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Newsletter

No. 171

December, 1972

L. J. DeHayes, P. Curb, W. Hagstrum and J. L. Sudmeier
Programmable Frequency Divider 1

H. P. Kellerhals
Improved Technique for CW O^{17} Experiments 4

P. Diehl
Postdoctoral Position Available 7

D. J. Frost
Analysis of Non-Conjugated Alkenic Fatty Acids; NMR Consumer Research? 8

A. Allerhand
How to Get ^{13}C Fourier Transform NMR Spectra Nine Times Faster Than on the Varian XL-100 and Similar Bruker and Jeol Equipment 11

R. Mańkowski-Favelier, F. Mathey and G. Mavel
Phosphorus Heterocycles 12

R. Spear and S. Sternhell
Allylic Coupling in the Region $\phi = 90°$ 16

G. W. Buchanan
^{13}C NMR of Benzophenones 21

J. den Hollander
CIDNP of Azomethane 24

G. E. Maciel
FT Spectra on Metal Nuclei 27

G. Widenlocher and E. Dayan
Temperature Dependence of Proton Resonance Shift of Water 28

W. Herres and D. Ziessow
CW- and FT-NMR Spectroscopy Controlled by a PDP-11 Computer 30

R. E. Sievers and J. A. Cunningham
Single Crystal Structural Results for NMR Shift Reagents 32

H. Kessler and D. Rosenthal
Z,E-Isomerization of Aromatic Diazoketones 34

B. Neijzen, J. Biemond and C. MacLean
NMR Electric Field Effects in 2,4,6-trifluoronitrobenzene 36

(Cont'd. inside on p. (i))

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J. D. Roberts
Europium-Induced Abnormal ^{13}C Shifts in Amines 40

J. Reuben
For Lovers of Linear (Shift Reagent) Plots 42

C. L. Khetrapal and A. C. Kunwar
PMR Spectra of Oriented Trimethylene Oxide and Trimethylene Sulphide 43

B. Blank, H. Fischer and A. Henne
CIDNP Determination of the PMR Spectrum of Vinyl Alcohol 44

O. Hartman and B. Gestblom
Line Shapes in Saturated AB Spectra 47

D. M. Wilson, R. W. Olsen and J. J. Chang
Dual Phase Detection Benefits in FT NMR 48

J. M. Briggs
Noise Decoupling of ^{19}F from ^{13}C in Fluoroaromatics 50

R. B. Johannesen
Tungsten-Fluorine Chemistry 53

Deadline Dates:	No. 172: 1 January 1973
	No. 173: 5 February 1973

All Newsletter correspondence, etc. should be addressed to:

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

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DEPARTMENT OF CHEMISTRY

RIVERSIDE, CALIFORNIA 92502

November 10, 1972

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

Programmable Frequency Divider

Dear Dr. Shapiro:

We have recently completed construction of a FT NMR spectrometer built around a Varian 14kG wide gap magnet. Our Magnion PG302 pulse programmer lacked versatility and stability with regard to pulse timing and triggering of our Fabri-Tek 1074. To overcome these problems we built an inexpensive (~$150, including power supply) Digital Programmable Frequency Divider.

As can be seen in the accompanying diagram the unit has four programmable (via switches) dividers. We use the outputs from these dividers to provide sweep width pulses (Dwell Time) for the Fabri-Tek and to trigger the first pulse of each sequence (Recycle). The auxiliary delay and tau delay counters are used in conjunction with plug in cards to generate delayed sweep trigger pulses and to trigger the second pulse in the PRFT sequence. The auxiliary delay card allows us to delay data accumulation for 1-15 dwell times after the final pulse, while the tau delay unit provides a variable interval between the first and second pulses. The card for this unit can be easily modified to produce the Carr-Purcell sequence. Additional counters and cards can be easily and inexpensively added to the unit to produce any desired pulse sequence.

The entire unit runs off the crystal controlled spectrometer operating frequency (7.54 MHz for C-13). This provides a very stable clock for timing and synchronizing the pulses. The sweep width unit is

particularly useful as it allows spectral widths to be set accurately in ppm (from 6 to 12, 500 ppm) regardless of the nucleus being run.

Sample ranges for the unit are shown below for some common C-13 sweep widths. Detailed schematics are available on request.

Sincerely yours,

Louis J. DeHayes
Phillip Curb
William Hagstrum
James L. Sudmeier

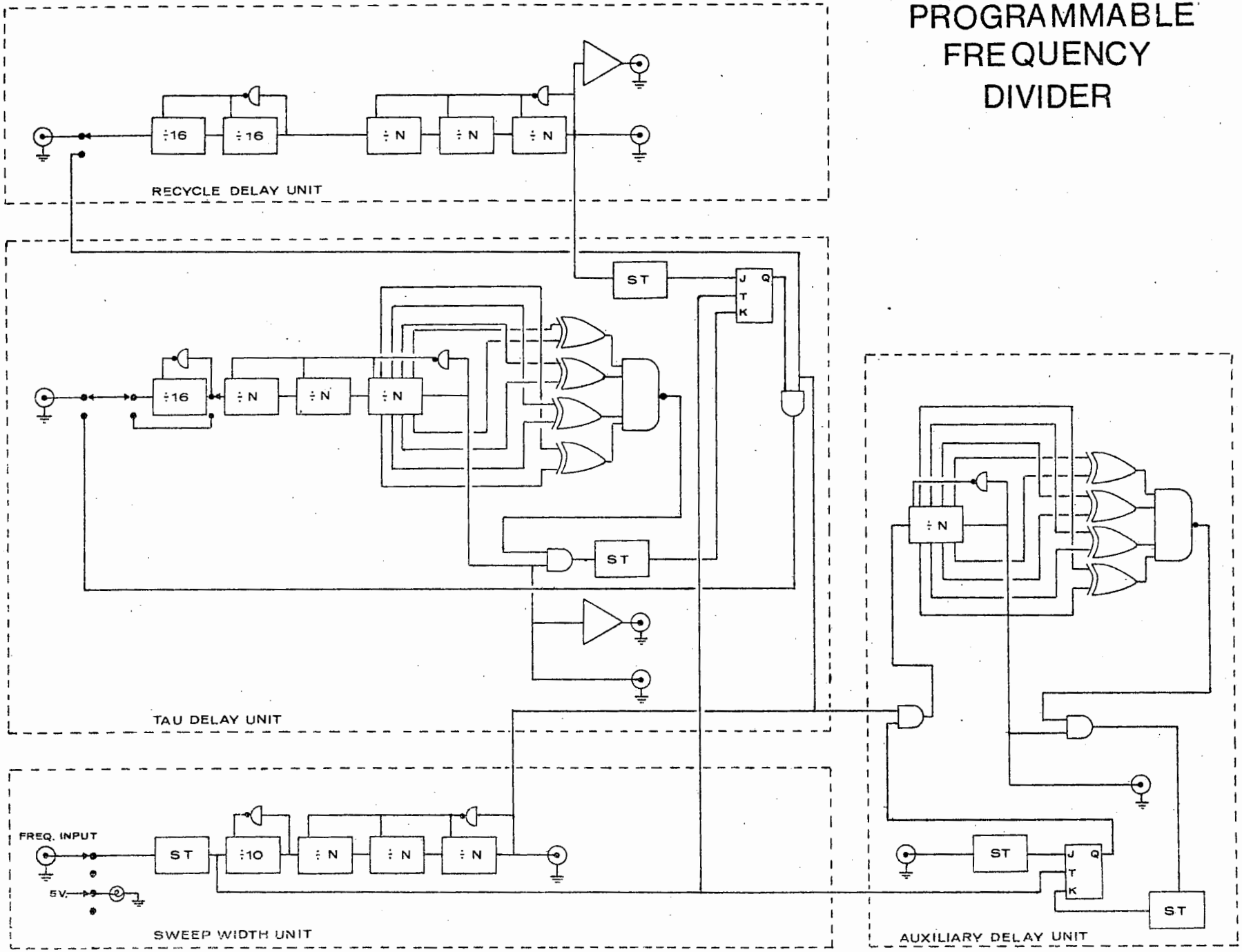
LJD/ngc

Enclosure

SYNTHESIZER FREQUENCY (MHZ): 7.544
RESONANCE FREQUENCY (MHZ) : 15.088
MAXIMUM SWEEP WIDTH (PPM) : 250.
MINIMUM SWEEP WIDTH (PPM) : 25.
SWEEP WIDTH INTERVAL (PPM) : 25.

SWEEP WIDTH		DWELL TIME	SWITCHES	TAU RANGES		RECYCLE RANGES	
(PPM)	(HZ)	(USEC)	(OCTAL)	MIN(USEC)	MAX(SEC)	MIN(MSEC)	MAX(SEC)
250	3772.0	132.6	0143	132.6	9.2	67.9	139.0
225	3394.8	147.3	0156	147.3	10.3	75.4	154.4
200	3017.6	165.7	0174	165.7	11.5	84.8	173.7
175	2640.4	189.4	0215	189.4	13.2	97.0	198.6
150	2263.2	220.9	0245	220.9	15.4	113.1	231.7
125	1886.0	265.1	0307	265.1	18.5	135.7	278.0
100	1508.8	331.4	0371	331.4	23.1	169.7	347.5
75	1131.6	441.9	0514	441.9	30.8	226.2	463.3
50	754.4	662.8	0763	662.8	46.1	339.3	695.0
25	377.2	1325.6	1747	1325.6	92.3	678.7	1389.9

PROGRAMMABLE FREQUENCY DIVIDER



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

October 31, 1972

re: Improved technique for CW O^{17} Experiments

Dear Prof. Shapiro:

Recently we performed some experiments in order to obtain improved results for O^{17} - CW resonance.

Because of very rapid relaxation, one works with rather high irradiation power so that leakage becomes the most significant problem.

Leakage can be suppressed in three ways:

a) geometrical isolation with orthogonal coils (together with electrical compensation)
b) field modulation or
c) pulsed free induction (PFP) (sometimes called "time-sharing")

In a CW spectrometer c) or a combination of a) and b) are used.

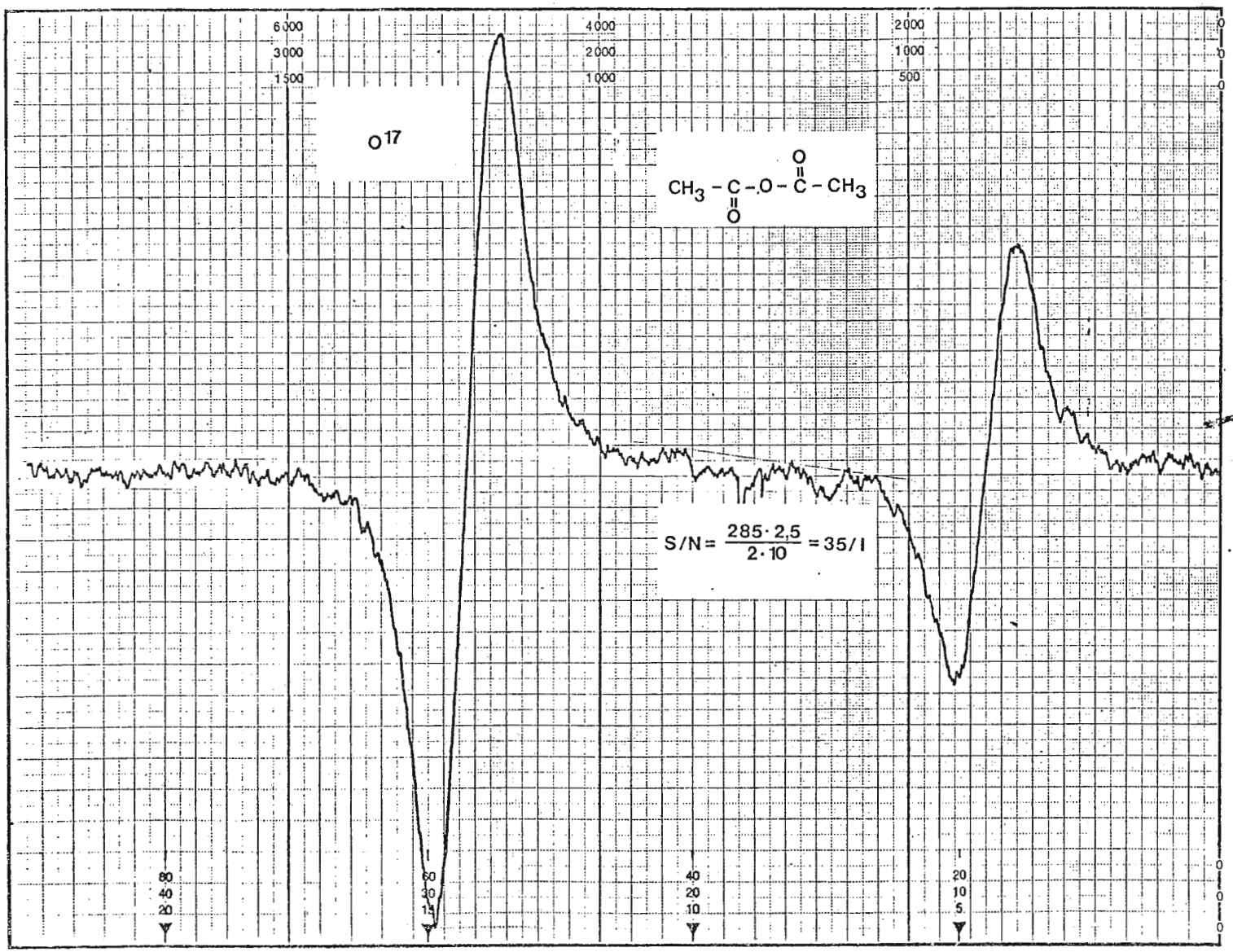
How ever for O^{17} resonance, we obtained improved results combining b) and c). On one hand leakage in this way is suppressed by two different mechanismes and on the other hand c) allows working with a single coil and therefore power transmission to the spin system is optimum.

The attached spectrum shows a single scan experiment for O^{17} in natural abundance.

Sincerely yours,

Hp. Kellerhals

Dr. Hp. Kellerhals



No ____

12.2 (Frequency) MHz O17 (Nucleus) Spectrum

Sample Essigsäure Anhydrid

Concentration 100 % in ____

Int. Standard ____

on H¹ ☐ F¹⁹ ☐ D² ☐ ____ ☐

Temperature: ambient ☒ ____ °K ☐

15mm Probe

Signal f_1

Normal	Fourier
Attenuation 0 db	Pulse Width ____ µsec
Time Const 20 sec	Points ____

Sweep

Width: f_1 100 Hz/cm f_2 ____ Hz/cm

Offset: f_1 6500 Hz f_2 ____ Hz

Time: 5000 sec times 1 scans

Decoupling f_2

Broad Band	☐	Off Resonance	☐
Continuous	☐	INDOR	☐
Frequency ____ Hz		Attenuation ____ db	

Date 8.8.72

Operator J.Merkli, C.Delseth
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Basel, November 7, 1972/ho

Prof. Dr. P. Diehl

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

Postdoctoral Position Available.

