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Prensa

Illinois
Institute of
Technology
N – M – R
Newsletter

No. 93
JUNE, 1966

Deadline Dates: No. 94: 15 July 1966
No. 95: 15 August 1966

TMC/BP

Please address any reply to
THE DIRECTOR
and quote: MS 5/8/01
Your reference:

Division of Molecular Science

20th May, 1966

Dear Dr. Shapiro,

Relaxation in Polyethylene Oxide: Spin Diffusion mechanisms.

Continuing our studies of the relaxation properties of oxide polymers, we have measured T_1's as a function of temperature for some low molecular weight polyethylene oxides with and without methyl endgroups.   In samples of molecular weight 550 and 750 (with <u>one</u> CH_3 end group) containing only 4.3% and 6.4% of their protons as methyl end groups we find that well defined motional minima in the temperature region corresponding to methyl group rotation ($118°K$) are nevertheless obtained.   On the other hand, samples with molecular weights 600 and 6000 containing no methyl groups (checked by running high resolution spectra) show no motional minima in this temperature region, T_1 being an order of magnitude larger.

Attempting to account for these results on the basis of a spin-diffusion mechanism, we have slightly modified the normal theory developed for the case of paramagnetic impurities in alkali halides (Abragam. p 378 et seq.) and find that whilst the temperature dependence of T_1 in the neighbourhood of the minimum is reasonably well reproduced, the absolute values of T_1 found are too small.   This is a common failing of most absolute calculations of T_1, particularly those based on BPP theory (which these are in part), which frequently predict more potent relaxation mechanisms than those observed experimentally .   We hope to shed further light on these relaxation mechanisms by low field relaxation studies in the rotating frame.

This work is in course of publication in 'Polymer' and preprints are available if any one is interested.

Yours sincerely,

Tom Connor

T.M. Connor

Dr. B.L. Shapiro,
Dept. of Chemistry,
Illinois Institute of Technology,
Technology Centre,
CHICAGO, Illinois, 60616,
U.S.A.

Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

Prof.B.L.Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
CHICAGO (Ill.)
U.S.A.

Uw kenmerk	Uw brief van	Ons kenmerk	JS/WS	Delft, Nederland, Lorentzweg 1, tel. 01730-33222

24th May 1966 toestel: 5394

Onderwerp

Dear Prof.Shapiro,

Thank you very much for your reminder. We submit now for the
I.I.T.N.M.R.-Newsletter the following contribution:

NMR of $F_2C = CH_2$ at high pressures

We are doing N.M.R.-work on 1.1.difluoro ethylene, especially
looking at the chemical shifts for proton-resonance (δ_H) and
for fluorine-resonance (δ_F). Two results of this work we should
like to mention here.

1. Chemical shifts in 1.1.difluoro ethylene as a function of den-
sity.

According to Buckingham and Pople (1) we write the screening
constant σ for a pure, nonperfect gas as a virialseries:
$\sigma = \sigma_o + \sigma_1/v_m + \sigma_2/v_m^2 + \ldots$, or, taking the molar density $\rho = 1/v_m$
as a variable: $\sigma = \sigma_o + \sigma_1\rho + \sigma_2\rho^2 + \ldots$
Taking only binary collisions into account, Buckingham and
others (2) showed that σ depends linearly on ρ (only σ_o and σ_1
are unlike zero); this is confirmed by experiment (3) for pro-
ton-resonance. Nevertheless there must be deviations from this
linear dependence, due to higher-order collisions. To find these
deviations, one should look to the chemical shift at high densi-
ty, from a heavy nucleus: First the calculations, mentioned in
(2), show that σ_1 is bigger for a heavy nucleus than for a pro-

ton, because its vaster electroncloud. If one assumes that the deviations from the linear shift-pressure-relation increase with increasing shift, they will be much easier be demonstrated with ^{19}F-resonance. So we took a fluid with ^{19}F-nuclei (and protons as well: see below). A second consideration was that near the critical point one has great densities and many higher-order collisions. So we took $F_2C = CH_2$: critical temperature $30^{\circ}.1$ C, critical pressure 43.8 atm, critical density 6.3 gmole/l. (4).

We work with sealed capillaries, with a well-known volume. They are filled by condensation from a much bigger, also known volume, into which the gas is led in up to a definite pressure.

By varying this pressure, we can vary the amount of fluid in the capillary. The spectra were recorded on a Varian DP-60 spectrometer, at a temperature of $32^{\circ}C$, $2^{\circ}C$ above the critical temperature. References were: $Si(Me)_4$ (proton-resonance), CF_3COOH (fluorine-resonance); we used a substitution-technique for the δ-measurements.

The proton-spectra are at low field from $Si(Me)_4$, the fluorine-spectra at high field from CF_3COOH.

Within the errors, caused principally by the uncertainty in the density, δ_H vs. ρ is a straight line. For δ_F vs. ρ we cannot make a definite statement. We can take δ_H as a measure for ρ, which is justified by a. the results of Gordon and Daily (3) who measured the shift of C_2H_4 up to 300 at., b. our own results. A plot of δ_H vs. δ_F gives fig.1[*) which is somewhat puzzling.

We will continue the work on this subject; we don't believe that a straight line will be the final result. But in order to be more sure about ρ we need a better equation of state of our stuff; the equations given in (4) are not very consistent in the critical region. If anybody knows a better equation of state for $F_2C=CH_2$ or knows a laboratory where one can determine this equation for us, please let he write us.

[*) In fig.1. increase of δ_H-values and decrease of δ_F-values correspond to lower field-values.

2. <u>Cha...es in the spectrum of $F_2C = CH_2$ near the critical point.</u>
When the capillaries are heated, the change of state is iso-
choric. Some of these isochors come very near to the critical
point. We have put the capillary which comes nearest to the
critical point in the spectrometer and than let the tempera-
ture raise from a value below T_c to a value somewhat above,
with a speed of appr. $0^\circ.1$ C/min. From visual observation we
know that the meniscus grows vague and finally disappears when
the capillary is heated, and that the meniscus becomes gradual-
ly visible when the capillary is cooled afterwards. We also
know that the meniscus does not raise or fall. Geometry: the
pick-up coil was 1 cm below the meniscus.
The results of these recordings are shown in fig.2. First one
has liquid (I; for a discussion of the spectrum see (4)). After
2 min. one gets II, which can be interpreted as two spectra (one
vapour, one liquid), about 0,08 ppm apart. After again $1\frac{1}{2}$ min.
we get III: one of the spectra has grown considerably, and so
we know which of the two is vapour and which is liquid. Finally
one gets IV; a gas-phase spectrum. When this interpretation is
correct, we see two things:
a. When going from liquid to vapour, the spectrum shifts to
   higher field; this shift is correct according to fig.1. The
   distance between the spectra of 0.08 ppm corresponds <u>for va-</u>
   <u>pour</u> with a density-difference of 1 gmole/l. This leads to
   the conclusion that there are important structural differen-
   ces between the vapour and the liquid.
b. We must suppose that under the condition of fig.2. II and III
   there are vapour- and liquid-clusters, with such a lifetime
   that they give distinct spectra. From the distance $\Delta\nu$ of the
   spectra one deduces with $2\pi.\Delta\nu.\tau \geqslant 4$ (6): $\tau \geqslant 0,1$ sec.

(1) A.D.Buckingham   Disc.Faraday Soc. <u>22</u>, 17 (1956)
     A.D.Pople

(2) W.T.Raynes   J.Chem.Phys. <u>36</u>, 3481 (1962
     A.D.Buckingham   and following papers of this series
     H.J.Bernstein

(3) S.Gordon   J.Chem.Phys. <u>34</u>, 1084 (1961)
     B.P.Dailey

(4) W.H.Mears and   Ind.Eng.Chem. <u>47</u>, 1449 (1955)
     coworkers

(5) G.W.Flynn   J.Chem.Phys. 38, 226 (1963)
     J.D.Baldeschwieler

(6) J.A.Pople   High Resolution N.M.R.
     W.G.Schneider   New York 1959, p.223.
     H.J.Bernstein

$\longrightarrow \rho(\text{mole/l})(\text{app.})$

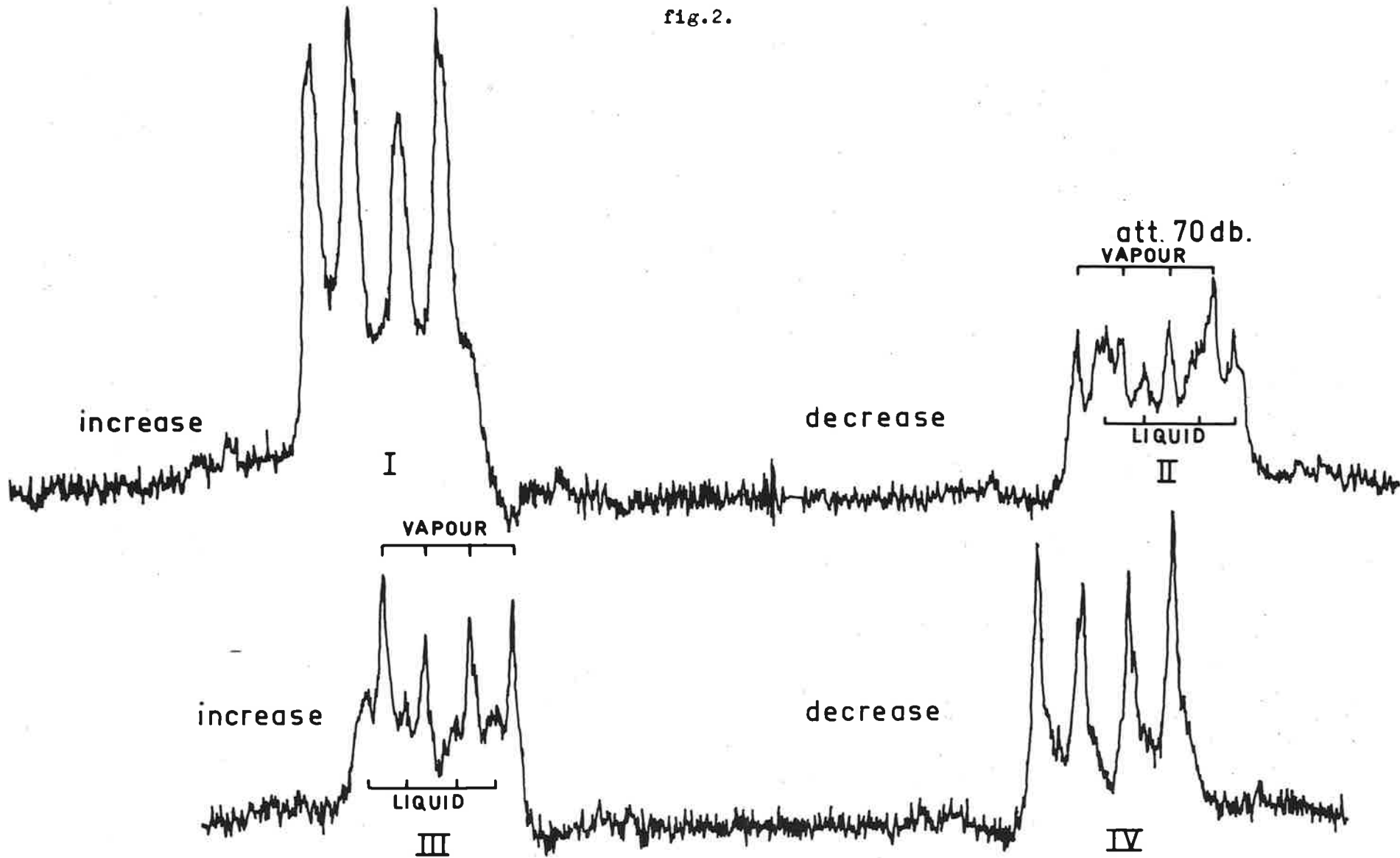fig.1. $\longrightarrow \delta_H(\text{ppm})$
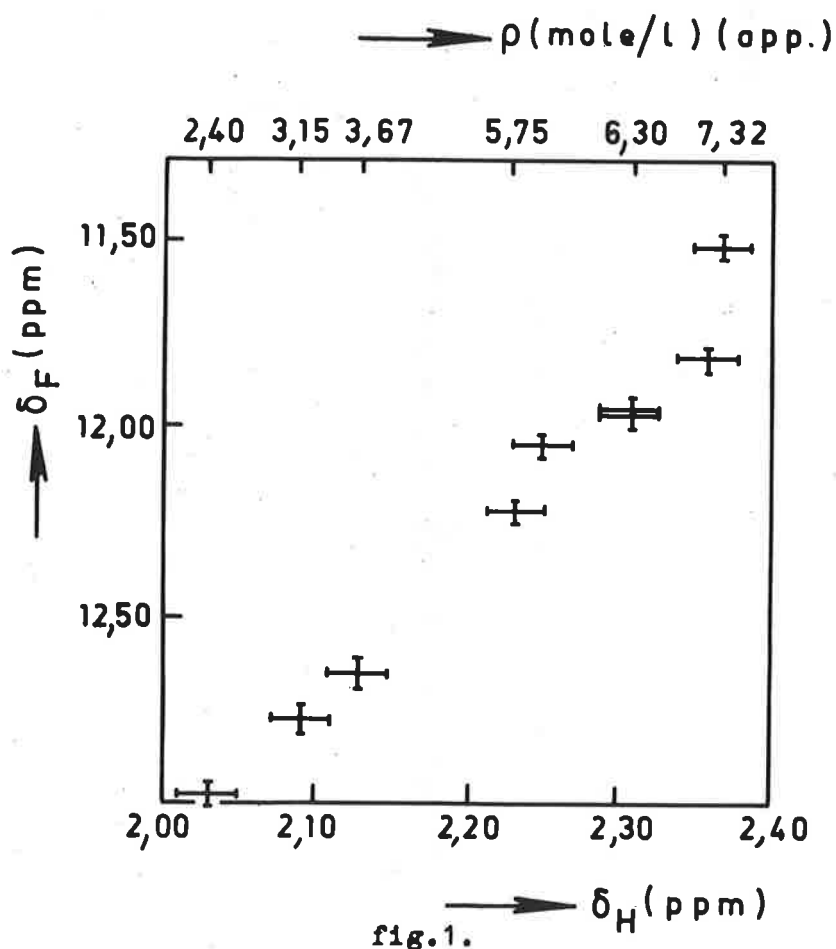
A.J.H.Schouten.   W.H.Wisman.   J.Smidt.

fig.2.

att. 70 db.

DIVISION OF PHYSICAL CHEMISTRY

THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70
SWEDEN

Cable address: Technology

SFn/MH

May 25, 1966

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center

CHICAGO, Illinois 60616

USA

Dear Barry:

Subjects: a) Spectral parameters of 1-indanone
           b) NMDR on 2-hydroxy-3-methoxy-benzaldehyde
              (the sign of yet another l.r. coupling!)
           c) transient and steady state Overhauser
              experiments (homonuclear).

In our latest letter we promised a presentation of some recent
experimental results. Here they are. We have studied proton
resonance spectra of 1-indanone at 40, 60 and 100 Mc/sec prompted
by the recent article by Hecht (Theor.Chim.Acta $\underline{3}$, 202 (1965)).
His results seemed rather improbable to us, in particular the
magnitudes he found for the geminal couplings in the A_2B_2 spectrum
of the five membered ring were in obvious disagreement with those
predicted on the basis of the correlations suggested by Pople and
Bothner-By (J.Chem.Phys. $\underline{42}$, 1339 (1965)). We obtained the para-
meters at 100 Mc/sec (ca $\overline{10}$ % CS_2 solution)

$$\nu_A - \nu_B = 55.43 \text{ cps}$$
$$N = 12.14 \text{ cps}$$
$$L = 5.16 \text{ cps}$$
$$K = -36.33 \text{ cps}$$
$$M = 1.76 \text{ cps}$$

Hecht found similar parameters except for K which he gave as
+3.8 cps. The coupling constants obtained in the 40 and 60 Mc/sec
spectra agree well within the experimental error with those ob-
tained from the spectrum at 100 Mc/sec. It is interesting to note
that the generalized A_2X_2 treatment of Gestblom $\underline{\text{et al}}$. gives the
correct parameters at 60 Mc/sec ($\nu_A - \nu_B = 33.0$ cps; N = 12.10;
L = 5.13; K = -36.51; M = 1.79 cps) in spite of the fact that the
spectrum is so strongly coupled that certain "A"-transitions
occur in the "B" region of the spectrum and vice versa.

93-8

Obviously the parameters obtained by us are in good agreement
with those predicted from the Pople, Bothner-By correlations.

In one of our recent published works (J.Mol.Spectroscopy $\underline{17}$, 13
(1965)) we describe how the signs of the long-range aldehyde
coupling in benzaldehydes was obtained through a general double
irradiation experiment. Theoretical spectra were calculated by
numerical diagonalization of the full ABCX NMDR Hamiltonian and
the predicted asymmetry in the aldehyde band at a certain irra-
diation frequency in the ring proton band was experimentally
established thus giving the sign of the long range aldehyde
coupling.

