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Newsletter

Brian H. Lykes

No. 138
MARCH, 1970

Retcofsky, H.L.; Friedel, R.A. ³³ S NMR Spectrum of Thiophene	1
Bystrov, V. Once Again About Combination Signals (Triple Resonance With a Strong rf Field)	2
Freyman, R. Nuclear Spin-Spin Relaxation in Pure Gases at Low Pressures	6
Rummen, F.H.A. A Simple Model for σ_a	8
Johannesen, R.B. Small Effects of Long-Range Coupling	10
Johannesen, R.B. A Mystery Solved!?	11
Slopp, G. An Interesting Degenerate ABX Case	12
Kellerhals, H.P.; Diehl, P. Modification in Error Computation for LAOCOON-type Programs?	16
Kuhlmann, K.F. What is "Shim"? CAT-Teletype Interfacing.	18
Andose, J.; Egan, B.; Mislow, K. Magnetic Nonequivalence of Enantiomers Which Owe Their Chirality to Tervalent Nitrogen	20
Slocum, D.W.; Jennings, C.A. The Hydroxyl Proton Spectra of o- and m-Methoxybenzyl Alcohol	22
Lunazzi, L. Proton-Mercury Coupling Constants in the Isomers of Dithienyl- and Difuryl Mercury	25
Wendisch, D.; Hähner, B. Bemerkungen Zum Einsatz Des "Spectro System 100" Von Varian, Ass.	28
Bryant, R.G. Potassium-39 Relaxation Times	30
Benezra, C. Angular Dependence of Vicinal ³¹ P, ¹ H Coupling	31

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Dürr, H. Einige Beispiele der Spektrenvereinfachung Durch Spinentkopplung	33
Reeves, L.W. Hindered Barriers in Dimethylamides	36
Shapiro, B.L. Postdoctoral Fellowship Available	38
Pehk, T.; Lippmaa, E. CIDNP Phenomena in ^{13}C Spectra at Natural Abundance	39
Smidt, J. THD Research Fellowship; Miscellaneous	42
Engle, J.L. R.F. Field Measurement	43
Cooper, M.A.; Manatt, S.L. "PASADENA"	44
Sherwood, J.N.; Lockhart, N.C.; Bladon, P. Line Narrowing Measurements on Single Plastic Crystals Using an R10 Spectrometer	48
Kaptein, R.; den Hollander, J.A.; de Kanter, F.J.J. Calculation of CINP Spectra	50
Thomas, W.A. The NMR Spectrum of L-azetidine-2-carboxylic Acid, a Novel Four-membered Ring	52
Berlin, K.D. Phosphorylated Aziridines, Preferred Invertomer; Correlation of J_{PNCH} Coupling with Structure	55
Katritzky, A.R.; Fletcher, I.J.; Bordignon, E.; Signor, A.; Lea, J.R. NMR Study of a Borohydride Reduction of a Pyridine	56

<p>Deadline Dates: No. 139: 6 April 1970 No. 140: 4 May 1970</p>
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All Newsletter correspondence, etc., should be addressed to:

Bernard L. Shapiro
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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

February 7, 1970

Dear Barry:

Although the first observation of an ^{33}S NMR signal (carbon disulfide) was reported by Dharmatte and Weaver in 1951, very few data for other pure compounds are currently available. We are exploring the sulfur-33 technique as a possible probe for coal-structure studies and wish to report here the

^{33}S NMR SPECTRUM OF THIOPHENE

The ^{33}S NMR spectrum of thiophene to which 10% carbon disulfide had been added as an internal chemical shift standard is shown on the right. The resonances were observed using the dispersion mode and broadline techniques. The peak at high field is due to carbon disulfide ($\delta = 0$ ppm) and exhibits some slight modulation broadening. The broader peak is that due to thiophene ($\delta = -231$ ppm; ΔH at half height is 710 Hz).

Attempts to observe the resonance in the tetrahydro analogue using essentially the same experimental conditions proved unsuccessful despite the fact that the magnetic field was scanned 30 gauss on either side of the carbon disulfide resonance. It is likely that quadrupole effects lead to excessive broadening of the resonance in this latter case.

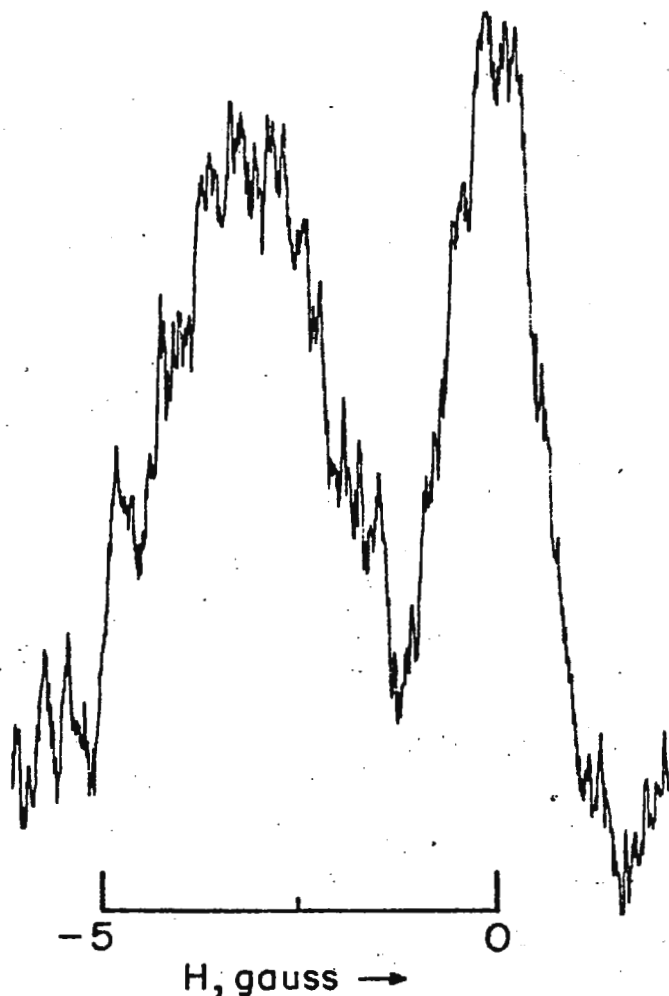
Sincerely yours,

Herb

H. L. Retcofsky

Rus

R. A. Friedel



ИНСТИТУТ ХИМИИ
ПРИРОДНЫХ СОЕДИНЕНИЙ
АН СССР

Dr. V.F. Bystrov
INSTITUTE FOR CHEMISTRY
OF NATURAL PRODUCTS
ACADEMY OF SCIENCES OF USSR
Ul. Vavilova, Moscow, USSR

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

26 December 1969

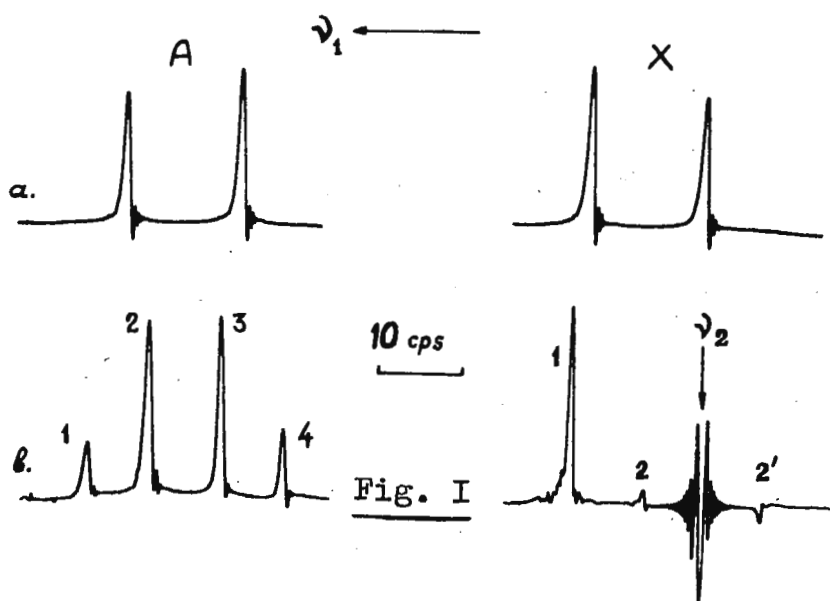
Dear Barry:

Title: Once again about
combination signals (triple
resonance with a strong rf
field).

In addition to the previously examined cases of exiting signals on combination frequencies [triple tickling of AMX spin-system (1) and double-quantum transitions in a AB system (2)] I wish to communicate the results of experiments on triple resonance with a strong rf field H_2 . E. Kundla (3) has theoretically considered the influence of an additional weak rf field H_3 on the double resonance spectrum obtained by the action of a strong rf field H_2 .

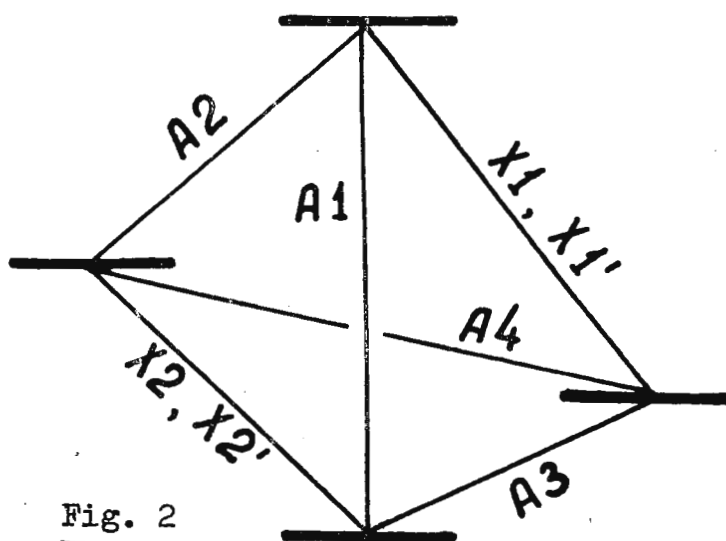
The experiments were carried out on the AX spectrum of the olefinic protons of trans-chloroacrylic acid ($\gamma_0 \delta^1 = 121.6$ cps, $J = 13.6$ cps) at 100 Mc/sec and frequency sweep (Fig. 1a). Irradiation of the high field X line by the relatively strong rf field H_2 (of the magnitude $h_2 = \gamma H_2 / 2\pi = 7.2$ cps) yields the double resonance spectrum in which the forbidden transitions are now allowed (Fig. 1b). The new system of energy levels is shown schematically on Fig. 2.

The influence of an additional weak rf field H_3 on the double resonance spectrum must be very similar to the effect on a mono resonance spectrum. In particular, one could expect splitting of the lines into doublets due to progressive and regressive transitions and the actuation of signals on

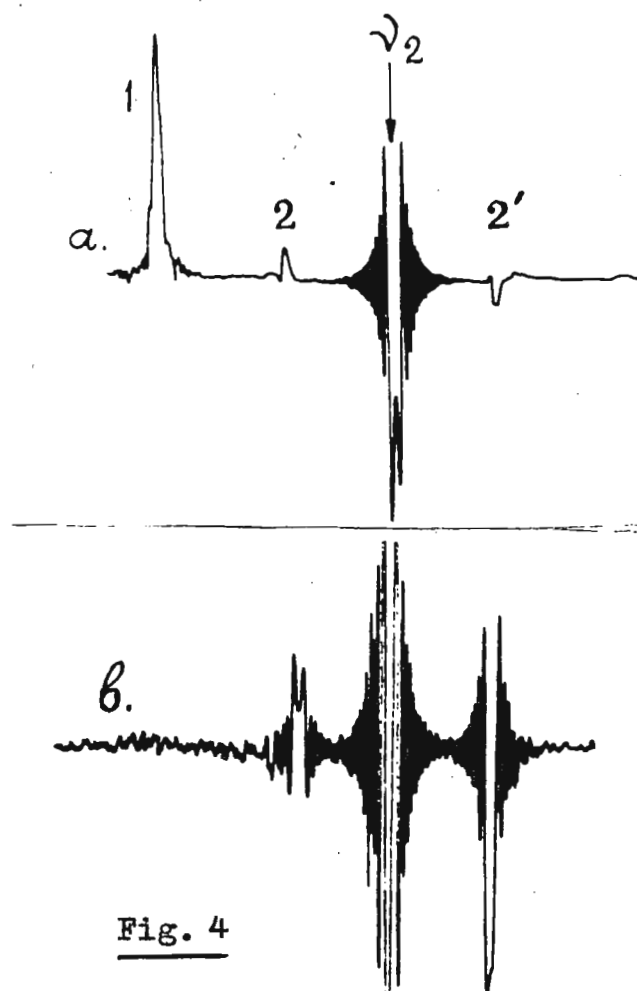
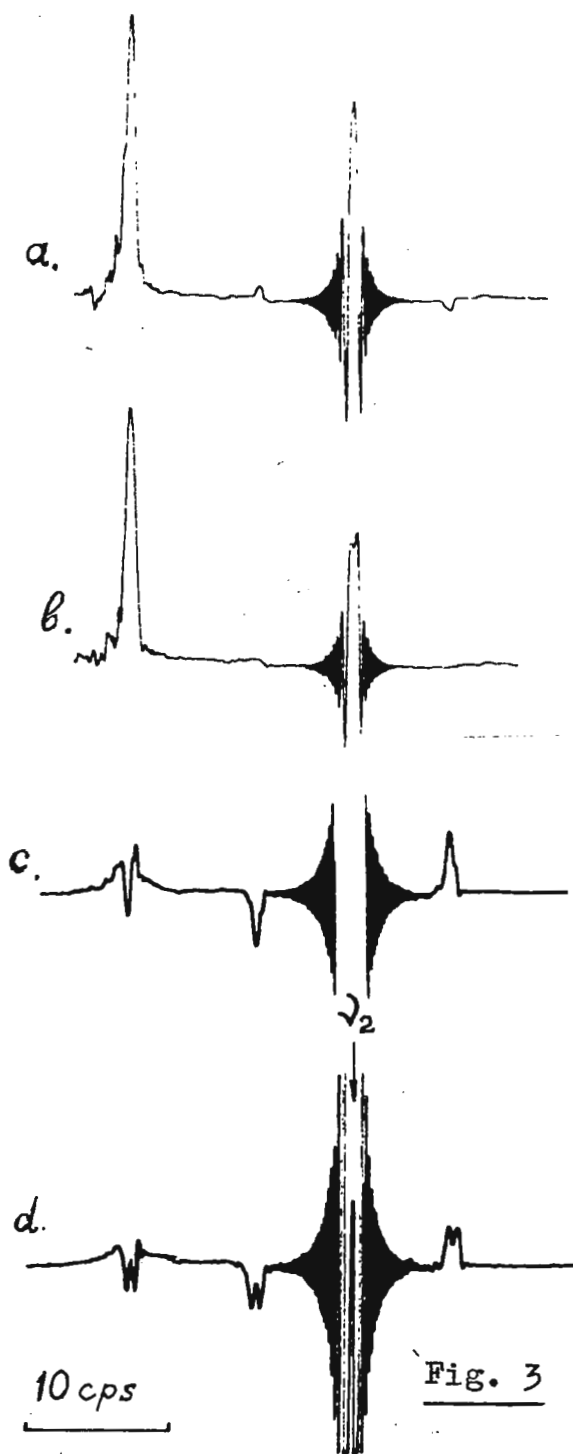


combination frequencies (3). However such a similarity is restricted in some cases only to the qualitative side of the phenomenon.

Fig. 3 shows the X-part of the double resonance spectrum with additional irradiation of the A1 line by the weak rf field H_3 . On increasing the amplitude of this field [$h_3 = 0.04(\underline{a})$, $0.12(\underline{b})$, $1.0(\underline{c})$ and $1.7 \text{ cps}(\underline{d})$] inversion of the X2 and X2' signals and their splitting into doublets observed. The XI line also undergo considerable change in shape.



The appearance of a signal on a frequency that is a combination of the basic frequencies was observed in experiments shown on Fig. 4. The method for detecting these signals has been described earlier (I,4). For successful results it is



necessary to irradiate two (out of three) transitions by weak rf fields in an interconnected three level fragment of the energy diagram shown on Fig. 2.

When the A3 and A4 lines are ir-

radiated by weak fields with ν_3 and ν_4 frequencies ($h_3 = h_4 = 0.54$ cps) two combination signals simultaneously appear (Fig. 4b). Zero beats are observed when the sweep frequency Γ coincides with the combination signal frequencies $\nu_{\text{comb.}} = \pm(\nu_3 - \nu_4) + \nu_2$, of which one corresponds to the X2 transition and the other to the X2' transition frequency. The transitions A3, A4, X2(X2') form a closed triangle in the energy diagram on Fig. 2.

The principal results of the experiments confirm the theoretical conclusions (3). Some effects as for instance these associated with the shape of the signals (Fig. 3) require additional theoretical consideration.

