$  Hz. At  $-70^\circ$  the ring protons appear as two overlapping AB quartets, demonstrating slow ring inversion, while the methyl group protons remain a simple triplet, showing that nitrogen inversion is still fast on the NMR time scale. However, the methylene protons of the ethyl groups appear as two sextuplets, showing their non-equivalence. We confirmed this by spin-decoupling; irradiation at the methyl resonance frequency collapsed the methylene signals to an AB quartet. The non-equivalence of the methylene proton arises because the nitrogen atoms are centres of chirality in the non-inverting ring regardless of the conformations of the ethyl groups. The free energy of activation for the ring inversion process was calculated to be ca. 12.0 Kcal Mole from the coalescences of the various methylene proton signals.

Yours sincerely,

*L. Angiolini* *R.A.Y. Jones* *A.R. Katritzky*

L. Angiolini R.A.Y. Jones A.R. Katritzky

BRYN MAWR COLLEGE  
BRYN MAWR, PENNSYLVANIA 19010

DEPARTMENT OF CHEMISTRY

9 March 1971

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

Dear Barry:

Student Exercise in NMR Calibration

Using the AFM sample of the NMR Subcommittee, Joint Committee on Atomic and Molecular Physical Data, NBS, an exercise was designed to instruct students in physical chemistry in the use and calibration of the College's A-56/60A spectrometer. The AFM sample includes 2.4% TMS, 6.0% 3,3-diethylpentane, 11.9% methylacetate, 1.2% methanol, 14.8% methylformate, 7.4% methylene chloride, 23.9% o-dichlorobenzene in 32.4%  $\text{CCl}_4$  in a Wilmad 528-PP sample tube.

Students were instructed in the concepts of chemical shift and (weak) spin-spin coupling, as well as in the usual homogeneity adjustments and controls on the spectrometer. A bare three hours was invested on two groups of four to six students in this instruction, after which the class was invited to tune up the spectrometer, and measure the TMS-methylene chloride separation using audio sidebands, plus the separation of one to four other lines from TMS by the same technique. Each student, or pair of students, worked until they got stuck, and then called on myself, the lab instructor (a Ph.D. candidate in NMR) or some other knowledgeable person to bail them out.

The results, except for a bout with Varian downtime, were encouraging. All students have mastered, by their own hands-on experience, the use of the spectrometer at a level somewhat above the "routine." The range of "answers" is interpreted best by a mixture of inexperience and hindsight, although in the most favorable cases measurements over the class fell within a range of less than 0.25 Hz.

Data was analyzed by a brief program NMRCAL, whose input is chart positions (mm) and sideband frequencies (Hz), and whose output is line frequencies (Hz) and error estimates. A limited number of writeups for the exercise and program are available.

Sincerely yours,



Jay Martin Anderson



DEPARTMENT OF CHEMISTRY

RIVERSIDE, CALIFORNIA 92502

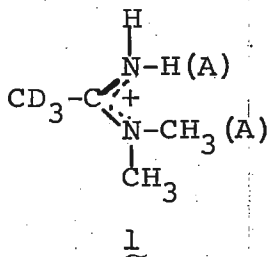
March 10, 1971

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

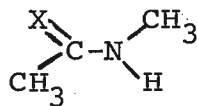
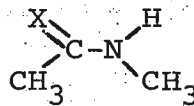
Title: Isomer Distributions in N-CH<sub>3</sub> Substituted  
 Amides, Thioamides and Amidinium Ions.

Dear Barry:

Dr. Violet Jonas has completed a study of the comparative rotational barriers about the C-N bonds in N,N-dimethyl amides, thioamides, and amidinium ions, and another dealing with ion-pairing of amidinium salts in dimethyl sulfoxide. These have been sent to J. Phys. Chem. During the first study we needed to know if a measurable steric interaction existed between NH(A) and NCH<sub>3</sub>(A) in 1.



To test for this, Ellen Logue synthesized the monosubstituted N-CH<sub>3</sub> amidinium ion (2, X = NH<sub>2</sub><sup>+</sup>) and determined the

2a2b

isomer distribution between 2a and 2b. The data are contrasted with those available for the analogous amide and thioamide in Table I.

Table I. Isomer Distributions for the Compounds  
 $\text{CH}_3(\text{X})\text{NHCH}_3$  (2a and 2b) in Solution

X	Solvent	<u>2a</u> (%)	<u>2b</u> (%)
O	Neat <sup>a</sup>	98	2
	$\text{H}_2\text{O}$ <sup>b</sup>	97	3
S	$\text{CCl}_4$ <sup>b</sup>	97	3
	$\text{C}_6\text{H}_6$ <sup>b</sup>	97	3
$\text{NH}_2^+\text{Cl}^-$	$\text{D}_2\text{O}$ <sup>c</sup>	96	4
$\text{NH}_2^+\text{NO}_3^-$	$\text{D}_2\text{O}$ <sup>c</sup>	96	4
	$\text{DMSO-d}_6$ <sup>c</sup>	97	3

(a) K. Anderson, unpublished results. (b) J. Sandström and B. Uppström, Acta Chem. Scand., 21, 2254 (1967). (c) Determined by E. Logue.

These results suggest that the interaction is insignificant; however they could, in part, reflect more favorable H bonding of solvent to the NH proton of  $\text{NHCH}_3$  in isomer 2a.

Sincerely yours,

Robert C. Neuman, Jr.  
 Associate Professor of Chemistry

RCN:mmm



# University College of Swansea

Department of Chemistry

Professor C H Hassaji PhD ScD FRIC  
Professor and Head of Department  
Professor J H Purnell BSc PhD MA PhD ScD  
Professor of Physical Chemistry

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15th March 1971

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

Dear Dr. Shapiro,

## New Computer Programme for Spectral Analysis:

LACX (Laocoon with Chemical Equivalence X Factorisation)

(C.W.H.)

Readers may recall the programme LAME, based on the Bothner-By-Castellano approach, which included magnetic equivalence and other improvements. There are four features which may be used to factorise spin Hamiltonians: (a) magnetic equivalence; (b) chemical equivalence; (c) total z-component; (d) total z-component for isotopic species. The new programme uses the last three of these. Previous programmes have incorporated chemical equivalence at the iteration stage; and isotopic differences (the X approximation) have been used to neglect appropriate off-diagonal elements. The novel feature now incorporated is the actual factorisation of the Hamiltonian.

A hypothetical illustration may serve. Either isomer of cis 1, 2-bis (chloromethyl)-3-chloro-3-fluoro cyclopropane possesses an effective plane of symmetry (assuming free rotation). If we neglect  $^5J_{HH}$ , the spin system can be described as  $[A_2B]_2 X$  (ref.1). Earlier programmes would factorise the Hamiltonian as simply ABCDEFG. LAME would factorise it as  $A_2BC_2DE$ . LACX factorises it as  $[ABC]_2X$ . The dimension of the largest subdivision of the Hamiltonian which requires separate diagonalisation is in the three cases cited 35, 18 and 10 respectively. When one recalls that storage requirements vary as the square of matrix dimensions, and diagonalisation times (often a major factor) roughly as their cubes, the advantages become clear. In one particular  $[AX]_2B$  case, the use of LACX instead of LAME halved the computing time.

New options include the printing of standard deviations and correlation coefficients for parameters, and/or error eigenvectors. Some or all of the partial differentials of transition frequencies w.r.t. parameters can also be printed. This may be helpful at the assignment stage; and it also clarifies



the quantum-mechanical structure of the problem less cumbrously than a complete set of eigenvector matrices.

A special feature of the write-up is a detailed discussion and full instructions for conversion of the FORTRAN programme for different, smaller or larger computers. The programme has already been widely circulated and used in different kinds of machines. Full details will be sent to interested enquirers.

### Bis(pentafluorotellurium) Oxide ( $\text{TeF}_5$ )<sub>2</sub>O

(P.B. and C.W.H.)

This<sup>2</sup> is an interesting example of an  $[\text{AB}_4]_2$  system<sup>1</sup>, which can usefully be discussed in  $(\text{AB}_4)_2$  terms<sup>3</sup>. Not many such systems have been studied<sup>4</sup>. Comparison of the low-resolution 56.445 MHz  $^{19}\text{F}$  spectrum (fig. 1) with ref. 5 shows excellent agreement with an  $\text{AB}_4$  calculation having  $|J|/(\nu_B - \nu_A) = 0.30$ . Clearly then all three four-bond couplings are small.

Examinations of the high-field A lines under high resolution gave no indication of either  $J_{\text{AA}}$  or the long-range  $J'_{\text{AB}}$  being resolvable; e.g. line H (figs. 1 and 2 c), which in the  $\text{AB}_4$  approximation is the single unmixed A line arising from the  $I_B = 0$  submatrix, is extremely sharp. Each of the twelve low-field B lines, predicted in the  $\text{AB}_4$  approximation, shows splitting vaguely resembling a binomial quintet (e.g. fig 2a), suggesting  $|J_{\text{BB}}|$  is about 2 Hz. If one uses products of  $\text{AB}_4$  eigenfunctions as zero-order wave-functions, first-order perturbation theory (taking symmetry properly into account) predicts that the 'quintet' components will be broadened, that intensity will be transferred within each 'quintet', and that weak outer lines will appear. The pattern of changes is sensitive to the relative sign of  $J_{\text{BB}}$ . Some of the A lines are, from symmetry considerations, predicted to manifest additional peaks at about  $\pm J_{\text{BB}}$  from the central one (e.g. multiplet I, figs. 1 and 2d) and some also at about  $\pm 2J_{\text{BB}}$ . Even though  $J_{\text{BB}}$  is so small, several pairs of zero-order eigenvalues are nearly degenerate, and hence second-order effects further perturb the spectrum. Refinement by means of the computer programme LAME is proceeding; the present parameters are  $(\nu_B - \nu_A) = 595.5$ ,  $J_{\text{AB}} = \mp 180.0$ ,  $J_{\text{BB}} = +2.0$ ,  $J_{\text{AA}} = J'_{\text{AB}} = 0.0$  Hz. The agreement presently achieved is seen in fig. 2a and b.

Tellurium possesses an isotope of spin  $\frac{1}{2}$ , namely  $^{125}\text{Te}$ , in 7.0% natural abundance. We are investigating the usual 'outer' satellites arising from one-bond Te-F coupling. But we now report the observation of 'inner' satellites which arise from the three-bond coupling of Te to the axial fluorine A. This is most clearly seen in the weak pair of additional peaks in figure 2c, whose intensities are correct. Other multiplets in the A part of the spectrum also show such peaks, and they can be seen faintly in fig. 2d. Hence  $|^3J_{\text{TeF(axial)}}| = 7.9$  Hz. Such 'inner' satellites, arising from long-range coupling to a nucleus of low natural abundance, are most

frequently so heavily overlapped by the principal absorption as only to be detectable e.g. by INDOR methods; this is true for most  $^{13}\text{C}$  'inner' satellites. It is also true in this case for the 'inner' satellites of the equatorial B fluorines.

