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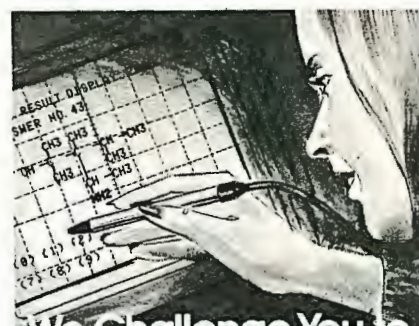DEADLINE DATES:  No. 211:  5 April 1976
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Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX  77843  U.S.A.

December 9, 1975

Prof. B. L. Shapiro

Department of Chemistry
Texas A&M University

College Station,   Texas 77843 / U. S. A.

Dear Professor Shapiro:

<u>An Empiric Rule for the Determination of the Substitution Type of Poly - pyrroles Related to Natural Products by Means of ^{1}H-NMR Spectroscopy.</u>
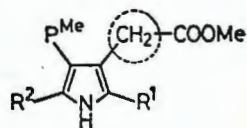
In the course of the investigation of the [1]H-n. m. r. spectra of a series of pyrrole derivatives which were prepared as building blocks for the synthesis of several polypyrrolic compounds related to uroporphyrin III [1a], 12-decarboxyuroporphyrin III [1b] and phyriaporphyrin III (18-decarboxy-uroporphyrin III) [1a] an interesting relationship was observed between the chemical shifts of the signals associated with the methylene protons of ß-standing acetic ester residues and the nature of the groups attached to the vicinal $\alpha$-positions. Thus, only such substituents at the $\alpha$-position which exert a conjugative electron-withdrawing effect on the pyrrole ring bring about a quite constant paramagnetic displacement of the chemical shift of methylene protons at the neighbouring ß-positions of about 0. 3 ppm as compared with the corresponding values for derivatives lacking such substituents (c. f. table 1). In this connection it is noteworthy that the (3-pyrrol-in-2-yliden)-methyl group as it occurs in the bilatrienes (e. g. 8) has no conjugative electron withdrawing effect (c. f. table 1).

The average values given in table 1 are rather independent of other substituents present in the molecule. They are therefore also valid, within a series of related compounds, for pyrrole derivatives as well as for many linear polypyrroles such as dipyrrylmethanes (5), tripyrrene hydrobromides (6, 13), biladienes-ac salts (7, 14), bilatrienes (8), and bilanes (9).
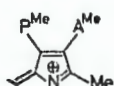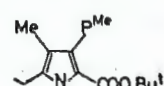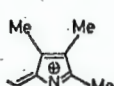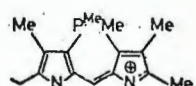
Table 2 shows the application of the above empiric rule to several biladiene-ac salts and bilatriene derivatives, most of which were prepared as the key intermediates for the synthesis of polypyrrolic compounds probably involved in the biosynthesis of heme, chlorophyll, and vitamin - $B_{12}$.

Table 1 . Dependence of the chemical shift of the methylene protons
of ß-standing acetate groups on the nature of the vicinal
α -substituent in pyrrole derivatives.



Me = CH₃
A^Me = CH₂—COOCH₃
P^Me = CH₂—CH₂—COOCH₃

| No. | R¹ | R² | δ (ppm) CDCl₃ |
|-----|------|--------|--------|
| 1 | H | CHO | 3,52 |
| 2 | J | CHO | 3,49 |
| 3 | Me | COOBuᵗ | 3,45 |
| 4 | CH₂OAc | COOBuᵗ | 3,52 |
| 5 | (pyrrole, COOCH₂Ph) | COOBuᵗ | 3,51 |
| 6 | (dipyrrylmethene) | COOBuᵗ | 3,58 |
| 7 | (dipyrrylmethene) | (pyrrole) | 3,54 |
| 8 | (dipyrrylmethane, COOMe) | (pyrrole, COOMe) | 3,54 |
| 9 | (pyrrole, COOMe) | (dipyrrylmethane, COOMe) | 3,42 |

| No. | R¹ | R² | δ(ppm) CDCl₃ |
|-----|-----------|------|--------|
| 10 | COOCH₂Ph | Me | 3,82 |
| 11 | COOMe | COOH | 3,76 |
| 12 | COOH | CHO | 3,92 |
| 13 | (pyrrole, Me) | (pyrrole, COOBuᵗ) | 3,73 |
| 14 | (pyrrole, Me) | (dipyrrylmethene, Me) | 3,74 |

On the basis of the assignments made for the methylene protons of acetate
side-chains in the corresponding ¹H-n.m.r. spectra we could exclude the
possibility of scrambling reactions [2] during the synthesis of our biladienes-
ac. Particularly, in the cases of biladiene-ac salts without terminal con-
jugative electron-withdrawing groups (e. g. I. 4) the existence of the expec-
ted arrangement of the ß-substituents could be confirmed by signals at
δ = 3.80 ppm (2H) and 3.52 ppm (4H) for the methylene protons of the
C-7 and the C-2, C-18 acetate groups, respectively. Furthermore, we
synthesized a biladiene-ac derivative I.7 of the 12-decarboxyuroporphyrin-I
type. As expected three signals for the methylene protons at the C-7, C-17,
and C-2 acetate side-chains at δ = 3.81 ppm (2H), 3.76 ppm (2H) and
δ = 3.50 ppm (2H), respectively, are observable.
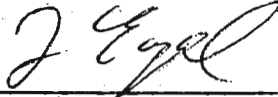
Table 2. Assignments of the $^1$H-n.m.r. signals to the methylene protons of ß-standing acetate groups in bilatriene and biladiene-ac derivatives.
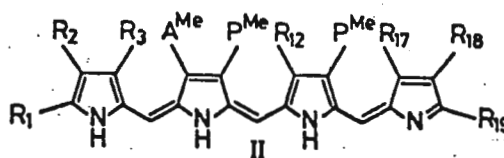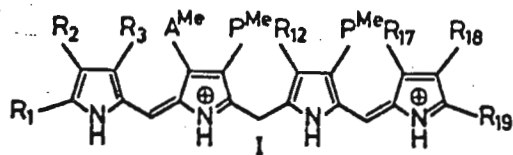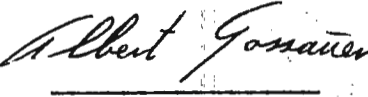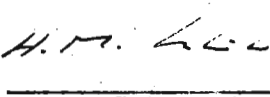


| No. | $H_{12}$ | $R_1$ | $R_{19}$ | $R_2$ | $R_3$ | $R_{17}$ | $R_{18}$ | $CH_2$(C-2) | $CH_2$(C-18) | $CH_2$(C-17) | $CH_2$(C-7) | $CH_2$(C-12) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I.1 | Me | H | H | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.57 | 3.57 | - | 3.86 | - |
| 2 | $A^{Me}$ | H | H | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.57 | 3.57 | - | 3.84 | 3.54 |
| 3 | Me | H | H | Me | Me | Me | Me | - | - | - | 3.81 | - |
| 4 | Me | Me | Me | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.52 | 3.52 | - | 3.80 | - |
| 5 | $A^{Me}$ | Me | Me | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.54 | 3.54 | - | 3.87 | 3.39 |
| 6 | Me | Me | Me | Me | Me | Me | Me | - | - | - | 3.74 | - |
| 7 | Me | Me | Me | $A^{Me}$ | $P^{Me}$ | $A^{Me}$ | $P^{Me}$ | 3.50 | - | 3.76 | 3.81 | - |
| 8 | Me | J | J | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.57 | 3.57 | - | 3.84 | - |
| 9 | Me | Me | H | Me | Me | Me | Me | - | - | - | 3.73 | - |
| 10 | Me | Me | H | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.49 | 3.53 | - | 3.78 | - |
| 11 | $A^{Me}$ | Me | H | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.52 | 3.58 | - | - | 3.39 |
| 12 | Me | Me | J | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.53 | 3.57 | - | 3.79 | - |
| 13 | $A^{Me}$ | Me | J | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | Me | 3.52 | - | - | 3.86 | 3.46 |
| II.1 | Me | $CO_2CH_2Ph$ | $CO_2CH_2Ph$ | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.72 | 3.72 | - | 3.47 | - |
| 2 | Me | $CO_2Et$ | $CO_2Et$ | Me | Me | Me | Me | - | - | - | 3.57 | - |
| 3 | Me | $CO_2Me$ | $CO_2Me$ | $A^{Me}$ | $P^{Me}$ | $P^{Me}$ | $A^{Me}$ | 3.74 | 3.74 | - | 3.57 | - |

In the case of the biladiene-a, c-dihydrobromide I.13, which was cyclized [1a] to the heptamethylester of the natural occuring phyriaporphyrin III, the correct substitution pattern could be shown by three singlets at $\delta$ = 3.46 ppm (2H), 3.52 ppm (2H), and 3.86 ppm (2H) for the methylene protons of the C-12, C-2, and C-7 acetate groups, respectively.

Yours sincerely

J. Engel          A. Gossauer          H. M. Schiebel

1 a)  J. Engel and A. Gossauer : Liebigs Ann. Chem., submitted to publication.
   b)  J. C. S. Chem. Comm. 1975, 570 and 713.

2)   A. H. Jackson, G. W. Kenner, G. S. Sach : J. Chem. Soc. (C) 1967, 2045.

From Prof.Dr.G.Hägele

4000 Düsseldorf, 20.1.1976

Institut für Anorganische
und Strukturchemie
der Universität Düsseldorf

Universitätsstr. 1

Dear Professor Shapiro,

We are very sorry to bother you with two reminders for our
contribution to TAMU NMR NEWSLETTERS. We spent about three
months with moving into and setting up our facilities in some
pretty new established buildings. Finally we got the necessary
power supplies to restart our Bruker Spectrometer.

We continued looking into the properties of alkylsubstituted
phosphorous compounds: After synthesizing the ten possible
homologues $RR'P(S)Br$ (R, R' = $CH_3$, $C_2H_5$, $iC_3H_7$, $tC_4H_9$) we
measured the 60-, 100-, 220-, 270- MHz- $^1$H-NMR-spectra.
Ethylgroups and – to a lesser degree – isopropylgroups gave
rise to highly second order spectra of $ABC_3X$ and $AB_3C_3X$ type.
Spectralanalysis and simulation proved to be unusually diffi-
cult because of overlapping multipletts. $^1$H-$\{^{31}P\}$-INDOR-
spectra done under conditions used previously [1], (power in
$H_2$ stronger than necessary for NOE, about tickling range)
yielded the $\delta_P$-values for $RR'P(S)Br$. $\delta_P$ will follow the total
number of $\beta$-carbonatoms $N_c$= k+1 in
$[(CH_3)_kCH_{3-k}][(CH_3)_lCH_{3-l}]P(S)Br$ fairly linearly indicating
the $\beta$-deshielding effect. No simple correlation between the
proton chemical shift and $N_c$ was detected. But the coupling
constants $^2J_{PH}$ for the methylgroup of $CH_3[(CH_3)_kCH_{3-k}]P(S)Br$
and $^4J_{PH}$ for the t-butylgroup in $t-C_4H_9[(CH_3)_kCH_{3-k}]P(S)Br$
appears to be linearly dependend on the number of $\beta$-carbon-
atoms k.