I am very grateful to Dr. S. Brownstein for presenting the opportunity of carrying out these experiments in the Division of Applied Chemistry, National Research Council of Canada (Ottawa).

With best wishes,

Your sincerely



Vladimir Bystrov

References:

1. V.F. Bystrov, IIT NMR II8-4 (1968); J. Molec. Spectry, 28, 81 (1968).
2. V.F. Bystrov, TAMU NMR I34-28 (1969).
3. E. Kundla, Bull. Acad. Sci. Estonian SSR, Phys. Mathem. Sci. Ser., 17, 475 (1968).
4. L.R. Anders and J.D. Baldeschwieler, J. Chem. Phys. 43, 2147 (1965).

Paris, January 12, 1970

70006/RF/MCP

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

TEXAS 77843 (U. S. A.)

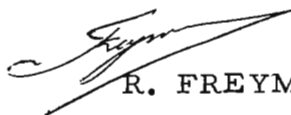
"Nuclear spin-spin relaxation in pure gases at low pressures"

Dear Professor SHAPIRO,

I will report here some results achieved by Drs DAYAN and CHIGLIEN at my laboratory on proton nuclear relaxation. They used a Varian A. 60 spectrometer at room temperature and measured linewidths (it's not a quite ideal method, but an easy one) for protons in gaseous CH_4 , C_2H_2 , C_2H_6 , C_2H_4 , $(\text{CH}_3)_2\text{O}$ and Si Me_4 (in vapor state) from 0.2 to 1.3. bar (*). However the figure herewith shows the values for spin-spin relaxation time T_2 v. s. pressure (at low pressures, it's admitted pressure and density about equal).

More over they have investigated the molecules H_2 , C_2H_2 and $(\text{CH}_3)_2\text{O}$ in mixtures with other gases and they related relaxation time T_∞ (in infinite dilution) to molecular quadrupole moments (when known) : it appears it's possible to determine approximately quadrupole moment's values ; a paper on this point will be published soon.

With best wishes, yours sincerely,



R. FREYMANN.

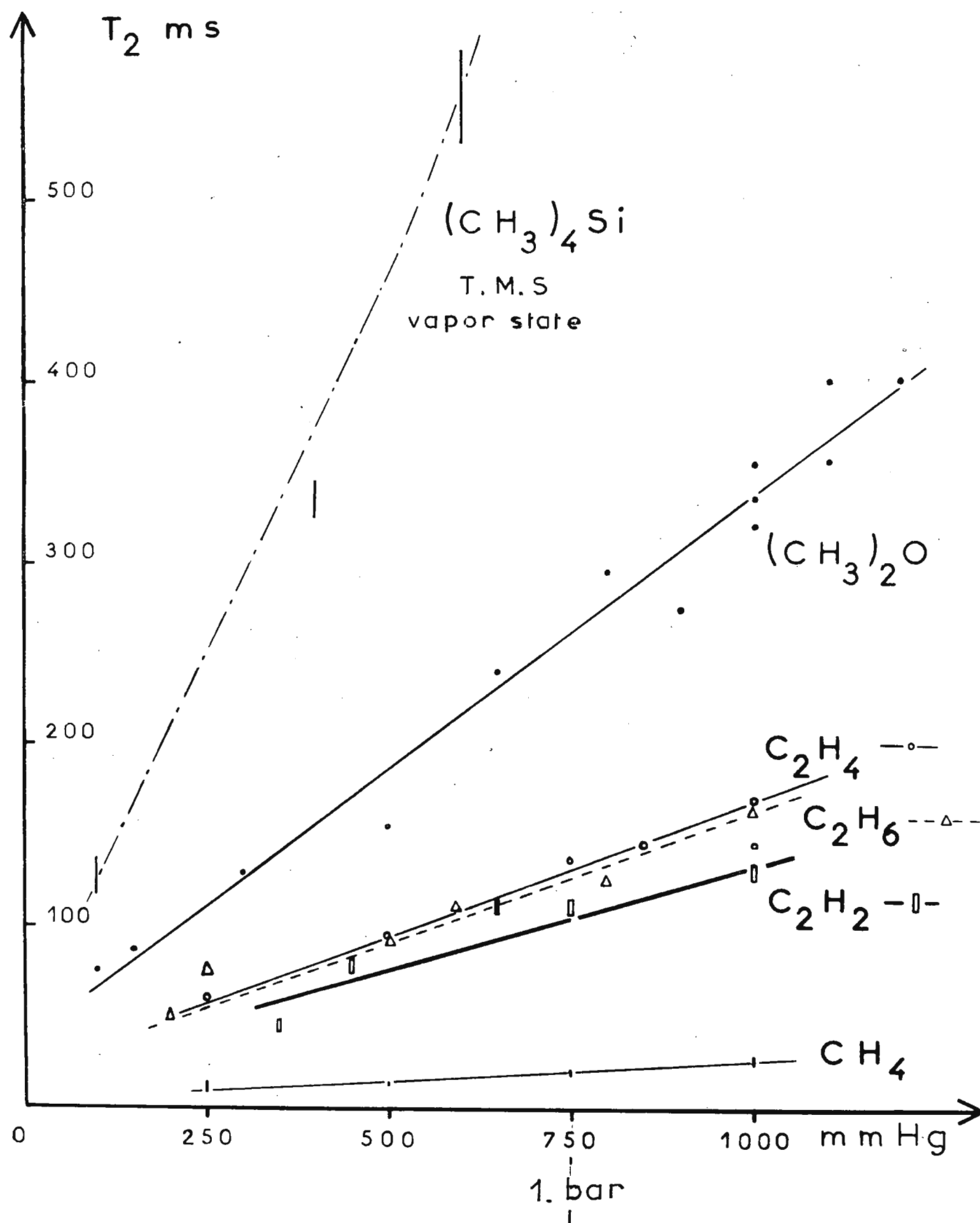
* Pressure N. M. R. tubes were described in :

Mellon N. M. R. 1963 N° 58 for pressures up to 200 bars

Mellon N. M. N. 1963 N° 62 for pressures up to 1,5 bar.

GAZ PURS

pure gases





UNIVERSITY OF SASKATCHEWAN REGINA CAMPUS

DEPARTMENT OF CHEMISTRY

REGINA SASKATCHEWAN

February 5, 1970

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

Dear Dr. Shapiro:

A Simple Model for ∇_a

The Neighbour Anisotropy Effect ∇_a still is a baffling phenomenon that is the preoccupation of many. Recent developments (Schug 1966, Homer 1967, Becconsall 1968) seem to require an ever increasing model-complexity. In an attempt to swing back the pendulum, I have developed the following simple equation:

$$\nabla_a \text{ (ppm)} = + 1.08 / \sqrt[6]{V_1} \quad (1)$$

where V_1 is the molar volume of the solute in the neat liquid state. The factor 1.08 contains a number of solvent parameters (shape factors in particular) as well as an empirical adjustment factor. Equation (1) applies to infinite dilutions of non polar solutes in benzene at 30°C. Details on the derivation of equation (1) have been submitted to J.A.C.S. but at the present it is perhaps only necessary to say that equation (1) is based on the complete absence of complex formation or preferred orientation. Table I gives some results (in fact, these are all I have at the moment!).

The ∇_w contributions have been calculated according to Rummens, Raynes and Bernstein (J. Phys. Chem. 72, 2111 (1968)). The bulk susceptibility term was taken as $\nabla_b = -1.267$ ppm.

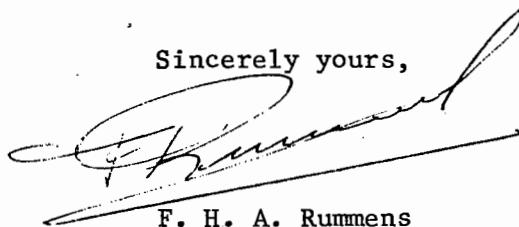
TABLE I

Proton Gas-to-Liquid shieldings (ppm) of
non-polar solutes in Benzene at 30°C

SOLUTE	σ_{exp}	σ_{w}	$\sigma_{\text{exp}} - \sigma_{\text{b}} - \sigma_{\text{w}}$	σ_{a} (calc) eq. (1)
CH ₄	-1.051	-0.206	+0.422	+0.452
C(CH ₂ CH ₃) ₄	-0.893	-0.105	+0.479	
(CH ₂)				+0.456
	-0.963	-0.150	+0.454	
(CH ₃)				
C(CH ₃) ₄	-0.998	-0.212	+0.481	+0.479
C ₆ H ₁₂	-0.962	-0.186	+0.491	+0.490
C ₆ H ₆	-1.001	-0.255	+0.521	+0.505

The conformity between the last two column's of Table I is embarassingly good (standard deviation $\pm 3\%$). The major conclusion is that σ_{a} depends on the solute only in a minor way, which in turn allows the separation of σ_{a} into a product of a solvent factor and a solute factor. The results on C₆H₁₂ indicate that the "site factor" for σ_{a} is unity (or very close to it) as predicted before (F.H.A. Rummens I I T - NMR Newsletter 110, 14 (1967) and Molecular Physics, in press).

Sincerely yours,



F. H. A. Rummens
Assoc. Prof. of Chemistry

FHAR/tag



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

6 February 1970

Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77840

SMALL EFFECTS OF LONG-RANGE COUPLING

Dear Barry:

The Program UEANMR3 referred to elsewhere in this newsletter allows calculation of spectra of quite large systems when magnetic equivalence is present. The n.m.r. spectrum of 3,3-diethylpentane, $(C_2H_5)_4C$, does not show sharp lines, such as are found in other ethyl compounds. It was thought that small long-range coupling over four or more bonds might be responsible for this effect. Thus, the following model systems were calculated: (1) A_2B_3 , (2) $A_2A_2' B_3B_3'$ with all long-range couplings equal zero, and (3) $A_2A_2' B_3B_3'$ with $J_{AA'} = 0.2$ Hz and remaining long-range couplings equal zero. In all three cases $\nu_B - \nu_A = 45.0$ Hz, $J_{AB} = J_{A'B'} = 7.2$ Hz. The result of the calculations gave identical spectra for cases 1 and 2. However, in case 3, even though $J_{AB'}$ and $J_{BB'}$ were zero, the effect of the long-range coupling was manifest in causing each of the lines from the simpler case to be split into a multitude of closely spaced lines. It is apparent from these results that only a very small long-range coupling in a system of this sort is sufficient to cause all of the lines to appear appreciably broadened; nevertheless, there is no single splitting that one can point to and say this is the magnitude of the long-range coupling.

Yours very truly,

Rolf B. Johannesen

Rolf B. Johannesen
Inorganic Chemistry Section



6 February 1970

Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77840

A MYSTERY SOLVED!?

Dear Barry:

I was interested to see the letter by Crutchfield and Heitsch, TAMUNMR 136, about the 40.5 MHz P-31 spectrum of methyl ethylene phosphite and the speculations about causes of the asymmetry observed in this spectrum. The computer program UEANMR3 (Harris, TAMUNMR 125) allows the calculation of the spectrum including the coupling to the methoxyl group. Using the parameters found from analysis of the proton spectrum¹, the P-31 spectrum was calculated at both 1.4092 and 2.3487 T (60 MHz and 100 MHz for protons). The phosphorus spectrum is calculated to be asymmetric and the resemblance between the calculated and observed spectrum is fairly good. Thus there is no need to suppose that there is more than one kind of phosphorus present in the system.

The program UEANMR3 uses magnetic equivalence factoring where possible in order to reduce the sizes of the matrices. The program has recently been revised to allow iterative calculations to be done. Listings are available in Europe from Dr. R. K. Harris, University of East Anglia, University Plain, Norwich NOR 85 C, England. Listings in the United States may be obtained from J. A. Ferretti (IBM 360), National Institutes of Health, Bethesda, Maryland, or from the undersigned in a form best suited for a UNIVAC 1108 computer.

Yours very truly,

Rolf B. Johannesen

Rolf B. Johannesen
Inorganic Chemistry Section

¹P. Haake, J. P. McNeal, and E. J. Goldsmith, J. Am. Chem. Soc., 90, 715 (1968).

THE UPJOHN COMPANY

KALAMAZOO, MICHIGAN 49001
TELEPHONE (616) 382-4000

February 9, 1970

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

Re. An Interesting Degenerate ABX Case

Dear Barry:

We have been interested in deceptively simple ABX spectra for some time. Several examples were cited in earlier letters (IITNMR, 116/36 and TAMUNMR 127/21).

Recently we found an example of an ABX subspectrum in which the AB part (P and Q in Figure 1) had the required degeneracy and the degenerate singlet was observed inside the origins of the other AB quartet. This would therefore be an example of the rare (at least to us) unlike-sign case referred to earlier.

The OPQRS portion of the spectrum was analyzed by construction techniques and the analysis was refined by LAOCN 3 considering only coupling of four bonds or less. The analysis converged to a solution with 0.310 RMS error:

W(O) = 4.96612	A(OS) = 2.321
W(P) = 4.56609	A(PQ) = 12.272
W(Q) = 4.52081	A(PR) = 0
W(R) = 4.04953	A(PS) = -0.443
W(S) = 3.77501	A(QR) = -0.149
A(OP) = 0	A(QS) = 7.647
A(OQ) = 0	A(RS) = 7.414
A(OR) = 8.671	

The calculated spectrum is shown in Figure 2.

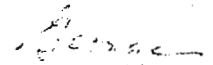
Professor B. L. Shapiro

-2-

February 9, 1970

The long-range couplings APS and AQR were correlated with the angles observed in a Dreiding model according to the theories of Barfield [*J. Chem. Phys.*, 41, 3825 (1964)]. For AQR $\phi_1 = \phi_3 = 60^\circ$, $J_{\text{calc'd.}} = -0.15$. The PQ coupling could not be treated accurately because of the uncertainty of the conformations of P and S because of the rotation of the benzhydryl group and the uncertainty of the geometry of the four-membered ring but the sign and magnitude seemed reasonable.

