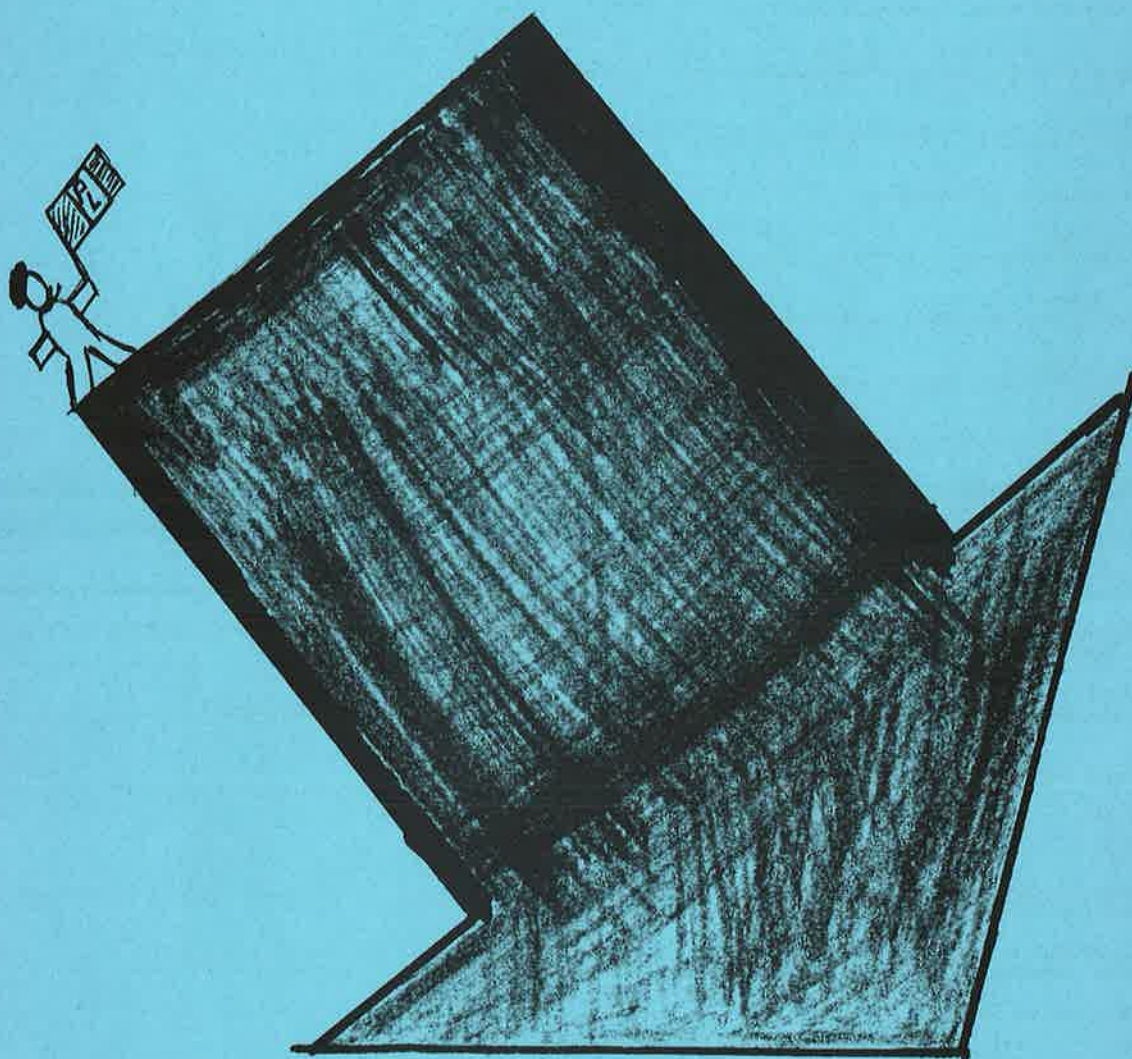


Illinois
Institute of
Technology
N - M - R
Newsletter

No. 79
APRIL, 1965

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Deadline dates:	No. 80:	19 May 1965
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A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".



THE UNIVERSITY OF MANCHESTER,

DEPARTMENT OF CHEMISTRY,

MANCHESTER, 13.

TELEPHONE: ARDWICK 3333

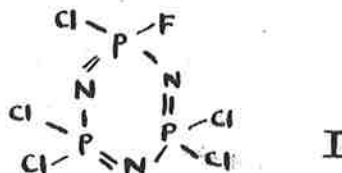
19th March, 1965.

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

Dear Dr. Shapiro,

Currently, work is in progress on the analysis of the spectra of several non-substituted triphosphonitrilic chlorides, as examples of AB_2X_n and $AB_2P_nX_n$ system. The relative signs as well as the magnitudes of the spectral parameters are being determined.

So far, only the 1-fluoro-triphosphonitrilic chloride (I) has been analysed completely.



This is an AB_2X system, and due to the large coupling constants involved, the two AB_2 -type sub-spectra of the phosphorus resonances are quite distinct. (Diag. II. The two sets are distinguished by the primed and double-primed line numbers; line X is an impurity). This enables the determination of the magnitudes of all the parameters. The relative signs were then obtained by calculating the ^{19}F spectrum and comparing with experiment. Satisfactory agreement could be obtained only if J_{BX} and J_{AB} were both of opposite sign to J_{AX} . The relevant data is given below :

$$\begin{aligned} \nu_A - \nu_B &= -219 \text{ cps at } 25 \text{ Mc/s} \\ J_{AX} &= 1014 \pm 2 \text{ cps} \quad J_{BX} = -9.8 \pm 0.5 \text{ cps.} \quad J_{PB} = -81 \pm 2 \text{ cps.} \end{aligned}$$

These results are in agreement with those obtained by Hefferman & White (1) for 1,1,-difluoro-triphosphonitrilic chloride. As they point out, J_{AX} can be taken as positive, since the two nuclei are directly coupled. The other two involve interaction via π electrons to some extent which perhaps accounts for their negative sign.

The ^{31}P spectrum was obtained at 25 Mc/s on an A.E.I. RS.2 machine and calibrated by sidebands.

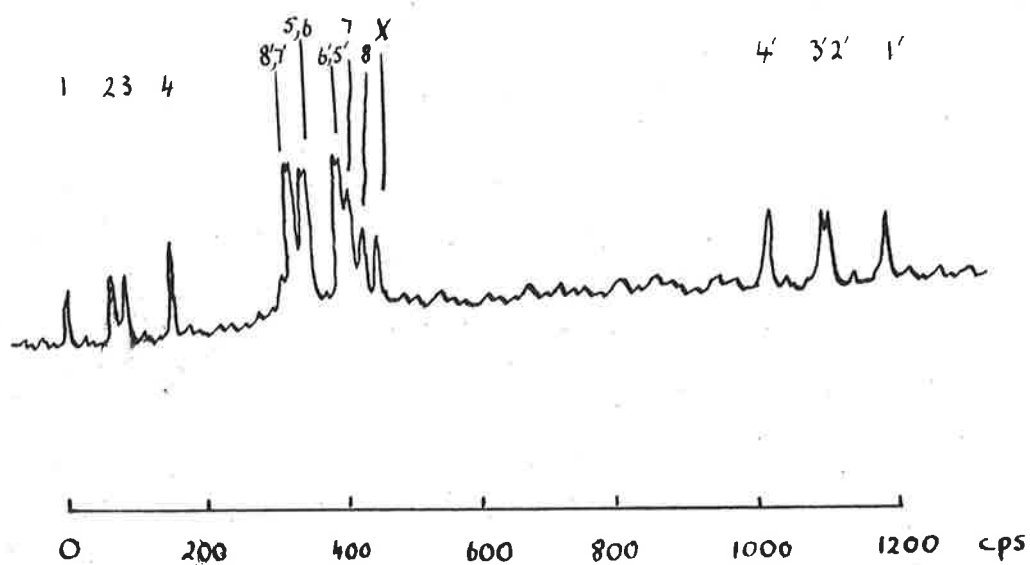
The other compounds being investigated are the methoxy and 1,1,1-trifluoro-ethoxy- mono-substituted compounds. To obtain better high-resolution ^{31}P spectra, a 7mm spinning probe is being constructed for the A.E.I. machine.

With apologies for the delay in sending this contribution.

Yours Sincerely,

F. Heatley
G. Allen

(1) Hefferman and White, J.C.S. p.1382 (1961)



II ^{31}P spectrum of 1-fluoro-triphosphonitric
chloride at 25 Mc/s

University of East Anglia

School of Chemical Sciences
 Wilberforce Road, Norwich NOR 54H
 Telephone Norwich 52651

16th March 1965

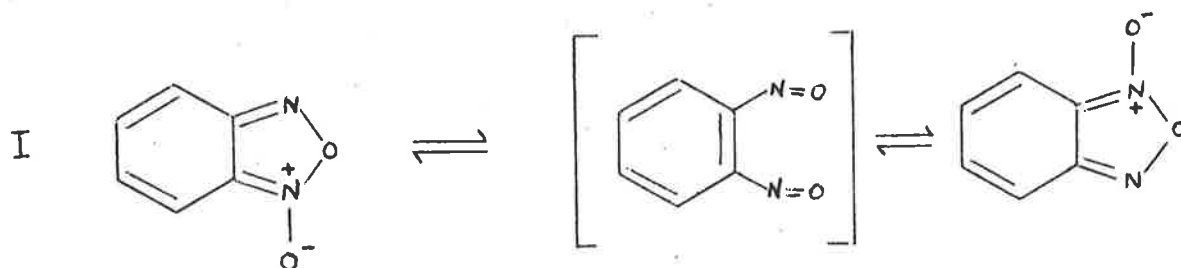
Dear Dr. Shapiro,

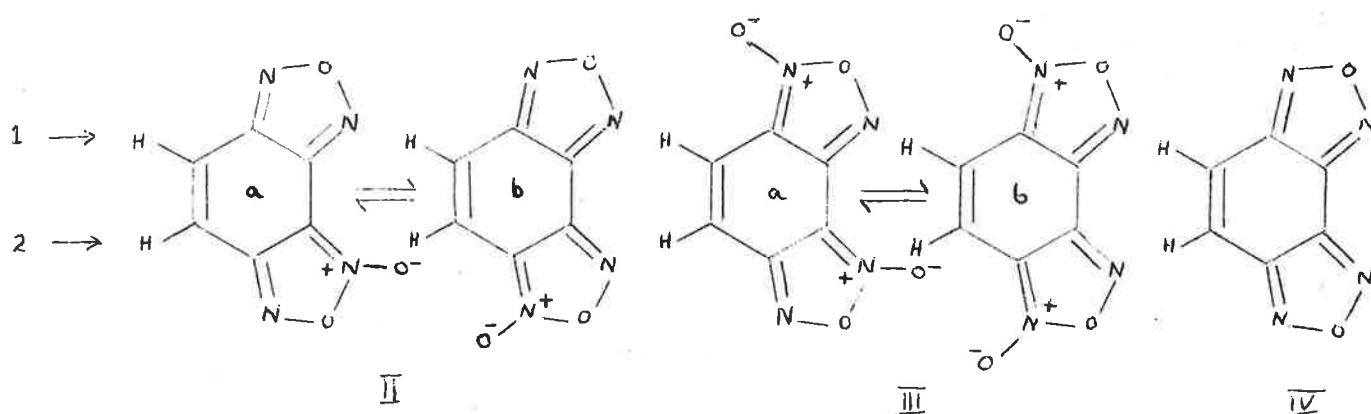
Furazanobenzofuroxan and Furoxanobenzofuroxan

Recent n.m.r. studies on benzofuroxans have shown that simple members of this series (I) undergo rapid tautomerism in solution, but that the oxadiazole-oxide structure represents the stable form. Variable-temperature work on various nitro-, dinitro-, and methoxy-derivatives has given coalescence points for the spectra of pairs of tautomers corresponding to free energies of activation of tautomerism between 12 and 15 kcal/mole.

We have now made a similar study of the tricyclic compounds furazano- and furoxanobenzofuroxan (II, III). Room temperature spectra in various solvents show sharp peaks for the individual tautomers of each compound, two AB quartets in (II) and an AB and an A₂ in (III). The AB coupling constants (~ 10.0) are the highest ortho-coupling constants yet recorded for benzo-furoxans or -furazans.

High-temperature measurements were made in diglyme, and showed coalescence at over 130°C to an AB quartet for (II) and to an A₂ singlet for (III). Estimates for the free energy of activation (ΔG^\ddagger) at the coalescence temperature are about 8 kcal/mol. higher than the corresponding values for the benzofuroxan series; if the transition state for the tautomerism be assumed close to the (presumed) o-dinitroso intermediate, it seems fair to deduce that the difference in resonance energy between the o-quinonoid system and the bis-o-quinonoid is less than that between the benzenoid and the o-quinonoid. However, comparison of the chemical shifts in acetone of benzene, benzofuroxan and benzofurazan with II, III, and IV would suggest that the reverse is true of the differences in ring current between the three series. We are not yet sure how to reconcile these conclusions.





	τ , ppm.	J, c/s	$T_c, ^\circ K$	ΔG^*
II	a { 1 2.05 2 2.15 }	9.9	417 414	21.8 22.2
	b { 1 2.18 2 2.42 }	10.0		
III	a { 1 2.45 2 2.37 }	10.2	410	21.7
	b { 1 2 }	2.63		
IV	{ 1 2 }	1.86		
Acetone (34°C) Diglyme				

Spectra were measured at 34°C on a 40Mc/s Perkin-Elmer permanent magnet spectrometer, and at other temperatures on a Varian Associates A60 with temperature control.

With best wishes to you and all our n.m.r. colleagues.

Yours sincerely,

A. J. Boulton

A. J. Boulton

A. C. Gripper Gray

A. C. Gripper Gray

A. R. Katritzky

A. R. Katritzky

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

SANDOZ LTD.

BASLE (SWITZERLAND)

Dr. P. Niklaus

PRIVATE

Ein aromatisches Proton bei $\delta = 5,45\text{ppm}$!

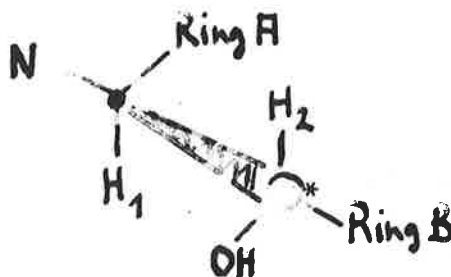
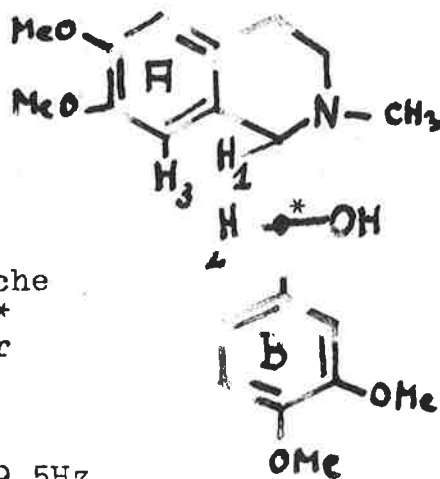
Hydroxylandanosin

kommt in zwei (α, β) diastereomeren Formen vor, welche sich in der Konfiguration an C* unterscheiden. Das Spektrum der α -Form zeigt ein Singlett bei 5,45ppm, vier H's im normalen aromatischen Absorptionsgebiet und ein AB-System mit $J_{\text{beob.}} = 9,5\text{Hz}$ für H_1 und H_2 .

Im Spektrum der β -Form erscheint das Singlett bei 5,86ppm und H_1 koppelt mit H_2 mit ca 3,8Hz.

