Dec. 65

Previous

Illinois Institute of Technology N-M-R Newsletter

No. 86
NOVEMBER, 1965

OVER

(continued)

Deadline Dates:	No. 87:	18 December 1965
	No. 88:	18 January 1966

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".

Socony Mobil Oil Company, Inc.

BOX 1025, PRINCETON, NEW JERSEY 08540

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

RESEARCH DEPARTMENT
CENTRAL RESEARCH DIVISION LABORATORY

October 13, 1965

Dear Barry:

COMPUTER PROGRAM FOR $A_{n_A}BX_{n_X}$ SPECTRA

Since our last communication (No. 74-53), in which we let your readers know about the availability of a computer program for $A_{n_A}B$ spectra, the debugging has been completed for an $A_{n_A}BX_{n_X}$ program (n_A, n_X any integers; all nuclei with spin ½). The computer program is based upon the expressions published in J. Mol. Spect., 8, 193 (1962), and was written by our Math Group at Socony Mobil.

The Hamiltonian for this system may be expressed as a single 2x2 matrix. Diagonalization of this matrix gives two eigenvalues and two eigenvectors, and all possible transition frequencies and intensities are given by eight recursion formulas. Therefore, a minimum of computer storage is required. We felt that this program might be of particular interest to people who have access to a computer, but the computer is too small to permit use of the general 8-spin system of Reilly and Swalen or the general 7-spin system of Bothner-By. Our $A_{n_A}BX_{n_X}$ program requires approximately 2700 decimal storage locations and less than 200 FORTRAN statements.

If n_X is set equal to zero, the program operates as an $A_{n_A}B$ program. n_A and n_X are limited to 99 (since only two columns are allowed for each), so the program is limited to 199 spin ½ nuclei. Any challenges for the "largest" NMR program? FORTRAN listings are available on request.

Sincerely,

R. C. Hirst

P. L. Corio

/ecc

86-2

ANORGANISCH-CHEMISCHES LABORATORIUM
DER
TECHNISCHEN HOCHSCHULE MUNCHEN

8 MUNCHEN 2, den Arcisstraße 21
Ruf-Nr. 5592/330
331

18.1o.1965

Herrn
Professor Dr. B.L. S h a p i r o
Department of Chemistry
Illinois Institute of Technology
Technology Center
C H I C A G O , Ill. 6o616
USA

Sehr geehrter Herr Professor S h a p i r o !

Im Rahmen unserer Untersuchungen über Heteroatom-Proton-Kopplungskonstanten wurden von uns die PMR-Spektren von Selenophen, α, α' -Dimethylselenophen sowie der entsprechenden Chromtricarbonyl-Komplexe vermessen. Tabelle 1 enthält die Meßergebnisse. Sie zeigt die Verschiebung der Resonanzsignale nach höheren Feldern, wie sie bei π-Bindung aromatischer Systeme im Komplex im Vergleich zum freien Liganden auftritt. Ferner ist bemerkenswert, daß die Kopplung zwischen den Protonen und Selen 77 (I = 1/2, natürliche Häufigkeit 7,5%) im α,α'-Dimethylselenophen sich bei der Komplexierung zum α,α'-Dimethylselenophen-chrom-tricarbonyl nicht ändert. Als Erklärung ist hier das Vorliegen einer gerichteten Bindung anzunehmen, wie sie von L.DAHL für das Thiophen-chrom-tricarbonyl angegeben wird.

Mit freundlichen Grüßen
Ihre

Heinz P. Fritz (H.P.Fritz) und Karl E. Schwarzhans (K.-E.Schwarzhans)

Tab. 1 Chemische Verschiebungen und ^{77}Se - ^{1}H-Kopplungskonstanten.

		Selenophen	α,α'-Dimethyl-selenophen	Selenophen-$Cr(CO)_3$	α,α'-Dimethyl-selenophen-$Cr(CO)_3$
Hz	α-H	464	-	354	-
	β-H	427	393	346	327
	α-CH_3	-	142	-	139
J Hz	^{77}Se-αH	47	-	x)	-
	^{77}Se-βH		7		7
	^{77}Se-α-C-H_3	-	1o		1o

x) zu wenig löslich

86-4

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

October 22, 1965

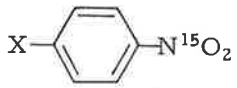
Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Chemical Shifts of para-Substituted N^{15}-Nitrobenzenes

Ring Inversion in 2,2-Difluoro-cis-decalin

The N^{15}-chemical shifts of nine para-substituted nitrobenzenes have been measured. The results are collected below. It is interesting to note the relatively small range of the shifts (8.23 p.p.m.). This may be compared with the F^{19}-chemical shifts in para-substituted fluorobenzenes (24.35 p.p.m.[1]) and the C^{13} shifts in para-substituted toluenes (1 p.p.m.[2]) for the same substituents. The intermediate range of chemical shifts is as expected if the paramagnetic term, σ_p^{AA}, dominates the shielding constants for these nuclei.[3] When the N^{15}-chemical shifts are plotted against the C^{13} or the F^{19} shifts, a good linear correlation is obtained. This would seem to confirm that similar factors are operative in determining the chemical shifts of N^{15}, C^{13}, and F^{19} nuclei.



Substituent (X)	Chemical Shift (p.p.m.)
NH_2	4.38
OMe	4.38
F	3.57
$NHCOCH_3$	3.07
Cl	2.09
Br	1.32
H	0.00
CN	-2.58
NO_2	-3.85

Examination of models suggest that the gem-difluoro group of 2,2-difluoro-cis-decalin should be found in two magnetically distinct environments corresponding to the two possible "enantiomeric" forms.

The fluorine-19 spectrum of this compound at -70° is a set of two overlapping AB quartets, thus confirming the above suggestion. As the temperature is raised, the spectrum finally coalesces to an overaged AB quartet. Employing a FORTRAN IV program based on Alexander's density-matrix treatment of such exchanges[4] to generate theoretical spectra, we estimate the activation energy for this process to be 14 ± .8 kcal/mole. Substituents at the ring-juncture lower the energy barrier somewhat but 3-methyl and 6-methyl-2, 2-difluoro-cis-decalin appear to be "frozen"; these latter compounds give only one temperature independent AB spectrum.

(1) R. W. Taft, et al., J. Am. Chem. Soc., 85, 3146 (1963).
(2) P. C. Lauterbur, Ann. N. Y. Acad. Sci., 70, 841 (1958).
(3) J. A. Pople, J. Chem. Phys., 37, 53 (1962).
(4) S. Alexander, J. Chem. Phys., 37, 974 (1962).

With all good wishes,

Very truly yours,

J. T. C. Gerig

David Clark

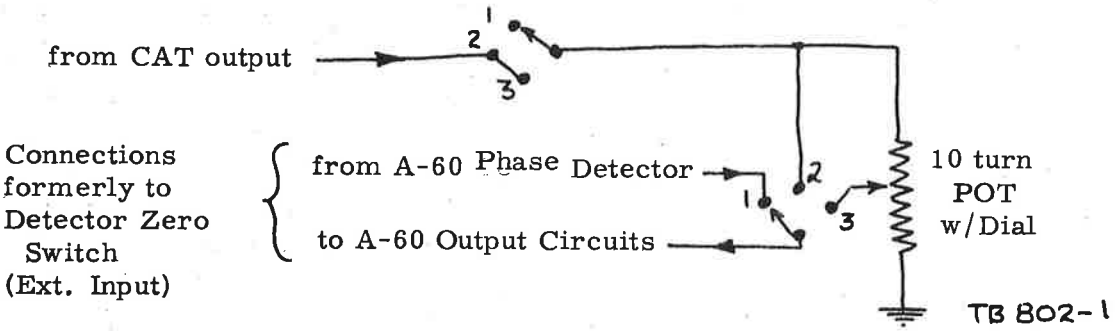
John D. Roberts

UNION CARBIDE CORPORATION
PLASTICS DIVISION
RIVER ROAD, BOUND BROOK, N J 08805

CAT 1024 Experiences

Our CAT 1024 was delivered some months back. We carried out the installation ourselves on our rather ancient A-60 with the help of Varian's adequate instructions in less than two hours. Its operation to date has been satisfactory. We operate almost exclusively in the NMR trigger mode to reduce long-term drift problems.

For certain types of data handling (e.g., when the graphical output data are to be compared visually), it is desirable to adjust the output amplitude so that certain features in the repeated spectra are presented equally. The only provision for output amplitude adjustment on the CAT is the factor-of-two-stepping vertical range control. Our need for a continuously variable control moved us to modify slightly the CAT-A-60 interface on the A-60 side.



Switch Position	label
1	NORMAL
2	CAT — DIRECT
3	CAT — ATTENUATED

The leads were removed from the Detector Zero control-operated external input switch. This permits the use of a 10-turn pot in the Detector Zero control (for the benefit of those of us without the lock-pickers touch). The switch and pot were mounted in a convenient place on the A-60 front panel.

UNION CARBIDE CORPORATION
PLASTICS DIVISION
RIVER ROAD, BOUND BROOK, N. J. 08805

For our modification, a value of 500 Ω was chosen for the CAT attenuator pot. Below this value, there appears to be some danger of overloading the CAT output circuitry (one must stay within the range which the CAT reads its memory linearly). Unfortunately, due to the shunt R 827-R 828, the A-60 recorder circuits have an input impedance of 4.7 K, which is low enough to cause up to a 2.6% (relative) negative error in the linearity of the signal attenuation. The calculated error is a maximum over the range 30-70%, but drops to zero at 0% and 100% attenuation. Observations bear these calculations out. If for some reason the error must be eliminated, an operational amplifier could be used to drive the A 60. However, it is possible to work with the error.

Bill.

William F. Beach

86-8

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
800 BUCHANAN STREET
ALBANY, CALIFORNIA 94710

October 18, 1965

AIRMAIL

Professor Bernard Shapiro
Chemistry Department
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Read-in-Time versus Read-out-Time Discrepancies in the C-1024 Time Averaging Computer. Two Solutions.

We agree with Tom Conner's conclusions in IITNMR #83 regarding read-in-time versus read-out-time discrepancies in the C 1024 Time Averaging Computer. Some time ago we attacked the same problem and came up with two solutions somewhat different in approach that might be of interest.

Since our CAT is coupled to several spectrometers, we decided that an ounce of prevention was worth several pounds of cure.

As Conner states, the read-in-time is quite stable. We decided to use the same digital timing circuitry for read-out purposes. In the TMC CN 1024 (non-Varian) this can be done with no modification. We refer to the CN 1024 because we are using the standard TMC Analyzer in conjunction with a TMC modified 202 CAT Logic Unit plug-in (purchased prior to announcement of Varian C 1024). Basically our unit is very similar to the Varian C 1024 except for the input A-D conversion and inclusion of spectrometer sweep ramp circuitry.

The address and arithmetic information displayed on the internal scope in the accumulate mode is simultaneously available for external display. This is the one volt high level analog output for recorder use. In the CN 1024 this output is brought directly from the Binary to Analog Converter card B7490 to an external jack.

Procedure to read out spectral information using accumulate address advance times is as follows:

1. Set the channel advance switch to a position compatible with the recorder time base. On the A-60 we generally use a 250 second chart sweep.

2. To avoid picking up additional arithmetic counts in the accumulate mode the A-D converter output must be inhibited so that it will not reach the arithmetic binary circuitry. Using the 202 CAT Logic Unit this is accomplished by front panel switching from Converter to Direct mode of operation. How to accomplish this in the Varian C 1024 will have to be left up to the user.

3. Finally, switch to Accumulate, start recorder time base and then trigger the CAT sweep at the trigger point on the recorder chart.

A second method of utilizing the accomulate address sweep times for readout is accomplished by a very minor modification on the function switch (PWR-ACCUM-DISPLAY-READOUT). This method allows normal setup for Readout except that sweep time circuitry controls address advance in Readout rather than the readout oscillator. In the CN 1024 a 3 volt inhibit is applied to the ΔT input of the memory cycle circuit except in Accumulate (pin B of Memory Cycle Card SCB 2812). If this inhibit voltage is removed in Readout, then the accumulate sweep time is enabled as in Accumulate. In the Function Switch circuit of the CN 1024 (schematic B 7860) it is only necessary to disconnect switch position 2 (Readout) of S3-3. CN 1024 circuitry is such that arithmetic counts are inhibited from reaching the arithmetic binaries in all positions of the function switch except Accumulate; therefore step 2 of the previous method is eliminated. One further condition must be satisfied -- the readout-display oscillator (card B 7464) must be disabled in Readout to prevent both timing circuits from activating the address advance. In the CN 1024 this is accomplished simply by switching the X-Y readout switch on the chassis rear to EXT. This inhibits the internal readout-display oscillator in Readout only. Since it is not necessary to externally inhibit arithmetic accumulate with the function switch in Readout, this second method may be most convenient for C 1024 owners. Procedure for readout using this second method is the same as normal except that address advance must be triggered manually. Readout does not automatically start when switching to Readout.

A warning to all CN 1024 owners: we found that the differential linearity of the B-A converters which feed the analog recorder output was very poor. The amplitude of every fourth step was about equal to the sum of the intervening three steps. The performance of the ramp can be easily

checked on a recorder as counts are fed into the address or arithmetic binaries at a rate sufficiently slow for the recorder to see individual steps. Linearity may also be affected by recorder input impedance because of loading effects on the B-A converter circuitry. The high level one volt recorder analog output for readout is connected directly across 800 ohms in a critical point of the B-A circuitry. We eventually were able to eliminate most of this trouble by trimming a number of the current-limiting resistors.

Sincerely yours,

R. E. Lundin, Principal Chemist

R. H. Elsken, Electronics Engineer
Molecular Structure Investigations
Wool and Mohair Laboratory

RICHFIELD OIL CORPORATION

RESEARCH AND DEVELOPMENT • 1900 CRESCENT AVENUE • ANAHEIM, CALIFORNIA 92803 • P. O. BOX 3883

October 19, 1965

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr. Shapiro:

QUANTITATIVE ANALYSES USING ^{13}C-H SATELLITES AS INTERNAL STANDARDS

Recently we had occasion to quantitatively estimate small amounts (0-5%) of various aromatic compounds dissolved in acetic acid. We preferred a non-destructive, non-contaminating method for analysis so chose n.m.r. Comparison of the integrals of the aromatic and acetic acid methyl proton resonance peaks was found to lead to large errors, apparently because of the necessarily vast differences in gain settings for the two peaks. However, by the use of the downfield acetic acid $^{13}CH_3$ satellite peak at -1.58 ppm as a quantitative internal standard (taken as 0.554%) reliable analyses were obtained. Some data taken from analyses of standard solutions are shown in the table below.

	Analyses, mole %	
Compound	Actual	Found
Benzoic acid	0.504	0.495
	2.28	2.06
Phthalic anhydride	1.01	1.07
o-Toluic acid	0.877	0.880
o-Xylene	2.73	2.80

This method is extremely convenient because no weighings are necessary. It can be used whenever the proton resonances of the substances to be analyzed and one of the ^{13}C-H satellites of an organic solvent occur where they can be integrated free from interference from other peaks.

