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Newsletter

No. 170

November, 1972

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Deadline Dates: No. 171: 4 December 1972
No. 172: 1 January 1973

All Newsletter correspondence, etc. should be addressed to:

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University of East Anglia

From: Dr. R. K. Harris

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

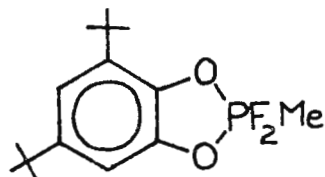
18th October 1972

Dear Barry,

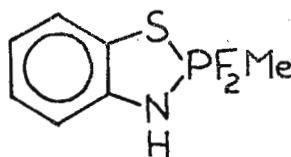
PSEUDOROTATION AT PHOSPHORUS IN A FIVE-MEMBERED RING.

For many years I have wondered what your famous pink forms were like, since the blue ones have sufficed to activate me. Now at last I have received a pink one, and seen its deadly doubly-underlined phrases. However, I hope this letter is sufficient to transfer me from the sinners' side of your ledger to the saints' side. I might just add that since the Newsletter takes six weeks to reach us I still don't know what the "deadline date" is which your pink form refers to.

However, I would like to mention some interesting (to us!) work we are doing in collaboration with Professor Reinhard Schmutzler of the Technical University in Braunschweig (German Federal Republic). There are several projects involved concerning NMR studies of intramolecular motion in phosphorus-containing compounds, but I will mention only one. This uses 4,6-di-*t*-butyl-2-methyl-2,2-difluoro-1,3,2-benzodioxaphosphole (I) and 2-methyl-2,2,-difluoro-1,3,2-benzothiazaphosphole (II), prepared by Michael Eisenhut at Braunschweig (who also carried out some of the NMR work). In each case it is anticipated that the ring will occupy one

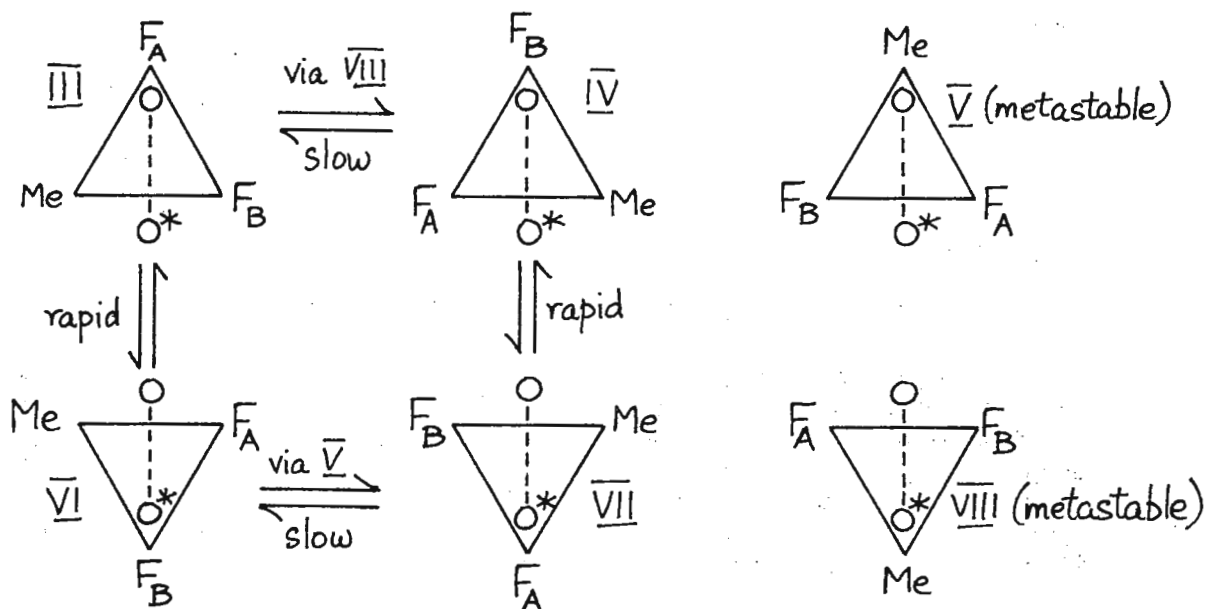


I



II

axial and one equatorial position at phosphorus (thus violating the usual rule that axial positions are preferably occupied by the most electronegative substituents). There are then six possible conformers, excluding mirror images, as shown in III to VIII, viewed in the projection we find most useful^{1,2} (in the plane of the ring, symbolised by 0----0*). Since the asymmetry in system I is not substantial, conformers III, IV, VI and VII, which all have an axial fluorine, will be roughly of the same energy, whereas V and VIII will be metastable. At room temperature interconversion



between all conformers is rapid, F_A and F_B are equivalent, and the ^{19}F spectrum is a simple doublet (ignoring or B irradiating the protons). At low temperatures interconversion between III and IV is slow on the NMR timescale, as it is between VI and VII, because the metastable forms V and VIII are involved. However the interconversions $\text{III} \rightleftharpoons \text{VI}$ and $\text{IV} \rightleftharpoons \text{VII}$ remain rapid. Thus F_A and F_B become non-equivalent. The chemical shift induced between them depends for its existence on the population difference between III and VI, and on the (perhaps small) intrinsic effects of the lack of symmetry, since axial \rightleftharpoons equatorial interconversion is not prevented. We find that the difference is 4.2ppm for I (at -88°C) and 1.9ppm for II (at -70°C), compared to ca. 40ppm for a normal axial-equatorial difference.

We have carried out bandshape analysis of the ^{19}F resonance for the two systems on an $\text{ABX} \rightleftharpoons \text{BAX}$ basis, in practice using one of the $\text{ab} \rightleftharpoons \text{ba}$ subspectra. The spectra were obtained at 94.1 MHz with a varian HA 100 spectrometer, digitized via a d-Mac pencil follower and iteratively fitted using an I.C.L. 1905E computer to obtain pre-exchange lifetimes. In both cases it was necessary to correct for the variation of the chemical shift difference with temperature. So far the coupling to protons has been dealt with by using an appropriate non-exchange linewidth, but we plan to carry out $^{19}\text{F}-\{^1\text{H}\}$ studies shortly. Eyring plots give provisional results for the thermodynamic activation parameters (with a transmission coefficient of $\frac{1}{2}$) as follows:

	ΔH^\ddagger	ΔS^\ddagger	ΔG_{220}^\ddagger
I	11.3 kcal mol ⁻¹ 47 kJ mol ⁻¹	10.7 cal deg ⁻¹ mol ⁻¹ 45 J K ⁻¹ mol ⁻¹	9.0 kcal mol ⁻¹ 38 kJ mol ⁻¹
II	11.1 kcal mol ⁻¹ 46 kJ mol ⁻¹	6.2 cal deg ⁻¹ mol ⁻¹ 26 J K ⁻¹ mol ⁻¹	9.9 kcal mol ⁻¹ 41 kJ mol ⁻¹

These parameters are calculated on the assumption that the energy difference between III and VI is negligible; to put it another way, the values given will be functions of the equilibrium constant between III and VI. The errors in the values of ΔH^\ddagger and ΔS^\ddagger are probably considerably larger than those in ΔG_{220}^\ddagger . The data for II appear to be more reliable than those for I. We hope to improve the accuracy of these results in the near future.

Even if it achieves nothing else, I hope this work succeeds in re-instating us on the mailing list.

Best wishes,

Robin Harris *Martin Murray*

R. K. Harris, M. Murray.

1. R. K. Harris and C. M. Woodman, Mol. Phys. 10, 437 (1966).
2. R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray and R. Schmutzler, Ber. Bunsengesell. Phys. Chem. 76, 44 (1972).

Dr. B. L. Shapiro,
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Texas A and M University,
College of Science,
College Station,
Texas 77843,
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RKH/PMR

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26 September 1972

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

Dear Professor Shapiro,

Chemical Shifts of the Methoxyl
in Anisole Derivatives

My apologies for this late contribution and hope that this continues my subscription.

Kerr constant measurements,¹ infrared and ultraviolet² spectra and dipole moment measurements³ have shown that in the anisole with an ortho-substituent the methoxyl lies to the other side of the benzene ring from the substituent, and with di-ortho substitution it is perpendicular to the plane of the ring.

We have obtained the chemical shift of the methoxyl of a number of substituted anisoles. The Table shows that in CCl_4 the methoxyl resonance shifts upfield with di-ortho-alkyl substitution, relative to anisole or ortho-alkyl substitution. However, this shift is not observed in the case of di-ortho-chloro substitution. In benzene the methoxyl resonance exhibits the aromatic solvent induced shift (ASIS), and this shift is larger with ortho than with di-ortho substitution. In the mono-ortho-substituted derivatives the methoxyl resonance shows a doublet structure, consistent with spin-spin coupling with the ortho-proton ($J \approx 0.20 \text{ Hz}$).

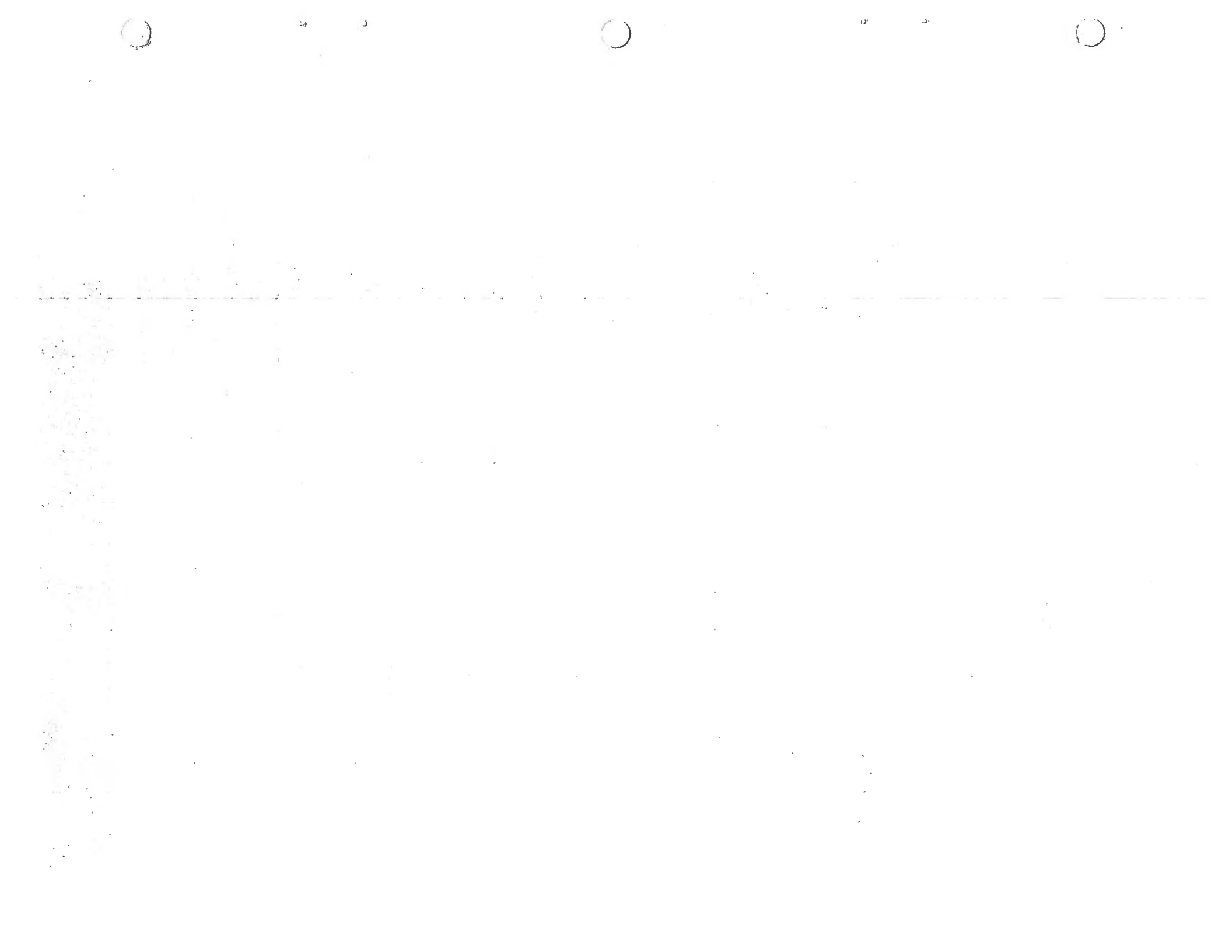
Table. Chemical Shifts of the Methoxyl Protons of Anisole Derivatives in CCl_4 and Benzene (2% W/W solutions at 34°C , relative to TMS).

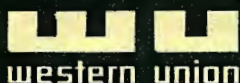
Anisole	CCl_4	C_6H_6
	Hz	Hz
Anisole	225.6	198.6
2-Me	227.4	200.8
2,6-di-Me	219.7	202.9
2-t-Bu	229.9	200.1
2,6-di-t-Bu	220.0	203.9
2-Cl	231.8	193.6
2,6-di-Cl	232.7	213.3

1. M.J. Aroney, M.G. Corfield, and R.J.W. LeFevre, J. Chem. Soc. 2954 (1964).
2. A. Balasubramanian, J.C. Deardin, W.F. Forbes, and N.F. Cheetham, Canad. J. Chem., 43, 2603 (1965)
3. N.L. Allinger, J.A. Maul, and M.J. Hickey, J. Org. Chem., 36, 2747 (1971).

Yours sincerely,

Soon Ng
(Soon Ng)



**Telegram**

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~~Please address reply to:~~

3rd October, 1972

Prof. B.L. Shapiro,
 Texas A & M University,
 College Station, TEXAS 77843.

Dear Professor Shapiro,

Effect of lanthanide shift reagents on spectra of simple
 secondary amides

We have recently submitted to Chemical Communications a preliminary account of observations on the effect of lanthanide reagents on the ^1H -n.m.r. spectra of simple secondary amides. Eu(dpm)_3 and Eu(fod)_3 can induce in the spectra of CDCl_3 solutions of amides, such as N-methylacetamide, signals for a minor component, the molar percentage of which increases with increase in lanthanide concentration. This minor component shows a different dependence of induced shift on lanthanide concentration and gives a chemical shift/lanthanide concentration plot that at low concentrations is not rectilinear.

The effect depends on the reagent used. Thus, for Eu(dpm)_3 - and Eu(fod)_3 -substrate molar ratios of 0.5, the induced shifts (downfield) for the N-methyl protons of N-methylacetamide were 4.3 and 3.9 p.p.m., respectively, for the major component, and 4.4 and 1.4 p.p.m., respectively, for the minor component; the molar percentages of minor component were ca. 10 and ca. 22, respectively. Pr(fod)_3 induced similar, but upfield, shifts.

Since N-methylacetamide normally exists largely as the trans isomer, it is reasonable to suppose that the major and minor components are associated with partially-complexed trans and cis isomers, respectively. An alternative explanation in terms of relatively slow complexing of one conformational isomer, either separately or simultaneously, at the oxygen and nitrogen atoms is considered unlikely, since at reagent/substrate ratios > 1.0 , we observed little further change in the proportion of minor components, and the rate of increase of the induced shifts was greatly reduced.

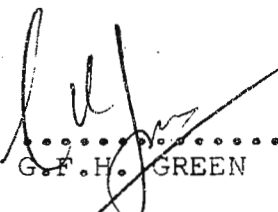
Yours sincerely,



 J.E. PAGE



 R.A. FLETON



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

-2 OCT 1972

Dear Professor Shapiro,

^1H and ^{31}P Spectra of $\text{H}_2\text{Ir}[\text{PET}_3]_4^+$

The octahedral complex $\text{cis-H}_2\text{Ir}[\text{PET}_3]_4^+$ an $\text{A}_2\text{BB'XX'}$ spin system gives the frustratingly simple spectrum (a) in the metal hydride region. It is clearly difficult to extract the 5 coupling constants (J_{BX} , $J_{\text{BX'}}$, J_{AX} , J_{BB} , J_{XX}) contained in this XX' portion although the large splitting is presumably $|J_{\text{BX}} + J_{\text{BX'}}|$ and the smaller splitting J_{AX} .

The completely proton decoupled ^{31}P spectrum (b) gives the A-B chemical shift difference and J_{AB} but does not further help in the analysis. However, on selectively decoupling the ethyl protons (not too much power or the hydrides are off-resonance decoupled), we obtain spectrum (c) which contains enough lines to give the tentative coupling constants.

$$J_{\text{AB}} = 16; \quad J_{\text{AX}} = 20$$

$$J_{\text{BX}} \text{ or } J_{\text{BX'}} = \pm 16 \text{ or } \mp 109$$

$$J_{\text{BB}} = 6; \quad J_{\text{XX}} = 22$$

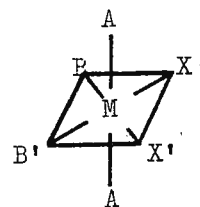
The hydride spectrum is invariant to temperature between $+100^\circ\text{C}$ and -100°C .

