

Primer

Illinois
Institute of
Technology
N - M - R
Newsletter

No. 89
FEBRUARY, 1966

Melera, Sternhell	1
Significant Long-Range Coupling in Non-W Configuration - A Negative Result	
Douglas	2
V-2100B Voltage Monitor and Interlock Modification and Mars Recorder Pen Modification	
McCall, Anderson, J. E., Slichter, W. P., Douglass, Jones, G. P.	8
Spin-Echo Studies of Self-Diffusion in Solutions of Non-Electrolytes; NMR Studies of the Pressure-Dependence of Self-Diffusion in Four Organic Solids; Nuclear Magnetic Relaxation of n-Alkanes in the Rotating Frame	
Maire	11
Nuclear Magnetic Resonance Study of p-Fluorophenylchlorostannanes: A_2B_2X Spectra	
van Gorkom	14
Diastereo-Isomeric Pairs of 2 Tetrahydropyran Derivatives	
Mark	16
Analysis of Steric Conditions by NMR; The Environment Around Phosphorus in Some of Its Esters	
Williamson	22
Substituent Effects on Long-Range J_{HF} in a Bicycloheptene System	
Connor	24
Pulse Programmer	
Lansbury	25
Long Range Coupling in Conformational Analysis of 7,12-Dihydropleiadenes	
Poranski, Moniz	28
J_{vic} in Substituted Propanes	
Durr, Eistert	29
NMR Study of Keto-enol Equilibria	
Bartle, Jones, E. W. Pearson	32
"Interpretation of High-Resolution NMR Spectra" - A Short Course	
Elie, Martin, R. J. L.	34
Effect of t-Butyl Substituent on Proton and Fluorine Resonance in Substituted Cyclohexanes	
Gil	37
On $^2J_{HH}$, $^3J_{HH}$, $^4J_{HH}$ and Inductive and Hyperconjugative Effects	
Bladon, Brown	40
Difluoroboron and Tetrafluorophosphorus Chelates	
Colson, Kanski	42
HA-100 Modification for a Mouse	
Schraml	44
Accidentally Simplified Spectra of Vinylsilanes	
Klein, Phelps	45
Proton Stabilization for P^{31} Resonance. AGC to Reduce AM Accompanying Phase Modulation	
Strauss	48
Extended Sweep Range of Perkin-Elmer Model R-10	
Burke	50
The Shielding Effect of the Cyclopropane Ring	

Hall, G. E., Roberts, D. G. Methyl Oleate Monohydroperoxide	53
Serge, Gatti Ring Inversion in Tetrahydropyrane	56
Cohen Spin Decoupling with the Varian A-60 System	58
Samek Conformations of Two 7-Membered Epoxide Rings in Steroids	60

Deadline Dates: No. 90 - 18 March 1966 No. 91 - 18 April 1966
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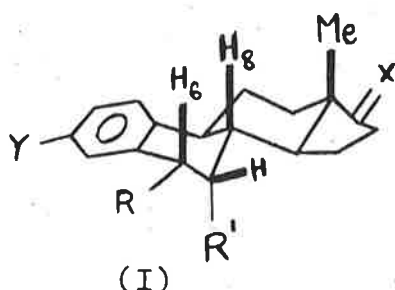
Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois, U.S.A.

11th January, 1966

SIGNIFICANT LONG-RANGE COUPLING IN NON-W CONFIGURATION
A NEGATIVE RESULT

Dear Barry,

The report by Osawa and Neeman¹ that $J_{6,8}$ in I ($R = R' = Cl$) was 1.8 c/s has been considered^{2,3,4,5} as a major anomaly⁶. We have exam-



ined, among others, the closely related compounds⁷ (I, $R = OAc$, $R' = Br$; I, $R = R' = OAc$ and I, $R = OAc$, $R' = \beta OAc$) by double resonance at 100 Mc/s and found no evidence for the presence of this type of interaction.

Thus, either this coupling is abnormally substitution dependent or the earlier results need reexamining. We do however find significant (approx. 1.5c/s) coupling between H_6 and H_9 in some compounds in this series which we consider to be of a "homobenzylic" type, related to analogous interactions between vicinal methyl groups^{8,9,10}.

Yours sincerely,

A. Melera

A. MELERA - Varian A.G., Zurich.

S. Sternhell

S. STERNHELL - University of Sydney.

1. Osawa and Neeman, JACS, 85, 2856(1963). 2. Sternhell, Rev. Pure. Appl. Chem., 14, 15 (1964). 3. Barfield, J.Chem.Phys., 41, 3825(1964).
4. Grant, Ann.Revs.Phys.Chem., 15, 489(1964). 5. Bhacca and Williams "Applications of NMR in organic chemistry", Holden-Day, p.121. 6. Small coupling across four bonds in non-W configuration is non unknown c.f. reference 2) and Ramey and Messick, Tetrahedron letters, 4423(1965).
- Laszlo's cases (Laszlo and Musher, Bull.Soc.Chim.Fr.(1964)2558) have a carbonyl group. 7. Wintersteiner, Moore and Cohen, J.Org.Chem., 29, 1325 (1964). 8. Gronowitz and Gestblom, Arkiv.Kemi, 18, 513(1962) and previous papers in this series. 9. Takahashi, Kanda and Matsuki, Bull. Chem. Soc. Japan., 38, 1799(1965) 10. Cohen and McLaughlan, Mol. Physics, 9, 49(1965)

**THE DOW CHEMICAL COMPANY**

MIDLAND, MICHIGAN

January 21, 1966

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

Title: V-2100B Voltage Monitor and Interlock Modification
and Mars Recorder Pen Modification

Dear Dr. Shapiro:

Enclosed are some diagrams (Figures I through III) showing how I modified our V-2100B magnet power supply so that any interlock condition or power interruption which causes magnet shutdown results in the magnet staying off until someone manually resets it. The V-3520 heat exchanger pump is also turned off so cool water does not continue to flow through the magnet while it is conducting no current. Both this unit and then the V-2100B must be manually restarted after a shutdown.

The only difficult item is that a magnet current overload must be reset either with a separate 115 VAC source, or the heat exchanger restart has to be held down while reset is accomplished, as the pump will not continue to run, after this modification, with the high voltage switch off.

The safety features provided by the original interlock circuit are not interfered with in any way by this modification.

Figure IV shows a voltmeter circuit we installed for monitoring of the 220 VAC 3 ϕ input and the output of the autotransformer. Three readings at each source give all three possible line-to-line voltages.

Since Mars recorder pens write like paintbrushes, I have had built a modification which uses a K. and E. lettering pen point and the original ink reservoir of the Mars pen. The feed tube also comes from the Mars pen, merely having been pulled up and cut off to a desirable length. The design is shown in Figure V. C. B. Pratt and H. D. Woodcock of the Chemical Physics Research Laboratory of Dow are gratefully thanked for their assistance in designing and constructing this modification.

Please credit this contribution to the subscription of Dr. J. P. Heesch, same address as mine.

Yours truly,

A. W. Douglas, Chemical Physics Research Laboratory, 1603 Bldg.

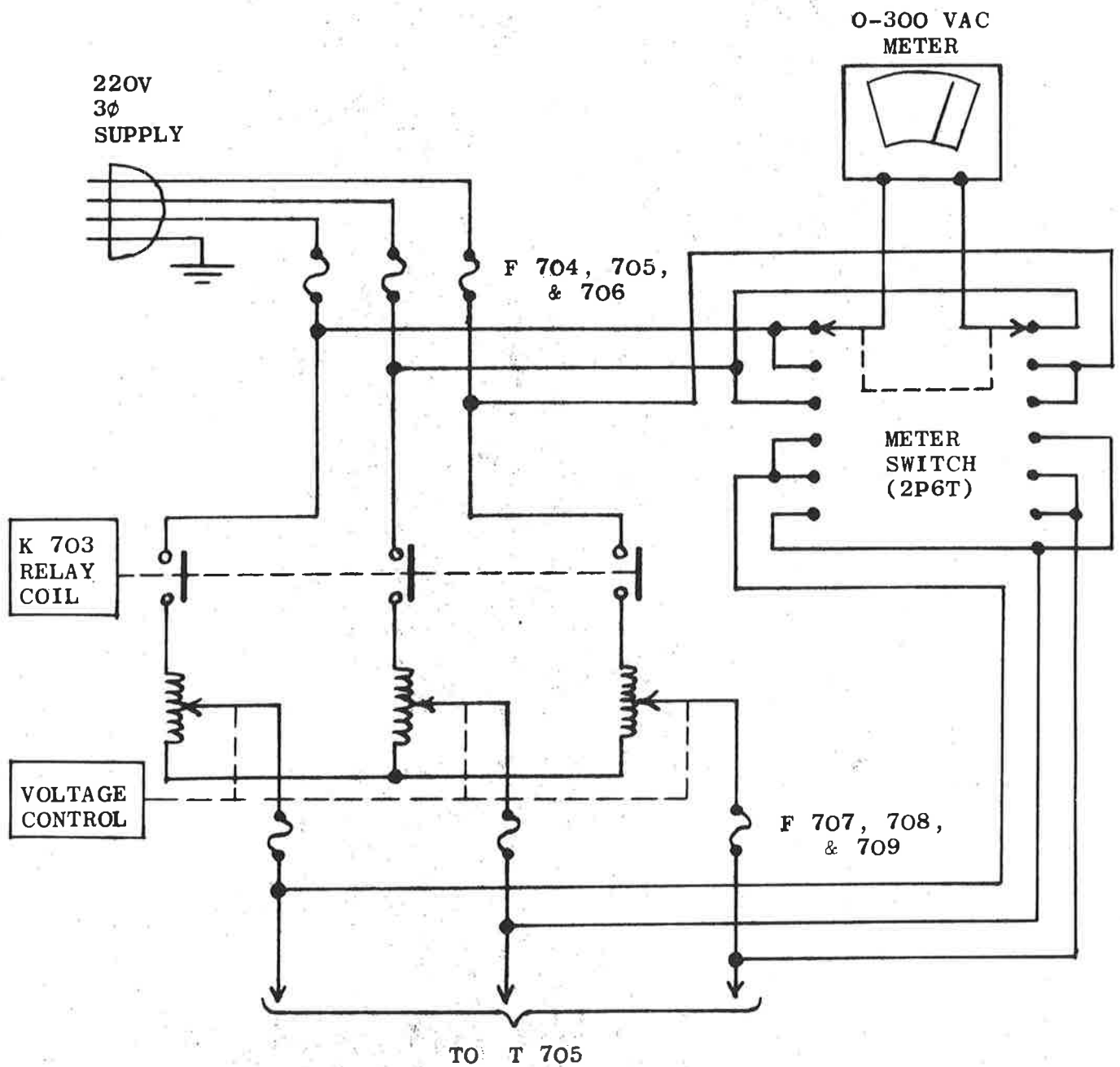
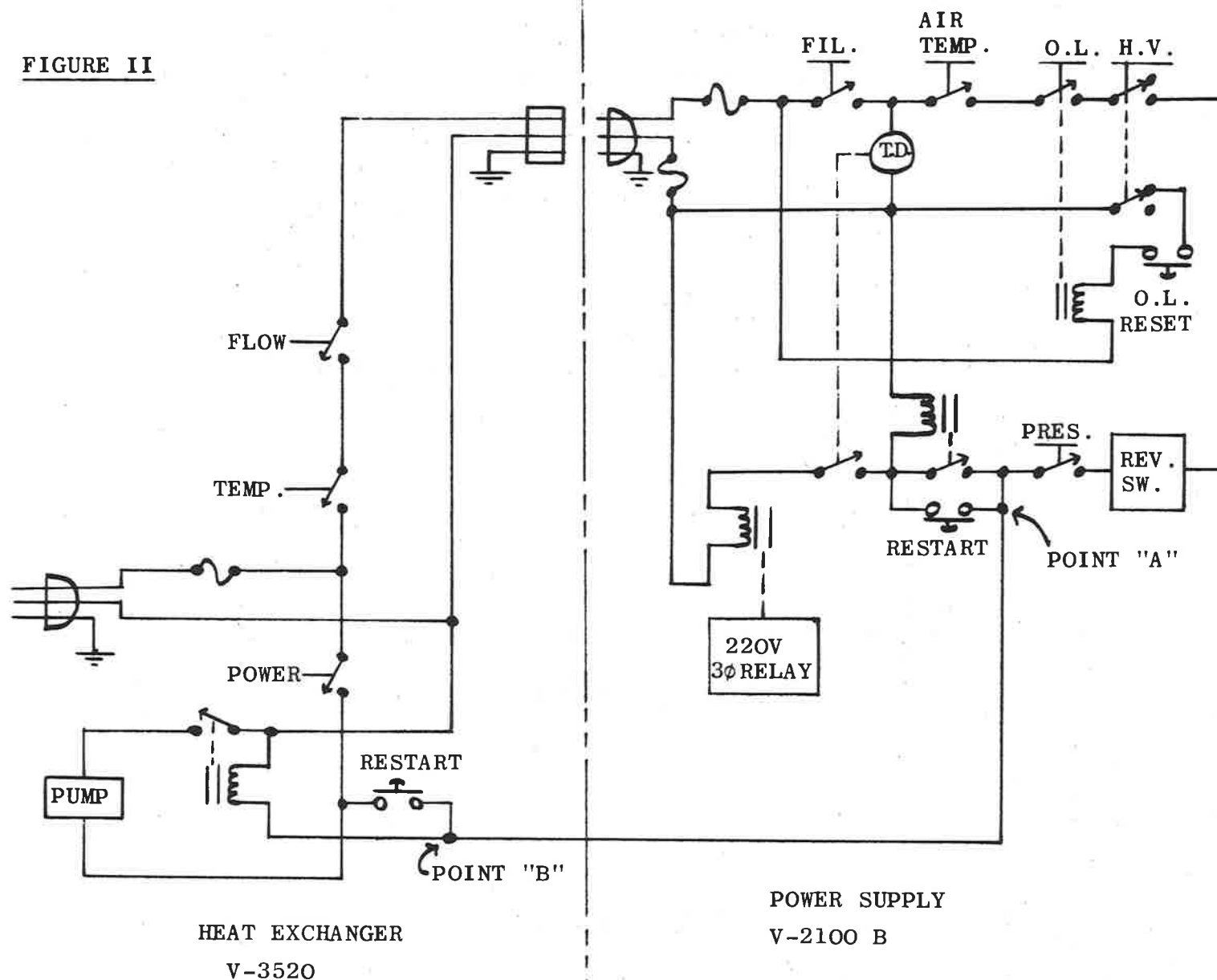


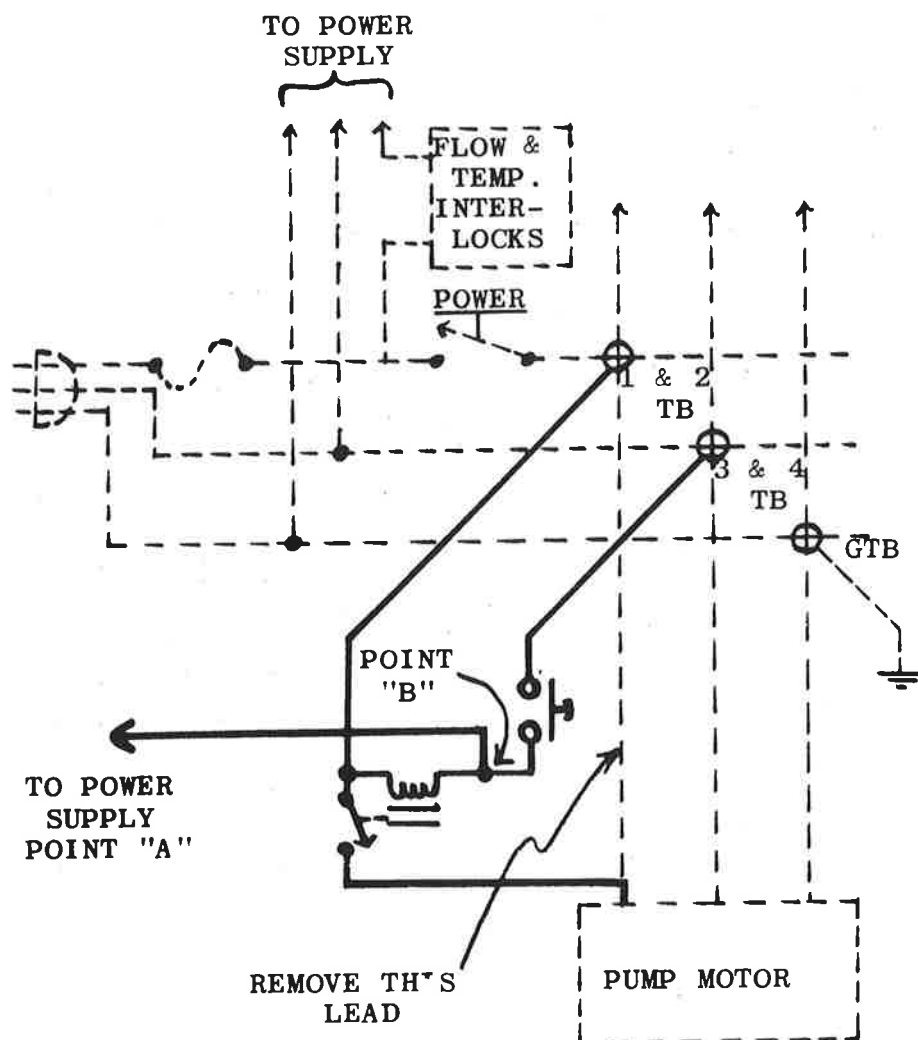
FIGURE I
3 PHASE METER CIRCUIT
FOR V-2100 B POWER SUPPLY

FIGURE II



SCHEMATIC OF COMPLETE INTERLOCK CIRCUIT AFTER MODIFICATION
(ONLY ESSENTIAL COMPONENTS SHOWN)

FIGURE III

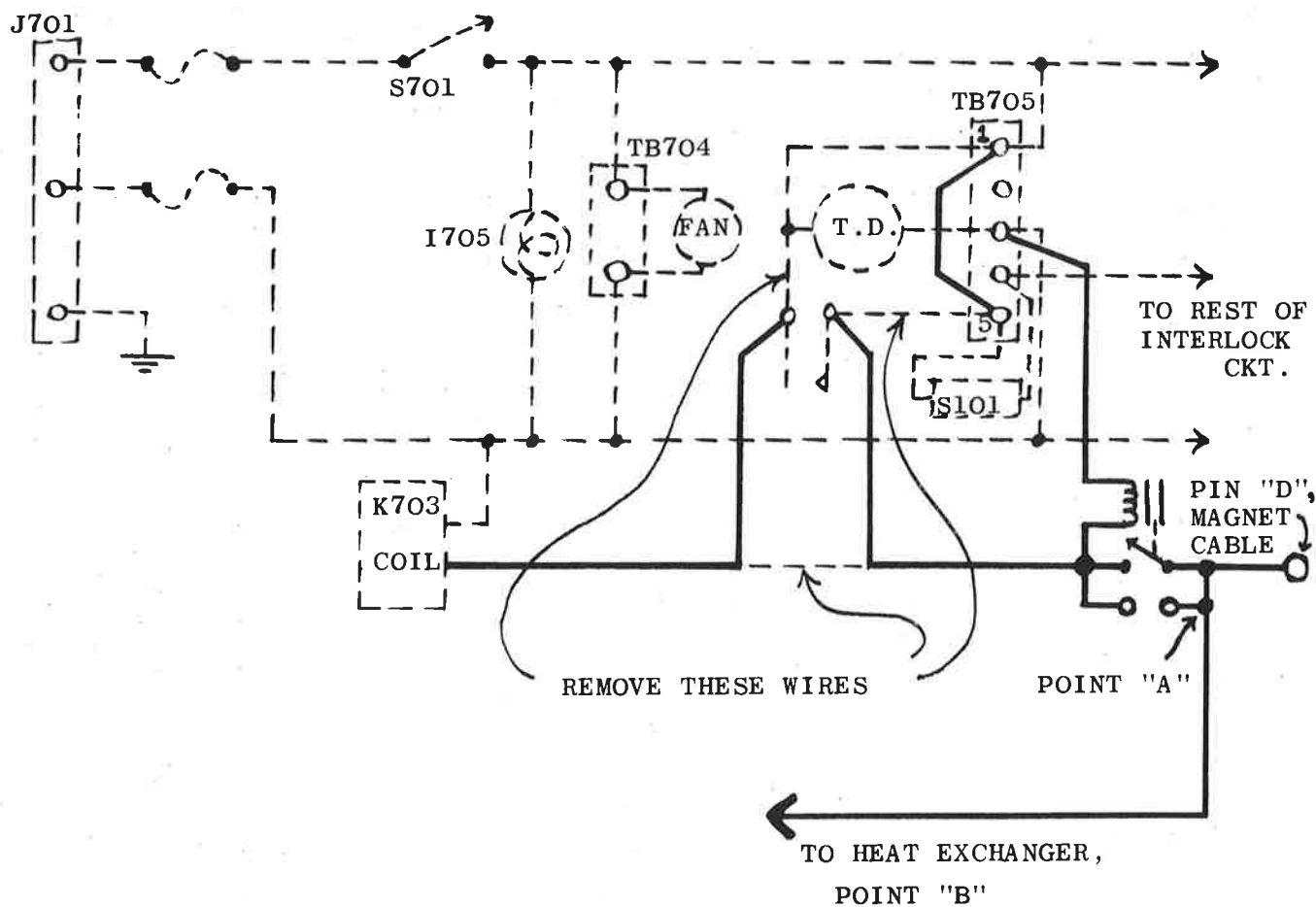


NUMBERS, e.g., 1 and 2 TB, REFER TO POSITIONS ON THE LEFTMOST TERMINAL BOARD (FACING THE EXCHANGER) WITH #1 AT BOTTOM.