Results:

$\delta_P \quad = \quad 66,64 + 13,77 \cdot N_c \quad (ppm); \quad rms \quad = \quad 2,1$

$^2J_{PH} \quad = -13,03 + 0,524 \cdot k \quad (Hz); \quad rms \quad = \quad 0,05$

$^4J_{PH} \quad = \quad 20,53 + 0,692 \cdot k \quad (Hz); \quad rms \quad = \quad 0,10$

Table 1:   Calculated And Experimental Values of $^{31}$P Shifts

| | $R_1$ | $R_2$ | $N_c$ | $\delta_{P_{exp}}$ | $\delta_{P_{calc}}$ |
|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | 0 | 64.60 | 66.65 |
| 2 | $CH_3$ | $C_2H_5$ | 1 | 80.73 | 80.40 |
| 3 | $CH_3$ | $i\text{-}C_3H_7$ | 2 | 93.19 | 94.17 |
| 4 | $C_2H_5$ | $C_2H_5$ | 2 | 96.36 | 94.17 |
| 5 | $CH_3$ | $t\text{-}C_4H_9$ | 3 | 105.40 | 107.94 |
| 6 | $C_2H_5$ | $i\text{-}C_3H_7$ | 3 | 110.24 | 107.94 |
| 7 | $C_2H_5$ | $t\text{-}C_4H_9$ | 4 | 122.63 | 121.71 |
| 8 | $i\text{-}C_3H_7$ | $i\text{-}C_3H_7$ | 4 | 124.05 | 121.71 |
| 9 | $i\text{-}C_3H_7$ | $t\text{-}C_4H_9$ | 5 | 135.57 | 135.47 |
| 10 | $t\text{-}C_4H_9$ | $t\text{-}C_4H_9$ | 6 | 146.64 | 144.24 |
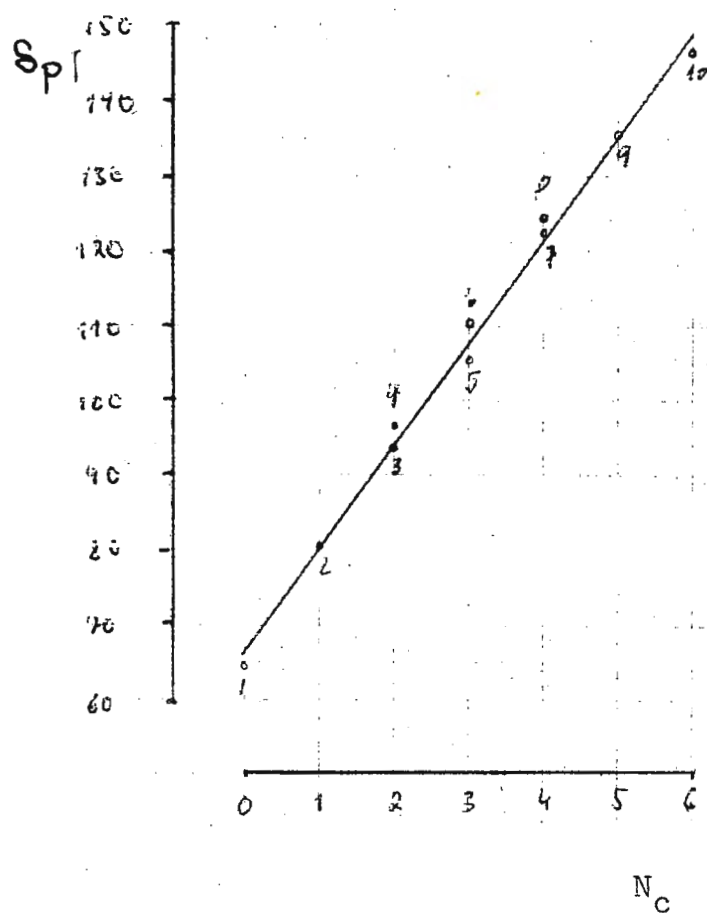
$\delta_P$ (ppm) of RR'P(S)Br vs $N_C$



$^1H-\{^{31}P\}-$ INDOR

$10\,Hz/cm$

$CH_3(iC_3H_7)P(S)Br$

Yours sincerely

G.Hägele

W.Peters

# University of Bristol     School of Chemistry

Telephone: Bristol 24161 Ext.

Cantock's Close
Bristol
England BS8 ITS

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

28th. January, 1976.

Dear Professor Shapiro,

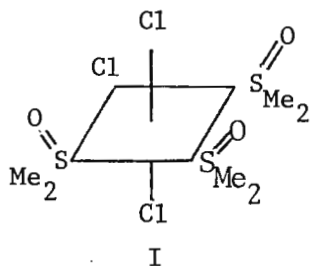### $^1H$ $^{103}Rh$   INDOR Measurements

The results of our INDOR study of $^{195}Pt$ chemical shifts in platinum(II) complexes should soon appear in J.C.S.Dalton. We are now investigating how far the same conclusions apply to platinum(IV) systems and to $^{103}Rh$ chemical shifts. The double resonance approach is particularly appropriate for $^{103}Rh$ because of its 100% abundance and low sensitivity under direct observation. Normally in our INDOR measurements, we monitor a peak maximum and scan the 'hetero' region using 'tickling' power levels. However, where $J_{RhH}$ is small ($\leqslant 0.5Hz$) we get better results observing the centre of the proton doublet and doing what is essentially a decoupling experiment (although the power levels are still low).

In general, we do not observe the small proton couplings in the $^{103}Rh$ spectrum but for $CH_3O_2CC_5H_4Rh(C_2H_4)_2$ we clearly resolved five of the nine lines due to coupling to the ethylene protons. This was particularly interesting because the proton resonance itself was a very broad hump at the temperature concerned due to coalescence of the two types of proton resonances on the ethylene ligands.

Successive replacements of chloride by bromide (or iodide) in platinum(II) complexes result in regular upfield shifts (the opposite direction to that implied by changes in the electronic spectra). This also applies to Pt(IV) and Rh(III) although changes are greater and smaller respectively. Thus in comparable situations, replacement of chloride by bromide produces changes of shift of 240, 350 and 170 p.p.m. for Pt(II), Pt(IV) and Rh(III) respectively. For platinum(II), these changes in $\delta_{Pt}$ are affected by the nature of the cis ligands as well as those in the trans position. Such cis effects are noticeably less for Pt(IV) and probably insignificant for Rh(III).

The effect of different neutral ligands does follow the sense of changes of the electronic spectra. Comparisons are not straightforward because successive replacements can result in very different changes in shift. As far as we can judge, the effects are of similar magnitude for platinum(II) and (IV) but rather larger for Rh(III) so that for the latter they predominate more over the effects of halides.

Already we have found $^{103}$Rh measurements to greatly assist the understanding of some unexpected quirks of rhodium chemistry. An example is mer $[RhCl_3(Me_2SO)_3]$ which does not show the two types of methyl group expected for structure I but the complex spectrum shown in the Figure.
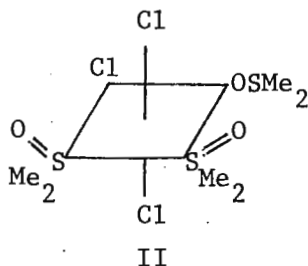


| I | II | III |
|---|---|---|
| $\Xi_{Rh}$ 3,170,990 | $\Xi_{Rh}$ 3,173,061 | $\Xi_{Rh}$ 3,175,540 |

Peaks A to D show the coupling to $^{103}$Rh expected for S-bonded DMSO (ca. 0.5Hz.), E and F are singlets with chemical shifts typical of O-bonded DMSO[1], and G corresponds to free DMSO. INDOR measurements on peaks B and D showed they were coupled to the same rhodium atom and since their intensities are approximately equal to E we assign them to structure II. INDOR measurements on C gave two rhodium resonances. To separate out the components of C, we have observed the $^1H\{^{103}Rh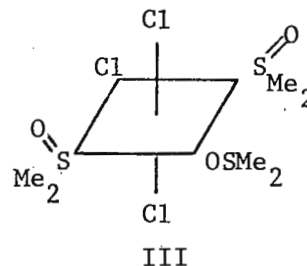\}$ spectrum at regular intervals across C. Our recently acquired Pacific Measurements model 1028A frequency synthesizer is invaluable for such experiments as the source of the audio sideband frequency for $^1H$ observation. Using the usual lock frequencies on our HA100 we can observe at switched intervals of 0.1Hz. whilst by reducing the lock frequency to approx. 1 kHz. we can use the next lower range giving intervals of 0.01 Hz. The heights of the observed $^{103}$Rh signals are plotted against $^1H$ frequency in the Figure from which we identify three resonances. From intensities and rhodium shift we assign C1 and C3 to structure I. Since C2 and F both grow with time we assign them to structure III. Having found the rhodium resonance associated with A, we subtracted (using our CAT) normal runs from those where this rhodium was decoupled. This revealed another proton signal under C. The chemical shifts ($\Xi_{Rh}$ = 3, 172, 407Hz.) and presence of free DMSO suggest a complex with some other ligand, probably water, in the place of the O-bonded DMSO in structure II.

Yours sincerely,

*Robin Goodfellow*

R.J. Goodfellow

1. J.H. Price, A.N. Williamson, R.F. Schramm and B.B. Wayland, Inorg.Chem., 1972, 11, 1280.

$^1$H Spectrum of $[RhCl_3(Me_2SO)_3]$ in dichloromethane
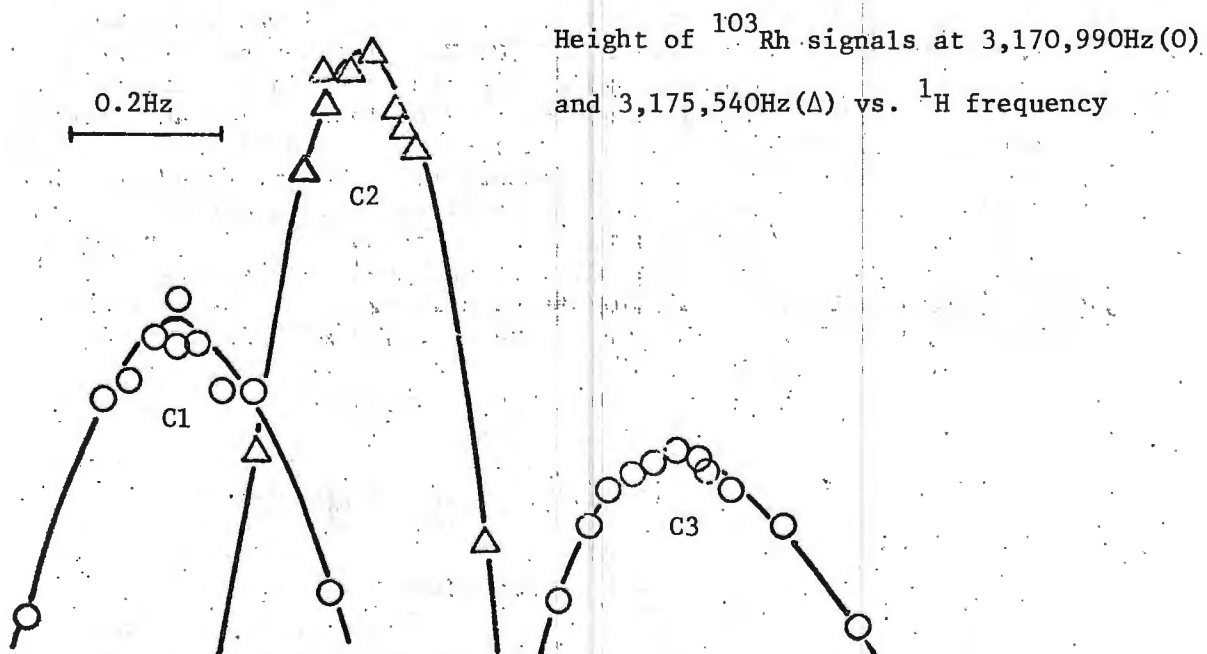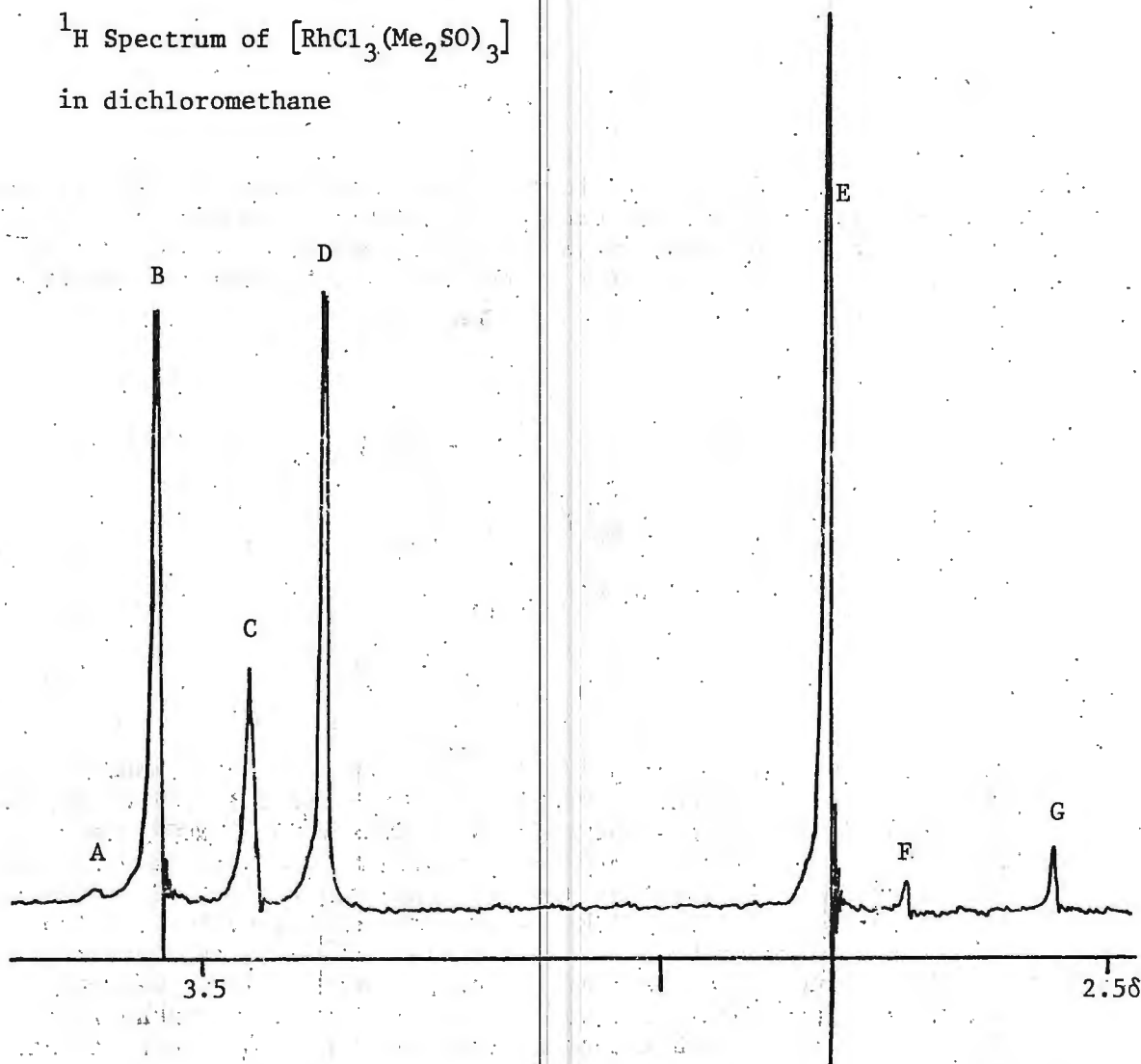