Sincerely yours,



P. Bladon,  
Strathclyde University, Glasgow

C.W. Haigh  
Swansea

1. C.W. Haigh, J. Chem. Soc. (A) 1682 (1970)
2. For preliminary results, see P. Bladon, D.H. Brown, K.D. Crosbie and D.W. A. Sharp, Spectrochim. Acta 26A, 2221 (1970).
3. B. Gestblom, R.A. Hoffman and S. Rodmar, Acta Chem. Scand. 18, 1222 (1964).
4. E.G. Finer and R. K. Harris, Spectrochim. Acta 24A, 1939 (1968)
5. J.W. Emsley, J. Feeney and L.H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy' vol.1, p.340, fig.8.15, Pergamon, Oxford, 1965.

5.2.76	4.3F	50uV	1/2	8	0.05	22.22	1152.7
Group	A B C	D	E	F	G H I	J K L	M

F  
P3  
F5Te22

100 Hz

Fig.1

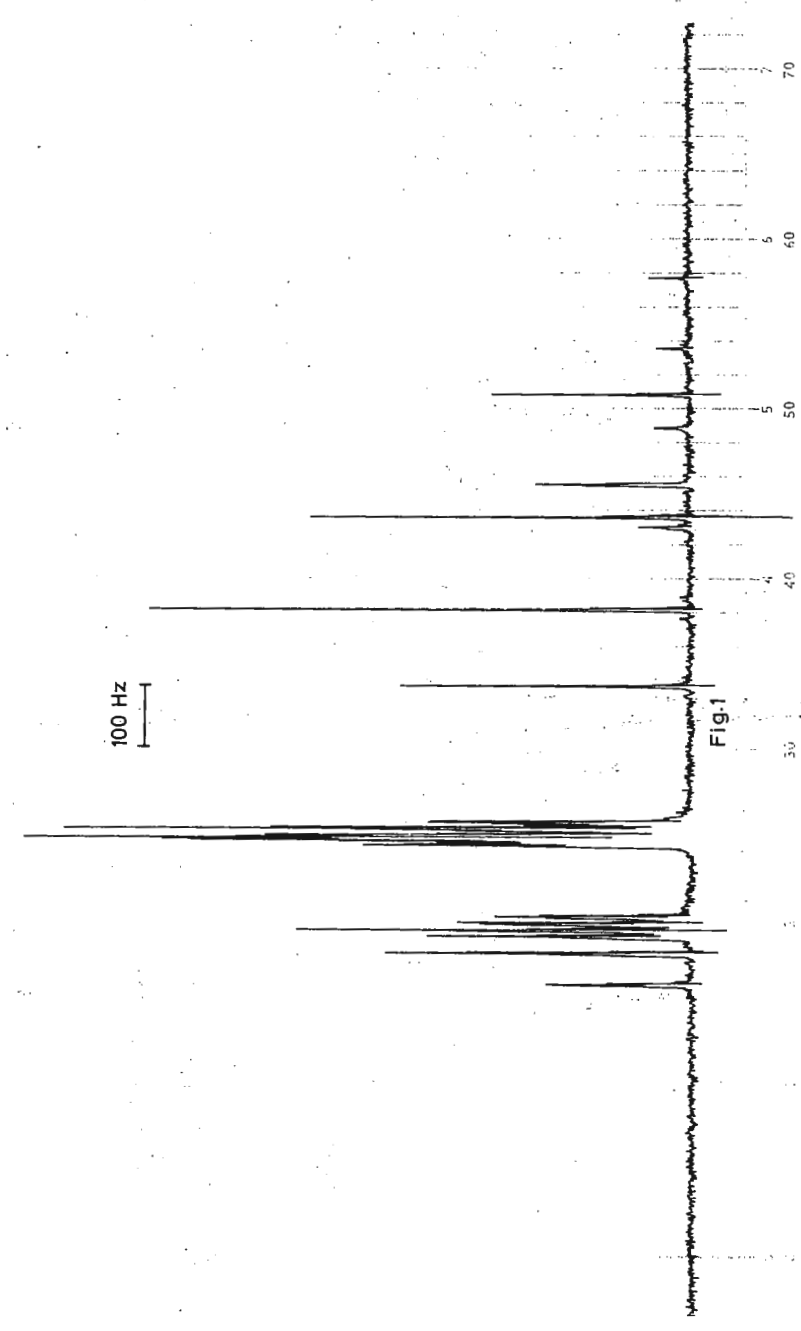
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151-9

N<sub>2</sub>T

P3



a. Multiplet C  
Spectrum

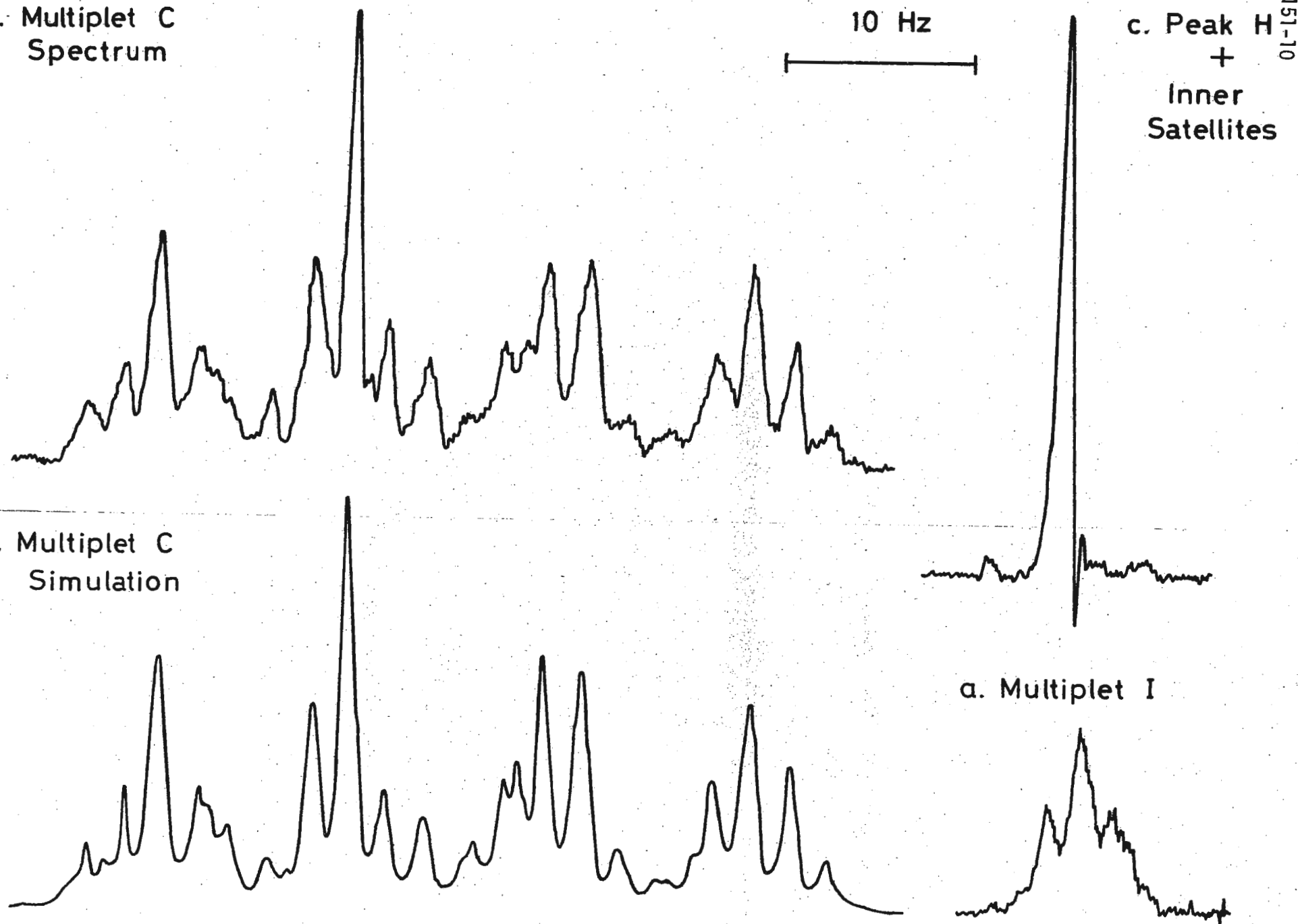
10 Hz

c. Peak H  
+  
Inner  
Satellites

b. Multiplet C  
Simulation

a. Multiplet I

Fig.2



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 SUISSE

# GROUPEMENT AMPERE

LE PRESIDENT

TEL. 022 24.12.68

Genève, le 15 mars 1971

GJB/hl

Professeur Bernard L. SHAPIRO  
 Department of Chemistry  
 Texas A & M University  
 College of Science  
 College Station, Texas 77843  
 U.S.A.

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 3 mars dernier.

1. AMPERE INTERNATIONAL SUMMER SCHOOL II  
 "PULSED MAGNETIC AND OPTICAL RESONANCES"

Podgora Hotel, Basko polje near Split, Yugoslavia, 2-13 September 1971  
 organized by The "Jozef Stefan" Institute, Ljubljana, Yugoslavia

Outline of programme

The programme of the School will include: Present state of experimental techniques in pulsed NMR, Present state of experimental techniques in pulsed EPR, Recent developments in double resonance, High resolution NMR in solids, Fourier transform spectroscopy, Pulsed optical resonance (self-induced transparency, photon echoes, etc.), Selected applications in solid state physics, chemistry and biology.

Lecture notes will be available in the beginning of the School.

The list of the invited speakers will be given in the second circular.

English will be the official language of the meeting.

Participants

The Ampère International Summer School II "Pulsed Magnetic and Optical Resonances" is intended for graduate students and young research workers in the field. The total number of participants will be limited to about 60. A limited number of brief research communications by the participants will be accepted.



Prof. Bernard L. SHAPIRO, College Station, Texas

- 2 -

#### Accommodation and transport

The location of the C.A. School will be the Podgora Hotel at Basko polje, an attractive swimming resort at the Adriatic coast. Sundays and early afternoons of the weekdays will be free for swimming or other activities.

At Podgora Hotel double-bedded rooms and apartments will be on disposal for the School. The price will be from 80 to 125 din (7 - 10 U.S. \$), according to the room, per person per day (meals included). A few single rooms will be available on special request.

As for transport, there will be special buses from Split at the Adriatic coast (train terminal and airport) to Podgora Hotel in Basko polje (some 60 km distance) and back. The time schedule will be given later.