Sincerely,


George Slomp
Physical and Analytical
Chemistry Research

mjc

enclosures

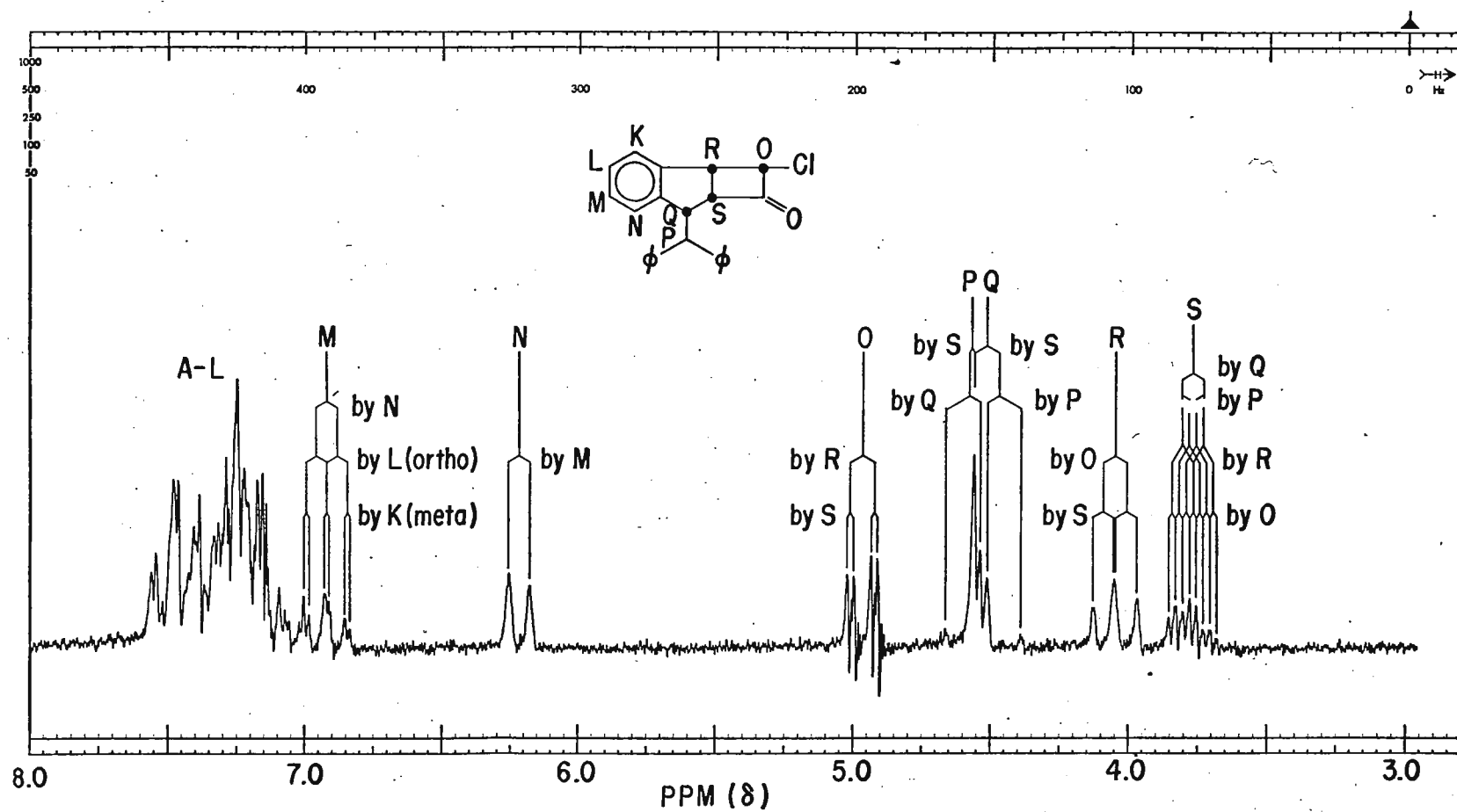
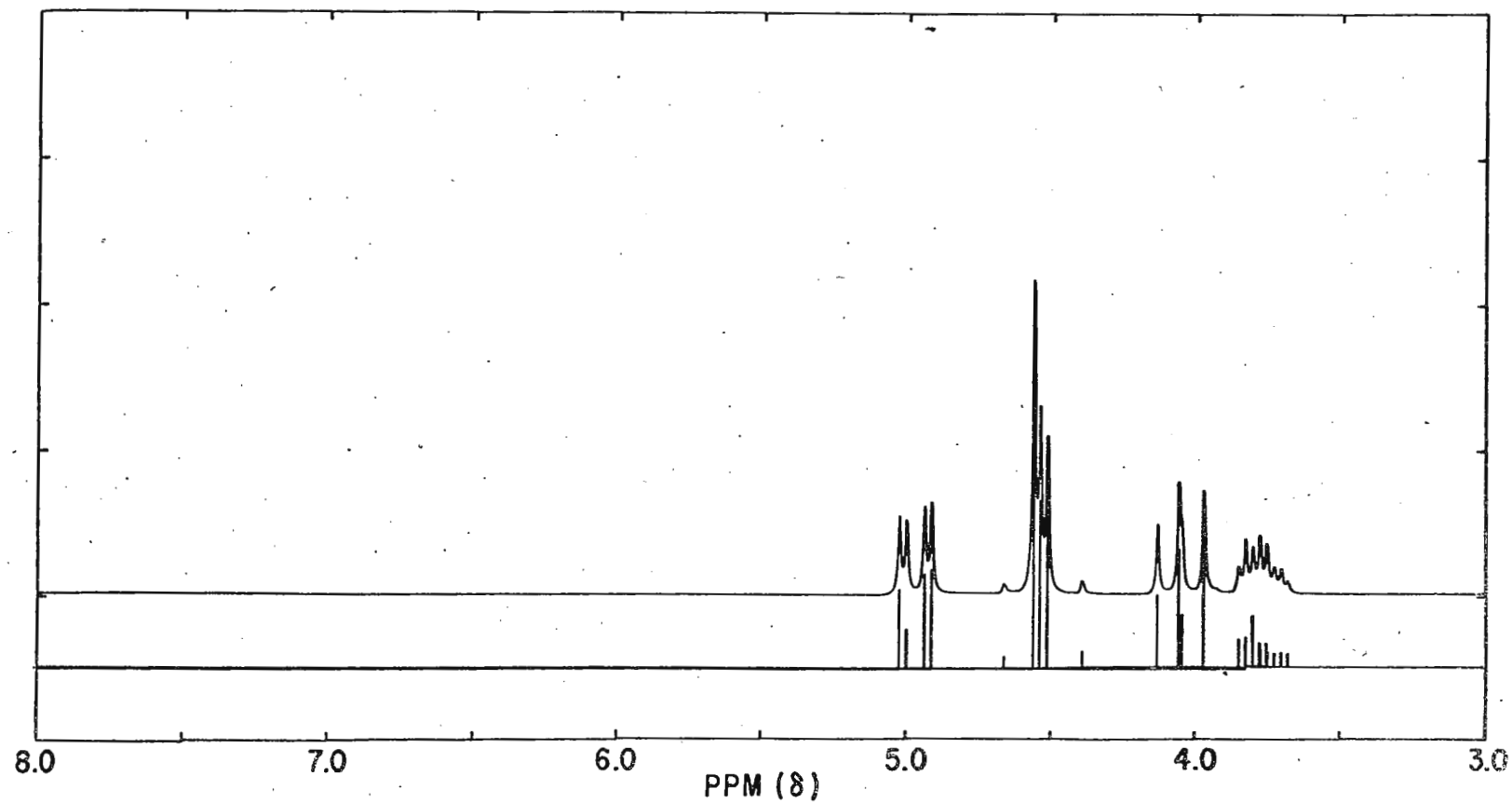
Figure 1. 100 MHz. NMR Spectrum of the Indane Product (N) in CDCl_3 .

Figure 2. . Computed NMR Spectrum for the α -Substituted Hydrogens of the Indane Product (IV).



PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 - TEL. 43 04 22
VORSTEHER: PROF. DR. P. HUBER

Basel, February 10, 1970

Prof. Dr. P. Diehl
Dr. H. P. Kellerhals

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

T e x a s - 77843

USA

Modification in error computation for LAOCOON-type programs?

Dear Barry,

In their original publication on the LAOCOON-program (JCP 41, 3863, 1964) Castellano and Bothner-By mentioned in a footnote that in strongly coupled spectra large errors would definitely be nonlinearly related to the parameters and the calculated probable errors should be regarded with skepticism.

As spectra of oriented molecules are usually "strongly coupled" and errors have a definite meaning in terms of imprecision of molecular shape, we were, of course, worried by this statement.

We modified the error computation so that its validity was no longer limited to weak coupling. The following result was obtained:

Whereas the procedure of the LAOCOON-programs leads to a parameter-error (δ_j) of:

$$\delta_j = \Delta F \sqrt{\sum_{i=1}^n [(D^T D)^{-1} D^T]_{ji}^2} \quad (1)$$

where

$$\Delta F = \sqrt{\sum_{i=1}^n (F_i - v_i)^2 / (n-k)}$$

with

- F_i = observed frequencies
- v_i = calculated frequencies
- n = number of observed frequencies
- k = number of parameters
- D = matrix of partial differentials, $(\partial v_i / \partial p_j)$

our modification gave the following result:

$$\delta_j = \Delta F \sqrt{\sum_{i=1}^n [(D^T D + Z)^{-1} D^T]_{ji}^2} \quad (2)$$

where

$$Z_{\alpha\beta} = \sum_{i=1}^n \left(\partial^2 / \partial p_\alpha \partial p_\beta \right) \left\{ v_i(p_j) [v_i(p_j) - F_i] \right\}$$

For weak coupling Z is zero, as, of course, it had to be and eq. (2) degenerates into (1).

Great, however, was our disappointment when we found that our modification in all practical cases we looked at never changed the error by more than 5 %. (of the error!).

We now think that the footnote mentioned above was over-cautious and that the modification is not necessary.

Yours sincerely,

H.P. Kellerhals

P. Diehl

H. Kellerhals

Peter



Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry · TEL. (603) 646-2501

February 10, 1970

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

Brief Title: What is "shim"? CAT-Teletype interfacing.

Dear Barry,

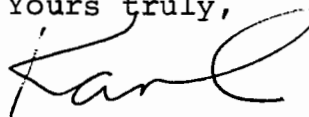
In a relatively idle moment recently I wondered what one is actually recording on a Varian internal lock machine when the "shim" switch is on. I hope that some newsletter readers will be interested in the following simple calculation. The function of the shim switch is to change the reference frequency of the analytical channel from the sweep oscillator to the manual oscillator (on frequency sweep mode). Then the two phase sensitive detectors in the controller are both referenced to the same frequency. Ideally the two reference voltages are exactly 90° out of phase, but with the simple phase shifting network used this can only occur for one frequency. Assuming that the exact quadrature holds, the lock channel reference voltage can be represented by $\sin\omega t$ and the analytical channel by $\cos\omega t$. The simplest model of a phase sensitive detector (mathematically) is a multiplier followed by a low pass filter. Using the identities $\sin^2\omega t = 1/2(1 - \cos 2\omega t)$ and $2\sin\omega t \cos\omega t = \sin 2\omega t$, it is easy to see that the effect of the detector is to pick out the part of the signal in phase with the reference. The signal input to the controller is an audio frequency voltage $S(t) = u(\cos\phi\sin\omega t + \sin\phi\cos\omega t) + v(\cos\phi\cos\omega t - \sin\phi\sin\omega t)$, where the phase angle ϕ is determined by the rf reference phase, and u and v are proportional to the dispersion and absorption NMR signals. The DC output of the lock channel phase detector is thus $E = 1/2(u\cos\phi - v\sin\phi)$. The field control feedback loop adjusts u and v until this is zero. The feedback loop thus requires that $\tan\phi = u/v$. The output of the analytical channel phase detector, which appears on the recorder, is $S' = 1/2(u\sin\phi + v\cos\phi)$. Using the feedback equation to eliminate ϕ , we get $S' = \frac{1}{2}\sqrt{u^2 + v^2}$. Thus the output voltage is proportional to the amplitude of the signal. This result was somewhat surprising to me because my first expectation was that the phase sensitive detector would naturally give me the absorption mode. The point is that the feedback loop changes the result. Of course the

- 2 -

practical effect is nearly the same. If the phase angle is chosen carefully the error signal, E , will vanish because u vanishes. Then the output is the amplitude of the absorption peak. However it may be useful sometimes to be aware of the subtle difference.

We have been spending some time on an inexpensive interface between our C 1024 and the Dartmouth Timesharing System. The problem is to get the data out of the CAT into a Teletype for transmission to the computer or to be punched on tape at as low a price as possible. We have pretty well solved the problem for our system, but I would like to hear from anyone who has worried about this problem in the past and might have suggestions. We are also willing to share our ideas.

Yours truly,

A handwritten signature in cursive script, appearing to read 'Karl', written in dark ink.

Karl F. Kuhlmann

P.S. Please mark this down in Dick Shafer's box.

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

10 February 1970

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

MAGNETIC NONEQUIVALENCE OF ENANTIOMERS WHICH
OWE THEIR CHIRALITY TO TERVALENT NITROGEN

Dear Barry:

Enantiomers are expected (1) to exhibit different nmr spectra in an optically active solvent, and ample evidence has been provided in support of this principle, mainly through the work of Pirkle et al. (2). We wish to report an example which may be of interest to some NEWSLETTER readers.

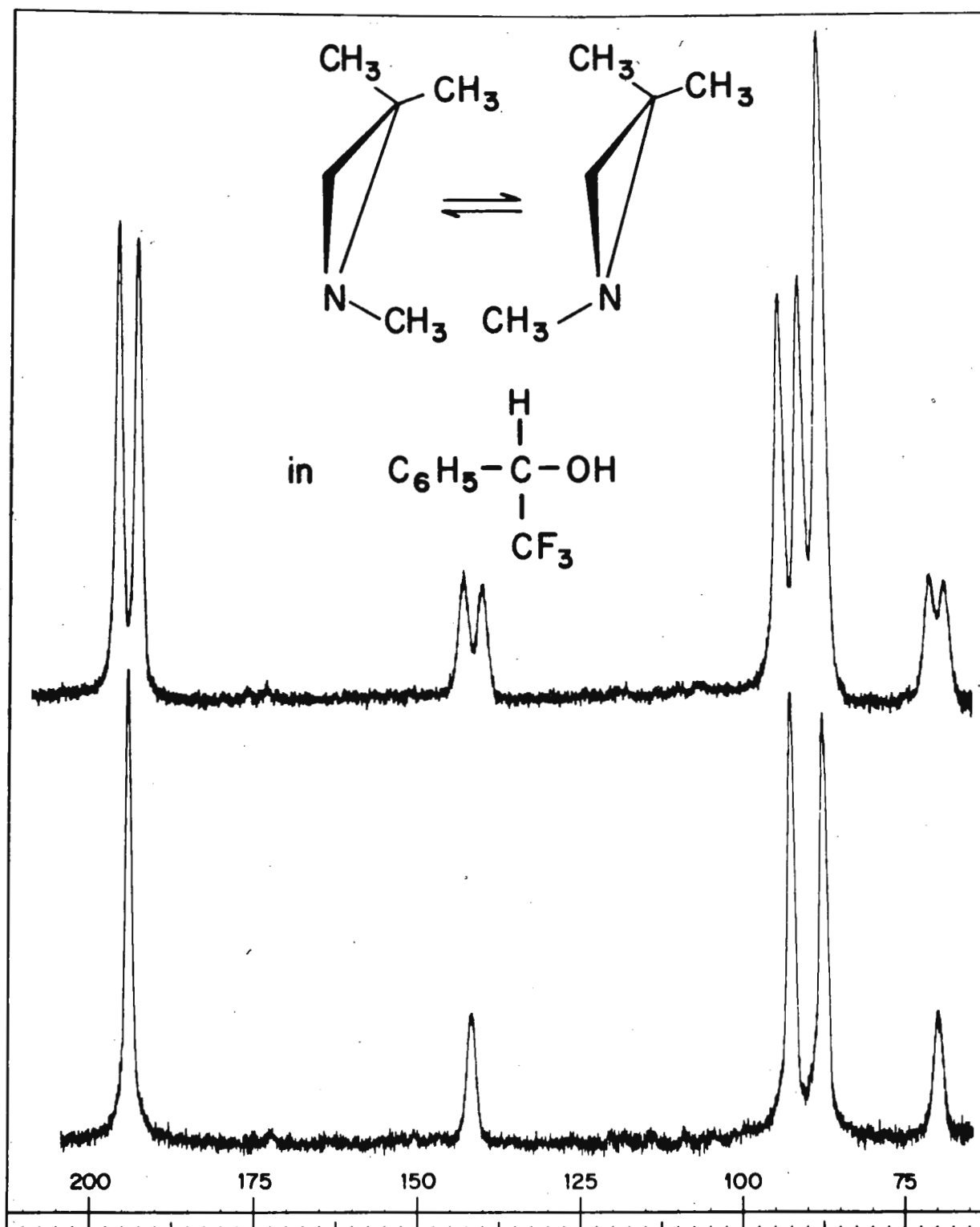
Pyramidal inversion interconverts the enantiomers of 1,2,2-trimethylaziridine, 1 (3). In racemic 1-phenyl-2,2,2-trifluoroethanol, 2, as in achiral solvents (3), the gem-methyl protons on C-2 and the gem-protons on C-3 exhibit magnetic nonequivalence of groups whose diastereotopism is due to slow (on the nmr time scale) inversion at the nitrogen center. However, in optically active 2, resonance doubling of all signals is observed (Figure 1): the enantiotopic N-methyl protons now exhibit two signals ($\Delta\delta 0.03$ ppm), and two sets of signals due to each of the gem-protons on C-3 are discernible. Because of accidental coincidence, only three of the four expected resonances for the gem-methyl protons on C-2 are observed.

We have been unable to discern magnetic nonequivalence in the enantiotopic protons of benzylmethylisopropylamine or 1-phenyl-2,2-dimethyl aziridine, in which nitrogen inversion is expected to occur at a substantially greater rate than in 1, under chiral conditions as described in the caption of Figure 1.

Yours sincerely,

Joe *Bill* *Kurt*
Joe Andose, Bill Egan, Kurt Mislow

- (1) K. Mislow, "Introduction to Stereochemistry, W. A. Benjamin, Inc., New York, 1965, p. 53.
- (2) For example see, W. H. Pirkle and S. D. Beare, J. Amer. Chem. Soc., 90, 6250 (1968).
- (3) M. Jautelat and J. D. Roberts, *ibid.*, 642 (1969).



Southern Illinois
University

CARBONDALE, ILLINOIS 62901

Department of Chemistry

February 10, 1970

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

THE HYDROXYL PROTON SPECTRA OF o- AND m-METHOXYBENZYL ALCOHOL

Dear Dr. Shapiro:

During investigation of the nmr spectra of various alcohols we observed, in accord with earlier observations, that dilution of the alcohol with inert solvent led to an upfield shift of the hydroxyl proton resonance.¹ In addition we have found that in non-hydrogen bonding solvents which have been distilled from carbonate² that the multiplicity of the hydroxyl proton resonance of various primary and secondary alcohols was concentration dependent. An internally hydrogen bonded alcohol should upon dilution 1) exhibit very little change in chemical shift, and 2) exhibit no change in multiplicity. A recent study of salicylaldehyde has provided an example of a phenol -OH which exhibits little change in chemical shift upon dilution in an inert solvent.³

To test the above ideas we performed a dilution study on an internally hydrogen-bonded alcohol, namely, ortho-methoxybenzyl alcohol and on its meta analog, which can only hydrogen bond intermolecularly.⁴ The results as summarized in Table I do not entirely correspond with the above predictions. Both the meta and ortho isomer exhibited significant upfield shift upon dilution; only the ortho isomer exhibited hydroxyl proton multiplicity. The upfield shift of the -OH proton in the ortho isomer suggests there is a change in structure upon dilution, i.e., that there

is significant intermolecular hydrogen bonding present. The lack of multiplicity observable at any concentration in the meta isomer is harder to explain, although it is quite possible that this merely reflects our inability to remove all traces of acid in spite of our care in sample preparation.

