13.2.67

Prof. H. Primas

Illinois Institute of Technology N-M-R Newsletter

No. 100
JANUARY, 1967

OVER

Deadline Dates: No. 101 - 15 February 1967
No. 102 - 15 March 1967

ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, 60616 Ill.

DEPARTMENT OF CHEMISTRY

Concerning the Future of the [IIT] NMR Newsletter

This Newsletter was started at Mellon Institute in October 1958 by A. A. Bothner-By and myself. When I moved to IIT in February 1964, the Newsletter came with me. Thus the present issue is the one hundredth consecutive month that this Newsletter has appeared. From the original mailing list of 30-40 people, the Newsletter has grown to a present circulation of 260. The growth rate during the past year has been particularly high. Since one must contribute to the Newsletter in order to get it, and since I have been somewhat ruthless about cutting off delinquent subscriber-participants, the growth of the Newsletter must be attributed to the explosive growth in the number of NMR practitioners.

I feel that the time has now come to let someone else enjoy the proprietorship of this Newsletter. There are two kinds of associated burdens which I do not feel that in conscience we can maintain much longer. The first of these burdens is financial. Rating both secretarial and my own time as zero, each issue of the Newsletter you get still costs approximately $1.75 per copy to put in your hands. When you do the necessary arithmetic you will see that this sums to a distinctly non-trivial amount of money per year. There is no outside financial support for this endeavor and the cost has been borne first by Mellon Institute and in more recent years by Illinois Institute of Technology via our Chemistry Department budget. I have decided that I can no longer ask the school to continue an expense of this magnitude for our special benefit; I wish to make it clear that this feeling is mine - IIT has not in any way tried to back out. Indeed the IIT administration has always been and still is very favorably disposed toward the Newsletter.

The second burden to which I would refer is the fact that the sheer size of the NMR world and the Newsletter subscriber list has raised the amount of my time required past an acceptable level. The correspondence, bookkeeping and other clerical chores of a non-productive nature just take too much time and I feel very much the need to spend this time on other things.

For the reasons outlined, therefore, there seem to me to be only two courses of action. First, the Newsletter can simply cease to exist. (Perhaps the time for this has in fact come, although the continuously increasing interest in the Newsletter seems to argue otherwise.) Second, one of our present subscribers can elect to take over the Newsletter. Thus I am calling for volunteers to take over the Newsletter and to run it in whatever way they feel will most benefit the NMR community. Anyone interested in or willing to do this is urged to get in touch with me to discuss particulars. In any event, I wish to terminate my involvement in the Newsletter no later than the May 1967 issue.

B. L. Shapiro

B. L. Shapiro
13 January 1967

varian/611 hansen way/palo alto/california 94303/u.s.a./415/326-4000

December 16, 1966

Mlles. Miriam Rae
and Catherine Ruth Shapiro
3100 South Michigan Avenue
Apartment 502
Chicago, Illinois 60616

Dear Miriam and Catherine:

Time-averaged Vapor Phase NMR Spectra

Theoretical calculations of shielding constants require comparison with the chemical shifts observed in isolated gaseous molecules, in order to eliminate the effects of intermolecular interactions(arising from the anisotropic diamagnetic susceptibility of neighboring molecules, the induced reaction field of the medium, van der Waals or dispersion interactions, specific interactions such as hydrogen bonding, complex formation, etc.) Conversely, the contribution of solvent and liquid state effects may be studied by measuring the difference between condensed and vapor phase chemical shifts.

Using commercially available NMR probes, such gas or vapor phase measurements were typically performed by enclosing the volatile materials in sealed glass tubes at pressures up to 20 or 30 atm {Cf., W. G. Schneider, H.J. Bernstein, and J.A. Pople, J. Chem. Phys. 28, 601 (1958)}. It would obviously be more convenient.....not to mention, safer..... to employ ordinary pressures and leave the labor of signal enhancement to a time-averaging device. The latter, in turn, presupposes some manner of field-frequency control in the NMR equipment. One method of achieving this would be to lock the field to a capillary of TMS or other liquid reference material (R) within the sample tube. Vapors from the analytical sample (S) could then be introduced around the capillary and time-averaged. The observed chemical shift, however, would require correction for the bulk magnetic susceptibility (χ) of TMS and the "liquid association shift" (D) of TMS (defined by Schneider et al, ref. cit.):

$$D_R \equiv \left\{ \delta_R(1) - \delta_R(g) \right\}_{obs} - \frac{2\pi}{3} \chi_R$$

$$\left\{ \delta_S(g) - \delta_R(g) \right\} = \left\{ \delta_S(g) - \delta_R(1) \right\}_{obs} + \left\{ D_R + \frac{2\pi}{3} \chi_R \right\} =$$

$$= \left\{ \delta_S(1) - \delta_R(1) \right\}_{obs} + \left\{ D_R + \frac{2\pi}{3} \chi_R \right\} - \left\{ D_S + \frac{2\pi}{3} \chi_S \right\}$$

$$= \left\{ \delta_S(1) - \delta_R(g) \right\}_{obs} - \left\{ D_S + \frac{2\pi}{3} \chi_S \right\}$$

Alternatively, we have found that the HA-100 spectrometer will lock on TMS vapor in 5 mm O.D. tubes at pressures of the order of 1 atm. Operationally, one merely places a minute drop of TMS at the bottom of the sample tube. The ambient temperature of the probe (about 35°C) is slightly above the boiling point of TMS, but a commonplace plastic pressure cap will easily sustain the equilibrium vapor pressure. Another droplet of a second volatile substance can be introduced at the bottom of the tube, and the quantity $\{\delta_S(g) - \delta_R(g)\}$ directly determined by means of the C-1024 computer. (Mixture of miscible liquid droplets will reduce the vapor pressure of each component. For this case, and in the case of relatively non-volatile materials, the system might be heated with the variable temperature control unit.)

Relaxation times in the gas phase are generally shorter than those encountered in solution work, and all spectral lines observed so far exhibit linewidths of 2-3 Hz under the aforementioned conditions. Thus, the larger spin-coupling constants, such as those between vicinal protons, may still be resolved. The lock signal derived from TMS vapor is nothing to brag about, but it is adequate for utilization of the Autoshim* accessory. Sample spinning is no longer critical.

With fairly simple volatile compounds, and molecules containing a healthy complement of hydrogen nuclei, the absorption of interest may be observed in a single scan. For example:

$$\delta_{CHCl_3(g)} - \delta_{TMS(g)} = 7.10 \text{ ppm}$$

$$\delta_{C_6H_6(g)} - \delta_{TMS(g)} = 7.24 \text{ ppm}$$

could be determined in one pass at ambient conditions. The results of some time-averaging experiments are depicted in the accompanying figure. In the case of CH_3CHO, the small coupling between the methyl group and the aldehydic proton was incompletely resolved. Incidentally, acetic acid vapor has also been examined, and the $CH_3C^{=O}$ chemical shift is again 1.91 ppm. In the ethanol vapor spectrum at the bottom of the figure, the suppression of hydroxyl exchange is reflected in the methylene splitting pattern; the hydroxyl absorption in the absence of significant hydrogen bonding has moved considerably upfield and is partially obscured by the C^{13} satellite of the TMS lock signal.

From the equations presented earlier, it is clear that the quantity $(D_S + \frac{2\pi}{3}\chi_S)$ may be determined from the direct gas phase measurement and one liquid capillary experiment. Knowledge of χ_S at the temperature of the investigation then yields the desired liquid association shift.

At this juncture, I would like to propose that all proton chemical shifts be referenced to TMS(g), as far as practicable. The numbers forthcoming would be termed **€** - values (for yours truly, since God helps those who help themselves).