Nach anfänglichen Zweifeln kamen wir zur Ueberzeugung, dass das Singlett bei 5,45- respektive 5,86ppm dem aromatischen Wasserstoffatom H_3 zuzuschreiben ist.

Beim α -Hydroxylandanosin muss H_1 mit H_2 einen Winkel von ca 180° einschliessen und die Rotation um die Einfachbindung stark gehindert sein (wegen $J = 9,5\text{Hz}$). Die O° -cis-Stellung kommt nicht in Frage, weil diese ohne weiteres in die energieärmere "staggered"-Position mit $J = \text{ca } 2\text{Hz}$ übergehen könnte. Die aussergewöhnliche chemische Verschiebung von H_3 lässt sich nur damit erklären, dass H_3 direkt über der Ebene des aromatischen Rings B steht. Damit folgt für α -Laudanosin die Konfiguration an C* wie hier angegeben:



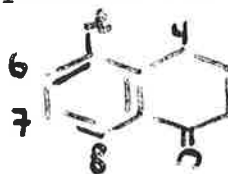
SANDOZ LTD.

BASLE (SWITZERLAND)

PRIVATE

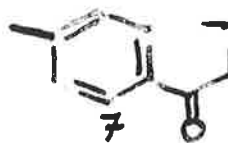
Bemerkung zu IIT N-M-R Newsletter No 76, long range coupling in Tetralone:

W.Brügel diskutiert das Spektrum von 5-Chlor-1-tetralon



und schreibt dabei die Absorption bei tiefstem Feld provisorisch dem H an C₆ zu.

Wie aus eigenen Messungen ähnlicher Substanzen hervorgeht muss H an C₈ das bei tiefstem Feld absorbierende sein. Der Einfluss⁸ der Ketogruppe ist in allen Fällen sehr gross, während die Chlorsubstitution die Lage der aromatischen H's nur wenig beeinflusst. Um nur ein Beispiel anzugeben: C₇-H in



absorbiert bei 458Hz (TMS=0 / CDCl₃) --- also fast an der gleichen Stelle, wo das tiefste H von 5-Chlor-1-Tetralon erscheint. Die zwei übrigen aromatischen Wasserstoffe kommen etwa 20Hz höher. Trotz bester Auflösung sind die Linien aller aromatischer Protonen stark verbreitert, was wiederum auf long range Kopplungen schliessen lässt.

17.3.65

P.Niklaus

Niklaus



הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

17 March, 1965

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois
U.S.A.

Dear Professor Shapiro:

Enclosed please find our contribution to IITNMR Newsletter.

NMR Studies of Methyl Isonitrile and Nitrile

The N^{14} C^{13} and H^1 nmr spectra of CH_3CN and CH_3NC were measured in neat compounds and various solvents. Some of the results are given in the attached Table.

The width of the C^{13} resonances could not be determined with our equipment.

The shift of C^{13} resonances in CH_3NC in methanol are to higher fields and indicate H bond formation to carbon. The same argument applies to the N^{14} shift in CH_3CN (in H_2O and CH_3OH), indicating H bond formation to the nitrogen.

We have also studied the OH shift of methanol in CH_3NC as a function of the concentration at 30, 0 and $-20^\circ C$. The results indicate that a 1:1 complex is formed with a very high complexation constant and low temperature dependence (small ΔH).

Another aspect studied are the extremely narrow resonances of N^{14} in CH_3NC .

A comprehensive report on the subject is being prepared for publication.

Yours sincerely,

A. Loewenstein

A. Loewenstein

Y. Margalit

Y. Margalit

NMR Parameters of CH_3NC and CH_3CN CH_3NC

Solvent	H^1 (ref. TMS)		N^{14} (ref. NH_4Cl sat.)		C^{13} (ref: CH_3 in CH_3CN)	
	Position (ppm)	Width (cps)	Position (ppm)	Width (cps)	Position (ppm)	
					<u>CH_3</u>	<u>NC</u>
Neat	3.17	< 0.5 triplet $J_{\text{NH}}=2.35$	- 136	~0.5 quartet $J=2.3$	24	156
CHCl_3 (1/1 vol.)	3.12	< 0.5	—	—	$\text{CH}_3\text{NC} = 132$	
CCl_4 (1/1 vol.)	3.17	< 0.5	- 136	~0.5	$\text{CH}_3\text{NC} = 130$	
H_2O (~10% vol.)	—	—	-136	~0.5	—	
$\text{CH}_3\text{OH}^{(a)}$	3.08-3.15	< 0.5	-135	~0.5	$\text{CH}_3\text{NC} = 103 \text{ to } 133$	

 CH_3CN

Neat	2.00	< 0.5	-228	81	0	123
$\text{CCl}_4^{(a)}$	2.00	< 0.5	-228 to -232 ^(a)	100	—	—
H_2O (1/1 vol)	2.05	< 0.5	-228 to -218 ^(a)	113	—	—
CH_3OH (1/1 vol)	2.07	< 0.5	-228 to -224 ^(a)	81	0	123

(a) Studied over a complete range of concentrations in given solvent.

CSIRO

DIVISION OF COAL RESEARCH

P.O. BOX 175, CHATSWOOD, N.S.W. TELEPHONE 88 0261. TELEGRAMS FUELRES CHATSWOOD N.S.W.

22nd March, 1965.

Dr. B.L. Shapiro,
Chemistry Department,
Illinois Institute of Technology,
CHICAGO, ILLINOIS.
U.S.A.

Dear Dr. Shapiro,

This is my first contribution to IITNMR, and I trust that the inclosed information may be of interest.

This Division has been interested for some considerable time in deuterium exchange in organic compounds with D_2O over metal catalysts. The role of p.m.r. in this programme is to estimate the position and quantity of H exchange. In most cases this can be done quite simply; however in some cases the spectra of partially exchanged compounds are complex, and quantitative information is difficult to obtain. More information can sometimes be obtained by study of a more fully exchanged compound.

Quinoline is such a case and will be briefly described here. In a "neat" solution of Quinoline H(2), H(3), H(4) and H(8) can be readily detected, but H(5) H(6) and H(7) cannot be separated. (see Fig 1 for partially exchanged sample). However in the more highly exchanged sample it seems apparent that of H(5), H(6) and H(7), the one preferentially exchanged is H(7). (See Fig 2). The spectrum shows residual H(8) downfield, and 2 AB systems as marked. The coupling constant of H(5) H(6) is ≈ 8.3 cps in agreement with P.J. Black and M.L. Heffernan.¹ (H(6) H(7) $J = 6.81$ cps) also H(6) is broadened as compared to H(5) indicating that it is ortho to D. Also of interest is the single peak (somewhat broadened) of H(4) due to molecules in which H(3) has been replaced by D.

Yours sincerely,

P. Collin

P. Collin

¹ P.J. Black, M.L. Heffernan.
Australian J. Chem. **17** 558-66 (1964)

PC/at

H Distribution

H →

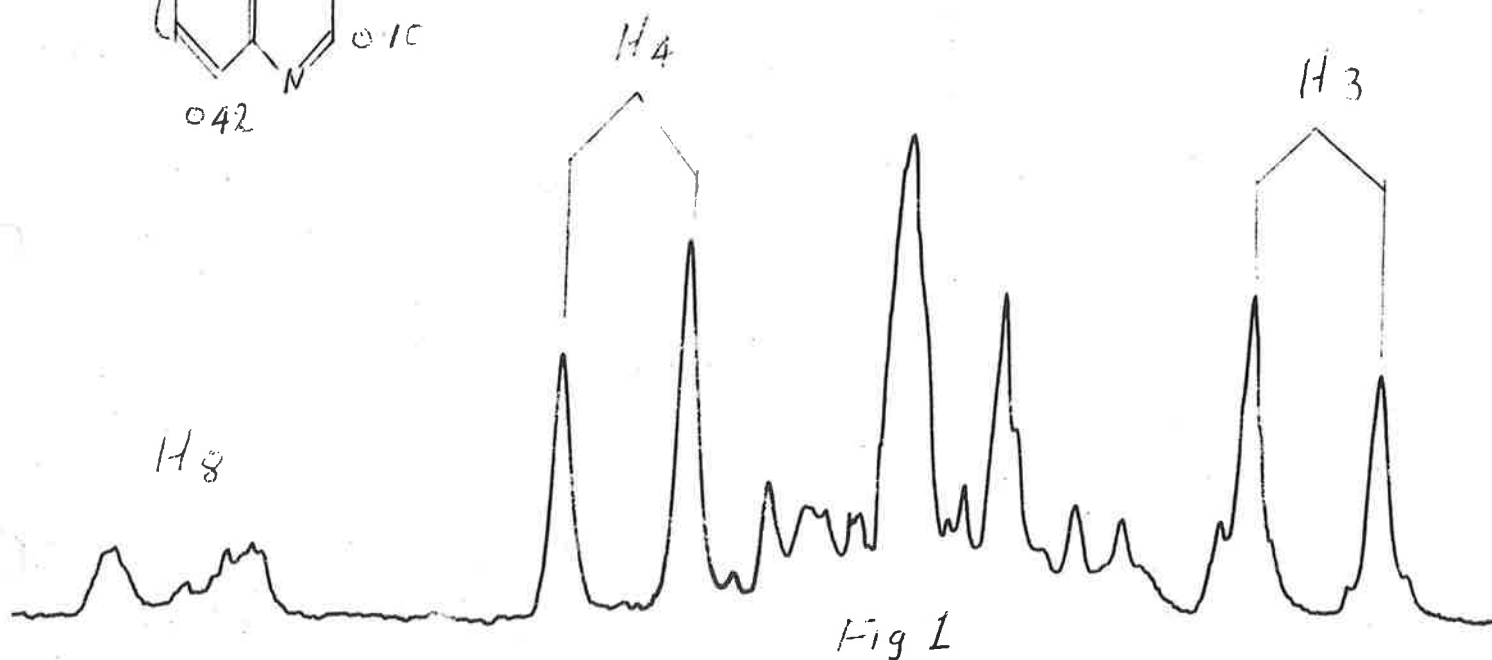
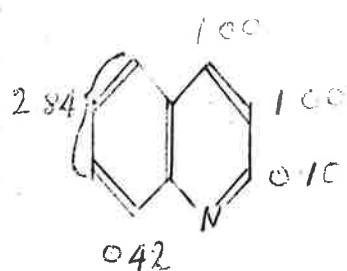
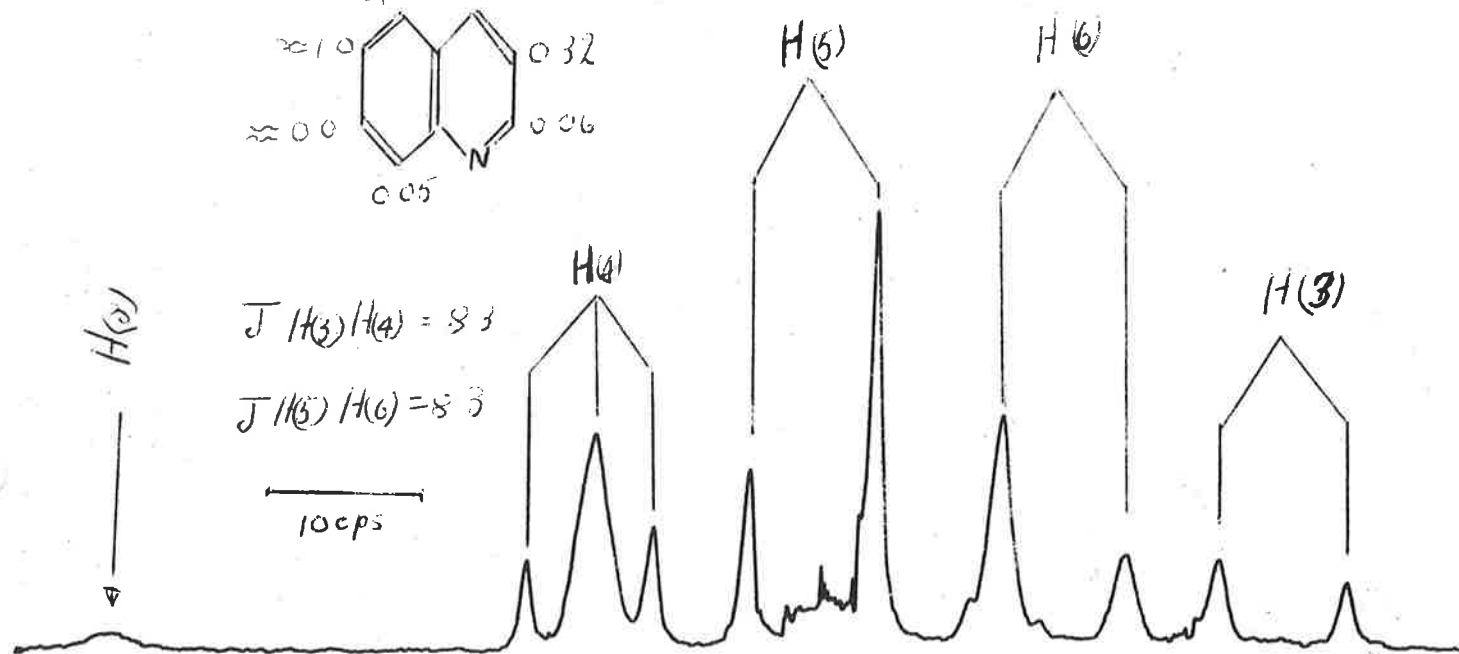
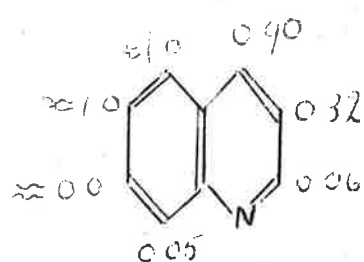


Fig 1

H →

H distribution

$$J(H(3)/H(4)) = 8.3$$

$$J(H(5)/H(6)) = 8.3$$

10 cps

Fig 2

LABORATORIUM FÜR PHYSIKALISCHE
CHEMIE UND ELEKTROCHEMIE DER
TECHNISCHEN HOCHSCHULE, STUTTGART, Germany

Dr. H. Dreeskamp

7 STUTTGART N
Wiederholdstraße 15
Telefon 29978393

March 22nd, 1965

Dear Dr. Shapiro:

J_{X-C-H} and $J_{X-C-C-H}$ in ethylcompounds. $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$.

Let us assume our determination of the absolute signs of hetero-nuclear coupling constants in group IV hydrides, tetramethyl- and tetraethylcompounds [see IITNMR Newsletters 66-31 and the proceedings of the XIII Colloque Ampere] and their interpretation is essentially correct. Then one begins to wonder what instead of going vertically through the Periodic Table one might find by going horizontally. Here hydrides and nuclei with spin $\frac{1}{2}$ are hard to come by but the magnitudes and relative signs of J_{X-C-H} and $J_{X-C-C-H}$ in some ethylcompounds are fairly well known. However, two entries have still been missing: $SeEt_2$ and $TeEt_2$. Together with V. Breuninger we prepared and measured these:

$SeEt_2$: $J_{Se^{77}-C-H} = \pm 10.6$ cps , $J_{Se^{77}-C-C-H} = \pm 10.8$ cps

$TeEt_2$: $J_{Te^{125}-C-H} = \pm 24.8$ cps , $J_{Te^{125}-C-C-H} = \pm 22.0$ cps

In both cases the same sign, similar to FC_2H_5 .

Next I would like to plot a "coupling factor" $K = \frac{J_{X-C-H}}{J_{X-H}}$ but the J_{X-H} 's are mostly unavailable.

Still we believe that the ratio of J_{X-C-H} divided by $J_{X-C-C-H}$ has some significance. [The normalized $J'_{X-C-C-H}$ most probably do not change sign and we will say some more on this in the full paper].

