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Elguero, J.; Fruchier, A. 1
Effet Longue Distance Du Groupement Methyle

Becconsall, J.K. 4
$\delta = \sigma(\text{sample}) - \sigma(\text{reference})$

Smith, W.B. 6
Summary of Current "Best" Q Values

Martin, J.C. 7
NMR in Chiral Solvents

Holder, B.; Ward, R.; Happe, J.; Maddux, A. 8
Phase Modulation of RF Signals

Moriarty, R.M.; Stirling, C.J.M. 10
The Equivalence of Diastereotopic Protons in an Isotopically Chiral Molecule

Pawliczek, J.B.; Günther, H. 12
Precise Coupling Constants for Naphthalene, Anthracene, and 1.1-Difluoro-benzocyclopropene

Berlin, K.D. 15
Nonequivalence of Protons in Cyclic Isomers

Kanski, E.L.; Marr, D.H. 16
HA 100 Slave Recorder - Odds and Ends

Schaefer, T. 19
Internal Rotation in α,α, 2,4,6-pentachlorotoluene

Dickson, F.E. 20
The Use of NMR in Petroleum Characterization

King, R.W. 21
Another Linear Correlation: $\delta^{29}Si$ vs. σ

Barfield, M. 22
Substituent Effects on $^4J_{HH'}$

Gast, R.; Hilbers, C.; MacLean, C. 26
Electric Field Effects in the ^2D Spectrum of Deutero-Nitrobenzene

Sutcliffe, L.H.; Tiddy, G.J.T. 30
The Signs of "Through-Space" F-F Coupling Constants

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OVER

Mannschreck, A. 32
Diastereoisomers of an Oxaziridine; Diastereoisomers of an Enamine

Tewari, K.C. 34
Effect of Mercury(II) on the PMR Spectra of Cytidine

Gestblom, B.; Hoffman, R.A. 36
Lineshape in High-resolution NMR; Relaxation and Chemical Exchange

Lauterbur, P.C.; Runde, E.J. 40
IBM 1800 Control of a Varian HR-100

Strauss, P.A.; Swinehart, J.S. 45
Triple Resonance Experiments

Deadline Dates: No. 131: 4 August 1969
No. 132: 3 September 1969

All Newsletter correspondence, etc., should be addressed to:

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

FACULTÉ DES SCIENCES
DE MONTPELLIER

R. JACQUIER
Professeur

Place Eugène Bataillon
Tél. : (67) 72.29.44 — 72.16.00 — 72.28.58
Poste 803

Montpellier, le 4 Juin 1969

Professeur B. L. SHAPIRO
Department of Chemistry
Texas A and M University
College of Science
College Station
TEXAS 77843
U. S. A.

Titre : EFFET LONGUE DISTANCE DU GROUPEMENT METHYLE.

Cher Professeur Shapiro,

Nous avons déja effectué un essai (1) d'utilisation de la formule d'ApSimon-Whalley (2) pour le calcul de l'effet produit par l'introduction d'un groupement méthyle, à la place d'un proton, sur les autres protons du système AA'BB' de quelques pyrazolines-2.

Pour cela nous avons évalué numériquement l'intégrale correspondant au méthyle en libre rotation en utilisant comme anisotropies et susceptibilités des liaisons C-H et C-C les valeurs données par Whalley (3) [voir aussi (4)].

Toutefois, aussi bien dans les travaux d'ApSimon et Whalley (2,4) que dans le nôtre (1), le $\Delta\sigma_T$ est calculé en évaluant $\Delta\sigma_{CH}$ et $\Delta\sigma_{CC}$ avec la formule d'ApSimon corrigée pour un dipole non ponctuel, tandis que le terme $\Delta\sigma_{Me}$ est calculé avec l'équation de McConnell. Si la correction apportée par ApSimon à la formule de McConnell est importante, cette façon de calculer $\Delta\sigma_T$ risque de rendre inutile le soin apporté au calcul de $\Delta\sigma_{CC}$ et de $\Delta\sigma_{CH}$.

Nous avons donc calculé le terme $\Delta\sigma_{Me}$ du méthyle en libre rotation en intégrant l'équation d'ApSimon, et constaté que, dans de nombreux cas, la correction apportée par le second terme n'est pas négligeable (Tableau I).

Un autre facteur susceptible d'influencer le $\Delta\sigma_T$ et, par conséquent, les paramètres d'anisotropie calculés selon la méthode itérative d'ApSimon (2,4), est la distance entre le centre du dipole et l'atome de carbone de la liaison C-H.

Plusieurs auteurs (5,6,7) ont utilisé pour cette distance la valeur du rayon de Van der Waals du carbone, soit 0,77 Å. ApSimon (2) utilise cette valeur pour le calcul de $\Delta\sigma_{CH}$, mais pour le calcul de l'effet du méthyle en libre rotation, il prend la valeur correspondant à la moitié de la liaison C-H, soit 0,546 Å. Dans nôtre précédent travail, nous avons fait de même (1).

Les calculs de $\Delta\sigma_{Me}$ que nous avons repris en considérant le centre du dipole à 0,77 Å (Tableau II) montrent que les modifications apportées ne sont pas négligeables.

Faute d'un choix justifié théoriquement, nous préférons, pour des raisons de cohérence, prendre 0,77 Å aussi bien pour $\Delta\sigma_{CH}$ que pour $\Delta\sigma_{Me}$.

Enfin, comme ApSimon l'a signalé (8), le problème majeur dans les calculs de blindages longue distance est celui de la détermination de l'importance relative des termes magnétiques, électriques, de Van der Waals et de solvant, en évitant de majorer arbitrairement l'une des contributions. L'obtention d'une bonne corrélation entre $\Delta\sigma_{obs}$ et $\Delta\sigma_{magn}$ seulement ne peut que conduire à des paramètres d'anisotropie magnétique erronés.

Références :

(1) J. ELGUERO, A. FRUCHIER et R. GIL, Bull. Soc. chim., 1968, p. 4403.
(2) J. W. ApSIMON, W.A. CRAIG, P.V. DEMARCO, D. W. MATHIESON, L. SAUNDERS et W. B. WHALLEY, Tetrahedron, 1967, 23, 2339.
(3) W. B. WHALLEY, IITNMR Newsletter, 1967, 101, 12.
(4) J. W. ApSIMON, W. A. CRAIG, P. V. DEMARCO, D. W. MATHIESON, L. SAUNDERS et W. B. WHALLEY, Tetrahedron, 1967, 23, 2373.
(5) J. R. DIDRY, J. GUY et F. CABARET, Cr. Acad. Sci. Paris, 1963, 257, 1466.
(6) D. W. DAVIES, Mol. Phys., 1963, 6, 489.
(7) J. HOMER et D. CALLAGHAN, J. chem. Soc., (A), 1968, p. 439.
(8) J. W. ApSIMON et H. BEIERBECK, TAMUNMR Newsletter, 1968, 122, 42.

Dans les deux tableaux suivants, $\Delta\sigma_A$ est calculé au moyen de l'équation de McConnell, tandis que $\Delta\sigma_B$ est la correction apportée par ApSimon. On a la relation $\Delta\sigma_{Me} = \Delta\sigma_A + \Delta\sigma_B$.

Tableau I : Le centre du dipôle de la liaison C-H est pris à 0,77 Å de l'atome de carbone pour $\Delta\sigma_{CH}$ et à 0,546 Å pour $\Delta\sigma_{Me}$.

R	γ	$\Delta\sigma_{CC}$	$\Delta\sigma_{CH}$	$\Delta\sigma_A$	$\Delta\sigma_B$	$\Delta\sigma_T$
2,15	76,99	0,431	0,232	0,086	0,027	0,313
2,40	66,00	0,178	0,098	0,069	0,013	0,162
2,60	84,00	0,257	0,147	0,090	0,014	0,133
2,62	42,88	-0,128	-0,086	0,061	0,006	0,025
2,80	31,00	-0,204	-0,138	0,053	0,004	-0,010

Tableau II : Le centre du dipôle de la liaison C-H est pris à 0,77 Å de l'atome de carbone pour $\Delta\sigma_{CH}$ et pour $\Delta\sigma_{Me}$.

R	γ	$\Delta\sigma_A$	$\Delta\sigma_B$	$\Delta\sigma_T$
2,15	76,99	0,132	0,029	0,361
2,40	66,00	0,085	0,013	0,178
2,60	84,00	0,045	0,016	0,171
2,62	42,88	0,051	0,005	0,015
2,80	31,00	0,039	0,003	-0,024

Veuillez croire, cher Professeur Shapiro, à l'assurance de nos sentiments les meilleurs,

J. ELGUERO

A. FRUCHIER

130-4

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5th June, 1969

Your Ref.

Our Ref. JKB/AR

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

Dear Barry,

$$\delta = \sigma(\text{sample}) - \sigma(\text{reference})$$

Under this rallying cry, may I inaugurate a counter-campaign against the "positive chemical shifts in the direction of increasing frequency" part of the conventions proposed by Grant and Jones (TAMU NMR Newsletter 128-27), and also strongly advocated by a number of my friends in the British nmr community (NMRDG meeting, Waltham Abbey, December 1968).

The end product of a high resolution nmr experiment, assuming a successful analysis of the spectrum, is a set of chemical shifts and coupling constants. The present argument is about the convention to be adopted in reporting chemical shifts. It is generally agreed that for well-known reasons the best form is a non-dimensional one (usually multiplied by 10^6 and described as parts per million). The important quantity most closely related to this form is the nuclear screening σ. This is also the quantity that one attempts to calculate in any theoretical treatment of the chemical shift. If one conveniently measures the chemical shift relative to some reference compound such as TMS, this leads directly to the quantity δ defined as above.

Cont/.....

FROM: J.K. Becconsall SHEET NO.: 2

TO: Dr. B.L. Shapiro DATE: 5.6.69.

To reverse the sign of δ, then to attempt to rationalise this by bringing the resonance frequency back into the discussion, is unnecessary and a potential source of confusion.

Of course, if we choose a reference with a high σ, as for TMS when used as a proton reference, most of the δ's defined as above will be negative. This is not an inconvenience, but a useful reminder of what one is doing.

Yours sincerely,

Jack Becconsall

J.K. Becconsall

0030A 8/66 Baden 27034

130-6

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129

Department of Chemistry

June 9, 1969

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

Dear Barry:

Summary of Current "Best" Q Values

As you know, we have found our empirical extention of Schaefer's Q parameter a useful means of further probing substituent effects on aromatic proton chemical shifts (I. I. T. NMR 112-14, TAMUNMR 121-32, and J. Phys. Chem., 73, 1043, 1046. 1049 (1969). Predictions regarding the chemical shifts of protons adjacent to various substituents can be made, and information regarding substituent conformations can also be obtained.

We have now obtained quite a list of values, and our most up-to-date set is given below. $Q_{(1)}$ values should be used for groups flanked on both sides by hydrogens. $Q_{(2)}$ values are used when a second substituent replaces one of the ortho hydrogens. Groups with cylindrical symmetry show only one value. No doubt groups such as acetyl and formyl will show $Q_{(2)}$ values different from their $Q_{(1)}$ values but these have not yet been determined.

	$Q_{(1)}$ Values (first)	$Q_{(2)}$ Values (second)	
NH_2	-0.67	-0.03	
OCH_3	0.54	----	
OH	0.30	1.20	
F	1.04*	----	
CH_3	1.72	----	
H	2.28*	----	
t-B_u	2.50	----	
Cl	2.25*	----	
C_6H_5	3.0	2.1	
Br	3.16	----	
CN	3.43	----	
CF_3	3.71	----	
I	3.98*	----	
CHO	4.90		
CCl_3	5.15	----	
$COCH_3$	5.20		
COCI	6.00	----	
NO_2	6.33	4.00	

* Schaefer's original values.

Yours sincerely,

Bill

W.B. Smith
Chairman
Department of Chemistry

WBS/mjb

UNIVERSITY OF ILLINOIS
Department of
CHEMISTRY AND CHEMICAL ENGINEERING
URBANA
61801

East Chemistry Building

June 6, 1969

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

Dear Barry:

You may be interested to know that the study of chiral nmr solvents being conducted by William Pirkle and his students is continuing to yield interesting results. Latest (and preliminary) findings are that, in chiral solvents such as 2,2,2-trifluorophenylethanol (1) and 2,2,2-trifluoro-α-naphthylethanol (2), the enantiomers of amine oxides and phosphine oxides exhibit dissimilar spectra.

For example, in $CDCl_3$, racemic N-methyl-N-ethyl-aniline-N-oxide has the expected simple spectrum. However, in chiral 2 (78% optical purity) the N-methyl resonances of the two enantiomers differ in chemical shift by 0.035 ppm, the diastereotopic methylene protons, which show an initial chemical shift difference of 0.012 ppm now show additional nonequivalence of 0.034 ppm, while the C-methyl resonances differ by 0.055 ppm.

In the case of phosphine oxides, methylphenyl-t-butyl phosphine oxide in chiral 1 serves as an example. The first order spectrum observed in $CDCl_3$ changes, on addition of 1, giving nonequivalence in the p-methyl group amounting to 0.032 ppm. However, the p-t-butyl protons of the enantiomers showed no observable difference in chemical shift.

