

Texas
A
M[&]
University
N - M - R
Newsletter

No. 128
MAY, 1969

Dowden, B.F.; Lusebrink, T.R. Varian HA-100/IBM 1800 Interface; Difficulties in Obtaining the Correct Solution for an ABCD System	1
Olah, G.A.; Jewell, C.L.; White, A.M. ¹³ C INDOR; Shifts in Cumyl Cations	4
Dürr, H. Konformationsisomerie von Tetraarylsubstituierten Cyclopenten	6
Banas, E.M.; Wenzel, B.E.; Croteau, P.G.; Dinerstein, R.A.; Slupski, D.J. Varian HR-52 NMR Spectrometer Conversion to DA-60-IL System	11
Lambert, J.B.; Oliver, W.L. Jr. Conformation of the Phosphorus Analogue of Piperidine; Heteronuclear Decoupler and Integrator/Decoupler for Sale	12
Reuben, J. On the Distinction between Transverse and Longitudinal Electron Relaxation Times	14
Carey, P.R.; Turpin, M.A.; Kroto, H.W. Reconsideration of CFC1 ₃ as a Reference Signal	16
Parmakovich, V. Modification on the 2200B Power Supply	18
Mavel, G. Coupling Mechanisms in Unsaturated Phosphorus Compounds	20
Krüger, U.; Hettler, H. Anisotropy Effects on Shifts in N-substituted 3-amino-benzisothiazole-S-dioxides	23
Randall, E.W. Postdoctoral Fellowship	26
Jones, A.J.; Grant, D.M. A Campaign for TMS and Positive Chemical Shifts in the Direction of Increasing Frequency or Why Not Logic?	27
Saika, A. Magnetic Anisotropy in the Acetylene Molecule	28
Vold, R.L. Analysis of NMR Spectra with Chemical Exchange and Quadrupole Relaxation	30
Lunazzi, L. P.M.R. Investigation on the "syn" and "anti" Isomerism in Aromatic Sulphines	32
Sewell, M.J. Hindered Rotation and Long-range Proton-fluorine Coupling (5-bonds) in N-trifluoroacetyl Compounds	34

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.

O V E R

Ramey, K.C. NMR Studies of Bridged Polycyclic Compound	35
Bennett, J.; Maire, J.C.; Vignollet, Y. PMR Determination of SiMe_3 Group Electronegativity - One More Linear Correlation	38
Connor, T. Molecular Motions in Urea- d_4 Adducts T_1 and $T_{1\rho}$ Measurements	40
Lustig, E. Operating Instructions for the A-60/C-1024 Combination	41
Willcott, M.R. Deuterium Decoupling: An Aid to the Determination of the Structure of Several Deuterated Vinylcyclopropanes	42
Haigh, C.W. Notation for Spin Systems	44
Brey, W.S. Jr. Broadband Homonuclear Decoupling	50

<p>Deadline Dates: No. 129: 2 June 1969 No. 130: 1 July 1969</p>
--

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

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



2670 Hanover Street
Palo Alto, California 94304
415/327-2300

International Business Machines Corporation

March 27, 1969

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

Dear Barry:

We have recently interfaced our Varian HA-100 to an IBM 1800 computer operating under a time sharing monitor for spectroscopic type experiments (1). At the present time the interface is minimal and we merely use the computer to digitize the high resolution spectra for off-line analysis. The system is also capable of performing time averaging experiments under computer control.

An INDOR kit purchased from Varian AG (2) has also just been installed. The installation is very easy and it is a very simple matter to perform excellent INDOR experiments.

While testing ASSIGN on an ABCD system (2-Cyanopyridine), we obtained some results which point out the hazards of assuming that an excellent match of calculated and experimental spectra signify that the correct NMR parameters have been found. This was originally discovered when using a "spectrum" calculated from published parameters (3). A total of eight assignments were found, one, of course, giving essentially a perfect fit. However, three additional assignments were close enough so that it seemed that if one had iterated to any one of them, that assignment could be considered a satisfactory solution, especially if an experimental spectrum had been used for the original data. Accordingly, we ran a slow sweep spectrum at 100 MHz and used DECOMP to find the line positions and intensities. These experimental values were then used by ASSIGN to find all the assignments consistent with frequency and intensity sum rules using tolerances suitable for the experimental spectrum. Again, several assignments were found, 4 of which were virtually indistinguishable in so far as goodness of fit is concerned. A line by line comparison of the observed and calculated frequencies and intensities showed none of the assignments to be preferable over the others.

To conserve space I have not shown the entire output, however, the parameters and statistical data are shown below:

Two Assignments for 2-Cyanopyridine

	Assignment 1	Assignment 6
1	-863.047	-863.047
2	-751.651	-751.626
3	-766.822	-766.824
4	-784.803	-784.824
12	-4.78	-4.75
13	-0.96	-0.97
14	-1.74	-1.76
23	-1.20	1.52
24	-7.74	7.51
34	-7.73	-7.78
Sum of squares of residuals	0.00012	0.00082
Sum of squares of energy level errors	0.0054	0.0053
Average frequency deviation	0.020	0.021
Average intensity deviation	0.085	0.086
Largest frequency deviation	0.069	0.066
Largest intensity deviation	0.304/1.4 (Peak height)	0.261/1.5 (Peak Height)

Assignment 1 is correct as verified by tickling experiments and assignment 6 can be seen to be almost equally as good not only in the sum of the squares of residuals and energy level errors but in the averages of frequency and intensity deviations. In fact it can be seen that the largest frequency and intensity deviations occur in the correct assignment. From the above comparison it is likely that one would consider the first of these assignments he obtained as correct unless he had additional information to the contrary. Even if all possible assignments are available, it is still not possible to choose the correct assignment without more experimental data.

This additional information could be prior knowledge about the type of system, eg. the relative signs of the coupling constants in the pyridine system, if such information were available. In the general case, however, it would seem desirable to be able to carry out the entire analysis on the basis of a self contained set of experiments. One way to do this would be to carry out a double resonance tickling, INDOR, or Torrey oscillation experiment. Another way might be to run the spectrum at a second frequency and compare with the

Prof. B. L. Shapiro

Page 3

March 27, 1969

spectra calculated at that frequency using the parameters obtained at the first frequency. A test of this latter approach was made by using the parameters for the two assignments to calculate two 60 MHz spectra. Although the spectra are quite similiar in appearance, it should be possible to select the correct one by comparison at 60 MHz even though it would not be possible at 100 MHz.

Sincerely yours,

B. F. Dowden
B. F. Dowden
IBM Research
San Jose, Calif.

T. R. Lusebrink
T. R. Lusebrink
IBM Scientific Center
Palo Alto, Calif.

TRL:BFD/cp

1. H. M. Gladney, J. Comp. Physics, 2 255 (1968)
2. U. Scheidegger, TAMUNMR 126 p. 28
3. V. J. Kowalewski & D. G. de Kowalewski, J. Chem. Phys., 37 2063 (1962)

Subjects: Varian HA-100/IBM 1800 Interface
Difficulties in Obtaining the Correct Solution for an ABCD System

April 7, 1969

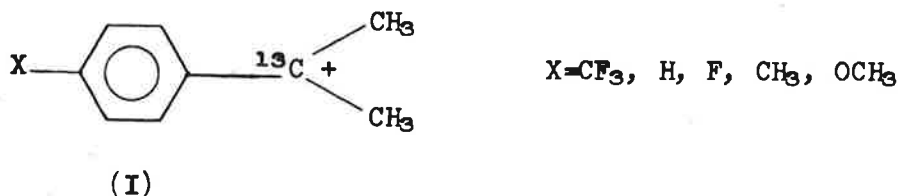
Professor Bernard L. Shapiro
Texas A&M University
Department of Chemistry
College Station, Texas 77843

Dear Barry:

^{13}C INDOR. Shifts in Cumyl Cations.

We have recently obtained a Monsanto 3100A Digital Frequency Synthesizer and as an initial application have adapted it for ^{13}C Indor operation on the HA100. Obtaining the variable irradiating frequency (25.15 MHz) proved to be a particularly simple operation since 26 MHz is available internally from the synthesizer. Mixing this with the variable 0-1.2 MHz output provides the desired irradiating frequency. We are currently driving the synthesizer with the voltage ramp output of a C1024 although we plan to go over to digital programming sometime in the near future.

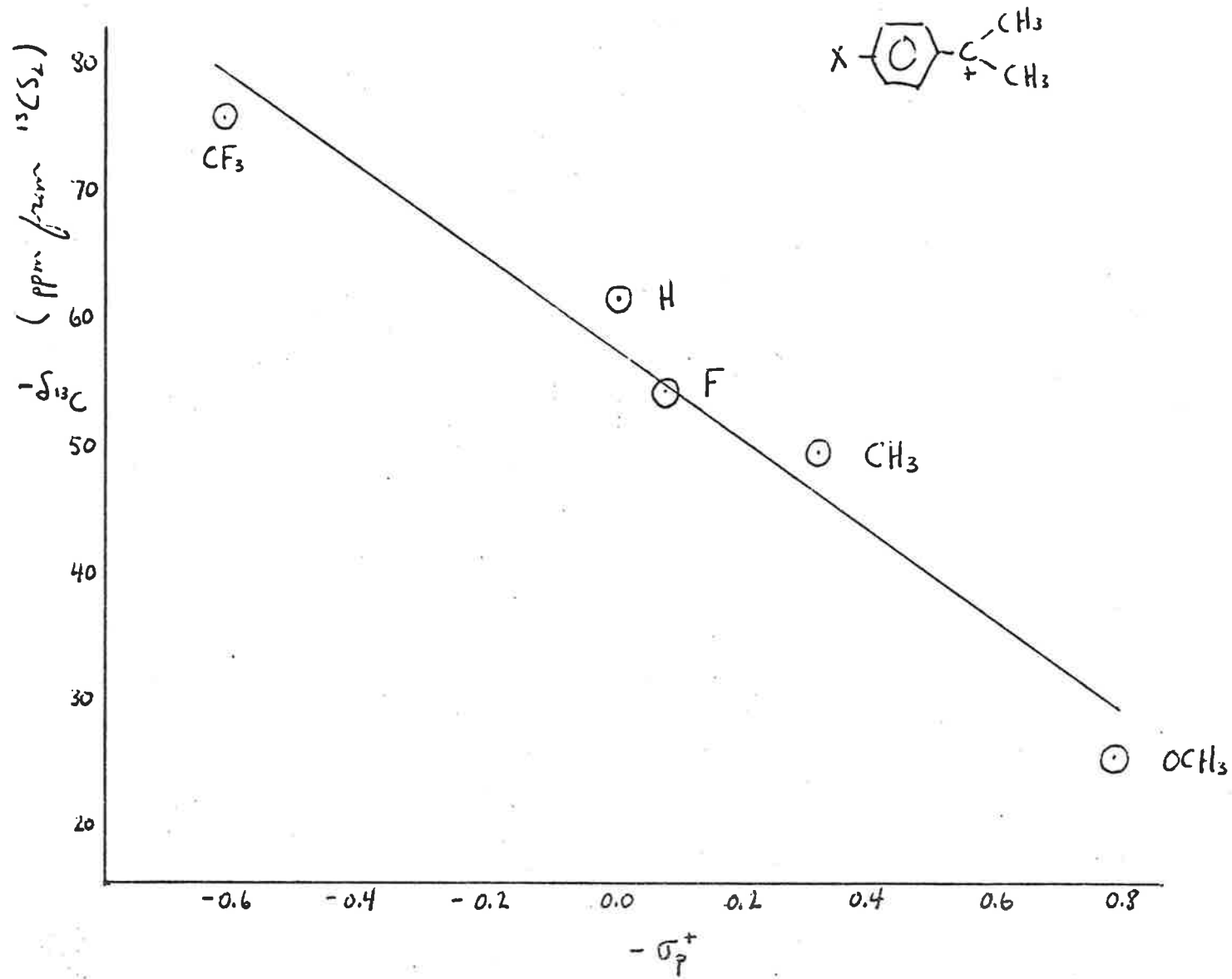
One of the ^{13}C projects underway at the present time is an investigation of the effect of para-substitution on the shifts in cumyl cations (I). These were generated from the corresponding chlorides or alcohols in $\text{SbF}_5\text{-SO}_2$ solution, ^{13}C Indor spectra being obtained at -60° using the satellites of the methyl proton resonance (the long-range coupling, J_{CCH} is about 6 Hz). The substituents so far examined give a



spread of ^{13}C shifts of 50 ppm and are correlated best with σ_p^+ substituent constants derived from solvolysis of the corresponding cumyl chlorides (see Figure). This in our minds, provides some justification for the assumption that the electronic requirements of the solvolysis transition state resemble those of the intermediate carbonium ion.

Yours sincerely,


G. A. Olah
C. L. Jewell
A. M. White

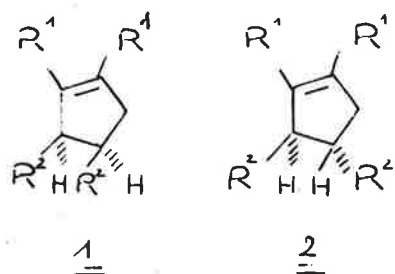


To
Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Konformationsisomerie von tetraarylsubstituierten
Cyclopenten

Dear Dr. Shapiro,

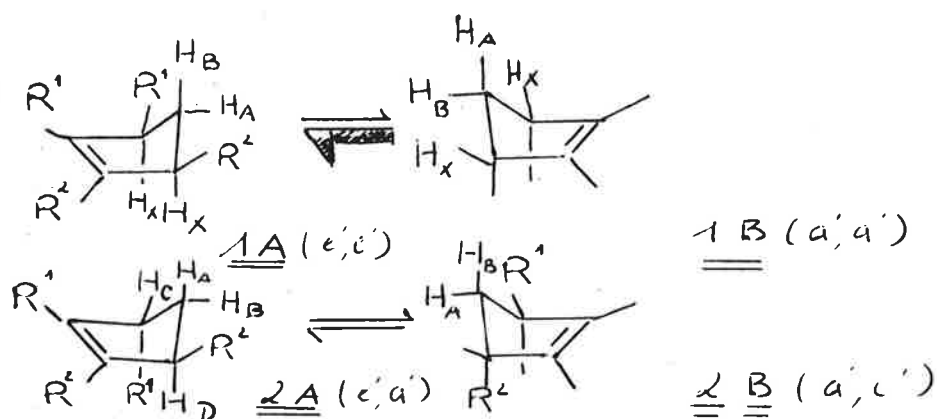
Die Photolyse von tetraarylsubstituierten Bicyclo[3.1.0]hexenolen führt zu den Tetraaryl-Cyclopenten 1 und 2(1,2).



	a	b	c	d	e
R ¹	∅	Py	∅	∅	∅
R ²	∅	Py	C ₆ H ₅	C ₆ H ₅	∅

∅ = C₆H₅, Py = 2-pyridyl
e = H_x = D

Diese können in zwei verschiedenen Konformationen A und B, begründet durch den nicht-ebenen Bau des Cyclopenten-Ringes(3), vorliegen, und zwar sind je zwei Konformere für cis-1 und trans-2 möglich:



Im Falle von cis-1 sind die beiden Konformeren 1A und 1B nicht

energiegleich, d.h. die großen Phenylsubstituenten sollten ausschließlich in der quasi-äquatorialen Stellung 1-A (e', e') stehen. 1-A sollte praktisch als einheitliches Konformeres auftreten. Bei trans-2 sind die beiden Konformere 2-A und 2-B praktisch energiegleich, so daß beide Konformere existent sind.