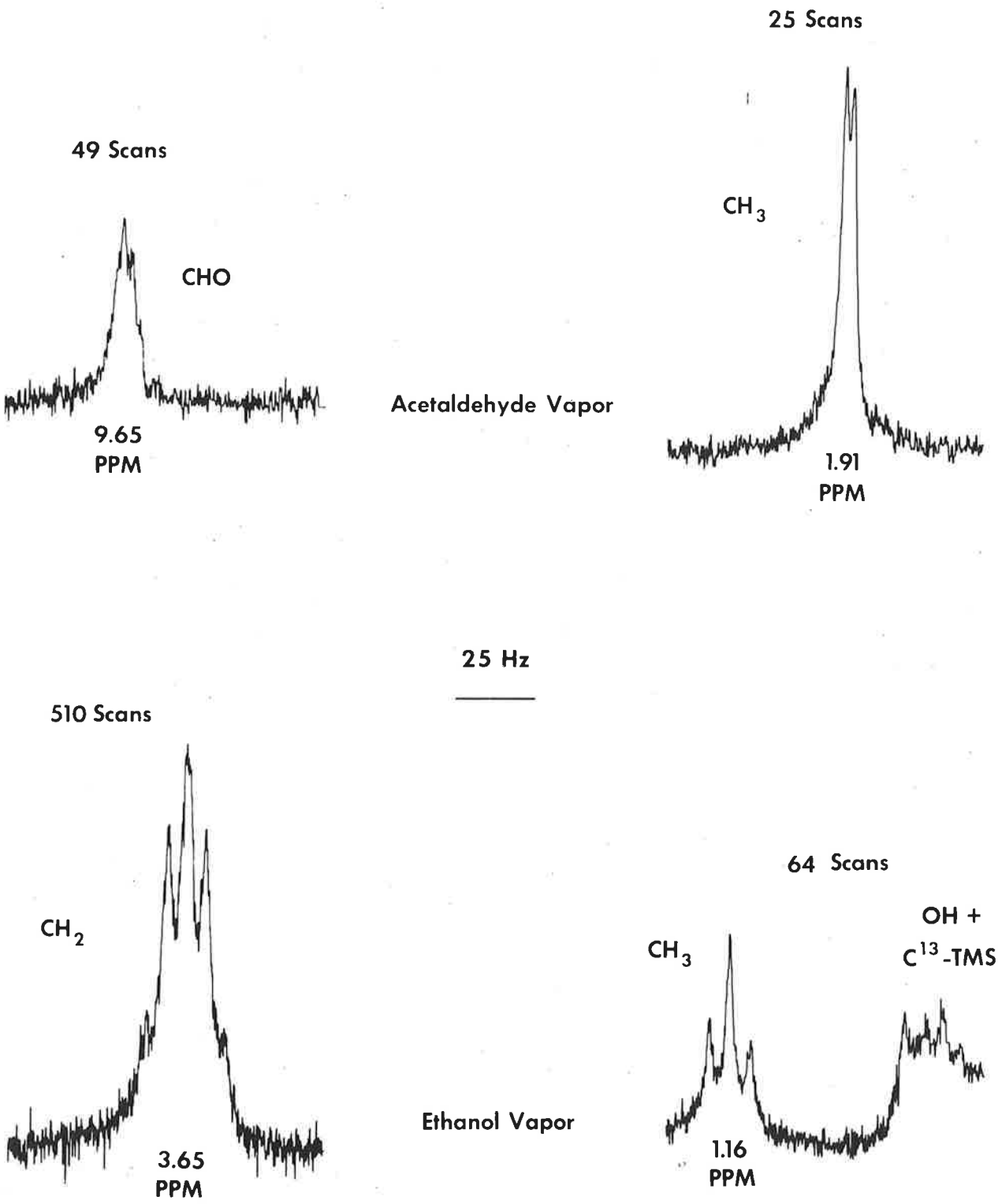
Say hello to Daddy

Ray €

Raymond Ettinger
Spectroscopy Applications Laboratories
Analytical Instrument Division

* Trademark

RE:jc



Time-averaged Vapor Phase NMR Spectra at 100 MHz

HA-100 Locked on TMS Vapor, 35°C

Battelle Memorial Institute · COLUMBUS LABORATORIES

505 KING AVENUE COLUMBUS, OHIO 43201 · AREA CODE 614, TELEPHONE 299-3151 · CABLE ADDRESS: BATMIN

December 16, 1966

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois 60616

Dear Professor Shapiro:

I hope that my new address and this subscription will serve to initiate me into the ranks.

The iteration[1] and "exact"[2] schemes for analysis of 3-spin spectra are complimentary. As most IITNMR subscribers know, Reiley & Swalen's[1] NMREN of the NMRIT/NMREN programme (QCPE 33-35) uses the transition frequencies to give a least-squares adjusted set of energy levels. Castellano & Waugh's[2] quartic-equation analysis approach uses the (3-spin only) energy levels referred to their center of gravity.

We have modified NMREN1 by adding a loop that refers the energy levels to the center of gravity, for the 3-spin case, which subsequently calls a routine to do the "exact" analysis. The programme is called NMREN3 (apologies to R & S).

The "exact" analysis routine, which may be used independently of NMREN3, is called QORTIC whose input is the seven energy parameters needed[2] and whose output is J's and δ's. The quartic is solved by two methods simultaneously, 1) The J.C.P. Miller method for <u>real</u> roots, and 2) A Laguerre iteration for <u>all</u> roots. Although the Ferrari solution is exact, it requires retaining many significant figures during the calculation (the roots are accurate to about 1/4 of the number of significant figures retained throughout) and is lengthy to programme. Methods 1) and 2) above, although manifestly different in approach, have always yielded the same <u>real</u> roots. Comments are printed when various things go wrong. If the roots are all complex, a numerical plot of the function is given, indicating, a) either erroneous input, or, b) an unresolvable degeneracy. In the latter case, the real part of the roots represent the "best" solution.

In all cases (about 30 analyses) both the iteration and the "exact" analyses gave the same results except when either failed to work, in which case both failed. The programmes are coded in FORTRAN II for IBM 7090/7094, and execute in two or three minutes on the above machines. NMREN3 requires no additional input other than that used for NMREN1.

A flow diagram, a short write-up and a test deck are available on request. QORTIC has about 200 FORTRAN CARDS. I am a bit disorganized and quite busy at the moment and therefore wish to ask that no requests be made for a deck unless it is needed now.

Sincerely,

Seán Cawley

---

1 J.C.P. 37, 21 (1962).

2 J.C.P. 34, 295 (1961).

Glaxo Research Limited

Greenford · Middlesex

TELEPHONE: BYRON 3434 TELEGRAMS: Glaxotha, London, Telex CODE: New Standard, Bentleys

100- 5

30th November, 1966.

[redacted]

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

Dear Professor Shapiro,

Micro-tubes and A60-Cooling Systems

Our experience with micro-tubes for routine use has not been very happy and we would welcome comments from other users.

In our hands, the Varian micro-tubes frequently leaked and did not always give reproducible spectra. We obtained better results by drilling a vertical, axial hole of 1 mm diameter in a Varian, lower, nylon plug and using the modified plug in an ordinary spinner tube. About 3 mg of sample, dissolved in 0.2 ml of solvent, were pipetted into the spinner tube and the plug, spherical-side downwards, pushed down until the liquid just rose in the axial hole. In this way, vortex formation in the spinning tube was prevented and it was still possible to filter the solution by pushing firmly to the bottom of the tube a small tuft of cotton-wool. Careful adjustment of the tube along the Y-axis of the magnet was, of course, necessary. The plug is removed from the tube with the Varian adjusting tool. The Varian, upper, plug can also be modified for use in an ordinary spinner tube.

Reasonable results have been obtained with the integral-sphere micro-tubes supplied by N.M.R. Specialities. Instead of the Hamilton 25 µl syringe, we use an ordinary 5 ml syringe fitted with an 18.5 cm needle (obtained from Allen and Hanburys Ltd., Bethnal Green, London, E.2.) for cleaning the micro-tubes. The tubes can then be readily flushed with relatively large volumes of solvent and air (for drying).

We notice a further report (IITNMRN, No. 97, p. 46) of difficulty with the A60-cooling system. After early trouble from algae, we circulated in the cooling system of our A60 distilled water containing 100 p.p.m. of dichlorophen ("Panacide" from British Drug Houses Ltd.). Since then, we have had no trouble from either organic growth or corrosion (see MOLLONMR, No. 56, p. 28 and IITNMRN, No. 74, p. 1). In fact, we have, except for slight topping up, only changed the cooling-water once during the last four years and when changed the water was still in good condition.

Yours sincerely,

James E Page — Dr. J.E. Page

[signature] — G.F.H. Green

J.E. Staniforth — J.E. Staniforth

100-6

HOOKER CHEMICAL CORPORATION

Niagara Falls, New York

December 19, 1966

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

Re: Modification of the Slow Sweep Unit and Integrator to Aid in Fluorine and Phosphorus

Dear Dr. Shapiro:

We have recently made several improvements in our HA100 to aid in running spectra, particularly Fluorine and Phosphorus.

In Fluorine spectra we have been using the modification suggested by Douglas and find it a great help. To make sure no peaks are missed however, we often run an HR scan, necessitating going in and out of lock. To speed up this process we have changed our 3521A Integrator-Decoupler to a 2500 Hz output. This now permits a direct transfer from HR to HA. By judicious setting of R219 and 220 we do not even need a phase shift on the 4311. This modification consists only of substituting for R201 a 301K resistor.

We have also utilized the Douglas modification for running Phosphorus using a P_4O_6 lock. This has proven to be much easier than the method by R. Johnson of using the instrument "as is" for running this nucleus.

A second modification is an Increase-Decrease relay-switch system to indicate the direction of the previous sweep when the I.D. switch is in neutral. This derives its greatest use in Fluorine and Phosphorus. We will be glad to send a copy of this improvement to anyone desiring it.

Very truly yours,

HOOKER CHEMICAL CORPORATION

James G. Colson

Eugene L. Kanski

/lo

HOOKER CHEMICALS PLASTICS

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

December 20, 1966

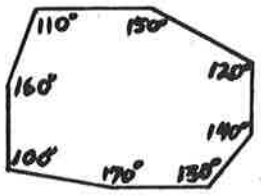
Dr. Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

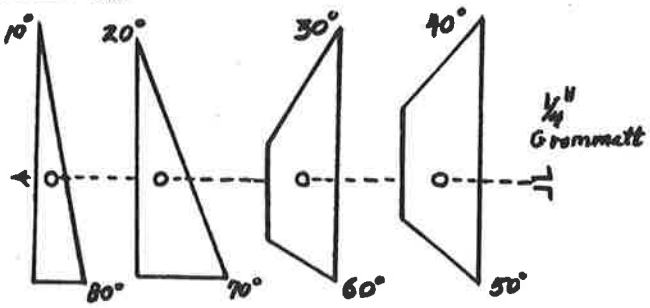
Dear Dr. Shapiro:

Those of your readers who frequently find themselves struggling to insert a protractor in the right position into molecular models to measure dihedral angles may find the following gadgets useful.

The "gadgets" consist of angular pieces which can be inserted into the spaces of stereomodels more easily than the usual protractor. Two pieces can be made to cover the angles from 10 to 170° inclusive. One covers angles greater than 90° in a single polygon, while the other includes the smaller angles. The latter is actually made up of four pieces fastened together in such a way that the desired angle may be rotated into position for measurements. Any of a variety of materials may be used for construction. Ordinary 3 x 5 file cards are satisfactory and give gadgets of dimensions suitable for use with Dreiding stereomodels.