DETAIL OF CHANGES IN HEAT EXCHANGER
(V-3520)

ADDITIONS MADE IN MODIFICATION SHOWN IN HEAVY LINES

FIGURE IV

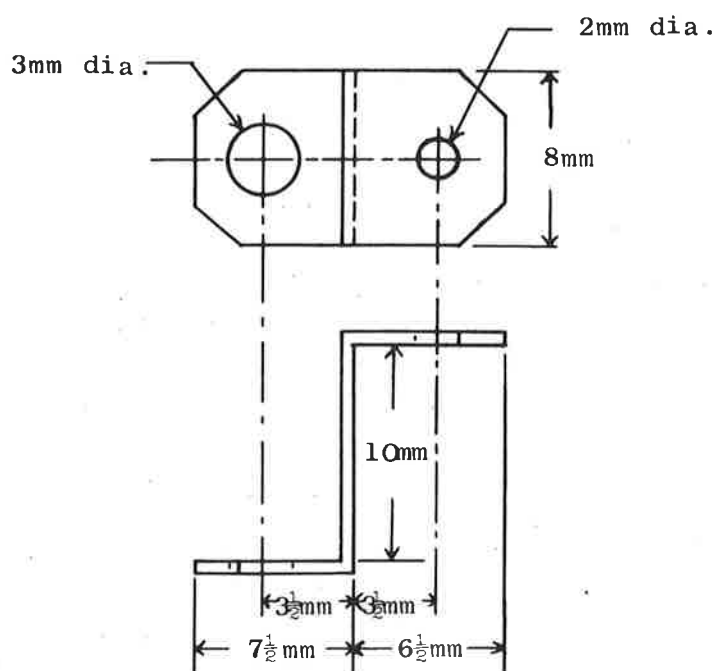


DETAIL

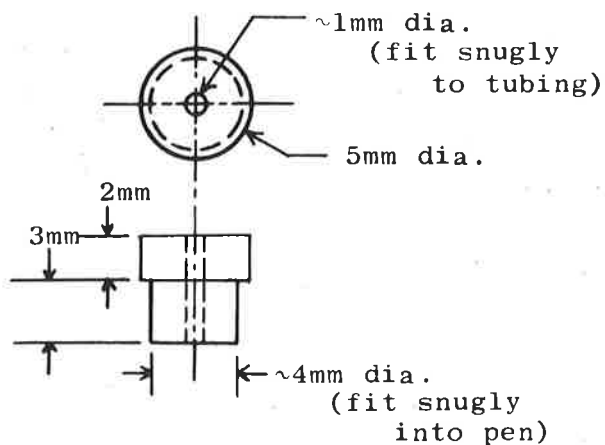
POWER SUPPLY MODIFICATIONS
(V-2100B)

ADDITIONS MADE IN MODIFICATION SHOWN IN HEAVY LINES

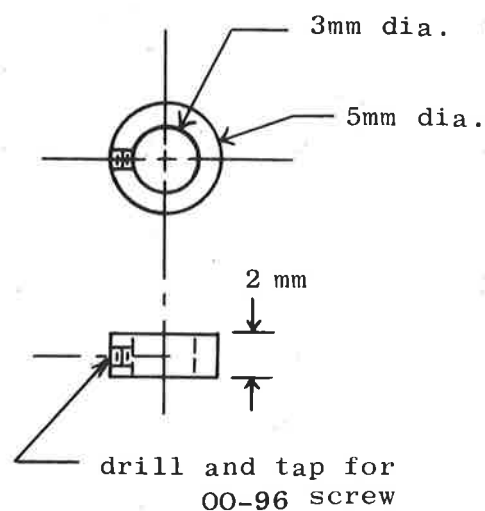
FIGURE V
MARS RECORDER PEN MODIFICATION



PIECE #1
(OF BRASS SHEET $\sim \frac{1}{2}$ mm. THICK)

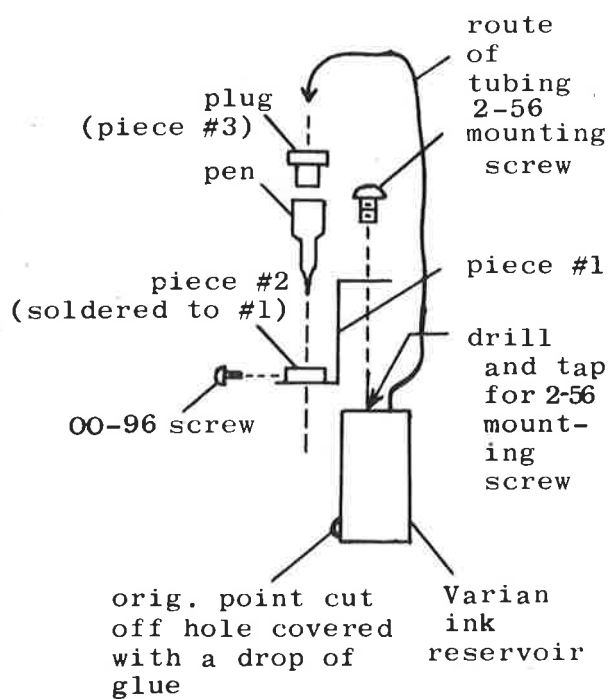


PIECE #3
(OF DUPONT TEFLON[®])



PIECE #2
(OF BRASS)

ASSEMBLY (SCHEMATIC)



BELL TELEPHONE LABORATORIES

INCORPORATED

MURRAY HILL, NEW JERSEY 07971

TELEPHONE

AREA CODE 201

582-3000

January 25, 1966

PROFESSOR BERNARD L. SHAPIRO
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Sorry you had to prompt us. I enclose two recent abstracts. Preprints are available from Dean Douglass or Bill Slichter. My own work has been concerned with further use of spin-echo methods to study self-diffusion. Present studies are in binary solutions of non-electrolytes. Using deuterated compounds we obtain self-diffusion coefficients for both species and get an estimate of the isotope effect on diffusion. The systems: benzene-cyclohexane, acetone-water, acetone-benzene, and acetone-chloroform. Similar measurements on aqueous solutions of tetra-alkyl ammonium salts have been completed.

Sincerely yours,



D. W. McCALL

MH-1513-DWM-MC

NMR STUDIES OF THE PRESSURE-DEPENDENCE
OF SELF-DIFFUSION IN FOUR ORGANIC SOLIDS

by

J. E. Anderson^{*} and W. P. Slichter
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey 07971

ABSTRACT

NMR pulse techniques have been used to study the influence of hydrostatic pressure on self-diffusion in four organic solids composed of nearly spherical molecules: cyclohexane, 2,2-dichloropropane, t-butyl chloride, and t-butyl bromide. The self diffusion was studied from the pressure and temperature dependence of T_2 , the spin-spin relaxation time, at pressures between 1 and 680 atm, and at temperatures within 10-50 degrees of the melting point. The measured activation volumes were 8-15 percent of the molar volumes. Comparable ratios have been previously observed for rotational motion in similar solids. The activation enthalpies for self-diffusion were 5-6 kcal/mole, somewhat exceeding the values for rotational motion. Comparisons are made with the latent volumes and enthalpies of fusion.

* Present address: Scientific Laboratory, Ford Motor Company,
Dearborn, Michigan

NUCLEAR MAGNETIC RELAXATION OF n-ALKANES IN THE
ROTATING FRAME

by

D. C. Douglass and G. P. Jones*
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

ABSTRACT

The rotating frame nuclear magnetic relaxation time $T_{1\rho}$ has been measured for ten normal alkanes ranging from C_4H_{10} to $C_{94}H_{190}$. Data were obtained within the range $-200^\circ C$ to $+70^\circ C$ for $C_{94}H_{190}$, $C_{40}H_{82}$ and C_6H_{14} . The high-temperature region is characterized by a process of high activation energy ascribed to chain rotation while the low temperature region exhibits a $T_{1\rho}$ minimum arising from coupling of the entire spin system to the methyl group rotation via spin diffusion. This information and the analogous T_1 data yield an activation energy of 2.6 Kcal/mole for the methyl group rotation. The remaining compounds were examined in the vicinity of the $T_{1\rho}$ minimum at $-190^\circ C$ and relaxation times characterizing the intrinsic methyl relaxation and spin diffusion process have been extracted from the data for three rf field strengths. Theoretical estimates of the spin diffusion coefficients at low fields and methyl proton relaxation times are in satisfactory agreement with the observed quantities.

*Present address: Physics Department, University College of North Wales, Bangor, Caernarvonshire, North Wales, Great Britain.

FACULTÉ DES SCIENCES DE MARSEILLE - SAINT-JÉROME

TRAVERSE DE LA BARASSE - MARSEILLE (13^e)

TÉLÉPHONE: 64.31.61

DÉPARTEMENT DE CHIMIE ORGANIQUE

LABORATOIRE DE CHIMIE M.P.C.

J. C. MAIRE: MAÎTRE DE CONFÉRENCES.

27 Janvier 1966

Professor B.L. SHAPIRO
 Department of Chemistry
 Illinois Institute of Technology
 CHICAGO, Illinois 60616 (U.S.A)

Nuclear magnetic resonance study of p-fluorophenylchlorostannanes: A_2B_2X spectra

Dear Dr. SHAPIRO,

I feel very sorry that you had to remind me about my contribution to ITNMR News letter.

We are continuing our study of the spectroscopic properties of the organotin compounds, and three NMR studies are now being carried out :
 Sn - H, Sn - CH and Sn - C - CH coupling constants in organotin hydrides, Sn - CH and Sn - C - CH coupling in diethyl tin compounds, and a systematic study of the various substituted phenylchlorostannanes. I shall restrict my contribution to the latter.

p-fluoro phenylchlorostannanes ($F - \text{C}_6\text{H}_4 - \text{SnCl}_3$) n Sn Cl₄ - n have been recently studied.

The aim was to obtain some evidences of p π - d π bonding between the tin atom and the benzène ring. The observed spectra are of A_2B_2X type, and were conveniently analysed as two superimposed simple A_2B_2 multiplets.

The experimental values of the nine parameters - the chemical shifts - and 6 coupling constants are given in the table below. The numbering of the nuclei is given on figure 1 and notations such as J_{15} are self understanding. F_{19} spectra have been run on a DP 60 and proton spectra 1H on a A-60 spectrometer. F_{19} chemical shift is given with C_6F_6 as internal reference and a positive figure means a down field shift - typical F_{19} and H_1 spectra are shown in figures 1 and 2.

n	$\nu_A - \nu_B$	J_{15}	J_{35}	J_{23}	J_{13}	J_{12}	J_{34}	σ_F c.p.s. C_6F_6
1	22,30	5,46	8,40	8,38	0,23	2,39	2,29	3372
2	25,90	5,70	8,64	8,02	0,40	2,57	1,77	3161
3	25,0	5,96	8,96	8,07	0,34	2,45	1,62	3000
4	22,30	6,18	9,35	7,63	0,40	2,51	1,42	2909

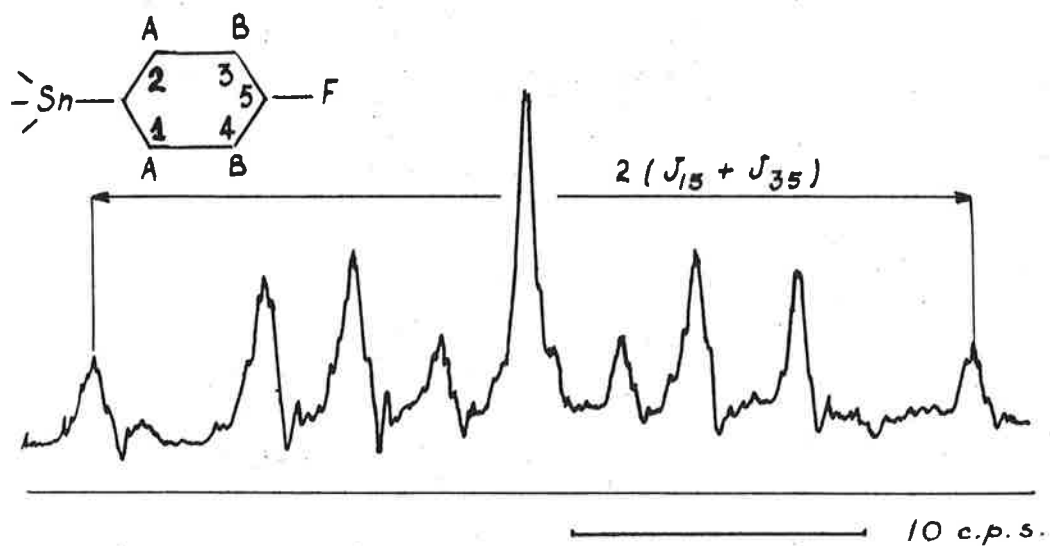


Fig 1: ^{19}F -spectrum of p-fluorophenyltrichlorostannane

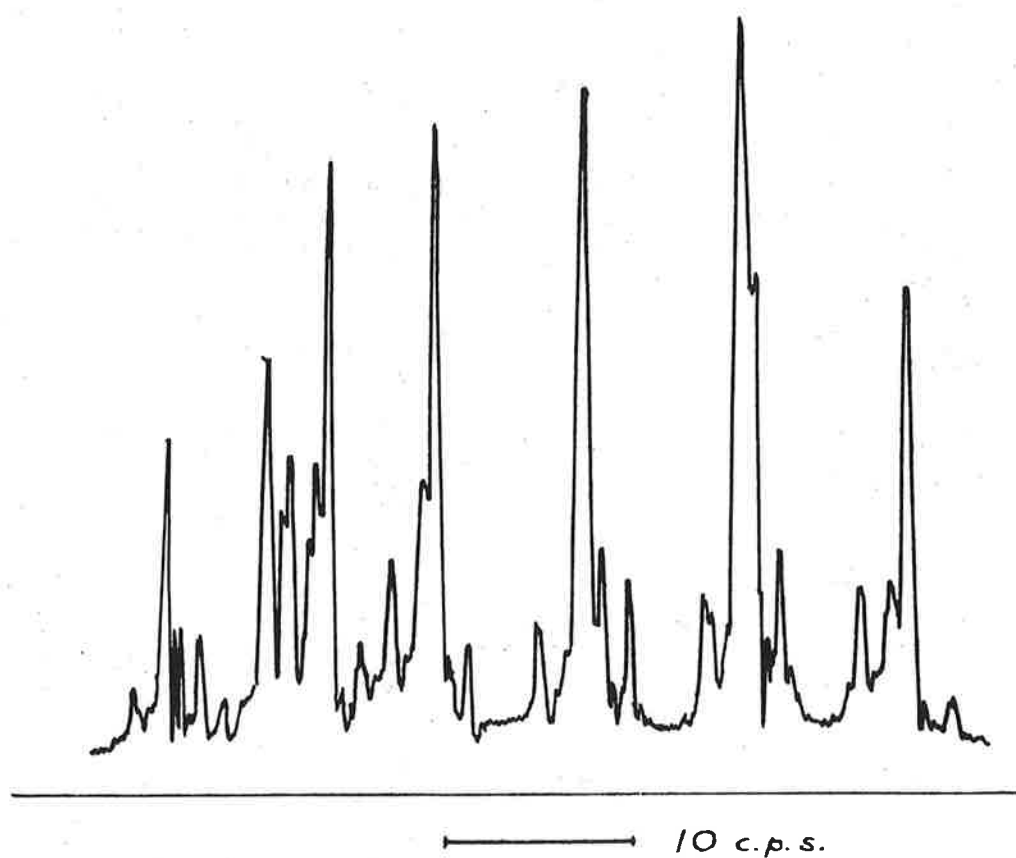


Fig 2: ^1H -spectrum of p-fluorophenyltrichlorostannane

For the analysis of the spectra the procedure was following:

$J_{15} + J_{35}$ was directly obtained from the F_{19} spectrum. From the $A_2 B_2$ part of the spectrum 35 we could get approximate values of J_{35} and J_{15} using the splitting between the main bands of the two superimposed 35 15 spectra. In a similar way we can get $J_{23} + J_{13}$. J_{13} para coupling, is likely very small and we have, a good approximation for J_{23} . Then the $A_2 B_2$ was picked out and considered as nearly an $A_2 X_2$ and a reasonable guess was made for J_{12} and J_{34} .

The spectrum was computed using FREQUINT IV program and J_{12} and J_{34} adjusted to obtain the best agreement with experimental spectrum.

Then we used the approximate parameters and NMRIT program to have the energy levels, then NMREN program to get the corresponding transitions, and again NMRIT with ten iterations to obtain the parameters given in table 1. J_{15} and J_{35} are found to be of the same sign, but the assumption that J_{15} and J_{35} are of the same sign as the proton-proton couplings is only tentative; the asymmetry in the F part of the spectrum being not resolved.

This work will be published in details as soon possible.

I wish to acknowledge my indebtedness to professor GUTOWSKY in whose laboratory I performed during the last summer the most part of this work and to Dr. JONAS for NMR computing programs placed at my disposal.

Sincerely yours.


J.C. MAIRE

UNILEVER RESEARCH LABORATORIUM

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 POSTBUS 114 - TELEFOON (01898) 46 41 - (010) 14 16 22 - TELEX 23261

Ref.

Vlaardingen, February 3, 1966.

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

Dear Dr. Shapiro,

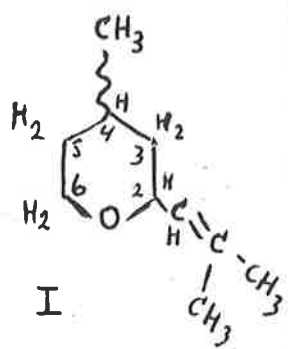
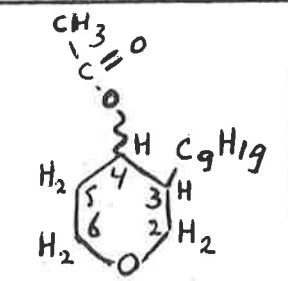
My contribution to IIT NMR is entitled "Diastereo-isomeric pairs of 2 tetrahydropyranderivatives"

- I.- From chemical evidence I knew, which of the two 2-isobutenyl-4-tetrahydropyrans was cis(IC) and which was trans (IT). See table for structure formulae and relevant n.m.r.-data. Rapid interconversion of the two conformers of IT results in a simpler p.m.r.-spectrum than for the rigid cis-isomer.(e.g. hydrogen on C₆ in IT exhibits a sharp triplet). Also H on C₂ in IT resonates at lower field than in IC, where it is a purely axial proton.
- II.- As a product of the Prins reaction 4-acetoxy-3-nonyl-tetrahydropyran became available to me as the cis (II C) and trans (II T) isomer. These were separated by fractional crystallization. In this case an averaging ^(process) is expected for the cis compound (ax-eq \longleftrightarrow eq-ax). The assignment of the simpler spectrum to II C is in agreement with all measured p.m.r.-parameters. Notable is the sextet, originating from the one proton on C₄ in II T with relative, nonbinomial intensities of 1:1:2:2:1:1. It is a result of coupling with one eq. proton on C₅ and about equal coupling constants with the ax. protons on C₃ and C₅.

VERVOLG No. 2

AAN:

TABLE. (A-60 spectrometer)

	Sub-stance	δ (1 st order) ref = TMS	$ J $ in c/s	Intens.	Multi- plicity	Assign- ment, H on
 <p>I</p>	IC in CCl ₄ (or C ₄ Cl ₆)	5.08 3.1-4.1	7.8 and 1.4 -	1 3	> 10 complex	C=C C ₂ and C ₆
	IT in CCl ₄ (or CS ₂)	5.22 4.26 3.57	7.3 and 1.4 7.0 and 4.5 5.4	1 1 2	> 10 broad quartet, triplet	C=C C ₂ C ₆
	IIC in CCl ₄ (or CS ₂)	5.07 3.3-3.8	4.0	1 4	quartet (broaden- ed) > 5	C ₄ C ₂ and C ₆
 <p>II</p>	IIT in CCl ₄ (or C ₄ Cl ₆)	4.56 2.8-4.1	4.5 and 9.0	1 4	sextet complex	C ₄ C ₂ and C ₆

The spectra did not change significantly in the temperature range 310-400°K (IC and II T) or from 253-310°K (IT and II C).

Sincerely yours,



Drs. M. van Gorkom

HOOKER CHEMICAL CORPORATION

Niagara Falls, New York 14302

Analysis of steric conditions by n.m.r.

The environment around phosphorus in some of its esters.

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois

February 7, 1966

Dear Dr. Shapiro:

Recently we acquired an HA-100 spectrometer and thus direct access to your NMR Letters now really becomes a must. Please accept the following note to start our "subscription". Although much of the data presented below was gathered a few years ago and is in the process of publication in a joint paper with Dr. J. R. van Wazer of Monsanto Company, I wish to use the content of this letter to call attention to the high accuracy of certain linear correlations between structure and chemical shifts in several series of related molecules. Deviations from this linear relationship can be used to detect conditions which can be ascribed to either the creation or the removal of steric interactions around the central phosphorus atom.

Last year we described the synthesis of tri-tert-butyl phosphite and some of its derivatives*, and characterized the products by, among others, phosphorus and proton n.m.r. spectroscopy. Comparing the P^{31} n.m.r. data with those of the analogous ethyl esters, a consistent shielding of phosphorus in all of the quadruply connected structures but not in tri-tert-butyl phosphite proper was noted.

P^{31} Chemical Shifts, p.p.m., (85% $H_3PO_4 = 0$) $\Delta\delta$

$(EtO)_3P$	-137.1	$(t-BuC)_3P$	-138.2	- 1.1
$(EtO)_3PO$	+ 1.2	$(t-BuC)_3PO$	+ 13.8	+ 12.6
$(EtO)_3PS$	- 68.0	$(t-BuC)_3PS$	- 41.2	+ 26.8
$(EtO)_3PSe$	- 72.1	$(t-BuC)_3PSe$	- 31.1	+ 41.0

Looking for an explanation of the non-conforming behavior of the tri-valent phosphorus ester, the hybrid structures between triethyl and tri-tert-butyl phosphite were synthesized and analyzed by n.m.r. These intermediate esters were also transformed into the corresponding oxo-, thio- and seleno-esters and characterized, in turn, by P^{31} and H^1 n.m.r.

* V. Mark and J. R. van Wazer, J. Org. Chem., 29, 1006 (1964).

-2-

Examination of the P^{31} data indicated a gradual shielding of the phosphorus, as the ethoxy substituent became successively replaced by the tert-butoxy, in all of the derivatives except in tri-tert-butyl phosphite proper. The latter showed a marked deshielding of the phosphorus nucleus compared with the hybrid structures, viz. tert-butyl diethyl and di-tert-butyl ethyl phosphites.

Analysis of the data revealed a quantitative relationship between chemical shift and composition. The upfield shifts in the P^{31} n.m.r. spectra caused by the replacement of an ethoxy by a tert-butoxy substituent suggested that the enhanced shielding might be caused by the enhanced inductive electron releasing property of the tert-butyl substituent. Accordingly, through the relay by the intervening oxygen, the tert-butyl substituents create inductively a higher electron density around the central phosphorus than was present in the ethyl homolog. A plot (Fig. 1) of the chemical shifts versus the sum of the inductive constants of the alkyl substituents shows an excellent linear correlation for all compounds except for tri-tert-butyl phosphite.

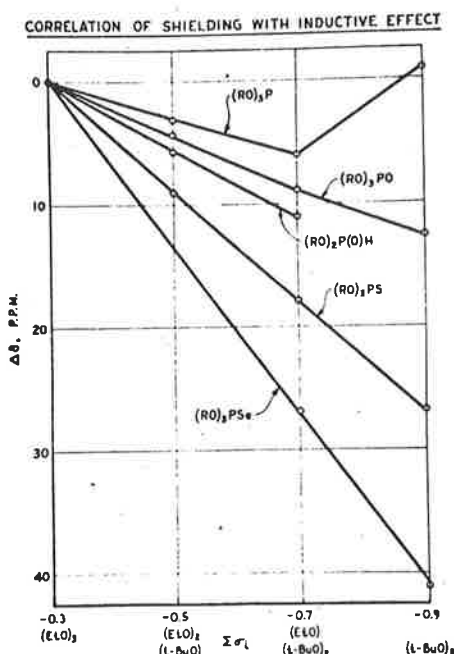


Fig. 1

The deviation in the P^{31} n.m.r. behavior of tri-tert-butyl phosphite from all of the other esters investigated suggested that the presence of three bulky substituents in the triply, but not in the quadruply, connected phosphorus derivatives affects the shielding of the phosphorus nucleus in some unique way. To test whether this is a general phenomenon, several series of phosphorus esters with various bulky, branched alkyl substituents were synthesized and analyzed by n.m.r.

Inspection of the data confirmed the pattern observed with the tert-butyl esters: a linear relationship between chemical shifts and composition was found to exist in all series of quadruply and triply connected esters, except for the tri-tert-alkyl phosphites, which showed sharp deviations from linearity in the same direction as was found with tri-tert-butyl phosphite. A few of the chemical shift versus composition plots are reproduced in Fig. 2 for the triply and in Fig. 3 for the quadruply connected derivatives:

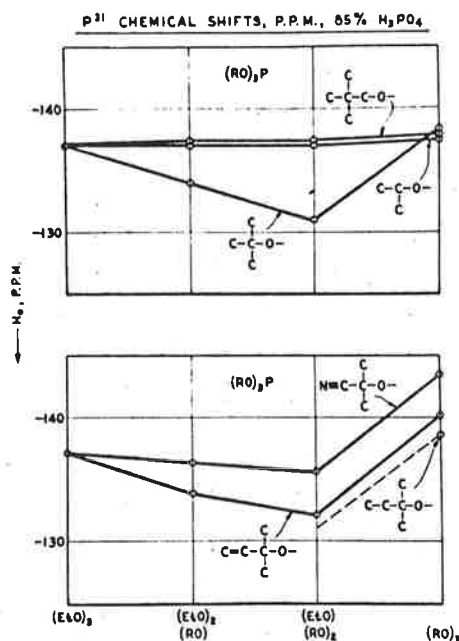


Fig. 2

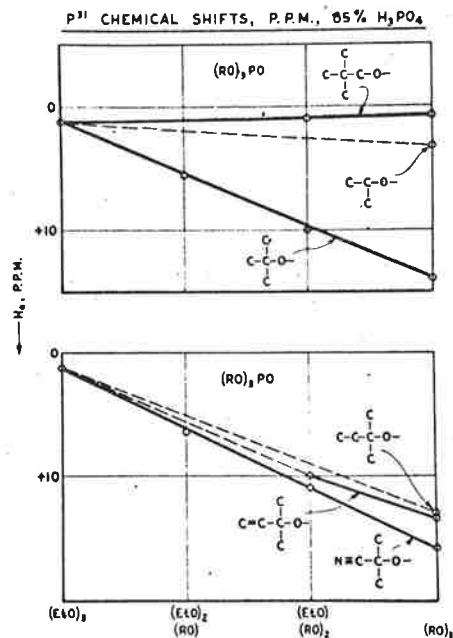


Fig. 3

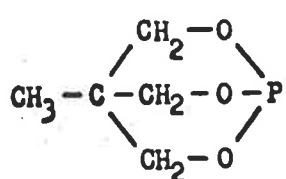
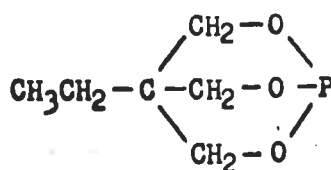
All of the tert-alkyl esters, which included the derivatives of tert-pentyl alcohol, α,α -dimethylallyl alcohol and acetone cyanohydrin, showed in their spectra a behavior very similar to that of the tert-butyl esters, in both kind and degree. Esters derived from secondary alcohols (isopropyl alcohol and sec-butyl alcohol) showed in their spectra the effects observed with the tert-alkyl esters, but in a much reduced degree. Interestingly, but, a posteriori, understandably, the behavior of the neopentyl-esters was essentially undistinguishable from that of the reference ethyl esters.