Height of $^{103}$Rh signals at 3,170,990Hz(O)
and 3,175,540Hz($\Delta$) vs. $^1$H frequency
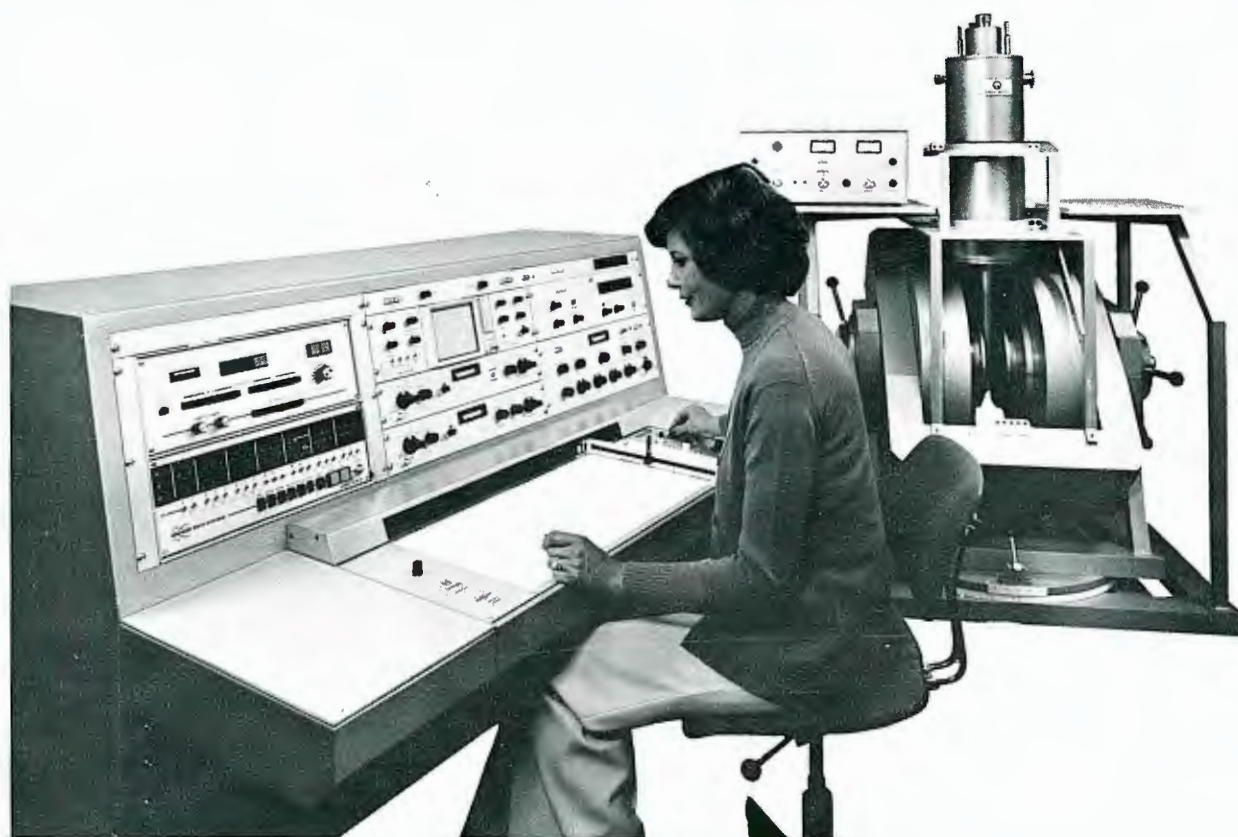
# Southern Research Institute

KETTERING-MEYER LABORATORY

2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35205
TELEPHONE 205-323-6592

February 2, 1976

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

Title: A Curious $^{13}C$ Spectrum

Dear Barry:

I have been living in daily dread of the pink notice. It has not yet arrived, so perhaps I can beat it by writing about a curious $^{13}C$ spectrum.
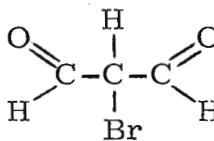


The proton-decoupled spectrum of the above compound (86 mg/0.4 ml DMSO-$d_6$) is predictable and uninteresting: $\delta\ C_1\ (C_3) = 175.98$ ppm, $\delta\ C_2 = 104.07$ ppm. The proton-coupled spectrum, however, is quite unexpected. $C_1$ and $C_3$ appear as a doublet of doublets ($^1J_{CH} = 178.2$ Hz, $^3J_{CCCH} = 1.8$ Hz). $C_2$ unexpectedly shows no $^1J_{CH}$ splitting, and appears as a triplet with $^2J_{CH} = 30.2$ Hz. The methine proton is apparently acidic enough to exchange at a rate which prevents observation of $^1J_{C_2H_2}$.

The overall pattern was the same in acetonitrile, though the chemical shifts and coupling constants were slightly different. Unfortunately, the compound is not sufficiently soluble in chloroform to determine the $^{13}C$ spectrum in that solvent.

Sincerely,

Martha Thorpe
Senior Chemist

MT/jkw

# Unilever Research

Port Sunlight Laboratory
Unilever Limited
Port Sunlight
Wirral Cheshire L62 4XN    Telephone 051-645 2000
                          Telex 627235


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


| Your ref | Our ref | EGS/KRC | Tel Ext | Date | 29 Jan 76 |

Dear Professor Shapiro

## $T_1$ STUDY OF WET NYLON FIBRES

In recent studies of chain motion in wet nylon 6.6 fibres we were able to
obtain separate $T_1$ data for 'amorphous' chain segments above their glass
transition temperature, $T_g$, by direct measurement from the FID component.



(FID for fibre above the $T_g$)          (Fibre-chain structure)
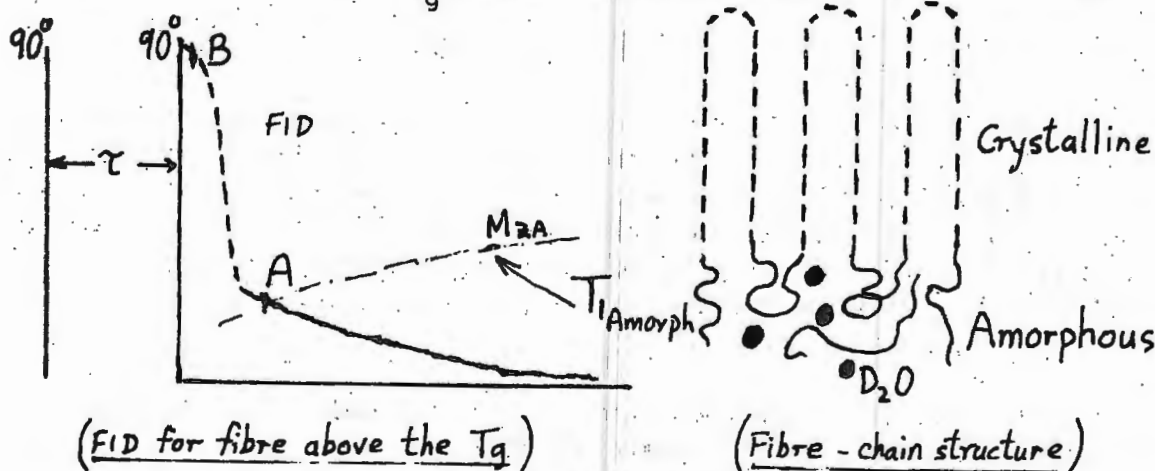
By monitoring signals at A and B using the Box-car integrator with
'gate' position fixed, (trigger with second $90°$ pulse) $M_{BA}$ for 'mobile'
(amorphous) and $M_{BB}$ (total) could be conveniently followed as $\tau$ is varied
and $T_{1\ amorph}$ and $T_{1\ rigid}$ determined. This enabled us to investigate
the influence of water ($D_2O$) molecules and $Mn^{2+}$ ions on the relaxation/
temperature behaviour for each phase. In dry fibres we found no difference
between $T_{1A}$ and $T_{1R}$ over the temperature range studied. Upon wetting
the fibres in $D_2O$, the divergence of $T_{1A}$ and $T_{1R}$, we believe results from
a reduction in efficiency of 'spin-diffusion' between 'mobile' and 'rigid'
chain segments due to the penetration of the 'plasticizing' $D_2O$ molecules
between amorphous chains in accessible regions. The $T_1$/temp curves reflect
the different mobility processes occurring in each phase.
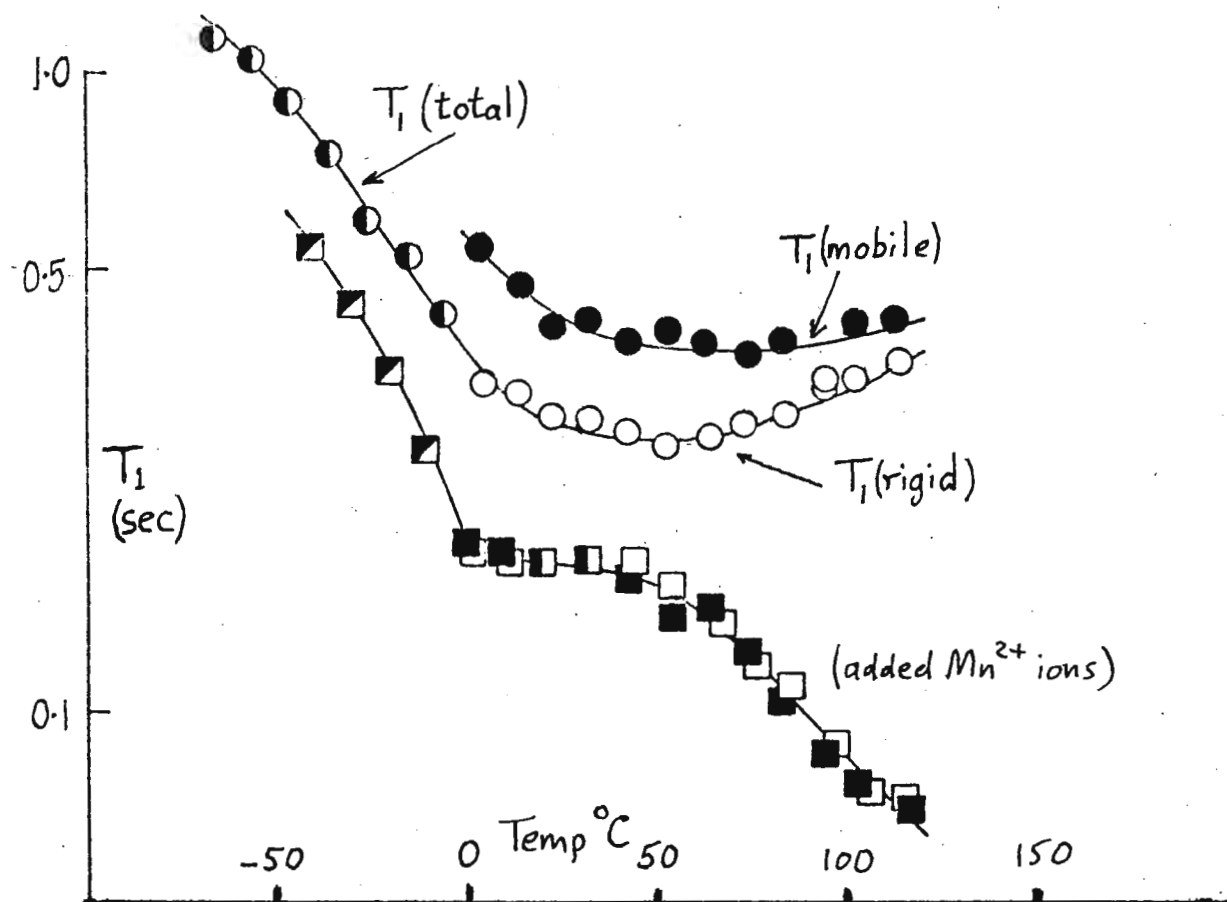
When we introduced $Mn^{2+}$ ions into the samples, paramagnetic effects determined the $T_{1A}$ and $T_{1R}$ behaviour equally; this we have discussed in terms of the penetration of these ions between chain segments close to the crystallite surface.