The same technique has now been applied to determine the long
range hydroxyl coupling J_{OH-4} in 2-hydroxy-3-methoxy benz-
aldehyde. Fig. 1a displays the single resonance spectrum of the
ring protons as obtained with a decoupling field centered at
the methoxyl signal. The long range hydroxyl coupling is now
nicely resolved in the band of the H-4 proton at 551-563 cps
(internal cyclohexane reference). Fig. 1c, d and e represent
respectively the hydroxyl proton signal, the aldehyde proton
signal and the doublet assigned to the methoxy group (J_{OCH-4} =
= 0.25 cps.)Experimental and theoretical double resonance spectra
obtained with an irradiation amplitude of $\gamma H_2/2\pi$ = 7.2 cps are
shown in Fig. 2. Fig. 2a shows the unperturbed hydroxyl signal
(J_{OH-4} = 0.62 cps). Fig. 2b and c show double resonance frequency
sweep spectra of the hydroxyl signal obtained with the irradiation
frequencies ν_2 = 550.2 cps and ν_2 = 549.0 cps respectively. The
theoretical spectra were calculated by superimposing eight
Lorentzian lines having a full width at half height of 0.20 cps.
Set I was calculated on the assumption that J_{OH-4} carries the
same sign as the ring couplings and Set II was obtained by re-
versing the sign of J_{OH-4}. It is interesting to note that the
high reproducibility of the experimental line shape as obtained
with NMR spectrometers employing internal proton stabilization
is sufficient to provide unambiguous evidence as to the sign of
J_{OH-4} from the line shape of a line with a full width at half
height of 0.65 cps and only one resolved peak as in Fig. 2b.
Clearly this would hardly have been born out if the theoretical
spectrum had been given as a "needle diagram".

In IITN-M-R Newsletter $\underline{86}$, 55 Surick and Anderson pointed to
the strong parallelism that exists between chemical exchange
and relaxation. We have also noted this similarity, in particular
as regards longitudinal relaxation and we have adopted the double
resonance technique developed for investigating chemical exchange
to the study of relaxation processes by means of transient and
steady state Overhauser experiments. Fig. 3 displays the expo-
nential decays obtained with double irradiation experiments on a
sample of formic acid at +29°C (A represents the formyl proton
and B the hydroxyl proton). The graph shows a semi-logarithmic
plot of the recovery of the signal intensity of the observed
peak after an adiabatic rapid passage of this same signal as
obtained with continuous saturation of the second signal. The
steady state Overhauser enhancements were 22.5 % for the formyl

proton and 17.5 % for the hydroxyl proton as compared with a theoretical maximum of 50 % if mutual dipole-dipole interactions were the only relaxation mechanism.
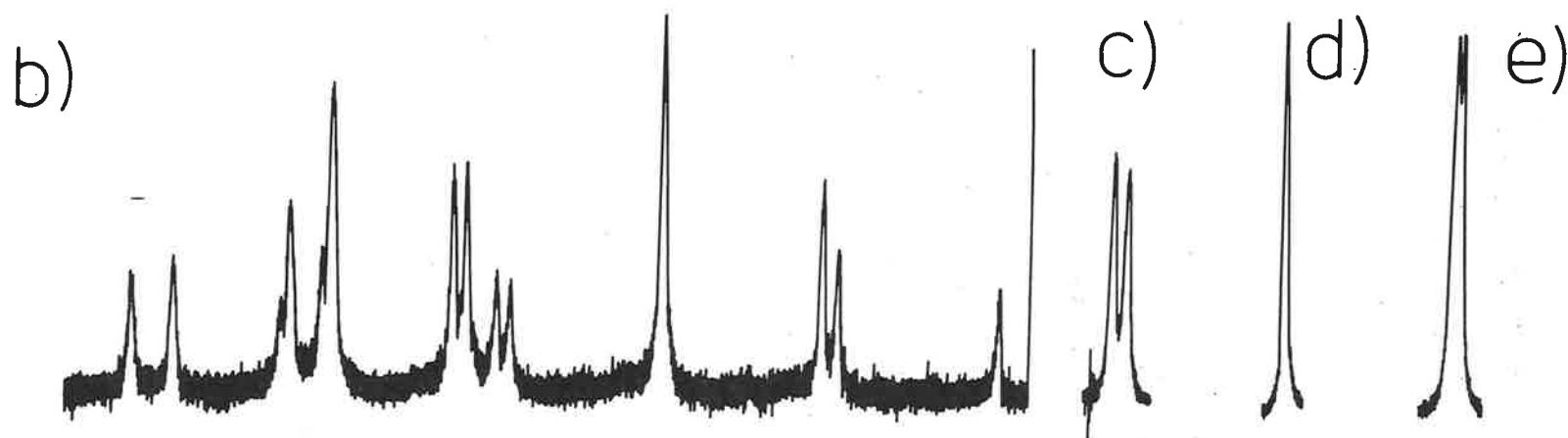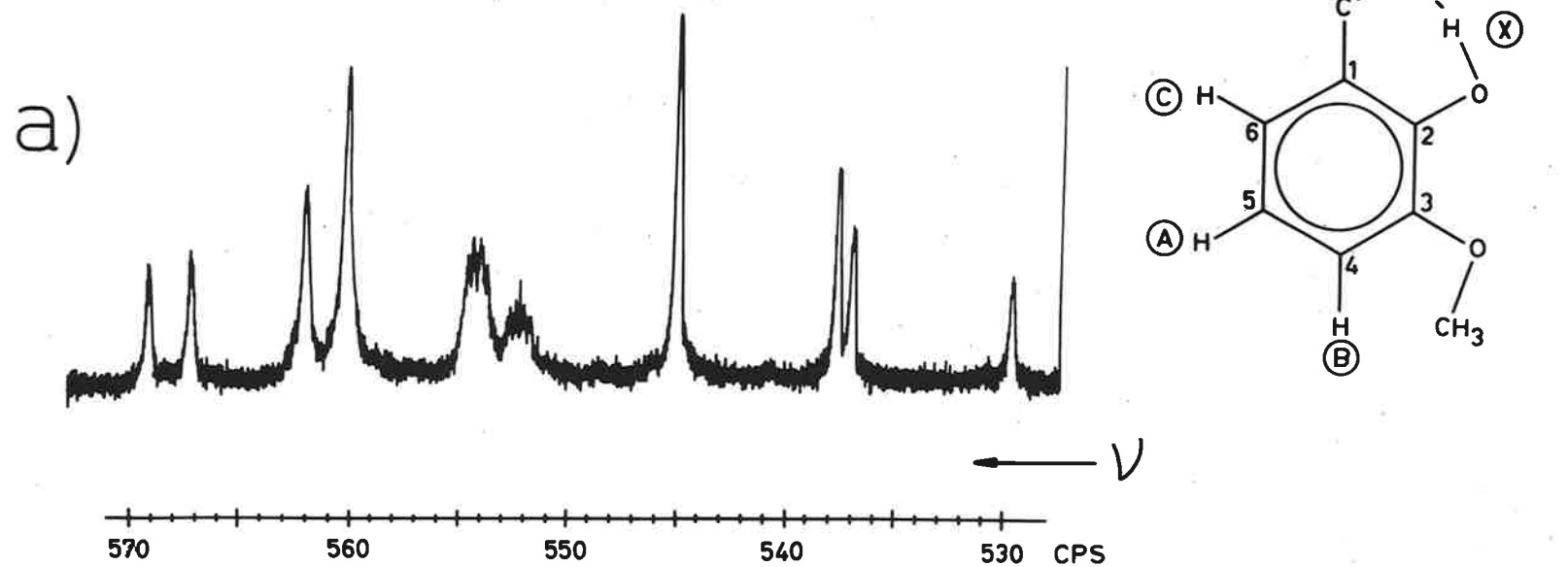
Fig. 4 displays the decay of a steady state Overhauser enhancement of the aldehyde magnetization in acetaldehyde as obtained by release at time t=0 of a saturating r.f. field centered on the methyl group band. The steady state enhancement in this sample amounted to 21 %. The sample employed was a standard Varian sample. We prepared another acetaldehyde sample from a bottle left over in a cupboard. This sample was used without further purification and after having been allowed to settle down for a fortnight in a pressure sealed sample tube, this second sample displayed longer relaxation times and a steady state Overhauser enhancement of 23.8 % for the aldehyde signal. Room for improvements Varian?
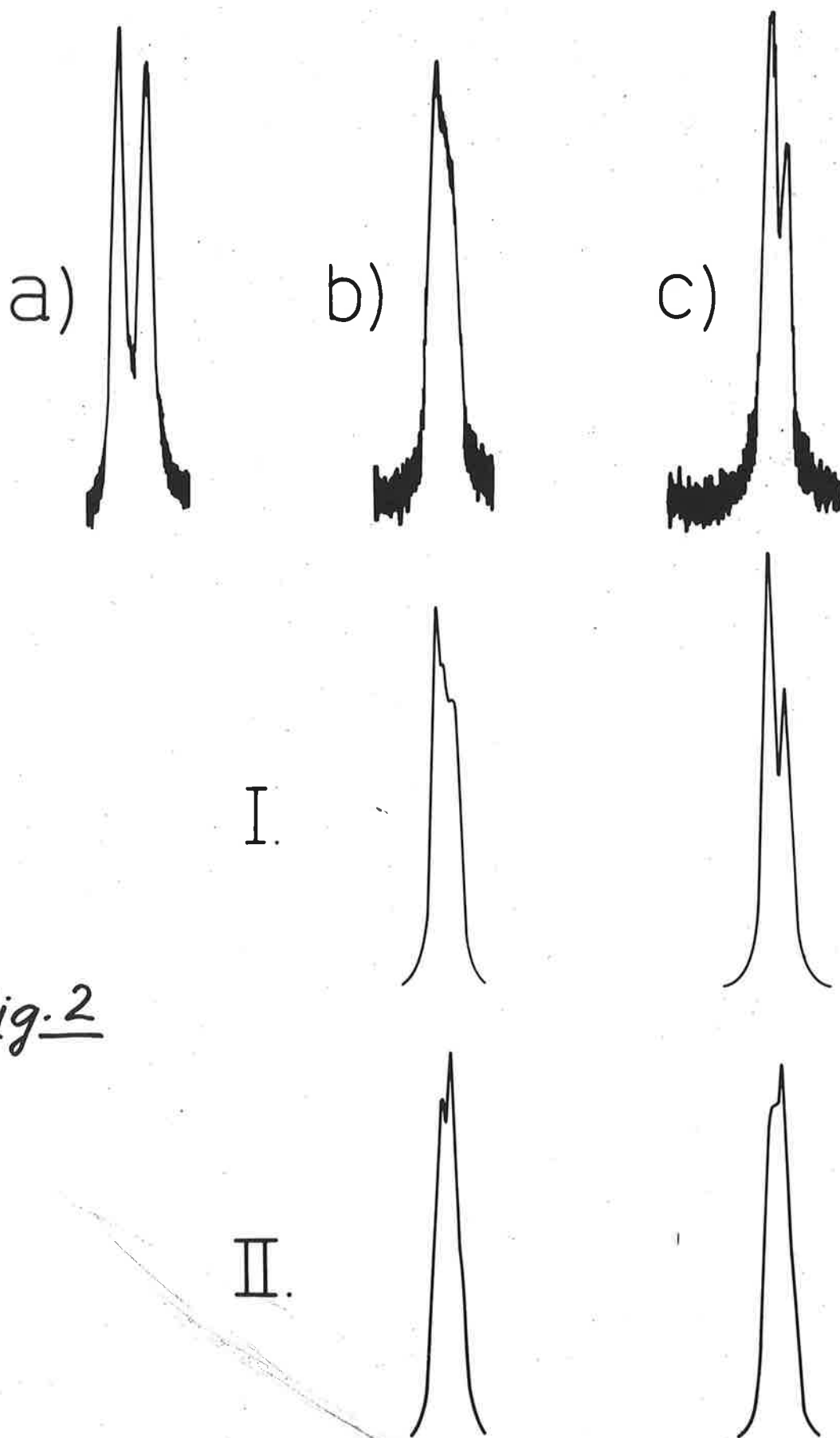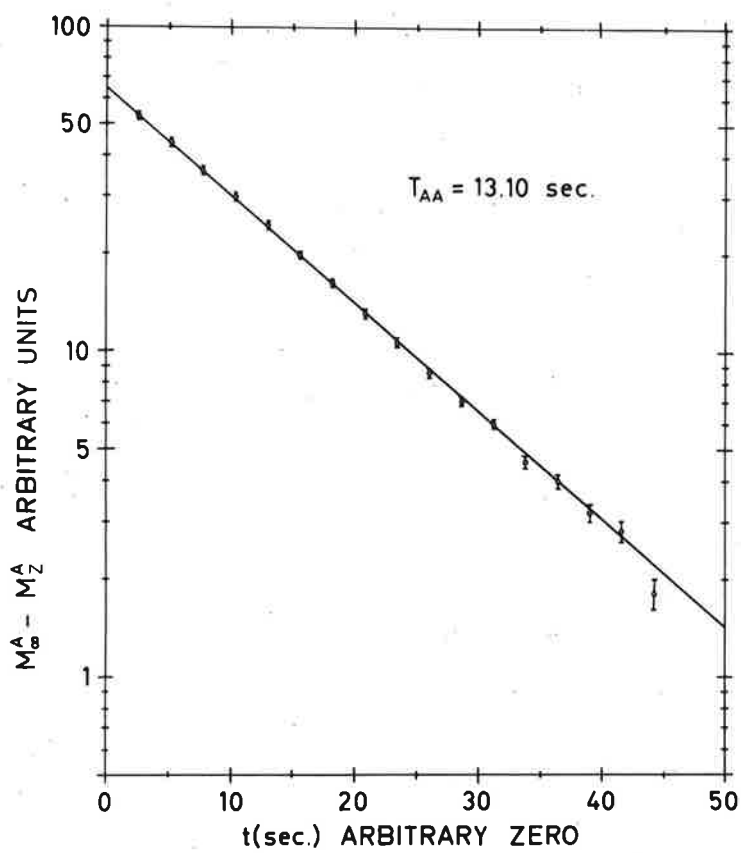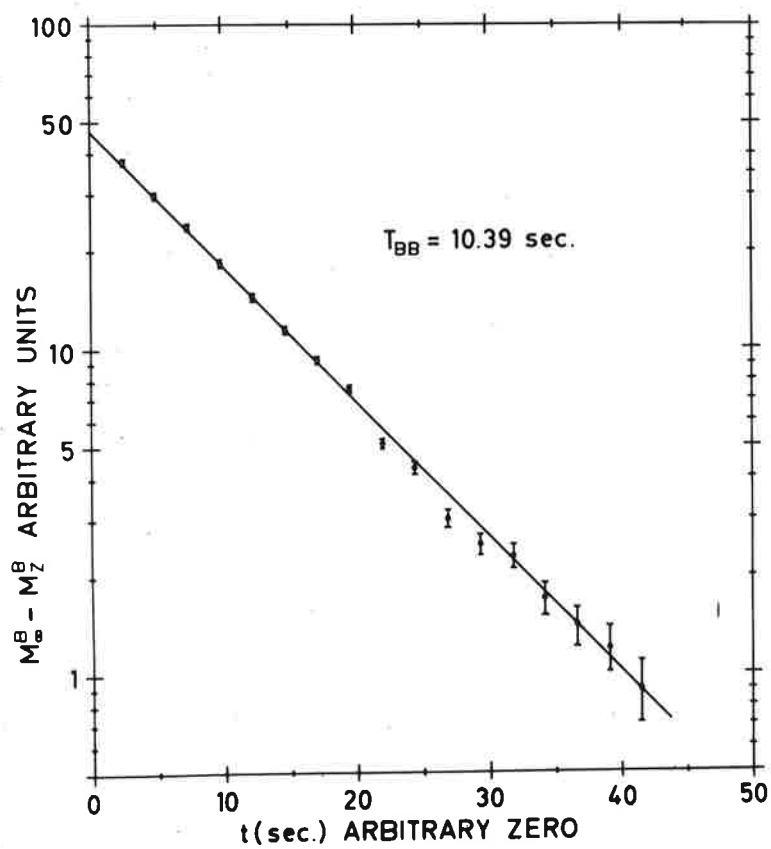
                      Best regards,

Sture Forsén   *Ragnar A. Hoffman*
Sture Forsén   Ragnar A. Hoffman

P.S. Please credit this letter to the NMR Group at the
     Royal Institute.

Fig. 1

Fig. 2

$T_{AA} = 13.10$ sec.

$M_\infty^A - M_z^A$ ARBITRARY UNITS

t(sec.) ARBITRARY ZERO

Fig.3

$T_{BB} = 10.39$ sec.