The number of angles used depends upon the desired accuracy; however, 10° increments seem to be a fair compromise between reasonable accuracy and the number of angles required. Angles can be measured to $\pm$ 5° in this manner, which suffices for many purposes. As an added convenience, the approximate coupling constants derived from the Karplus equation may be added to the angles; however, the user must be well aware of the hazards involved [M. Karplus, J. Am. Chem. Soc., 85, 2870 (1963)].





Sincerely yours,

Lois J. Durham

Lois J. Durham, Ph. D.
NMR Spectroscopist

LJD:df

100-8

DEPARTMENT OF THE AIR FORCE
AIR FORCE MATERIALS LABORATORY: RTD (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

REPLY TO ATTN OF: MAYH/Roger E. Rondeau/255-2280

20 DEC 1966

SUBJECT: Degassing NMR Samples

TO: Dr. Bernard Shapiro
Dept. of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr. Shapiro,

Here is my first installment for subscription to the NMR Newsletter.

The two usual methods of degassing NMR samples involve either freeze - pump - thaw cycling or flusing the sample with an inert gas. Both methods are rather time consuming and relatively inefficient compared to the technique described below and depicted in the attached figure.

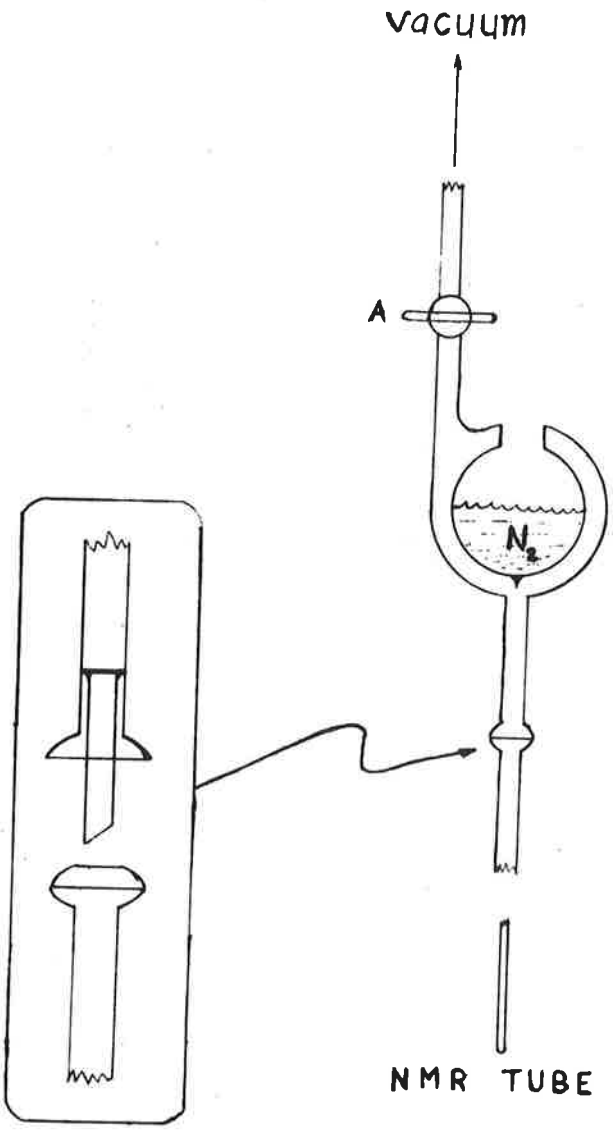
The NMR tube containing the sample is attached to the bottom of a borosilicate glass cold trap (with an O-ring adapter or with a greaseless joint, etc.) and frozen with liquid nitrogen, or some other appropriate coolant. With the sample frozen, valve A is opened and the air above the sample is removed. After this preliminary pumping, the valve is closed and the liquid nitrogen is removed from around the sample tube and poured into the cold trap. Condensation of the liquid sample occurs as a thin layer along the bottom of the spherical cold wall. The last trace of air that was previously inextricably trapped in the liquid column can now be quickly removed by pumping on the thin, exposed layer of sample. After pumping, the valve is closed and the liquid nitrogen is removed from inside the cold trap by blowing into it with an air hose. The sample is then allowed to drip back into the tube by liquid nitrogen pumping (and gravity) where it is sealed under vacuum.

The insert depicts a simple ball and socket connecting tube fabricated with a ring seal and drip tube to prevent the returning liquid from contacting the vacuum grease on the joint.

Roger E. Rondeau

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division
AF Materials Laboratory

1 Atch a/s


Vacuum
A
N_2
NMR TUBE

OKLAHOMA STATE UNIVERSITY · STILLWATER

Department of Chemistry
FRontier 2-6211, Ext. 7215—7218

74074

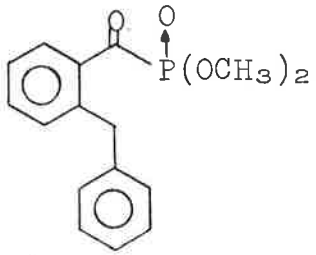
December 22, 1966

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

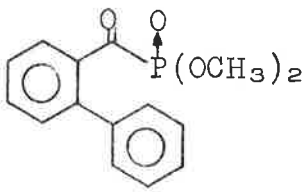
Dear Dr. Shapiro:

Chemical Shifts and J_{POCH} Values In Bulky Acylphosphonates

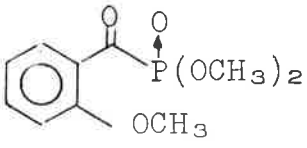
Our contribution this time revolves around our continuing study of J_{POCH} constants in hindered acylphosphonates. The following five compounds did not show nonequivalence of the methyl protons in CCl_4. In our letter



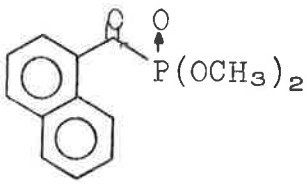
ν = 222 cps; J_{POCH} = 11 cps



ν = 223 cps; J_{POCH} = 11 cps



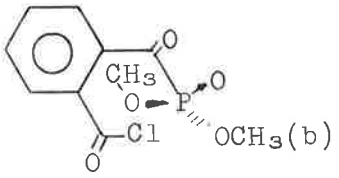
ν = 227 cps; J_{POCH} = 11 cps



ν = 234 cps; J_{POCH} = 11 cps

Dr. B. L. Shapiro -- December 22, 1966

of last April we noted nonequivalence of the methyl protons in I.



ν_a = 242 cps; J_{POCH} = 10.5

ν_b = 220 cps

Sincerely yours,

K. D. Berlin
Professor

KDB:djm

TELEGRAMS : TECHNOLOGY

TELEPHONES : 37121
37122
37123
37124
37125
36180

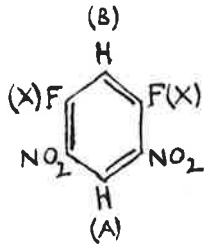
INDIAN INSTITUTE OF TECHNOLOGY KANPUR (INDIA)
DEPARTMENT OF PHYSICS

I. I. T. Post Office
KANPUR 17th Dec. 1966

Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
chicago, Ill.,
U.S.A.

Dear Prof. Shapiro:

We have recently looked at the H^1 and F^{19} high resolution NMR spectra of 1,3-Difluoro-4,6-dinitrobenzene. This compound is studied in solvents as it is a solid at room temperature. The coupling constants are solvent dependent. The labelling of the nuclei in the molecule is shown in the figure. This is an ABX_2 spectrum with negligible AB coupling. The proton spectrum has two 1:2:1 triplets and the F^{19} spectrum has four lines almost of equal intensity. The analysis can be carried out in a straightforward manner by standard methods[1]. But the coupling constants J^o_{HF} and J^m_{HF} change from solvent to solvent. The values at 10 per cent concentration are given below:



	Benzene	$CDCl_3$	CH_2Cl_2	Acetone	CH_3CN	T.H.F.	Dioxane
J^m_{HF}	7.00	7.49	7.61	7.66	7.70	7.65	7.73
J^o_{HF}	10.01	9.69	9.93	10.61	10.53	10.58	10.61
ε	2.27	4.67 ($CHCl_3$)	8.79	20.4	36.2	8.2	2.2

The experimental accuracy of these parameters (standard deviation) is 0.05 cps. We could see the variation in a

marked manner in the sum ($J^{o}_{HF}+J^{m}_{HF}$) which can be obtained from the fluorine spectrum directly with about the same standard deviation as above. Following the line of previous work on this type of observations[2-4,6], the manner of variation suggests the following: In the first four solvents the variation is roughly linear with dielectric constant indicating that it may be due to reaction field effect[5] (electric field produced at the solute molecule due to a polarization of the medium by the solute itself). In the last three cases such a correlation does not exist and here the variation seems to be due to the formation of donor accepter complexes[4].

We have also looked at the concentration dependence in d-chloroform and dioxane. No such dependence is unambiguously recognizable. The concentration is varied from 5 to 25 per cent. The apparent concentration independence of coupling constants within experimental errors could in several cases be due to the limited range of concentrations which could be studied (limited by solubility, signal to noise ratio considerations etc.) rather than the absence of any solvent effects.

We are submitting this as a downpayment for your :Newsletter:.

