Texas A & M University N-M-R Newsletter

IN 5/23/72

No. 164

May, 1972

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	No. 166: 3 July 1972

All Newsletter correspondence, etc. should be addressed to:

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

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

April 3, 1972

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

Dear Barry:

Title: Angular Dependence of Dihomoallylic Coupling Constants

Recently we have studied several 1,4-cyclohexadiene systems and have attempted to predict the ring conformation from the values of the relatively large five-bond homoallylic coupling constants. Garbisch and Griffith[1] used equation 1 in their study of 1,4-dihydrobenzene but omitted the derivation of this equation. The angles φ and ω are defined in Fig. 1.

$$\frac{^5J_c}{^5J_t} = \frac{(\sin^2\varphi)^2 + [\sin^2(\omega-\varphi)]^2}{2\,[\sin^2(\omega-\varphi)\,\sin^2\varphi]} \qquad \text{Eq. 1}$$

Assuming that $\omega = 120^\circ$, this equation predicts that for all φ $J_c \geq J_t$ and that $J_c = J_t$ only for $\varphi = 60^\circ$, i.e., only for the planar conformation of the 1,4-cyclohexadiene ring.

In our work and at least one other case[2] reported in the literature, the conformation predicted by equation 1 does not agree with the conformation predicted by other coupling constants. Equation 1 was derived from the Karplus treatment[3] of long-range coupling constants. Accordingly, ^5J_c and ^5J_t for conformations I and II are given by:

$$^5J_c^I = k(\sin^2\varphi\sin^2\varphi+\sin^2\varphi\sin^2\varphi) = k\,2(\sin^2\varphi)^2$$

$$^5J_c^{II} = k(\sin^2\varphi'\,\sin^2\varphi' + \sin^2\varphi'\,\sin^2\varphi') = k2(\sin^2\varphi')^2 = k2[\sin^2(\omega-\varphi)]^2$$

$$^5J_t^I = k[\sin^2(\omega-\varphi)\,\sin^2\varphi + \sin^2(\omega-\varphi)\sin^2\varphi] = k2\sin^2(\omega-\varphi)\,\sin^2\varphi$$

$$^5J_t^{II} = k[\sin^2(\omega-\varphi')\,\sin^2\varphi' + \sin^2(\omega-\varphi')\sin^2\varphi'] = k2\sin^2(\omega-\varphi')\sin^2\varphi' = k2\sin^2(\varphi)\,\sin^2(\omega-\varphi)$$

where $\varphi = \omega - \varphi'$ from inspection of Fig. 1.

If X is the fraction of molecules having conformation II and 1-X is the fraction of molecules having conformation I and if the two conformations are rapidly interchanging then:

$$^5J_c^{avg} = (1-X)J_c^I + XJ_c^{II} = (1-X)\,2k(\sin^2\varphi)^2 + X2k\,[\sin^2(\omega-\varphi)]^2$$

$$^5J_t^{avg} = (1-X)J_t^I + XJ_t^{II} = (1-X)\,2k\sin^2(\omega-\varphi)\,\sin^2\varphi + X2K\,\sin^2(\omega-\varphi)\,\sin^2\varphi$$

$$\frac{^5J_c}{^5J_t} = \frac{(1-X)\,(\sin^2\varphi) + X\,\sin^2(\omega-\varphi)^2}{\sin^2(\omega-\varphi)\,\sin^2\varphi} \qquad \text{Eq. 2}$$

This equation reduces to equation 1 when X = 0.5, i.e., when the two conformations are of equal energy as in unsubstituted 1,4-dihydrobenzene. When the substituent R is other than H, it is reasonable to expect that one conformation will be energetically preferred. In this case, equation 2 predicts (1) J_c/J_t can be either greater than or less than 1 depending on φ and X; (2) for all values of X, $J_c/J_t = 1$ for $\varphi = 60^\circ$ and (3) for $X \neq 0.5$ there is an additional angle at which $J_c/J_t = 1.0$. A plot of equation 2 for X = 0.0, 0.1 and 0.5 is given in figure 2.

The fact that J_c/J_t can be 1 for an angle other than 60° would explain the anomalous results reported for 1,4-dihydronaphthoic acid[2] (III). Reported coupling constants were $J_{14} = J_{14'} = 3.93$ Hz, $J_{34} = 4.60$ Hz and $J_{34'} = 2.44$ Hz. The difference in vicinal coupling constants J_{34} and $J_{34'}$ requires a nonplanar ring while the insertion of the dihomoallylic coupling constants into equation 1 predicts a planar ring. On the other hand, equation 2 allows for $J_{14} = J_{14'}$ in a nonplanar structure.

Of course, no information about φ can be obtained until X has been determined. We are presently attempting a variable temperature study of our system in hopes of shedding some light on the conformational population. We hope to report our findings in the near future.

Please credit this contribution to the Standard Oil of Indiana subscription which is in the name of B. E. Wenzel.

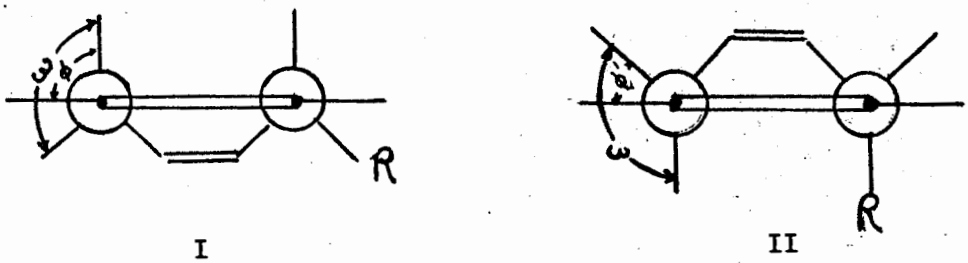
Sincerely,

Joe Ray

G. J. Ray

GJR/ch

1) E. W. Garbisch, Jr. and M. G. Griffith, J. Am. Chem. Soc., 90, 3590 (1968).
2) J. L. Marshall and T. K. Folsom, J. Org. Chem., 36, 2011 (1971).
3) M. Karplus, J. Chem. Phys., 33, 1842 (1960).



I II

Fig. 1

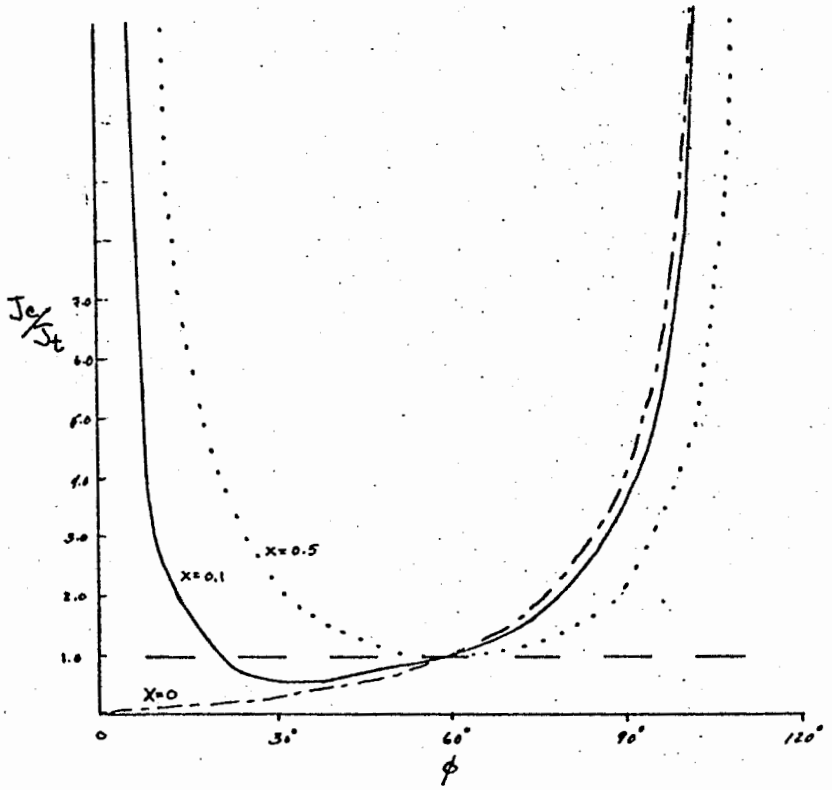
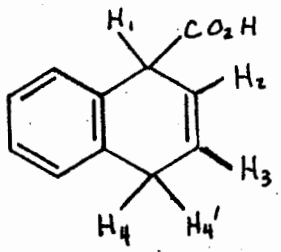


Fig. 2



III

Fig. 3

varian/new york area office
analytical instrument division
#25 route 22/springfield/new jersey 07081
telephone (201) 376-6620

April 5, 1972

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

Dear Barry:

Installation of our Springfield application laboratory XL-100-15 is complete and running smoothly. During the installation, Charley Peters and I were doing some homonuclear proton decoupling in cw mode and of course we asked ourselves why couldn't we do the same in ft mode.

Ordinarily, homonuclear decoupling is performed in the XL-100 by mixing the observing and decoupling fields in the console prior to going to the probe. Naturally, in ft mode the fields are only present at the sample during the pulse. Consequently, no decoupling is possible. However, we got around this problem by pushing the hetero button on the gyrocode decoupler, selecting the same gyrocode matrix elements, and using the decoupling matching network appropriate for decoupling ^{1}H or ^{19}F while observing ^{19}F or ^{1}H. The tuning capacitors on the matching network are tuned for maximum leakage after nulling the insert with the box connected.

Enclosed is a copy of the first experiments performed. The nice feature about this is that it can be done on a completely standard XL-100-Ft Spectrometer without modification. Obvious applications are, in addition to homonuclear decoupling, solvent (e.g. H_2O in biochemical solutions) saturation to remove any dynamic range problem, cleaner spectral presentation, and the speed of ft operation over cw operation.