TABLE I
Chemical Shifts of Hydroxyl Proton Resonance
of o- and m- Isomers of Methoxybenzyl Alcohol at
Various Concentrations in CCl_4

Mole %	δ (Hz) o-Methoxybenzyl Alcohol ^a	δ (Hz) m-Methoxy- benzyl Alcohol ^a
100	280 (s)	301 (bs)
80	269 (t)	290 (bs)
66	258 (t)	286 (bs)
50	242 (t)	275 (bs)
33	228 (t)	262 (bs)
20	201 (t)	244 (bs)
10	175 (t)	219 (bs)
5	151 (t)	178 (bs)
2	119 (t) ^b	132 (bs)
1	110 (t) ^b	111 (bs)
0.5	102 (t) ^b	---

^aChemical shifts obtained relative to benzene ring protons but converted relative to TMS.

^bTMS in solvent tended to catalyze loss of multiplicity for o-methoxybenzyl alcohol at approximately 4 mole percent. These results obtained for solutions not containing TMS. Also these are inferred triplets since it was the methylene doublet that was actually observed.

References

1. J. C. Davis, Jr., K. S. Pitzer and C. N. R. Rao, J. Phys., Chem., 64, 1744 (1960); T. M. Connor and C. Reid, J. Mol. Spectroscopy 7, 32 (1962).
2. J. M. Bruce and P. Knowles, Proc. Chem. Soc., 294 (1964); J. Chem. Soc., 5900 (1964).
3. I. Yamaguchi, Bull. Chem. Soc. Japan, 34, 353 (1961).
4. Both alcohols were distilled from anhydrous NaCO_3 before use.

Yours very truly,

D.W. Slocum

D. W. Slocum
Associate Professor

C. A. Jennings

C. A. Jennings
NASA Fellow

DWS:CAJ:s11



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

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

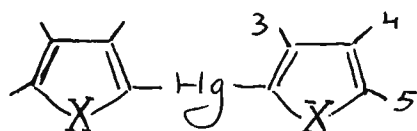
li February 11, 1970

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

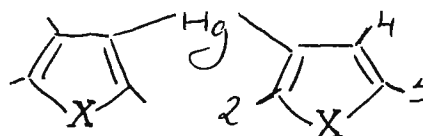
Title: Proton-mercury coupling constants
in the isomers of dithienyl- and
difuryl mercury.

Dear Professor Shapiro,

we have been recently interested in the measurements of
proton-mercury couplings in heterocyclic derivatives as (I) and (II):



(I)



(II)

X = O
= S

The analyses of their satellite spectra allowed the determination of the values and of the relative signs of the 'long-range' $H-Hg^{199}$ coupling constants.

A sample spectrum of some satellites of 2,2' difuryl mercury [(I), X = O] is reported in the first figure. The computer simulated spectra (LAOCOON III) have been obtained using the Hg-H couplings with all the signs alike (a) and and Hg-H₃, Hg-H₄, Hg-H₅ each with opposite sign to the remaining couplings (spectra b, c, d, respectively).

A linear relationship was observed between these Hg-H couplings and the corresponding constants of thiophene and furan (TAMU Newsletter, 131). This fact could be interpreted as an indication that the Fermi's contact term gives probably the main contribution to the mechanism of proton-mercury coupling as it does for the proton-proton coupling. (Figure 2).

A more detailed account of this work is expected to appear in the next months on the J. of Molecular Spectroscopy.

Sincerely yours

L. Lunazzi
L. Lunazzi

Fig. 1

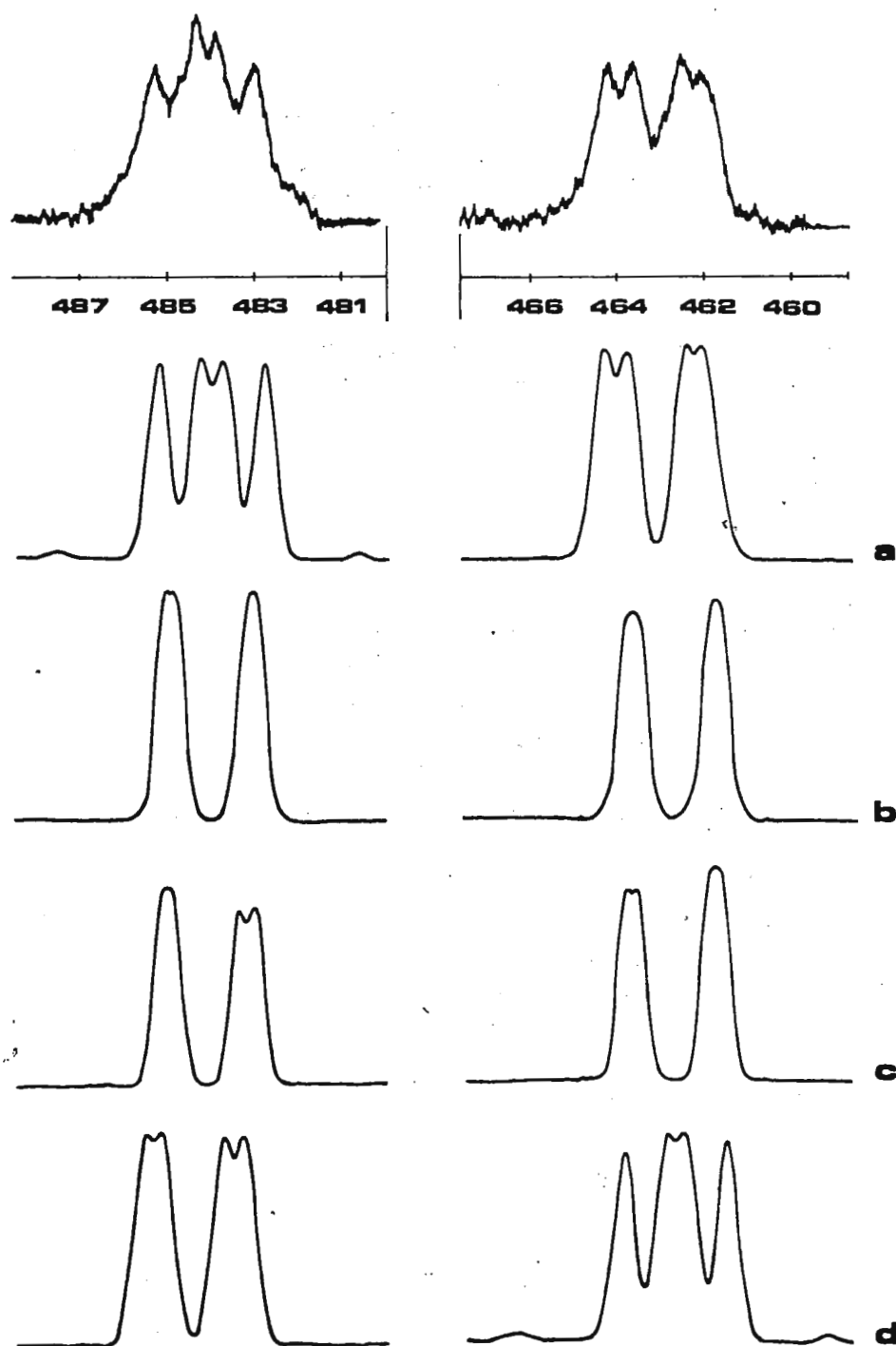
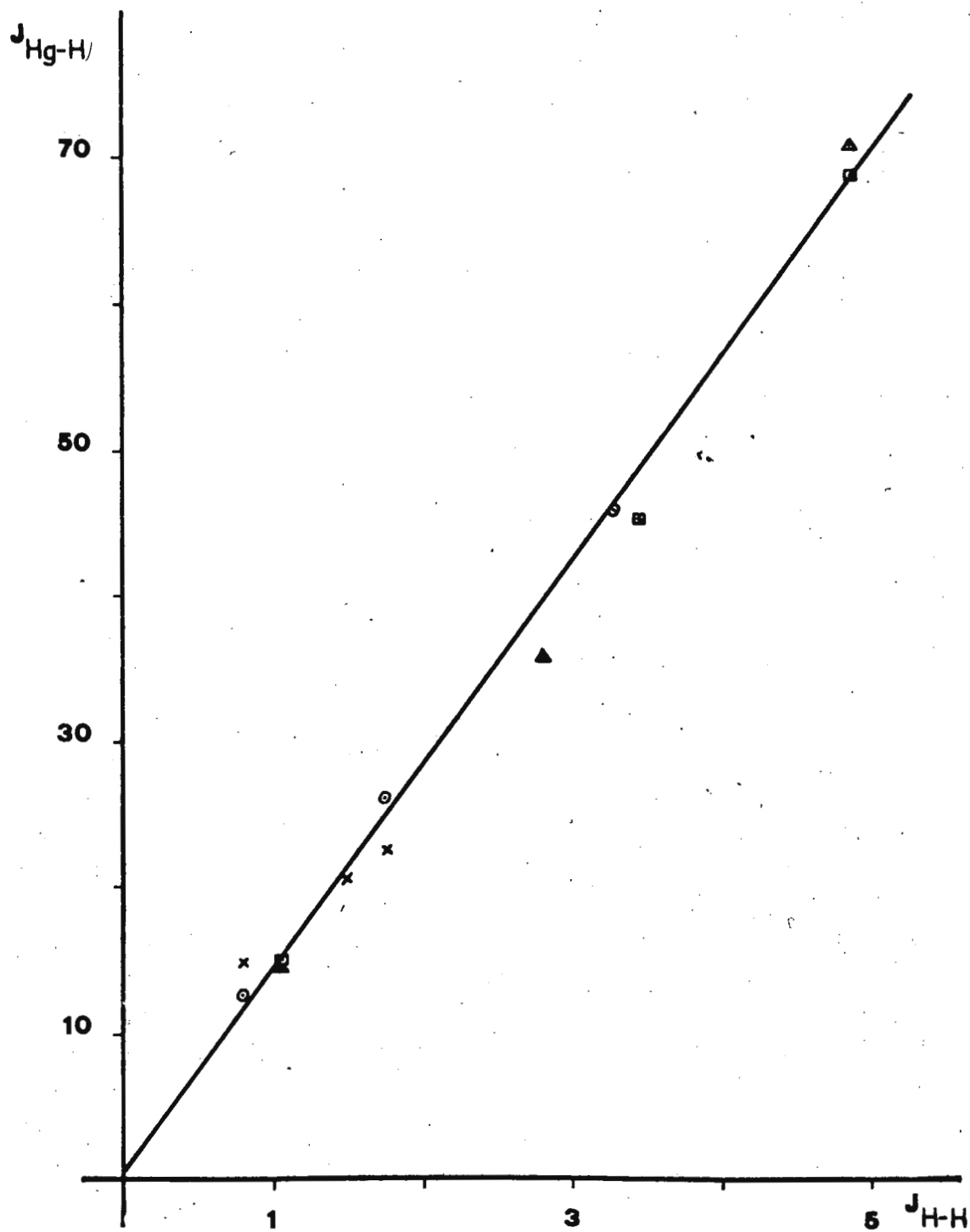


Fig. 2





Dr.D.Wendisch und B.Hähner in Firma
Ing.-Abt. Angewandte Physik 10

Farbenfabriken Bayer AG

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

Telefon: Leverkusen 301 (Vermittlung)
Telex: 8510881
Telegramme: Farbfabrik Leverkusen
Konten: Postscheckkonto Köln 37 82
Landeszentralbank Köln-Mülheim 378/82

U S A

Ihre Zeichen

Ihre Nachricht

Unsere Zeichen
Wec/Hä/Ko

Telefon-Durchwahl
02172/30 .5546

509 Leverkusen-Bayerwerk
den 12.2.1970

Betr.: Bemerkungen zum Einsatz des "Spectro System 100" von
Varian, Ass.

Sehr geehrter Herr Dr.Shapiro!

Zunächst bitten wir zu entschuldigen, daß unser bereits fälliger
Beitrag erst von Ihnen angemahnt werden mußte.

Wir hoffen, daß Sie unsere hier gemachten Bemerkungen zum Einsatz
des "Spectro System 100" als Beitrag anerkennen werden.

Im Zuge der Automatisierung unserer spektroskopischen Labors haben
wir u.a. das "Spectro System 100" für die Kernresonanz eingeführt.

In der derzeitigen Ausbaustufe betreiben wir ein Varian-A60-D-Spektro-
meter im ON-LINE-Betrieb mit dem Computer "620/i" des "SS 100", wobei
uns momentan nur eine 4K-Software zur Verfügung steht. Insbesondere
verwenden wir das System zur verbesserten Spektrenakkumulation
(CAT-Verfahren). Die Möglichkeit der automatischen Wahl des SHIM-
Programmes zwischen den Einzelscans hat sich nach unseren bisherigen
Erfahrungen als sehr positiv erwiesen. Wir konnten so Langzeitmes-
sungen (60-70 Stunden) bei Proben extrem geringer Konzentration ohne
nennenswerten Auflösungsverlust durchführen. Das SHIM-Programm in
der 4K-Version ist für Einzelmessungen (Single Scan) nicht sonderlich
brauchbar, da Zeitaufwand und Ergebnis nicht in vertretbarem Verhält-
nis stehen.

- 2 -

Bei der Charakterisierung von Polymeren (z.B. Auffindung von geringen Verzweigungen) sowie Strukturermittlungen von Metaboliten geringster Konzentrationen konnten wir das nunmehr verbesserte CAT-Verfahren mit Erfolg einsetzen.

Das uns derzeit zugängliche 4K-Programm von Varian zur Berechnung und graphischen Darstellung von Systemen bis maximal 5 Spins arbeitet hingegen nicht völlig einwandfrei. Da uns zu diesem Programm nur das Band und keine Statement-Liste zur Verfügung stehen, konnten wir die ermittelten Schwächen des 4K-Programmes nicht beseitigen.

Als Schwächen des 4K-Simulationsprogrammes haben wir insbesondere die folgenden festgestellt:

1. Spin-Systeme mit "magnetic equivalence" werden nicht korrekt berechnet; durch geringfügige Änderungen der Parameterwerte (Aufhebung der magnetic equivalence) können jedoch sinnvolle Näherungen erhalten werden.
2. Das Ausschreiben (PLOT) des berechneten Spektrums (Frequenzen, Intensitäten) gelingt nicht in jedem Fall einwandfrei und ohne Störungen. Dabei werden u.a. Linienintensitäten falsch wiedergegeben und bestimmte Linien wahllos wesentlich schneller registriert, wobei Intensität und Signalform verfälscht werden. Die Wahl des scale factors ist offensichtlich nicht ohne Einfluß auf die genannten Phänomene, wobei die Kausalität hierfür ohne detaillierte Programmkenntnis nicht empirisch von uns ermittelt werden konnte.

Diese vergleichenden Untersuchungen des genannten Programmes wurden von uns unter Benutzung des LAOCN 3- bzw. - LAOCOON II-Programmes durchgeführt.

Es bleibt zu hoffen, daß in der angekündigten 8K-Software diese Mängel beseitigt sein werden.

In Kürze glauben wir auch unser HA-100- und HR-220-Spektrometer an das "SS 100" anschließen zu können, wobei vorläufig nicht an einen Simultanbetrieb gedacht ist.

Mit freundlichen Grüßen

Wolfgang Kundlich Bernhard Nahr

DEPARTMENT OF CHEMISTRY

139 CHEMISTRY BUILDING • MINNEAPOLIS, MINNESOTA 55455

February 13, 1970

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

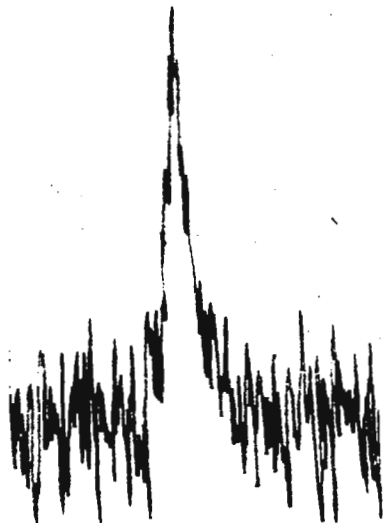
Potassium-39 Relaxation Times

Dear Barry:

I have recently been exploring the possibility of using potassium-39 relaxation times to study important potassium interactions in biology. Because I know of no other work on this nucleus in aqueous solution, my first results may be of interest to some.