In Fig.1 a semi-graphical representation of these and similar ratios are given ordered according to the group of the element X and the principal quantum number of the valence electrons of X as a parameter. [Values are from: G. Klose, Ann.Physik 9 p.275 (1962), S. L. Stafford and J. D. Baldeschwieler JACS 83 4473 (1961), J. E. Lancaster Mellonmr 62-2]

Evidently some conclusions might be drawn from this:

- 1) More than the atomic number the group number determines this ratio.
- 2) Be careful drawing conclusions on the "hybridisation"

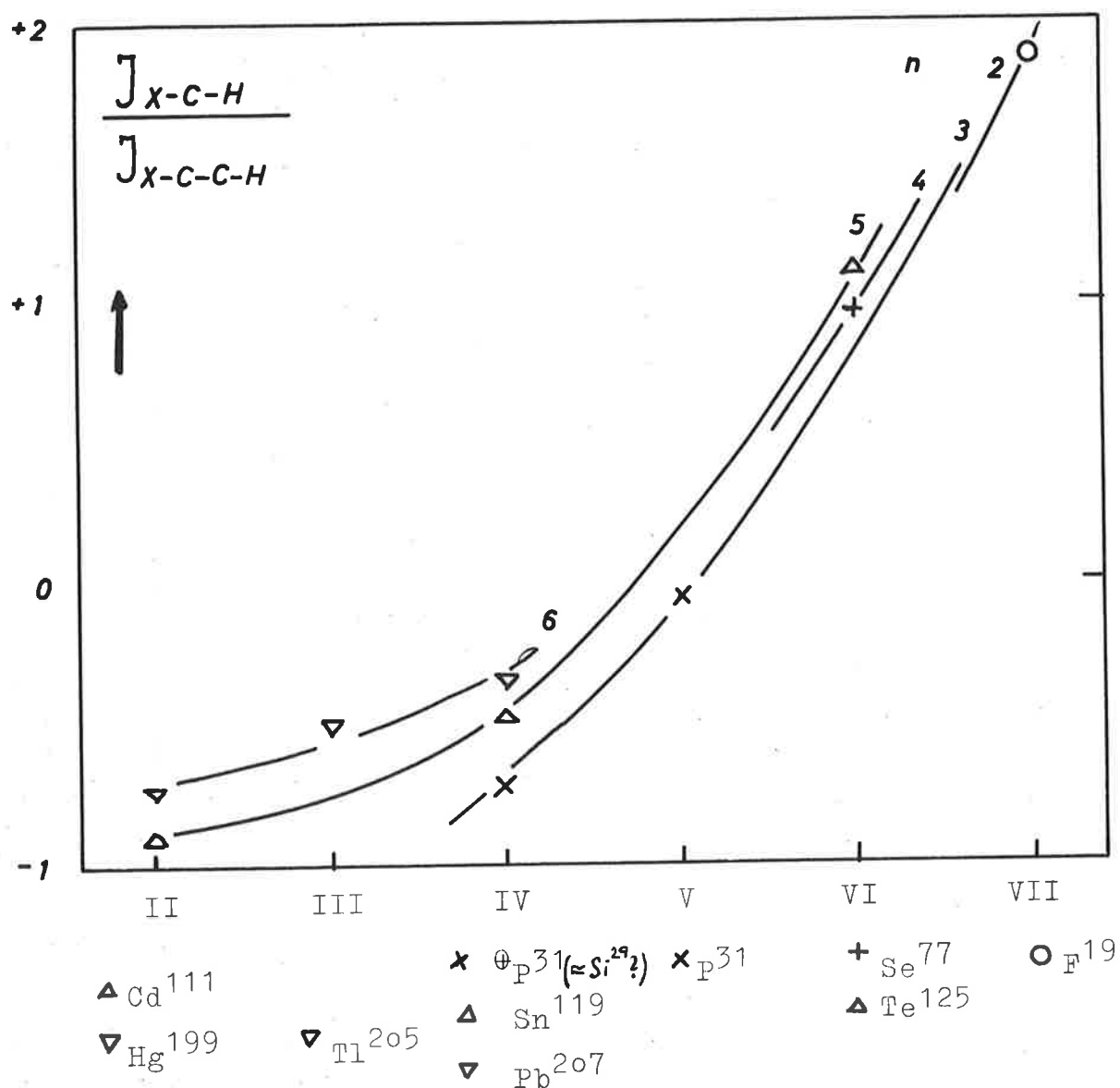


Fig.1

of X when you only know J_{X-C-H} but nothing about K_{X-C-H} .

3) There ought to be some reasonable simple theoretical model accounting for these regularities. Perhaps a few words on this later.

Sincerely yours,

4. *Freehand*

TELEPHONE NO. 78555



Department of Chemistry,
THE UNIVERSITY,
SHEFFIELD, 10.

25th March, 1965.

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

Dear Professor Shapiro,

The C^{13} -H satellites of pyridazine have recently been the subject of a paper by Tori and Ogata (Chem. Pharm. Bull. Japan, 12, 272 (1964)). However, the first-order analysis they give (similar to that of the C^{13} -H satellites of furan by Reddy and Goldstein, J. Am. Chem. Soc., 84, 583 (1962)) is incorrect. In fact the C^{13} -H satellites for A_2X_2 type molecules are the X-spectra of ABMX systems.

We have obtained the satellite spectra of pyridazine with a Varian HR-100 spectrometer. The high-field satellite corresponding to the 4,5 protons is shown in the figure. The proton coupling constants (in c.p.s.) obtained from an ABMX analysis are as follows:

$$J_{34} = 5.05 (4.9)$$

$$J_{35} = 1.85 (2.0)$$

$$J_{45} = 8.00 (8.4)$$

$$J_{36} = \pm 1.40 (3.5)$$

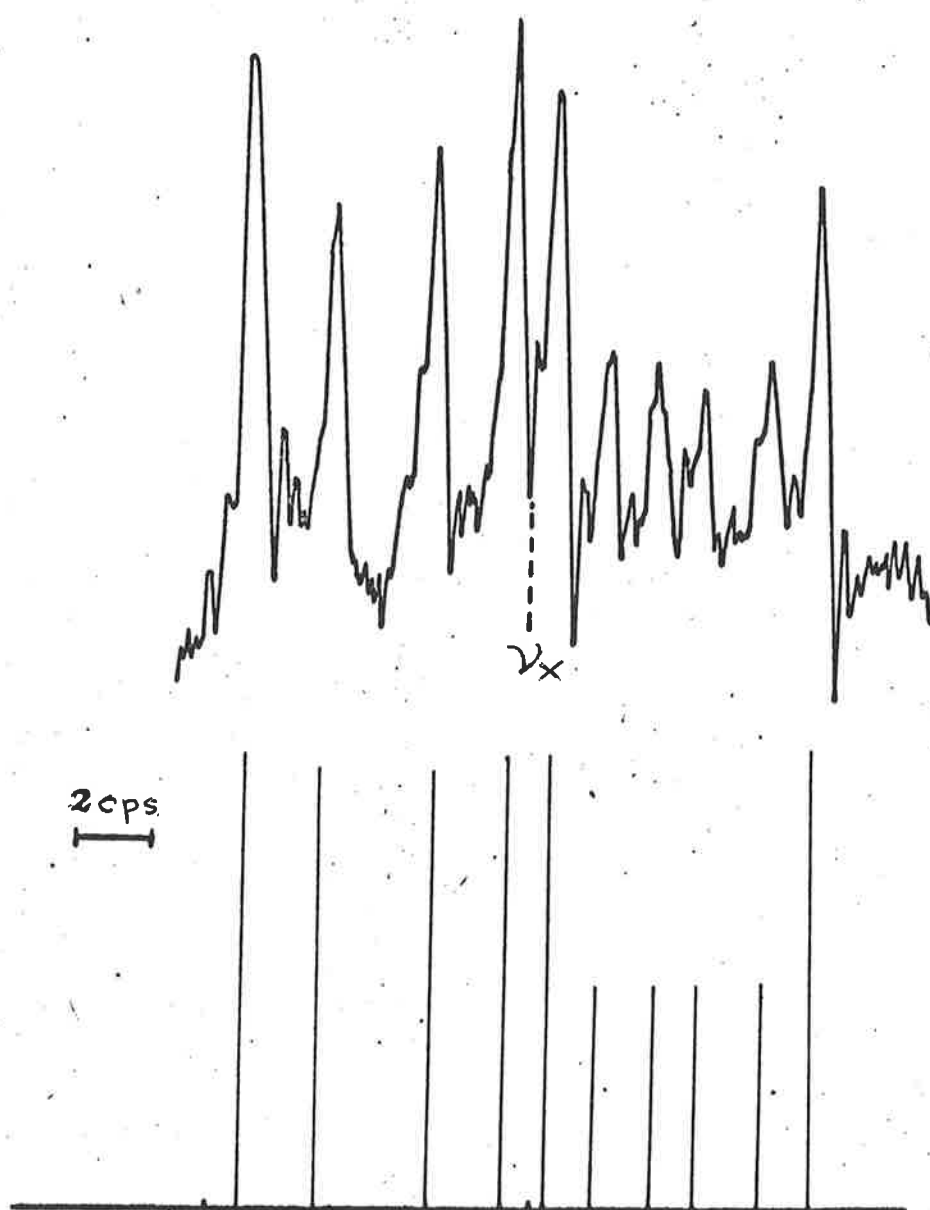
The values in brackets are those reported by Tori and Ogata.

With this communication I hope to be counted among the subscribers of IITMERN.

Yours sincerely,

Victor M S Gil

Victor M.S. Gil.



The high-field C^{13} -H satellite for the
4,5 protons of pyridazine.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

March 25, 1965

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

Dear Barry:

Sorry for the tardiness of my contribution for I.I.T. N.M.R. - part of the reason is my being absent from Melbourne spending six months study leave with John Baldeschwieler's research group. For some time now, Peter Black and I have been interested in obtaining the proton chemical shifts for various six and five-membered ring heterocyclic compounds, mainly N containing ones. The aim has been to collect such data and then to try and work back to the electron distribution in these compounds by applying a series of corrections for known effects. Lloyd Jackman is also interested in the general problem and we have often discussed ways and means of finding "a path through the thickets without getting completely bushed". Having obtained such "experimental" estimates of the electron distribution, one is in a position to make some comparison with the predictions of molecular orbital theory. We think (for reasons other than megalomania) that the VESCF method, a variant of the Pariser-Parr-Pople method, could be particularly suited to discussion of charge distributions in heterocyclic systems. We are still working on this but I include here a few interim results on the simpler systems. There are many pitfalls and uncertainties in such work, of course, and it is wise to work on these problems only on days when one feels optimistic!

Unfortunately, the situation in unsymmetrical molecules like quinoline is not even fully determined because there are only seven chemical shifts and ten atoms in the conjugated system. After allowing for the normalization condition this then leaves two unknown charges to be fixed by appeal to some other criterion; we have used

the theoretical predictions to fix these values and then applied a least squares conditioned observations theory to obtain the best overall agreement between the experimental observations and the calculated charge densities. This problem does not arise for symmetrical molecules and only such examples are given in the table.

The way we process the row data is as follows. The chemical shifts (δ_{rel}), measured where possible in dilute solution in a non-polar solvent, are referred to the benzene resonance as origin.

(a) The ring current contribution (δ'_{rc}) is obtained by the method of Hall and Hardisson except that we use the VESCF, rather than the Pople SCF, method. Since the results obtained are probably too large on an absolute scale, we use the theoretical ratio to benzene to scale the "experimental" value for the deshielding in benzene, taken as 1.55 p.p.m. This scaled value is then referred to benzene as origin.

(b) The magnetic anisotropy of the neighbouring tertiary N atoms is calculated by the method of Murrell and Gil, where only the components of the paramagnetic susceptibility are calculated and the chemical shift contribution is calculated by a dipole approximation. The calculation is again made relative to the benzene system and the difference in proton deshielding between the molecule and benzene (δ'_{MA}) is estimated. A similar treatment is used for furan-type 0.

(c) In molecules containing atoms with lone pairs there will be an electric field associated with these atomic dipoles and the effect of this field on the proton shifts may be estimated by means of the Buckingham or Musher equations. We have carried out calculations (δ'_D) using the Musher equation although the Buckingham equation gives similar predictions.

The corrected shifts (δ_{corr}) are thus obtained as

$$\delta_{corr} = \delta_{rel} + \delta'_{rc} + \delta'_{MA} + \delta'_D.$$

Table. Comparison of "experimental" and calculated charge distributions

Molecular Position	δ_{rel}	δ'_{rc}	δ'_{MA}	δ'_D	δ_{corr}	q_{exp}	q_{VESCF}
Pyridine							
1						1.116	1.096
2	-1.30	0.06	-0.35	-0.41	-0.60	0.933	0.964
3	0.00	0.06	0.00	-0.18	0.12	1.024	0.997
4	-0.37	0.06	0.00	-0.14	-0.29	0.970	0.984
Pyridazine							
1						1.049	1.062
3	-1.80	0.06	-0.35	-0.60	-0.91	0.912	0.951
4	0.04	0.06	0.00	-0.33	0.31	1.039	0.980
Pyrimidine							
1						1.082	1.094
2	-1.96	0.07	-0.70	-0.83	-0.50	0.935	0.928
4	-1.45	0.07	-0.35	-0.56	-0.61	0.932	0.947
5	-0.09	0.07	0.00	-0.38	0.22	1.038	0.990
Pyrazine							
1						1.062	1.080
2	-1.20	0.06	-0.35	-0.61	0.30	0.969	0.960
Pyrrole							
1						1.824	1.719
2	0.94	0.74	--	--	0.20	1.034	1.070
3	1.33	0.74	--	--	0.59	1.051	1.071
Furan							
1						1.933	1.795
2	0.00	0.83	-0.35	-0.40	-0.08	0.995	1.046
3	1.04	0.83	0.00	-0.20	0.41	1.038	1.056

Page 3

March 25, 1965

These corrected shifts, we believe, should represent the contributions arising from the electric field produced by the unequal charge distribution in the molecule. Although these contributions are dominated by the π -electron density on the adjacent C atoms, we find that the other atoms also make a contribution, particularly in the case of secondary N atoms where there is probably a significant positive charge. An "experimental" estimate can be made of the charge distribution on the various centers by working back, via the Musher equation, from the corrected shifts to the electric field causing them. This process is solved iteratively on a computer.

Although the theoretical models normally used for these systems assume that only the π -electrons are polarized, the "experimental" charge distributions deduced from the corrected shifts are really the total charges on the various centers. In this regard, it was interesting to see the results being obtained by Professor Lauterbur, as mentioned in a recent contribution to the Newsletter, from C^{13} studies which implied that there was probably some σ -electron polarization in these systems. We have compared the above results with the VESCF M.O. calculations. The agreement is reasonable although the results for five-membered ring systems are not as good as for the six-membered rings. It seems that careful use of chemical shift data can lead to estimates of the ground state charge distribution in heterocyclic systems although there is still need for much caution. The appearance of independent estimates from C^{13} spectra is an encouraging development.

Yours sincerely,

Michael L. Heffernan

Peter J. Black
Michael L. Heffernan

MLH:mo

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY 4, CALIFORNIA
Building No. 3

March 22, 1965

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

Dear Barry:

Our last contribution, IITNMR-68, entitled "The Structure of 'Ethylmetaphosphate' (Langheld Ester), has appeared in completed form in JACS 87, 591 (1965). Our current contribution is an extension of that work and depended heavily on P^{31} nmr results. Preprints of this paper are available.