Yours sincerely,

Anil Kumar

(Anil Kumar)

B.D. Nageswara Rao

(B.D. Nageswara Rao)

References:

1. Pople, J.A., Schneider,W.G., and Burnstein, H.J.,High Resolution Nuclear Magnetic Resonance, McGraw Hill(1959) Ch.6.
2. Sapiro, B.L., Ebersole, S.J., and Kopchik,R.M., J.Mol.Spec. 11, 326,(1963) and J.Chem.Phys.39, 3154 (1963).
3. Watts,V.S., and Goldstein,J.H., J.Chem.Phys. 42, 228 (1965) and J.Mol.Spec. 11, 325 (1963).
4. Bates,P., Cawley,S., and Danyluk,S.S., J.Chem.Phys.40,2415 (1964).
5. Buckingham,A.D., Schaefer,T., and Schneider,W.G., J.Chem. Phys. 32, 1227 (1960) and Canad.J. Chem. 38,300 (1960).
6. Soon Ng, Jane Tang and Sederholm, C.H.,J.Chem.Phys. 42, 79(1965), and ibid 40, 2090 (1964).

100-14

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Telex: 62655 ICIMONDIVHQ, RCN

21st December, 1966

Your Ref.

Our Ref. JKB/MAV

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

Dear Professor Shapiro,

Although another contribution to I.I.T.N.M.R. Newsletter from this laboratory is not yet due, I would like to use your pages to make some comments on a solvent effect whose importance for polar solutes has come to be recognised in the last few years, namely the electric reaction field shift first discussed by Buckingham (Canad. J. Chem., 38, 300, (1960)). Emsley and Phillips have recently studied solvent effects on F^{19} chemical shifts in aromatic compounds (Mol. Phys., 11, 437, (1966)), and in the final paragraph of their paper they make a comment on some of our earlier results (Mol. Phys., 10, 21, (1965)) which shows a misunderstanding of our conclusions.

We have not in fact suggested that the effective permittivity ϵ_{eff} giving the reaction field is in all cases nearer to n^2 (n = optical refractive index) than to the static permittivity ϵ, but only that this appears to be so for methyl iodide dissolved in certain polar solvents that we used (chloroform, dichloromethane, and methyl iodide itself). In general the value of ϵ_{eff} in a polar solvent depends on the relationship between the dielectric relaxation time τ_r for the solvent and the correlation time τ_c for thermal reorientation of the solute molecule. In the two extreme cases:

if $\tau_c \ll \tau_r$, $\epsilon_{eff} \approx n^2$

and if $\tau_c \gg \tau_r$, $\epsilon_{eff} \approx \epsilon$ (if we neglect dielectric saturation, see below).

Unfortunately it is not in general possible to calculate ϵ_{eff} because our knowledge of the correlation times and dielectric relaxation times is inadequate. One can, however, take the discussion a little further by noting that the dielectric relaxation time τ_r is closely related to the thermal reorientation correlation time τ_c' for solvent molecules, and has the same order of magnitude; this is evident from a consideration of the statistical

contd ....

FROM J.K. Becconsall

TO B.L. Shapiro

DATE: 21st December, 1966

nature of the relaxation process in a liquid. An important parameter in determining ϵ_{eff} is therefore the ratio τ_c/τ_c'. The correlation times themselves will be strongly influenced by the respective volumes, moments of inertia and shapes of the molecules. Thus, for relatively bulky and heavy solute molecules in a solvent of small and light molecules, we have $\tau_c/\tau_c' \gg 1$, giving $\epsilon_{eff} \approx \epsilon$, while for small solute molecules in a solvent of large heavy molecules, $\tau_c/\tau_c' \ll 1$, giving $\epsilon_{eff} \approx n^2$. When the solute and solvent molecules are of similar size and mass, ϵ_{eff} will be intermediate between these extremes.

The use of the static permittivity ϵ to calculate the reaction field experienced by a polar molecule in a polar solvent is indefensible except when the solute molecule is heavy and/or bulky compared with the solvent molecules. In all other cases the solvent molecule simply cannot on average stay in one orientation long enough for the local solvent polarisation to reach equilibrium.

The above discussion neglects the effect of dielectric saturation in the immediate neighbourhood of the solute molecule. For methyl iodide our calculations suggest that the innermost layer of solvent molecules experiences an electric field much stronger than any obtainable on a macroscopic scale in the laboratory, and certainly sufficient to result in a very marked dielectric saturation effect. Owing to this effect one expects to find an effective permittivity somewhat less than the static permittivity ϵ for the bulk medium, even if $\tau_c \gg \tau_r$. This effect is, however, expected to be much less serious for solutes having bulkier molecules, as the nearest solvent molecules are then further away from the effective dipole centre.

In the measurements reported by Emsley and Phillips, the fluorinated aromatic molecules studied are probably sufficiently more bulky than some of the solvent molecules (e.g. dichloromethane, nitromethane, acetonitrile) to make τ_c appreciably greater than τ_c'. One would not expect this to be the case, however, for solvents such as o-xylene or n-butyl ether.

Emsley and Phillips suggest that the lack of an obvious correlation between our measured proton and C^{13} solvent shifts and the static permittivity ϵ may be due to van der Waals shifts. This explanation fails to account for the strong correlation that we found between proton and C^{13} solvent shifts (see p. 25 of our paper).

Yours sincerely,

J.K. Becconsall

J.K. Becconsall

(Short title: Electric reaction field shifts)

UNIVERSITÉ DE LYON FACULTÉ DES SCIENCES

V Réf. :

N Réf. : J. DELMAU - J. DUPLAN

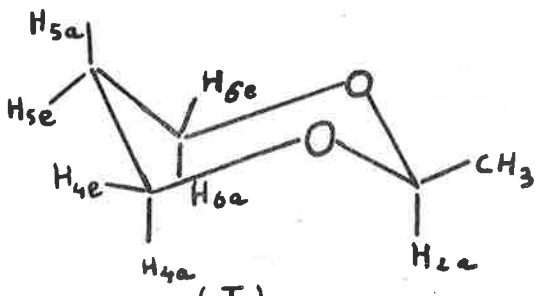
Villeurbanne, le 7 décembre 1966

Professor B.L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
Tecnology Center
CHICAGO , Illinois 60 616

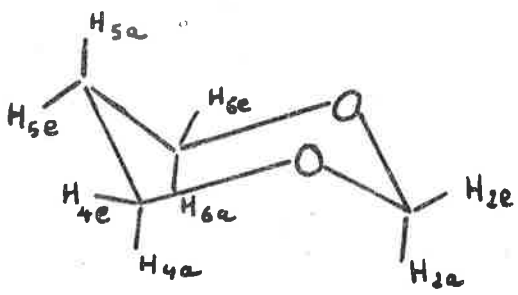
Cher Professeur Shapiro,

Nous avons récemment soumis pour publication à "Tetrahedron " un article où nous étudions en particulier les résonances "anormales" des protons en 5 dans les dioxannes-1,3 . En effet dans les dioxannes-1,3 c'est le proton axial qui résonne vers les champs faibles et le proton équatorial vers les champs forts contrairement à ce qui est observé dans les dérivés cyclohexaniques.

Pour expliquer ce phénomène , nous avons,à cette occasion ,fait intervenir , entre autres facteurs , le moment dipolaire électrique de la molécule (2,15 D pour le dioxanne lui-même). Nous nous proposons aujourd'hui de vérifier sur un autre dioxanne,le méthyl-2-dioxanne-1,3 , l'importance du moment dipolaire sur la position des résonances des protons en 5 . A cet effet il est utile de rapprocher les déplacements chimiques de ce dérivé de ceux obtenus à partir du spectre du dioxanne-1,3 , à-100°C , donné par Anteunis et coll. (Bull. Soc. Chim. Belge 75 , 396 ,(1966)).



(I)



(II)

Adresse : 43, boulevard de l'Hippodrome - Villeurbanne. Rhône
Téléphone : 52-07-04 . 52-07-05 . 52-07-20 . 52-07-49 . 52-07-52 . 52-07-55 . 52-07-73 . 52-07-80 . 52-07-92

	Méthyl-2-dioxanne-1,3 (I)	Dioxanne-1,3 (II)
Protons 4a et 6a	3,63 ppm	3,6 ppm
Protons 4e et 6e	4 ppm	4 ppm
Méthyle en 2 (équ.)	1,18 ppm	
Proton axial 2a	4,55 ppm	4,55ppm
Proton 5a	2,02 ppm	2,15ppm
Proton 5e	1,23 ppm	1,35ppm

Notons que la présence du méthyle équatorial en 2 n'a pas affecté le déplacement chimique du proton en 2.

Les spectres sont naturellement très voisins, toutefois si les déplacements en 2,4 et 6 sont identiques , les changements pour les protons en 5,bien que faibles,sont néanmoins significatifs: l'ensemble des deux protons est ramené de quelque 0,12 ppm vers les champs forts quand on passe du dioxanne-1,3 au méthyl-2-dioxanne-1,3. Ce déplacement des protons en 5 pour deux molécules ayant au demeurant même forme ne saurait être attribué à une influence des anisotropies de liaison (étant donné l'éloignement du substituant en 2). Le changement le plus important lors du passage d'une molécule à l'autre semble par contre une variation sensible du moment dipolaire.

M.R. Walker et D.W. Davidson (Can. J. Chem. 37, 459,(1959)) ont donné les moments dipolaires électriques du dioxanne-1,3 (2,15 D)et du méthyl-2-dioxanne-1,3 (1,89 D). Les champs électriques créés par ces moments apportent une contribution d'écran des protons H_{5a} et H_{5e}. Cette contribution est , dans l'approximation dipolaire , proportionelle au moment dipolaire. (A paraître).