Dear Barry,

I will have funds available for a postdoctoral position for one year beginning April 1st 1973 (or later). The work will involve NMR-research exclusively (oriented molecules). We have access to an HX-90 with FT capabilities for ^{1}H, ^{2}D, ^{13}C, ^{19}F and ^{31}P as well as to a Bruker Supercon-Spectrometer.

The salary amounts to Swiss Francs 27'000.- per year. There is no travel allowance. Any person interested should write to me as soon as possible.

Sincerely yours

Peter

Prof. Dr. P. Diehl

Unilever Research

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Olivier van Noortlaan 120
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Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843
U.S.A.

uw ref. | onze ref CR/2674/as | toestel | datum 19 Oct 72

Dear Professor Shapiro,

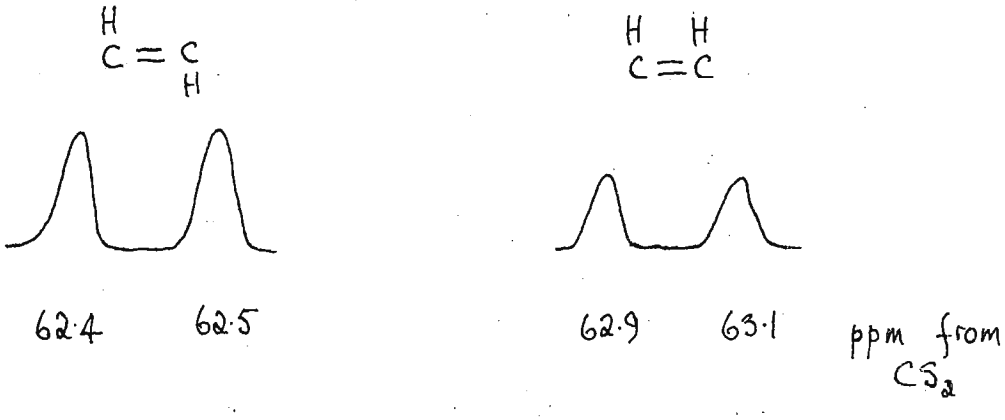
Analysis of non-conjugated alkenic fatty acids; NMR consumer research?

Following on from our work on cis alkenic fatty acids (Anal. Chem. 43, (1971), 1316), with the help of Professor Gunstone (Univ. St. Andrews, Scotland) we have been able to extend our correlations to cover compounds containing cis and/or trans double bonds. We have now obtained the 220 MHz spectra (in CCl_4) of nearly 100 compounds falling into this category, and conclude that it should be possible to identify the vast majority of the several thousands of such fatty acids conceivable. For the most commonly occurring C_{18} acids, the most taxing cases concern the positioning of a single cis or trans double bond in the chain, and we were fortunate in having available the whole series of positional isomers of cis and trans methyl octadecenoates. Apart from some difficulty in distinguishing between Δ10 and Δ11 isomers (which may be resolved by shift reagents), the 220 MHz spectra immediately pinpoint the position of unsaturation. To our previous list of deshielding effects along an alkyl chain (in ppm in CCl_4) we can add:

Group	α	β	γ	∂	ε
H H -C=C	0.732	0.065	0.021	0.014	0.005
H H -C=C-C-CH=CH	0.768	0.073	0.025	0.024	0.009
H -C=C H	0.683	0.052	0.003	0.000	0.000
H -C=C-C-CH=CH H	0.700	0.066	?	0.000	0.000

Apart from the well-documented difference between the α-effects of the cis and trans bonds, their notably different long-range effects are interesting - that of the cis extending over 4-5 carbon atoms, whilst that of the trans being virtually negligible after 2 carbon atoms. This may be qualitatively explained if we assume that both bonds exert a similar deshielding effect transmitted through the chain, but that the effect of the cis is further supplemented by the steric hindrance between its alkyl groups.

Present work is extending our results to acetylenic, epoxy, cyclopropyl and hydroxy acids, and I should be most interested to hear from anyone in a position to supply model compounds. We are also optimistic of the results to be obtained from C13 NMR in this line - the spectrum below (run for us by Varian some time back) of the olefinic carbons of a 2:3 mixture of cis and trans methyl $\Delta 9$ octadecenoates, shows not only the expected difference between cis and trans, but also a clear separation of the C9 and C10 atoms in the same molecule.



The past few months have involved seemingly endless discussions before reaching a decision on the choice of a new FT system. All great fun, perhaps, and certainly something of a diversion. Of course, every individual must make his own choice, but I wonder if there isn't some scope for more concerted action on the part of 'consumers'. It might be valuable to all concerned if, for example, an independent body, like the TAMUNMR Newsletter, carried out a survey to establish a few 'facts', sounding out what equipment is in use, reliability experienced, etc. etc.

Yours sincerely,

UNILEVER RESEARCH VLAARDINGEN

David Frost

D.J. Frost

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Total memory capacity is 2048 words, 24 bits long. The upper 12 bits store the final average while the lower 12 may be used to store the integral. Averaged spectra may be stored in halves of memory and added to or subtracted from one another.

Digital integration is built-in and does not destroy the original spectrum thus allowing simultaneous display of spectrum and integral. Baseline correction can be accomplished during display of the integral to assure optimal results.

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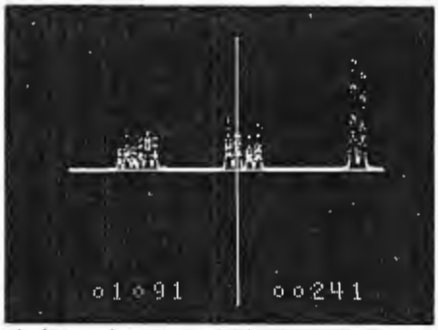
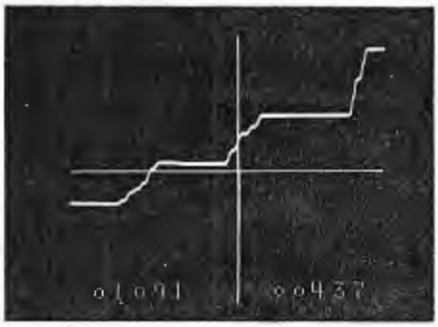
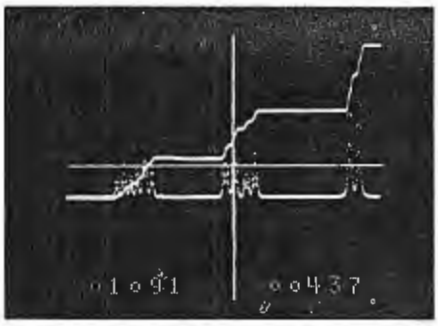


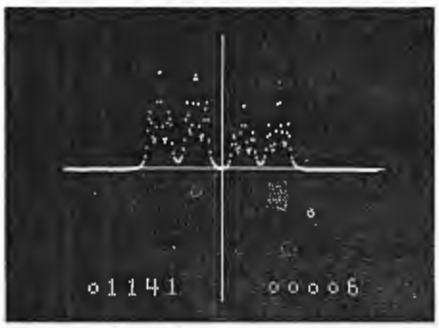
1. Averaged spectrum of 2-butyl-1, 2-dihydropyridene with spectrum expanded on amplitude scale by a factor of 2.



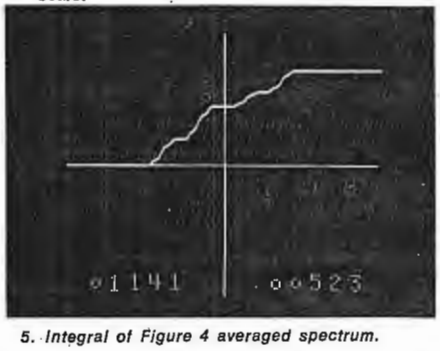
2. Integral of Figure 1 averaged spectrum.



3. Figure 1 spectrum and Figure 2 integral displayed simultaneously.



4. Averaged spectrum expanded by a factor of 4 on both the amplitude scale and the frequency scale.



5. Integral of Figure 4 averaged spectrum.

In Europe: Nicolet Instrument GmbH, Goerdeler Strasse 48, D-605 Offenbach am Main, West Germany, 0611/852028, Telex: 841/4185411

INDIANA UNIVERSITY
Department of Chemistry
CHEMISTRY BUILDING
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November 9, 1972

TEL. NO. 812—

Professor Barry Shapiro
TAMU NMR
Department of Chemistry
Texas A and M University
College Station, Texas 77843

How to get ^{13}C Fourier Transform NMR Spectra Nine Times Faster than on the Varian XL-100 and Similar Brucker and Jeol Equipment.

Dear Barry:

Together with my co-workers, Dr. R. F. Childers, Dr. E. Oldfield, Mr. R. Komoroski, Mr. R. A. Goodman, and Mr. X. Ysern, we concluded some time ago that the sensitivity of existing Fourier transform NMR equipment was not sufficient for many of our ^{13}C studies. For example, although it was possible to obtain good-looking natural-abundance ^{13}C spectra of proteins, single-carbon resonances were not being observed unambiguously.

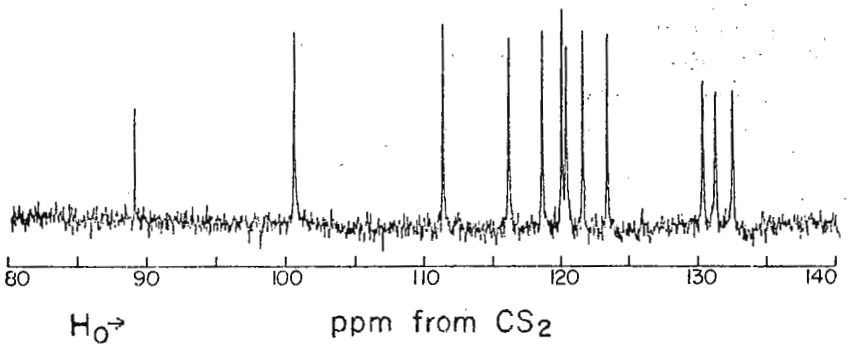
We have recently constructed a probe for spinning sample tubes of 20 mm outside diameter. This has led to an increase in sensitivity of about a factor of 3 with respect to 12 mm and 13 mm tubes. The new probe was incorporated into our existing Fourier transform system. We use a Varian 12" electromagnet at 14.2 kG (15.18 MHz ^{13}C, 60.37 MHz ^{1}H). The homogeneity is surprisingly good. 0.3 Hz inhomogeneity broadening is routine.

We show below a proton-decoupled ^{13}C spectrum of 0.04 M aqueous sucrose, obtained in 37 minutes of accumulation time. A comparable spectrum on the latest commercial instruments would require about TEN times as much signal averaging time. The resolution is comparable to that in spectra kindly supplied by Varian and Jeol.

We can now observe numerous single-carbon resonances of proteins of low molecular weight. The 20 mm probe has greatly extended the range of applications of ^{13}C NMR in our laboratory.

Sincerely yours,

Adam Allerhand
Professor of Chemistry



0.04 M Sucrose
1024 scans
37 minutes

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Pr. Bernard L. SHAPIRO
Department of Chemistry
TEXAS A&M UNIVERSITY
College of Science
College Station,
TEXAS 77843

COl GM/mg 3711

Vert le Petit, le October 31, 1972

Dear Barry,

During a recent investigation of the reaction of benzoyl chloride with various phospholes[a], our Organic Synthesis Lab. obtained 2-hydroxy 2-phenyl 1,2-dihydrophosphorine oxides (A) which rearrange into 7-phenyl 1-oxa 2-phosphacyclohepta-4,6-dienes (B) (with sodium hydride as a catalyst) Representatives of these two families have been studied using proton resonance in $CDCl_3$ (with proton- and ^{31}P- decoupling when necessary). Typical data (including phosphorus chemical shifts upfield from P_4O_6) are reported in the following tables along with corresponding 1-aza 2-phosphacycloheptadienes (C) for comparison. Some bref comments are possible :

- PCOH couplings appear in A when hydroxyl-exchange is blocked by the geminal and vicinal phenyl groups[b], it is not so reproducible when a butyl group is attached to the phosphorus atom and does not appear at all with a vicinal methyl group.

- PCH and P C - C(CH_3) couplings in A have the same sign ; this is

a) F. MATHEY, Tetrah., to appear (see also Tetrah., 28, 4171 (1972))

b) Such couplings have been reported by C.E. Griffin and S.K. Kundu (J. Org. Chem., 34, 1532 (1969) and T. Bottin - Strzalko and J. Seyden-Penne (Tetrah. Lett., p. 1945 (1972).

in contradistinction with results obtained on vinyl phosphine oxides [c] or, as well, on 2-phosphole derivatives [d];

- long range couplings appear in B (and C) compounds, between phosphorus and (C_5) CH_3 (as checked by phosphorus decoupling) ; their magnitude is greater than between phosphorus and (C_4) CH_3.

- the non-equivalence of the PCH_2 protons in B does not exist in C when X = O (actually, the CH_2 doublet is some-what skewed showing only a slight non-equivalence). Except for that, feature B and C (X = O) only differ by slight proton downfield shifts (and appreciable phosphorus downfield shift) from C to B, as predictable from the change in electronegativity from 1-aza to 1-oxa. In the case of C when X = S, one clearly detects a tautomeric mixture (ca. I : I) of the thiono- and thiolo-forms. After phosphorus decoupling, one can assign for the phosphorus-proton couplings within the non-equivalent CH_AH_B system, low field pattern : P - CH_A 20.0 Hz PCH_B 9.0 Hz (same sign) Dδ (CH_A-CH_B) 0.31 ppm high field pattern : P-CH_A 14.1 Hz PCH_B 6.7 Hz (same sign) Dδ (CH_A-CH_B) 0.15 ppm.

The investigation of this family is going on.

Very best regards,

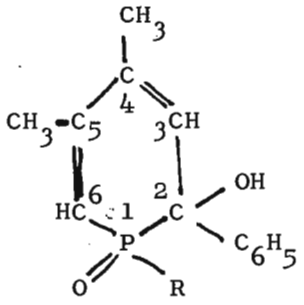
R. MANKOWSKI-FAVELIER
F. MATHEY
G. MAVEL

P.S. - By the way, what's about the "AFM" survey of proton line frequency determination in which we participated in December 1970. Are conclusions published now? Thanks for further details.

---

c) G. MAVEL, R. MANKOWSKI-FAVELIER, J. Chim. Phys., 64, 1808, 1967

d) F. MATHEY, R. MANKOWSKI-FAVELIER, Bull. Soc. Chim. France, 12, 4433, 1970 (in the latter case, no phosphole oxides - which dimerize - but only phosphole sulfides and related phosphoniums were investigated).