Yours sincerely,

*E G Smith.*

E G Smith

# LABORATORIUM VOOR FYSISCHE CHEMIE

Toernooiveld
Nijmegen
Telefoon (080) 55 88 33

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

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

Uw kenmerk          Uw brief van          Ons kenmerk

Datum January 30, 1976

Onderwerp Temperature dependence of Lanthanide Induced Shifts

Dear Professor Shapiro,

An important problem involved in the use of lanthanide shift reagents as structural probes in solution, is the determination of the fermi contact (FC) contribution to the lanthanide induced shift (LIS). One way to tackle this problem is based on theoretical predictions of the temperature dependence of pseudo contact (PC) and FC shifts. Bleaney's analysis has predicted the PC shift in $Pr^{3+}$ complexes to vary as $T^{-2}$ (1), whereas the FC shift varies as $T^{-1}$ (2).

We have measured the temperature variation of LIS in the complexes of $Pr(fod)_3$ with 1,2-dimethoxyethane (DME), 1-methoxy-2-n-octyloxyethane (MOE) and 4,5-dimethylveratrole (DMV), respectively, which all contain the binding moiety
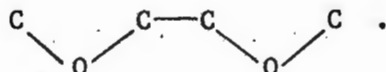


Grotens et al. found that these compounds bind bidentally. This gives rise to high binding constants ($\approx 5 \times 10^3$ $M^{-1}$) while it prevents the formation of 1 : 2 complexes and minimizes chemical exchange effects in samples where the $Pr(fod)_3$/substrate ratio is slightly higher than unity.

An example of the observed temperature dependence is shown in Figure 1, where the induced shift of the 7-protons of MOE is plotted versus $T^{-1}$.
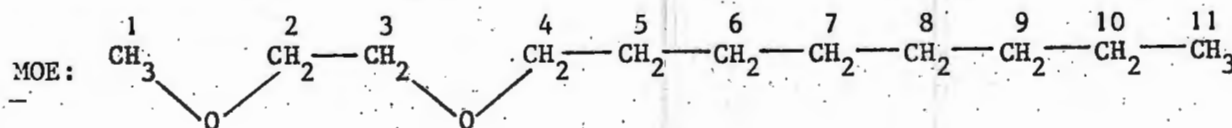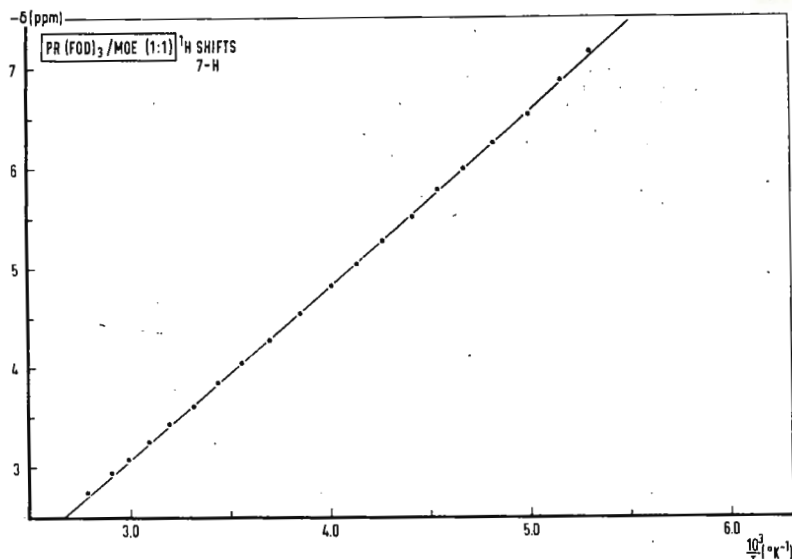
One observes, that even for these MOE protons, which are not expected to exhibit a large FC shift, the shift is almost linear in $T^{-1}$ between +75 to $-95^{\circ}C$, while the intercept at $T^{-1} \longrightarrow 0$ is large. A least squares analysis of the observed shift in terms of the relation

$$\delta = a_0 + a_1 T^{-1} + a_2 T^{-2}$$

yields similar results for all protons in DME, MOE and DMV and the $^{13}C$ nuclei in MOE: both $a_0$ and $a_1 T^{-1}$ are large but opposite in sign, whereas $a_2 T^{-2}$ is only a minor contribution. For instance, the result for the 7-protons of MOE at $31^{\circ}C$ is

$$a_0 = 1.7 \text{ ppm}$$
$$a_1 T^{-1} = -4.9 \text{ ppm}$$
$$a_2 T^{-2} = -0.3 \text{ ppm}$$

These results are completely in disagreement with the predicted $T^{-2}$ dependence. Objections against Bleaney's treatment were raised by Horrocks et al. (3) based on the observation that the ligand field splittings in rare earth complexes are not small compared to kT at temperatures normally used in NMR on liquids. The predictions of Horrocks et al., i.e. a $T^{-1}$ dependence of the shifts and non negligible $a_0$, agree qualitatively with our experimental results.

In conclusion, the present experiments demonstrate that the temperature dependence of lanthanide induced shifts cannot be used to separate the FC and PC contributions to the total shift. A more detailed discussion of our results is submitted for publication in J. Magn. Resonance.

References

1. B. Bleaney, J. Magn. Resonance 8, 91 (1972).
2. J. Reuben and D. Fiat, J. Chem. Phys. 51, 4909 (1969).
3. W. DeW. Horrocks, Jr., J.P. Sipe, III and D. Sudnick in "Nuclear Magnetic Resonance Shift Reagents", R.E. Sievers, Ed., Academic Press, New York, 1973.

Sincerely yours,

J.W.M. de Boer        C.W. Hilbers        E. de Boer

# QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

PRINCIPAL   Sir Harry W. Melville, K.C.B., F.R.S.
REGISTRAR  R. P. Tong, O.B.E., M.A.
DEPARTMENT OF CHEMISTRY

MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811

Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843,
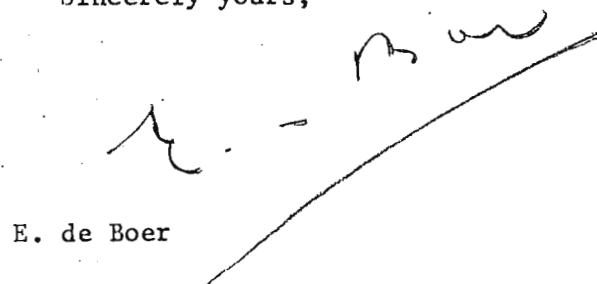U.S.A.                                                    30th January, 1976

Dear Barry,

### $^{15}N$ NMR With Off-Resonance $^1H$ Decoupling

Some readers may have seen a recent communication to J.Mag.Res.[1] in which
we briefly mentioned that problems may occur when employing "off-resonance"
CW $^1H$ decoupling for the observation of multiplicities of $^{15}N$ resonances.
The basic problem arises from the different power requirements in the $^1H$
decoupling field which are necessary, to produce an NOE effect (which for
$^{15}N-|^1H|$ experiments is negative) on the one hand, and a reduction in the
$^{15}N-^1H$ scalar coupling, on the other. The $^{15}N$ spectra shown in the figure
were obtained in this laboratory some years ago by Les Farnell (who has since
left the group) on a Bruker HFX system with the B-SV 2 decoupler unit. The
sample is $^{15}N$-enriched ammonium sulphate in sulphuric acid, and the conditions
employed were to vary the $^1H$ frequency offset from close in to the proton
doublet (spectrum a) to a large offset (spectrum f) using a constant power
for the decoupling. Spectrum g is without any second irradiation. Spectra
a-c clearly show both a reduction in the $^{15}N-^1H$ scalar coupling and the
negative $^{15}N-^1H$ NOE. While the effective deocupling powers employed for
spectra d-f were not sufficient to significantly perturb the $^{15}N-^1H$ coupling,
some very unusual intensity changes have occurred. In particular note the
nulling of the central line in spectra e, f and the double sign inversion
of line 4 between spectra c, d and d, e.

These effects have been studied in much greater detail for both $^{15}N$ and $^{13}C$
observation with $^1H$ double irradiation by Bill Litchman while visiting this
laboratory for a year (1974-1975). Some may recall the paper presented by
Alex Bain and Ruth Lynden-Bell at the St. Andrews meeting last July in which

they described a theory which they had obligingly produced to account for
the unusual intensity effects in such double resonance experiments. The
experiments and theory have been combined in two manuscripts currently in
preparation.

Best wishes from Ed.

Yours sincerely,

Dr. G.E. Hawkes.

[1]G.E. Hawkes, W.M. Litchman and E.W. Randall, J.Mag.Res., 19, 255 (1975).
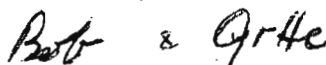
## POSTDOCTORAL POSITION AVAILABLE

Dear Barry

A postdoctoral position for a physical chemist is available in our laboratory, starting September 1976. The research is aimed at distinguishing effects of molecular size and shape from those of attractive intermolecular forces in liquids. This will involve measurements of $^{13}C$, $^{2}H$, $^{14}N$ and $^{17}O$ in a variety of small rigid molecules and use of standard descriptions of "effective correlation times" for anisotropic motion. In addition, opportunities exist for analyzing spin lattice relaxation of strongly coupled proton spin systems in order to use the effects of cross correlation between different dipolar interactions to obtain information about molecular motion (cf. J. Chem. Phys. 64, 900 (1976)).

Qualified candidates should contact us as soon as possible.

Best Regards

Robert L. and Regitze R. Vold
Department of Chemistry
University of California, San Diego
La Jolla, CA  92037

February 6, 1976
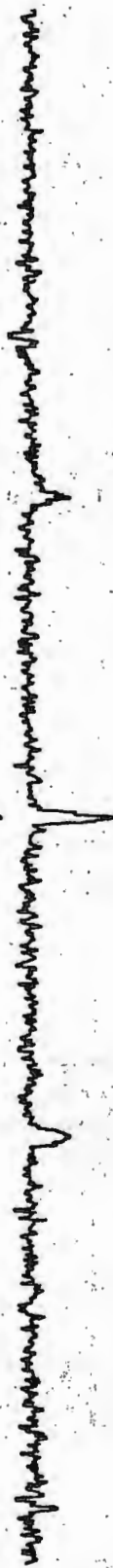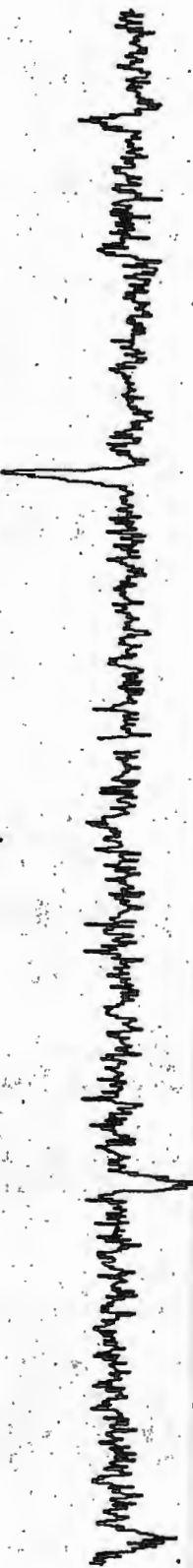
# NAVAL RESEARCH LABORATORY

### WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6120-40:WBM:mjt

10 February 1976

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

Title: Low Cost Video Terminal

Dear Barry:

Much of the interplay between the operator and the computer in an FT system consists of trivia of which no permanent record is required. In the process, a good deal of teletype running time and paper are consumed. A low cost solution to this problem has come to our attention. It is the "TV Typewriter", or video terminal, written up in the February 1975 Radio Electronics Magazine. Southwest Technical Products Corporation* (219 W. Rhapsody, San Antonio, Texas 78216) sells kits based on the terminal. The terminal works in conjunction with a slightly modified portable television set.