Die Klärung dieser beiden Probleme erlauben die NMR-Spektren von 1 und 2, die in Tab. 1 und 2 wiedergegeben sind.

Die Spektren der Cyclopentene 1 und 2 sind als 4-Spin-Systeme recht komplex und zwar sind sie von ABX_2 - oder ABCD-Typ.

Problem a) kann relativ einfach mit Hilfe des NMR-Spektrums von 1b (ABCD- bzw. ABXY-Typ) entschieden werden, da in diesem zwei verschiedene Methin-Signale als Triplets bei $\tau=5.36\text{ppm}$ (H_C) und bei $\tau=5.02\text{ppm}$ (H_D) mit Kopplungskonstanten von $^3J_{AC}=8.0$ und $^3J_{AD}=9.0$ Hz vorhanden sind. b) Die cis-Cyclopentene 1 liegen - wie weiter oben betont - als einheitliche e', e' -Konformere vor und ergeben NMR-Spektren vom ABX_2 - (1a, c) oder ABXY-Typ (1b). Wie eine genaue Rechnung zeigt, können diese Spektren noch 1. Ordnung analysiert werden (die Abweichung im AB-Teil beträgt lediglich $\approx 0.01\text{ppm}$ bei der Berechnung der chemischen Verschiebung).

Aus den vicinalen Kopplungskonstanten von $^3J_{AX}=6.1$ und $^3J_{BX}=9.1$ Hz läßt sich mit der Karplus-Gleichung (4):

$$J = \begin{cases} 8,5 \cos^2 \varphi & \text{für } 0^\circ \leq \varphi \leq 90^\circ \\ 9,5 \cos^2 \varphi & \text{für } 90^\circ \leq \varphi \leq 180^\circ \end{cases}$$

der Dieder-Winkel zwischen den koppelnden Protonen zu $\varphi \approx 13^\circ$ ($H_A-C-C-H$) und $\varphi \approx 132^\circ$ ($H_B-C-C-H_X$) abschätzen. Die beiden Phenylkerne in 2.5-Stellung sollten durch ihre relative Elektronegativität keinen großen Einfluß auf die vicinalen Kopplungskonstanten aufweisen.

Einen interessanten Effekt beobachtet man bei 1b. Die Methin-Triplets sind hier noch weiter aufgespalten, und zwar näherungsweise in Dubletts. Diese Aufspaltung kommt durch eine Homallylkopplung der chemisch nicht äquivalenten C_6H_5-C-H - und $Py-C-H$ -Protonen über 5-Bindungen zustande. Die Kopplungskonstante von $^5J=2.5$ Hz ($H-C-C=C-C-H$) ist in der Größenordnung für analoge Systeme (5).

Die Zuordnung der Signale zu den entsprechenden Protonen bei 1 wird durch ein Spinentkopplungsexperiment gestützt. So kann in 1a durch Sättigung des Kerns X ($\nu_X - \nu_B = -71$ Hz) das Signal des Protons B zu einem Dublett ($^2J=13,5$ Hz) vereinfacht werden. Wird Kern B gesättigt, ($\nu_B - \nu_A = -68,5$ Hz), so wird Proton A zu einem Triplet ($^3J=8$ Hz) entkoppelt.

Die trans-Cyclopentene 2 (Tab. 2) ergeben wesentlich komplexere NMR-Spektren als cis-1, da in 2 das Spin-Muster in einem ABCD-Typ übergeht, herrührend von der geringeren Differenz der chem. Verschiebung der beteiligten Kerne. So zeigt das Spektrum von 2b zwei verschiedene Methin-Protonen H_C und H_D bei $\tau=5.24$ ($^3J=6.5$ und $^5J=2.5$ Hz) und 4.83 ($^3J=6.5$ und $^5J=2,5$ Hz) als Triplets mit einer Feinstruktur, herrührend von der 5J -Homo-allylkopplung (5). Die Methylenprotonen H_A und H_B fallen in ein komplexes Multiplett bei $7.7-6.8$ ppm zusammen. Ein Spektrum bei 220 MHz (6) ergibt eine Aufspaltung des H_A - und H_B -Protons in zwei Multiplette bei 7.41 und 7.18 ppm.

Was bedeutet nun dieses Resultat in Bezug auf das Konformergleichgewicht 2 A \rightleftharpoons 2 B?

Wäre die Gleichgewichtseinstellung 2 A \rightleftharpoons 2 B sehr schnell, d.h.

$$k = \frac{1}{\tau}$$

k = Umklappgeschwindigkeit
A \rightleftharpoons B

τ = Lebensdauer von A bzw. B

k sehr groß, so müßte ein Mittelwertsspektrum beobachtbar sein, d.h. ein Triplet für H_D und H_C und ebenfalls ein Triplet für H_A und H_B .

Die Lebensdauer τ der einzelnen Konformeren 2 A und 2 B ließe sich bei einem Abstand der beiden Linien der Methylen-Protonen vom $\nu_A - \nu_B$ (bei 220 MHz) mit Hilfe der Gleichung:

$$\tau = \frac{\sqrt{2}}{2(\nu_A - \nu_B) \pi} \quad (\text{sec})$$

abschätzen. Diese Methode ist jedoch nur erlaubt für $R^1=R^2$ also für 2a. Bei 2b müssen H_A und H_B stets eine verschiedene Verschiebung aufweisen, so daß hier keine Aussage für τ möglich ist.

Yours sincerely


(Dr. Heinz Dürr)

Tab. 1: NMR-Spektren der tetrasubstituierten Aralkyl-cyclopentene 1 ($\tilde{\nu}$ in ppm; J in Hz)

Verbindung	Solvens	H _A	H _B	H _C H _X	H _D H _Y	arom. Protonen übrige Protonen		
<u>1a</u>	CDCl ₃	7.87 (² J _{AB} =13.5) (³ J _{AX} = 8.0) doppl. t 1H	6.81 (³ J _{BX} =9.0) doppl. t 1H	5.53 (³ J=8.5) t 2H	-	2.97 10H	2.71 10H	
<u>1b</u>	CDCl ₃	7.71 (² J _{AB} =13.0) (³ J _{AD} = 8.0) (³ J _{AC} = 9.0) 1H	6.78 1H	5.63 1H	5.02 1H	3.04 16H	2.70 2H	
<u>1c, d</u>	CCl ₄	<u>CH₃</u> 9.06 (³ J=6.5) t 6H	<u>CH₃</u> 9.03 t	<u>CH₂</u> 7.71 q	<u>CH₂</u> 7.40 q	8.57 m	5.83 (³ J=8) (⁵ J=2) 1H	2.96 10H

Tab.2: NMR-Spektren der Aryl-cyclopentene 2

Verbindung	Solvens	H _A	H _B	H _C	H _D	arom.Protonen	übrige Protonen
trans- <u>2a</u>	C ₆ D ₆	7.12 ^{a)} _q 2H	6.53 ^{a)} _q	6.01 ^{a)} _d 1H	5.62 ^{a)} _d 1H	3.0-3.7 20H	
trans- <u>2b</u>	CDCl ₃	7.41 [7.7-6.8 ^{c)}] m 1H	7.18 ^{b)} m 1H	5.24 [5.24] (³ J=6.5) (⁵ J=2.5) t 1H	4.83 [4.83] (³ J=6.5) (⁵ J=2.5) t 1H	2.2-3.2 [2.4-3.2] m 16H	156 [1.56] 2H

a) Multiplette zentriert bei den angegebenen chem.Verschiebungen

b) Aufgenommen bei 220 MHz

c) Werte bei 60 MHz in Klammern

Literatur

- 1) H. Dürr, Tetrahedron Letters [London] 1966, 5829.
- 2) H. Dürr, Chem.Ber. 101, 3047 (1968).
- 3) H.H. Jakobsen, Tetrahedron Letters [London] 1967, 1991.
- 4) H. Suhr, Anwendung der kernmagn. Res. i.d.org.Chemie, Springer Verlag, Berlin, 1965, u.a..
- 5) R. Knorr, IIT-Letters, 115, 20 (1968).
- 6) Für die Aufnahme des Spektrums bei 20 MHz sei Herrn Dr. W. Brügel, B A S F, Ludwigshafen/Rhein gedankt.



AMERICAN OIL COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT 2500 NEW YORK AVENUE WHITING, INDIANA 46394

April 11, 1969

Subject: Varian HR-52 NMR
Spectrometer Conversion
to DA-60-IL System

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

Dear Barry:

At the present time we are involved in having our Varian HR-52 NMR Spectrometer converted to the DA-60-IL system. There are some features of our original system which we feel are worth mentioning, even though similar things have appeared in the NMR Newsletter from time to time.

The water circulating system for the magnet is unusual in that it has a heater rather than only cooling. To give more details, the water circulating through the magnet quite typically is in a closed loop with a pump and reservoir. The water returning from the magnet passes through a heat exchanger which has water, cooled by a chiller, continuously circulating through it. It then returns to the reservoir, which contains heaters. The temperature of the reservoir is monitored and if the water is too cold it is heated. The advantage of this design is that magnet water is flowing continuously since there are no solenoid valves. In addition, absence of solenoids firing eliminates a possible source of noise spikes.

The closed loop magnet water system has a flow interlock, in addition to the Pressuretrol on the magnet. This turns off the V-2100 in case of water flow cessation.

We monitor the temperature of the magnet by means of the thermocouples buried in the energizing coils. If for some reason either or both of energizing coils get too hot, the V-2100 is turned off.

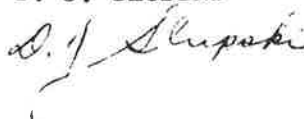
Good use has been made of the old V-2101 Magnet Current Regulator by modifying it and the V-2100 so that now twelve 304 TL's are used. Windows have been installed so that a visual check can be made of all 304 TL's as well as the 872A's.

Sincerely,


E. M. BANAS
B. E. WENZEL
P. G. CROTEAU

R. A. DINERSTEIN

D. J. SLUPSKI



NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

April 9, 1969

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

Dear Barry:

The problem of the location of the N-proton in piperidine has challenged chemists for several years. Evidence has been presented that it is mostly axial, mostly equatorial, or equally distributed between the two positions. Most people do agree that there are substantial amounts of both isomers. For comparison, we have now synthesized the phosphorus analogue and found that it is almost entirely axial.



Phosphorinane has a number of recommending qualities. In particular, the P-proton exchanges sufficiently slowly that the coupling to the vicinal ring protons can be observed. Axial protons are easily recognized because J_{trans} is quite large (J_{trans} for an equatorial proton is often smaller than J_{cis}). We have analyzed the spectrum of the P-proton and found that J_{trans} is 12 Hz and J_{cis} is 2.5 Hz. These parameters can only be interpreted in terms of a predominantly axial P-proton. The spectra were taken at -50° in Freon 11 on the Bruker HFX-10 at 90 MHz.

The axial preference of the proton is particularly interesting because the lone pair in phosphines resides in a nearly directionless s orbital. Much has been said about the "steric requirements" of the lone pair. The concept does not have an operational meaning. In this system the proton shows an inherent axial preference, even though there is "nothing" in the equatorial position.

Professor Bernard L. Shapiro
Page Two
April 9, 1969

Because of a recent change in our instrumentation, we have two nmr items we wish to sell:

- (1) NMR Specialties SD-60B Heteronuclear Decoupler, suitable for decoupling ^2H , ^{31}P , or other nuclei from proton (or vice versa) on the A-60 or HA-60. Used less than a year.
- (2) Varian Integrator-decoupler for HA instruments. Hardly used at all.

Sincerely,



Joseph B. Lambert



Wallace L. Oliver, Jr.

JBL/kc

Title: Conformation of the Phosphorus Analogue of Piperidine;
Heteronuclear Decoupler and Integrator/Decoupler For Sale

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

The School of Medicine

JOHNSON RESEARCH FOUNDATION

DEPARTMENT OF

BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

April 8, 1969

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

Dear Professor Shapiro:

It has been pointed out, that in the terms of the dipolar contribution to the transverse relaxation rate (1) (as well as in the hyperfine ones (2)) of a nucleus in a paramagnetic complex, one should distinguish between the longitudinal and transverse relaxation times of the electron. This distinction is important in interpreting data for complexes for which the tumbling time is longer than the electron relaxation time and the latter is the effective correlation time. In paramagnetic macromolecules, e.g., enzymes containing bound paramagnetic ions, this may often be the case.

It can be shown that the longitudinal nuclear relaxation rate is given by:

$$1/T_1 = \frac{2}{15} S(S+1) \gamma_I^2 g^2 \beta^2 r^{-6} \left[\frac{\tau_{c_2}}{1 + (\omega_I - \omega_S)^2 \tau_{c_2}^2} + \frac{3\tau_{c_1}}{1 + \omega_I^2 \tau_{c_1}^2} + \frac{6\tau_{c_2}}{1 + (\omega_I + \omega_S)^2 \tau_{c_2}^2} \right] \\ + \frac{2}{3} S(S+1) (A/\hbar)^2 \left[\frac{\tau_{e_2}}{1 - (\omega_I - \omega_S)^2 \tau_{e_2}^2} \right]$$

where $1/\tau_{c_1} = 1/\tau_{e_1} + 1/\tau_r$, $1/\tau_{c_2} = 1/\tau_{e_2} + 1/\tau_r$, $1/\tau_{e_1} = 1/T_{1e} + 1/\tau_M$, $1/\tau_{e_2} = 1/T_{2e} + 1/\tau_M$, and τ_M is the mean residence time of the nucleus in the complex. This follows from the equations describing the time-dependence of the expectation value of the longitudinal, z , component of the angular momentum of two unlike spins (3), using an argument similar to that of Connick and Fiat (1). The hyperfine term is that given by Abragam (2).

Sincerely yours,


Jacques Reuben

References:

- (1) R.E. Connick and D. Fiat, J. Chem. Phys. 44, 4103 (1966).
- (2) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, 1961, p. 311, eq. 127.
- (3) Ibid., p. 295.

Title: On the distinction between transverse and longitudinal electron relaxation times.



UNIVERSITY OF SUSSEX
 THE CHEMICAL LABORATORY FALMER BRIGHTON BN1 9QJ
 Telephone Brighton OBR 3 66755

11th April, 1969.