Pour cette contribution le calcul donne pour le dioxanne

$$\Delta\sigma_{5a} = -0{,}99 \text{ ppm}$$

$$\Delta\sigma_{5e} = -0{,}51 \text{ ppm}$$

tandis que pour le méthyl-2 , on trouve :

$$\Delta\sigma_{5a} = -0{,}87 \text{ ppm}$$

$$\Delta\sigma_{5e} = -0{,}44 \text{ ppm}$$

Ce calcul suppose que le moment dipolaire à même ~~ne change pas de~~ direction ~~entre les~~ dans ces deux molécules , ce qui est une approximation suffisante étant donné le type de calculs effectués.

Les considérations précédentes font donc prévoir des déplacements vers les champs forts des protons en 5 du méthyl-2-dioxanne -1,3 par rapport à ceux du dioxanne-1,3 .

On obtient $\Delta\delta_{5a} = +0{,}12$ ppm

$\Delta\delta_{5e} = +0{,}07$ ppm

ce qui conduit , à partir des δ du dioxanne , à des déplacements chimiques pour le méthyl-2-dioxanne-1,3 .

$\delta_{H_{5a}} = 2{,}03$ ppm (valeur expérimentale 2,02 ppm)

$\delta_{H_{5e}} = 1{,}28$ ppm (valeur expérimentale 1,23 ppm)

Ainsi la comparaison de deux dioxannes (dioxanne-1,3 et méthyl-2-dioxanne-1,3) de moments dipolaires électriques différents montre l'influence de ce moment dans la différenciation des protons en 5 . Toutefois il ne semble pas que le moment dipolaire permette , à lui seul, de rendre compte du grand déplacement relatif

$\Delta\delta_{e-a} \simeq$ - 0,8 ppm des résonances de ces protons en 5;

il faut faire intervenir d'autres facteurs tels que l'anisotropie des liaisons C-O, influence des orbitales p des oxygènes cycliques.....

Croyez , cher Monsieur , en nos sentiments les meilleurs.

J. DELMAU et J. DUPLAN

100-20

RIJKSUNIVERSITEIT GENT
LABORATORIUM
voor
ORGANISCHE CHEMIE
Dir.: Prof. Dr. F. GOVAERT

GENT, December 29th 1966.

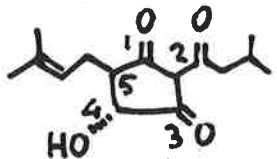
J. Plateaustraat, 22 Tel. 23.38.21

Assoc. Prof. B. L. SHAPIRO,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,

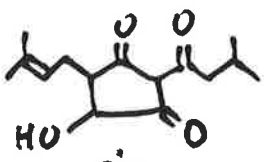
CHICAGO - ILLINOIS 60616.

Dear Prof. Shapiro,

Correlation of shift values and structure, especially in making a choice between possible geometric isomers, has become powerfull. We remarked earlier (1) that shift values of the CHOH absorption in I and II depends on wether this proton stays cis or anti with the alkyl substituent R-5, and upfield shifts for H-5 when nearly eclipsed with an OH (alt. OAc) were also noted



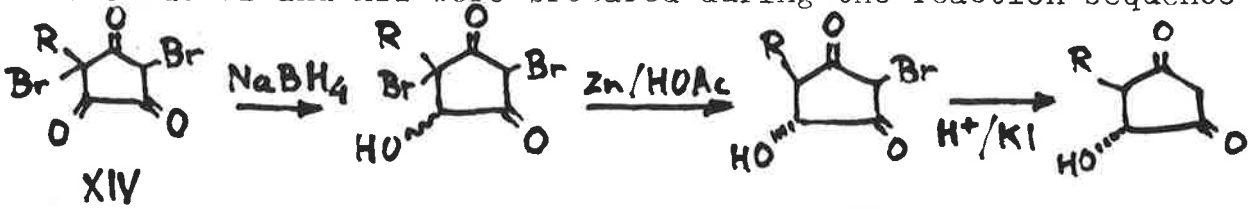
anti
I Humulinic Acid A



cis
II HAB

	HAA	HAB
δ (H-5)	2.72	3.14
δ (H-4)	4.08	4.40
$J_{H4,H5}$	4.4	~7.3

We have now some further interesting exemples (table I) obtained through synthesis (4). In most of the cases it is easy to decide between cis and anti (between OH-4 and R-5), simply by recognizing the higher $J_{H4,H5}$ in the cis compound (resp. 2.5 to 5.0 in trans; 6.3 to 7.3 in cis). From the table it is noteworthy that the shifts of a 5-Me substituent is also to higher fields when eclipsed with an OH-4 or OAc-4, except for the 2-bromo derivatives V. With the 2,5-dibromo compounds (VI) the situation is again in the general trend. In the latter case structure assignation could not be done on the above mentioned criterium, but follows from chemical evidence. The compounds VI and XII were prepared during the reaction sequence :



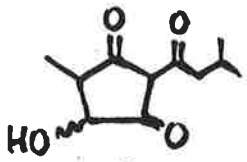
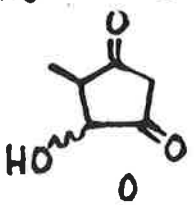
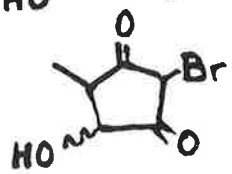
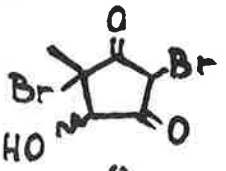
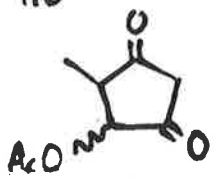
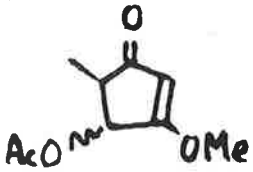
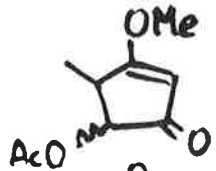
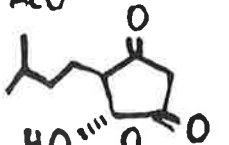
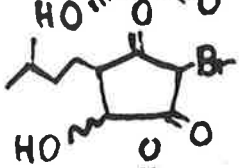
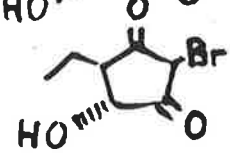
XIV
XV

VI R = Me
XII R = $CH_2CH_2CH(CH_3)_2$

V
XI

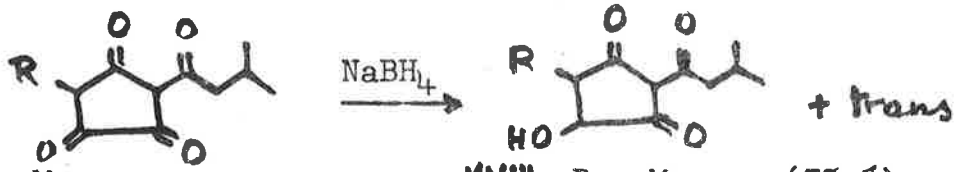
VII
X

.../...

Compound			-CH_3-group δ	Δδ	J	>CH-OR group δ	Δδ	J	Solvens
	cis	III_c	1.22	0.17	6.50	4.72	0.40	7.30	$CDCl_3$
	trans	III_t	1.39		7.42	4.32		5.00	$CDCl_3$
	cis	IV_c	1.37	0.05	7.03	4.92	0.36	6.60	pyridine
	trans	IV_t	1.41		7.27	4.56		2.81	pyridine
	cis	V_c	1.45	-0.06	7.2	4.89	+0.39	6.27	pyridine
	trans	V_t	1.39		7.22	4.50		2.58	pyridine
	cis	VI_c	1.32	+0.55	-	4.48	+0.09	-	D_2O
	trans	VI_t	1.87		-	4.39		-	D_2O
	cis	VII_c	1.20	+0.24	7.12	5.97	+0.40	7.16	pyridine
	trans	VII_t	1.44		7.40	5.57		2.50	pyridine
	cis	$VIII_c$	1.07	+0.21	7.6	5.86	+0.43	6.54	$CDCl_3$
	trans	$VIII_t$	1.28		7.58	5.43		2.50	$CDCl_3$
	cis	IX_c	1.08	+0.26	7.4	5.31	+0.44	7.0	$CDCl_3$
	trans	IX_t	1.36		7.30	4.87		2.95	$CDCl_3$
	trans	X				4.69		2.59	pyridine
	trans	XI				4.70		2.57	pyridine
	cis	XII_c				5.12	+0.68	-	$CDCl_3$
	trans	XII_t				4.44		-	$CDCl_3$
	trans	XIII				4.72		2.55	pyridine

.../...

Reduction of the trione XIV (R = Me) with $NaBH_4$ gives a mixture of two isomers in 90/10 ratio. From XV (R = isoPe) however a 68/32 mixture is obtained. It is assumed that the structures formed in smallest amount in each series have identical geometric relationships (i.e. 10 % cis from XIV and 32 % cis from XIV). That the compound formed in excess (resp. 90 % and 68 %) is the anti product is obvious in the light of the data obtained through reduction of XVI (R = Me) and XVII (R = isoPe).

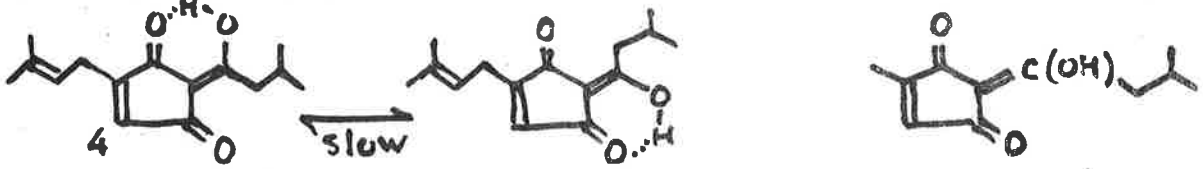


XVI R = Me
XVII R = $-CH_2CH_2CH(CH_3)_2$

XVIII R = Me (72 %)
XIX R = isoPe (100 %)

Here cis compounds are formed preferentially, but the more with R = isoPe (3). Thus a Me group is less space demanding during BH_4^- attack, resulting in formation of some 30 % of the trans compound.
Therefore the analoguous increase of 68 → 90 % in comparing XV with XIV must be attributed to the trans-series. The fact however that here the trans compounds are formed preferentially must be due to the influence of the vicinal bromine substituent.