We purchased the terminal system, keyboard and encoder, manual cursor control, power supply, and UART serial interface (RS-232 compatible), for a total cost of under $300. Our NIC-80 is equipped with the dual teletype board. The video terminal uses the RS-232 port. Standard baud rate is 110, but we obtained the additional parts to add to the terminal's serial interface board which allow rates up to 1200 baud.

The terminal does have some limitations: a maximum of 32 characters per line x 16 lines (one page) may be displayed at a time from the two pages of terminal memory. The keyboard does not have particularly good action. And the builder has to supply some sort of chassis and frame to hang everything on.

The terminal has operated successfully with the NIC-80. We are now debugging the software which will cause the FT program to respond to whichever device flags it. We will be happy to supply Newsletter subscribers with the software when it is ready.

Sincerely,

C. F. Poranski, Jr.      W. B. Moniz

*Reference to a company or product name does not imply approval or recommendation of the product or services by any agency of the U. S. Government to the exclusion of others that may be suitable.

# Nicolet News

# Nicolet Announces A New, *Complete System* For Fourier Transform Infrared Spectroscopy To Be Demonstrated At Pittsburgh Conference

MADISON, Wis.—Nicolet Instrument Corporation (a leader in Fourier Transform NMR Spectroscopy) has acquired the Infrared Interferometer product line of EOCOM Corporation.

This means that, for the first time, one company manufactures both the interferometer *and* the data system. This combination of capabilities has produced a complete Fourier Transform Infrared Spectrophotometer instrumentation system for basic analytical or routine laboratory work.

The system contains automatic ratio recording with better than $0.07$ cm$^{-1}$ resolution throughout the spectral range of 4000 to 400 cm$^{-1}$. It includes a Michelson interferometer with germanium on KBr beam splitter, laser reference and white light reference system, and variable mirror drive rates of 0.05 cm/sec to 4 cm/sec. It has a total optical retardation length of 16 cm and a nominal aperture of 2" diameter. Options are available for operation in the visible, near and far infrared regions, and for operations with a cooled detector.

Information is collected, processed and displayed from a Nicolet 1180 data system having 40K words of solid state, 20-bit memory storage, dual 4.8 megaword disk memory, a high speed digital plotter and CRT display.

Some major features of this data system are its 15-bit analog-to-digital converter (ADC) with automatic gain ranging, the ability to plot while processing and/or acquiring, the ability to collect and transform up to 512K data points, an optimized instruction set for fast Fourier transformations, and a very complete software package. An option is available to replace the data system with an ADC interfaced to a 9-track magnetic tape system and a complete Fortran software package for an IBM 360 system.

# Nicolet Technology Announces Fourier Transform Mass Spectrometer

MOUNTAIN VIEW, Calif. — Nicolet Technology Corporation, which previously specialized in interfacing data systems to nmr spectrometers, has announced plans for a new, high resolution Fourier Ion Resonance Mass Spectrometer called FIRMS. Capable of working with samples of lower volatility than usable in conventional mass spectrometers this new spectrometer offers greatly improved resolution and sensitivity along with the ability to examine higher molecular weight compounds. Since Fourier transform ion resonance spectroscopy detects the entire spectrum at once, rather than one element at a time as in the conventional scanning spectrometer, a given spectrum may be obtained 100 to 1000 times faster. Because of this speed the chemist can observe ion-molecule reactions.

# More Details Offered

MADISON, Wis.—For details on the FT-IR System please write or phone Nicolet Instrument Corporation, 5225 Verona Road, Madison, WI 53711, Phone: 608 / 271-3333. For information on the FT Mass Spectrometer please write or phone Nicolet Technology Corporation, 145 East Dana Street, Mountain View, CA, 94041, Phone: 415 / 969-2076.

# VI INTERNATIONAL SYMPOSIUM ON MAGNETIC RESONANCE

# VIᵉ SYMPOSIUM INTERNATIONAL SUR LA RÉSONANCE MAGNÉTIQUE

BANFF, ALBERTA, CANADA
MAY 21-27 MAI 1977

Please address correspondence to/Veuillez adresser correspondance à:
R. W. Dolan, Executive Secretary, VI International Symposium on
Magnetic Resonance, c/o National Research Council of Canada,
Ottawa, Canada K1A 0R6

February 3, 1976

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Comité national

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  Co-président

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

The 6th International Symposium on Magnetic Resonance

Dear Barry,

    This is to officially announce the title symposium which will
be held in the Banff Springs Hotel, Banff, Alberta, May 21-27, 1977.

    The first bulletin regarding this symposium has been mailed
out during the last week of January.  Anyone who is interested, but
who has not received that bulletin # 1 is requested to write to:

        Mr. R.W. Dolan
        Executive Secretary
        VI International Symposium on Magnetic Resonance
        Office of International Conferences
        National Research Council
        Ottawa, Ontario
        Canada    K1A 0R6

    With thanks for opening the TAMU-NMR Newsletter pages for this
kind of contribution (non-countable, of course).

                                        Best regards,

                                        F.H.A.   Rummens, D.Sc.
                                        Professor

FHAR:11

F. H. A. Rummens
Dept. of Chemistry
University of Regina, REGINA, S4S 0A2
Canada (Tel. 306-584-4259)

J. A. Weil
Dept. of Chemistry and Chemical Engineering
University of Saskatchewan, SASKATOON, S7N 0W
Canada (Tel. 306-343-3240)

# UNIVERSITY OF CALIFORNIA, SANTA BARBARA

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO          SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106
February 17, 1976

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

"Molecular Motion in Sephadex G75"

Dear Barry:

Various commercially available cross-linked dextrans (Sephadexes) have been
used for a number of years as supports for the immobilization of proteins.  As
part of a study of polysaccaride-enzyme conjugates we recently examined the
carbon-13 spectrum of Pharmacia's Sephadex G-75.  According to the manufacturer
this gel is formed by cross-linking dextran of 70,000 molecular weight with
epichlorohydrin.  The carbon spectrum of Sephadex G-75 at 38°, obtained with a
Varian CFT-20, consists of six major lines corresponding to the six carbon atoms
of the glucose monomer units of the polysaccharide chains.  The approximate chemi-
cal shifts of these peaks and their spin-lattice and transverse relaxation times
are given in Table I.  The relaxation data, coupled with an estimate of the nOe
on the signals (~2), allows an estimate of the correlation times for nuclear
motion in the gel.

Assuming the applicability of the Woessner equations,[1] we searched for values
of $\tau_c$, the overall correlation time of the molecule, and $\tau_i$, the correlation
time characteristic of internal rotation, that would reproduce our $T_1$, $T_2$ and
nOe data.  Only when $\tau_c = 12 \pm 2$ nsec and $\tau_i = 0.4 \pm 0.05$ nsec could one obtain
reasonable agreement with experiment for all three observables.

While it is not completely clear that the model used for Woessner's equations is
appropriate to the present case, it does appear that large domains of the gel
undergo a relatively leisurely reorientation ($\tau_c$) while the individual glucose
units rotate rapidly about an axis parallel to the polymer chain.

Sincerely yours,

A. J. Benesi
Postgraduate Research Chemist

J. T. Gerig
Associate Professor

[1] D. E. Woessner, J. Chem. Phys., 36, 1 (1962).

TABLE I

Carbon-13 NMR Data for Sephadex G-75

| Carbon | $\delta$, ppm[a] | $T_1$ msec | $T_2$, msec |
|--------|-----------|-----------|------------|
| $C_1$ | 98.0 | 70 | |
| $C_2$ | 73.8 | 61 | |
| $C_3$ | 71.8 | 60 | ~25 |
| $C_4$ | 70.5 | 60 | |
| $C_5$ | 70.0 | 61 | |
| $C_6$ | 65.9 | 33 | 20 |

[a] Chemical shifts in ppm downfield from TMS; ± 0.2ppm.
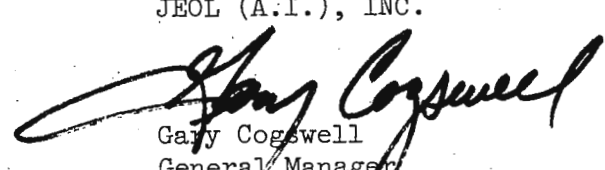
---

Dear Dr. Shapiro:

We are pleased to announce the opening of two positions for employment in JEOL (A.I.), Inc. The first is a technical sales/applications position in the Cranford Application and R & D Laboratory. The second is a field sales position in the Midwest.

Persons interested in either of these positions should contact:

Mr. Robert Martin
JEOL A.I., INC.
235 Birchwood Avenue
Cranford, New Jersey 07016
(201) 272-8820

Sincerely,

JEOL (A.I.), INC.

Gary Cogswell
General Manager

Professor L.W. Reeves
UNIVERSIDADE DE SÃO PAULO
## INSTITUTO DE QUÍMICA
CIDADE UNIVERSITÁRIA - CAIXA POSTAL, 20.780
SÃO PAULO — (BRASIL)

February 4, 1976.

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

Dear Barry:

### Nuclear Quadrupole Couplings for Deuterium from Spectra
### of Oriented Molecules

The reason for the excessive delay in providing a letter for
TAMUNMR is linked with the mail strike which occurred in Canada, my lack of sec-
retarial help and the geographical location.  This contribution is thus necess-
arily late.  I have asked the home base in Waterloo to use letterhead from here
to round out the more exotic addresses you publish.

I annex a deuterium spectrum of oriented methanol taken by Douglas
Chen sometime ago and included in his thesis at Waterloo (July 1975).  The analysis
previously made by Emsley, Lindon and Tabony (1973) gives the spacings shown in
the figure for the dipole-dipole coupling between deuterium nuclei.  Six peak
separations give a best average value for D of 2.7±0.4Hz.  Derived from the same
spectrum the deuterium quadrupole coupling constant is obtained via an assumed
geometry.  Using the angle D-C-D as 109°2', a CD bond length of 1.10A and the
quadrupole doublet splitting measured leads to a quadrupole coupling constant
($\eta=0$ assumed) of 150±22KHz.  The large uncertainty is a result of the small mag-
nitude of the dipole-dipole coupling.  A second measurement using a mixture of
$CD_3OH$ and $CH_3OH$ dissolved in the same lyotropic medium uses the dipole-dipole
coupling between methyl protons to determine appropriate order parameter via the
geometry, and then the deuterium quadrupole doublet gives the quadrupole coupling
constant.  The result we obtained was 125±1KHz.  The large systematic but low
random error shows up immediately.  A reasonable value is near 170KHz.  The chief
problem in the direct measurement from the same deuterium spectrum is the precision
with which the small dipole-dipole coupling constant can be measured.  Nematic
solvents which impose higher degrees of order would help, but paying the price of
a 36 fold decrease in magnitude of the dipole coupling which determines order para-
meters seems too large.  In a rigid molecule of course one can determine order
parameters from protons and use these to determine a quadrupole coupling in a
selectively deuterated position from a known geometry.

I am prompted to these remarks by reading on January 22 the J.
Mag. Resonance of September 1975 (just arrived) the short comment of Deihl and
co-workers on the same subject.

Kind regards from the Tropic of Capricorn.