Yours sincerely,

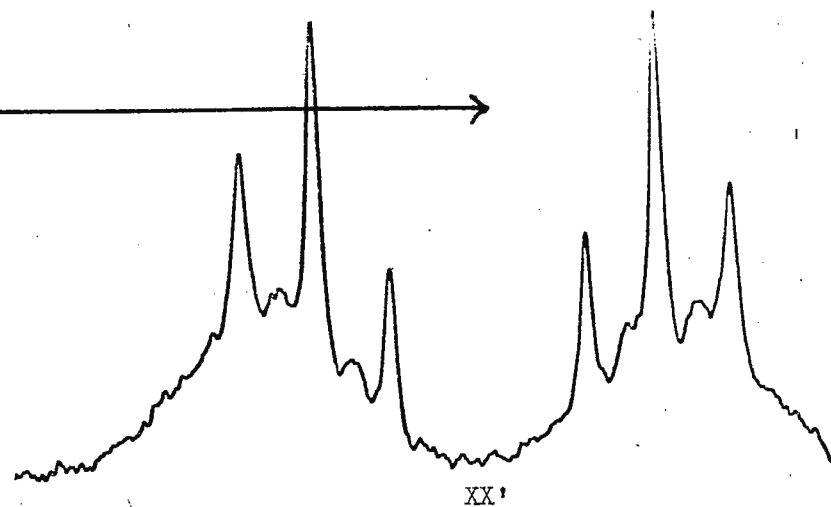
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(a)

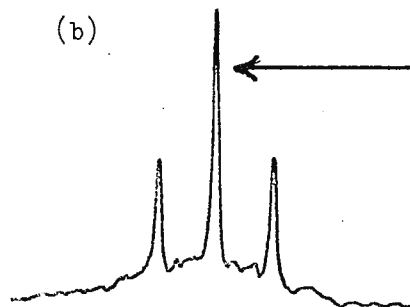


TMS 14.4 ppm



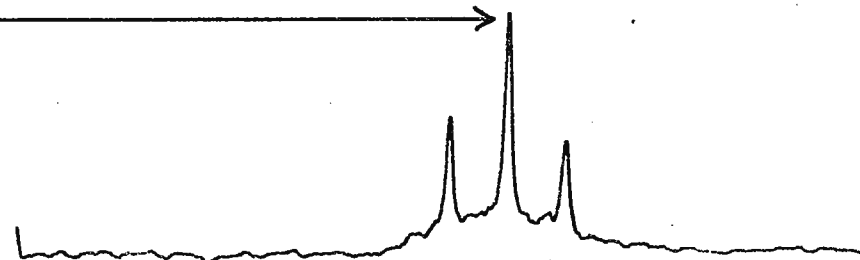
^1H Hydride spectrum

(b)



A2

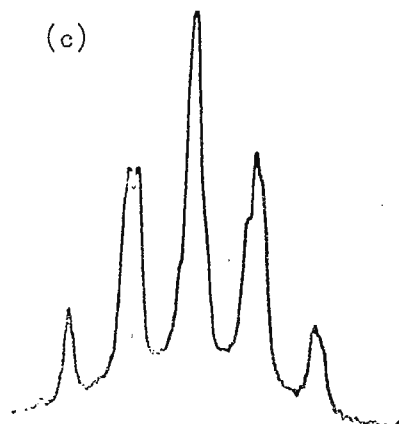
10 ppm



BB'

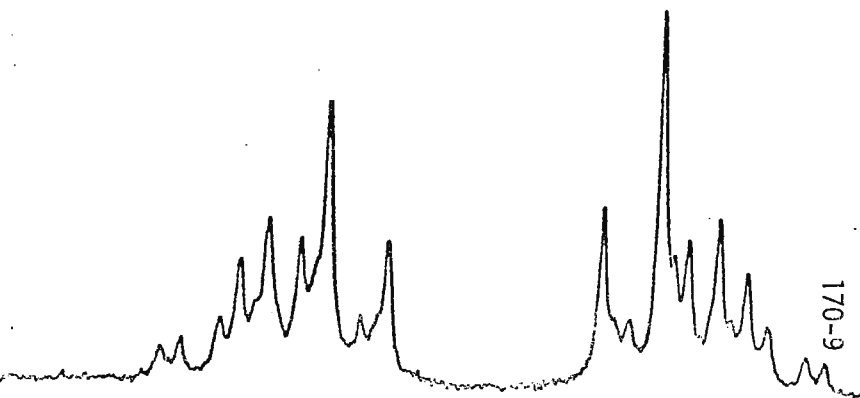
^{31}P spectrum, all protons decoupled

(c)



A2

^{31}P spectrum ethyl protons decoupled



BB'

170-9



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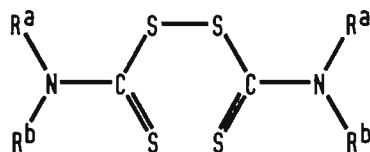
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Datum September 29, 1972

Onderwerp NMR of ethylthiuram disulfide and complexes.

Dear Dr. Shapiro,

Recently we investigated hindered rotation around the S_2C-NR_2 bond of N,N,N',N'-tetraalkylthiuram disulfides (see figure 1) and their complexes with Zn, Cd and Hg(II) halides.



We measured the NMR spectra as a function of the temperature from + 10 to + 110 degrees centigrade and obtained the thermodynamic constants of this process by comparison of experimental spectra with computer simulations. Somewhat to our surprise, the NMR patterns of the ethyl compounds measured at temperatures lower than + 10° centigrade reveal the existence of a second process that interchanges inequivalent alkyl groups. In fig. 2 some low temperature spectra of the CH_2 -groups of $CdI_2 \cdot (Et_4tds)$ in $CDCl_3$ are presented. It is shown that the low field CH_2 quartet broadens more than the high field one and yields one structureless signal at - 29 °C whereas the high field multiplet can still be identified as a broadened quartet. At - 60°C this part of the spectrum shows three broad signals for all CH_2 groups.

The crystallographic structure of $\text{HgI}_2 (\text{Me}_4\text{tds})$ is known¹⁾. It shows that the sulfur atoms in the seven-membered ring are not equivalent. From a structure model one learns that a ring inversion process may interchange the positions of the sulfur atoms and consequently the two alkylgroups a and also the alkylgroups b (fig. 1) interchange. The changes at low temperatures in that part of the spectra where the CH_2 groups resonate can be explained, as we will show, by the inversion process. That the ring inversion does not affect the CH_3 signals of the ethyl groups is probably due to the larger distance between the CH_3 groups and the ring compared to that of the CH_2 group and the ring.

The three broad signals, representing the NMR pattern of all CH_2 groups in $\text{CdI}_2 (\text{Et}_4\text{tds})$ and $\text{HgI}_2 (\text{Et}_4\text{tds})$ at -60°C can be analyzed as a superposition of four signals A, B, C and D, each arising from one CH_2 group. The positions of the peaks A, B, C and D are presented in fig. 2. The computer simulations have been carried out by adding the line pattern, resulting from the interconversion between the two sites A and D, to that of the interconversion between the sites B and C, each process taken with a statistical weight of 1.0.

In figure 2 the CH_2 absorption signals are shown for $\text{CdI}_2 (\text{Et}_4\text{tds})$ in CDCl_3 at temperatures lower than $+10^\circ$ centigrade together with the simulations. Figure 3 shows the Arrhenius plots for the ring inversion in $\text{CdI}_2 (\text{Et}_4\text{tds})$ and in $\text{HgI}_2 (\text{Et}_4\text{tds})$ dissolved in CDCl_3 . The thermodynamic constants derived from these plots are given in table 1. The values for ΔE_{act} and ΔG^\ddagger have the same order of magnitude as those reported in the literature for inversion of rings containing heteroatoms.

1) P.T. Beurskens, J.A. Cras, J.H. Noordik and A.M. Spruyt,
J. Cryst. Mol. Struct. 1, (1971)

Table 1

Thermodynamic constants for the ring inversion
in $\text{CdI}_2 (\text{Et}_4\text{tds})$ and $\text{HgI}_2 (\text{Et}_4\text{tds})$ in CDCl_3^x

compound	$\text{CdI}_2 (\text{Et}_4\text{tds})$	$\text{HgI}_2 (\text{Et}_4\text{tds})$
ΔE_{act} (kcal mole ⁻¹)	13.0	14.5
$^{10}\log k_o$ (k_o in s ⁻¹)	14	17
ΔG_{273}^\ddagger (kcal mole ⁻¹)	11.5	9.5
ΔH_{273}^\ddagger (kcal mole ⁻¹)	12.5	14.0
ΔS_{273}^\ddagger (e.u.)	4	16

^x The inaccuracy in ΔE_{act} , ΔG^\ddagger and ΔH^\ddagger is approximately 0.5 unit, for $^{10}\log k_o$ and ΔS^\ddagger approximately 1 unit.

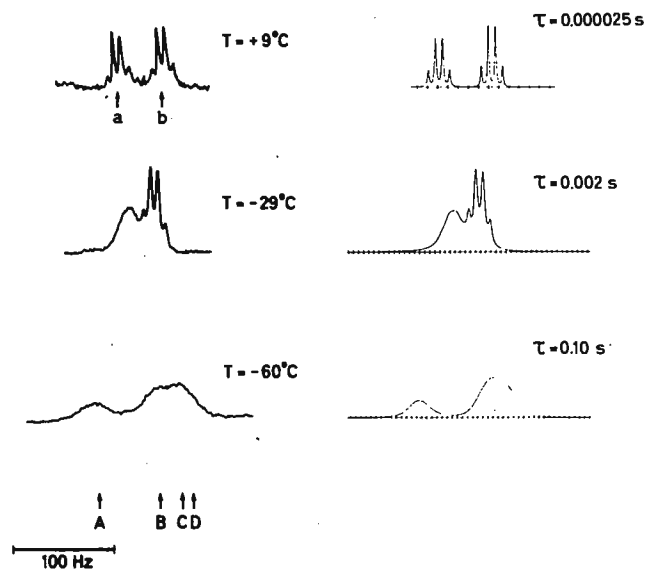


Fig. 2

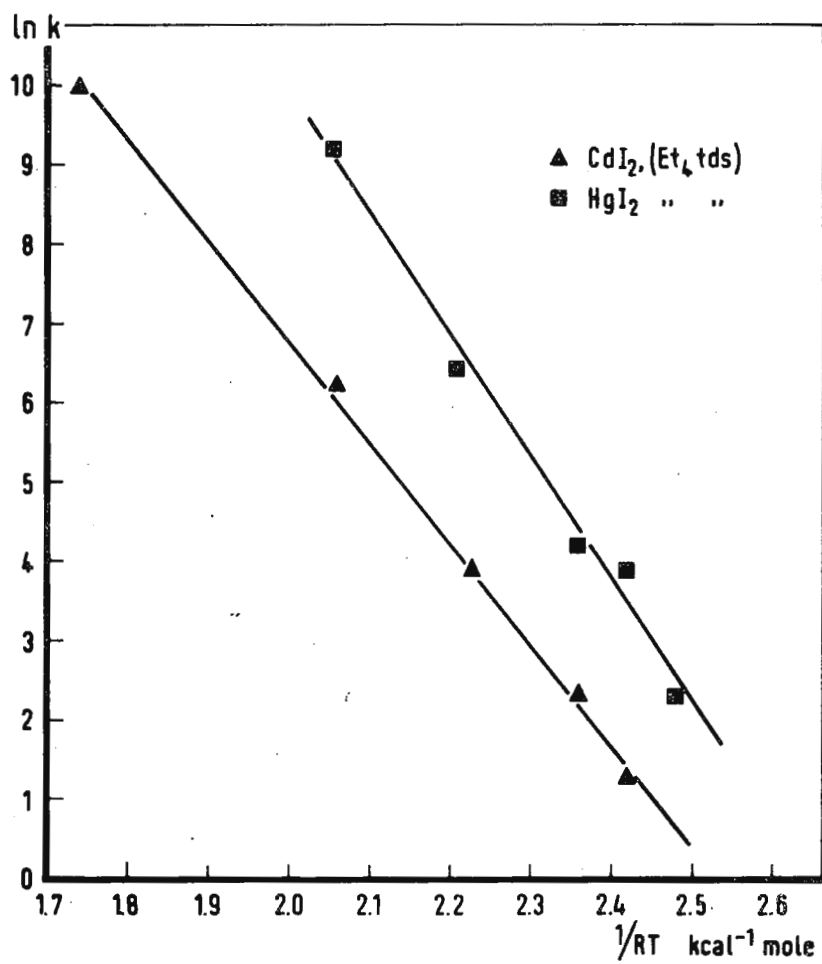




Fig. 3

Sincerely yours,


(Dr. F.W. Pijpers)
(Drs. A.M. Grotens)



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October 4, 1972

Department of Chemistry

Phone (617) 969-0100
Ext. 2225, 2236

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

Dear Barry:

Kajimoto and Fueno [Tetrahedron Lett., 3329 (1972)] recently reported that substituent-induced variations in the ^{13}C chemical shifts of trans-1-substituted butadienes alternate down the chain in a manner reminiscent of the alternating induced charges found by Pople and Gordon in their CNDO studies of substituent effects:



I would like to point out here the similarity between these results and the positional dependence of substituent effects on $^4J_{\text{HH}}$ in propanes which we have found, and to suggest a connection between the two types of behavior.

If one considers a π -system, such as butadiene, in the Hückel approximation, then the effects of substituents on charge densities can be treated by perturbational molecular orbital methods. Assuming for simplicity that the substituent produces only a change in the coulomb integral ($\delta\alpha_i$) of the carbon to which it is attached (i), the substituent-induced change in the charge density at carbon atom j is

$$\Delta q_j = q_j' - q_j \approx \delta\alpha_i + \sum_{\mu}^{occ} \sum_{\nu}^{unocc} \frac{c_{\mu i} c_{\mu j} c_{\nu i} c_{\nu j}}{E_{\mu} - E_{\nu}}$$

where the c's are a.o. coefficients. The coupling constant between two nuclei i and j can be written (with a number of

simplifications) as

$$J_{cc'} = K \sum_{\mu}^{occ} \sum_{\nu}^{unocc} \frac{C_{\mu i} C_{\mu j} C_{\nu i} C_{\nu j}}{E_{\mu} - E_{\nu}}$$

where K is a collection of constants. Combining the expressions, we anticipate

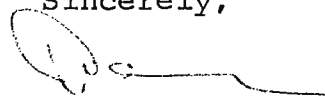
$$\Delta g_j \approx \sum \alpha_i + J_{cc'} / K$$

Since cc coupling constants are not easily accessible, let's use instead long-range HH couplings in π -systems, which are known to be dominated by the π -contributions. Since the signs of such couplings invariably alternate, depending on the number of intervening bonds, one therefore predicts alternating induced charges, depending on the number of bonds separating the substituted carbon from the "probe" carbon, as is observed.

Finally, since variations in the terms under the double summation can be assessed qualitatively in terms of selective depopulation of orbitals of specific symmetry types, I suspect that all of the above phenomena can be treated in a unified manner.

I would welcome comments from your readers.

Sincerely,



Dennis J. Sardella
Associate Professor

DJS/sh

title: chemical shifts, coupling constants and orbital symmetry



Dartmouth College HANOVER • NEW HAMPSHIRE • 03755

Department of Chemistry • TEL. (603) 646-2501

October 5, 1972

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

Perkin-Elmer R-24 Performance

Dear Professor Shapiro:

We wish to present our experience over the past seven months with a Perkin-Elmer R-24 spectrometer. This may be of interest to those readers contemplating purchasing a low-cost nmr spectrometer from the several commercial models currently available.

After some initial problems in providing a suitable environment for the instrument were solved, it became a real workhorse, reliably providing routine spectra (3000 to date) for inexperienced operators and requiring virtually no regular maintenance or adjustment. A draft from a nearby window (in February) at first prevented the magnet from achieving thermal stability. A satisfactory draft shield was conveniently constructed from three sections of the packing crate in which the R-24 arrived.

For reasons not yet understood, the instrument exhibited a slow steady change in the shape of the field, observed as a drifting "Y" gradient. After some trial and error this was halted by supporting the instrument's frame on four small wooden blocks, lifting the instrument from its own feet.

Despite our initial skepticism, the recorder (which uses precalibrated roll charts) has proved to be quite practical. Its parameters seem well matched to the spectrometer and it has required key operator attention only when chart rolls need changing. The pen has performed reliably for seven months without failing or clogging once. The recorder "pen-up" switch is only momentary and inconvenient for "dry-run" scans of integrals, etc. A positive action toggle switch was installed locally to complement this.

Probe removal for cleaning has been necessary only once and was accomplished without difficulties. An occasional (three times in seven months) "vacuum cleaning" with the devices supplied has satisfied all other probe cleaning needs. Spinner turbines originally supplied with the R-24 failed to perform satisfactorily; the manufacturer voluntarily replaced these with an improved design which has given no problems.