#### Participation fee

A participation fee of \$ 35 is foreseen, payable at the reception desk of the School. This participation fee is reduced to \$ 25 for the members of the Groupement Ampère.

#### Enrolment

The deadline for application is 1 July, 1971. The completed application form should be sent to:

Miss T. Matoh, Adm. Secretary,  
Institut "Jozef Stefan"  
P.O.B. 199, 61001 LJUBLJANA, Yugoslavia.

Additional application forms and information can be obtained by writing to the same address.

## 2. TRAVAUX RECENTS DU DEPARTEMENT DE PHYSIQUE DE LA MATIERE CONDENSEE DANS LE DOMAINE DES RESONANCES MAGNETIQUES

### a) Georges J. Béné - Echos de spins en champ moyen nul

Note aux C.R. Acad. Sc. Paris B271, 1235 (1970)

L'analyse phénoménologique des échos de spins, facilitée par leur mise en oeuvre dans le référentiel du laboratoire, met en évidence le rôle du gradient du champ magnétique appliqué. Elle permet de montrer les relations des diverses techniques employées et de suggérer une méthode d'observation en l'absence d'un champ magnétique homogène et constant.

./.

Prof. Bernard L. SHAPIRO, College Station, Texas

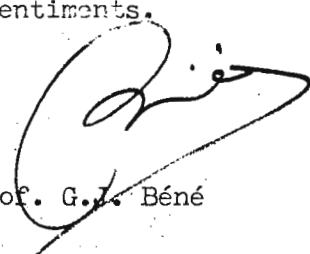
- 3 -

- b) Georges J. Béné - Description simple des échos de spins et de leurs perturbations

Société de Physique et d'Histoire Naturelle de Genève, Séance du  
4 mars 1971

Le phénomène fondamental qui est à la racine de toute les techniques connues d'échos de spins est décrit en détail. On montre ensuite comment, par une rotation de référentiels (plan de dispersion des moments, axe du système...) on peut en déduire toutes les techniques de production et d'observation d'échos. Cette analyse rend compte simplement des perturbations axiales apportées aux échos de spins et suggère des méthodes nouvelles de mise en oeuvre de ces phénomènes.

Croyez, cher Professeur Shapiro, à mes meilleurs sentiments.



Prof. G.J. Béné

151-14

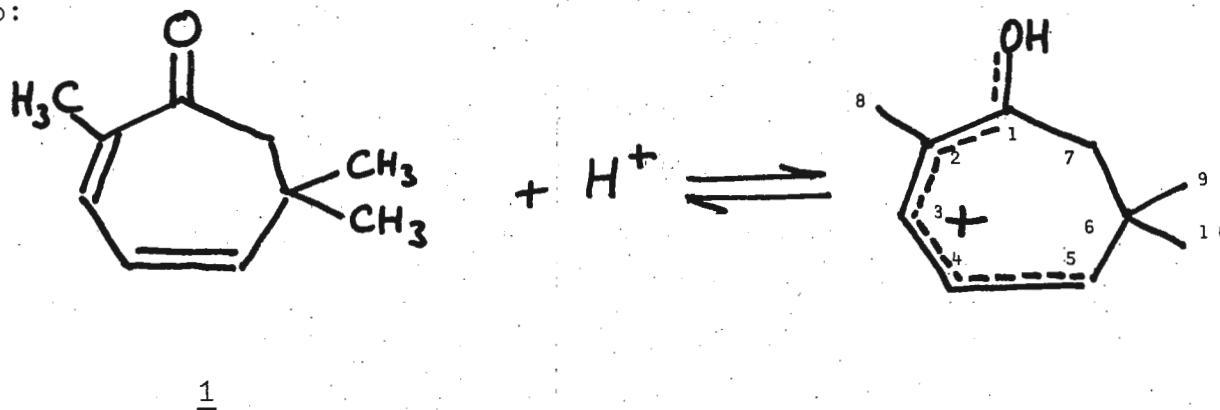
Professor B.L. Shapiro  
 Department of Chemistry  
 Texas A&M University  
 College Station, Texas 77843 U.S.A.

March 22, 1971

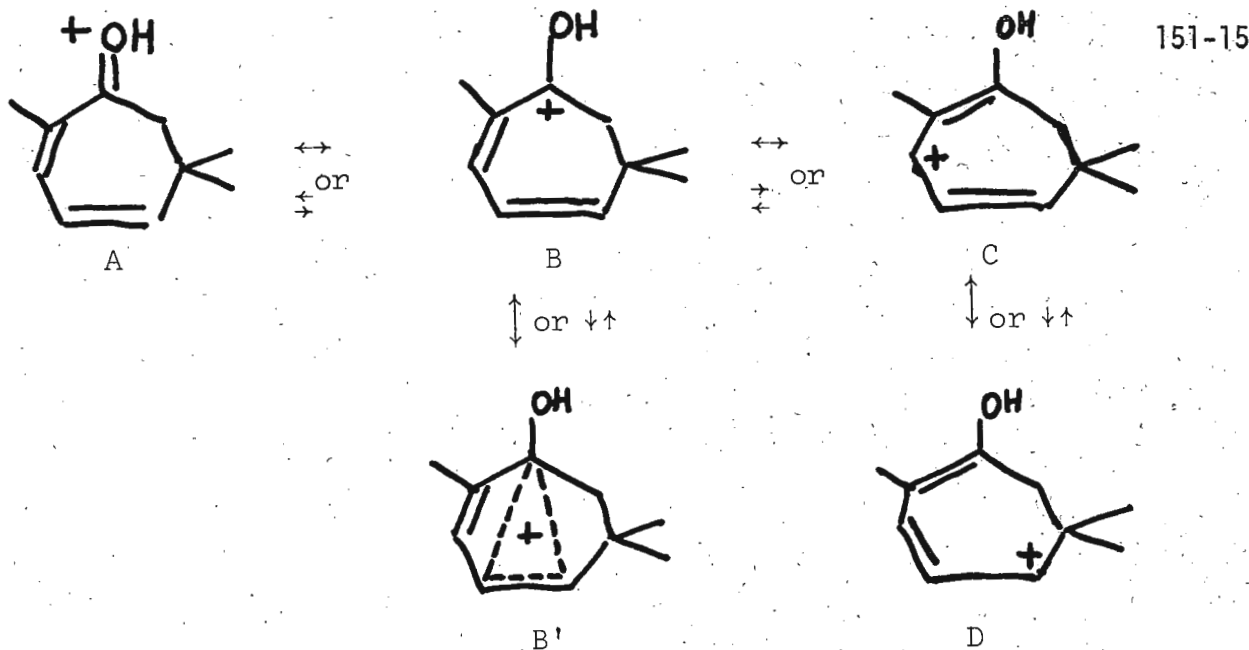
Electronic distribution in protonated eucarvone.

Dear Barry,

Recently, in the course of another investigation, we became interested in various cationic species originating with eucarvone (1). Its basicity is rather weak for an  $\alpha$ - $\beta$  unsaturated ketone, with a  $pK_a$  of -4.9<sup>1</sup>. It is protonated according to:



The shift towards higher wavelengths of the U.V. maximum in sulfuric acid (398 nm in 96%  $H_2SO_4$  compared to 298 in MeOH - lit. 300<sup>2</sup>) suggested the formation of a delocalized ion, according to:



We could obtain information about the resultant charge distribution from  $^1\text{H}$  and better yet from  $^{13}\text{C}$  protonation shifts:

POSITION	$^1\text{H}$ PROTONATION SHIFTS (ppm)	$^{13}\text{C}$ PROTONATION SHIFTS (ppm)
1	-	-7.1
2	-	+4.2
3	-1.42	-32.6
4	-0.75	-3.9
5	-0.87	-19.5
6	-	-1.5
7	-0.74	+4.6
8	-0.31	+2.2
9 10	-0.37	+3.3

They imply delocalization of the positive charge partially unto  $\text{C}_1$ ,  $\text{C}_3$ ,  $\text{C}_5$  and possibly  $\text{C}_4$ , and show a marked predominance of the resonance forms C and D.

In line with this observation, the  $^4J_{\text{CH}_3(8)-\text{H}(3)}$  coupling has its magnitude substantially reduced<sup>5</sup>. An upper limit of 0.6 Hz is found in  $\text{FSO}_3\text{H}$  versus 1.5 Hz for eucaryone neat<sup>6</sup> or in  $\text{CCl}_4$  solution.

With best regards,  
Sincerely yours,

*André Cornélis*  
André Cornélis

*Pierre Laszlo*  
Pierre Laszlo

- <sup>1</sup> The  $pK_a$  was determined by U.V. titration according to the method described by C.T. DAVIS and T.A. GEISSMAN, J. Amer. Chem. Soc., 76 3507 (1954);
- <sup>2</sup> E.J. COREY and H.J. BURKE, J. Amer. Chem. Soc., 78 177 (1956);
- <sup>3</sup> Obtained through the courtesy of Dr. PRICE, Bruker Instruments, Karlsruhe, German Federal Republic;  
The carbon shifts are roughly 20-25 times more sensitive than proton shifts to the presence of charge in the  $p_z$  orbital on carbon, which is consistent with a number of earlier observations; "proportionality" constants of ca 180 and 10 ppm per unit of charge are often quoted for the paramagnetic part of the carbon chemical shift and for the proton chemical shift.
- <sup>4</sup> Change in chemical shift between  $CCl_4$  and  $FSO_3H$  solution referred to internal cyclohexane;
- <sup>5</sup> E.C. FRIEDRICH, J. Org. Chem., 33 413 (1968) had already noticed, in various methyl-substituted 4-methyl-4-dichloromethylcyclohexa-2,5-dienones, a  $^4J_{CH_3, H^{n\pm 1}}$  of 1.5 Hz in  $CCl_4$  and of ca 0 in  $H_2SO_4$ .  
Those  $^4J_{CH_3-H}$  coupling constants depend upon the  $\pi$  bond order in the  $CH_3-C=C$  fragment:  
D.J. BLEARS, S.S. DANYLUK, and T. SCHAEFER, Can. J. Chem., 46 654 (1968). H. ROTTENDORF and S. STERNHELL, Aust.J.Chem., 17 1315 (1964).  
But this is clearly not the only factor to be considered here: eucarvone being non planar, conformational changes occur upon protonation. The mean excitation energy is also affected somewhat.
- <sup>6</sup> A.A. BOTHNER-BY and E. MOSER, J. Amer. Chem. Soc., 90 2347 (1968).



## STANFORD UNIVERSITY

STANFORD, CALIFORNIA 94305

March 23, 1971

DEPARTMENT OF CHEMISTRY

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

Dear Barry:

Thanks for the reminder. I had hoped that this would be a more complete report, but will tell you of our progress now to keep the subscription going.