KINETICS OF THE HYDROLYSIS AND ALCOHOLYSIS OF TETRAPOLYPHOSPHATE ESTERS
("ETHYL METAPHOSPHATE")

Abstract

"Ethyl metaphosphate" or tetrapolyphosphate esters are a potentially useful starting material for the preparation of polynucleotides. The kinetics of the reactions of the esters with excess water and ethanol have been measured by means of P^{31} nmr and I.R. spectroscopy. Upon the addition of specific amounts of water or ethanol, substances could be prepared which consist mainly of linear tetrapoly-, tripoly- or pyrophosphate esters containing smaller amounts of other polyphosphates and orthophosphates in an equilibrium composition. Diethyl hydrogen orthophosphate reacts with cyclic polyphosphate esters to open the ring; with linear esters it reacts to form polyphosphates with lesser degree of condensation. This latter reaction also proceeds to an equilibrium. No reactions between linear and cyclic polyphosphate esters were observed at room temperature, which implies that the rates of the disproportionation of the linear polyphosphate esters were low. Some organic solvents previously employed for the dehydrating polymerization of sugars, amino acids or nucleotides destroy the tetrapolyphosphate esters. The various substances now available from tetrapolyphosphate esters by the action of water or reactive solvents will differ in their capabilities of producing the dehydrating polymerization reaction. Thus, one may expect that very different products might result from very small differences in reaction conditions.

Sincerely yours,



Gottfried Burkhardt*
Melvin P. Klein

MPK/dem

*Postdoctoral fellow of the Deutscher Akademischer Sustauchdienst (Germany)

INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MARBURG
DIREKTOR: PROF. DR. MAX SCHMIDT

355 MARBURG, 28. III. 1955
Gutenbergstraße 18
Fernruf 731, Nebenstelle 3614
bei Durchwahl 733614

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

Chemical Shifts and Coupling Constants of Isosteric Compounds

Dear Professor Shapiro,

Our recent investigations were dedicated to isosters and isoelectronics of siloxane compounds. Along with preparation, chemical properties and infrared spectra of these substances we have now studied their NMR-spectra in some detail. To our surprise NMR turned out to be an excellent method to demonstrate the isosterism relation in this group of compounds. This was to be observed with corresponding coupling constants as well as with the chemical shift values.

The 1 : 1 adduct of trimethylaluminum and trimethylphosphinic oxide (Ia) is the isoster of the basic organosiloxane member hexamethyldisiloxane (Ib) :



The same holds for the corresponding symmetric ethyl derivatives IIa and IIb.

In contrast to Ib and IIb the isosters Ia and IIa are sparingly soluble in alkanes or haloalkanes (as C_6H_{12} and CCl_4 , etc.. With the latter, moreover, chemical reaction occurs.) Only benzene showed satisfactory solvent properties for both types of compounds. To avoid significant solvent effects in this dangerously anisotropic solvent we have kept exactly equal concentrations for the compounds to be compared. Cyclohexane was used as an internal reference.

Ia shows the expected dublett for the $\text{CH}_3\text{-P}$ protons and a singlett for $\text{CH}_3\text{-Al}$ protons. The chemical shifts of these resonances yield an arithmetic mean $\bar{\delta} = 1/2 (\delta_{\text{CH}_3\text{P}} + \delta_{\text{CH}_3\text{Al}})$ which is surprisingly close to the value of the siloxane isoster Ib. (Table 1)

The complex A_3B_2 and A_3B_2X multipletts of IIa are not so easy to solve, as small internal shift differences and partial overlap lead to quite complicated features. At present we have determined only the δ and J values listed in the table, others remain to be done. [The constants of IIb have already been reported (1).] Again, however, a simple relation can be detected between $\bar{\delta} = 1/2(\delta_{CH_3CH_2P} + \delta_{CH_3CH_2Al})$ of IIa and $\delta_{CH_3CH_2Si}$ of IIb, though less convincing.

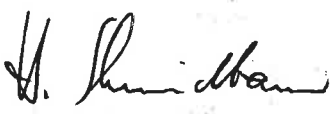
In addition to this chemical shift relationship between the isosters the coupling constants $J(^1H-^{13}C)$ showed a quite similar behaviour, which made our results more reliable and less fortuitous: Here the mean value of $J(^1H-^{13}C-Al)$ and $J(^1H-^{13}C-P)$ of Ia is now in good agreement with $J(^1H-^{13}C-Si)$ of Ib. (Table 1).

Unfortunately the $J(^1H_2-^{13}C)$ values of IIa and IIb could not yet be determined because of the difficulties mentioned above, but we are convinced that they should show the same relations.

The data of the unsymmetrical compounds III and IV listed in the table are also worth considering, but we think that a similarly simple arithmetic treatment would oversimplify the problem in these cases.

Yours sincerely


(Fritz Schindler)


(Hubert Schmidbaur)

1. H. Schmidbaur und H. Hussek, J. organometal. Chem. 1, 235 (1964), H. Schmidbaur und F. Schindler, ibid. 2, 466 (1964), H. Schmidbaur, J. Amer. chem. Soc. 85, 2336 (1963), Angew. Chem. 77, 170 (1965), H. Schmidbaur und I. Ruidisch, Inorg. Chem. 3, 599 (1964).

NMR-data of some siloxanes and their isosteric phospha-alumoxanes

(All values in cps; cyclohexane as an internal reference in benzene solution; conc. = 2.35 mol%; Varian A 60, 60 Mc; 35°C.)

		$\delta_{\text{CH}_3\text{P}}$	$\delta_{\text{CH}_3\text{Al}}$	$\bar{\delta}$	$\delta_{\text{CH}_3\text{Si}}$	$J(\text{H}^1\text{ }^3\text{CP})$	$J(\text{H}^1\text{ }^3\text{CAL})$	\bar{J}	$J(\text{H}^1\text{ }^3\text{CSi})$
Ia	$\text{Me}_3\text{POAlMe}_3$	+42.0 ^x)	+107.0	+74.5	-	127	108.5	117.8	-
Ib	$\text{Me}_3\text{SiOSiMe}_3$	-	-	-	+76.5	-	-	-	118.0
IIa	$\text{Et}_3\text{POAlEt}_3$	+45.5 ^{xx})	-8.0	+18.8	-	-	-	-	-
IIb	$\text{Et}_3\text{SiOSiEt}_3$	-	-	-	+24.0 ^{xxx})	-	-	-	-
IIIa	$\text{Me}_3\text{POAlEt}_3$	+39.0	-7.0	+16.0	-	127	-	-	-
IIIb	$\text{Me}_3\text{SiOSiEt}_3$	-	-	-	+76.0(Me) +24.5(Et)	-	-	-	-
IV	$\text{Et}_3\text{POAlMe}_3$	+47.0	+106.0	+76.5	-	-	109.0	-	-

^x) $J(\text{H}^1\text{-C-}^3\text{P}) = 13.5$; ^{xx}) $J(\text{H}^1\text{-C-C-}^3\text{P}) = 16.5$; ^{xxx}) $J(\text{H}^1\text{-C-C-}^1\text{H}) \sim 8.0$

**TEXAS CHRISTIAN UNIVERSITY**

Fort Worth, Texas 76129

Department of Chemistry

March 30, 1965

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

Dear Dr. Shapiro:

I would like to report here some data which will appear several months hence in J. Phys. Chem. The coupling constants are for the A_2B_2 ring spectra for the various systems.

Yours sincerely,

William B. Smith

William B. Smith
Professor of Chemistry

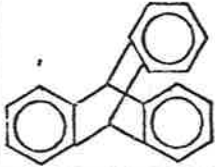
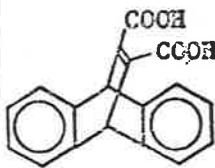
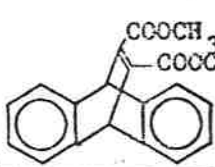
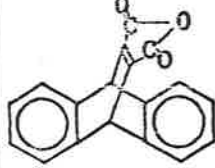
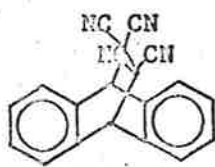
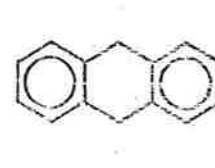
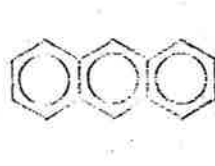
The NMR Spectra of Some 9,10-Bridged -9,10-Dihydroanthracenes

Abstract

The chemical shifts for a series of arylalkanes have been determined along with the values of $J_{C^{13}-H}$ for the alkyl protons. The observation that the alkyl protons in triptycene are more shielded than that of triphenylmethane led to the determination of the NMR parameters for a series of 9,10-bridged-9,10-dihydroanthracenes. The results of this study are presented.

Table II

Chemical Shifts and Coupling Constants in Acetone

COMPOUND	$\tau_{A_2B_2}$	Δ_{AB} cps	τ Bridge- head H	J_{AB}	$J_{AB'}$	$J_{AA'}$	$J_{BB'}$
	2.75	28.26	4.40	7.60	1.20	0.00	7.70
	2.72	27.46	3.98	7.60	1.20	0.00	7.70
	2.71	27.06	4.33	7.60	1.20	0.00	7.70
	2.68	30.76	4.21	7.60	1.20	0.00	7.70
	2.33	15.00	4.18	8.30	1.20	0.00	7.50
	2.75	7.14	6.09	7.93	1.47	0.00	7.10
	2.17	33.70	1.52	3.30	1.20	0.00	6.50



Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich

8006 ZÜRICH, March 29, 1965
Universitätstrasse
Tel. (051) 32 7330

Pr/bz

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

Renormalization in Quantum Chemistry and Theory of Chemical Shift

Dear Professor Shapiro:

For years we have been trying to understand a bit better the phenomenon of chemical shift, but as J.I. Musher wrote (MELLONMR No. 63-25), "we do not know as much about chemical shifts as we think we do". Of course, we accept the Ramsey formula as mathematically correct, but in spite of its correctness it obscures the relevant physical situation badly. We were never able to acquire a taste for the average energy ΔE -method; there is no excuse for such a crime. Of course we all know about the success of such semiempirical concepts as the ring current, bond susceptibility, polar groups etc. but these concepts were never derived in a correct way from the first principles of quantum mechanics. As Leon Brillouin says: "A mixture of different (and often incompatible) approximations is bound to be wrong, because some corrections will be counted twice, some other corrections may be used in problems where they do not apply, and finally some absolutely necessary corrections (too difficult to guess) will simply be ignored. Beware of semiempirical methods!"

One way out of this dilemma is a renormalization program for quantum chemistry. "Renormalization" means that we want to replace the mathematical ("bare") quantities in the theory by their physical counterparts ("dressed" quantities). Apart from quantum electrodynamics such a procedure is well known in classical thermodynamics, where by a Legendre transformation the primary quantities are replaced by more convenient ones (e.g. the Gibbs function G and the temperature T). A similar transformation is possible in quantum mechanics, and one can replace the bare 1- and 2-particle potentials in the Hamiltonian by the operationally much more significant 1- and 2-Greenfunctions.

After this long introduction we will explain what our nmr-group is now working on:

- a) Exact, renormalized theory of the linear chemical shift. In the renormalized version we do not ask "What is the chemical shift of a molecule when the Hamiltonian is given" but "Are there relations between the chemical shift and other observable quantities?" This approach proved to be fruitful. We could show that there is a close connection between the 3-dimensional charge density and the induced current density. For a molecule in a non-degenerated state this implies that besides of small correlation effects (usually in the order of a few percent) the chemical shift is just due to the first N natural currents which can be calculated from the first N natural orbitals. This means, that contrary to the impression that Ramsey's formula gives, we do not need any information about excited states, but that the information contained in the unperturbed ground state wavefunction is enough to explain the main part of the chemical shift.
- b) Theory of the higher order effects to the chemical shift tensor. This topic is of interest to us because the knowledge of these quantities allows us to get exact empirical information about the natural orbitals of a molecule.
- c) A good part of our current effort is being devoted to the development of the necessary equipment to measure higher order effects. These effects are tiny, of course, but would be most informative. We are hoping that there are no significant reasons why it should be impossible to measure chemical shift differences with an extreme accuracy, say of 0.0001 cps. We are optimistic and we will try it, but may be there are some pitfalls. If you have to remind us again for our contribution to your excellent IIT NMR Newsletter this does not mean that we do not esteem it but just that there were still unexpected difficulties either in 100 kV supply or in the 0.0001 cps detecting system.

With the very best regards.

Yours sincerely,

Hans Primas

Hans Primas

Adalbert Huber

Adalbert HUBER

Jürg Riess

Jürg RIESS

Bruno Hilti

Bruno HILTI



THE COLLEGE OF ADVANCED TECHNOLOGY

GOSTA GREEN, BIRMINGHAM, 4

DEPARTMENT OF CHEMISTRY

Telephone:

ASTon Cross 3611

Your Ref.

Our Ref.

Head of Department:

W. G. S. Parker, Ph.D., F.R.I.C., A.F.R.A.c.S.

Professor B.L.Shapiro,
 Department of Chemistry,
 Illinois Institute of Technology,
 Technology Center,
 Chicago 16, Illinois 60616,
 U.S.A.

Dear Professor Shapiro,

Please accept my apologies for the delay in sending my, by now overdue, subscription to the I.I.T. N-M-R newsletter.

Since my last contribution I have moved to the College of Advanced Technology, Birmingham (University of Aston in Birmingham Designate) and set up an N.M.R. laboratory based on a Perkin-Elmer R.10 spectrometer. The equipment allows ^1H , ^{19}F , ^1H - ^1H decoupling (frequency sweep) and shortly ^{31}P and variable temperature studies.

To provide some idea of the fields of interest in this laboratory it is probably most convenient to list the work ready for publication:

1. The identification of the isomers of 1,3,5 - trimethyl - 1,3,5-triphenylcyclotrisiloxane and 1,3,5,7-tetramethyl - 1,3,5,7 tetraphenyl-cyclotetrasiloxanes by proton magnetic resonance.
2. ^{19}F resonance studies of perfluoro - and highly fluorinated norbornanes.*
3. A method for the experimental determination of the effective dipolar centres of certain molecules.

Probably of more interest to some readers of I.I.T N-M-R would be comments on our (with Mr. P.J.Huck) progress with the problem of ^{19}F - ^{19}F decoupling with the R.10; neither the equipment nor the best method of doing this being available from Perkin-Elmer. So far I have not found anyone who has succeeded in this, but, needless to say, I should be extremely interested to hear from anyone who has. Because of routine service commitments the problem reduced to finding the best method with as little modification to normal instrument operation as possible. The solution, or more correctly partial solution, is surprisingly simple and enables ^{19}F - ^{19}F field sweep decoupling experiments to be carried out by two methods, both being possible because of the wide working

frequency range of the phase-detection system.

Method 1 The RF carrier (56.454 Mc/sec) is suppressed as completely as possible and the following procedure followed.

(a) Plug (PD-PL7) on the front of the phase detector unit is removed and a signal at a frequency ν equivalent to the chemical shift of the nuclei of interest is taken to pin 4 of SKT 7 to produce outputs of 1v at SKT1 and SKT2,

(b) The signal to be saturated is observed on the scope at 56.454 Mc/sec $\pm \nu$ (upper or lower sideband) in the conventional manner.

(c) The R.F level is raised suitably for saturation and the bridge balanced.

(d) The upper bridge control is off-balanced to give a 5-6 v reading on the front panel meter and the homodyne supply to the R.F amplifier removed (There is now sufficient 56.454 Mc/s $\pm \nu$ entering the R.F. amplifier to act as homodyne for effective detection of signals at the carrier frequency.

(e) The decoupled signal now appears on the 'scope at the carrier frequency, either as a result of incomplete carrier suppression or by the introduction of carrier from the 200 mV homodyne through the channel 2 attenuators to the probe.

Upper sideband mode of operation is used to observe the more shielded and lower sideband the less shielded of the decoupled nuclei. By this method J's of up to 30 c/sec can be eliminated. Further, by frequency variation of the L.F. input to the phase detector, at a rate comparable with that of the field sweep, decoupling can be extended over a much wider range.