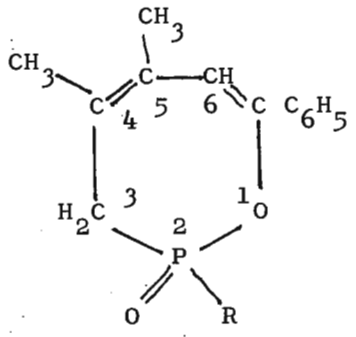


(A)

	R = C_6H_5	R = nC_4H_9	R = CH_3
$C_{(2)}\underline{OH}$ (H-P coupling)	2.41 (10.6)	4.33 (11.8)	4.38 (sing.)
$C_{(3)}\underline{H}$ (H-P coupling)	6.24 (14)[a]	5.85 (14.2)[b]	5.87 (15.3)[b]
$C_{(4)}\underline{CH_3}$ (singulet)	2.17	1.98	1.98
$C_{(5)}\underline{CH_3}$ (H-P and HC_6H couplings)	2.02 (2.7-1.2)	1.88 (1.6-1.6)	1.88(1.7-1.7)
$C_{(6)}\underline{H}$ (H - P coupling)	6.13 (15.5)	5.85 (14.2)[b]	5.87 (15.3)[b]
Phosphorus chem. shift	90.5	-	-

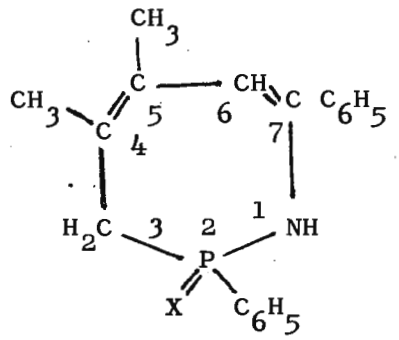
a) This corrects earlier assignments (F. Mathey, Tetrah., 28, 4171 (1972)).

b) Both olefinic protons appear as a single doublet as checked by double resonance and can't be distinguished.



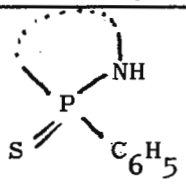
(B)

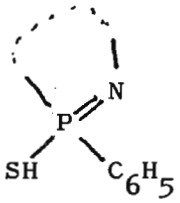
	R = C_6H_5	R = nC_4H_9	R = CH_3
$C_{(3)}\underline{H_2}$ (non equivalent)	2.73 - 3.37	2.57-3.13	2.57 - 3.15
$C_{(4)}\underline{CH_3}$ (H-P coupling)	1.57 (2.4)	1.80 (2.8)	1.81 (-)
$C_{(5)}\underline{CH_3}$ (H-P coupling)	1.88 (5.3)	1.92 (3.5)	1.93 (3.1)
Phosphorus chem. shift	52	33.7	-



(C)

	X = O	X = S a)
$C_{(3)}\underline{H}_2$ (H-P coupling)	2.74 (18.6)	2.52 - 3.39 (non equivalent)
$C_{(4)}$ $\underline{CH}_3$ (H-P coupling)	1.36 (3.1)	1.21 (2.7)
$C_{(5)}$ CH_3 (H-P coupling)	1.82 (5.3)	1.73 (6.0)
Phosphorus chem. shift	70.2	30

a) This compound is actually a mixture of  (thiono)

and  (thiolo) (approximatively 1 : 1).

71-16
TELEPHONE: 660 0522.

The University of Sydney

SYDNEY, N.S.W. 2006
Department of Organic Chemistry

IN REPLY PLEASE QUOTE:

November 7th, 1972

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

Allylic Coupling in the Region $\phi = 90°$

Dear Barry,

We have recently established[1] that the relative magnitudes of cisoid and transoid allylic coupling constants (see diagram for definitions) for the region embracing substantial negative values (say ϕ = 0-50 and 130-180°) are in qualitative agreement with Barfield's INDO calculations[2] (Fig. 2) but not with the earlier[3] VB treatment (Fig. 1), in particular as regards the presence of a cross-over point.

For $\phi = 90°$, the two treatments predict clearly different sets of values:

	VB	INDO
J_{cisoid} (J_{AC})	+0.43	-1.15
$J_{transoid}$ (J_{BC})	+0.80	-0.54

Published experimental data are scarce[3,4] and, while they establish that both are 'small', meaningful[5] comparative and quantitatively reliable data for $\phi = 90°$ are confined to (I)[6], and even here the signs are insensitive to experimental parameters[7]. No sign determinations are available for any of the subsequently quoted data. We have therefore synthesised the relatively rigid compounds (II) - (IV) and demonstrated that Bothner-By's findings for (I) appear to be general, i.e. $|J_{cisoid}| > |J_{transoid}|$ for $\phi = 90°$.

In a number of [redacted] derivatives of [2.2.1]bicycloheptane[8] the reverse has been observed and our data for methylene camphor (V) are typical for this series, while equal allylic coupling constants have been reported[9] for camphene (VI) by Stothers. In these systems, ϕ is about 70-80° (= 100-110°), but the results may not be of general significance because of strain. However, data[10] for (VII) and (VIII), which appear to be somewhat distorted (by the criterion of allylic coupling to C-2 methylene group) from the $\phi = 90°$ relation in (III), suggest that $|J_{transoid}|$ is indeed larger than $|J_{cisoid}|$ for unstrained systems as well, for values of ϕ which are ca 10-20° larger or smaller than 90°.

Fig.1

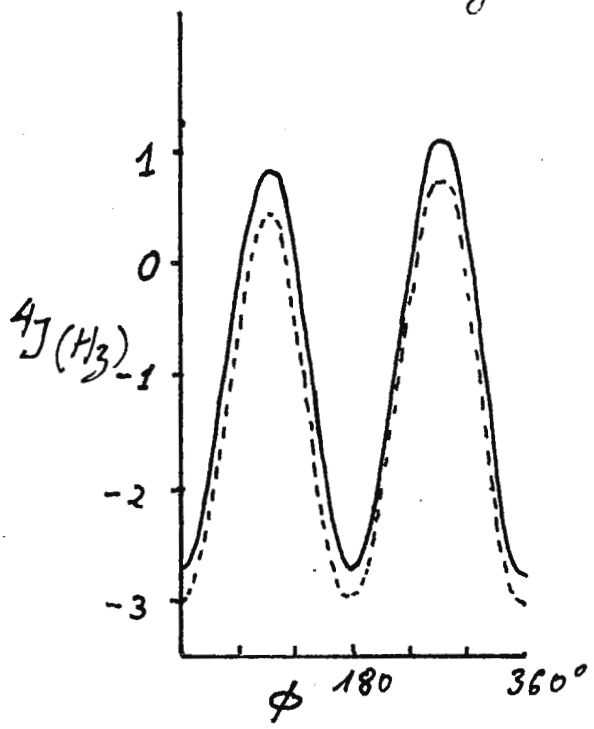
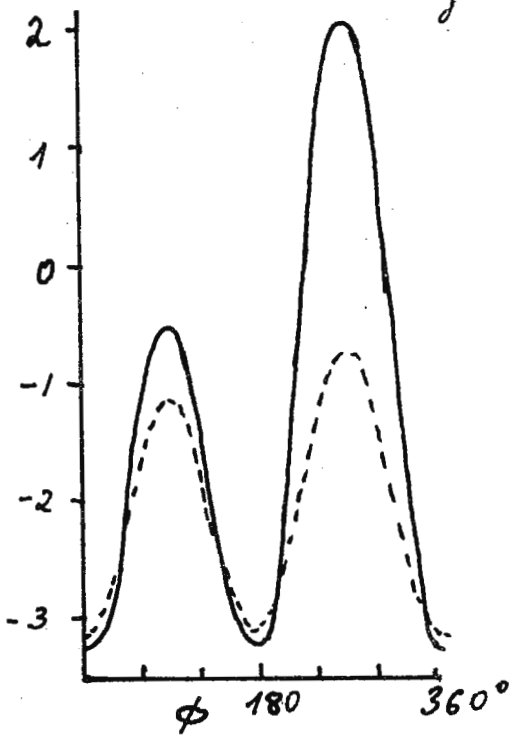
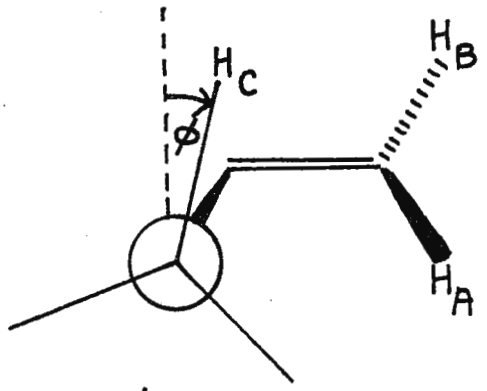


Fig.2

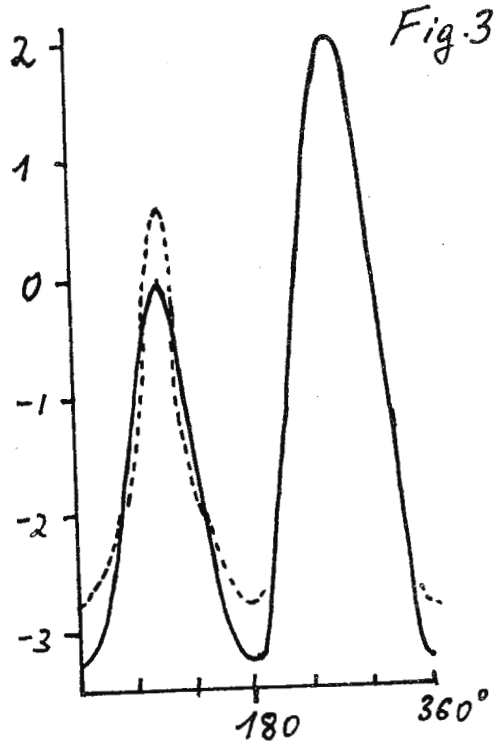


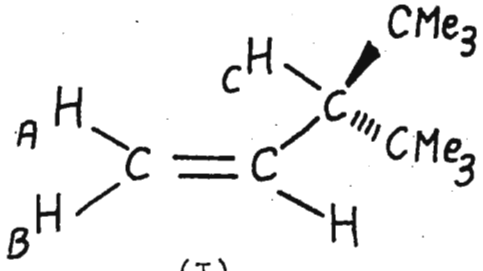


$^4J_{AC} = J_{ALLYLIC\ CISOID}$:-----

$^4J_{BC} = J_{ALLYLIC\ TRANSOID}$:——

Fig.3

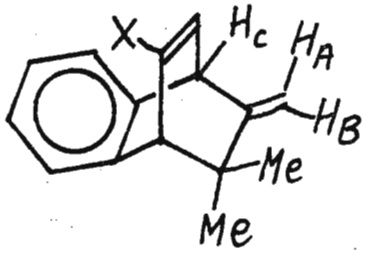




(I)

J_{AC} = −0.63

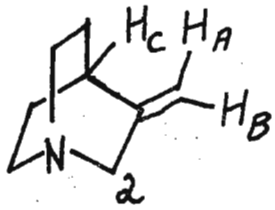
J_{BC} = −0.10



(II, X=H)

J_{AC} = 0.6 ± 0.1

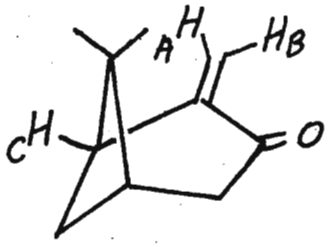
$J_{BC} \leq$ 0.3



(III)

J_{AC} = 0.53

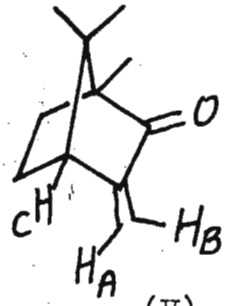
$J_{BC} \leq$ 0.15



(IV)

$J_{AC} \leq$ 0.45

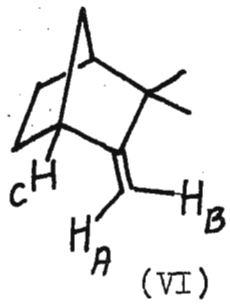
$J_{BC} \leq$ 0.1



(V)

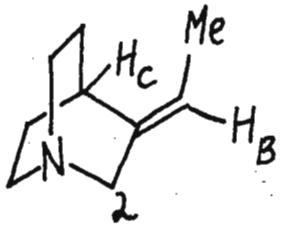
$J_{AC} \leq$ 0.4

J_{BC} = 0.8±0.1



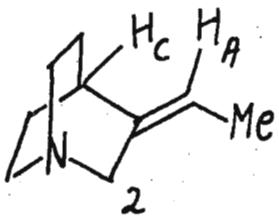
(VI)

$J_{AC} = J_{BC}$ = 0.55



(VII)

J_{BC} = 0.4



(VIII)

J_{AC} = "nil"

Accepting the generality of the above two sets of observations as a working hypothesis[11] and bearing in mind (a) that both J_{cisoid} and $J_{transoid}$ assume substantial negative values as ϕ approaches 0° (or 180°) and (b) that a crossover point exists (at ca -2 Hz)[1] below which $J_{transoid}$ is more negative[12], these experimental data may be summarised as follows:

1. $|J_c^{90}| > |J_t^{90}|$
2. $|\tilde{J}_c^{100}| < |\tilde{J}_t^{100}|$
3. $-J_c^{\sim 120} > -J_t^{\sim 120}$ (see however footnote 12)
4. $-J_c^{180} < -J_t^{180}$
5. $|J_c^{90}| > |J_c^{\sim 100}|$
6. $|J_t^{90}| < |\tilde{J}_t^{100}|$

In turn, the obvious way to combine the above points in terms of a regular dependence of $J_{allylic}$ on ϕ is in terms of the curves shown in Fig. 3 - unlikely as it looks (see also footnotes 12 and 13). An obvious test lies in the sign of J_{cisoid} in (I) (which should be positive) and we are re-preparing (I) and will report the results later. Sign determinations on other compounds available to us have proved difficult, but we would also predict that both of the allylic coupling constants in camphene (VI) should be negative.

Note that the cisoid curve in Fig. 3 has a break - to our knowledge there are no directly pertinent experimental data for this region. Note also that for structural work the situation is quite clear: allylic coupling constants for the region near $\phi = 90°$ are indeed 'small'.

With best regards,

Yours sincerely,

Robert Spear

R. SPEAR

Sev Sternhell

S. STERNHELL

1. Newsoroff and Sternhell, *Aust. J. Chem.*, 25, 1669 (1972).
2. Barfield, *JACS*, 93, 1066 (1971).
3. Barfield, *J.Chem.Phys.*, 41, 3825 (1964); Barfield and Chakrabarti, *Chem. Rev.*, 69, 757 (1969).
4. Jackman and Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon 1969, Ch.4-4; Sternhell, *Quart.Rev.*, 23, 236 (1969).
5. We have pointed out elsewhere [ref.1 and Newsoroff and Sternhell, *Tet. Lett.*, 6117 (1968)] that only data for molecules containing a $C{=}CH_2$ group are really reliable for the purpose of comparing cisoid and transoid allylic coupling constants.
6. Bothner-By, Naar-Colin and Günther, *JACS*, 84, 2748 (1962).
7. Bothner-By, private communication.
8. Garbisch, *Chem. and Ind.*, 1715 (1964) and *JACS*, 86, 5561 (1964); Kossanyi, Furth and Morizur, *Tetrahedron*, 26, 395 (1970).
9. Grover and Stothers, *JACS*, 91, 4331 (1969).