The R-24 has been tolerant and unaffected by wide variations in line voltage and by power supply noise generated by compressors and motors on the same line.

The instrument has proved useful for virtually unsupervised operation by students in our first-year Organic chemistry course.

While the R-24 will perform usefully for extended periods (up to three or four weeks) with no attention from a skilled operator, we have found that about five minutes attention daily is enough to keep it performing substantially better than specifications, both in resolution and sensitivity.

With regard to operating costs one factor should be mentioned. The cost of chart paper is outrageously high--more than 8 cents per chart. This is at least twice the cost of other nmr spectrometer charts and this difference can run to several hundred dollars per year.

Please credit to the account of P. R. Shafer.

Sincerely yours,

Gordon W. Gribble

Gordon W. Gribble
Assistant Professor
of Chemistry

Kenneth A. Clark

Ken Clark

GWG:wo

INDIANA UNIVERSITY

Department of Chemistry

CHEMISTRY BUILDING

BLOOMINGTON, INDIANA 47401

October 6, 1972

TEL. NO. 812—

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

Dear Professor Shapiro:

¹H Line Narrowing in Membranes

Recently we¹ have been investigating the possibilities of line-narrowing in enhancing the resolution of our lipid and membrane spectra,¹ and we have obtained preliminary results on gel and liquid crystalline lecithins in D₂O, spinning at high frequency at the "magic angle".

The gel spectra show (Fig 1a) only a slight narrowing of a single resonance attributable to a moderately rapidly anisotropically reorienting -NMe₃ group ($\tau = 6.8$ ppm), and this is only apparent at $\omega_{\text{rot}} = 3.5$ kHz. Egg lecithin shows, however, even at the low ω_{rot} of 500 Hz, narrowing of terminal CH₃ and -NMe₃ groups. At 3.5 kHz the narrowing is quite pronounced (Fig 1b). This must mean that the motion of these groups is highly anisotropic, with the presence of associated modes with $\tau_c \sim 10^{-4}$ s. This is surprising. However, the likelihood of any purely mechanical effect influencing the spectra seems small since runs spaced only a few seconds apart, at $\theta = 90^\circ$ and $\theta = \sec^{-1} \sqrt{3}$ show dramatic narrowing at the "magic angle" (Fig 1c,d). In the frequency range we are working (60 MHz) and at the concentrations used it also appears that the linebroadening is purely dipolar.^{2,3}

The fact that the CH₃- and -NMe₃ groups are the only ones to narrow at our highest attainable frequencies is consistent with this $\omega_{\text{rot}} \gg \Delta\nu_{\frac{1}{2}}$ only for these groups in these systems.

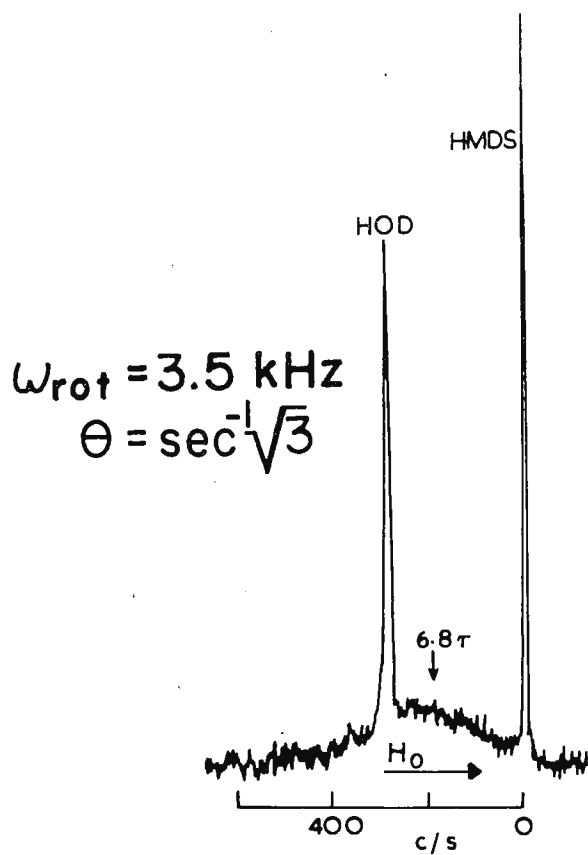
Yours sincerely,



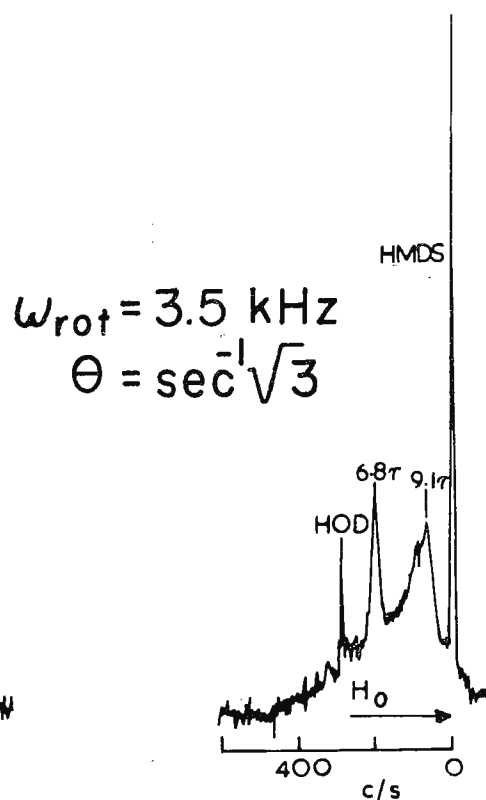
Eric Oldfield

EO:esm

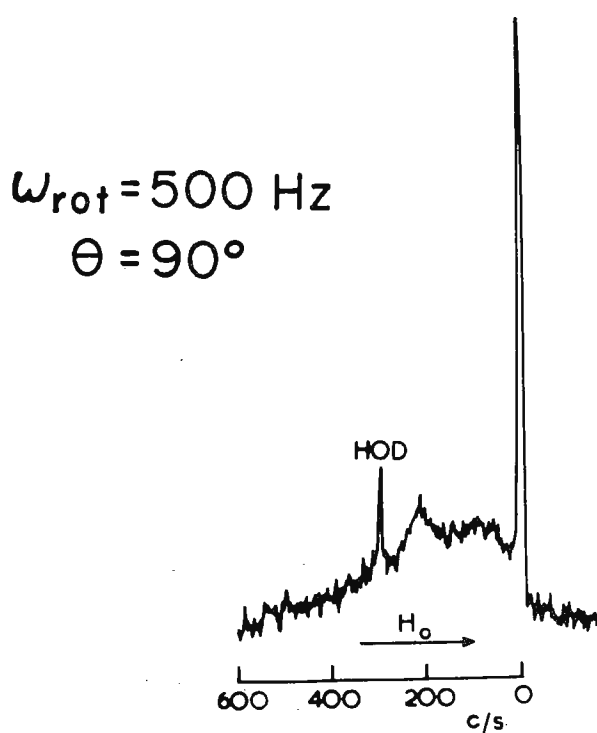
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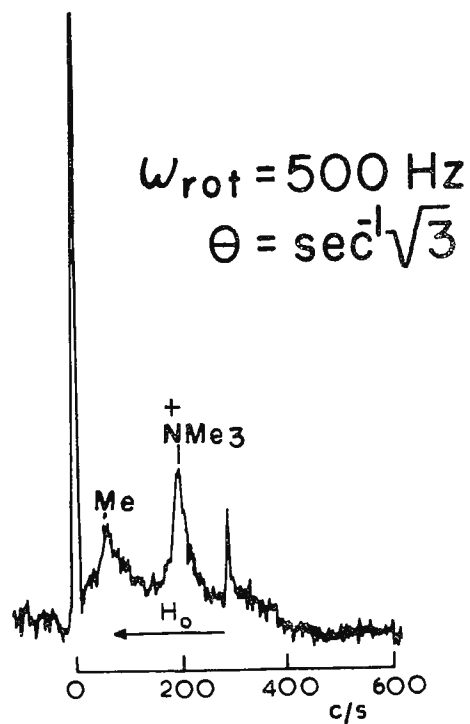
(a)



(b)



(c)



(d)

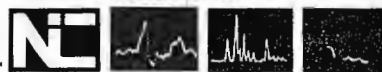


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FACULTY OF PHARMACY
19 Russell Street

TORONTO 181, ONTARIO

October 10, 1972

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

Dear Barry:

 ^{13}C Chemical Shifts Accompanying Helix Formation

In the course of our investigations of biochemical systems utilizing ^{13}C -FT NMR, we have become interested in the sensitivity of ^{13}C -NMR to the detection of helix-coil secondary structure transitions. Recent reports^{1,2} have dealt with ^{13}C studies of this phenomenon for homopolypeptides in non-aqueous solvents. The results indicated a consistent pattern of ^{13}C chemical shifts for the C- α , C- β , and C_o (carbonyl) carbons upon transition from the coil to helical states. Since non-aqueous solvents are not generally appropriate for biochemical studies, we have investigated the pH dependent helix-coil transition of poly-L-glutamic acid (PGA) (MW ~ 30,000) in aqueous solution. For comparative purposes, we have also carried out a study of the ^{13}C shifts for L-glutamic acid (Glu) as a function of pH. All experiments were run on our Varian XL-100-15 spectrometer (16K-620i computer system).

In Figure 1 are plotted the ^{13}C chemical shifts of the α -carboxyl carbon (C_o) of Glu and the α -carbonyl carbon (C_o) of PGA versus pH in the pH region 3 - 12. The titration results for the remaining four carbons of the glutamic acid systems are presented in Figure 2. For the amino acid, the results indicate the effects of protonation of the α -amino group in the pH range 8 - 12 and the side-chain carboxyl (C_o- γ) in the pH region 3 - 6. The α -carboxyl titration, which occurs at a lower pH ($\text{pK}=2.19^3$), is not shown, but overlaps to some extent the C_o- γ titration⁴. The pH profiles for Glu are consistent with the ^{13}C results of other amino acid titrations⁴⁻⁷, as in general the carbons are shielded upon protonation and each pH transition of the amino acid is reflected in the ^{13}C shift of every carbon. The polyamino acid ^{13}C shifts reflect only the C_o- γ protonation and remain essentially constant in the pH region 6.5 - 12. The differences in chemical shifts (both in magnitude and direction) in the pH region ~ 6.0 - 8.0 between the free amino acid and the polymer are in agreement with the previous ^{13}C -NMR shifts attributed to peptide bond formation^{5,8}.

Below pH 5.5, the chemical shifts of the C- α and C_o carbons of PGA undergo a sharp downfield transition, and most strikingly, the shifts are in the opposite direction to those seen in the amino acid titration. This

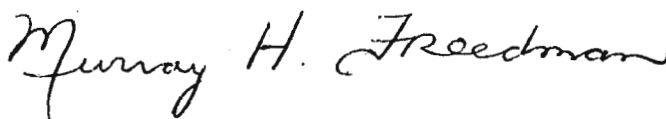
very likely reflects the cooperative transition in secondary structure from a coil to a helix; the helical structure having a significantly deshielded environment for C- α and C $^{\circ}$ relative to that of the "random" coil⁹. The β -carbon of PGA also displays a significantly different pH dependence of chemical shift below pH 5.5 when compared to Glu, but is more difficult to differentiate, being in the same direction as that for the amino acid. The pH profiles for the C- γ and C $^{\circ}$ - γ carbons of PGA in the pH region 4.5 - 5.5 suggest that these shifts are dominated by the C $^{\circ}$ - γ protonation effects. Unfortunately, highly concentrated aqueous PGA solutions aggregate strongly below pH 4.6¹⁰ precluding the possibility of observing the transition to maximum helical content. At pH 4.6, the estimated helical content is > 75%¹¹.

In Table 1, the PGA shifts observed on helix formation are compared with those reported for poly-N-carbobenzoxy-L-ornithine (PCBO)¹ and poly- γ -benzyl-L-glutamate (PBLG)² in the non-aqueous chloroform: trifluoroacetic acid solvent system. The values for aqueous PGA were calculated assuming the same contribution to the shift difference from the C $^{\circ}$ - γ protonation in PGA as in glutamic acid. The transition values attributed to the aqueous PGA do not represent the complete transition to maximum helical content, as is the case for the non-aqueous values. However, the similarity in direction and magnitude of the values in each system suggests that ¹³C chemical shifts can be used as an index of helix formation.

To test the above hypothesis in a more complicated system, we have investigated selectively ¹³C-enriched ribonuclease (RNase). A synthetic 1-15 amino-terminal peptide of RNase in which phenylalanyl residue #8 was uniformly labelled to ~ 15 atom% ¹³C has been prepared^{12,13}. This peptide was complexed with the S-protein of RNase (residues 21-124) to give a complex having essentially the same enzymatic activity as native RNase S¹². In the RNase S crystal structure, residues 2-13 are known to be in an α -helix¹⁴ while the free 1-15 amino-terminal peptide seems to be devoid of substantial secondary structure¹⁵ in solution. Thus, the ¹³C shifts in the phenylalanyl residue in the peptide versus complex may reflect the secondary structure transition. The differences in chemical shift are given in Table 1 and indeed the direction of the shifts for C $^{\circ}$, C- α , and C- β carbons upon complex formation is the same as that in PGA upon coil to helix transition. Although it cannot be determined with certainty that the ¹³C shift differences in the phenylalanyl residue between the free peptide and the complex arise solely from the random coil to α -helix configurational change, the parallel with the various homopolyptide results is apparent and suggests the general applicability of ¹³C-NMR in detecting secondary-structure transitions.

With best wishes,

Sincerely yours,



MHF:jl
Encls.

Murray H. Freedman, Ph.D.
Associate Professor of Biochemistry

Murray H. Freedman and James R. Lyster, Jr., Faculty of Pharmacy, and
Brian H. Barber, Department of Medical Cell Biology, University of Toronto,
Toronto, Ontario, Canada.

TABLE I

¹³C Chemical Shift Data Upon Helix-Coil Transition

Carbon	$\Delta^{a,b}_{PGA}$	Δ^c_{PCBO}	Δ^d_{PBLG}	Δ^e_{RNase}
C- α	-2.31	-3.4	-3.1	-0.72
C- β	+0.76	+1.0	+1.2	+0.50
C _O	-2.25	-2.8	-2.0	-1.33

^a Δ values are given in ppm and represent the difference between the chemical shift in the helical form minus the coil. A negative value indicates the carbon is deshielded in the helical form relative to the coil.

^bFor PGA, Δ equals the difference in chemical shift between the values at pH 4.7 and pH 8.0. Also, allowance has been made for the contribution of the C_O-Y titration.

^cData taken from reference 1.

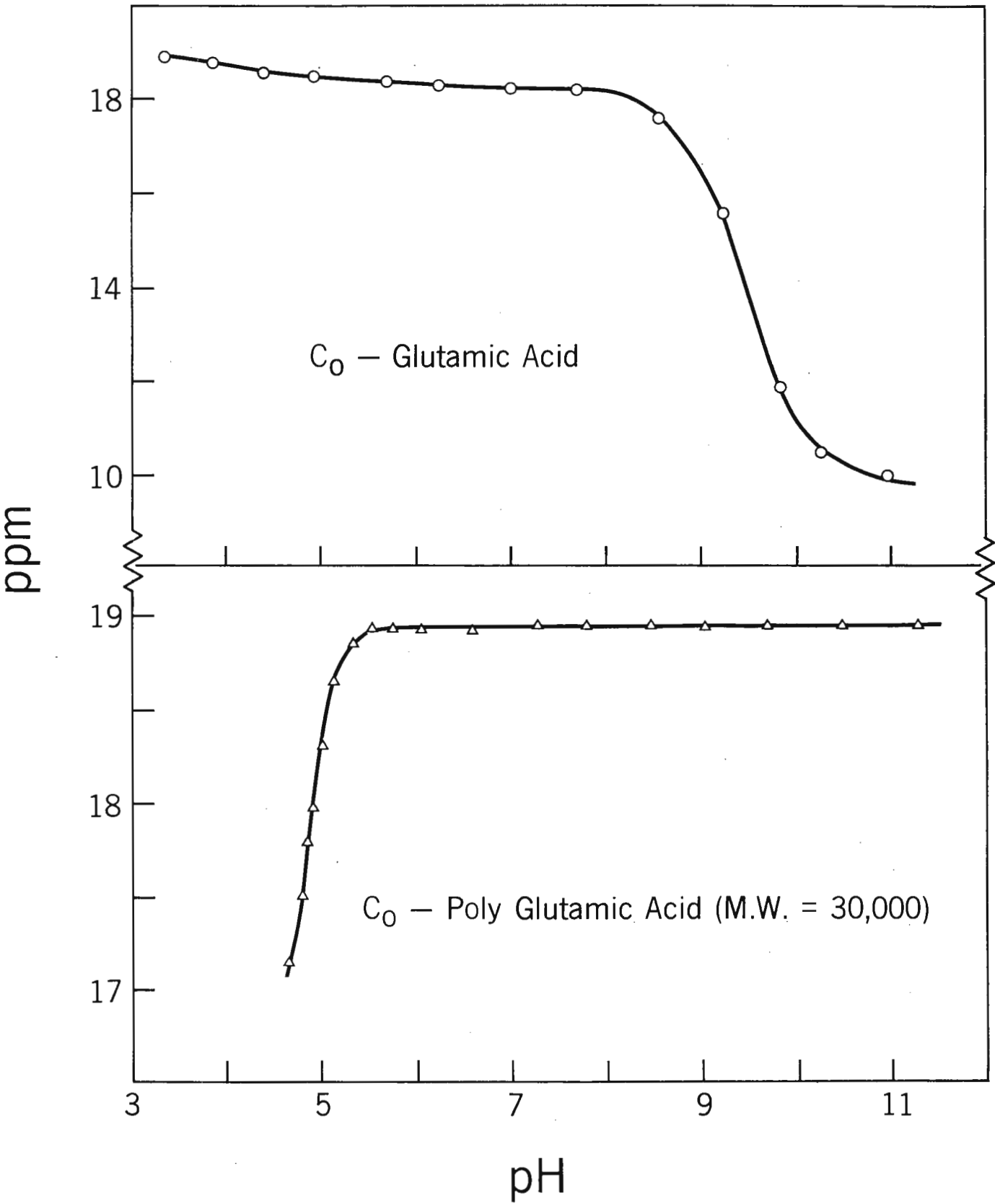
^dData taken from reference 2.