$M_\infty^B - M_z^B$ ARBITRARY UNITS

t(sec.) ARBITRARY ZERO
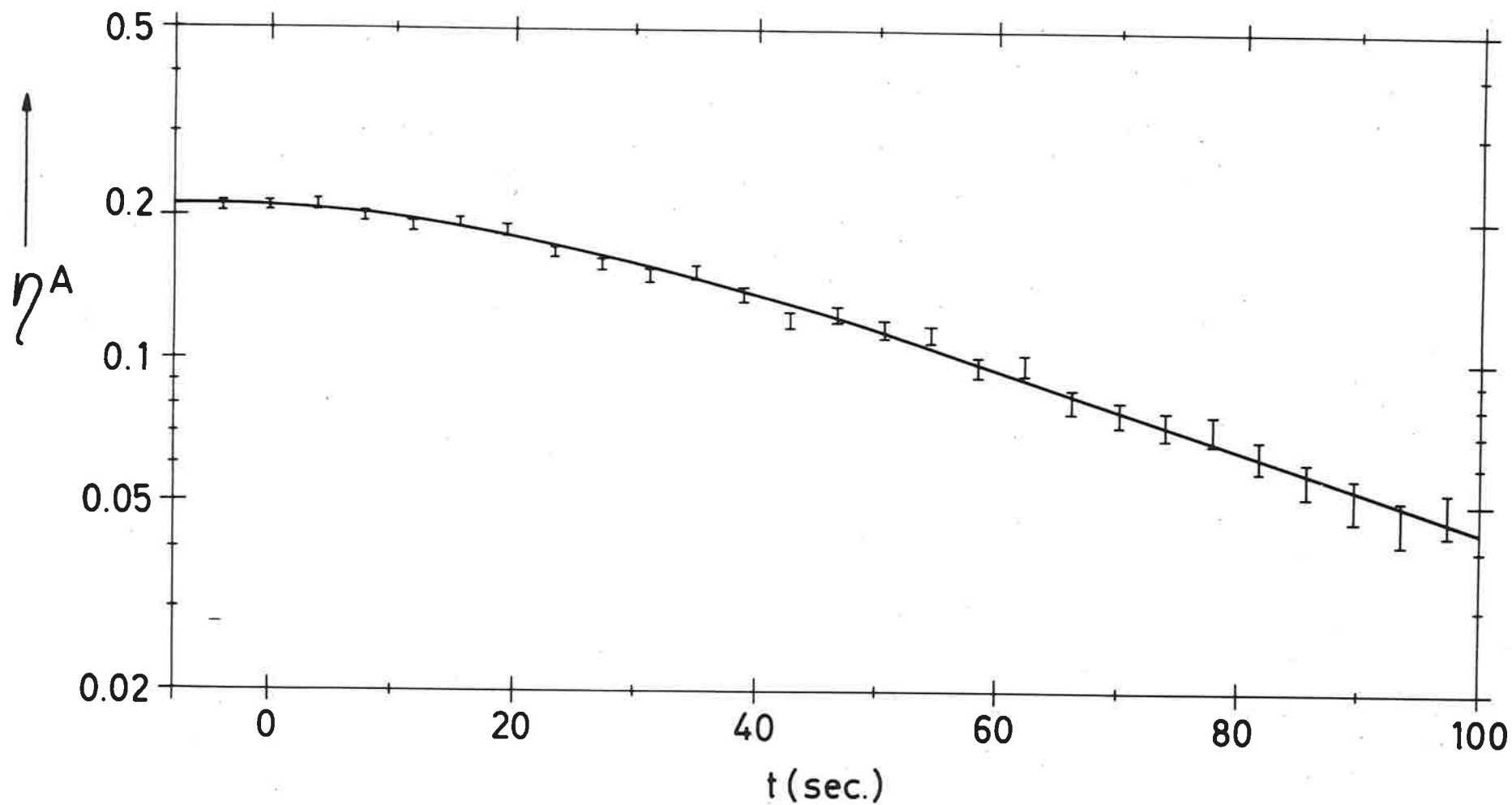
Fig. 4

UNIVERSITY OF EXETER

Department of Chemistry

Tel. 77911

Dr. K. G. Orrell

Stocker Road,
Exeter

25th May, 1966.

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

Dear Professor Shapiro,

Diels-Alder Adducts From Perfluorocyclopentadiene

In the Diels-Alder reaction, perfluorocyclopentadiene acts (a) as a diene in its thermal reactions with ethylene(I), butadiene(II) and norbornadiene(III), for example,

(I)   (II)   (III)
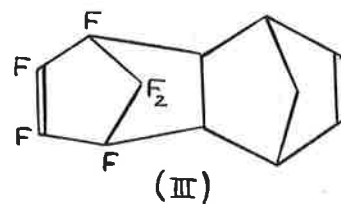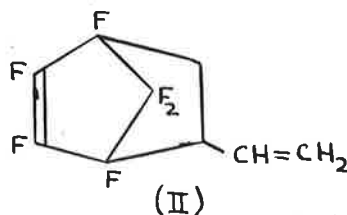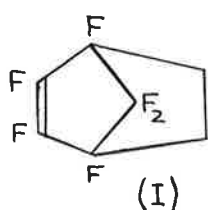
(b) as a dienophile when heated with anthracene(IV) and (c) as both a diene and dienophile when heated with cyclopentadiene, (V) and (VI).

(IV)   (V)   (VI)
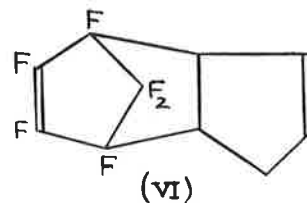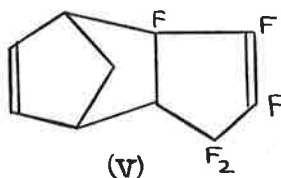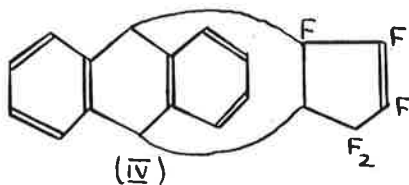
N.M.R. studies of these adducts were of great help in establishing their structures. The basic problem was how to distinguish between compounds containing a dienic residue (A), i.e. arising from 1,4-addition to perfluorocyclopentadiene, and those containing a dienophilic residue (B), i.e. arising from 1,2-addition to perfluorocyclopentadiene.

(A)   (B)
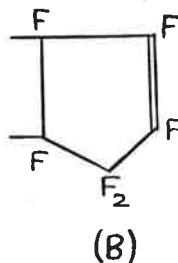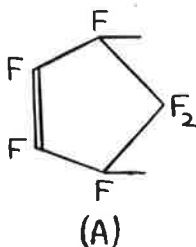
Professor B. L. Shapiro.   -2-   25th May, 1966.

This problem was solved by studying the spectra of perfluorocyclopentadiene itself and those Diels-Alder adducts for which convincing structural evidence had been obtained by chemical or other spectroscopic means. Thus, it was found that an adduct containing the element of structure (A) gives an ^{19}F absorption pattern with characteristic parameters easily distinguishable from those associated with the presence of element (B). These characteristic parameters are as follows:

(1)   The AB pattern (or single band if the nuclei are equivalent) due to the $-CF_2-$ group of the type present in (A) is centred at ca. 60 p.p.m. (to high field of external CF_3CO_2H) whereas a $-CF_2-$ group of type (B) occurs at ca. 30 p.p.m.

(2)   The geminal coupling constant $|J_{gem}|$, for the $-CF_2-$ group in (A) is of the order of 175 c/s whereas for the $-CF_2-$ group in (B) it is ca. 250 c/s.

(3)   The tertiary fluorines in a compound containing structure (A) absorb at a much higher applied field (at ca. 130 p.p.m. relative to CF_3CO_2H) than those in a compound containing structure (B) where there is also a considerable chemical shift difference between fluorine types

$$\diagdown\!\!CF\!\!-\!\!CF_2\!- \qquad \text{and} \qquad \diagdown\!\!CF\!\!-\!\!CF\!\!=\!\!.$$

These distinctive features of the spectra of the residues (A) and (B) have enabled the structures of nearly a dozen adducts to be established with considerable certainty (Refs. 1, 2). Data for adducts I-VI are given in the table below.

I continue to find your newsletter a most valuable and interesting publication.

Yours sincerely,

Keith G. Orrell

References:

1)   Banks, Harrison, Haszeldine, and Orrell, Chem. Comm., 1965, 41.

2)   Banks, Harrison, Haszeldine and Orrell, J. Chem. Soc., to be published.

KGO/LL

Table

^{19}F (56.46 Mc/s) Spectral Parameters of Diels-Alder Adducts

of Perfluorocyclopentadiene

Adduct	Chemical Shift Assignments (p.p.m. to high field of CF_3CO_2H)				$\left|J_{gem}\right|$ (c/s)
	$-CF_2-$	$=CF-CF\big\langle$	$=CF-CF_2-$	$\big\rangle CF$	
I	68.3	81.9	–	130.4	177
II	65.4	75.4	–	129.4	180
		81.8		131.4	
III[a]	59.0	71.5	–	126.9	175
	57.4	69.8		125.4	175
IV[b]	32.1	66.7 73.0	85.8	96.2	248
V[b]	37.3	66.3 75.4	95.3	103.8	260
VI	61.4	75.4	–	128.8	179
		76.4			

a) Values refer to two stereoisomers.

b) Assignments of the vinylic and tertiary fluorines are not yet established with any certainty.

Koninklijke/Shell - Laboratorium, Amsterdam

BADHUISWEG 3   AMSTERDAM - N.

TELEFOON (020)-6 11 11

Dear Dr. Shapiro,

T_2 in a scalarly coupled two-spin system

In a paper soon to appear in the Journal of Chemical Physics we have discussed the problem of transverse relaxation in systems of two non-identical spins which are coupled by a time-independent scalar spin-spin interaction. Transverse relaxation rates are affected by the presence of a scalar coupling and we have derived the appropriate formulae on the basis of the Redfield[1] formulation.

The spins are denoted by S and I $(S = I = \frac{1}{2})$ and the relaxation mechanism is supposed to be provided by the dipole-dipole interaction between the spins. The rates of relaxation, without and with a spin-spin coupling, are denoted by T_2^{-1} $(J_{SI} = 0)$ and T_2^{-1} $(J_{SI} \neq 0)$, respectively.

If the dipolar interaction between the spins in the same molecule provides the relaxation, we have

$$T_2^{-1}(J_{SI} = 0) = \tfrac{3}{4}\gamma_S^2\gamma_I^2 \hbar^2 \cdot [\tfrac{1}{6}J(0) + \tfrac{1}{24}J(\omega_S-\omega_I) + \tfrac{3}{4}J(\omega_S) + \tfrac{3}{2}J(\omega_I) + \tfrac{3}{8}J(\omega_S+\omega_I)]. \qquad (1a)$$

(see, for instance, ref. 2)

$$T_2^{-1}(J_{SI} \neq 0) = \tfrac{3}{4}\gamma_S^2\gamma_I^2 \hbar^2 \cdot [\tfrac{1}{6}J(0) + \tfrac{1}{24}J(\omega_S-\omega_I) + \tfrac{3}{4}J(\omega_S) + \tfrac{3}{4}J(\omega_I) + \tfrac{3}{8}J(\omega_S+\omega_I)]. \qquad (1b)$$

The introduction of a scalar coupling causes T_2^{-1} to decrease. Since $J(0):J(\omega_{I,S}):J(\omega_S+\omega_I) = 6:1:4$ the decrease is by a factor of 17/20.

If non-identical spins on different molecules interact, the time dependence results from translation rather than from rotation. As the corresponding spectral densities are in general different from the ones in eqns. (1a) and (1b), we use primed spectral densities.

If $J_{SI} = 0$, the expression for T_2^{-1} is the same as (1a). On the other hand, if $J_{SI} \neq 0$, we have:

$$T_2^{-1}(J_{SI}\neq0) = \tfrac{3}{4}\gamma_S^2\gamma_I^2 \hbar^2 \cdot [\tfrac{1}{6}J'(0) + \tfrac{1}{12}J'(\omega_S-\omega_I) + \tfrac{3}{4}J'(\omega_S) + \tfrac{9}{4}J'(\omega_I) + \tfrac{3}{4}J'(\omega_S+\omega_I)].$$

The introduction of J_{SI} leads to an "inverted three-halves effect": $T_{2S}^{-1}(J_{SI}\neq0)/T_{2S}^{-1}(J=0) = 3/2$.

The transverse relaxation of S spins, if caused by S-S interaction, is not dependent on a spin-spin coupling constant:

$$T_{2S}^{-1}(J_{SI}\neq0) = T_{2S}^{-1}(J_{SI} = 0) = \tfrac{3}{4}\gamma_S^4 \hbar^2 [\tfrac{3}{8}J_S''(0) + \tfrac{15}{4}J_S(\omega_S) + \tfrac{3}{8}J_S''(2\omega_S)],$$

where the double prime denotes that the spectral density results from interaction between two S spins.

I-I interactions do not affect T_{2S}^{-1} if $J_{SI} = 0$. However, if $J_{SI} \neq 0$, a transition of an I spin broadens an S line:

$$T_{2S}^{-1}(J\neq0) = \tfrac{3}{4}\gamma_I^4 \hbar^2 [\tfrac{1}{24}J_I''(0) + \tfrac{3}{4}J_I''(\omega_I) + \tfrac{3}{8}J_I''(2\omega_I)].$$

With kind regards,

E.L. Mackor   C. Maclean

Amsterdam,   5th May 1966

1. A.G. Redfield, I.B.M. J. Research Develop. 1 (1957) 19.
2. A. Abragam, The principles of nuclear magnetism, Oxford University Press (1963).

Koninklijke/Shell - Laboratorium, Amsterdam

BADHUISWEG 3   AMSTERDAM - N.

TELEFOON (020)-6 11 11

Dear Dr. Shapiro,

<u>Anisotropy of fluorine chemical shift in $CHFCl_2$</u>

A recent paper[1] described an investigation carried out by us to determine the sign of the spin-spin coupling constant (J_{HF}) in the molecule $CHFCl_2$. We followed a relaxation method in which the effect of a cross term between two relaxation mechanisms that operate simultaneously is measured. In this particular experiment these mechanisms are (1) the dipole-dipole interaction between the spins in the molecule and (2) the anisotropy of the fluorine chemical shift. Analysis of the method shows[1] that the sign of the coupling constant can only be given in terms of the sign of the anisotropy of the chemical shift; the latter is defined as ($\sigma_\parallel - \sigma_\perp$).

In this note we report briefly on experiments from which the sign of $\Delta\sigma$ has been determined. The method, which has been described by Andrew and Tunstall[2], consisted in studying the wide-line NMR spectrum of a polycrystalline sample. At sufficiently high values of the external magnetic field this spectrum shows a pronounced asymmetry caused by the anisotropy of the chemical shift. The experimental spectrum, measured at 56.4 MHz, is known in figure 1. (Since dipolar fields tend to mask the asymmetry, the deuterated compound $CDFCl_2$ was chosen.)

To interpret this spectrum, we have plotted in fig. 2a and 2b the NMR line shape of a polycrystalline sample, the spins of which have an axially symmetric chemical shift; in the bottom spectrum dipolar broadening has been superposed on the component lines. A perpendicular CF-bond is much more likely than a parallel one; this is reflected in the high intensity near $H_0(1 - \sigma_\perp)$ and the low intensity near $H_0(1 - \sigma_\parallel)$.

Comparison of the experimental spectrum with fig. 2 shows that the anisotropy of the chemical shift is negative. From the field dependence of the second moment one can also obtain its magnitude:

$$\sigma_\parallel - \sigma_\perp = - 205 \text{ ppm.}$$

Combining this result with the relaxation data, one finds $J_{HF} = + 53.6$ Hz. Tiers[3] has performed relative sign determinations of this coupling constant with respect to $J(^{13}C-H)$ and $J(^{13}C-F)$ so that the absolute sign of all three coupling constants can be given:

$$J_{HF} = + 53.6 \text{ Hz}$$
$$J_{^{13}C-H} = + 220.0 \text{ Hz}$$
$$J_{^{13}C-F} = - 293.8 \text{ Hz}$$
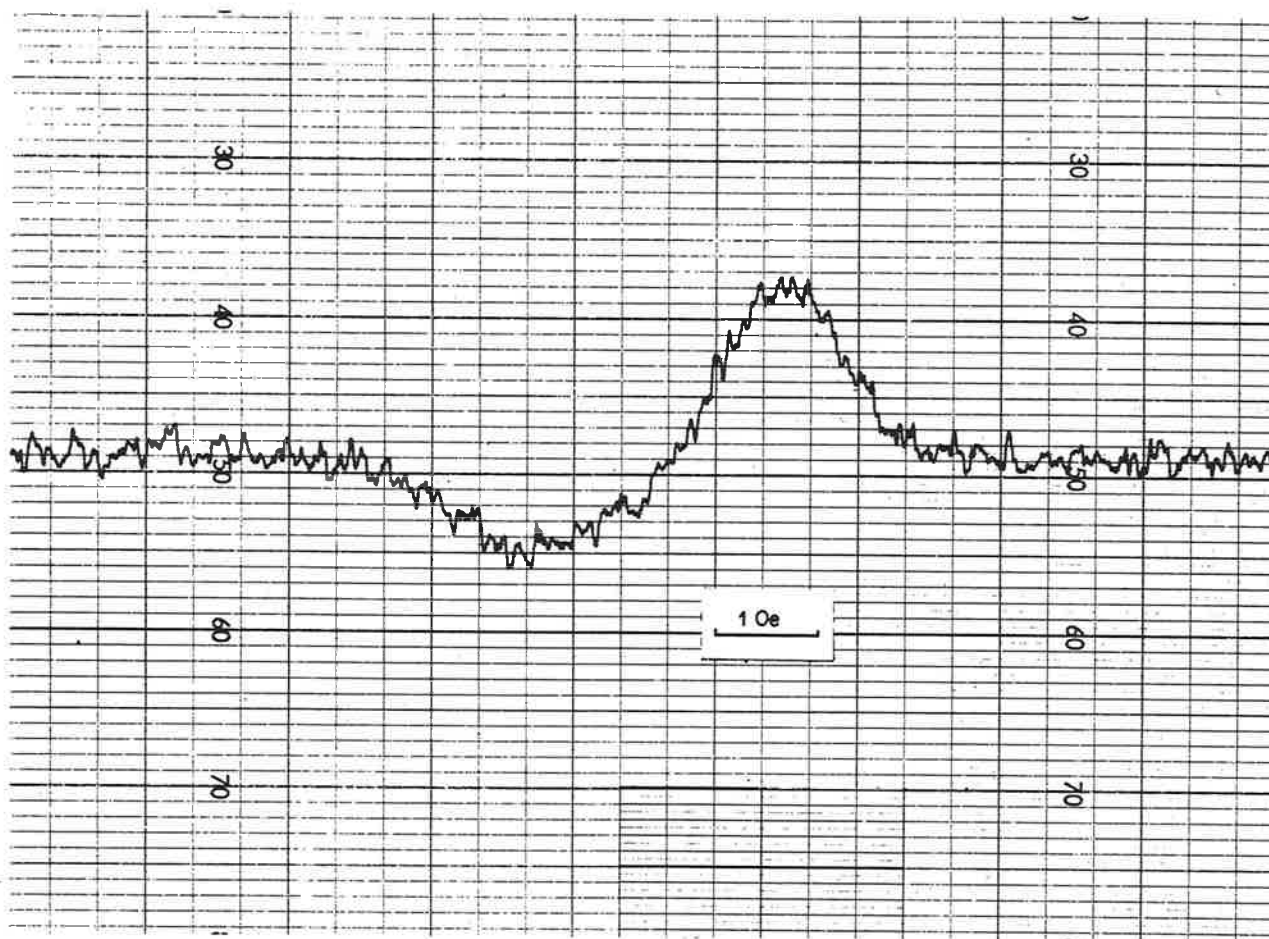
With kind regards,

E.L. Mackor   C. Maclean

2 Figures

Amsterdam, 5th May 1966

----

1. E.L. Mackor & C. Maclean, J. Chem. Phys., <u>44</u> (1966) 64.
2. E.R. Andrew & P.P. Tunstall, Proc. Phys. Soc., <u>81</u> (1963) 986,
3. G.V.D. Tiers, J. Am. Chem. Soc., <u>84</u> (1962) 3972.