Sincerely yours,

RICHFIELD OIL CORPORATION

Fred Caserio Jr

F. F. Caserio, Jr.
Research Associate

FFC:ka

86-12

GROUPEMENT AMPERE

ATOMES ET MOLÉCULES PAR ÉTUDES RADIO-ÉLECTRIQUES

SECRÉTARIAT
Institut de Physique de l'Université de Genève
Boulevard d'Yvoy
GENÈVE - SUISSE
Ø 25 22 10
Chèques postaux I. 6319
Tél. 022 - 24 12 68

GJB/cp

Genève, le 25 octobre 1965

Professor B. L. Shapiro
Illinois Institute of Technology

Chicago 16 - Illinois

U. S. A.

Cher Docteur Shapiro,

Je pense qu'un certain nombre de nos collègues seront intéressés de savoir que le groupement AMPERE, qui réunit depuis 1952 un grand nombre de chercheurs, en majorité européens, intéressés par l'Etude des Atomes et Molécules Par Etudes Radio Electriques organise chaque année un colloque international sur les problèmes de Résonance et Relaxation Magnétiques et Electriques.

La prochaine réunion qui aura lieu à LJUBLJANA, en Yougoslavie, est prévue pour la semaine du 5 au 10 septembre 1966. Elle portera sur un certain nombre de questions d'actualités se rapportant à la résonance et la relaxation magnétiques. Le Compte Rendu de cette rencontre, comme ceux des derniers colloques: notamment celui de Louvain 1964, sera édité par North Holland Publishing Company, Amsterdam.

Les renseignements concernant cette rencontre sont publiés dans le Bulletin Ampère (Abonnements: Imprimerie Kundig, 10, rue du Vieux-Collège, Genève, Suisse) ou peuvent être demandés directement au soussigné ou au Secrétariat d'Organisation du Colloque Ampère de Ljubljana (septembre 1966) à qui toute correspondance concernant le colloque peut être adressée.
Ecrire à:

Secretary 14th Colloque Ampère
Nuclear Institute J. Stefan
LJUBLJANA - Yougoslavie

Avec mes meilleures amitiés

Prof. G. J. Béné

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH, PA. 15213

20 October 1965

Professor Barry L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, ILLINOIS 60616

Dear Barry:

We have been running frequency sweep spectra with our HR-60 and RSI spin decoupler with a sweep unit that we have recently built that may be of interest to some of your readers. Instead of mechanically driving an oscillator, which was found to be noisy, unstable and non-reproducible, we now externally control a General Radio 1161-A frequency synthesizer. This is accomplished by taking the output from a mercury battery and integrating and amplifying it with a Heath Operational Amplifier (Model EUW-19A). The sweep time can be selected by varying the RC time constant with any one of four resistors. The sweep range is determined by the regulated output across any of three resistors and the synthesizer decade which is being swept. The synthesizer has four decades (10, 100, 1000 and 10,000 c.p.s.) and a continually adjustable decade of -1 to 10 c.p.s. This, in conjunction with the sweep range switch, gives a variety of ranges from 2 to 10,000 c.p.s. per 25 cm.

The output of the synthesizer is only 2 volts. In order to up this output to about 20 volts we connected the two amplifiers of the V 4240 sweep amplifier unit in series. This was accomplished by means of a switch connecting pins 3 and 4 of J 406 to pin 5 of V 405 and V 406, respectively. The diagram of the sweep set-up and block diagram are shown in figures 1 and 2. A Moseley X-Y recorder (model 7030A) is used to display the spectrum.

We have found the unit to be very linear and reproducible spectra can be recorded easily. The spectrum can be calibrated by stopping the recorder at several points and reading the frequency from the counter. An alternate method is to record the spectrum and then return the pen and read the frequencies of the individual peak by stopping the pen on the peaks. The reproducibility is $\pm$ 0.1 c.p.s., or the limit of the frequency counter (10 sec. count). Figure 3 shows an example of the resolution which can be obtained. This is a 10 c.p.s. scan of a small portion of the resonance signal of the inner fluorine in 1,1,3-trifluorobutadiene. The sweep time was 60 sec.

So far we have been quite pleased with the performance of the unit. The only "bug" we have not worked out is that of the phase change that occurs over larger sweep widths (50 c.p.s. or greater). Since we normally

use sweep widths less than this, this has not been a serious problem. Perhaps the biggest drawback to the system is the cost of the frequency synthesizer, about $4,000. This price seems less when one realizes how nicely the synthesizer is suited for introducing sidebands. The frequency of the sideband can be dialed in and internally calibrated to 7 significant figures (to one thousandth of a c.p.s.). The sideband frequency can then be changed by simply changing any of the 4 decade dials while the one thousandth c.p.s. accuracy is maintained.

Sincerely,

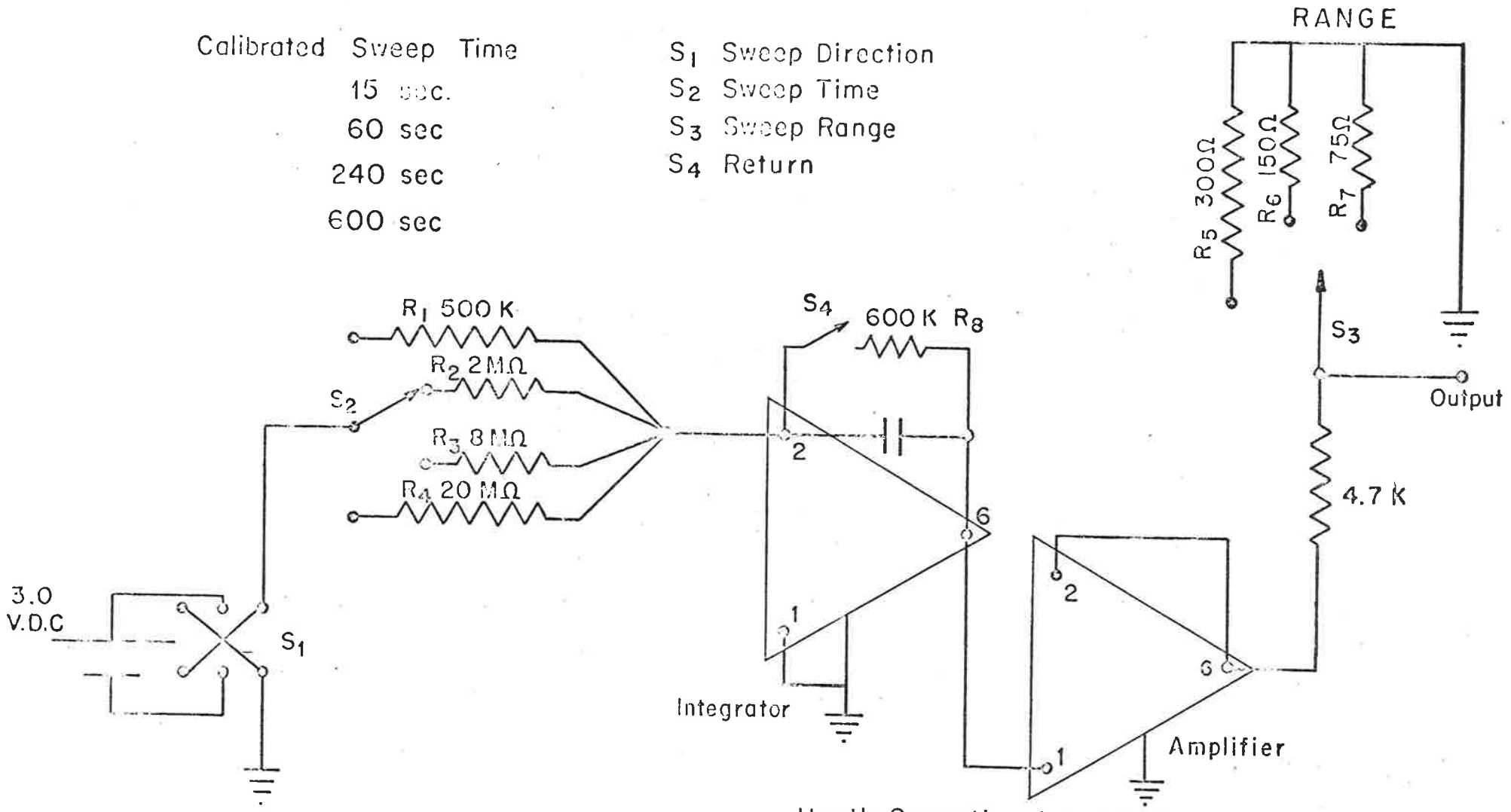
Aksel A. Bothner-By

David F. Koster

Dennis E. Wisnosky

DFK:hb

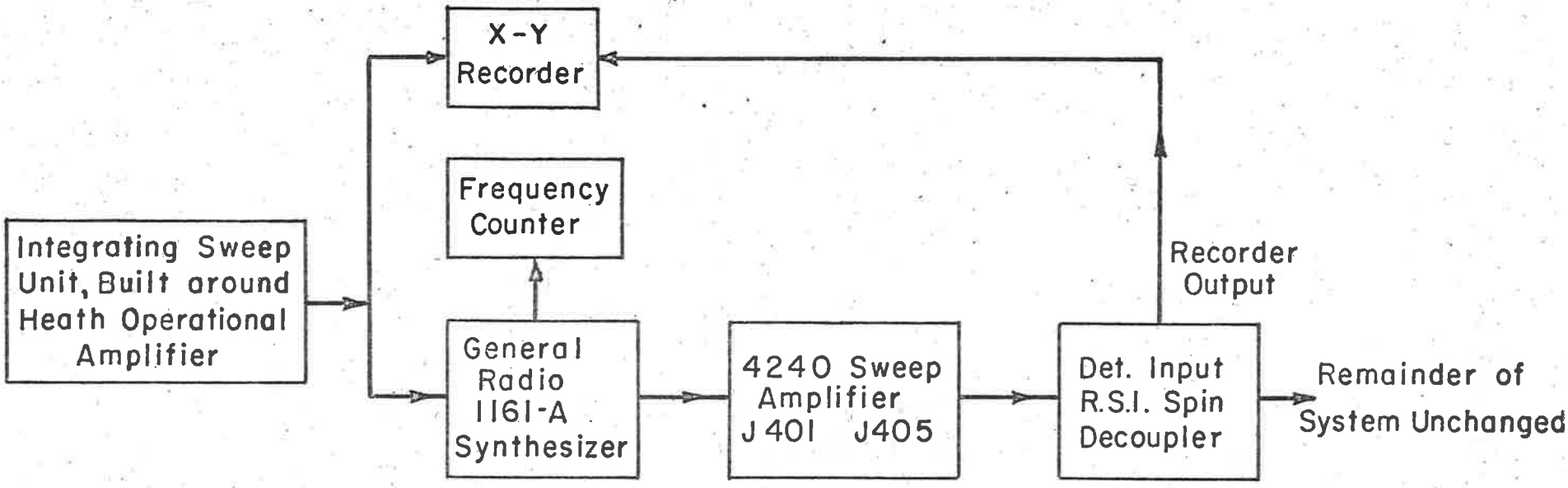
Figure 1.



Resistors all $\frac{1}{2}$ Watt Capacitor, 1mfd, 600 V.D.C.

Frequency Sweep Unit

Figure 2.



BLOCK DIAGRAM

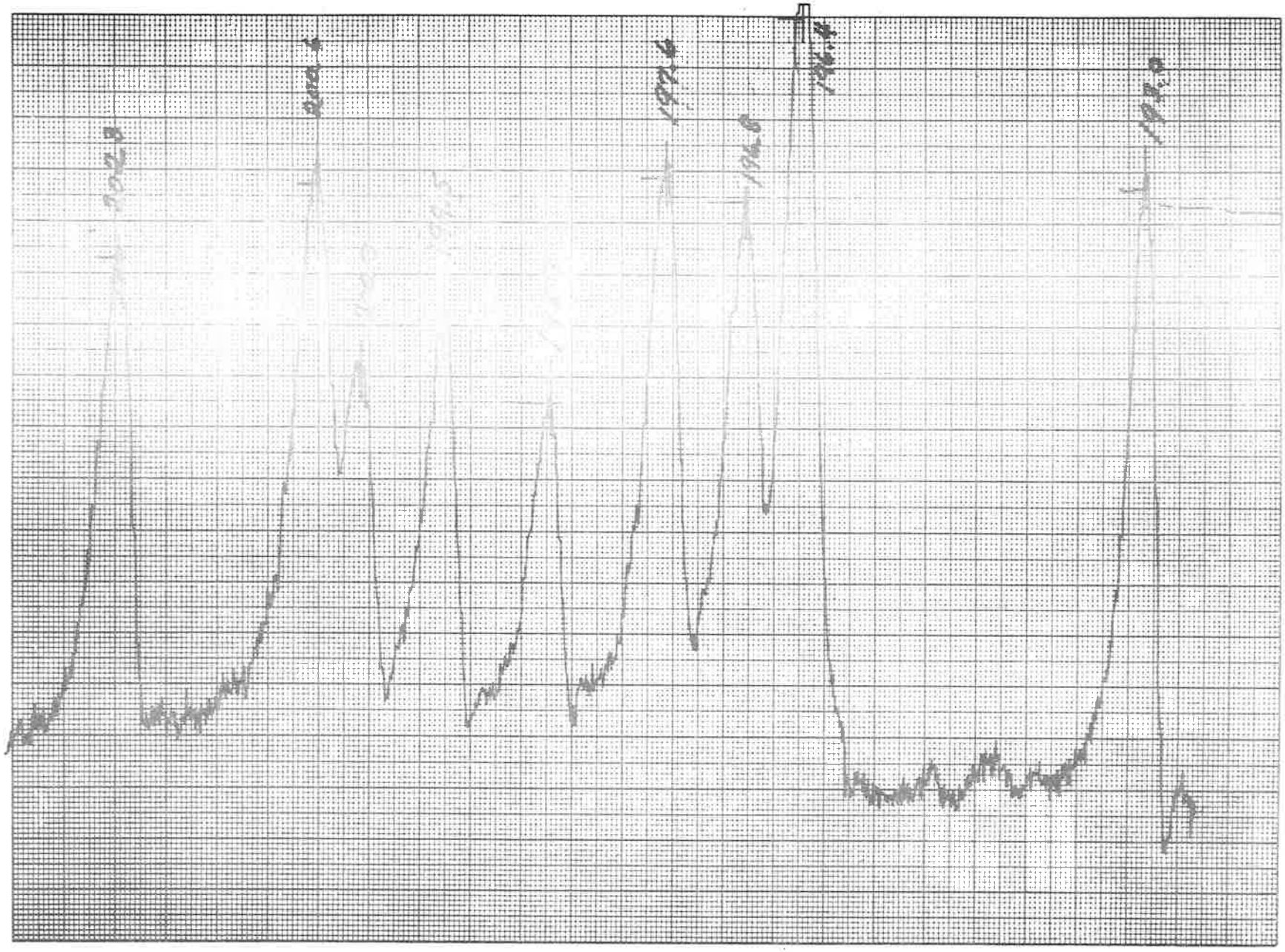


Figure 3.