The potassium line width (full width at half height) in a 4 M potassium chloride solution is $6.5 \text{ Hz} \pm 0.5 \text{ Hz}$ when recorded in a 15 mm non-spinning sample tube. The line width is unchanged on using smaller sample tubes so that contributions to the line width due to inhomogeneity is apparently negligible.

Signal to noise ratio is not all that could be hoped for; however the sample spectrum below for 1 M potassium chloride indicates that S/N is sufficient to provide a useful approach to the study of potassium ion interactions where potassium ion is critical such as in certain enzymatic reactions.



This spectrum was recorded on a Varian 4300 nmr spectrometer system employing a V-4210A r.f. unit operating at 2.65 MHz. A Princeton Applied research Model 121 Lock-in amplifier was a part of the detection system and operated at an audio frequency of 400 Hz.

I would like to thank Professors Paul Lauterbur and J. E. Ramirez of the Chemistry Department, State University of New York at Stony Brook for making their 2-4 MHz probe available for this work.

Sincerely,

Robert G. Bryant
Robert G. Bryant
Assistant Professor

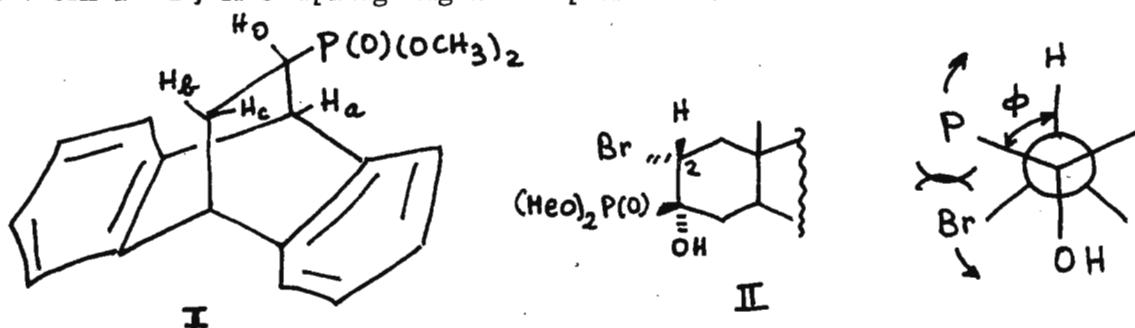
RGB:cmg

February 16, 1970.

Professor Bernard L. Shapiro,
Texas A and M University,
College of Science,
College Station, Texas 77843,
U. S. A.

Dear Professor Shapiro,

The NMR spectrum of the adduct I of dimethyl phosphite-dibenzobicyclo[2.2.2]octadienone provides information concerning the vicinal ^{31}P , ^1H coupling angular dependence.



The couplings are the following: $J_{\text{PH}_a} (\phi \approx 60^\circ) = 6.4 \text{ Hz}$, $J_{\text{PH}_b} (120^\circ) = 6.0 \text{ Hz}$, $J_{\text{PH}_c} (0^\circ) = 16.0 \text{ Hz}$. Those results are in agreement with a Karplus-type relationship (1) of the $^3J_{\text{PH}}$ coupling. This gives now a much more reliable value for $^3J_{\text{PH}}(60^\circ)$. The quite large value (12 Hz) indicated earlier (2) for a steroidal phosphonate II must then correspond to a dihedral angle $\phi < 60^\circ$, which would take into account the strong gauche interaction between the bulky bromine and dimethylphosphono group. This explanation is certainly not sufficient to account for this large difference and surely other factors should be considered.

Please credit this contribution to Dr. R. R. Fraser
of our Department.

Sincerely yours,

Claude Benezra

Claude Benezra,
Assistant Professor
of Chemistry.

- 1) C. Benezra, Tetrahedron Letters, 4471 (1969).
 - 2) C. Benezra and G. Ourisson, Bull. Soc. Chim. France, 1966, 1825.
- Short title: Angular dependence of vicinal $^{31}\text{P}_1$ ^1H coupling.

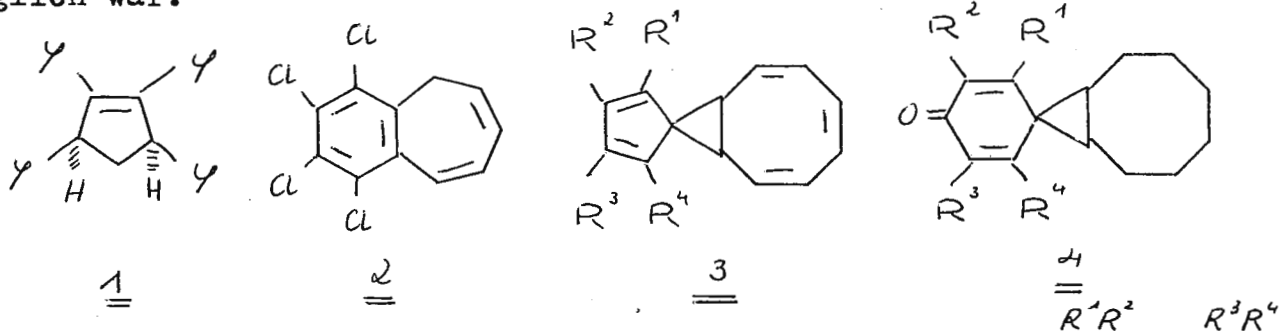
CB:ws

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

Dear Dr.Shapiro,

Title: Einige Beispiele der Spektrenvereinfachung durch Spin-
entkopplung

Im Laufe unserer Untersuchungen der Photochemie kleiner Ringe¹⁾ erhielten wir eine Reihe von cyclischen Verbindungen, die sehr komplexe NMR-Spektren aufwiesen. Mit Hilfe der Spinentkopplung - also Doppelresonanzexperimenten - ist es uns gelungen, die NMR-Spektren der Verbindungen 1-4 so zu vereinfachen, daß eine eindeutige Analyse möglich war.



3 u. 4: o-Phenylen o-Phc-
nylen

Die Spektren der Produkte 1-4 wurden gemessen in:

1(CDCl₃, 20 %), 2(CDCl₃, 10 %), 3 und 4(CDCl₃, 15 %).

Alle Spektren wurden mit einem Gerät der Varian Associates vom Typ A 60 aufgenommen. Für die Spinentkopplung wurde das Zusatzgerät V-6058 A eingesetzt, d.h. alle Doppelresonanzexperimente^{sind} mit der "field-sweep-decoupling"-Methode durchgeführt worden.

In der Abbild. 1 und 2 sind die durch Spinentkopplung vereinfachten Spektren von 1-4 wieder gegeben.

Bei dem Tetraphenyl-cyclopenten(1) kann das NMR-Signal von H_B (τ = 6.81) durch Einstrahlen bei H_X (τ = 5.53) zu einem Dublett(AB-System) mit J_{AB} = 13.5 Hz entkoppelt werden. Einstrahlen von H₂ bei H_B ergibt annähernd ein Triplet für H_A (τ = 7.87) mit einer Kopplungskonstanten J_{AX} = 8.5 Hz(AX₂-System). Das NMR-Spektrum des Tetrachlor-5H-Benzocycloheptens(2) kann folgendermaßen vereinfacht werden: Einstrahlen von H₂ bei τ = 4.3-3.8(H_D) ergibt ein Singulett bei τ = 6.78 für H_E (umgekehrt vereinfacht sich das doppelte Dublett von H_D zu einem Dublett bei Einstrahlen von H₂ bei H_E (J_{CD} = 9.5 Hz). In entsprechender Weise kann H_B (τ = 3.24) in ein doppeltes Dublett(Kopplung mit H_E (J_{AB} = 12) und H_C (τ = 3.76) in ein Dublett(Kopplung mit H_B) J_{CD} = 9.5-10 Hz) entkoppelt werden.

Eine eindeutige Auflösung des Multipletts bei ca. 4τ im NMR von 3 und 4 erbrachte ebenfalls ein Doppelresonanzexperiment. Durch Einstrahlung der jeweiligen Resonanzfrequenz bei H_A ($\tau=4.34$) wird das H_B ($\tau=3.87$) zu einem Singulett zu einem Singulett^A entkoppelt und umgekehrt ($J_{AB}=12$ Hz). Das H_C -Proton ($\tau=4.04$) weist nur geringe Kopplung auf²). ^{AB}
Analog verhält sich das Spektrum von 4.

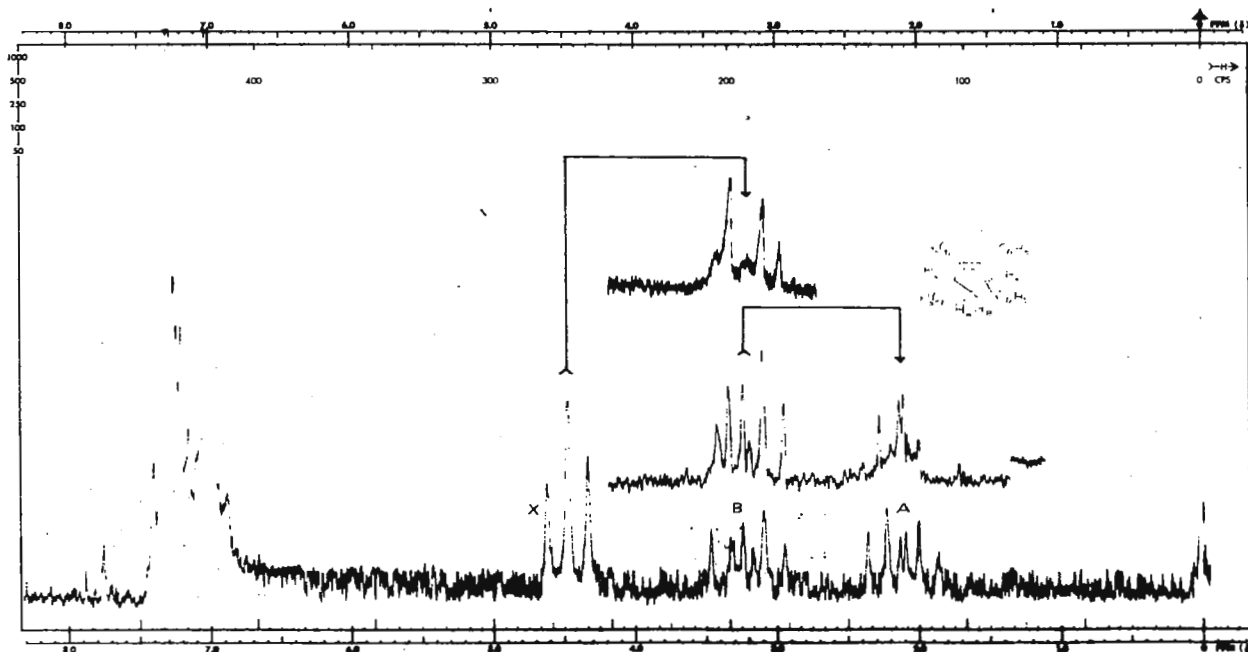
Yours sincerely



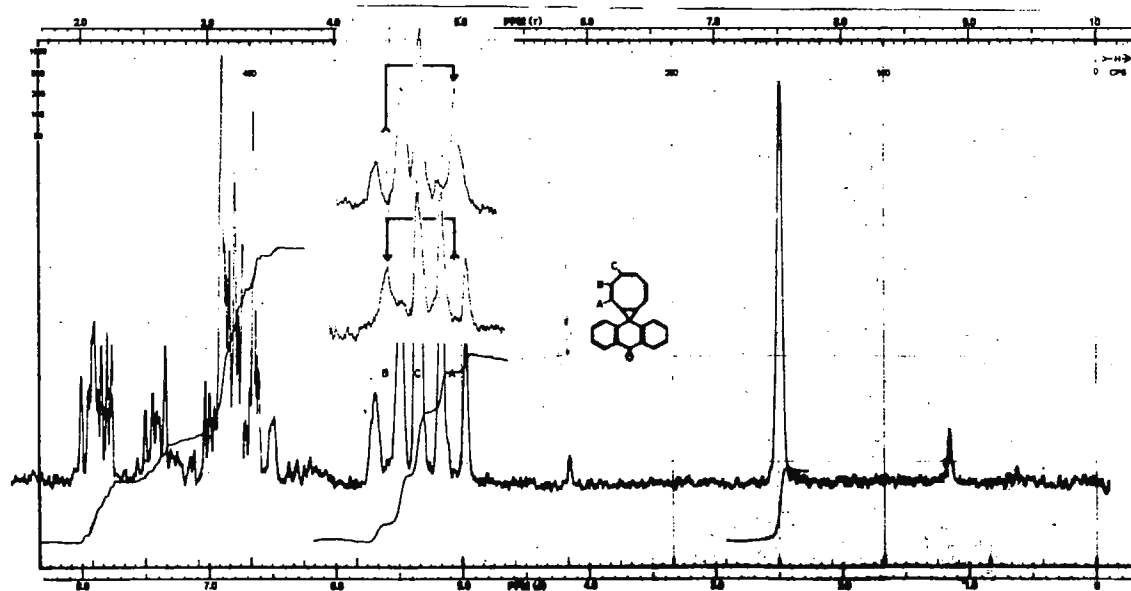
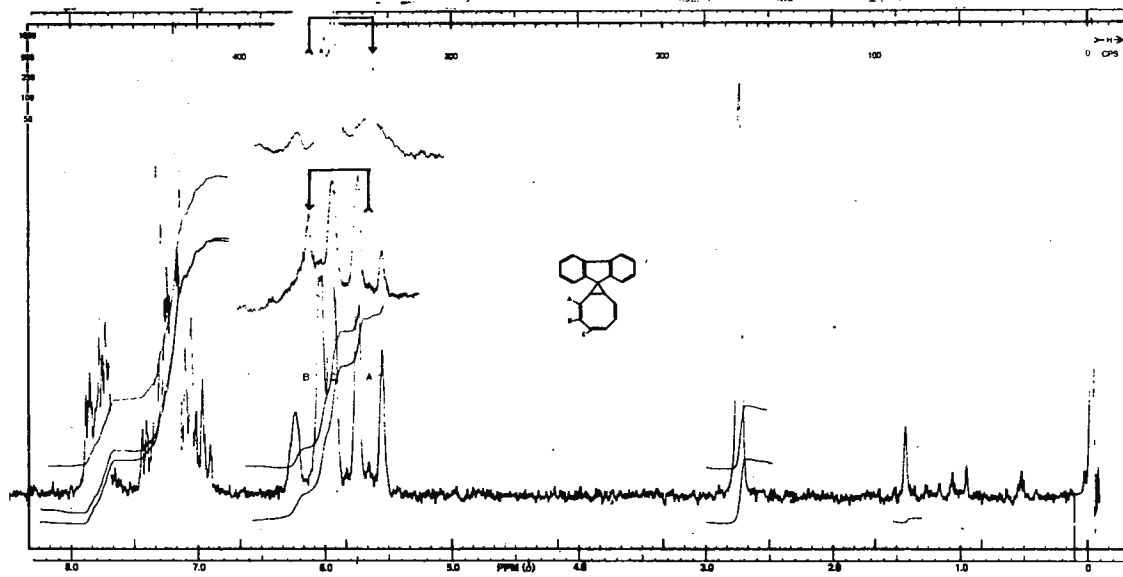
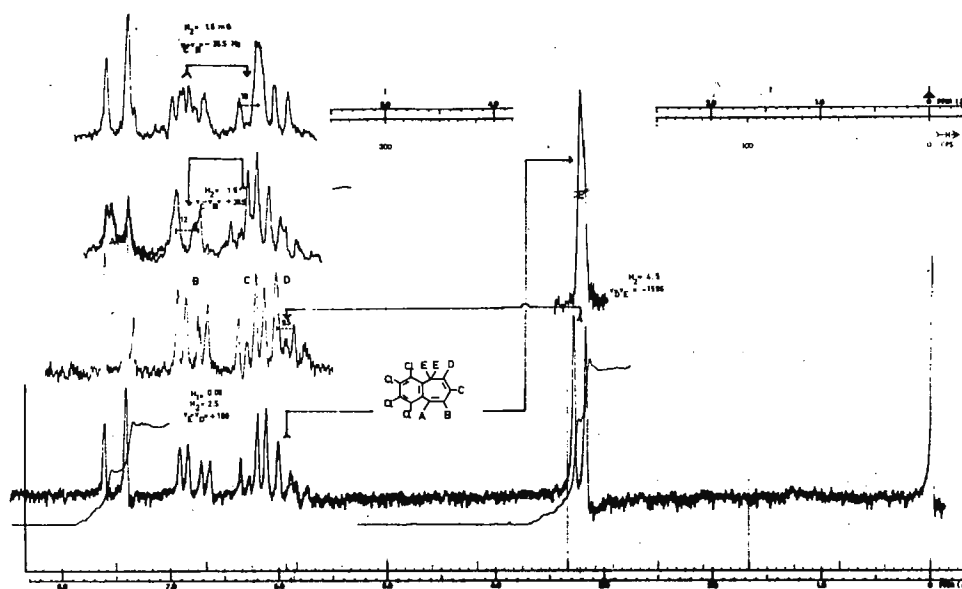
(Dr.H.Dürr)

Literatur

- 1) H.Dürr und L.Schrader, Chem.Ber. 102, 2026 (1969) und frühere Arbeiten.
- 2) H.Günther und H.H.Hinrichs, Tetrahedron Letters [London] 1966, 787.