In talking with Clarence Gust of Case Western Reserve, we learned that it might be possible to improve the sensitivity of our rather ancient A-60 by installing a six-turn insert in the variable temperature probe. Though the A-60 itself is over nine-years-old, the variable temperature accessory was added several years later and new shim coils were installed at that time. In the hope that the new shim coils would be able to handle the six-turn insert, we had Clarence install one for us.

The results look very promising. The resolution attainable with the new insert appears to be at least as good as with our three-turn insert type probes (0.2 to 0.25 Hz), and the sensitivity seems to be at least doubled. More specific statements would be made if it were not for the rather perverse nature of our A-60 which developed a loss in sensitivity while the probe was out being modified. This made a "before and after" comparison on the same probe with three and six-turn inserts rather meaningless. However, our room temperature (V-6030) probe and our variable temperature (V-6031) probe with three-turn insert have had a history of similar sensitivity and resolution, so we can make the comparison on that basis with the instrument under the same conditions. The spectra of ODCB (30% in  $\text{CCl}_4$  + TMS) and the 1% ethylbenzene quartet were run with each probe over a period of two days. The transmitters, receivers, and probes were returned before the data was obtained.

The improvement in signal to noise is shown clearly in the 1% ethylbenzene quartets, though normally we have had better sensitivity on the room temperature probe to start with (up to 12/1) after making some modifications which were recommended in Clarence Gust's "A-60 Service Program." Hopefully, when we complete that program and locate the source of our present loss of sensitivity we will have even better than the 16/1 S/N obtained recently with the six-turn insert.

For those readers who have later models of A-60's and are thinking that this is just now getting up to what theirs has always been, I'd like to point out that this "original" A-60 started out with an S/N specification of 5/1. Thus, we feel that pushing it up to where it is now is something of an accomplishment.

Sincerely yours,



Lois J. Durham

Suggested title: Upgrading A-60

1% Ethylbenzene in  $\text{CCl}_4$

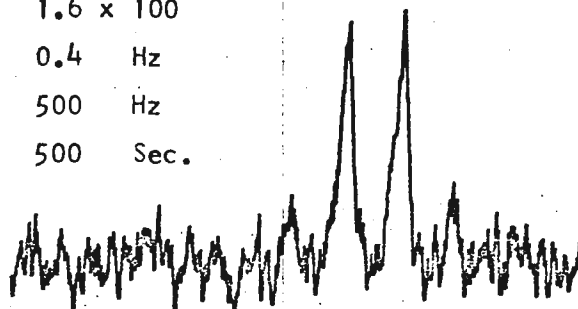
RF Power 0.15 mG

Spec.Amp.  $1.6 \times 100$

Filter 0.4 Hz

Sweep Width 500 Hz

Sweep Time 500 Sec.



30% ODCB in  $\text{CCl}_4$  + TMS

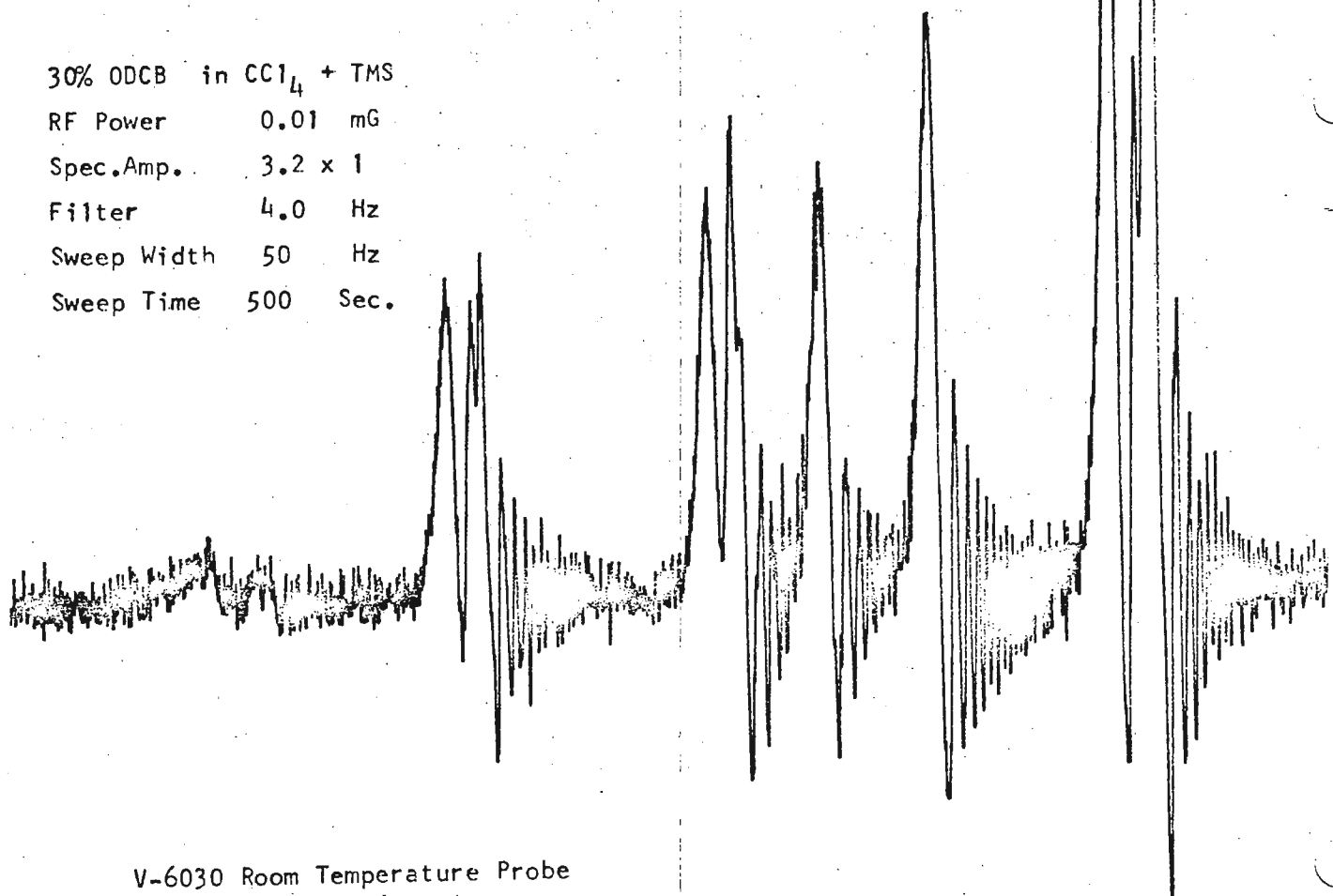
RF Power 0.01 mG

Spec.Amp.  $3.2 \times 1$

Filter 4.0 Hz

Sweep Width 50 Hz

Sweep Time 500 Sec.



V-6030 Room Temperature Probe  
with three turn insert

1% Ethylbenzene in  $\text{CCl}_4$

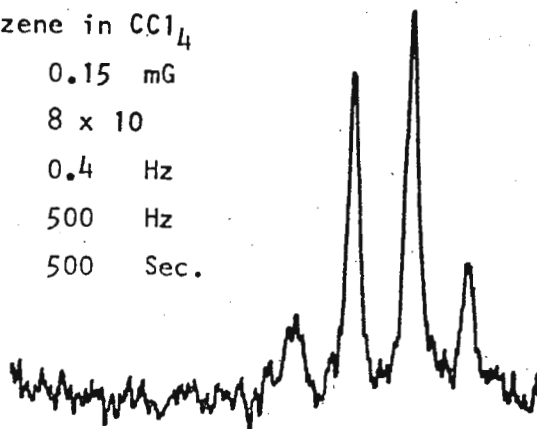
RF Power 0.15 mG

Spec.Amp.  $8 \times 10$

Filter 0.4 Hz

Sweep Width 500 Hz

Sweep Time 500 Sec.



30% ODCB in  $\text{CCl}_4$  + TMS

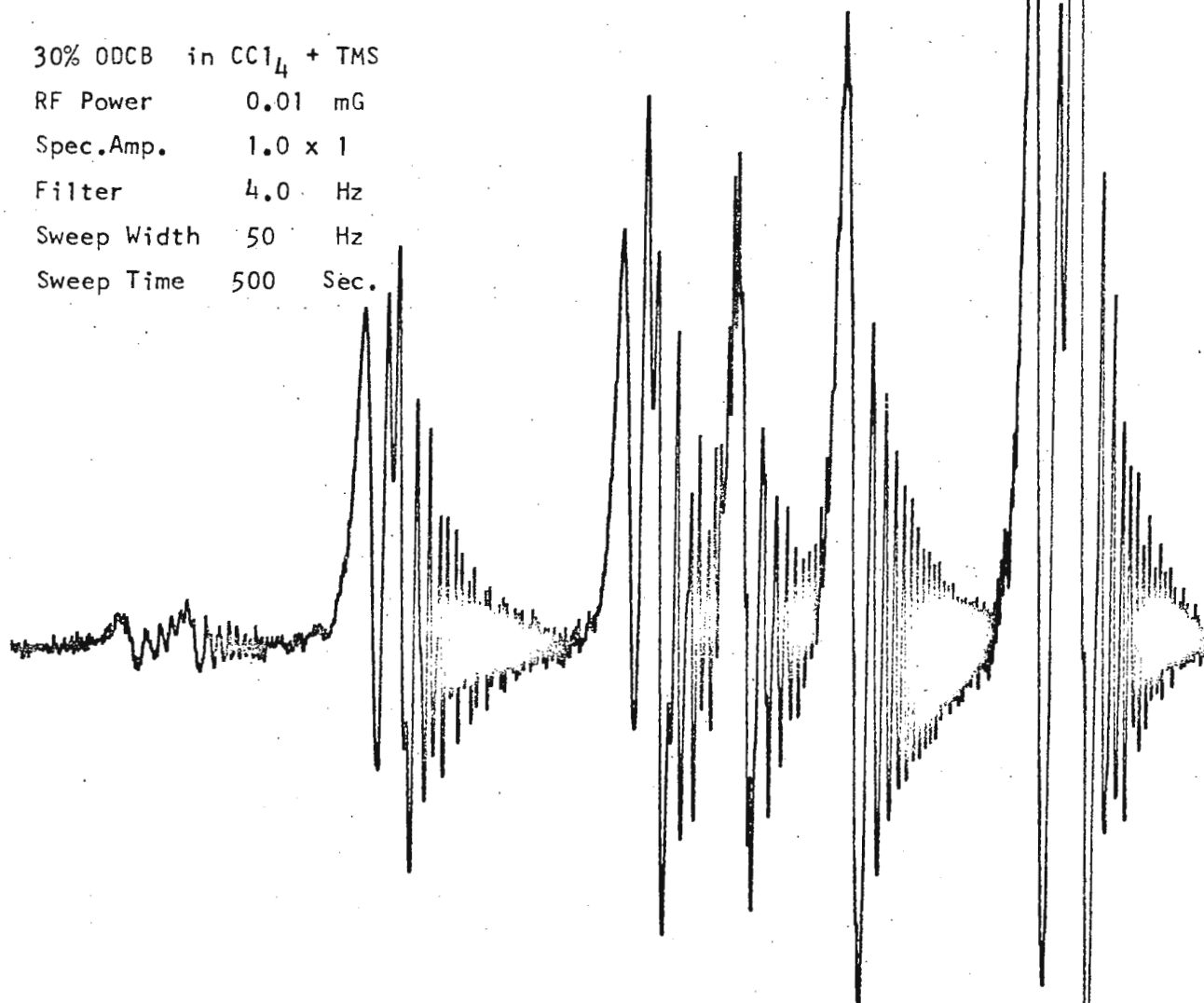
RF Power 0.01 mG

Spec.Amp.  $1.0 \times 1$

Filter 4.0 Hz

Sweep Width 50 Hz

Sweep Time 500 Sec.