10. Martin *et al. Bull. Soc. Chim. Belges*, 74, 506 (1965).
11. Possibility that we are in a region of ϕ values where allylic coupling is unusually susceptible to secondary effects, e.g. substituent effects must not be dismissed. Such a region is certainly apparent for transoid allylic coupling constants near ϕ = 270° [c.f. Bauer, Bell, Brophy, Bubb, Sheinin, Sternhell and Wright, *Aust. J. Chem.*, 24, 2319 (1971)] and we were somewhat surprised that both of the allylic coupling constants in (II, X = Br), which was prepared for sign determinations, were substantially reduced when compared with those in (II, X = H). The relative magnitudes remain unchanged.
12. This relation has been considered[13] inherent in well known data for e.g. propene [Bothner-By and Naar-Colin, *JACS*, 83, 321 (1961)] and flexible six-membered rings[1]. However (this is a key point) it is yet to be established for any rigid systems with an exocyclic methylene group and we are working on this as well. It is ironic that this relationship which is one of the earliest regularities proposed for allylic coupling should now be seriously questioned. Should this relationship be <u>not</u> confirmed, i.e. if J_{cisoid} is more positive than $J_{transoid}$ for <u>all</u> values of ϕ between 0 and 180° (except where they are nearly equal due to secondary effects) the strange curve depicted in Fig. 3 would be scrapped and replaced by what is qualitatively the reverse of the curve shown in Fig. 1 for this region (i.e. dashed line <u>above</u> solid line between ϕ = 0 and 180°).
13. The propene case has been treated[14] as corresponding to the average of ϕ = 90,210 and 330° and while this gives a fair consistency with calculated values (also for homoallylic cases in butenes), it gives no direct evidence for or against the correctness of point 3 in our list. The case of flexible six-membered rings[1] can be treated as corresponding to two equally populated conformers for all compounds so far investigated[1] but only some of the dihedral angles are in the range where point 3 is pertinent.
14. Barfield, *JACS*, 93, 1066 (1971); Barfield and Sternhell, *JACS*, 94, 1905 (1972).

CARLETON UNIVERSITY

OTTAWA CANADA
K1S 5B6

DEPARTMENT OF CHEMISTRY

November 3, 1972

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77845
U. S. A.

^{13}C NMR of Benzophenones

Dear Barry:

In collaboration with Dr. G. Montaudo we have initiated a ^{13}C NMR study of a series of Ar-X-Ar compounds. For benzophenones the CMR shieldings are presented in the Table.

As the degree of ortho-substitution increases the C=O resonances are deshielded, reflecting steric interference to phenyl - C=O conjugation.

Using semi-empirical methods we have calculated the preferred conformations of these molecules, and accordingly the two phenyl torsional angles θ and ϕ. A plot of $\cos^2 \theta + \cos^2 \phi$ vs. the C=O shift for the methyl benzophenones gives a linear relationship as illustrated. Please credit this contribution to John ApSimon's account.

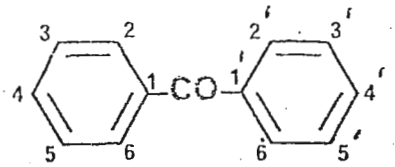
Best regards,

G. W. Buchanan
Assistant Professor

GWB:ap
Enc.

TABLE 1

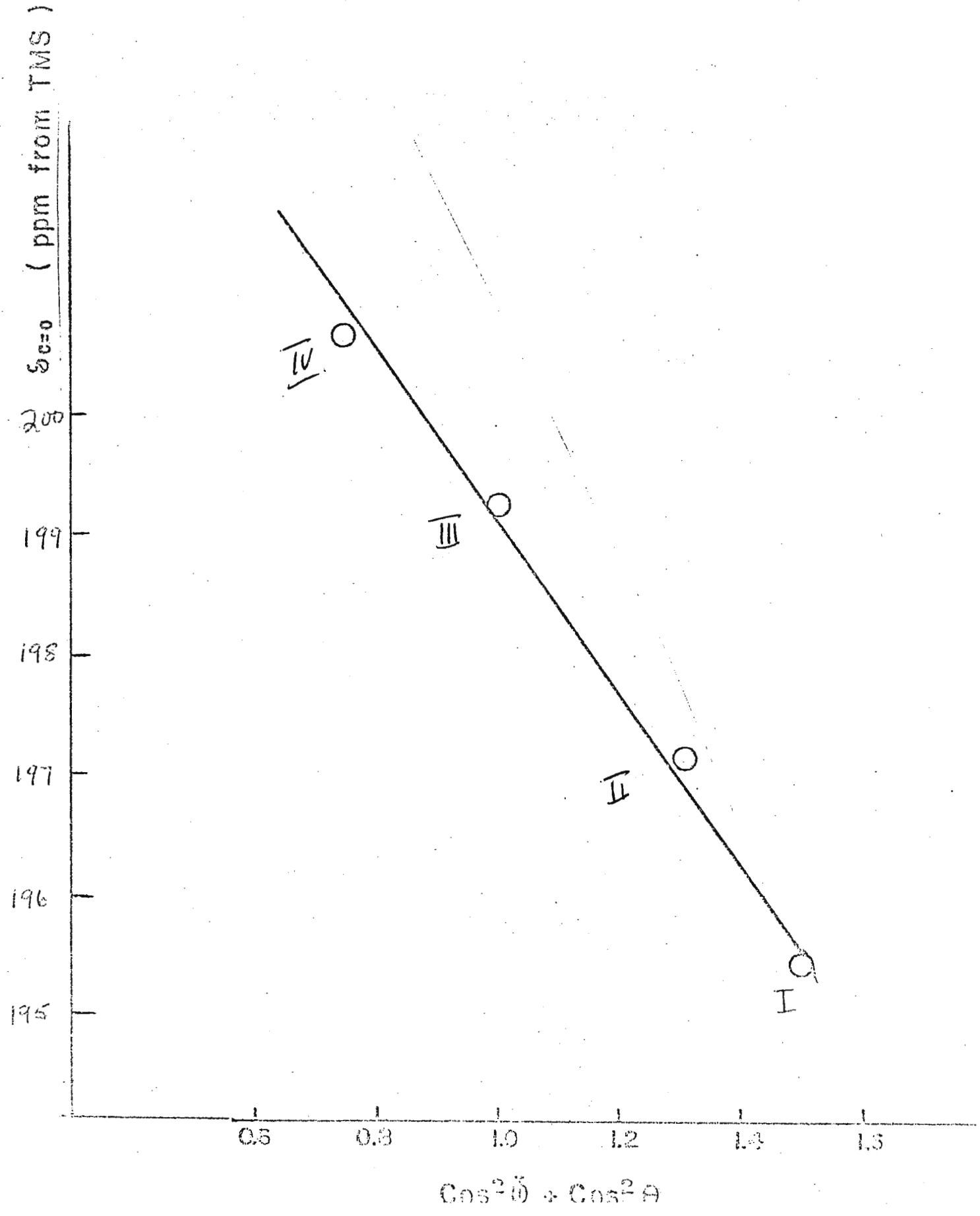
^{13}C NMR Chemical Shifts for Benzophenones (ppm from TMS ± 0.1)[a]



Compound		I	II	III	IV	V	VI	VII	VIII	IX
Subst. Position	CH_3	--	2	2,4,6	2,4,6,2'	--	--	2	2,4,6	2,4,6
	OCH_3	--	--	--	--	4'	2',4'	2',4'	2',4'	4'
	C=O	195.5	197.2	199.3	200.7	193.3	193.9	195.5	197.0	197.7
	(C=O)[b]	196.3	200.1	206.9		194.9	194.8			
	C-1	137.0	137.9	137.6	138.6	136.9	135.9	139.8	139.3	136.5
	C-2	129.2	135.8	133.3	133.1	128.1	126.5	135.3	132.9	132.3
	C-3	127.6	130.2	127.8	127.3	126.7	125.2	128.6	127.5	126.7
	C-4	131.6	130.3	136.2	137.0	130.3	129.0	129.4	136.8	135.8
	C-5	127.6	124.5	127.8	127.3	126.7	125.2	123.9	127.5	126.7
	C-6	129.2	129.5	133.3	133.1	128.1	126.5	127.4	132.9	132.3
	C-1'		137.1	136.6	137.4	128.7	118.7	120.9	120.6	129.1
	C-2'		129.2	128.4	135.9	130.9	158.4	159.6	161.1	130.1
	C-3'		127.7	127.5	130.8	112.3	96.1	98.5	98.5	112.6
	C-4'		132.8	132.5	130.9	161.5	162.2	163.0	164.3	163.0
	C-5'		127.7	127.5	124.7	112.3	102.3	104.5	104.7	112.6
	C-6'		129.2	128.4	130.5	130.9	129.3	132.2	133.9	130.1
	2-CH_3		19.1	18.5	18.5			20.0	19.1	18.6
	4-CH_3			20.4	20.7				20.9	20.4
	2'-CH_3				20.1					
	2'-OCH_3						55.3	55.3	55.4	
	4'-OCH_3					55.1	55.3	55.3	55.4	55.3

[a] 0.5 M in $CDCl_3$.

[b] Shifts for corresponding acetophenones.


δc=o (ppm from TMS)
200
199
198
197
196
195
IV
III
II
I
0.6
0.8
1.0
1.2
1.4
1.6
Cos² δ + Cos² θ

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT
Afd.:
Wassenaarseweg
Leiden
Telefoon 4 83 33

LEIDEN, 2 november 19 72

Drs. J.A. den Hollander.

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

Dear Professor Shapiro,

CIDNP of Azomethane.

The influence of the magnetic field strength on CIDNP is recognized already for a number of years [1,2].
Moreover it appears that these effects are rather well understood at the moment [3,4].
A simple example we studied is the fotolysis of azomethane in carbon-tetrachloride. On irradiation of azomethane the following reaction occurs:

$$CH_3-N=N-CH_3 \xrightarrow{h\nu} CH_3-N=N-CH_3^* \longrightarrow 2CH_3\cdot + N_2\uparrow$$
$$2CH_3\cdot \longrightarrow CH_3-CH_3$$
$$CH_3\cdot + CCl_4 \longrightarrow CH_3Cl + CCl_3\cdot$$

So one forms two methyl radicals which can recombine to form ethane, or react with the solvent to methylchloride.
When the reaction is carried out in a high magnetic field (i.e.in the probe of the NMR spectrometer) one predicts according the simple rules of Kaptein [5] that there will be no polarization in the recombination product ethane. (We have a symmetrical pair, i.e. $\Delta g = 0$).
Indeed it is impossible to find any polarization in the formed ethane. (Thus the situation is different from the thermal decomposition of acetylperoxide, where one observes emission in ethane [6]).
However, when the reaction is carried out in the field of an auxiliary magnet and one transfers the sample very quickly (i.e. within the nuclear relaxation time) to the probe of a NMR spectrometer one do find a polarization of ethane, dependent on the magnetic field strength of the auxiliary magnet.

We observed an emission, which is maximal at about 40 Gauss, and which disappears at higher magnetic field (we saw no polarization when the magnetic field was higher then 250 Gauss). This behaviour is reproduced by the calculations [4] when we assume that the reaction proceeds from the singlet state. It is necessary to include all nuclear spins in the calculations.
So where in this case one gets no information from the high field CIDNP experiment it is possible to extract the usual information from the low field experiment.

Yours Sincerely,

J.A. den Hollander

Jan den Hollander.

1). H.R. Ward, R.G. Lawler, H.Y. Loken, R.A. Cooper
J. Amer. Chem. Soc. 91, 4928 (1969).

2). M. Lehnig, H. Fischer
Z. Naturforsch., A, 24, 1771 (1969).

3). J.I. Morris, R.C. Morrison, D.W. Smith, J.F. Garst
J. Amer. Chem. Soc. 94, 2406 (1972).

4). R. Kaptein, J.A. den Hollander
J. Amer. Chem. Soc. 94, 6269 (1972).

5). R. Kaptein
Chem. Comm. 1971, 732.

6). R. Kaptein, J. Brokken-Zijp, F.J.J. de Kanter
J. Amer. Chem. Soc. 94, 6280 (1972).

WE EXTEND THE SEASONS GREETINGS TO ALL READERS WITH

BEST WISHES FOR PEACE AND JOY FOR THE COMING YEAR.

BRUKER

COLORADO
STATE UNIVERSITY
department of chemistry
FORT COLLINS
COLORADO
80521

November 8, 1972

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

In re: FT Spectra on Metal Nuclei

Dear Barry:

I decided to reply to your blue notice on "Blue Wednesday" following the election. In addition to listening to political dialogue these past few months, we (primarily Marie Borzo and Jerry Dallas) have also spent considerable time performing FT experiments on metal nuclei, especially with heavy metals. As one might expect, FT experiments on nuclei such as ^{113}Cd, ^{199}Hg, and ^{207}Pb can be carried out by virtually the same techniques as those used in ^{13}C FT work. Relaxation times are roughly of the same order of magnitude, and NOE's do not dominate the spectra (as they often do with ^{29}Si). The main operational difference is that one must be far more careful in the heavy metal work to make sure that he is observing the frequency window of his choice, and not a fold-over or reflection (with respect to the pulse frequency).

As expected from earlier work on heavy metals, huge chemical shift ranges are observed. The spectra are also very sensitive to details of complexation, as reflected in very large solvent and temperature effects. This sensitivity is now being explored to elucidate such details.

The configuration that we have been employing is a Bruker HFX-90 spectrometer and Digilab FTS/NMR-3 data system and 400-2 pulser with 410 plug-in unit for the 15-20 MHz frequency range. The pulse frequency (f_1) is obtained from a frequency synthesizer. A second synthesizer provides a signal at f_1 + 2.05 MHz, which is used to provide the mixing frequency for generating the 2.05 MHz I.F. utilized in the Bruker receiver circuitry; mixing these two synthesizer outputs provides the 2.05 MHz reference for the I.F. section. Of course, by judicious application of frequency mixers, one can avoid using more than one synthesizer. This kind of technique is quite versatile, and has been used in our laboratory for the nmr detection of a dozen metal nuclides.

Sincerely,

Gary E. Maciel
Professor

GEM:sj

71-28

PHYSIQUE EXPÉRIMENTALE MOLÉCULAIRE
FACULTÉ DES SCIENCES
1, Quai Saint-Bernard - 75 - PARIS (5e)
Tél. : 336-25-25 - Poste 40-53
Tour 22 - 1er étage

PARIS, 7 NOVEMBER 1972

Professor BERNARD L. SHAPIRO
Department Of Chemistry
Texas A and M University
College Station
TEXAS 77843.