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

Dear Professor Shapiro,

Reconsideration of CFCl_3 as a reference signal

We are continuing our study of the splitting in the 'reference' peak of CFCl_3 due to the presence differing proportions of chlorine isotopes¹. CFCl_3 exists in four chlorine isotopic modifications $\text{CF}^{35}\text{Cl}_3$ (42.0%), $\text{CF}^{35}\text{Cl}_2^{37}\text{Cl}$ (42.9%), $\text{CF}^{35}\text{Cl}^{37}\text{Cl}_2$ (13.6%), and $\text{CF}^{37}\text{Cl}_3$ (1.5%). For many variations of solvent and temperature the peaks due to the three most abundant isotopic species are clearly resolved - see figure. The peak due to $\text{CF}^{37}\text{Cl}_3$ has not been definitely identified due to the low abundance of this species.

The measured peak to peak separation of the two main peaks under a variety of conditions is listed below. All solutions are approximately 5% by volume.

Although these results only represent preliminary observations, two conclusions seem to be emerging. Firstly the species of 13.6% abundance has always come to high field - in accordance with an established empirical rule for molecules containing the heavier isotopes². Secondly a lowering of temperature produces a substantial increase in the splitting. This second conclusion in particular needs substantiating by more experimental evidence. At any rate we feel that CFCl_3 's role as a universal locking and reference signal for fluorine NMR must be seriously reconsidered in the light of these results.

- (1) P.R. Carey, H.W. Kroto, M.A. Turpin Chem. Comm. 188, (1969)
- (2) H. Batiz-Hernandez, R.A. Bernheim Progr NMR Spectroscopy 1967, 3, 63.

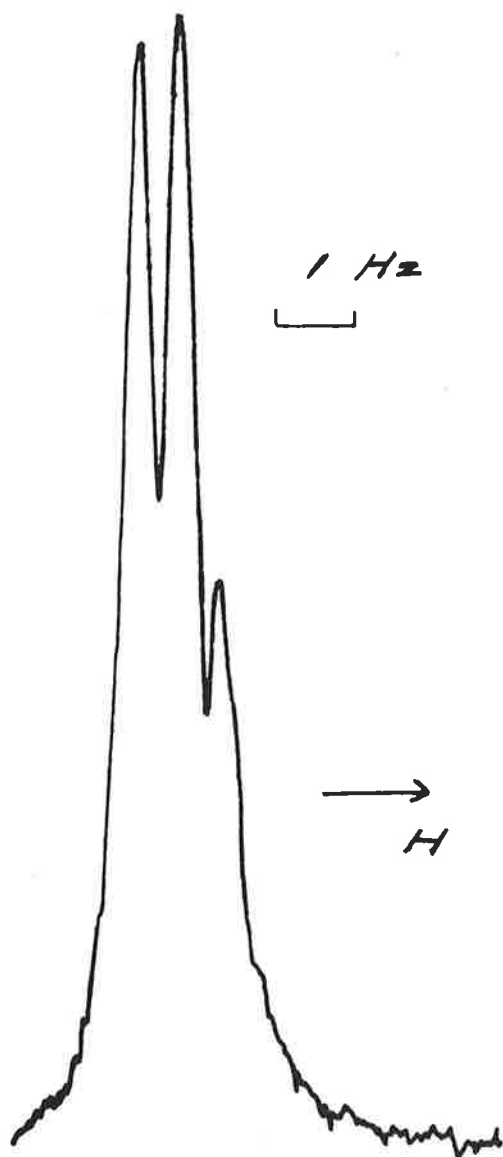
Please credit this contribution to Professor J.N. Murrell's subscription

Yours sincerely,

P.R. Carey,

M.A. Turpin,

H.W. Kroto.



5% CFCl_3 by volume in
DMSO at 30°C

Solvent	Temp. ($^\circ\text{C}$)	Splitting (Hz)
Methanol	30	0.45
Chloroform	30	0.5
Acetonitrile	30	0.5
"	-20	0.65
"	-40	0.7
Pyridine	30	0.55
DMSO	30	0.55
Cyclopentane	30	0.4
	-80	0.8

The total width of the signals at
half-height varied between 1.0 and 1.6

Columbia University in the City of New York | New York, N.Y. 10027

DEPARTMENT OF CHEMISTRY

Evemugor Hall

April 15, 1969

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

Modification on the 2200B Power Supply

Dear Professor Shapiro:

Recently we designed and installed a conversion for the V-2100B regulated power supply of our Varian HA 100 spectrometer. Since the power supply was located in the same room with the spectrometer and other instrumentation, we encountered great difficulty in providing enough air for the proper cooling of the power supply as well as maintaining constant temperature in the room especially during the summer.

Several months ago we replaced the eight 304 TL tubes of the power supply with a single 3 CW 5000 TL tube. The characteristics of this water cooled triode approximated most closely the existing eight 304 TL tubes. We are pleased to report that this replacement solved all our problems with respect to constant room temperature and heat control within the power supply.

To cool the tube, we use the same raw water which runs through the magnet coolant control system. This amount of water is more than sufficient to cool the tube. The magnet coolant control system and the tube are connected in series with respect to the raw water. We used 30 feet of polyurethane hose 1/2" ID, 11/16 OD in both the water supply and the drain line to make sure that there exists a high resistance path to ground through the cooling water. Both the water supply and the drain line hose are wound on an aliptical wooden frame which is located in the same place as the old tubes inside the power supply. Only a few feet of the hose is placed outside the machine. The leads from the thermal interlock switch S 101 are connected to a Shur-Flo switch which is located at some distance from the tube in the drain line.

The filament transformer T 702 could be replaced with F 751 Stancor Primary 115/230 V, Secondary 7.75 V, 5I A, C.T., but for reasons of simplicity, we kept the existing one. If the original transformer is used, 5 V secondary coils are connected in series and then the 10 V secondary voltage is dropped

Professor B. L. Shapiro
 April 15, 1969
 Page 2

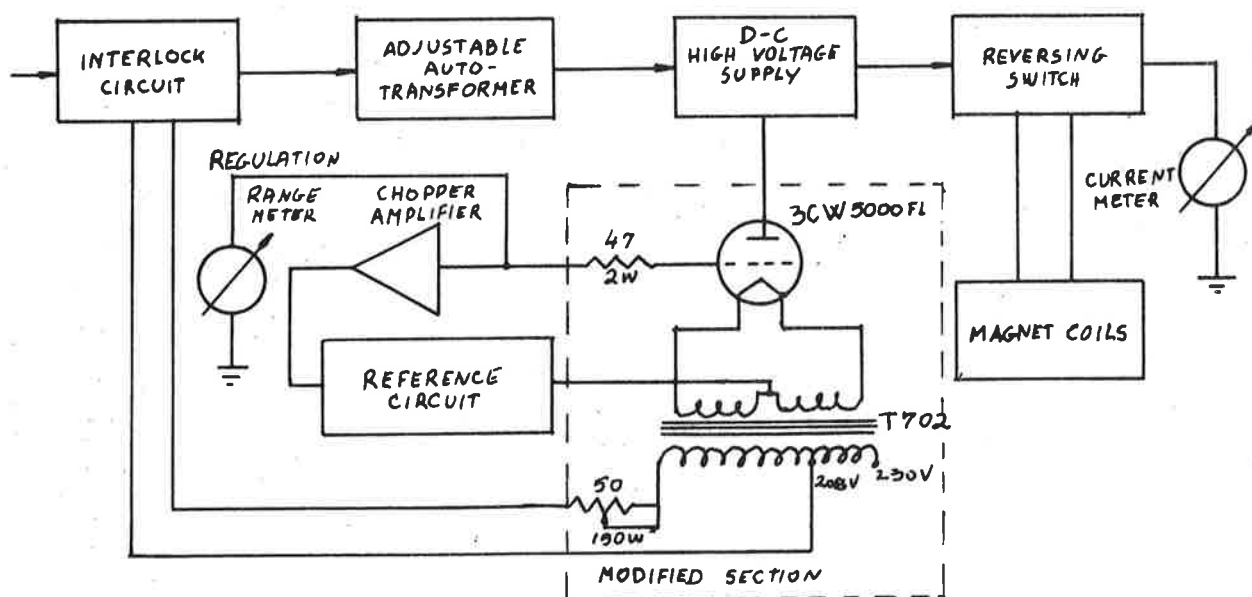
to 7.5 V by means of a 50 Ohm, 150 W resistor in series with the primary coil. Even with such a loss of power on the dropping resistor we still use less than 50% of the filament power necessary with eight tubes. Furthermore, the price of the new tube, if purchased directly from EIMAC Division of Varian, is \$ 216 while a set of eight 304 TL tubes cost \$ 480. It was standard practice to replace the whole set of tubes since we always had the problem of matching a new tube to the remaining old tubes. The modification is shown at the V-2100 High Voltage Circuit.

I would like to thank Mr. W. R. Barkley, who consulted with us in our choice of tube and gave us very helpful advice.

Sincerely,

Vinka Parmakovich

Vinka Parmakovich
 Senior Staff Associate
 Department of Chemistry
 Columbia University



V-2100 High Voltage Circuit

Institut
national
de recherche
chimique
appliquée

établissement public à caractère
industriel et commercial,
12 quai Henri IV, Paris 4
rc Seine 58 b 7806
n° d'entreprise 971 75 104 9051
ccp Paris 9065 96 au nom
de l'agent comptable de l'ircha

Direction générale
Service de Paris

12, quai Henri-IV, Paris-4°
téléphone : 272 82 70

Professeur Bernard L. SHAPIRO
TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
College Station, Texas 77843

Paris, le 16 Avril 1969

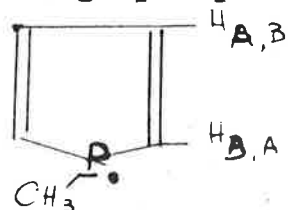
Coupling mechanisms in unsaturated phosphorus compounds.

Dear Barry,

We have recently been visited by R.M.N. (French for N.M.R.) and I seize this opportunity to drop you a line before leaving for a trip to the U.S.A. (on an exchange basis of course). The problem of sign changes of $P^{31}-H^1$ (and as well $P^{31}-C^{13}$ (1) remains quite puzzling; its stereospecificity seems now well documented (2) but sound explanations are still lacking: 'hyperconjugation' in the $CH_3P...$ moiety; 'thru-space' contribution (as suggested by recent results presented here (3) or 'normal extension' of Pople-Santry theory (4). Instead of debating this, I would point out that similar effects appear in unsaturated homologs. Couplings in trivinyl-phosphine are well-known (5):

$P(CH=CH_2)_3$ $P..H$ gem +11.7 Cis \pm 13.6 trans \pm 30.2

turning to the homolog 'phosphole' (6) with a fixed conformation.



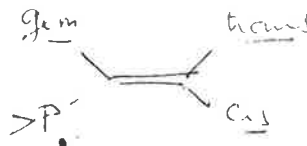
$P..H_A (H_B)$ 13.9 39.5

one is tempted to admit for trivinyl-phosphine (with $p_{\pi} - d_{\pi}$

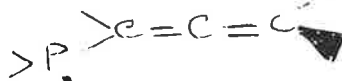
....

- 2 -

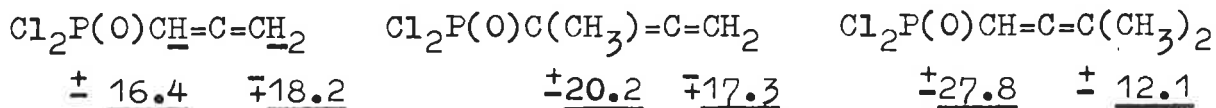
stabilization between phosphorus and the sp_2 carbon) the following geometry:



All couplings having the same sign (positive?), it appears that the two 'closer' are lower than the 'farthest' (this remains true for phosphoryl derivatives, vinyl phosphonates, 2-phospholene oxides...). In methylated derivatives, comparison of these anomalous couplings for the proton and the methyl cases often reveals no sign change from one to the other (contrary to expectations based on 'perfect pairing') and a greater modulus - or nearly - for the $\underline{PC(CH_3)}$ than for the \underline{PCH} . Same trends appear for allenic derivatives (for which γ positions are evidently equivalent, but rather far from the phosphorus atom):



Compare (7)



Once again, stereospecific effects appear unquestionable, but the question of their origin remains open.

Kind st regards,

G. Mavel
G. MAVEL

P.S. - Just received your blue note, we are dead-head.

....

- (1) W. Mc FARLANE. Proc. Roy. Soc. A. 306, 185, 1968.
G. MAVEL, M. GREEN. Chem. Comm., 1968, p. 742.
 - (2) G. MAVEL. J. Chim. Phys., 65, 1692, 1968.
JP. ALBRAND, D. GAGNAIRE, J. MARTIN, J.B. ROBERT. Bull. Soc.
Chim. France, 1969, p. 40.
 - (3) S.O. GRIM, TAMU. 125-33.
 - (4) E.G. FINER, R.K. HARRIS. Chem. Comm., 1968, p. 110.
 - (5) S.C. MANATT, G.L. JUVINALL, R.I. WAGNER, D.D. ELLEMAN.
J. Am. Chem. Soc., 88, 2689, 1966.
 - (6) L.D. QUIN, J.G. BRYSON, ibid., 5984, 1967 and private
Comm., 1968.
 - (7) M.P. SIMONNIN, C. CHARRIER. Compt. Rend. C, 267, 550, 1968.
Org. Magn. Resonance 1, 27, 1969.
-

Uwe Krüger
Hans Hettler

Institut für Organische Chemie
der Techn. Universität
Braunschweig, 10th March 1969

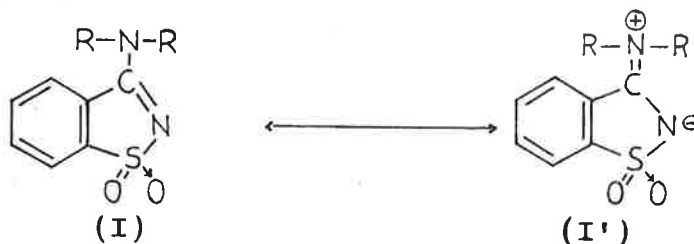
Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

Anisotropy Effects on Shifts in N-substituted 3-amino-benzisothiazole-S-dioxides

Dear Professor Shapiro,

some results we obtained on restricted rotation may be of general interest. We wonder, whether they could be reproduced in "NMR-Newsletters".

When looking into solvent influences on rotational barriers in N-substituted 3-amino-benzisothiazole-S-dioxides ¹⁾²⁾³⁾ (I,I') by means of proton-NMR



(Ia) R= -CH₃
(Ib) R= -CH₂CH₃
(Ic) R= -CH(CH₃)₂

we were puzzled by the fact, that comparable protons i.e. protons at approximately the same distance from the amidine-system $-\text{N}=\text{C}-\text{N}-$ in the sequence $-\text{CH}_3$, $-\text{CH}_2-\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$ should give rise to greatly different values for maximum separation of signals ($\Delta\nu_\infty$) at sufficiently low temperatures in one and the same solvent.