Fig. 1

Derivative of the fluorine wide-line spectrum of $CDFCl_2$ in hexadeuteroacetone at -196 °C (56.4 Mc/sec.). The scale (1 Oe) is indicated in the spectrum; the field increases from left to right. The asymmetry in the spectrum is caused by the anisotropy in the chemical shift.

(a)

$\sigma_{||} > \sigma_{\perp}$

(b)

$\sigma_{||} > \sigma_{\perp}$
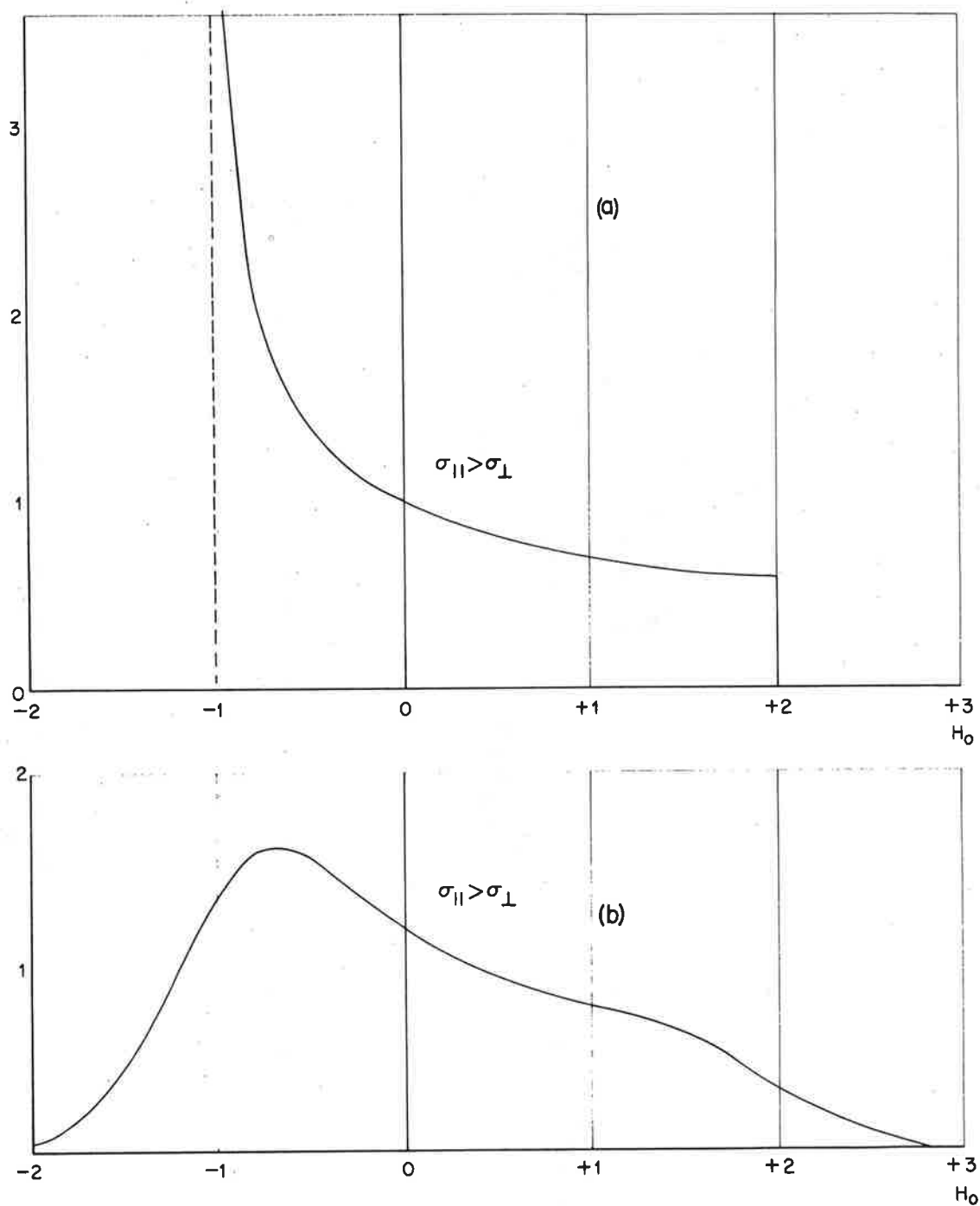
Fig. 2

(a) Line shape in a polycrystalline specimen due to
an axially symmetric chemical shift.

(b) Ditto, after superposition of gaussian broadening
of the component lines.

University of Durham

TELEPHONE DURHAM 3541-8

CHEMISTRY DEPARTMENT,
SOUTH ROAD,
DURHAM CITY.

27th May, 1966.

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

Dear Professor Shapiro,

The note in the 83rd newsletter from Dr.Pascoe on the improvement in signal to noise ratio of an A60 achieved by using 6CW4 Nuvistor valves prompts us to say that we too have used this valve to the same end in our A.E.I. RS 2 machine. We have replaced the ECC 81 valve in the pre-amplifier by two Nuvistors. At first we did not make any other changes at all and observed an improvement of about a factor 2 in the S/N ratio, however, after running for several weeks we found that the valves were overheating and we have now dropped the total voltage across the cascode chain from 250 to 150 by placing a dropping resistor in series. The valves have been in place now for about a year and function quite satisfactorily.

One other experimental tip may be of interest to fellow A.E.I. users. We have found that an improvement in the stability of the magnetic field and drift control can be achieved by ageing the Mallory Cells before use. This is done by shorting the terminals through a load of 100 ohms for 12 hours. The life of the cells is of course reduce by this process, but the improvement in field stability justifies the procedure.

We are in the process of constructing a field-frequency locking device using the circuit of Noggle (Rev.Sci.Inst.) and if anyone else is doing the same thing for an A.E.I. machine we would be very interested to hear from them and to pool our experiences.

Yours sincerely,

J.W.Emsley,
J.D.Dyson.

<div align="center">

D E P A R T M E N T   O F   C H E M I S T R Y

THE UNIVERSITY OF MICHIGAN · ANN ARBOR, MICHIGAN

June 3, 1966

</div>

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

<div align="center">

Shielding of Cyclopropyl Protons by
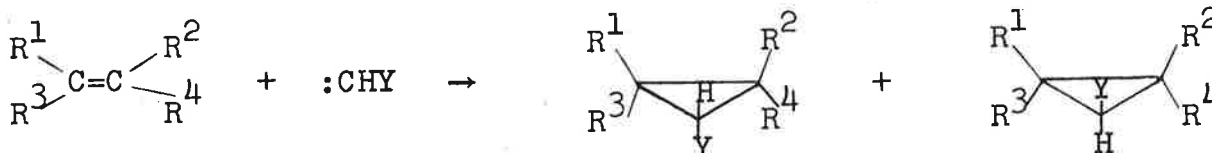
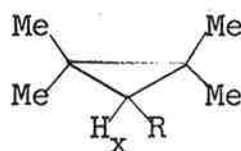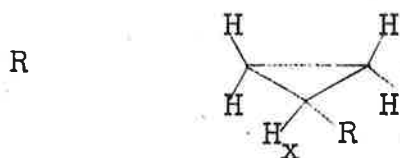Carbon-Carbon Single Bonds

</div>

Dear Barry:

A pair of stereoisomeric cyclopropanes results from the addition of unsymmetrically substituted carbenes to olefins lacking a center of symmetry (eq. 1). In such cases structural assignments are frequently made by examination of ring proton coupling constants. In most known cases the cis coupling constants in cyclopropanes are larger than the trans coupling constants.

A similarity in the diamagnetic effects of carbon-carbon single bonds on cyclopropyl protons and on axial/equatorial cyclohexyl protons has been suggested.[1] In a few cases the shielding effect of a cis alkyl group has been used to assign structures to isomeric cyclopropanes.[2] In the accompanying table are recorded the chemical shifts of the methine protons, H_x, in a variety of substituted cyclopropanes and the corresponding tetramethylcyclopropanes. In every pair the methine proton in the tetramethyl compound appears at significantly higher field. Analogously to the axial and equatorial protons in cyclohexane it appears that cyclopropyl protons are shielded by vicinal cis carbon-carbon bonds and deshielded by vicinal trans carbon-carbon bonds.

As an example of the utilization of this phenomenon in structure determination, consider the isomeric compounds I, II, and III. Within a given pair of isomers structural assignments have been made, as shown, solely on the basis of the relative magnitudes of the cyclopropyl coupling constants.[3] The same assignments result on the basis that the isomer with the methine proton, H_x, at higher field is the one in which that proton is cis to the greater number of alkyl groups. We are examining the generality and usefulness of this approach.
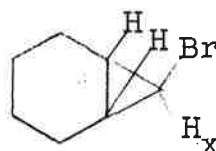
(eq. 1)

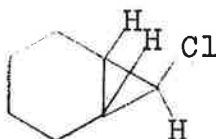| R				
Br	τ	7.14	τ	7.38
-OCMe$_3$		6.90		7.61
-OAc		5.92		6.68
-OCOØ		5.6		6.41
-CO$_2$Me		8.4[4]		8.90[6]
-CH$_2$OH		8.95[5]		9.53[6]

I $\underline{J}$ 8.0 cps τ 6.81 $\underline{J}$ 3.7 cps τ 7.42
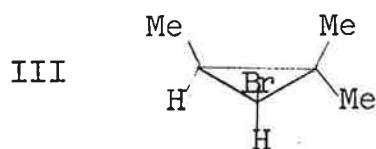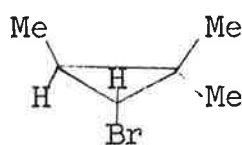
II $\underline{J}$ 7.5 τ 6.86 $\underline{J}$ 3.7 τ 7.44

III $\underline{J}$ 7.2 τ 6.77 $\underline{J}$ 3.8 τ 7.23

References

1. U. Schöllkopf and J. Paust, Ber., 98, 2221 (1965).
2. Cf. Ref. 1 and G. L. Closs, R. A. Moss, and J. J. Coyle, J. Am. Chem. Soc., 84, 4985 (1962).
3. D. Seyferth, H. Yamazaki, and D. L. Alleston, J. Org. Chem., 28, 703 (1963).
4. NMR Spectra Catalog, Varian Associates, Palo Alto, California, 1962.
5. A. Abrahams, S. E. Wiberley, and F. C. Nachod, Appl. Spectry., 18, 13 (1964).
6. P. S. Wharton and T. I. Bair, J. Org. Chem., 30, 1681 (1965).

Sincerely yours,

Daniel T. Longone

Alfred H. Miller

INDEPENDENCE MALL WEST PHILADELPHIA, PA. 19105 TELEPHONE (215) 592-3000

REPLY TO: **Rohm and Haas Company**
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALA. 35807
(205) 876-9042

**ROHM
AND
HAAS
COMPANY**

June 14, 1966

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

Dear Barry,

We have done some additional work on the compound $N_2F_4 \cdot 2SbF_5$
[J. Ruff, J. Am. Chem. Soc., **87**, 1140 (1965)]. Spectra were run
in liquid SO_2 at -70°C, in SO_2 at 25°C and on the pure molten material
at 120°C. All the spectra were very similar; the -70°C traces had
slightly better resolution and are shown in Figure I.

The upfield resonances are due to SbF's - the relative areas of
the peaks are 1.0 (91.7ϕ): 8.3 (112.7ϕ): 1.9 (134.5ϕ).
R. J. Gillespie (private communication) has observed the $Sb_2F_{11}^-$ ion
in HF. This anion consists of two octahedra sharing an apex; thus there
are three types of fluorine in the ratios 1(b-bridging) : 8(e-equatorial) :
2(a-apical). Gillespie has found J_{ae} and J_{be} to be 100 cps and 53 cps
respectively; our values of 93 cps and 60 cps in fair agreement con-
sidering our rather poor resolution.

The low-field fluorine spectra are not unreasonable for the
$N_2F_3^+$ cation. Three groups of peaks having relative areas of 1.0
(-189.8ϕ): 1.05(-155ϕ): 0.97(-130ϕ) are observed. The pattern
is ABX - the best sets of possible coupling constants are J_{AB} = 379 cps,
J_{AX} = 81 cps (or 82), J_{BX} = 45 cps (or -50). A structure such as:

(I.)

$$ \underset{F_2}{\overset{F_1}{\diagdown}} N^+ = N \diagup^{F_3} $$
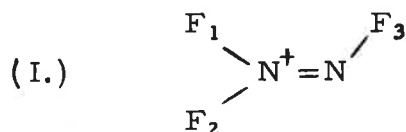
may be expected not to show free rotation about the N N bond, thus
having three different fluorines.

We are unable to assign the observed fluorine resonances to
atoms in (I) without ambiguity. One might expect that F_1 and F_2
would have similar chemical shifts; a geminal J_{FNF} of 380 cps seems
about right since we have observed J_{FF} gem of 600 cps in nonionic

compounds. On the other hand, the largest coupling in $CF_2=NF$ (which is isoelectronic with $N_2F_3^+$) appears to be trans (D.H. Dybvig, private communication) as in the fluorocarbon olefins. The two larger coupling constants of $N_2F_3^+$ are also strikingly similar to the J_{FF}'s in cis and trans N_2F_2 [Noggle, Baldeschwieler and Colburn, J. Chem. Phys., 37, 182 (1962)].

We originally considered the possibility of hindered rotation of a symmetrical Lewis acid: base adduct. However, the lack of changes with temperature and, most convincingly, the presence of $Sb_2F_{11}^-$ appear to settle this point.
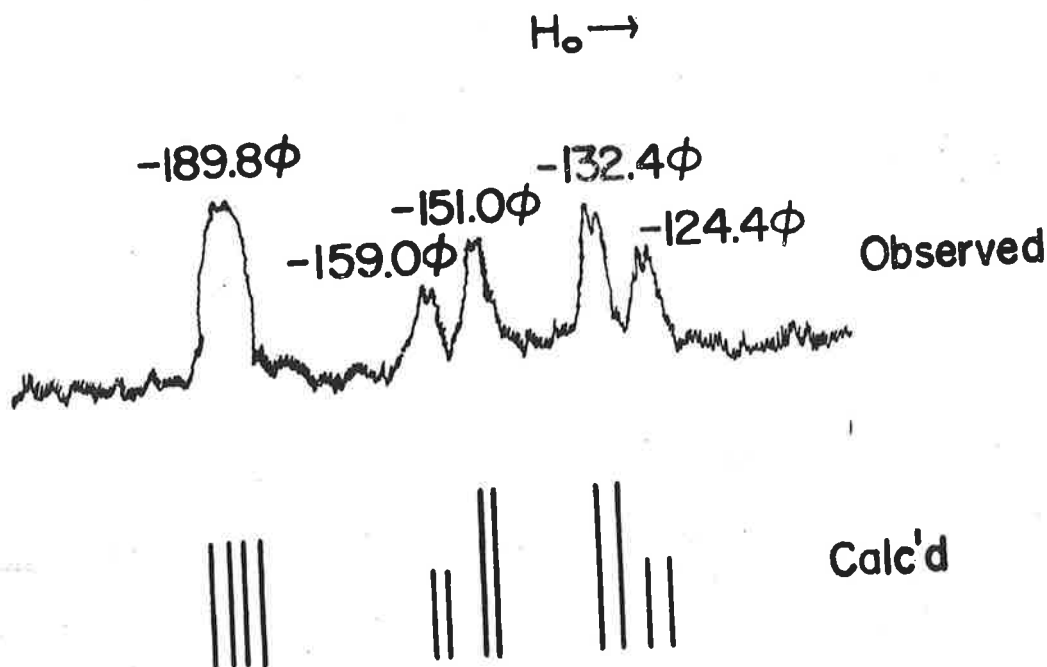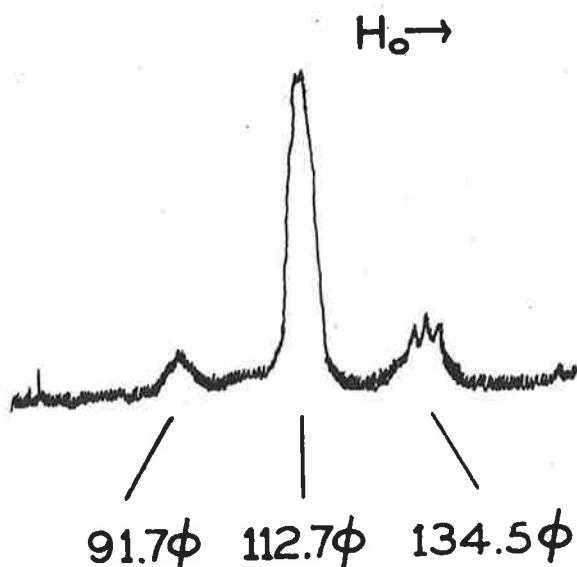
Sincerely,

Fred

F. A. Johnson

John

John K. Ruff

Carolyn

Carolyn Haney

$H_o \rightarrow$

91.7φ   112.7φ   134.5φ

$H_o \rightarrow$

-189.8φ
-151.0φ
-159.0φ
-132.4φ
-124.4φ   Observed

Calc'd

June 7th, 1966

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

Subject: Magnetic Equivalence of Diastereomeric Protons where
          Asymmetry is Due to CHD-OH.   Temperature Studies.