To end with, it is perhaps interesting that we encountered a further exemple of a structure where two intramolecular H-bridge forms are existing one next to the other, and thus are differentiated in their PMR spectrum. This was reported earlier for XX (a and b)(5) which are products derived from natural occurent substances.



XXa XXb XXIa

This is substantiated i.e. by the occurence of two olefinic H-4 proton patterns (δ 6.39 & 6.48). Now compound XXI has been synthetised (4) and is entirely analoguous to XX with respect to the olefinic H-4 behaviour, the PMR spectra showing two quartets (resulting from XXIa and XXIb)(J = 1.6 c/s δ 6.52 and 6.60). For a discussion see (5).

(1) F.Alderweireldt, M.Anteunis; Bull.Soc.Chim.Belg., 73, 285 (1964).
(2) In connection with shielding effects between H and Me-substituents by β interaction (1,3 interaction) in pentacyclic compounds (M.Anteunis, F.Alderweireldt; B.S.C.B., 73, 903 (1964)and M.Anteunis, F.Alderweireldt; B.S.C.B., 73, 889

.../...

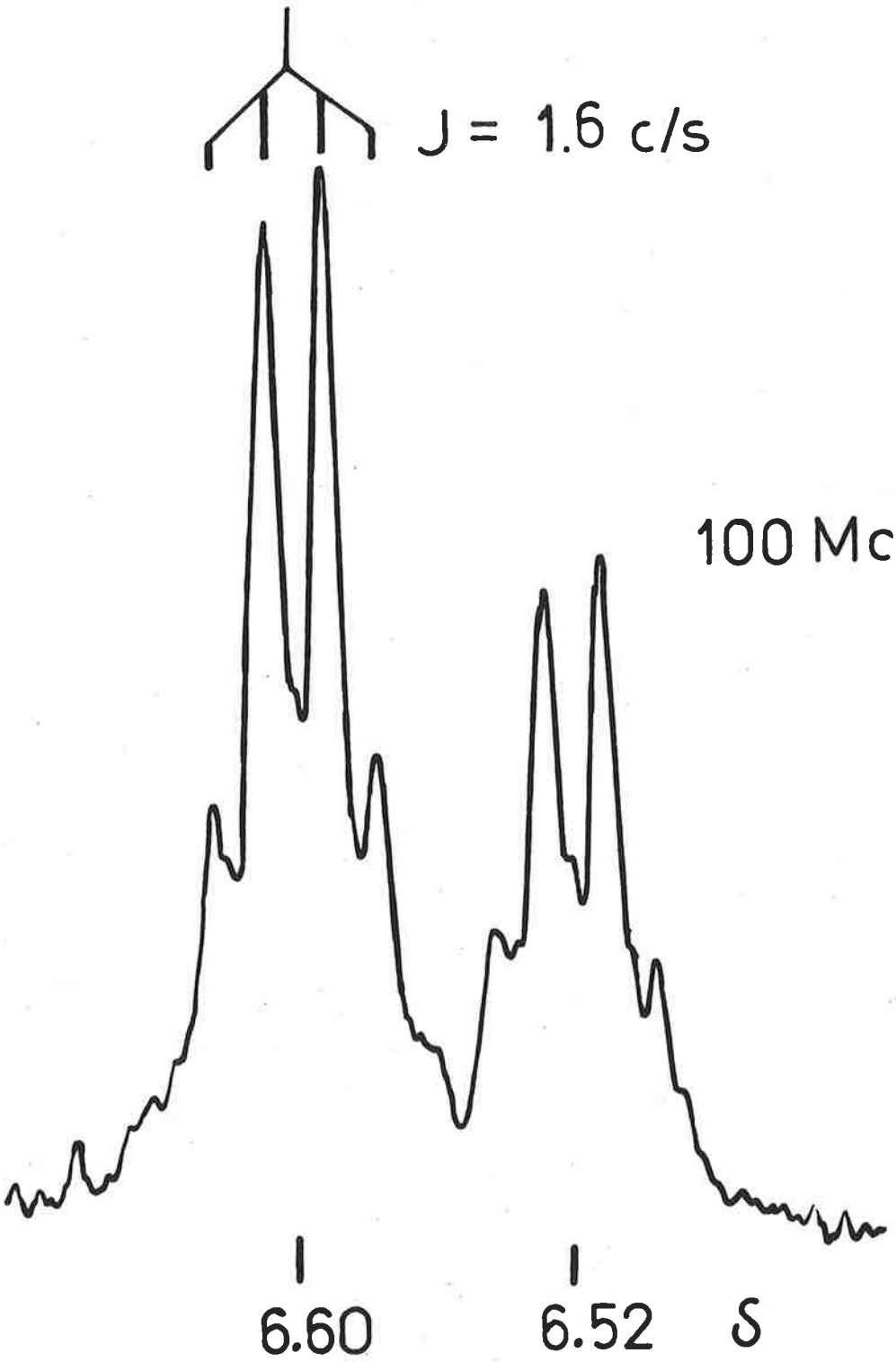
.../...

(1964)) the effect resulting in a downfield shift as stated (loc.cit.) must actually be reversed. The attribution of cis resp. trans isomers indeed must be reversed, i.e. the cis 2,4-dimethyl-1,3-dioxolane being the most stable compound, in contrast with the published assumption.

(3) A. Lepoivre, F.Alderweireldt, M.Anteunis & M. Verzele; Bull.Soc.Chim.Belg., 73, 275 (1964).
(4) M. Vandewalle, F. Compernolle; to be published.
(5) M. Anteunis & F. Alderweireldt; IITNMR 72-22 (1964).

Sincerely yours,

M. ANTEUNIS



100- 24

Académie des Sciences de Tahiti
Service de la Physique Expérimentale
et Résonance Magnétique
Avenue Louis de Bougainville, 13
Papeete

le 4 janvier 1967

M. le Professeur B. L. SHAPLIERO
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616 U.S.A.

Mon cher Barrie,

Lors de votre récent passage à notre laboratoire, vous avez sollicité une communication digne de la centième édition de l'I.I.T.N.M.R.

Depuis quelque temps nous étudions les signes relatifs des constantes d'intéraction spin-spin à longue distance dans certains extraits de l'huile de coprah. Au cours de ce travail nous avons éprouvé quelques difficultés à établir le réseau des niveaux d'énergie pour certains systèmes de deux groupes de spins nucléaires, par exemple A_2X_3 (selon la nomenclature de POPLE). Le problème a été résolu par une nouvelle méthode de construction graphique qui s'explique par l'exemple suivant.

On trace d'abord sur le graphique (Fig. 1) le profil du spectre A_2X_3, se rappelant qu'un quadruplet 1:3:3:1 doit être décomposé en quadruplet (1:1:1:1) auquel on superpose un doublet (2:2) par dessus les deux lignes centrales, tandis qu'un triplet (1:2:1) est décomposé en triplet (1:1:1) avec un singulet central. Ainsi chaque résonance est en réalité deux sous-spectres[1] qui doivent être traités séparément.

Avec un compas centré sur chaque ligne d'un sous-spectre A quelconque, on trace des arcs qui se coupent avec d'autres arcs (à rayon r égal) centrés sur les lignes d'un sous-spectre X. Les intersections de ces arcs définissent les niveaux d'énergie, et, dans ce cas particulier de deux sous-spectres A et deux sous-spectres X, établissent quatre systèmes indépendants de niveaux (voir la figure ci-contre). Les transitions entre niveaux d'énergie peuvent être identifiées par l'origine de l'arc générateur.

Par dessus le marché, la méthode se prête facilement à la prédiction des spectres à deux quanta. Chaque parallélogramme sur le graphique engendre une transition à deux quanta dont la fréquence correspond à la mi-hauteur du parallélogramme (on doit tourner la figure pour que la direction énergie soit verticale). Le cas A_2X_3 donne naissance à un quadruplet de transitions à deux quanta, avec les intensités relatives 1:4:4:1, en accord avec l'expérience de KAPLAN et MEIBOOM[2] sur l'alcool éthylique.

Cette méthode s'étend sans difficultés à d'autres systèmes à couplage faible, A_nX_m. On laisse au lecteur le soin de construire (en deux dimensions) les graphiques appropriés aux systèmes $A_nM_mX_p$ (trois groupes de spins inégaux).