The anisotropy of the amidine group (when there is no rotation around the C-N bond) obviously affects methyl-, methylen- and methine protons in a different way.

In acetone (spectrograde)-d as a solvent we observed the following values of maximum separation of signals:

1) J.A. Jesurun

Ber. Deut. Chem.Ges. 26,2286
(1883)

2) C.H. Grogan, E.E. Reid and L.M.Rice J.Org.Chem. 20, 1425 (1955)

3) H. Hettler

Z. f. analyt. Chem. 220,9 (1966)

	$\Delta\nu_{\infty}$
$\text{--}\underline{\text{CH}_3}$	0,40 ppm
$\text{--}\underline{\text{CH}_2}\text{--CH}_3$	0,30 ppm
$\text{--}\underline{\text{CH}}(\text{CH}_3)_2$	0,99 ppm

In other solvents the same general feature was observed.

This unexpected result can be rationalized as follows:

- i) We assume that alkyl groups at temperatures sufficiently low to bar rotation around the C-N-bond (in this case below 0°C) are fixed in sterically favourable positions only permitting bending vibrations. In this way rotamers are formed. The methyl groups in (Ia) naturally will continue to rotate.
- ii) The model developed by PAULSEN + TODT⁴⁾ explaining the effect of anisotropy in amides can be applied to this case, too.

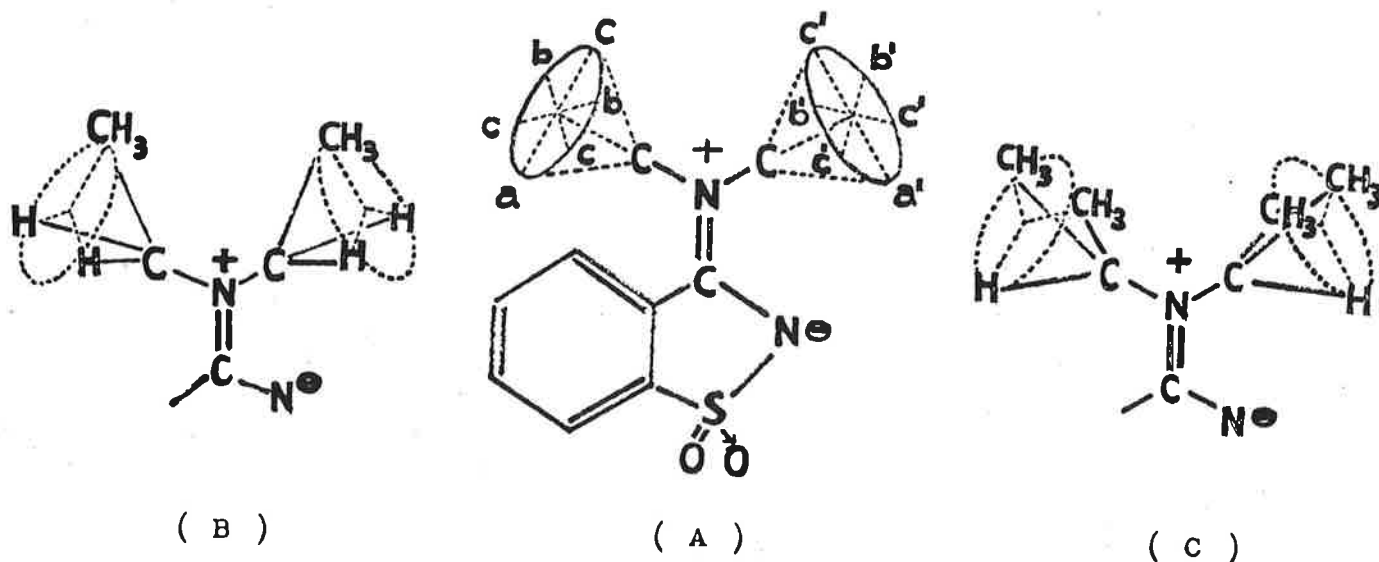


FIG. 1
The Paulsen-model⁴⁾

⁴⁾ H. PAULSEN and K. TODT Angew. Chem. 78, 943 (1966)

⁵⁾ A complete x-ray analysis of (Ic) has been carried out,
c.f W. SAENGER and H. HETTLER Chem. Ber. in press

The PAULSEN-model⁴⁾ (Figure 1)

According to Paulsen there are two kinds of distinguished positions namely a and b which substituents can occupy. In these positions the substituents will show the greatest differences in chemical shifts when a is compared with a' and b with b'. They are called equatorial = a, a' and axial = b, b' positions. The intermediate positions c and c' will not present appreciable differences. Paulsen⁴⁾ was able to show that a proton in the equatorial position is more shielded in a than in a'; b' is more shielded than b.

In the case of ethyl substitution (Ib) the CH₂-protons at low temperature will essentially occupy the c, c' positions [Fig. 1 (B)]. One would expect relatively weak splitting. For the methyl protons, too, splitting should be weak since the methyl group is free to rotate even at low temperature and thus an average value will result.

We may assume that in the diisopropyl derivative (Ic) the -C-H group is fixed in position a [Fig. 1 (C)]. The high field signal should then originate from -C-H in position a. Unfortunately this conclusion cannot be proved by dilution experiments with benzene, since the bulky methyl groups keep the aromatic solvent molecules too far away from the -C-H proton.

This assumption would account for the abnormally high values for maximum separation of signals in the case of the -C-H (methine) proton would therefore support the suggested structure of the diisopropyl compound (Ic) at low temperature.⁵⁾

A full account of the results will be given in Z. f. Physik. Chem. This is a contribution from the Department of Organic Chemistry, Technical University, Braunschweig and Max-Planck-Institut für Experimentelle Medizin, Göttingen.

V. J. J. J.
J. J. J. J.

QUEEN MARY COLLEGE

(UNIVERSITY OF LONDON)

MILE END ROAD - LONDON - E.1.

Telephone: ADVANCE 4811

DEPARTMENT OF CHEMISTRY



PROFESSOR K. W. SYKES,
M.A., B.Sc., D.Phil.
PROFESSOR B. C. L. WEEDON,
D.Sc., Ph.D., F.R.I.C.
PROFESSOR D. C. BRADLEY,
D.Sc.

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

17th April 1969

Dear Barry,

Postdoctoral Fellowship

I have an award for a foreign (i.e. non-British) post-doctoral fellow for work on orientated molecules containing ^{15}N and ^{14}N . The salary is £1,320 and the position is renewable for a second year. A candidate with experience of nuclear quadrupole spectroscopy, or of the n.m.r. of orientated molecules would be preferred.

We have an HA100 with excellent heteronuclear double resonance facilities (see Newsletter#123) and hope to obtain shortly a Varian FS100-15 system (or equivalent) with an SS 100 control unit.

Yours sincerely,

Edward W. Randall
Reader in Chemistry

THE UNIVERSITY OF UTAH

SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

April 18, 1969

Dr. B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843TITLE: A Campaign for TMS and Positive Chemical Shifts in the Direction
of Increasing Frequency or Why Not Logic?

Dear Barry,

We wholeheartedly endorse Gary Maciel's attempt¹ to introduce some logic into adopting TMS as a reference not only for ¹H but also ¹³C and ²⁹Si chemical shifts. TMS provides the additional attraction associated with proton decoupling techniques - enhanced signal and greater accuracy².

As McFarlane³ has pointed out, apart from the obvious course of referring chemical shifts to one of the "accepted" standards for a particular nucleus there is also the attractive possibility of relating the resonance frequencies of all nuclei to a single standard (TMS) using the relationship³:

$$X_{\text{TMS}} = 10^8 X_{\text{obs}} / (10^8 + f - 100 \delta).$$

If this system were adopted it does not seem unreasonable to also ask that present and future generations of ¹³C spectroscopists adopt a "δ"-scale with positive shifts in the direction of increasing frequency from TMS.

As we are about to submit a ¹³C review article (with data referred to benzene) we are concerned to hear the opinions of others working in this area. This would seem an ideal opportunity not only to force us to recalculate all our own ¹³C values but also to influence the "future generations" towards some logical system.

Sincerely yours,


 Alan J. Jones


 David M. Grant

AJJ:fjc

1. G. E. Maciel, TAMU IEMR Newsletter, No. 125, 14 (1969).
2. E. G. Paul and D. M. Grant, J. Am. Chem. Soc., 86, 2977 (1964).
3. W. McFarlane, Ann. Rev. IEMR Spec., Academic Press, London, 1968, p. 135.

See also R. W. Mattoon IITMNR Newsletter, No. 114, 24, (1968).

Department of Chemistry
Kyoto University
Kyoto, Japan

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

Title: Magnetic Anisotropy in the Acetylene Molecule

Dear Professor Shapiro:

Magnetic anisotropy due to multiple bonds is of interest to us to investigate long-range shielding effects in NMR spectroscopy. Estimates of the magnetic anisotropy of the acetylenic group ($\Delta\chi_{C\equiv C}$) vary considerably with the methods employed, as seen in Table I. The estimates (I) and (II) were obtained theoretically by the variation method and the gauge-invariant atomic orbital method simplified under several approximations, respectively. The estimates (III) and (IV) were derived indirectly for interpretations of the experimental proton shifts and Cl^3-H coupling constants of acetylenes respectively.

A general theory of diamagnetic susceptibility was given by Van Vleck, and for the z component of susceptibility tensor,

$$\chi_{zz} = -\frac{Ne^2}{4mc^2} \sum_i \langle 0 | x_i^2 + y_i^2 | 0 \rangle + \frac{Ne^2}{2mc^2} \sum_{n \neq 0} \frac{|\langle 0 | L_z | n \rangle|^2}{E_n - E_0}$$

$$= \chi_{zz}^d + \chi_{zz}^p$$

We calculated the susceptibility of C_2H_2 using a single-determinant SCF MO wavefunction obtained by Palke⁵. The paramagnetic term χ^p is deduced from the rotational magnetic moment which was obtained from the recent molecular beam experiment of C_2H_2 by Cedeberg⁶. The results are shown in Table II. Our estimates may be fairly reliable, since they are of the same order of magnitude with the experimental values for N_2 , which has similar electronic structure. The anisotropy has been found mainly due to the diamagnetic term contrary to some previous conjectures.

This work has been done in collaboration with Professor Y. Kato.

Table I. Susceptibility and Anisotropy in C_2H_2 . (Units in 10^{-6} emu.mole $^{-1}$).

	$\bar{\chi}$	$\Delta\chi_{(C\equiv C)}$	Author	Reference
(I)	-12.26	-1.61	Tillieu et al.	1
(II)	--	-19.4	Pople	2
(III)	--	-34 -38	Zeil et al.	3
(IV)	--	-16.5	Reddy et al.	4

Table II. Estimated Values of the susceptibility of C_2H_2 , together with the experimental valued for N_2 . (Units in 10^{-6} emu.mole $^{-1}$).

Molecule	$\chi_{ }$	χ_{\perp}	$\bar{\chi}$	$\Delta\chi$
C_2H_2	-20.64	-17.53	-18.57	-3.11
N_2	---	---	-13.3-3.	-8.65

REFERENCES

1. J.Tillieu and J.Guy, Compt.Rend., 241, 382 (1955); ibid., 242, 1279, 1436 (1956).
2. J.A.Pople, J.Chem.Phys., 37, 53,60 (1962).
3. H.Heel and W.Zeil, Z. Elektrochem., 64, 962 (1960).
4. G.S.Reddy and J.H.Goldstein, J.Chem.Phys., 36, 2644 (1962); ibid., 39, 5309 (1963).
5. W.E.Palke and W.N.Lipscomb, J.Am.Chem.Soc., 88, 2384 (1966).
6. J.W.Cederberg, C.H.Anderson, and N.F.Ramsey, Phys.Rev., 136, A960 (1964). Theoretical estimate for under the truncated sum approximation reaches at most one half of that deduced from the rotational magnetic moment ($+42.01 \cdot 10^{-6}$ emu.mole $^{-1}$).

id zero for linear molecules.

Yours sincerely,

A. Saika

A. Saika

Analysis of NMR Spectra with Chemical Exchange and Quadrupole Relaxation

Determination of lifetimes of protons on magnetically nonequivalent sites is a relatively simple matter when a single rate process contributes to the line-width. Here we consider the combined effects of chemical exchange and quadrupole relaxation on the NMR lineshape, with a view towards separating experimentally the former from the latter.

Specifically, consider the case of exchange of a proton between two sites (populations p_a and p_b) chemically shifted by Ω rad/sec, with forward and reverse specific rates k_{ab} and k_{ba} . Assume also that spins in site b are coupled (A rad/sec) to a nucleus of spin 1 relaxing at rate R_1 . Such systems occur in aqueous amides and amines, for example.

The lineshape equation can be written

$$I(\omega) = -\operatorname{Re}\{\underline{1} \cdot (\underline{A} - i\omega \underline{I})^{-1} \cdot \underline{M}(0)\} \quad (1)$$

where $\underline{M}(0)$ is a weight vector, and \underline{A} is the matrix form of Alexander's equations. To simplify Eq. (1) for the specific case at hand, we apply a set of similarity transformations to \underline{A} which diagonalize the submatrix of terms proportional to R_1 , and symmetrize the chemical exchange terms. When $\underline{1}$ and $\underline{M}(0)$ are correspondingly transformed, Eq. (1) requires only four of the inverse matrix elements. These can readily be found by the method of cofactors, and the resulting lineshape is

$$I(\omega) = -\operatorname{Re}\{p_b \alpha + p_a (\beta + \eta) - 4kp_a p_b / [\alpha(\beta + \eta) - 4k^2 p_a p_b]\} \quad (2)$$

where

$$\alpha = -R_2^0 - k_{ab} + i(p_b \Omega - \omega) \quad (3)$$

$$\beta = -R_2^0 - k_{ba} + i(-p_a \Omega - \omega) \quad (4)$$

$$\eta = \frac{2}{3} A^2 (\beta - 0.6R_1) / [(\beta - 0.6R_1)(\beta - R_1) + A^2/3] \quad (5)$$

and

$$k = 1/2(k_{ab} + k_{ba}) \quad (6)$$

Eqs. (2)-(6) represent an extension of the Hahn-Maxwell-McConnell equations, to which they reduce when \mathcal{A} (and η) are zero. An interesting limiting case arises when $\mathcal{A}/R_1 \ll 1$, i.e., fast quadrupole relaxation. Eq. (5) then reduces to

$$\eta \approx -2/3 \mathcal{A}^2 / (R_1 + k_{ba}) \quad (7)$$

and for fast chemical exchange, one line is predicted with width R/π and

$$R = R_2^0 + \Omega^2 p_a p_b / 2k + \frac{2}{3} p_b \mathcal{A}^2 / (R_1 + k_{ba}) \quad (8)$$

For slow exchange, and fast quadrupole relaxation, two lines are predicted, with widths R_a/π and R_b/π where

$$R_a = R_2^0 + k_{ab} \quad (9)$$

$$R_b = R_2^0 + k_{ba} + \frac{2}{3} \mathcal{A}^2 / (R_1 + k_{ba}) \quad (10)$$

Thus for slow exchange, fast quadrupole relaxation, the lifetime of a spin in site B is not easy to determine from the linewidth of B. It is not fair to subtract $\frac{2}{3} \mathcal{A}^2 / R_1$ as an estimate of the quadrupolar broadening. The lifetime in site a is however, not affected by quadrupole relaxation.