- 3 -





Waterloo, Ontario, Canada

Faculty of Science
Department of Chemistry

13th February, 1970.

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

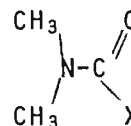
Hindered Barriers in Dimethylamides

Dear Barry,

Life has been extremely busy since I came to Waterloo and I apologise for not anticipating your reminders.

We have a large task here to set up an enlarged NMR laboratory but we are now close to having two instruments fully operational, namely, a HA100 and a completely refurbished HR60. Our next task will be to re-establish the home built Spin-Echo spectrometer. We have a Fabritek 1074 which will act as a buffer between our instruments and an 'on line' IBM 360/44. We shall be able to do many types of NMR experiments.

As a contribution I thought I might refer to some very careful measurements of hindered barriers in molecules of the type:



These are old and well worn systems, but still good data is rare. We have a reasonable variation of X between cyanide, chloride, bromide and hydrogen. We find that in normal organic solvents the barriers are sensibly independent of solvents and concentration. Two figures are attached, one of which plots the activation energy from our NMR data against the total change in π -energy considering delocalisation over

in the ground state but over $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{X} \end{array}$ only in the transition state. The calcu-

lations were of the ω -type Huckel variety where coulomb and resonance integrals were determined to give the best results for calculations of spectral data in the related series of acetyl-X compounds. It is clear that the π -energy appears to be the major contributor to the energy barrier but that π -bonding in the C-X bond which is not possible with hydrogen, makes this an exceptional substituent in the series studied. In the second figure a similar observation is made. The π character in the C-N bond obtained from the same calculations is plotted against the activation energies.

The kinetic data was obtained from line shape fits; in the case of the hydrogen substituent using a four site analysis because of the long range coupling. The data and calculations have been obtained in collaboration with Rick Hobson and Keith Shaw.

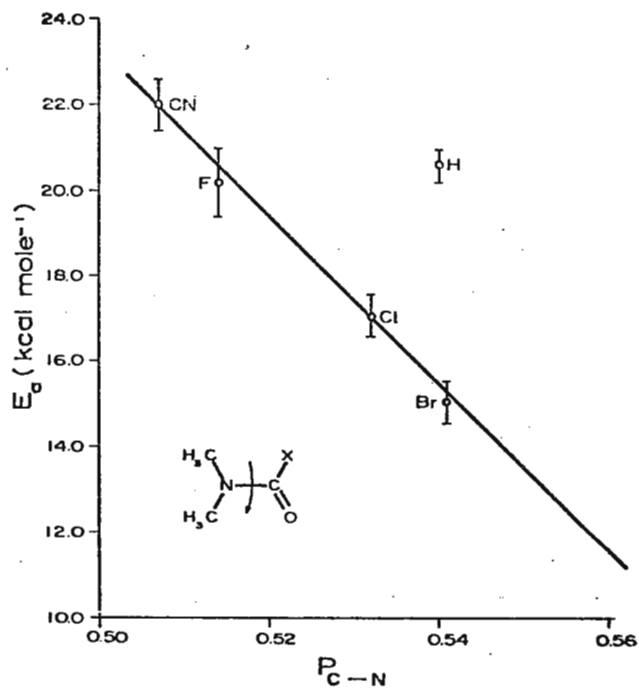
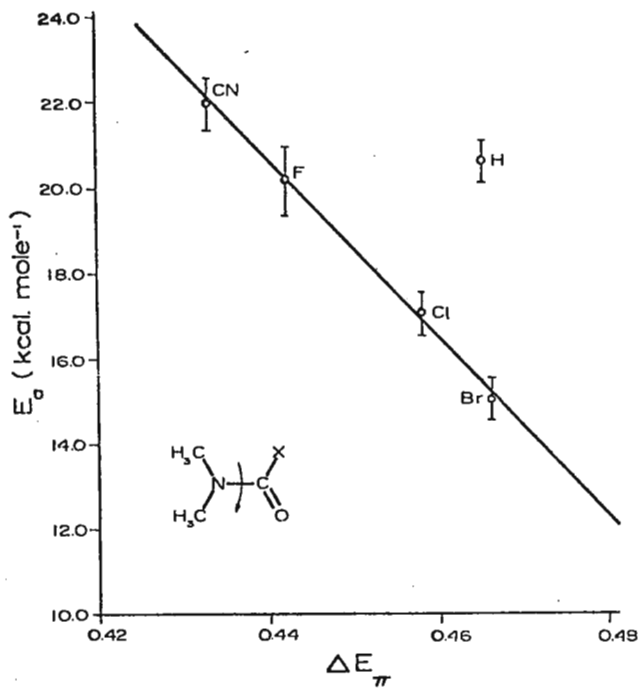
I hope soon to give you some news of our work at Waterloo.

Best wishes,

Yours sincerely,



Leonard W. Reeves,
Chairman,
Chemistry Department.



TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

10 March 1970

POSTDOCTORAL FELLOWSHIP AVAILABLE

There will be an opening for a postdoctoral research associate in my group available as of May 1 of this year, through the award to me of a research grant from The Robert A. Welch Foundation of Houston.

The research itself will involve both synthesis and NMR studies, and the relative proportions of these can vary somewhat depending on the tastes and background of the person involved. Initially, we will be restricted to proton and fluorine NMR, but it is hoped and expected that carbon-13 studies will also be involved fairly soon.

The postdoctoral fellowship can begin May 1, 1970, or as shortly thereafter as is possible. Some NMR experience is very highly desirable and the more the better, of course. If mutually satisfactory, this fellowship could be extended for at least a second year, and other things being equal, I would prefer someone to whom this is at least a reasonable possibility. Anyone interested should write directly to me, sending the usual résumé, date available, and the names of those from whom letters of reference have been requested. All inquiries will be acknowledged.



Bernard L. Shapiro

BLS/jc

EESTI NSV TEADUSTE AKADEEMIA
KÜBERNEETIKA INSTITUUT

Tallinn, Lenini puistee 10
Telef. 406-42, 490-72



АКАДЕМИЯ НАУК ЭСТОНСКОЙ ССР
ИНСТИТУТ КИБЕРНЕТИКИ

Таллин, Бульвар Ленина д. 10
тел. 406-42, 490-72

Nr. _____

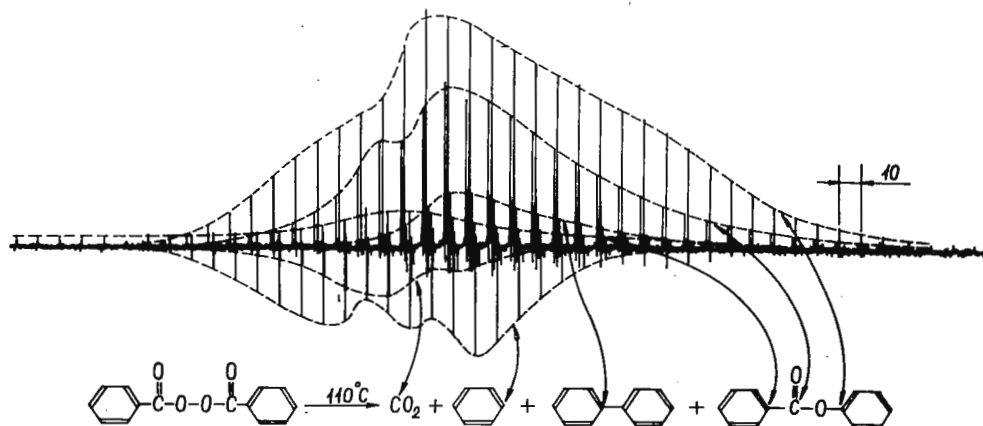
February 13, 1970 a./r.

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

CIDNP Phenomena in ^{13}C Spectra at Natural Abundance

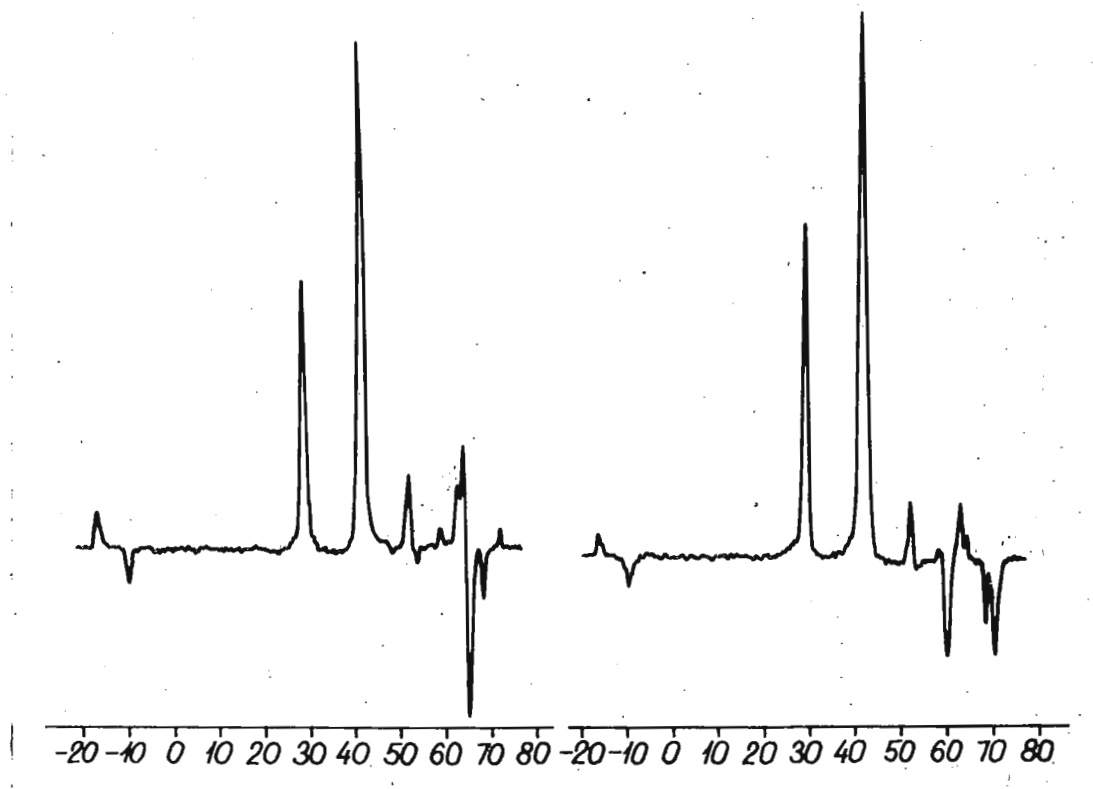
Dear Professor Shapiro,

We have recently been investigating chemically induced dynamic nuclear polarization (CIDNP) phenomena in ^{13}C spectra at natural abundance. It appears that such spectra provide much more information about the polarization phenomena than the proton spectra. The nuclear polarization is at least an order of magnitude



larger than in proton spectra and each polarized carbon atom, including those without attached protons, gives a signal. The thermal decomposition of dibenzoyl peroxide (26 per cent in cyclohexanone) at 110°C is depicted in Fig. 1. The spectrum was scanned each 10 sec and accumulated. Both single and double resonance with total decoupling of hydrogen nuclei were used and all spectra were ran at 15.1 MHz. Of the main reaction products

benzoic acid was not polarized, but the minor component, phenyl benzoate, gave most of the strong peaks in Fig. 2. (double resonance at the left, single resonance at the right). The carboxyl carbon absorbs at 28.7 ppm, the substituted carbon of the phenol moiety at 41.5 ppm and the substituted carbon atom of benzoyl group at 63.2 ppm (from carbon disulfide). The weak lines at 64.1 and 72.0 ppm belong to ortho-carbon atoms of both aromatic rings. The negative-going doublet at 59.7 and 70.3 ppm (or 65.0 ppm in the double resonance spectrum) belongs to benzene and the other negative peak at 68.3 ppm to carbon dioxide. The central carbon atoms of diphenyl absorb at 52.1 ppm, and just as in the case of phenyl benzoate the other carbon atoms are not polarized.



The line at - 16.2 ppm belongs to the unpolarized carbonyl group of the cyclohexanone solvent and the negative peak at -9.7 ppm to some reaction product of the solvent. As a general rule only the carbon atoms in or adjacent to the reaction center are polarized and the polarization of ^{13}C is positive in recombination products, negative in radical decomposition or hydrogen abstraction products. The signs of ^1H and ^{13}C polarization are in some cases opposite.

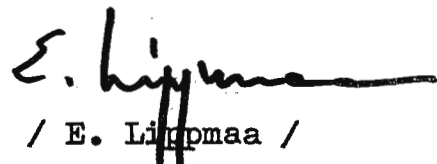
The multiplet effect that is so prominent in ^1H spectra is overshadowed by the very much stronger energy polarization in ^{13}C spectra and very weak. All these results are in accord with the conclusion that chemical polarization (CIDNP) appears at the very moment of the formation of stable reaction products and not as the result of dipole-dipole or scalar relaxation processes in the free radical itself.

A full account of the results will be given in the Chemical Physics Letters and Doklady AN SSSR.

Yours sincerely,



/ T. Pehk /



/ E. Lippmaa /



Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

Prof.dr. B.L. Shapiro
TEXAS A AND M UNIVERSITY
College of Sciences
College Station
TEXAS 77843
U.S.A.

Uw kenmerk

Uw brief van

Ons kenmerk

Delft, Nederland, Lorentzweg 1, tel. 01730-33222

February 17, 1970 toestel:

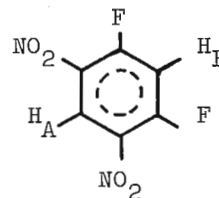
Onderwerp

Dear Professor Shapiro,

Thank you very much for your reminder of 3-2-70, which prompted me to write the following small contribution:

Title: THD Research Fellowship; Miscellaneous

1. Per 1971 there is the possibility of a THD research fellowship in our Magnetic Resonance Group (THD = Technische Hogeschool Delft) Anyone who is interested in measurement of nuclear magnetic relaxation times in liquids and/or solids and likes to work in our group for a period of one year, is invited to contact me for further information.
2. In the autumn of 1969 our high resolution specialist, Dr.H. Angad Gaur, left us and went over to the Research Laboratory of A.K.Z.O. in Arnhem. In April his place will be filled by Drs. W. Bovée.
3. We are developing a system with which we can measure T_1 en T_2 of the separate peaks in a N.M.R.-spectrum. That it is not always necessary to use a sophisticated system in order to find out that these relaxation times may be different, is proven by the following 60 MHz proton spectrum:



Yours sincerely,

Prof.dr. J. Smidt

THE INSTITUTE FOR CANCER RESEARCH

7701 BURHOLME AVENUE

FOX CHASE • PHILADELPHIA, PENNSYLVANIA 19111

215 FIDELITY 2-1000 • CABLE ADDRESS: CANSEARCH

February 18, 1970

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

R.F. Field Measurement

Dear Dr. Shapiro:

This letter is to report on a modification of J. S. Leigh's method (Review of Scientific Instruments, Vol. 39, No. 10, 1594-1595, October 1968) of measuring the effective radio frequency field intensity experienced by the sample in an NMR experiment. Leigh's method is as follows: A single narrow resonance line found in a sample such as benzene is given a sudden burst of r.f. by decreasing the transmitter attenuation by ~ 40 dB. The net magnetization precesses about the rotating r.f. vector at a low rate, for example 2 Hz. The transient ringing signal may be recorded on a chart recorder, storage oscilloscope or oscilloscope camera. Having recorded and measured the ringing frequency one calculates the effective r.f. field, H_1 , from the formula $\Omega = \gamma H_1$ where $\Omega = 2\pi \times$ ringing frequency and γ is the gyromagnetic ratio. The value of H_1 at any other attenuation dB setting may be found from the equation $20 \log_{10} H_1/H_1' = \text{dB} - \text{dB}'$.

Leigh used a Varian DA-60 whose lock signal comes from a "piggyback" probe. When one tries the method on the Varian HA100 with internal lock the strong signal in the analytical channel disturbs the weaker signal in the lock channel, the resonance position shifts, and the recorded ringing frequency is too high. A good solution of the problem is as follows: Generate a very strong lock signal (approximately the same amplitude as the analytical signal). A broad line (e.g. from doped water) is used, which will not saturate. Keep the transmitter output high throughout the measurement. Using a low audio modulation level in the analytical channel find a narrow line such as that of 2% t-butanol dissolved in the doped water. Suddenly increase the modulation to some standard setting and record the ringing. A convenient calibration of frequency especially on an oscilloscope, can be obtained by adding a separate line of 60 Hz hum to the same recording.