These results indicate that the attachment to the trivalent phosphorus of three alkoxy substituents, in which the alpha carbon is fully branched (tert-alkyl), creates conditions which result in a marked deshielding of the phosphorus with respect to other related esters. Partial branching on the α -carbon causes only slight effect, whereas branching on the β -carbon alone is apparently without effect on the shielding of the phosphorus.

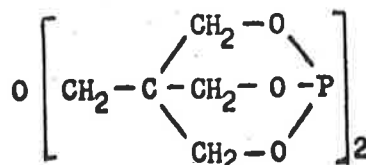
Since the data indicate that the cause of the relative deshielding is, most likely, of steric nature and arises from the crowding of the three bulky substituents in the triply but not in the quadruply connected derivatives, the opposite effect would probably be provoked by decreasing the steric interactions present even in the simplest alkyl esters, e.g. triethyl phosphite. Based on the effect on basicity of tying together the alkyl substituents of triethylamine to form quinuclidine, several analogous bicyclic phosphorus esters were synthesized and analyzed by n.m.r.

-4-

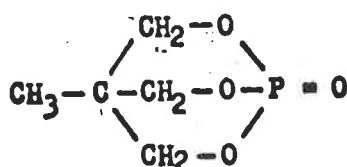
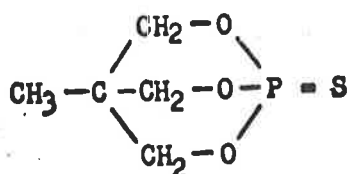
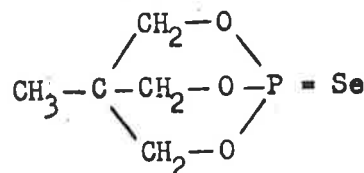
The results confirmed fully the expectations: a strong shielding of the phosphorus, with reference to triethyl phosphite, was observed in all of the triply connected esters, but only a mild shielding in the quadruply substituted esters. Some of the data are summarized below:

A. - 91.8 p.p.m.^a

B. - 94.0 p.p.m.

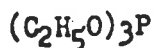


C. - 93.4 p.p.m.

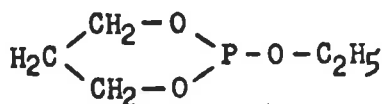
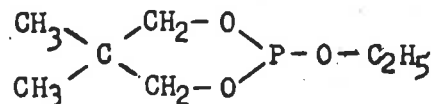
+ 8.2 p.p.m.^a- 57.2 p.p.m.^a

- 60.8 p.p.m.

Even the monocyclic analogs of the bicyclic structures above show a definite, although smaller, shielding effect relative to the open chain esters, e.g.

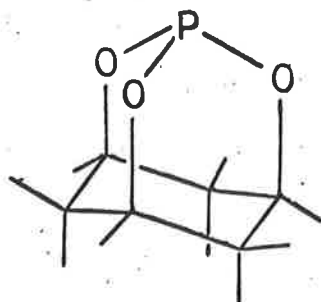
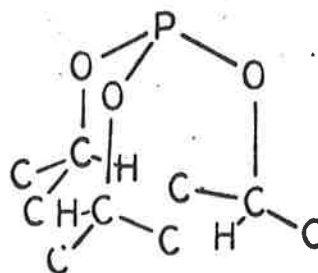


- 137.1 p.p.m.

D - 132 p.p.m.^c

E. - 122.2 p.p.m.

Since increasing the bulkiness of the alkoxy substituents results, most likely, in an increase of the bond angles of phosphorus and the tying together of the alkoxy substituents in a decrease, the observed relative deshielding and shielding effects can be ascribed to the relative increase and decrease, respectively, of the OPO angles. Significantly, the cyclic phosphorus ester with the very stable and rigid adamantane skeleton has a chemical shift^b practically identical with that of the reference triisopropyl ester.

F. - 137 p.p.m.^b

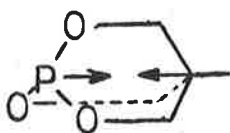
- 137.5 p.p.m.

^a The P^{31} a.m.r. data of several of these compounds became available, after the conclusion of our investigation, from the work of Dr. J.G. Verkade and coworkers.^b

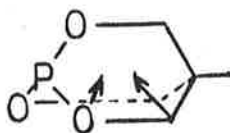
^b J.G. Verkade and R.W. King, J. Inorg. Chem., 1, 1948 (1962), and subsequent publications.

^c C.M. Blackburn, J.S. Cohen, and L. Todd, Tetrahedron Letters, 2873 (1964).

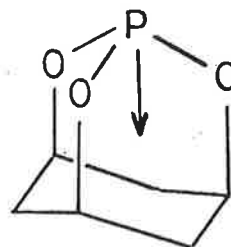
To account for the high shielding of A, B and C, but for the normal behavior of F, decreased O-P-O bond angles in the former three compounds - but not in F - are postulated. The smaller bond angles of phosphorus in A-C could be the result of the nonbonded repulsion between phosphorus and the bridgehead carbon. Although neither bond angle nor bond distance data seem to be available for compounds A-C, it is very likely that the distance between phosphorus and the quaternary carbon is less than the sum of their van der Waals radii, i.e. $1.6 + 1.9 = 3.5 \text{ \AA}$.^d The back sides of the other atoms of the skeleton of A-C point to the open spaces between rings, hence there is only bridgehead bumping and, therefore, elongation of the molecule only along the P-quaternary carbon axis is the most likely consequence of the steric interaction. An analogous situation is not present in F: here, like in adamantane^e, the bridgehead atoms are backed only by intraskeletal holes, hence the steric interactions in this molecule, like in its open chain analogs, are probably minimal.



A.



A.



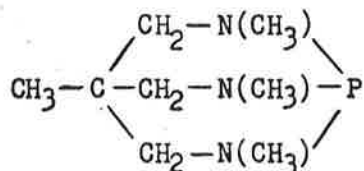
F.

There are many examples in the literature of P^{31} chemical shifts which lend support to the conclusions reached above^f and provide data for the effects of both the steric congestion around phosphorus, resulting in a relative deshielding effect, and the reduction of phosphorus bond angles, resulting in a relative shielding effect^h. Extreme examples of the latter are the chemical shifts of compounds which

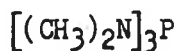
^d This argument is modeled after the one suggested by R.C. Fort and P. von R. Schleyer to account for the low reactivity of 1-bromobicyclo [2.2.2] octane^e, the carbocyclic analog of A-C.

^e R.C. Fort and P. von R. Schleyer, Chemical Reviews, 64, 277 (1964).

^f The nitrogen analog of A is also strongly shielded relative to the non-cyclic model:



- 83.6 p.p.m.^g



- 122.0 p.p.m.

^g B.L. Laube, G. Casedy and J.G. Verkade, Abstracts of Papers presented at the 150th Meeting, ACS, September 1965, p. 14-0.

^h If the dependence of chemical shifts on bond angles is of the magnitude indicated by the semiempirical correlation of Muller-Lauterbur-Goldensonⁱ and Parks^j, that is ca. 50 p.p.m. per degree, then by P^{31} n.m.r. one can detect and follow changes in bond angles even as small as one minute.

ⁱ N. Muller, P.C. Lauterbur and J. Goldenson, J. Am. Chem. Soc., 78, 3557 (1958).

^j J. R. Parks, ibid., 79, 757 (1959).

contain the P_3 triangles present in elemental phosphorus (P_4 tetrahedron, $\delta + 450$ to 488 p.p.m.) and still intact in some of its derivatives (P_4S_3 , $\delta + 122$ p.p.m.^k; P_4Se_3 , $\delta + 106$ p.p.m.^l).

The direction and magnitude of the observed effects can be conveniently interpreted by considering the effect of the narrowing or spreading of the bond angles on the hybridization state of an atom^m. A decrease in the bond angles of the trivalent phosphorus results in an increase of the p character of the bonds and in an increase of the s character of the nonbonding electrons, the net result of which is an enhanced shielding of the phosphorus nucleus. The opposite effect, a relative deshielding, is effected by increasing the p character of the nonbonding electrons by the spreading of the phosphorus bond angles. This change results in a decrease in the density of the unshared electrons around phosphorus and, therefore, in a deshielding of the latter.

Sincerely,

Victor Mark

Victor Mark
Research Associate

- ^k C.F. Callis, J.R. van Wazer, J.N. Shoolery and W.A. Anderson, ibid, 79, 2719 (1959); the isolated phosphorus has $\delta -72$ p.p.m.
- ^l K. Irgolic, R.A. Zingaro and M. Kudchacker, Inorg. Chem., 4, 1421 (1965); the isolated phosphorus has $\delta -38$ p.p.m.
- ^m H.A. Bent, Chem. Reviews, 61, 275 (1961).

DEPARTMENT OF CHEMISTRY
 CORNELL UNIVERSITY
 ITHACA, NEW YORK 14850

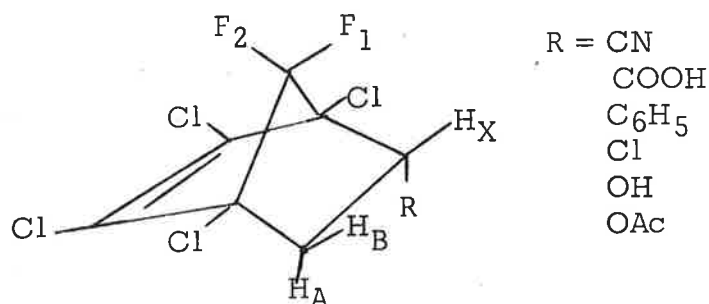
February 4, 1966

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

Dear Barry:

SUBSTITUENT EFFECTS ON LONG-RANGE
 J_{HF} IN A BICYCLOHEPTENE SYSTEM

To study the effect of various substituents on J_{HF} over four saturated bonds we have synthesized and analyzed the n.m.r. spectra of the following:



The analysis of this five spin system was straightforward because we have previously analyzed the three spin system in which two chlorine atoms replace the fluorine atoms. The chemical shift between the two fluorine atoms is about 1000 c.p.s. so that an AB type F^{19} spectrum is observed on which proton couplings are superimposed. Fluorine F_1 is downfield from fluorine F_2 .

The following points are noteworthy: J_{AB} , J_{AX} and J_{BX} are about the same as were observed for the hexachloro compounds. The largest long-range J_{HF} is between F_2 and H_A (~ 5 c.p.s.). Protons in similar geometry have been observed to couple in bicycloheptenes. If the assumption is made that all the coupling constants in this system must decrease algebraically as the substituent electronegativity increases then most of the long-range J_{HF} couplings are negative. However J_{F_2X} must, by this criterion, be given a positive sign. LAOCOON II fitting is being completed.

I presented this work at the International Symposium on N.M.R. in Tokyo last September.

Sincerely yours,

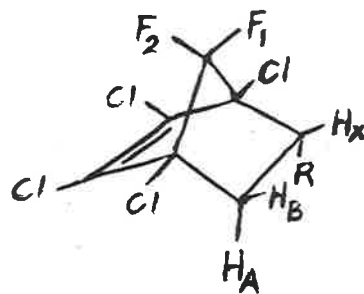
Kenneth L. Williamson
 Visiting Professor

KLW:ksh

Coupling Constants of 5-Substituted-7,7-Difluoro-2,2,3,4-

tetrachlorobicyclo[2.2.1]-2-heptenes

R	J_{AB}	J_{AX}	J_{BX}	J_{AF_1}	J_{AF_2}	J_{BF_1}	J_{BF_2}	J_{XF_1}	J_{XF_2}	$J_{F_1F_2}$
CN	-13.0	4.7	9.3	-1.5	-4.6	-2.6	-0.6	-2.3	1.1	-174 ± 3
COOH				-1.7	-3.1	-2.5		-2.7	1.0	-174 ± 3
C ₆ H ₅	-12.6		8.8	-1.2	-4.7	-2.4	-0.5	-2.7	1.0	-174 ± 3
Cl	-14.1	3.6	8.8	-1.7	-5.1	-3.1	-0.8	$(-2.9-3.5)$	0.8	-178 ± 1
OH	-13.0	2.7	7.8	-2.1	-5.4	-3.3	-0.5	$(-2.7-3.2)$	0.5	-182 ± 1
OAc	-13.5	2.8	7.9	-1.9	-5.3	-3.4	-0.8	-3.2	0.6	-179 ± 1





Please address any reply to
THE DIRECTOR
and quote: MS 5/8/01
Your reference:

Ministry of Technology
NATIONAL PHYSICAL LABORATORY
TEDDINGTON, Middlesex
Telex: 262344 Telegrams: Physics, Teddington, Telex
Telephone: TEDDINGTON Lock 3222, ext. 813/826

DIVISION OF MOLECULAR SCIENCE

7th February, 1966.

Dear Dr. Shapiro,

PULSE PROGRAMMER

I thought readers of this news letter might be interested in brief details of a pulse programmer which we've constructed, the circuit being a modification of one previously used by Tony Hartland. The programmer is built from a variety of transistorized plug-in units (Binary and decade dividers, pulse shapers, gates etc. made by Venner were used but no doubt any similar units could be employed) and will deliver the standard pulse sequences required in spin-echo work, i.e. two pulses separated by a given time interval and the Carr-Purcell sequence. The output pulses are derived from a variable frequency sine-wave input, the pulse spacing being determined by this frequency and the setting of a train of three decade dividers. The sequence repetition rate is also controlled by a sine-wave input, conveniently derived internally from the 50 cps mains frequency which may be divided by a chain of 8 binary units and a decade unit. Alternatively sequence rate pulses may be supplied from another external source. Provision is also made for manual triggering of pulse sequences. For Carr-Purcell sequences a train of three decade units allows 10, 100 or 1000 pulses to be produced, the time for which pulses are delivered also being controllable manually. The outputs are suitable for driving Tektronix 163 pulse shapers or similar units.

We can supply anyone interested with a circuit diagram.

Yours sincerely,

Tom Connor

T. M. CONNOR

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

STATE UNIVERSITY OF NEW YORK AT BUFFALO

College of Arts and Sciences

Formerly The University of Buffalo, Founded 1846

Department of Chemistry

Acheson Hall

Chemistry Road

Buffalo, New York 14214

Telephone 831 - 3014

Area Code 716

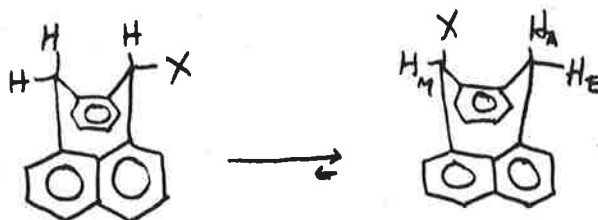
February 8, 1966

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

LONG RANGE COUPLING IN CONFORMATIONAL
 ANALYSIS OF 7,12-DIHYDROPLEIADENES

Dear Dr. Shapiro:

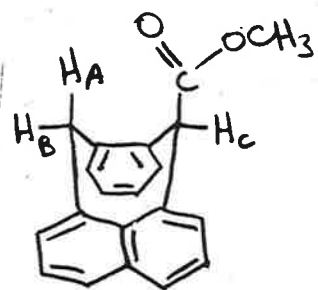
We have used line width measurements of C_7 - and C_{12} - proton signals in 7-substituted dihydropleiadenes (DHP) to assign configurations to the single detectable conformer present in solution in the $+40$ to -60° range.

X = Cl, COOCH₃

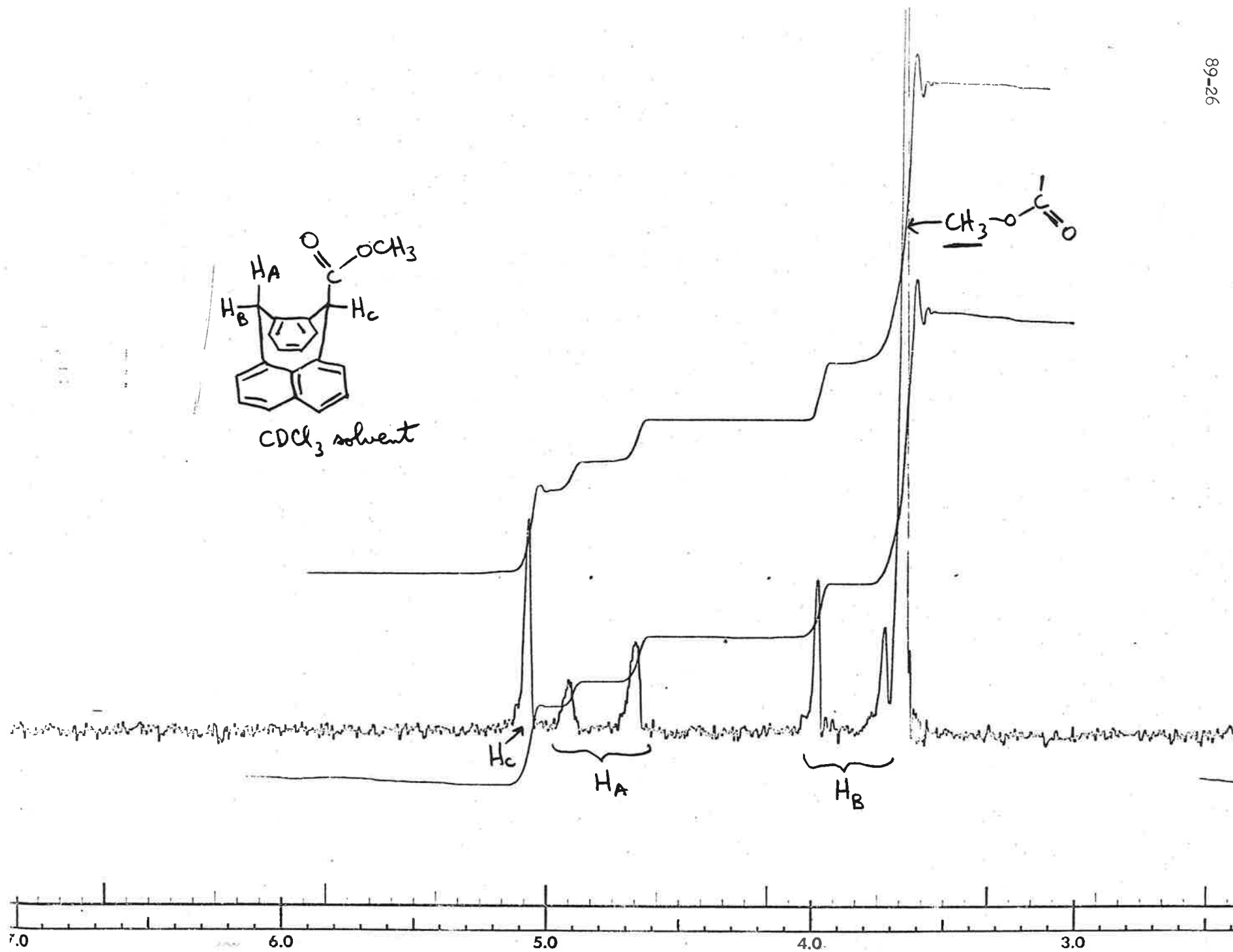
The C_{12} -methylene quartet shows the low-field doublet lines to be broader than the upfield doublet; this is because the former signal is due to the "axial" proton (H_A above), which is long-range coupled to aromatic protons more effectively than the "equatorial" protons, $H_E \leftrightarrow H_M$. The 7-Cl isomer gave values of line width at half-height ($W_{h/2}$) as follows: $H_E = H_M = 1.9$ cps., $H_A = 2.8$ cps. (and 1.9 cps. after decoupling the aromatic protons). Thus, if $W_{h/2}$ for the C_7 -methine signal in a 7-subst. DHP is comparable to that of the C_{12} -equatorial proton doublet, the substituent must be axial, whereas the equatorial position would be indicated if $W_{h/2}$ for $H_A \approx H_M$. These findings of stereoelectronic preferences for side-chain to ring proton couplings are in agreement with previous studies (e.g. Sternhell, Rev. Pure & Appl. Chem., 14, 15 (1964)). We are enclosing partial n.m.r. spectra of several 7-substituted DHP's, which illustrate the points mentioned above.