For fast chemical exchange, the last term in Eq. (8) may become small much faster than the second term, particularly for small p_b . In this case one can neglect quadrupole relaxation altogether. Moreover, when the last term in Eq. (8) is not dominant, fairly large errors in \mathcal{A} and R_1 can be tolerated as long as their ratio is correct, and the exchange rates can still be determined accurately.

Robert L. Vold
Assistant Professor of Chemistry
University of California at San Diego
La Jolla, California 92037



dr. L. Lunazzi

Istituto di Chimica Organica e di Chimica Industriale
dell'Università di Bologna

li April, 18 1969

Viale Risorgimento, 4 - Tel. 42.18.80
c.a.p. 40136

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

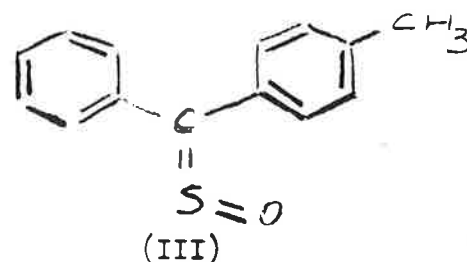
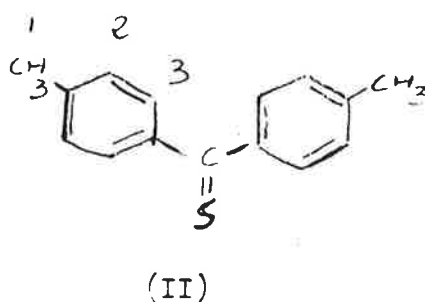
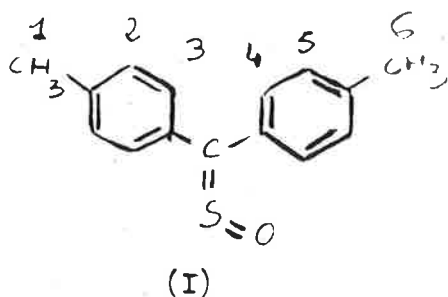
Title : P.M.R. investigation on the "syn"
and "anti" isomerism in aromatic
sulphines.

Dear dr. Shapiro,

after my postdoctoral fellowship in Ottawa at the N.P.C. I am now back in Europe, and I had the opportunity to enjoy the warm hospitality of Ueli Schneiderger and of his Varian 100MHz. in Zurich. There I could investigate on the problem of the isomerism in the aromatic sulphines; I hope you will find my preliminary results of some interest. The 100 MHz. spectrum of (I) shows (Fig. 1a) the presence of two different signals for the methyl groups, with different fine structure patterns clearly due to the couplings with the two different aromatic rings. The decoupling at the frequency of protons 3 actually affect only one of the two signals (Fig. 1b).

This unambiguously shows that the C=S=O group is a rigid and non linear system. The spectrum of (II) presents, as only aliphatic signal, a septet (Fig. 2a) which has been decoupled by irradiating the protons 2 and 3 (Figs. 2b and 2c): this seems suggest that also in (I) the septet is likely to belong to the CH₃ group in a situation closer to that experienced by the -CH₃ in (II), namely the "anti" in respect to the C=S=O.

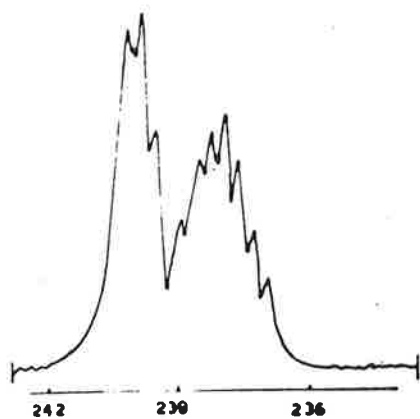
By using a molecule with only one -CH₃ in one of the two ring is thus possible to foresee the existence of two isomers; they actually has been detected in the crude reaction mixture and one of them (m.p. 58-60°) has been isolated. Its spectrum shows only one signal in the aliphatic region (Fig. 3) and its fine structure and position seems to indicate that we are in presence of the "syn" isomer (III). Works are in progress to isolate also the other isomer and to make a complete spectral analysis of both the aliphatic and aromatic bands.



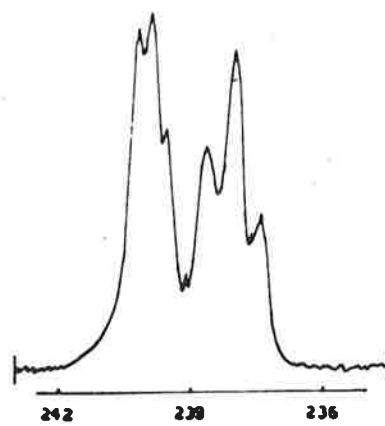
Sincerely yours

(Lodovico Lunazzi)
Lodovico Lunazzi

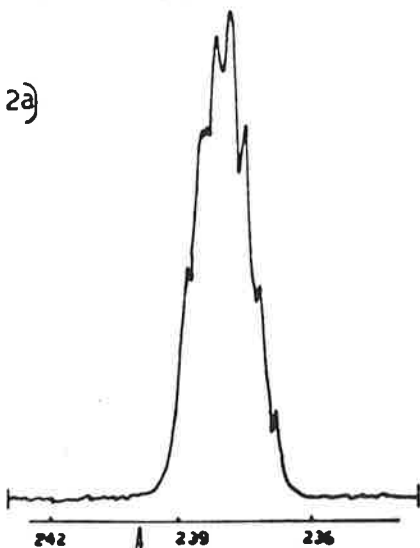
1a)



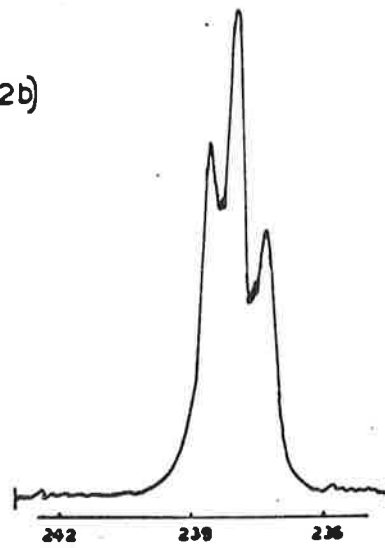
1b)



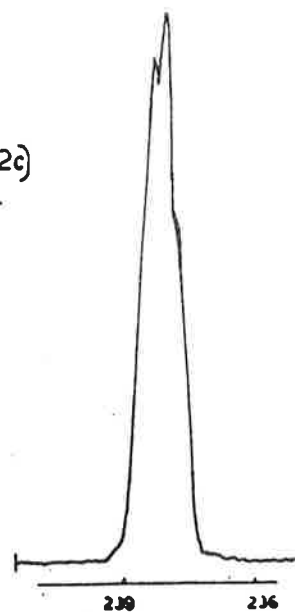
2a)



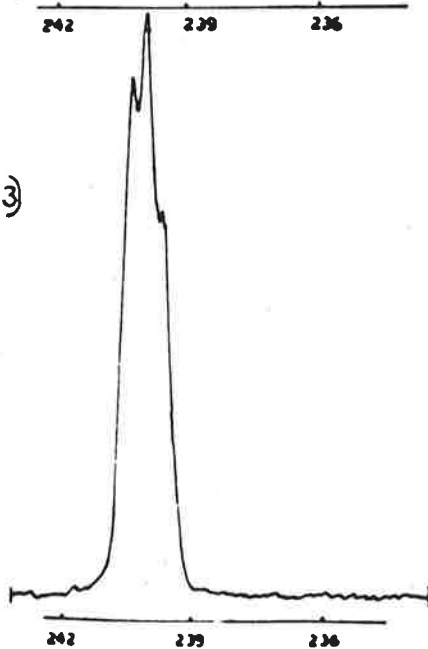
2b)



2c)



3)





Sandwich, Kent. Telephone: Sandwich 3511. Telegrams: Pfizer (Telex) Sandwich. Telex: 96114.

MJS/lmd

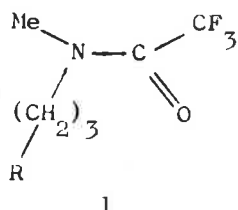
17th April, 1969.

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

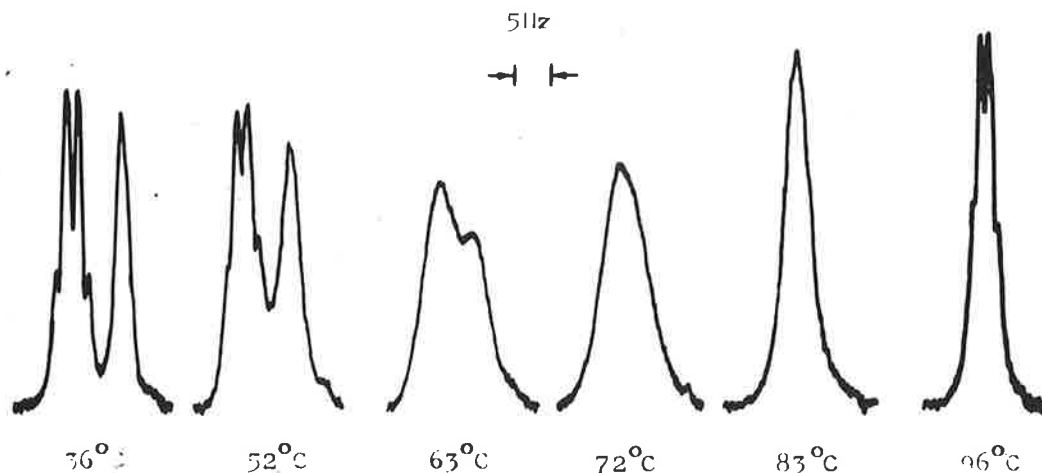
Dear Professor Shapiro,

Hindered rotation and long-range proton-fluorine
coupling (5-bonds) in N-trifluoroacetyl compounds

The N-methyl resonance of a compound of type 1 gave two separate absorptions at normal spectrometer temperatures (36°C), as shown in the Figure.



This suggested hindered internal rotation about the N-C bond. A subsequent variable temperature study of the compound in CCl_4 confirmed this, with $\Delta G^{\ddagger} \approx 18$ Kcal/mole (from coalescence temperature measurements).



Figure

In one form (36°C) the N-methyl resonance was experiencing an observable coupling of 1.6 Hz, whereas the other appeared as a broad singlet. In the final averaged case (96°C) the coupling was 1.2 Hz.

Yours sincerely,

M. J. Sewell

M. J. Sewell

Chemical Research Department.

PFIZER LIMITED

Chairman and Managing Director P V Colebrook A M I Chem E

F Goulding M P S C J Jones M A K J Lyles B Sc, Ph D

Directors H J Bragg F P S

R D Douglas B A

J K Morrison B Sc, M B, Ch B

B J G Page, M C, I, C, A



File: 001-3-1-1

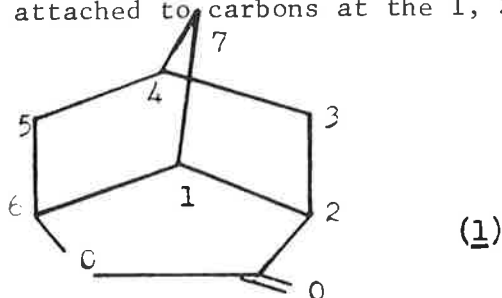
April 15, 1969

NMR Studies of Bridged Polycyclic Compound

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

Dear Barry:

In the course of our study of the NMR spectra of certain bridged bicyclo(2.2.1)-heptyl^{1,2} and bicyclo(2.2.2)octyl systems unusually large solvent induced shifts were noted for the various protons attached to carbons at the 1, 2, 5, and 6 positions.




The spectrum of compound(1) exhibits a strikingly different pattern in C_6D_6 solution relative to that in $CDCl_3$. As shown in Fig. 1 ($CDCl_3$ solution) the pattern for the 6-exo and 1 protons approach that of a triplet and the former may be interpreted as the A part of an AMXY system, where the 6-exo, 1, 5-exo and 5-endo protons correspond to A, M, X and Y respectively, and $J_{AX} \approx J_{AM}$ and $J_{AY} = 0$. On this basis the couplings may be approximated by a first order analysis, $J(6ex-1) = 5.2$ Hz and $J(6ex-5ex) = 7.0$ Hz, in good agreement with expectations based upon results observed for related compounds.^{1,2} In C_6D_6 solution (Fig. 2) the spectrum of compound 1 is surprisingly simple particularly with respect to the upfield resonances which indicates that the 5-exo and 5-endo protons are equivalent as well as those attached to carbon atoms 3 and 7. Note that the 6-exo resonance pattern has undergone a significant change and now appears as a doublet of triplets, $J(6ex-1) = 5.2$ Hz and $J(6ex-5ex) = J(6ex-5en) = 3.8$ Hz. These couplings were confirmed by spin decoupling and the results are depicted in Figs. 2b and 2c. Irradiation of the 5-exo, endo protons $\delta = 1.12$ removed the small triplet from the 6-exo resonance, while irradiation of proton 1, $\delta = 2.42$ removed the larger doublet (Fig. 2c).

While these results may be interpreted as simply another case of virtual coupling, they are probably best represented by a change of the spin system from an AMX_2 to an $AMXY$. Furthermore the A and M portions of the spectrum are strongly dependent upon $\Delta \int_{xy}$.

References:

- (1) R.M.Moriarty, H.Gopal, H.G.Welsh, K.C.Ramey and D.C.Lini, Tetrahedron Letters 38, 4555 (1966).
- (2) K.C.Ramey, D.C.Lini, R.Moriarty, H.Gopal and H.G.Welsh, J.Am. Chem.Soc. 89, 2401 (1967).