Sincerely,

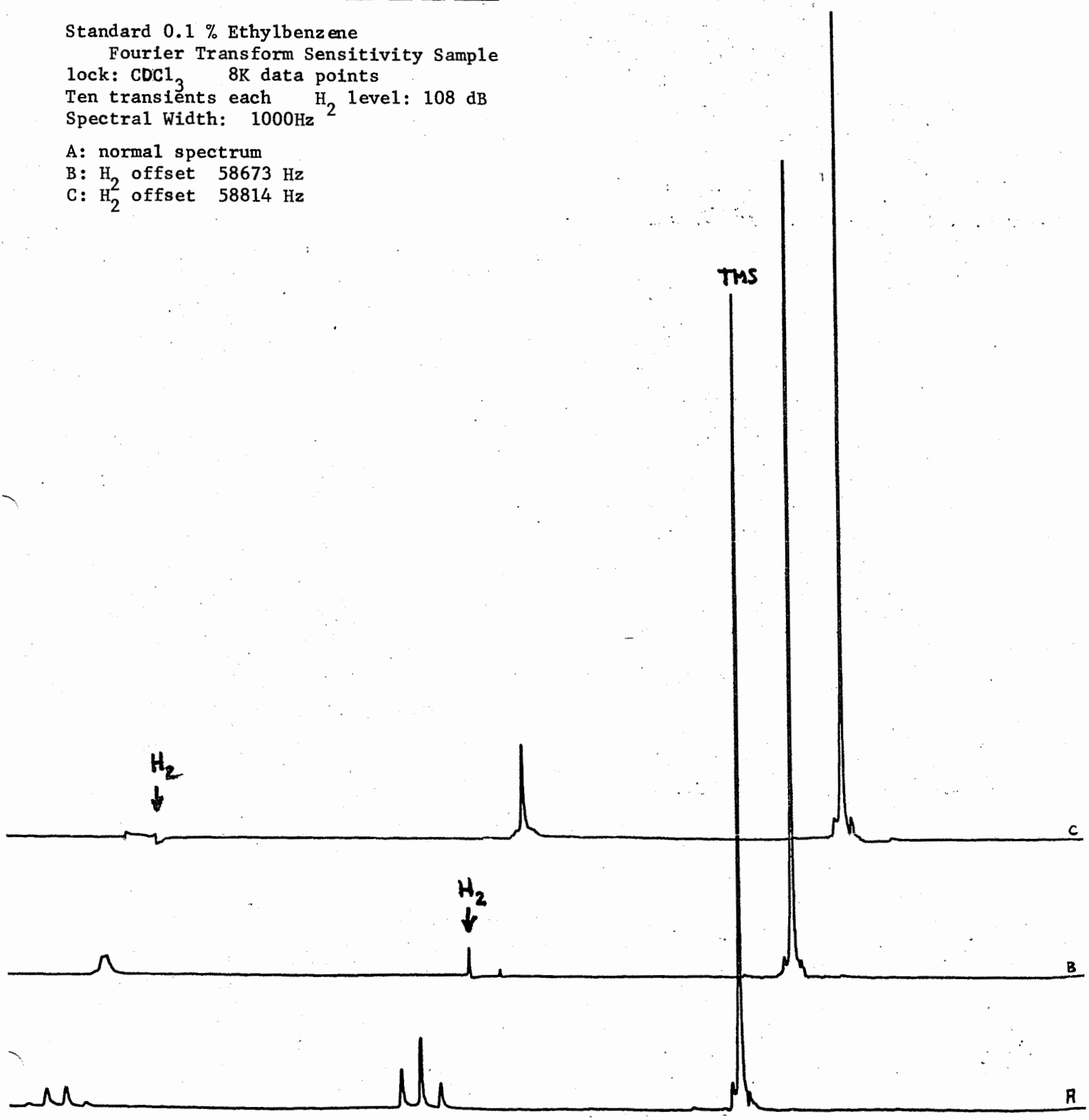
George Gray
Sr. Applications Chemist

im
Enc.

Homonuclear Proton Decoupling in FT Mode

Standard 0.1 % Ethylbenzene
Fourier Transform Sensitivity Sample
lock: $CDCl_3$ 8K data points
Ten transients each H_2 level: 108 dB
Spectral Width: 1000Hz

A: normal spectrum
B: H_2 offset 58673 Hz
C: H_2 offset 58814 Hz



NICOLET INSTRUMENT CORPORATION
5225 Verona Road, Madison, Wisconsin 53711
Phone: 608/271-3333 TWX: 910-286-2713
(formerly Fabri-Tek Instruments, Inc.)

April 6, 1972

Dr. B. L. Shapiro
TAMUNMR Newsletter
College of Science
Texas A & M University
College Station, Texas 72843

Dear Barry:

"Oscillating Baselines in FT-NMR"

We have been investigating the cause and cure for the sinusoidal baseline that occurs occasionally in the Fourier transform nmr experiment. This seems to occur when a high powered pulse is used followed by a delay insufficient to minimize pulse feed-through appears as a spike in the free induction decay, introducing an impulse in what ought to be purely a collection of sine waves.

The transform of such an impulse function is a sine wave, which is then combined with the frequency domain spectrum. While we recommend slowly adjusting the delay time in small increments until the feed-through disappears, we report here a simple method of removing the feed-through from a spectrum in which the delay time was for some reason too short.

There are several mathematical "windows" which may be applied to the free induction decay to get rid of this feed-through spike, but the one we have found easiest to use and implement is the linear trapezoidal-type apodization function. Figure 1 shows the unmodified free induction decay, and Figure 2 its Fourier transform. Figure 3 shows the trapezoidal window used, where points 1 - 50 are multiplied by the diagonal line such that the first data point is multiplied by 1/50, the second by 2/50 and so forth up to point 50 which is multiplied by 50/50 or 1.00. Figure 4 shows the apodized FID.

In Figure 5, we show the Fourier transform of this FID, clearly showing the improvement available by this simple process. Finally, in Figures 6 and 7, 100 addresses are apodized. This last spectrum clearly has an extremely flat baseline. It also indicates something of the cost the spectroscopist may pay for this scheme since as this window is extended it distorts the line shape so that the peaks each appear to have

a "moat" around them. While it may be possible to bridge this moat with a more complex apodization function, the mathematical dragons occupying it have persuaded us to prefer this simpler approach.

We wish to thank Dr. Chris Tanzer of Bruker Scientific for providing us with the free induction decay spectra.

Regards,

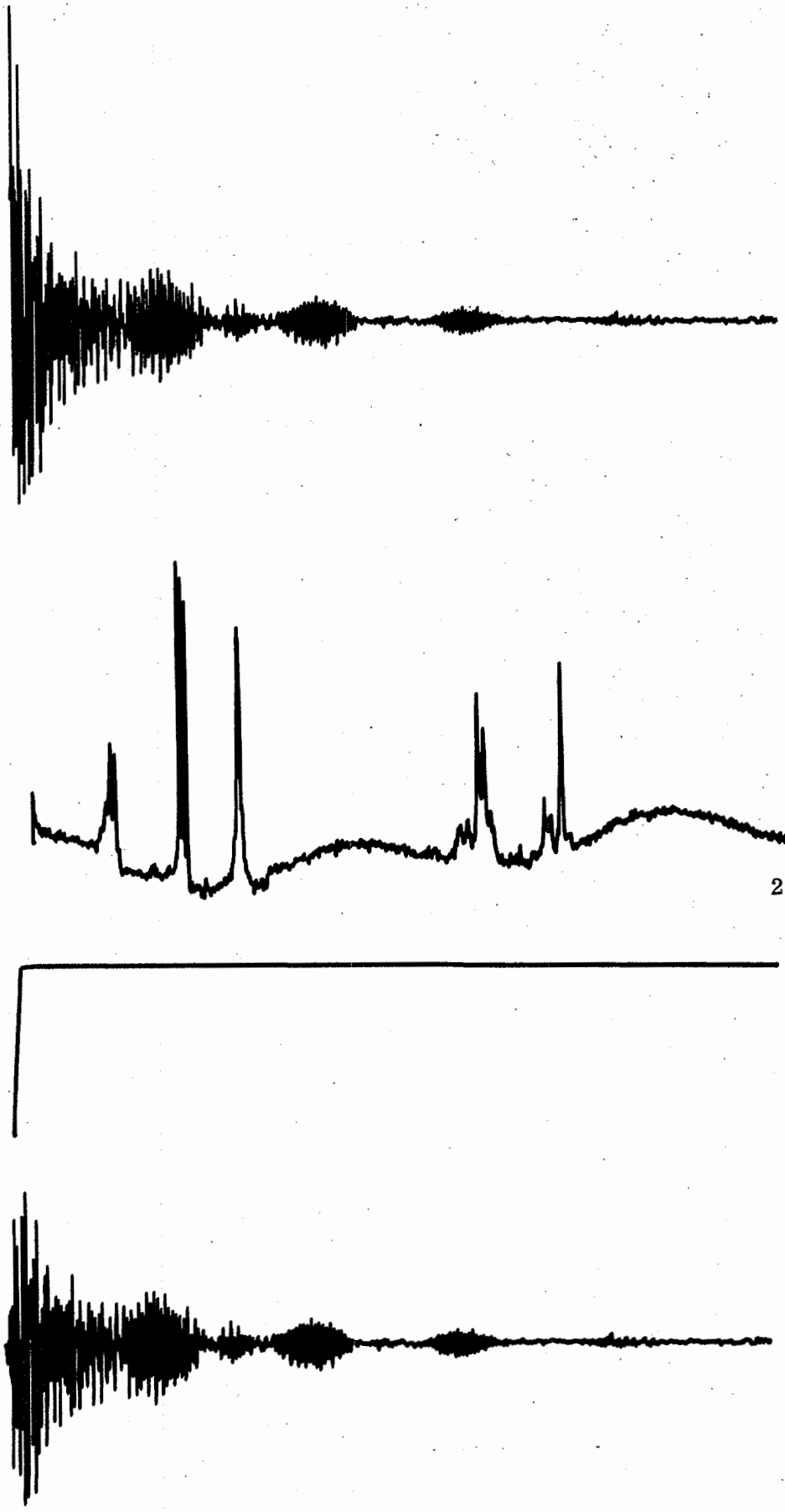
Jim Cooper

James W. Cooper

Bob Addleman

Robert E. Addleman

re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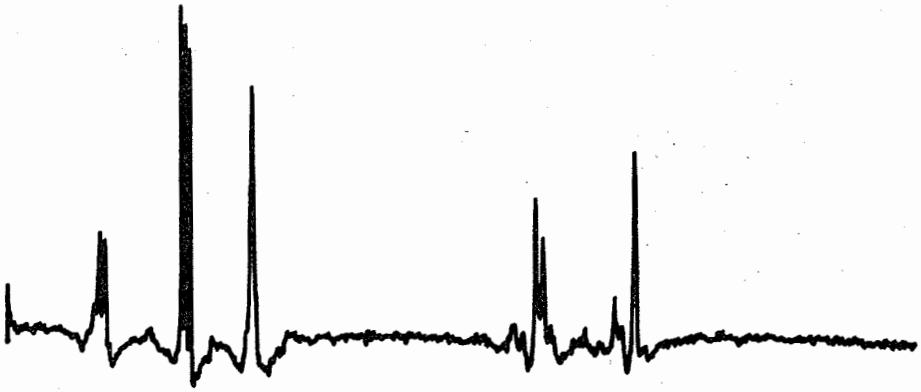

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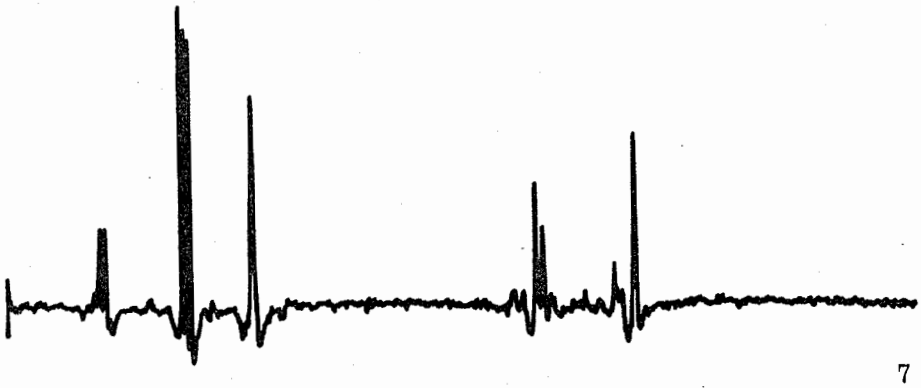

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CALIFORNIA STATE COLLEGE AT LONG BEACH
90801

DEPARTMENT OF CHEMISTRY

April 6, 1972

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

Dear Professor Shapiro,

Magnetic non-equivalence in an ortho ester.