86-18

UNIVERSITY OF ILLINOIS URBANA 61803

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

THE WILLIAM ALBERT NOYES LABORATORY

October 29, 1965

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

One of our group, Dick Meinzer, has recently completed a detailed study of the temperature and pressure dependences of the ^{1}H and ^{19}F shifts and some of the coupling constants in several gases, including the deuteromethanes, fluoromethanes, H_2 and HD. The results are summarized in the abstract of his Ph.D. thesis as follows:

"The proton and fluorine chemical shifts of gaseous CH_4, CH_3D, CH_2D_2, CHD_3, CH_3F, CH_2F_2, and CF_4 were measured as a function of temperature and density relative to reference liquids. The temperature dependence of the proton chemical shift of gasesou H_2 and HD was similarly measured. It was found that these results are fitted by the following empirical equation:

$$\sigma(\rho T) = aT + b\rho + c\rho T + e$$

The temperature dependent shift of the reference liquid is included in the a term. The absolute temperature dependence, however, of the reference liquids was also determined. With this information, the a term can be corrected so that the above equation represents only the changes in the chemical shift of the gas as a function of the two variables. Since the chemical shift is equal to the differences in the magnetic shielding constants of the sample and reference, the above equation actually gives the functional dependence of the magnetic shielding constant of a gas on the two variables. Measurements made in the critical temperature region of methyl fluoride and fluroform indicate that the same equation might also be applicable to the chemical shift of the liquid. The change through the critical region was approximately proportional to the b and c terms.

"The a and e terms result from intramolecular effects, and their origin is discussed. The b and c terms result from intermolecular effects. They include contributions from the bulk susceptibility correction, polar effects, van der Waals attractive forces and repulsive exchange forces. The b term corrected for the bulk susceptibility of the medium and the c term are both proportional to the spin-rotation constants.

"In addition, the nuclear spin-spin coupling constant was measured in these compounds as a function of the same two variables. The J_{HF} coupling constant in the fluoromethanes is density dependent, and it is different in the gaseous and liquid states. The changes in the coupling constant can be explained by the orbital currents produced by the surrounding molecules. These orbital currents also produce part of the density dependent chemical shift, and thus the changes in chemical shift and coupling constant are related. The sign and magnitude of the change are related to the bond anisotropy."

I hope that the above will pay my subscription for a while. A short title of this is "P and T dependence of ^{1}H and ^{19}F shifts and of J_{HD} and J_{HF} in $CH_{4-n}D_n$, $CH_{4-n}F_n$, H_2 and HD."

With best personal regards,

H. S Gutowsky

HSG:ljz

University of East Anglia

School of Chemical Sciences
Wilberforce Road, Norwich NOR 77H
Telephone Norwich 52651

26th October, 1965.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
Chicago, Illinois, 60616.

PMR SPECTRA OF SOME CYCLIC N-NITROSAMINES

Dear Barry,

We wish to report some research being carried out here into the P.M.R. spectra of cyclic nitrosamines. There were four aims of this research, namely:-

(a) To obtain information about the long-range effect on chemical shifts by the nitroso group.

(b) To find out how the presence of the nitroso group affects the relative stability of a neighbouring methyl group in the axial or equatorial position for six-membered rings.

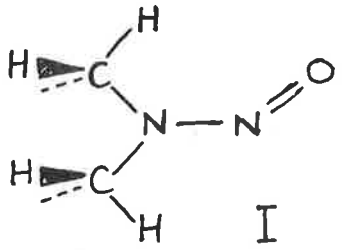
(c) To see if evidence for the twist form (or at any rate deviations from the chair form) of N,N-dinitrosopiperazines could be obtained.

(d) To assign configurations to the γ - and δ -2,3,5,6-tetramethyl-piperazines (abbreviated to γ- and δ- TMP) by examining the spectra of their dinitroso derivatives. Although this might seem the most trivial of the four aims, it was in fact the original problem which suggested the rest of the research!

Most of our results to date are summarised in the table. We hope to obtain further information shortly when homonuclear double resonance facilities become available here. Detailed consideration of the data, including related published values, enable us to arrive at the following tentative conclusions:-

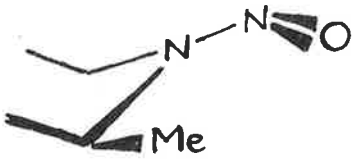
(a) Using the value reported for dimethylnitrosamine[1], we find that for the α -protons in the plane of the nitroso group, the one cis to the oxygen atom gives a signal ca. 0.4 p.p.m. to low field of that from the proton trans to the nitroso group. On the other hand for the α -protons not in the nitroso group plane, the trans proton is to low-field by ca. 1.4 p.p.m.

The conformation shown in I is assumed:-



I

(b) Methyl groups cis to the nitroso oxygen atom would have a very strong interaction with the nitroso group if they were in the equatorial position as in II.



II

We believe that such a situation does not occur, but, for instance, that ∝-dinitroso TMP exists with all four methyl groups axial as in III (probably with some distortion from the chair form).

III

In other cases the molecule is forced to assume the twist form (see (c)).

(c) It is found that:-
(i) Certain unexpected values for vicinal coupling constants (e.g. for the transoid-∈-TMP-isomer a value of 10.6 c/s is found for a coupling which, if the molecule were in the chair form, would be the average of J_{aa} and J_{ee}) lead us to suppose the existence of the twist form.
(ii) There exist non-additivities in chemical shift effects of the position of the two nitroso groups for TMP derivatives. By this we mean that the chemical shift difference between the resonances of a given ring proton for the two possible orientations of the nearer nitroso group depends on the orientation of the further nitroso group. Consequently in such cases (as for dinitrosopiperazine[2]) the cisoid and transoid forms probably have somewhat different ring conformations.

(d) We believe that the assignments of γ - and δ -dinitroso TMP are as below (the plus and minus signs refer to the position of methyl groups above and below the "plane" of the ring). The other three possible isomers of TMP had already been assigned on the basis of the NMR spectra of their dihydrochlorides[3].

γ δ

References

1. Looney, Phillips and Reilly, J.A.C.S. 79, 6136 (1957)

2. Harris, J.Mol.Spect. 15, 100 (1965)

3. Harris and Sheppard, J.Chem.Soc., to be published.

Best wishes,

Yours sincerely,

Robin Harris — Richard Spragg

R.K. Harris. — R.A. Spragg.

TABLE: SOME CHEMICAL SHIFTS OF CYCLIC NITROSAMINES IN SOLUTION.

(a) Mononitroso compounds

	αCH_2 τ		$\Delta\tau$	αCH τ		$\Delta\tau$	αCCH_3 τ		$\Delta\tau$
1-methyl-4-nitrosopiperazine	6.29	5.80	0.49						
N-nitroso-piperidine	6.31	5.82	0.49						
N-nitroso-2-methylpiperidine X	6.35	5.55	0.80				8.96	8.51	0.45
							8.92	8.58	0.34
cis-N-nitroso-2,6-dimethylpiperidine				?	?	< 0.5	8.97	8.37	0.60
trans " "				5.0	6.1	-1.1	8.66	8.40	0.26
N-nitroso-2,2,6,6-tetramethylpiperidine									
N-nitrosomorpholine	6.30	5.79	0.51						
N-nitrosopyrrolidine	6.60	5.82	0.78				8.63	8.45	0.18
N-nitroso-2,2,5,5-tetramethylpyrrolidine									
N-nitroso-hexamethylene-imine	6.49	5.73	0.76						
Nitroso-γ-2,3,4,5,6-pentamethylpiperazine				5.2	5.2	<0.3	8.97	8.62	

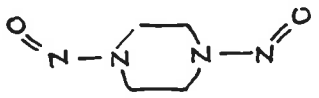
(b) Dinitroso compounds. * +

	CH_2 τ		$\Delta\tau$	CH τ		CCH_3 τ		$\Delta\tau$
cisoid 1,4-dinitrosopiperazine	6.18	5.39	0.59					
transoid "	5.98	5.49	& 0.69					
cisoid α-dinitroso TMP				5.0		8.89	8.41	0.37 & 0.35
transoid "				5.0		8.76	8.52	
cisoid ϵ- "				4.64	5.96	9.05	8.13	
transoid "				5.30 &	5.67	8.78	8.20	
transoid γ "				5.13 &	5.41	8.92	8.30	
transoid δ "				4.50	5.91	8.97	8.36	

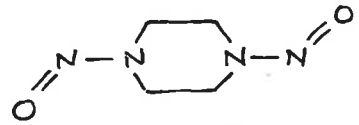
X two isomers involved.

* TMP is used as an abbreviation for 2,3,5,6-tetramethylpiperazine.

\+ The terms cisoid and transoid refer to the relationship of the two nitroso groups as IV and V.



cisoid



transoid

86-24

PROFESSOR SIR EDMUND HIRST, C.B.E., F.R.S.
PROFESSOR T. L. COTTRELL, D.Sc.

TELEPHONE: EDINBURGH NEWINGTON 1011

DEPARTMENT OF CHEMISTRY
WEST MAINS ROAD
EDINBURGH, 9

1st November 1965.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago,
Illinois 60616, U.S.A.

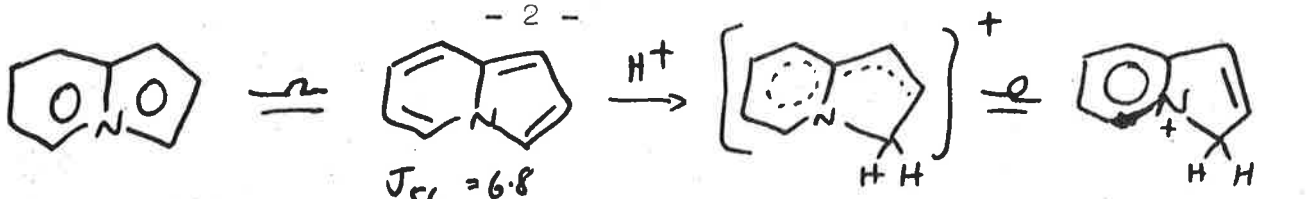
Dear Professor Shapiro,

Thank you for your reminder. N.M.R. is being used in this department by two main research groups whose interests are carbohydrates and heteroaromatic compounds. I shall restrict my contribution to the latter in this Newsletter. One of the aspects which excited us at one time was the change in coupling constants in bases and their corresponding salts. We noticed that J_{AB} in the system $CH_A-CH_B-\overset{\oplus}{N}$ of an aromatic system was particularly sensitive to the electronic state of the N atom, increasing in the salts, quaternary salts and N-oxides. When we first found this it appeared to be a largely novel observation but other research groups were apparently also aware of it. Some of our unpublished results are given in the Table.

Thinking that this was likely to prove a general phenomenon we thought this would be useful to determine the site of protonation, quaternisation and N-oxidation of azines where alternative sites were possible. The application to cinnoline seemed worthwhile and the N.M.R. results strongly suggest that protonation and quaternisation occur at the 1-position.[1] However the position is not completely clear since Ames and Kucharska in a series of closely interwoven papers proposed that quaternisation of cinnoline occurs at the 2-position.[2] We cannot explain this anomaly: some of the degradative work used by these workers may be incorrect since rearrangements were possible (and considered) in some of the reactions. Perhaps the coupling constant changes in cinnoline are different; we are looking into this possibility, but the observations with cinnoline-1- and 2-oxides certainly fit with the quinoline and isoquinoline data. We are interested to hear any comments upon the experimental work.

We know of course that exceptions to the general rules will occur. Some obvious ones are the systems with near classical bond orders - i.e. approaching alternate single-double bonds; if protonation changes the degree of aromaticity markedly, then the coupling constants in a near double bond (in the base) will fall. Take the indolizines as an example; some figures are shown below.

1. Palmer & Semple, Chem. and Ind., 1965, 1766
2. Ames & Kucharska, J. chem. Soc., 1964, 283.



$J_{56} = 6.8$
$J_{67} = 6.4$
$J_{78} = 8.9$ c/s

$J_{56} = 6.5$
$J_{78} = 7.5 - 8.5$ c/s
(Various comps.)

Table of Coupling Constant Changes ($\Delta J_{ij} = J_{ij}^{N} - J_{ij}^{+}$)

Pyridines		J_{25}	J_{24}	J_{34}	J_{35}	J_{45}	J_{46}	J_{56}
2Br	N			7.6	1.0	7.3	2.5	4.7
	A			8.3	1.8	7.2	2.0	5.4
2Cl	N			8.2	1.1	7.5	2.1	4.8
	A			c.8.5	c.1.4	c.7.5	2.0	c.6.2
3Br	N	0.8	0.8			8.3	1.9	4.8
	A	0.4	2.0			8.7	1.3	5.7

Quinolines		J_{23}	J_{34}	J_{24}	J_{56}	J_{68}	J_{78}
5,6-Cl_2	N	4.2	8.6	1.7			9.1
	A	5.4	8.6	1.5			9.3
7CF_3	N	4.2	8.2	1.8	8.7	1.7	
	A	5.3	8.5	1.4	8.7	1.4	

Isoquinolines		J_{13}	J_{34}	J_{56}	J_{68}
None	N	0.5	5.7		
	A	0.9	6.7		
7Cl	N	0.5	5.8	8.8	1.8
	A	0.8	6.8	8.9	1.8
7Meo	N	0.5	5.7	8.9	2.6
	A	0.7	6.5	9.0	2.5

I hope that this contribution will prove satisfactory.

Can any reader run a very small number of ^{14}N or ^{17}O spectra for me?

Yours sincerely,

M.H. Palmer.

(M.H. Palmer) M.H. Palmer & B. Semple.

86-26

RÉPUBLIQUE FRANÇAISE
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TÉL. 87-50-11

Laboratoire de
Chimie Organique Physique

Professor B.L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
Technology Center
C H I C A G O, Illinois 60.616
U.S.A.

RÉFÉRENCE A RAPPELER : G/ COP-1/65-588

VOTRE RÉF. :

VOTRE LETTRE DU

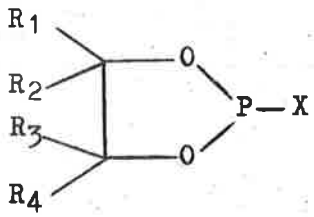
GRENOBLE, LE 2 Novembre 1965

MEL 6

Stereochemistry of Tricoordinate Organophosphorus Compouds. Analysis of Spectra AA'BB'X and AA'MM'XX'.