Sincerely,



Kermit C. Ramey

KCR:LH

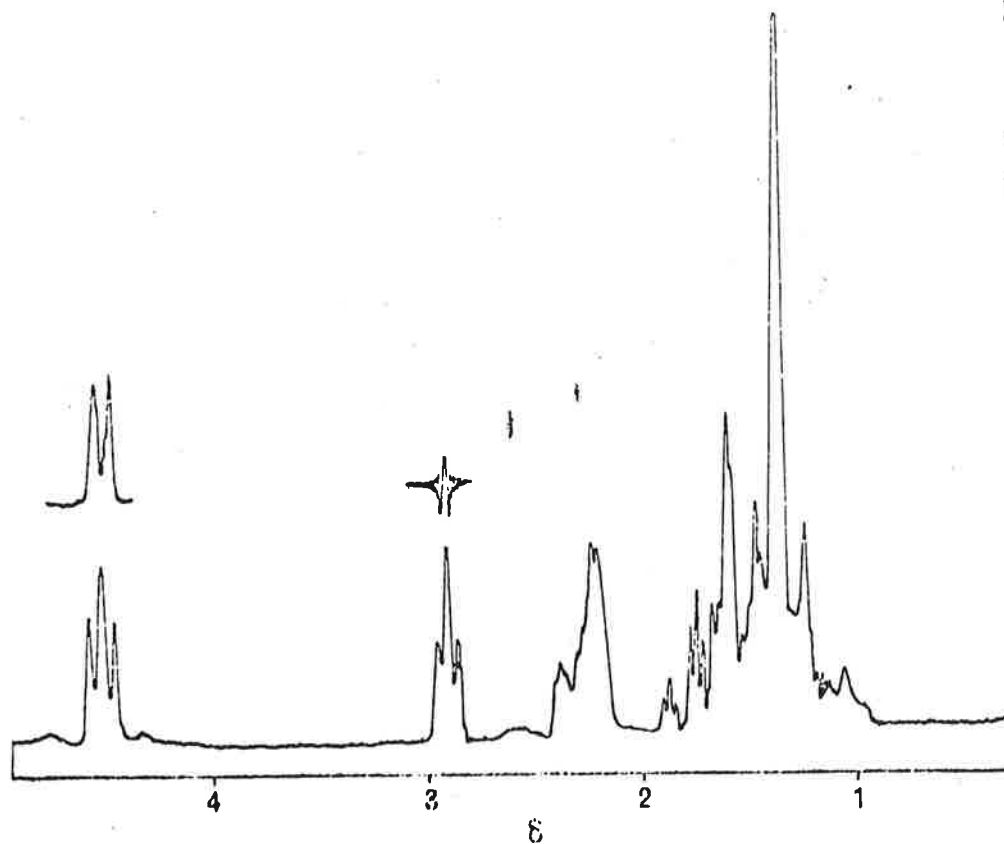


FIG. 1. NMR spectra of compound 1 in solution in CDCl_3 (100 MHz); A, normal, and B, decoupled.

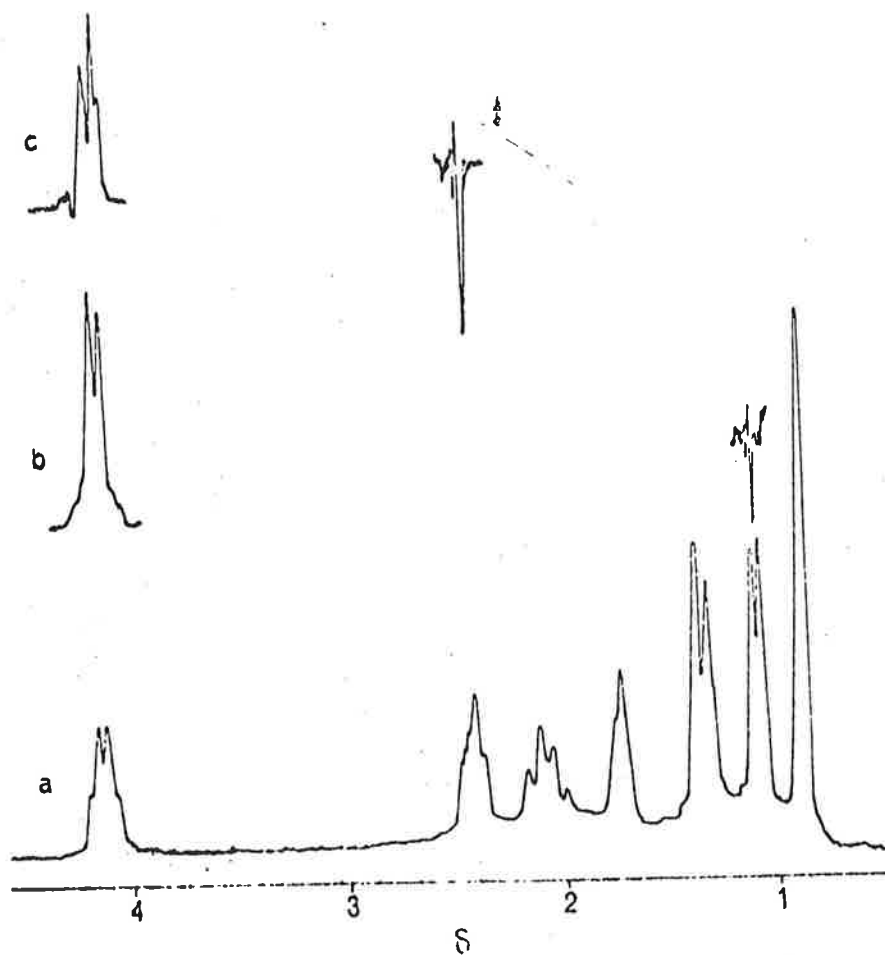


FIG. 2. NMR spectra of compound 1 in solution in C_6D_6 (100 MHz); A, normal, and B and C, decoupled.

DÉPARTEMENT DE CHIMIE ORGANIQUE

April 23 th 1969

LABORATOIRE DES ORGANOMÉTALLIQUES

PROFESSEUR J. C. MAIRE

Professor Bernard L. SHAPIRO

Department of Chemistry

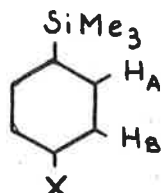
Texas A&M University

College Station, Texas 77843

Pmr DETERMINATION OF SiMe_3 GROUP ELECTRONEGATIVITY
 - ONE MORE LINEAR CORRELATION

Dear Dr. Shapiro:

We are currently investigating by a number of spectroscopic methods the question of d-orbitals participation (1) in the aromatic silicon derivatives. In aromatic trimethylsilyl compounds electron back donation effect ($\text{C} \rightarrow \text{Si}$) is more than balanced by the electron releasing effect of the three methyl groups. We have shown by a study of a series of p-substituted phenyltrimethylsilanes, 1 to 5, that if a second electron donating substituent is enhancing the conjugation effect, π - $d\pi$ bonding becomes significant.



In this series the proton-proton ortho coupling constant J_{AB} is related linearly to the electronegativity E_X of substituent X, as results from Table 1 and fig.1 (continuous line).

X	E_X	E_{SiMe_3}	J_{AB} , Hz
<u>1</u> , D	2,1	3,10	8
<u>2</u> , NH_2	3,31	2,34	8,36
<u>3</u> , OMe	2,95	2,15	8,25
<u>4</u> , NO_2	3,7	2,35	8,15
<u>5</u> , F	4	(2,25) 2,8	8,63

This conclusion is in agreement with the one of COX (2) whose results were used to estimate the electronegativity of SiMe_3 group. We considered the dotted line (fig.1) for compounds 1, 2, 3, 5 (X and Y both electron releasing) and broken line for compound 4 (NO_2 is electron withdrawing) together with our values of J_{AB} to obtain $E_X + E_{\text{SiMe}_3}$, and therefore E_{SiMe_3} . The obtained values are shown in table 1. The last one corresponding to $X = \text{F}$ is obviously too large. But fluorine atom can be considered as a strong electron donor, by conjugation, and in that case, SiMe_3 is induced to act as an electron acceptor through its 3d-orbitals. The SiMe_3 group electronegativity in compound 5 is then to be obtained from the broken line as $E_{\text{SiMe}_3} = 2,25$ in excellent agreement with the others. Moreover previous unpublished theoretical work using an iterative process based on free atoms electronegativities, and Pauling formula, allowed us to calculate the electronegativity of $-\text{SiMe}_3$ group bonded to a phenyl ring as 2,25. The variation of J_{AB} with the nature of substituent X can be explained by the inductive effect, as measured by E_X .

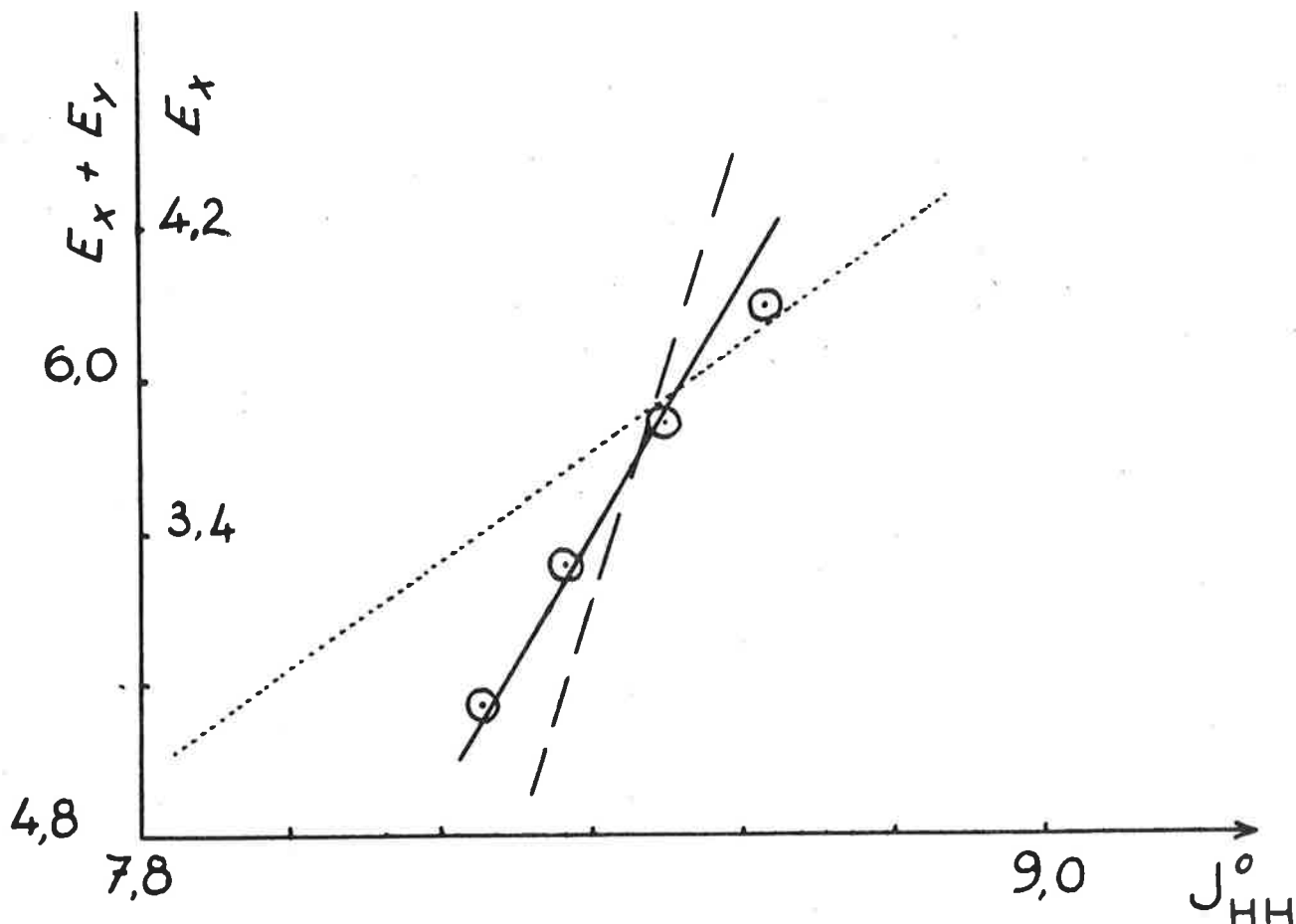


Figure 1 : $\left. \begin{array}{l} \text{-----} \\ \text{.....} \\ \text{-----} \end{array} \right\} \begin{array}{l} E_X + E_Y = f(J_{HH}^0) \text{, from reference 2. see text.} \\ E_X = f(J_{HH}^0) \text{, when } Y = \text{SiMe}_3. \end{array}$

The agreement between experimental and calculated E_{SiMe_3} electronegativity, although perhaps casual favors that idea. But when $X=F$, to SiMe_3 account for the observed J_{AB} , we have to consider that SiMe_3 is electron acceptor. This can be achieved only if there is a participation of the Silicon d-orbitals favored by the presence of a strong π electron donor on para position.

Despite the harsh charge of S.I. MILLER and G.R. WILEY against "linear correlators fraternity" I would like to add two points to their diagram (3) mentioning the study of p-substituted acetanilides. In this series

$$\begin{aligned} \delta_{\text{CH}_3} &= 0.206 + 0.127 \sigma_p \\ \delta_{\text{NH}} &= 0.996 + 0.723 \sigma_p \end{aligned}$$

Yours sincerely.

J.R. Bennett

J. BENNETT

J.C. MAIRE

Y. VIGNOLLET

References

- (1) J.C. MAIRE, Y. VIGNOLLET, M. WITANOWSKI, Chem. Comm. 1187 (1963)
- (2) P.F. COX, J. Amer. Chem. Soc. 85, 380 (1963).
- (3) TANU News letter 124-25. Fig. 6 (Fig. 1 in the text).



DIVISION OF MOLECULAR SCIENCE

Ministry of Technology

NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

Telex: 262344 Telegrams: Physics, Teddington, Telex

Telephone: TEDDINGTON Lock 3222, ext.

24th April 1969

Please address any reply to
THE DIRECTOR

and quote: MS 5/9/10C

Your reference:

Dear Dr. Shapiro,

Molecular Motions in Urea-d₄ AdductsT₁ and T_{1ρ} measurements

In conjunction with Dai Blears who was then spending a few weeks at the Chemistry Department at Manchester University, we have studied molecular motions in the adducts of urea-d₄ with palmitic and stearic acids, by measuring the relaxation times in the laboratory (T₁) and rotating frames (T_{1ρ}) as a function of temperature. These adducts had been previously studied by broadline nmr (Umemoto, K. and Danyluk, S.S., J.Phys.Chem., 71, 3757, 1967) and we thought it would be of interest to make measurements at two widely different frequencies in order to detect and characterize the different motions more thoroughly. Three separate processes are evident in both the T₁ and T_{1ρ} data for both the adducts, the two at lower temperatures being second order processes, whose activation energies have been determined from the shifts of the minima with frequency. The high temperature process seems to be first order, showing no shift with change of frequency, and corresponding roughly in position to the major drops in $\langle H_2^2 \rangle$ seen in the broadline data. The molecular assignments are not clear, although the lowest temperature process probably corresponds to terminal methyl group reorientation, whilst the first order process may be due to rotation of whole acid molecules in their channels. This work is in course of publication and preprints are available.