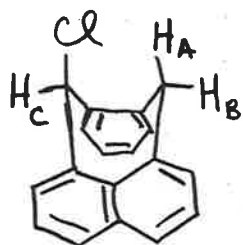
Sincerely yours,

P. T. Lansbury
 Professor of Chemistry

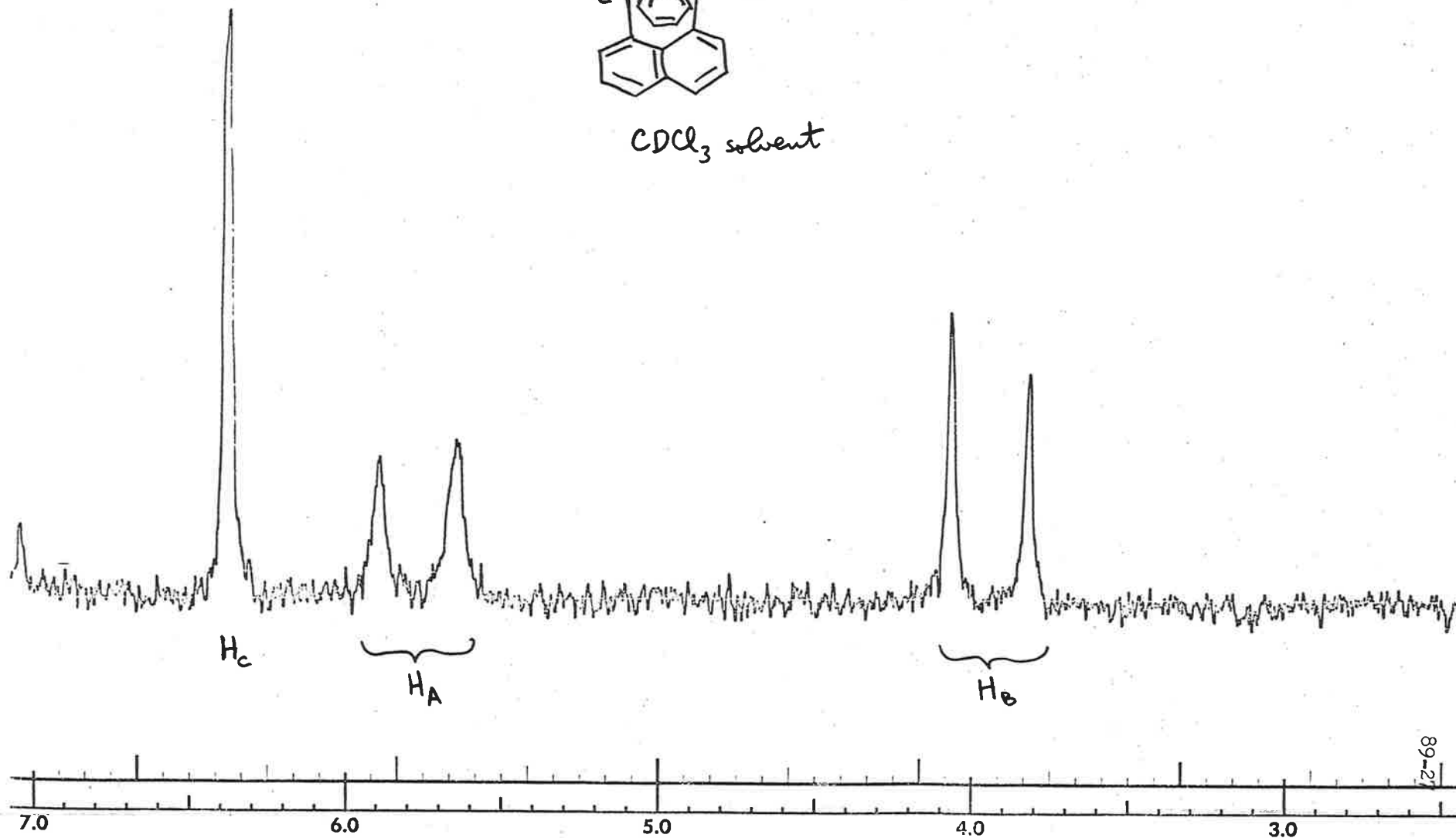


CDCl_3 solvent



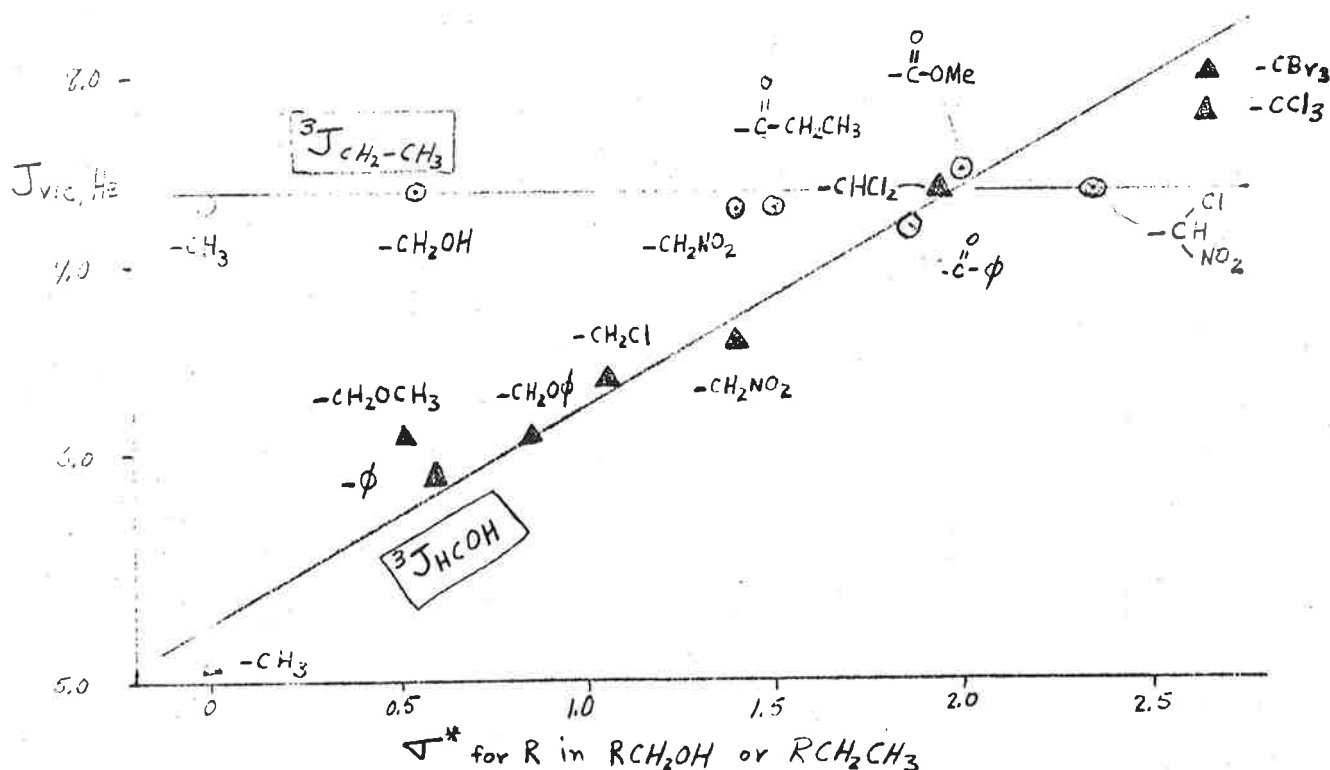


CDCl₃ solvent



J_{vic} in substituted propanes

The magnitude of $^3J_{HCOH}$ in primary alcohols RCH_2OH is quite sensitive to the electronegativity of R measured in terms of the Taft substituent parameter, σ^* . Furthermore, J_{HCOH} varies directly with electronegativity, rather than inversely, as is the usual case. We recently studied some substituted propanes, $R-CH_2CH_3$, to see if similar phenomena prevail in the C-C system. The results are shown graphically below.* Included are representative data for some primary alcohols.



Perhaps an insensitivity of J_{vic} in saturated C-C systems to inductive effects one carbon away was to be expected. The factors which operate in the alcohol series are obviously absent in the C-C bond. The oxygen lone pair electrons, or the polarizability of the C-O bond apparently are intimately involved in the effects observed in the alcohols.

*Propane data from R. C. Ferguson and D. W. Marquardt, J. Chem. Phys. 41, 2087 (1964); others obtained at 100 Mc, 5-10% CCl_4 solutions. For J_{HCOH} 's, see J. Am. Chem. Soc. 88, 190 (1966).

C. F. Poranski

C. F. Poranski

W. B. Moniz

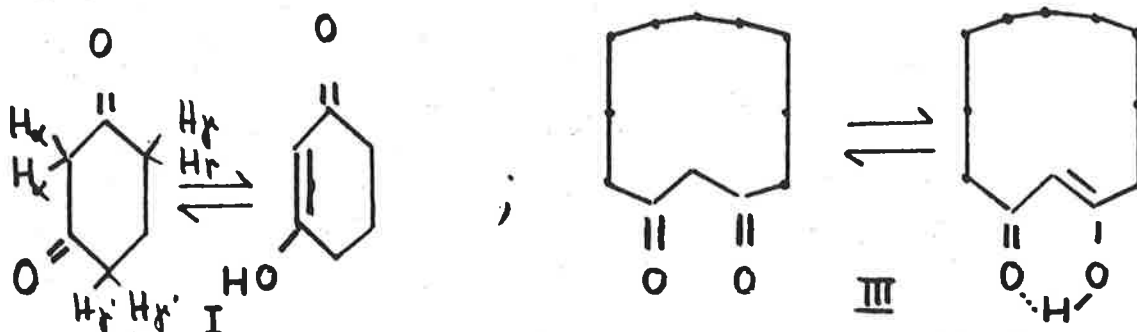
Institut für organische Chemie
der Universität des Saarlandes
Saarbrücken 15
Germany

66 Saarbrücken 15, den February 9, 1966
Telefon 21351

Dr. Bernard L. Shapiro
Associate Professor of Chemistry
Illinois Institute of Technology
Technology Center
Chicago/Illinois 60616

Dear Dr. Shapiro,

For a study of the thermodynamical data of the keto-enol-equilibrium in cyclic systems we chose cyclohexane-(1,3)-dione(I), cycloundecane-(1,3)-dione (II) and cyclododecane-(1,3)-dione(III)^{1,2)}. These compounds represent two extreme cases: I is a "trans-fixed" 1,3-diketone^{3,4)} which cannot form a cis-enol-chelate at all; II and III are ring systems which are just large enough to adopt a cis-enol-chelate-structure again^{1,2)}. For this reason one would expect quite interesting results for the ΔH -, ΔS - and ΔG -values of this compounds.



The NMR-spectra of I, II and III exhibit the following signals (temp.: 37°, 10 % solutions in DCCl_3):

I) at 2.03 ppm a broad multiplet and a triplet at 2.41 ppm. These signals are caused by the C-5- resp. the γ - and the γ' -protons. The α -CH₂-protons give a singlet at 3.45 ppm resulting from the diketone-system.

III) shows at 1.37 ppm and 1.63 ppm the signals due to the C-5- up to the C-11-protons. At 2.48 ppm the signals caused by the γ, δ - and γ', δ' -protons and at 3.59 ppm the α -CH₂-singlet of the diketo-compound are observed. The triplet at 2.34 ppm and the singlet at 5.72 ppm are due to the enol. The enol O-H-signal is observable in high concentrations only (50 % sol. in CCl₄: 14.60 ppm).

The determination of the concentration of the enol in the equilibrium mixture of I, II and III (I: 0.893, II: 0.552, III: 0.51 molar sol.) was carried out by integration of the α -CH₂- and the =C-H-signals. To such integration values were measured and from the average value the percentage of enol was calculated. These data gave the equilibrium constant $K_{E/K}$ (E = enol, K = diketone) and with $K_{E/K}$ the figures of ΔH and ΔS were graphically determined. The ΔG -value can be obtained from the equation:

$$\Delta G = - RT \ln K = \Delta H - T \Delta S \quad (1)$$

Tab. 1: ΔH -, ΔS - and ΔG -values of the cycloalkane-(1,3)-diones

Table 1 shows the detailed values of ΔH , ΔS and ΔG .

ΔG is equivalent to the classical "tendency of enolisation"^{5,6)} The more negative ΔG is, the larger is the concentration of enol in the equilibrium mixture. I has a ΔG -value of ~ -1.6 kcal/mole resulting from the large enolisation (~ 90 % of enol). This negative ΔG is due to the formation of strong intermolecular hydrogen-bonds producing thus "trans-anti" chelating. In II and more pronouncedly in III an intramolecular "cis-syn" chelate-ring is possible. But this system is less favorable because of conformational effects. This is the reason too for the low $\Delta G = \sim 0$ in ~~II and III~~.

- 3 -

Tab. 1: ΔH -, ΔS - and ΔG -Values of I, II and III^{a)}

diketone	ΔH (kcal)	ΔS (cal/o)	$T \Delta S$ (kcal)	$\Delta G^b)$ (kcal)
I	- 3.7 ₅	- 7	- 2.12	- 1.6
II	1.3 ₅	- 1	- 0.32	1.6
III	0.5 ₂	0.9	0.26	0.2

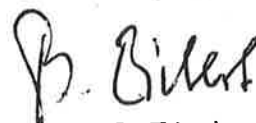
a) temperature range for ΔH , ΔS and ΔG : from $T = 250^\circ$ to 330° Kb) values based on $T = 290.5^\circ$ KReferences

- 1) B.Eistert and K.Schank, Tetrahedron Letters(London) 8, 429(1964)
- 2) K.Schank, B.Eistert and J.Felzmann, Chem.Ber. (in print).
- 3) B.Eistert and W.Reiss, Chem.Ber. 87, 92, 108 (1954).
- 4) B.Eistert, E.Merkel and W.Reiss, Chem.Ber. 87, 1513 (1954).
- 5) G.Briegleb, W.Strohmeier and I.Höhne, Ztschr.f.Elektrochemie 56 3,240 (1952).
- 6) G.Briegleb and W.Strohmeier, Angew.Chemie 64, 409 (1952).

Sincerely yours



(Dr. Heinz Dürr)



(Prof. Dr. Bernd Eistert)



Bradford Institute of Technology

BRADFORD 7

Principal E G EDWARDS PhD BSc FRIC Bradford 29567

DEPARTMENT OF CHEMICAL TECHNOLOGY

Professor R L Elliott BSc PhD FRIC FTI FSDC

DWJ/JH

10th February, 1966.

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

Dear Professor Shapiro,

Thank you for copies of the I.I.T. N.-M.-R. Newsletter.

Short Course: INTERPRETATION OF HIGH-RESOLUTION N.-M.-R. SPECTRA

We should like to announce that our next course on the interpretation of high-resolution nuclear magnetic resonance spectra will take place from 11th to 13th May, 1966.

The accent will be on proton spectra from organic compounds. The lectures, each of which will be followed by a question and discussion period, will include the topics of double resonance and the calculation of spectra. There will also be two sessions during which participants will attempt to solve spectra under the guidance of tutors drawn from the speakers and the undersigned. It is hoped to make some division between participants having some and negligible interpretation experience.

PROGRAMME

WEDNESDAY 11TH MAY

Introduction to N.M.R. Spectra - Dr. D. W. Jones (Bradford Institute of Technology)

Qualitative Interpretation of N.M.R. Spectra - Dr. P. R. Brook (University of Leeds)

/cont.

- 2 -

THURSDAY 12TH MAY

Analysis of Spectra I - Dr. J. W. Emsley (University of Durham)

Spectra Interpretation
Session I.
Chemical Applications of
Double Resonance - Dr. R. K. Harris (University of East Anglia)

Spectra Interpretation
Session II

FRIDAY 13TH MAY

Analysis of Spectra II - Dr. J. W. Emsley (University of Durham)

Analytical Applications of
N.M.R. - Dr. A. Mathias (I.C.I. Ltd., Dyestuffs
Division)

Registration and Location

The course fee is £5, including tea and coffee but not lunches; intending registrants should apply to the Registrar, Bradford Institute of Technology, Bradford 7, England. There are no arrangements for residential accommodation, but a hotels' list may be requested. Meetings will be held in lecture theatres N3 and N4 on floor N of the tall main building.

A registration form is enclosed.

K. D. Bartle

K. D. Bartle

Yours sincerely,

D. W. Jones
D. W. Jones

J. E. Pearson
J. E. Pearson

REGISTRATION FORM

Short Course on Interpretation of High-resolution N.M.R. Spectra.
Wednesday, 11th May - Friday, 13th May, 1966.

NAME.....
(Last) (First)

NAME OF ORGANISATION.....

POSITION IN ORGANISATION.....

ACADEMIC/PROFESSIONAL QUALIFICATIONS.....

ADDRESS FOR CORRESPONDENCE.....

.....

Previous experience of N.M.R. Spectra: None/Slight/Appreciable.

This form, should be completed and sent, together with fee of £5,
to The Registrar, Bradford Institute of Technology, Bradford, 7. England.

University of Notre Dame

College of Science

Notre Dame, Indiana 46556

Department of Chemistry

February 12, 1966

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

Re: Effect of t-Butyl Substituent on Proton and Fluorine Resonance in
Substituted Cyclohexanes

Dear Barry:

We were pleased to be put on the mailing list of the IIT-NMR Newsletter and have read the first two issues we received with great interest. Since Anteunis and Tavernier (No. 87, p. 27) referred to some of our results on geminally disubstituted cyclohexanes, I felt your readers would be interested in the NMR spectra of mixtures of cyclohexanone dimethyl ketal (I) and 3-t-butylcyclohexanone dimethyl ketal (II) (Fig. 1) and I and 4-t-butylcyclohexanone dimethyl ketal (III) (Fig. 2). The averaged signal of the methoxy methyl groups in I does not fall midway between the signals for the axial and equatorial methoxyls in II but it does fall midway between these two signals in III. Since the spectra recorded are those of mixtures (I + II and I + III, CCl₄ solvent, shifts in c./s. at 60 mc./s. from TMS), differences in magnetic susceptibility cannot come into play and Fig. 1 would therefore seem to indicate that a 3-t-butyl group has a differential effect on the chemical shifts of axial and equatorial methoxyls. The tentative conclusion from Fig. 2 that a 4-t-butyl substituent has no such differential effect is less secure: the experiment would not reveal an effect of the 4-t-butyl substituent on the methoxyl shift which would move the axial and equatorial signals equally in opposite directions. Moreover, the limit of perception is probably ± 0.05 c./s. which could cover up a 5%-effect on shift from the midpoint, since the total shift is only 1.0 c./s. Other experiments in our laboratory which will be published soon in full suggest, however, that a 4-t-butyl substituent does, in fact, have little influence on proton shifts at C₁ in cyclohexane.

As shown in Figs. 3 and 4, the situation is entirely different in F¹⁹ resonance. Fig. 3 refers to the F¹⁹ spectrum of mixtures of 1,1-difluorocyclohexane (IV) and 4-t-butyl-1,1-difluorocyclohexane (V)

Professor B. L. Shapiro
Page 2

February 12, 1966

(which both we and J. D. Roberts and coworkers have succeeded in synthesizing). Fig. 4 refers to the F^{19} spectrum of a mixture of IV and 3-t-butyl-1,1-difluorocyclohexane (VI). (Both spectra were recorded at 56.4 mc./s. in CCl_4 with internal side-bands, shifts are in c./s. and the relatively small H^1 splittings are not indicated.) Clearly the t-butyl substituent produces a large differential shift of axial and equatorial fluorine (over 100 c./s. from the average position) and the direction of this differential shift is opposite in conformationally analogous 3- and 4-t-butyl isomers. At the moment we are puzzled as to the source of so large a shift and we would be anxious to have suggestions from readers of the Newsletter as to its possible origin. That the shift is quite real is confirmed by F^{19} measurements on cyclohexyl fluoride and cis- and trans-4-t-butylcyclohexyl fluoride soon to be published.

Sincerely yours,



Ernest L. Eliel
(with R. J. L. Martin)

ELE:pa

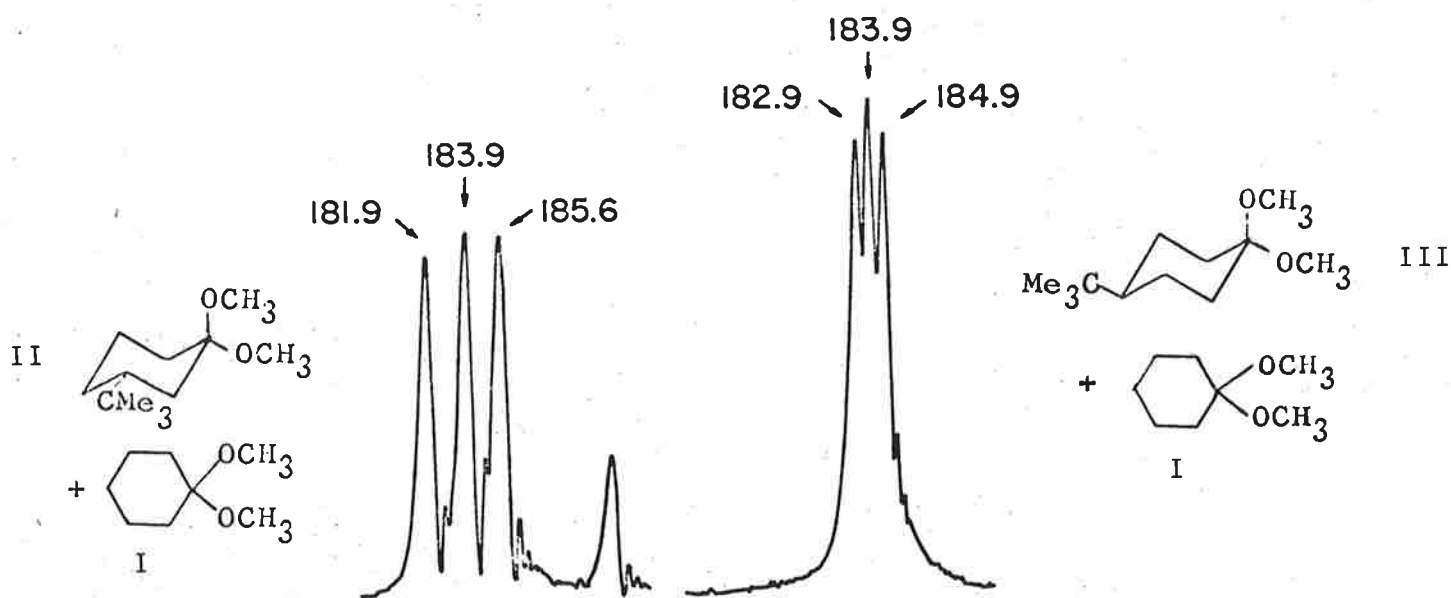


Fig. 1

Fig. 2

1,1-Difluorocyclohexanes

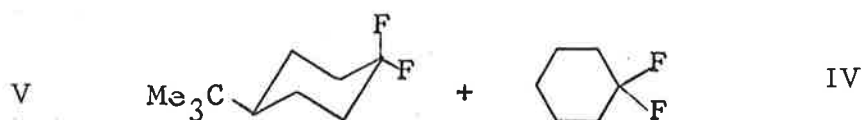
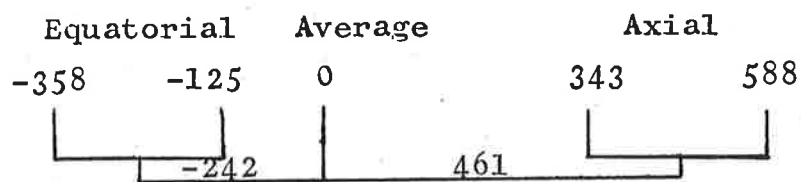


Fig. 3

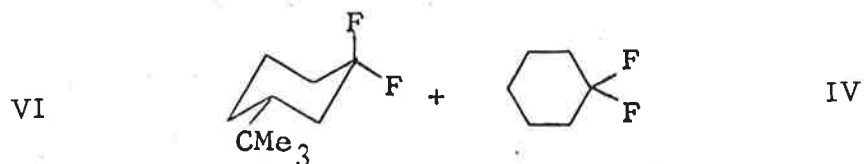
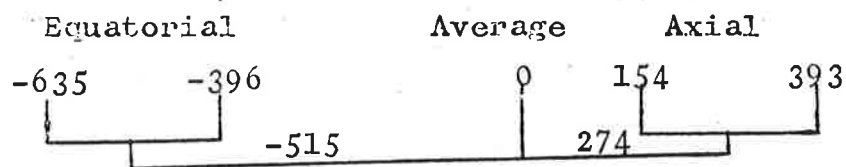


Fig. 4



UNIVERSIDADE DE COIMBRA

LABORATÓRIO QUÍMICO DA FACULDADE DE CIÊNCIAS

COIMBRA--PORTUGAL--TELEF. 22026

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

14th February, 1966

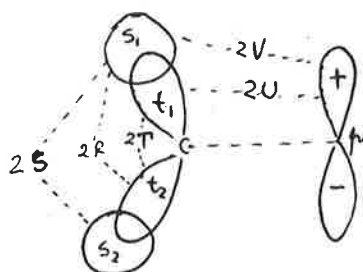
Dear Professor Shapiro,

On $^2J_{HH}$, $^3J_{HH}$, $^4J_{HH}$ and inductive and hyperconjugative effects.

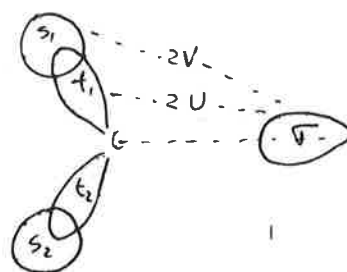
$^2J_{HH}$

We have resumed part of the study by Pople and Bothner-By (J. Chem. Phys. 42, 1339 (1965)) of substituent effects on the spin coupling constant between geminal protons, from a slightly different point of view.

Having obtained an expression for the mutual polarizability of the hydrogen atoms of two CH bonds in terms of the various π resonance integrals leading to $\sqrt{\pi}$ -electron delocalization (Murrell and Gil, Theoret. Chim. Acta, to appear; see also, Pople and Santry, Mol. Phys. 9, 311 (1965)), we used the same approach in the calculation of $\pi_{S_1 S_2}$ (i.e. $\frac{^2J_{HH}}{h}$) for the following systems:



(A)



(B)

where the atomic orbitals σ and p are considered, alternatively, vacant and filled. π_{S,S_2} is calculated by making use of the relationship $\pi_{\mu\nu} = \partial^2 E / \partial \alpha_\mu \partial \alpha_\nu$, that is, besides introducing the delocalization terms R, S, T, U, V into a set of localized molecular orbitals, we also include small perturbations D_1, D_2 to the coulomb integrals of S_1 and S_2 ; π_{S,S_2} is then given by the coefficient of $D_1 D_2$ in the perturbation expansion of the total electronic energy E of the system. This is obtained by first diagonalizing the secular matrix ^{with} $D_1 = D_2 = 0$, and then introducing D_1 and D_2 and using second-order perturbation theory to evaluate the perturbation of the energy that is proportional to $D_1 D_2$. The diagonalization can be accomplished by making use of the local symmetry on the CH_2 group and making the simplifying assumptions $S=T$ and $U=V$. In these circumstances and assuming all coulomb integrals equal, we get for

Case (A), p vacant,

$$(1) \quad \pi_{s_1 s_2} = \frac{1}{\beta^3} (R^2 - T^2) + \frac{24}{\beta^4} U^2 T + \frac{8}{\beta^4} U^2 R;$$

n filled,

$$(2) \quad \pi_{s_1 s_2} = \frac{1}{\beta^3} (R^2 - T^2) + \frac{8}{\beta^4} U^2 (R - T)$$

For case (B), The first terms are the same and the β^{-4} terms are symmetric of those above.