N/Réf : E.D/KG-72/261

Title : "Temperature dependence of proton resonance shift of water",

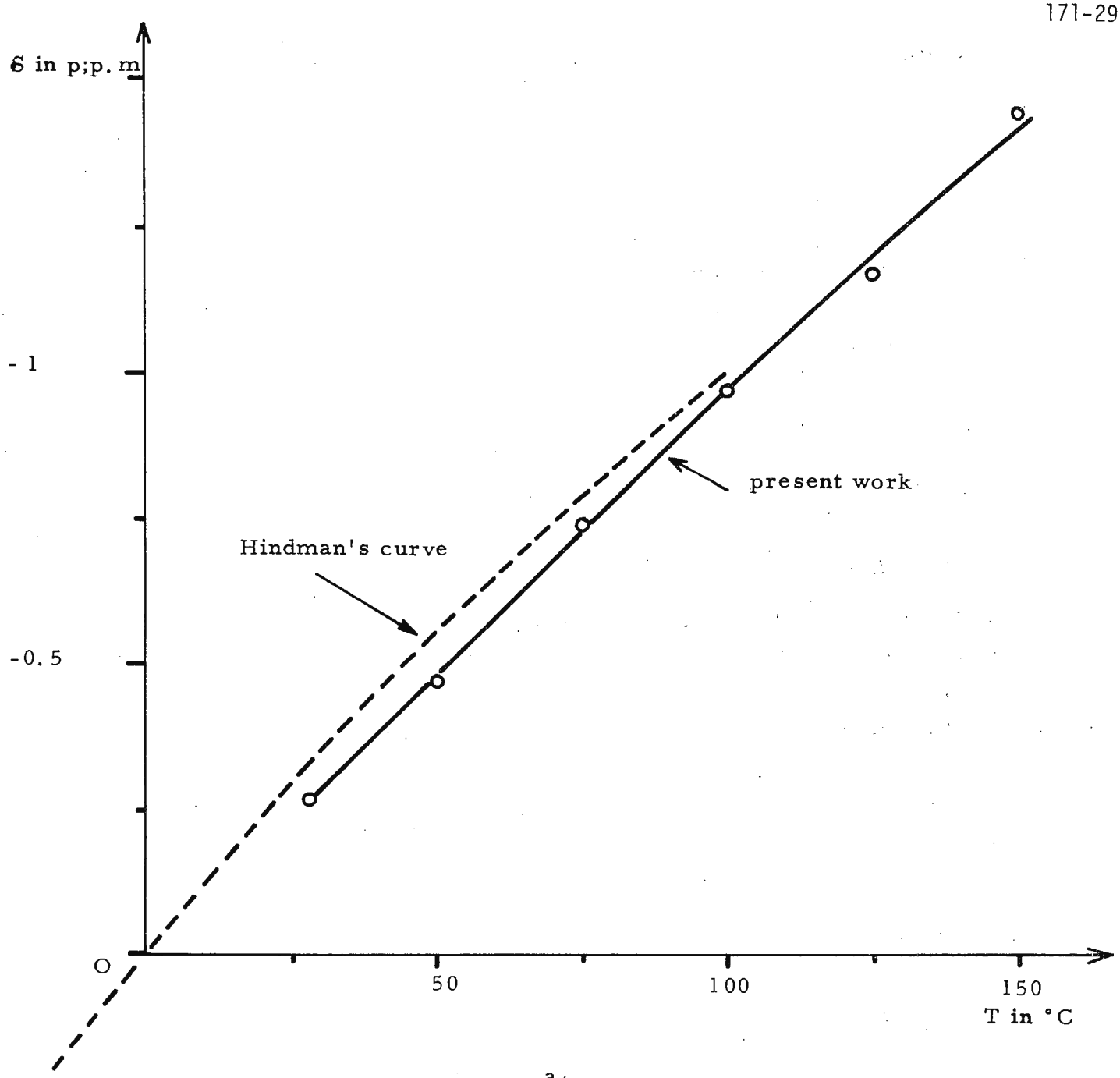
Dear Professor Shapiro,

We would tell you, here, about some experiments done on liquid water. Our cell (described already in Mello NMR Newsletter 1963 N°58) allows us to work under pressure, so we have studied proton resonance shift of water from 30°C to 150°C in liquid state (above 100°C, the liquid is under pressure). We know the interesting work of Dr Hindman * on this subject (up to 100°C) : our data are only complementary and one must note a slight disagreement (see figure hereby). We hope our results might yield information concerning the complex interpretation of water.

Sincerely Yours.
G.WIDENLOCHER and E.DAYAN

* Hindman J.c: J. Chem. Phys 44. 1966. p 4582.

Please credit this contribution to Professor Freymann subscription.



Chemical shift of water as[a] function of temperature (susceptibility corrected shift lines in both cases) our results were obtained relative to CH_4 gas, corrected here to δ_{H_2O} at 0° C = 0 for comparison.

Iwan N. Stranski-Institut
II. Institut für Physikalische Chemie
der Technischen Universität Berlin

1 Berlin 12, den 11/11/1972
Straße des 17. Juni 112
Tel.: (0311) 314 (Durchwahl)

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

Title: CW- and FT-NMR Spectroscopy controlled by a PDP-11 Computer

Dear Dr. Shapiro:

Since June we have been engaged in developping the software and hardware for controlling a BRUKER HFX-90 by a PDP-11/20 (16K) computer, supplemented with a fixed-head disc (256K) and a DEC Disc Operating System Program (DOS). Alphanumeric dialog and graphic display is accomplished by means of a Tektronix display terminal, Model 4010. Both the DOS Monitor and the Tektronix terminal proved to be convenient and fast in programming the PDP-11. The DOS Monitor is designed to load and execute one user program, e.g. for data aquisition or data calculations. However, efficient computer utilization in the laboratory environment quite often requires simultaneous core residence of two or more independent program modules which may interact. Real-time-task or Time-sharing System programs, supplied by computer manufacturers, do meet this need but are disadvantageous in our case since these programs occupy a considerable part, or almost all, of our available core. The program length can be cut down by taking into account the specific requirements of the anticipated experiments and dismissing the more general features. For this reason, we have written an EXECUTIVE-PROGRAM 'EXEC' which resides in upper core (0.6K). EXEC is basically an Assembler program providing faster and more efficient file handling than the DOS Monitor. EXEC is loaded from disc by a short loader program which in turn is run under the supervision of the DOS-11 Monitor, which resides in a 3K region low core. EXEC interacts with DOS-11

11/11/1972

with respect to disc surface information, conversion routines (ASCII-BINARY) and in particular the disc driver. For example, while running a data collection routine, EXEC swaps on command a 4010 Plot routine from disc to core to check the accumulated data, or a service routine to check spectrometer conditions, or a data treatment routine which does preliminary tests. The operator interacts with EXEC in a dialog mode. All program modules are written in position-independent code.

Interfacing the spectrometer and the PDP-11 is eased by the DEC Modul DR 11, a 16 bit Input and Output Register (TTL). The BRUKER recorder of the HFX 90 proved to be extremely amenable with respect to controlling it by the PDP-11, both for spectrum scanning and plotting.

Interested readers can be provided with more details. Please credit this contribution to the subscription of Dr. E. Lippert

Sincerely yours

W. Herres

D. Ziessow

DEPARTMENT OF THE AIR FORCE
AEROSPACE RESEARCH LABORATORIES (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

13 November 1972

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

Dear Professor Shapiro:

Single Crystal Structural Results for NMR Shift Reagents

In order to provide accurate structural parameters for complexes of the type $Eu(L)_3D_x$, where x = 1 or 2, D is an organic nucleophile, and L is the ligand fod or thd, we have undertaken single crystal structure determinations of several of these compounds. The following adducts have been isolated in crystalline form and are being studied by x-ray diffraction techniques:

$$Eu(thd)_3(DMF)_2$$
$$Eu(thd)_3(DMSO)$$
$$Eu(thd)_3(DEF)_2$$

wherein DEF is the abbreviation for N, N-diethylformamide, and DMF and DMSO carry their usual meaning.

A complete three-dimensional structure determination of the octa-coordinate complex $Eu(thd)_3(DMF)_2$ has just been successfully completed and we wish to quickly pass on these results and several thoughts and criticisms which we have concerning some of the methods used for the evaluation of LIS data.

In contrast to the coordination geometry displayed by the bis adducts of 4-picoline and pyridine with $Eu(thd)_3$, the two DMF molecules, each coordinated through an oxygen atom, are cis on the same square face of a distorted square-antiprism. The bonding pattern of the bidentate thd's is such that none of these ligands span an edge joining the two square faces of the coordination polyhedron. This motif is reminiscent of the molecular stereochemistry exhibited by both $La(acac)_3(H_2O)_2$ and $\left[Y(acac)_3(H_2O)_2\right]\cdot H_2O$ and $\left[Y(acac)_3(H_2O)_2\right]\cdot H_2O$ in the crystalline state. Four monomeric $Eu(thd)_3(DMF)_2$ molecules utilize a triclinic unit cell of symmetry $P\bar{1}$; thus in the structure determination process we had to locate and refine the positions of one hundred independent carbon and heavier atoms comprising two complete, independent molecules. At the present stage of refinement, we are now attempting to locate the positions of the hydrogen atoms.

Pertinent bond lengths and angles, averaged where appropriate, are:

Bond Type	Distance, A
$Eu\text{-}O_{DMF}$	2.47 (average of 4 values)
$Eu\text{-}O_{thd}$	2.35 (average of 12 values)
Angle Type	**Angle, deg.**
$\angle Eu\text{-}O\text{-}C_{DMF}$	134

All other bond lengths and angles are similar to those found in other complexes of this type.

A quick perusal of the available x-ray structural data clearly shows the $Ln\text{-}O_{\beta\text{-dik}}$ bond lengths lie within the expected ranges. In particular for Eu^{3+} this range is approximately 2.30 - 2.40A with 2.35A as the average value. The $Ln\text{-}X_{adduct}$ bond lengths observed are naturally dependent not only upon the radius of the lanthanide ion but also upon the nature of the coordinating atom, X. Even in the extremely unstable bis pyridine adduct, previously mentioned, this bond length does not exceed 2.66A; the range of reported Eu-donor lengths (40 bonds) for $Eu(\beta\text{-diketonate})_3$ complexes is 2.3 - 2.7A. In light of these data we feel that any treatment of LIS data should be based on the assumption that the Eu-X bond length has a value in this approximate range. It does not seem justified to ignore structural information about bond lengths in crystals and vary the adduct bond length over unreasonable large values just to obtain better computer fits of the NMR spectral data.

We would also like to point out that of the five completed x-ray structures of shift reagents and related complexes, three are of bis monodentate adducts. It, therefore, seems quite probable that even at moderate values of the ratios [D] / [shift reagent], more than one species is present in solution. Consequently it will be necessary to work at low values of [D] / [shift reagent] to minimize formation of the bis adduct.

Sincerely,

Robert E. Sievers

ROBERT E. SIEVERS

James A. Cunningham

JAMES A. CUNNINGHAM

171-34 Institut für Organische Chemie
der Johann Wolfgang Goethe-Universität
Frankfurt am Main
Prof. Dr. H. Kessler

6 Frankfurt/M., den Nov. 10, 1972
Sandhofstr.
Telefon 6301-6 0 3 3

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University

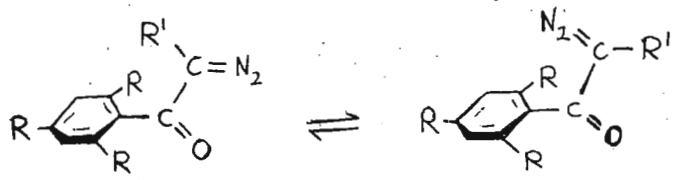
College Station, TX 77843

U S A

Dear Dr. Shapiro:

Z, E-Isomerization of Aromatic Diazoketones

The conformation of aromatic diazoketones has been studied in ortho-substituted ones.



Z ⇌ E

	R'	R
1	H	H
2	H	CH_3
3	H	i-C_3H_7
4	CH_3	H
5	CH_3	i-C_3H_7

In spite of earlier measurements of 1 [1] we were able to detect both isomers in 2, 3 and 5. This was explained by twisting the aryl-ring-plane respect to the diazo-carbonyl-plane[2]. Kinetic datas has been determined by complete line shape studies (table). The assignement to the Z or E- conformation was made with Eu(fod)$_3$-measurements in which the group R' in the E-conformation is more deshielded. The free enthalpy of activation $\Delta G^{\ddagger}$ increases slightly with increasing size of R (2 ⟶ 3) and R' (3 ⟶ 5).

Yours sincerely

H. Kessler D. Rosenthal

H. Kessler and D. Rosenthal

Table. Signals of R' in Aromatic Diazoketones[a].

No	R' [ppm]		Intensity [in %]		T_c [°K]	$\Delta G^{\ddagger}_{298}$ [kcal/mol]	E_a [kcal/mol]	lgA
	Z	E	Z	E				
1	5.84		>98	<2				
2	5.45	5.36	76	24	298	15.0	15.7	13.0
3	5.50	5.37	78	22	301	15.5	16.9	13.8
4		2.12	<2	>98				
5	1.39	1.84	23	77	335	16.8[b]	13.3[b]	10.2[b]
						16.7[c]	17.2[c]	14.2[c]

a) Shift and intensity measurements at 263°K in $CDCl_3$;

b) Solvent: C_6H_5Br; c) Preliminary measurements in $CDCl_3$ below T_c.

References

1) F. Kaplan u. G. H. Meloy, JACS 88, 950 (1966).

2) The same phenomenon was observed in acetanilides
H. Kessler and A. Rieker, Liebigs Ann. Chem. 708, 57 (1967).

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, November 10, 1972

Uw ref.:

Onze ref.: 72166/BN/aa

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

Dear Dr. Shapiro,

NMR electric field effects in 2,4,6-trifluoronitrobenzene

NMR electric field experiments have been carried out on the molecule 2,4,6-trifluoronitrobenzene. At sufficiently high voltages, direct spin-spin dipolar and quadrupolar electric field effects appear, as reported before for several related molecules (1). With these effects a value can be obtained for the alignment, $\langle 3\cos^2\varphi - 1\rangle_E$, of the molecules. We wish to report here the first experimental results.

In fig. 1 the experimental ^{19}F-NMR spectra are given without (a) and with (b) an applied electric field (70 kV/cm). The low field absorptions originate from the fluorine spins in paraposition (4), while the high field multiplet represents the fluorine spins in orthopositions (2,6). Likewise, the isotropic (a) and anisotropic (b) ^{1}H-NMR spectra are given in fig. 2. The spectral parameters σ, J and D are collected in table 1. The values for σ and J have been obtained from the interpretation of isotropic ^{1}H- and ^{19}F-NMR spectra. The D-couplings in table 1 correspond with an average orientation of $\langle 3\cos^2\varphi - 1\rangle_E = 3.0 \times 10^{-4}$. The experimental spectra are in good agreement with the theoretical ones, computed with a modified LAOCOON III program.

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DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

Table 1

Spectral parameters used in the simulation of the 2,4,6-trifluoronitrobenzene spectra.
Values are given in Hz. D-couplings correspond with an orientation $\langle 3\cos^2\measuredangle - 1\rangle_E = 3.0 \times 10^{-4}$.

Chemical shift	J-couplings	D-couplings
W(2) = W(6) = 964	J(2,3) = J(5,6) = 10.01	D(2,3) = D(5,6) = - 1.56
W(4) = 0	J(2,4) = J(4,6) = 9.34	D(2,4) = D(4,6) = - 0.16
	J(2,5) = J(3,6) = - 2.04	D(2,5) = D(3,6) = 0.02
	J(3,4) = J(4,5) = 8.53	D(3,4) = D(4,5) = - 0.01
	J(2,6) = - 2.66	D(2,6) = 0.14
	J(3,5) = 2.20	D(3,5) = 0.22

Comparison of the isotropic and anisotropic spectra shows that, especially in the orthofluorine- and protonspectra, the separation between the peaks becomes smaller under the influence of an applied electric field, while there is no visible change in the spectrum of the fluorine spins in paraposition.

From the orthofluorinespectra as well as from the protonspectra a value was extracted for the ratio of the alignment and the square of the electric field strength in the liquid. The average value for both experiments is: $\langle 3\cos^2\measuredangle - 1\rangle_E/E^2 = 0.55 \times 10^{-8}$ (e.s.u.).