We have also looked at nuclear relaxation (T₁ and T_{1ρ}) as a function of molecular weight in a series of ^{well} characterized linear atactic polystyrenes, preprints of this work also being available. We are also starting some high resolution studies of polymers in solution aiming to follow up some work of myself and Keith McLauchlan on polyethylene oxide (J.Phys.Chem., 69, 1888, 1965), where our interest was in determining gauche/trans ratios of bonds in the chain. Roger Pritchett has just joined our group, and is primarily concerned with this aspect of our work.

Yours sincerely,

Tom Connor

TOM CONNOR

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



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
WASHINGTON, D.C. 20204

FOOD AND DRUG ADMINISTRATION

Operating Instructions for the A-60/C-1024 Combination

May 1, 1969

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

Dear Barry:

We now also have available a set of operating instructions for the A-60/C-1024 combination, "which (we think) are compact, complete, easy-to-follow and (we hope) free of errors" (see TAMUNMR 118,10).

Again, anyone interested in these directions is welcome to a set for the asking.

Best regards.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "Ernest", is written below the typed name.

Ernest Lustig, Ph.D.
Division of Food Chemistry
and Technology
Bureau of Science

UNIVERSITY OF HOUSTON

CULLEN BOULEVARD
HOUSTON, TEXAS 77004
UNITED STATES OF AMERICA

DEPARTMENT OF CHEMISTRY

28 April 1969

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

Title: Deuterium Decoupling: An Aid to the Determination of the Structure of Several Deuterated Vinylcyclopropanes.

Dear Barry:

We have been using 100 MHz NMR to determine the position of the deuterium atom in 2-deuterio-1-vinylcyclopropane with reasonable success. We have even been able to analyze various cis:trans mixtures by simple integration. There are some accidental degeneracies which simplify the spectra, but that is not the subject of this letter.

When the cis-2,3-dideuteriovinylcyclopropane (I) was heated at 325°C for 50 minutes, we obtained a reaction mixture which consisted of nothing but deuterated vinylcyclopropane. The spectrum shown at the top of the page indicates the deuterium atoms were epimerized. However, this spectrum was obtained even after care was exhibited in the operation of the spectrometer, and is fuzzy, indefinite, unconvincing, and perhaps useless. Since at this point our investment in time was considerable, we carried the sample to Ben Shoulders' spectrometer and laboratory in Austin and decoupled the deuterium atoms. Our initial results were disappointing, as we had a great deal of trouble with long relaxation times. In desperation, we cooled the sample, condensed the vinylcyclopropane in the carbon tetrachloride layer, and operated using more or less normal conditions. The results are shown in the lower spectrum. The deuterium decoupled spectrum is a reasonable super-position of the individual spectra of the three isomers which are illustrated below. The qualitative assignments of parameters are also indicated. Computer analysis of the coupling constants and chemical shifts for these deuterated compounds are underway and we hope to be able to report them soon.

It seems particularly inappropriate to mention to the entire NMR community the name change which the Aggies have requested.

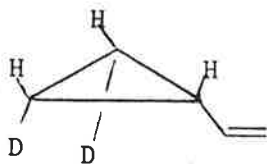
Sincerely,

Bob

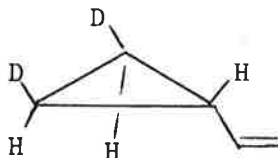
M. R. Willcott
Associate Professor of Chemistry

MRW:la
Enclosure

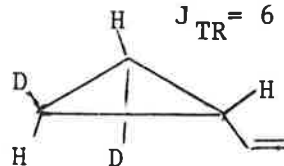
$\delta = 0.6$ $J_C = 8$ Hz



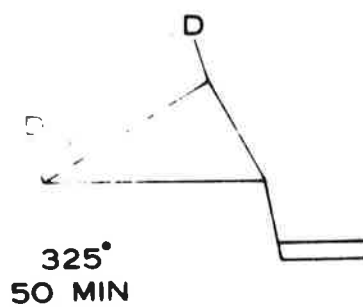
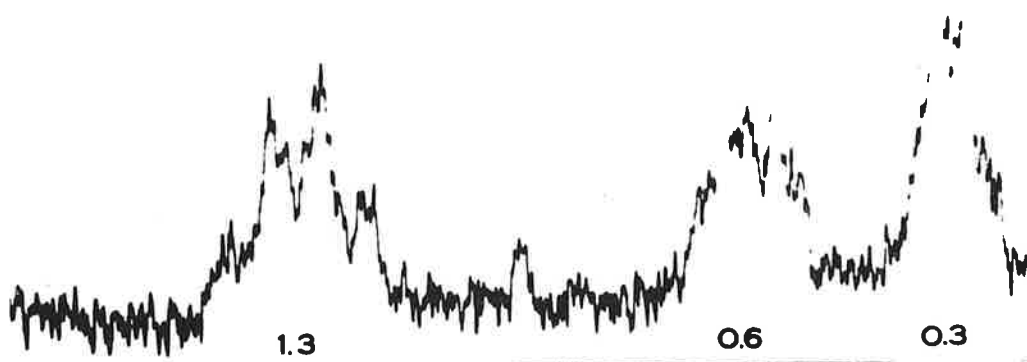
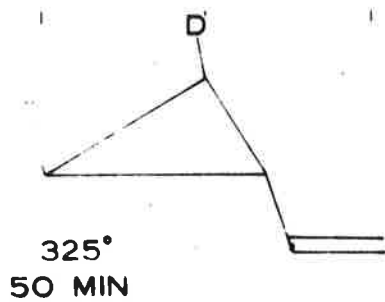
$\delta = 0.3$ $J_{TR} = 5$ Hz



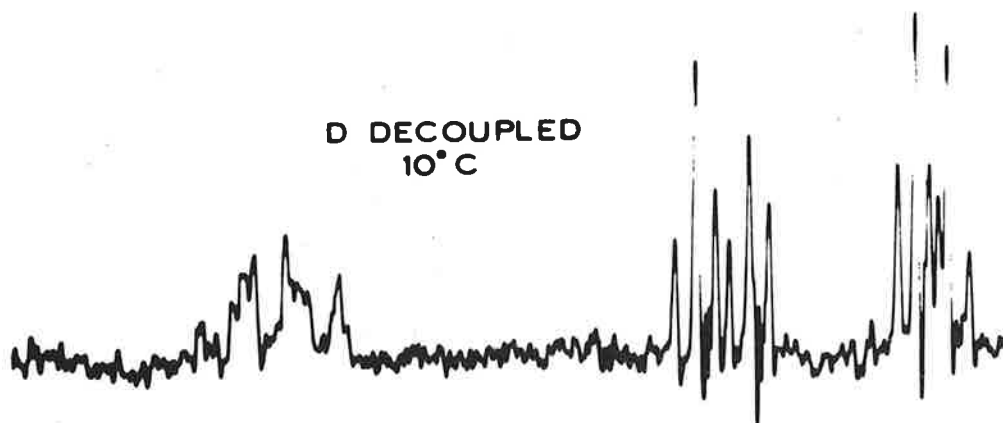
$\delta = 0.6$ $J_C = 8$ Hz
 $J_{TR} = 6$ Hz



$\delta = 0.3$ $J_C = 6$ Hz
 $J_{TR} = 5$ Hz



D DECOUPLED
10°C





28th April, 1969

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

Dear Dr. Shapiro,

Notation for Spin Systems

A group of British N.M.R. spectroscopists has been concerned about the above question. A sub-committee of the British N.M.R. Discussion Group (now affiliated to the (London) Chemical Society) has met and corresponded. Some of you may have seen a short summary of our proposals in Bishop, at p.95 of Ann. Rev. in N.M.R. Spectroscopy, ed. Mooney, vol. 1, Academic Press 1968. The members of the sub-committee were Professor Sheppard, F.R.S., and Drs. Bishop, Bladon, Harris, R. G. Jones, Lynden-Bell, Mooney and Woodman; I am most grateful to them, and particularly to Dr. Woodman for the detailed thought he has given these problems.

I append our suggestions, and welcome any comments, either directly, or via the Newsletter. In particular, I am not happy about example 17 (see footnote 2).

Sincerely yours,

C. W. Haigh

Notation for Spin Systems in N.M.R.

The A, B, P, X notation for magnetic nuclei introduced by Bernstein, Pople and Schneider in their classic 1957 paper has been universally adopted. But it does not distinguish between magnetically equivalent (me) and magnetically non-equivalent

(mne) nuclei. (See Waugh and Dodds, J.C.P. 31, 1235 (1959).) E.g. in methylene fluoride, the protons have the same chemical shift (are isochronous), and so are the ¹⁹F nuclei; further each proton is equally coupled to each fluorine, so that the protons are me, and so are the fluorines. However, in any of the isomers of difluoroethylene, although the protons (and also the fluorines) are isochronous, they are unequally coupled to the two fluorines, and are therefore mne. Yet on this notation, both are described as A₂X₂ systems.

This problem was recognised quite early, and two alternative notations have been proposed. It was apparently Richards and Schaefer (Mol. Phys. 1, 331 (1958)) who first proposed that isochronous but mne nuclei should be represented by one or more primes. Accordingly, where no primes are added, this implies all isochronous nuclei are me. Secondly, Diehl and Pople (ibid. 3, 537 (1960)) proposed that isochronous nuclei that are me should be denoted by an asterisk. By implication, though not explicitly, the absence of asterisks implies that nuclei are mne. The notation was certainly understood in this sense by Lynden-Bell (ibid. 6, 601 (1963)). The present situation is summarised and illustrated in table I. Column IV presents the suggestions embodied in this memorandum and discussed below.

<u>Molecule</u>	<u>Table I</u>			
	<u>System</u>			
	<u>I. B., P. & S.</u>	<u>II. R. & S.</u>	<u>III. D. & P.</u>	<u>IV.</u>
CH ₂ F ₂	A ₂ X ₂	1. A ₂ X ₂	1. A ₂ [*] X ₂ [*]	[A ₂ X ₂]
C ₂ H ₂ F ₂	A ₂ X ₂	2. AA'XX'	2. A ₂ X ₂	[AX] ₂

The systems and the notational principles will be referred to, following the table, as I, II.1, II.2, III.1, III.2 or IV. It should be added that system II has been very popular, whereas III has gained little acceptance.

These systems have been extremely useful. However, in my opinion the present situation has three principal disadvantages. Firstly, the notation A₂X₂ can mean three different things, following I, II.1 or III.2: this can be confusing and even possibly ambiguous. An appropriate example is given by the -CH₂.CH₂- grouping in some rings: this was often referred to as A₂B₂ (correctly in system I), and analysed as A₂B₂ (system II.1) until it was recognised as a special case of A₂B₂ (system III.2). Secondly, the use of primes, i.e. II.2, in quite simple but highly symmetrical cases can be very cumbersome and inelegant. A recent paper (Jones and Walker, ibid. 10, 363 (1966)) used the symbols AA'A"A'XX'X'X' repeatedly for the first few pages; on the eighth page, they finally gave up and introduced (without comment) a new notation which provided much of the stimulation for the present approach, though it was not eventually incorporated. Lynden-Bell (loc. cit.) poured scorn on the notation AA'A"A'XX'(II.2), preferring A₄X₂(III.2). Thirdly, the current notations include no economical way of signifying that a similar group of nuclei is repeated once

or several times in the molecule. That the notations for such systems, following II, can get very cumbersome is amply illustrated by the table II.

The following suggestions are designed to overcome these objections. Firstly, it is suggested that the use of only capital letters and subscript numbers should connote nothing about magnetic equivalence or non-equivalence. In other words, the ambiguous usages II.1 and III.2 should be dropped, leaving only the usage I implied when one merely writes A_2X_2 . This 'portmanteau' usage will be chiefly of use to chemists when they are not concerned with the finer details of the spectra.

Secondly, the following new rule is proposed (henceforth termed system IV):

"Square brackets (with subscript numbers) shall be used to indicate repeated, symmetry-related, magnetically non-equivalent groups of nuclei. All strictly isochronous nuclei within a square bracket are to be considered magnetically equivalent unless the contrary is specified by the use of further square brackets. In the same way, the square bracket (without a subscript) shall be used to denote the magnetic equivalence of iso-chronous nuclei inside it".

The following explanatory notes are added:

1. Each square bracket represents a specific symmetry operation or set of operations e.g. for cyclobutene, represented $[[A]_2X]_2$, the inner brackets represent the ring plane, the outer brackets the perpendicular plane.
2. In cases of ambiguity, which can occur where threefold or higher symmetry axes may be present, the relevant point-group must be appended in brackets (see also Jones and Walker, loc. cit.). Where free rotation is assumed, in simple cases the rule due to F. S. Mortimer, (J. Mag. Res. 1, 1 (1969).) is to be applied, namely that the relevant symmetry to be used is that for the most symmetrical conformer: the symbol 'rot.' should be added in this case. These two points are well illustrated by examples 13 and 14 in table II: in 14, with C_{2v} symmetry - the molecular plane is redundant - there are three distinct $J_{AA's}$. In 13, however, where free rotation is assumed, and the conformation of highest symmetry is chosen (namely that with the ring planes perpendicular), only two distinct $J_{AA's}$ are discernible².
3. Accidental equality of chemical shift (not related to symmetry) is specifically excluded from consideration.

¹ In more complicated cases, ordinary point group notation is inadequate (Altman, Proc. Roy. Soc., A298, 184 (1967). and refs. cited therein.)

² Where sets of atoms lie on different types of special positions in a point group, the suggested approach is illustrated by example 17.

The square bracket³ is uniquely characteristic of the new notation IV, just as the prime was of II and the asterisk for III. There should therefore be neither confusion nor ambiguity. It is also worth noting that the number of distinct couplings of a different type is always implicit in the notation, as in the examples just cited. (Of course, to say which is which in a particular case a diagram must be drawn and the A nuclei etc. numbered).

It is hoped that table II adequately illustrates the suggestions introduced in this memorandum, and demonstrates their increased clarity and succinctness compared with previous systems⁴.

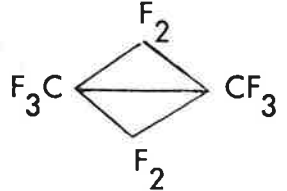
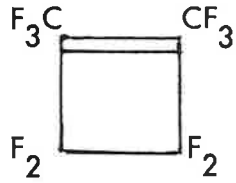
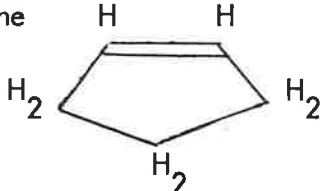
³ Square rather than round brackets have been specified to avoid any possible confusion with the usage of Gestblom et al. (Acta Chem. Scand. 18, 1222 (1964)).

⁴ The extension of this notation to anisotropic media (see e.g. C. M. Woodman, Mol. Phys. 13, 365 (1967), footnote on p. 368) is straightforward. Nuclei with spin greater than $\frac{1}{2}$ can also be included by writing the value of the spin as a right superscript; otherwise, spin $\frac{1}{2}$ is to be assumed. Furthermore, one can extend this notation to the terminology of sub-spectral analysis, and write of, say, the two $[ab]_2$ sub-spectra in an $[AB]_2X$ system.