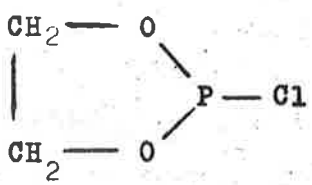
Cher Docteur SHAPIRO,

Nous étudions actuellement par R.M.N. des dérivés phosphorés, et en particulier des molécules du type général suivant :



en vue de préciser la stéréochimie du phosphore tricoordiné. En particulier, le spectre du dérivé chloré (fig.1)

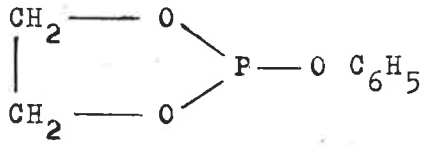
(*)



(*) Nous remercions M. WOLF, de la Faculté des Sciences de Toulouse, pour les échantillons qu'il nous a ainsi aimablement fait parvenir.

est du type AA'BB'X. La non-équivalence des protons provient de la structure tétraédrique du phosphore ; il n'y a pas inversion rapide de la liaison P-Cl. Cette non-équivalence existe aussi dans le dérivé (2) :

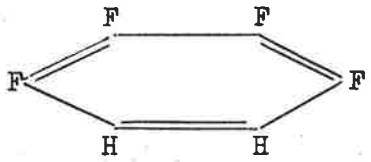
(2)



et se retrouve jusqu'à la température de 250°C. Le temps d'inversion est supérieur à $1,4.10^{-2}$ s, à cette température.

L'analyse du spectre du dérivé chloré peut se faire en le décomposant en deux sous-spectres AA'BB' (fig. 2) dans lesquels seul le δ relatif est différent. Une analyse approximative, basée sur les raies algébriquement calculables, donne avec les notations habituelles : M = 0, N = -2, L = -15, avec J_{P,H_A} = 1,2 c.p.s. et J_{P,H_B} = 10 c.p.s. L'analyse exacte est en cours au laboratoire de calcul de SACLAY (C.E.A.) à l'aide du programme de REILLY et SWALLEN. Ce programme a d'autre part été utilisé dans l'analyse du spectre du dérivé fluoré (3) :

(3)



pour lequel les raies algébriques ont été préalablement déterminées (spectre du type AA'MM'XX'). [1]

D. GAGNAIRE J.B. ROBERT

Laboratoire de Chimie Organique Physique

[1] C. BARBIER, H. FAUCHER et D. GAGNAIRE, Journal de Chimie Physique, à paraître.

FIG 1

86-28

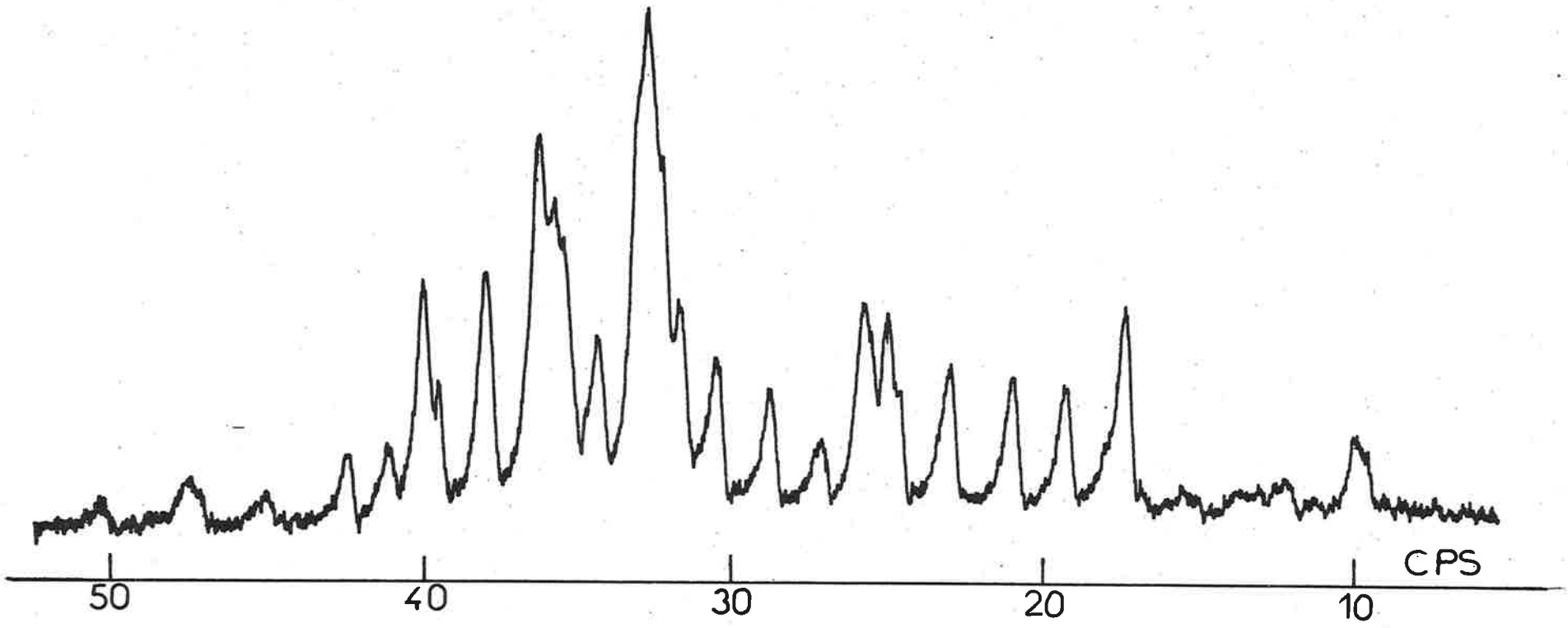
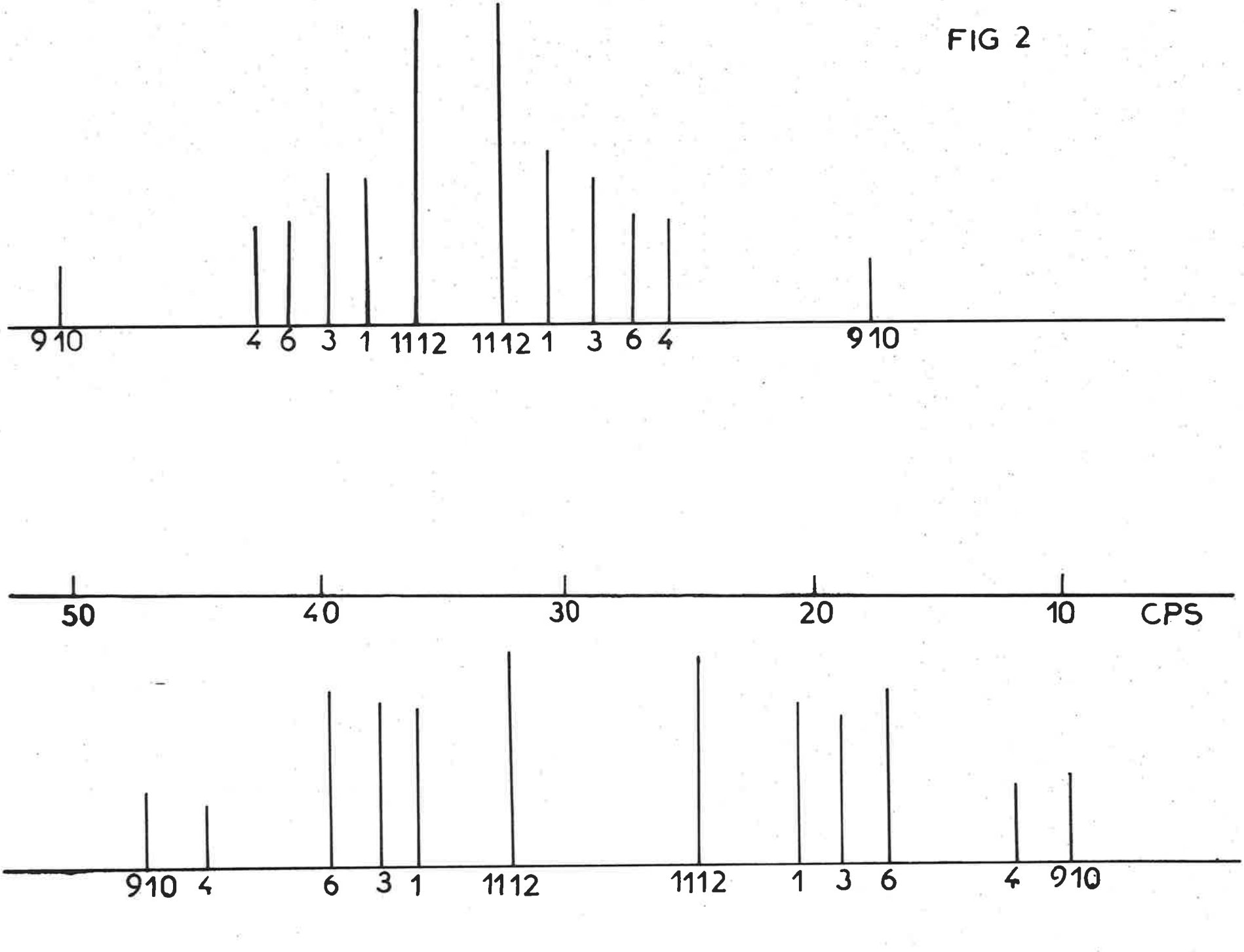


FIG 2


9 10
4 6 3 1 1112 1112 1 3 6 4
9 10
50
40
30
20
10
CPS
9 10 4
6 3 1
1112
1112
1 3 6
4 9 10

86-29

86-30

Prof. Dr. H.-H. Perkampus und Dipl.-Chem. Uwe Krüger
Abteilung für Molekülspektroskopie
im
INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. H. H. INHOFFEN

33 BRAUNSCHWEIG
SCHLEINITZSTRASSE
Tel. Hochschule 4781
Durchwahl Institut 47825
Vorwahl 0531

Herrn
Prof. Dr. Bernard L. Shapiro
Illinois Institute of Technology

60616 Chicago

U S A

13. 10. 1965

Sehr geehrter Herr Professor Shapiro!

Innerhalb unserer NMR-spektroskopischen Untersuchungen über zwischenmolekulare Wechselwirkungen haben wir eine Reihe von EDA-Komplexen untersucht. Dabei zeigte sich, daß bei starken Elektronen-Akzeptoren wie z. B. Tetracyanoäthylen und Chloranil eine Beeinflussung der Protonen-Resonanzsignale der Donator-Komponenten praktisch nicht zu beobachten ist. Als Elektronen-Donatoren haben wir verschiedene Methylbenzole und mehrkernige Aromaten untersucht.

Dagegen zeigte sich, wenn der Elektronen-Akzeptor Wasserstoffatome enthält, daß in Abhängigkeit vom Elektronen-Donator eine Verschiebung der Protonen-Resonanzsignale des Akzeptors zu beobachten ist. Als Elektronen-Akzeptor wurde von uns Parabenzochinon untersucht. Die Ergebnisse dieser Untersuchungen sind in der folgenden Tabelle zusammengestellt. Bezogen auf den τ-Wert des Parabenzochinons in CCl_4 erfolgt in Abhängigkeit vom Donator eine Verschiebung zu höheren Feldstärken. Die Verschiebung folgt der Basizitätsabstufung der Donator-Komponenten.

Die Messungen wurden mit dem HA 100 NMR-Spektrometer der Firma Varian durchgeführt. Die genauen Frequenzen wurden mittels eines Frequenzzählers mehrmals reproduziert. Der Fehler dürfte in der Größenordnung von 0,01 ppm liegen.

	τ (ppm)	$\Delta\tau$
Chinon	3,29	0
" + Benzol	3,35	+0,06
" + Toluol	3,36	+0,07
" + o-Xylol	3,39	+0,10
" + m-Xylol	3,38	+0,09
" + p-Xylol	3,38	+0,09
" + 1,2,3-Trimethylbenzol	3,40	+0,11
" + 1,2,4-Trimethylbenzol	3,38	+0,09
" + Durol	3,42	+0,13
" + Hexamethylbenzol	3,54	+0,25
" + Naphthalin	3,46	+0,17
" + 1-Methylnaphthalin	3,49	+0,20
" + 2-Methylnaphthalin	3,49	+0,20

τ-Werte der Chinonprotonen einiger CT-Komplexe des p-Benzochinons mit Benzol- und Naphthalinderivaten. Lösungsmittel: CCl_4; Chinon-Konzentration: 0,25 molar; Aromat-Konzentration: 0,5 molar; Raumtemperatur.

Mit vorzüglicher Hochachtung

Ihre

H. U. Perkampus

M. Krüger

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

November 4, 1965

Dr. Bernard L. Shapiro
Illinois Institute of Technology
Chicago, 60616
U. S. A.

Dear Barry:

Thanks for the reminder on my contribution. We have plenty of data now on our kinetic work using the Spin-Echo method. I presented this at a recent meeting in Japan but have not completed writing it up yet. We use the closed form expression for two sites devised by Bloom, Reeves and Wells. (J. Chem. Phys. 42 2115 (1965)) and independently by Gutowsky and Allerhand (J. Chem. Phys. 42 1587 (1965)).

We have thoroughly tested the dependence of the exchange contribution to the Carr-Purcell time constant 'r' in the presence of chemical exchange with 90° / 180° pulse interval 't'

The time constant;

$$r = K - \frac{1}{2\tau} \operatorname{Sinh}^{-1} F \qquad (1)$$

where

$$F = \frac{K}{(w^2-K^2)^{1/2}} \operatorname{Sin}[2\tau(w^2-K^2)^{1/2}] \qquad W > K$$

$$F = \frac{K}{(K^2-W^2)^{1/2}} \operatorname{Sinh}[2\tau(K^2-W^2)^{1/2}] \qquad W < K$$

W = half chemical shift in radians
K = mean rate constant for 2 site exchange equal population.

In the limits $K\tau \ll 1$ $W\tau \ll 1$ this simplifies to

$$r = \frac{2}{3} kW^2\tau^2 \qquad (2)$$

The equally populated two site case is a special one as indicated in our theoretical work. Using the expression (1) and (2) and various techniques

to experimentally determine T_2 to greater accuracy we have derived activation parameters and rates for hindered inversion in NN dimethylnitrosamine and NN dimethyl trifluoro-acetamide. The agreement between high resolution studies we have done, the original study of Phillips [Am N.Y. Acad Sci 70 817 (1958)] and our present spin-echo study is very good. The activation energy from the spin-echo results is 22.9 ± 1.6 Kcals mole $^{-1}$ with a normal frequency factor. The results for NN dimethyltrifluoroacetamide give an activation energy 20.6 ± 1.4 Kcals mole^{-1}. This last result does not agree with Rogers Woodbury (J. Phys. Chem. 66 540 1962). It is however a poor case for high resolution work because of the small splitting between inequivalent methyl groups.

I have long since been appalled at the price of deuterated materials. In spite of recent competition the price deuterated solvents is of course being reduced but the specifically deuterated material will always be in demand for special problems. Many of these chemicals are bought and gather dust after use on chemical lab. shelves. In most spectroscopic - particularly NMR - work the research is non-destructive and even in the case of NMR solvents the contamination is merely a case of added solute. I am trying to interest a commercial concern in a rental service. In this way the same compound could be used several times over for different research purposes. A short term rental service could offer chemicals at a fraction of the present listed prices. I wonder if readers of IITNMRN would indicate their interest in such a service by writing to me and even indicating perhaps the types of compounds they might require. This would help to evaluate whether such a service is needed and help with any persuasion. It seems to me that the service ought perhaps to include enriched ^{13}C and ^{15}N compounds. Very often different types of NMR interests such as signs of coupling, double irradiation experiments, kinetic experiments, NMR of enriched nucleus, and relaxation phenomena co-incide in the same molecule. It is very rare that the same laboratory wants to tackle all these varied problems.