V-6031 Variable Temperature Probe  
with six turn insert

Department of Chemistry



FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW 463, ONTARIO

24 March 1971

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

Concerning the Porosity of Plastic NMR Tube Caps

Dear Professor Shapiro,

We were interested in the recent communication concerning porosity of plastic NMR caps. Some of our kinetic work involves use of capped samples stored over several days. The reported rate of solvent loss was higher than anticipated, so we decided to examine a few samples. Our results confirm the bad news and indicate that, short of heat sealing the glass itself, little can be done to alleviate the problem.

The data in the Table represent three solvents in three qualities of tube, all sealed by plastic (NMR Specialities) caps. As can be seen, little dependence on tube quality is found. Thus uniformity of outer bore and the nature of the glass surface are not major problems. Sealing the cap-tube interface with Fisher Sealit (column b) had only a small effect as did completely sealing the interface and cap (column c). Sealing with a heavier picene wax appeared to produce results but unfortunately it is soon evident that the escaping solvent is simply being trapped in the wax.

The tubes were kept throughout in the magnet housing of our HA 100 at 32°C. They contained about half a ml of solvent (actual weight given in Table), and weight losses as a percentage of original per day were calculated from the linear plots of weight-loss versus time.

Our systems are extremely sensitive to catalysis by water, and a study of the time-dependence of the kinetics tends to confirm the previously reported impermeability of the caps to atmospheric water vapour.

.../2

- 2 -

TABLE  
Weight Loss as a Percentage Per Day

Solvent Tube	CCl <sub>4</sub> (1.2 gms.)				C <sub>6</sub> H <sub>6</sub> (0.6 gms.)				CHCl <sub>3</sub> (1.1 gms.)			
	a.	b.	c.	d.	a.	b.	c.	d.	a.	b.	c.	d.
Cheap Throwaway	0.85	0.75	0.52	0.05	1.30	1.10	0.94	0.07	1.40	1.30	1.40	0.05
Medium Cost Ground Glass	0.81	0.76	0.56	0.06	1.20	1.10	0.90	0.04	1.70	1.54	1.76	0.11
Best Quality Smooth Bore	1.00	0.86	0.71	0.10	1.30	1.27	1.02	0.07	1.90	1.78	1.92	0.12

a= untouched cap. b= sealed at edge. c= cap totally covered. d= picene wax seal

Yours sincerely,

*Clive E. Holloway* *R. Ward*

C. E. Holloway.

R. Ward

CEH/RW:pc



## University of East Anglia

From The Dean  
Professor N. Sheppard F.R.S.

School of Chemical Sciences  
University Plain, Norwich NOR 88C  
Telephone Norwich (0603) 56161  
Telegraphic Address UEANOR  
23rd March 1971

Dear Barry,

A Study of the Solvation of  $Mg^{2+}$  Ions in Water/Acetone

I am replying to your recent memorandum reminding me that my subscription for the TAMU NMR Newsletter is due for renewal.

I should like to briefly describe some work on the solvation of  $Mg^{2+}$  ions in water/acetonitrile that was carried out by Dr. Robert D. Green who recently spent a one year postdoctoral period in this laboratory.

Similar techniques were employed as in a previous highly successful study of aluminium perchlorate in water/acetonitrile<sup>1,2</sup> except that separate 'bound' and 'free' resonances from water and acetone molecules could only be obtained in the present case by cooling below  $-70^{\circ}C$ ; with the aluminium salt such measurements were possible at room temperature. In anhydrous acetone, the number of molecules in the first solvation shell was found to be 5, and the addition of water to the system caused molecule-for-molecule replacement of acetone by solvated water. Further addition of water led to a final solvation number of 6, as previously reported in the literature.<sup>3,4</sup>

We interpret these findings in terms of uniform 6-fold coordination of  $Mg^{2+}$ , with a perchlorate ion occupying one place until the final stages when it also is replaced by water. In this case 'free' water resonances appeared well before the 'bound' water resonances had increased to its maximum intensity; this shows that the comparative strength of solvation of water to magnesium is less than to aluminium, where the 'free' water resonance only appeared after the 'bound' shell was virtually complete.

Once again, in the solutions containing less water, six different 'bound' water signals were observed corresponding to mono-aquo up to hexa-aquo solvated species with relatively long lifetimes; equilibrium constants have been derived for the co-existence of these different solvated species. The Figure shows the resonances from different aquated species in solutions with  $[H_2O]/Mg^{2+} = 5.6$  and 1.3.

Structure in some of the 'free' water resonances is thought to distinguish between molecules in the second coordination sphere of  $Mg^{2+}$  and other 'free' water molecules which interact only with acetone neighbours.

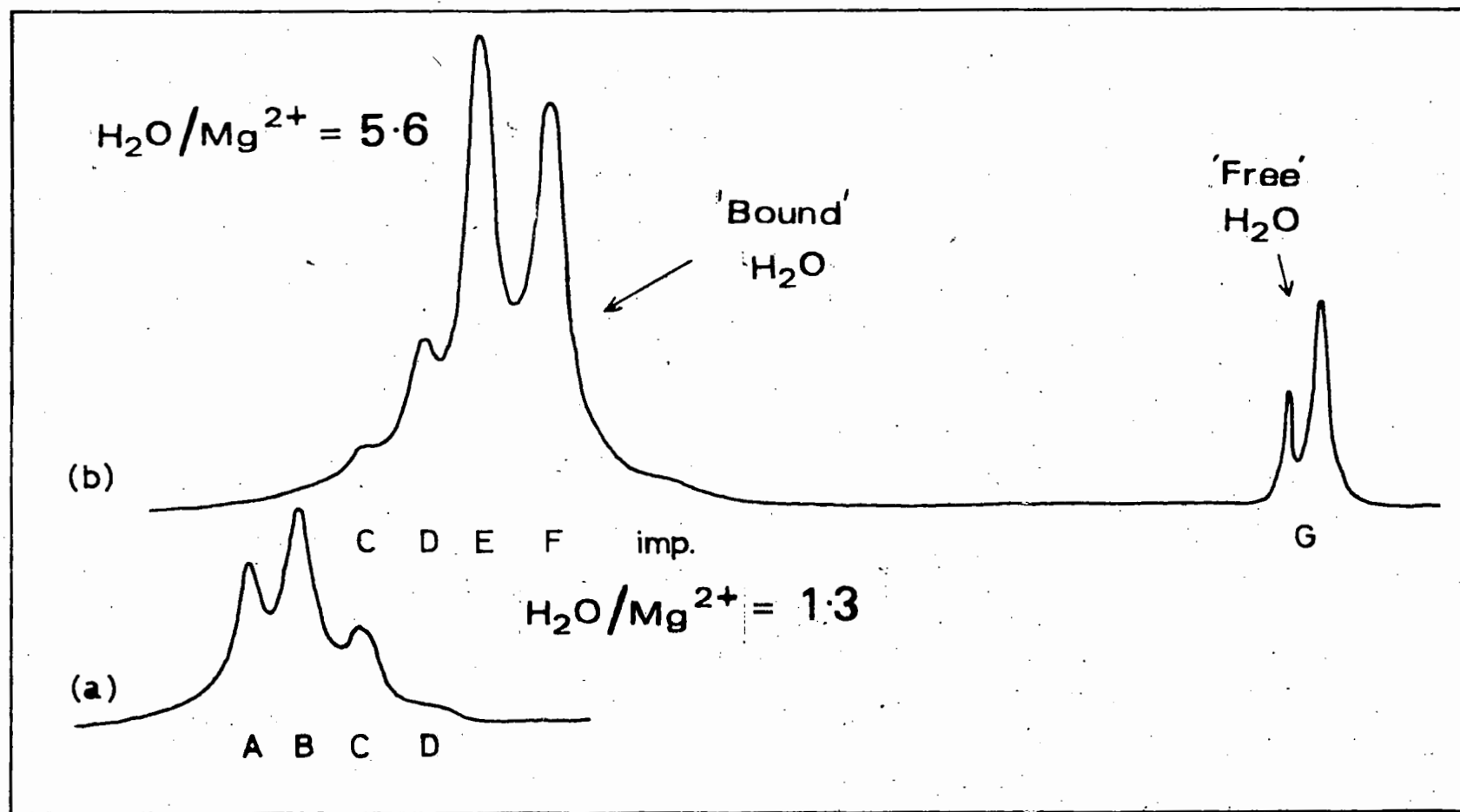
Yours sincerely,

*N. Sheppard*  
N. Sheppard.

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

NS/ML.

# $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}/\text{Acetone}$



## SUMMER SCHOOL ON ELECTRON SPIN RELAXATION IN LIQUIDS

A Summer School on this subject sponsored by NATO will be held at "Spåtind", Norway, between August 16-28, 1971.

The scientific programme includes the following lectures:

L.T. Muus, Aarhus, Density Operators, Superoperators and Time-Ordering

I. Oppenheim, M.I.T., Linear Response Theory

J.M. Deutch, M.I.T., Generalized Brownian Motion  
Multiple Time Scale

D. Kivelson, U.C.L.A., Electron Spin Relaxation in  
Liquids (I)

J.H. Freed, Cornell, Electron Spin Relaxation in Liquids (II)

P.W. Atkins, Oxford, Spin Rotation Theory

R.G. Gordon, Harvard, Asymmetric Line Broadening in  
Viscous Liquids

G.R. Luckhurst, Southampton, Rotational Relaxation in  
 $^6\text{S}$  State Ions

Molecular Motion in Liquid Crystals.

The School is open to Research Scientists and Graduate Students interested in the field.