The spectrum shown reveals non-equivalence of the methylene protons of triethyl - 1 - bromoorthopropionate and since the compound gives a very similar spectrum at 130° in 1,1,2,2-tetrachloroethane (TCE) it seems reasonable to conclude that the non-equivalence is intrinsic to the molecule. This is interesting in view of the separation of the methylene protons from the asymmetric centre.

Decoupling on the methyl protons ($-OCH_2\underline{CH_3}$) at ambient in CCl_4 causes collapse of the methylene multiplet to an AB quartet from which one may deduce, $\Delta\nu_{AB}$ = 11.7, J_{AB} = 9.0 and J_{HH} = 6.9 Hz. From the peak heights of the AB quartet, $i_2/i_1 = i_3/i_4$ = 4.6 (calc. 4.35); peak assignments are shown in the figure. At 130° (TCE) analysis of the spectrum reveals $\Delta\nu_{AB}$ = 12.0 and J_{AB} = 7.0 Hz.

Thanks are due to Dr. D. Z. Denney (Rutgers University) and PCMU (Harwell) for nmr spectra. I trust this contribution will permit my re-instatement to the TAMUNN circle, the newsletter has been missed!

Yours sincerely,

C.D. Hall.

C. D. Hall
P.G. LeGrâs P.G.L.

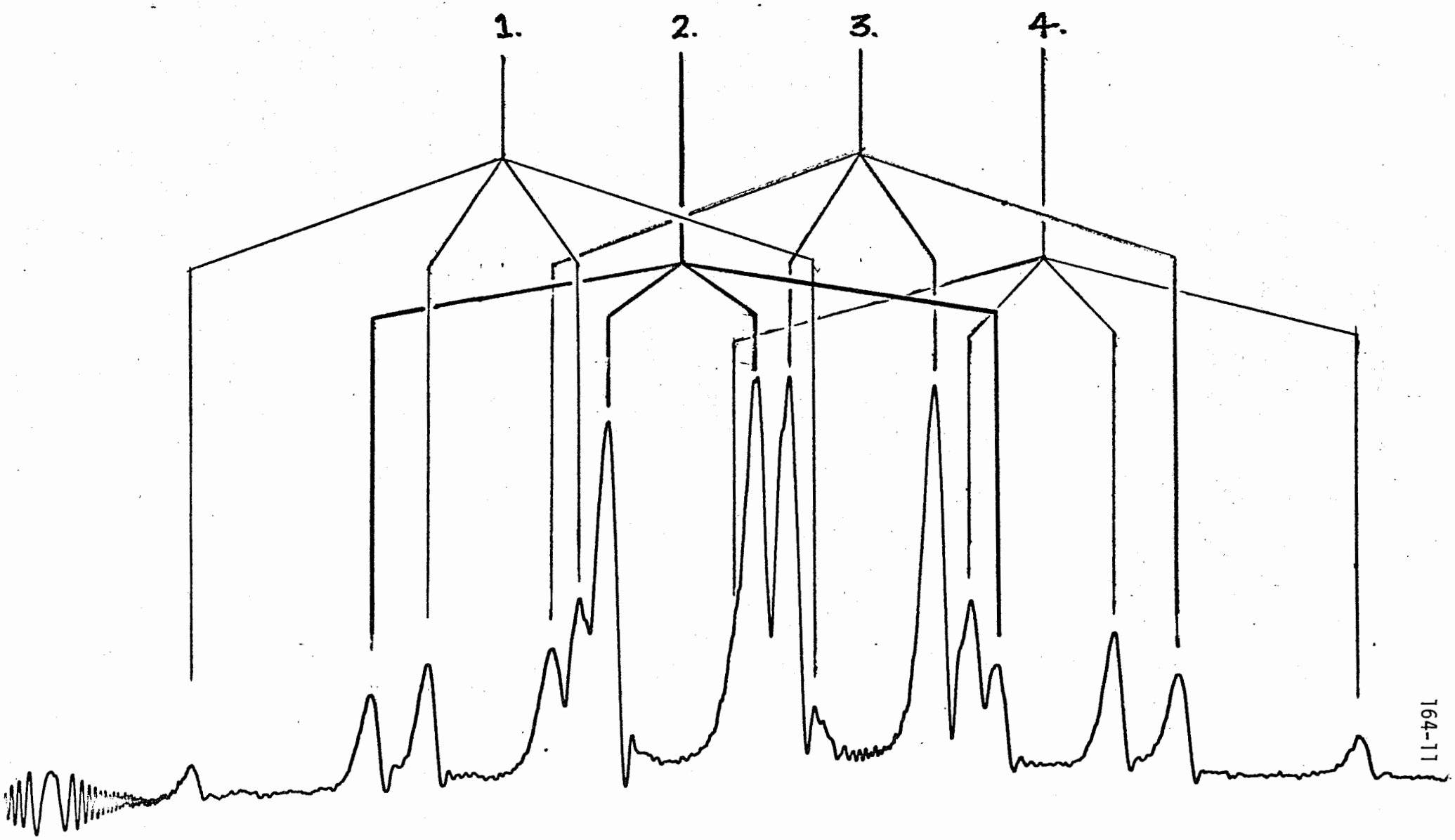
P.S. The above address is temporary until August 1972 when I return to Kings' College, London.

CDH:pl

$CH_3CHBrC(OCH_2CH_3)_3$, 100 MHz nmr in CCl_4 (ambient)

$-OC\underline{H}_2CH_3$

S.W. 100 Hz ; S.T. 250 s



Department of Chemistry

BROCK
University

St. Catharines, Ontario

Glenridge Campus
684-7201 Ext. 317

April 7, 1972.

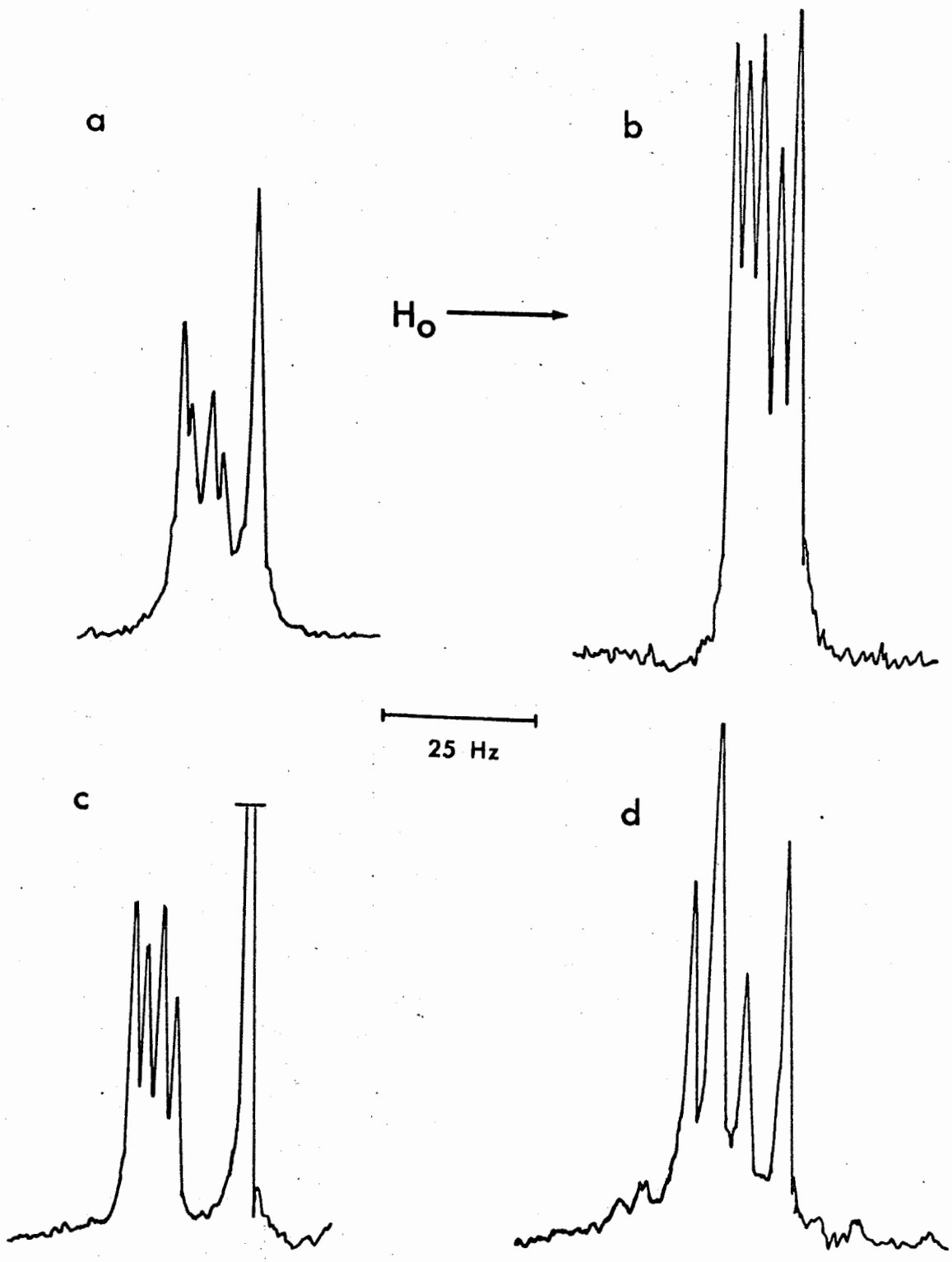
Dr. B. L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station,
Texas, 77843,
U. S. A.

Dear Dr. Shapiro:

Barriers to Rotation in Ureas: Enhancement by BF_3 Complexation

In the course of our studies of alkylurea - BF_3 adducts (1) we have observed that the very low barriers to rotation about the central C-N bonds of sym- and unsym-dialkylureas ($(RNH)_2CO$ and $R_2NC(O)NH_2$ respectively) are greatly enhanced by complexation with BF_3. A similar effect has been reported recently for the $SbCl_5$ adducts of sym-dialkylureas (2).