Dear Dr. Shapiro:

We have been interested in the effect of molecular asymmetry
upon the chemical shifts of diastereomeric nuclei.   Numerous examples
of this phenomenon have been reported for geminal nuclei in an
asymmetric environment.   For a system such as $CabcCH_2-X$, purely on
symmetry grounds, it is evident that the geminal protons of the three
conformers (i, ii, iii) are different.
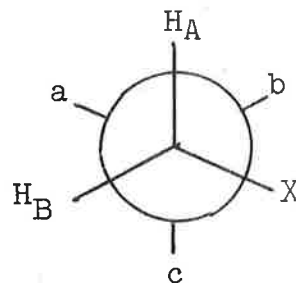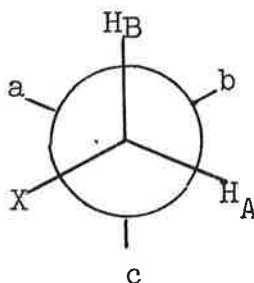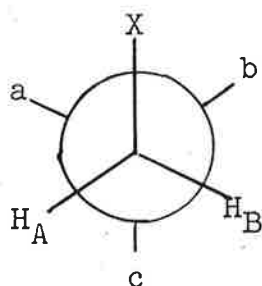
Even though protons H_A and H_B are always different, even when
$Xi = Xii = Xiii$, observation of separate lines corresponding to H_A and
H_B ($\nu_A \neq \nu_B$) requires that their respective magnetic environments
differ.

In order to learn whether the contribution to molecular asymmetry
supplied by the group, CHD-OH, could cause detectable magnetic
inequivalence the spectra of $(CH_3)_2CH-CHDOH(I)$ and $(C_6H_5)_3SiCH_2-CHDOH(II)$
were studied.   The three staggered conformations for I are presented
below:
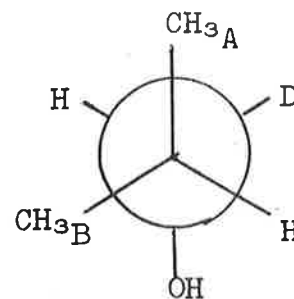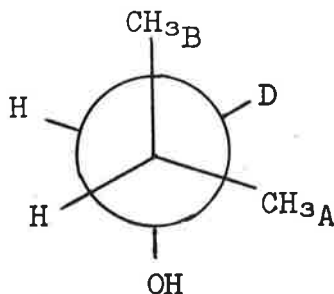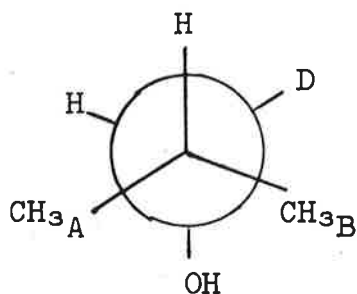
-2-

In neither I nor II was any evidence observed for magnetic inequivalence of the diastereomeric nuclei. For I, the methyl protons of the isopropyl group appeared as a doublet, J vicinal = 7.0 c.p.s. The conclusion drawn from these results is that in spite of the stereochemical non-equivalence of the diastereomeric protons, insufficient magnetic inequivalence is imposed by the asymmetry of the CHDOH group for $\nu_A \approx \nu_B$.

Temperature Variation of Geminal CHD Coupling for $(CH_3)_2CHCDH-OH(I)$

The room temperature spectrum of I shows a doublet of triplets pattern for CHD proton. The principal splitting is due to CH-CH vicinal coupling, J = 6.2 c.p.s. and the subsidiary triplets result from deuterium hydrogen geminal coupling, J = 1.5 c.p.s. This pattern remained unchanged upon addition of catalytic quantities of acid or base. Cooling of the sample to -30° caused a progressive collapse of each of the triplets to singlets ultimately resulting in a simple doublet pattern with the same coupling constant as the principal doublet mentioned above. That this was not due to a slowing of the hydroxyl proton exchange at lower temperatures was demonstrated by the fact that the urethane also showed the same collapse of the

$$CH_3$$
$$\quad CH-CHDO-\overset{\overset{\displaystyle O}{\|}}{C}-NH-C_6H_5$$
$$CH_3$$
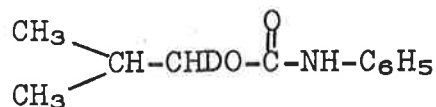
doublet of triplets to a simple doublet pattern. We believe that we are observing the first example of decoupling of the deuterium hydrogen geminal coupling due to an increase in the efficiency of the quadrupolar relaxation of the ^2H dipole at lower temperatures.[3] Cooling slows down the molecular motion and spin-lattice relaxation arising from the fluctuating electric field gradient becomes faster. Splitting should disappear when the correlation time, τ, becomes short with respect to the coupling constant

$$\tau \approx \frac{5}{2\pi J} \approx 0.5 \text{ sec}^{-1}$$

Phillips and Meutterties[1] have observed this type of effect for $N^{14}-F$ (coalescence temp. = -205°) and Roberts[2] has observed coalescence of the $N^{14}-H$ triplet for a number of amines as a temperature dependent function.

Sincerely yours,

Robert M. Moriarty

Robert M. Moriarty
Associate Professor of Chemistry

John P. Kim

John P. Kim
Lecturer

(1) E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 81, 1084 (1959).

(2) J. D. Roberts, J. Am. Chem. Soc., 78, 4495 (1956)

(3) Details will be published with John Kim (C.U.A.) and Ernest Lustig (F.D.A.)

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH, PA. 15213

13 June 1966

Prof. Barry Shapiro
Illinois Institute of Technology
Dept. of Chemistry
Chicago, Illinois 60616

Dear Barry:

"Semel in Anno....Communicare Necesse Est" and this seems to be my turn. Here there are some results obtained at Mellon Institute which I think fit very well with the findings of Drs. Kowalewski's (IITNN 92, 34), of Dr. Bernstein (IITNN 92,12) and of Dr. Martin (IITNN 82,22):

a) We have completely analyzed the proton spectrum of pyridine decoupled from the ^{14}N nucleus. Labelling the protons from 1 to 5 around the ring (the same labelling scheme is used later for monosubstituted benzenes),the best fit of the spectrum (r.m.s. = 0.028 cps) was achieved with the following set of parameters (all data in cps. at 60 Mcps.):

Chemical shifts

W(1) = W(5)	516.510
W(2) = W(4)	427.428
W(3)	450.108

Coupling constants

J(1,2) = J(4,5)	4.882
J(1,3) = J(3,5)	1.842
J(1,4) = J(2,5)	0.995
J(1,5)	-0.132
J(2,3) = J(3,4)	7.666
J(2,4)	1.366

These data agree well with those of Diehl, Jones and Bernstein[1] whenever the comparison is possible, but differ substantially from the old results of Schneider, Bernstein and Pople.[2] The negative sign of J(1,5) is in nice agreement with the results of the Kowalewski's on β-acetyl pyridine.

b) About one year ago we published the analysis of the spectrum of phenylacetylene. In our paper[3] we emphasized the fact that the values of the two vicinal coupling constants [J(1,2) = J(4,5) and J(2,3) = J(3,4)] were, in that compound, closer in magnitude than in any other monosubstituted benzene whose spectral analysis had been published at that time. Today after having analyzed more than 30 monosubstituted benzenes, this

MELLON INSTITUTE

B. L. Shapiro   -2-   13 June 1966

statement is still true indicating, in our view, that the presence of an
acetylenic group on the aromatic ring affects only slightly the magnitude
of the vicinal coupling constants. The parameters found in our analysis
were:

	neat liquid	10% sol. in CCl_4
J(1,2)	7.76	7.77
J(2,3)	7.58	7.60

It seems to us that the excellent agreement between their averaged values
(7.67 and 7.68 cps.) and the value found by Dr. Bernstein and coll. in
benzene (7.7 cps.) completely confirms our previous observation.

c) We have performed a complete analysis of the spectrum of
benzaldehyde both as neat liquid and as 10% solution in CCl_4. The coupling
constant between the aldehyde hydrogen and the meta protons are respectively
0.399 cps. and 0.379 cps. in excellent agreement with the data of Dr.
Martin on monosubstituted benzaldehydes. It is interesting that in both
cases the computer furnished a value of -0.062 cps. for the coupling between
the aldehyde proton and the ortho hydrogens. This value borders the limit
of experimental error and therefore is not too much reliable; it is however
very interesting to observe the reversal of sign which has been confirmed
in the analysis of the spectrum of benzoylfluoride; for this molecule the
long range coupling constants have the following values: $J_{FHortho} = -0.601$ cps.
$J_{FH meta} = 1.330$ cps. $J_{FH para} = -0.023$ (?)

---

[1] P. Diehl, R. G. Jones and H. J. Bernstein, Can. J. Chem. 43, 81 (1965).

[2] W. G. Schneider, H. J. Bernstein and J. A. Pople, Can. J. Chem. 35, 1487 (1957).

[3] S. Castellano and J. Lorenc, J. Phys. Chem. 69, 3552 (1965).

I have done my duty, I don't want to continue receiving
threatening letters from your secretary and .....arrivederci until next year.

Cordially yours,

S. Castellano

SC:HB

Southern Research Institute

May 27, 1966

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

Intermolecular Exchange of Anilino and Methylamino Groups Attached to Silicon

Dear Barry:

Some of our recent nmr work on acyclic silazanes allowed us to observe intermolecular exchange of methylamino and anilino groups attached to silicon. Although intermolecular exchange has been reported for other functional groups attached to silicon, particularly alkoxy, dimethylamino, and chloro groups,[1-3] we do not believe intermolecular exchange between anilino and methylamino groups has been previously reported.

For our work, bis(methylamino)dimethylsilane, I, and dianilinodimethylsilane, II, were mixed in a 2.4:1 molar ratio, sealed under vacuum in an nmr sample tube, and the spectrum recorded periodically.
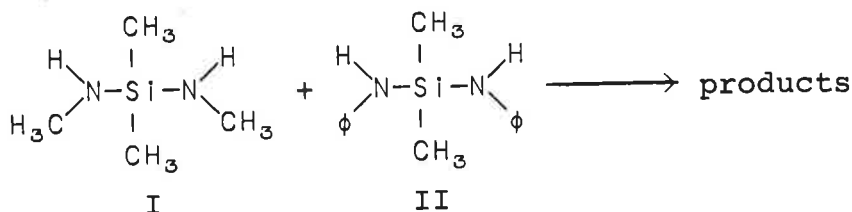
The exchange was conveniently followed by observation of the appearance and growth of a new SiCH$_3$ peak, intermediate in chemical shift between the SiCH$_3$ peaks of I and II, at the expense of the SiCH$_3$ peaks of I and II.
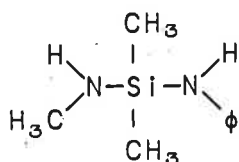
Southern Research Institute
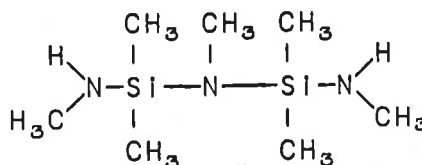
May 27, 1966

Dr. B. L. Shapiro
Chicago, Illinois

-2-

The possible products of this reaction were:

III

IV
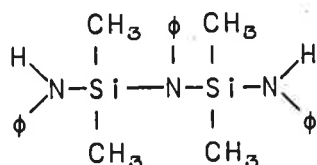
V
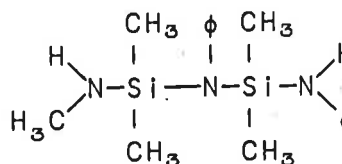
VI
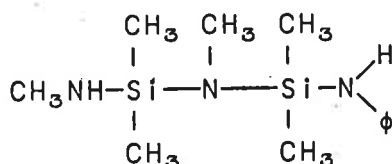
VII

From the nmr spectrum, we felt that III was the product, and
this was confirmed by gas chromatography, infrared spectroscopy,
and elemental analysis.

This exchange took place readily under mild conditions
(room temperature except when in probe at 38°C), and equilibrium
was reached within 24 hours. At equilibrium, the mixed species,
III, was present in larger proportion compared with I and II than
would be predicted for a random distribution of functional groups.
This non-random distribution was reported by Van Wazer and
Moedritzer[1-3] for exchange between chloro and dimethylamino groups,
while a random distribution was reported for exchange between
alkoxy and dimethylamino groups, or between different alkoxy groups.

Southern Research Institute

May 27, 1966
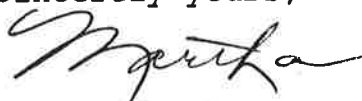
Dr. B. L. Shapiro
Chicago, Illinois

-3-

The most interesting feature of this exchange lies in the fact that the labile bond is the Si-N bond, since there is no evidence of any species with other than two methyl groups attached to silicon, or with two phenyl groups (or two methyl groups) attached to the same nitrogen atom.

In the March 1966 Journal of Organic Chemistry more of our work on azido-tetrazole equilibria appeared. A few reprints are available.

Sincerely yours,

Martha C. Thorpe
Research Chemist

1. J. R. Van Wazer and K. Moedritzer, J. Inorg. Nucl. Chem., 26, 737 (1964).

2. K. Moedritzer and J. R. Van Wazer, Inorg. Chem., 3, 268 (1964).

3. J. R. Van Wazer and S. Norval, Inorg. Chem., 4, 1294 (1965).

mct jis

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

May 27, 1966
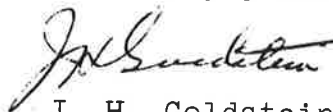
Professor Bernard L. Shapiro
Illinois Institute of Technology
Department of Chemistry
Chicago, Illinois 60616

Dear Barry:
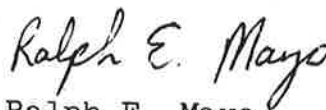
There seems to have been some disagreement in the recent litera-
ture with regard to the assignments of coupling parameters in
4-pyrone. This molecule is an AA'BB' system and the question
concerns the distinction between $J_{AA'}$ and $J_{BB'}$, both which
are long-range cross-ring couplings with the approximate val-
ues 1.1 and 2.7 cps. Four previsouly published reports are
evenly divided on these assignments.

We have re-examined this problem and on the basis of a variety
of evidence again conclude that $J_{26} = 1.15$ cps and $J_{35} = 2.78$
cps. Similar conclusions are reported by Garbisch[a]. Thus,
it appears that in 4-pyrone the long-range coupling transmit-
ted through the structure C - O - C is the smaller of the two.

Sincerely yours,

J. H. Goldstein

Ralph E. Mayo

JHG:lt

[a] Chem. and Industry 1715 (1964).

THE UPJOHN COMPANY

KALAMAZOO, MICHIGAN

June 10, 1966

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

Dear Barry:

I would like to submit some news from our laboratory for the NMR news-
letter.

We have been studying the chemical shifts of hydrogens which are influ-
enced by nearby nitrogen atoms in organic molecules. The data on satu-
rated and olefinic types are presented in the attached tables arranged
alphabetically according to the Varian structure code for the hydrogen.
(Full-size charts are available on request.) The effect of the nitrogen
in various structural environments is consistent and additive. The de-
shielding due to the N is 0.1 to 0.5 δ at a hydrogen three bonds removed,
0.8 to 1.3 δ two single bonds removed and about 2.0 δ when the hydrogen is
on the chromophore (Type-4). The effect of protonating the nitrogen is
more variable.

We recently converted our DP-60 spectrometer to an HA-100. The new instru-
ment has a S/N of 32 and a line width of 0.35 c.p.s. determined in the
usual way. We are now becoming more familiar with its operation. Incidently,
the conversion left us with some un-needed components that we would like to
dispose of. These include the old 14.1 kg. magnet with homogeniety control
unit, 40 and 60 mc. R.F. units and probes, and some other miscellaneous
components.

I wish also to tell the readers of the newsletter about an opening we have
in our NMR laboratory. We have a group of investigators who are active in
structure determination by NMR, IR, UV, mass spectrometry and X-ray dif-
fraction. We now wish to add a Ph.D. to provide more depth in the theo-
retical aspects of NMR. The specific job would depend a lot on the capa-
bilities of the recruit but would probably start with the objective of
preparing a computer program for the IBM 360/30 to analyze NMR spectra.

I hope this letter will stimulate some replies from interested readers.

Best personal regards.

Very truly yours,

George Slomp
Physical and Analytical Chemistry

alb

ORGANIZATION OF NMR DATA ON NITROGEN-CONTAINING COMPOUNDS

George Slomp and James G. Lindberg

The table is limited to primary interactions with nitrogen functions. Long-range effects are not covered nor are interactions with non-nitrogen functional groups except for a few examples of olefins. The table makes only a few distinctions between aliphatic and cyclic chromophores. Aromatic chromophores are noted. In the analysis of resonance hybrids only the form with the largest contribution was considered.

1. Code

   The effect of alkyl substituents (A, B, C or D) was about the same and these possibilities have therefore been combined in the charts. Thus the meaning of the term "A, B, C or D" is that one and only one of these groups is attached to the chromophore.

   When no lower-case letters appear in the code it is understood that only H or saturated-C substituents such as a, b, c or d are attached. Deshielding substituents including N, O, S, halogens or multiple bonds, when present, are shown in the code. The effect of j-, k-, l-, m-, or v-substituents was about the same and these possibilities have therefore been combined wherever possible. Thus, the meaning of the term "j, k, l, m or v" is that one and only one of these groups is present unless otherwise specified. In some cases the inclusion of o, p, q and s made no difference in the absorption frequency and these were therefore included in the code designation.

   The semicolon is used to separate the various functional groups attached to the chromophore. A plus sign followed by a lower-case letter signifies that one such substituent is attached to the functional group. Thus, the term "B, C or D + j, k, l, m or v" signifies that the group may be B, C or D and that one substituent of the type j, k, l, m or v is attached and that the rest of the substituents are a, b, c, d and/or h, as required.