From this value and from quadrupolar electric field effects in the ^{14}N-NMR spectra the quadrupolar coupling constant of ^{14}N in this molecule can be computed. Our calculation yields: $(e^2qQ)/h = 0.78$ MHz. For comparison we give the value of the quadrupolar coupling constant of ^{14}N in nitrobenzene (deduced from (2)): $(e^2qQ)/h = 0.95$ MHz.

We have also tried to estimate the anisotropy in the chemical shifts of the fluorine nuclei. Assuming axial symmetry of the CF bonds in the

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DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

molecule a value can be calculated for $(\sigma_{//} - \sigma_{\perp})$, in the manner described by Buckingham and Pople (3). In the quantity $(\sigma_{//} - \sigma_{\perp})\ \sigma_{//}$ is defined as the chemical shift in the direction of the CF bond. From our data only a very approximate value can be derived for the anisotropy in the chemical shift of the parafluorine nucleus:

$$(\sigma_{//} - \sigma_{\perp})_{\text{parafluorine}} = -50 \pm 100 \text{ p.p.m.}$$

Sincerely yours,

B. Neijzen J. Biemond C. MacLean

(1) NMR-Basic Principles and Progress,
Vol. 7, C.W. Hilbers and C. MacLean,
Springer-Verlag, Berlin, 1972

(2) Sears, R.E.J. and E.L. Hahn,
J.chem.Phys., 45, 2753, (1966)
Ibid., 47, 348 , (1967)

(3) Buckingham, A.D. and J.A. Pople,
Trans. Faraday Soc., 59, 2421, (1963)

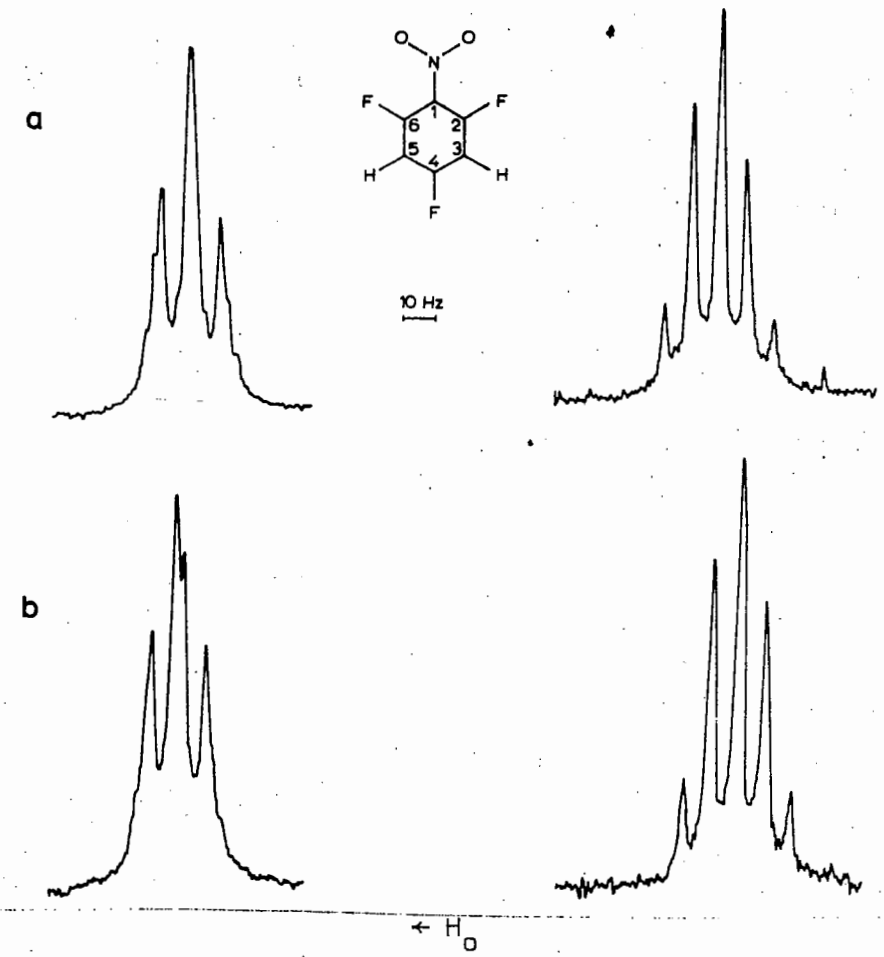


Fig. 1. ^{19}F-NMR spectra of 2,4,6-trifluornitrobenzene at room temperature without (a) and with (b) an applied electric field (70 kV/cm).

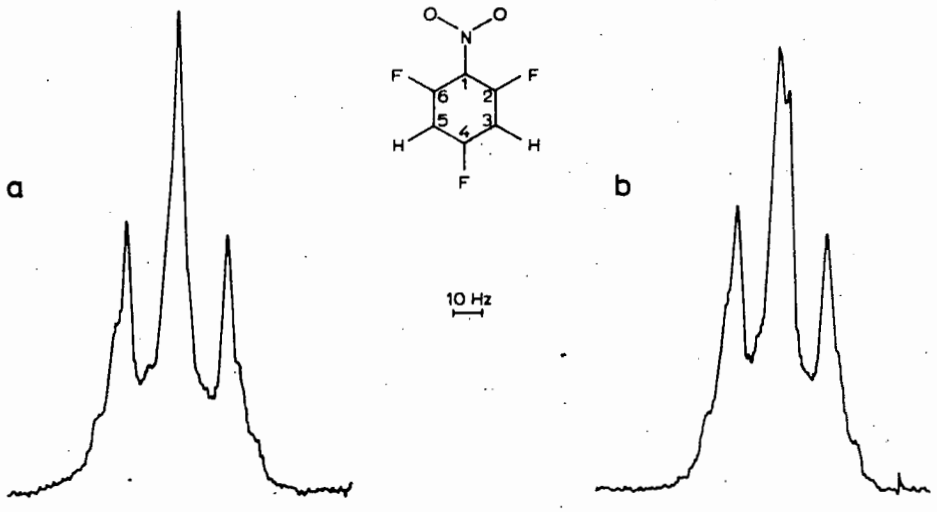


Fig. 2. ^{1}H-NMR spectrum of 2,4,6-trifluornitrobenzene at room temperature without (a) and with (b) an applied electric field (70 kV/cm).

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS
PROFESSOR OF ORGANIC CHEMISTRY

November 14, 1972

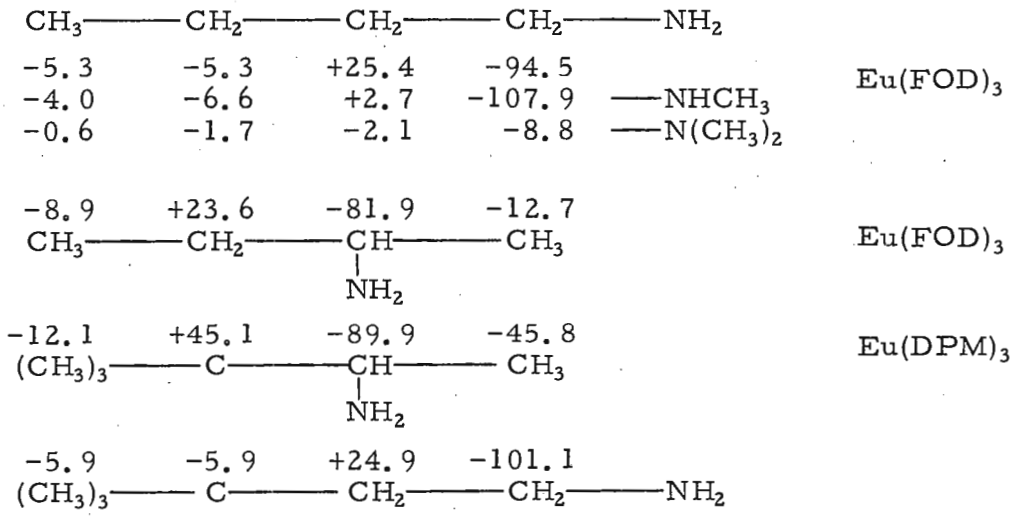
Professor B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

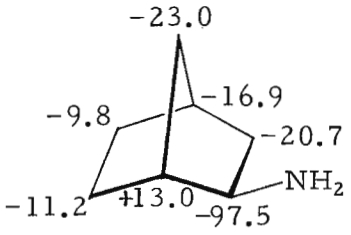
Europium-Induced
Abnormal ^{13}C Shifts in Amines

Dear Barry,

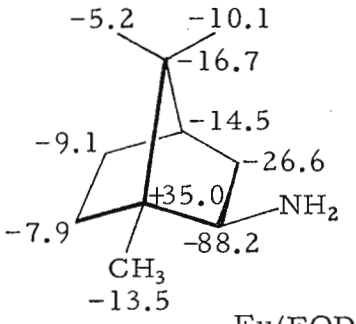
Some of your readers may be interested in the kind of structural variations found by Claude Marzin, Robert Cooper, Geoffrey Hawkes, and Klaus Herwig, which are associated with the 'wrong-way' β ^{13}C shifts induced in amines by europium chelates, and which were independently discovered by Cushley, Anderson, and Lipsky (Chem. Commun., 636 (1972)) and mentioned in my ENC talk at Asilomar last April.

The spectra were taken of $CDCl_3$ solutions at 15.01 MHz using the PFT 'Brukarian' spectrometer developed from our time-honored Varian DFS spectrometer and a Bruker probe, ^2H stabilization, pulse amplifier and receiver. These supposedly incompatible components were interfaced with a Varian pulse box and 620 i computer with great skill by Bruce Hawkins, now at Lausanne, with helpful suggestions from Chris Tanzer and Rudy Nunlist of Bruker. The shifts, which were strictly linear with concentration and determined for several concentrations, are normalized to 1 M concentrations of amine and chelate. The proton shifts in all of these substances were essentially normal and uncomplicated.



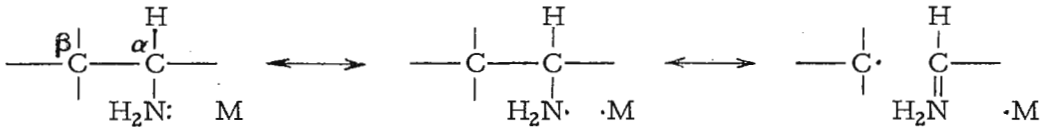


Eu(DPM)$_3$

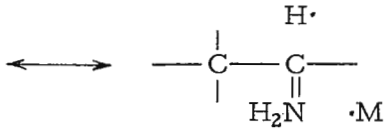


Eu(FOD)$_3$

These data show clearly that the degree of the abnormal β shift is quaternary > tertiary > secondary > primary carbons. We interpret this in terms of hyperconjugation of which the key structure for the abnormal shift is III.



I II III



IV

The greater the degree of substitution of the β carbon, the more important III is. The analogous structure for hydrogen hyperconjugation IV is apparently much less important because the degree of contribution of contact shifts to the hydrogen resonance positions is small, if not zero.

With all good wishes,

Very truly yours

Jack

171-42

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOT · ISRAEL רחובות · ישראל

ISOTOPE DEPARTMENT מחלקת איזוטופים

Prof. Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

November 7th 1972

Dear Barry:

Much as one would like, plots of the shifts induced by shift reagents versus the reagent-to-substrate ratio are not always linear. However, by suitable mathematical manipulations they can be made linear as has been convincingly demonstrated by ApSimon, Beierbeck and Fruchier, Can. J. Chem., 50, 2725 (1972). Unfortunately, the physicochemical meaning of these manipulations may be somewhat obscure. The method proposed, opere citato, reduces to the following procedure, which is recommended to all the lovers of linear plots. Take a set of n random numbers I_i , $i = 1, 2, \ldots, n$, and generate a new set $J_i = I_i/C$, where C is a constant. Plot I_i versus J_i . A perfect linear plot of slope C and zero intercept will result. If a non-zero intercept of value δ is required, add δ to your I_i's.

Sorry about that.

Sincerely yours,

Jacques

Jacques Reuben

Title: For lovers of linear (shift reagent) plots.

JR:dr

CABLE ADDRESS: WEIZINST (Israel) מען למברקים: PHONE: 951721 טלפון:

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

National Centre of the Government of India for Nuclear Science and Mathematics

Telegrams: ZETESIS HOMI BHABHA ROAD, BOMBAY 5. Telephone: 213141

DR. C.L. KHETRAPAL

November 14, 1972

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

Title: PMR Spectra of Oriented Trimethylene Oxide and Trimethylene Sulphide

Dear Professor Shapiro,

We have studied the Proton Magnetic Resonance spectra of trimethylene oxide and trimethylene sulphide oriented in the nematic phase of liquid crystals. The chemical shifts, the direct and the indirect spin-spin couplings are determined. The interpretation of the direct couplings in terms of the molecular structure shows that the ring skeleton of these molecules is not rigidly planar due to ring puckering vibrations. Mean amplitudes for the vibrations are estimated assuming fixed values for the bond distances and for the HCH bond angles. The results obtained are in good agreement with the earlier microwave studies.

This work has been done in collaboration with Dr. A. Saupe of the Liquid Crystal Institute, Kent State University, Kent, Ohio.

Yours sincerely,

C.L. Khetrapal (C.L. Khetrapal)

A.C. Kunwar (A.C. Kunwar)

Prof. Dr. Hanns Fischer

Physikalisch-Chemisches Institut
der Universität Zürich

CH-8001 Zürich
Rämistrasse 76
Telefon 01 / 32 26 20

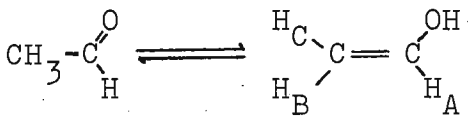
November 23, 1972

Professor Dr. B.L. Shapiro
TEXAS A&M UNIVERSITY
Department of Chemistry
College Station
T e x a s 77843 U.S.A.

CIDNP Determination of the PMR Spectrum of Vinyl Alcohol

Dear Dr. Shapiro:

Under equilibrium conditions at ≈ 25°C, the concentration of acetaldehyde (1) is believed[1] to exceed that of its enol, vinyl alcohol (2), by a factor of at least 10^7. This explains why the PMR-spectrum of(2) has not been reported, so far.