For application blank and further information please contact:

Professor L.T. Muus  
Chemistry Department  
140 Langelandsgade  
DK-8000 Aarhus C, Denmark

before May 15.

MONTECATINI EDISON S. p. A.

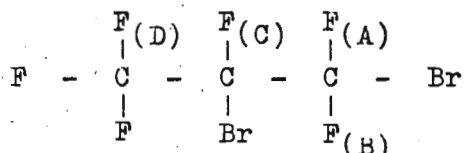
STABILIMENTO PETROLCHIMICO  
PORTO MARGHERA

Porto Marghera 26 march 1971

Prof. Bernard L. Shapiro  
Texas A & M University  
College of Science  
Department of Chemistry  
College Station, Texas 77843  
U.S.A.Centro Ricerche Petrolchimiche  
Montecatini Edison S.p.A.  
Stabilimento Petrolchimico  
Via dell'Elettricità, 41  
30175 - Porto Marghera (Venezia)  
ITALY

Subject: NMR Spectrum of 1,2-dibromo-hexafluoro-propane.

We have analyzed 1,2-dibromo-exafluoro-propane (I), contained as impurity in a sample of symmetric 1,2-dibromo-tetrafluoroethane. (I) was obtained by distillation and chromatographic separation and it was identified by MS, IR and NMR analysis.  $^{19}\text{F}$  NMR spectra of (I) were studied and its parameters extracted at 56,4 Mc. The fluorine nuclei of (I) are labelled according to the following formula:



The NMR data relative to this compound are reported in the following table.

Table 1

NMR parameters of 1,2-dibromo-exafluoropropane (50%  $\text{CFCl}_3$ - $\text{CDCl}_3^*$  solution)

$\delta^*$ (A)	=	56.93 ppm
$\delta^*$ (B)	=	58.92 ppm
$\delta^*$ (C)	=	132.95 ppm
$\delta^*$ (D)	=	74.65 ppm
$J$ (A.B)	= $\pm$	176.8 Hz
$J^{\text{AV}}$ (A.C)	= $\mp$	14.9 Hz
$J^{\text{AV}}$ (B.C)	= $\mp$	15.3 Hz
$J^{\text{AV}}$ (A.D)	= $\pm$	9.7 Hz
$J^{\text{AV}}$ (B.D)	= $\pm$	11.6 Hz
$J^{\text{AV}}$ (C.D)	= $\mp$	8.7 Hz

The RMS obtained between experimental and theoretical lines is 0.08 Hz. With the  $J^{\text{AV}}$  notation we have indicated average coupling constants because of the free rotation about C-C bonds at room temperature.

(\*) This solvent was used to lower the vapor pressure of the mixture.

TABLE 1

Best values of the NMR parameters of 2,4 dichloro-1-pentene ( $C_6D_6$  1% solution) and their probable errors. These data were obtained with the aid of the iterative program.(°)

$\nu(A)$	=	$237.30 \pm 0.02$
$\nu(B)$	=	$217.52 \pm 0.02$
$\nu(X)$	=	$502.11 \pm 0.02$
$\nu(Y)$	=	$479.82 \pm 0.02$
$\nu(K)$	=	$402.56 \pm 0.02$
$J(A.B)$	=	$- 14.58 \pm 0.02$
$J(A.X)$	=	$- 0.12 \pm 0.03$
$J(A.Y)$	=	$- 0.93 \pm 0.03$
$J(A.K)$	=	$7.92 \pm 0.03$
$J(B.X)$	=	$- 0.35 \pm 0.03$
$J(B.Y)$	=	$- 1.06 \pm 0.03$
$J(B.K)$	=	$5.76 \pm 0.03$
$J(X.Y)$	=	$- 1.42 \pm 0.02$
$J(K.X)$	=	$0.00$
$J(K.Y)$	=	$0.00$

The RMS obtained between theoretical and experimental lines is 0.09 Hz  
The following data from first order analysis have been determined:

$$\nu(Z) = 111.60$$

$$J(K.Z) = 6.60$$

---

(°)The frequencies (TMS as reference) and the coupling constants are reported in Hz.



TABLE 2

NMR parameters of 2,4-dichloro-1-pentene-1d<sub>1</sub> (Hz) (C<sub>6</sub>D<sub>6</sub> 3% solution)

These data were obtained without iterative programs.

	3% C <sub>6</sub> D <sub>6</sub>	3% C <sub>6</sub> D <sub>6</sub>	30% C <sub>6</sub> D <sub>6</sub>	30% C <sub>6</sub> D <sub>6</sub>	30% C <sub>6</sub> H <sub>5</sub> Cl	30% C <sub>6</sub> H <sub>5</sub> Cl	30% CDCl <sub>3</sub>	30% CDCl <sub>3</sub>	10% CD <sub>3</sub> COCD <sub>3</sub>	10% CD <sub>3</sub> COCD <sub>3</sub>
	cis	trans	cis	trans	cis	trans	cis	trans	cis	trans
ν (A)	237.51	237.51	245.81	245.81	256.39	256.39	274.48	274.48	277.19	277.19
ν (B)	217.73	217.73	229.10	229.10	243.71	243.71	264.14	264.14	275.55	275.55
ν (Y)	479.49	501.66	489.52	505.68	504.85	513.12	523.49	526.10	535.62	527.75
ν (X)	403.00	403.00	407.24	407.24	415.53	415.53	429.29	429.29	433.78	433.78
ν (Z)	111.97	111.97	121.52	121.52	134.08	134.08	152.78	152.78	153.64	153.64
J (A.B)	- 14.62	- 14.62	- 14.55	- 14.55	- 14.50	- 14.50	- 14.54	- 14.54	- 12.07	- 12.07
J (A.Y)	- 0.89	- 0.15	- 0.87	- 0.20	- 0.87	- 0.16	- 0.88	- 0.17	- 0.89	- 0.17
J (A.X)	7.93	7.93	7.82	7.82	7.78	7.78	7.73	7.73	8.51	8.51
J (A.D)	- 0.02	- 0.14	- 0.03	- 0.13	- 0.02	- 0.13	- 0.03	- 0.13	- 0.03	- 0.14
J (B.Y)	- 1.02	- 0.20	- 1.00	- 0.29	- 0.99	- 0.25	- 0.86	- 0.28	- 0.94	- 0.35
J (B.X)	5.74	5.74	6.06	6.06	6.09	6.09	6.17	6.17	5.22	5.22
J (B.D)	- 0.03	- 0.16	- 0.04	- 0.15	- 0.04	- 0.15	- 0.04	- 0.13	- 0.04	- 0.14
J (Y.D)	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22	- 0.22
J (X.Z)	6.52	6.52	6.51	6.51	6.48	6.48	6.49	6.49	6.54	6.54

Although the sign of the geminal coupling constant  $J(A.B)$  at the saturated carbon atom of (I) cannot be determined from the ABX analysis, it was assumed as negative as it is usual for a geminal coupling constant in a saturated carbon atom (1).

The allylic cis and trans coupling constants  $J(A.X)$ ,  $J(A.Y)$  and  $J(B.X)$ ,  $J(B.Y)$  were considered negative as reported in (1).

The geminal coupling constant  $J(X.Y)$  at the unsaturated carbon atom is considered negative as in vinyl chloride (2,3). The coupling constants  $J(A.K)$  and  $J(B.K)$  between the A and B nuclei and the  $-CHCl-$  proton, are vicinal coupling constants and therefore both positive (4).

The same situation is true for the coupling  $J(K.Z)$  between methyl and  $-CHCl-$  groups. In addition we have an average vicinal coupling constant because of the free rotation of  $CH_3-$  about C-C bond.

Yours sincerely

*Giorgio Gurato*  
(Giorgio Gurato)

(Adelio Rigo)

*Adelio Rigo*

- 1) -J.W. Emsley, J. Feeney and L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol.2, Pergamon Press, Oxford 1965, p. 682
- 2) -W.S. Brey and K.N. Scott, J. Phys. Chem., 72, 4351 (1968)
- 3) -W. Brüghel, Nuclear Magnetic Resonance Spectra and Chemical Structure, Vol. I, Academic Press, New York, 1967, p.91
- 4) -L.M. Jackman and S. Sternhell, Applications of Nuclear Resonance Spectroscopy in Organic Chemistry, Pergamon Press, Oxford 1969, p. 280

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The paper will be envoyed to Organic Magnetic Resonance Journal.

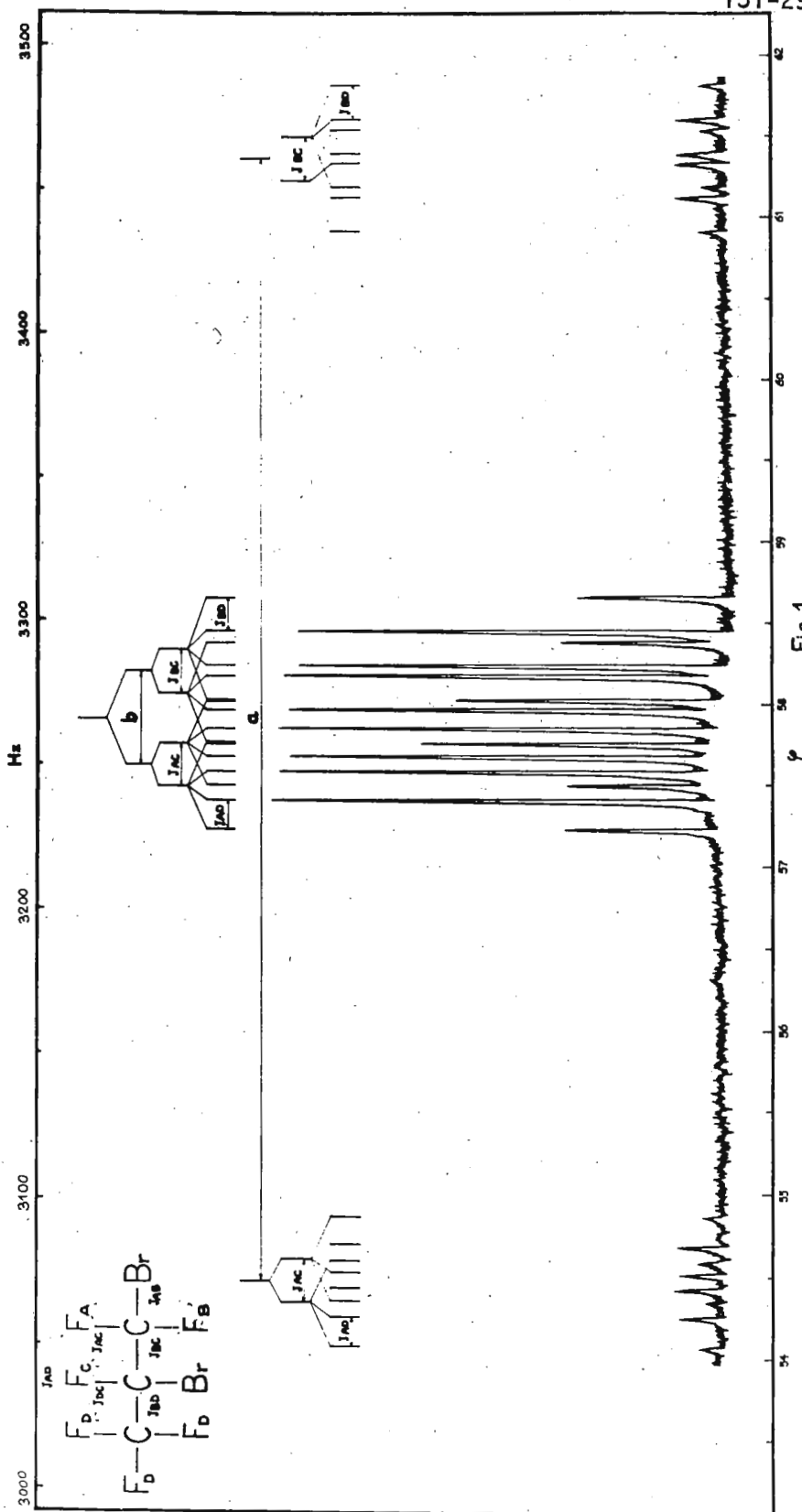


Fig. 1

MONTECATINI EDISON S. p. A.