These expressions are in agreement with the conclusions of Pople and Bothner-By (T and R are negative quantities). The second term in (2) is only a correction to the value for an "isolated" CH_2 group and does not reflect any transfer of electrons.

$$\underline{{}^3J_{HH} \text{ and } {}^4J_{HH}}$$

In the NMR Newsletter no. 81 we reported some MO calculations of proton coupling constants in benzene and pyridine. The agreement with

experiment was surprisingly good, but no insight was gained on the "paths" through which the various couplings occur, nor on the effect of replacing a CH group in benzene by a N atom to give pyridine. Using the same set of parameters we have performed similar calculations on benzene-like molecules with $\alpha_{C_1} = \alpha_N$ and/or $\beta_{C_1C_2} = \beta_{CN}$; and on pyridine with $\alpha_N = \alpha_{C_1}$ and $\beta_{CN} = \beta_{C_1C_2}$, or $\alpha_N \neq \alpha_{C_1}$ and $\beta_{CN} = \beta_{C_1C_2}$, or $\alpha_N = \alpha_{C_1}$ and $\beta_{CN} \neq \beta_{C_1C_2}$, aiming at isolating the various effects. (In principle, it should be possible to do a study of inductive and hyperconjugative effects, at least on $^3J_{HH}$ where the mechanism of coupling is best known, along lines similar to those for $^2J_{HH}$). Those effects are: Δ^{lp} , due to the presence of the lone-pair instead of the C_1H bond; Δ^α , the contribution arising from $\alpha_N \neq \alpha_{C_1}$; and Δ^β the contribution due to $\beta_{CN} \neq \beta_{C_1C_2}$.

They are given below for J_{23} and J_{26} :

	Δ^{lp}	Δ^α	Δ^β	$\Delta^{lp} + \Delta^\alpha + \Delta^\beta$	Pyridine - Benzene (calc.)	
J_{23}	-1.2	-0.7	-1.6	-3.5	-2.9	c.p.s.
J_{26}	-1.5	-0.2	-0.7	-2.4	-1.8	c.p.s.

It is found that Δ^α and Δ^β can be added to reproduce $\Delta^{\alpha,\beta}$ (simultaneous change of α_{C_1} and $\beta_{C_1C_2}$) almost exactly, but differences occur between $\Delta^{lp,\alpha}$ and $\Delta^{lp} + \Delta^\alpha$ (+0.3 for J_{23} and +0.6 for J_{26}) and between $\Delta^{lp,\beta}$ and $\Delta^{lp} + \Delta^\beta$ (+0.3 for J_{23} and 0.0 for J_{26}).

The comparatively small sensitivity of J_{23} and J_{26} to α_{C_1} and the large effect of the lone pair in the position 1 are consistent with the observed increases in J_{23} and J_{26} of azines when the nitrogen lone pair becomes involved in a bond, e.g. on protonation (Palmer and Sample, Chem. Ind. 1766, (1965)), although changes in Δ^β and in the molecular geometry may also be important.

Yours sincerely,

Victor M. S. Gil

(Victor M. S. Gil)



University of Strathclyde

Professor: Patrick D. Ritchie
 Professor: Peter L. Pauson
 Professor: Manfred Gordon
 Professor: D. W. A. Sharp

Department of Pure and Applied Chemistry

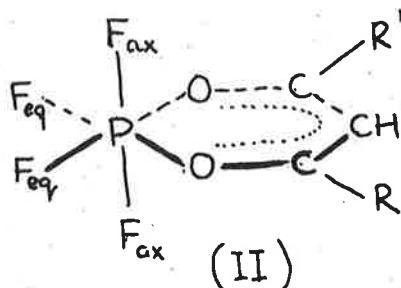
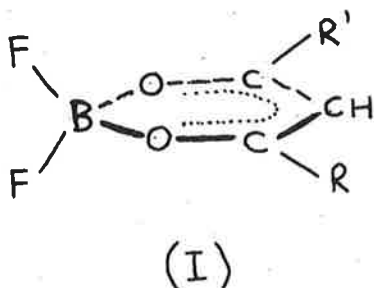
Thomas Graham Building,
 Cathedral Street, Glasgow, C.1 Tel: Bell 4400

15th February, 1966

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

Dear Barry,

In an earlier letter¹ we mentioned the proton spectra of some difluoroboron chelates (I). We have also run the fluorine spectra (at 37.64 Mc/s) of these compounds and we think that the results are worthy of comment. All the compounds show two sharp lines in the fluorine spectrum separated by an average value of 2.3 c/s or 0.06 p.p.m. and we ascribe this phenomenon to a ^{10}B - ^{11}B isotope shift. The relative intensities of the lines are consistent with this interpretation, the low field line being less intense than the high field line. This phenomenon is not new², but these compounds give perhaps the best example so far of the predicted effect³. No evidence of fluorine-boron spin-spin coupling was found and we could attribute this to either of two extreme situations: (a) a very unsymmetrical electronic environment around the boron atom, causing the quadrupole relaxation of the boron spins to be very fast (not inconceivable in view of the high dipole moments¹), or (b) a very symmetrical situation around the boron atom allowing little relaxation of the boron spins, in this case the boron-fluorine coupling constant would need to be very small. Of these we felt that (b) was the most likely and we were able to confirm this through the courtesy of Dr. Michael Green of Perkin-Elmer Ltd., Beaconsfield, who kindly ran ^{11}B spectra of (I, R = R' = Me; I, R = Me, R' = Ph; I, R = R' = Ph) at 19.3 Mc/s. All of these had relatively sharp resonance lines, that of (I, R = R' = Me) having a width at half height of 9.6 c/s compared with that of the aq. NH_4BF_4 reference line (7.7 c/s). The chemical shifts (relative to aq. NH_4BF_4) were between -2.1 and -3 p.p.m.



An extension of this work in which β -diketones were reacted with PF_5 instead of BF_3 has given us a series of compounds (II). One of these (II, $\text{R} = \text{R}' = \text{Me}$) had a fluorine spectrum consisting of 24 clearly resolved lines (28 non-combination lines are expected for the $\text{A}_2\text{B}_2\text{X}$ spectrum) and a proton spectrum with methyl and 'para' hydrogen resonances in the expected positions. The parameters for CDCl_3 solution are:- CH_3 doublet at τ 7.68, $J_{\text{PH}} 2\text{c/s}$; 'para-H' τ 3.86. $\phi F_{\text{ax}} + 53.8$; $\phi F_{\text{eq}} + 73.4$. $J_{\text{PF(ax)}} \pm 828\text{ c/s}$; $J_{\text{PF(eq)}} \pm 740\text{ c/s}$; $|J_{\text{F(ax.)F(eq.)}}| 58.2\text{ c/s}$. There was no coupling of the fluorines to any of the protons.

Yours sincerely,

Peter Bladon

Peter Bladon

Norman Brown

Norman Brown

References

1. IITNMRN, No. 70 p.30
2. J. Bacon, R. J. Gillespie, and J. W. Quail,
Canad. J. Chem., 41, 3063 (1963)
3. J. V. D. Tiers, J. Inorg. Nuclear Chem., 16, 363 (1961).

HOOKER CHEMICAL CORPORATION

Niagara Falls, New York 14302

February 15, 1966

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

Dear Dr. Shapiro:

HA-100 MODIFICATION FOR A MOUSE

I would like to submit the following as an initial comment in order to receive your IIT newsletters.

We have now been running our HA 100 since June and have had fairly good luck with it. In order to extend its usefulness to our specific applications, we have built a little MOUSE, a 1a Robertson, using relays rather than tubes and have used the same circuit for event-marking on our slave G-14 recorder. The accompanying diagram is self-explanatory. In order to utilize the MOUSE as MOUSE "B" (see Robertson), a 0.01 frequency response has been added to our filter network.

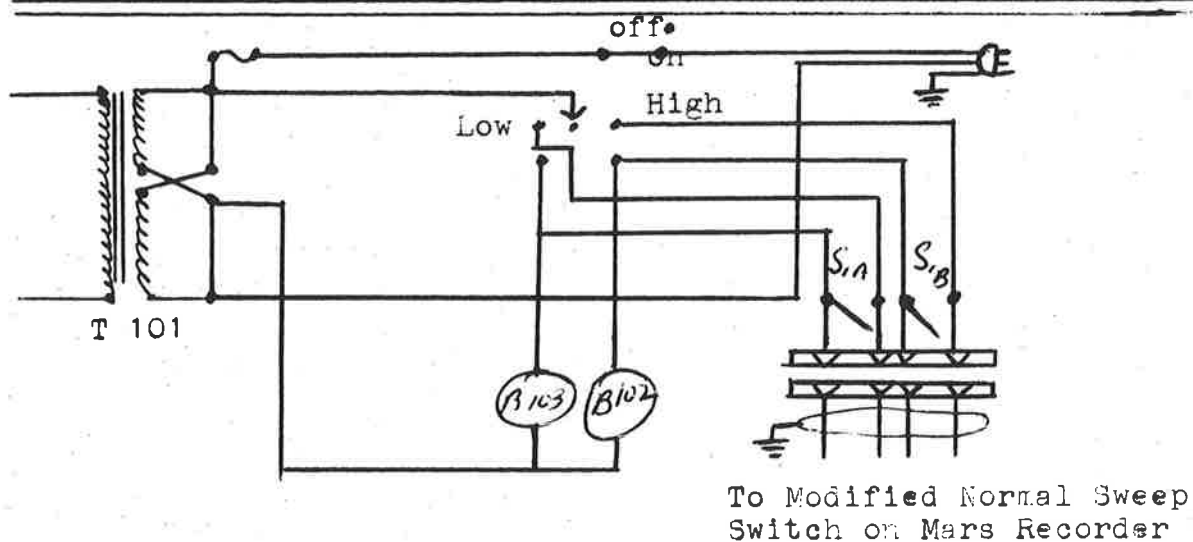
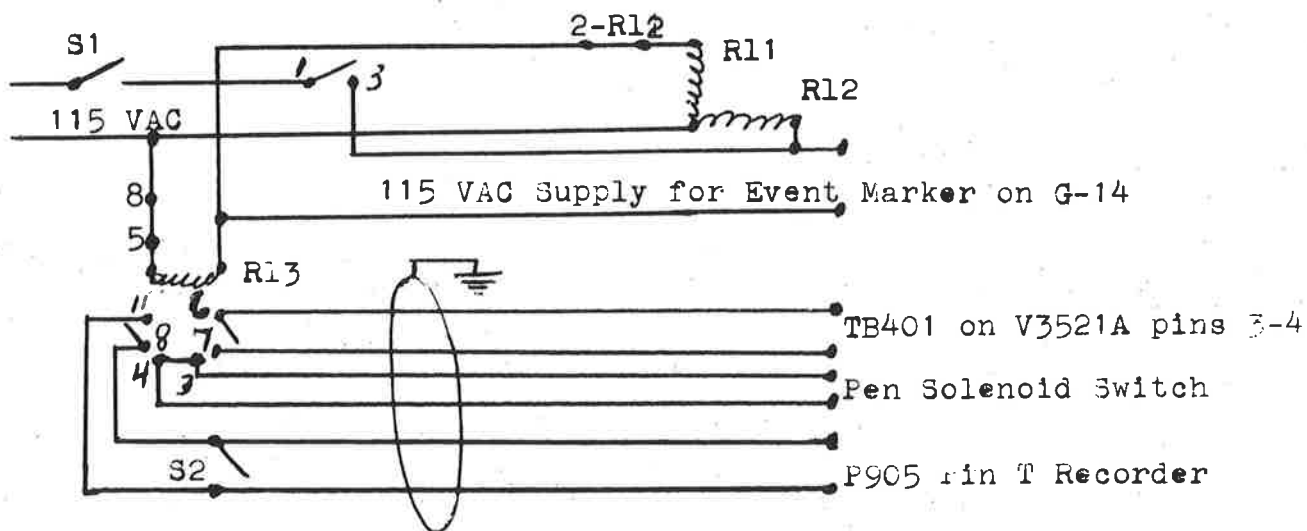
Along with hydrogen and fluorine, a great deal of our work concerns phosphorus. I would greatly appreciate hearing any comments on methods of determining P chemical shifts with a precision of ± 0.01 PPM. At present, we use a series of nine internal standards each containing a known P-H or PF coupling. This obviates the need for modulation. I would also like to receive any comments on shifts due to amplitude modulation (see Tiers).

Yours truly,


James G. Colson


Eugene Kanski

:mea



Parts for Mouse

- | | |
|-------------------------------------|--------------|
| 1 Cornell Dubilier Time Delay Relay | 3870003 |
| 1 Cornell Dubilier Time Delay Relay | 3879995 |
| 1 Phillips Advance Relay | GHP/30/115VA |
| 2 Single Pole Single Throw Switches | |

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

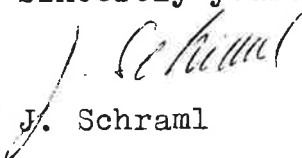
Re: Accidentally simplified spectra of vinylsilanes

Dear Professor Shapiro:

Some years ago it was noticed¹ that the P.M.R. spectrum of vinyltrichlorosilane consists only of one line (neglecting satellites), all the three vinylic protons having the same chemical shifts. Later we observed the same behaviour of protons in tris (trimethylsiloxy) vinylsilane and tri(t-butoxy) vinylsilane². The spectrum of triethoxy vinylsilane while reported³ as similarly collapsed into a single line in vinylic region, shows at 60 Mc/s some structure (see the spectrum in ⁴. This spectrum is probably analysable at 100 Mc/s with the help of our previous results² on methylethoxy-vinylsilanes and of recent work of Bishop⁵.

Recently, before leaving Harvard, I had an opportunity to measure the spectrum of vinylsilane itself ($\text{CH}_2 = \text{CHSiH}_3$) and, surprisingly, it is also very strongly coupled so that it gives at 60 Mc/s only one broadened signal of vinylic protons and a doublet of Si-H protons. Isn't it strange so many accidentally simple spectra among closely related compounds?

Sincerely yours,


 J. Schraml

References:

1. Hobgood, R. T.; Goldstein, J. H.; Reddy, G. S.; J. Chem. Phys. 35, 2038, (1961).
2. Schraml, J.; Chvalovsky, V.; Coll. Czech. Chem. Comm., in press (1966), (or the same authors in one of 1964 issues of IITNMR-N).
3. Razuvaev, G. A.; Jegorockin, A. N.; Chidekel, M. L.; Mironov, V. F.; Lzv. Akad. nauk SSSR, otd. chim. nauk 1964, 928.
4. Bhacca, N. S.; Johnson, L. F.; Shoolery, J. N.; N. M. R. Spectra Catalog, Spectrum No. 219, Varian Associates, Palo Alto, 1962.
5. Bishop, E. O.; Mol. Phys. 10, 49 (1965).

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY, CALIFORNIA 94720

February 15, 1966

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

Dear Professor Shapiro:

Proton Stabilization for P^{31} Resonance. AGC
to Reduce AM Accompanying Phase Modulation

The advent of P_4O_8 provides a P^{31} sample suitable for field-frequency locking by the conventional sideband techniques. Such stabilization is, of course, a prerequisite for successful continuous averaging. While awaiting our samples of P_4O_8 we decided to construct an internal lock system by locking on protons at 60 mcs while observing P^{31} at 24.3 mcs. Unless one employs a frequency synthesizer, which will maintain the exact H/P frequency ratio, this scheme serves primarily to compensate for slow drifts in the field. These drifts are the most troublesome sources of "horizontal" noise, as they preclude the long-term registration of high resolution spectra. The usual crystal oscillators in the RF units have sufficient stability, both short and long term, to satisfy all but the most exacting requirements.

To satisfy the requirements for double or simultaneous resonance, we resorted to double tuning of both the transmitter and receiver coils of the V-4300 probe. For convenience we use the 25 mcs receiver insert in the 60 mcs probe with the circuitry given in Figure 1. The combination $L_1C_1C_2C_3$ resonate about 28 mcs while $L_2C_4C_5$ are resonant about 55 mcs. When coupled together, the overall circuit resonates at 24.3 and 60 mcs. With care in the selection of the circuit parameters, very good proton signals are obtained while sacrificing only about 10 percent of the phosphorus signal. The transmitter circuitry is much less critical, as there is almost always an excess of power available for observation. The combination $L_3C_6C_7$ is already contained in the 60 mcs probe. L_4C_8 are in parallel resonance at 60 mcs, and prevent the 60 mcs power from leaking out; they are permanently installed in the probe body. At the lower frequency, L_4 and L_3 are in series, and are in turn shunt resonated by C_9C_{10} . This latter arrangement is quite standard for introducing power for heteronuclear decoupling.

For an arbitrary pair of crystals in the two RF oscillators, there is little probability that the ratio of frequencies will be correct to simultaneously resonate H^1 and P^{31} , so that rather high modulation frequencies may be required to achieve simultaneous re-

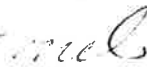
-2-

sonance. In our particular case, for 2 Kcs phosphorus sidebands, 11 Kcs proton sidebands were required. The heavy aluminum body of the V4300 probe clearly precludes field modulation at this frequency, so we employed the phase modulation capabilities of the RF units. This approach is satisfactory except for the fact that an intolerable amount of amplitude modulation accompanies the phase modulation, resulting in an audio signal large enough to totally mask the NMR signal. We have incorporated an automatic gain control into both RF units which reduces the incidental AM to tolerable levels. The circuit for this modification, which was developed by Bob Acker, is shown in Figure 2. With this modification it may be possible, in many instances, to forego field modulation in favor of phase modulation. This will have the reward that it is simpler to maintain a constant modulation index for frequency swept spectra with phase modulation than when field modulation is employed.

The u-mode paddles are somewhat frequency dependent so that it is not possible to simultaneously balance the probe to zero leakage at both frequencies. We have found it best to operate with the best balance at 25 mcs and reduce the 60 mcs receiver gain sufficiently so that the leakage is not excessive.

We have in the works some field effect transistor preamplifiers which look promising, and when evaluation is complete the results will be communicated ecumenically.

Sincerely yours,



Melvin P. Klein
Donald Phelps

MPK:el

NMR DOUBLE RESONANCE PROBE SCHEMATIC

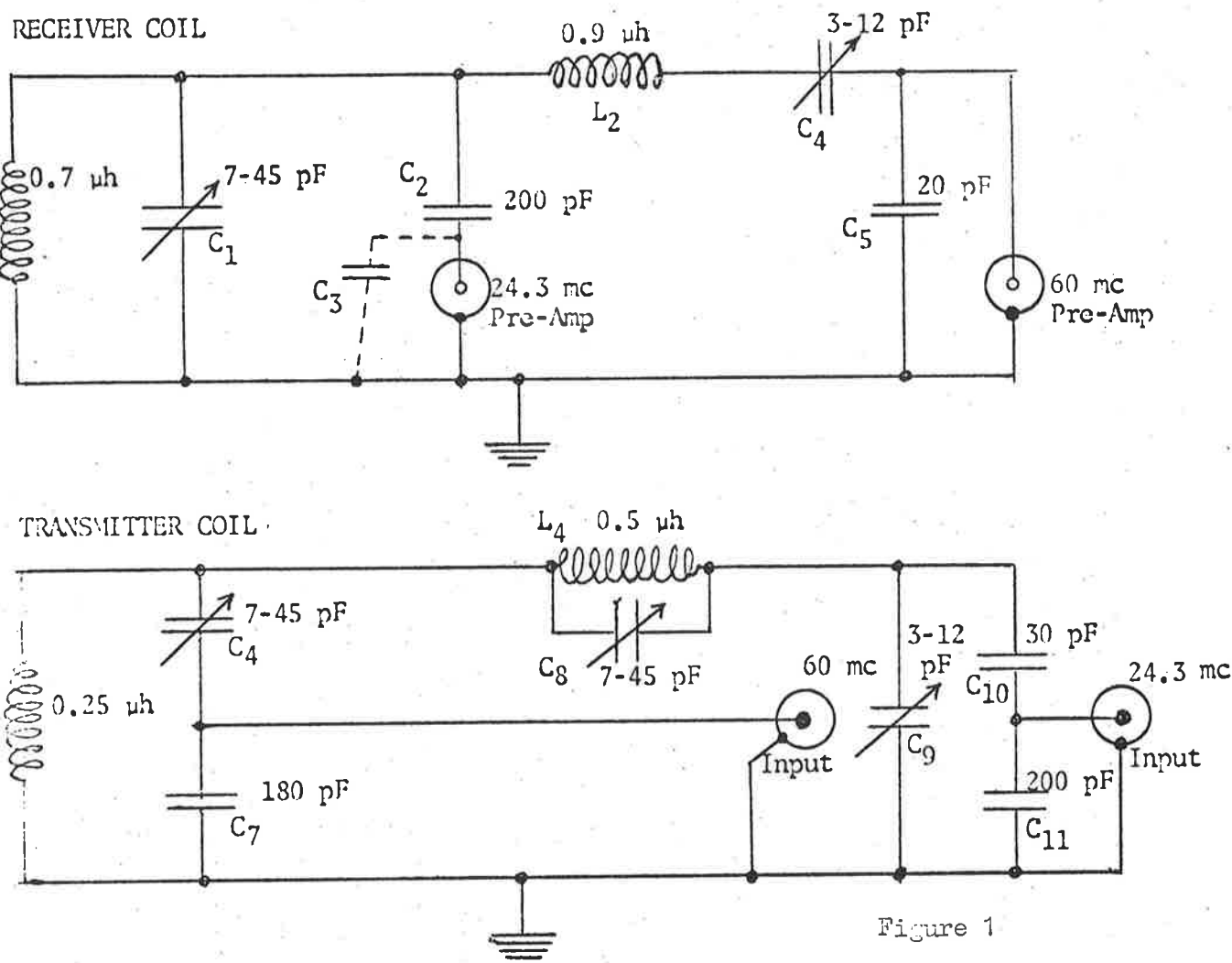


Figure 1

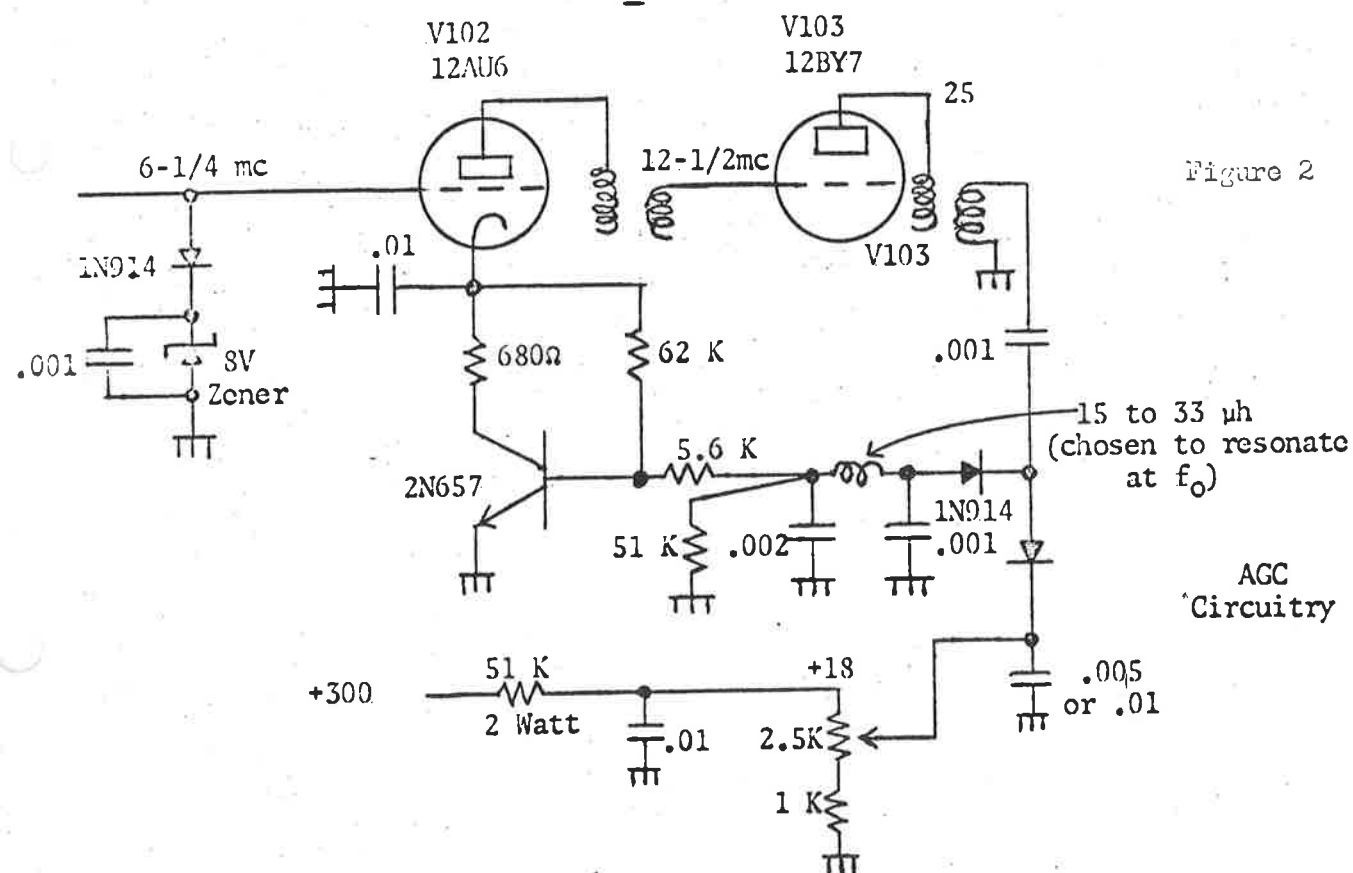


Figure 2

PERKIN-ELMER

THE PERKIN-ELMER CORPORATION

NORWALK, CONNECTICUT 06852

TELEPHONE: (203) 847-0411

CABLE: PECO-NORWALK

February 14, 1966

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

Subject: Extended Sweep Range of Perkin-Elmer Model R-10

Dear Barry:

Thank you for your dues notice. I spent some time at our laboratory in the U.K. a few months ago and have just gotten around to sorting things out.