^eRepresents the difference in chemical shift between the RNase complex and the free 1-15 peptide, data taken from reference 13.

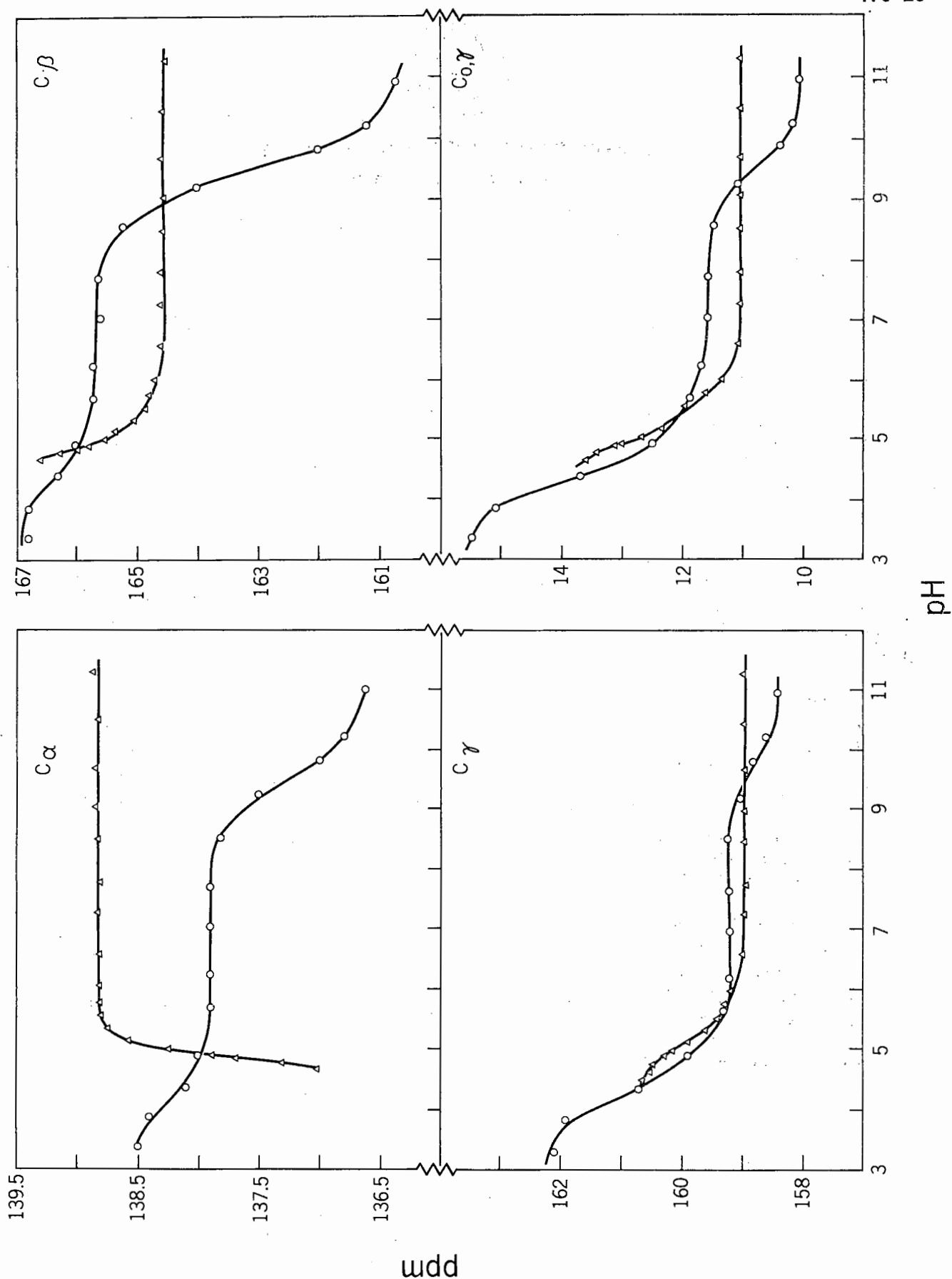
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C₀ TITRATION CURVES FOR GLUTAMIC AND POLYGLUTAMIC ACIDS



1. The ¹³C chemical shifts of the α-carboxyl carbon of L-glutamic acid (circles) and the α-carbonyl carbon of poly-L-glutamic acid (triangles) as a function of pH. Chemical shifts are ppm upfield from CS₂.



2. The ^{13}C chemical shifts of the C- α , C- β , C- γ , and C0- γ carbons of L-glutamic acid (circles) and poly-L-glutamic acid (triangles) as a function of pH. Chemical shifts are ppm upfield from CS_2 .



UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

Department of Chemistry
(803) 777-5263

September 29, 1972

Professor Barry Shapiro
1101 Merry Oaks
College Station, Texas 77840

TITLE: Carbon-13 Chemical Shifts of the Fluoromethanes, Fluoroethylenes, Fluoroallenes, and Fluoroacetylene.

Dear Barry:

I hope this puts me back in good standings-but I just had to see the fabled "pink letter" with my own eyes. I would like to relate some of our experimental fluorocarbon work to the Newsletter readers. The work on the fluoroallenes and fluoroacetylene is being done by Mr. A. P. (Toby) Zens of our department.

In the enclosed Table I have listed the ^{13}C chemical shifts of these compounds with respect to several references: the fluoromethanes are reported with respect to CH_4 , the fluoroethylenes are reported with respect to C_2H_4 , fluoroacetylene is reported with respect to acetylene, and the fluoroallenes are reported in two ways-the terminal carbons are reported with respect to the terminal carbons in allene, and the central carbons are reported with respect to the central carbon in allene. All positive shifts denote chemical shifts to higher shieldings. The various conversion factors are given at the bottom of this Table.

These systems are of tremendous theoretical interest because of their inherent simplicity with respect to structure and numbers of atoms. Furthermore, they have all the necessary substituents to investigate mesomeric and inductive contributions to the ^{13}C chemical shifts in these systems. Detailed discussions of these data with comparisons to gauge invariant atomic orbital ab initio chemical shift calculations (via Robert Ditchfield) will be submitted for publication in the near future.

Best wishes,

A handwritten signature in cursive script, appearing to read "Paul D. Ellis".

Paul D. Ellis
Assistant Professor
of Chemistry

PDE/pw

Enclosure

^{13}C Chemical Shifts of the Fluoromethanes,
Fluoroethylenes, Fluoroallenes, and Fluoroacetylene

Compound Chemical Shift^a

Fluoromethanes, $\text{CH}_{4-n}\text{F}_n$:

CH_4	0.0 ^b
CH_3F	-77.5
CH_2F_2	-111.3
CHF_3	-118.7
CF_4	-123.9

Fluoroethylenes, $\text{C}_2\text{H}_{4-n}\text{F}_n$:

	C_α	C_β
$\text{H}_2\text{C}_\alpha=\text{C}_\beta\text{H}_2$	0.0 ^c	0.0 ^c
$\text{H}_2\text{C}=\text{CHF}$	34.3	-24.9
$\text{H}_2\text{C}=\text{CF}_2$	58.9	-38.2
<u>trans</u> $\text{HFC}=\text{CFH}$	-21.4	-21.4
<u>cis</u> $\text{HFC}=\text{CFH}$	-13.1	-13.1
$\text{HFC}=\text{CF}_2$	2.2	-35.2
$\text{F}_2\text{C}=\text{CF}_2$	-21.2	-21.2

Fluoroallenes, $\text{C}_3\text{H}_{4-n}\text{F}_n$:

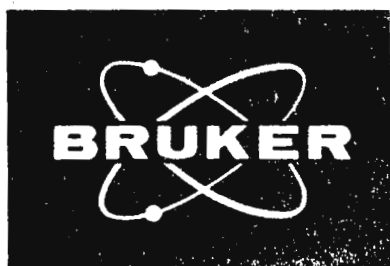
	C_α	C_β	$\text{C}_{\alpha'}$
$\text{H}_2\text{C}_\alpha=\text{C}_\beta=\text{C}_{\alpha'}\text{H}_2$	0.0 ^d	0.0 ^e	0.0 ^d
$\text{H}_2\text{C}=\text{C}=\text{CHF}$	-19.1	31.3	-55.0
$\text{HFC}=\text{C}=\text{CFH}$	-57.4	55.0	-57.4
$\text{H}_2\text{C}=\text{C}=\text{CF}_2$	-30.0	50.1	-81.4
$\text{HFC}=\text{C}=\text{CF}_2$	-59.0	81.7	-71.0
$\text{F}_2\text{C}=\text{C}=\text{CF}_2$	-65.8	113.4	-65.8

Fluoroacetylene

	C_{α}	C_{β}
$HC \equiv C_{\alpha} H_{\beta}$	0.0^f	0.0^f
$HC \equiv CF$	57.6	-16.9

Footnotes

- All chemical shifts are reported in ppm with respect to the corresponding parent hydrocarbon. Negative values for the chemical shift denote resonances to lower shielding.
- Chemical shift with respect to TMS is 2.3 ppm.
- Chemical shift with respect to TMS is -123.3 ppm.
- Chemical shift with respect to TMS is -74.8 ppm.
- Chemical shift with respect to TMS is -231.5 ppm.
- Chemical shift with respect to TMS is -73.7 ppm.



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October 5, 1972

Prof. Bernard L. Shapiro
Dept. Chemistry
Texas A & M University
College Station
Texas 77843

Title: NMR spectra for people without a spectrometer.

Dear Barry Shapiro:

I would like to use your pages to state that I have now relocated from the University of Stanford to the West coast office of Bruker Scientific, and to inform avid readers of the TAMU newsletter that some of the time on our Palo Alto instruments will be available for service work. Naturally as a newly established office & laboratory we are interested in interfacing with the needs of scientists in industry and universities.

The first of our instruments to be installed, the HX90E, is now operational here in Palo Alto and has of course multinuclear and F.T. capabilities.

The aquisition of additional hardware, such as disk attachment to the BNC computer, and more exotic nuclei will be made according to demand.

Consequently we would like to invite enquiries from those who are frustrated by the lack of NMR spectra.

Sincerely,

Malcolm R. Bramwell
Malcolm R. Bramwell

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Ns. Rif. Prot. N.

Prof. B. L. Shapiro
 Department of Chemistry
 Texas A. and M. University
 College station
 Texas 77843

U.S.A

Dear Professor Shapiro,

Once again our contribution has fallen due, and we hope the following will suffice.

"Parameter set errors obtained from computer analysis of spectra of partially oriented molecules"

We have analysed the spectra of Ethylene carbonate and thiocarbonate partially oriented in the nematic phase of N-(p-ethoxybenzylidene)-p-n-butylaniline, the results of which will appear fairly soon in J. Mag. Res.

In each case five spectra were obtained, and since the AA'A'A'A'' spectra of the CH₂-CH₂ fragment is capable of explicit analysis¹ we were thus able to analyse each spectrum individually, and so obtain the "true" standard deviation of each parameter. Averaging the frequencies and analysing using a modified version of LAOCOON3² then gave us the "Parameter set errors". As can be seen from the results given below the differences are significant.

Parameter	Ethylene Carbonate		Ethylenethiocarbonate	
	Computer Analysis	Explicit Analysis	Computer Analysis	Explicit Analysis
D _{gem}	+4977.6 ±0.3	+4977.6 ±1.6	+3901.2 ±0.3	+3901.7 ±2.2
D _{vic}	-1040.8 ±0.3	-1039.8 ±4.2	-308.5 ±0.3	-308.4 ±1.0
D _{trans}	+16.5 ±0.3	+16.5 ±0.9	+100.8 ±0.3	+100.8 ±1.0



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 29.52.78 - 29.54.82 - 29.60.71

NS. Rif. Prot. N.

As can be seen, with the exception of D_{cis}^{vic} for the carbonate and, to a lesser extent, D_{gem} for the thiocarbonate, while the actual values of the dipolar coupling constants are identical, the error values are greatly different. While the large errors for the two above mentioned parameters may be at least in part ascribable to spectrometer drift between successive spectra, nevertheless this only reinforces the conclusion that the parameter set errors as given by LAOCOON3 are serious underestimates of the true errors.

It has been suggested in the case of isotropic phase spectra³ that the parameter set errors should be multiplied by a factor of five, and our results indicate that a similar factor should be used in the case of nematic phase spectra.

Yours faithfully,

(Dr. P.F. Swinton)

P. Swinton

(Dr. G. Gatti)

G. Gatti

References

- 1) J. Bulthuis, J. Gerritsen, C.W. Hilbers and C. Maclean
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- 2) P.F. Swinton and G. Gatti
Spectroscopy Letters, 3, 259 (1970)
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Tetrahedron Letters, 5205 (1967)

Gesellschaft für Molekularbiologische Forschung mbH

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Bahnhof: Expreßgut Braunschweig Hbf
Stückgut Braunschweig HGbfAbt.:

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

Stöckheim, den 5.10.1972

Rüdiger Lawaczek

"The Formation of Weak Complexes Studied by PMR.
 On the Origin of the Variability in K_{app} for Different Protons".

Dear Professor Shapiro,

In the course of our experiments on the interaction of nucleic acid constituents with amines of aromatic amino acids we obtained different results in the apparent association constant K_{app} depending on the proton whose chemical shift was followed. These differences were observed by other groups, too, studying weak complexes by PMR techniques. We observed these differences in linearised computations like Benesi-Hildebrand and Scatchard models and also in nonlinear direct least square fits of our data. The data are the observed chemical shifts of the protons of the fixed partner by varying the concentration of the other partner. Foreman et al. (1) proposed that these differences in K_{app} might be due to deviations from the 1:1 stoichiometry imposed by the linear models. We observed these facts with other stoichiometries and in some other approximations (especially in an isodesmic approximation), too, so we started with regard to this problem some computer simulations which support the proposed assumption of Foreman et. al.

We have chosen a model system consisting of the free partners A_f , B_f , the heterocomplexes AB , A_2B and one self-association complex AA . The stoichiometric concentrations were:

$$A_o = A_f + 2AA + AB + 2A_2B$$

$$B_o = B_f + AB + A_2B.$$

Selecting appropriate sets of the three association constants K_i for the three complexes we computed the various concentrations of the complexes and their respective mole- or proton-fractions by varying the concentration of one partner while the concentration of the other partner was fixed. Choosing chemical shifts Δ_i of the three pure complexes as another set of parameters we computed hypothetical (observed) chemical shifts in the limiting case of fast exchange which are the sums over the products of the proton fractions of each complex and the respective chemical shifts. In this manner the hypothetical (observed) chemical shifts were calculated for the protons of the fixed partner as a function of the concentration of the other partner. These data were now used to compute apparent association constants by the Scatchard method, which includes only a 1:1 complex and neglects self-association and formation of higher complexes. With such a simulation it was possible to look at K_{app} as a function of the two sets of parameters K_i ; Δ_i ($i = AA, AB, A_2B$). We have done these computations in two steps, first holding fixed A_0 and varying B_0 and then vice versa.