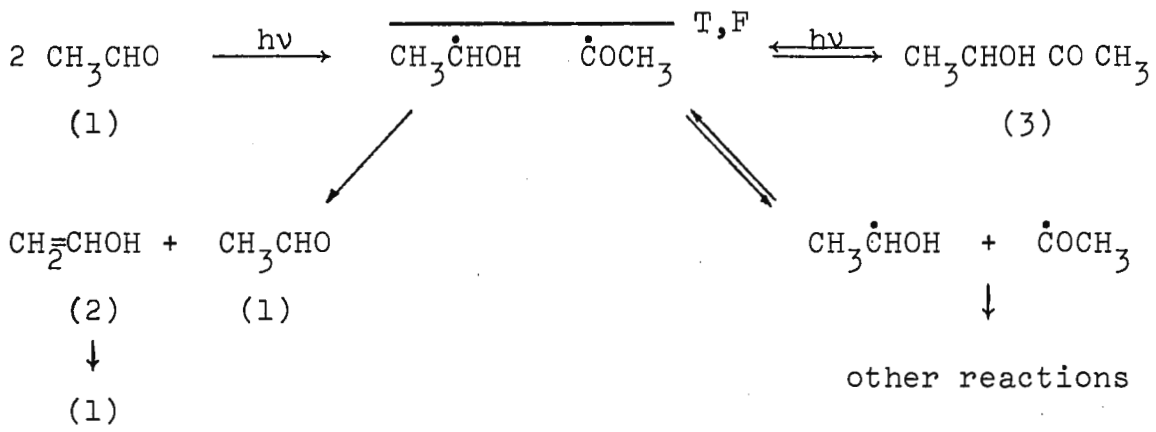
(1) (2)

During photoreactions of (1) or acetoin (3) at ≈ 25°C in benzene, cyclohexane and other solvents, we have recently observed PMR-CIDNP effects (100 Mc/sec) of an intermediate which is characterized by an olefinic ABC-system (δ_A = 6.27, δ_B = 3.91, δ_C = 4.13 ppm, J_{AB} = 6.5, J_{AC} = 14.0, J_{BC} = 1.8 sec^{-1}, TMS, benzene). We assign these transitions to the A,B,C-protons of (2), and support the assignment as follows:

1. The spectral parameters are consistent with an -OR substituted vinylgroup only[2,3].

2. The transitions can not be observed if traces of acids which catalyze the equilibration are added to the solutions. They are also not observed after the reaction, and therefore are not due to a stable vinylether.

3. The signs of the CIDNP-effects (H_A: E+A/E, H_B, H_C: A+A/E) are consistent with those predicted from CIDNP theory, the known ESR-parameters[4,5] of $CH_3\dot{C}O$ and $CH_3\dot{C}HOH$, and the reaction mechanism



This mechanism is supported by ESR observation[4] of $CH_3\dot{C}HOH$, the photochemistry[6] of (3), and the signs of the CIDNP effects of (1) and (3).

The HO-proton of (2) is not detected and not predicted to be polarized. From the linewidth of the transitions of (2) ($\approx$1.3 sec^{-1}), we guess a lifetime of about 1 sec or longer.

The figure shows the observed CIDNP-pattern of (2) (a) and a CIDNP-pattern simulated[7] on the basis of the diffusion model, the known radical parameters and the choice $J_{AB}>0$, $J_{AC}>0$, $J_{BC}<0$ (b).

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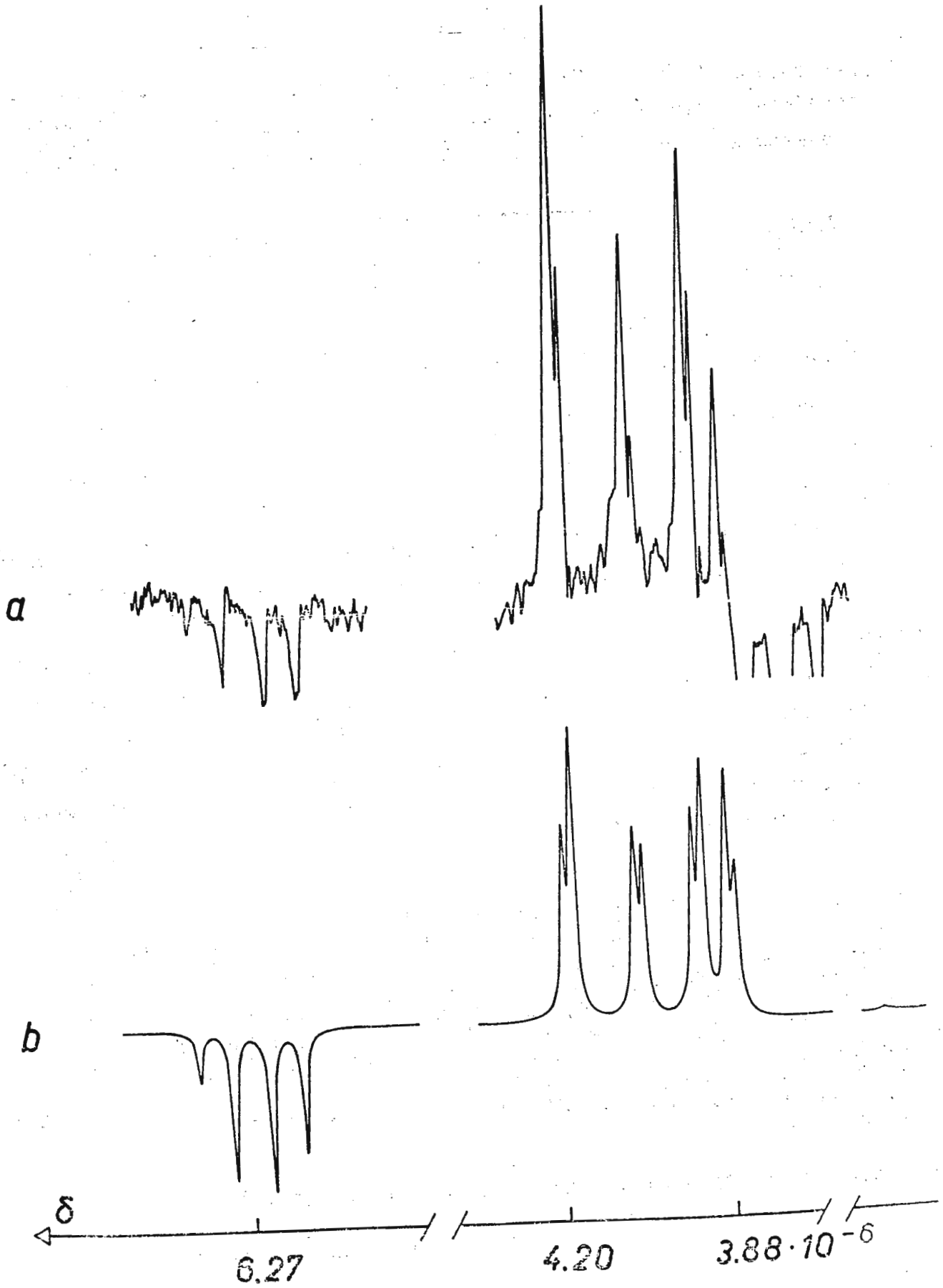
3. J.W. Emsley, J. Feeney, L.H. Sutcliffe, High Resolution NMR, Pergamon (1966), p 710 ff
4. H. Zeldes, R. Livingston, J.Chem.Phys.47, 1465 (1967)
5. J.F. Bennett, B. Mile, Trans.Farad.Soc.67, 1587 (1971)
6. E.J. Baum, L.D. Hess, J.R. Wyatt, J.N. Pitts,Jr., J.Am.Chem.Soc.91, 2461 (1969)

7. We thank Dr. J.A. den Hollander, Leiden, for a copy of his CIDNP program.

We apologize for being late in sending our contribution.

Sincerely yours,

B. Blank H. Fischer A. Henne



CIDNP OF $H_2C{=}CHOH$

Uppsala universitet
Fysiska institutionen

University of Uppsala
Institute of Physics

1972-11-20

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

Line shapes in saturated AB spectra

We have been studying AB spin systems and recorded slow-passage single resonance spectra at high rf amplitudes when saturation and overlap of spectral lines is appreciable. The line-shapes of the strongly saturated spectrum gives information about the relaxation mechanisms. A study of random field interactions on the line-shapes has been presented (J. Magn. Resonance 8, 230, 1972)

Recently we have studied the line-shapes in an AB system where the dipole-dipole interaction is of the same order of magnitude as the random field interactions. It has been possible to obtain values for the relaxation parameters from comparisons with computer-calculated spectra. Especially the behaviour of the double quantum peak is strongly dependent of the dipole-dipole interaction, (cf. Harris & Worvill, Chem.Phys. Lett. 14, 598, 1972).

An unfortunate non-linearity in our instrumentation has however made the comparison with the computer calculated spectra troublesome, and delayed the investigation considerably. We hope to be able to return to this point later on.

Sincerely yours,

Ola Hartman

Bo Gestblom

UNIVERSITY OF CALIFORNIA, BERKELEY

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SPACE SCIENCES LABORATORY

BERKELEY, CALIFORNIA 94720

21 November 1972

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

Dear Professor Shapiro:

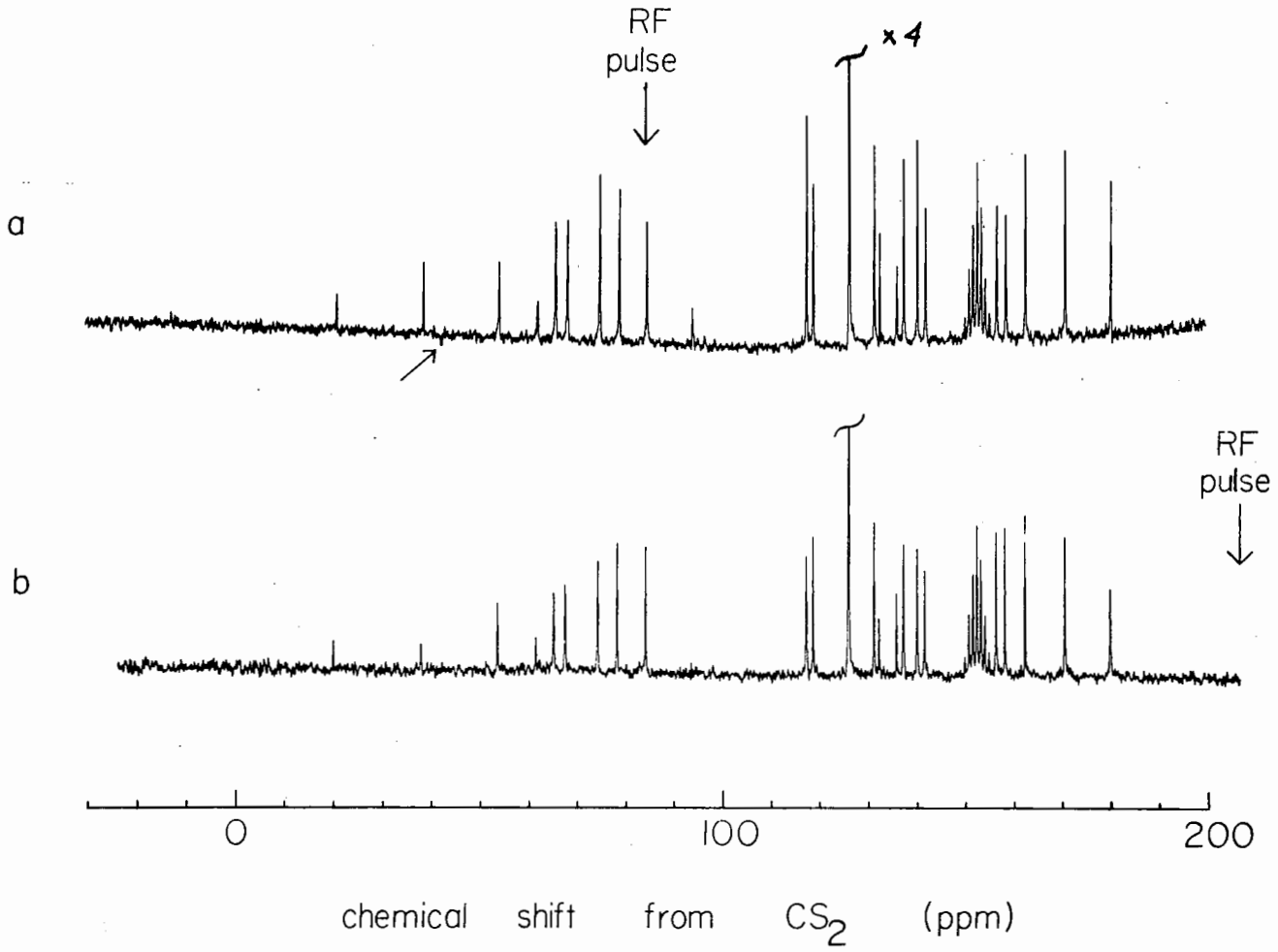
Dual Phase Detection Benefits in F.T. NMR

A principal instrumental goal in this laboratory is reduction of sample quantity requirements for characterization of naturally occurring compounds by ^{1}H and ^{13}C NMR. We are aware of at least two laboratories (1,2) which are already employing the method of dual lock-in detection, i.e. accumulation of separate free-induction decays from phase detectors working in quadrature with respect to each other. This gives essentially twice the number of scans in the same accumulation time, and one expects a S/N enhancement improvement of $\sqrt{2}$.

Another benefit derives from the ability to pulse in the middle of a spectrum in the dual-phase mode. The angle between the "effective field" around which precession occurs during an RF pulse and that of the irradiating H_1 field, is given by $\beta = \arctan(4\,\Delta\,\tau_{90})$ where Δ is the frequency difference (in Hz) between the RF carrier frequency of the pulse and the resonance frequency of the nucleus, and τ_{90} is an instrumental characteristic, the pulse width required to flip a nucleus near resonance by 90°. Although Jones and Sternlicht (3) have devised methods to optimize the pulse flip angle and pulse repetition rate for a nucleus of given T_1, individual ^{13}C T_1's in complex molecules have been shown to typically differ by an order of magnitude (4). Under these circumstances, with the additional requirement of enough sampling time to give the desired spectral resolution in the Fourier transformed result, the only solution for obtaining approximately accurate line intensities is to keep β as small as possible. Dual phase detection helps accomplish this by halving Δ.

We have replaced the final 40.96 KHz phase-detection stage of our Varian XL-100 spectrometer with dual phase detectors, wherein the reference signals are provided by a phase-locked 163.84 KHz oscillator, thus assuring reliable quadrature separation of the two channels by a few parts in 10^4. Matched 4-pole Butterworth filters and alternate sampling of their outputs by the A/D converter complete the hardware modifications. Software modifications were trivial, inasmuch as we found the previously used linear phase correction to be adequate. The figure shows a comparison of dual-phase detected (a) and single phase detected (b) ^{13}C pulsed Fourier-transform proton-decoupled spectra of 20 mg of the alkaloid Vincamajine in dimethyl sulfoxide-D_6 at 75°C. 40° 200-watt RF pulses were applied at the positions indicated at 1.5 sec intervals for 17 hours in each spectrum. The fact that dioxane was added in excessive quantity as an internal reference serves to illustrate that "imaging" is not a problem, since its "image" at the diagonal arrow in (a) is attenuated by more than 40 db and would have been unobservable if a more prudent amount had been added.

Finally, it should be emphasized that no additional computer memory is required to achieve the same resolution as in single-phase detection, since the sampling rate for each channel is halved. It appears to us that any presently working F.T. system should require only minor hardware or software changes to implement this technique, even those which destroy the data while Fourier transforming it.



D. M. Wilson

R. W. Olsen

J. J. Chang

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2. J. D. Ellett, M. G. Gibby, U. Haeberlen, L. M. Huber, M. Mehring, A. Pines, and J. S. Waugh, ibid., p. 117.
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171-50

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Dept. of Chemistry

28.11.72.

Dr. B.L.Shapiro,

Department of Chemistry,

Texas A & M University,

College Station, Texas 77843.