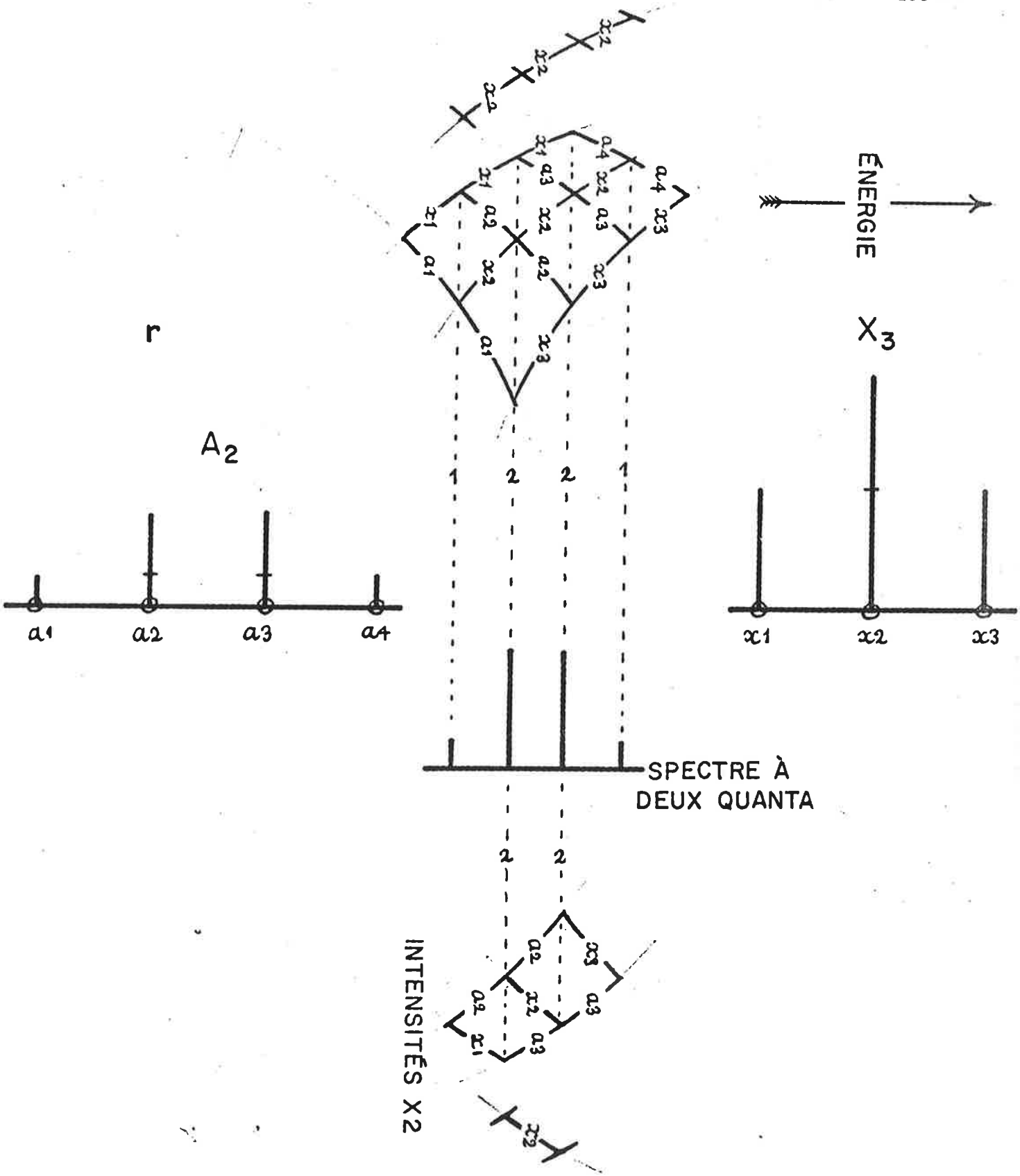
Sincères salutations,

Sue

(Mlle) Suzanne Perchery

1. Voir par exemple P. DIEHL, 6 ième Congrès de la R.M.N. Expérimentale (6th E.N.C.) Pittsburgh, 1965; Helv.Chim.Acta, 48, 567 (1965).
2. J. I. KAPLAN et S. MEIBOOM, Phys.Rev. 106, 499 (1957).

Titre: Niveaux d'énergie A_nX_m.


r
A2
a1
a2
a3
a4
ÉNERGIE
X3
x1
x2
x3
1
2
2
1
SPECTRE À
DEUX QUANTA
2
2
INTENSITÉS X2

100-26

20th December, 1966

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

Dear Professor Shapiro,

Thank you for your reminder. Here is my contribution to the NMR Newsletter:

Enhanced conjugation in sterically hindered molecules.

Usually, π electron conjugation between two molecular groups R,R' is reduced whenever the orientation of R with respect to R' is influenced by steric effects (cf. the conjugation between the NH_2 and the phenyl groups in aniline and its 2,6-dimethyl derivative).

However, situations can be envisaged in which conjugation can increase, or arise, due to steric effects. This seems to be the case in cis-azobenzene as compared to the trans-isomer, as far as the nitrogen lone pair orbitals are concerned. Whereas the latter is planar, the interaction between the two rings prevents coplanarity for the cis-isomer. The conjugation between the rings and the nitrogen π orbitals is, thus, reduced, but that with the lone pair orbitals of the nitrogen atoms becomes possible. The π-electron densities in the benzene rings of cis-azobenzene are, therefore, expected to be similar to those of aniline.

The proton NMR spectra of cis-and trans-azobenzenes give support to this hypothesis. The spectrum of the latter (in CCl_4) looks of the AA'XX'Y type, consisting of two groups of lines with relative intensities 2:3, around τ=2,1 and τ=2,6, respectively; the low-field multiplet is assigned to the ortho protons. The spectrum of the cis-compound is similar to that of the trans-isomer except that the multiplet of intensity 3 appears around τ=2,8 and the multiplet of intensity 2 is centred around τ=3,2. Although a full analysis of these spectra is required, it looks as though the ortho protons are more shielded in cis-azobenzene by ca. 1.1 p.p.m. than in trans-azobenzene; the meta and para protons signals also moves to high field going from the trans- to the cis-compound.

These shifts, particulary that of the ortho protons, are too large to be due to a neighbouring ring current effect. Also, the proton shifts of cis-azobenzene relative to benzene parallel those observed for aniline. They are, therefore, ascribed to the increased π-electron density on the ring carbon atoms through conjugation with the nitrogen lone pairs, in the cis-isomer.

Yours sincerely,

Happy New Year!

Victor M.S. Gil

INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. PHIL., DR. MED. h. c. H. H. INHOFFEN

- Dr. Claus-Dieter Mengler -

33 BRAUNSCHWEIG
SCHLEINITZSTRASSE
Tel. Hochschule 4781
Durchwahl Institut 4782225
Vorwahl 0531

3. Januar 1967

Herrn
Professor Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology

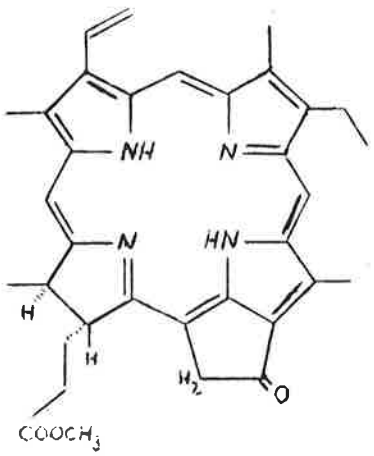
CHICAGO, ILL. 60616

U. S. A.

Sehr geehrter Herr Professor Shapiro!

Trideuterierung der C-5-Methylgruppe im Pyromethylphäophorbid a
Bestätigung der Zuordnung des C-5-NMR-Signals.

Eine Reihe von Publikationen (1, 2, 3) beschreibt den Austausch der C_{10}-Protonen in Chlorophyll-Derivaten gegen Deuteronen mittels CH_3OD oder D_2O. Diese Reaktion wurde im hiesigen Institut am Pyromethylphäophorbid a (I) durch Kochen von I in Pyridin mit D_2O durchgeführt.

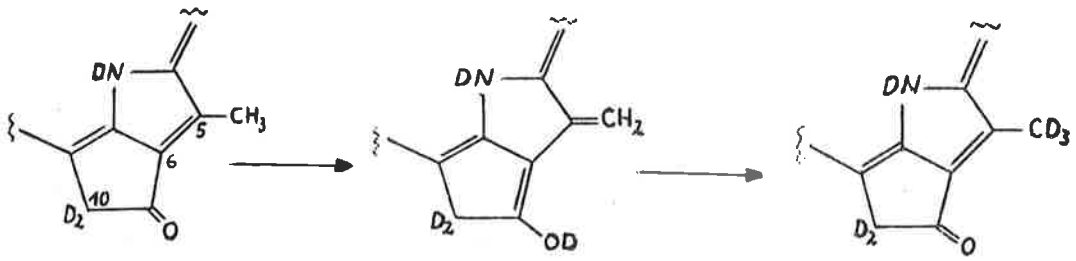


I

Messung des NMR-Spektrums nach 48-stündigem Kochen zeigte den erwarteten vollständigen Austausch der beiden C_{10}-Protonen. Der von Woodward und Skaric (4) beschriebene Austausch des δ-Methinprotons war unter diesen Bedingungen nicht zu beobachten. Auffallend war jedoch die bisher nicht

beschriebene deutliche Verkleinerung des Signals bei δ = 3. 59 ppm, das in Übereinstimmung mit Pennington et al. (5) der 5-Methylgruppe und der 7''-$COOCH_3$-Gruppe zugeordnet wird. Nach 7-tägigem Kochen in Pyridin/D_2O zeigte das NMR-Spektrum für dieses Signal eine Verkleinerung um 3 Protonen.

Bei Messung einer Probe mit einer Konzentration von ca. 0. 3 Mol/l an einem Varian A 60-NMR-Spektrometer war das 5-CH_3-Signal bei δ = 3. 21 ppm verschwunden, während das 7''-$COOCH_3$-Signal unverändert geblieben war. Es werden also durch Enolisierung der 9-Carbonylgruppe nicht nur die C_{10}-Methylenprotonen gegen Deuteronen ausgetauscht, sondern genauso, wenn auch beträchtlich langsamer, die Protonen der 5-Methylgruppe. Dabei dürfte die durch die Starrheit des Cyclopentenonringes garantierte Coplanarität der beteiligten Gruppen ein wesentlicher Faktor sein.