Sincerely,



James L. Engle

JLE/deh



JET PROPULSION LABORATORY California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103

13 February 1970

Refer to: 328-MAC/SLM:cls

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

"PASADENA"

Dear Barry:

For the sake of brevity we shall not spend our first sentence apologizing for the tardiness of our contribution.

Readers of TAMUN may be interested in hearing of some experiments we have performed on ^{19}F using digital sweep and proton noise decoupling. The spectra were taken on a Varian Associates HA-100 spectrometer, modified as detailed below. The "sweep oscillator amplifier" and "sweep network" cards were removed from the V-4354A unit, and in their place the output from a Hewlett-Packard 5100A synthesizer was fed into the "sweep oscillator out" jack of this unit. Digital frequency sweep was obtained by use of a Barry Research* LSC-7A Linear Sweep Controller. This digital programmer is configured to sweep a Hewlett-Packard 5100A Frequency Synthesizer over ranges from 10 to 10^4 Hz. The time for sweeping any of these ranges may be varied between 5 Hz/sec and 0.01 Hz/sec in convenient multiples.

In the present case, all of the signals examined were close to, and down-field from the hexafluorobenzene (C_6F_6) signal which was used for control. Thus the procedure was to lock on C_6F_6 using the internal-lock system with a frequency of ca 2 kHz, and to sweep an audio sideband, which in this instance was never greater than 7 kHz from the lock. In this range, there is no need to adjust the phases of the locking and observing frequencies independently, although this would be required with a sideband of ca 10 kHz or larger. This adjustment could be made quite easily, and is commonly used in the more usual method of obtaining field/frequency locked ^{19}F spectra. In the latter method, it is the lock frequency which is taken externally, and the internal sweep oscillator, which is restricted to a range of 2500 to 3500 Hz, is maintained.

* Available from Barry Research, 934 East Meadow Drive, Palo Alto, California 94303.

Prof. B. L. Shapiro

-2-

13 February 1970

We have determined that the times taken by the pen carriage on our HA-100 to traverse the flat bed recorder are accurate to better than 0.05%. Thus our procedure for taking spectra was to select a sweep range and sweep rate on the digital programmer and to start the latter and the recorder carriage simultaneously. The resultant spectrum is of excellent linearity and by suitable combination of sweeper and recorder times can be made in a variety of convenient and accurate expansions.

We have used the present setup in conjunction with complete proton decoupling for the extraction of $F \dots F$ coupling constants in a number of systems where they might otherwise be tedious to obtain (Table 1). A convenient aspect emerges when ^{13}C satellites are of interest. We describe this with reference to the proton decoupled spectrum of meta-difluorobenzene (Fig. 1). The satellites occur ca 120 Hz either side of the main ^{12}C band, which itself is ca 4960 Hz downfield from C_6F_6 . Thus, with a locking sideband of 1890 Hz, the main band signal occurs at a sweep frequency 6850 Hz, which was arranged to be in the center of the digital sweep as the latter decreased from 6900 to 6800 Hz. By sweeping from 7000 to 6900 Hz, the low and high field ^{13}C satellites could be obtained respectively. Thus the low field satellites were recorded with the synthesizer set to 6900 Hz, to which the swept 100 Hz frequency is added. As soon as the satellites had been recorded, the synthesizer was punched manually to give a reading of 6800 Hz, without interrupting the remaining sweep settings, and the ^{12}C band was recorded with suitable reduction in the output gain controls. Finally, the synthesizer was set to 6700 Hz, and the upfield satellite was recorded. Thus all five signals of interest are recorded in one continuous sweep and the values of $^4J_{\text{FF}}$, $^1J_{^{13}\text{C}-\text{F}}$, chemical and isotope shifts can be conveniently obtained. We must stress that the values of $^1J_{^{13}\text{C}-\text{F}}$ and the isotope shift need strictly speaking to be obtained by a full ABX analysis. In practice the corrections required are often negligible or may be easily calculated to sufficient accuracy (± 0.1 Hz). The switching time of the synthesizer is very small, of the order of microseconds for electronic switching, although no doubt more when switching manually, but in a series of control experiments no hiatus in the sweep caused by switching could be detected.

Although the system can be developed further, we have already obtained some most useful results from it and have christened it "PASADENA," for "Provides Accurate Sweeps and Digitally Enables Nicer Analyses." We did consider "PALO ALTO" for "Provides A Linear Observation And Lines Tumble Out," but did not wish to infringe "RFTI" (Ray Freeman's Territorial Impertative).

Regards,

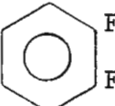
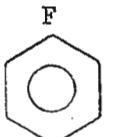
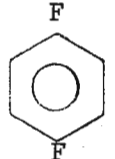
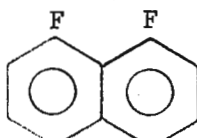
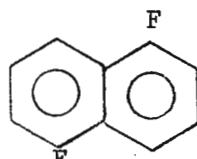
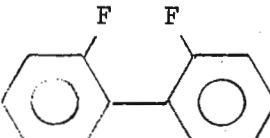
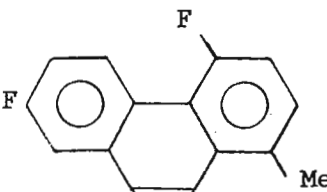


M. Ashley Cooper



Stanley L. Manatt

Table 1
A Partial List of F ... F Couplings Obtained from
 ^{19}F Spectra with Complete ^1H Decoupling

Mol.	$ J_{\text{FF}} $ Hz	Comments
	20.9 20.5	CCl_4^* TMS
	6.6	CCl_4
	17.6	CCl_4
	58.4	$\text{Me}_2\text{CO}^\dagger$
	4.1	$\text{Me}_2\text{CO}^\dagger$
	18.2	pyridine
	0.8	‡

* cf. M. A. Cooper, Org. Mag. Res., 1, 363 (1969)

† Kindly loaned by Prof. F. B. Mallory, Bryn Mawr College.

‡ Kindly loaned by Prof. K. L. Servis, University of Southern California.

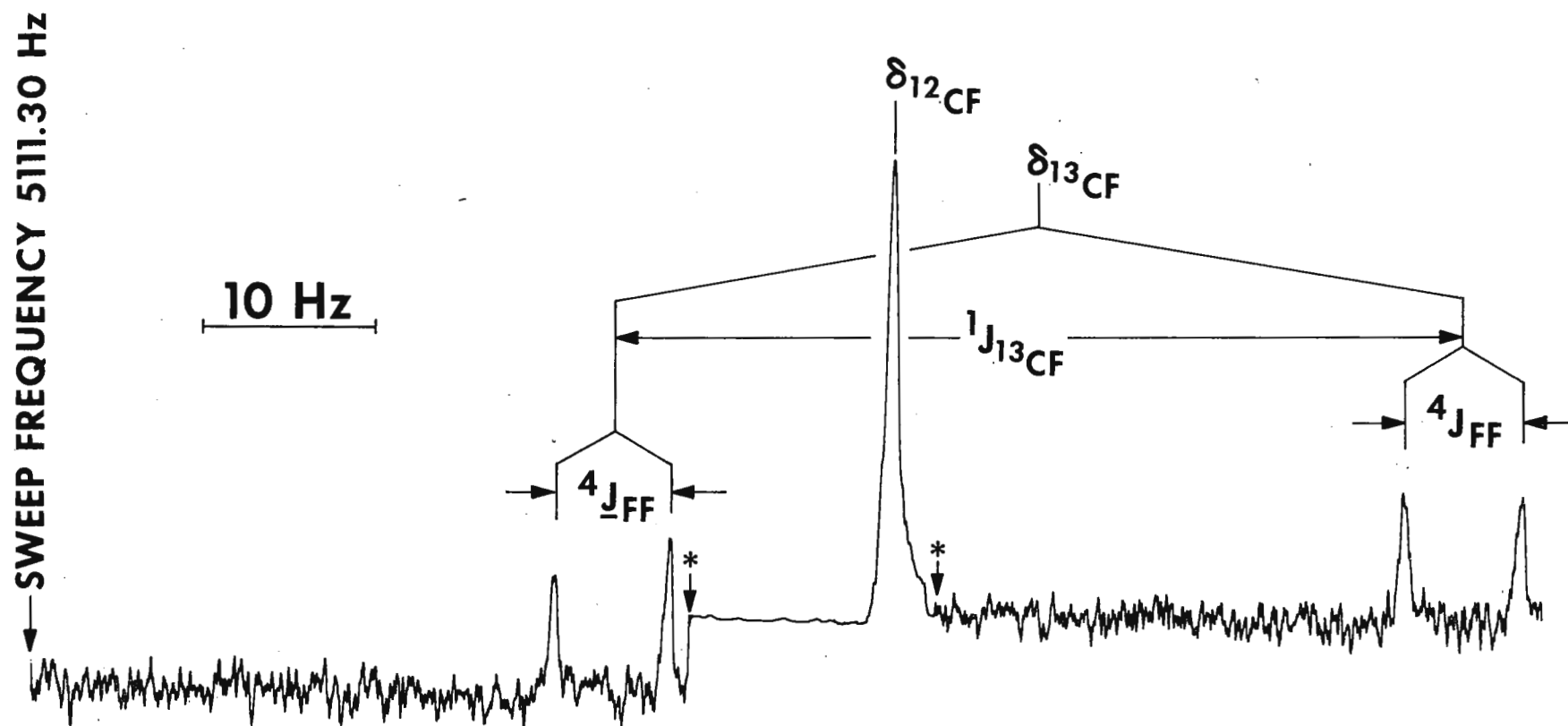


Fig. 1 Digital Frequency Sweep of Proton Decoupled m-Difluorobenzene, Showing ^{12}C band and ^{13}C satellites. Asterisk indicates positions where Synthesizer was switched (see text)



University
of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building Cathedral Street, Glasgow, C.1
Telephone: Bell 4400 STD 041-552 4400

20th February, 1970.

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

Line Narrowing Measurements on Single Plastic
Crystals Using an R10 Spectrometer

Dear Barry,

Line-narrowing and relaxation time studies of plastic organic crystals reveal evidence of translational motion at high temperatures¹. This line-narrowing process which has been ascribed to lattice self-diffusion yields activation energies, which, however, are not in agreement with those obtained from the more direct tracer studies². Possible reasons for this discrepancy lie in the purity and perfections or rather the lack of these qualities, in the specimens. In order to resolve this discrepancy we have examined the high-temperature line-narrowing in a series of highly pure single plastic crystals: cyclohexane, pivalic acid, camphene, succinonitrile, perfluorocyclohexane, triethylene diamine, 2,2-dichloropropane, neopentane, hexamethylethane, and 1,1,1-trichloroethane.

Most previous work of this nature has used broad line n.m.r. spectrometers, but the nature of these materials: in all but two cases all of the protons (or fluorines) have chemical shift equivalence, and the fact that even 60° below the melting points the half width of the lines are of the order of 2KHz, has allowed the use of

our Perkin Elmer R10 high resolution instrument. This provided the advantage of good temperature accuracy and reproducibility and the ability to measure narrow lines near the melting points.

The series of materials used covers the full plastic crystal range. We find good agreement between tracer and n.m.r. studies with the compounds of high entropy of fusion, and poor agreement in the cases of compounds with low entropy of fusion. We ascribe this variation to the nature of point defects in this peculiar class of compounds.

Yours sincerely,

John N. Sherwood

Dr. J. N. Sherwood

Neville C. Lockhart

N. C. Lockhart

Peter Bladon

Dr. P. Bladon

¹ E. R. Andrews and R. G. Eades, Proc. Roy. Soc., 216A, 398 (1953).

² G. M. Hood and J. N. Sherwood, J. Chim. Physique, 63, 121 (1960)

CHEMIE-COMPLEX
DER RIJKS-UNIVERSITEIT

Afd.: Prof. Dr. L. J. Oosterhoff
Wassenaarseweg (Drs. R. Kaptein)
Postbus 75
Leiden
Telefoon 4 83 33

LEIDEN, February 20 19 70

Prof. B. L. Shapiro,
Texas A & M University
College of Science
College station / Texas 77843
U.S.A.

ref.: GmH
subject:

Dear Dr. Shapiro,

Calculation of CIMP spectra

During our study of Chemically Induced Nuclear Polarization we felt the need for another extension of NMR spectrum simulation. In order to describe the wild intensity changes, which appear in the enhanced CIMP spectra, we modified a simulation program with magnetic equivalence factoring^{1,2}) so that populations (N_i) of zero order energy levels can be used as input parameters. In this way, however, one cannot simulate multiplet effects (both emission (E) and absorption (A) within a multiplet). The populations N_i of the levels corresponding to the eigenstates are calculated as follows:

$$N'_j = \sum_i c_{ij}^2 N_i$$

where c_{ij} are elements of the eigenvectors. The intensities I_{kl} are proportional to $(N'_k - N'_l)$

To calculate the populations we used a theory, explaining CIMP multiplet effects in products from cage recombinations of radical pairs, published recently⁴). We derived a formula for the relative population rates for the levels of nuclear states χ_i :

$$P_i \sim 1 - \frac{2 a_i^2 \tau^2}{1 + 4(J^2 + a_i^2)\tau^2}$$

where τ is the lifetime of the radical pair, J is the exchange integral and

$a_i = \langle S \chi_i | H | T \chi_i \rangle$ is a Singlet - Triplet mixing coefficient. The coupling of electrons with nuclei is responsible for this mixing. If the nuclear relaxation rates of the NMR lines do not differ much then $N_i \sim P_i$.

As an example of the calculations, the experimental and calculated ^{13}C -spectra (15.1 Mc) of ethane formed during thermal decomposition of Diacetylperoxide -2,2'- ^{13}C (56% enriched) in Hexachloro-acetone are shown in the figure. The spectrum is actually a superposition of mono- and di- ^{13}C -ethane. A strong A/E quartet of $^{13}\text{CH}_3\text{Cl}$ can also be observed.

The nice agreement between calculated and experimental spectra gives some confidence that the theory is essentially correct.

√ (This is a step further than Lehnig and Fischer³), who used the polarization as input parameter)

Please credit this contribution to the subscription of Drs. Th.J.Sekuur.

Sincerely yours,

Robert Kaptein

R. Kaptein

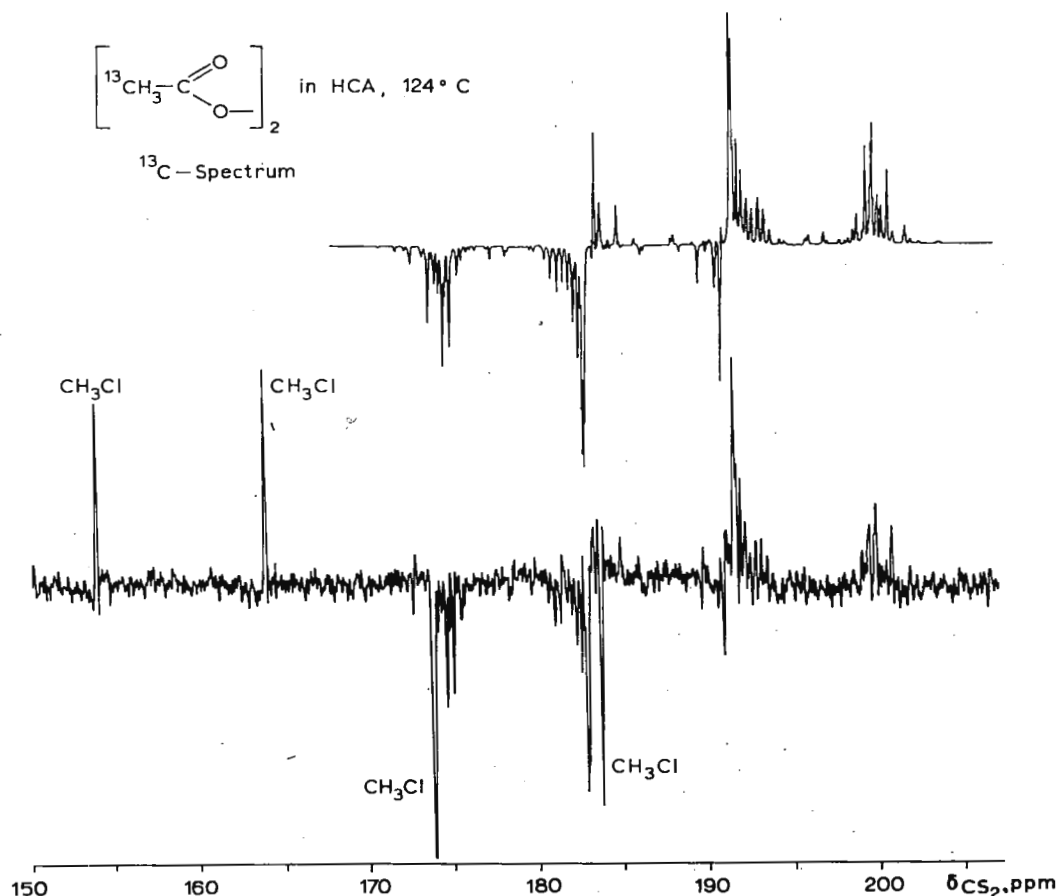
J.A. den Hollander

J.A. den Hollander

F.J.J. de Kanter

F.J.J. de Kanter

- 1) C.W. Haigh, TAMU NMR News Letters 121,54
- 2) R. Kaptein and J.A. den Hollander, TAMU NMR News letters 127,46
- 3) M. Lehing and H. Fischer, in press.
- 4) R. Kaptein and L.J.Oosterhoff
Chem. Phys. letters 4 (1969) 195, 214



^{13}C -spectrum of decomposition of ^{13}C -enriched Diacetyl-peroxide in HCA at 124°C. Computer simulated spectrum is a superposition of mono- and di- ^{13}C -ethane.