Yours,

J. C. Martin
Professor of Chemistry

Short title: Nmr in Chiral Solvents

cb

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
P.O. BOX 808
LIVERMORE, CALIFORNIA 94550

TELEPHONE (415) 447-1100
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TWX 910-386-8339 AEC LRL LVMR

June 3, 1969

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

Dear Prof. Shapiro:

Phase Modulation of RF Signals

The theory of the various types of modulated nmr signals has been examined in the literature (1), (2). Occasionally it is desirable to produce modulated signal without resorting to field or frequency modulation. We would like to point out some interesting aspects of phase modulation (PM) and one way it can be implemented. The distribution of rf power in the sidebands of a phase modulated signal is similar to that for a frequency modulated signal with the same modulation index. The modulation index, β, for a sinusoidal modulated FM wave is the maximum frequency deviation divided by the modulation rate. The modulation index for PM is the maximum angular deviation expressed in radians (3).

$$\beta_{FM} = \frac{\Delta\omega_{max}}{\omega_m} \quad ; \quad \beta_{PM} = \Delta\theta_{max}$$

During the development of a multinuclei spectrometer, utilizing a Hewlett-Packard Frequency Synthesizer, we wished to provide a 60 MHz field frequency internal lock system without the use of field or frequency modulation. A 30 MHz signal from the H-P Synthesizer Driver is fed into a phase modulator driven by a 2.5 kHz square wave (see Fig. 1). The modulator is a tuned rf amplifier whose center frequency can be shifted by means of a voltage-controlled capacitor. The 30 MHz rf signal is subjected to a square wave type phase shift through the amplifier as it is alternately tuned above and below 30 MHz at the audio rate. Biasing and amplitude controls tune the voltage-controlled amplifier and adjust the modulation index. If these are adjusted to alternately shift the amplifier's upper and lower 3 db points to 30 MHz, reasonable modulation index can be obtained with negligible accompanying AM. The modulation index is doubled when the frequency is doubled to 60 MHz although the deviation rate (which sets the side band spacing) remains the same.

Sincerely yours,

Bert Holder

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

(1) W. A. Anderson; N.M.R. and E.P.R. Spectroscopy, Pergamon Press, Inc., N.Y. 1960.
(2) O. Haworth and R. E. Richards; Progress in N.M.R. Spectroscopy, Pergamon Press, Ltd., London, 1966.
(3) H. S. Black; Modulation Theory, D. Van Nostrand & Co., Inc., N.Y. 1953.

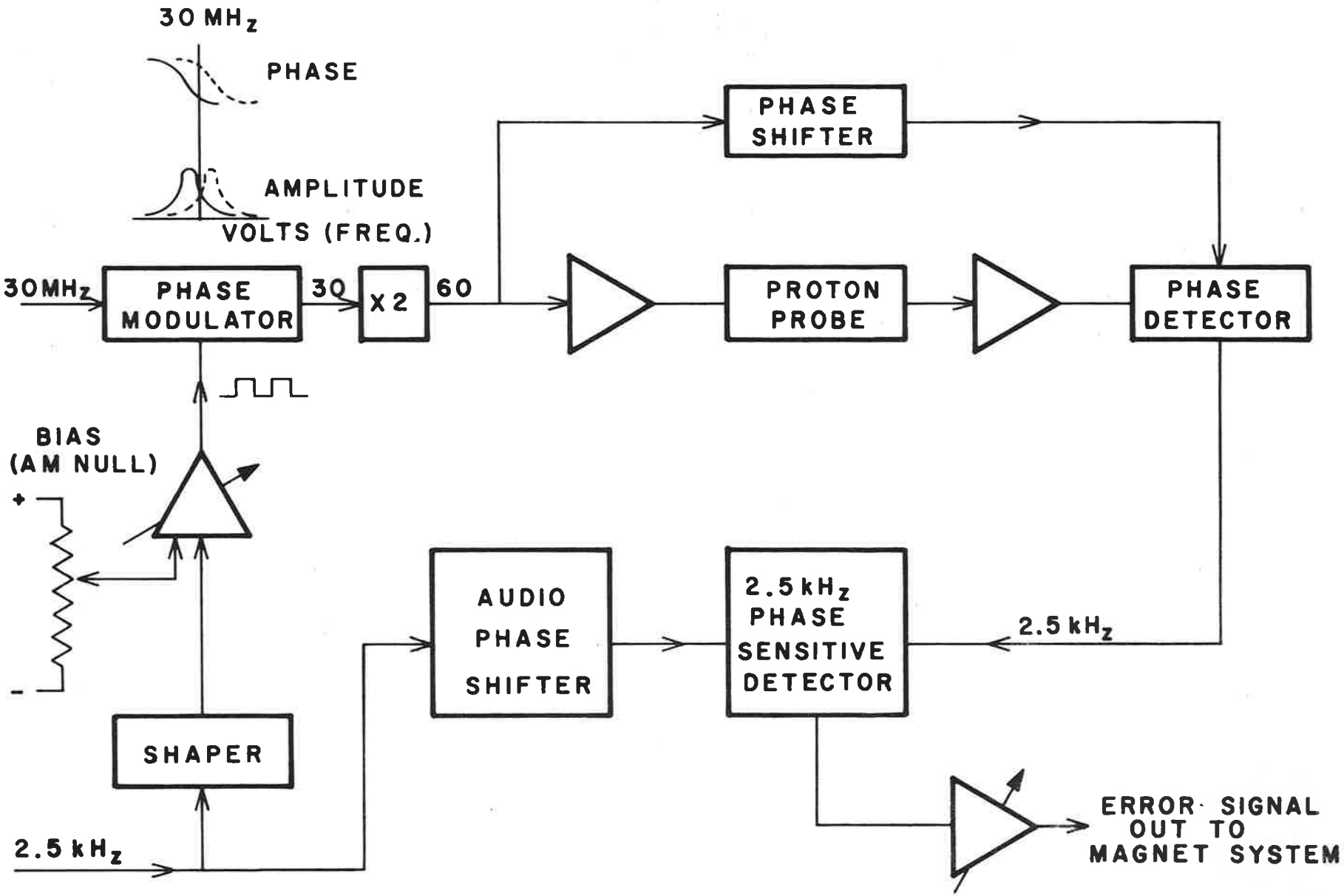


FIGURE I. BLOCK DIAGRAM OF FIELD-FREQUENCY LOCK SYSTEM USING PHASE MODULATION.

University of Illinois at Chicago Circle

130-10

College of Liberal Arts and Sciences
Department of Chemistry
(Box 4348) Chicago, Illinois 60680
Telephone: 663-3161

June 5, 1969

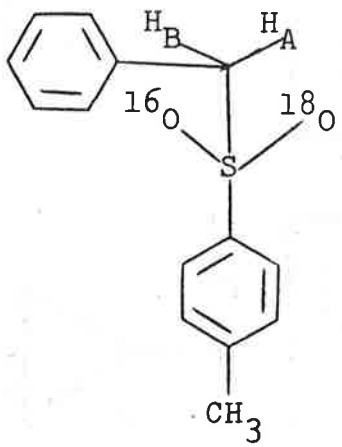
Professor B. L. Shapiro
Department of Chemistry
Texas A. & M. University
College Station, Texas 77843

The Equivalence of Diastereotopic Protons in an Isotopically Chiral Molecule

Dear Professor Shapiro:

The chemical and magnetic nonequivalence of geminal diastereotopic protons in chiral molecules is familiar. We wish to report our work on the investigation of this phenomenon in molecules where chirality is due to isotopic differences.[1]

The benzylic protons in the chiral molecule (-)-benzyl p-tolyl [$S^{16}O^{18}O$] sulfone[2] (1) are diastereotopic and therefore anisochronous.



1

It was of interest to determine whether their anisochronous nature might be manifested in an observable chemical shift difference. Spectra determined at 60 MHz and 100 MHz for $CDCl_3$ of (1) showed only A_2 behavior for the benzylic protons.

Similar results were obtained in several other achiral solvents.

Finally the spectrum of (1) was measured at 220 MHz.[3] The benzylic protons appeared as sharp singlet resonances with no tendency towards splitting.

The non-observation of splitting is perhaps not surprising in what may be described as a system of mildly diastereotopic protons.

Sincerely,

Robert M. Moriarty
University of Illinois
Chicago Circle Campus

C. Stirling

C. J. M. Stirling
University College of North Wales
Bangor, Wales
~~England~~ U K.

RMM:nb

1. For an earlier contribution to this problem see J. Kim and R. M. Moriarty, IITNMR, 93, 26(1966).

2. C. J. M. Stirling, J. Chem. Soc., 5741 (1963).

3. We wish to thank Prof. J. M. Lehn, Institut de Chimie, Strasbourg, for arranging this measurement.

130-12

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Dr. H. Günther

5 KÖLN, June 2, 1969
ZÜLPICHER STRASSE 47
TELEFON: 20 24 22 39

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

Precise Coupling Constants for Naphthalene, Anthracene, and 1.1-Difluoro-benzocyclopropene.

Dear Barry:

We have joint the group of resonators, that is trying to analyse some of the basic molecules of organic chemistry more properly as this was possible in the early days of high resolution nmr. After the excellent analysis of benzene by Read et al. [1] it was especially tempting to reanalyse naphthalene (I) and anthracene (II). For both compounds, earlier investigatioms [2] were based on 4-spin approximations, neglecting completely inter-ring couplings. This introduced necessarily large experimental errors in the measured transition frequencies, as can be seen from fig. 1a for the case of I. Brügel has shown, that J_{18} in I may be as large as 0.8 Hz [3]! The longrange coupling constants in I and II, therefore, were not determined with any accuracy.

We have synthesized 1.2.3.4-tetra-deutero-I and 9.10-di-deutero-II and measured the ^{1}H-nmr spectra using H-{D}-decoupling [4]. For both compounds all 24 transitions of the AA'BB'-systems could be resolved (see fig. 1b for I). Analysis was performed by the direct method [5], using Laocoon II [6] for a refinement of the data. Results are shown in the table. The errors in the coupling constants are believed to be smaller than 0.05 Hz.

We have also completed the final analysis of 1.1-difluoro-benzocyclopropene (III). With the aid of H-{^{19}F}-decoupling [4] all 24 lines of the AA'BB'system were recorded (fig. 2). The analysis was staightforward and yielded the data shown in the table. The coupling constants obtained now differ considerably (especially with regard to J_{45}) from those we reported earlier [7]. Our first assignment missed the small intensity line g in the undecoupled spectrum

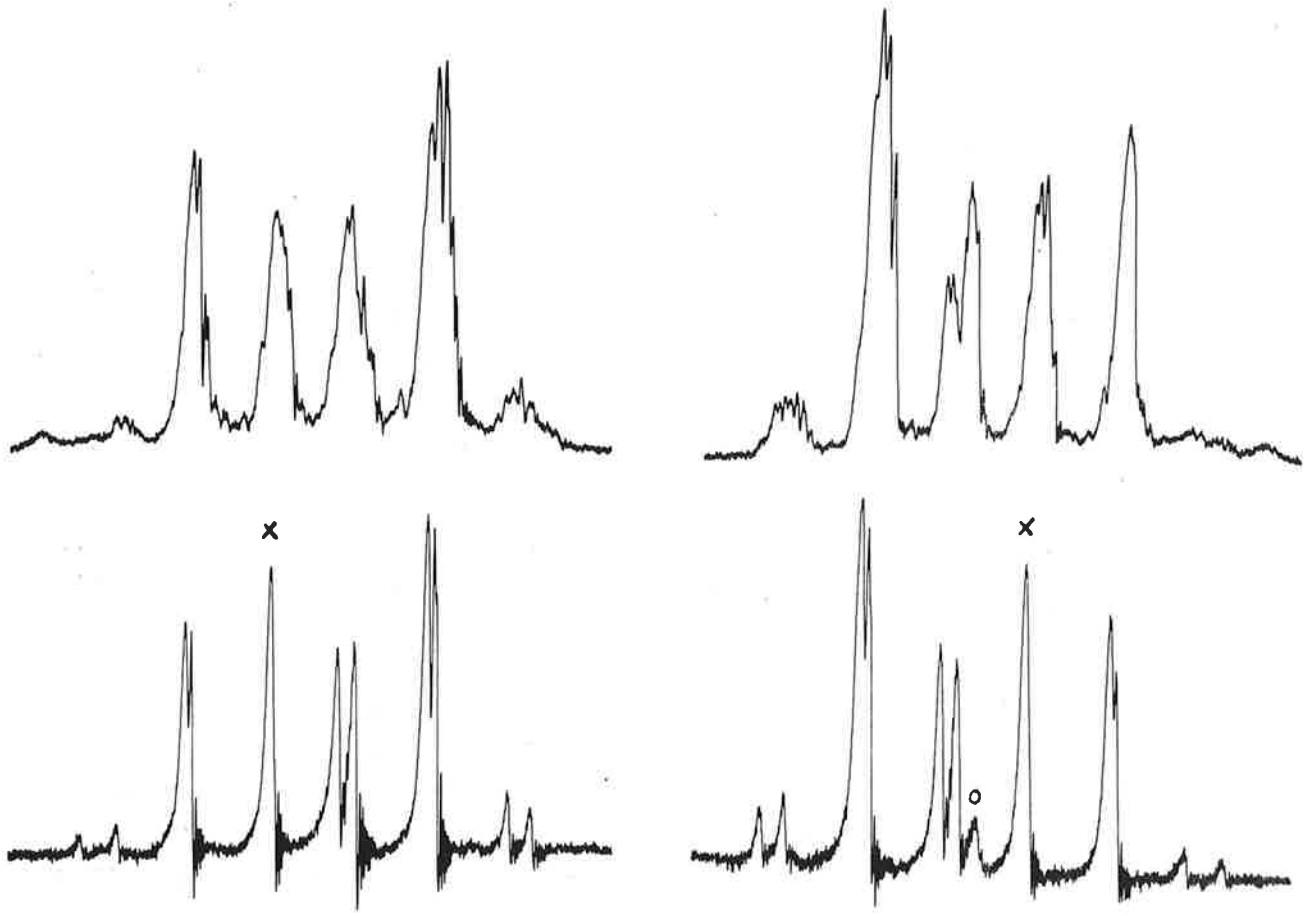
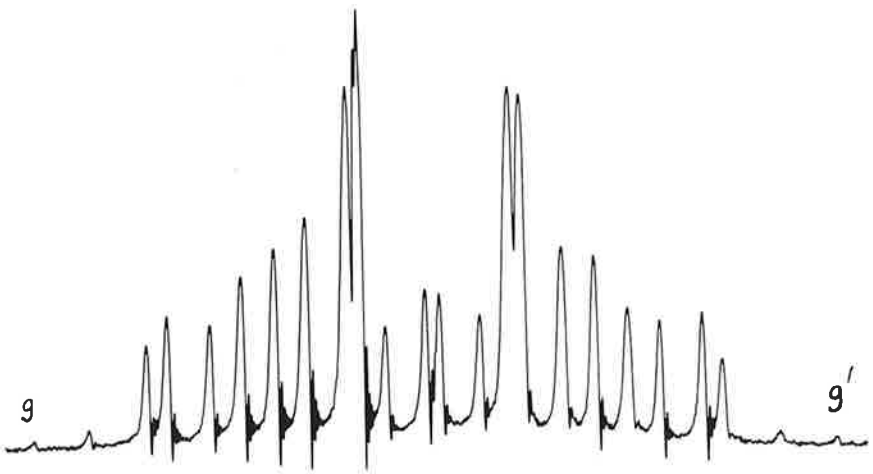
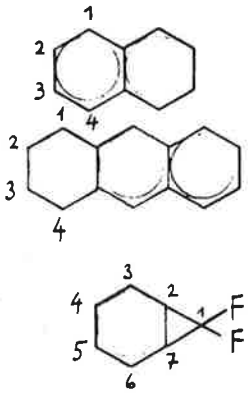


Figure 1: a) 100-MHz-spectrum of naphthalene

b) 100-MHz-spectrum of tetradeutero-naphthalene with H-{D}-decoupling. The lines marked with (x) were resolved as doublets at slower sweep rate. At (o) impurity of, presumably, trideuterated material.