2. Structure

   A dangling single bond signifies a hydrogen or saturated-carbon atom is attached. A dangling double bond signifies that a carbon or nitrogen atom is attached by a double bond. The symbol ❷ signifies that an unsaturated carbon or unsaturated nitrogen atom is attached in the manner shown.

3. Chemical Shift

   Solid lines represent values for the structures shown. Values for protonated derivatives are shown as dotted lines. Values differing by 8 c.p.s. or less are connected and show the highly populated regions. Spurious values may arise from special long-range effects.

4. Range

   The range of the highly populated region is reported. Where this was not known the individual results are recorded using commas where applicable.

GS:alb

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
I-B,C or D + n	CH₃-C-N<		1.28-0.93 / 1.60 1.23	20 / 22
I-B,C or D + j,k,l,m or v + n	CH₃-C-N<		1.45-1.32 / 1.63,1.30	6 / 2
I-C or D + nn	CH₃-C-N<		2.96	1
I-Jn	CH₃-C-N<		2.78-1.88	28
I-L + j,k,l,m or v	CH₃-C-N< or CH₃-C-N<		2.96-2.00 / 2.36-2.20	60 / 5
I-Lin	CH₃-C-N<		2.64-1.92	43
I-L + m	CH₃-C-N<		2.03-1.67	11
I-Lmm	CH₃-C-N<		2.76-2.37 / 2.48-2.33	25 / 5
I-Lmn	CH₃-C-N<		2.57	1
I-Lmo	CH₃-C-N<		3.87	1
I-N	CH₃-N<		2.44-2.00 / 3.13-2.70	34 / 25
I-N + j,l,m or v	CH₃-N<		3.22-2.57 / 3.26-2.96	63 / 14
I-N + 2[j,k,l,m or v]	CH₃-N<		3.85-2.86 / 4.06-3.73	43 / 6
I-N❷	CH₃-N<		3.35-3.16	11
I-Om	CH₃-O-N=		3.85	1
I-On	CH₃-O-N<		4.03	1
I-Sn	CH₃-S-ARYL+N		2.43,2.38	2
I-X	CH₃-ARYL+N		2.76-1.96 / 2.57-2.22	82 / 10

Table 1

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
2-A,B,C or D; B,C or D + n	-CH$_2$-C-N<		.75-.52 / 1.58-1.62	11 / 6
2-B,C or D; B,C or D + n	CH$_2$ N (ring)		2.02-1.58 / 2.47-2.10	23 / 8
	CH$_2$ N (ring)		1.75-1.38 / 1.87-1.72	26 / 10
	CH$_2$ N (ring)		1.70-1.53	14
2-A,B,C or D; C or D, + j,k,l,m,n,p or v + n	-CH$_2$-C-N< (θ)		2.13-1.87 / 2.54, 2.23	3 / 2
2-B,C or D + j or l, B,C or D + n	>C-C-CH$_2$-N<		2.08-1.87	7
2-A,B,C or D; Jn	-CH$_2$-C-N< (=O)		2.32-1.87	6
	-CH$_2$-C-N<		3.02-2.63	6
2-B,C or D + n; J,K or L	>C-CH$_2$-C-N<	aliphatic / cyclic	3.05-2.77 / 3.00-2.94 / 2.63-2.38 / 3.26-2.80	3 / 4 / 7 / 2
2-B,C or D + m; L	>C-CH$_2$-C-N<		2.88	1
2-A,B,C or D; L + a or b + m	-CH$_2$-C=N<		2.37	1
2-A,B,C or D; Lhl	-CH$_2$-C=C-N<		1.67	1
2-A,B,C or D; Lll	-CH$_2$-C=N<		2.68-2.46 / 3.02	7 / 1
2-A,B,C or D; Llm	-CH$_2$-C=N< or -CH$_2$-C=N<		2.97-2.54	19
2-A,B,C or D; Lln	-CH$_2$-C-N<		2.87-2.60 / 2.52, 2.24	8 / 2
	-CH$_2$-C-N< conj		2.72-2.43	13
2-A,B,C or D; Lmm	-CH$_2$-C=N<		3.10-2.50	5
2-A,B,C or D; Ml	-CH$_2$-N=C- conj		4.07-3.95	3
2-A,B,C or D; Mm	-CH$_2$-N=N-		4.43	1

Table 2

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
2-A,B,C or D, N	-CH$_2$-N<	aliphatic / cyclic	2.95-2.37 / 3.42-2.78 / 2.90-2.20 / 3.68-3.10	13 / 20 / 29 / 21
2-A,B,C or D; N + j,k,l,m,n or v	-CH$_2$-N< (θ or N<)	aliphatic / cyclic	3.54-3.05 / 3.28 / 3.92-2.92 / 3.78	14 / 1 / 39 / 1
2-A,B,C or D; N + 2 j,k,l,m,n or v	-CH$_2$-N< (θ or N<)	aliphatic	4.05-3.64	10
2-B,C or D + j,k,l,m or v; N + a,b,c,d,h,i,k,l,m or v	=B,C-CH$_2$-N< C,H or θ=	aliphatic / cyclic	2.93-2.63 / 3.32-3.25 / 3.17-2.63 / 3.40-3.38	7 / 4 / 10 / 3
2-A,B,C or D; Nn	-CH$_2$-N< N<		2.92-2.87	5
2-A,B,C or D; Om	-CH$_2$-O-N=		4.78, 4.37, 4.15	3
2-J + a,b,c,d,m,n or v; N / 2-K; N	C,O or θ-C-CH$_2$-N< (=O)		3.55-3.45 / 3.85-3.80	3 / 4
2-J + a,b,c,d,m,n or v; N + j,k,l,m or v / 2-K; N + j,k,l,m or v	C,O or θ-C-CH$_2$-N< θ= (=O)		4.07-3.86	7
2-L + l or m; N	θ=C-CH$_2$-N<		3.34-3.14 / 3.58-3.57	5 / 3
2-L + l or m; N + j,k,l,m or v	θ=C-CH$_2$-N< θ=		4.05-3.70 / 4.30-3.86	59 / 7
2-Lll; N	-N C=C-CH$_2$-N<		3.87, 3.83	2
2-Llv; N	Aryl C=C-CH$_2$-N<		3.78-3.70	5
2-Llv; N	Aryl conj-C=C-CH$_2$-N<		4.26-4.08 / 5.07, 4.82	6 / 2
2-Lmn; N	-N C=N-C-CH$_2$-N<		3.88	1
2-N; V	(ring)-CH$_2$-N<		3.80-3.54 / 4.43-4.17	3 / 4
2-N; V + j,k,l,m or v	(ring)-CH$_2$-N< θ=		4.85-4.30	13
2-N; V + 2 (j,k,l,m or v)	(ring)-CH$_2$-N< θ=		5.25, 4.96, 4.57	3
2-Om; Vbb	(ring)-CH$_2$-O-N<		4.65 / 4.93	1 / 1

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
3-A,B,C or D; A,B,C or D; B,C or D + n	-ĊH-Ċ-N<		2.30 , 1.65 3.47 , 2.56	2 2
3-A,B,C or D; A,B,C or D; Jn	-ĊH-Ċ-N< (O)		2.62	1
3-A,B,C or D; A,B,C or D; L in	-ĊH-Ċ-N< (C)		2.04-1.94	2
3-A,B,C or D; B,C or D + n; J,K or L	>C-ĊH-Ċ-N<		3.50-2.93 3.47	8 1
3-A,B,C or D; A,B,C or D; N	-ĊH-N<		2.87-2.78 3.74-3.38	4 10
3-A,B,C or D; A,B,C or D; N + j,k,l, m or v	-ĊH-N< (∅)		3.84-3.38	9
3-A,B,C or D; B,C or D + j,k,l, m or v; N + a,b,c,d,h,j,k,l, m or v	=∅-Ċ-ĊH-N< (C,H or ∅)		4.10 , 3.55 5.08-4.65	2 6
3-A,B,C or D; J,K,L,M or V; N	-ĊH-N< (∅)		4.80-3.75 4.34 , 3.97	11 3
3-A,B,C or D; J,K,L,M or V; N + j,k,l, m or v	-ĊH-N< (∅)		4.72-4.61 4.63	5 1
3-B,C or D + j,k,l, m or v; J,K,L,M or V; N + j,k,l, m or v	=∅-Ċ-ĊH-N< (∅)		4.96-4.72	8

Scale: PPM (δ) 5.0 4.0 3.0 2.0 1.0

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
4-A,B,C or D; A,B,C or D	-C=N- (H)		7.26-7.22	2
4-A,B,C or D; J,K,L,M or V	-C=N-∅- (H)			
4-A,B,C or D; M	-C=N-N- (H)			
4-A,B,C or D; N	-C=N-N< (H)		8.12, 8.62	2
4-A,B,C or D; O,P,Q or S	-C=N-O- or -S- (H)			
4-J,K,L,M or V; A,B,C or D	=∅-C=N- (H)		8.27	1
4-J,K,L,M or V; O,P,Q or S	=∅-C=N-O- or -S- (H)		8.27-8.02	6
4-J,K,L,M or V; J,K,L,M or V	=∅-C=N-∅- (H)		8.17-8.05	6
4-J,K,L,M or V; N	=∅-C=N-K (H)		7.96-7.66	7
4-N; A,B,C or D	>N-C=N- (H)			
4-N; J,K,L,M or V	>N-C=N-∅- (H)		7.90	1

Scale: PPM (δ) 9.0 8.0 7.0 6.0 5.0

Table 1

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
5 - B,C or D + n ; H ; H			5.90–5.52 / 5.96–5.60	10 / 3
5 - H ; H ; B,C or D + n 5 - H ; B,C or D + n ; H			5.26–5.02	19
5 - Jn ; H ; H			6.15	1
5 - H ; H ; Jn 5 - H ; Jn ; H			5.60 / 6.25	1 / 1
5 - N ; H ; H			6.86	1
5 - H ; H ; N 5 - H ; N ; H			4.13 / 4.37	1 / 1
6 - N ; A,B,C or D				
6 - A,B,C or D ; N				
6 - N + j ; Jn or K			8.00 7.75	2
6 - Jn or K ; N + j	N or O–		5.95–5.90	2
7 - Jn ; Jn	aromatic		6.78	1
7 - Jn ; L	aromatic		6.45	1
7 - L ; Jn				
7 - N + j ; Jn or K	aromatic		8.00–7.62	7
7 - Jn or K ; N + j			5.95–5.73	7
7 - N + j, h, l, m or v ; A,B,C or D			5.80–5.70 / 5.83–5.78	3 / 2
7 - A,B,C or D ; N + j, h, l, m or v			6.12–6.03 / 6.20–6.16	2 / 2
7 - N + j or l ; L	aromatic		7.68–7.30	8
7 - L ; N + j or L			6.73–6.53	8
7 - Ml ; N + l	aromatic		7.13	1
7 - N + l ; Ml			7.13	1

Table 2

CODE	STRUCTURE	CHEMICAL SHIFT	RANGE	NO.
8 - N + j ; V			4.42	1
8 - V ; N + j			4.93	1
9 - A,B,C or D ; K ; N + l			4.90	1
9 - B,C or D + o ; N + j ; A,B,C or D			4.90	1
9 - B,C or D + o ; N + j ; B,C or D + v			5.56–5.30	2
9 - Jn ; A,B,C or D ; A,B,C or D			5.80	1
9 - J ; A,B,C or D ; N			5.01	1
9 - J ; N + j ; A,B,C or D			5.66–5.26	5
9 - J ; N + j ; B,C or D + v			5.96–5.70	7
9 - J + l ; N + j ; A,B,C or D			5.63–5.56	2
9 - J + l ; N + j ; B,C or D + v			6.12, 5.96, 5.76	3
9 - K ; Jn ; N + v			5.96	1
9 - L + j, h, l, m or v ; A,B,C or D ; Ml			5.75–5.70	2
9 - L + j, h, l, m or v ; A,B,C or D ; N			5.15, 4.88	2
9 - L + j, h, l, m or v ; A,B,C or D ; N + j, h, l, m or v			5.83–5.56	4
9 - N ; A,B,C or D ; A,B,C or D			5.43–5.40	3

IOWA STATE UNIVERSITY
of Science and Technology
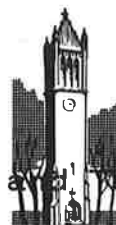
AMES, IOWA 50010

Department of Chemistry

June 10, 1966

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

Dear Barry, <u>Line Shapes from the A-60</u>

Dr. J. G. Verkade and I have been analyzing the methylene multiplets of complexes of the type <u>trans-$[CH_3C(CH_2O)_3P]_2M(CO)_x$</u>, where M=Ni, Fe, Cr, Mo, Co, W, to obtain values for J_{PP}. Some results have recently appeared in print (Inorg. Chem. $\underline{5}$, 639 (1965).

The system was treated as $X_nAA'X'$ with $J_{XX'} = 0$ (cf. Harris, Can. J. Chem., 42, 2275 (1964)) with the further assumption that $J_{AX'}$ is zero. With J_{AX} at 4-5 cps (Hz) the multiplet appeared from a clean doublet ($J_{PP} = 0$) through intermediate stages to a near-1:2:1 triplet for $J_{PP} = 300$ cps (Hz). We wrote a simple program for the IBM 7074 to calculate and plot the envelope of the CH_2 multiplet with suitable scale factors for superimposition on the A-60 trace; J_{AX}, $J_{AA'}$ and the line width were then juggled for best fit by eyeball iteration.

The point of all this is that we achieved surprisingly good fits using a pure Lorentzian line shape. The A-60 was run at a sweep width of 50 cps (Hz), RF field 0.01 milligauss and sweep time 250 or 500 seconds. The line widths observed (0.6-0.9 cps (Hz) at h/2) were rather larger than the instrumental line width, probably because of traces of paramagnetic species, which may account for the good Lorentzian shape. I recall only one report of envelope analysis in these pages (Colebrook, IITNMR 84, 6) and would be interested to hear from anyone who has done detailed line shape analysis with single- or crossed-coil instruments.

As may be seen, my frequency units are still in a state of flux. Maybe the student (cf. ApSimon, IITNMR 92, 46) was right when he referred to the subject as "unclear magnetic resonance".

Sincerely yours,

Roy W. King

The University of Newcastle upon Tyne,
Department of Inorganic Chemistry,
School of Chemistry,
The University,
Newcastle upon Tyne, 1.

Telephone: Newcastle 28511.

14th June 1966.

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

Dear Professor Shapiro,

Remote Bridge Balancing.

The N.M.R. spectrometer at Newcastle is an A.E.I.
Ltd. type RS2. We have had, on the whole, good results from
this though some modifications have been necessary, particularly
to the bridge (the Tuttle-Anderson bridge is used) and to the
lock in detector.

It has been found necessary to stiffen the bridges mechanically
to eliminate mechanical back-lash from the balancing controls and for
broad line work, to introduce remote balancing, since at high R.F.
inputs the bridge remains mechanically too unstable. This was
achieved by putting back-biased (Varactor) diodes across the
balancing capacitors and adjusting their capacity with a remotely
adjustable biasing voltage. The circuit is given in fig 2.2. The
diodes used were standard switching diodes though it would be better
to use high "Q" diodes. These are obtained from S.T.C. in this
country or from Philco in the U.S.A. A battery power source was
used as this should give a very steady output, though smoothing was
added in case any short term fluctuations occurred, especially
towards the end of the battery life. The unit has immensely
improved the spectrometer handling and is recommended to users of
instruments with similar bridge circuits. None of the values of
fig 2.2 is critical though I have arranged that the diode bias
shall never fall to zero so as to avoid loading the bridge with
conducting diodes. Also, wire wound potentiometers should be
used as these are free from back-lash. The condenser C_c is the
one placed across the sample coil and is sensitive to smaller
variations in capacity than is C_r, hence the dissimilar voltage
dividers.