University College of Swansea

Department of Chemistry

19th February 1970

19th February 1970

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

The n.m.r. spectrum of L-azetidine-2-carboxylic acid,
a novel four-membered ring.

Dear Barry,

The recent publication of the crystal structure of L-azetidine-2-carboxylic acid (I)¹ prompted me to complete an analysis of the proton spectrum of this unusual amino-acid. The spectrum (HA-100, 30 mgs/0.5 ml. D₂O, Bu^tOH reference and locking signal) is shown in the Figure together with the best computed spectrum using the iterative programme LAME. The splittings measured on a first-order basis enable a good approximation to the actual coupling constants to be obtained, and the chemical shifts were confirmed from the 220 MHz spectrum (by courtesy of I.C.I. P. and P. Division). The ABMNX spectrum is sensitive to the relative signs of the two ²J_{HH} values, agreement only being obtained for signs opposite to those of ³J_{HH}. The sign of the long-range coupling has not yet been determined.

Table of Best Parameters

W(1) 355.54 ± 0.03 Hz	J ₁₂ 0.04 ± 0.04 Hz	J ₂₄ 9.34 ± 0.05 Hz
W(2) 285.43 ± 0.04	J ₁₃ 0.69 ± 0.04	J ₂₅ 8.23 ± 0.04
W(3) 269.14 ± 0.03	J ₁₄ 9.98 ± 0.04	J ₃₄ 6.02 ± 0.05
W(4) 154.99 ± 0.03	J ₁₅ 8.00 ± 0.04	J ₃₅ 9.74 ± 0.04
W(5) 130.64 ± 0.03	J ₂₃ -10.58 ± 0.04	J ₄₅ -12.15 ± 0.04

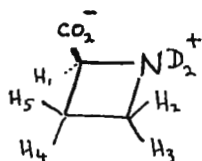
RMS deviation 0.09 Hz

Chemical shifts in Hz from Bu^tOH

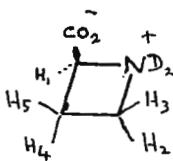
2.

The fairly large errors in the results are unfortunately due to the near equality of many of the coupling constants, leading to much overlapping of peaks.

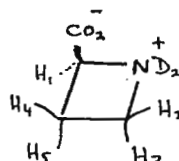
Having analysed the spectrum, it remains to assign $H_{1 \rightarrow 5}$ to the ring protons of the molecule. H_1 is clearly the α -proton, but the other protons can be assigned in four different ways, assuming that the central multiplet (250 \rightarrow 300 Hz) belongs to the CH_2 -N protons.



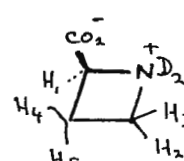
(I A)



(I B)



(I C)



(I D)

After searching the literature, it appears that whereas the evidence is slightly in favour of the $-COOH$ group shielding protons adjacent to it, this is reinforced in amino-acid zwitterions, where the negative charge associated with the carboxylate anion will increase the shielding effect. Therefore the protons on the same side of the ring as the $-CO_2^-$ group in (I) will be at higher field than the trans protons, and since from the Table these are H_3 and H_5 in their respective pairs, (IB) is concluded to have the correct assignment. The coupling constants are in agreement with this, in that the general rule for four-membered rings states that

$$^3J_{cis} > ^3J_{trans} \quad \text{i.e.} \quad J_{15} < J_{14} ; J_{25} < J_{24} \quad \text{and} \quad J_{34} < J_{35}.$$

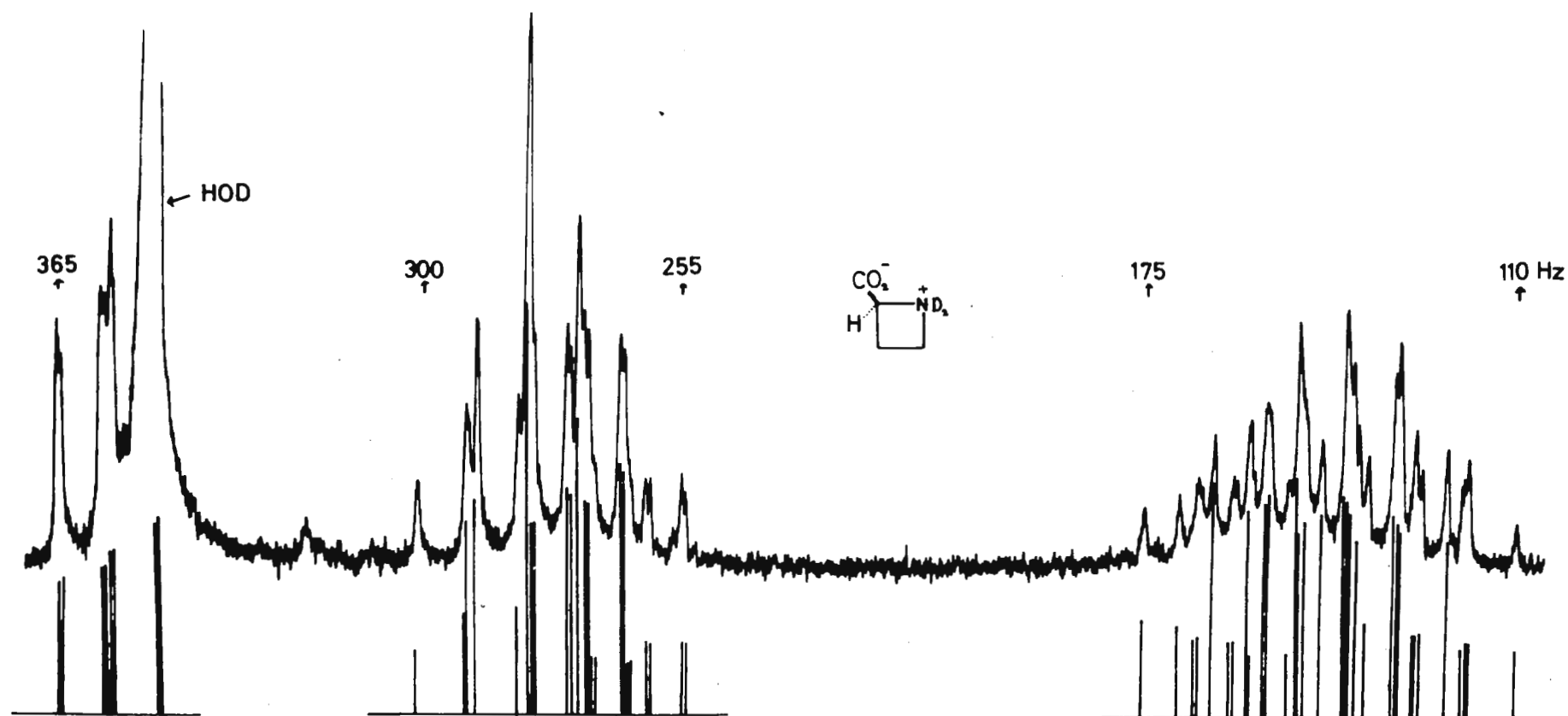
The major long-range coupling occurs between trans protons (J_{13}). Knowing the inadequacies of the Karplus treatments for four-membered rings, I hesitate to make firm conclusions about the non-planarity of the ring. However the differences in the vicinal couplings observed for trans-oriented protons may reflect some deformation from planarity, in addition to electronegativity effects. This and other effects are being further investigated.

With best wishes,

Yours sincerely,

W.A. Thomas.

1. H.M. Berman, E.L. McGardy, J.W. Burgnar II and R.L. Van Etten, J. Amer. Chem. Soc. 1969, 91, 6177



Oklahoma State University

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

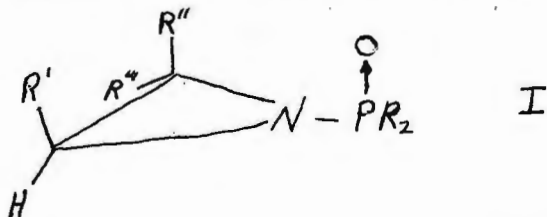
March 5, 1970

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

Short Titles: Phosphorylated Aziridines, Preferred Invertomers;
Correlation of J_{PNCH} Coupling with Structure

Dear Dr. Shapiro:

Recent studies of a series of phosphosylated aziridines I have



provided for the first time accurate J_{PNCH} , J_{HH} (cis - $\text{R}''' = \text{H}$), and J_{HH} (trans- $\text{R}'' = \text{H}$) values. Analysis of the systems over a wide temperature suggests the inversion on nitrogen is slow. In the example, where $\text{R}' = \text{aryl}$ and $\text{R}''' = \text{methyl}$, only one signal is obtained for the methyl resonance in the NMR spectrum at room temperature. Preference of one invertomer is suggested. Stereospecific chemical degradation of the aziridine precursor of I to a specific alkene places the stereochemical assignments from NMR analysis on a firm basis.

Sincerely yours,

Darrell

K. D. Berlin
Professor

KDB:jw

From the Dean
Professor A. R. Katritzky

School of Chemical Sciences
University Plain
Norwich NOR 88C
Telephone Norwich (0603) 56161

12th February 1970.

Dear Dr. Shapiro,

NMR Study of a Borohydride Reduction of a Pyridine

The reduction of 3,5-dinitro-2-methylaminopyridine has been carried out using sodium borohydride in water and deuterium oxide, and using sodium borodeuteride in water and deuterium oxide to yield the tetrahydropyridines (1 - 4). The 100 MHz. n.m.r. spectra of the products show the structure, conformational preference and mechanism of reduction.

The proton H_A is deshielded by the adjacent nitro group and appears as a complex multiplet at 4.81 τ , being coupled by 3-5 Hz. with the protons H_B - H_E . H_A is obviously the 5-proton and the chemical shift is in good agreement with the values observed for similar protons in cis and trans 4-t-butylnitrocyclohexanes¹ and in 3-nitrocyclohexene². Proton H_B is coupled to H_C by 15 Hz. and H_D to H_E by 19 Hz. They thus form two geminal CH_2 groups, the lower field positions of H_B and H_C indicate that they are in the 6-position adjacent to the ring nitrogen atom, whilst H_D and H_E occupy the 4-position. This is consistent with the values of 7.38 and 8.13 τ observed for the 6- and 4-protons respectively in 1,2-dimethyl-1,4,5,6-tetrahydropyridine.³

The individual assignments of H_B and H_D to the equatorial protons and of H_C and H_E to the axial protons in 5 is based on three criteria. Firstly, molecular models indicate values of 30°, 45°, 55° and 65° for the dihedral angles of H_A with H_E , H_C , H_B and H_D respectively, the observed coupling constants of 5, 3.5, 3 and 3 Hz. being in reasonable agreement with these values. Secondly, equatorial protons adjacent to an axial nitro group have been shown to be deshielded for cis 4-t-butylnitrocyclohexane,¹ as is observed in this case for H_B and

H_D . Finally, a small coupling of 1.5 Hz. is observed between H_B and H_D . This value is typical of a coupling over four bonds between two protons which are in a planar zig-zag configuration,⁴ i.e. both these protons occupy equatorial positions.

As far as the partially deuterated compounds (2, 3 and 4) are concerned, the spectra indicate that hydride attack occurs, as expected, in the 4- and 6-positions, whilst the hydrogen atoms in the 1- and 5-positions originate from the solvent. Furthermore, in the case of 2 and 4, the relative values of the integrals of H_B , H_C , H_D and H_E indicate that approximately equal amounts of the four possible stereoisomers are formed. This may be explained either by the attack of borohydride being completely non-stereospecific, or by assuming the proton H_A to be labile, when randomisation can occur by easy inversion at the 5-carbon atom, which is perhaps the more likely.

Yours sincerely,

 
A. R. Katritzky I. J. Fletcher

E. Bordignon* A. Signor* J. R. Lea

References

1. A. C. Huitric and W. F. Trager, J. Org. Chem., 1962, 27, 1926.
2. A. A. Griswold and P. S. Starcher, J. Org. Chem., 1966, 31, 357.
3. Z. Ksandr, Z. Samek, V. Spirko and M. Ferles, Coll. Czech. Chem. Comm., 1966, 31, 3003.
4. M. Barfield and J. Chakrabati, Chem. Revs., 1969, 69, 757.

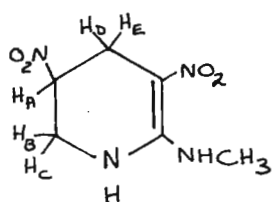
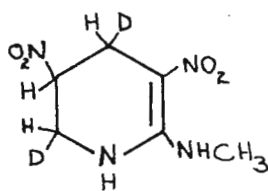
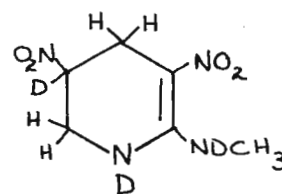
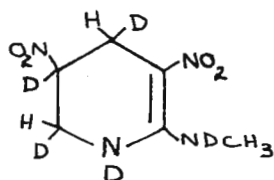
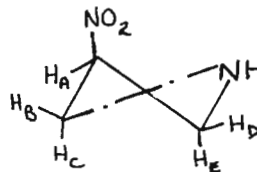
* Istituto di Chimica Organica, Via Marzolo No. 1, Padova, Italy.

Table 1

Compound	Chemical Shift τ values in ppm							Integrals					
	NH	H _A	H _B	H _C	H _D	H _E	NMe	NH	H _A	H _B	H _C	H _D	H _E + Me
1	ca.	2.0	4.81	5.61	5.97	6.14	6.92	6.90	1.07	0.95	1.08	1.97	4.00
2	ca.	2.0	4.81	5.63	5.97	6.16	--	6.91	1.29	0.66	0.49	0.49	3.50
3	--	--	5.62	5.98	6.14	6.94	6.91	--	--	0.95	1.82		4.00
4	--	--	5.64	5.98	6.16	--	6.91	--	--	0.46	0.47	0.47	3.50

Coupling Constants in Hz.

	J _{AB}	J _{AC}	J _{AD}	J _{AE}	J _{BC}	J _{BD}	J _{DE}	J _{NH/Me}
1	3	3.5	3	5	15	1.5	19	5
2	3	3.5	3	-	-	1.5	-	5
3	-	-	-	-	15	1.5	19	-
4	-	-	-	-	-	1.5	-	-

(1) reduced with
NaBH₄/H₂O(2) reduced with
NaBD₄/H₂O(3) reduced with
NaBH₄/D₂O(4) reduced with
NaBD₄/D₂O

(5)

Author Index - TAMU NMR Newsletter No. 138

Andose, J.	20	Katritzky, A.R.	56
Benezra, C.	31	Kellerhals, H.P.	16
Berlin, K.D.	55	Kuhlmann, K.F.	18
Bladon, P.	48	Lea, J.R.	56
Bordignon, E.	56	Lippmaa, E.	39
Bryant, R.G.	30	Lockhart, N.C.	48
Bystrov, V.F.	2	Lunazzi, L.	25
Cooper, M.A.	44	Manatt, S.L.	44
Diehl, P.	16	Mislow, K.	20
Dürr, H.	33	Pehk, T.	39
Egan, B.	20	Reeves, L.W.	36
Engle, J.L.	43	Retcofsky, H.L.	1
Fletcher, I.J.	56	Rummens, F.H.A.	8
Freymann, R.	6	Shapiro, B.L.	38
Friedel, R.A.	1	Sherwood, J.N.	48
Hähner, B.	28	Signor, A.	56
den Hollander, J.A.	50	Slocum, D.W.	22
Jennings, C.A.	22	Slomp, G.	12
Johannesen, R.B.	10,11	Smidt, J.	42
de Kanter, F.	50	Thomas, W.A.	52
Kaptein, R.	50	Wendisch, D.	28

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