L.W. Reeves.

for
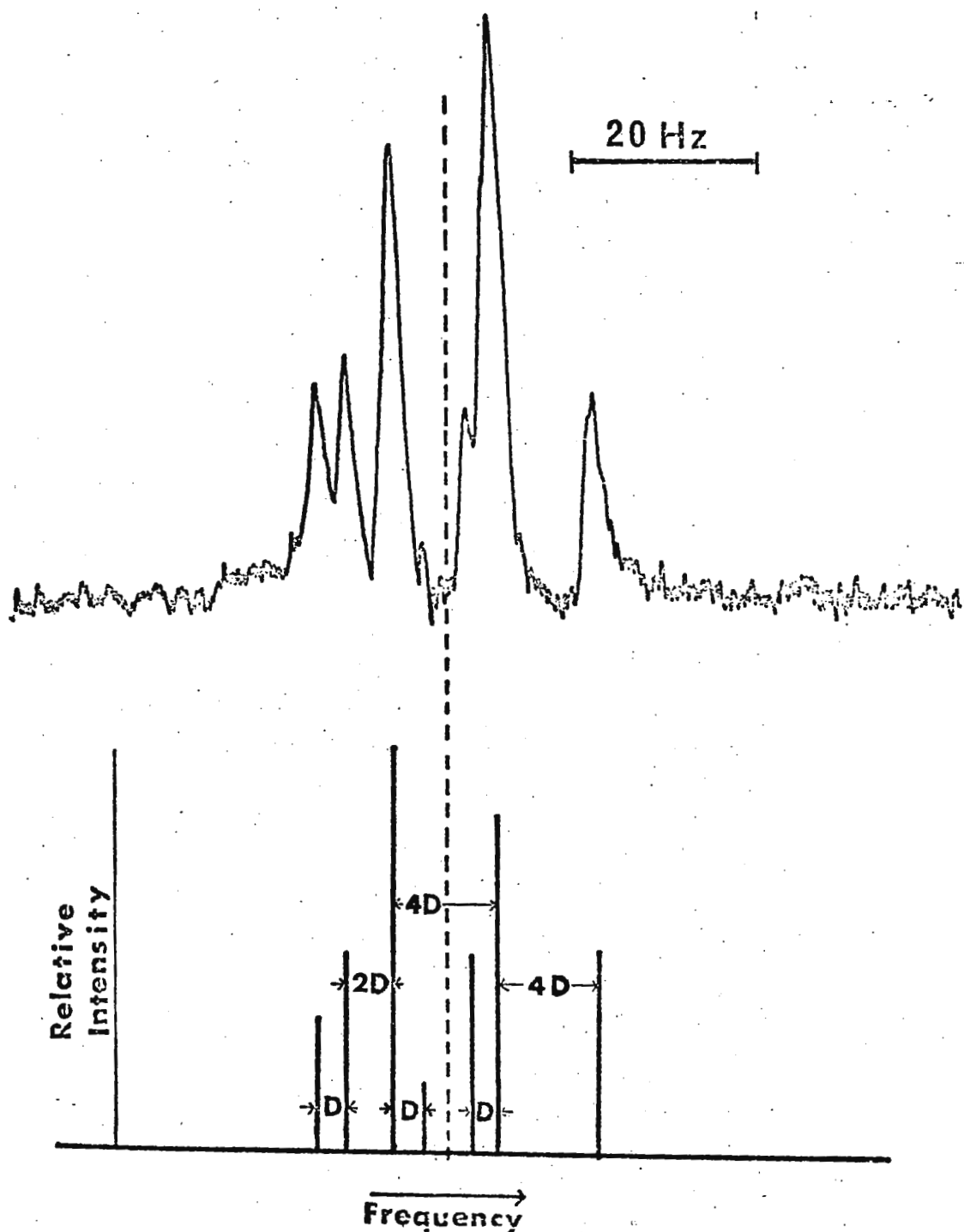
Top figure:  High frequency half of the $^2$D doublet due to the methyl deuterons of oriented methanol.  The spectrum was obtained by the pulse method with 512 scans after the sample was left spinning overnight in the magnet.  Bottom figure:  Predicted spectrum for a $-CD_3$ group when the quadrupole coupling and the deuteron-deuteron dipole coupling terms are of opposite sign.  The dotted line indicates the position of the $^2$D quadrupole doublet in the absence of dipole splitting.

# University
# of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL  Tel: 041-552 4400

6th February, 1976

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

Dear Barry,

Here are the results of some preliminary experiments that
have recently been obtained here on the proton n.m.r. spectrum of
water in the outermost layer of skin (the stratum corneum).
Samples of this layer ($\sim$20 microns thick) separated from samples
of human skin removed at autopsy were suspended on a glass frame
that allowed reasonably accurate alignment of the sample at any
chosen angle to the magnetic field.  Under these conditions spectra
obtained by FT methods (JEOL PS100 – PFT 100, typically 100 pulses)
showed two peaks (A and B) clearly due to water (both removed by
drying, reappearing on standing in humid air), and a third peak (C)
which is probably due to more firmly bound water.  Peaks A and B
had half widths of $\sim$ 150 Hz and $T_1$'s of 0.35 and 0.42 secs
respectively.   Peak C was much broader and had $T_1$ $\sim$0.2 secs
and can only really be seen properly when the A and B peaks are
removed by drying.   The three peaks have different chemical
shifts and peak A is interesting in that its position is dependant
on the orientation of the sample, being   600 Hz to low field of B
when the plane of the sample is at right angles to the field and
600 Hz to high field when the sample is parallel to the field.  The
plot of shift against angle is sinusoidal.  This effect, possibly due
to chemical shift anisotropy, could indicate that one of the types
of water has restricted freedom of translational or rotational
motion (or both).   Further work on this intriguing phenomenon
is in hand.

Yours sincerely,

P. Bladon        M. I. Foreman.

# University of Wisconsin ⚞✹⚟ Madison

**CENTER FOR HEALTH SCIENCES**
**School of Pharmacy**
425 North Charter Street
Madison, Wisconsin 53706
Telephone: 608/262-1416

March 3, 1976

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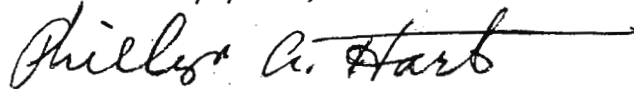Texas A and M University
College Station, Texas   77843

Dear Professor Shapiro:

### Phosphorus-Proton Nuclear Overhauser Effects

I have been working for some time to adapt the phosphorus-proton
NOE (see P. L. Yeagle, W. C. Hutton and R. B. Martin, JACS, 97, 7175
(1975)), to the conformational analysis of phosphorus-containing co-
enzymes, nucleotides and oligonucleotides and have had some success
with ATP and thiamine pyrophosphate.  As has been demonstrated time-
and-again good phosphorus NMR requires the rigorous exclusion of para-
magnetic impurities and that includes oxygen.  Thus, all glassware
must be soaked in basic EDTA and solutions must be treated with Chelex
(column percolation preferred) then the final solution must be degassed.
This seems to be the best protocol, though I haven't tried bubbling $H_2S$
through the solutions as Ian Smith suggested recently.  Extraction
procedures (e.g., dithizone in $CCl_4$) give variable results at best and
are difficult to carry out on the rather small quantities of aqueous
solutions ordinarily encountered.  One loses critical information if
maximum precautions are not exercised.  The very important enhancements
(see Table) of the terminal phosphorus of both ATP and thiamine pyro-
phosphate are nearly completely lost if oxygen is not removed and, of
course, no enhancements are seen at all if paramagnetic metals are
present.

| Compound | Irradiation Mode | %Enhancement $\alpha$P | $\beta$P | $\gamma$P |
|---|---|---|---|---|
| ATP | broad-band | 65 | 17 | 26 |
| Thiamine PP | broad-band | 49 | 33 | |

Sincerely yours,

Phillip A. Hart

PAH:is

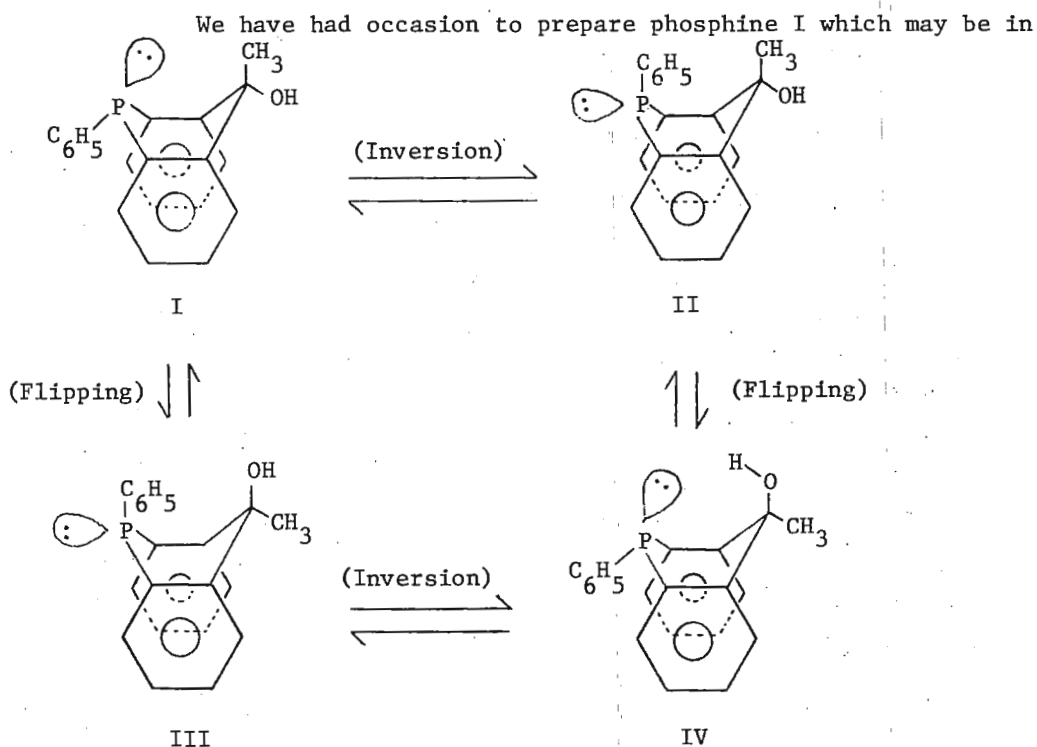# Oklahoma State University

*Department of Chemistry / (405) 372-6211, Ext. 7215 / Stillwater, Oklahoma 74074*

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

February 12, 1976

Dear Barry:

### Flipping of Phosphaanthracene Systems

We have had occasion to prepare phosphine I which may be in



equilibrium with phosphine IV.  In $HCCl_3$ at R.T., a doublet appears for the
methyl protons which coalesces to a singlet at $-20°$.  In benzene a doublet of
doublets are visible at R.T. .  Irradiation of phosphorus leaves a doublet
which suggests two conformers.  This novel strained system apparently has only
two major conformers, and we suspect III and IV as being strained and in low
concentration.  Efforts are in progress to separate out the energetics for the
individual steps, flipping versus inversion.  I trust this will serve as our
contribution.  Best regards.

Sincerely yours,

*Darrell*

K. D. Berlin
Regents Professor

KDB:pjp

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH

NATIONAL INSTITUTE OF
ENVIRONMENTAL HEALTH SCIENCES
P.O. BOX 12233
RESEARCH TRIANGLE PARK. N.C. 27709

February 19, 1976

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

Dear Dr. Shapiro:

The Chemistry Section of this Institute within the Environmental
Biology and Chemistry Branch is looking for suitable applicants
(one or possibly two positions) who are eligible for sabbatical
leave and qualified to accept a Visiting Appointment for one to
two years at this Institute in the general areas of bioorganic
and bioinorganic chemistry. We are particularly interested in
the application of these approaches to the study of environmental-
biological chemistry problems using NMR as a primary tool.

One Visiting Scientist would aid in establishing the use of $^{13}C$
enriched compounds as a complement to $^{14}C$ labeled compounds for
studying the biological interactions and reactions of diverse
environmental agents. Consideration for appointment would receive
immediate attention, and the salary would be open depending on the
qualifications, experience and desire of a suitable applicant. We
presently have a Varian XL-100 NMR spectrometer.

Interested persons should write to me as soon as possible enclosing
a Curriculum Vitae and bibliography.

Sincerely,

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

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT · ISRAEL          רחובות · ישראל

ISOTOPE DEPARTMENT                February 17, 1976                מחלקת איזוטופים

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

Dear Barry:

We have been interested for some time in <u>aqueous lanthanide shift reagents</u>.  As
is well known, the use of the trivalent lanthanide ions is restricted to the
acidic side of neutral pH due to hydrolysis and precipitation of hydroxides at
higher pH values.  The EDTA chelates, however, can be used as shift reagents for
a variety of ionized substrates over a sufficiently wide pH range.  Particularly
large shifts were obtained for the anions of salicylaldehyde and of <u>ortho</u>-
nitrophenol.  For example, with PrEDTA at $\rho = 2.32$ the proton ortho to the
hydroxyl in salicylaldehyde is shifted downfield by more than 21 ppm.  With the
potentially chelating ligands the internal shift ratios are different for
lanthanides, suggesting that the system is devoid of axial symmetry.  Also line-
broadening effects are observed arising from the modulation by chemical exchange
of the shift difference between complexed and uncomplexed substrate molecules.
These broadenings are reduced at higher $\rho$ values.