Varying the K_i values and taking a constant set of the parameters Δ_i leads to self-evident results. However the change to fixed K_i and variable Δ_i values is of real interest. In analogy to actual systems we have chosen the fixed K_i values in such a manner that the AB complex is predominant. Table 1 shows the results of such a computation with the fixed values $K_{AA} = 1 \text{ M}^{-1}$, $K_{AB} = 10 \text{ M}^{-1}$ and $K_{A_2B} = 10 \text{ M}^{-2}$; we looked hypothetically at the protons of the A species. For example with these K_i values and $A_0 = 0.05 \text{ M} = \text{const.}$ the concentrations of the three complexes (in percentage of A_0) at $B_0 = 0.4 \text{ M}$ are : AA 0.2 %, A_2B 0.8 % and AB 77 %. As Table 1 indicates the computed values for an apparent association constant K_{app} by the Scatchard method depend very much on the choice of the parameters Δ_i . This situation resembles chemical systems consisting of more than one complex but mainly governed by the AB complex. The K_i values are fixed by the chemical affinities, but the various protons will experience different magnetic environments in the various complexes; this is expressed by different sets of the Δ_i parameters for each proton.

This leads to the following conclusion: one apparent association constant for different protons will be observed only in the case that there is one complex. If more than one complex is present then in general differences in K_{app} from proton to proton will be observed. These differences will be larger the higher the concentrations of complexes of different stoichiometries and the larger the deviations of the Δ_i parameters for different protons.

Table 1 Computed values of the apparent association constants (K_{app}) in a Scatchard approximation for a 1:1 complex as a function of the parameters Δ_i ; x_i ; the values for the parameters K_i are fixed ($K_{AA} = 1 \text{ M}^{-1}$, $K_{AB} = 10 \text{ M}^{-1}$, $K_{A_2B} = 10 \text{ M}^{-2}$).

Δ_{AA}	Δ_{AB}	Δ_{A_2B}	$K_{app}^{1:1}$
0.6	0.7	0.1	7.6
0.6	0.7	0.35	7.9
0.6	0.7	0.7	8.2
0.6	0.7	1.0	8.6
0.6	0.7	1.4	9.0

x_i in ppm, the Δ_i values are the differences in the chemical shifts with respect to the i free partner.

I thank Dr.K.G.Wagner for valuable discussions.

Yours sincerely ,

Rüdiger Lawaczeck

Rüdiger Lawaczeck

- (1) Foreman, M.I., Foster, R. and Twiselton, D.R.
Chem. Communications 1318 (1969).

University of Notre Dame
College of Science
Notre Dame, Indiana 46556

Department of Chemistry

October 17, 1972

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

(For TAMU Newsletter)

Dear Barry:

Faculty Position Available

Our department is interested in adding a faculty member whose research interests revolve around ^{13}C resonance in the general area of organic or bioorganic chemistry with teaching interests in organic chemistry. We currently have an XL-100, as well as an A-60A, and have the resources to add fourier transform.

Interested persons should send a complete vita to myself or Professor Jeremiah Freeman. All inquiries will be kept confidential.

Sincerely yours,



Daniel J. Pasto
Professor of Chemistry

DJP:tg



18th October, 1972.

הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

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

Dear Barry,

NMR OF SYMMETRIC MOLECULES IN NEMATICS.SELF DIFFUSION OF AMINES.

R. Ader is extending our study of deuterium and hydrogen nmr of symmetric or almost symmetric small molecules dissolved in nematic liquid crystals. A preliminary report on CD_4 , CHD_3 , CH_2D_2 , CH_3D , CH_4 and $(CH_3)_4C$ has appeared recently in Mol. Phys. We have measured the concentration dependence of the dnmr splittings. The results indicate that the apparent orientation of the solute molecules changes with its concentration. We are presently measuring the corresponding derivatives of Si and Ge and hope to be able to present the results in the very near future.

E. Glaser has measured self diffusion coefficients in liquid CH_3ND_2 and $(CH_3)_3N$. Some results are presented in the following table.

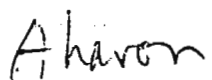
CH_3ND_2		$(CH_3)_3N$	
$T^\circ K$	$D \times 10^5 \text{ cm}^2/\text{sec}$	$T^\circ K$	$D \times 10^5 \text{ cm}^2/\text{sec}$
194	1.05	183	1.06
209	1.8	209	2.3
225	2.5	225	2.8
250	3.8	247	4.3
272	5.3	271	5.3
297	8.2	298	7.9

Professor B.L. Shapiro

18th October, 1972.

These results together with current measurements of $(\text{CH}_3)_2\text{ND}$ and other results are being interpreted in terms of molecular reorientations and translations.

Yours sincerely,

A handwritten signature in cursive script, appearing to read 'A. Loewenstein'.

A. Loewenstein

AL/s1



UNIVERSITY OF LONDON KING'S COLLEGE

TEL: OI-836 5454

STRAND LONDON WC2R 2LS

DEPARTMENT OF CHEMISTRY

CDH/BW

12th October, 1972

Dear Professor Shapiro,

Hammett substituent constants by n.m.r.

Your recent letter serves as a sharp reminder of the quicksilver ebb of time! Therefore, in the absence of more significant results may we offer the following snippet arising from work with benzylidene malonitriles and related compounds.^{1,2}

The Table shows the chemical shifts (in acetone) of the vinyl protons of a series of substituted benzylidene malonitriles, $\text{XC}_6\text{H}_4\text{CH}:\text{C}(\text{CN})_2$. The chemical shifts show an excellent correlation (correlation coefficient, $r = 0.993$) with the σ^\pm values³ of the aromatic substituents and this provides a convenient method for the determination of σ^\pm parameters. For instance, the correlation predicts a σ^- value for the p-2,2-dicyanovinyl group of +0.68 (± 0.05) in reasonable agreement with the value of +0.75 suggested by Sheppard and Henderson.⁴ Regrettably, the changes in chemical shift of the vinyl protons are not sensitive enough to allow a clear choice of σ^\pm or σ as the appropriate substituent constants. Thus using the σ parameters one

Benzylidene malonitriles, $\text{XC}_6\text{H}_4\text{CH}:\text{C}(\text{CN})_2$
 100 MHz nmr in CD_3COCD_3

Compound X =	δ ppm (TMS) vinyl proton	σ^+ , or σ^-	σ
p-Me ₂ N	2.21	-1.70	-0.83
p-MeO	1.93	-0.78	-0.27
p-Me	1.85	-0.31	-0.17
H	1.73	0	0
p-Cl	1.72	+0.11	+0.23
p-Br	1.73	+0.15	+0.23
M-NO ₂	1.51	-	+0.71
p-NO ₂	1.49	+1.24	+0.78
p-CH:C(CN) ₂	1.60	-	-

obtains, $r = 0.987$ predicting for $-\text{CH}:\text{C}(\text{CN})_2$, $\rho = +0.48 (\pm 0.04)$. We hope current investigations of the ^{13}C spectra will be more definitive.

Yours sincerely,

Richard L. Powell

R.L. Powell

Isaac Posner

T. Posner

Dennis Hall

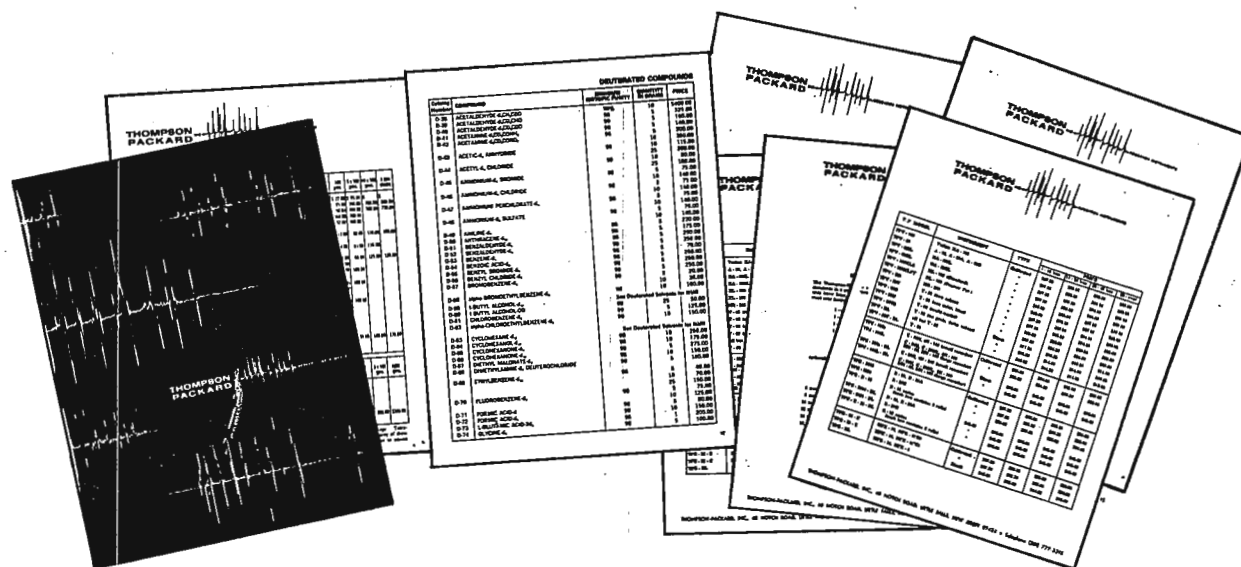
C.D. Hall

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Standard Oil Company (Indiana)

Standard Oil Research Center
Post Office Box 400
Naperville, Illinois 60540
312-420-5111

September 26, 1972

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

Dear Barry,

After having our Bruker NMR Spectrometer (HFX-90/7-12/4) for a little more than two years now, your subscribers may be interested in our experiences with its performance. Generally the two criteria which concern most people are sensitivity and resolution. Quite typically we can easily get a proton S/N of 50/1 for the traditional quartet of 1% ethylbenzene. On a quiet day and with more effort we have obtained better than 75/1. Regarding resolution, again it takes little effort to resolve two peaks separated by $\frac{1}{2}$ Hz. With more effort and patience one can resolve two peaks separated by about 0.3Hz as, for example, in the time honored o-dichlorobenzene.

Long term stability is another matter. It was found that the Bruker B-MT 30/50 magnet water cooling system simply did not hold the temperature of the magnet system constant (within $\frac{1}{2}^{\circ}\text{C}$) for long periods of time. We thus found it necessary to purchase a Neslab Instruments, Inc. model HX-300 refrigerated recirculating heat exchanger. This unit has the 55P pump option (6gpm at 45 psi) and also a water cooled compressor. Since receiving the Neslab HX-300 in January of this year, the long term stability of the spectrometer has been greatly improved. Time averaging for 26 hrs. is quite easy now with longer periods possible.

I realize that there is a stigma and taboo against mentioning water systems in the NMR Newsletter; however, I feel it is important to note it here because a number of other Bruker owners have already obtained or anticipate obtaining a better water system. Although I have not seen it reported in the newsletter, I do know subscribers who have purchased a Neslab or Haskris chiller or have constructed their own.

Returning to the performance of the Bruker spectrometer, I have included an example of its operation for homonuclear proton INDOR. The upper trace of Figure 1 shows the normal sweep (f_1 channel) of the aromatic portion of 7.4 wt % trimethyltrimellitate in CDCl_3 with field frequency stabilization (f_0 channel) on TMS. From this spectrum the following values were measured:


$\nu(\text{A}) = 696.4\text{Hz}$	$\text{J}(\text{AB}) = 7.99\text{Hz}$
$\nu(\text{B}) = 737.0$	$\text{J}(\text{BC}) = 1.68$
$\nu(\text{C}) = 756.9$	$\text{J}(\text{AC}) = 0.52$

Homonuclear INDOR is easily accomplished with the Bruker spectrometer. With the sweep pushbutton in the f_1 (observing) channel one turns a position control until the counter reads the frequency of a peak to be monitored. Next the f_2 (decoupling) channel button of the sweep is pushed and recording is begun. Examples of this are shown in the middle and lower traces of Figure 1. Naturally to obtain the best INDOR spectra time is spent optimizing r.f. power levels, receiver gain, f_1 position, and f_2 scanning speed (0.24Hz/sec. in this case). For the example here, it took about a day to obtain the best INDOR spectra for all four of the C lines.

In the usual manner, progressive and regressive transitions are assigned to pairs of lines from the upward and downward excursions of the pen. Finally, the full energy level diagram is constructed as shown in Figure 2. This could be considered an experimental example of the discussion given by Friedman and Gutowsky, J. Chem. Phys., 45, 3158 (1966). In this example all couplings are the same sign and positive.

I hope that the above contribution serves to stave off the Newsletter subscription wolf for another nine months!

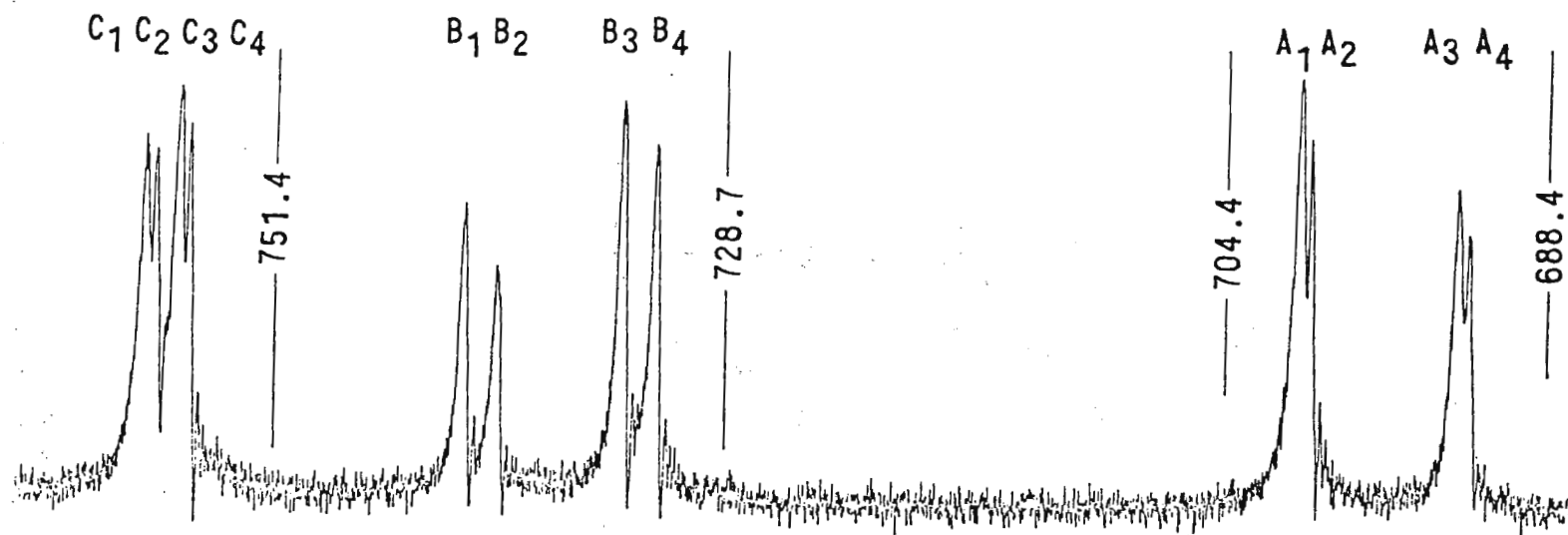
Best regards,



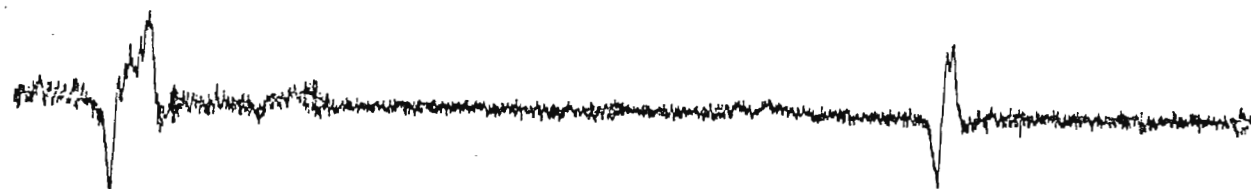
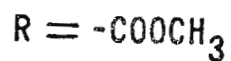
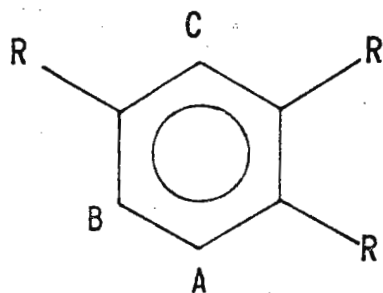
Bruce Wenzel
BEW/ch

Title: Experience with a Bruker Spectrometer; An Example of
Homonuclear INDOR

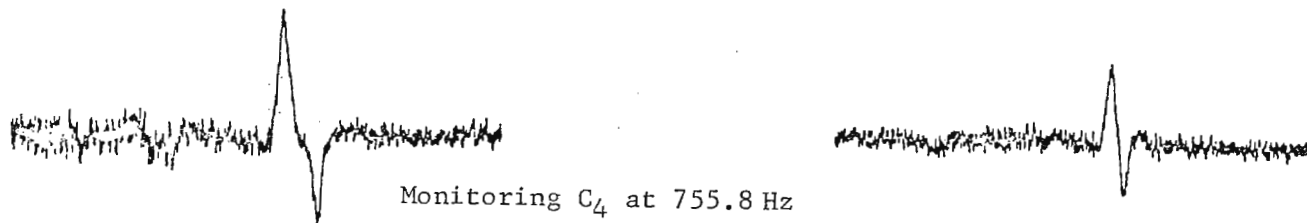
cc: R. M. Alm
R. R. Hopkins
E. M. Banas
G. J. Ray