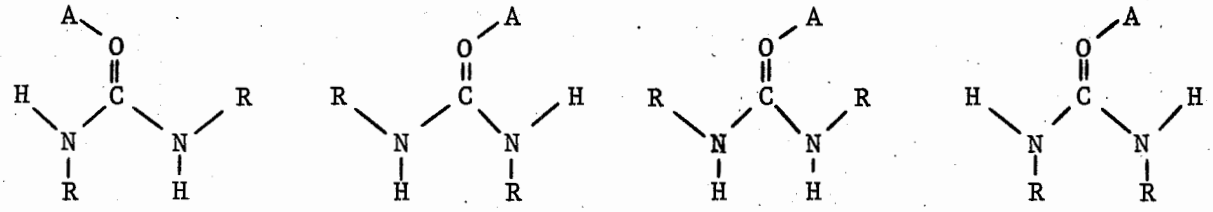
The Figure shows -20° ^1H nmr spectra of methylene chloride solutions of sym-dimethylurea and BF_3 in the ratios 1:0.50 (a and c) and 1:0.75 (b and d) at 60 MHz (a and b) and 100 MHz (c and d). Only the methyl region is shown. The peak at highest field in each of the spectra arises from the uncomplexed urea. The change in field strength identifies the two spin-spin doublets (J_{HCNH} = 5.0 Hz) which arise from the 1:1 adduct of sym-dimethylurea with BF_3. The adduct chemical shifts are somewhat concentration-dependent. As in the sym-dialkylurea-$SbCl_5$ adducts (2), the two doublets collapse to give a single spin-spin doublet at room temperature. However, unlike the $SbCl_5$ adducts, the two methyl environments have unequal intensities (39:61) at -20°. This was confirmed by the preparation of the deuterated adduct $(MeND)_2CO.BF_3$. Deuterium



-20° ^1H spectra of sym-dimethylurea - BF_3 solutions in methylene chloride

substitution collapsed the doublet splittings and gave two broadened singlets of unequal intensity which collapsed above -20°.

To account for the two equally populated alkyl environments in the $SbCl_5$ adducts, Stilbs and co-workers proposed that due to steric effects the only two conformers present are I and II, which interconvert by a concerted shift of substituents.



I II III IV

(A = $SbCl_5$ or BF_3)

Since in the BF_3 adduct there are unequally populated alkyl environments, there must be at least one additional conformation present, perhaps III or IV. Since only two alkyl resonances are detected, some of the conformational differences which must exist do not give rise to distinguishable nmr signals.

By analogy with amides (3) we expect separate signals for methyls cis and trans to the carbonyl oxygen if there is slow rotation about the central C-N bonds. Separate signals due to cis-trans orientation of a Lewis acid about a carbonyl group have been detected only at very low temperatures (4) and are not likely to be observed at -20°. Thus the enequal intensities of the methyl signals probably arise from differing populations of methyls cis and trans to the carbonyl group, as in amides. $SbCl_5$ has greater steric requirements than BF_3, so we would expect differences in conformer populations between the BF_3 and $SbCl_5$ adducts.

Unsym-dimethylurea.BF_3 gives two methyl resonances of equal intensity at -20°, confirming that the methyls cis and trans to the carbonyl give rise to the separate signals. The diethylureas give

similar results. The sym adduct shows two unequally populated ethyl environments while the unsym adduct shows two equally populated ethyl environments.

Yours sincerely,

Steve Hartman

J. S. Hartman, G. J. Schrobilgen.

JSH:hk

(1) J. S. Hartman and G. J. Schrobilgen, Can. J. Chem. in press; TAMU - NMR #144-29.

(2) G. Olofsson, P. Stilbs, T. Drakensberg and S. Forsen, Tetrahedron, 27, 4583 (1971).

(3) W. E. Stewart and T. H. Siddall, III, Chem. Rev., 70, 517 (1970).

(4) U. Henriksson and S. Forsen, Chem. Comm., 1229 (1970).

164-16

MRC
Medical Research Council

MRC Molecular Pharmacology Unit
Medical School, Hills Road
Cambridge CB2 3EF

telephone Cambridge 45171

reference

11th April, 1972

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

Dear Barry,

Elimination of Solvent Bands in Proton Fourier Transform Spectra

In company with several other groups of workers we have been worrying about the problem of coping with large solvent bands when recording proton Fourier transform spectra. By virtue of the differences in T_1 relaxation times between the solvent and solute molecules it is often possible to discriminate against the solvent signals (1,2). Using the Varian inversion-recovery T_1 routine as supplied with the XL 100 $(\pi - t - \pi/2 - T)_n$ one can adjust the values of t and T to arrange for the M_z magnetisation of the solvent nuclei to be zero and the solute magnetisation to be positive immediately preceding the $\pi/2$ observing pulse and this effectively eliminates the solvent signal. Immediately following the π pulse we apply a homogeneity spoiling pulse (3). The values of t and T for solvent elimination in a multiple pulse experiment can be calculated from the relationship (2),

$$\exp\left\{-\left(T_1(\text{solvent})\ 1n2 + T\right)/T_1(\text{solvent})\right\} + \exp\left\{-\left(T_1(\text{solvent})\ 1n2 - t\right)/T_1(\text{solvent})\right\} = 1$$

This equation holds after the first cycle of pulses when a steady state is established. To use this method without modification of the Varian software the first few pulse sequences must be suppressed by using a minimum spectrum amplitude setting after which it is adjusted to the appropriate level.

In practical terms the solvent T_1 value is first determined and then for a chosen value of T the corresponding t value can be calculated. Using this approach we have obtained excellent proton Fourier transform spectra for proteins and small molecules at concentrations as low as 10^{-4}M in aqueous solution (see Figure). For the purpose of comparison we also show in the Figure the spectrum of Ribonuclease A obtained with a steady state pulse sequence of $(\pi/2 - T)_n$. One obvious advantage of the inversion recovery method of eliminating the solvent signal is that spectral information from signals in close proximity to the solvent band is retained. The values of t and T require less critical adjustment when the solvent has a long T_1 value.

Best wishes,

Fred Benz Jim Feeney Gordon Roberts

F. W. Benz, J. Feeney, G. C. K. Roberts

REFERENCES

1. S. L. Patt and B. D. Sykes, J.Chem.Phys. 56 - 3182 - 72.
2. F. W. Benz, J. Feeney and G. C. K. Roberts, J.Magnetic Resonance, In Press.
3. This is a field gradient pulse applied to the shim coils which requires the Varian millisecond T_1 program and hardware modification.

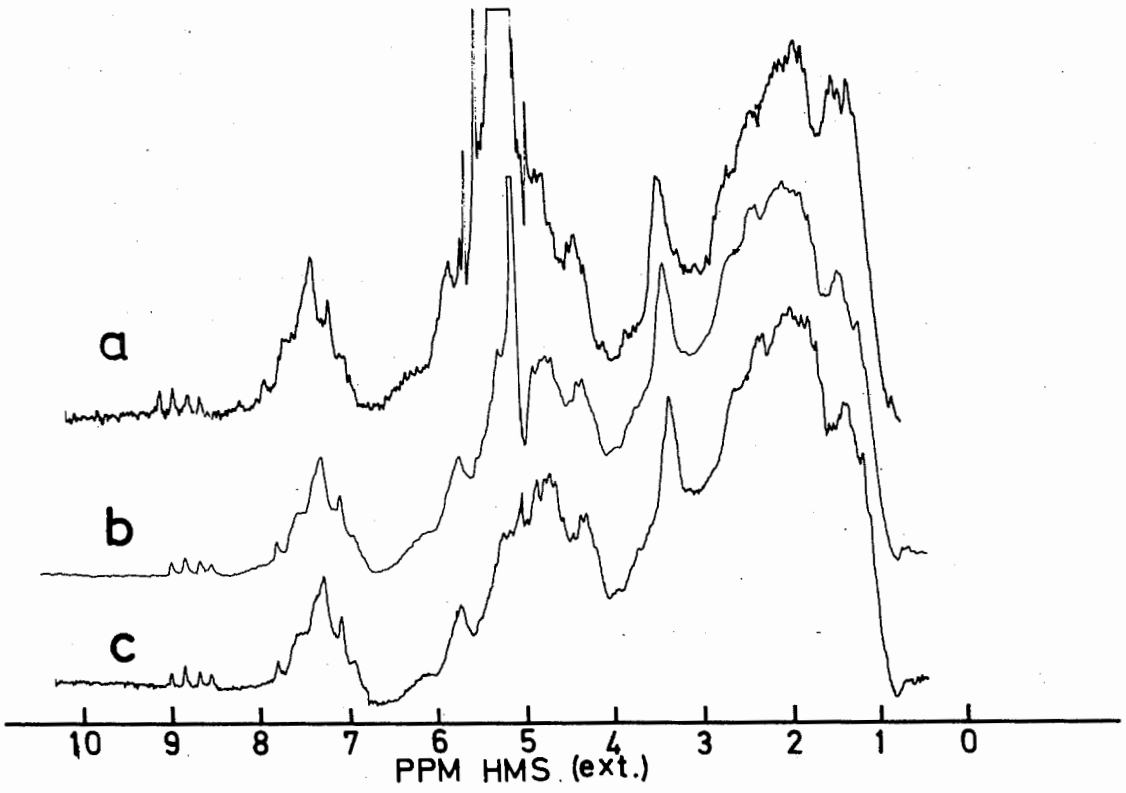
Figure

Proton NMR spectra at 100 MHz of ribonuclease A (2×10^{-3}M) in 0.2M deuteroacetate buffer pH 5.5.

(a) Continuous wave spectrum: Sweep width 1000 Hz; Sweep time 250 sec.

(b) Steady state sequence: $(\pi/2 - T)_n$ Spectral width 1000 Hz; T = 1.00 sec; sensitivity enhancement time constant 0.5 sec; 250 transients.

(c) Inversion recovery sequence: $(\pi -$ HSP $-t- \pi/2 - T)_n$ Spectral width 1000 Hz; T = 1.40 sec; t = 1.200 sec; 250 transients. HSP = Homogeneity spoiling pulse.



Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

BUENOS AIRES, April 10, 1972.-

Prof. Bernard L. Shapiro
Texas A & M. University
College Station, Texas 77843
USA

Title: Poor Man's Spectrum Plotter

Dear Dr. Shapiro:

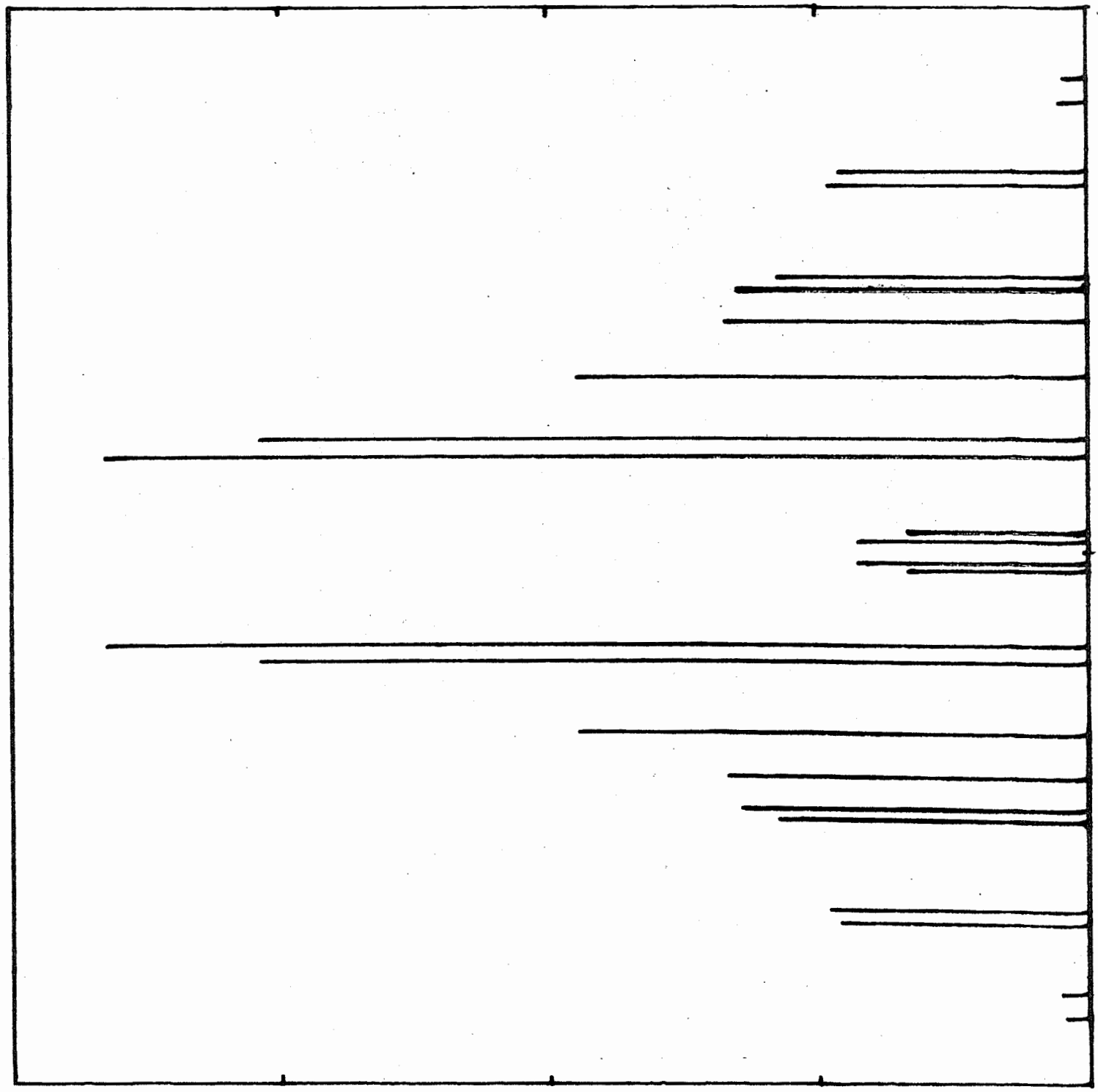
Due to a major break down, we have been left for some time without our lorenzian line spectrum plotter. Since quite often just a stick plot is enough, we have thought of a way to aleviate the task of spectrum plotting. The result is the circuit included, which can be used if a spare X-Y plotter is available.

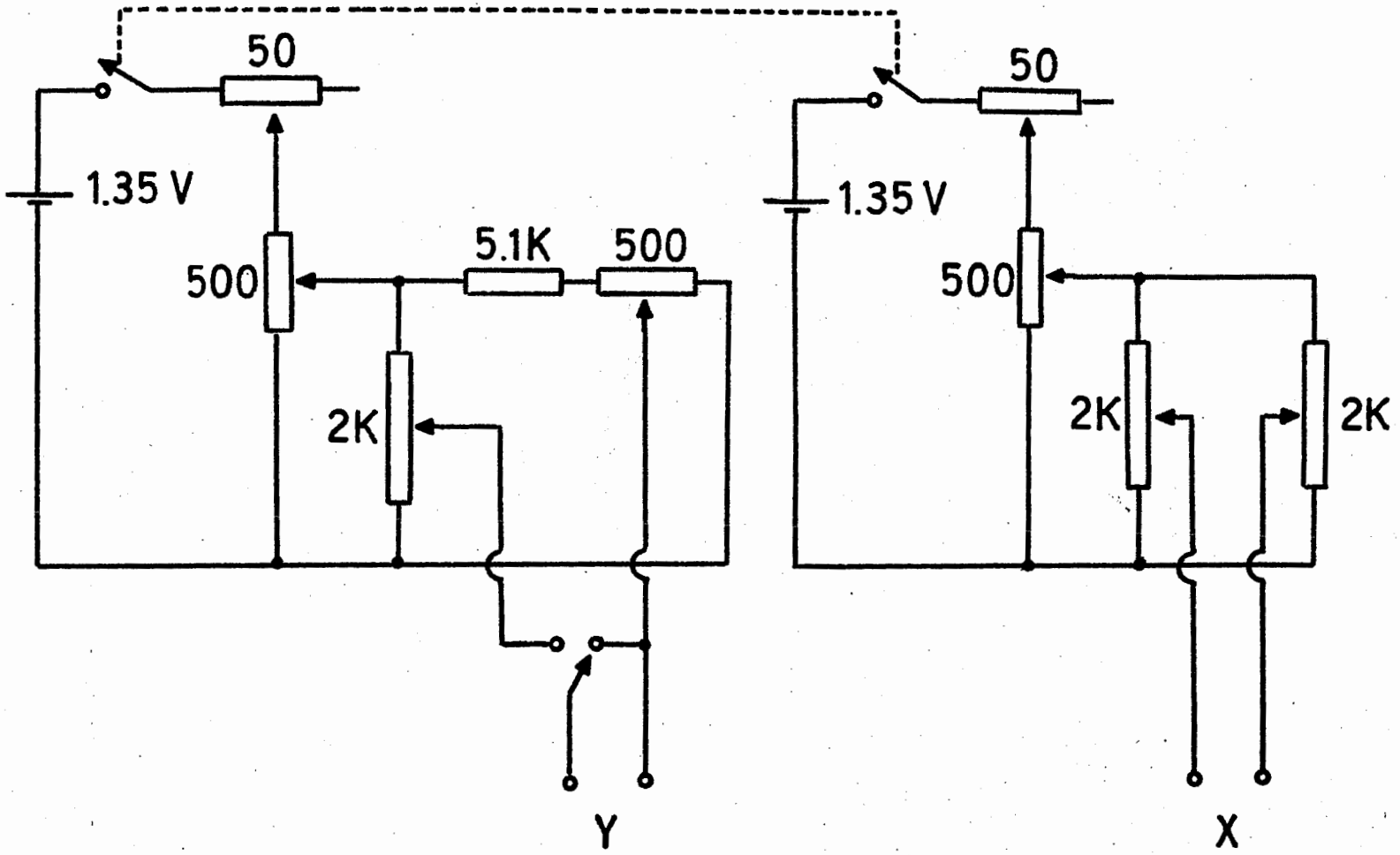
The results obtained can be appreciated in the graph, which is a plot of a classical A_2B_2 spectrum (o-dichloro-bencene).

In truth, we cannot claim much originality, since there are some similar commercial devices, of the push-button type. We use ten turn, big size Helipot dials which I have never seen used for this purpose. Besides, ours is a lot cheaper.

Yours sincerely,

Dr. V.J. Kowalewski
Professor

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1.35 V
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Koninklijke/Shell-Laboratorium, Amsterdam
-Handelsregister Amsterdam no. 111841-
(Shell Research N.V., gevestigd te 's-Gravenhage)

Telegramadres:
Konshellab-Amsterdam
Rechtstreeks (020)
Via telefoniste (020) 209111

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

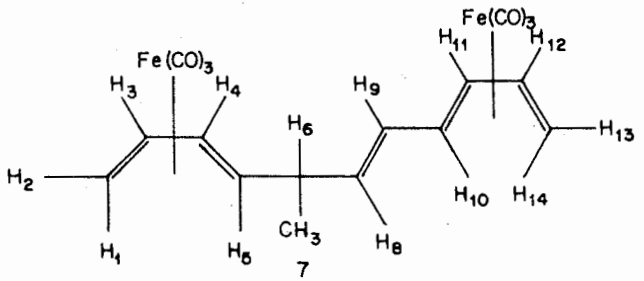
Referentie: Brief no.:

Amsterdam-N., 21st April 1972
Badhuisweg 3
Postbus 3003

Dear Professor Shapiro,

Structure determination of a polyene iron carbonyl complex with the aid of ^{13}C NMR and 220 MHz double-resonance experiments

During the investigation of iron carbonyl complexes we obtained an interesting product which high-resolution mass spectrometry showed to have the molecular formula $C_{12}H_{16}Fe_2(CO)_6$. Structure determination by means of PMR and CMR revealed that the product consists of two diastereomers of syn, syn-5-methylundeca-1,3,6,8,10-pentaene-1,3,8,10-diiron hexacarbonyl.



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The presence of the $Fe(CO)_3$ groups complexed to the terminal diene moieties is confirmed by: (1) the presence of two high-field triplets (163 ppm relative to $^{13}CS_2$) in the proton-coupled ^{13}C spectrum, and (2) the presence of two high-field proton absorptions at 0.28 and 0.47 ppm, whose positions and multiplicities are characteristic of protons in the anti position of terminal methylene groups in dienyl iron complexes. The arrangement of the four carbons linking the two dienyl iron groups, including the position of the CH_3 group, may be deduced from the 220 MH_3 spectrum and the results of the double-resonance experiments. For example, the two absorptions at 5.38 and 5.58 ppm are typical of protons attached to a trans substituted double bond (J = 15 Hz). The absence of absorptions between 1.95 and 5.15 ppm indicates that the carbons linking the two diene systems are attached in a syn manner. Anti substitution would require that protons 5 and 10 should absorb in the region between 2.5 and 3.0 ppm.

Koninklijke/Shell-Laboratorium, Amsterdam

d.d.

The presence of diastereomers is indicated by doubling of the absorptions of the two carbons, $\geq$CH-CH$_3$ and also of the protons 6, 7 and 8. The relative intensities within these doubled absorptions depend on the degree of separation achieved by chromatography.

The chemical shifts and coupling constants are presented in the attached table. The double-resonance experiments were carried out in the field sweep mode. We are very grateful to Ir. P.E.J. Verwiel of the Central Laboratory, TNO, Delft, who performed these experiments.

Please, credit this contribution to Dr. R. Prins.

Yours sincerely,

A.D.H. Clague (A.D.H. Clague)

M. Anderson (M. Anderson)

P.A. Couperus (P.A. Couperus)

PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS

Shift, ppm	Assignment	Coupling constants, Hz
0.28	1	$J_{1,3}$ = 9.0 $J_{1,2}$ = 2.0
0.47	14	$J_{12,14}$ = 9.0 $J_{13,14}$ = 2.5
0.82	5	$J_{4,5}$ =, $J_{5,6}$ = 9.0
1.12	7	$J_{6,7}$ = 6.5
1.75	2, 10, 13	
1.95	6	$J_{5,6}$ = 9.0 $J_{6,7}$ = 6.5 $J_{6,8}$ = 7.0
5.14	3, 4, 12	
5.24	11	$J_{10,11}$ = 8.5 $J_{11,12}$ = 5.0
5.38	9	$J_{8,9}$ = 15.0 $J_{9,10}$ = 9.5
5.58	8	$J_{8,9}$ = 15.0 $J_{6,8}$ = 7.0

THE UNIVERSITY OF LEEDS

KDB/HS

School of Chemistry
Leeds
LS2 9JT
Telephone 31751

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

7th April, 1972.