We have built a really historic instrument around a magnet generously donated by Shell Development Company. This 'Original' Varian Magnet used by Charlie Reilly for some years was, I believe, the first one Varian marketed back in the early 50's. It has one coil shorted to the yoke but fires very well on three each side and still gives remarkable resolution at 40 Mc. The old 4310 A R.F. unit delivered here in 1956 is now powered by Lambda supplies and we generate a sweep off a Tektronix 545A oscilloscope which we use as part of our spin-echo machine on the same magnet. It turns out that our Tektronix sweep is much more stable and linear than the slow sweep unit produced by Varian through the Stabiliser. It is also a much more expensive sweep but we happened to be using the Scope on the same magnet anyway. The original Varian high resolution probe has been modified by adding higher voltage break down capacitors and will take300 Watt pulses needed for our spin-echo work, then take a high resolution spectrum 5 minutes later. The switch over is very rapid. Perhaps I should describe our sweep circuit in a later letter.

Best Wishes,

Len

Len Reeves.

LR/ds

86-34

GENERAL ELECTRIC COMPANY

WATERFORD, NEW YORK 12188 . . . . . AREA 518—TELEPHONE 237-3330

SILICONE PRODUCTS DEPARTMENT

October 29, 1965

Use of Corrosion Inhibitors in A-60 Cooling System

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Professor Shapiro:

Recently I had the opportunity of seeing a copy of the " I I T NMR Newsletter." I think this is an excellent idea and would like to have this letter considered as my initial contribution.

A number of NMR spectroscopists have had problems with algae, corrosion, etc., with the cooling systems of their magnets. Perhaps our experience using a corrosion inhibitor will be of help to some spectroscopists.

We have an A-60 instrument equipped with the V-6020 heat exchanger. After eight months of operating with only distilled water, it was decided to add a corrosion inhibitor as a precautionary measure.

Fifty-seven grams of potassium chromate (0.5%) were added. Within three weeks after adding the chromate, the pump seal failed. A second pump was installed and the reservoir was filled with 0.5% chromate solution. This pump developed a leaky seal one month after it was installed. There was a slow steady drop in the pressure at the outlet of the heat exchanger. A third pump was installed and the reservoir was filled with plain distilled water. The third pump has been in operation three and one-half months with no detectable leak.

Our conclusion is that the chromate attacks the organic parts of the pump. The composition of the organic material used in the pump is not known.

On many A-60 instruments the recorder bed vibrates and causes an annoying noise. We solved this problem by cementing two pieces of silicone rubber to the under side of the recorder bed and between the metal grill and paper holder.

Sincerely yours,

Carl A. Hirt

C. A. Hirt, Chemist
Analytical Services

CAH:jp

Prof.V.V.Voevodskii
Institute of Chemical
Kinetics and Combustion
Siberian Department of the
USSR Academy of Sciences
Novosibirsk, 90

19 oktober,1965

Prof. B.L.Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616
U.S.A.

Dear Professor Shapiro

A number of iron-group coordination compounds were investigated in our NMR-group this year. Among these are: Co^{+2} pyridinates (1), Fe^{+3} xanthogenates and dialkyldithiocarbamates (2) and pyridine N - oxides adducts of Co^{+2} and Ni^{+2} acetylacetonates. This communication is a summury of the results on acetylacetonates. Our experimental technique and calculations are mainly the same as those of Hope and Ward (3), and W.D.Horrocks, R.C.Taylor and G.N.La Mar (4). We used dilution in a large excess of free ligand in the absolute shifts determination (1). The shifts measured (in ppm. from free ligand) are shown in fig.1. The analysis of the results lead us to the following preliminary conclusions:

1.The shifts observed in Ni^{+2} complexes are dominated by contact interaction whereas in Co^{+2} complexes there is a significant contribution of pseudocontact terms.

2.Unpaired spin density is delocalized through the π - system or N -oxides.

3.The angle between the axis of N -oxide molecule and z axis (fig.2) is about 50-60°. The methyl group of α -methylpyridine N -oxide may have only one orientation because of steric hindrance, while in other N -oxides both orientations ("up" and "down") are possible.

A new fact that we could not explain up to now is the difference of two β -proton shifts in α -methylpyridine - N - oxide adduct.

A more detailed description will be published in "Journ.Struct.Chem." USSR.

Sincerely yours

V.Voevodsky

Molin

V.V.Voevodskii
Yu.N.Molin
E.E.Zayev

R e f e r e n c e s:

1.E.E.Zayev, G.L.Skoobnewskay, Yu.N.Molin,
J.Struct.Chem.,USSR, 6, N4,639 (1965).

2.E.E.Zayew, S.W.Larionow, Yu.N.Molin,
Dokl.Akad.Nauk USSR, (to be published).

3.J.A.Happe and R.L.Ward,
J.Chem.Phys., 39,1211 (1963).

4.W.D.Horrocks, R.C.Taylor and G.N.La Mar,
J.Am.Chem.Soc., 86,3031, (1964).

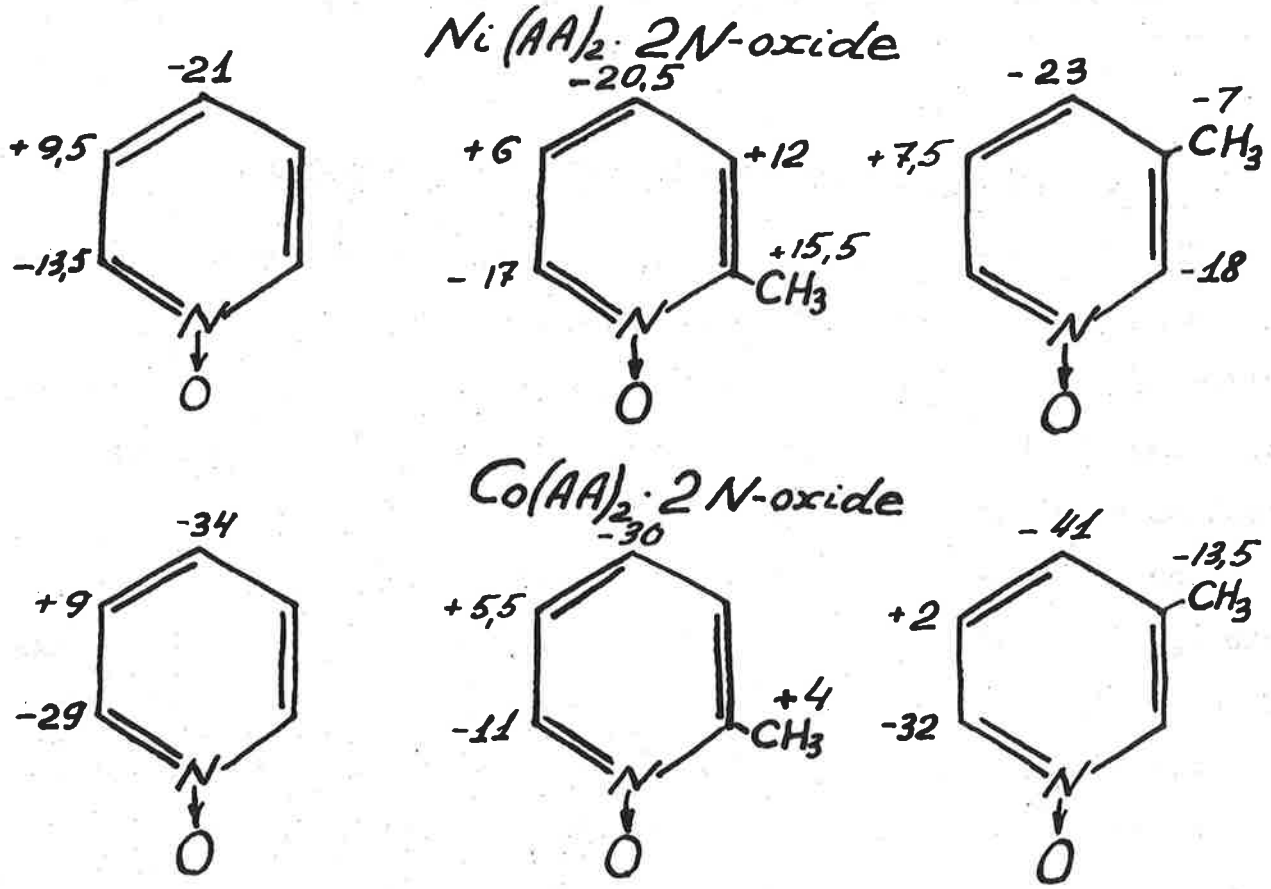

Ni(AA)2·2N-oxide
-21
+9,5
-13,5
-20,5
+6
+12
-17
+15,5
CH3
-23
-7
CH3
+7,5
-18
Co(AA)2·2N-oxide
-34
+9
-29
-30
+5,5
+4
-11
CH3
-41
-13,5
CH3
+2
-32
O
N

Fig. 1

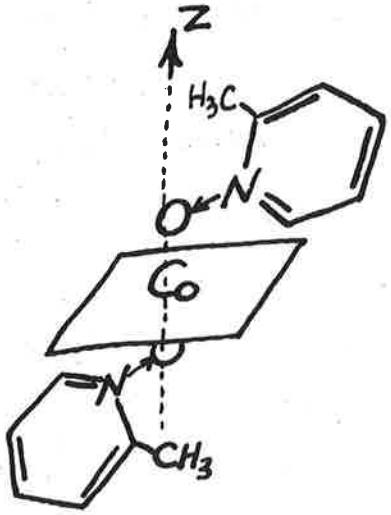

z
H3C
N
O
Co
CH3

Fig. 2

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UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

833 South Wood Street • P.O. Box 6998

FOURTH NUCLEAR MAGNETIC RESONANCE WORKSHOP

The fourth Workshop on High Resolution Proton Magnetic Resonance will take place on this Campus, Wednesday (8:00 A.M.) through Friday (6:00 P.M.) (inclusive) December 15 - 17, 1965. The Workshop will consist of a series of lectures, discussions, problem-solving sessions and laboratory demonstrations.

The lectures will cover a variety of topics such as theory of spin-spin coupling, multiple irradiation techniques, the use of NMR in the study of equilibria and rate processes and to the study of the structure of polymers. Each lecture will be followed by a question and answer period. Additional time will be available during the discussion sessions to examine problems submitted by registrants. The laboratory for the advanced section will consist of the demonstration of the Varian A-56-60 and HA-100 spectrometers, the A-60 Spin Decoupler and the C-1024 Computer of Average Transients. In addition, registrants will be able to see the Varian E-3 electron spin resonance spectrometer which will be on display.

A supplementary program is planned for those scientists without any previous knowledge in the field. The first day is primarily devoted to them and will consist of two lectures and a discussion period designed to provide ample background for them to understand the ensuing lectures. In the laboratory, the beginning section will be introduced to the A-60 spectrometer by a series of demonstrations which will include the determination of a spectrum of an unknown, integration, the microcell and the temperature probe.

The Laboratory will be open to all registrants on the first two evenings, December 15 and 16.

PROGRAM

Wednesday, December 15 - Suggested for Beginners only.

"Elementary Theory of NMR Spectroscopy"	Dr. S. Danyluk Argonne National Laboratories
"Application and Elementary Interpretation"	Dr. Charles L. Bell University of Illinois at the Medical Center

Thursday and Friday, December 16 and 17

"Multiple Irradiation Techniques in Structure Determination"	Dr. Leroy Johnson Varian Associates
"Carbon-13 Magnetic Resonance"	Dr. David M. Grant University of Utah
"Calculation of Spectra"	Dr. Aksel Bothner-By Mellon Institute
"Coupling Constants and Hybridization"	Dr. Joseph Lambert Northwestern University
"Conformational Isomerism and Rate Process Studies by NMR Spectroscopy"	Dr. Fred Kaplan University of Cincinnati
"Elucidation of Polymer Microstructure by High Resolution NMR Spectroscopy"	Dr. Raymond C. Ferguson E.I. du Pont de Nemours & Co.

GENERAL INFORMATION

The registration fee for the Workshop will be $40.00. This sum covers tuition, laboratory fees, Workshop materials and three luncheons.

LOCATION

All sessions will be conducted in the College of Pharmacy Building, 833 South Wood Street, Chicago, Illinois. Lunch will be served each day in the Students Union Building.

REGISTRATION

To ensure a place in the Workshop, please register in advance by completing the enclosed registration form and mailing it together with your check made payable to the UNIVERSITY OF ILLINOIS, to

Dr. Ludwig Bauer
Department of Chemistry, College of Pharmacy
University of Illinois
P. O. Box 6998
Chicago, Illinois 60680

Your registration fee will be refunded promptly if you should find it necessary to cancel your enrollment at any time up to five days before the Workshop begins on December 15, 1965.

HOUSING

A block reservation has been made at the LaSalle Hotel for the nights of December 14, 15, and 16. Rates per person are as follows:

SINGLE	$12.00
DOUBLE	$15.00
TWIN	$18.00

Should you desire accommodation at the LaSalle Hotel, please contact Mr. David Murray, Reservation Office, LaSalle Hotel directly prior to December 1 and refer to the Workshop. Their address is 10 North LaSalle, Chicago, Illinois (telephone: Area code 312 - FR 2-0700).

TRANSPORTATION

The College of Pharmacy is easily reached in about fifteen minutes from the LaSalle Hotel by walking to the Monroe station of the Dearborn Street "L". Then take the Douglas Park "B" train from the Monroe "L" Station to the Polk Street "L" Station (Medical Center). The College is two blocks west of the Polk Street Station.

REGISTRATION FORM

NUCLEAR MAGNETIC RESONANCE WORKSHOP, DECEMBER 15 - 17, 1965

UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER

Name _____
(Last) (First)

Name of Organization you represent _____

Position in Organization _____

Address _____
(Number) (Street)

_____
(City) (State) (Zip Code)

☐ Enclosed is my check for $40.00 for payment of the registration fee. Your check will be acknowledged.

☐ I plan to drive a car. You will receive a parking permit by mail.

I plan to arrive in time for registration (8:00 to 9:00 A.M.)

☐ Wednesday, December 15

☐ Thursday, December 16

Experience in NMR

☐ I can handle simple interpretation of NMR spectra and would like to be placed in the somewhat more advanced section.

☐ I would like to be placed in the beginner's section. I am not at all acquainted with interpretation.

Your check (made out to the UNIVERSITY OF ILLINOIS) and this form should be mailed at your earliest convenience to

Dr. Ludwig Bauer
Department of Chemistry, College of Pharmacy
University of Illinois
P. O. Box 6998
Chicago, Illinois 60680

Additional registration forms are available or this form may be reproduced.