Scan of the aromatic region of the spectrum of Trimethyl trimellitate
(7.4 wt % in CDCl₃)



Monitoring C₁ at 758.3 Hz



Monitoring C₄ at 755.8 Hz

FIGURE 1

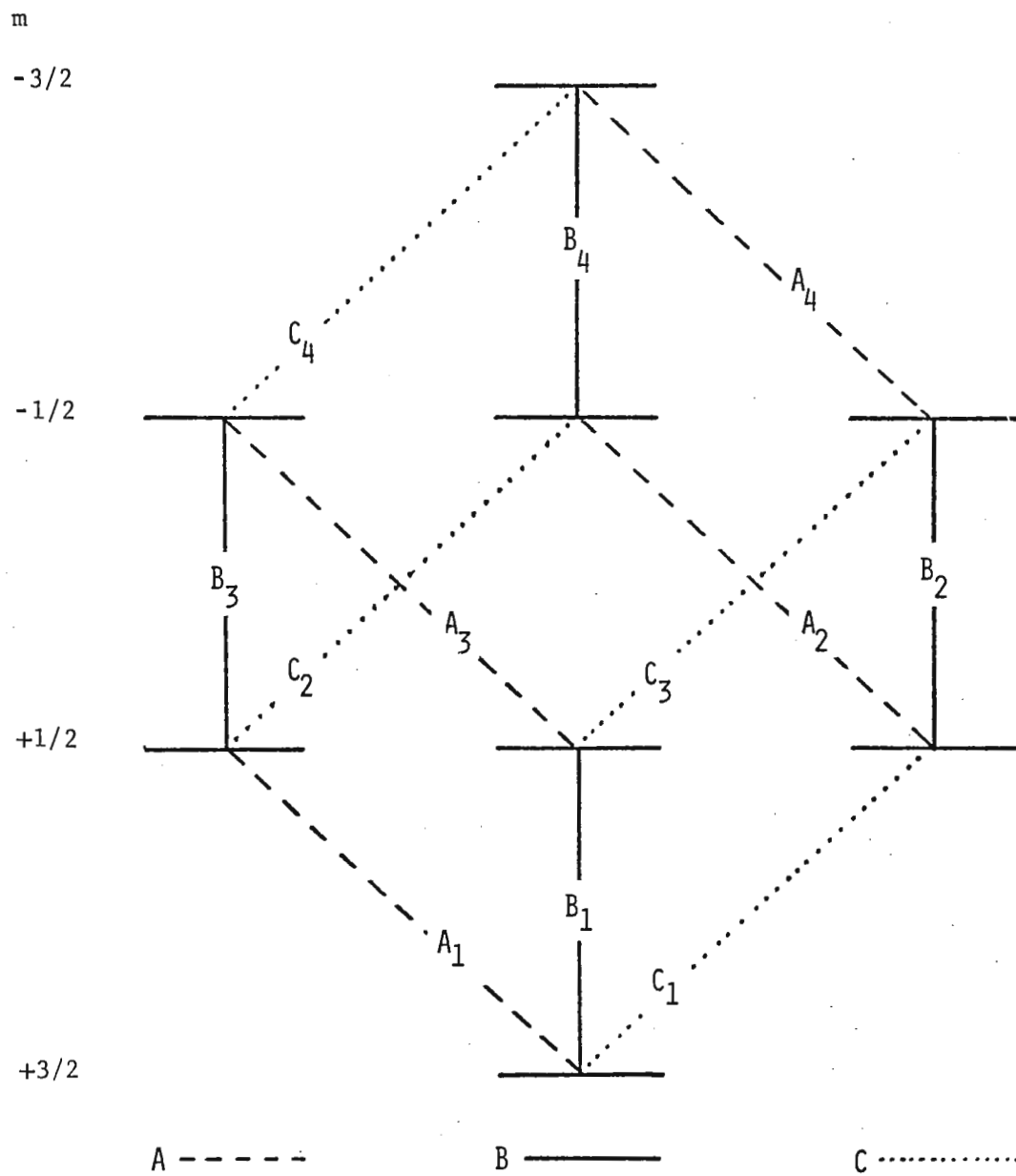
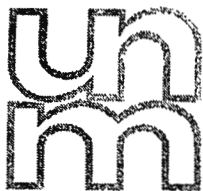


FIGURE 2 Energy level diagram obtained from the
INDOR experiments on Trimethyl trimellitate.



THE UNIVERSITY OF NEW MEXICO ALBUQUERQUE, NEW MEXICO 87106

DEPARTMENT OF CHEMISTRY
TELEPHONE 505: 277-2821

25 October 1972

Dr. Barry Shapiro
Chemistry Department
Texas A&M University
College Station, Texas 77843

Dear Dr. Shapiro,

Thank you for your reminder.

I can mention some work performed recently in connection with a ^{15}N relaxation study. We needed to know the viscosity of pure ND_3 as a function of temperature since the viscosity is useful in determining the importance of various relaxation mechanisms. We found that only three values of the viscosity for ND_3 have been reported. An extensive study of the viscosity of NH_3 has been done with these data readily available. We measured the viscosity of ND_3 from -65°C to $+30^\circ\text{C}$. We found that the viscosity of ND_3 is greater than that of NH_3 by a factor of $1.19 \pm .03$ which is constant over the entire range studied. This contrasts with the $\text{D}_2\text{O}-\text{H}_2\text{O}$ ratio which varies with temperature. The work will be published soon in J. Chem. Phys.

A new XL-100 will be installed at UNM within a month with capability of observing ^1H , ^{19}F , ^{13}C , ^{15}N , and ^{31}P . I would be very interested in hearing from any graduate students or prospective graduate students who have interests in Nuclear Magnetic Resonance studies in physical chemistry.

Sincerely,

Wm. M. Litchman
Wm. M. Litchman

Title: Viscosity of ND_3

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

Homonuclear INDOR in the spectrum of codeine

Dear Dr. Shapiro,

We have recently been evaluating the INDOR facility of the Model R32, and mention of codeine (TAMUNMR 163-30) prompts us to describe some results from this molecule. At 90MHz the five protons of the cyclohexene ring appear as a nearly first order system with eight couplings resolved. (Figure). Although many lines overlap it is still possible to extract information very simply by concentrating on the non-degenerate outermost lines of the various multiplets. The single INDOR scan shown is sufficient to fix the relative signs of all eight coupling constants. The results of interest are that $^4J_{57}$ and $^5J_{614}$ are both positive.

As long as a non-degenerate line is being monitored the sense of the INDOR peaks (up or down) is irrelevant to the sign determination, and construction of any energy level diagram is unnecessary. If a degenerate line is monitored reference to an energy level diagram is required. An example occurs if H-1 is monitored to locate the 10-CH₂ buried among other methylene resonances. H-1 appears as a pair of poorly resolved triplets because the two four bond couplings are nearly equal. Monitoring the centre of one such triplet gives INDOR spectra interpretable in terms of AMX sub-spectra with lines A₂ and A₃ monitored simultaneously (see below). As can be seen the relative sign information is contained in the sense of the INDOR peaks. This particular example has that least common combination of signs, all negative.

Yours sincerely,

R.A. Spragg

R.A. Spragg

Abt.f.Physik.Chem.d.Kunststoffe
im Institut f. Physik. Chemie
Prof. Dr. Kosfeld

51 Aachen, den 19. Okt. 1972
Templergraben 59
Telefon: (0241) 422-2770

Herrn

Prof. Bernard L. Shapiro
Texas A + M University
College of Science
College Station
Department of Chemistry

T e x a s 77843 / U.S.A.

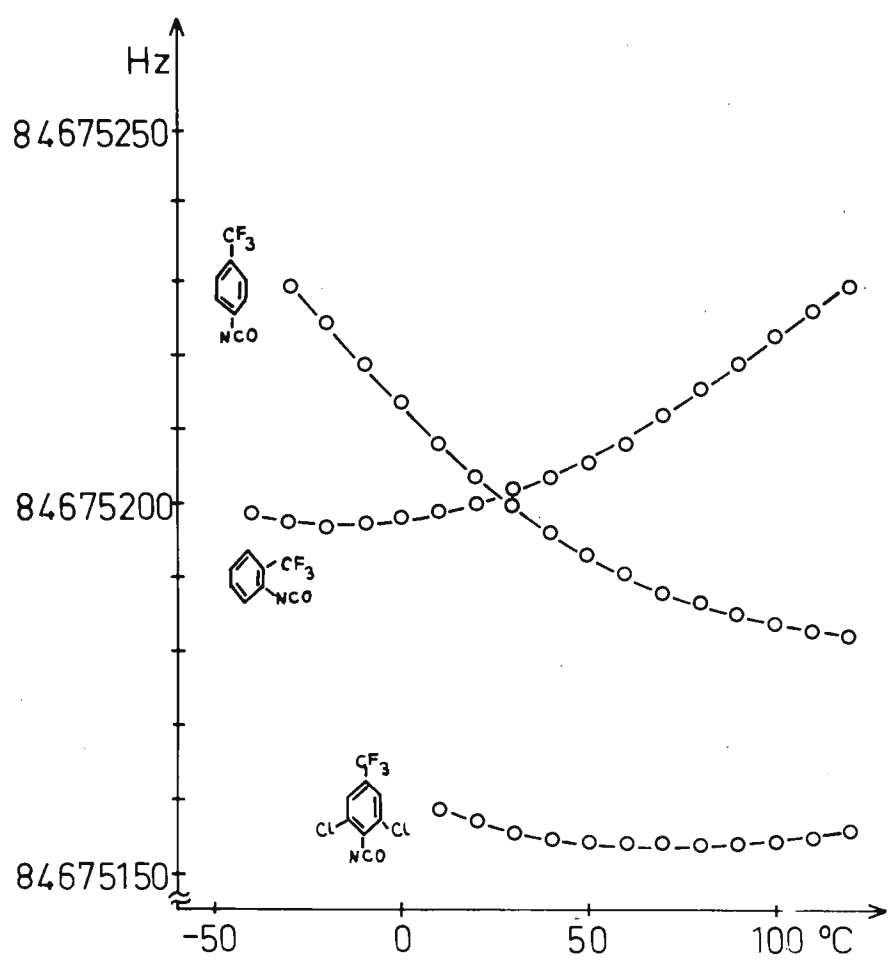
Dear Professor Shapiro !

TEMPERATURE EFFECTS ON THE CHEMICAL SHIFT OF FLUORINE NUCLEI
IN SOME TRIFLUOROMETHYLPHENYLISOCYANATES.

We have investigated the influence of the temperature on the chemical shift of the fluorine signals of trifluoromethylphenylisocyanates in the temperature range of -60°C to 120°C . The values of the chemical shifts have been measured directly with a frequency counter in relation to the internal standard TMS.

We found a quite different temperature dependence for the chemical shifts of the various substances which is determined by the kind and the position of the substituent to the CF_3 -group.

The chemical shifts of the ortho - trifluoromethylphenylisocyanate, 3 - chloro, 4-trifluoromethylphenylisocyanate and 3,6 - dichloro, 4 - trifluoromethylphenylisocyanate increase with rising temperature. The shielding of the fluorine nuclei in the investigated trifluoromethylphenylisocyanates decreases with rising temperature, if the CF_3 -group is surrounded by the substituents Cl or NCO in orthoposition.



Chemische Verschiebung der Fluor-
signale in Abhängigkeit von der
Meßtemperatur

CHIMIE ORGANIQUE PHYSIQUE

UNIVERSITÉ DE NANTES
U E R DE CHIMIE

38, Bd Michelet - 44 - NANTES
B. P. 1044
Tél. (40) 74-50-70

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

TEXAS 77 843

U.S.A.

SPECTRAL RESOLUTION OF ALLENIC ENANTIOMERS
REQUEST FOR INFORMATION

Cher Professeur SHAPIRO,

Du fait de l'éloignement mutuel des substituants d'un squelette allénique les interactions diastéréoisomères impliquant un motif allénique dissymétrique risquent d'être moins différenciées que dans le cas des carbones ou hétéroatomes asymétriques. A cet égard, bien que les écarts de déplacements chimiques observés soient relativement faibles, des diastéréoisomères comportant un système allénique et un carbone asymétrique sont susceptibles d'être distingués par leurs spectres R.M.N. (1). La création de diastéréoisomères labiles entre un solvant chiral et des énantiomères alléniques doit donc permettre en principe la résolution spectrale de ces derniers (2) (3). Toutefois, les non équivalences créées dans des mélanges d'alcools alléniques et de (-) α (naphtyl-1)-éthylamine ou de cétones ou oxydes de phosphines alléniques et de (-) menthol sont restées insuffisantes pour être décelées à 60 MHz. Par contre le spectre du composé $(\text{CH}_3)_3\text{C} \cdot \text{CH} = \text{C} = \text{C}(\text{C}_6\text{H}_5) \text{PO}(\text{C}_6\text{H}_5)_2$ (I) dilué dans CCl_4 en présence de tris [(t butyl-hydroxy méthylène)-3 camphorate] d'euporium optiquement actif (4) fait apparaitre 2 doublets d'égales intensités pour le proton allénique. La différence de déplacements chimiques entre les raies des 2 énantiomères

atteint 4 Hz à 60 MHz pour une concentration ρ = nombre de moles de complexe/nombre de moles d'allène = 0,36 ($J_{P\sim H} = 10,4$ Hz).

La détermination de la pureté optique des composés alléniques dissymétriques difficile à réaliser par les méthodes habituelles peut donc être obtenue aisément par R.M.N.

*
x x

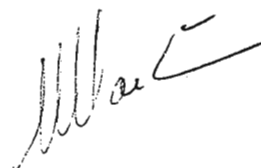
Nous serions très heureux d'obtenir des informations sur les problèmes d'interface entre une mémoire à disque ou à bande magnétique et un calculateur Varian 620 f pour F.T.

*
x x

Nous vous prions de croire, Cher Professeur SHAPIRO, à nos sentiments les meilleurs.

François LEFEVRE

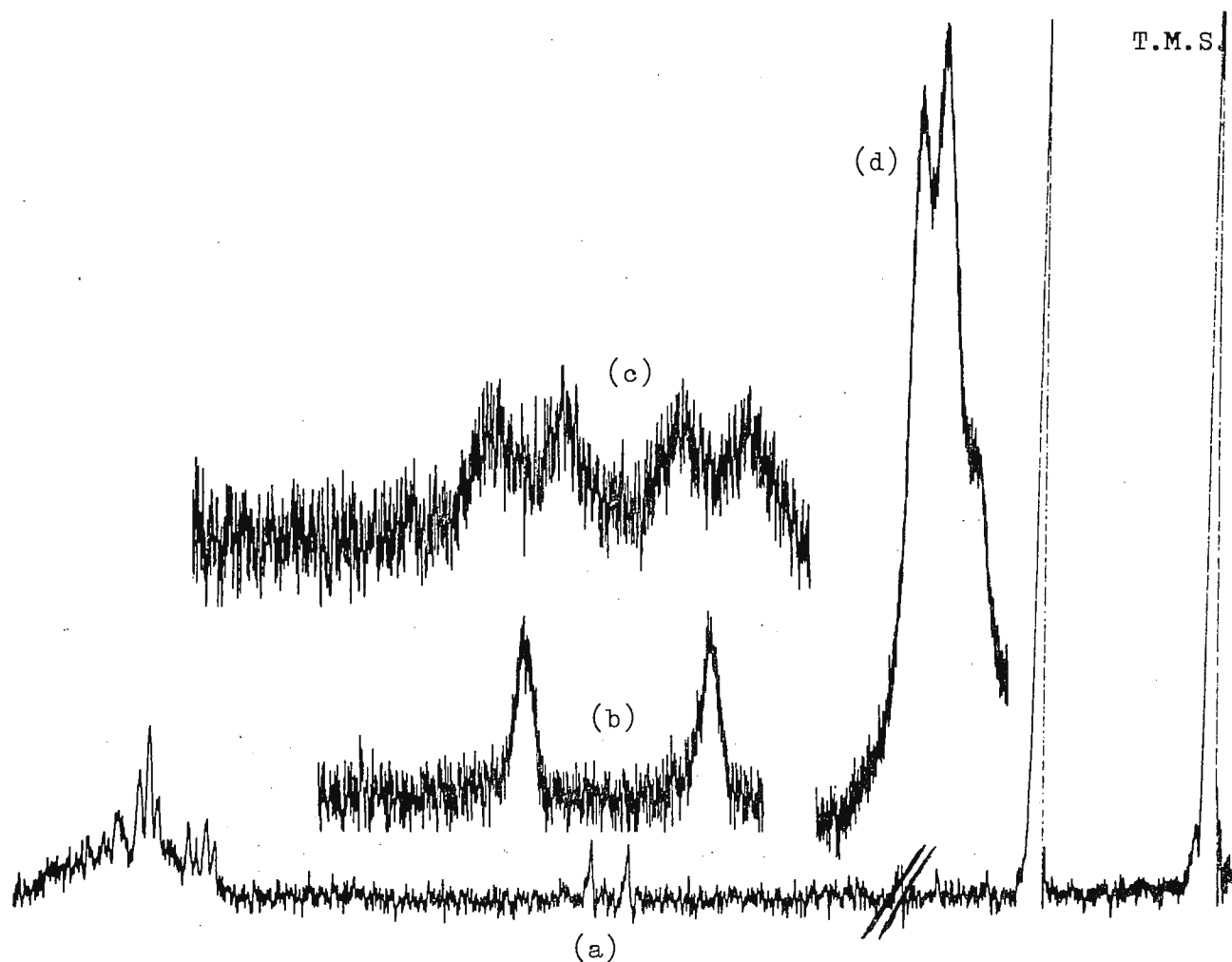
Maryvonne L. MARTIN



- (1) M.L. MARTIN, R. MANTIONE, G.J. MARTIN - Tetrahedron Letters 48,4809,1967-
- (2) W.H. PIRKLE - J. Amer. Chem. Soc. 88, 1837, 1966 -
- (3) M. RABAN, K. MISLOW - Topics in Stereochemistry 2, 199, 1967 -
- (4) G.M. WHITESIDES, D.W. LEWIS - J. Amer. Chem. Soc. 92, 6979, 1970 -

a) et b) Spectres de I dans CCl_4 .

c) et d) Spectres de $=\text{CH}$ et $(\text{CH}_3)_3\text{C}$ en présence de tris [(t butyl-hydroxyméthylène)-3 camphorate] d'euporium





E. I. DU PONT DE NEMOURS & COMPANY
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WILMINGTON, DELAWARE 19898

CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION

September 12, 1972

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

TRACK-FIELD SWEEP DECOUPLING ON
THE VARIAN HR-220 NMR SPECTROMETER (1)

Track-field sweep (pseudo frequency sweep) decoupling can be done on an HR-220 by addition of a voltage-controlled oscillator (VCO), driven by a voltage proportional to the sweep current. The decoupling sideband is thus swept so that the irradiating frequency is always $\omega_2 = \gamma H_0$.