Fiure 2: 100 MHz-spectrum of 1.1-difluoro-benzocyclopropene with H-{^{19}F}-decoupling.



	$\nu_o\delta^a$	J_{12}	J_{13}	J_{14}	J_{23}	Δf^b	rms^c
	36.33	8.28	1.24	0.74	6.85	0.03	0.02
	52.80	8.55	1.20	0.82	6.59	0.04	0.02
	$\nu_o\delta^a$	J_{34}	J_{35}	J_{36}	J_{45}	f^b	rms^c
	11.93	6.83	0.32	1.89	7.43	0.04	0.03

a) at 100 MHz; b) experimental error in relative line positions; c) rms error in fitting observed and calculated spectrum with LAOCOON II.
All values are in Hz.

This resulted in large errors mainly for the spectral parameters K and M. The conclusions drawn from the earlier data [7] with regard to the structure of III are now not justified anymore.
Dr.'s Cooper and Manatt recently informed us, that they succeeded in analysing the hydrocarbon benzo-cyclopropene. Their results, which they kindly communicated to us, are in good agreement with our findings.
The exact data now available for the aromatic compounds make it worthwhile to reinvestigate the bond order - ^3J relationship [8]. We hope to report on the results of this investigation in a full paper in the near future.

Sincerely yours,

Pawliczek (J.B.Pawliczek) Günther (H.Günther)

[1] J.M.Read et al., J.molecular Spectr. 22, 419 (1967).
[2] B.Dischler and G.Englert, Z.Naturf. 16a, 1180 [1961]; N.Jonathan, S.Gordon and B.P.Dailey, J.Chem.Phys. 36, 2443 (1962), and several other papers.
[3] W.Brügel, private communication.
[4] HA-100, using a Schlumberger frequency synthesizer FSX 3000 and a NMR-Specialities probe adapter.
[5] B.Dischler, Z.Naturforschg. 20a, 888 (1965).
[6] S.Castellano and A.A.Bothner-By, J.Chem.Phys. 41, 3863 (1964).
[7] E.Vogel, S.Korte, W.Grimme, and H.Günther, Angew.Chemie 80, 279 (1968); see also IIT-NMR-Newsletter No. 112/59.
[8] Ref. 2b; W.B.Smith et al., J.Am.Chem.Soc. 89, 1438 (1967); H.Günther, Tetrahedron Letters 1967, 2967.

Oklahoma State University

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

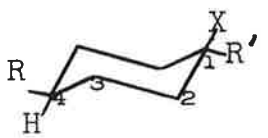
June 16, 1969

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

Nonequivalence of Protons In Cyclic Isomers

Dear Dr. Shapiro:

Because of a major breakdown in our NMR system for nearly 12 weeks, our research effort in NMR has been greatly slowed. Thus the reason for the delay in our contribution. to TAMU. We have observed a very interesting chemical shift different as much as 10 Hz in the protons of alkyl groups at C-4 in the systems I and II which are cis-trans isomers. We



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II

have actually isolated isomers in certain examples. We are currently performing experiments to determine if there is a nuclear Overhauser effect involving R and X or R and R'. I trust this will serve as our contribution this time and I promise to be on time with a more substantial contribution in the future.

Sincerely yours,

K D Berlin

K. D. Berlin
Professor

KDB/dm

130-16

hooker research center

NIAGARA FALLS, NEW YORK 14302, PHONE (716) 773-2345

May 23, 1969

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

Dear Barry:

HA 100 SLAVE RECORDER - ODDS AND ENDS

As mentioned in a recent NMR newsletter there are a couple of ways to obtain duplicate NMR spectra. We decided the slave-recorder route was more appropriate for our particular needs since the copies are obtained simultaneously and on 8 1/2" x 11" chart paper which is ideal for notebook storage. Although I am sure a number of people have done this previously in quickly scanning back issues of the Newsletter I could find no mention of it. Since for one reason or another we did encounter some problems I thought this might be of interest to your readers.

Fig. 1 gives the simple wiring diagram for the system. R904A is a triple gang 500 ohm Helipot we had especially built by Beckman. This replaces the double gang pot on the original equipment. A 6.8 V D.C. regulated power supply provides the necessary voltage to drive the third pot. The recorder we are using is a Varian F-130 X-Y recorder. Installing the slave-recorder in the circuit upset the response of the Mars recorder. This problem was eliminated with the ground lead as shown. Using T-60 chart paper and doubling the cps. calibration gives us 100 MHz spectra calibrated in Hz.

Recently we broke another of the variable temperature probe spinner caps. Jim Lappegard of Varian suggested a modification of the cap which has been tried successfully and I thought worthy of being passed on. This involves removal of the bottom 1/4" of the

cap and replacement with an identical piece fashioned from aluminum. This is made with a threaded top so that it can be screwed into the body of the cap which is also threaded.

Finally a plea for help. Although this is an NMR newsletter I am sure it is seen by many ESR users. We have recently acquired an E-4 and will shortly be receiving the variable temperature apparatus. We are considering programming the variable temperature unit to change automatically and would like to know if anyone has done this. Also if anyone has computer programs for spectral simulation or electron density calculations we would like to obtain these.

Sincerely yours,

Eugene L. Kanski

David H. Marr

DHM/srd

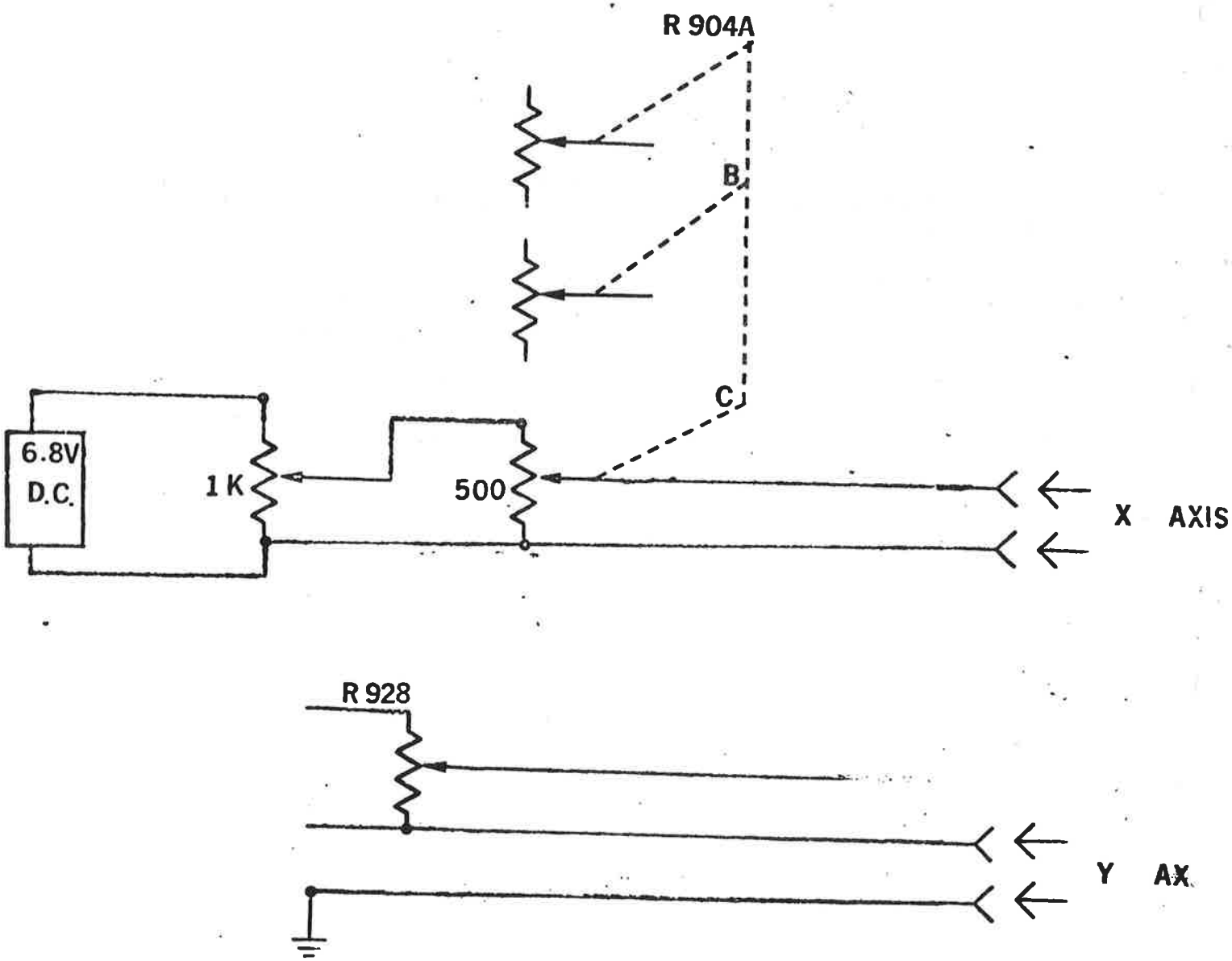


FIG. I

THE UNIVERSITY OF MANITOBA

DEPARTMENT OF CHEMISTRY WINNIPEG, CANADA

June 18, 1969

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

Dear Barry:

Short Title: Internal rotation in α,α,2,4,6-pentachlorotoluene.

Following a note in Can. J. Chem. 46, 2187 (1968) on similar behaviour in α,α,2,6-tetrachlorotoluene, we have been doing a full line-shape analysis (based on a density matrix treatment) of the PMR spectra of the pentachlorocompounds in a variety of solvents. For example, in toluene-d_8 at -40°C the spectrum is ABX where $\nu_B-\nu_A=0.235$ ppm, $J_{AB}=2.1$Hz, $J_{AX}=0.5$Hz, $J_{BX}=0.08$Hz. At 60°C we have an A_2X spectrum. The line shape fitting takes into account changes in internal shift as the temperature changes, as well as changes in T_2. In some of the solvents we deal with an ABC spectrum and plan to apply Professor Binsch' method. When the chlorine atoms on the ring are replaced by bromine there is slow rotation on the NMR time scale even at body temperature. We are getting a good deal of amusement from ringing the changes on the substituents.

Bryan Fuhr and Bruce Goodwin have done the hard work and are leaving for doctoral work shortly. They are good men! The aid of Dr. Hutton is proving as useful as always.

Yours sincerely,

Ted Schaefer
Professor

TS:ck

Gulf Research & Development Company

A. Bruce King
DIVISION DIRECTOR
PHYSICAL SCIENCES

P. O. Drawer 2038
Pittsburgh, Pa. 15230

June 18, 1969

Reference: 6251AA10-1

Via Airmail

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

Dear Barry: The Use of NMR in Petroleum Characterization

Since coming with Gulf Research & Development Company, I have been engaged in the study of petroleum residuals by NMR and other spectroscopic techniques. I would like to submit the following brief summary for the purpose of renewing our subscription to the TAMU NMR Newsletter. Gulf Research & Development Company's subscription is entered under Dr. L. Petrakis's name and can be continued that way. A more complete description of this work is scheduled to appear shortly in ANALYTICAL CHEMISTRY.

It has been suggested that the structure of petroleum residuals is a composite of "unit sheets", particles (composed of associated and/or bonded "unit sheets"), and micelles (composed of associated particles). Various standard methods have been employed to obtain molecular weights of petroleum residuals, all of which measure entities which to some degree are associated. Therefore, molecular weights of residuals reported in the literature show a wide degree of inconsistency depending on the methods employed. Colligative property measurements, for example, will be seriously affected by association and may yield molecular weights abnormally high.

We have suggested that by the application of certain empirical equations, NMR data on gel permeation fractions of residuals can yield "unit sheet" weights, the weight of the fundamental particles of the residual. NMR "unit sheet" weights agree with mass spectroscopy and vapor pressure osmometry data in residual fractions where no association occurs. In this regard NMR is shown to be an extremely valuable tool in the characterization of petroleum residuals.

Sincerely,

Frank E. Dickson

IOWA STATE UNIVERSITY
of Science and Technology
AMES, IOWA 50010

Department of Chemistry

June 26, 1969

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

Another Linear Correlation: $\delta^{29}Si$ vs. σ

Dear Barry,

In response to your dunning letters, I wish to report yet another example of a linear relation of chemical shift to Hammett σ constants, hoping that this will not call down the same editorial response as did magnet cooling problems some time back.