86-42

SHELL DEVELOPMENT COMPANY
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EMERYVILLE, CALIFORNIA

November 8, 1965

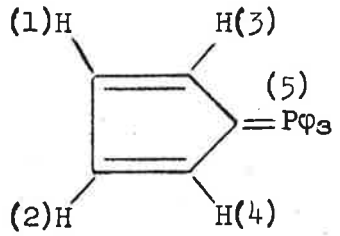
Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry,

Cyclopentadienylidenetriphenylphosphorane

The above is still another horrible example of what happens when contributors to your Newsletter supply their own titles.

In a recent Newsletter (No. 81), Professor Smith of Texas Christian University asked for help with the spectral analysis of the following compound (named in the title):



He sent us a sample to see what we could do with it. We have run the normal and the P decoupled spectra (frequency swept) with our 100 MHz spectrometer (P decoupler at 40.5 MHz) and have made an iterative analysis of both spectra with our computer program, MARIP. The spectra of the 4 ring protons are shown in the enclosed Figures and the parameters are given in the following Table.

	Normal	P Decoupled	"Best"
$\delta_1 = \delta_2$	6.277 ppm from TMS	6.276 ppm from TMS	6.277 ppm from TMS
$\delta_3 = \delta_4$	6.445 ppm from TMS	6.447 ppm from TMS	6.446 ppm from TMS
δ_5	--	-9.8 ppm from TMP*	
J_{12}	+2.75 Hz	+2.85 ± 0.04 Hz	+2.80 ± 0.05 Hz
$J_{13} = J_{24}$	+3.85 Hz	+3.83 ± 0.05 Hz	+3.84 ± 0.05 Hz
$J_{14} = J_{23}$	+1.88 Hz	+1.89 ± 0.06 Hz	+1.89 ± 0.06 Hz
$J_{15} = J_{25}$	±3.6 Hz	--	±3.6 ± 0.1 Hz
$J_{35} = J_{45}$	±5.6 Hz	--	±5.6 ± 0.1 Hz
J_{34}	+2.13 Hz	+2.19 ± 0.07 Hz	+2.16 ± 0.07 Hz

* TMP = Trimethylphosphate (~~+0.9~~ -2.4 ppm from H_3PO_4).

The interproton couplings are all of the same sign and the P-H couplings are also of the same sign. In order to determine the signs of one set relative to the other it would be necessary to appeal to the phosphorus spectrum. The values for the coupling constants suggest that this compound should be classed as an aromatic rather than as a diene.

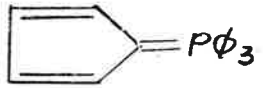
Yours sincerely,

Charlie

C. A. Reilly

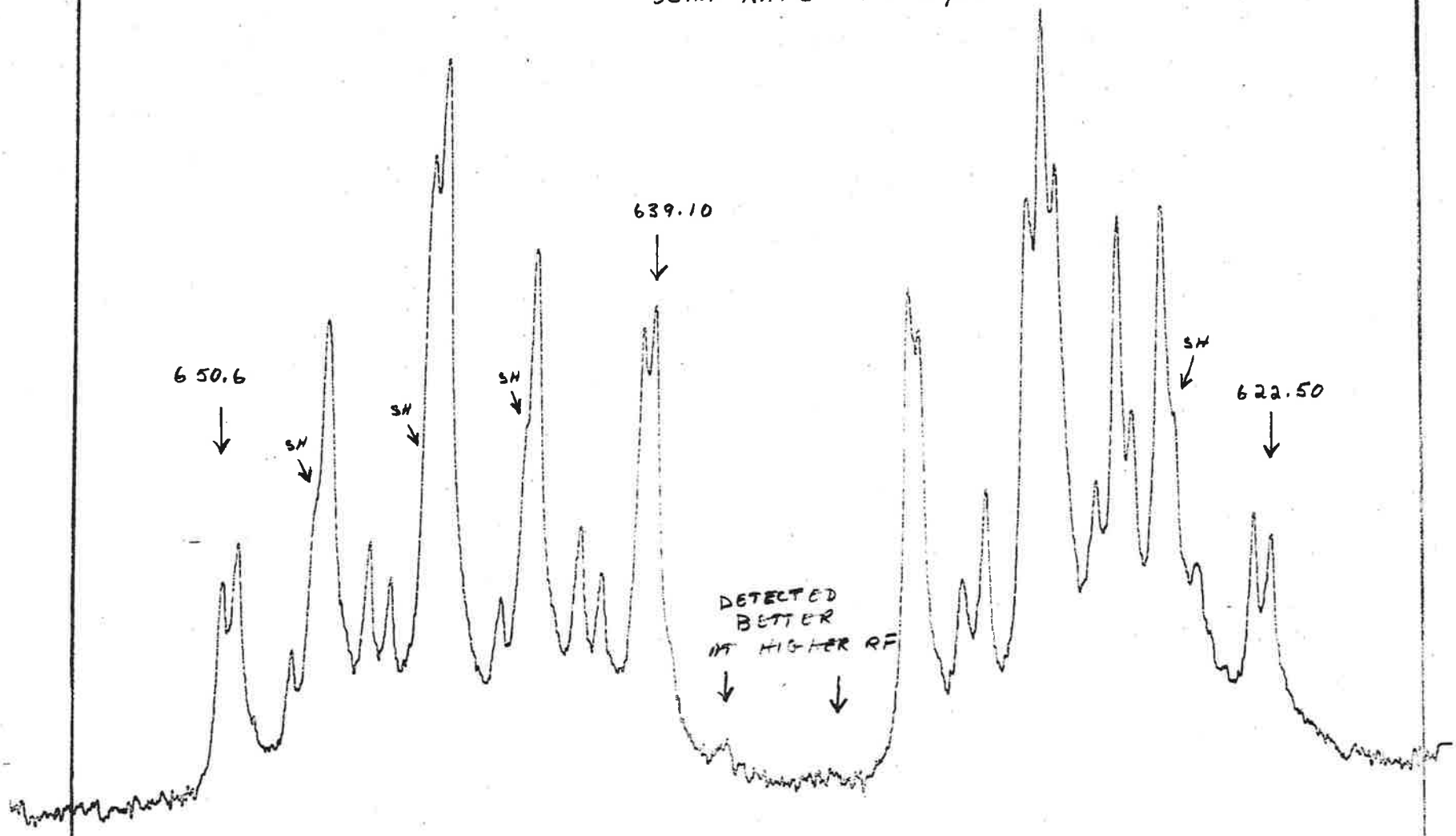
CAR:jel
Encl.

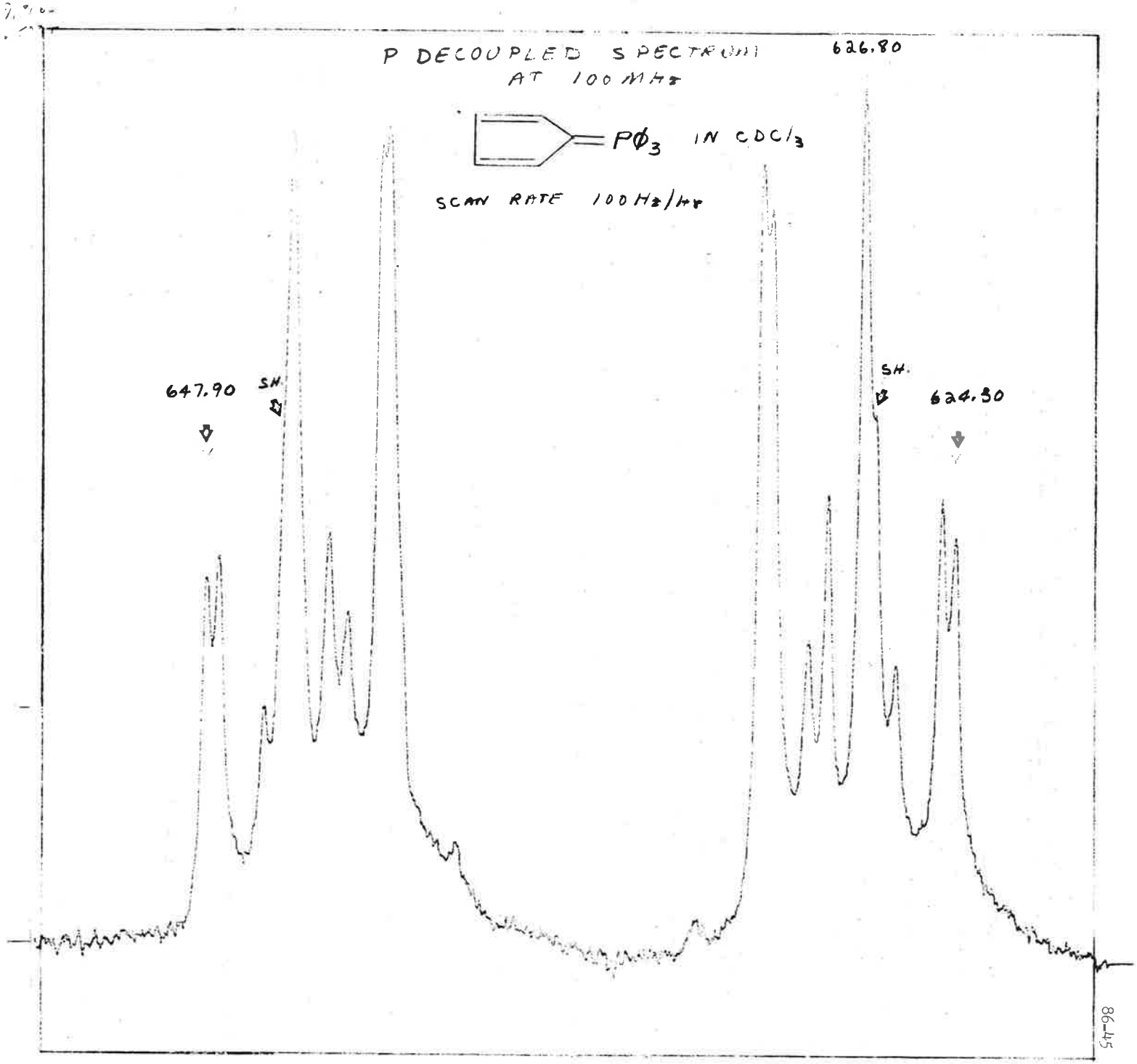
NORMAL SPECTRUM AT 100 MHz



IN $CDCl_3$

SCAN RATE 100 Hz/Hr




P DECOUPLED SPECTRUM
AT 100 MHz
626.80
PØ3 IN CDCl3
SCAN RATE 100 Hz/Hr
647.90
SH.
SH.
624.30
86-45

7th ENC (E X P E R I M E N T A L N M R C O N F E R E N C E)

7th ENC Committee

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Address correspondence to:

A. A Bothner-By
Mellon Institute
4400 Fifth Ave.,
Pittsburgh, Pa. 15213

or

B. L. Shapiro
Dept. of Chemistry
Illinois Institute
of Technology
Chicago, Ill. 60616

The Seventh Experimental NMR Conference will be held Thursday through Saturday, 24-26 February 1966, at Mellon Institute, Pittsburgh, Pennsylvania. The Conference is devoted to advances in instrumentation and experimental design and techniques; it does not compete with Workshops or courses offering an introduction to the field.

Sessions will consist largely of invited papers. A limited number of contributed papers may be accepted, and manuscripts or applications to read a paper should be sent to the appropriate session chairman, or to the conference chairman. Topics of sessions and chairmen are:

Topic	Chairman	Address
Pulse Techniques	A. Allerhand	Dept. of Chemistry Johns Hopkins Univ. Baltimore, Md.
Stability Improvement	E. B. Baker	Physical Research Lab. The Dow Chemical Co. Midland, Michigan
Sensitivity Improvement	T. J. Flautt	The Procter and Gamble Company Miami Valley Labs., Box 39175 Cincinnati, Ohio 45239
Resolution Improvement	S. Glarum	Bell Telephone Labs., Inc. Murray Hill, New Jersey
Variable Environment-Temperature	R. J. Kurland	Chemistry Department Carnegie Institute of Technology Pittsburgh, Pa. 15213
Variable Environment - Gas, Clathrates, etc.	L. C. Snyder	Bell Telephone Labs., Inc. Murray Hill, New Jersey
Superconducting Solenoid Systems	R. Dawson	Physics Department Texas A and M College Station, Texas
Spectral Analysis	R. C. Hirst	Socony-Mobil Oil Co. P.O. Box 1025 Princeton, New Jersey
Instructional Methods	P. Bender	Department of Chemistry University of Wisconsin Madison, Wisconsin
Less Receptive Nuclei	J. B. Stothers	Department of Chemistry University of Western Ontario London, Ontario, Canada

ADDITIONAL INFORMATION AND THE APPLICATION TO ATTEND 7th ENC MAY BE OBTAINED ONLY BY RETURNING THE ENCLOSED POST-CARD (DON'T FORGET TO PUT A STAMP ON THE POST-CARD!) OR BY OTHERWISE INFORMING EITHER THE CHAIRMAN OR THE SEC'Y-TREAS. OF YOUR INTEREST. PLEASE BE SURE TO DO THIS PROMPTLY -- CERTAINLY NO LATER THAN DECEMBER 15 - IF YOU CONTEMPLATE ATTENDING; IT MAY BE NECESSARY TO LIMIT ATTENDANCE BECAUSE OF RESTRICTED PHYSICAL FACILITIES.

The 1966 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held February 21-25, 1966. The program includes three symposia: "NMR Spectra of Polymeric Materials", Tuesday p.m., February 22; "Magneto-optic Rotatory Dispersion", Wednesday a.m., February 23; and "Nuclear Magnetic Double Resonance", Wednesday p.m., February 23. In addition, there will be an ESR symposium on Monday p.m., February 21 and contributed papers on both NMR and ESR topics on Monday evening, February 21. Instrument exhibits will be open 9:00 a.m. - 8:30 p.m. Tuesday, 9:00 a.m. - 6:00 p.m. Wednesday, 12:00 a.m. - 8:30 p.m. Thursday, and 9:00 a.m. - 12:00 a.m. Friday.

Instructions for Speakers and Contributors

I. Lengths of invited and contributed papers will be assigned by Session Chairmen so as to leave ample time for discussion in each session.

II. Abstracts and supplementary material (figures, tables, etc.) in no case exceeding 6 pages should be sent, by February 1, to:

Dr. S. M. Castellano
7th ENC Arrangements
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

They will be printed and distributed to the conferees. Additional material, either too long or too late to have been printed, may be reproduced by the author and arrangements will be made to distribute it at the Conference. A distribution center will also be provided for commercial material of possible interest to the conferees. Authors are urged to submit detailed abstracts and drawings, schematics, spectra, etc., if at all possible. Participants in past conferences have found such a printed record to be quite valuable. In addition, the presentation of undigestible masses of data, complicated schematics, etc. on slides or blackboard is obviated, saving time and easing communication.

III. Abstracts of papers and contributions not accepted for formal presentation will be printed in a Supplementary Program and may be discussed at any appropriate session if time permits. The deadline and length limitation are the same as for other abstracts.