Dear Dr. Shapiro,

It's hard to realise that we've had 9 months relaxation since our last subscription reminder; may we be excused.....accumulation times are much longer for mono-substituted perfluorobenzenes than for their protonated counterparts.

^{19}F wideband decoupling with our Bruker BSV-2 has proved somewhat difficult since the range of ^{19}F chemical shifts, even in C_6F_5X compounds, is rather large (30 ppm) for this unit. However, by using wideband techniques at 2 different frequencies, we have managed to observe the aromatic ^{13}C nuclei in C_6F_5X where X has been F, Cl, Br, I, OH, OCH_3, NH_2, CH_3, CH_2Br, $CH{:}CH_2$, CHO, CO_2H, SH, NO_2, C_6H_5, and CN. Fortunately, the power output is sufficient to remove ^{13}C-^{19}F couplings at ranges greater than one bond, and in cases such as C_6F_5H, when the m and p ^{19}F signals are irradiated, the m and p ^{13}C signals show no coupling to the o^{19}F nucleus (see fig.), and vice versa. This greatly assists the ^{13}C assignment.

Qualitative comparisons of ^{13}C decoupled from ^{19}F with ^{13}C attached to ^{1}H in the same molecule suggests that there is little or no Overhauser enhancement in $^{13}C\{^{19}F\}$ experiments; the observation is given further weight by direct comparison of decoupled and un-decoupled spectra of tri-fluoro acetic acid, and by comparison of the $^{13}CF_3$ and $^{13}CO_2H$ signals which show no differential NOE to within the rather wide limits of measurement. There may be significant contributions of spin rotation or even chemical shift anisotropy relaxation

mechanisms to T_1 in these systems.

Chemical shifts of the ring ^{13}C nuclei have been compared with those in C_6H_5X and C_6H_4FX. C1 and C4 give good linear correlations whilst C3 remains virtually constant ($\pm$ 0.5 ppm), and C4 (w.r.t. $^{13}C_6F_6$) correlates linearly with δ_{F4} in C_6F_5X (w.r.t. $C_6{}^{19}F_6$).To add further fuel to the linear free energy relationship fire, δ_{C4} correlates well with Taft's σ_I and σ_R using the formula;

$$\delta_{C4} = 10.41\sigma_R + 4.01\sigma_I + 3.07 \text{ ppm}$$

obtained by throwing a least mean squares fit of 12 chemical shifts to 3 variables. (Chemical shifts are on the δ scale in ppm to low-field of $^{13}C_6F_6$.)

Please credit this contribution to the account of Dr. E.W.Randall, from whom, greetings.

Yours sincerely

J.M.Briggs

Suggested title. Noise decoupling of ^{19}F from ^{13}C in fluoroaromatics.

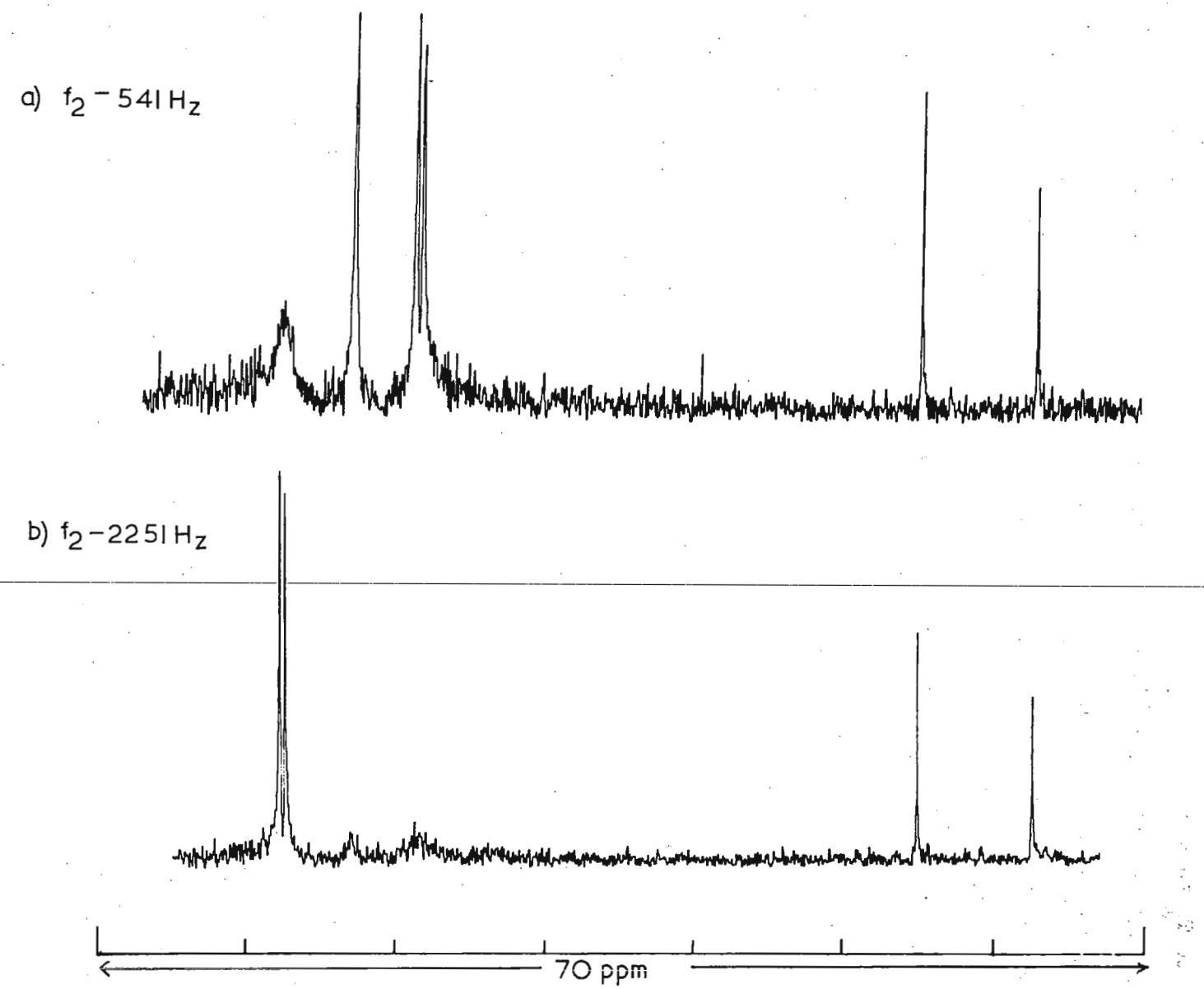


Fig 3 ^{13}C spectra of C_6F_5H at 22·63 MHz noise decoupled from ^{19}F

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

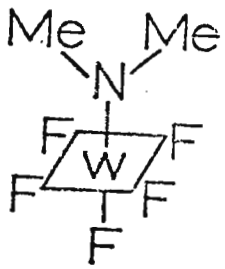
November 29, 1972

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

Tungsten - Fluorine Chemistry

Dear Barry:

We have run into some unexpected nmr results in our examination of the new compound $(CH_3)_2NWF_5$ prepared here by Fred Brinckman.



In proton nmr, the methyl signal is at exceedingly low field: 7.0 ppm downfield from TMS. At room temperature in C_6F_6, the signal is a reasonably good sextet with $J_{HF} \simeq 1.9$ Hz. However, at -65 °C in $CHFCl_2$ as solvent, the signal becomes a doublet of quintets; $J_{HF(ax)} = 2.7$ Hz and $J_{HF(eq)} = 1.5$ Hz.

So far no real problem. The fluorine spectrum is more difficult to understand. At room temperature in $CHFCl_2$, all fluorines on tungsten, including WF_5 present in excess as well as the axial and equatorial fluorine signals from the $-WF_5$ group, are at least 50 Hz broad (FWHM approximately). The WF_6, although broad, is within 15 Hz or less of its position in a separate tube containing only WF_6 in $CHFCl_2$. The axial F signal is so broad and weak it is almost impossible to find by direct observation at room temperature, although an approximate chemical shift can be obtained by decoupling fluorine from the observed methyl proton signal. That the entire content of the tube is paramagnetic is disproved by the observation that the solvent signal, $CHFCl_2$, consists of its normal sharp doublet.

As the temperature is lowered, the $-WF_{5(eq)}$ signal becomes sharp (it is a doublet with $J_{FF} \simeq 53$ Hz, with $J_{HF} \simeq 3$ Hz superimposed) and ^{183}W satellites are observed. The temperature must be dropped another 20° or so before the WF_6 signal becomes sharp. The $-WF_5$ (axial) signal even at -55° is still very broad, with the 3 center lines of the expected quintet visible with widths of roughly 20-30 Hz. Attempts to decouple ^{14}N in an effort to sharpen the axial fluorine signal have been to date unsuccessful. All of the fluorines on tungsten exhibited little or no chemical shift between room temperature and -55°.

A number of questions put themselves:

(1) Why is the methyl signal at such low field?

(2) How do we observe structure due to HF coupling in the proton spectrum while the fluorine signals are very broad?

(3) If the fluorines on tungsten are being broadened by an exchange process, why do we fail to observe the signals moving closer together as they become broader?

(4) Is the axial fluorine signal really strongly broadened by the ^{14}N quadrupole? If this is the case it will be shown by improved experimental arrangement. In this connection it is interesting to note that the axial fluorine signal in WF_5Cl is unusually broad, and the suggested explanation is that the axial fluorine is strongly coupled to the trans chlorine and broadened by the chlorine quadrupole (1).

Suggestions from readers, either of possible explanations or for further experiments, will be welcomed.

One final observation, puzzling to me at least, has been made on several MWF_5 compounds, where M = RO- or R_2N-. In each case, the fluorine signals from axial and equatorial fluorines were separated by several hundred to several thousand Hertz. Yet when the protons in the R group were observed, the signal was always collapsed to a single line by irradiating fluorine in either axial or equatorial position, rather than giving the expected doublet or quintet. The fluorine irradiating power was assuredly not strong enough,

nor the frequency noisy enough, to irradiate the entire fluorine chemical shift range. This phenomenon may be connected with the large coupling constant (55 - 65 Hz) between axial and equatorial fluorines in these compounds.

Yours very truly,

Rolf

Rolf B. Johannesen
Inorganic Chemistry Section

Reference (1): G. W. Fraser, C. J. W. Gibbs and R. D. Peacock, J. Chem. Soc. A, 1708 (1970).

AUTHOR INDEX

Allerhand, A. 11
Biemond, J. 36
Blank, B. 44
Briggs, J. M. 50
Buchanan, G. W. 21
Chang, J. J. 48
Cunningham, J. A. 32
Curb, P. 1
Dayan, E. 28
DeHayes, L. J. 1
Diehl, P. 7
Fischer, H. 44
Frost, D. J. 8
Gestblom, B. 47
Hagstrum, W. 1
Hartman, O. 47
Henne, A. 44
Herres, W. 30
den Hollander, J. 24
Johannesen, R. B. 53
Kellerhals, H. P. 4
Kessler, H. 34
Khetrapal, C. L. 43
Kunwar, A. C. 43
Maciel, G. E. 27
MacLean, C. 36
Mankowski-Favelier, R. 12
Mathey, F. 12
Mavel, G. 12
Neijzen, B. 36
Olsen, R. W. 48
Reuben, J. 42
Roberts, J. D. 40
Rosenthal, D. 34
Sievers, R. E. 32
Spear, R. 16
Sternhell, S. 16
Sudmeier, J. L. 1
Widenlocher, G. 28
Wilson, D. M. 48
Ziessow, D. 30

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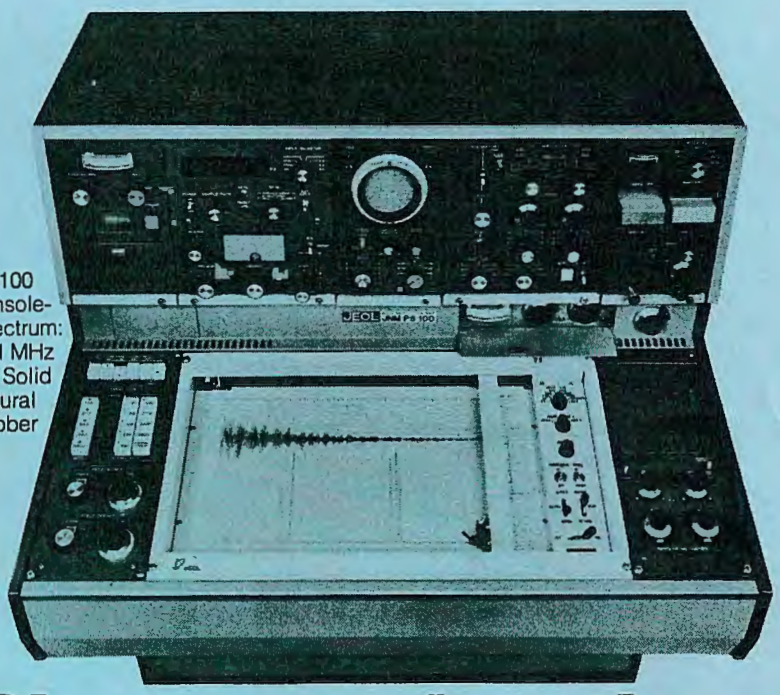

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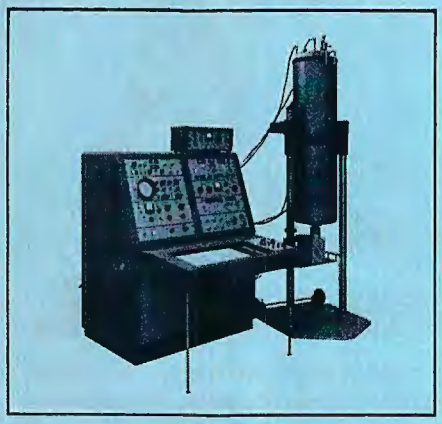

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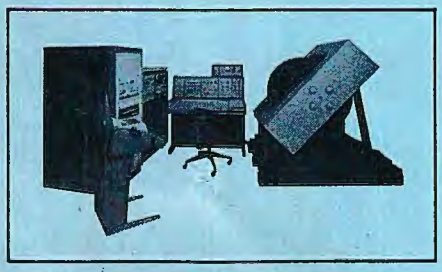

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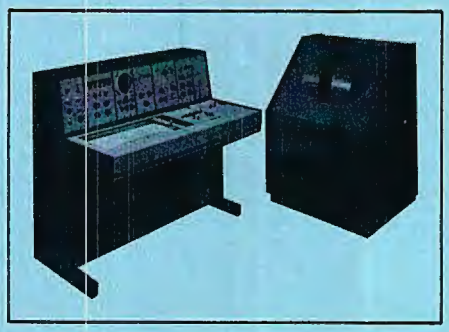

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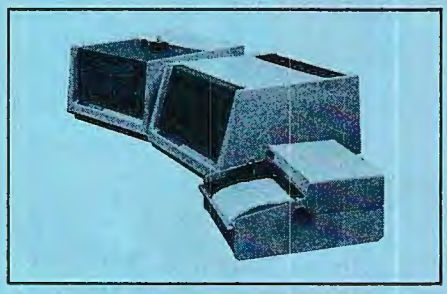

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