In a series of compounds p-$XC_6H_4Si(CH_3)_3$, where X = NMe_2, OC_6H_5, H, F, Br, COOH and NO_2, the silicon-29 shift shows quite a good linear correlation with substituent sigma constant. The fit was less good when σ^+, σ_R or Taft's combined parameter was used. The slope is -2.0 p.p.m./σ unit, shifts being determined by the INDOR method relative to the protons of TMS at 60.002000 MHz and corrected to p.p.m. downfield from the ^{29}Si resonance of TMS. This slope is fairly small compared to Spiesecke and Schneider's ring ^{13}C (-17) or ^{1}H (-0.65, with much less paramagnetic contribution) or Taft's ^{19}F (-18) results. Some d-p interaction must occur, as invoked by Sakurai and Ohtsura to explain methyl proton shifts in a similar series, but is much less than in a silicon-halogen bond. We have observed solvent shifts of up to 35 p.p.m. in a chlorosilane.

Work continues on this until September, when I move to the University of Florida.

Best regards,

Roy W. King

RWK/ld

THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

June 23, 1969

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

Dear Barry:

Substituent Effects on $^4J_{HH'}$

The dependence of long range coupling on substituents is complex. Presented here is a qualitative MO description which is completely analogous to that used by Pople and Bothner-By (1) to discuss $^2J_{HH'}$. The predicted trends have been used to rationalize long-range substituent trends in a variety of saturated and unsaturated hydrocarbons (2).

The nodal behavior of the eight MO's and the corresponding symmetry designations for the all trans arrangement of a propanic fragment is depicted in Fig. 1. The ordering of the energies of the MO's follows from the same considerations which were used for CH_2 (1). In the MO description the H-H coupling is proportional to the mutual atom-atom polarizability.

$$\pi_{tu} = 4 \sum_{ij} [\epsilon_i - \epsilon_j]^{-1} c_{it} c_{ju} c_{jt} c_{ju},$$

where the sum is over the occupied (i) and unoccupied (j) MO's. The signs of the products of the coefficients of the 1s orbitals on H_1 and H_3, $c_{ih}c_{ih'}c_{jh}c_{jh'}$ are entered in the second column of Table 1 for each of the possible transitions from occupied to unoccupied MO's. Transition energies in the first column are given in order of increasing separation.

Consider the effect of the introduction of an electron withdrawing group at the C_2 carbon atom. Electron density will be withdrawn from the bonding regions of the symmetric MO, ψ_1 resulting in a decrease of the 1s atomic orbital coefficients, c_{1h} and $c_{1h'}$. The 1s coefficients in the other symmetric MO's will be increased accordingly, but they will be unchanged for the antisymmetric MO's. The changes in the magnitudes of the products $c_{ih}c_{ih'}c_{jh}c_{jh'}$ are given in the fourth column. Since the positive shifts outweigh the negative shifts, it appears that the overall effect of substitution of an electron withdrawing group at the C_2 carbon atom

should be to produce a positive shift in the value of $^4J_{HH'}$. Using analogous arguments positive shifts are also predicted for substitution of an hyperconjugative substituent at C_2. The changes in $^4J_{HH'}$ due to inductive and hyperconjugative substituents at the C_1 and C_3 carbon atoms are more subtle, but just the opposite trends are anticipated (2).

1. J. A. Pople and A. A. Bothner-By, J. C. P., 42, 1339 (1965).

2. M. Barfield and B. Chakrabarti, Chem. Rev., to be published.

Sincerely yours,

Mike

Mike Barfield

MB/rlw

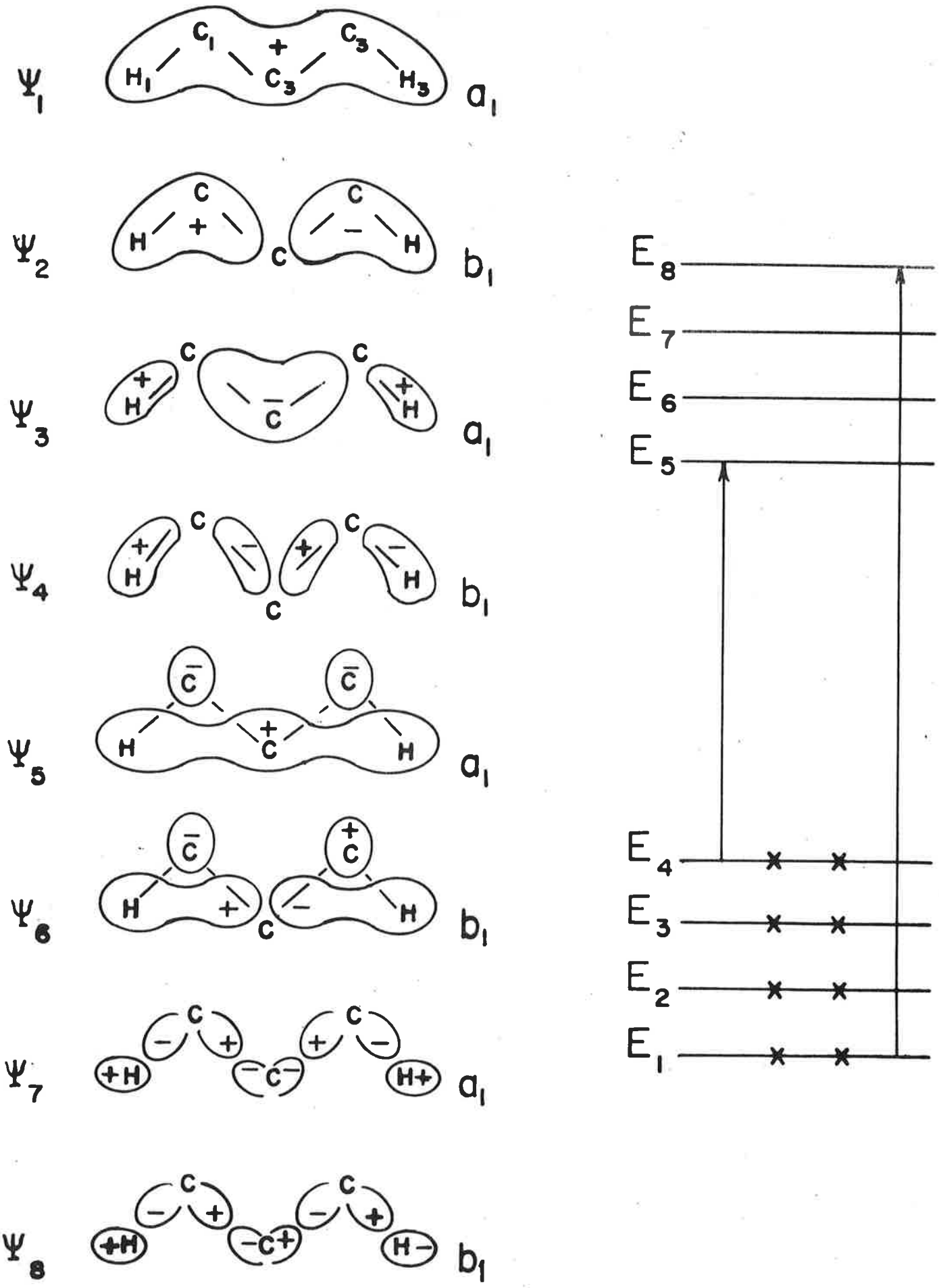

Ψ1
C1
C3
H1
H3
a1
Ψ2
b1
Ψ3
a1
Ψ4
b1
Ψ5
a1
Ψ6
b1
Ψ7
a1
Ψ8
b1
E8
E7
E6
E5
E4
E3
E2
E1

TABLE I. Changes in the magnitude of $^4J_{HH'}$ due to inductive and hyperconjugative substituents at the C_2 and C_1 carbon atoms of a propanic fragment.

Transition	Sign of $c_{ih}c_{ih'}c_{jh}c_{jh'}$	Sign of $^4J_{HH'}$	Change of $^4J_{HH'}$,-C_2 Substitution		Change of $^4J_{HH'}$,-C_1 Substitution	
			Inductive	Hyperconjugative	Inductive	Hyperconjugative
4 →5	-	+	>+	>+	>+	. . .
3 →5	+	-	>-	. . .	>-	. . .
4 →6	+	-	. . .	>-	>-	. . .
2 →5	-	+	>+	<+	. . .	>+
3 →6	-	+	>+	>+	>+	. . .
4 →7	-	+	>+	>+	>+	. . .
1 →5	+	-	. . .	. . .	. . .	>-
2 →6	+	-	. . .	. . .	. . .	>-
3 →7	+	-	>-	. . .	>-	. . .
4 →8	+	-	. . .	>-	>-	. . .
1 →6	-	+	<+	>+	. . .	>+
2 →7	-	+	>+	<+	. . .	>+
3 →8	-	+	>+	>+	>+	. . .
1 →7	+	-	. . .	. . .	. . .	>-
2 →8	+	-	. . .	. . .	. . .	>-
1 →8	-	+	<+	>+	. . .	>+

130-26
SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, June 23, 1969

Uw ref.:

Onze ref.:

"Electric Field Effects in the ^{2}D Spectrum of Deutero-Nitrobenzene"

Dear Dr. Shapiro,

When an electric field is applied to a polar liquid the molecular electric dipoles tend to align themselves along the field. In competition with this effect the thermal motion disturbs the ordering, so that only a partial alignment results. Such an alignment may modify the N.M.R. spectrum since the dipole or nuclear quadrupole interactions do not average out completely. Several attempts have been made to detect the molecular alignment due to electric fields via the dipolar interactions by means of N.M.R., but they are a matter of controversy[1,2,3].

We have detected the quadrupolar electric field effect on the ^{14}N N.M.R. signal of polar liquids like nitrobenzene and nitromethane[4,5]. To make the experiment successfull strong electric fields had to be applied, up to 60 kV/cm. Also the electric conduction through the samples should be rigorously suppressed. This has been reached by application of electrodialytic membranes[5].

In this letter we report experiments on the ^{2}D-nuclei of deuterated nitrobenzene. The quadrupole coupling constant $e^{2}qQ/h$ in deuterobenzene is about 200 kHz[7] and the line-splittings expected are smaller (a factor 5 à 10) than those of ^{14}N nuclei. On the other hand the line widths are of the order of 1 Hz so that electric fields effects may well be detectable.

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, June 23, 1969.

Uw ref.:

Onze ref.:

If the magnetic- and the electric field are parallel, as was the case in our experiments, the induced line splitting $\Delta\nu$ is given by the following equation[6]

$$\Delta\nu \; \frac{3}{8} \; \frac{e^2qQ}{h} \; \langle 3\cos^2\theta - 1 \rangle_E \; (3\cos^2\alpha - 1) \qquad (1)$$

α is the angle between the molecular electric dipole moment $\vec{p}$ and the axis of the electric field gradient at the ^2D nuclei for which axial symmetry has been assumed; θ is the angle between the axis of the electric field gradient and the magnetic field. In nitrobenzene $\alpha_{para} = 0^\circ$, α_{meta} and $\alpha_{ortho} \simeq 60^\circ$.

^2D NMR spectra of deuterated nitrobenzene are reproduced in fig. 1. The spectrum of fig. 1a was recorded without an applied electric field using a normal high resolution sample tube. The low field line is attributed to the ortho-deuterons; the high field line to the para- and meta-deuterons. In fig 1b the same spectrum has been measured using the electric field sample cell[5]. The homogeneity is somewhat worse. The effect of applying an electric field of 43 kV/cm is shown in fig. 1c.

The angles α of the ortho- and meta deuterium nuclei are approximately 60° and the splittings caused by the electric field are accordingly small (see eqn. 1). Line splitting of the ortho- and meta deuteron signals have nevertheless been accomplished and was only limited by the magnetic field inhomogeneity caused by the sample cell

(compare fig. 1a and 1b). Due to their chemical shift difference a triplet is obtained (fig. 1c).

The lateral lines in fig. 1c result from the para deuteron. The splitting for this deuteron is expected to be the largest since $\alpha_{para} = 0$.

The quadrupole coupling constants of the nuclei may be somewhat different and for a known molecular geometry it should be in principle possible to evaluate these couplings constants from the electric field experiments. Reversily for a known molecular geometry and quadrupolar coupling constants it is possible to determine experimentally the direction of the molecular dipole moment with respect to the molecular frame.

The alignments $\langle 3\cos^2\theta - 1 \rangle_E$ of nitrobenzene have been determined as a function of the applied electric field[4,5]. The ^{14}N and ^{2}D electric field spectra are in agreement if the ratio $(e^2qQ)_{14N}/(e^2qQ)_{2D} = 5{,}46$. In nitrobenzene $(\frac{e^2qQ}{h})_{^{14}N} = 0{,}98$ MHz (deduced from ref. 8), which means that $(\frac{e^2qQ}{h})_{^{2}D} = 180$ kHz $\pm$ 10. This is in reasonable agreement with the result of Rowell at all[9] for deuterobenzene (192 kHz).

R. Gast C. Hilbers C. MacLean

---

1) Buckingham A.D. and McLauchlan K.A., 1963, Proc.chem.Soc., 144; Progress in N.M.R., Vol. II (Pergamon Press).

2) Macomber J.D., Ham N.S., and Waugh J.S., 1967, J.Chem.Phys., 46, 2855.