IV. Projectors for 3-1/2 x 4 inch and 2 x 2 inch slides will be available at all sessions. Unusual requirements of any sort should be transmitted in advance to the Session Chairman.

Application of Group Theory to Spectrum Analysis

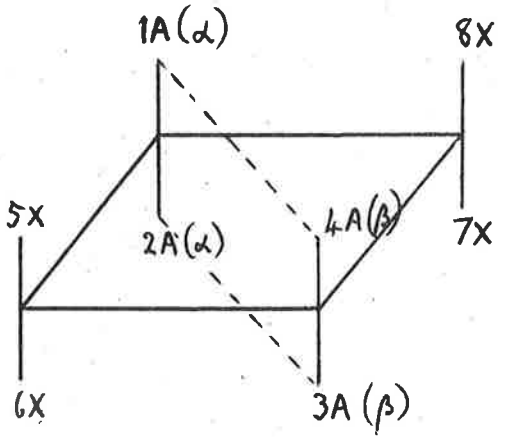
J. Feeney,
(Varian Associates, Molesey Road, Walton-on-Thames).
L.H. Sutcliffe and S.M. Walker,
(Donnan Chemical Laboratories, The University, Liverpool).

In the analysis of simple spin systems it is unnecessary to use group theoretical methods. For such systems possessing a high degree of magnetic equivalence, for example AB_4, the explicit energy levels may be derived simply by the complex particle method. However, group theory is useful for the analysis of multi-spin systems having little magnetic equivalence but much chemical equivalence. An example is the AA'A''A'''XX'X''X''' spin system. By invoking the molecular symmetry, the maximum number of explicit energy levels can be obtained. A different spectrum analysis results for each molecular symmetry.

A convenient shorthand notation has been devised for multi-spin systems and this will now be outlined. The basis functions are denoted by the positions of the β spins only, thus simplifying the tabulation of these functions and enabling matrix elements to be derived by inspection. An example is $\alpha(1)\alpha(2)\beta(3)\beta(4)$ which becomes 34; another is $\alpha(1)\alpha(2)\alpha(3)\alpha(4)$ which is written 0 (zero). For the first example the coupling constant terms in the diagonal element are

$$+ J_{12} - J_{13} - J_{14} - J_{23} - J_{24} + J_{34}$$

The numbering system for the spin positions must follow that used in the construction of the symmetrised spin product functions. Taking a cyclobutane derivative, the A spins are numbered successively as shown



D_{2h}

The real value of this shorthand method becomes apparent when the symmetrised spin functions have to be displayed. For example,

$(\beta\beta\alpha\alpha + \alpha\alpha\beta\beta)(\beta\beta\alpha\alpha + \alpha\alpha\beta\beta)$ becomes $(12 + 34)(56 + 78)$.

86-50

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OUR REF. Res/G.2050(B)/ACC/DJM/JS. YOUR REF. DATE 9th November 1965.

Dr. B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago,
Illinois 60616,
U.S.A.

N. M. R. Spectra of the X_n A A' X'_n Type

Dear Dr. Shapiro,

Because nuclear spin systems of the type $X_6AA'X'_6$ are often encountered and the complete quantum mechanical analysis is extensive, Harris (1) derived general expressions for the calculation of the energies and associated relative intensities of the X spectrum, subject to three limitations.

1. $J_{XX'} = 0$.
2. Only nuclei of spin $\frac{1}{2}$ considered.
3. The chemical shift between the A and X nuclei is large compared with the coupling constants.

We have derived similar equations for the calculation of the A transitions, subject to the same limitations.

Energy (E_A) and Intensity (I_A) Equations:

The total spin (in the field direction) of the X_n and X'_n groups of nuclei given as p and m, take the values $n/2$, $n/2 - 1$, .., $-n/2$.

Case A $m = p$

$$E_A = {}^{m}/_{2} \ (J_{AX} + J_{AX'})$$

$$I_A = \left({}^{n}C_{(\frac{n}{2} + m)}\right)^2$$

Case B $m \neq p$

$$E_A = \pm \tfrac{1}{2} \left(A + J' J_{AA'} + (m + p)(J_{AX} + J_{AX'})\right)$$

$$I_A = (1 - J' J_{AA'}/A) \ {}^{n}C_{(\frac{n}{2} + p)} \ {}^{n}C_{(\frac{n}{2} + m)}$$

contd/-

where $A = ((m - p)^2 (J_{AX} - J_{AX'})^2 + J_{AA'}^2)^{\frac{1}{2}}$ and $\delta = \pm 1$.

The ^1H and ^{31}P spectra of some hypo- and pyro- phosphate compounds have been examined and the calculated N.M.R. parameters are listed in Table 1. Due to the intrinsic broadness and poor signal/noise ratio of the ^{31}P spectra the analyses were performed on the ^1H spectra using the equations of Harris. Confirmation of the analysis is achieved by comparing the ^{31}P spectrum with that calculated from the equations given above. Calculations were made with the aid of an Elliott 803 computer. Due to the large number of transitions encountered in the spectra of the ethyl compounds, only the simpler spectra of the methyl compounds are discussed. Tetramethyl pyrophosphate and tetramethyl hypophosphate are excellent examples of X_n A A' X'_n systems as discussed and illustrated by Harris (1). The ^1H spectra in Figure 1 demonstrate that the pyrophosphate system is of the general type in which $J_{AA'}$ and $(J_{AX} + J_{AX'})$ are of similar magnitude, whereas the spectrum of the hypophosphate is of the 'deceptively simple' type in which $J_{AA'} >> (J_{AX} + J_{AX'})$. From the comparison of the experimental and theoretical ^{31}P spectra made in Figure 2 it can be seen that the A spectrum is also deceptively simple when $J_{AA'} >> (J_{AX} + J_{AX'})$.

In the deceptively simple case it is only possible to estimate the magnetude of $J_{AA'}$ from the line width of the centre component of the triplet of the X spectrum. In the case of tetramethyl hypophosphate the centre component is about $^3/_2$ times as wide as the outer components and $J_{AA'}$ is taken to be of the order of 200 c/s.

Yours sincerely,

A.C.Chapman, D.J.Mowthorpe.
Research Department.

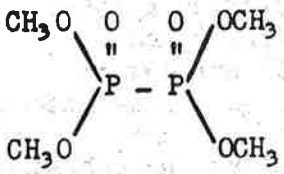
(1) Harris, R.K. Can. J. Chem 42 2275 (1964)

TABLE 1.

Compound	τCH_2	τCH_3	$J_{CH_3-CH_2}$	J_{CH_2-P} (J_{AX})	J_{CH_3-P} (J_{AX})	J_{P-P} ($J_{AA'}$)	($J_{AX'}$, $J_{XX'}$)
Tetraethyl hypophosphate	5.87	8.70	6.8	8.2	0.5	200*	0
Tetramethyl hypophosphate	-	6.15	-	-	11.2	200*	0
Tetraethyl pyrophosphate	5.84	8.64	7.0	≈ 8	≈ 0.7	≈ 14	0
Tetramethyl pyrophosphate	-	6.10	-	-	11.6	14.3	0

* These values estimated (see text).

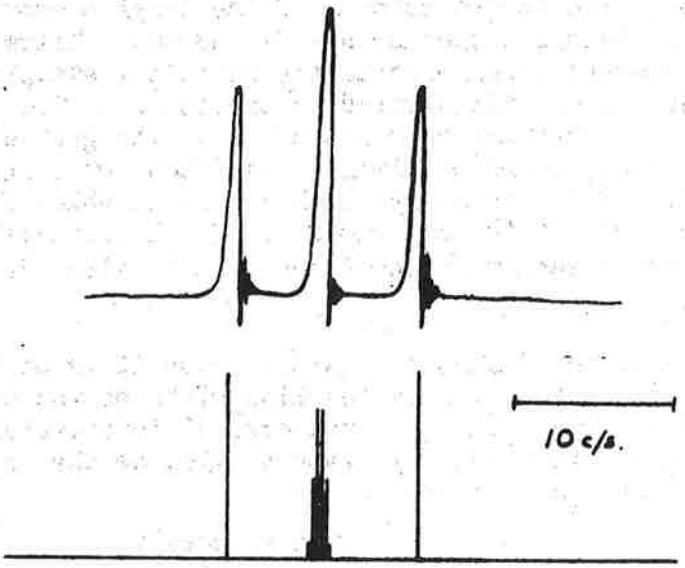
Fig. 1. 60 Mc/s, ^1H SPECTRA

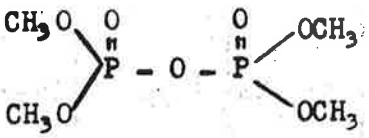


TETRAMETHYL HYPOPHOSPHATE

$J_{AA'}$ = 200 c/s.

J_{AX} = 11.2 c/s.





TETRAMETHYL PYROPHOSPHATE

$J_{AA'}$ = 14.3 c/s.

J_{AX} = 11.6 c/s.

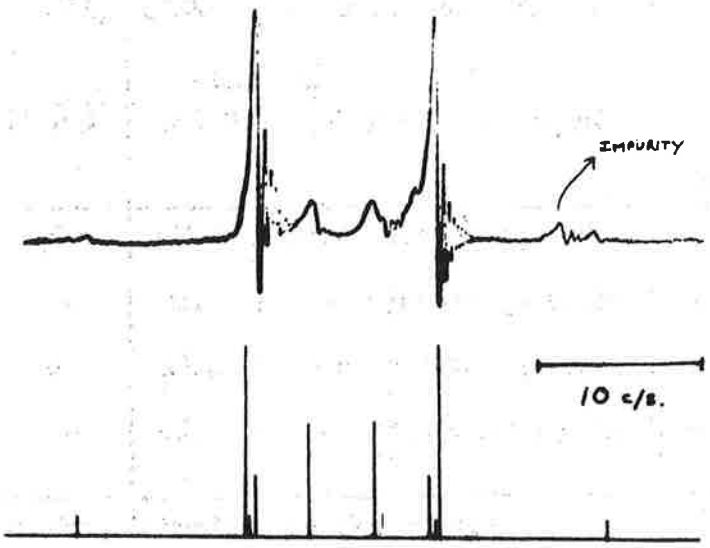
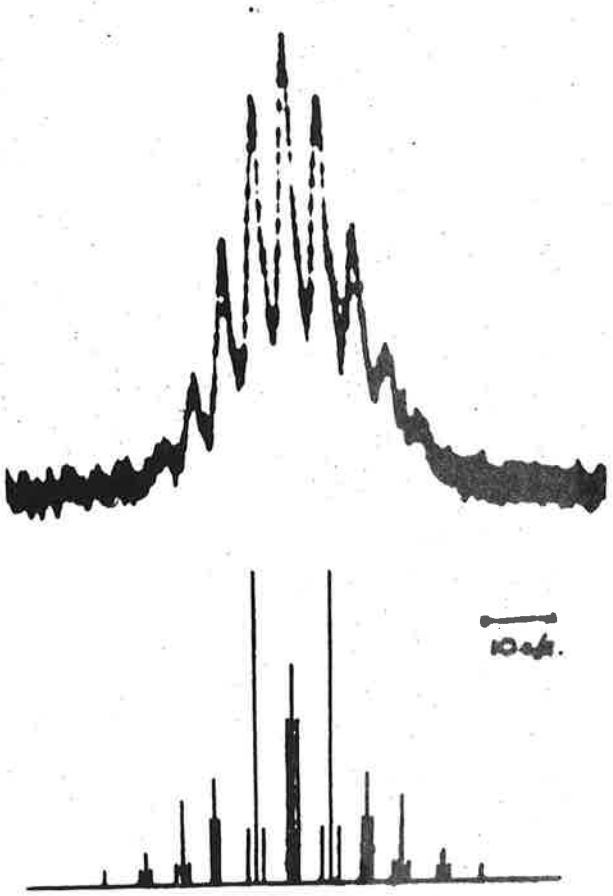
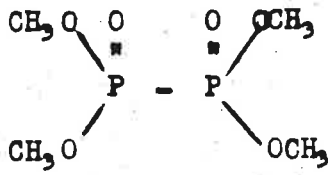


Fig. 2. 25 Mc/s, ^{31}P SPECTRA

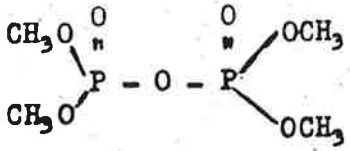




TETRAMETHYL HYPOPHOSPHATE

$J_{AA'}$ = 200 c/s.

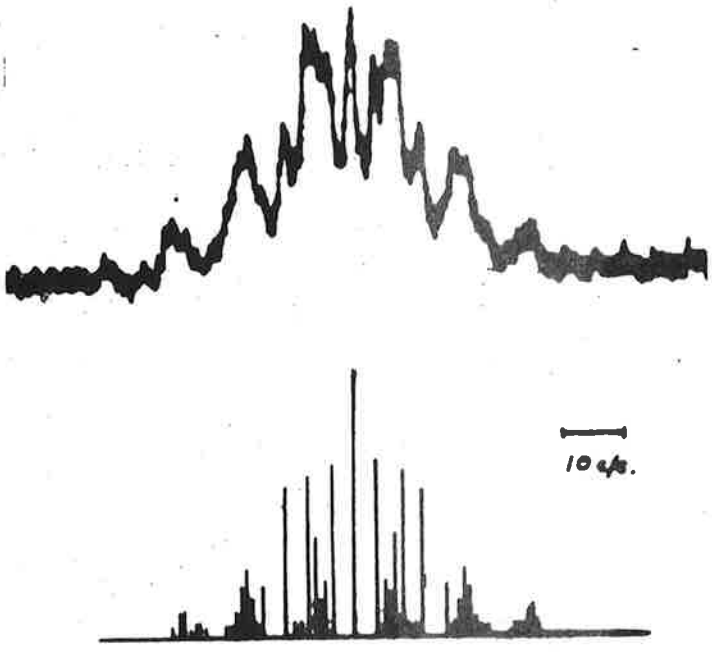
J_{AX} = 11.2 c/s.



TETRAMETHYL PYROPHOSPHATE

$J_{AA'}$ = 14.3 c/s.

J_{AX} = 11.6 c/s.



86-54

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November 10, 1965

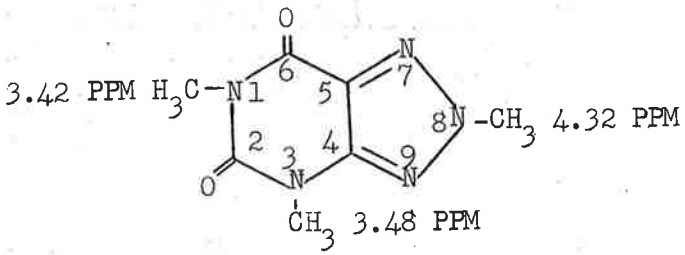
Dr. B. L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Dr. Shapiro:

We would like to report some work on the following:

Assignment of N-Methyl peaks in an 8-aza-purine

Using related aza-purines of known structure and the N-Methyl assignments for caffeine and two caffein homologs[1] we were able to establish the structure of I as shown.