Table II

Molecule	Systems			
	I	II	III	IV
1. o-dichlorobenzene $C_6H_4Cl_2$	A_2B_2	$AA'BB'$	A_2B_2	$[AB]_2$
2. β -propiolactone $\underbrace{CH_2 \cdot CH_2 \cdot COO}_1$	A_2B_2	$AA'BB'$	A_2B_2	$[AB]_2$
3. Sulphur tetrafluoride SF_4	A_2B_2	A_2B_2	$A_2^*B_2^*$	$[A_2B_2]$
4. Pyridine C_5NH_5	A_2B_2C	$AA'BB'C$	A_2B_2C	$[AB]_2C$
5. s-trifluorobenzene $C_6H_3F_3$	A_3X_3	$AA'A''XX'X''$	A_3X_3	$[AX]_3 (C_{3v})$
6. Diphosphine P_2H_4	A_4X_2	$AA'A''A'''XX'$	A_4X_2	$[[A]_2X]_2$
7. Cyclobutene C_4H_6	A_4X_2	$AA'A''A'''XX'$	A_4X_2	$[[A]_2X]_2$
8. Bis(3,5-dichloro-2,4,6-trifluorophenyl)	A_4X_2	$A_2A_2'XX'$	$A_2^*A_2^*X_2$	$[A_2X]_2 (rot.)$
9. Tetrahydrofuran $\underbrace{CH_2CH_2CH_2CH_2-O}$	A_4X_4	$AA'A''A'''XX'X''X'''$	A_4X_4	$[AX]_4 (C_{2v})$
10. Bis(4-chloro-2,3,5,6-tetrafluorophenyl)	A_4X_4	$AA'A''A'''XX'X''X'''$	A_4X_4	$[AX]_4 (D_{2d}, rot.)$
11. Bicyclo [1.1.1] pentane $HC[CH_2]_3CH$	A_2X_6	A_2X_6	$A_2^*X_6^*$	$[A_2X_6]$
12. Mesitylene s- $C_6H_3(CH_3)_3$	A_3X_9	$AA'A''X_3X_3'X_3''$	$A_3X_3^*X_3^*X_3^*$	$[AX_3]_3 (C_{3v})$
13. Diphenyl $(C_6H_5)_2$	$A_4B_4C_2$	$CBB'AA'A''A'''B''B'''C'$	$A_4B_4C_2$	$[[AB]_2C]_2 (D_{2d}, rot.)$
14. Anthracene $C_{14}H_{10}$	$A_4B_4C_2$	$BB'AA'CC'A''A'''B''B'''$	$A_4B_4C_2$	$[[AB]_2C]_2 (C_{2v})$

Table II (Contd.)

<u>Molecule</u>		<u>Systems</u>			
		<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
15. a.		$A_6 M_2 X_2$	$A_6 MM'XX'$	$A_6^* M_2 X_2$	$A_6 [MX]_2$
b.	$F_2C=C(CF_3).C(CF_3)=CF_2$	$A_6 M_2 X_2$	$MXA_3 A'_3 X' M'$	$A_3^* A_3^* M_2 X_2$	$[A_3 MX]_2$
c.		$A_6 X_4$	$A_3 XX'X''X'''A_3'$	$A_3^* A_3^* X_4$	$[A_3 X]_2$
16.	1,9 bisdehydro[16]annulene (=CH.CH=CH.C≡C.CH=CH.CH=) ₂	$A_4 B_4 X_4$	$ABXX'B'A'A''B''X''X'''B'''A'''$	$A_4 B_4 X_4$	$[ABX]_4 (C_{2v})$
17.	Cyclopentene 	$A_2 B_4 X_2$	$AA'BB'B''B'''XX'$	$A_2 B_4 X_2$	$[A]_2 [B]_4 [X]_2 (C_{2v})$

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

DEPARTMENT OF CHEMISTRY

May 2, 1969

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

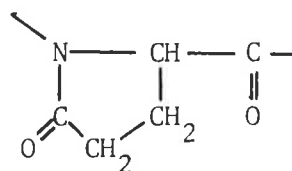
Dear Barry:

Subject: Broadband Homonuclear Decoupling

We are in the process of acquiring an HA-100 spectrometer with Varian's new 15-inch, wide-gap magnet. Eventually this system will include a noise decoupler, which is, of course, designed primarily for heteronuclear decoupling. Pending receipt of this unit, Vincent Heuring has developed a method of spectrum simplification by broadband homonuclear decoupling, and the results have been very satisfactory.

His procedure is essentially that of sweeping the irradiating frequency over that portion of the spectrum to be decoupled at a rate fast compared with $1/T_2$ for the peaks being irradiated. This "stirring" of the spins effectively decouples a number of them simultaneously from the remainder of the spin system and thus from the signal which one wishes to observe. A Wavetek model 114 function generator was swept internally with a sawtooth ramp at a rate of approximately 100 Hz, setting the upper and lower limits of the sweep to correspond to the frequency range to be irradiated. This signal was fed into the HA-100 exactly as would be a fixed oscillator output for ordinary decoupling.

A particular problem solved by this technique by Dr. Katherine N. Scott is illustrated in the accompanying spectrum. The sample was an unknown, from the laboratory of Dr. Clyde M. Williams, Department of radiology, University of Florida, and was found to contain the structural unit:



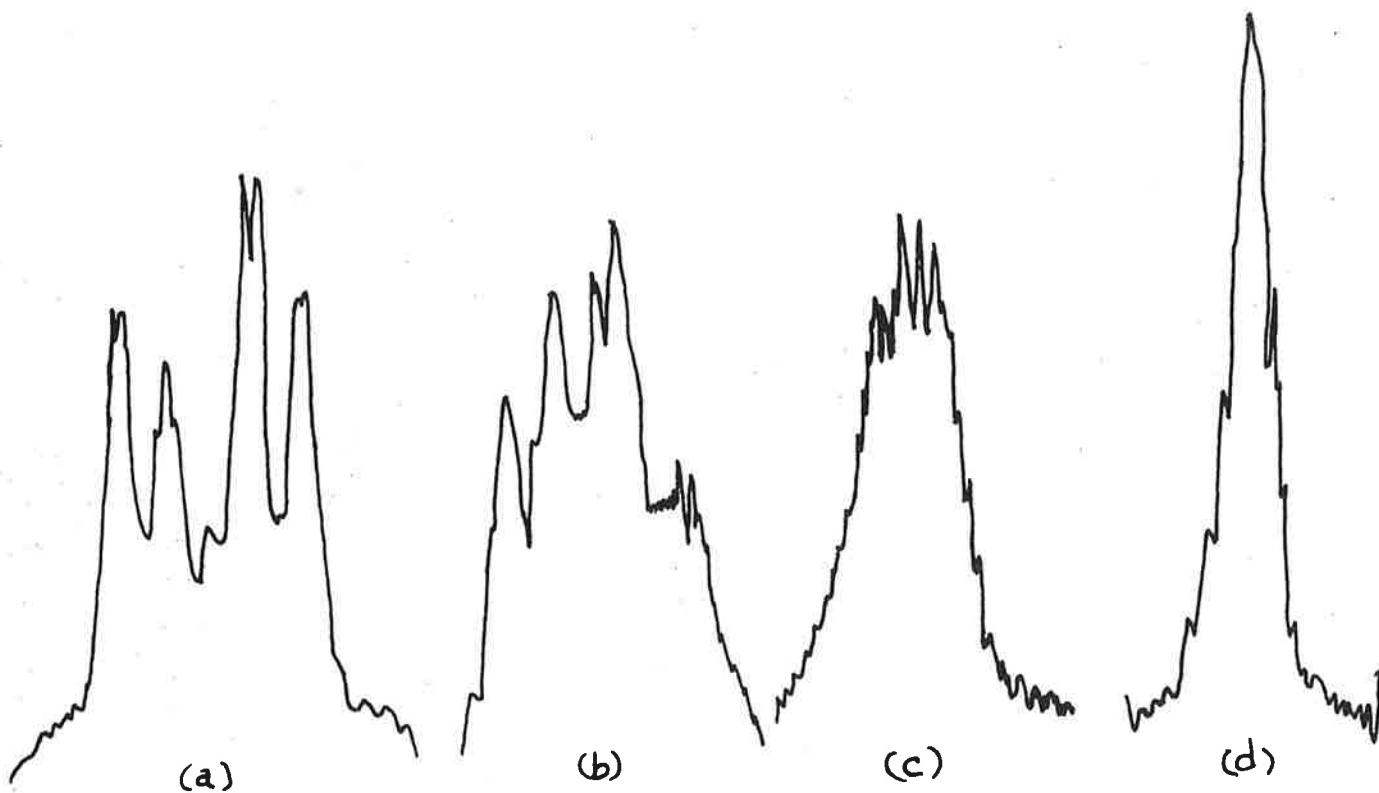
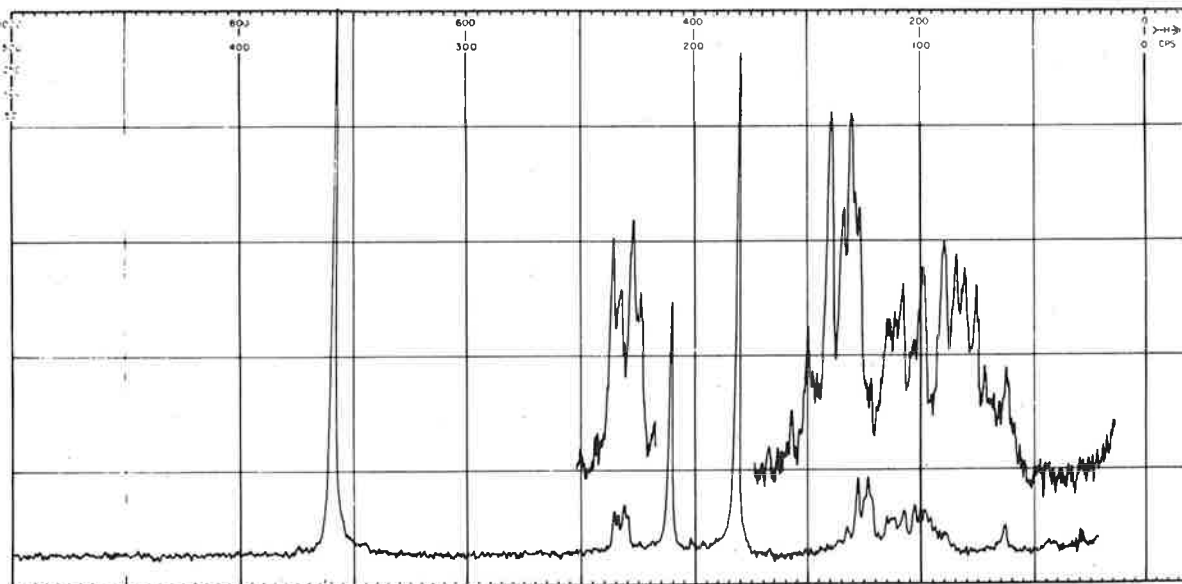
It was desired to establish that the splitting in the methine hydrogen resonance at about 470 Hz downfield from the lock was the result of spin-spin coupling to the methylene protons in the upfield portion of the spectrum. The Wavetek was swept from about 170 to 270 Hz, so as to cover the upfield region. The appearance of the methine multiplet, as a function of irradiating voltage as determined from the scope, is shown in four stages: (a) 10 mv, (b) 100 mv, (c) 200 mv, and (d) 400 mv. It can be seen that the multiplet collapses nicely to a singlet, and this collapse was achieved without the need of detailed searching for an optimum single decoupling frequency.

There seems to be no reason why, with several function generators or with a sawtooth ramp with a discontinuity in it, one could not decouple any desired group of peaks from the remainder of the spectrum. An additional benefit of the method is that beat notes of the irradiating frequency are not seen; the only beats are those from the sweep rate, a quantity which can be varied over a rather wide range with little effect on the spectrum.

Cordially yours,

Wallace

W. S. Brey, Jr.



Author Index - TAMU NMR Newsletter No. 128

Banas, E.M.	11	Lusebrink, T.R.	1
Bennett, J.	38	Lustig, E.	41
Brey, W.S. Jr.	50	Maire, J.C.	38
Carey, P.R.	16	Mavel, G.	20
Connor, T.	40	Olah, G.A.	4
Croteau, P.G.	11	Oliver, W.L. Jr.	12
Dinerstein, R.A.	11	Parmakovich, V.	18
Dowden, B.F.	1	Ramey, K.C.	35
Dürr, H.	6	Randall, E.W.	26
Grant, D.M.	27	Reuben, J.	14
Haigh, C.W.	44	Saika, A.	28
Hettler, H.	23	Sewell, M.J.	34
Jeuell, C.L.	4	Slupski, D.J.	11
Jones, A.J.	27	Turpin, M.A.	16
Kroto, H.W.	16	Vignollet, Y.	38
Krüger, U.	23	Vold, R.L.	30
Lambert, J.B.	12	Wenzel, B.E.	11
Lunazzi, L.	32	White, A.M.	4
		Willcott, M.R.	42

Sponsors of the TAMU NMR Newsletter

AKU (Algemene Kunstzijde Unie N.V.), (Arnhem, The Netherlands)
Albright and Wilson (Mfg.) Ltd. (England)
American Cyanamid Company
American Oil Company
The Atlantic Richfield Company
Badische Anilin- & Soda-Fabrik AG (Ludwigshafen, Germany)
The British Petroleum Company Limited (England)
Bryn Mawr College
Bureau of Mines, U.S. Department of Interior
Dartmouth College
Diaprep Incorporated
Digital Equipment Corporation
The Dow Chemical Company
Dow Corning Corporation
Eastman Kodak Company
Farbenfabriken Bayer AG (Germany)
J. R. Geigy S.A. (Switzerland)
Glaxo Group Limited (England)
The Goodyear Tire and Rubber Company
W. R. Grace and Company
Gulf Research & Development Company
F. Hoffmann-La Roche & Company (Switzerland)
Hooker Chemical Corporation
Hunter College of the City University of New York
IBM Corporation
Imperial Chemical Industries Limited (Great Britain)
IRCHA (France)
Library Research Department BROCADES (Holland)
The Lilly Research Laboratories, Eli Lilly and Company
E. Merck AG (Darmstadt, Germany)
Monsanto Company
Montecatini Edison S.p.A. (Italy)
National Institutes of Health
National Research Council of Canada
Nuclear Magnetic Resonance Specialties, Inc.
N.V. Philips-Duphar (The Netherlands)
The Perkin-Elmer Corporation
The Procter and Gamble Company, Miami Valley Laboratories
The Royal Institute of Technology (Sweden)
Shell Development Company
Southern Research Institute
Stauffer Chemical Company
Texas A&M Research Foundation
Texas A&M University
Texas Christian University Research Foundation
Union Carbide Corporation
Varian
Wilmad Glass Company, Inc.