Method 2. For best results this method necessitates building a phase splitter to produce two equal intensity, 90° phase differing, signals at 4Kc/sec. A circuit similar to that used by the manufacturers is satisfactory. The procedure is as follows:-

(a) The absorption of the nucleus to be saturated is observed on the 'scope. Select a suitable R.F. saturation level, balance the bridge and then off-balance to give a 5-6 V front panel meter reading and remove homodyne.

(b) The 4 Kc/sec signal at pin 2 of the phase detector SKT 7 is taken to the auxiliary phase splitter and the outputs from this to pins 4 and 12 of R.F.S.1 (care in selecting the correct quadrature connections)

(c) To minimize complications throw the 4 kc/sec switch in the R.F. compartment to R.F.S. 2.

(d) An L.F. signal from an external oscillator is split to give a low level $\leq 5V$ and a high level $\leq 26V$ supply at frequency ν . The

former is taken to modulation input E.M.3 (close modulation switch), and the latter to phase detector SKT.7 pin 4 for reference.

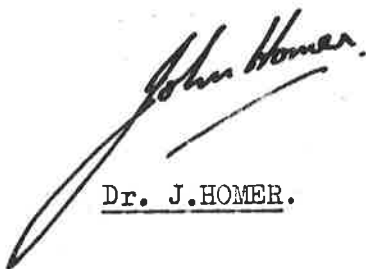
(e) The decoupled signal now appears on the 'scope.

In both methods complete elimination of unwanted signals from the saturated nuclei can be achieved by careful adjustment of the bridge controls.

Fig. 1 illustrates the application of Method 2 to cis - 1-hydro, heptafluoro but -2- ene.* The fluoromethylene ^{19}F absorption is normally symmetrical with two sets of four quadruplets each. Strong irradiation of the fluoromethyl group, whilst simultaneously observing the fluoromethylene absorption, results in partial decoupling and two of the quadruplets are collapsed to single lines in the high field portion of the observed spectrum.

It should be pointed out that neither of the two methods are suitable for decoupling nuclei with small shifts. Work is in progress on overcoming this problem and I will inform you of the results when they become available.

Yours sincerely,

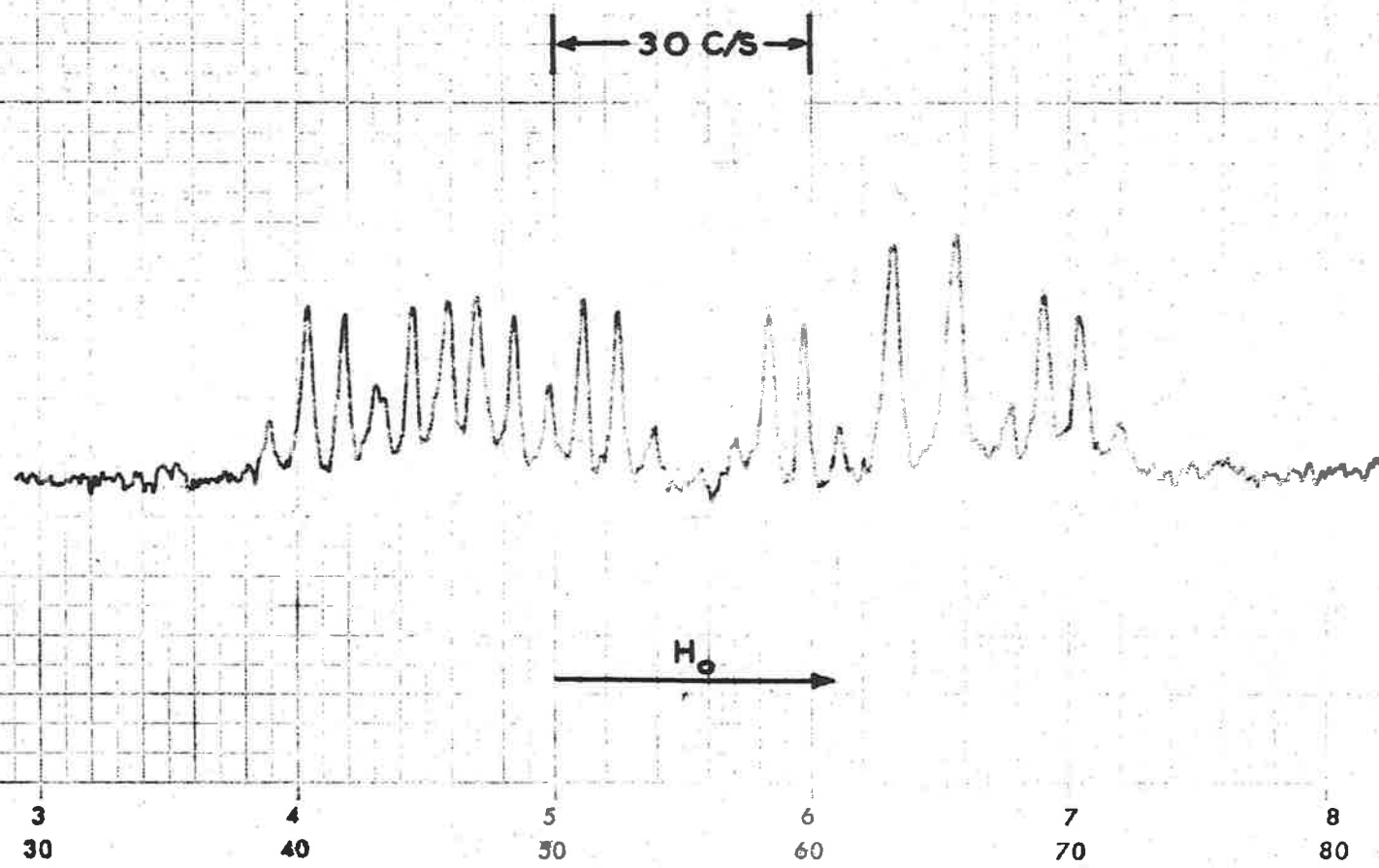


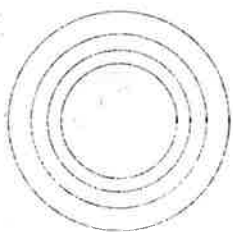
Dr. J.HOMER.

* Provided by Dr. R. Stephens, Department of Chemistry, The University of Birmingham.

FIGURE 1.

THE PARTIALLY DECOUPLED $-\text{CF}_2-$ ^{19}F SPECTRUM OF $\text{CF}_3\text{C}(\text{F})=\text{C}(\text{F})\text{CF}_2\text{H}$





VARIAN associates

611 HANSEN WAY

PALO ALTO, CALIFORNIA

326-4000

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

Dear Barry,

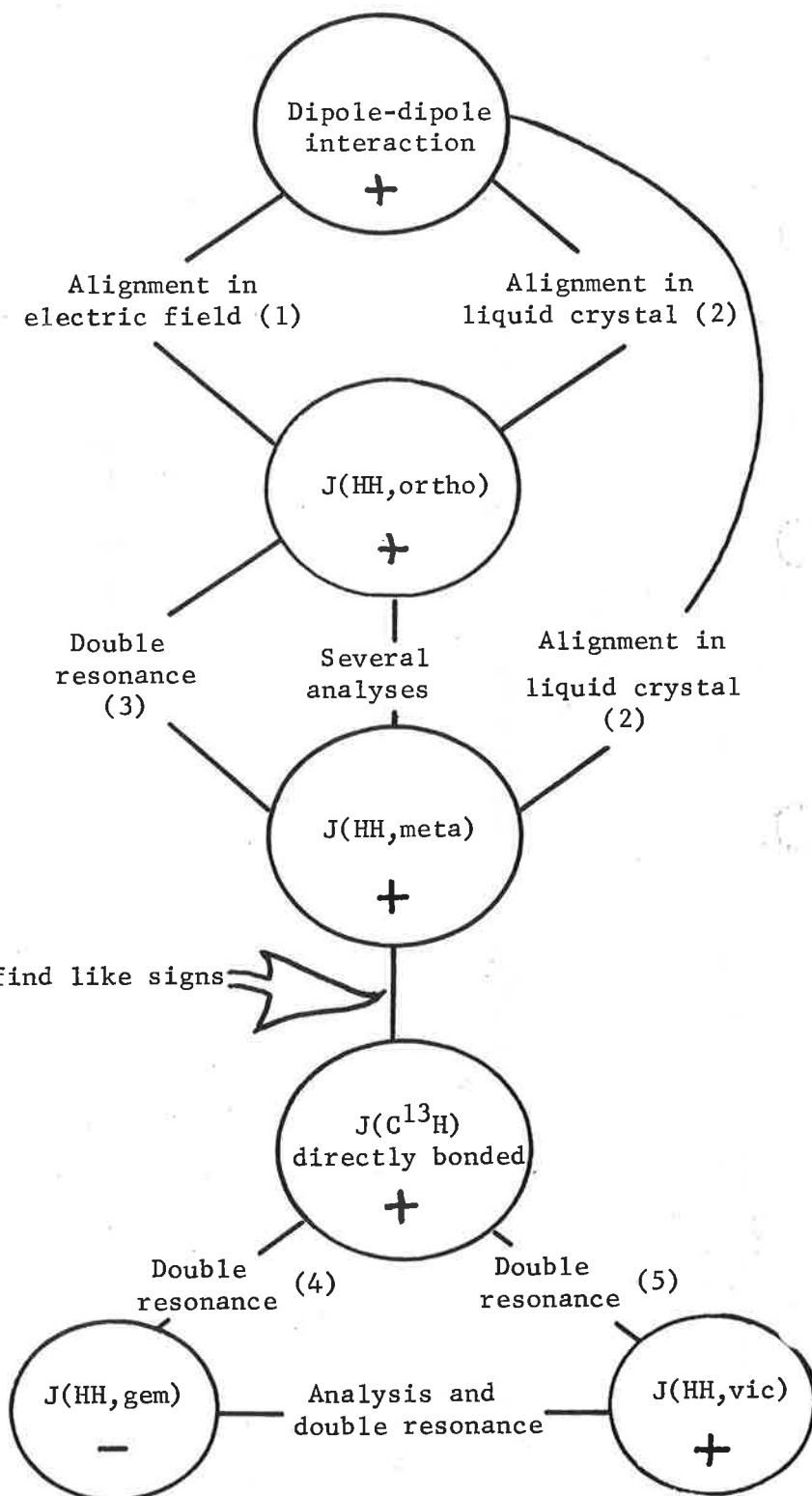
Just a short
tale about a relative sign
determination that

may turn out to be
one of the last
links required
to connect the
"absolute" sign
of the proton-
proton ortho

coupling in
benzene with
the aliphatic

series. With
acknowledgments
to Lewis Carroll;
Buckingham and
McLauchlan (1);
Saupe and Englert (2);
Freeman, Bhacca, and
Reilly (3); Anet (4);
Lauterbur and Kurland (5).

Pulsed spin decoupling and
pulsed tickling were both
used to record the inner
 C^{13} satellites of 1,3,5-
trichlorobenzene. We find like signs



Yours sincerely

Ray

Ray Freeman

THE SQUIBB INSTITUTE

FOR MEDICAL RESEARCH

NEW BRUNSWICK, N.J.

March 25, 1965

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

Dear Doctor Shapiro:

Recently, we have investigated hydrogen bonding of steroids at concentrations outside the range recommended for infrared studies and found some significant information concerning hydrogen bonding.

In a recent study of the chemistry of 11,12-oxygenated progesterones, a compound, ultimately assigned the structure of 11-keto-12 α -hydroxyprogesterone, was obtained which exhibited an unbound hydroxyl infrared frequency (3600 cm^{-1} , 0.001M CCl_4) and a NMR hydroxyl resonance band near 5.7 τ (ca. 0.2M CDCl_3).² Previous correlations of intramolecular hydrogen bonding by NMR and IR spectroscopy^{3,4} has led to the generalizations shown in Figure 1. For the compound under consideration, a chemical shift, of 5.7 τ would suggest strong hydrogen bonding. Further examination at various concentrations demonstrated that the hydroxyl chemical shift is extremely concentration dependent (0.23M, 5.67 τ ; 0.16M, 5.94 τ ; 0.08M, 6.40 τ) and the I.R. spectra showed the intermolecular bound form predominates at concentrations greater than 0.05M. From I.R. considerations, Cole and Muller⁵ suggest the triterpenoid α -ketol cerin may intermolecularly hydrogen bond by cyclic dimerization. We feel our spectral evidence establishes this mode of hydrogen bonding in a large molecule where it is sterically permitted. The change in chemical shift is proportional to the number of molecules involved in molecular association.

In our initial survey, we find that chemical shifts of intramolecularly bound hydroxyl protons are essentially concentration independent over a four-fold change in concentration (ca. 0.2 to 0.05M). At concentrations of 0.2M or less hydroxyl groups involved in linear intermolecular bonding resonate at 7.5 τ or greater while compounds involved in the cyclic dimerization of their ketols or diols resonate at lower fields.

Barbara T. Keeler
Barbara T. Keeler

Yours truly,

Allen I. Cohen
Allen I. Cohen

Professor B. L. Shapiro

- 2 -

March 25, 1965

1. L. P. Kuhn, J. Am. Chem. Soc., 74, 2492 (1952).
2. E. J. Becker, R. M. Palmere, A. I. Cohen and P. A. Diassi,
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B. J. Junta, R. M. Palmere, and P. Diassi, Steroids, 5, 57(1965).
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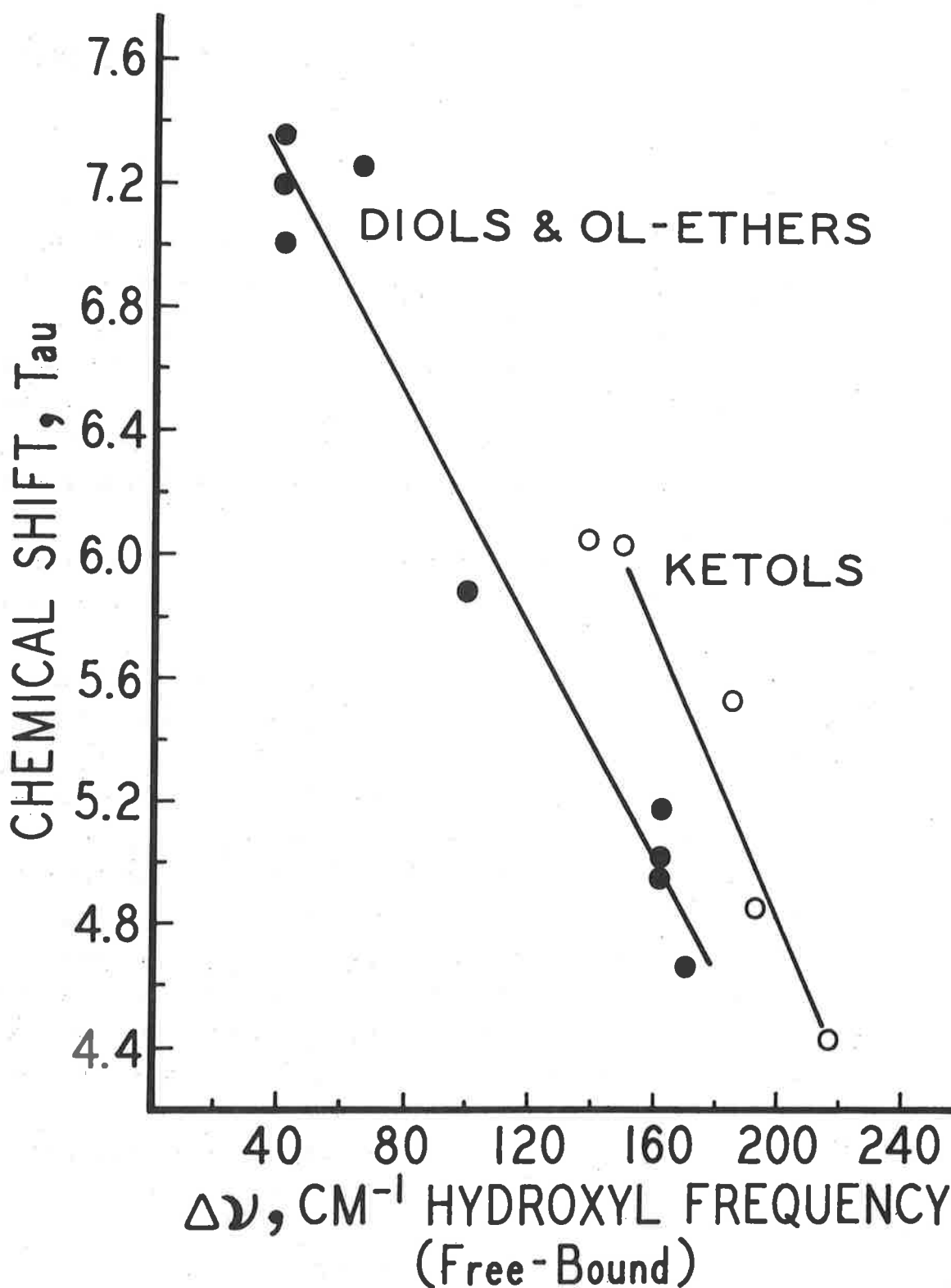


Figure 1 - The variation of the hydroxyl chemical shift as a function $\Delta\nu$ cm^{-1} of the hydroxyl infrared band

INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES
 GIF-SUR-YVETTE (S.-&O.)