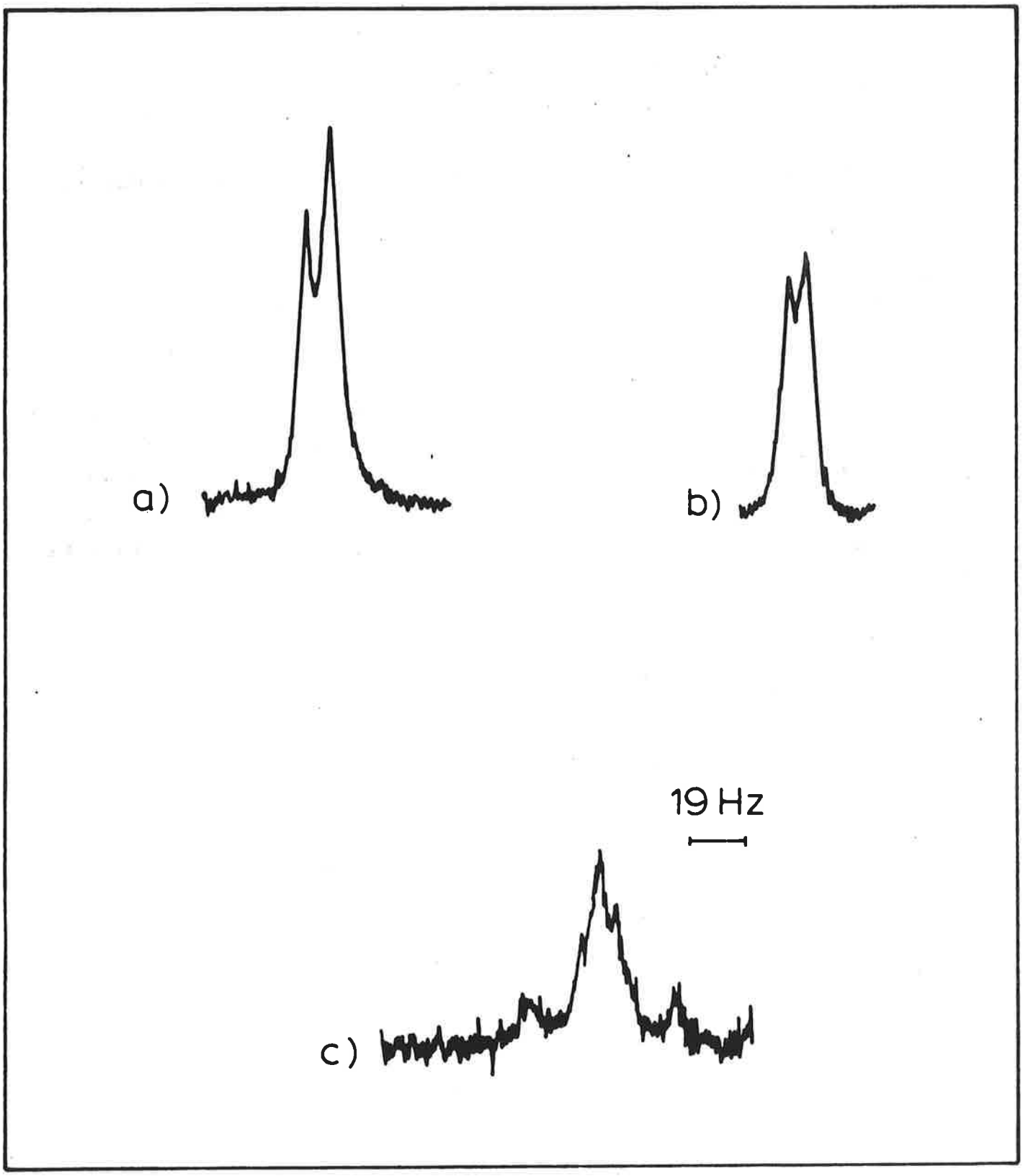
3) Sears R.E.J. and Hahn E.L., 1966, J.Chem.Phys., 45, 2753; Ibid., 47, 348.

4) Hilbers C.W. and MacLean C., 1968, Chem.Phys. Letters, 2, 445.

5) Hilbers C.W. and MacLean C., 1969, Molec. Phys., 16, 275.

6) Buckingham A.D. and Lovering E.G., 1962, Trans. Faraday Society, 58, 2077.

7) Rowell J.C., Phillips W.P., Melby L.R. and Panar M., 1965, J.Chem.Phys., 43, 3442.


a)
b)
19 Hz
c)

FROM THE DEPARTMENT OF INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY

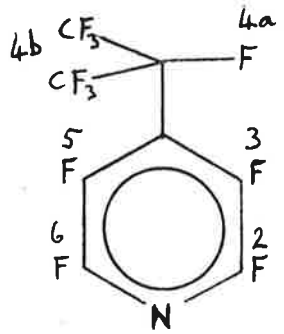
DONNAN LABORATORIES GROVE STREET P.O. BOX 147 LIVERPOOL L69 3BX TEL: 051 – 709 - 6022 EXT.

The University of Liverpool

The Signs of "Through-Space" F-F Coupling Constants

by L.H. Sutcliffe and G.J.T. Tiddy.

In conjunction with Professor W.K.R. Musgrave and Dr. R.D. Chambers, both of Durham University, we are studying some related perfluoroalkyl derivatives of fluoroaromatic compounds[1,2]. From a series of double irradiation experiments we have established the majority of signs and magnitudes of the F-F coupling constants. The simplest example will be given here, namely, perfluoro-4-isopropylpyridine:



J(2,3)	=	-21.0 c s^{-1}	J(3,6)	=	+30.2 c s^{-1}
J(2,5)	=	+29.0	J(4a,4b)	=	6.0
J(2,6)	=	14.0	J(4a,5)	=	0
J(3,4a)	=	+86	J(4a,6)	=	2.5
J(3,4b)	=	3.1	J(5,6)	=	-22.0
J(3,5)	=	8	J(4b,5)	=	+20.8

Assignments were made by making chemical shift comparisons with related compounds and by performing double irradiation experiments. The signs which were determined are based on the assumption that ortho F-F coupling constants are negative. It may be seen that the large four-bond

coupling constant J(3,4a) and the five-bond coupling constant J(4b,5) are both positive. Indeed, all the compounds we have studied in this series have positive F-F coupling constants when there is clearly a large "through-space" contribution. There is obviously a need to establish whether this contribution to fluorine-fluorine coupling is invariably positive.

1. R.D. Chambers, J.A. Jackson, W.K.R. Musgrave, L.H. Sutcliffe and G.J.T. Tiddy, Chemical Communications, 178 (1969).

2. R.D. Chambers, J.A. Jackson, W.K.R. Musgrave, L.H. Sutcliffe and G.J.T. Tiddy, Tetrahedron, in press.

130-32

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT
Albrecht Mannschreck

69 HEIDELBERG, Tiergartenstraße
Tel. 483/2411
bei Durchwahl 483/ 2433

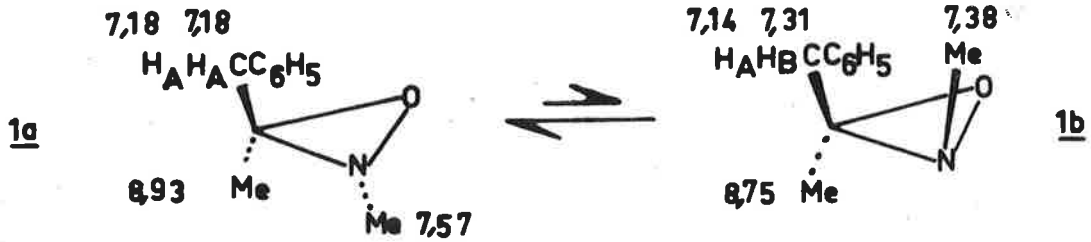
June 26, 1969

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

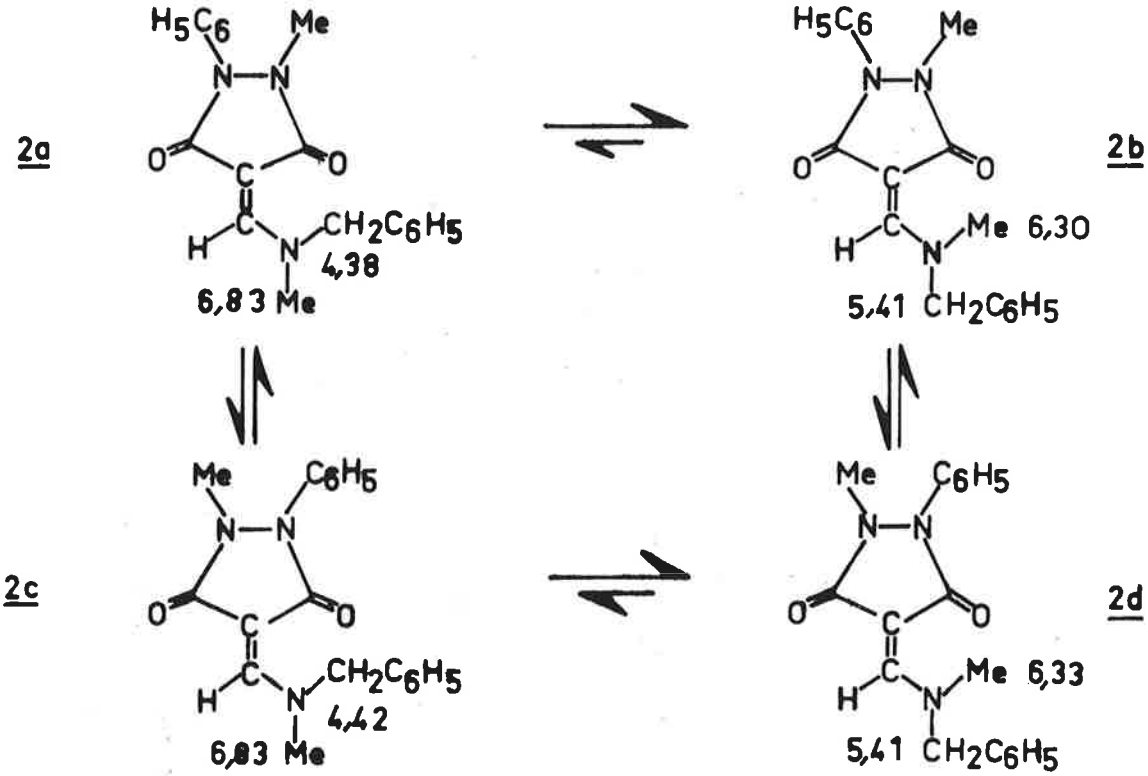
Diastereoisomers of an Oxaziridine. Diastereoisomers of an Enamine

Dear Professor Shapiro:

The first separation of the invertomers of an oxaziridine has been accomplished with 1a and 1b by Miss Linss and Mr.Seitz[1]. The compounds were assigned the structures shown, due to the fact that 1a predominated to the extent of 79% in the equilibrium which was slowly established in C_2Cl_4 solutions at 120°, no matter which invertomer was chosen as starting material. We were surprised by the extent to which 1a is favored. However, the isomer ratio of 2,3-dimethyl-3-benzyldiaziridine[2] proved to be quite similar. The above equilibration resulted in barriers as high as $\Delta G^{\neq}_{a}$ = 32.4 and $\Delta G^{\neq}_{b}$ = 31.4 kcal/mole. We conclude that inversion in these oxaziridines occurs more slowly than in any amine investigated to date. All measurements were performed by taking advantage of the spectral differences between 1a and 1b. The τ-values (benzene, 36°) are given with the formulae.



Mr.Koelle has identified the first enamines which are rotamers with respect to the =C-N bond[3]. He obtained a 1:1 mixture of 2b and 2d with a melting point of 130°. When equilibrated, the $CDCl_3$ solution at 13° contained 20% of both 2a and 2c as well as 30% of 2b and 2d. The time dependence of the isomer ratio resulted in $\Delta G^{\neq}$=21.3 kcal/mole for the =C-N ro-



tation 2b ⟶ 2a, whereas a lower $\Delta G^{\neq}$-value of 19.2 kcal/mole was measured by coalescence at 70° in $Cl_2CHCHCl_2$ for 2b ⟶ 2d, the corresponding motion at the C=C bond[4]. The C=C isomers are tentatively assigned the τ-values ($CDCl_3$, 30°) given with the formulae. The correlation of the C-N rotamers again rests on the above equilibrium, assuming that the steric interaction of the carbonyl group is less severe with N-Me than with $N\text{-}CH_2C_6H_5$.

Sincerely yours,

Albrecht Mannschreck

Albrecht Mannschreck

---

1) A.Mannschreck, J.Linss, and W.Seitz, Liebigs Ann. Chem., in press. Preprints available.
2) A.Mannschreck and W.Seitz, Angew.Chem. 81, 224 (1969); Angew.Chem.Internat.Edit. 8, 212 (1969).
3) A.Mannschreck and U.Koelle, Angew.Chem., in press. Preprints available.
4) Cf. Y.Shvo, E.C.Taylor, and J.Bartulin, Tetrahedron Letters 1967, 3259; A.Mannschreck and U.Koelle, Tetrahedron Letters 1967, 863.

130-34

DUQUESNE UNIVERSITY
PITTSBURGH, PENNSYLVANIA
15219

June 26,1969

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

Effect of Mercury(II) on the PMR Spectra of Cytidine

Dear Professor Shapiro:

Professor Norman C. Li, who is preparing to leave for Taiwan and Australia for the summer, has shown me your letter re the TAMU NMR NEWSLETTER, and has asked me to send you a contribution. I hope this will do.

Cytidine is a pyrimidine nucleoside, and in aqueous solution, the C_5-H, C_6-H and H_1' are doublets. Figure 1 gives plots of the C_5-H, C_6-H and H-1' frequencies (using t-butanol as internal reference at 60 MHz) vs. pH for solutions containing 0.2 M cytidine and the following concentrations of $Hg(NO_3)_2$: 0.049,0.10 and 0.15 M. It is seen that C_5-H moves downfield with increasing concentration of $Hg(NO_3)_2$. On the other hand, the C_6-H and the H-1' signals move upfield with increasing concentration of $Hg(NO_3)_2$. A plausible explanation of the shifts of C_5-H and C_6-H in opposite directions may be as follows:

Ts'o,Chan and co-workers[1] have reported that purine and pyrimidine nucleosides associate in aqueous solution by a mechanism involving vertical stacking of bases. The upfield shift of C_6-H and H-1' in cytidine in the presence of mercury(II) therefore may result from stacks which have a partially overlapped orientation so that the C_6-H and H-1' are both shielded. The C_5-H is close to the site of mercuration, the amino group or the N-3 atom, so that downfield shift is experienced. From the chemical shifts of C_5-H as a function the concentration of $Hg(NO_3)_2$, we are calculating the equilibrium constants for the formation of the 1:1 and 1:2 mercury-cytidine complexes.