STABILIMENTO PETROLCHIMICO

PORTO MARGHERA

Porto Marghera 26 march 1971

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

Centro Ricerche Petrolchimiche  
 Montecatini Edison S.p.A.  
 Stabilimento Petrolchimico  
 Via dell'Elettricità, 41  
 30175 - Porto Marghera(Venezia)  
 ITALY

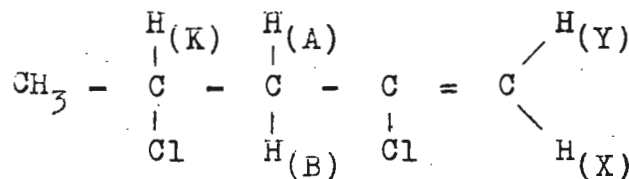
Subject: NMR spectrum of 2,4-dichloro-1-pentene and of 2,4-dichloro-1-pentene- $\text{d}_1$

Dear Professor Shapiro,

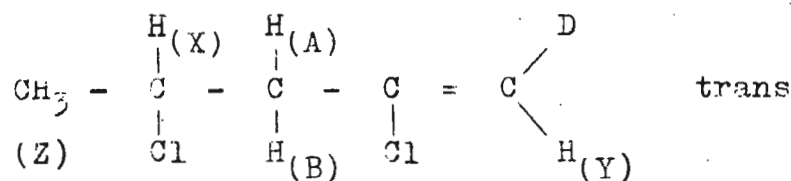
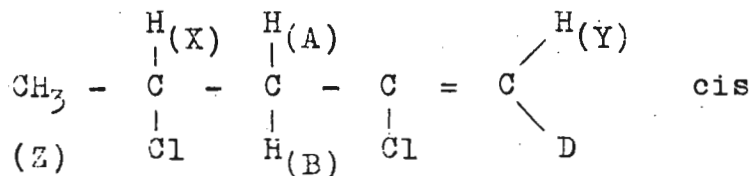
sorry we needed reminding about our contribution.

In the course of a study of short chain branching in polyvinyl chloride it was necessary to synthesize  $\text{CH}_3\text{-CHCl-CH}_2\text{-CCl=CH}_2$  (I) and  $\text{CH}_3\text{-CHCl-CH}_2\text{CCl=CHD}$  (II).

We have investigated the NMR spectrum at 100 MHz of these compounds. The data obtained for the solution in  $\text{C}_6\text{D}_6$  are reported in table 1 and 2. These data were calculated by computer -(LAOCN III program). The protons of (I) are labelled according to the following formula:



We have used the following labels for the cis and trans isomers of (II)



The  $\text{CF}_3$ - pattern is a doublet of doublets of doublets, the  $\text{CFBr}$ - pattern is an overlapping doublet of doublet of quartets and  $\text{CF}_2\text{Br}$  - is a AB system ( $\nu_A - \nu_B = 112.05 \text{ Hz}$ ) of doublets of quartets. We have reported in fig. (1) the pattern of  $\text{CF}_2\text{Br}$  - moiety. (\*)

We have found a good agreement between our and literature data (1-2) of the similar molecule 2-chloro-exafluoro-1-iodopropane. The  $\rho^*$ 's of the two compounds are referred to  $\text{CFCl}_3$  as internal standard.

It was also possible to assign the relative signs of the coupling constants according to the data of Evans on the relative signs of fluorine coupling constants (3).

- 1) -E.F. Mooney. Annual Reports on N.M.R. Spectroscopy - Volume 3  
Academic Press - London and New York (1970) pag.266
- 2) -R.E. Banks, A. Braithwaite, R.N. Haszeldine and D.R. Taylor  
J. Chem. Soc. (C) 2593, 1968
- 3) -D.F. Evans - Discussions of the Faraday Soc. 34-35-36; 139(1962-1963)

We hope to have accomplished to our duty towards TAMU NMR NEWSLETTER and we beg You to send to us the No. 132 SEPTEMBER 1969 which we have never received.

Faithfully yours

(Giorgio Gurato)

*Giorgio Gurato*

(Giorgio Zenoni)

*Giorgio Zenoni*

---

(\*) In the theoretical spectrum reported in fig. 1 we have not considered multiplet's intensities.-

TELEX 335313 LAWRADLAB BERK  
TWX 910-366-7172 LAW RAD LAB  
CABLE UCLRL BERKELEY

March 31, 1971

CIDNP in  $^{13}\text{C}$  Satellites
$$\begin{aligned} (\text{RCO}_2)_2 &\rightarrow \text{R} \cdot \xrightarrow{\text{R}'_2\text{CHI}} \text{RI} + \text{R}'_2\text{CH} \cdot \\ 2\text{R}'_2\text{CH} \cdot &\rightarrow \overline{2\text{R}'_2\text{CH} \cdot} \rightarrow \text{R}'_2\text{CH}^* \cdot \xrightarrow[\text{R}'_2\text{CHI}]{\text{R}'_2\text{CH}^* \cdot} \text{R}'_2\text{CH}^* \text{I} \end{aligned}$$
$$a_{\beta} = \oplus \quad \text{H}_{\beta} - \text{C} - \underset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{H}_{\alpha} \quad a_{\alpha} = \ominus \quad \longrightarrow \quad \text{H}_{\beta} \quad \text{J}_{\beta} = \oplus \quad \text{H}_{\alpha} \\ \text{C} - \text{C} - \text{I}$$
$$\text{C}_6\text{H}_5\text{C}(=\text{O})\text{H} \quad \text{a}^{\text{H}} = \ominus$$

$$\text{a}^{\text{C}} = \oplus$$

The positive sign of  $a_{\text{benzyl}}^{\text{C}}$  is also predicted by using reasonable estimates of spin densities and the Karplus-Fraenkel equation<sup>3</sup>. Although in this particular case the results are not very surprising, they do show the feasibility of using CIDNP in proton spectra to obtain the sign (and when more than one type of proton is involved, the magnitude) of hyperfine splittings from  $^{13}\text{C}$  and possibly other nuclei which are coupled to protons in a product molecule. Conversely, if the signs of the hyperfine splittings are known, the sign of the heteronuclear spin-spin splitting can be obtained.

1. H.R.Ward, R.G.Lawler and R.A.Cooper, Tetrahedron Letters, 527 (1969).
2. R.Kaptein and J.A. den Hollander, TAMU NMR Newsletters, 149, 7 (1971).
3. M.Karplus and G.K.Fraenkel, J.Chem.Phys., 35, 1312 (1961).

Sincerely yours,



Ronald G. Lawler  
Brown University  
(Visiting Professor,  
U.C., Berkeley)

## AUBURN UNIVERSITY



SCHOOL OF ARTS AND SCIENCES

Department of Chemistry

March 31, 1971

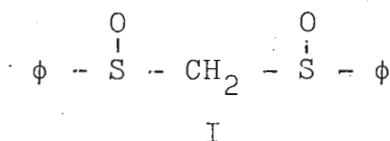
Telephone 826-4043  
Area Code 205

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

Title: Use of a Chemical Shift Reagent to Assign the Structure  
of meso- and d,l-Bis(phenylsulfinyl)methane

Dear Professor Shapiro:

We have synthesized the meso and d,l isomers of bis-(phenylsulfinyl)methane (I). Both isomers are crystalline



solids, one melting at 183° and the other at 118°. NMR should provide a means of assigning the structures of these compounds. The methylene protons in the d,l isomer are equivalent while those of the meso are not. However, the NMR spectra of the methylene protons of both compounds (Figure 1) shows a sharp singlet for the methylene protons. This is due to the accidental equivalence of the methylene protons in the meso isomer.

The spectra of both compounds in the presence of tris-(dipivalomethanato) europium<sup>1</sup> (Eu(DPM)<sub>3</sub>) is shown in the upper part of figure 1. In the presence of the shift reagent, the protons in the lower melting isomer are split into an A B quartet (J = 13 cps). Thus the lower melting isomer may be assigned the meso structure. The higher melting isomer is unaffected by the shift reagent and is the d,l isomer.

1. J. K. M. Sanders and D. H. Williams, J. Am. Chem. Soc. **93**, 641 (1971).

Sincerely yours,

*Joseph L. Greene, Jr.*  
Joseph L. Greene, Jr.