Dr. L. Cary picks up the necessary voltage from the recorder sweep pot through a high variable resistance (2). We have used this method, but recalibration of the VCO input voltage is required for each sweep width. It is more satisfactory to pick up the voltage from the 70-ohm resistor R326 in the V4353 sweep unit; this directly tracks the current in the field sweep coils. An operational amplifier is required (Fig. 1). The output is connected to the input of a Wavetek Model 111 Voltage-Controlled Generator (VCO).

A frequency counter is needed for calibration and is helpful, though not essential, for decoupling experiments. Calibration of the VCO input voltage requires adjustment of pot " ω_2 cal." The decoupling frequency is set by placing the recorder

pen at the desired position in the spectrum, and adjusting the base frequency of the VCO to equal the modulation frequency (10 KHz or 20 KHz). If a counter is not available, this frequency can be set by observing the beat frequency between ω_2 and ω_1 . Field sweep decoupling can still be performed by disconnecting the voltage ramp to the VCO.

Another helpful modification suggested by Cary (1) is a modulation amplitude control for the observing sideband, ω_1 . Replacing pot R273 in the V3523 Integrator/Audio unit by the circuit in Figure 2 provides independent control of H_1 to optimize S/N for any H_2 .

Raymond C. Ferguson

Raymond C. Ferguson

Howard M. Records

Howard M. Records

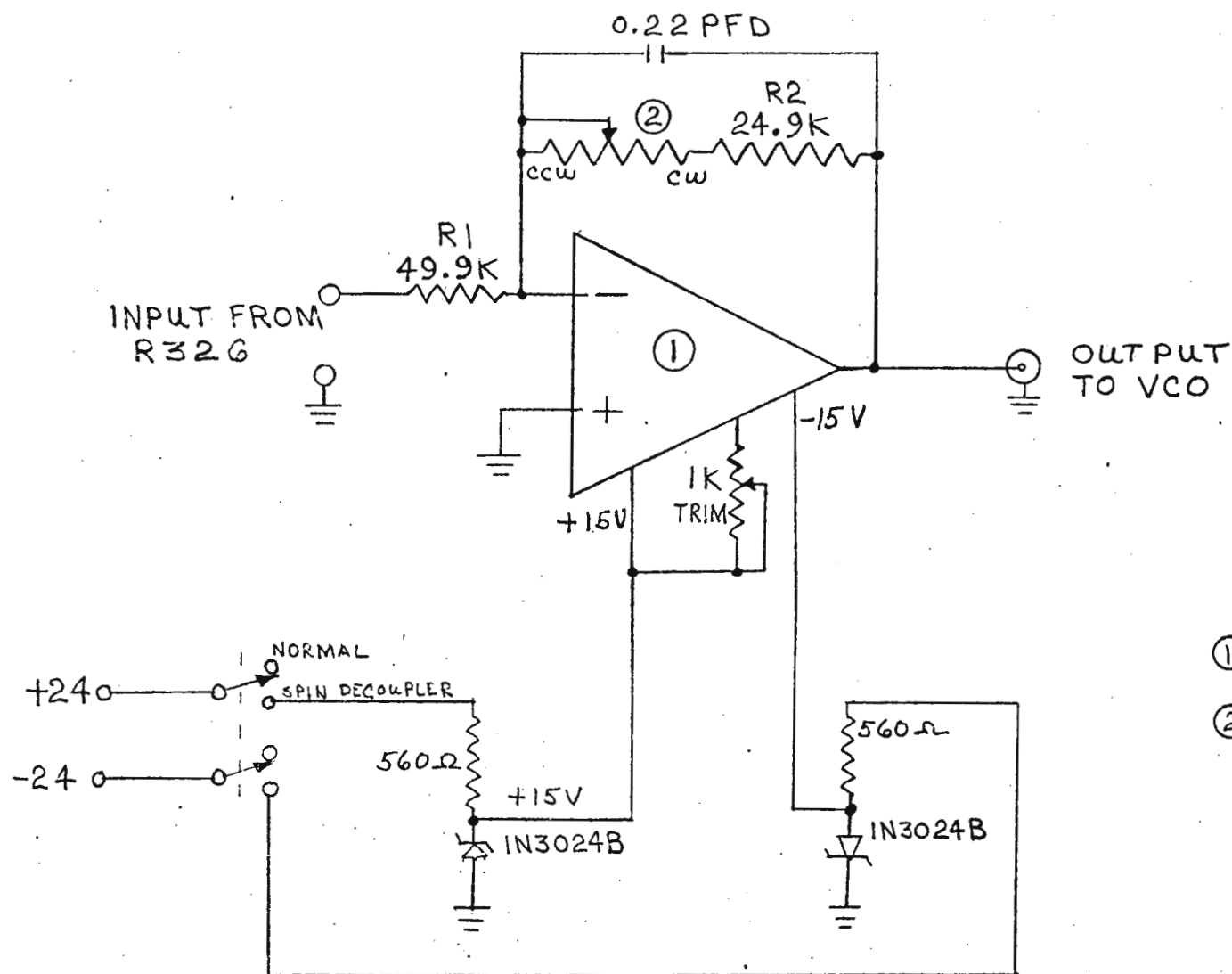
RCF:HMR/dew
9/12/72

- (1) Contribution No. 1988, Central Research Department
- (2) L. Cary (Varian Associates, Analytical Instruments Division, Palo Alto, Calif.), private communication.

OPERATIONAL AMPLIFIER CIRCUIT - HR 220 TRACK FIELD SWEEP DECOUPLER

170-56

FIGURE 1



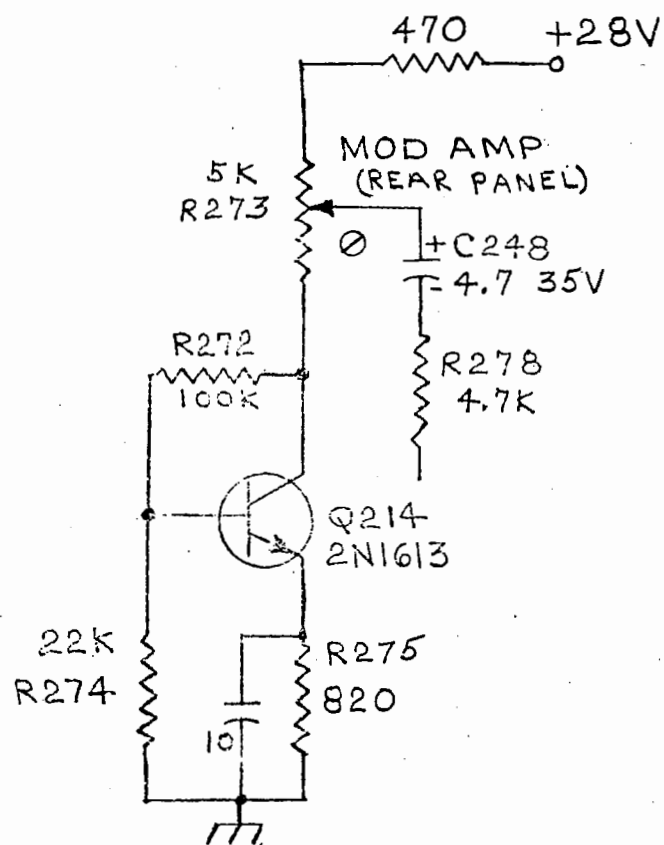
① PHILBRICK NEXUS 1009

② "W₂ CAL" 100K 10TURN

R1 AND R2 ARE 0.5% TOL.

5-15-72
H.R.

OLD CIRCUIT



REVISÉD CIRCUIT

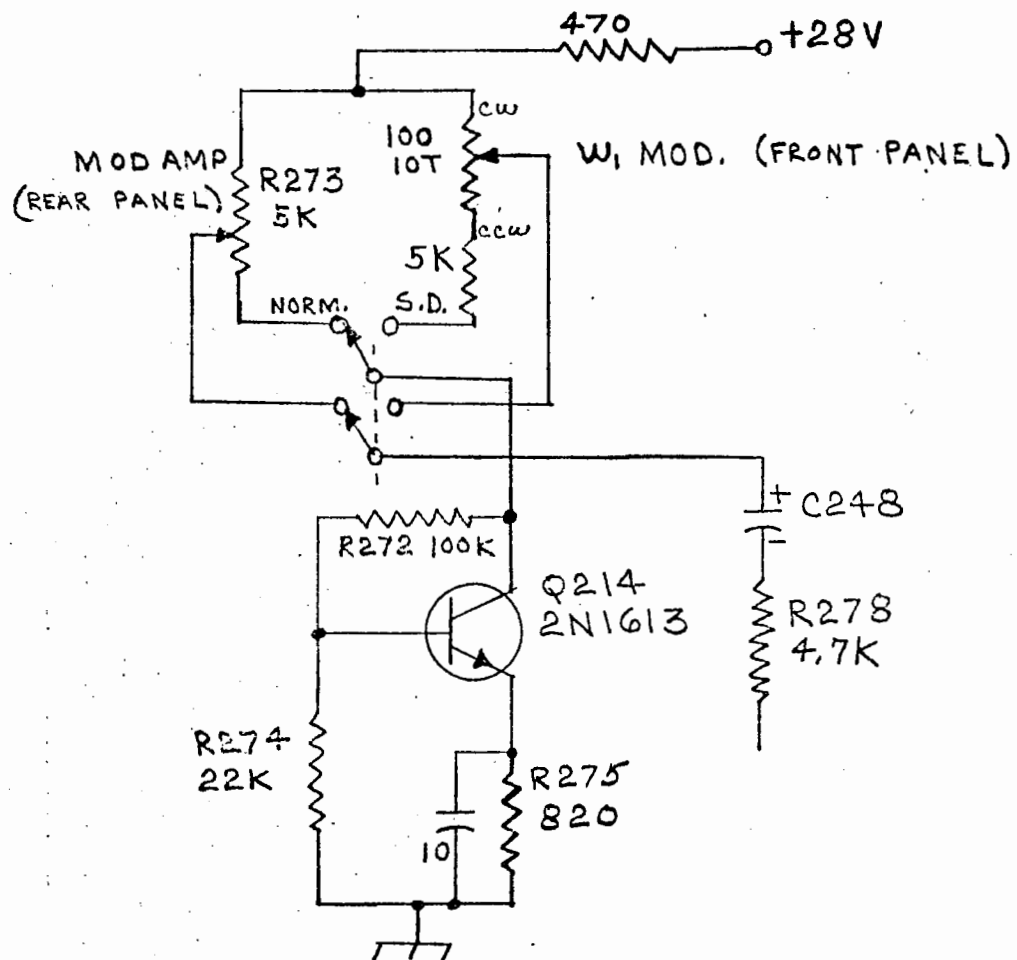


FIGURE 2

5-15-72
H.R.

Research Laboratory

International Business Machines Corporation

Monterey & Cottle Roads
San Jose, California 95114
408 / 227-7100

October 27, 1972


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

Dear Barry:

Since learning about the new technique for high-resolution nmr in solids developed a couple of years ago by Bleich and Redfield, I have been interested in using it to obtain fluorine and proton spectra of isolated molecules. The basic idea is to dilute the molecule of interest (which contains the nuclei to be studied) in a solvent containing different, but abundant nuclei. The spins which have been made rare by dilution are then detected via cross-relaxation in the rotating frame with the abundant nuclei in the surrounding solvent molecules. Thus, the technique can be used to obtain high-resolution ^1H and ^{19}F spectra in the solid. In the accompanying figure, I show some results which we obtained when we mixed a small amount of CF_3CCl_3 into adamantane. No spectrum is obtained with a pure adamantane sample, or when either of the necessary conditions for double resonance (matching the rotating frame energy levels of rare and abundant spins, or heating the rare spins) is deliberately not met. The spectrum should probably be isotropic judging from work by Dave Woods on epr in an adamantane matrix; however, the linewidth (~ 250 Hz) is bewildering and may be due to a specific association of CF_3CCl_3 with the adamantane. We will be doing more experiments to learn why the resolution is so poor, and will be looking at some anisotropic ^1H and ^{19}F spectra.

We used the Bleich-Redfield method here, but the Pines-Gibby-Waugh technique could be used just as well.

Sincerely yours,


C. S. Yannoni

mar

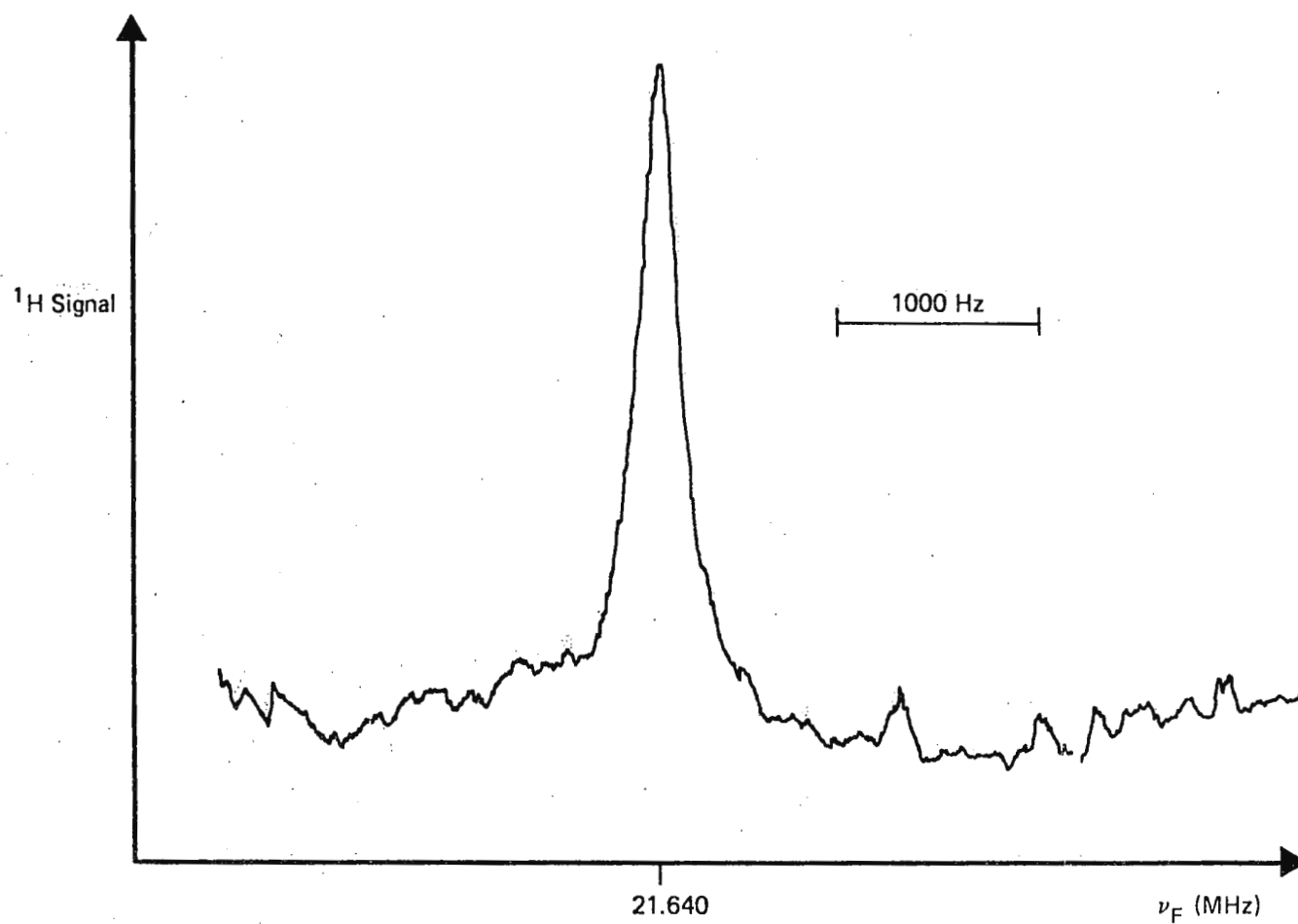


Fig. 1 ^{19}F double resonance spectrum of 1, 1, 1-trifluorotrichloroethane (CF_3CCl_3) in adamantane ($\text{C}_{10}\text{H}_{16}$) at 80°C . Full width at half-height is 250 Hz. The off-resonant (matching) rf field on ^{19}F is 21.609 MHz with $H_1 \approx 2$ gauss. The ordinate is the magnitude of the adamantane proton signal, and the abscissa shows the frequency of the saturating rf field (≈ 20 milligauss) swept through the ^{19}F spectrum.