The lock in detector gives trouble in that with L.F.
modulation applied (23 cps) one obtains beats between this,
its harmonics and the 50 cps mains frequency which give an
intense output at about 3 cps. In order to reduce the 3 cps
noise several modifications were made which, basically,
consist in reducing the LID amplifier gains and improving the
H.T. decoupling. To date I have obtained about a 3:1 improve-
ment in signal/noise ratio for the Ga^{71} signal from 2m $GaCl_4^-$.
I am willing to send details of these modifications to
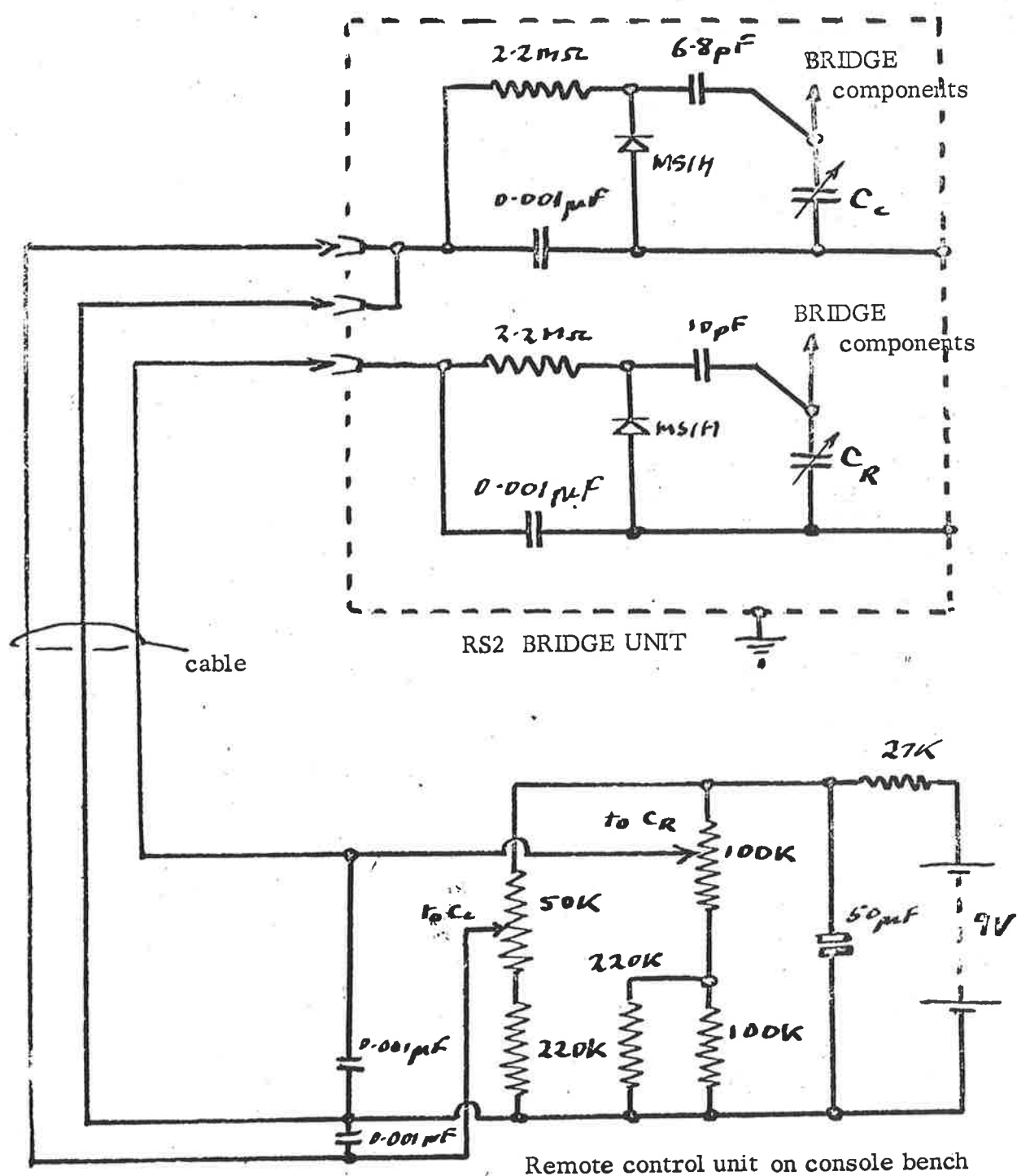anyone interested.

Yours sincerely,

J.W. Akitt

Fig. 2-2   Remote Balancing Circuit

fig 2-1

93-42

THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY · INDIANAPOLIS 6, U.S.A. · 317 MELROSE 6-2211

June 14, 1966

Dr. B. M. Shapiro
Associate Professor of Chemistry
Illinois Institute of Technology
Chicago, Illinois - 60616

Dear Barry:

RE: RING ANISOTROPIES IN HETERO-
AROMATIC COMPOUNDS

We have been looking at the PMR spectra of some phenyl-substituted
heteroaromatic ring compounds. We find a strong paramagnetic
shift (~0.3 - 0.6 ppm.) of the ortho protons of the phenyl, unless
the two aromatic rings are restricted from being coplanar. Lynch
and Hung first pointed this out for the pyrazoles. Thus far, the

B. M. Lynch and Y. Y. Hung, Can. J. Chem., _42_, 1605 (1964)

data fall into three general classes. (1) The ortho multiplet is
cleanly separated from the meta-para multiplet. This indicates
coplanarity, and occurs in those compounds having one or no
protons on the heterocyclic ring that are alpha to the point of
phenyl substitution (cf. esp. Table II). (2) The presence of two
alpha protons is sufficient to destroy much of the coplanarity, as
for examples, in diphenyl and in 4-phenyl pyrazole. Here the
ortho effect is not clearly seen, but the resonance is definitely
a multiplet. (3) The phenyl protons appear as a singlet or very
nearly so, in compounds having even one substituent in the alpha
position.

The shift difference between ortho and the meta-para protons shown
in the following tables is a rough measure of the magnetic aniso-
tropic effect of each heteroaromatic ring on the ortho protons of
the phenyl ring. In some of these compounds the ortho phenyl
protons are a fixed distance away in the plane of the hetero-
aromatic ring. This approach to anisotropies bears on the twin
questions: (1) How aromatic are these heterocompounds, and, (2) How
much of the magnetic anisotropy of a ring is due to contributions
from individual atoms and how much from an induced ring current?

In order to properly interpret these data, we are busy extracting
better chemical shift data for the meta and para protons, via
deuterated compounds and computer spectral analyses. Part of
these data will appear soon in the Journal of Organic Chemistry.
C. Ainsworth contributed to the discussion; P. Landis, L. Spangle,
and T. Elzey provided the NMR data.

Sincerely yours,

Lowell G. Tensmeyer
Chemical Research Division

jb
Attach. 2 Tables

Table 1

Phenyl Proton Chemical Shifts δ of Phenyl Pyrazoles Measured in
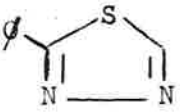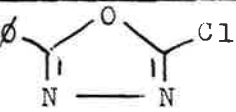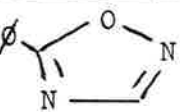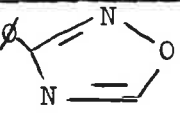Deuterochloroform, ppm. from Internal TMS
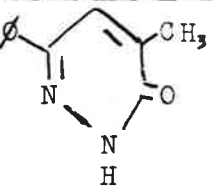
Compound Class	No. of Compounds Tested	Singlet δ (all protons)	Multiplet, δ		
			Ortho	Meta, Para	$\delta_o - \delta_{m,p}$
1-Phenyl (5-position substituted)	4	7.41 ± 0.02^a	-	-	-
1-Phenyl (5-position <u>not</u> substituted	2	-	7.7 - 7.8	7.2	0.5
5-Phenyl (N-R)	5	7.44 ± 0.03^a	-	-	-
3-Phenyl (N-R)	5	-	7.82 ± 0.01	7.39 ± 0.03^b	0.43 ± 0.04
3(5)Phenyl (N-H)	7	-	7.73 ± 0.02	7.37 ± 0.02^b	0.36 ± 0.01

[a]   The two values superscript[a] are not significantly different;
     average δ 7.43 $\pm$ 0.03 ppm.

[b]   Observed chemical shift of benzene in deuterochloroform is 7.37 ppm.

Table 2

Aromatic Resonances of Additional Mono-Substituted Benzenes
(ppm. from internal TMS)

Compound	Ortho Shift δ	Meta, Para Shift $\delta_{m,p}$	$\delta_o - \delta_{m,p}$	Heteroaromatic Proton Shift	Solvent
(phenyl-thiazole structure)	7.92	~7.44	0.48	9.17	$CDCl_3$
(phenyl-oxadiazole-Cl structure)	8.05	~7.42	0.63	–	$CDCl_3$
(phenyl-oxadiazole structure)	8.12	~7.53	0.59	8.51	$CDCl_3$
(phenyl-oxadiazole structure)	8.08	~7.45	0.63	8.72	$CDCl_3$
(phenyl-CH₃ heterocycle structure)	7.78	~7.40	0.38	7.60	$CDCl_3$

MICHIGAN STATE UNIVERSITY EAST LANSING · MICHIGAN 48823

COLLEGE OF NATURAL SCIENCE · DEPARTMENT OF CHEMISTRY · CHEMISTRY BUILDING

June 14, 1966

Professor Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

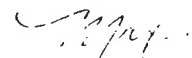<div align="right">Re: Manual for V-4331 Probes</div>

Dear Barry:

We have quite a stock of Varian manuals for the DP-60 of various vintages and find it easy, especially for those just learning the operation of the instrument, to miss some key information buried therein.
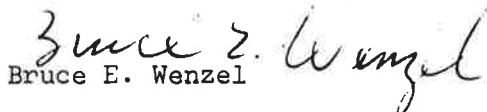
Since we frequently change probes, the material from various Varian manuals covering the V-4331 has been brought together, along with a few notes of our own, into an eight-page "Manual for the V-4331 Probe". If anyone is interested we will be glad to send them a copy.

Another case of temporarily misplaced Varian literature caused us some lost hours recently. An old V-4310 RF unit was being used for wide line work but we could not get calibrating audio sideband through it. Somehow it had escaped the necessary modification described in Varian Publication No. 87-100,026 Revision A which is supplied with the "Modification Kit for Adapting V-4310 and V-4311 R. F. units to V-3521 NMR Integrators". The filter unit in the old RF units filters out the audio and must be rebuilt. If anyone inherits one of these old units it might be well to check that the modification has been made.

Yours sincerely,

Max T. Rogers

Bruce E. Wenzel

nh

SUMMER INSTITUTE
IN
MASS SPECTROSCOPY
AND
ADVANCED NMR

INTERPRETATION OF SPECTRA
AND COMPUTER TECHNIQUES

A Special Merit Program, designed
to meet the needs of scientists
in industry, sponsored by Stevens
Institute of Technology and par-
tially funded by The Department
of Commerce under the State Tech-
nical Services Act of 1966.

DATE: AUGUST 15 - 19, 1966

STEVENS INSTITUTE
OF TECHNOLOGY
Hoboken, New Jersey

PROGRAM

A one-week program designed primarily for
chemists who have some knowledge of nuclear
magnetic resonance (NMR) but little or no
background in mass spectroscopy or computers.
Personnel from industrial, government, and
academic institutions are invited to par-
ticipate.

The course will emphasize the more advanced
aspects of high resolution NMR; such as
computer analysis of spectra, spin decou-
pling, structure and stereochemistry,
applications to polymer and biochemistry.
Sessions will be held on the fundamentals,
high resolution methods and computer tech-
niques of mass spectroscopy. No previous
training in computers is assumed. Emphasis
will be on the complimentary aspects of
these powerful techniques for basic and
applied research, development and quality
control.

Formal lectures will be held each morning.
Afternoons will be devoted to NMR, mass
spectral and computer laboratories; prob-
lem sessions, and seminars. Evenings will
be available for supplementary discussions
and laboratory work.

LECTURE TOPICS

Monday, August 15, 1966

Mass Spectra and NMR of Natural Products

Dr. Ajay K. Bose
Stevens Institute of Technology

Introduction to Computers and Computer Language

Dr. Myron White
Stevens Institute of Technology

Fundamentals of Mass Spectroscopy

Dr. Phillip T. Funke
Stevens Institute of Technology

Tuesday, August 16, 1966

Introduction to Complex NMR Spectra

Dr. Edmund R. Malinowski
and
Dr. James van der Veen
Stevens Institute of Technology

Computer Programming

Dr. Myron White
Stevens Institute of Technology

Wednesday, August 17, 1966

Mass Spectral Fragmentation

Dr. Ajay K. Bose
Stevens Institute of Technology

Computer Analysis of NMR Spectra

Dr. Salvatore Castellano
Mellon Institute
Pittsburgh, Pennsylvania

Thursday, August 18, 1966

Isotopes in Mass Spectroscopy

Dr. Phillip T. Funke
Stevens Institute of Technology

NMR Double Resonance

Dr. Jay Anderson
Bryn Mawr College
Bryn Mawr, Pennsylvania

NMR of Polymers

Dr. Frank Bovey
Bell Telephone Laboratories
Murray Hill, New Jersey

Friday, August 19, 1966

NMR of ^{13}C and ^{15}N, Biochemical Applications

Dr. Edmund R. Malinowski
and
Dr. Ajay K. Bose
Stevens Institute of Technology

High Resolution MS and Computer Techniques

Dr. Klaus Biemann
Massachusetts Institute of Technology
Cambridge, Massachusetts

BANQUET, Thursday, August 18, 1966

Stevens Center, 6:30 p.m.
Banquet Speaker: Dr. James Shoolery
Varian Associates, Palo Alto, California

"Future Prospects of NMR and Mass Spectroscopy"

ENROLLMENT FORM

Mail To:

Dr. Edmund R. Malinowski
Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Castle Point Station
Hoboken, New Jersey 07030

Telephone: 201 - 792 - 2700   Ext. 344

Enclose:

Check made payable to Stevens Institute of Technology in the amount of $200.00 (this fee includes $10.00 for banquet).

Please indicate experience in	None	Some	Much
NMR			
MS			
Computers			

Name _____

Position _____ Telephone _____

Organization _____

Mailing Address _____

Home Address _____

Parking facility requested   Yes ☐ No ☐   Accommodation on campus requested   Yes ☐ No ☐

(Air-conditioned room, $7.00 per person, two persons per room)   (Cafeteria facilities are available at Stevens Center)

THE UNIVERSITY OF SUSSEX

THE CHEMICAL LABORATORY   FALMER   BRIGHTON   SUSSEX

Telephone: Brighton 66755

9th June, 1966.

Dr. Shapiro,
Department of Chemistry,
The Illinois Institute of Technology,
Chicago 60616,
U.S.A.

Dear Dr. Shapiro,

In the chemical physics group at the University of
Sussex we are using the Pople-Santry approach for the
calculation of spin-spin coupling constants. One project
which we have recently completed is an evaluation of the
theory for quantitative predictions of directly-bonded
coupling constants between fluorine and other first row
elements. The results we have obtained are shown in the
enclosed figures, and are very satisfactory.

The details of the parameterization cannot be given
in this short letter, except to say that the most important
requirement is to use a Mulliken-type approximation for the
resonance integrals, $\beta_{AB} = kS_{AB}(\alpha_A + \alpha_B)$, where k is a
constant for all elements. The formula $\beta = kS_{ab}$ can not
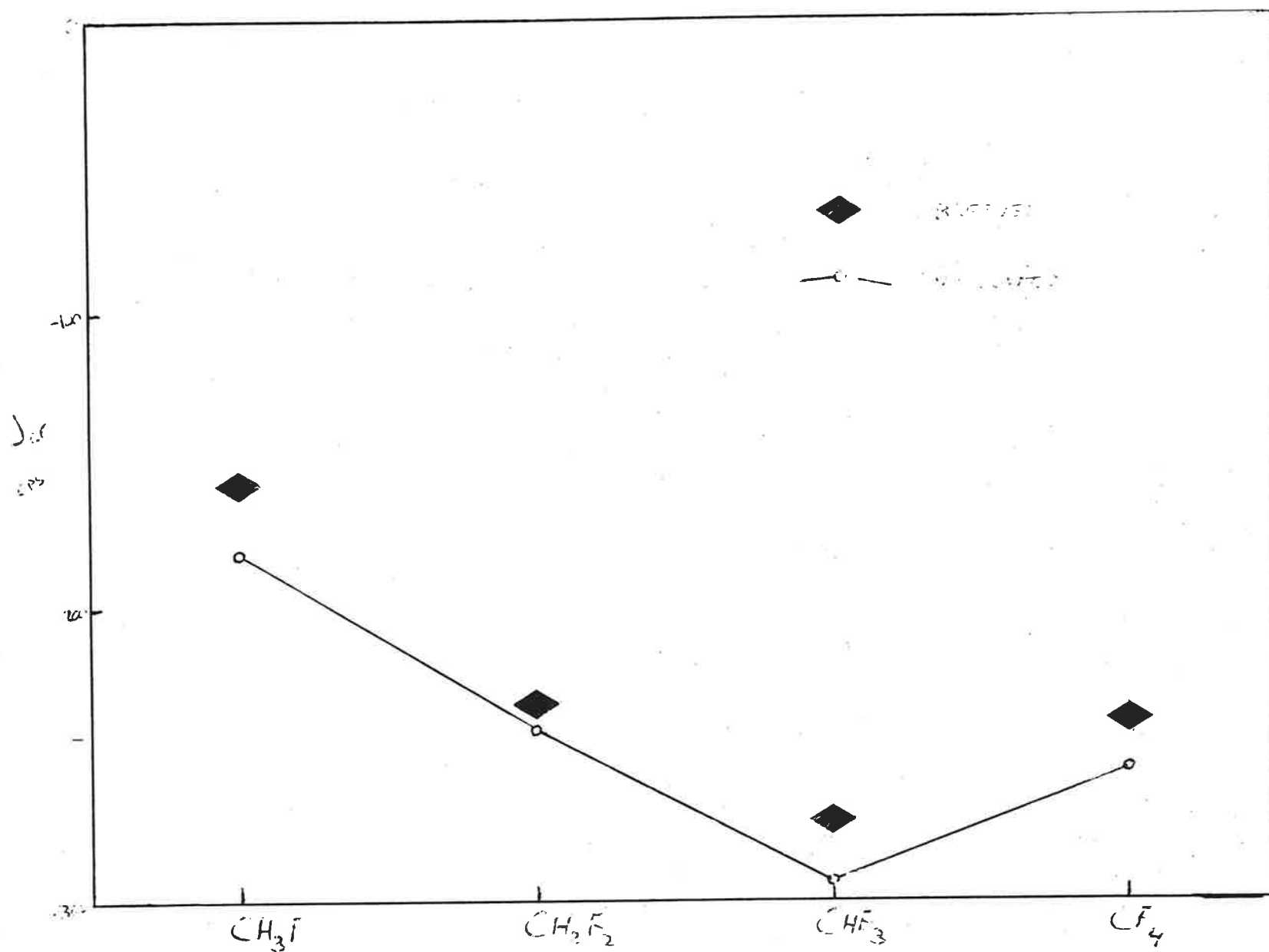encompass both F and H couplings.