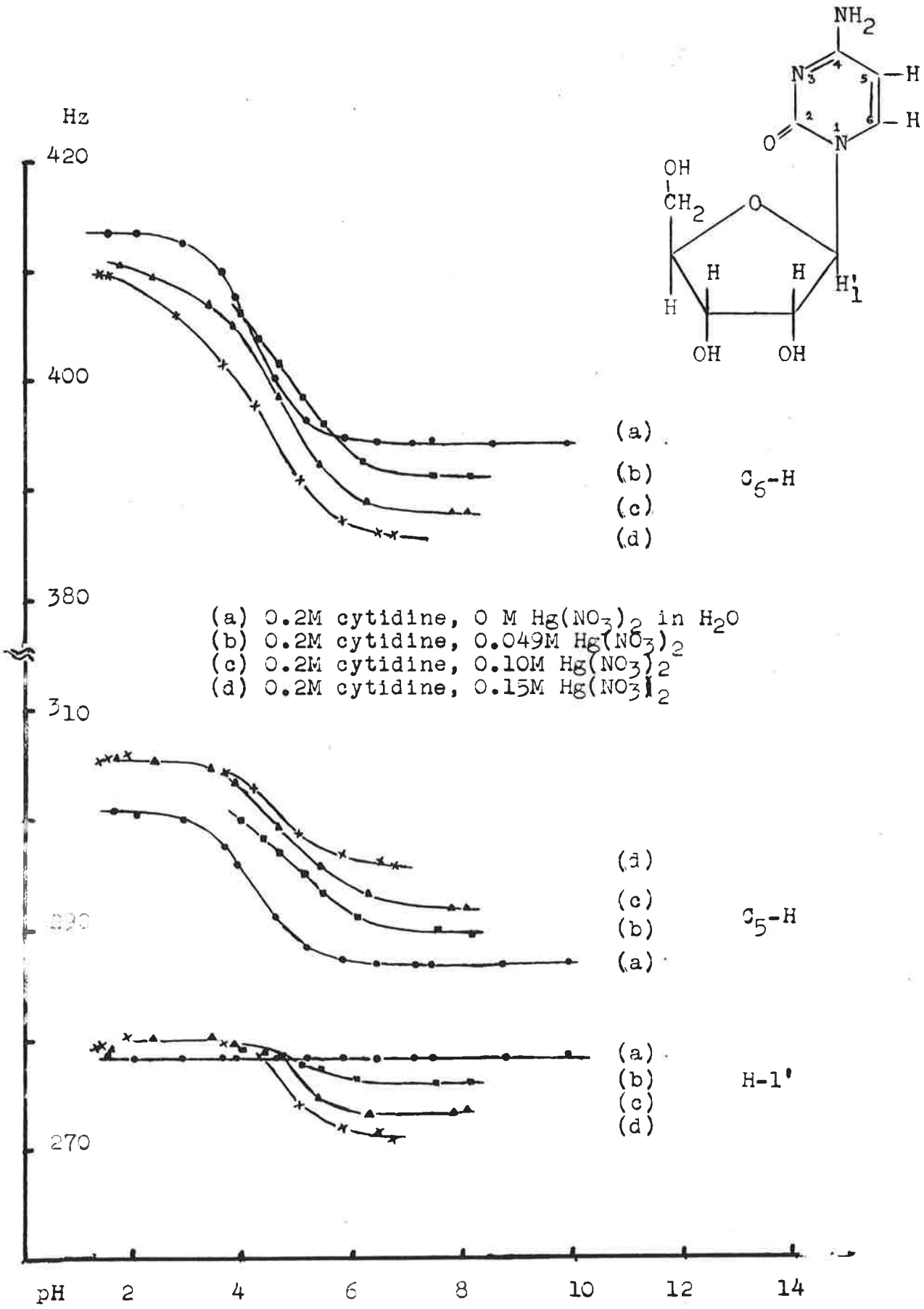
Sincerely yours,

K.C.Tewari

K.C.Tewari

Research Associate

(1) M.P. Schweizer,S.I.Chan,and P.O.P.Ts'o,J.Am.Chem.Soc., 87, 5241 (1965).


Hz
420
400
380
310
270
pH 2 4 6 8 10 12 14
(a)
(b)
(c)
(d)
C_5-H
(a) 0.2M cytidine, 0 M $Hg(NO_3)_2$ in H_2O
(b) 0.2M cytidine, 0.049M $Hg(NO_3)_2$
(c) 0.2M cytidine, 0.10M $Hg(NO_3)_2$
(d) 0.2M cytidine, 0.15M $Hg(NO_3)_2$
(d)
(c)
(b)
(a)
C_5-H
(a)
(b)
(c)
(d)
H-1'
NH2
N3
H
H
O
N
OH
CH2
O
H
H
H
H'1
OH
OH

Fysiska Institutionen, Uppsala 19 June 1969

Lineshape in High-resolution NMR: Relaxation and chemical exchange.

Dear Barry:

Last fall one of us (R.A.H.) wrote up an article on lineshape in high-resolution NMR that will appear in volume IV of Advances in Magnetic Resonance. The objective was to develop a formula $S = S(\omega)$ for the slow passage NMR signal amplitude S as a function of the frequency ω so as to obtain the spectrum as a single entity rather than as a list of transition frequencies, intensities and widths of the different lines.

Currently we are exploring the utility of this approach for investigating relaxation phenomena; in collaboration with colleagues at the chemistry department of the technical faculty in Lund we are furthermore investigating to what extent additional information on chemical rate processes might be obtainable by studying the lineshape in slow-passage spectra excited with strong rf fields.

The formalism is developed by the density matrix method of Bloch, Wangsness and Redfield aided by the concept of superoperators as discussed by Banwell and Primas. The final formula reads,

$$S(\omega) = i\gamma H_1 \, \mathrm{Tr}\{ F_+ \, \Omega^{-1} \, (F_+ - F_-) \} \qquad (1)$$

where Tr{} stands for the trace (diagonal sum or Spuhr) of the bracketed expression, F_+ and F_- are the well-known ladder operators of the resultant spin angular momentum:

$$F_\pm = F_x \pm iF_y \qquad (2)$$

γ is the gyromagnetic ratio of the nuclei studied, H_1 is the amplitude of the stimulating rf field and Ω^{-1} is the inverse of a superoperator Ω.

The superoperator Ω may be written:

$$\Omega = \Gamma + \lambda P - i\Lambda \quad , \qquad (3)$$

where Γ is the relaxation superoperator (whose matrix representative in the eigenbasis of the spin system is given by Redfield's relaxation matrix), λ is an arbitrary multiplier introduced to render Ω non-singular, P is a projection superoperator that projects any spin operator Q onto the identity operator $\hat{E}$:

$$PQ = Tr\{Q\}\,\hat{E} \qquad (4)$$

and Λ is the derivation superoperator generated by the rotating frame spin Hamiltonian <u>including</u> the stimulating H_1 field. The function $S(\omega)$ of eqn.(1) is complex, its real and imaginary parts correspond to the dispersion and absorption components, respectively, of the NMR signal.

In applications of eqn.(1) above, the formula is rewritten in a matrix representation and the problem of calculating the lineshape $S(\omega)$ reduces to the problem of inverting the matrix representative of Ω. The technique is thus essentially the same as that employed for lineshape analysis of spectra from systems undergoing chemical exchange, and allowance for exchange is readily made by the addition of an exchange superoperator to the relaxation superoperator Γ.

When saturation phenomena are negligible (i.e. within the domain of linear response) the dimensionality of the matrix inversion problem is given by the number of possible single quantum transitions (4X4 for a two-spin AB system, 15X15 for a three-spin system etc) but when the non-linear response is taken into account the matrix Ω is of order 4^N X 4^N for a system of N spins ‡ (16X16 for a two-spin system, 64X64 for a three-spin system etc.). Thus, the practical utility of eqn.(1) at present is restricted to spin systems holding no more than two or three spins. Theretically the formalism is more powerful inasmuch as appropriate perturbation expansions on the inverse superoperator Ω^{-1} allows one to re-derive the standard expressions for transition frequencies, intensities and widths in unsaturated spectra, or the so-called

direct analysis formulas of Banwell and Primas as well as Bloch's equations for the saturation of a simple line and Yatsiv's expressions for multiple quantum spectra. In small spin systems one may discard the perturbation methods, however, and perform the numerical calculations indicated by eqn.(1) directly on a digital computer; an advantage of this latter procedure is that one may evaluate all matrix elements in an arbitrary basis since the trace is the same in any representation.

So far we have obtained results for trans-1-Br-2-Cl-ethylene (I) and for monomethyl fumarate. Observed and calculated spectra for (I) are reproduced in Fig.1. The experimental[a] spectrum (center) was recorded with a sweep speed of 0.01 Hz/sec. at an rf amplitude of $\gamma H_1/2\pi = 0.177 \pm 0.003$ Hz, and saturation phenomena as well as a double quantum peak are clearly noticable. The leftmost[b] theoretical spectrum (displaced 2 Hz downfield for clarity) was calculated directly from eqn.(1) and the rightmost theoretical spectrum[c] was obtained from the former by convolution with a Lorentzian profile of 0.12 Hz width (full width at half height) to simulate instrumental line broadening.

Because the sample was doped with a paramagnetic relaxation catalyst, the relaxation mechanism was assumed to be one of random isotropic fields with parameters obtained by analysis of the saturated spectra. From very strongly saturated spectra the degree of correlation of the fields over the two protons could in fact be determined quite accurately and the correlation coefficient was found to have the value of 0.66 ± 0.03.

A slightly more detailed summary of our results has been written up as a preliminary report and may be obtained on request. We hope to have our experimental studies wound up for publication this coming fall.

Sincerely;

Bo Gestblom

Ragnar A. Hoffman

Institute of Physics
University of Uppsala
Box 530
751 21 Uppsala 1
SWEDEN

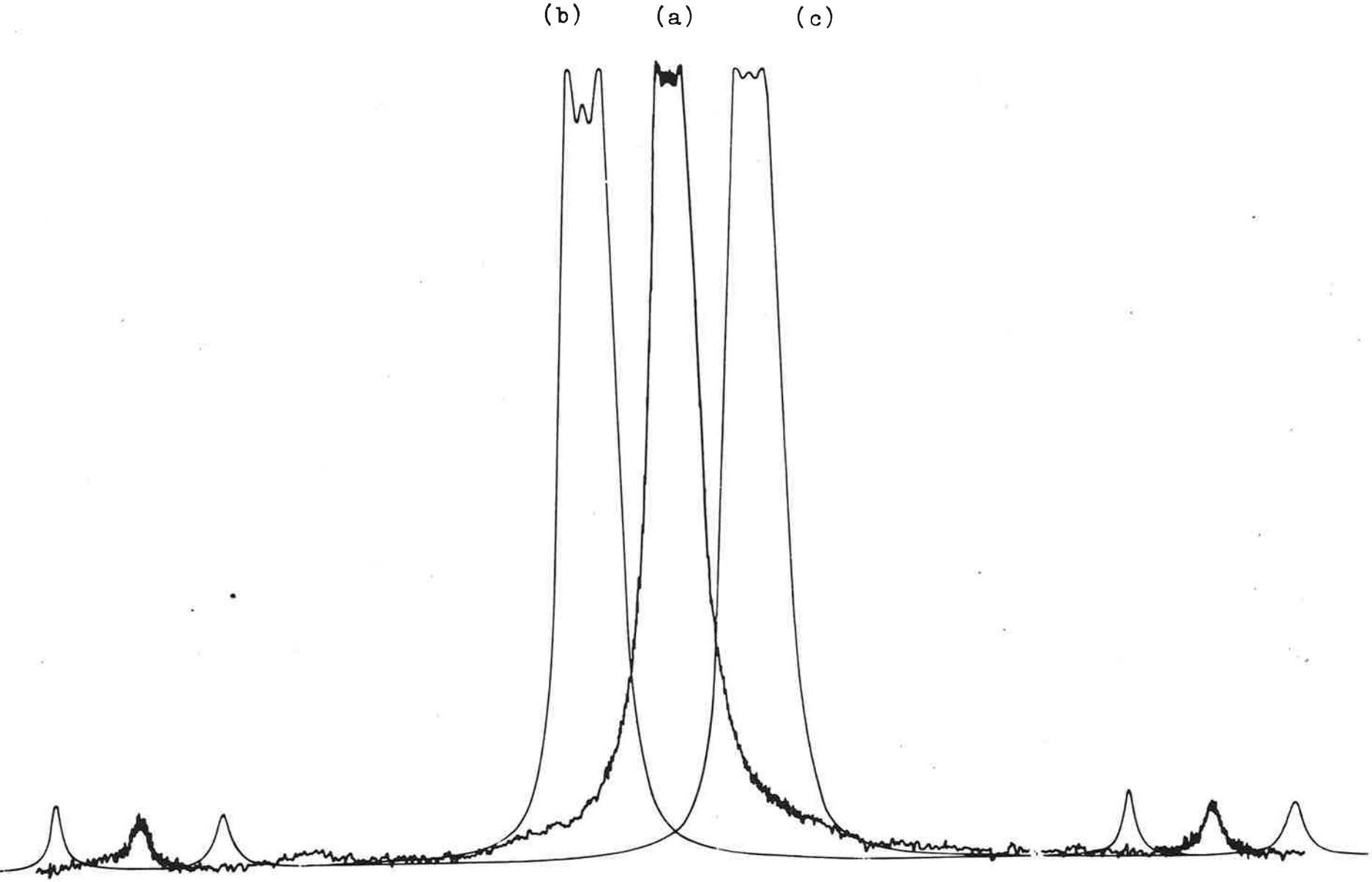


Fig. 1. Observed and calculated spectra of trans-1-Br-2-Cl-ethylene in C_6F_6 solution at 56.4 MHz. (a) experimental spectrum (center), (b) calculated spectrum (left) including only "natural" and saturation broadening and (c) right including a Lorentzian instrument width of 0.12 Hz.

STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

DEPARTMENT OF CHEMISTRY

STONY BROOK, N.Y. 11790

June 26, 1969

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

Dear Barry:

IBM 1800 Control of a Varian HR-100

We have recently coaxed into operation a system for partial control of our HR-100 spectrometer by an IBM 1800 computer. Since the ideas and techniques may be of some general interest in the NMR community, we are giving you a scoop for your eager readers before formal publication.

Our system has been saddled with the sobriquet CHEETAH, which might be an acronym for Computer Hickey* for Extended Experimental Time Averaging Haruspicy†, but actually derives from the common name of Acinonyx jubatus, a large "CAT" that can be trained to hunt.

The block diagram in Figure 1 shows the general organization of the system‡. Its operational principles are quite simple. The Operator sets up the spectrometer, using the Slow Sweep Unit in the normal way, until a satisfactory spectrum is obtained for any desired value of the sweep time. Data switches (to be replaced soon by a Teletype or equivalent) are then used to enter such

---

*"hick'ey (hik'i), n. A device or gadget;" Websters Collegiate Dictionary, 5th. ed., G. & C. Merriam Co., Springfield, Mass. (1948).

†"ha·rus'pi·cy (ha·rus'pi·si), n." Divination by entrails (ibid.) A reference to the intended use of the system to study the spectra of proteins and other sinuous biological molecules.

‡The IBM 1800 Computer configuration used by the present system has 16K of core, 1 tape drive, and 1 disc drive, and operates under the IBM TSX system, Version 3 Mod 6.

parameters as sweep time, rest period (between "Increase" and "Decrease" scans of the trapezoidal sweep), total number of scans, location of the "window" for the reference peak, and the parity and sign of the reference signal. The Slow Sweep Unit is switched to computer control, the program is called, and the operator goes home to bed. Meanwhile, the computer locates the highest peak in the reference window (when an odd multiplet or simple peak is used: with an even multiplet, such as a doublet, the average of the two highest peaks is used), and thereafter ensures, by flicking the Increase and Decrease switches on and off during the rest periods, that that peak will appear at the same place in each succeeding scan, despite whatever drifts may be occurring. Each spectrum is loaded onto a disk and then transferred to magnetic tape. The spectra on the tape may be added, deleted, trimmed, adjusted, filtered and generally fudged as necessary for a particular experiment, usually by using our IBM 360/67 computer, and recorded by a Calcomp plotter.

The whole CHEETAH system runs smoothly (even, in one case, when the Flux Stabilizer was mis-wired) except when some other 1800 user finds a way to "bomb" the system, (we time-share, of course, with other users in the Department) or when we are the victims of, in the immortal words of Donald H. Lemmon, a "Malicious Act of God". Even then, all data recorded prior to the disaster can be saved because they are kept on the magnetic tape.

We have used CHEETAH for ^{13}C and ^{59}Co spectra of liquids, and for ^{19}F spectra of solids. Figure 2 shows the result of a digital averaging run on the 59Co spectrum of an aqueous solution of ^{13}C enriched $K_3Co(CN)_6$. The total width of the spectrum is about 550 Hz. Spectrum b is the sum of 70 scans of 240 sec each; spectrum a is a single 240 sec scan. The system also works very well on the spectra of solids, if a sharp line from a liquid can be introduced as a reference. It scans any spectral width within the range of the Flux Stabilizer, and automatically acquires data for both increasing and decreasing sweep fields.

Many extensions and modifications are obvious. We shall shortly replace the modified C-1024 we use as an ADC with a couple of circuit boards, at about 1/50 the cost. The same scheme should work with a frequency sweep using a programmable synthesizer. Other computers, of course, could be used in the same way. If anyone should be interested in CHEETAH in her present configuration, we

shall shortly be able to supply program listings and a circuit diagram and parts list for the Slow Sweep Unit modification.

Keep TAMUNMRN coming!

Yours truly,

Paul

Paul C. Lauterbur

E. J. Runde

E. James Runde

PCL:st

Dear Paul:

I accept your invitation to scribble something to fill up the rest of this page. First, though, let me thank you for adding a little humor to the increasingly stodgy Newsletter!

I do not believe that Cheetahs can be taught to hunt, if I may push your analogy too far. However, I am told that the Cheetah is a famous go-go place, and was disappointed, therefore, not to see the rest of this page taken up by a picture of you - topless!

BLS

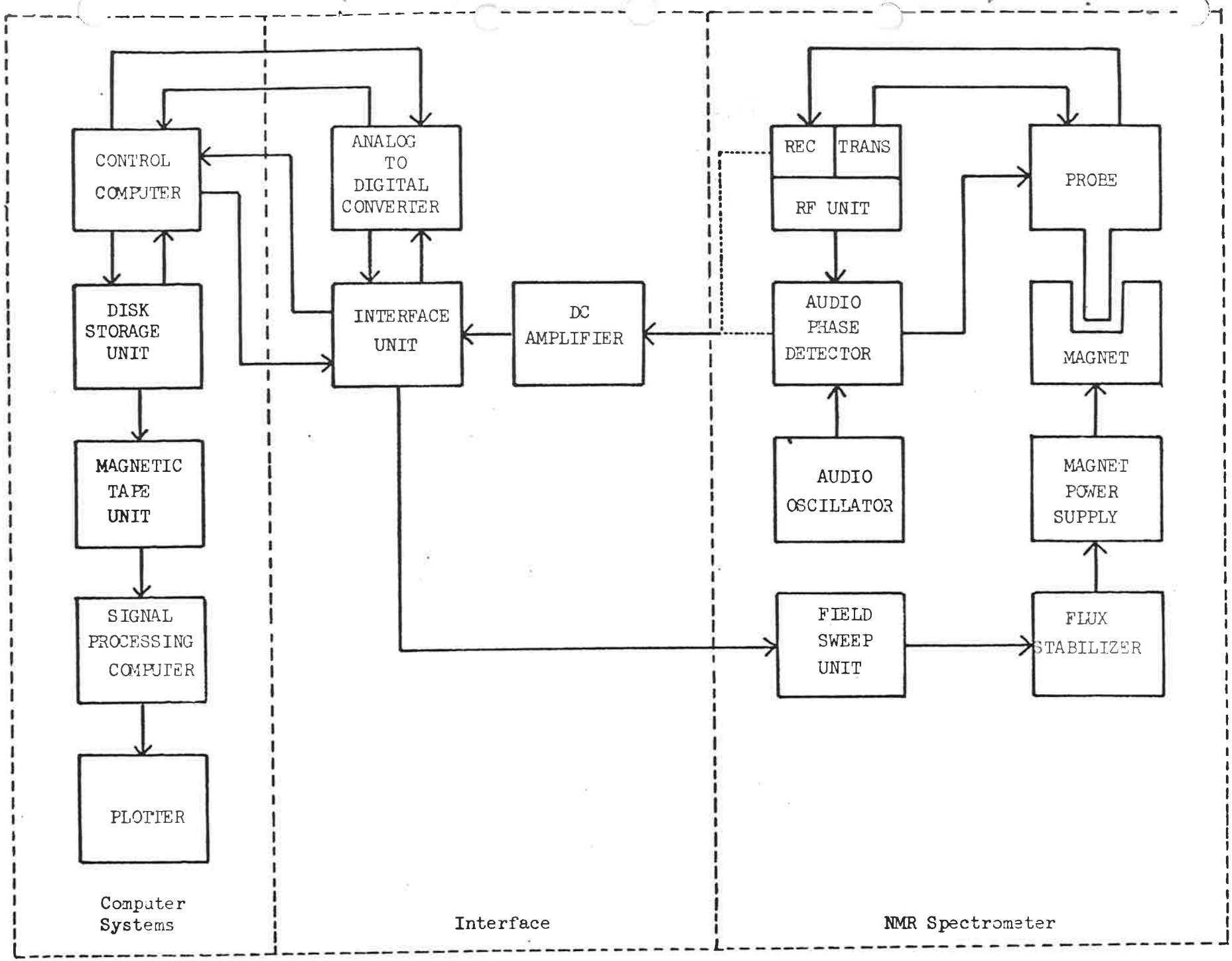


Figure 1

CHEETAH

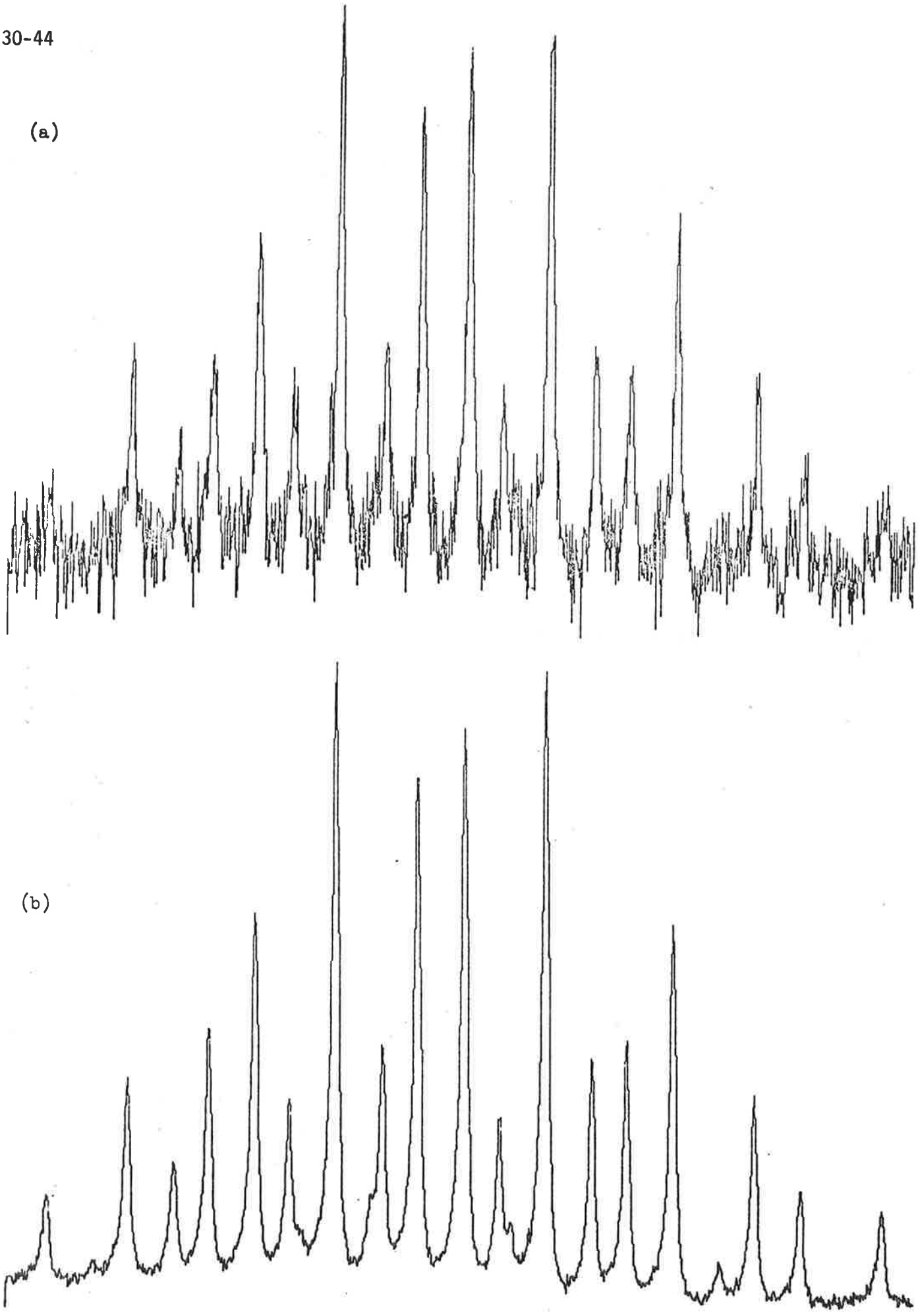


Figure 2

PERKIN-ELMER

THE PERKIN-ELMER CORPORATION
NORWALK, CONNECTICUT 06852
TELEPHONE: (203) 762-1000
CABLE: PECO-NORWALK

June 27, 1969

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

Title: Triple Resonance Experiments

Dear Barry,

We wish to report some triple resonance experiments which were performed to ascertain their utility to simplify interpretation and assignment of NMR spectra. The experiments were done on a Model R-20 equipped with two standard frequency-swept proton spin decouplers. Only a few "T" BNC connectors and a DC power source were required to connect the second decoupler to the spectrometer.

Figure 1 shows double and triple resonance experiments on crotonaldehyde. Irradiation of the methyl group gives the usual simplification of the vinyl proton resonances (middle scan). Irradiation of both methyl and aldehyde protons reduces the vinyl resonances further to a simple AB pattern. Coupling constant J_{bc} can be easily determined.

Figure 2 is a normal spectrum of exo-himic acid anhydride. The four upfield resonances are from the 7a and 7s protons, with complicated couplings to other protons.

The 7a proton is split into two triplets by geminal coupling with the 7s proton and vicinal coupling with the 1,4 protons. It is further split by long range coupling with the 5,6 protons. The coupling constant between 7a and 5,6 is almost the same as that between 7a and 1,4 which results in overlapping multiplets. These can be simplified by irradiation of the 5,6 protons with H_2 to produce two sharp triplets for the 7a resonance shown in trace 2 of Figure 3. By additional

irradiation the 1,4 protons with H_3 to produce triple resonance, the 7a resonance is reduced to the sharp doublets shown in trace 3 of Figure 3.