Eidg. Technische Hochschule
Zürich-Hönggerberg

Institut für Molekularbiologie
und Biophysik

Tel. (051) 57 57 70

8049 Zürich, October 27th 1972 KW/jr

Professor B. Shapiro
Dept. of Chemistry
Texas A and M University
College Station, Texas 77843
USA

Dear Professor Shapiro,

Since this is the first contribution from our laboratory, it may be appropriate to begin with a few general remarks on our activities. The group consists of physicists and chemists interested in biological problems. The current research projects include studies of the molecular conformations in peptides and proteins, investigations of the electronic states in hemoproteins, and work on the solvent interactions with biopolymers. Our main technique of investigation is NMR, and this brings me to our first title for T A M U N.

Some remarks on proton NMR investigation of intramolecular hydrogen bonding in peptides

Studies of intramolecular hydrogen bonding are an important part of the work involved in the elucidation of the molecular conformations in peptides, and proton NMR studies have contributed much to the understanding of the hydrogen bonding pattern, particularly in cyclic peptides. Several lines of evidence are used to distinguish between amide protons which are freely accessible to the solvent, and those which are shielded from interactions with the solvent, e.g. in transannular hydrogen bonds in cyclic peptides. Among these are the amide proton resonance positions and their dependence on temperature and solvent, and the rate of the amide proton exchange in deuterated protic solvents. From various observations we came to feel that great care has to be taken in such experiments. The following is one of several rather unexpected data which we encountered in the investigation of these phenomena.

If the cyclic hexapeptide $c(-\text{Gly-L-Pro-Gly-Gly-L-Pro-Gly-})$ is dissolved in DMSO it forms a β -structure with the amide protons of Gly(1) and Gly(4) involved in transannular hydrogen bonding (1-3). If D_2O is added to the solution in DMSO one would according to the generally accepted rules expect the amide protons in positions (1) and (4) to be exchanged more slowly than the remaining two amide protons which are more freely accessible to the solvent. We found that the relative rates of exchange of the two types of glycylic amide protons can be reversed by variation of the pH in the D_2O added. In these measurements

20 μ l of D_2O was added to 0.5 ml of 0.05 - M solution of the peptide in d_6 -DMSO. The 1H - and ^{13}C -resonance positions were not affected by this change in solvent composition (3,4), indicating that the same molecular conformation was maintained throughout the series of experiments.

pD of D_2O added	$t_{1/2}$ (minutes)	
	NH (3) and (6) at 8.6 ppm	NH (1) and (4) at 7.6 ppm
1.1	23	6
2.2	80	200
3.9	35	65
"neutral"	\sim 180	\sim 700
9.5	4	8

The table shows that the expected behaviour was observed in the pH range 3 to 10. At pH around 2 the exchange of both types of protons is unexpectedly slow, and at pH around 1 the apparently still hydrogen bonded protons exchange faster than those in positions (3) and (6).

Sincerely yours,

Ch. Grathwohl *K. Wüthrich*
Ch. Grathwohl K. Wüthrich

References

1. R. Schwyzer, J.P. Carrion, B. Gorup, H. Nolting and A. Tun-Kyi, *Helv. Chim. Acta* 47, 441 (1964)
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4. Ch. Grathwohl, R. Schwyzer, A. Tun-Kyi and K. Wüthrich, submitted to FEBS Letters

THE PENNSYLVANIA STATE UNIVERSITY

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College of Science
Department of Chemistry

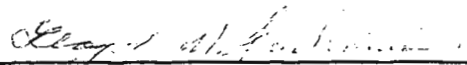
October 27, 1972

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

NMR Position Open

We are interested in hiring a full time person to operate our NMR facilities. These include primarily a JEOL PS 100-FT equipped with a Nicolet 1085 computer (with disc and tape) and a Varian MA-100 converted to FT operation. Strong preference for NMR and/or FT experience is desired. Electronics background helpful. Please submit resume to Dr. Lloyd Jackman 814-865-2269 (or 4221).


Joseph J. Villafranca


Lloyd Jackman

Gesellschaft für Molekularbiologische Forschung mbH

3301 Stöckheim über Braunschweig

Mascheroder Weg 1

German Federal Republic

Telefon 0531/60071 — Telex 9-52 667

Bahnstation: Expresgut Braunschweig Hbf
Stückgut Braunschweig HGbf

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

Abt.: Physikalische Messtechnik

2 November 1972

New address

Dear Barry,

As you already know, we will move to the above address on or about 1 February 1973.


One of us (DNL) will be a Senior Scientist in NMR, and the other (EL) will be heading the Division of Spectroscopy (Abt. Physikalische Messtechnik), and the NMR Section of this Division.


Requests for copies of the two programs SIMULATE2 and LAOCOON₁ as well as of the editing routine (TAMU NMR Newsletter 169-49) should in the meantime be addressed to

Dr. David N. Lincoln
26600 Haney Ave.
Damascus, Md. 20750
USA.

Thank you for having this change of address announced in the Newsletter.

Best wishes and regards.


David N. Lincoln


Ernest Lustig



THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

October 30, 1972

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

Extended Sweep Range for the HA-100

Dear Barry,

We have just completed testing the prototype of a new circuit card [PRAXIS PR-40] supplied by The Praxis Corporation* that replaces the sweep frequency amplifier card in the Lock Box of the Varian HA-100. This card quadruples the frequency of the sweep oscillator and thus gives additional sweep ranges of 4KHz and 2KHz to the HA-100. Because of the higher sweep frequency this unit also gives four times the normal offset range. This is a distinct advantage when recording ^{19}F spectra where the reference compound may not be close to the observed peaks. Enclosed you will find a ^{19}F spectrum and a ^{13}C spectrum using this new card. We have found that it works very well.

Best regards,

A handwritten signature in cursive script that reads "Ben A. Shoulders".

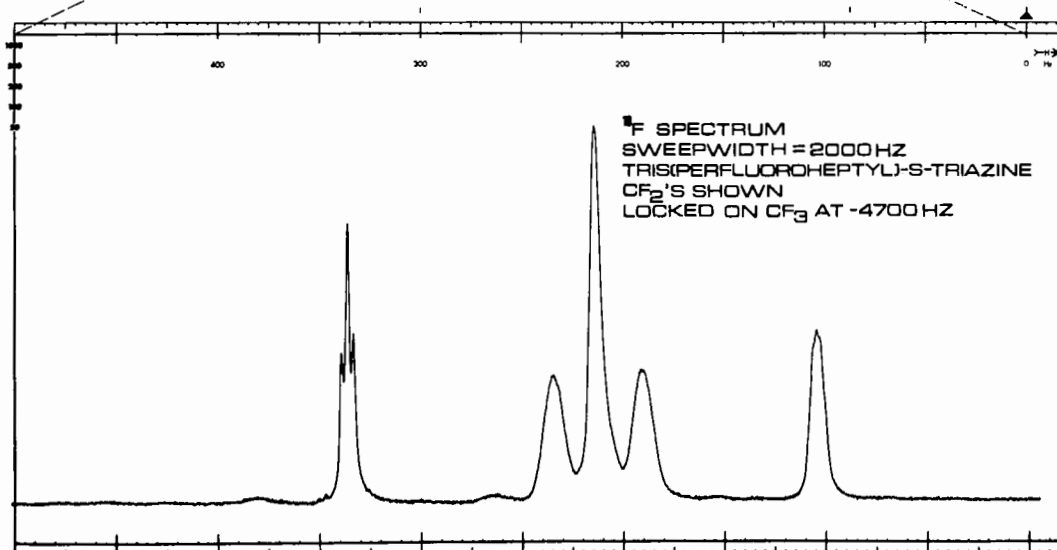
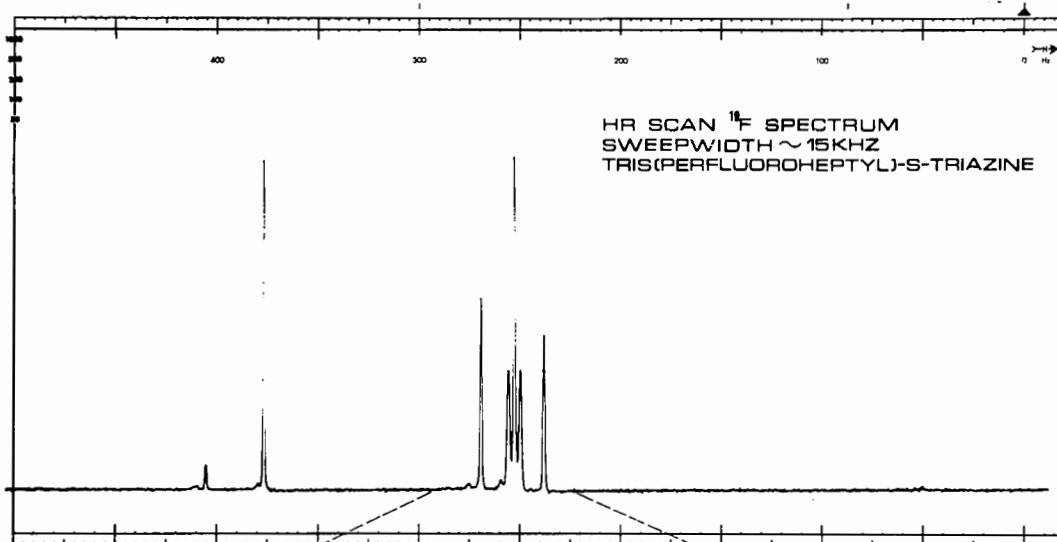
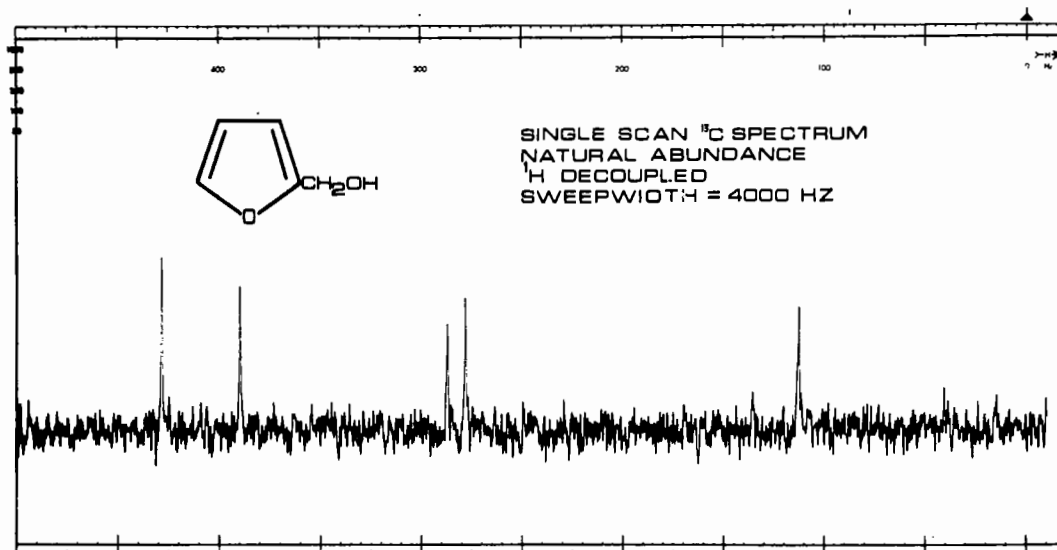
Ben A. Shoulders

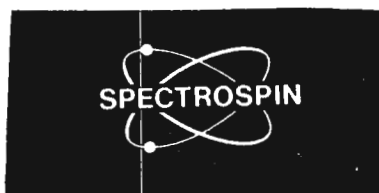
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Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University

College Station, Texas 77843
U S A

Fällanden, November 2, 1972

POSITIONS AVAILABLE

Dear Prof. Shapiro:

We have two openings for scientists with experience in magnetic resonance

1) BRUKER SPECTROSPIN FELLOWSHIP

This position is available in our research lab at Zurich where our aim is to study new NMR techniques in the high resolution field using super-conducting solenoids, computer and pulse methods. Other investigations are concerned with NMR of nuclei other than H^1 , Cl^{35} or F^{19} .

We are interested in a post-doctoral fellow with a strong background in high resolution NMR. Some experience in electronics and computer programming would be desirable but more important is this enthusiasm for new fields of NMR application.

2) EPR - SPECIALIST

The second position for an EPR-specialist is open at BRUKER's EPR Division at Karlsruhe, Germany. This scientist would at first take an active part in our research and development-group at Karlsruhe. Later on, he would lead an EPR application lab in the US.

Sincerely yours,

SPECTROSPIN AG

(Dr. Hp. Kellerhals)

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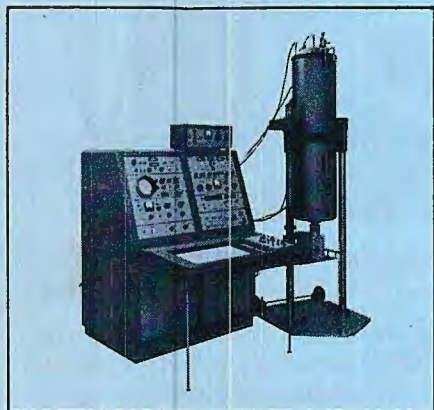
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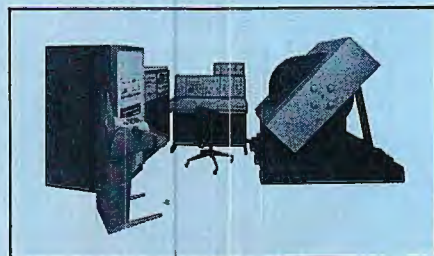
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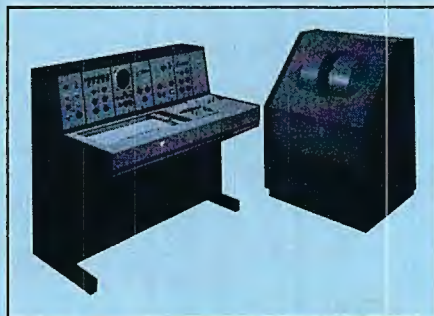
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A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz, and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments.

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A moderately priced 14-kG, ^{13}C research spectrometer offering the highest performance per dollar of any NMR system now available. Accessories include Fourier transform for ^{13}C , and other nuclei such as ^1H , ^{19}F and ^{31}P . It is a solid state, frequency swept spectrometer ideal for either high performance routine tasks, or for those research requirements demanding state-of-the-art capabilities along with versatile lock, spin decoupling, and variable temperature capability using 8mm sample tubes.

System T-60



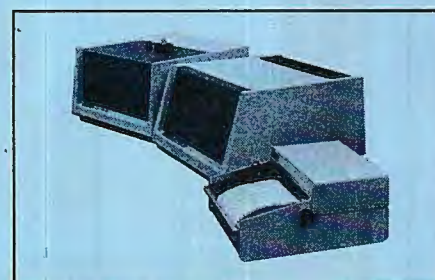
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