Our NMR equipment will be augmented in the near future, <u>inter alia</u>, with a Bruker
WH-270.  Those among the Newsletter readers who wish to spend their sabbatical
with us are welcome to contact Prof. Zeev Luz or me at the above address.

Sincerely,

Jacques

Jacques Reuben

# RUTGERS UNIVERSITY *The State University of New Jersey*

February 7, 1977

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

## $^{13}$C NMR Studies of P(V) Compounds

Dear Barry:

Bradley Campbell prepared some unique P(V) compounds by the reaction of various phosphites and dimethyldioxetane. I embarked on a study of their $^{13}$C nmr spectra in the hopes that we might gain some insight into the structure of these molecules. All I can say is that we find the data interesting but they do not uniquely establish the compounds structures. These molecules are all undergoing rapid, on the nmr time scale, permutational isomerization.

We are thrilled with our new phosphorus capability for the CFT- 20 — one hour after it arrived we were on the air.

Sincerely yours,

*Dorothy*

Dorothy Z. Denney



4
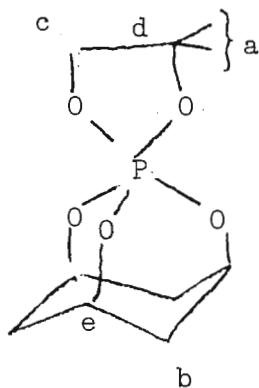
| | |
|---|---|
| a | 26.93 (6.7) |
| b | 34.47 (3.8) |
| c | 69.14 (4.4) |
| d | 75.90 (7.1) |
| e | 78.72 (6.4) |



5
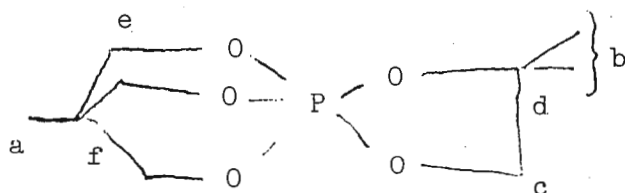
| | |
|---|---|
| a | 13.73 |
| b | 26.58 (6.6) |
| c | 68.10 (4.7) |
| d | 72.76 (3.8) |
| e | 77.29 (6.2) |
| f | 78.81 (5.8) |

δ

## 1



$(CH_3O)_3P$ with structure, labels a, b, c, d
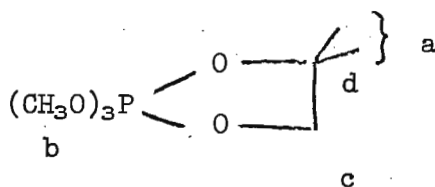
a   26.43 (6.1)

b   54.78 (10.5)

c   69.80 (2.9)

d   73.66

## 2



Structure with OCH₃ (b), labels a, c, d, e
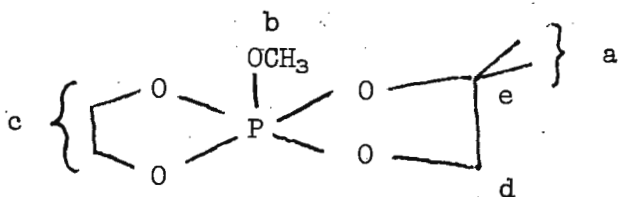
a   26.54 (6.9)

    26.81 (4.0)

b   54.81 (9.2)

c   58.74 (5.6)

    61.31 (3.7)

d   70.01 (4.5)

e   74.60 (2.8)

## 3



Structure with OCH₃ (b), labels a, c, d, e, f, g
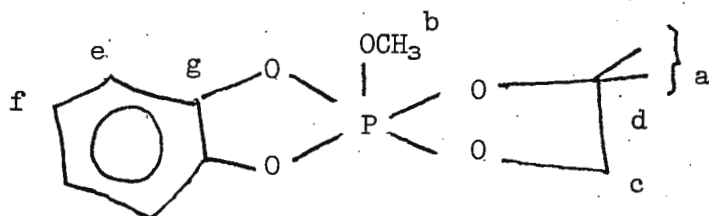
a   26.30 (7.5)

    26.62 (5.3)

b   55.63 (9.6)

c   70.40 (4.3)

d   76.30 (3.0)

e   109.74 (12.8)

    110.54 (14.4)

f   120.17

    122.22

g   142.26 (broad)

    144.42 (broad)

# University of Nottingham

Department of Chemistry

UNIVERSITY PARK NOTTINGHAM NG7 2RD
TEL. NOTTINGHAM 56101

HB/PS                                    9th February, 1976.

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

Dear Professor Shapiro,

### Equivalence and Non-Equivalence

In your issue No.206 (just received) Dr. DePuy describes
the lanthanide-induced non-equivalence of methoxy proton signals
(4 signals seen) in the four isomers of

$$CH_3CH(D)CH(CH_3)CH(CH_3)OCH_3 \qquad (1)$$
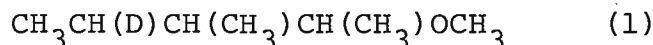
I believe that <u>no special explanation is required for this
observation.</u>  We have known for some time that methylene
protons some distance from a single chiral atom may be non-
equivalent, due to their possessing a different environment,
averaged over the conformations involved.  Similarly, in threo/
erythro type stereoisomers, e.g. (2) and (3), reference to the
conformations involved (e.g. by Newmann projection) shows that
it is unlikely that the averaged environment of $H_A$ (or $H_B$) will
be identical to that of $H_C$ (or $H_D$).
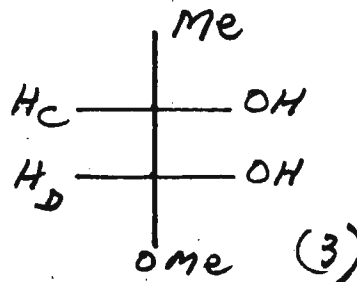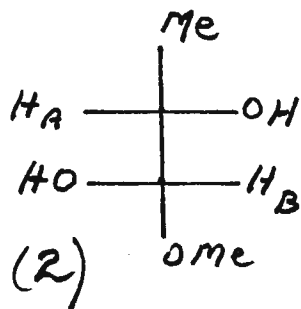


Further, the environment of the methoxy hydrogens in the
four diastereoisomers of (1) is <u>not</u> the same, and therefore
different chemical shifts are to be expected, although the
differences may be small.  Any alteration in the size or shape
of the methoxy, e.g. by complexation with an interactive solvent
or shift reagent, will clearly alter magnetic properties, leading
to enhanced (or diminished) chemical shift differences.  In a
chiral environment, e.g. optically active solvent or shift
reagent, <u>eight</u> methoxy signals are possible for (1), in theory.

Differences in chemical shift between corresponding nuclei in threo/erythro isomers have been observed without recourse to shift reagents. A couple of years ago we noted differences in $^{13}C$ chemical shifts between most carbons in (4) and their counterparts in (5).



(4)



(5)
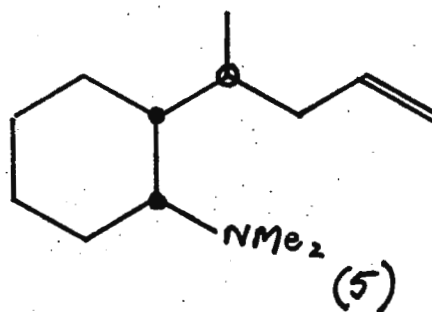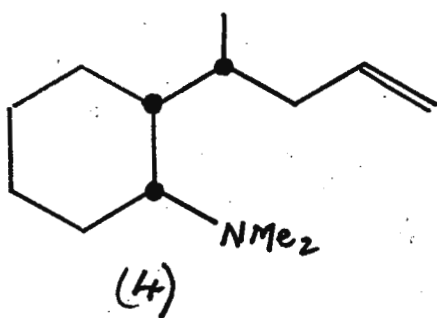
In all such cases, I maintain that non-equivalence is to be expected; indeed, it is, in general, equivalence which requires to be explained,* rather than non-equivalence!

Yours sincerely,

*Harold Booth*

Dr. H. Booth

---

* The explanation is usually either

(a) sheer coincidence; or

(b) identical environment (e.g. the methine hydrogens of meso-tartaric acid, which has one centrosymmetric conformation and two enantiomeric conformations.)

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

CH-8006 Zürich,
Universitätstrasse 16   February 18th, 1976
Tel. (01) 32 62 11

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

Integrated Line Intensities in FT Spectra

Dear Professor Shapiro,

Recently it has been shown that digitalisation may introduce large errors
in both signal height and integral [1]. For Lorentzian lines the magnitude
of these errors depend highly on the relative digital resolution, which
may conveniantly be expressed as the ratio between the absolute digital
resolution R (the frequency spacing between succesive data points) and
the true line width $\nu_{1/2}$ (full width at half height). If integration is
performed by simple summation of the measured values, the error in the
integral arises predominantely from the linear interpolation between the
measured values inherent in the integration by summation. The value found
for the integral will have its highest value, if the true line maximum
coincides with a data point. If the true line maximum falls exactly in the
middle of the interval between two data points, a minimal value for the
integral will be found.

We have estimated minimal and maximal integrated intensity for Lorentzian
lines as a function of the relative digital resolution $R/\nu_{1/2}$ under the
assumption, that no other error sources contribute to the result. The
results are summarised in Table 1. From these results it can be seen, that
for a relative digital resolution of 2 (e.g. true line width 0.6 Hz, data
points every 1.2 Hz) the integrated intensity may have an error of up to

± 10 %. To keep the errors in integrated intensity arising from the discussed source of errors below 1 % the (absolute) digital resolution should be equal or less than the true half width of the signal, i.e. there should be at least one data point per half width of the signal.

Table 1. Minimal and maximal integrated intensity as a function of the relative digital resolution.

| Relative digital resolution $(R/\nu_{1/2})$ | Integral intensity (% of true value) | |
|---|---|---|
| | maximum | minimum |
| 0.5 | 100.2 | 100.2 |
| 0.75 | 100.3 | 100.2 |
| 1.0 | 100.7 | 99.9 |
| 1.5 | 103.7 | 97.3 |
| 2.0 | 110.3 | 91.8 |
| 2.5 | 119.6 | 84.8 |
| 3.0 | 130.3 | 77.5 |
| 4.0 | 156.2 | 64.5 |

Yours sincerely

J. T. Clerc                    E. Pretsch

[1] H. P. Kellerhals, TAMU NMR Newsletter, 184, 28 (1974).

# JEOL

ANALYTICAL INSTRUMENTS, INC. • 235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016
INSTRUMENTS and APPLICATIONS CENTER • (201) 272-8820
TELEX NO. 13-8840

February 24, 1976

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

Dear Professor Shapiro,

## STACKING OF SELECTIVE HETERO-DECOUPLING EXPERIMENTS WITH THE DUAL $^{13}C/^1H$ PROBE

Further software updates for the JNM/FX-60 now permit computer stacking of selective decoupling experiments. With minimal hardware modification, up to 20 decoupling frequencies may be selected to the nearest 10Hz. Automatic, unattended operation is now possible for pre-selected computer control of both homo and hetero narrow-band decoupling frequencies.

Selective hetero-decoupling allows the full utilization of proton spectral information for rapid, unambiguous iden-tification of carbon peaks. Utilizing the dual frequency $^{13}C/^1H$ probe, proton decoupling frequencies can be read directly from the CRT display. Since probe change is not necessary, set-up is accomplished in a few minutes.

The insert on the accompanying figure shows the proton spectrum of ethylcrotonate. Points A through E show the five frequencies chosen for selective hetero-decoupling. After switching to carbon observation, the lower trace was acquired (noise decoupling) with 60 dB power. The mode was then changed to selective decoupling and power reduced accordingly. The five other spectra were automatically obtained overnight.