One of the things we did recently in our efforts to improve "other nucleus" capability was to extend the sweep range of the R-10. It is now possible to produce a single, continuous calibrated spectrum of 200 ppm width as shown on the enclosed phosphorous spectrum.

Sincerely,



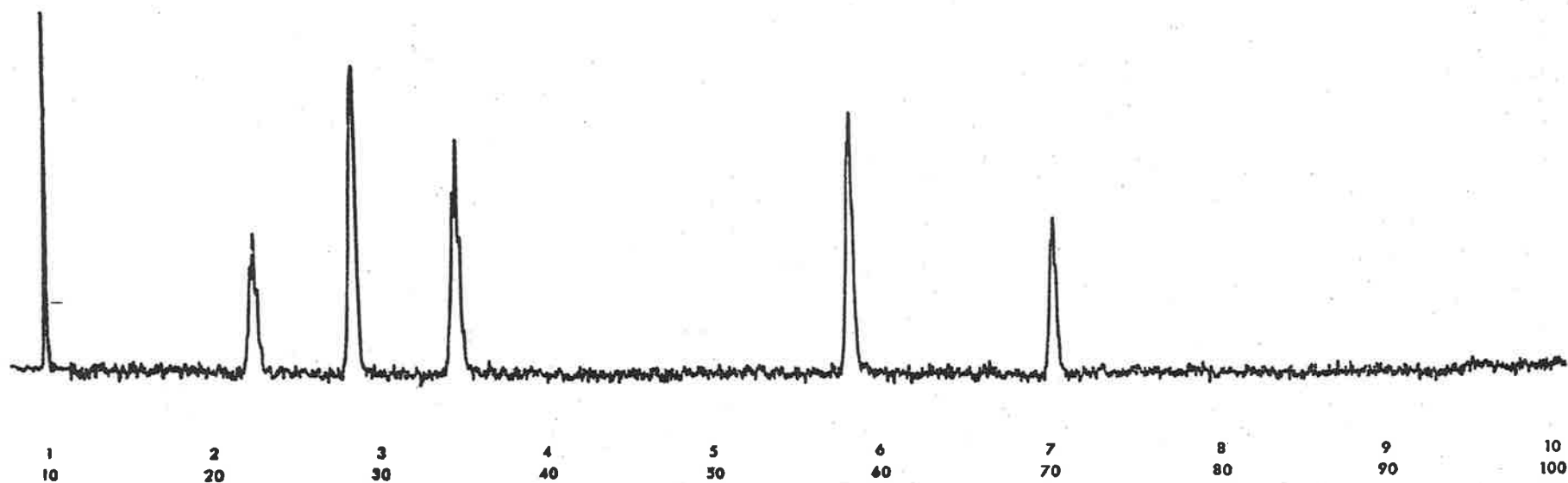
Paul A. Strauss

PAS:mjd
Enclosure

DEC. SHIFT	REF. STD.	R.F. FIELD	R.F. GAIN	REMARKS	SENSITIVITY	SWEEP RATE	TIME CONST.	SCALE FACT
	P ₄ O ₆	1mV	1/2	REFERENCE USED AS EXTERNAL STANDARD IN CAPILLARY.	NORM: 1 INT: ---	32 UNITS PER MIN	0.01 SECS 0.15 M SECS	2 ppm PER UNIT

³¹P SPECTRUM OF $(\text{EtO})_2\text{P}-\underset{\text{S}}{\underset{\text{O}}{\text{P}}}(\text{O}^i\text{Ar})_2$ CONTAINING AN IMPURITY OF $(\text{EtH})_2\text{P}-\underset{\text{S}}{\underset{\text{O}}{\text{P}}}(\text{O}^i\text{Ar})_2$

RANGE OF SCAN : 200 PPM.



MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH, PA. 15213

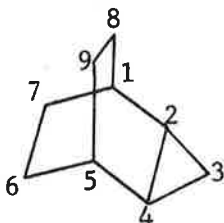
February 11, 1966

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

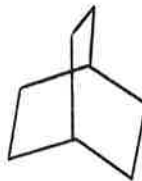
The Shielding Effect of the Cyclopropane Ring

Dear Barry:

Recently Tori and Kitahonoki reported on the shift differences between protons in several tricyclo-[3.2.2.0^{2,4}]nonane(I) derivatives and corresponding protons in the analogous bicyclo-[2.2.2]octane(II) compounds.¹



(I)



(II)

These shift differences were roughly correlated with carbon-carbon anisotropy effects in the cyclopropane ring assuming that carbon-hydrogen anisotropy effects were negligible. These authors found it necessary to use a high value for the C-C bond anisotropy ($-20 \times 10^{-30} \text{ cm}^3/\text{molecule}$) as compared with the ordinary value ($-5.5 \times 10^{-30} \text{ cm}^3/\text{molecule}$).

We felt that these shift differences might equally well correlate with the "ring current" model.²

With the help of Mr. Frederick M. Jones III of the University of Pittsburgh, we wrote a program to evaluate the shift induced by "ring current" using our previously reported data on cyclopropane.^{2,3}

MELLON INSTITUTE

Professor B. L. Shapiro

- 2 -

February 9, 1966

The results of our calculations, as well as those reported by Tori and Kitahonoki are shown in Table I.

Except for the calculations on the H_1 , H_5 protons, our results are in fairly good agreement with those of Tori and Kitahonoki. However, the observed shift values are not consistently predicted in all instances by either of the two calculations.

An examination of Dreiding models of (I) and (II) indicates that the H_1 , H_5 protons are quite likely to display large shift changes due to C-H anisotropy effects which change with molecular geometry. It therefore seems clear that neglect of C-H anisotropy effects is an oversimplification.

The "ring current" model, which works well for cyclopropane itself, * gives reasonably good predictions in these polycyclic systems, when applied to protons that are far enough removed from the cyclopropane ring so that C-H anisotropy effects are relatively small.

*The anisotropy model¹ does not fit the observed data for cyclopropane.


¹K. Tori and K. Kitahonoki, J. Am. Chem. Soc., 87, 386 (1965).

²J. J. Burke and P. C. Lauterbur, *ibid.*, 86, 1870 (1964).

³The method of Johnson and Bovey was used to make the ring current calculations.⁴

⁴C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958).

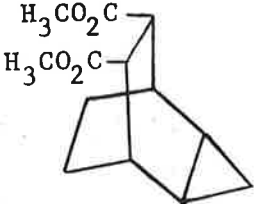
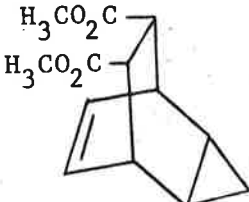
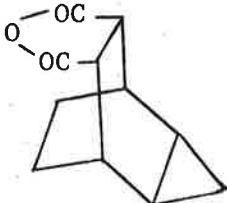
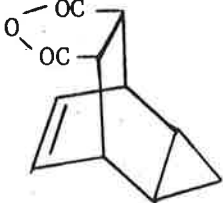
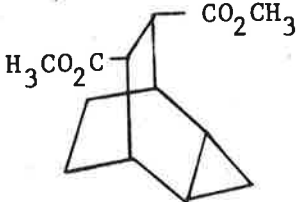
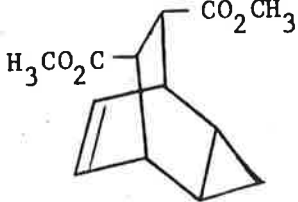
Sincerely,


John J. Burke
FELLOW

JJB:mlr

Enclosure

TABLE I

Tricyclo[3.2.2.0 ^{2,4}]nonane Compounds	Protons	(H ¹ Shift in Tricyclo[3.2.2.0 ^{2,4}]nonane - H ¹ shift in bicyclo[2.2.0]octane) (ppm)		
		Observed	Ring Current	Ref. 1
	H ₁ , H ₅	-0.30	-0.08	-0.36
	H ₈ , H ₉	-0.11	-0.19	-0.14
	H ₁ , H ₅	-0.23	-0.06	-0.28
	H ₆ , H ₇	+0.46	+0.34	+0.35
	H ₈ , H ₉	-0.09	-0.19	-0.14
	H ₁ , H ₅	-0.37	-0.08	-0.36
	H ₈ , H ₉	-0.17	-0.19	-0.14
	H ₁ , H ₅	-0.23	-0.06	-0.28
	H ₆ , H ₇	+0.43	+0.34	+0.35
	H ₈ , H ₉	-0.14	-0.19	-0.14
	H ₁ , H ₅	-0.37	-0.08	-0.36
	H ₈	-0.06	+0.08	+0.06
	H ₉	-0.15	-0.19	-0.14
	H ₆	+0.51	+0.34	+0.35
	H ₇	+0.50	+0.34	+0.35
	H ₈	-0.03	+0.08	+0.08
	H ₉	-0.14	-0.19	-0.14

Methyl Oleate Monohydroperoxide

We have recently had occasion to look at the NMR of the monohydroperoxide produced by chlorophyll-catalysed oxidation of methyl oleate. Our results indicate the following partial structure to be present. The parameters attached are those which we have deduced from single and double resonance spectra, followed by the use of LAOCOON II, parts I and II.

	p.p.m	cps
$ \begin{array}{c} \text{OOH} \\ \\ \text{H}^b - \text{C} = \text{C} - \text{CH}^d - \text{CH}_2^e - \\ \quad \quad \\ -\text{CH}_2^a \quad \quad \text{H}^c \end{array} $	δ_a 2.10 δ_b 5.60 δ_c 5.30 δ_d 4.11 δ_e 1.44	$J_{ab} \pm 6.25$ $J_{bc} \pm 15.59$ $J_{cd} \pm 8.04$ $J_{ac} \pm 0.96$ $J_{bd} \pm 1.17$

Figure I shows the single and double resonance spectra obtained using our P-E R-10 and both field (H) and frequency (ν) sweep for the spin-decoupling experiments. The letters A-D indicate which absorptions are being decoupled. The second figure shows the fit obtained between the experimental olefinic bands and the theoretical calculated using the above parameters.

G.E.HALL

G.E. Hall

D.G.ROBERTS

D.G. Roberts

Colworth House,
 Sharnbrook,
 Bedford.
 England.

Fig 1 METHYL OLEATE MONOHYDROPEROXIDE

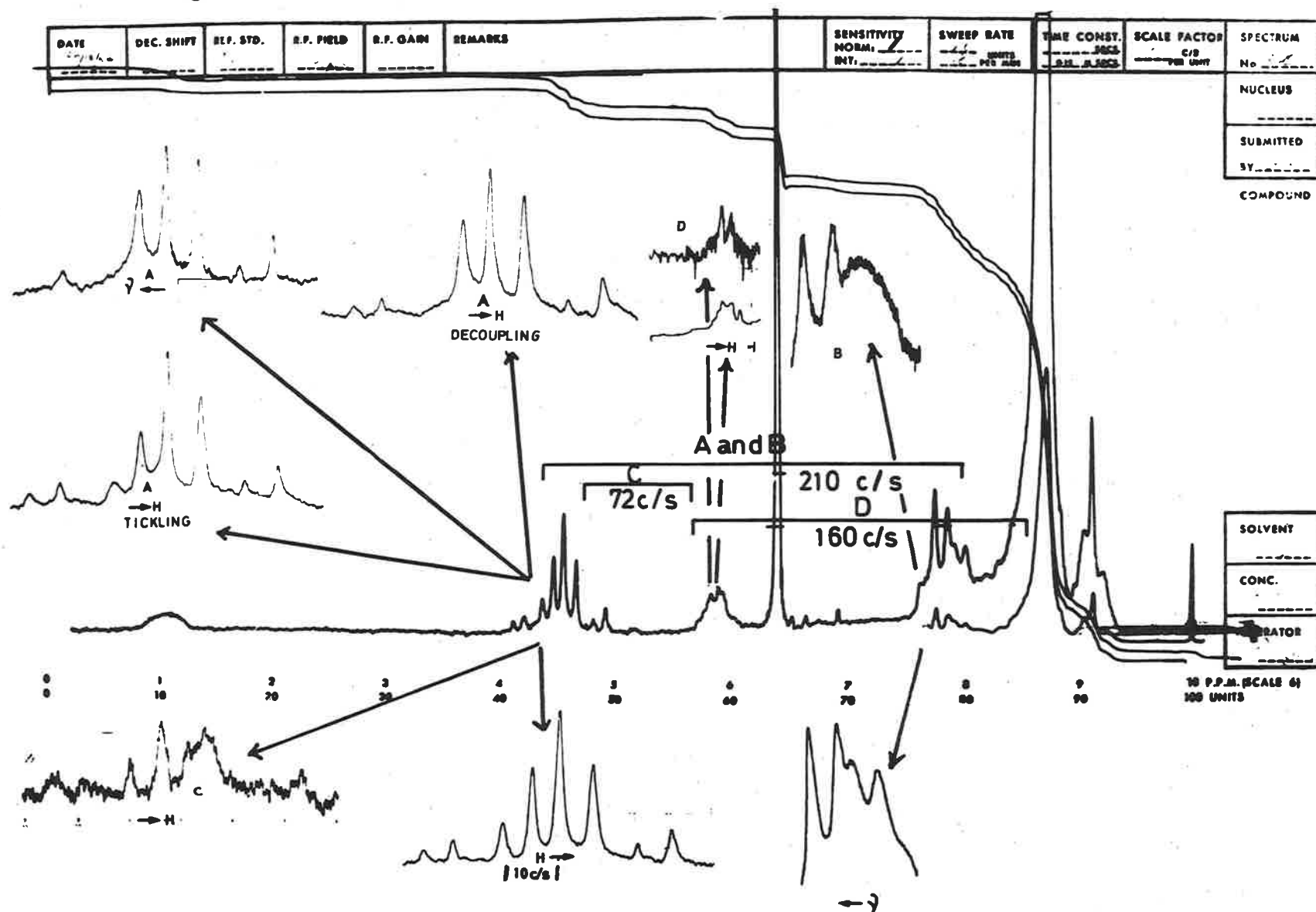
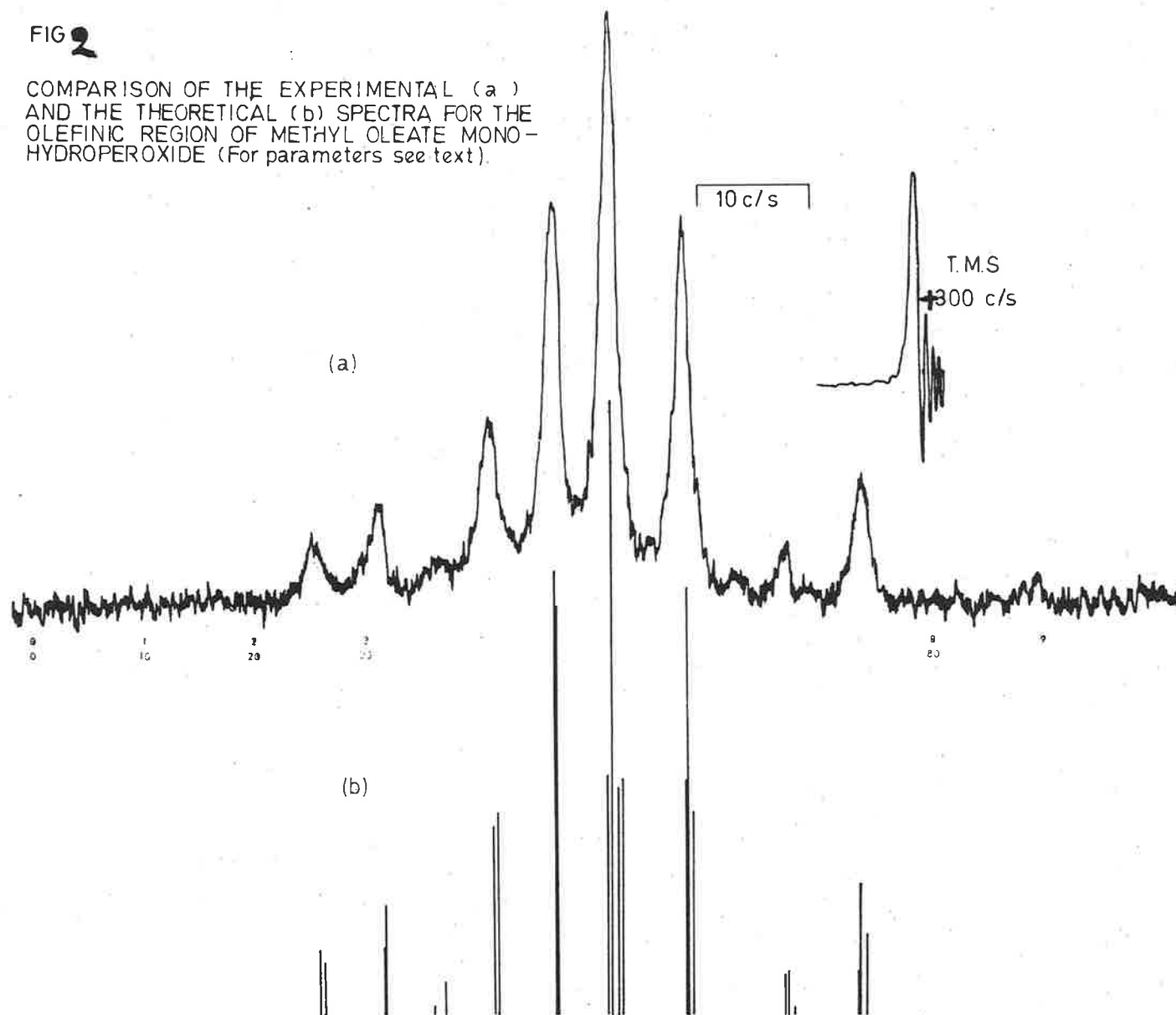


FIG 2

COMPARISON OF THE EXPERIMENTAL (a) AND THE THEORETICAL (b) SPECTRA FOR THE OLEFINIC REGION OF METHYL OLEATE MONO-HYDROPEROXIDE (For parameters see text).





ISTITUTO DI CHIMICA INDUSTRIALE
DEL POLITECNICO
PIAZZA LEONARDO DA VINCI, 32 - MILANO

MILANO, February 11, 1966

TELEF. { 292.125 - 292.126
292.105 - 106 - 107

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

Dear Professor Shapiro,

We hope that you can admit us in your mailing list. On this purpose, we send you the following short letter.

Ring Inversion in Tetrahydropyrane

We have used NMR technique for the study of the conformation of tetrahydropyrane. The NMR spectrum obtained at room temperature in 1% solution of CS_2 with a Varian HA-100 spectrometer shows two bands with complex structure centered at about 1.5 and 3.5 ppm. The intensities are 6 and 4 respectively. On the basis of the value of the chemical shift, the band downfield is assigned to the CH_2 linked to the oxygen atom. The band upfield can be assigned to the CH_2 groups in β and γ position. By irradiation at 1.5 ppm the CH_2 adjacent to the oxygen is decoupled and a clear singlet occurs at 3.46 ppm. In analogy with what has been found for cyclohexane, it is impossible at room temperature to observe the chemical shift between the equatorial and axial hydrogens. At low temperature the band at 3.46 ppm. broadens and at even lower temperatures and by irradiation at 1.5 ppm. splits into two doublets (See table).

T (°C)	-70	-75	-80	-85	-90	-95
$\nu_a - \nu_e$ (cps)	42	51	53.5	54.5	54.5	54.5

2)

The spectral pattern obtained under the conditions above is typical of a AX system with $\delta_{AX} = 0.55$ ppm and $J_{AX} = -12$ cps. The value of the observed J_{AX} is characteristic of a geminal coupling.

At the temperature in which coalescence occurs (-62°C) the rate constant calculated from the formula :

$$K = \frac{\pi}{\sqrt{2}} (\nu_a - \nu_e)$$

is 122.1 sec^{-1} .

Using Eyring's equation for ΔG^{\ddagger} a value of 10.2 kcal/mol is obtained. The value of ΔG^{\ddagger} calculated is of the same order of that of cyclohexane. It can then be concluded that the substitution of a CH_2 of the ring with an oxygen atom does not sensibly affect the conformational mobility. However, when a second oxygen atom is introduced in the ring in para position the conformational mobility is strongly enhanced as it is shown by the fact that p-dioxane at -95°C exhibits an unchanged spectrum.

(This work has been supported by the U.S. Department of Army, European Office, Contract DA 91-591-EUC-3079).

With best regards,

Your sincerely,

Ambrosio Segre Giuseppe Gatti

(A.L. Segre and G. Gatti)

THE SQUIBB INSTITUTE

FOR MEDICAL RESEARCH

NEW BRUNSWICK, N.J. 08903

February 17, 1966

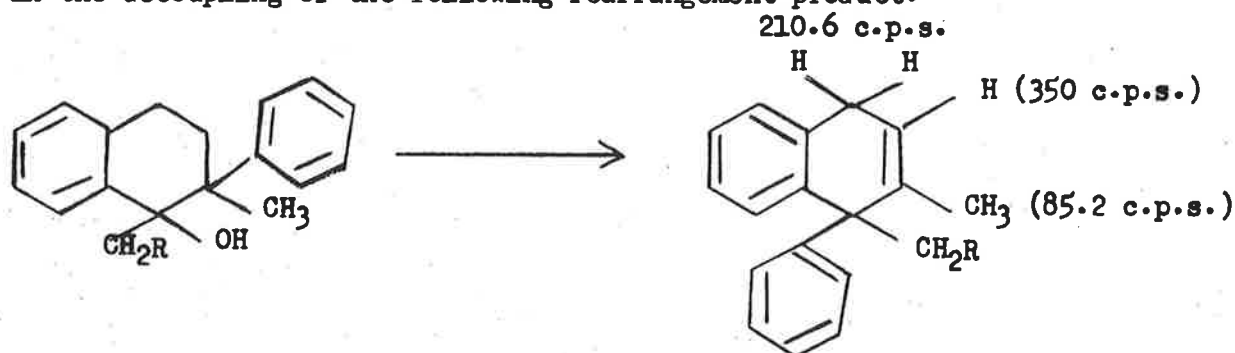
Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Ill. 60616

Subject: Spin Decoupling with the Varian A-60 System.

Dear Dr. Shapiro:

After considerable effort, the Varian field engineers have gotten our V-6058 spin decoupler to work pretty well. Some of the difficulty was attributed to the early vintage (serial No. 135) of our instrument.

An example of long-range coupling through five bonds is demonstrated in the decoupling of the following rearrangement product.