Yours sincerely,

J. N. Murrell,
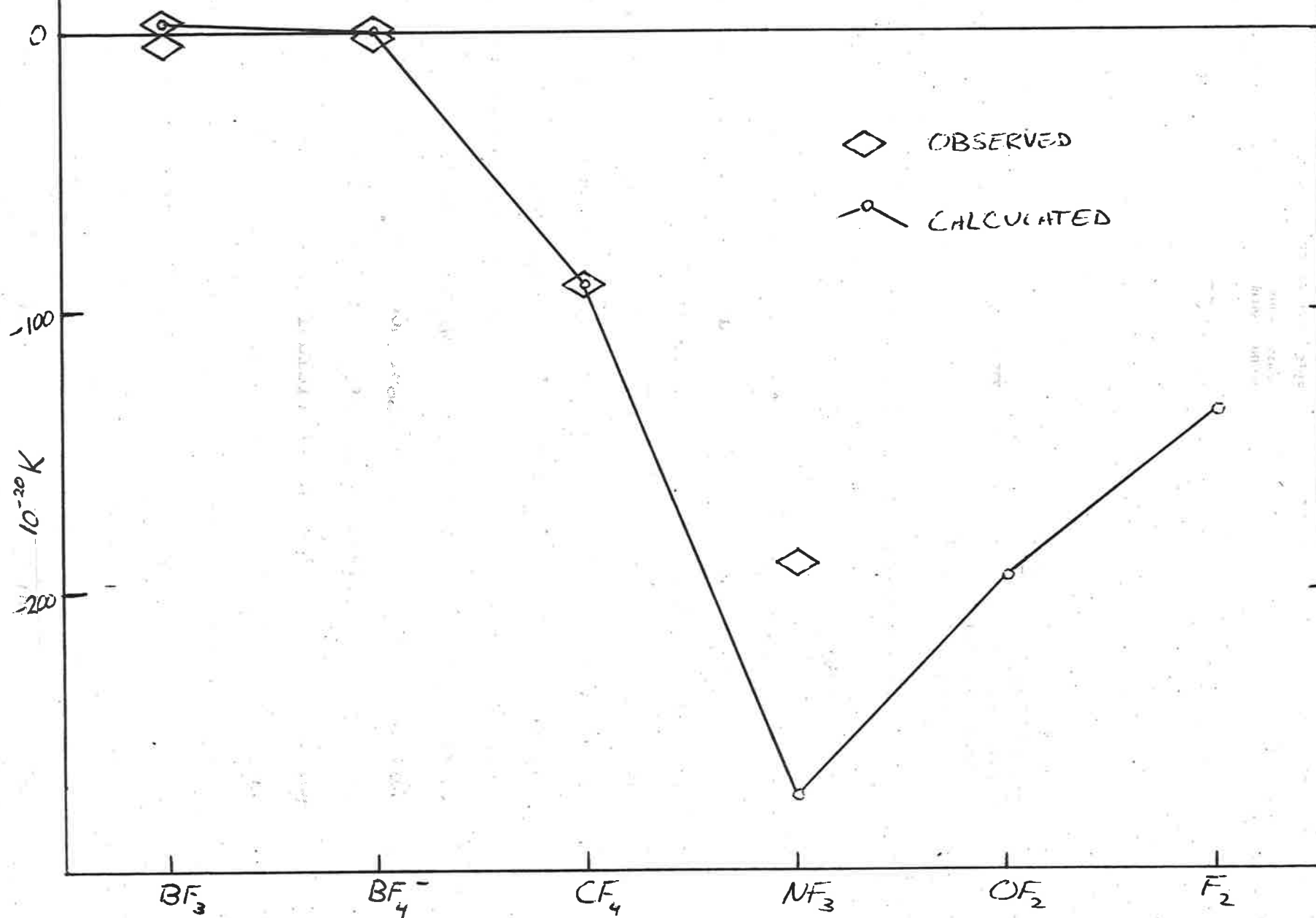G. T. Jones,
P. E. Stevenson.

CARBON - HYDROGEN COUPLING CONSTANTS
IN FLUOROMETHANES
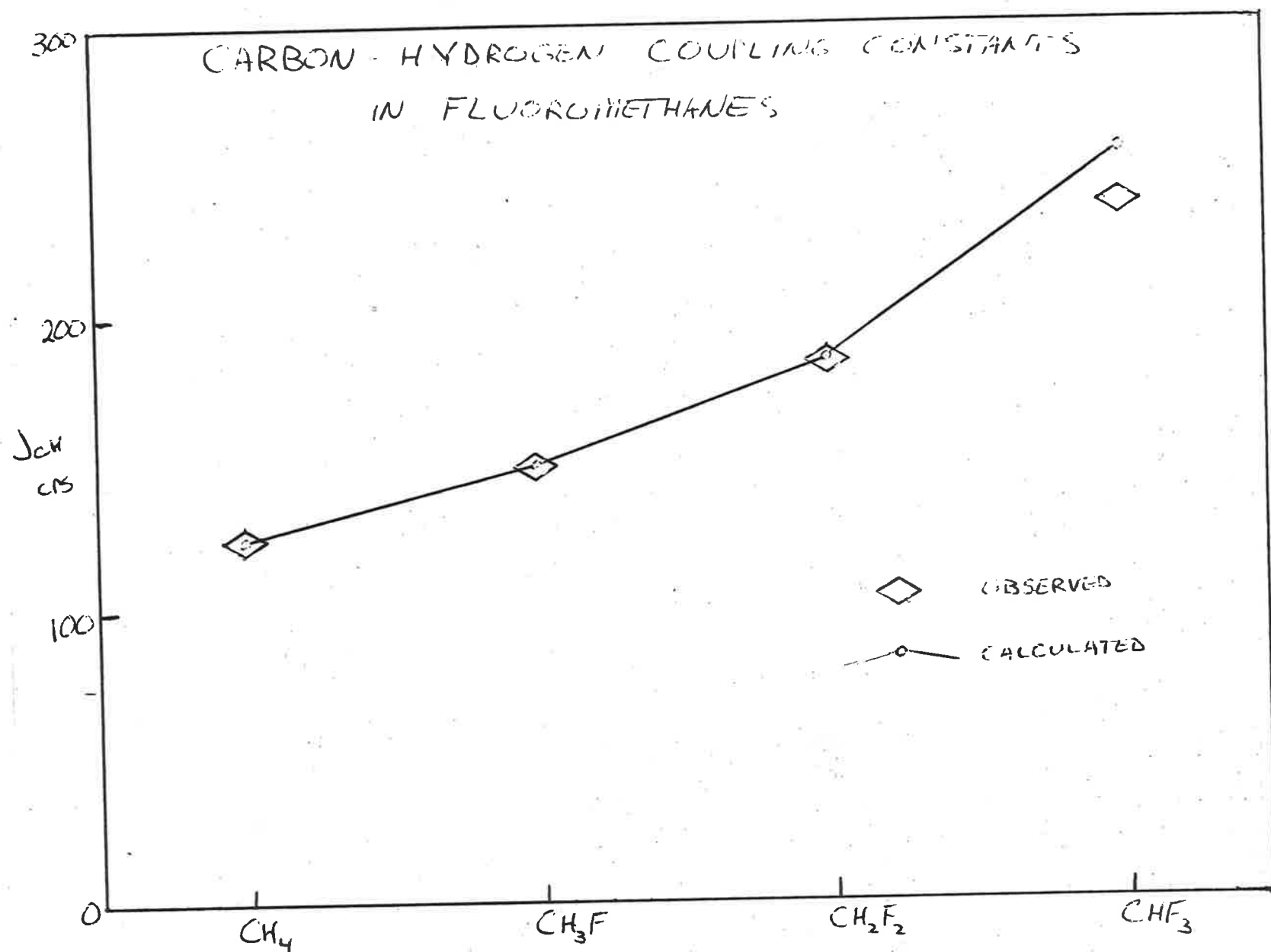
CARBON FLUORINE BOND DISTANCES IN FLUOROMETHANES

DIRECTLY BONDED COUPLING CONSTANTS (REDUCED) IN FIRST-ROW FLUORIDES

◇ OBSERVED

CALCULATED

$-10^{-20} K$

0

-100

-200

BF_3 BF_4^- CF_4 NF_3 OF_2 F_2

93-51

𝔄rgonne 𝔑ational 𝔏aboratorp

OPERATED BY THE UNIVERSITY OF CHICAGO

June 14, 1966

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

Electronic Scan for Time-Averaging with HA-100

Dear Barry:

Time-averaging with an HA-100 Spectrometer can normally be carried out only with the recorder in operation. The swept oscillator frequency used in scanning (frequency sweep mode) or for field-frequency stabilization (field-sweep mode) is determined by the position of the recorder arm, and data can be collected only when the recorder arm is in motion. This makes it impossible to use the C-1024 with the HA-100 in the same way as it can be used with an A-60. With the HA-100, the C-1024 must be used in external trigger mode, and the necessary trigger signals are provided by two micro switches at the ends of the recorder bed. Although the field-frequency stability of the HA-100 is sufficiently good to make the use of an external trigger practical, the continuous operation of the recorder has some serious disadvantages: (a) the life expectancy of the recorder and of the potentiometer controlled by the recorder arm is adversely affected; for even a 50 cps scan, the entire recorder bed must be traversed; (b) the length and time of scan is

determined entirely by the recorder controls; no scan under
50 cps in width or in less than 25 sec. can be made, a serious
drawback where a very large number of scans over a short interval
are desired. We have therefore devised a simple method whereby
the HA-100 can be used for time-averaging independently of
recorder operation. To achieve this end, a voltage-controlled
oscillator, driven by the ramp of the C-1024, replaces the sweep
oscillator of the V4354 unit.

Variable Frequency Oscillator. We have used for our
electronic scan unit a voltage-controlled oscillator available
from MF Electronics Corp., 118 East 25th Street, New York,
New York 10010. This oscillator operates at 2500 cps at zero
volts and 3500 cps at +10V. This is within the range of the
C-1024 ramp. The linearity of the oscillator is described as
better than 0.25% of the deviation band, and ours proved to be
better than 0.10%. The oscillator requires a power supply of
-28V ± 10% at 25 ma. max. A potentiometer on the oscillator
adjusts the output voltage, which is large enough to drive the
V4354 directly without further amplification. The necessary
interconnections are shown in Figure 1.

Frequency Sweep Mode. The sweep oscillator of the V4354
unit is disabled by removing card J1324 and the output of the
external voltage-controlled oscillator connected at sweep oscillator
"Out" position (J1307) of V4354. The starting position of the

scan is controlled by the frequency offset control on the V4354 unit, and the width of the scan is controlled by the sweep width control of the C-1024. The appropriate scanning rate is selected on the C-1024. The C-1024 function selector is turned to Internal Trigger, SUB.-STD. BY-ADD is turned to ADD, and the trigger source turned to Recur. The C-1024 triggers and continues to scan until the desired number of scans are collected. Since the triggering occurs as soon as the end of the ramp is reached, the flyback switch must be turned to OFF to operate in this trigger mode.

We find it convenient to monitor the output of the C-1024 with a digital voltmeter; 10 mv is equivalent to 1 cps. Since the potentiometer that controls the sweep width on the C-1024 is not linear, the actual range of scanning is determined by making one very slow scan and reading the terminal voltages.

Field-Sweep Mode. For some purposes, scanning in field-sweep mode is desirable. In field-sweep mode, the C-1024 must be modified to make possible the use of the flyback time control. This is necessary to ensure that the ramp decay time is made sufficiently slow to prevent collapse of the spectrometer lock. The necessary modifications are shown in Figure 2. A summation recognize zero pulse is generated when all the address binaries in the C-1024 are counted down to the logic 0. At this time, positive 5 volt search ramp advance pulses are generated. We
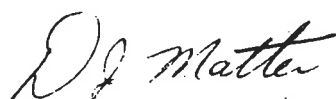
modify the C-1024 to use the very first search ramp advance pulse to give us an end of search (EOS). As in frequency sweep mode, the starting position of the scan is controlled by the frequency offset control on the V4354 unit; the sweep width and sweep time by the appropriate controls on the C-1024. The C-1024 trigger source is then turned to SIDEBAND, the function selector to NMR TRIGGER, and SUB.-STD.BY-ADD control to ADD.
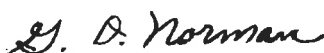
Read-Out. Exactly as in normal C-1024 operation. Since we scan from 2500 to 3500 cps, we take the data out backwards in order to have the usual presentation.

General Comments. In our experience, spectra secured by electronic scanning are equal in all respects to those obtained by the conventional procedure. The system is particularly useful for making large numbers of scans over a short (say 20 to 100 cps) section of the spectrum. The voltage controlled oscillator can also be used for decoupling (dynamic decoupling), and still other applications are being studied.
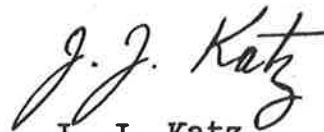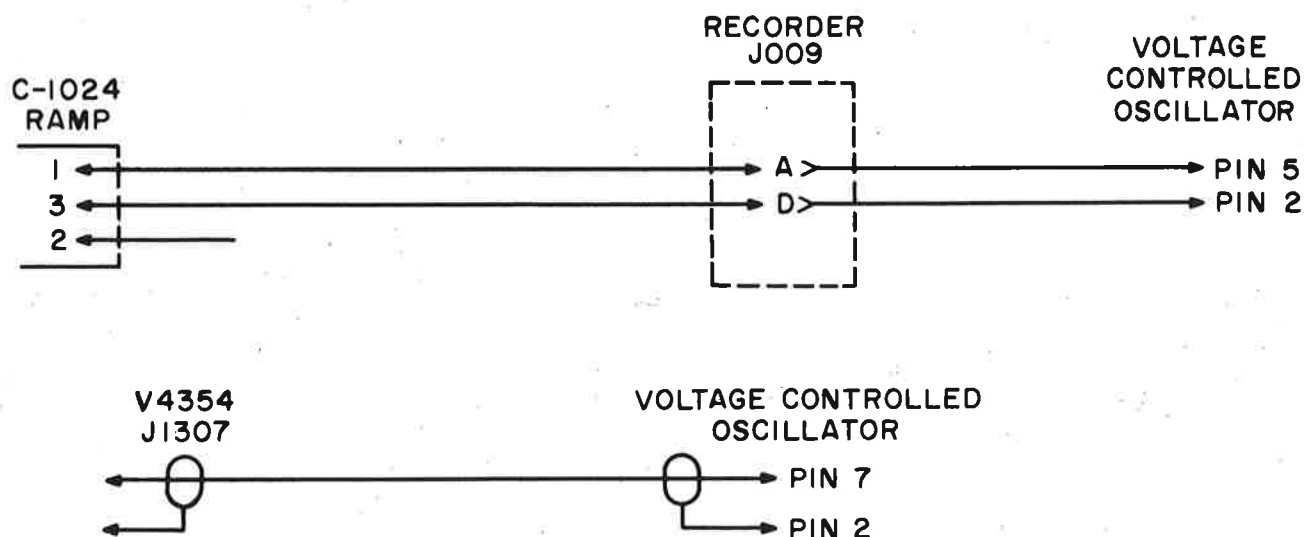
Sincerely yours,

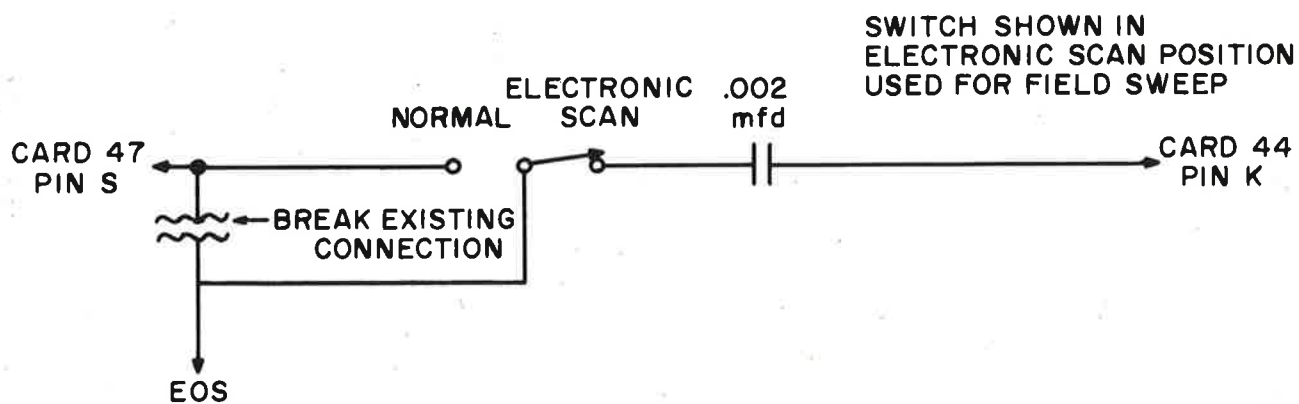D. J. Matter   G. D. Norman   J. J. Katz

FIGURE I   INTERCONNECTIONS for VOLTAGE CONTROLLED OSCILLATOR

FIGURE 2   MODIFICATION of C-1024

TEXAS A&M UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

COLLEGE STATION, TEXAS

Department of
CHEMISTRY

June 13, 1966

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

Dear Dr. Shapiro:

I am sorry to reply at so late a date to your reminders ---
sorrier still for the unhappy news I bear. Our group leader, Dr. Alfred
Danti, died of a coronary this May 17th.

Although his primary interest was that of far infrared vibrational[1-3]
spectroscopy, Dr. Danti was actually engaged, also, in NMR spectroscopy.

Many will remember his API efforts, in this regard, under Dr.
Bruno J. Zwolinski (API Research Project 44).

Work is continuing on variable temperature studies of acyclic
vinylic systems (IITNMR 83-48) and we shall report on this, shortly.

Would you please address subsequent issues of this newsletter
jointly to Drs. F. Sicilio and F. Smentowski.

Thank you.

Sincerely yours,

Tom Altpeter

Tom Altpeter

1.   D. Koster and A. Danti, PMR Studies of Diazomethane, J.
        Chem. Phys. 41, 582 (1964).

2.   D. Koster and A. Danti, PMR Studies of Ten Diolefins, J.
        Phys. Chem. 69, 486 (1965).

3.   M. Merkle, A. Danti and R. Hall, The Use of Nuclear Mag-
        netic Resonance in Determining the Structure of Isocil, 5-
        Bromo-6-Methyl-3-Isopropyluracil, Weed Research 5, 27
        (1965).