Dear Professor Shapiro,

P.m.r. of Polychlorobiphenyls

Since leaving Bradford University I have been an occasional contributor to TAMUNMR NEWSLETTER through Dr. D.W. Jones' group. However, I should now like to establish an independent subscription by describing features of the spectra of some polychlorobiphenyls (PCBs), separated by preparative gas chromatography from a commercial mixture.

Both combination g.c.-mass spectrometry[1] and high resolution m.s. alone[2] enable the number of chlorine atoms per PCB molecule to be determined, but offer no information on the position of substitution, the preliminary to discerning the detail of the mode of PCB metabolic action[3]; 209 chlorinated biphenyls are possible.

On the other hand, p.m.r. spectra can often be interpreted to identify PCBs even if reference compounds are not available. For example, a hexachlorobiphenyl gave a very simple spectrum consisting of two 8.3_0 Hz doublets and a pair of slightly broadened singlets. The 42 structural possibilities are thus immediately reduced to two: 2,3,4,2',4', 5'- or 2,3,6,2',4',5'-. Chemical shift arguments based on biphenyl[4] and trichlorobenzenes[5], checked by application to the unambiguously assigned 2',4',5' ring, favour the 2,3,4,2',4',5'- structure.

A tetrachlorobiphenyl gave a spectrum which could be interpreted as ABC, with coupling constants, extracted with LAOCOON III, 8.4_6, 2.4_4, and 0.3_8Hz. The possible structures (again 42) reduce to 2,4,2',4'-; 2,5,2', 5'-; or 3,4,3',4'-. Chemical shifts are consistent only with 2,5,2',5'-.

The heavy degree of chlorine substitution in PCBs makes it unlikely that more than three coupled protons will be encountered, although collapsed or overlapped spectra may be observed in some cases.

Yours sincerely,

K. D. Bartle

K.D. Bartle.

1. G.E. Bagley, W.L. Reichel, and E. Cromartie, J. AOAC, 53, 251 (1970).
2. O. Hutzinger, W.D. Jamieson, and V. Zitko, Nature, 226, 664 (1970).
3. J.L. Lincer and D.B. Peakall, Nature, 228, 783 (1970).
4. A.R. Tarpley and J.H. Goldstein, J. Phys. Chem., 75, 421 (1971).
5. B. Richardson and T. Schaefer, Can. J. Chem., 46, 2195 (1968).

UNIVERSITY OF KENTUCKY

LEXINGTON. KENTUCKY 40506

April 19, 1972

COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY
TELEPHONE 606-257-4741

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

Dear Dr. Shapiro:

The usual practice in preparing to run ^{11}B NMR spectra is to initially adjust the field homogeniety controls while visually observing on the oscilloscope the peak height and symmetry of the singlet arising from a Bf_3 etherate standard.

Naturally, this procedure does not allow the attainment of resolution better than a few Hz., but for most boron containing compounds it is adequate due to the linewidths generally encountered.

However, in the event that smaller splittings are present in an unknown sample, the varification of their being present and their measurement would normally be lost with this procedure because of the relatively poor field with which the operator started.

We have found that the highly symmetrical BF_4 anion in aqueous solution exhibits linewidths of $\leq$ 0.2 Hz. and readily shows B-F coupling of 1.8 and 1.1 Hz. for the sodium and ammonium salts respectively. These couplings are, of course, solvent dependent.

The figure given shows the ^{11}B NMR spectrum of a saturated solution ($\sim$ 1.2 molar) of the sodium salt of tetrafluoroborate obtained in HR mode at a sweep rate of approximately 0.24 Hz/sec and an RF attenuation of 45 db. The signals from fresh samples are reasonably intense at these concentrations but diminish over several days with the increasing production of hydrolysis products.

As a result, we have found it convenient to store a number of sealed ampules containing 65 milligrams of sodium tetrafluoroborate so that it is only a matter of breaking open the ampule and adding 0.5 ml of water when a fresh sample is needed to set up for an occassional boron analysis.

Unfortunately, we have not been able to use the natural abundant material as a locking signal for the HA mode of operation at 60 MHz due to the relatively low RF power levels necessary to avoid saturation. However, 100 MHz instrument

owners may find that they can lock onto this multiplet for field-lock operation either with the naturally occurring ~80% ^{11}B species or with further enrichment.

Sincerely,

Claude Dungan Stan

Claude H. Dungan
Stanford L. Smith

^{11}B NMR Spectrum of a 1.2 molar solution of Sodium Tetrafluoroborate in water obtained at 19.3 MC at a sweep rate of 0.24 Hz./sec and an R. F. attenuation of 45 db. J_{BF}=1.8 Hz.

UNIVERSITY OF FLORIDA
GAINESVILLE

DEPARTMENT OF CHEMISTRY

April 24, 1972

Dear Barry:

Subject: Spin-Spin Coupling in Fluoropropanes

We have been interested for some time in conformational effects in fluorocarbons. Looking back over data for temperature dependence accumulated on a variety of materials, it is possible to develop a self-consistent picture of the behavior of the F-F coupling constants. In general, if there is no conformational change, one finds the value of the three-bond or vicinal coupling diminishing slightly with increasing temperature, with a change of the order of several tenths hertz over 100° change. In the molecule $CFCl_2CFCFCl_2$, for example, the vicinal coupling is found to be independent of temperature and we assert with some confidence that this is the result of two opposing effects, a change in the conformational equilibrium offsetting the usual decrease in J with increasing temperature.

The vicinal couplings seem almost always to be larger for the gauche relation of the two fluorine atoms than for the trans relation, but the difference clearly diminishes as the electronegativity of the substituents becomes smaller; thus as each of the two values becomes larger, they approach one another. For the molecule $CFCl_2CFClCCl_3$, it appears that the trans value is larger than the gauche, for the coupling constant increases from 14 Hz at +100° to 17 Hz at -100°; these values, indeed, are rather large. The generalization, to which this molecule provides the exception , is merely an extension to propanes of trends found earlier for fluoroethanes by several other workers.

It appears clear that the four-bond couplings between fluorines become larger when the two atoms involved approach one another, whatever the mechanism of transmission of the coupling information may be. Rather interesting data has recently been obtained in our labs by Bill Tallon, for the molecule $CFCl_2CF_2CFClBr$, in which all four fluorines have distinct chemical shifts. The numbers are shown in the table. J_{13} and J_{14} nicely approach one another as the temperature rises, as do J_{23} and J_{24}. If the larger value is assigned to the gauche fluorine pair in each combination, then F-1 is gauche to F-4, which is trans to F-2, all in the favored conformation. This puts F-1 and F-2 on "opposite sides" of the molecule in the preferred conformation. It is reasonable that steric requirements are best satisfied by placing each fluorine atom in opposition to a halogen at the other end of the molecule. As a result, the two fluorines do not approach one another very closely at low temperatures, but display a steadily rising coupling constant as conformational averaging increases with rising temperature.

Fluorine-fluorine coupling constants (acetone (solution) for:

$$CFCl_2\text{--}CF_2\text{--}CFClBr$$
$$1 \quad 3,4 \quad 2$$

Temp., °C	J_{13}	J_{14}	J_{23}	J_{24}	J_{12}
+32	-4.52	-7.83	-10.70	-7.07	8.61
+4.5	-4.44	-8.08	-10.98	-7.09	7.80
-7.5	-4.29	-8.41	-11.11	-7.06	7.40
-44	-3.63	-9.00	-11.64	-6.80	5.92
-68	-2.94	-9.69	-12.19	-6.42	4.82

Sincerely yours,

Wallace

Wallace S. Brey, Jr.

LAWRENCE LIVERMORE LABORATORY

April 24, 1972

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

Dear Professor Shapiro:

^{35}Cl NMR and Mn (II) Nucleotide Triphosphate Chelates

For some time now we have been using the halide ion probe NMR method to study Zn (II) binding to both macromolecules and to smaller chelating molecules such as nucleotide di-and triphosphates and amino acids. Recently we have made some measurements on Mn (II) - nucleotide triphosphate chelates and we include some of the results in Figure 1. In 0.5 M NaCl solutions, Mn (II) is more than two orders of magnitude more effective in ^{35}Cl relaxation than is Zn (II). The formation of Mn (II) NTP chelates could for this reason be studied at the sub-millimolar concentration level.

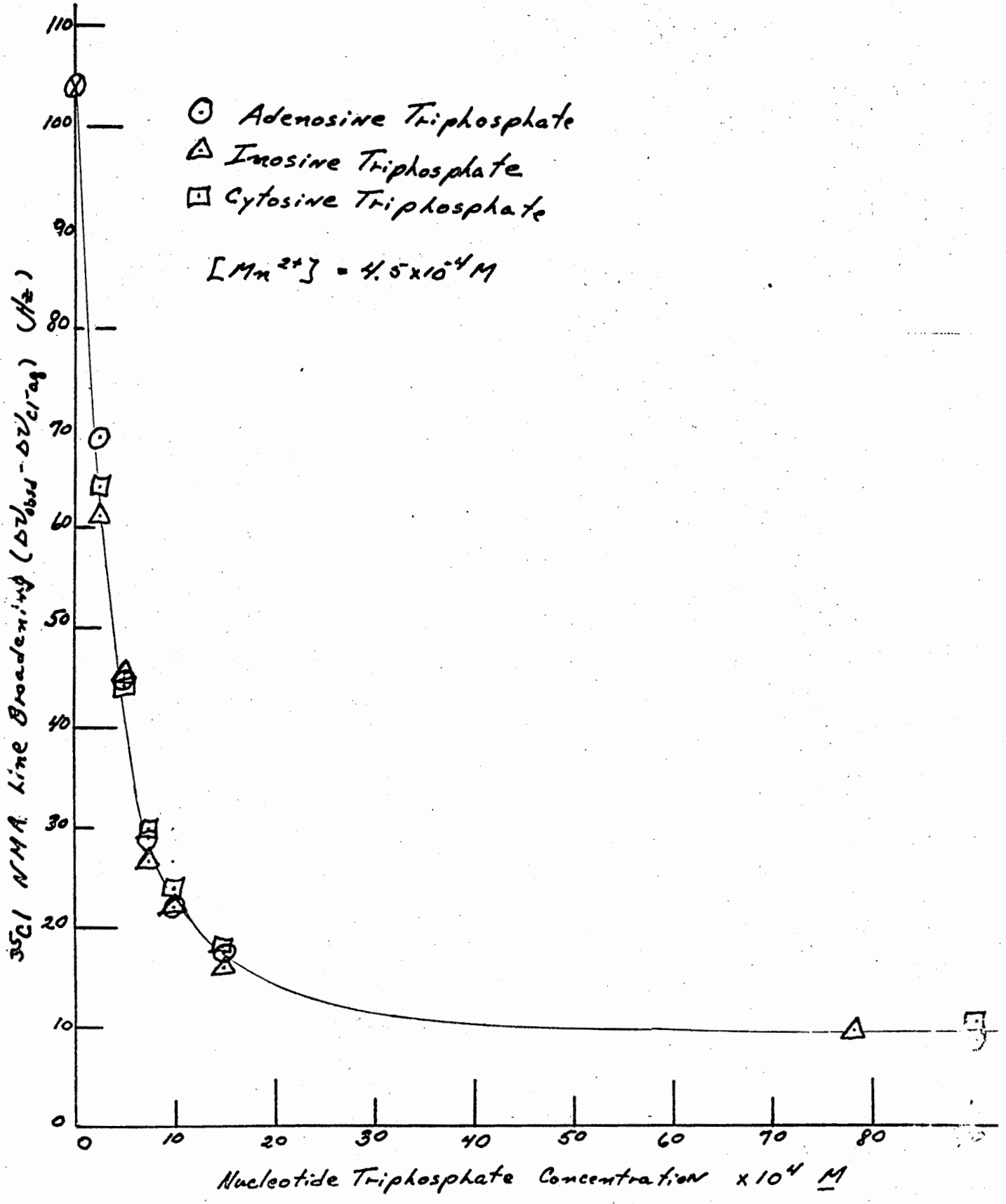
In the Figure we show titrations of $Mn^{2+}(aq)$ with three different nucleotide triphosphates. The Mn (II) concentration was held fixed at 4.5×10^{-4} M and the pH was 7.0. When the nucleotides are added, the $Mn^{2+}(aq)$ is chelated and the ^{35}Cl NMR line sharpens. The reason appears to be that Cl^- is less likely to form a Mn (II)—Cl^- bond when the Mn (II) is chelated. There is a rapid initial decrease in line broadening but a large excess of the nucleotides is necessary to chelate essentially all of the Mn (II). The remaining line broadening is that which the Mn (NTP) chelates can produce. As near as we can tell each of the Mn (II) NTP chelates produces the same ^{35}Cl relaxation. The structural implications of these observations are difficult to assess. It seems probable though that each of the chelates binds Cl^- equally-there being no dependance on the nucleotide base structure.