*Philip B. Shevlin*  
Philip B. Shevlin



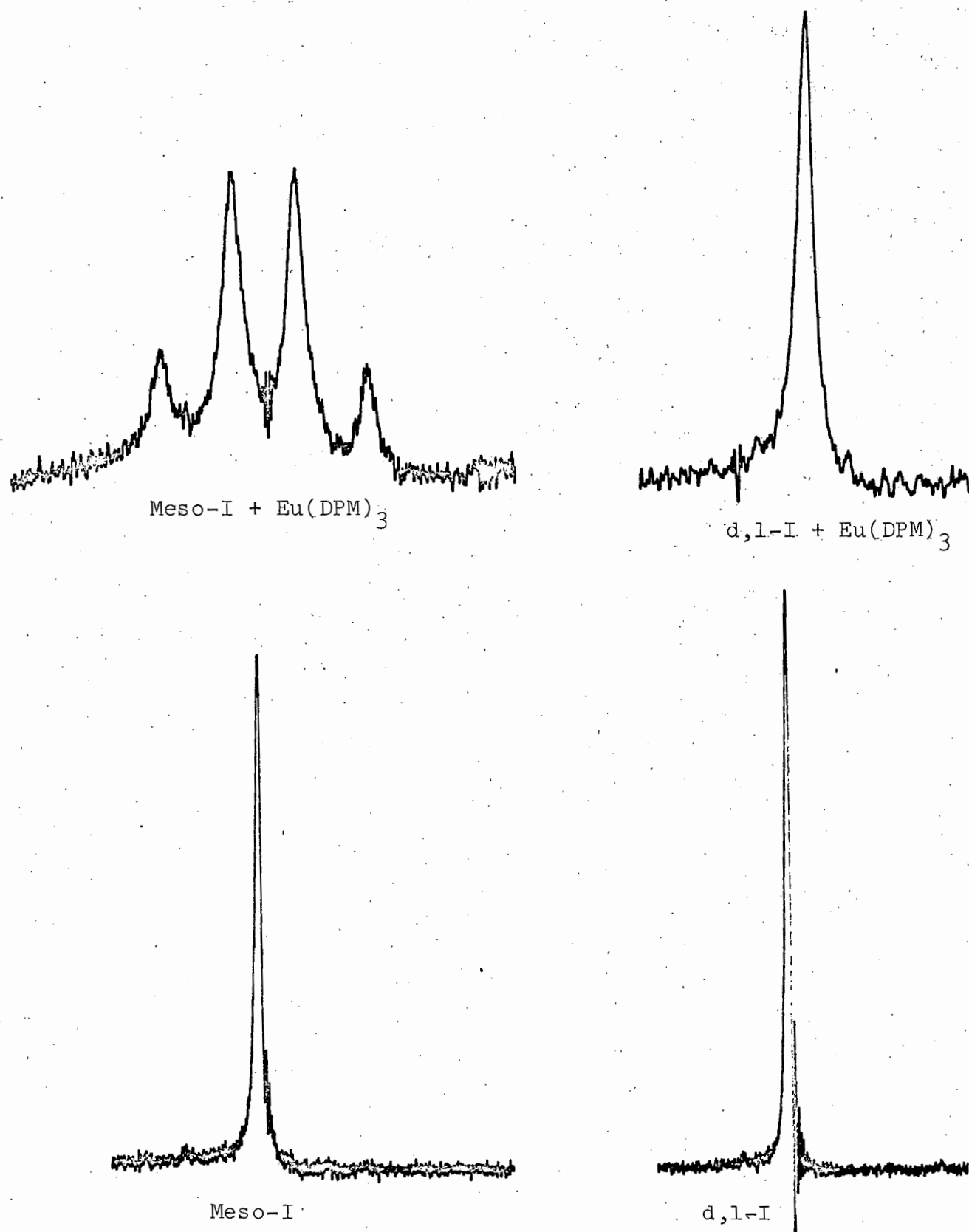


Figure 1 NMR spectra of meso- and d,l-bis(phenylsulfinyl)methane

UNIVERSITÉ DE LYON

## LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918  
69 - VILLEURBANNE

TÉL. (78) 52-07-04 et 52-12-29

Professeur J. DEU'AU

Villeurbanne, le 31 Mars 1971

Détermination de  $T_1$  à partir de signaux de faible intensité.

Cher Doctor Shapiro,

Nous nous intéressons à la détermination du temps de relaxation  $T_1$  (en haute résolution) de raies de faible intensité. Cela nous a amenés à concevoir un dispositif très simple (voir schéma) qui nous permet de réaliser ces mesures sur HA 100 avec l'aide du CAT 1024.

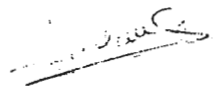
On se situe à la résonance. Un cycle de mesure de  $T_1$  comporte les opérations suivantes :

- 1) saturation suivant un temps  $\tau$ , la commande étant effectuée par une horloge.
- 2) coupure de la saturation, coupure qui déclenche l'application du champ  $H_1$  nécessaire à l'observation et en même temps déclenche le balayage du CAT.

La courbe de restauration du signal s'enregistre directement sur le CAT durant cette phase.

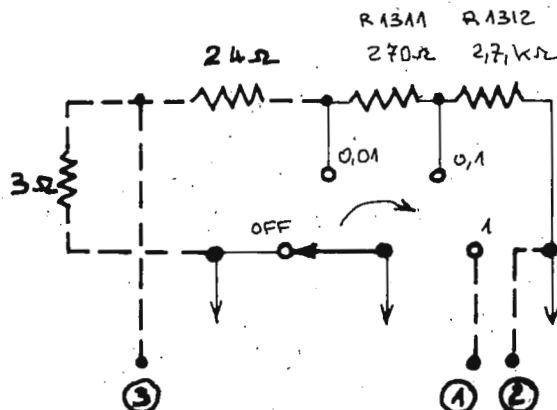
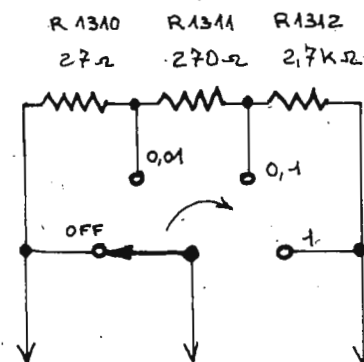
On peut ensuite accumuler un grand nombre de mesures. La méthode s'est avérée particulièrement intéressante dans l'étude de la relaxation des satellites du  $^{13}\text{C}$  (1)

Recevez mes meilleurs sentiments.

  
J.C. DUPLAN  
J. DEU'AU

(1) A. BRIGUET, J.C. DUPLAN, A. ERBEIA J. de Physique  
(1971), 32, 1, p.23.

## Modifications à apporter au commutateur S 1304 -----



liaisons | ①-② : Fonctionnement normal  
①-③ et position 1 : Facteur 0,001

## Temporisation de l'irradiation et de l'observation.

A | minuterie  
1 contact retardé a'  
de 20s à 12mn

B | minuterie  
1 contact non retardé b  
1 contact retardé b'  
de 20s à 12mn

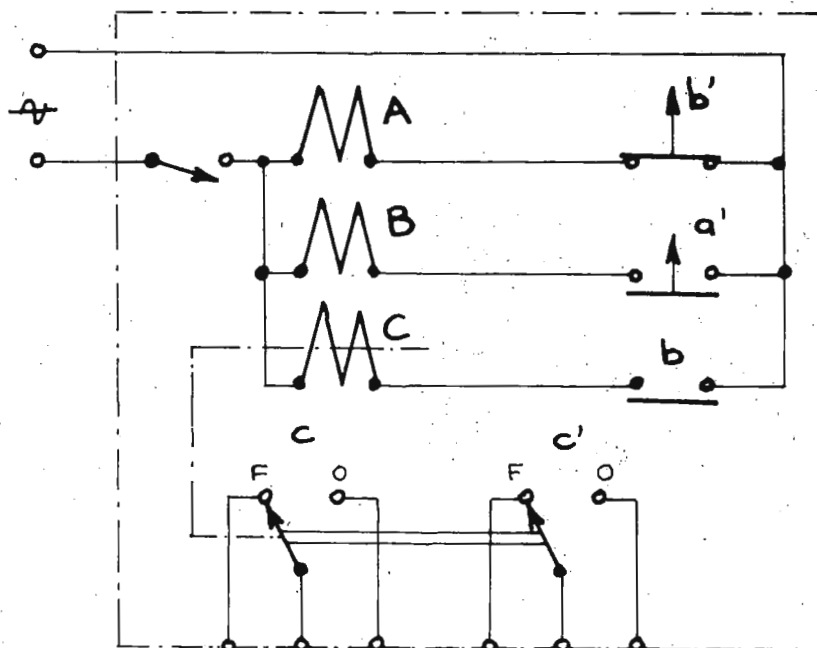
C | relais  
2 inverseurs C et C'

Minuteries A et B : par exemple

- marque OMRON
- type subminiature STP-M
- temporisation : 20s à 12mn

position de  
C et C'

- F : irradiation
- O : observation



C.A.T.

oscillateur  
extérieur

sweep  
frequency.

② ① ③

V. 4354A  
modifié

# THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

April 1, 1971

P. O. BOX 39175  
CINCINNATI, OHIO 45239

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

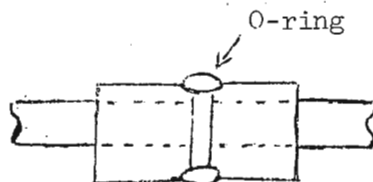
Dear Dr. Shapiro:

Mars Recorder Modification, T-60 Scope Modification,  
and  $^{29}\text{Si}$  NMR on the HA-100

The following notes on  $^{29}\text{Si}$  NMR on the HA-100, and some minor instrumental modifications may be of interest.

HA-100 Recorder

A modification to the Rulon bearings in the carriage of the HA-100 Mars Recorder has eliminated carriage binding by providing better bearing alignment and reducing friction. A groove was machined around the center of the bearing 0.08 inch deep to accommodate a number 10 O-ring ( $1/2'' \times 11/16'' \times 3/32''$ ) as per the following diagram. The O-ring secures the bearing in the housing but is flexible enough to allow the bearing to align with the carriage guides.



T-60 Scope Modification

After our T-60 scope kit was installed and in operation, it became evident that a way was needed to automatically reduce the beam intensity of the scope during recorder mode to prevent damage to the C.R.T. This was accomplished by installing an additional switch to the recorder-scope switch. When operating in scope mode, this switch shorts out a resistor placed in series with the scope intensity control. In recorder mode, the additional resistance is added in the brightness circuit reducing the intensity below the damage level.

Dr. Bernard L. Shapiro

April 1, 1971

Page 2

 $^{29}\text{Si}$  Spectroscopy

We have tried to obtain high resolution  $^{29}\text{Si}$  spectra on our HA-100. Although a signal-to-noise ratio of 5:1 was obtained after one scan in the HR mode for Silicone Oil and Tetramethylsilane, the signal in the HA mode was too weak to retain a lock, thus making signal-averaging impossible. The problem here is seen as being due to (1) inherent decrease in signal strength when switching from HR to HA mode; (2) necessity of using a very low RF power to avoid sample saturation; (3) a broad signal in the case of TMS possibly resulting from spin-coupling with the methyl protons, although we could not resolve the peak sufficiently to measure the coupling.

We would be interested to hear what success other people have had in obtaining  $^{29}\text{Si}$  spectra on the HA-100.

Very truly yours,

THE PROCTER & GAMBLE COMPANY  
Research and Development Department

I. D. Calvert, Research Division



C. D. Sazavsky, Research Division

0

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7/2

0

1) " 68

0



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