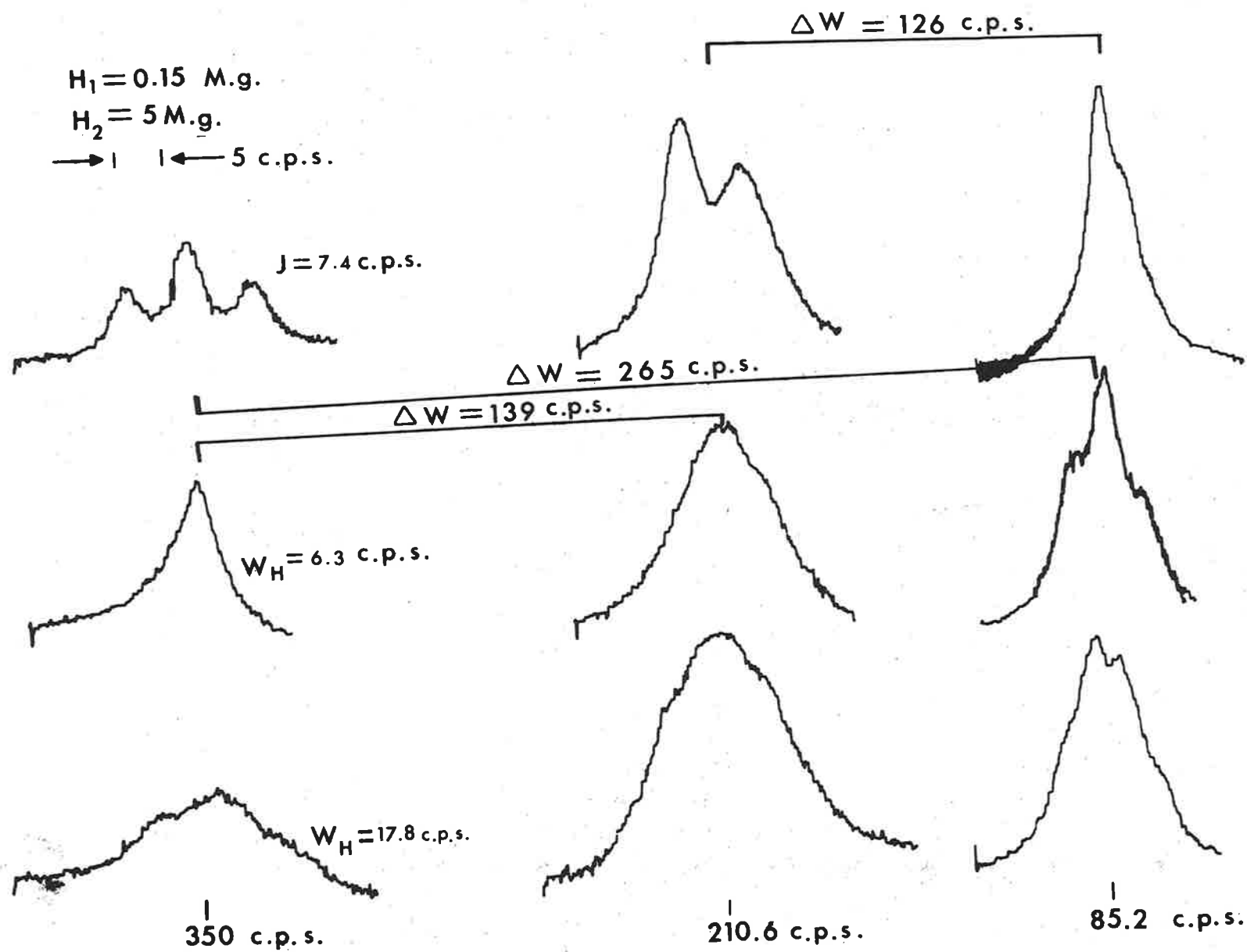
The peaks of the undecoupled protons are shown at the bottom of the curve and were scanned at a rate of 0.4 c/s per second. The decoupled spectra are shown in the upper traces. Coupling of all three proton types to each other is demonstratable from the decoupled spectra.

Yours truly,

Allen I. Cohen

Allen I. Cohen

AIC:mbg



CZECHOSLOVAK ACADEMY OF SCIENCE
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

FLEMINGOVO NÁM. 2

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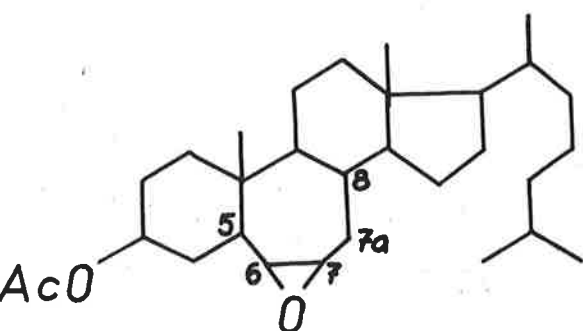
Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616
U. S. A.

February 14th, 1966

Dear Dr. Shapiro,

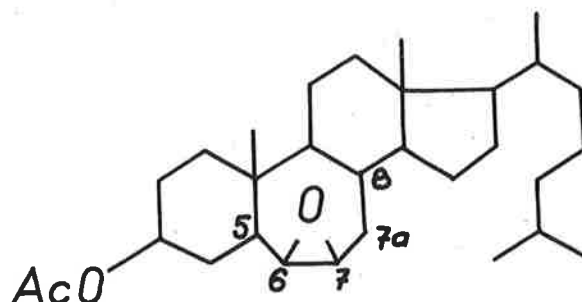
I refer to the last contribution from our Institute (Dr. J. Jonáš, No. 77, 1965) and should appreciate it if our NMR-people could be accepted again in the family of the readers of IITNN-Letters.

In connection with our investigations of conformations of the 7-membered rings we measured also the spectra of some unknown B-nor-epoxides of cholestane type. We found (first-order analysis, at HA-100, confirmed by frequency-swept decoupling experiments in CDCl_3 -solution) somewhat unusual J 's for epoxidal fragments (see table). The assignment of the two epoxides was carried out on the basis of zero vicinal couplings, by comparison with Dreiding-models. The observed J 's are interesting with regard to the dihedral-angle-dependence and ring-size effects and a more detailed discussion in connection with general-stereospecificity-rules for epoxidal couplings (see H. Buss and co-workers, Tetrahedron 21, 69, 1965) will be given in a forthcoming paper.



6 α ,7 α -oxide
"chair" conformation
of B-ring

3 α -H	5,35 τ
6 β -H	7,46 τ
7 β -H	7,02 τ
7a β -H	7,82 τ



6 β ,7 β -oxide
"chair" conformation
of B-ring

3 α -H	5,35 τ
6 α -H	7,37 τ
7 α -H	7,04 τ
7a β -H	7,68 τ

oxide	$^3J(5,6)$	$^3J(6,7)$	$^3J(7,7a\alpha)$	$^3J(7,7a\beta)$	$^2J(7a)$	$^3J(7a\beta,8)$
α, α	6,8	4,5	8,2	6,2	13,5	~ 0
β, β	~ 0	4,6	~ 0	6,4	14,2	~ 0

Yours sincerely

Z. Samek

"Trichodermin, a New Sesquiterpene Antibiotic"

W. O. Godtfredsen and S. Vangedal
Acta Chem. Scand. 19, 1088 (1965)

"The Reactions of Lignin during Sulphate Cooking. Part VIII.
The Mechanism of Splitting of β -Arylether Bonds in Phenolic
Units by White Liquor"

J. Gierer and L.-A. Smedman
Acta Chem. Scand. 19, 1103 (1965)

"Photochemical Studies. III. Photorearrangement of Methyl
Substituted Quinoline-N-oxides in Aqueous Solution and in
Potassium Bromide Discs"

O. Buchardt, J. Becher and CHR. Lohse
Acta Chem. Scand. 19, 1120 (1965)

"The Occurrence of Optically Active 3-Methyl-dodecanoic Acid
in Sperm Oil"

P. K. Christensen and R. A. Gehe
Acta Chem. Scand. 19, 1153 (1965)

"A Facile Ring-opening in the Thiophene Series"

S. Gronowitz and G. L. Borgen
Acta Chem. Scand. 19, 1180 (1965)

"Nuclear Magnetic Resonance Studies on 2-Phenyl-4-thiazolone
and Some Related Compounds"

S. Gronowitz, B. Mathiasson, R. Dahlbom and B. Holmberg,
K. A. Jensen
Acta Chem. Scand. 19, 1215 (1965)

"The Tautomeric Structures of Some Alkylsubstituted 3-
Hydroxythiophenes"

A.-B. Hornfeldt
Acta Chem. Scand. 19, 1249 (1965)

"Chemical Constituents of the Genus Dahlia"

F. Kaufmann and J. Lam
Acta Chem. Scand. 19, 1267 (1965)

"Über die Umsetzung von Boralkylen mit Isonitrilen"

G. Hesse und H. Witte
Ann. Chem. 687, 1 (1965)

"Umsetzung von Cycloalkenaminen mit Cyanallen und mit
Tetracyclon"

W. Ried und W. Kappeler
Ann. Chem. 687, 183 (1965)

"Einwirkung von Halogenen auf O- und p-Benzochinon-diazid"

W. Ried und E. Torok
Ann. Chem. 687, 232 (1965)

"Darstellung von 1,4-Dichlor-2,3-diaza-bicyclo_{2.2.2}octen-
(2) und dessen N²-Oxid"

W. Luttke und V. Schabacker
Ann. Chem. 687, 236 (1965)

"Molecular Susceptibility. The Determination of Molar Cotton-
Mouton Constants of Solutes at Infinite Dilution"

R. J. W. Le Fèvre, P. H. Williams, and J. M. Eckert
Aust. J. Chem. 18, 1133 (1965)

"Proton Magnetic Resonance Spectra of Some 1,2-Dithiole-3-
Ones and 1,2-Dithiole-3-Thinones"

L. F. C. Brown, I. D. Rae, and S. Sternhall
Aust. J. Chem. 18, 1211 (1965)

"Studies of Aromaticity by Nuclear Magnetic Resonance
Spectroscopy"

L. M. Jackman, Q. N. Porter, and G. R. Underwood
Aust. J. Chem. 18, 1221 (1965)

"Variations of the Lipid Phase of Living Microorganisms
during the Transport Process"

J. Cerbon
Biochim. Biophys. Acta 102, 449 (1965)

"The Proton Magnetic Resonance Spectra of Phenyltin Chlorides"

L. Verdonck, G. P. Van der Kelen
Bull. Soc. Chim. Belges 74, 361 (1965)

"Nuclear Magnetic Resonance Spectral Observations on the
Glycol-Scission of Deuterated D-Glucose"

W. Mackie and A. S. Perlin
Can. J. Chem. 43, 2645 (1965)

"Proton Magnetic Resonance Spectra of D-Glucopyranose
Polymers"

C. A. Glass
Can. J. Chem. 43, 2652 (1965)

"The Amino Proton Shifts of Some Substituted Anilines in
Cyclohexane"

T. Yonemoto, W. F. Reynolds, H. M. Hutton and T. Schaefer
Can. J. Chem. 43, 2668 (1965)

"Photo-Addition of N-Nitrosodialkylamines to Cyclohexene"

Y. L. Chow
Can. J. Chem. 43, 2711 (1965)

"Studies in the Pyrroline Series. V. ¹3,3-Dimethyl-1-
Pyrroline-1-Oxide"

R. Bonnett, S. C. Ho, and J. A. Raleigh
Can. J. Chem. 43, 2717 (1965)

"The Preparation of a Trivinyl Carbonium Ion"

T. S. Sorensen
Can. J. Chem. 43, 2744 (1965)

"Radiation-Induced Changes in the Unsaturation of Poly-
isoprene"

M. A. Golub and J. Danon
Can. J. Chem. 43, 2772 (1965)

"The Stereochemistry of the Tetrahydropimaric Acids"

J. W. ApSimon, P. V. Demarco, and J. Lemke
Can. J. Chem. 43, 2793 (1965)

"Correlation of Ethylenic Proton Coupling Constants with
the Electronegativity of Substituents. Interpretation of
the Deviations of Bromo and Iodo Substituents"

F. Hruska, C. Kotowycz, and T. Schaefer
Can. J. Chem. 43, 2827 (1965)

"Steroids and Related Natural Products. XXV. Photochemical
Transformation of 3 β -Nitrito-5 α -Lanostane"

G. R. Pettit, R. E. Kadunce, P. Sunder-Plassmann, and J.
Oocolowitz
Can. J. Chem. 43, 2872 (1965)

"Coordination Compounds of Olefins with Anhydrous Silver
Salts. II. An Infrared and Nuclear Magnetic Resonance
Investigation of Silver Tetrafluoroborate - Olefin
Complexes"

H. W. Quinn, J. S. McIntyre, and D. J. Peterson
Can. J. Chem. 43, 2896 (1965)

"¹³C-¹H for Substituted Aldehydes"

R. M. Hamaker
Can. J. Chem. 43, 2916 (1965)

"1,2-O-Isopropylidene- α -D-Glucofuranose-5-d and -5,6,6'-d₃1"

W. Mackie and A. S. Perlin
Can. J. Chem. 43, 2921 (1965)

"Bisaddukte aus Nitrilimin und Carbodiimiden"
R. Huisgen, R. Grashey, R. Kunz, G. Wallbillich und
E. Aufderhaar
Chem. Ber. 98, 2174 (1965)

"Die Saureisomerisierung von Methylen-cyclobutenen mit
Allylseitenketten"
R. Criegee, H. Hofmeister und G. Bolz
Chem. Ber. 98, 2327 (1965)

"Vergleichende spektrometrische Untersuchungen an α , β -
ungesättigten Steroidketonen"
H. Hoffmeister, C. Rufer, H. H. Keller, H. Schairer und
P. Karlson
Chem. Ber. 98, 2361 (1965)

"N.m.r. Studies of Rate Processes and Conformations. A
Double Rate Process"
J. C. Breliere and J. M. Lehn
Chem. Commun. 426 (1965)

"A Novel Substituent Effect in Vicinal Proton-Proton Couplings"
R. J. Abraham and W. A. Thomas
Chem. Commun. 431 (1965)

"Absolute Configuration of Some Derivatives of 1,4-Oxathian
S-Oxide"
K. W. Buck, A. B. Foster, A. R. Perry, and J. M. Weber
Chem. Commun. 433 (1965)

"The Condensation of Acetone with Urea: The Formation of a
Spirobishexahydropyrimidine"
H. H. Hatt and A. C. K. Triffett
Chem. Commun. 439 (1965)

"Carborane Analogues of Cobalticinium Ion"
M. F. Hawthorne and T. D. Andrews
Chem. Commun. 443 (1965)

"The Hexamethylstilbene-Hexamethyldihydrophenanthrene Inter-
conversion, an Example of a Reversible Photocyclization"
K. A. Muszkat, D. Gegiou, and E. Fischer
Chem. Commun. 447 (1965)

"Synthesis of 2,5-Di-t-butylpyrrole and of 2,3,5-Tri-t-butyl-
pyrrole"
R. Ramasseul and A. Rassat
Chem. Commun. 453 (1965)

"Long-range Coupling in the Proton Magnetic Resonance Spectra
of 1,4-Dihydrobenzenes"
L. J. Durham and J. Studebaker
Chem. Commun. 456 (1965)

"Magnetic Non-equivalence of the Epoxide Ring (C-6 and C-7)
Protons of Scopolamine"
S. R. Johns and J. A. Lambertson
Chem. Commun. 458 (1965)

"Spectroscopic Study of Keto-Enol Tautomerization in Phenol
Derivatives"
G. O. Dudek and E. P. Dudek
Chem. Commun. 464 (1965)

"Heterocyclic Studies. The Photoisomerization of 2,3-Dihydro-
5-methyl-6-phenyl-4H-1,2-diazepin-4-one and Derivatives"
W. J. Theuer and J. A. Moore
Chem. Commun. 468 (1965)

"Reactions of Enamines. XIII. Tautomerism of Enamines"
O. Cervinka and L. Hub
Collection Czech. Chem. Commun. 30, 3111

"Effet de température et de dilution sur la polarisation
nucléaire dynamique des noyaux de fluor"
J.-. Imbaud et G. Berthet
Compt. Rend. 261, 953 (1965)

"Étude par résonance magnétique nucléaire d'échanges d'ions
intervenant dans le mécanisme de l'effet «push pull» "
S. Kinastowski, René Lucas
Compt. Rend. 261, 961 (1965)

"Étude d'un spectromètre sensible à de faibles champs
statiques transversaux"
R. Ribotta et H. Ottavi
Compt. Rendus 261, 1670 (1965)

"Réduction des gem-dibromométhylène-cyclopropanes par le
sodium et le méthanol"
A. Bézaguet et M. Bertrand
Compt. Rend. 261, 1695 (1965)

"Synthèse d'amino-5 pentanol-1 ones-4 N-disubstituées"
R. Aguilera et G. Descotes
Compt. Rend. 261, 1702 (1965)

"Dimérisation du chloro-2 butadiène-2 . 3 oate d'éthyle"
R. Vessière et M. Verny
Compt. Rend. 261, 1868 (1965)

"Constantes de couplage $^{13}\text{C}-\text{H}$ en résonance magnétique
nucléaire et angles de valence, dans la série du thiazole"
E.-J. Vincent et J. Metzger
Compt. Rend. 261, 1964 (1965)

"Analyse itérative, sur calculateur électronique, des
spectres de résonance magnétique nucléaire."
B. Brailion et J. Barret
Compt. Rend. 261, 1967 (1965)

"Composés acétyleniques de l'aluminium"
H. Demarne
Compt. Rend. 261, 1992 (1965)

"Dérives acétyleniques de l'arsenic"
J. Benaim
Compt. Rend. 261, 1996 (1965)

"Analyse spectrale d'effets non linéaires dans des
transitions à plusieurs quanta"
J. Pommier
Compt. Rend. 261, 2091 (1965)

"Darstellung substituierter 2,6-Dioxo-2,3,4,6-tetrahydro-
pyrido[2,1-a]isoindole"
M. Viscontini, W. Kaiser und H. A. Leidner
Helv. Chim. Acta 48, 1221 (1965)

"Atropisomerie in der Dibenzo[a,d]cyclohepten-Reihe"
A. Ebnother, E. Jucker and A. Stoll
Helv. Chim. Acta 48, 1237 (1965)

"Zur Kenntnis der Hexaalkylbenzole. Seitenkettenreaktionen
des Hexa-(n-propyl)-benzols"
H. Hopff und A. Gati
Helv. Chim. Acta 48, 1289 (1965)

"Über die sogenannte anomale Claisen-Unlagerung"
A. Habich, R. Barner, W. von Philipsborn und H. Schmid
Helv. Chim. Acta 48, 1297 (1965)

"Konstellation und Solvolysengeschwindigkeit der 1-Decalyl-p-toluolsulfonate"

C. A. Grob und S. W. Tam
Helv. Chim. Acta 48, 1317 (1965)

"NMR.-Untersuchungen an einfachen Furenidonsystemen. Synthese des unsubstituierten Δ^2 -Furenidons-(4) (α -Hydoxyfuran)"

A. Hofmann, W. v. Philipsborn und C. H. Eugster
Helv. Chim. Acta 48, 1322 (1965)

"Über die Chemie des Vitamins K. Totalsynthese und Stereochemie von trans- und cis-(7'R,11'R)-Phyllochinon und verwandten Verbindungen)

L. M. Jackman, R. Ruegg, G. Ryser, C. von Planta, U. Gloor, H. Mayer, P. Schudel, M. Kofler und O. Isler
Helv. Chim. Acta 48, 1332 (1965)

"Alstophyllin, ein neues Indolalkaloid aus Alstonia macrophylla Wall"

T. Kishi, M. Hesse, C. W. Gemenden, W. I. Taylor und H. Schmid
Helv. Chim. Acta 48, 1349 (1965)

"Photoreaktionen von Acridin und Acridinabkömmlingen sowie von Arylketonen mit Methanol"

H. Goth, P. Cerutti und H. Schmid
Helv. Chim. Acta 48, 1395 (1965)

"Thionation of 3- β -N-Diethylaminoethyl-4-quinazalone: Isolation of Thiopegene-9,4-thione as a Byproduct"

A. P. Bhaduri, N. M. Khanna und M. L. Dhar
Indian J. Chem. 3, 284 (1965)

"Estimation of the Drift in the High Field in Nuclear Magnetic Resonance Experiments"

S. Visweswaramurthy
Indian J. Pure & Appl. Phys. 3, 220 (1965)

"Oxygen Exchange between Periodate and Water Studied by ^{17}O Nuclear Magnetic Resonance"

I. Pecht und Z. Luz
J. Am. Chem. Soc. 87, 4068 (1965)

"A New Boron Hydride, B_8H_{18} "

J. Dobson, D. Gaines, and R. Schaeffer
J. Am. Chem. Soc. 87, 4072 (1965)

"Organic Syntheses by Means of Noble Metal Compounds. XIII. Carbonylation of Butadiene- and Isoprene-Palladium Chloride Complexes"

J. Tsuji und S. Hosaka
J. Am. Chem. Soc. 87, 4075 (1965)

"Nitrogen-15 Magnetic Resonance Spectroscopy. V. Oxygen-Nitrogen Compounds"

J. B. Lambert und J. D. Roberts
J. Am. Chem. Soc. 87, 4087 (1965)

"Nuclear Magnetic Resonance Spectroscopy. Magnetic Non-equivalence Due to Slow Inversion in Amines"

D. L. Griffith und J. D. Roberts
J. Am. Chem. Soc. 87, 4089 (1965)

"Spin-Echo Nuclear Magnetic Resonance Studies of Chemical Exchange. VI. Rearrangement of Bullvalene and of its Silver Nitrate Complex"

A. Allerhand und H. S. Gutowsky
J. Am. Chem. Soc. 87, 4092 (1965)

"Cycloadditions. III. Reactions of Δ^2 -1,2,3-Triazolines with Phenyl Isocyanate and Phenyl Isothiocyanate"

J. E. Baldwin, G. V. Kaiser, und J. A. Romersberger
J. Am. Chem. Soc. 87, 4114 (1965)

"The Synthesis and the Decomposition of cis- and trans-3,5-Bis(p-anisyl)-1-pyrazolines"

C. G. Overberger, N. Weinshenker, und J-P. Anselme
J. Am. Chem. Soc. 87, 4119 (1965)

"Preparation and Chemistry of α -Chloroalkyllithium Compounds. Their Role as Carbenoid Intermediates"

D. F. Hoeg, D. I. Lusk, und A. L. Crumbliss
J. Am. Chem. Soc. 87, 4147 (1965)

"Studies in Phosphinemethylene Chemistry. XII. Triphenylphosphine-t-butylmethylene and Triphenylphosphine-trimethylsilylmethylene"

D. Seyferth und G. Singh
J. Am. Chem. Soc. 87, 4156 (1965)

"Synthesis and Reactivity in the Benzocalicene Series"

A. S. Kende und P. T. Izzo
J. Am. Chem. Soc. 87, 4162 (1965)

"Reactions in Frozen Systems. II. Enhanced Hydroxylaminolysis of Simple Amides"

H. E. Alburn und N. H. Grant
J. Am. Chem. Soc. 87, 4174 (1965)

"Photochemical Degradation of Flavins. II. The Mechanisms of Alkaline Hydrolysis of 6,7-Dimethyl-9-formylmethylisoxazine"

P.-S. Song, E. C. Smith und D. E. Metzler
J. Am. Chem. Soc. 87, 4181 (1965)

"Strained Systems. IV. The Tricyclo[1.1.0.0^{2,4}]butane System"

S. Masamune, M. Kato
J. Am. Chem. Soc. 87, 4190 (1965)

"Facile Addition of a Grignard Reagent to an Unconjugated Ethylenic Linkage"

J. J. Eisch, G. R. Husk
J. Am. Chem. Soc. 87, 4194 (1965)

"Ceanothine-B, a Naturally Occurring Oxazacyclononadiene"

E. W. Warnhoff, J. C. N. Ma, P. Reynolds-Warnhoff
J. Am. Chem. Soc. 87, 4198 (1965)

"A New 1- α -Amino Acid from Lepidoptera"

K. S. Brown, Jr.
J. Am. Chem. Soc. 87, 4202 (1965)

"Photochemical Transformations of a β,γ -Epoxy Ketone"

A. Padwa
J. Am. Chem. Soc. 87, 4205 (1965)

"Halogen Addition to Bicyclo[2.1.0]pentane"

R. T. LaLonde
J. Am. Chem. Soc. 87, 4217 (1965)

"Classification of Alcohols by Nuclear Magnetic Resonance Spectroscopy. A Cautionary Note"

J. G. Traynham, G. A. Knesel
J. Am. Chem. Soc. 87, 4220 (1965)

"Synthetic Routes to Emetine. Revised Structure of a Lactonic Intermediate"

J. A. Weisbach, J. L. Kirkpatrick, E. L. Anderson, K. Williams, B. Douglas, und H. Rapoport
J. Am. Chem. Soc. 87, 4221 (1965)

"The Halogenation of Diazomethane. Study of the Reactivities of Carbenes Derived from Halodiazomethanes"

G. L. Closs und J. J. Coyle
J. Amer. Chem. Soc. 87, 4270 (1965)

"Chlorination Studies of Unsaturated Materials in Nonpolar Media. IV. The Ionic Pathway for alkylated Ethylenes. Products and Relative Reactivities"