TÉL. : 928 46-76

5 Avril 1965

Information upon and from solvent effects;
Theory of allylic coupling.

A- Nous avons étudié l'effet des solvants sur $\text{ClH}_A\text{C}=\text{CH}_B\text{OC}_2\text{H}_5$, et mis en évidence ce que nous croyons le premier exemple d'une variation de $^3J_{\text{H-H}}$ dans une molécule rigide. J_{AB} varie de $4,2^5$ Hz (5% v/v dans $(\text{CH}_3)_2\text{SO}$) à 6,3 Hz (5% v/v dans C_6H_{12}), les valeurs intermédiaires sont observées pour d'autres concentrations et d'autres solvants ($\text{C}_6\text{H}_5\text{NO}_2$, C_6H_6 , CCl_4). On observe une assez bonne corrélation inverse de J_{AB} avec le déplacement chimique interne $|\nu_A - \nu_B|$, qui varie de 56,3 Hz (5% v/v dans C_6H_{12}) à 85,9 Hz (5% v/v dans $(\text{CH}_3)_2\text{SO}$), à 60 MHz. Il nous semble encore prématuré de nous prononcer sur l'origine du phénomène.

B- Nous avons mesuré les déplacements chimiques des groupes méthyles dans la méthyl-2 cyclohexanone (1), la diméthyl-2,2 cyclohexanone (2), la triméthyl-2,2,6 cyclohexanone (3), et la tétraméthyl-2,2,6,6 cyclohexanone (4), en solution diluée dans CDCl_3 , CCl_4 , et C_6H_6 . A partir des variations obtenues, qui recourent de très près les observations antérieures sur les cétones stéroïdes (1), nous avons pu vérifier que la géométrie relative de la cyclohexanone et du noyau aromatique était identique pour les complexes obtenus avec 1-3, et nous avons alors pu interpréter les singularités observées pour 4 comme résultant de la déformation en une chaise très aplatie ou une forme croisée. Les paramètres IR ($\nu_{\text{C=O}}$) et UV (λ_{max}) sont en accord.

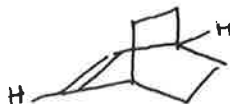
C- Les points suivants nous paraissent importants à discuter, compte-tenu des tentatives récentes de Garbisch (2) et de Barfield (3) :

a/ effet de la dimension du cycle.cf.(4)



$$^4J = +0,55$$

$$\theta \cong 20^\circ$$



$$^4J = +1,5$$

$$\theta \cong 0^\circ$$

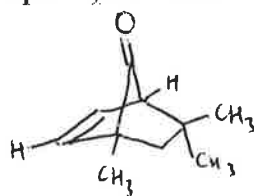
b/ exaltation du couplage allylique par une insaturation proche, par exemple :



$$^4J = 0,55$$

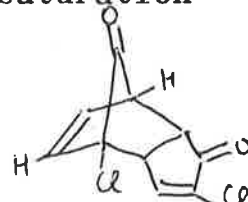


$$^4J = 0,95$$



$$^4J = 1,4$$

(5)



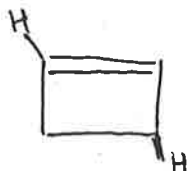
$$^4J = 1,8$$

(6)

un "principe" qui semble généralement admis dans l'étude du couplage entre protons de manière aussi implicite qu'intangible est que celui-ci intervient toujours par le chemin le plus court (celui qui comporte le plus petit nombre de liaisons) et seulement par le chemin le plus court.

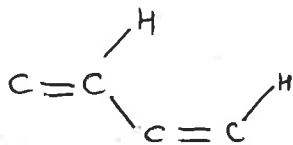
Rien ne permet de l'affirmer.

c/



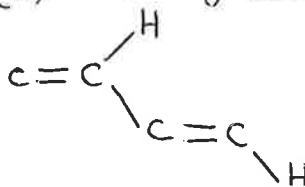
$$^4J = +1,55 \quad (7)$$

d/



$$^4J = -0,8$$

(8,9)



$$^4J = -0,9$$

- (1) N.S. Bhacca et D.H. Williams, *Tetrahedron Letters*, 3127 (1964)
- (2) E.W. Garbisch Jr, *Chem. Ind.*, 1715 (1964); *J. Am. Chem. Soc.*, 86, 5561 (1964)
- (3) M. Barfield, *J. Chem. Phys.*, 41, 3825 (1964)
- (4) P. Laszlo et P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1171 (1964)
- (5) J.J. Hurst et G.H. Whitham, *J. Chem. Soc.*, 710 (1963)
- (6) C.H. de Puy et al., *J. Org. Chem.*, 29, 3503 (1964)
- (7) S. Borčić et J.D. Roberts, *J. Am. Chem. Soc.*, 87, 1056 (1965)
- (8) E.O. Bishop et J.I. Musker, *Mol. Phys.*, 6, 621 (1963)
- (9) R.T. Hobgood et J.H. Goldstein, *J. Mol. Spectry*, 12, 76 (1964)

Le travail A résulte d'une collaboration avec le Dr.H.J.T.Bos, de l'Université d'Utrecht (Pays-Bas); B a été fait avec les Drs. (Mme.) S.Bory et M.Fétizon, de cet Institut, et D.H.Williams, de l'Université de Cambridge (Grande-Bretagne). Je peux expédier des exemplaires de ma thèse de doctorat, intitulée "Les constantes de couplage en résonance magnétique du proton", qui comporte entre autres la discussion du point C, à ceux qui seraient intéressés par sa lecture.

Veuillez croire, cher Barry, à mon amical souvenir (HOW BIG CAN YOUR "DEADLINE DATES" ARROW GROW ?)

I Wish you won't quash this pulsion !

Ciève

PIERRE LASZLO

UNIVERSITY OF CALIFORNIA, LOS ANGELES

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

 DEPARTMENT OF CHEMISTRY
 LOS ANGELES, CALIFORNIA 90024
 April 7, 1965

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

Dear Barry:

 ^1H Magnetic Resonance Spectrum of $(\text{CH}_3)_2\text{P}(\text{S})\text{H}$.

We wish to report the NMR spectrum of $(\text{CH}_3)_2\text{P}(\text{S})\text{H}$, Fig. 1 and Table 1, and in particular to note the relative signs of P-H and P-C-H coupling constants. In the free phosphines, CH_3PH_2 and $(\text{CH}_3)_2\text{PH}$, Whitesides, Beauchamp and Roberts (see Table 1) found that the relative signs of the above-mentioned coupling constants were the same. We find that in the phosphine sulfide the coupling constants are of opposite relative sign.

Table 1

Compound	Chemical Shifts (τ , p.p.m.)		Coupling Constants (cps)			
	CH_3	H	P-H	P-C-H	H-P-C-H	$^{13}\text{C-H}$
CH_3PH_2^*	9.02	7.37	± 186.4	± 4.1	8.2	
$(\text{CH}_3)_2\text{PH}^*$	8.94	6.87	± 191.6	± 3.6	7.7	
$(\text{CH}_3)_2\text{P}(\text{S})\text{H}^{**}$	8.20	3.08	± 455.0	∓ 14.30	4.65	128.0

*) G. M. Whitesides, J. L. Beauchamp and J. D. Roberts, J. Am. Chem. Soc. **85**, 2665 (1963).

**) This work.

The spectrum of dimethylphosphine sulfide is almost entirely first order, yet there is sufficient asymmetry in the methyl resonances due to some interaction with the nearby high field P-H septet that a determination of the relative signs of the P-H and P-C-H coupling constants is possible by computer techniques. The experimental and calculated spectra for the methyl peaks are shown in Figure 2. Above the observed spectrum are the calculated lines for opposite relative signs for P-C-H and P-H coupling constants. The low field doublet is broadened by interaction with the P-H septet (not shown here) which is in agreement with observed spectrum. In the calculated spectrum below the observed lines, broadening of the high field doublet is obtained, which is not in agreement with observed spectrum. In these calculations we used a modified NMRIIT program which takes into account symmetry factoring to save computer time, which was written by R. M. Stanley, D. W. Marquart and R. C. Ferguson (SHARE General Program Library, I.B.M. Inc., No. DPENMR (PA) 3165). The above-mentioned program is written for the IBM 7040 computer and was converted by us for use with the IBM 7094 of the U.C.L.A. Computer Facility.

Professor B. L. Shapiro
April 7, 1965
Page 2

Double resonance experiments were used to confirm the assignments of relative signs. Irradiation at the low field septet caused collapse of the high field doublet and irradiation of the high field septet collapsed the low field doublet.

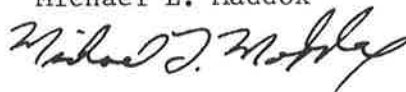
We believe it is the P-C-H coupling constant rather than the P-H coupling constant which has changed its absolute sign. In all probability, it has shifted by 17.9 c.p.s. from ± 3.6 c.p.s. in the free phosphine to ∓ 14.30 c.p.s. in the phosphine sulfide. This is in agreement with the conclusions of Manatt, Juvinal and Elleman (J. Am. Chem. Soc., 85, 2664 (1963)) that the P-C-H may have either a positive or a negative absolute sign in various organophosphorus compounds, but that the P-H coupling constant remains the same (and of positive) absolute sign. Preliminary results indicate that the effect of coordinating trimethylaluminum to dimethylphosphine also causes a change in the relative signs of the P-H and P-C-H coupling constants.

Best personal regards.

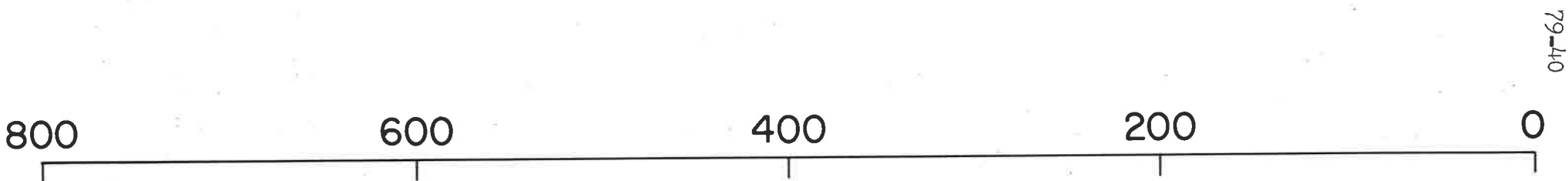
Herbert Kaesz



Michael L. Maddox

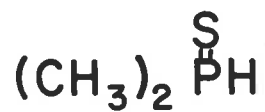


HK:MLM:smd



A. DIMETHYL PHOSPHINE SULFIDE

NEAT LIQUID/HMDSO
INTERNAL STANDARD

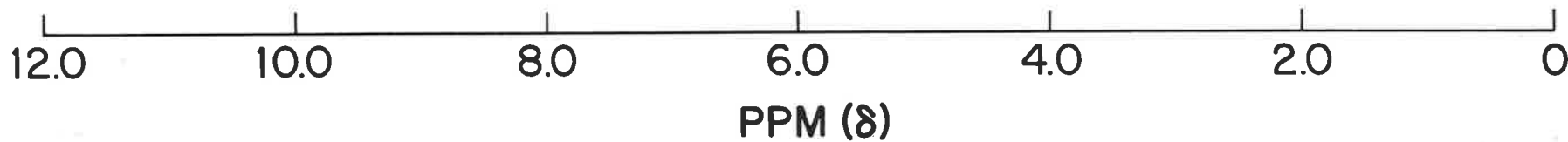


(a) (b)

(a) 1.79 ppm

(b) 7.00 ppm

(c) 2.17 ppm imp (Acetone)



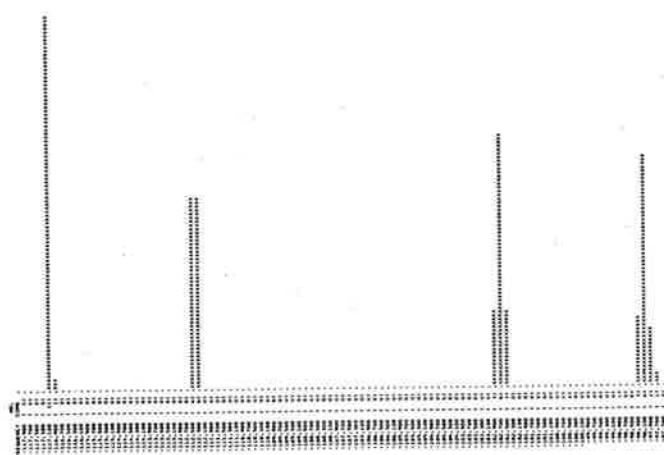
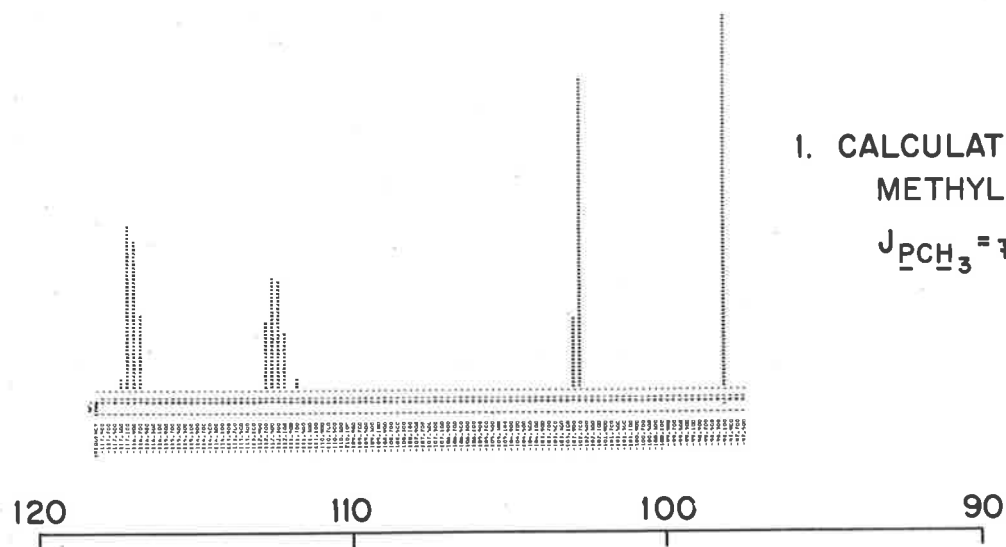


Fig 2

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT

69 HEIDELBERG, April 12, 1965
Tiergartenstraße
Tel. 483/2411
bei Durchwahl 483/..... mi

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

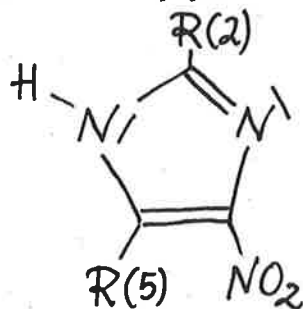
H/D Exchange of Imidazoles in 4/5-Position

Dear Dr. Shapiro:

We have continued studying the H/D exchange of azoles ^{1,2)}, this time looking at the 4- and/or 5-hydrogens of imidazoles.