Sincerely,

James A. Happe

James Happe
Bert Holder (subscription credit)
Al Maddux
Raymond Ward

Figure 1. The effect of Mn (II) nucleotide triphosphate chelate formation on ^{35}Cl nmr line broadening by 4.5×10^{-4} M Mn (II) in a 0.5 M NaCl solution.



UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *Urbana, Illinois 61801*

School of Chemical Sciences

April 26, 1972

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

Dear Barry:

Re: The Use of Shift Reagents in Studies of Chemical Exchange

We've been doing some experiments on the use of shift reagents to study chemical exchange, which may interest some of your readers. One limitation arises from the temperature dependence of electron relaxation in the shift reagent, which becomes slower at lower temperatures. This broadens the nmr lines and can obscure the chemical exchange effects. Also, many shift reagents have poor solubility at lower temperatures and produce correspondingly smaller shifts. However, two new shift reagents, $Eu(fod)_3$ and $Pr(fod)_3$,[1] were reported recently[2] to have smaller line-broadening effects and greater solubility, so we were prompted to investigate their use in measuring the internal rotation rates of dimethylformamide (DMF), dimethylacetamide (DMA), and dimethylpropionamide (DMP).

The amides were studied as 5 mole % solutions in tetrachloroethane (TCE), to which various amounts and types of shift reagent were added. Figure 1 compares the broadening of the α-methyl p.m.r. of DMA by $Eu(fod)_3$ with that by $Eu(thd)_3$ at temperatures between 270° and 370°K.[10] For both shift reagents, the line broadening increases exponentially with 1/T at low temperatures. However, the r = 0.15 curve for $Eu(fod)_3$ is displaced about 50° below that for $Eu(thd)_3$ even though it produces shifts which are of comparable magnitude. The broadening by $Eu(fod)_3$ is quite small above 310°K, and we can neglect it in the amides because the chemical exchange broadening occurs at higher temperatures. On the other hand, the shift reagent will obscure chemical exchange effects which have a low free energy of activation $\Delta G^{\ddagger}$ and a correspondingly low coalescence temperature T_c.

Figure 2 presents the combined effects of temperature and $Eu(fod)_3$ upon the separation $\Delta\nu$ between cis and trans α-CH_3 group resonances in DMF. The reagent shifts both proton

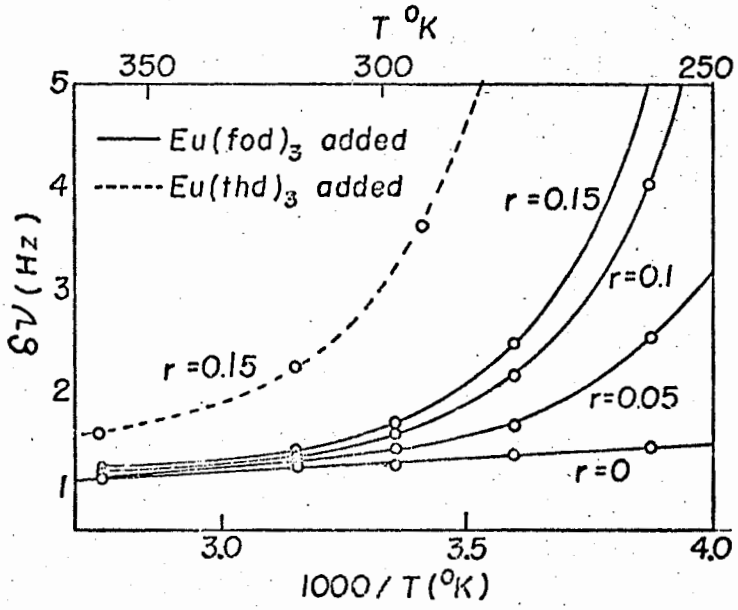


Fig. 1. Spin-exchange broadening of the α-CH_3 group p.m.r. in DMA by the chemical shift reagents Eu(fod)$_3$ and Eu(thd)$_3$ as a function of 1/T. The line width δν is the full width at half height; r is the molar ration of shift reagent to DMA in the TCE solutions.

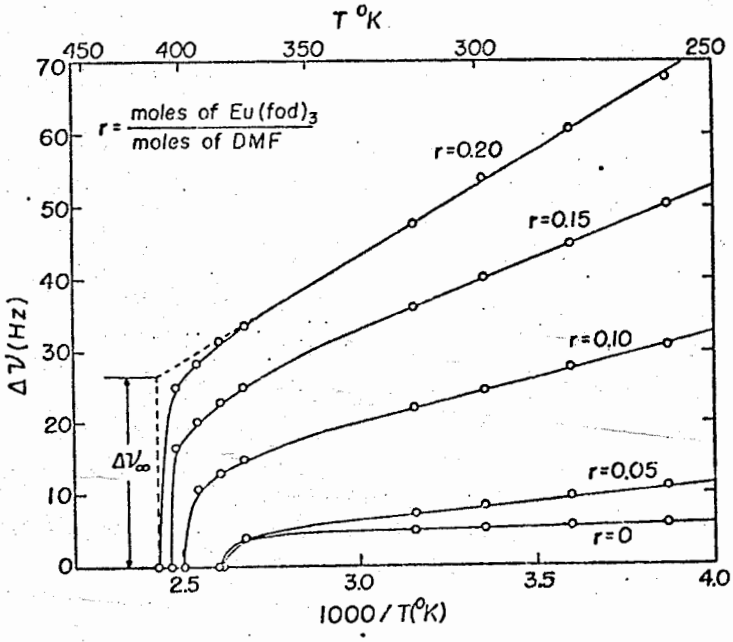


Fig. 2. The separation Δν between the p.m.r. lines of the two α-CH_3 groups in DMF at 60 MHz as a function of 1/T and the amount of shift reagent added.

lines downfield but the cis protons (upfield for r = o) experience a greater shift because of their proximity to the Eu atom in the amide - $Eu(fod)_3$ complex. This causes a reversal in the positions of the lines for $r \simeq 0.02$ but otherwise $\Delta\nu$ is linear in r at a given $T < T_c$. Also, for a given r, the dependence of $\Delta\nu$ upon 1/T is linear until the internal rotation begins to coalesce the lines. Moreover, the coalescence temperature increases with the addition of $Eu(fod)_3$ for $r > 0.04$ because of its effect upon $\Delta\nu_\infty$, the effective shift in the absence of chemical exchange.

The chemical exchange broadening is most sensitive to the exchange rate at T_c, for which $k_c = \pi\Delta\nu_\infty/\sqrt{2}$. Therefore we elected to determine T_c and $\Delta\nu_\infty$ as a function of r. Typical results for $\Delta\nu_\infty$ from the line-width at T_c are given in Table I along with the values of $\Delta G^\ddagger$ calculated from k_c via the Eyring equation.[4] The results are consistent with earlier work, except that $\Delta G^\ddagger$ appears to increase slightly with increasing T_c, especially for the DMF - $Eu(fod)_3$ solutions which cover a range in T_c of more than 50°.[4] This increase might be attributed to the association of the amide with the shift reagent.

Another possibility is that at least part of the increase is due to the temperature-dependent entropy term in $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. There is evidence that $\Delta S^\ddagger$ for internal rotation of amides is about -5 e.u., which would give an increase in $\Delta G^\ddagger$ with T_c of nearly the magnitude observed. The dependence of T_c and $\Delta G^\ddagger$ upon resonance frequency as well as upon r and the nature of the shift reagent are being investigated further to separate the two contributions. Such an approach could prove to be helpful in obtaining more accurate measurements of $\Delta S^\ddagger$.

H. N. Cheng

H. S. Gutowsky

References

(1) $Eu(thd)_3$ represents tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium (III), also designated as $Eu(DPM)_3$. $Eu(fod)_3$ represents tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium (III). $Pr(thd)_3$ and $Pr(fod)_3$ represent the praseodymium (III) complexes of the same anions.

(2) R. E. Rondeau and R. E. Sievers, J. Am. Chem. Soc., 93, 1522 (1971).

(3) D. R. Eaton, and W. D. Phillips, Adv. in Mag. Resonance, 1, 103 (1965); H. J. Keller and K. E. Schwarzhaus, Angew. Chem. Int. Ed. Engl., 9, 196 (1970).

Table 1. P.m.r. and activation parameters for internal rotation of amides with various molar ratios of $Eu(fod)_3$.[a]

r[a]	$\Delta\nu_\infty$, Hz[b]	T_c, °C	$\Delta G^{\ddagger}$[c]	lit. values, $\Delta G^{\ddagger}$, T_c, Ref
		Dimethylformamide (DMF)		
0.00	5.0	114.0	21.00	20.9 in TCE, 113°, 4
0.10	14.0	131.5	21.16	20.9 in TCE, 115°, 5a
0.30	40.5	152.5	21.40	21.7 neat, 116°, 5b
0.50	71.0	164.0	21.52	
0.60	76.0	167.5	21.63	
		Dimethylacetamide (DMA)		
0.00	5.3	66.0	18.27	18.5 in TCE, 73°, 4
0.05	6.8	69.5	18.30	18.2 neat, 75°, 6
0.10	15.1	82.0	18.42	
0.15	21.0	88.0	18.50	
		Dimethylpropionamide (DMP)		
0.00	4.4	51.0	17.55	18.0 neat, 54°, 7a
0.05	7.8	58.0	17.57	16.6 in CCl_4, 44°, 7b
0.10	16.0	70.0	17.73	
0.15	22.0	74.0	17.73	

[a] The molar ratio $Eu(fod)_3$/amide in TCE solutions with 5 mole % of amide.