M. L. Poutsma
J. Am. Chem. Soc. 87, 4285 (1965)

"Chlorination Studies of Unsaturated Materials in Nonpolar Media. V. Norbornene and Norticyclene"

M. L. Poutsma
J. Am. Chem. Soc. 87, 4293 (1965)

"Tetracyclo[3.3.0.0²,8.0⁴,6]octan-3-one. Preparation, Characterization, and Physical and Chemical Properties"

N. A. LeBel and R. N. Liesemer
J. Am. Chem. Soc. 87, 4301 (1965)

"The Polycondensation of Phenylsilanetriol"

J. F. Brown, Jr.
J. Am. Chem. Soc. 87, 4317 (1965)

"N-Fluoroalkylamines. I. Difluoroazomethines"

W. A. Sheppard
J. Am. Chem. Soc. 87, 4338 (1965)

"N-Fluoroalkylamines. II. N,N-Bis(trifluoromethyl)anilines"

F. S. Fawcett and W. A. Sheppard
J. Am. Chem. Soc. 87, 4341 (1965)

"Curtius and Lossen Rearrangements. I. The Benzenesulfonyl System"

W. Lwowski and E. Scheiffele
J. Am. Chem. Soc. 87, 4359 (1965)

"Epoxidation Studies. III. The Peracid Oxidation of Substituted Benzoylimines"

A. Padwa
J. Am. Chem. Soc. 87, 4365 (1965)

"Multiple Long-Range Couplings between Protons in the Bicyclo [3.2.1]octene-2 Skeleton"

C. W. Jefford, J. Gunsher, and K. C. Ramey
J. Am. Chem. Soc. 87, 4384 (1965)

"B-Phenyl-1,2-dicarboclovododecaborane(12) from B₉C₂H₁₁⁻² through an Insertion Reaction"

M. F. Hawthorne, P. A. Wegner
J. Am. Chem. Soc. 87, 4392 (1965)

"3a,6a-Diazapentalene (Pyrazolo[1,2-a]pyrazole)

S. Trofimenko
J. Am. Chem. Soc. 87, 4393 (1965)

"Long-Range Mercury-199-Proton Spin-Spin Coupling. I. Substituent Effects in Acyclic Systems"

E. F. Kiefer and W. L. Waters
J. Am. Chem. Soc. 87, 4401 (1965)

"Two Diisotactic Processes in the Anionic Polymerization of Isopropyl Acrylate with Phenylmagnesium Bromide"

T. Yoshino, and K. Kuno
J. Am. Chem. Soc. 87, 4404 (1965)

"A Proton Magnetic Resonance Study of Some Dialkylamino-phosphorus Derivatives"

A. H. Cowley and R. P. Pinnell
J. Am. Chem. Soc. 87, 4454 (1965)

"Magnetic Nonequivalence in Derivatives of α -Hydroxy Acids"

N. S. Bowman, D. E. Rice, and B. R. Switzer
J. Am. Chem. Soc. 87, 4477 (1965)

"The Facile Isomerization and Dimerization of 1,2,6-Cyclo-nonatriene"

K. G. Untch and D. J. Martin
J. Am. Chem. Soc. 87, 4501 (1965)

"Thermally Induced Reactions of Some Novel Allenes"

L. Skattebøl and S. Solomon
J. Am. Chem. Soc. 87, 4506 (1965)

"Cycloadditions. IV. Mechanism of the Photoisomerization of cis,cis-1,5-Cyclooctatriene to Tricyclo[3.3.0.0²,6]octane"

J. E. Baldwin and R. H. Greeley
J. Am. Chem. Soc. 87, 4514 (1965)

"The sym-Dibenzcyclooctatetraene Anion Radical and Dianion"

T. J. Katz, M. Yoshida, and L. C. Siew
J. Am. Chem. Soc. 87, 4516 (1965)

"Carbonium Ions. XIX. The Intense Conjugation in Cyclopropyl Carbonium Ions"

N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner
J. Am. Chem. Soc. 87, 4533 (1965)

"Nucleophilic Displacements on Three-Membered Rings"

J. A. Deyrup and R. B. Greenwald
J. Am. Chem. Soc. 87, 4538 (1965)

"The Synthesis and Spectra of α,β -Unsaturated Aliphatic Azo Compounds"

B. T. Gillis and J. D. Hagarty
J. Am. Chem. Soc. 87, 4576 (1965)

"The Preparation of Alkylhydroquinones by the Reductive Alkylation of Quinones with Trialkylboranes"

M. F. Hawthorne and M. Reintjes
J. Am. Chem. Soc. 87, 4585 (1965)

"Some Radical Exchange Reactions during Nitrite Ester Photolysis"

M. Akhtar, D. H. R. Barton, and P. G. Sammes
J. Am. Chem. Soc. 87, 4601 (1965)

"Glutarimide Antibiotics. IX. The Stereochemistry of the Dihydrocycloheximides and the Configuration of the Hydroxyl Group of Cycloheximide"

F. Johnson, N. A. Starkovsky, and A. A. Carlson
J. Am. Chem. Soc. 87, 4612 (1965)

"Steroids. CCLXXXIII. Stereochemically Controlled Simmons-Smith Methylenation of Homoallylic Alcohols of Low Reactivity. A New Synthesis of 10 α -Testosterone"

R. Ginsig and A. D. Cross
J. Am. Chem. Soc. 87, 4629 (1965)

"Long-Range Effects of Acyl Groups in the Solvolysis of Glycofuranosyl Halides. The Synthesis of 2,3-Di-*O*-benzyl-5-*O*-*p*-nitrobenzoyl- α -D-arabinofuranosyl Chloride and 2-*O*-Benzyl-3,5-di-*O*-*p*-nitrobenzoyl- α -D-arabinofuranosyl Chloride"

C. P. J. Glaudemans and H. G. Fletcher, Jr.
J. Am. Chem. Soc. 87, 4636 (1965)

"Selective Labilizing of α -Hydrogen Atoms by Chelation of α -Aminocarboxylic Acids"

D. H. Williams, D. H. Busch
J. Am. Chem. Soc. 87, 4644 (1965)

"Novel Products from the Reaction of Benzyne with Anthracenes"

B. H. Klanderma
J. Am. Chem. Soc. 87, 4649 (1965)

"Oxidation of Carbohydrates with Dimethyl Sulfoxide Containing Phosphorus Pentoxide"

K. Onodera, S. Hirano, N. Kashimura
J. Am. Chem. Soc. 87, 4651 (1965)

"A Novel Photochemical Cycloaddition Reaction of Benzene"

R. Srinivasan, K. A. Hill
J. Am. Chem. Soc. 87, 4653 (1965)

"Microbiological Synthesis of Aldosterone from Corticosterone"
E. Kondo, T. Mitsugi, K. Tori
J. Am. Chem. Soc. 87, 4655 (1965)

"Acid-Catalyzed Reactions of Phenols with Dimethyl Sulfoxide and Dicyclohexylcarbodiimide"
M. G. Burdon J. G. Moffatt
J. Am. Chem. Soc. 87, 4656 (1965)

"The Reactions of Phenols with Oxysulfonium Cations"
K. E. Pfitzner, J. P. Marino, R. A. Olofson
J. Am. Chem. Soc. 87, 4658 (1965)

"The Structures of the Spiramycins and Magnamycin"
M. E. Kuehne and Barrett W. Benson
J. Am. Chem. Soc. 87, 4660 (1965)

"The Structure of Magnamycin"
R. B. Woodward, L. S. Weiler, P. C. Dutta
J. Am. Chem. Soc. 87, 4662 (1965)

"Polymerization of Methyl Methacrylate under Ultrasonic Irradiation"
Z. Osawa and N. Igarashi
J. Appl. Polymer Sci. 9, 3171 (1965)

"Cis-Trans Isomers of Methyl Substituted Fluorocinnamic and 5-(O-,m-, and p-Fluorophenyl) pentadienoic Acids"
R. H. Wiley and H. C. Van der Plas
J. Chem. Engr. Data 10, 72 (1965)

"Cis-2-Oxa-3a,7a-dihydroindane (cis-3a,7a-Dihydrophthalan)"
L. F. Hatch, G. Bachmann, and T. E. Sample, Jr.
J. Chem. Engr. Data 10, 74 (1965)

"Nuclear Magnetic Shielding of Alkali Ions in Crystals and Dilute Aqueous Solutions"
D. Ikenberry and T. P. Das
J. Chem. Phys. 43, 2199 (1965)

"Strong Coupling in Nuclear Resonance Spectra. V. Perturbation Theory for the Extreme Coupling Case"
J. S. Waugh and E. L. Wei
J. Chem. Phys. 43, 2308 (1965)

"Concerning Structural Models for Water and Chemical-Shift Data"
N. Muller
J. Chem. Phys. 43, 2555 (1965)

"On the Detectability of the Quadratic NMR Electric-Field Effect in Liquids"
J. M. Deutch and J. S. Waugh
J. Chem. Phys. 43, 2568 (1965)

"On the Proton Knight Shift in Metallic VH"
D. S. Schreiber and L. D. Graham
J. Chem. Phys. 43, 2573 (1965)

"Buxus Alkaloids. Part IV. Isolation and Structure Elucidation of Eight New Alkaloids, Cyclomicrophylline-A, -B, and -C, Dihydrocyclocymicrophylline-A and -F, Cyclomicrophyllidine-A, Dihydrocyclocymicrophyllidine-A, and Cyclomicrobuxine, from B. microphylla Sieb. et Zucc. Var. suffruticosa Makino"
T. Nakano and S. Terao
J. Chem. Soc. 4512 (1965)

"The Janovsky Reaction"
R. J. Pollitt and B. C. Saunders
J. Chem. Soc. 4615 (1965)

"Isodrin in the Diels-Alder Reaction"
K. MacKenzie
J. Chem. Soc. 4646 (1965)

"The Biosynthesis of Phenols. Part IX. Asperugin, a Metabolic Product of *Aspergillus rugulosus*"
J. A. Ballantine, C. H. Hassall, and G. Jones
J. Chem. Soc. 4672 (1965)

"The Proton Magnetic Resonance Spectra of o-Phenanthroline and Some of its Metal Complexes in Non-aqueous Solution"
J. D. Miller and R. H. Prince
J. Chem. Soc. 4706 (1965)

"Perfluoroalkyl Derivatives of Nitrogen. Part XVI. Reaction of Trifluoronitrosomethane with Butadiene and with Isobutene"
R. E. Banks, M. G. Barlow, and R. N. Haszeldine
J. Chem. Soc. 4714 (1965)

"Hexachlorocyclopentadiene. Part IV. Reaction with 1,2-Diols and a Base at High Temperatures"
W.-H. Chang
J. Chem. Soc. 4744 (1965)

"Alkaloid Studies. Part XLVIII. The Structure of Apparicine, a Novel *Aspidosperma* Alkaloid"
J. A. Joule, H. Monteiro, L. J. Durham, B. Gilbert, and Carl Djerassi
J. Chem. Soc. 4773 (1965)

"Phosphorus-Nitrogen Compounds. Part XV. The π Nuclear Magnetic Resonance and Infrared Spectra of Some Mononuclear Phosphorus(v) Compounds containing the $P-NMe_2$ Grouping"
R. Keat and R. A. Shaw
J. Chem. Soc. 4802 (1965)

"The Reaction of Some cis-Dienes with Aromatic Thiols"
J. A. Claisse and D. I. Davies
J. Chem. Soc. 4894 (1965)

"8-Azasteroids. Part I. The Synthesis of 8-Azaestrone"
R. Clarkson
J. Chem. Soc. 4900 (1965)

"Biphenylenes. Part XIII. Diacylation of Biphenylene"
J. M. Blatchly, A. J. Boulton, and J. F. W. McOmie
J. Chem. Soc. 4930 (1965)

"Synthesis of Some Griseofulvin Analogues"
T. P. C. Mulholland, and R. I. W. Honeywood, H. D. Preston, and D. T. Rosevear
J. Chem. Soc. 4939 (1965)

"Transition-metal-Carbon Bonds. Part V. Hydrido-cyclo-octa-1,5-diene Complexes of Iridium(III)"
S. D. Robinson and B. L. Shaw
J. Chem. Soc. 4997 (1965)

"Giberellic Acid. Part XXXI. The Nuclear Magnetic Resonance Spectra of Some Gibberellin Derivatives"
J. R. Hanson
J. Chem. Soc. 5036 (1965)

"Polyfluoroheterocyclic Compounds. Part IV. Compounds Derived from 4-Aminotetrafluoropyridine"
R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave
J. Chem. Soc. 5040 (1965)

"Polyfluoroheterocyclic Compounds. Part V. Catalytic Reduction of Perfluoro- and Chlorofluoro-pyridines and the Preparation of Polyfluoropyridinecarboxylic Acids"
R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave
J. Chem. Soc. 5045 (1965)

- "Hydrolysis of 3,4-Dibromo- and 3,4-Dichloro-2,2-dimethyl-chroman"
R. Binns, W. D. Cotterill, and R. Livingstone
J. Chem. Soc. 5049 (1965)
- "Nucleotides. Part XLIX. The Reduction of the Adduct of Periodate-oxidised Adenosine-5' Phosphate and Methylamine"
D. M. Brown and A. P. Read
J. Chem. Soc. 5072 (1965)
- "Reactions of Organoaluminium Compounds with Cyanides. Part II. Alkyl Cyanides"
J. R. Jennings, J. E. Lloyd, and K. Wade
J. Chem. Soc. 5083 (1965)
- "3-Nitro-o-phenylenediamines: a New Route"
J. A. Elvidge, G. T. Newbold, A. Percival, and I. R. Senciall
J. Chem. Soc. 5119 (1965)
- "Solvent and Concentration Effects on ^{13}C -H Coupling Constants and Chemical Shifts in Some Dihaloethylenes"
V. S. Watts, J. Loemker, and J. H. Goldstein
J. Mol. Spectr. 17, 348 (1965)
- "Proton Spin-lattice Relaxation in Aqueous Ionic Solutions" by Jones and Powles"
B. P. Fabricand
Mol. Phys. 9, 399 (1965)
- "Determination des Signes Relais des Constantes de Couplage ^{31}P - ^1H dans le Tripropyl Phosphate par R.M.N. dans le Champ Magnetique Terrestre"
E. Duval, J. Ranft et G. J. Bene
Mol. Phys. 9, 427 (1965)
- "An NMR Study of Hindered Internatl Rotation in N, N-Dialkyl Amides"
R. M. Hammaker and B. A. Gugler
J. Mol. Spectr. 17, 356 (1965)
- "Reaction of α , α -Diphenyl- β -Picrylhydrazyl with Acids"
D. H. Solomon and J. D. Swift
J. Polymer Sci. A3, 3107 (1965)
- "Heteroaromatic Polymers. The Polybithiazoles"
D. T. Longone and H. H. Un
J. Polymer Sci. A3, 3117 (1965)
- "A Molecular Orbital Theory of Hydrocarbons. III. Nuclear Spin Coupling Constants"
J. A. Pople and D. P. Santry
Mol. Phys. 9, 311 (1965)
- "Double Long-range Spin-spin Couplings between Aldehydic and Aromatic Protons in the N.M.R. Spectra of Salicylaldehydes"
D. G. Kowalewski and V. J. Kowalewski
Mol. Phys. 9, 319 (1965)
- "Multiple Long Range Spin-spin Couplings in Di-substituted Benzaldehydes and Hindered Rotation"
D. G. Kowalewski and V. J. Kowalewski
Mol. Phys. 9, 331 (1965)
- "Electric Fields in Fluorocyclohexanes and the Magnitude of ^{19}F Chemical Shifts"
J. W. Emsley
Mol. Phys. 9, 381 (1965)
- "H-H and ^{13}C -H Coupling Constants in Pyridazine"
V. M. S. Gil
Mol. Phys. 9, 443 (1965)
- "Red Pigments of Dactynotus rudbeckiae and D. ambrosiae [Homoptera, Aphididae]"
U. Weiss and H. W. Altland
Nature 207, 1295 (1965)
- "Magnetic-Field Meter Utilizing Frequency Modulated NMR Detector"
S. Mito, K. Okumura and H. Mima
Osaka City Univ. Faculty Eng. Memoirs 6, 107 (1964)
- "Nuclear Magnetic Resonance in Metals Using Helicons"
P. R. Antoniewicz and S. Rodriguez
Phys. Letters 18, 249 (1965)
- "Magnetic Double Resonance Spectrometer for Dynamic Nuclear Polarization and Relaxation Time Measurements at 175 G"
H. Grützediek, K. D. Kramer, and W. Müller-Warmuth
Rev. Sci. Instr. 36, 1418 (1965)
- "Means of Reducing Ringing Times in Pulsed Nuclear Magnetic Resonance"
J. J. Spokas
Rev. Sci. Instr. 36, 1436 (1965)
- "Time-Sharing Modulation at 200 kc Applied to Broad and Narrow Line NMR for Base-Line Stability"
E. B. Baker, L. W. Burd, and G. N. Root
Rev. Sci. Instr. 36, 1495 (1965)
- "High Resolution NMR Probe Suitable for Use in a Superconducting Solenoid"
S. Meiboom and R. C. Hewitt
Rev. Sci. Instr. 36, 1509 (1965)
- "A π -Hexenyl Complex from Propene and Palladium Chloride"
I. I. Moiseev, A. P. Belov, and G. Yu. Pek
Russian J. Inorg. Chem. 10, 180 (1965)
- "N.M.R. Studies of Donor-Acceptor Interaction in Boron Trihalide Complexes—I. The Use of Boron-11 Chemical Shifts as a measure of Donor-Acceptor Interaction"
P. N. Gates, E. J. McLaughlan and E. F. Mooney
Spectrochim. Acta 21, 1445 (1965)
- "The Nuclear Magnetic Resonance Spectrum of Decaborane-14"
R. L. Williams, N. N. Greenwood, and J. H. Morris
Spectrochim. Acta 21, 1579 (1965)
- "Über die Protonen-Resonanzspektren der Exo-Endo-Isomeren 2-Substituierten Norbornene"
J. Paasivirta
Suomen Kemistilehti 38, 130 (1965)
- "La Cyclisation Thermique des Cetonnes Cycliques ϵ -Ethyleniques. Voie D'Acces Aux Cetonnes Polycycliques"
F. Rouessac, P. Beslin et J.-M. Conia
Tetrahedron Letters 3319 (1965)
- "Stereochemistry and P.M.R. Spectra of β -Lactams"
K. D. Barrow and T. M. Spotswood
Tetrahedron Letters 3325 (1965)
- "A General Synthesis of Medium-Sized Ring Amines"
M. G. Reinecke, L. R. Kray, and R. F. Francis
Tetrahedron Letters 3549 (1965)
- "Isomerization of 2,3',5',6-Tetra-*t*-Butylindophenol by Proton Magnetic Resonance Spectroscopy"
B. D. Gesner
Tetrahedron Letters 3559 (1965)

- "Synthesis of Cyclic Sulphonium Salts Involving Rearrangement of Carbonium Ions"
B. D. Tilak, R. B. Mitrao and C. V. Deshpande
Tetrahedron Letters 3569 (1965)
- "Alkaloids from Buxus Sempervirens L. V. Configuration of Buxtauine and Buxpiine"
Z. Voticky and J. Tomko
Tetrahedron Letters 3579 (1965)
- "Adducts of Dimethylketene With C=N Containing Compounds"
J. C. Martin, V. A. Hoyle, Jr., and K. C. Brannock
Tetrahedron Letters 3589 (1965)
- "Thalictrum Alkaloids I. Thalifendlerine and Thalifendine"
M. Shamma, M. A. Greenberg, and B. S. Dudock
Tetrahedron Letters 3595 (1965)
- "The Structure and Total Synthesis of Takatonine"
S. Kubota and T. Masui, E. Fujita, S. M. Kupchan
Tetrahedron Letters 3599 (1965)
- "Über Ein Vierring-Dicarben"
G. Maier
Tetrahedron Letters 3603 (1965)
- "1,6-Imino-Cyclodecapentaen (1,6-Imino-[10]Annulen)"
E. Vogel, W. Pretzer und W. A. Böhl
Tetrahedron Letters 3613 (1965)
- "A New Sesquiterpene Hydrocarbon from Laurencia Glandulifera"
T. Irie, Y. Yasunari, T. Susuki, N. Imai, E. Kurosawa, and T. Masamune
Tetrahedron Letters 3619 (1965)
- "Benzocyclopropan"
E. Vogel, W. Grümme und S. Korte
Tetrahedron Letters 3625 (1965)
- "The Alkaloid of the Leaves of Alstonia Scholaris R. Br."
A. Chatterjee, B. Mukherjee and A. B. Ray, and B. Das
Tetrahedron Letters 3633 (1965)
- "Stereochemical Studies by PMR Spectroscopy - III, Axial and Equatorial Acids"
C. R. Narayanan and N.K. Venkatasubramanian
Tetrahedron Letters 3639 (1965)
- "New Method for the Initiation of the Cyclisation Reaction of Isoprenoid Compounds"
W. A. Smit, A. V. Semenovskiy
Tetrahedron Letters 3651 (1965)
- "The Structure of Hinokiresinol"
Y. Hirose, N. Oishi, H. Nagaki, and T. Nakatsuka
Tetrahedron Letters 3665 (1965)
- "Quercetagenin 3,6-Dimethyl Ether"
A. O. Taylor and E. Wong
Tetrahedron Letters 3675 (1965)
- "The Stereoselectivity of Photobromination"
W. O. Haag and El-Ahmadi I. Heiba
Tetrahedron Letters 3679 (1965)
- "Epimerization of (+)-4',5,7-Trimethoxyflavan-4 β -OL to the -4 α -OL with Acetic Anhydride and Pyridine"
H. G. Krishnamurty and T. R. Seshadri and D. G. Roux
Tetrahedron Letters 3689 (1965)
- "Fragmentierung an Einigen Isochinuclidin-Alkaloiden"
U. Renner, K. A. Jaeggi und D. A. Prins
Tetrahedron Letters 3697 (1965)
- "Isomere der Thiathiophthene Aus Trithionen und Acetylenen"
H. Behringer und R. Wiedenmann
Tetrahedron Letters 3705 (1965)
- "The Photodimer of Thymine: An NMR Study"
R. Anet
Tetrahedron Letters 3713 (1965)
- "The Diterpenes of Dacrydium Colensoi. Part IV"
P. K. Grant and M. H. G. Munro
Tetrahedron Letters 3729 (1965)
- "Triterpenes of the Friedelane Series. Part V. Acids.
J. L. Courtney and W. Stern
Tetrahedron Letters 3733 (1965)
- "Dustanin: A New Pentacyclic Triterpenoid as a Fungal Metabolite"
Y. Tsuda and K. Isobe
Tetrahedron Letters 3737 (1965)
- "An Alternate Method to Identify Proton(s) on the Carbon Bearing a Hydroxyl Group"
C. R. Narayanan and K. N. Iyer
Tetrahedron Letters 3741 (1965)
- "Effects of Substituents on Intramolecular Hydrogen Bonds of 2-Hydroxy-4-Substituted Acetophenones"
Z.-I. Yoshida and Masami Haruta
Tetrahedron Letters 3745 (1965)
- "Über die Konformation des Latraxisols"
W. Sandermann und K. Bruns
Tetrahedron Letters 3757 (1965)
- "Mayurone, A C₁₄-Sesquiterpene Ketone"
G. L. Chetty and S. Dev
Tetrahedron Letters 3773 (1965)
- "New Constituents of Thujopsis Dolabrata"
S. Ito, K. Endo, H. Homma and K. Ota
Tetrahedron Letters 3777 (1965)
- "The Structure of Saikogenin A, A Sapogenin of Bupleurum Species"
S. Shibata, I. Kitagawa, and H. Fujimoto
Tetrahedron Letters 3783 (1965)
- "A Possible Zwitterion Intermediate in the Reaction of 3-Methoxy-1-Methylbenzimidazolium Iodide with Various Nucleophiles"
S. Takahashi and H. Kanō
Tetrahedron Letters 3789 (1965)
- "Linear Oligosiloxanes with Bis-(Trimethylsilyl)-amine Chain-terminating Groups"
C. Krüger and E. G. Rochow
Z. Anorg. Allgem. Chem. 338, 113 (1965)
- "Die Umsetzung Zwischen Phosphorsäure- und Thiophosphorsäureamiden mit Phosphorpentachlorid II"
M. Becke-Goeppert and W. Haubold
Z. Anorg. Allgem. Chem. 338, 305 (1965)