R.J.Gillespie and coworkers ³⁾ claimed that imidazole in D₂O during 4 hours at 250° is deuterated in the 4- and 5-position without exchange of the 2-proton. Since their result seemed to disagree with our findings ^{1,2)}, we repeated their experiment and found by NMR that the 2-proton as well as the 4- and 5-hydrogens are deuterated under the conditions given by the above authors. 1-Methylimidazole yields 1-methyl-2,4,5-d₃-imidazole by the same procedure.

Before investigating the H/D exchange of 4(or 5)-nitroimidazole (I), it was necessary to correlate its signals at

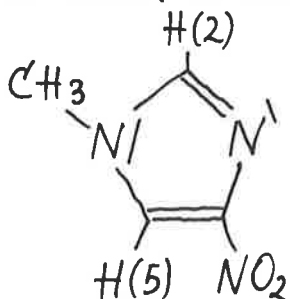


- I R(2) = R(5) = H
II R(2) = CH₃, R(5) = H
III R(2) = H, R(5) = CH₃

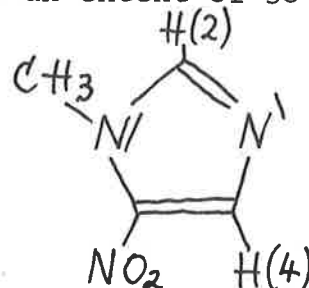
τ = 2.12 and 1.66 in dimethylsulfoxide (DMSO) to H(2) and H(5 or 4). This was done by comparison with 2-methyl-4(or 5)-nitroimidazole (II, $\tau_{5(or\ 4)}$ = 1.80 in DMSO) and 5(or 4)-methyl-4(or 5)-nitroimidazole (III, τ_2 = 2.36 in DMSO), the result being

$\tau_2 = 2.12$ and $\tau_{5(\text{or } 4)} = 1.66$ for nitroimidazole in contrast to all other imidazoles investigated ²⁾. Nitroimidazole (I) was heated in D_2O to 100° for 13 hours and analysed by NMR. The intensity ratio of the H(2) and H(5 or 4) signals was approximately 3:5, i.e. the exchange of the 2-hydrogen was faster than that of the 5(or 4)-proton.

1-Methyl-4-nitroimidazole (IV), treated in neutral solution as above, exchanged its 2-position to an extent of 50 % and its



IV



V

5-position to an extent of 90 %, whereas 100 % of H(2) and only 10 - 20 % of H(4) in 1-methyl-5-nitroimidazole (V) were deuterated under the neutral conditions mentioned above. (In these cases the methyl group protons served as an internal standard for integration, allowing approximate extents of deuteration to be determined.) The differences concerning H(5) and H(4) should be due to the neighborhood of the amino nitrogen to the exchanging proton in IV or of the aza nitrogen in V. The amino nitrogen is more electron deficient than the aza nitrogen and may, therefore, accelerate the exchange as observed.

With kindest regards,
Yours sincerely,

Hermann Irngartinger

Hermann Irngartinger

Albrecht Mannschreck

Albrecht Mannschreck

- 1) H.A.Staab, M.-Th.Wu, A.Mannschreck and G.Schwalbach, Tetrahedron Letters 1964, 845.
- 2) A.Mannschreck, W.Seitz and H.A.Staab, Ber.Bunsenges.Physic.Chem. 67, 470 (1963).
- 3) R.J.Gillespie, A.Grimison, J.H.Ridd and R.F.M.White, J.Chem.Soc. 1958, 3228.



CONTINENTAL OIL COMPANY

P. O. DRAWER 1267
PONCA CITY, OKLAHOMA
Research and Development Department

April 9, 1965

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

Dear Barry:

Cis and Trans β -Nitrostyrenes

We would like to report some preliminary data and conclusions on cis and trans isomers of three β -nitrostyrenes. The cpds. are β -nitrostyrene, α -methyl- β -nitrostyrene, and β -methyl- β -nitrostyrene. The cis isomers were prepared by solar irradiation of the trans compounds and were separated by silicic acid chromatography.

	$\delta(H_a)$	$\delta(H_b)$	$\delta(CH_3)$	Appearance of phenyl signal
	(ppm. from TMS)			
<hr/>				
$\emptyset CH = CHNO_2$				
trans	7.95	7.53	—	Singlet
cis	6.71	6.91	—	Multiplet
$\emptyset CH = C \begin{matrix} \diagup NO_2 \\ \diagdown CH_3 \end{matrix}$				
trans	8.00	—	2.40	S.
cis	6.34	—	2.30	M.
$\emptyset \begin{matrix} \diagdown \\ CH_3 \end{matrix} C = CHNO_2$				
trans	—	7.16	2.58	S.
cis	—	6.96	2.13	M.

Dr. B. L. Shapiro
Page 2

The assignments for β -nitrostyrene are on the basis of line width: deuteration experiments are in progress.

The cis isomers of these compounds are quite sterically hindered. Models indicate that the phenyl and nitro groups cannot both be coplanar with the ethylenic double bond.

We believe the magnitudes of the trans \rightarrow cis shifts observed indicate that in the cis isomer the nitro group remains in the plane and the phenyl group is twisted out of the plane. In each case, the trans \rightarrow cis change is greater for an α -substituent (in β -nitrostyrene; 1.24 ppm for an α -H, 0.62 ppm for a β -H). Also the multiplicity of the phenyl resonance in the cis isomer seems to indicate that the ortho hydrogens are in a different environment, as they should be if the phenyl group is twisted out of the plane.

Sincerely,

Pat W. Flanagan
Pat W. Flanagan

Donald B. Miller
Donald B. Miller

PWF/DBM-SS



Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9, England

Telephone: CHEETHAM HILL 1411 Telex: 66152/3/4 MANCHESTER

Telegrams: BRIDYCOR, MANCHESTER

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

Your Ref:

Our Ref: PL/PHY-5
Research Department.

Dear Dr. Shapiro,

Thank you for reminding us that a further contribution to the N.M.R. Newsletter is due. We now have some more C^{13} results obtained by the $H^1 - C^{13}$ double irradiation technique using our modified HR 100 spectrometer (for details of apparatus, etc., Allen, Beconsall and Turner, J.Sci. Insts. 41 673, 1964).

H^1 and C^{13} Solvent Dilution Shifts

We have studied the effects of various solvents on the chemical shifts of the CH_3 protons and natural abundance C^{13} nuclei in the polar compounds methyl iodide and acetonitrile. The electric "reaction field", which results from local polarisation of the medium by the permanent electric dipole of the solute molecule, is given by the simple spherical cavity model of Onsager as

$$R = \frac{2(K-1)(n_o^2-1) \cdot \frac{m_o}{\alpha}}{3(2K + n_o^2)}$$

(m_o = electric dipole moment of free solute molecule, α = polarisability of pure solute, K = dielectric constant of medium, n_o = refractive index of pure solute). Buckingham (Can. J.Chem., 38, 300 (1960)) has discussed the effect of R in distorting the solute molecule and thereby altering the chemical shift, and predicts a linear dependence of the chemical shift on R . If the chemical shifts for a given solute in a variety of solvents, extrapolated to infinite dilution, are plotted against

$$\frac{K-1}{2K + n_o^2}$$

(K being now the solvent dielectric constant), a straight line should then result.

Laszlo and Musher (J.Chem. Phys., 41, 3906 (1964)) have presented measurements of proton solvent shifts and shown that these simple assumptions do not adequately describe their results, which give curved plots.

The plots obtained from our results do not even approximate to smooth

FROM Imperial Chemical Industries Limited,
Dyestuffs Division, Manchester, 9, England.

CONTINUATION: Sheet No. 2

TO Dr. B. L. Shapiro, Illinois Institute of Technology, Date
Chicago, Illinois 60616, U.S.A.

curves, and suggest a very poor correlation between the solvent dilution shifts and R calculated as above. This could result from either or both of the following:

(i) the theoretical model is an inadequate description of the reaction field effect,

(ii) effects other than that of the reaction field are appreciable.

We consider that the reaction field is, in fact, the predominating effect, at least for the C^{13} shifts, which are much larger (e.g. up to 7 p.p.m.) than any expected magnetic anisotropy effects. Van der Waals effects could be more significant, but published results suggest that these too are of a smaller order of magnitude. We conclude, therefore, that the theoretical model is inadequate.

One inadequacy which does not appear to have been considered previously is that correlation times for random reorientation of the solute molecules may be comparable with dielectric relaxation times for at least some of the solvents, so that the effective dielectric constant is intermediate between the low-frequency value K and the high-frequency value n^2 (n = optical refractive index). We have found it possible to fit our results to straight-line plots on this assumption: we find that the effective dielectric constants are generally nearer to n^2 than to K . This would be consistent with solute molecule correlation times of the order of 10^{-11} second, which we believe to be not unreasonable.

Carbonyl C^{13} Shifts in Substituted Benzaldehydes

After measuring carbonyl C^{13} shifts in some substituted benzaldehydes by direct observation Stothers and Lauterbur (Can. J. Chem. 42, 1563, 1964) concluded that no correlation seemed to exist between the C^{13} shifts and Hammett parameters, in direct contrast to the H^1 and F^{19} results in substituted aromatic compounds. We have also looked at some carbonyl C^{13} shifts in substituted benzaldehydes, but by the indirect method. Table 1 shows the collected results from both sets of experiments. The indirect results were obtained relative to benzene and have an accuracy of ± 0.08 p.p.m. The value of + 65.0 p.p.m. for benzene relative to CS_2 has been used however to enable all the results to be related to CS_2 . The accuracy of the direct observations of Stothers and Lauterbur is ± 0.5 p.p.m.

Several points emerge from the results:-

(a) For substituents in the ortho position the carbonyl C^{13} shifts were found to correlate quite well with the shifts of the aldehydic proton. No correlation was found between these shifts for substituents in the meta and para positions.

(b) A plot of the carbonyl C^{13} shifts for meta substituted benzaldehydes against the Hammett σ_m parameters of the substituents was roughly linear for five of the examples. The last example, m-hydroxybenzaldehyde, was about 1.5 p.p.m. removed from the best line through the other five points. However this sample had to be examined in ethanol for solubility reasons, and the results obtained in the previous section show that a solvent effect in ethanol of 1.5 p.p.m.

(continued)

FROM Imperial Chemical Industries Limited,
Dyestuffs Division, Manchester, 9, England.

CONTINUATION: Sheet No. 3

TO Dr. B. L. Shapiro, Illinois Institute of Technology, Date
Chicago, Illinois 60616, U.S.A.

might easily be present. A plot using the separated Taft parameter σ_I showed no improvement over that using σ_m

- (c) Carbonyl C^{13} shifts for para substituted benzaldehydes showed no correlation with the Hammett σ_p or Taft σ_R parameters.

Two communications are about to be submitted for publication in which both the above topics are discussed more fully.

Yours sincerely,

J.K. Becconsall. A. Mathias. P. Hampson.

J.K. Becconsall
A. Mathias
P. Hampson

JKB/AM/PH/AYK.
Enc.

FROM Imperial Chemical Industries Limited
Dyestuffs Division, Manchester, 9, England.

CONTINUATION: Sheet No. 4

TO Dr. B. L. Shapiro, Illinois Institute of Technology, Date
Chicago, Illinois 60616, U.S.A.

TABLE 1.

CARBONYL C¹³ SHIFTS IN SUBSTITUTED BENZALDEHYDES

Substituent	p.p.m. from C ₆ H ₆	p.p.m. from CS ₂	S+L p.p.m. from CS ₂	Remarks
H	- 63.75	+ 1.25	+ 1.8	neat
O - Cl	- 60.61	+ 4.39		neat
m - Cl	- 62.72	+ 2.28		neat
p - Cl	- 61.62	+ 3.38		sat.soln. Et ₂ O
m - Br	- 61.89	+ 3.11		neat
o - OH	- 68.54	- 3.54	- 3.5	neat
m - OH	- 64.89	+ 0.11		Sat.soln. EtOH
p - OH	- 65.53	- 0.53		Sat.soln. EtOH
o - NO ₂			+ 5.0	Sat soln CHCl ₃
m - NO ₂			+ 4.0	Sat.soln.CHCl ₃
o - CH ₃			+ 0.9	neat
m - CH ₃			+ 1.4	neat
p - CH ₃			+ 1.9	neat
O - OCH ₃			+ 5.3	neat
m - OCH ₃	- 63.37	+ 1.63		neat
p - OCH ₃		+ 2.6	→	neat
p - N(CH ₃) ₂		+ 3.1	→	neat

MOUNT
HOLYOKE
COLLEGE

SOUTH HADLEY, MASSACHUSETTS 01075

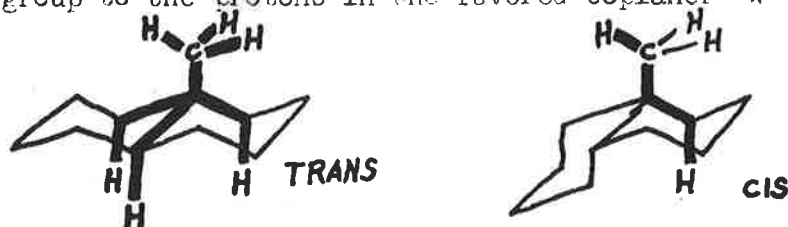
April 16, 1965

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

ANGULAR METHYL LINE WIDTHS TO DETERMINE
CIS-TRANS STEREOCHEMISTRY

Dear Barry,

Recently we have been measuring the line widths at half-height of the angular methyl group in a number of cis-trans pairs of decalins (See Table). In every case we have examined so far the line width of the trans-fused compound is wider than that of the corresponding cis-isomer. This is undoubtedly due to stereospecific long-range coupling of the methyl group to the protons in the favored coplanar "W" conformation:




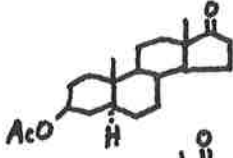

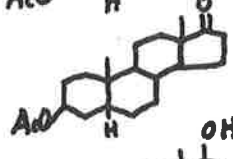
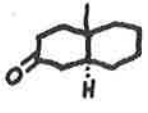
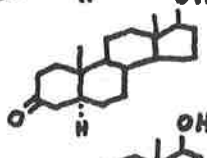
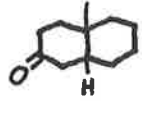
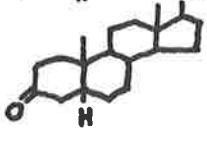
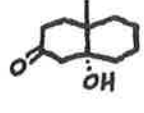
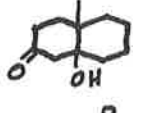
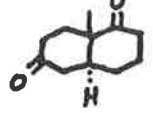
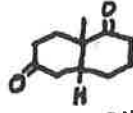
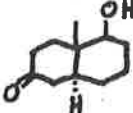
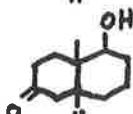
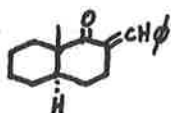
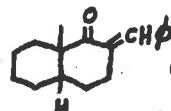
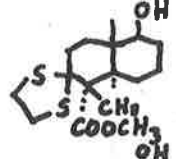
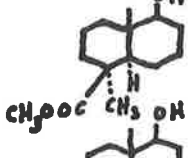
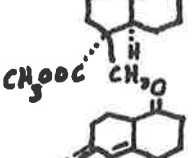
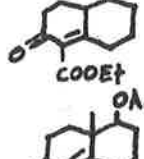
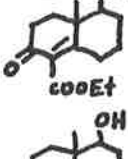
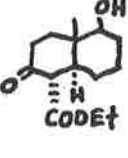
We have also examined the line widths of some cis-trans pairs of steroids. Here again the width of the C-19 methyl peak is greater in the trans-isomer than in the cis, but the differences are not great. It is also difficult to decide where the base line is in some of the steroids, so precise line width measurements are impossible.