The 7s proton shows complex splitting because of vicinal coupling with 1,4 protons and long range coupling with 2,3 protons. If 1,4 protons are irradiated, the 7a, 7b pair is simplified (trace 4, Figure 3). The fine structure in the 7s doublet is barely detectable because the 7s-2,3 coupling constant is so small. When the 2,3 protons are irradiated, triplets in the 7s resonance from coupling with the 1,4 protons are easily seen (trace 5, Figure 3). However, when the 7s proton is also coupled to the 2,3 protons (trace 1, Figure 3) fine structure makes $J_{7s-1,4}$ more difficult to see. Trace 6 shows simplification by simultaneous irradiation of the 2,3 and 1,4 protons. Lack of fine structure in the 7s doublet indicates that decoupling of the 7s with all other protons except 7a is complete.

Sincerely,

Paul A. Strauss

James S. Swinehart

PAS/JSS/rb

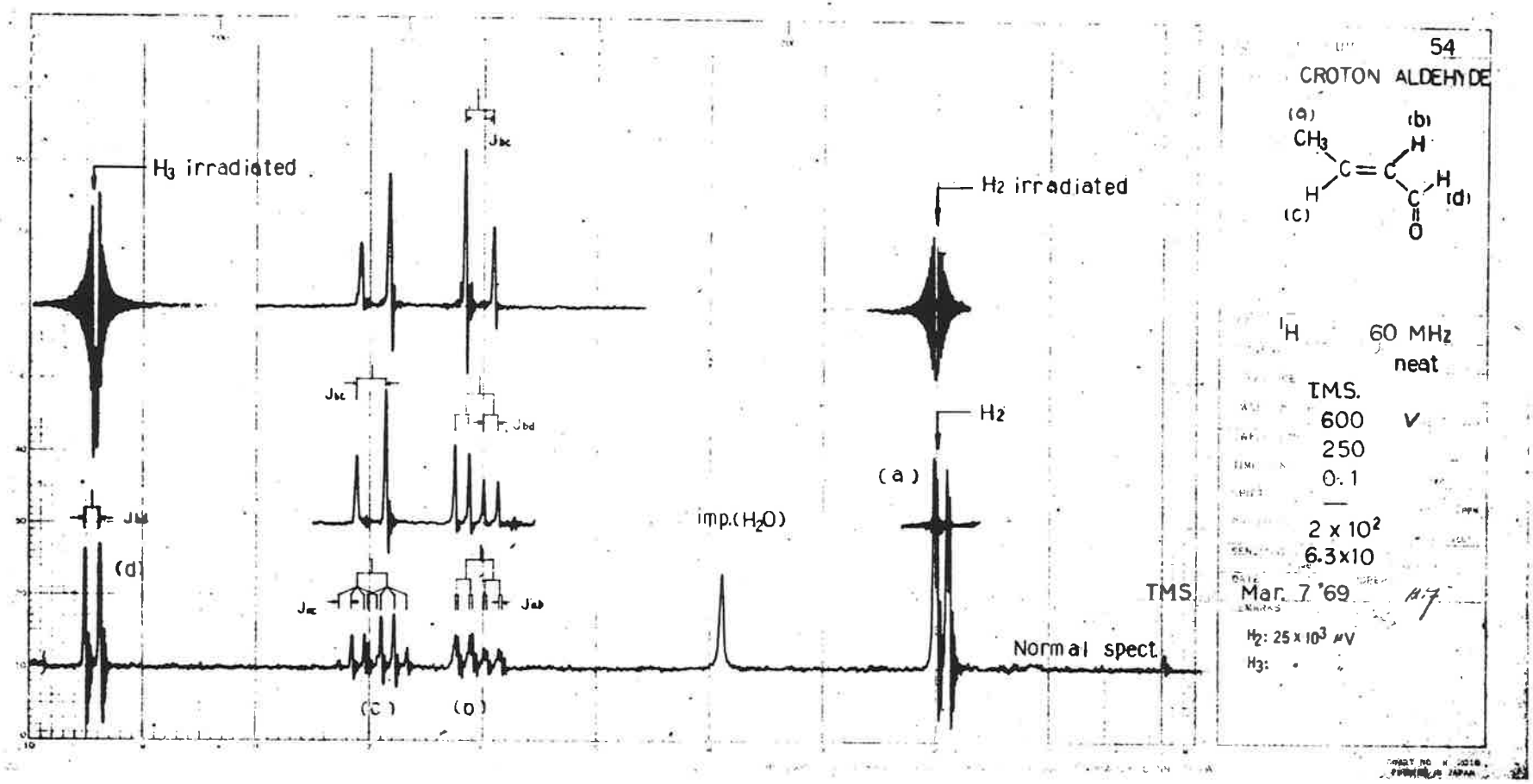

54
CROTON ALDEHYDE
(a)
(b)
(c)
(d)
^{1}H 60 MHz
neat
TMS.
600 V
250
0.1
—
2 x 10^2
6.3x10
Mar. 7 '69
H$_2$: 25 x 10^3 μV
H$_3$:
H$_3$ irradiated
H$_2$ irradiated
H$_2$
(a)
imp.(H$_2$O)
TMS
Normal spect.
(d)
(c)
(b)

Figure 1

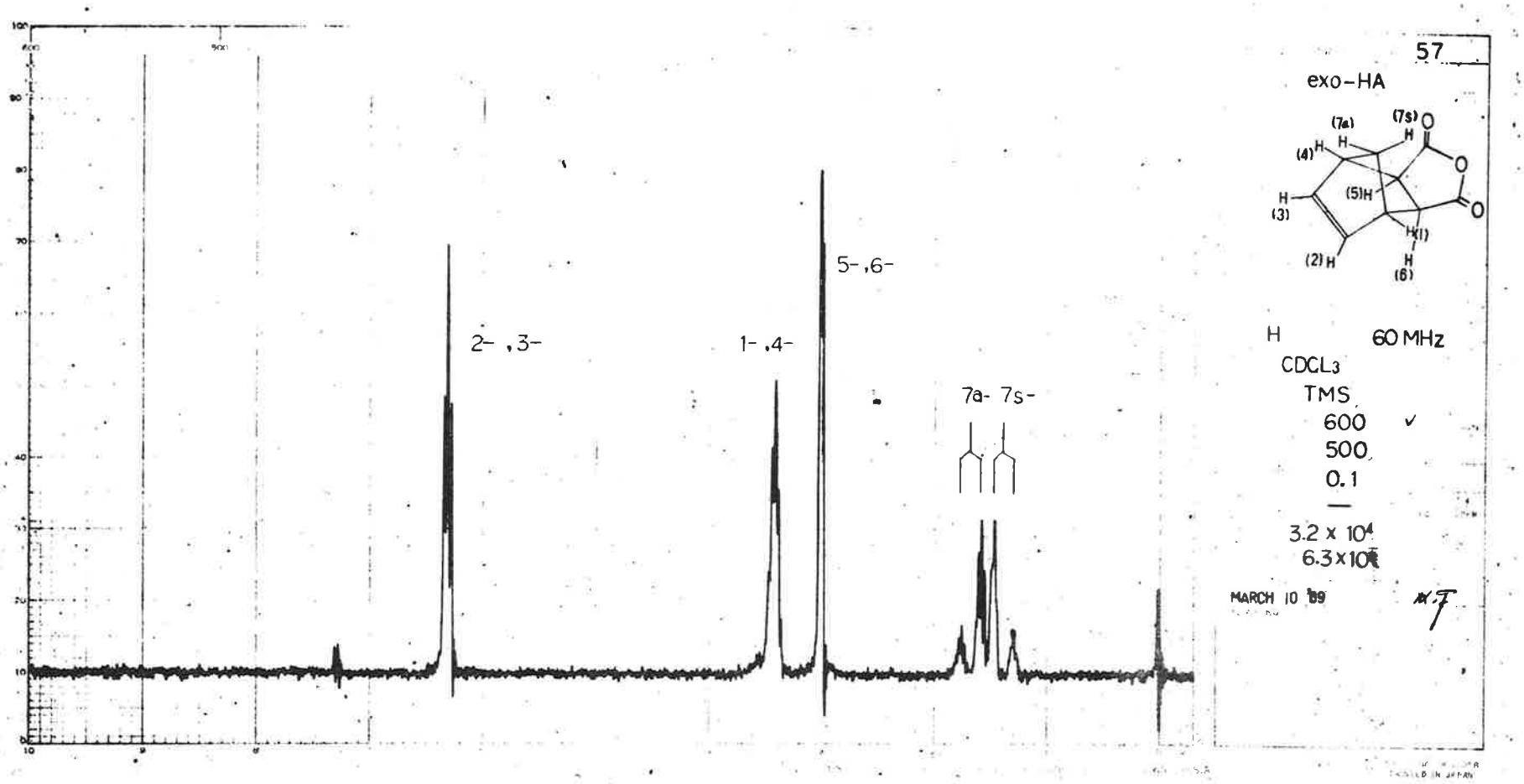

57
exo-HA
(7a)
(7s)
(4)
(5)
(3)
(1)
(2)
(6)
2- ,3-
1- ,4-
5- ,6-
7a- 7s-
H
60 MHz
CDCL3
TMS
600
500
0.1
3.2 x 10⁴
6.3x10⁴
MARCH 10 '89

Figure 2

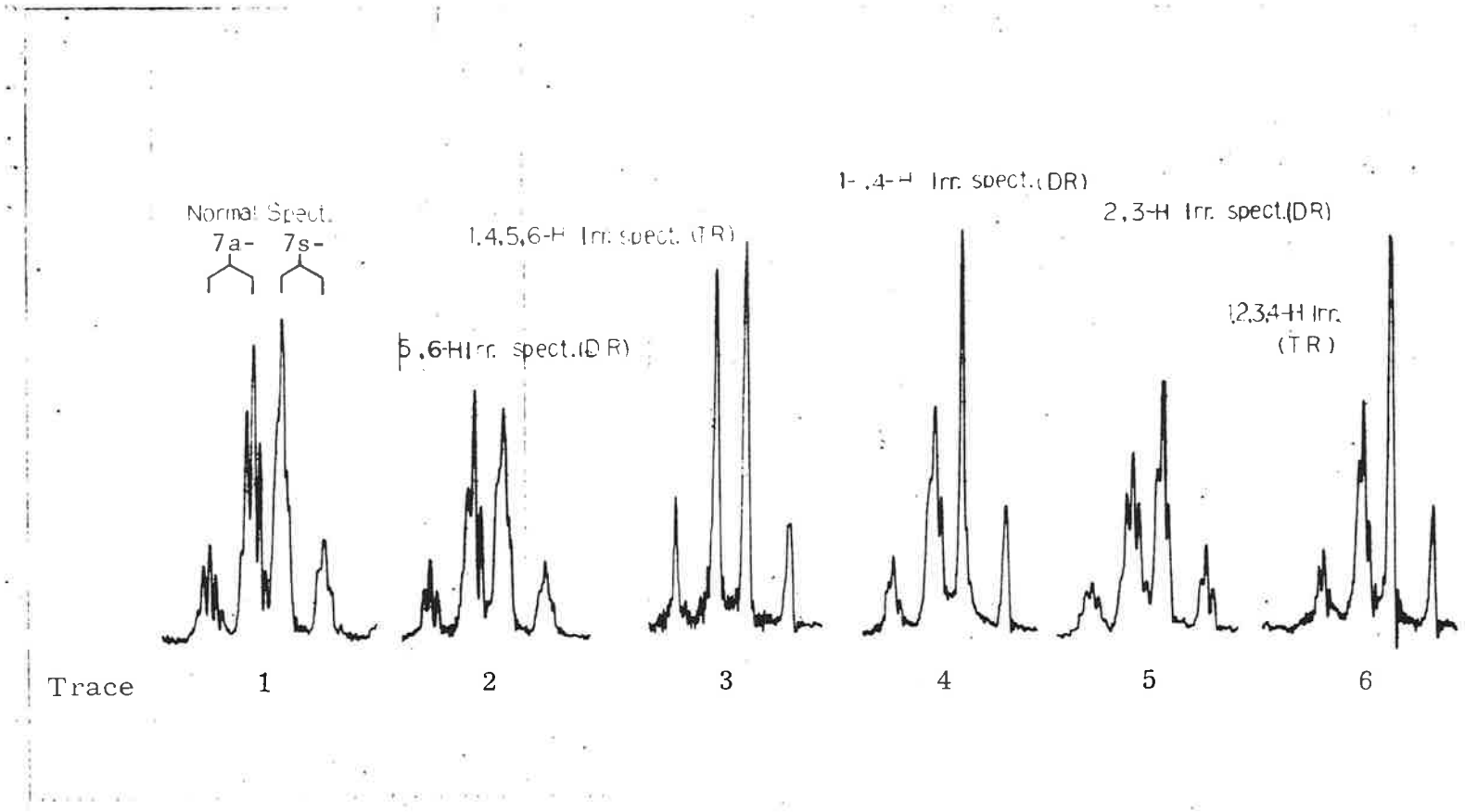

Normal Spect.
7a- 7s-
1,4,5,6-H Irr. spect. (TR)
5,6-H Irr. spect.(DR)
1-,4-H Irr. spect.(DR)
2,3-H Irr. spect.(DR)
1,2,3,4-H Irr.
(TR)
Trace
1
2
3
4
5
6

Figure 3

Author Index - TAMU NMR Newsletter No. 130

Barfield, M.	22
Becconsall, J.K.	4
Berlin, K.D.	15
Dickson, F.E.	20
Elguero, J.	1
Fruchier, A.	1
Gast, R.	26
Gestblom, B.	36
Günther, H.	12
Happe, J.	8
Hilbers, C.	26
Hoffman, R.A.	36
Holder, B.	8
Kanski, E.L.	16
King, R.W.	21
Lauterbur, P.C.	40
MacLean, C.	26
Maddux, A.	8
Mannschreck, A.	32
Marr, D.H.	16
Martin, J.C.	7
Moriarty, R.M.	10
Pawliczek, J.B.	12
Runde, E.J.	40
Schaefer, T.	19
Smith, W.B.	6
Stirling, C.J.M.	10
Strauss, P.A.	45
Sutcliffe, L.H.	30
Swinehart, J.S.	45
Tewari, K.C.	34
Tiddy, G.J.T.	30
Ward, R.	8

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