[b] The width at half-height of the 60 MHz p.m.r. at T_c.

[c] In kcal/mole, obtained from the Eyring equation, $k_c = (kT_c/h)\exp(-\Delta G^{\ddagger}/RT_c)$.

(4) The fact that $Yb(thd)_3$ increases T_c for DMF and DMA has been noted by C. Beauté, Z. W. Wolkowski, and N. Thoai, Chem. Comm., 70 (1971), but values are not given for $\Delta\nu_\infty$.

(5) (a) E. S. Gore, D. J. Blears, and S. S. Danyluk, Can. J. Chem., 43, 2135 (1965); (b) M. Rabinowitz and A. Pines, J. Am. Chem. Soc., 91, 1585 (1969).

(6) R. C. Neuman, Jr., and V. Jonas, J. Am. Chem. Soc., 90, 1970 (1968).

(7) (a) C. W. Fryer, F. Conti, and C. Franconi, Ric. Sci. Rend. Sci., A, 35, 788 (1965); (b) J. C. Woodbrey and M. T. Rogers, J. Am. Chem. Soc., 84, 13 (1962).

RIJKSUNIVERSITEIT GENT
LABORATORIUM voor ORGANISCHE CHEMIE

STATE UNIV. of GENT
ORGANIC CHEM. DEPT.
LAB. for NMR SPECTROSCOPY
Prof. M. ANTEUNIS
Krijgslaan 271 — GENT B — 9000
BELGIUM

B-9000 GENT, April 27th 1972.
KRIJGSLAAN 271 - S.4 Tel. (09) ~~32.60.05~~ 22.57.15
(België-Europa)

1° Example of "HR-300 MHz NMR at work"
2° Inquiry on interest for 300 MHz amino acid spectra.

Dear Barry,

1° A couple of months ago we had our new VARIAN HR-300 machine installed equipped with FFT facilities. Needless to say that we are "pouring" previous unsolved problems in it, which were at that time saved up "for better times". One of the problems we were confrontated came from our polymeric research team (Prof. E. Goethals), who asked us for a decision between two possible structures (1) and (2), a hydroxy-sulfonic acid derivative (L=H) they have prepared.

$$\underset{\underset{OL}{|}}{\text{ØCH}}\text{-CH}_2\text{SO}_3\text{Na} \qquad (1) \qquad \text{or} \qquad \underset{\underset{SO_3Na}{|}}{\text{ØCH}}\text{-CH}_2\text{OL} \qquad (2)$$

However the H-atom showed a too tightly coupled system, as to allow an analysis at 100 MHz. This is overcome by inspecting the 300 MHz detail (fig. 1). The three-spin system is of the ABM type, the AB-part forming a nice example of "embracing" quartets (P. Diehl; TAMU nmr Newsl. 106-33). This case therefore allows unambiguously the determination of relative signs of the couplings, giving J(A,B) = 9.5; J(A,M) = 4.5 and J(B,M) = -10.2 Hz (approximate values, as follows from ABX treatment; $\Delta\delta/J \triangleq 5.5$). Thus the B,M atoms are geminal. In view of a value found for propylene-sulton (R.W. Ohline, A.L. Allred and F.G. Bordwell; J.A.C.S. 87, 2768 (1965)), ^2J being -14.0 Hz, the observed value rather indicates that the methylene part bears the hydroxylgroup for which a lower value than -12.5 Hz may be expected (cf. M. Anteunis, G. Swaelens and J. Gelan; Tetrah. 27, 1917 (1971) and cf. ^2J(MeOMe) = -9.5). Thus structure (2) (L = H) actually is under consideration. It was prepared along the scheme :

$$\text{NaHSO}_3 + \text{Ø}\!\!\diagdown\!\!\diagup\!\!\text{O} \xrightarrow{H_2O} (1) \quad \text{or} \quad (2)$$

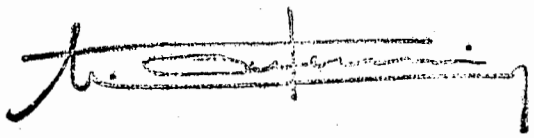
To confirm the validity of these deductions, acetylation was tried. After some difficulties (e.g. acetolysis of the sulfonic group, which points upon a mobile benzylic function) the acetylated derivative (2); L=Ac was obtained. The 300 MHz NPR spectrum (fig. 2) shows an ABX system (J(A,B) = -11.4 Hz; J(A,X) = 5.75 Hz and J(B,X) = 8.20 Hz), at resp. δ(A) = 4.84; δ(B) = 4.67 and δ(X) = 4.45. This shows uniquivocally that especially two protons have become deshielded against the original parent derivative.

Thus the compound contains a $-CH_2OAc$ unit, and not a $>CH-OAc$ unit. As expected $^2J(C\underline{H}_2OAc)$ is increased somewhat in absolute value by a withdraw mechanism of the O-p-orbitals.

2°- For the moment we are taking the 300 MHz spectra of twenty amino acids (D_2O; neutral-, acid- and alkaline medium). Although 60 (B. Smith and A.M. Ihrig "The NMR spectra of eighteen essential amino acids" Texas University Research Foundation, Forth Worth, Texas 76129 - Sept. 1969) and data on 220 MHz spectra (B. Bak, C. Dambmann, F. Nicolaisen, E. Pedersen and N. Bhacca; J.Mol.Spectr. 26 (1968) 78) are available, I wonder if research centra would be interested in possessing the spectra and details obtained at 300 MHz.

May I kindly invite interested people to contact me ? This would enable me to decide upon the mode of publication of these data.

Yours sincerely,



Prof. M. Anteunis.

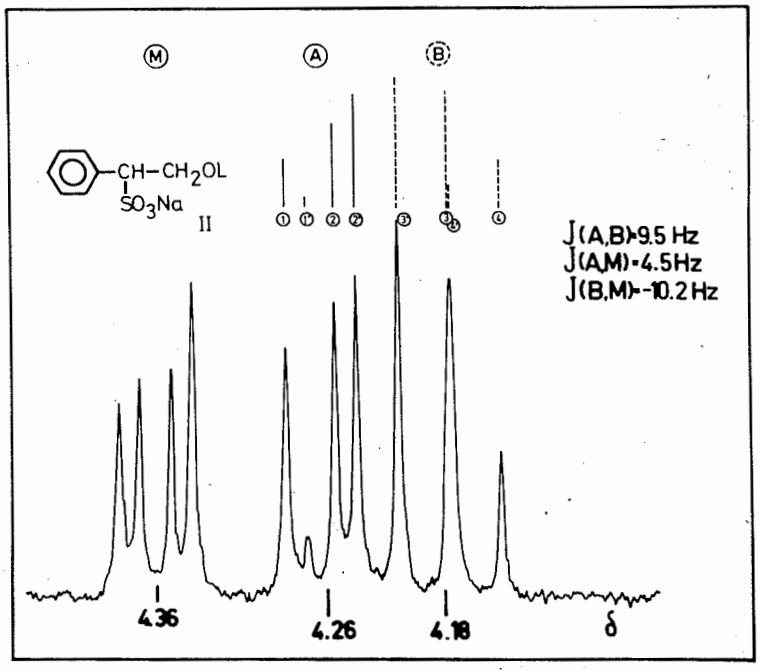
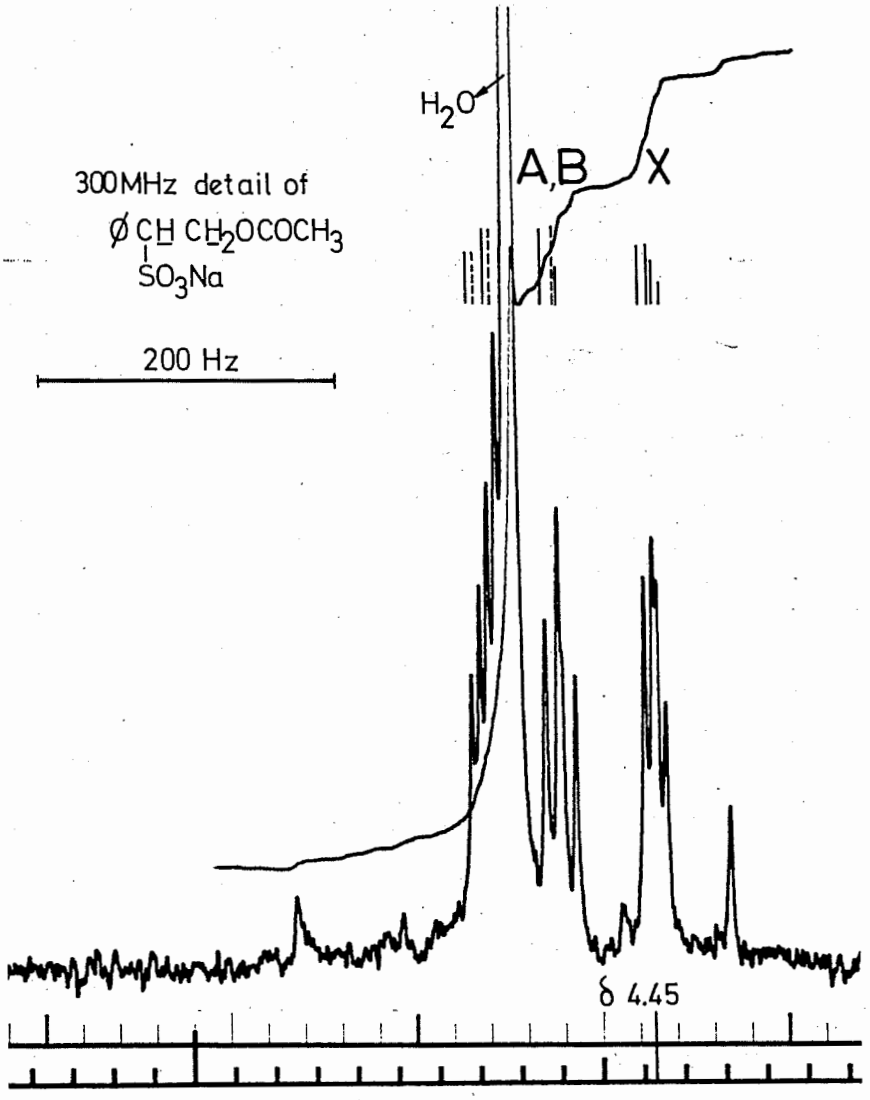


Figure 1 :
300 MHz detail of (2) in D_2O (sodium 2,2,3,3-tetradeutero-3-trimethyl-silylpropionate internal).
J and δ-values as indicated.

Figure 2 :

(2) L = Ac
Detail of the A,BX system obtained at 300 MHz in D_2O.
Same internal standard as for figure (1).



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