In making these measurements we always have the A-60 resolution at its best, the TMS width being ≤ 0.4 c.p.s. Great care is also taken to avoid saturation. We have noted no concentration effects or solvent effects in the solvents we have used (CS_2 , CDCl_3).

Sincerely yours,

Kenneth L. Williamson

Angular Methyl Line Width at Half-Height (c.p.s.)

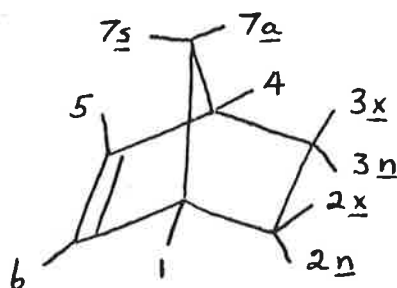
	1.2 trans		1.2 trans (AB ring)
	0.3 cis		0.8 cis
	1.9 trans		1.2 trans
	1.2 cis		0.9 cis
	1.4 trans	Some other examples, unpaired:	
	0.5 cis		
	1.0 trans		
	0.6 cis		
	1.3 trans		
	0.6 cis		
	0.75 trans		
	0.63 cis		
			1.6
			1.5
			1.4
			0.7
			0.9
			1.4

THE UNIVERSITY OF TEXAS
DEPARTMENT OF CHEMISTRY
AUSTIN 78712

April 3, 1965

Dear Dr. Shapiro,

We have been doing some proton-proton decoupling work on a variety of bicyclic compounds synthesized by Dr. Thomas Van Auken among which was a set of endo and exo substituted norbornenes. The decoupling was performed with the HR-60 integrator circuit. The compounds were:



<u>Compound</u>	<u>Substituent</u>	
	<u>2x</u>	<u>2n</u>
<u>I_n</u>	H	OH
<u>II_n</u>	H	COOCH ₃
<u>III_n</u>	H	CN
<u>I_x</u>	OH	H
<u>II_x</u>	COOCH ₃	H
<u>III_x</u>	CN	H

Of most interest was the fact that the endo-endo vicinal coupling (2n,3n) was consistently smaller than the exo-exo coupling (2x,3x). The 7a bridge peak was found to be sensitive to endo-exo substitution and several long-range couplings were found.

Jeff C. Davis, Jr.
Jeff C. Davis, Jr.

TABLE II FOOTNOTES :

- All other coupling constants not listed are zero.
- Coupling was not resolved but was indicated by sharpening of the lines by the decoupling frequency.
- Not observed in this work but proven by work in ref. 15 to be ~ 0.5 c.p.s. (Laszlo & Schleyer, J.A.C.S. 86, 1171 (1964).)

TABLE I
Chemical Shifts^a

H	<u>I</u> n	<u>II</u> n	<u>III</u> n	<u>I</u> x	<u>II</u> x	<u>III</u> x
1	174 (7.10)	188 (7.00)	190 (6.83)	163 (7.28)	173 (7.12)	190 (6.82)
<u>2</u> n	-	-	-	227 (6.22)	128 (7.83)	131 (7.82)
<u>2</u> x	261 (5.65)	174 (7.10)	171 (6.15)	-	-	-
<u>3</u> n	48 (9.20)	78 (8.70)	72 (8.80)	75 (8.75)	77 (8.72)	90 (8.50)
<u>3</u> x	118 (8.03)	112 (8.13)	126 (7.90)	103 (8.28)	112 (8.13)	115 (8.08)
4	164 (7.27)	172 (7.13)	178 (7.03)	163 (7.28)	179 (7.02)	181 (6.98)
5	359 (4.02)	353 (4.12)	369 (3.85)	355 (4.08)	366 (3.90)	362 (3.97)
6	376 (3.73)	366 (3.90)	378 (3.70)	365 (3.92)	366 (3.90)	368 (3.80)
<u>7</u> <u>a</u>	85 (8.55)	83 (8.62)	84 (8.60)	82 (8.63)	82 (8.63)	86 (8.57)
<u>7</u> <u>a</u>	73 (8.78)	78 (8.70)	72 (8.80)	93 (8.45)	90 (8.50)	93 (8.45)

a. c.p.s. downfield from TMS measured at 60 Mc. Values in parenthesis are shifts in τ units (p.p.m.).

TABLE II
Coupling Constants (c.p.s.)^a

<u>J</u>	<u>I_n</u>	<u>II_n</u>	<u>III_n</u>	<u>I_x</u>	<u>II_x</u>	<u>III_x</u>
$J_{1,7a}=J_{4,7a}$	1.4	1.3	1.3	1.3	1.4	1.4
$J_{1,7s}=J_{4,7s}$	1.8	1.9	1.9	1.9	1.8	1.8
$J_{2n,7s}$	-	-	-	2.9	3.0	3.0
$J_{3n,7s}$	2.8	3.0	3.1	2.9	3.0	3.0
$J_{5,7a}=J_{6,7a}$	<0.3 ^b	0.3 ^b	0.4	<0.3	<0.3	0.85
$J_{7a,7s}$	8.4	8.5	8.6	8.5	8.8	?
$J_{1,6}$	2.6	2.8	2.9	2.8	2.8	2.7
$J_{4,5}$	2.9	2.8	2.6	3.0	2.7	3.0
$J_{5,6}$	5.9	5.6	5.6	5.8	?	5.8
$J_{1,5}=J_{4,6}$	- ^c	- ^c	- ^c	- ^c	- ^c	- ^c
$J_{1,2n}$	-	-	-	0	0	0
$J_{1,2x}$	3.5	3.6	3.5	-	-	-
$J_{3n,4}$	0	0	0	0	0	0
$J_{3x,4}$	3.8	3.4	3.6	3.7	3.5	3.4
$J_{1,4}$	0	0	0	0	0	0
$J_{2n,3n}$	-	-	-	5.6	4.4	4.5
$J_{2x,3x}$	8.0	8.8	9.1	-	-	-
$J_{2n,3x}$	-	-	-	3.1	3.8	4.2
$J_{2x,3n}$	3.0	3.4	3.4	-	-	-
$J_{3n,3x}$	12.0	11.8	11.5	12.0	12.3	12.5

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13. APR. 1965

Prof. B.L. Shapiro,
 Dept. of Chemistry,
 Illinois Institute of Technology,
 Technology Centre,
CHICAGO,
 Ill. 60616,
 U.S.A.

Dear Prof. Shapiro,

Computer Programme

We are busy installing our new Varian HA-100 spectrometer. All other activities have consequently slowed down. We have been battling for quite some time to squeeze C.A. Reilly's iteration programme MARIP, a 7040 version of NMRI and NMREN, into our IBM 704, which has a rather small 8 K core storage only. We managed to do the job in the following way:

- (1) Restrict the programme to five spins only,
- (2) Treat NMREN as a separate programme,
- (3) Leave out the ERROR sub-routine altogether,
- (4) Split the main programme into three parts,
- (5) Write the programme on tape and use the loader PF PROG to get the various parts into the computer.

The programme has so far been tried on a four-spin problem and has worked well. If anyone faces the same problem of limited computer storage we will gladly supply a listing of the programme.

Yours sincerely,

A handwritten signature in dark ink, appearing to read 'K. Pachler'.

K. Pachler
 SENIOR RESEARCH OFFICER
 CHEMICAL PHYSICS GROUP
 NATIONAL CHEMICAL RESEARCH LABORATORY

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY

Frick Chemical Laboratory

April 17, 1965

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

Dear Barry:

Your reminder has prompted us to submit the following contribution to IIT NMR, in order to keep our subscription in force.

We have recently initiated a study of hydrogen bonding involving C-H bonds in heterocyclic molecules as proton donors. We are specifically interested in whether a hydrogen attached to a carbon flanked by two heteroatoms is sufficiently activated to detect complexing in the presence of bases. Infra red spectroscopic studies are made exceedingly complex by the presence in most cases of several types of magnetically non-equivalent hydrogen in the solution. We have chosen NMR as the tool for investigation, for here the various types of hydrogen are so separated on the NMR curve to allow for more easily interpreted results.

Some of our preliminary experiments and results are described below.

We have found that the resonance of H_2 (relative to TMS) of Benzthiazole (I) is shifted to lower field in a linear fashion upon replacing successive increments of CCl_4 with di-n-butyl ether. The sample concentration is not changed ($5 \mu l.$ in $0.4 ml$ solvent). The limiting chemical shifts are $\nu_{OH}(CCl_4) = 534.5$ cps and $\nu_{OH}(n-Bu_2O) = 539.0$. The total $\Delta(\nu_{OH}) = 4.5$ cps. By way of comparison, the data for $CHCl_3$, a known proton donor, are $\nu_{OH}(CCl_4) = 437$ cps and $\nu_{OH}(n-Bu_2O) = 456$ cps, $\Delta(\nu_{OH}) = 19$ cps. The chemical shift correlation with base

Dr. B.L. Shapiro

-2-

4/17/65

concentration again appears to be linear. A pertinent observation is also that the aromatic hydrogen absorption of I in appearance or shift does not change when effecting these solvent variations.

The simplest explanation of these results is that H_2 of I is involved in hydrogen bonding, albeit somewhat weaker than chloroform. Use of stronger bases show a greater chemical shift change in I, however substrate reaction with base leads to less clean results.

We are continuing our studies in this direction.

Sincerely,

L.B. Rodewald

L. B. Rodewald

Paul von R. Schleyer

Paul von R. Schleyer

Duke University
DURHAM
NORTH CAROLINA

DEPARTMENT OF CHEMISTRY

POSTAL CODE 27706
TELEPHONE 919-681-0111

April 16, 1965

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

Dear Barry,

We have been analysing some NMR exchange data for a collapsed unequal doublet, similar to the case observed for dilute aqueous hydrogen peroxide solutions (1) but for mixtures of water and hydrogen peroxide at the natural pH over the 0.05 to 1.00 mole fraction range of hydrogen peroxide (2). In this investigation we found it necessary to develop a fast, accurate analytical procedure for directly determining the half-height width of the exchange peak for values of the exchange parameter $\tau\delta$. We wished to eliminate the measurement of computer generated line-shapes which were used previously (1). We have used the lineshape equation of Gutowsky and Holm (3) in the derivation of two equations which give the exchange peak maximum and the width at half height. With these equations (cubic and quartic) a table of half-height widths of the exchange peak for given values of the proton fraction and exchange parameter $\tau\delta$ are easily calculated. A computer program was written in ALGOL for the IBM 7072, but other languages and computers should be suitable, since the program is simple and only about 15 sec. are required for each table. The analysis was successfully carried out using this procedure. Fuller details are available to those interested in this procedure. These are also described in a recently completed dissertation (4) which includes the kinetic results obtained.

Sincerely yours,



James J. McLeskey, III



Peter Smith

-2-

1. M. Anbar, A. Loewenstein and S. Meiboom, J. Am. Chem. Soc., 80, 2630 (1958).
2. P. E. Miller, Ph. D. Dissertation, Duke University, Durham, North Carolina, 1964; Diss. Abs., 25, 2784 (1964).
3. H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956).
4. J. J. McLeskey, III, Ph. D. Dissertation, Duke University, Durham, North Carolina, 1965.

Vlaardingen, 14th April, 1965.

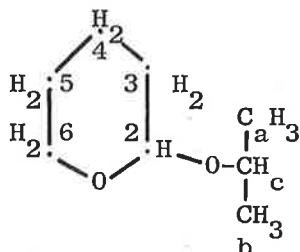
Dr. B.L. Shapiro, Associate Professor
 Department of Chemistry
 Illinois Institute of Technology
 Chicago, Illinois 60616
 U.S.A.

Dear Dr. Shapiro,

I hope you will accept this contribution, entitled "Two more examples of magnetic nonequivalence" as my subscription fee to IIT NMR Newsletter.

In the PMR-spectra, measured at 60 Mc (Varian A-60) of the following compounds, I have found "too many" lines:

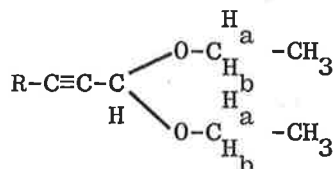
1)



2-Isopropoxytetrahydropyran gave the expected absorptions in CCl_4 -solution at 38°C . The H_c -septet ($\delta = 3.85$, $J = 5.8$) was superposed on the pattern from the protons on C_6 . Less expected was the methyl-"triplet" ($\delta = 1.12$, $J = 5.8$, int. = 6 protons), which I think is composed of 2 doublets. Compare the quartet absorption of the methyl

protons of the isopropylgroup α to the oxygen in the furanring of lunacrine (S. Goodwin, J.N. Shoolery and L.F. Johnson, J. Am. Chem. Soc. 81, 3065 (1959)). The value of ($\delta_{\text{aCH}_3} - \delta_{\text{bCH}_3}$) of 0.096 ppm decreases at temperatures above 38°C .

2)



In the spectrum of undecynaldiethylacetal, run neat or in solutions, at 38°C , the H_a and H_b protons show up as a multiplet of at least 12 lines.

At 70°C all 16 lines of the 4 AB-quartets are visible. In C_4Cl_6 (hexachlorobutadiene)-solution $\delta_{\text{H}_a} - \delta_{\text{H}_b}$ diminishes from 0.174 ppm at 38°C to

0.096 ppm at 180°C (except in the AB-system, quoted figures are first order). Compare G.M. Whitesides, D. Holtz and J.D. Roberts, J. Am. Chem. Soc. 86, 2628 (1964) for magnetic nonequivalence, due to molecular asymmetry. In the acetal, the lack of an "asymmetric" carbon atom (with 4 different groups) and the presence of a plane of symmetry are noteworthy.

The temperature dependence and SASM-molecule models ("montage compact") indicate that hindered rotation (and of course low symmetry) are the cause of the mentioned multiplicities.

Sincerely yours,

Drs. M. v. Gorkom
 Unilever Research Laboratory
 Mercatorweg 2
 Vlaardingen
 The Netherlands

"Preparation of 2-Acetyl-1,3-diketones from Acid Anhydrides and Isopropenyl Acetate"
F. Merényi and M. Nilsson
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L. M. Jackman and S. L. Jensen
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R. H. Martin, N. Defay, F. Geerts-Evrard et S. Delavarenne
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E. W. C. Wong and C. C. Lee
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"The Reaction of Unsaturated Carbohydrates with Carbon Monoxide and Hydrogen"
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Can. J. Chem. 43, 126 (1965)

"Oxygen-17 Nuclear Magnetic Resonance Study of the Chromate Reaction with Dichromate"

B. N. Figgis, R. G. Kidd and R. S. Nyholm
Can. J. Chem. 43, 145 (1965)

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