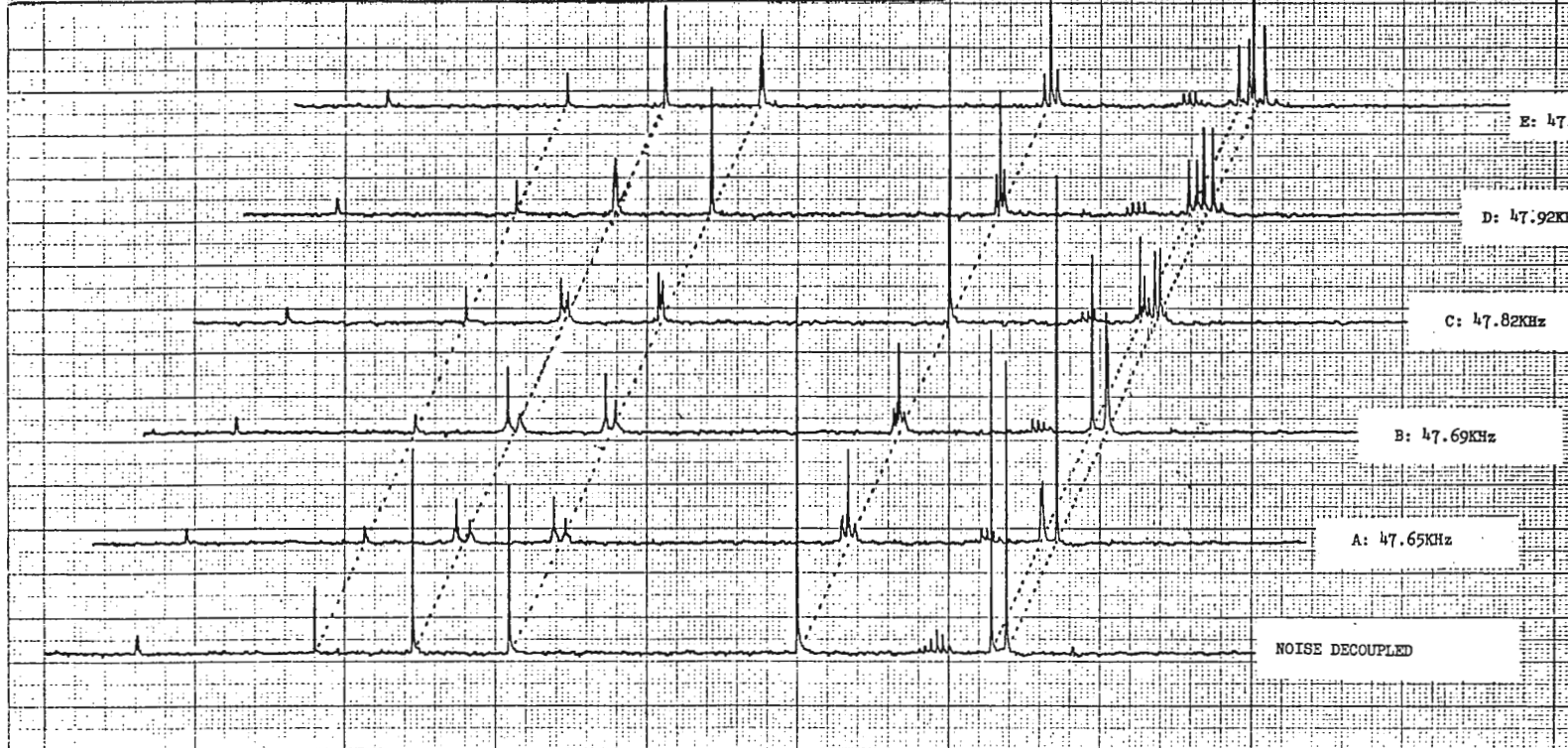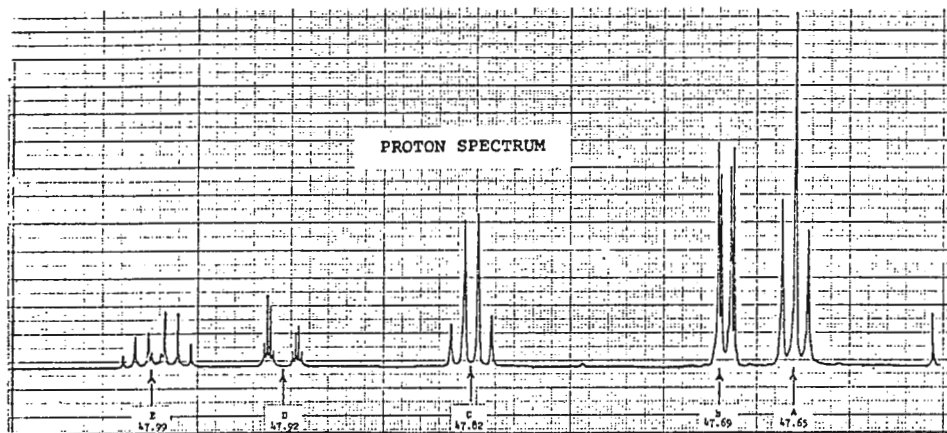Sincerely yours,

K. Goto          Dr. Ralph H. Obenauf          N. Odan
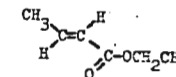
RHO/nc
Enclosures
**JEOL**      *"Bringing the Scientist Tomorrow's Capabilities Today."*

PROTON SPECTRUM

E 47.99  D 47.92  C 47.82  47.69  A 47.65

FX-60
CHART NO. ____
SAMPLE

Ethyl Crotonate

CH₃     H
  C=C
H     C-OCH₂CH₃
    O

E: 47.99KHz
D: 47.92KHz
C: 47.82KHz
B: 47.69KHz
A: 47.65KHz

NOISE DECOUPLED

SOLVENT/tube 10 mm
CONCENTRATION: 50%
REFERENCE ____
TEMPERATURE R.T.

NUCLEUS 13 C
  OBS.
  LOCK ☑D ☐F ☐H
  IRR. 1H
OFFSET
  OBS. 35.50 KHZ
  RR. AUTO-CHANGE KHZ
PULSE ☑SINGLE ☐MULTI
  WIDTH 9 μSEC. 60°
  INTERVAL ____ SEC.
  REPETITION 2.0 SEC.

DATA POINTS 8 K
WINDOW 5
NO. OF PULSES 100

SPECTRAL WIDTH 4 K HZ
RF GAIN 4
AMPLITUDE 2×10

DECOUPLING
  ☐CW ☑NOISE ☐PARTIAL
  ☐HOMO ☑-ETEROL 5°
  POWER 40db
LOCK
  RF LEVEL L-4
  RF GAIN 4
  AMPLITUDE 5×10

DATE 2/23/76
OPERATOR K. Goto

REMARKS

210-39

JEOL LTD.

MERCK SHARP & DOHME / *RESEARCH LABORATORIES*

March 3, 1976

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

Dear Barry:

Perhaps some information on vicinal $^{13}$C-H coupling which I am submitting to <u>Organic Magnetic Resonance</u> will be of interest to readers of the TAMU newsletter.

Values of long-range $^{13}$CH coupling through the double bond in a number of isopropenyl compounds are reported. Although the anticipated[1] dependance of the couplings upon substituent electronegativity is found, there is evidence that this dependance is not related linearly to that of H-H couplings in vinyl compounds. The ratio of $^3J_{CH}$ to $^3J_{HH}$ in analogous pairs of compounds appears to decrease with increasing substituent polarity. Table 1 presents values of $^3J_{CH}$ and $^3J_{HH}$.

Please credit this contribution to the subscription of Dr. B. H. Arison.

Sincerely yours,

Alan W. Douglas

ms

1  U. Vögeli and W. von Philipsborn, <u>Org. Mag. Res.</u>, 7, 617(1975).

Table 1

## Vicinal $^{13}$CH Coupling Constants in iso-Propenyl Compounds Compared with HH Couplings in Vinyl Compounds

| Substituent | Cpd. No. | $^3J^{13}CH$* | | | $^3J_{HH}$ | | | | Ratio $\dfrac{^3J_{CH}}{^3J_{HH}}$ | $^3J_{\underline{C}=C-CH_3}$ |
| | | cis | trans | sum | cis | trans | sum | Ref. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| F | 1 | 2.5 | 7.0 | 9.5 | 4.7 | 12.7 | 17.4 | a. | 0.55 | 3.6 |
| OAc | 2 | 3.4 | 8.1 | 11.5 | 6.4 | 14.0 | 20.4 | b. | 0.56 | 4.3 |
| OCH$_3$ | 3 | - | - | 12.5 | {7.0 / 6.6} | 14.1 / 14.4 | 21.1 / 21.0 | c. } d. | 0.59 | 3.9 |
| Cl | 4 | 4.2 | 8.6 | 12.8 | 7.2 | 14.8 | 22.0 | a. | 0.58 | 4.7 |
| Br | 5 | 4.5 | 9.0 | 13.5 | 7.2 | 15.1 | 22.3 | a. | 0.61 | 5.0 |
| COCl | 6 | 5.6 | 9.6 | 15.2 | 10.2 | 16.8 | 27.0 | b. | 0.56 | 5.5 |
| CO$_2$Me | 7 | 6.0 | 10.3 | 16.3 | 10.5 | 17.3 | 27.8 | b. | 0.59 | 5.8 |
| CN | 8 | 6.4 | 10.1 | 16.5 | 11.8 | 17.9 | 29.7 | e,f. | 0.56 | 6.2 |
| CH$_3$ | 9 | - | - | 17.3 | 10.0 | 16.8 | 26.8 | g. | 0.65 | - |
| Ph | 10 | 6.7 | 11.1 | 17.8 | 11.5 | 18.6 | 30.1 | h. | 0.59 | 5.9 |
| Ph-F(p) | 11 | 6.8 | 11.2 | 18.0 | - | - | - | - | - | 5.8 |
| C(Me)=CH$_2$ | 12 | 7.1 | 11.2 | 18.3 | 10.2 | 17.1 | 27.3 | i. | 0.67 | 6.2 |
| CMe$_3$ | 13 | 7.1 | 11.5 | 18.6 | 10.0 | 16.8 | 26.8 | b. | 0.69 | 6.0 |

* Coupling constants are reported to the nearest (averaged) 0.1 hz., although <u>theoretical</u> accuracy is not claimed to be better than 0.5 hz.

References

a. R. E. Mayo and J. H. Goldstein, <u>J. Mol. Spectr.</u>, 14, 173(1964).
b. A. W. Douglas, unpublished results.
c. R. T. Hobgood, Jr., G. S. Reddy and J. H. Goldstein, <u>J. Phys. Chem.</u>, 67, 110(1963).
d. J. Feeney, A. Ledwith, and L. H. Sutcliffe, <u>J. Chem. Soc.</u>, 1962, 2021.
e. R. T. Hobgood, J. R. E. Mayo, and J. H. Goldstein, <u>J. Chem. Phys.</u> 39, 2501(1963).

f. R. Freeman, <u>J. Chem. Phys.</u>, 40 3571(1964).
g. A. A. Bothner-By and C. Naar-Colin, <u>J. Am. Chem. Soc.</u>, 83, 231(1961).
h. E. I. Snyder, <u>J. Am. Chem. Soc.</u>, 85, 2624(1963).
i. R. T. Hobgood and J. H. Goldstein, <u>J. Mol. Spectr.</u>, 12, 76(1964).

RAMAN RESEARCH INSTITUTE

BANGALORE 6

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

February 21, 1976

Dear Professor Shapiro,

### Title: 'Oriented' N-methyl acetamide

In continuation of our work on the study of the planarity of the peptide unit using NMR spectroscopy of oriented molecules, we have now interpreted the spectrum of N-methyl acetamide dissolved in a nematic solvent. Unlike N-methyl formamide, this system provides spectrum due to trans species only. Analysis of the spectrum provides 5 different HH direct dipolar couplings.

In order to investigate the problem of the amide planarity, one has to check internal consistency of the 5 dipolar couplings for 3 order parameters using known geometry. If the results are self consistent, the planarity is indicated. The problem was studied under the following assumptions:

1) Influences of all types of vibrations were neglected
2) bond length and bond angle values were taken from the literature
3) free as well as hindered rotations of the methyl groups were considered
4) methyl groups themselves were assumed rigid
5) no coupled motion between the two methyl groups was considered.

Calculations were carried out for a rigidly planar structure as well as for the case when there is a rapid inversion through nitrogen atom such that the system has an 'effective' plane of symmetry.

It was found that the minimum root mean square error between the observed and the 'best-fit' calculated dipolar couplings is obtained when the dihedral angles C-C-N-H and C-C-N-C are differing by $10 \pm 4°$ from the values of 0° and 180° for a completely planar configuration. These results agree with those obtained for N-methyl formamide.

Yours sincerely,

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