I

In the course of the same work we were able to arrive at relative shielding values for the nitrogens in this type of compound. Based on our related models we found the order to be $N_8 > N_7 \cong N_9 >> N_3 > N_1$

Independent confirmation of our structure was established by comparison of the U.V. spectrum and melting point of our compound with those published by G. Niibel and W. Pfleiderer[2].

1. T. G. Alexander and M. Maienthal
Jour. Pharm. Sci 53, 962, (1964)

2. G. Niibel and W. Pfleiderer
Chem. Ber. 98, 1060, (1965)

Very truly yours,

W. Fulmor Van Conady Jr. G.O. Morton

W. Fulmor, V.L. Canady and G.O. Morton
Organic Chemical Research Section

WF:dk

86-55

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY TEL: (215) LA 5-1000

11 November 1965

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Prof. Shapiro:

The following is the abstract of a paper which has been submitted for publication. Preprints for the readers of IIT NMR Newsletter are available; comments from the readership are invited.

EFFECT OF CHEMICAL EXCHANGE
IN NUCLEAR MAGNETIC RESONANCE

The effect of chemical exchange in NMR spectra is analyzed by separating the Hamiltonian into time-independent and time-dependent parts. Exchange and relaxation may then be treated in a parallel fashion, using the notational simplification of Redfield's relaxation matrix. The result shows the strong parallel that exists between exchange and relaxation. An example of a two-spin system gives the appropriate slow- and fast-exchange limits.

Sincerely yours,

Elaine Surick

Elaine Surick

Jay Martin Anderson

Jay Martin Anderson

86-56

DCBRL: 904-1

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OTTAWA, ONTARIO

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OTTAWA, ONTARIO

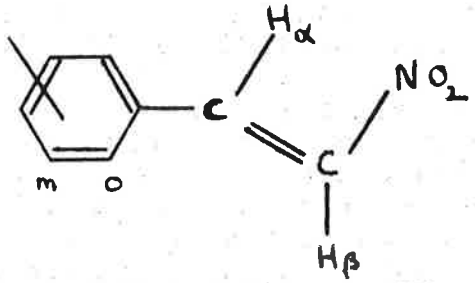
15 November, 1955.

Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois, 60616.

Solvent Effects in the N.M.R. Spectra of β-Nitrostyrenes

Dear Dr. Shapiro:

In previous work we showed (1) that, in benzalmalononitriles, the benzylic proton is solvated by acetone, and that in benzene solution association with two solvent molecules is required to explain the observed shifts. A similar study, by n.m.r., has now been carried out on β-nitrostyrenes, variously substituted in the aromatic ring.



The n.m.r. spectra determined in $CDCl_3$, acetone and C_6D_6 solutions show an AB pattern for the α and β protons. Assignment of the line origins were made on the basis of the spectra of a number of α or β-deuterated β-nitrostyrenes in which the remaining proton gave the expected triplet. In all compounds (substituents NMe_2, OMe, Me, Cl, NO_2 in ortho or para position) the α-β proton coupling constant is about 13.7 cps, indicating a trans relationship between the olefinic protons.

For the para - substituted compounds in chloroform solution only the protons ortho to the substituent show any marked substituent effect on their τ-values, and this in the expected direction. All other proton shifts are relatively substituent independent, resulting in an almost constant downfield shift ($\delta_{\alpha\beta}$ = 0.4 p.p.m.) of the α from the β proton. This $\delta_{\alpha\beta}$ is opposite to what might have been expected from considerations of electron densities and the acetone solvent shifts, and is probably due to the anisotropic effects of the nitro group. The acetone solvent shifts on the α-proton vary from 0.23 to 0.50 p.p.m., and on the β-proton

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Dr.B.L. Shapiro,
Chicago, Illinois.

DCBRL 904-1
15 November, 1965.

from 0.01 to 0.18 as the para substituent changes from NMe_2 to NO_2. These data are at present interpreted by a model in which acetone solvates the β proton, considered to be more electropositive. Unlike the benzalmalononitriles a large acetone solvent shift (0.03 to 0.50 p.p.m.) is also seen on the protons ortho to the benzylic group which, because of the trans configuration of the styrene, are close to the solvating molecule and hence under the influence of the anisotropic effects of the carbonyl group. In the ortho substituted β-nitrostyrenes, the acetone solvent effect is hardly any smaller than in the para-substituted analogues, and there is little evidence for intramolecular complexing of the β-proton.

In benzene solution the para-substituted derivatives show slightly smaller solvent shifts on the α than on the β-proton and these (β) vary from 0.23 to 0.98 p.p.m. for the substituent change NMe_2 to NO_2. These shifts cannot be explained, as was done for benzalmalononitriles, by a two solvent molecule association model, in which one benzene was over the benzylic α carbon, independent of substituent. To explain the large effects on the aromatic protons (0.54 to 1.44 p.p.m. on the proton ortho to the benzylic group) a model with at least two solvent molecules associated with the nitrostyrene may be postulated, but both rings now move with a change of substituent. With this type of model in which the solvent rings are parallel to the solute ring, three benzene molecules appear to be necessary to give the large solvent shifts in p-nitro-β-nitrostyrene. This situation is a little unsatisfying and further calculations are in progress.

Sincerely,
G. Gordon Nicholson

M.A. Weinberger

(1) M.A. Weinberger, R.M. Heggie and H.L. Holmes Can. J. Chem. 43, 2585 (1965)

86-58

ORGANISCH CHEMISCH
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nr.:

onderwerp:

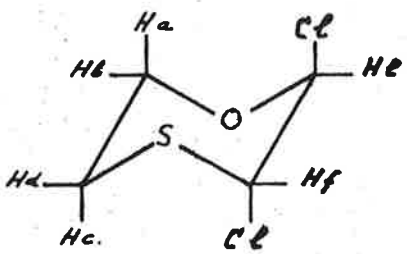
LEIDEN, November, 11 1965..

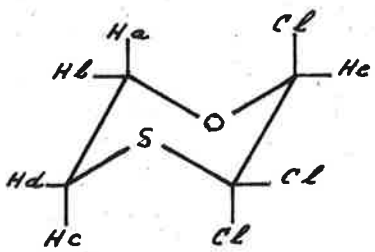
Dr B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
CHICAGO, ILLINOIS 60616
USA

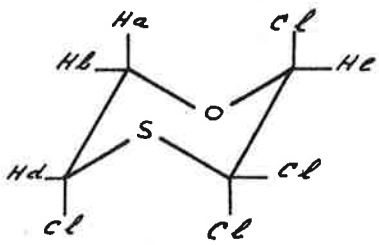
Dear Dr Shapiro,

We feel very sorry that you had to remind us about our contribution to the I.T.T.N.M.R. Newsletter and we hope you will put us back on the mailing list.

As you may know work is being done in our laboratory on the conformational analysis of small ring compounds. In the course of this work one of us, Mr N. de Wolf , prepaired trans 2,3 dichlorothioxane (1,4) [I] , 2,3,3, trichlorothioxane (1,4) [II] and 2,3,3,5 tetrachloro thioxane (1,4) [III] .







The compounds were investigated by n.m.r. In the three cases long range coupling of considerable value is present. The coupling through the sulfuratom is always larger than through the oxygenatom.

LONG RANGE COUPLING CONSTANTS IN SUBSTITUTED THIOXANES

	I	II	III
Jdf	1,4		
Jcf	0,6		
Jbe	0,6	0,4	<0,3
Jae	0,7	0,6	0,6
Jde	1,0	0,6	0,4
Jce	<0,3	<0,2	
Jbf	0,6		
Jaf	<0,3		

ORGANISCH CHEMISCH
LABORATORIUM,
Leiden

Vervolgblad van brief d.d. 11-11-1965, nr.....,
aan Dr B.L. Shapiro

We found these long range couplings to be of great value in the analysis of the (fixed) conformations of these and related compounds. The results of other measurements, in particular of dipole moments in solution, do not give unambiguous evidence with respect to the question of these conformations.

Yours Sincerely,

P. Henniger.

(P.W. Henniger)

Th. Sekuur.

(Th.J. Sekuur)

n de Wolf

(N. de Wolf)

86-60

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Research Department

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616.

Your Ref.

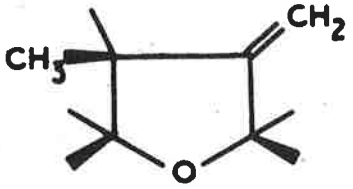
Our Ref.

22nd October, 1965

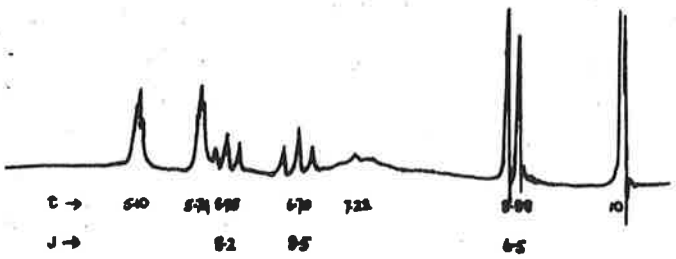
Dear Professor Shapiro,

A SURPRISING COUPLING IN A SUBSTITUTED TETRAHYDROFURAN

A compound which has recently been studied in these laboratories was shown by mass spectroscopy to have the molecular formula $C_6H_{10}O$. Combined evidence from NMR, IR and mass spectra has led us to conclude that the compound is 2,5-dihydro-3-methyl-4-methylenefuran. The exocyclic double bond is characterised by a band at 884 cm^{-1} in the infra-red.



The NMR spectrum (60 Mc/s; A.E.I. Ltd. RS2 spectrometer) does, however, show unexpected features, the only entirely predictable signals being those from the substituent methyl and methylene groups. The unusual features arise in the signals from the 2- and 3-hydrogens. We have assigned the triplets at



τ = 5.97 (J = 8.2 cps) and τ = 6.70 (J = 8.5 cps) to the 2-hydrogens, and the broad multiplet at τ = 7.35 to the 3-hydrogen, but we find it surprising that the cis and trans 2-hydrogens should have such similar coupling constants and such dissimilar chemical shifts. We wonder whether any of your readers have come across similar anomalies in their work which would justify these general assignments, and would also confirm our presumption that the lower signal should be assigned to the cis hydrogen.

We would be grateful if the IITNMR Newsletter could be sent to the first-named author.

Yours sincerely,

J.M. Rowe. A. J. Wilkinson

J.M. Rowe A.J. Wilkinson

"Die Silylierung als Hilfsmittel in der organischen Synthese"
L. Birkofer und A. Ritter
Angew. Chem. 77, 414 (1965)

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T. Sakai, K. Nishimura and Y. Hirose
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"Studies in the Pyrroline Series. Part IV. The Ultraviolet Absorption of the Unconjugated Azomethine Group"
R. Bonnett
J. Chem. Soc. 2313 (1965)

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"Steroids and Walden Inversion. Part LIV. The Grignard Oxygenation of Epicholesteryl Bromide and Partial Synthesis of 3α-Hydroxycholest-6-ene"
C. W. Shoppee, T. F. Holley, and G. P. Newsoroff
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"Ebenaceae Extractives. Part I. Naphthalene Derivatives from Macassar Ebony (Diospyros celebica Bakh)"
A. G. Brown, J. C. Lovie, and R. H. Thomson
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K. Feenan and G. W. A. Fowles
J. Chem. Soc. 2449 (1965)

"Steroids. Part XXIV. The Preparation and Nuclear Magnetic Resonance Spectra of Some 6-Substituted 4-Methylcholest-4-enes"
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J. Chem. Soc. 2476 (1965)

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J. Chem. Soc. 2492 (1965)

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K. Anderton and R. W. Rickards
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"Some Reactions of 2-2'-Pyrrolyl-1-pyrrolines"
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J. Chem. Soc. 2614 (1965)

"Aromatic Polyfluoro-compounds. Part XXIII. Polyfluoroazo-, -azoxy-, and -hydrazo-benzenes"
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"Addition Reactions of Heterocyclic Compounds. Part XXIII. The Formation of Kashimoto's Compound from 1,2,3,4-tetra-methoxycarbonylquinolizinium Perchlorate and Related Reactions"
R. M. Acheson, D. M. Goodall, and D. A. Robinson
J. Chem. Soc. 2633 (1965)

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R. M. Acheson
J. Chem. Soc. 2630 (1965)

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E. V. Aroskar, J. Burdon, J. G. Campbell, and R. Stephens
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J. E. Lloyd and K. Wade
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B. J. Calvert and J. D. Hobson
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A. J. Bellamy and R. D. Guthrie
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B. Milligan and J. M. Swan
J. Chem. Soc. 2901 (1965)

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"Studies in the Steroid Group. Part LXXVI. The Methylation of Enol Acetates and Bromo-ketones. Nuclear Magnetic Resonance Spectra of 11-Keto-steroids"
E. R. H. Jones and D. A. Wilson
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"Compounds of Silicon. Part IV. Reactions of Hexamethyldisilazyl-lithium with Chlorosilanes"
E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith
J. Chem. Soc. 2997 (1965)

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A. J. Birch and G. S. R. Subba Rao
J. Chem. Soc. 3007 (1965)

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C. W. Bird
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P. S. Steyn, W. J.Conradie, C. F. Garbers, and M. J. De Vries
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R. M. Acheson, M. W. Foxton, and G. R. Miller
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"Structure of 3-Alkyl-4-arylazoisoxazol-5-ones and Related Compounds"
L. A. Summers, P. F. H. Freeman, and D. J. Shields
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"Aspects of Stereochemistry. Part XIX. Isopropylidene Derivatives of Some Polyhydric Alcohols. Observations on the Hydrolytic Behaviour and Migration of Cyclic Ketals"
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J. Chem. Soc. 3382 (1965)

"Aspects of Sterochemistry. Part XXI. Absolute Configuration of Benzylidene Derivatives of Some Acyclic Polyhydric Alcohols"
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J. Chem. Soc. 3394 (1965)

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D. E. Applequist, R. Searle, M.-D. Steinhardt, E. C. Friedrich, and R. L. Litle
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"A one-step Synthesis of 10-Oxo-1,5-diazabicyclo[4,4,0]-dec-5-ene"
Johannes Dale and Raymond Coulon
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J. Chem. Soc. 3488 (1965)

"Fluorocyclohexanes. Part IX. Lithium Aluminium Hydride Reduction of 1H,2H,3H-Heptafluorocyclohexene, a Route 1,2,3-Trifluorobenzene"
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J. Chem. Soc. 3502 (1965)

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I. A. D'yakonov and R. R. Kostikov
J. Gen. Chem. USSR (Eng. Transl.) 34, 1735 (1964)

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S. L. Vail, R. H. Barker, and P. G. Mennitt
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"1-Phenylcyclopenten-3-one Derivatives and Their Conversion into Bis-π-(1-methyl-3-phenylcyclopentadienyl)titanium Dichlorides"
R. F. Heck
J. Org. Chem. 30, 2205 (1965)

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J. Gen. Chem. USSR (Eng. Transl.) 34, 1884 (1964)

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