Die Tabelle zeigt die Zuordnung der beteiligten Signale:

Chemische Verschiebungen (ppm), $CDCl_3$

Varian HA-100, 0. 05 m

	Pyromethylphäophorbid a (I)	I nach 7-tägigem Kochen in Pyridin/D_2O
δ -Methinproton	8. 47	8. 47
10-CH_2	5. 11	ausgetauscht
7''-$COOCH_3$	3. 59	3. 59
5-CH_3	3. 59	ausgetauscht

Dr. C.-D. Mengler c/o
Prof. Dr. phil., Dr. med. h. c. H. H. Inhoffen · Technische Hochschule Braunschweig

Varian A-60, ca. 0.3 m

	Pyromethylphäophorbid a (I)	I nach 7-tägigem Kochen in Pyridin/D_2O
δ-Methinproton	8.24	8.24
10-CH_2	4.94	ausgetauscht
7''-$COOCH_3$	3.57	3.57
5-CH_3	3.21	ausgetauscht

(1) J.J. Katz, M.R. Thomas und H.H. Strain
J. Amer. Chem. Soc. 84, 3687 (1962).

(2) J.J. Katz, R.C. Dougherty, F.C. Pennington, H.H. Strain und G.L. Closs
J. Amer. Chem. Soc. 85, 4049 (1963).

(3) R.C. Dougherty, H.H. Strain und J.J. Katz
J. Amer. Chem. Soc. 87, 104 (1965).

(4) R.B. Woodward und V. Skaric
J. Amer. Chem. Soc. 83, 4676 (1961).

(5) F.C. Pennington, H.H. Strain, W.A. Svec und J.J. Katz
J. Amer. Chem. Soc. 86, 1418 (1964).

Mit vorzüglicher Hochachtung

Ihr

Claus-Dieter Mengler

(Dr. Claus-Dieter Mengler)

100-30

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Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
CHICAGO, Illinois 60616
U. S. A.

Paris, le 6 Janvier 1967

SUBJECT : NMR OF P-PHENYL GROUPS.

Dear Barry,

Before receiving your reminder, I prefer to pick up from our last studies some preliminary data which may be of some interest. Lastly, we had representative phenyl-phosphonates, or -phosphinates (with sulfur and selenium homologs in some cases) and we obtained proton and phosphorus spectra on our R 10 machine. We have not yet tried to analyze the complete phenyl pattern, but the ortho protons are far enough from the other aromatic peaks to yield first-order data which may be useful for the moment.

	δ ortho	J(P-H ortho)	δ (OCH_3/ SCH_3)	J(P.. CH_3)	δ P
ϕ_2 P(O)OCH_3 (a)	7,81	12,0	3,63	11,3	80,0
ϕ_2 P(S)OCH_3 (a)	7,80	13,5	3,58	13,75	29,1
ϕ_2 P(Se)OCH_3 (a)	7,85	13,7	3,60	14,3	24,0
ϕ P(S) $(OCH_3)_2$ (b)	7,90	14,0	3,61	13,7	22,7
ϕ_2 P(O) SCH_3 (a)	7,94	12,7	2,13	11,85	69,7
ϕ_2 P(S) (SCH_3) (a)	7,94	14,0	2,21	14,7	-
ϕ P(S) $(SCH_3)_2$ (c)	8,05	15,1	2,27	16,05	29,0 (b)

.../...

a/ in $CDCl_3$; b/ neat ; c/ in CCl_4.
Proton chemical shifts in p.p.m. VS. T.M.S. ; couplings in Hz.
Phosphorus chemical shifts in p.p.m. upfield from P_4O_6 (for phosphoric acid, substract 112,5 p.p.m.).

Phosphorus resonance data may be handled on the basis of Letcher and Van Wazer analysis (J. Chem. Phys., 44, 815, 1966). From the following diagram (similar to fig. 9 and 10 in the above paper), one may grossly estimate the number of π electrons per phosphorus...

	n = 3	2	1	0
$\emptyset_n$ P(O) $(OCH_3)_{3-n}$	.5	1.0	-	1.6
$\emptyset_n$ P(S) $(OCH_3)_{3-n}$	$.1_5$	$.7_5$	1.1_5	1.3_5
$\emptyset_n$ P(Se) $(OCH_3)_{3-n}$	$.0_5$	.8	-	1.2_5
$\emptyset_n$ P(O) $(SCH_3)_{3-n}$	.5	.6	-	.8
$\emptyset_n$ P(S) $(SCH_3)_{3-n}$	$.1_5$	-	.4	.5

... and discuss these figures taking in account phosphorus-substituents conjugation and steric hindrance effects.

Independently, proton resonance enlights separately phosphorus conjugation with phenyl, OCH_3 and maybe SCH_3 groups. Phosphorus- ortho proton couplings deserve special comments, as they are quite sensitive to the molecular environment ; they are to be compared with :

- Ca. 3.5 Hz in $P\emptyset_3$ (Akitt et al., Chem. Comm. 1966, p. 134);*
- 6.5. - 7.0 in related substituted phosphines (Griffin, Tetrah. 20, 2399, 1964) ;
- 10.5 - 13.0 in phosphine oxides and phosphoniums (Griffin, op. cit. ; Griffin et al., Tetrah. 22, 561, 1966) ;

* See next page

.../...

When completed with the NMR study of lacking compounds in the series and may-be with some UV data, we hope to attain a better description of phosphorus bonding in such structures.

Looking for the pleasure to see you again (at the 8th ENC, I hope), with my sincere season's greetings to all of you numerous friends

and my best regards

G. MAVEL

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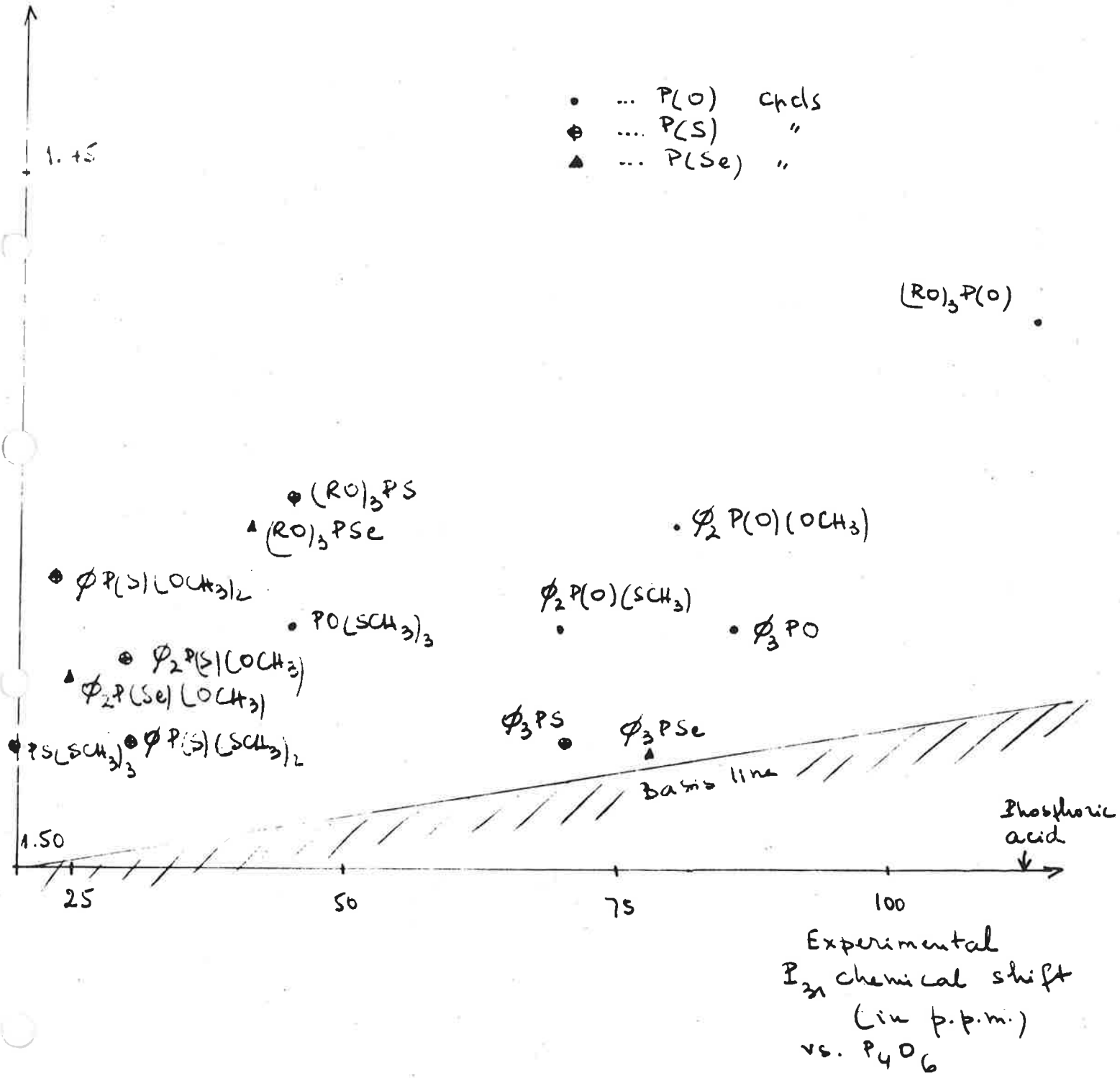
* We are not aware of a similar study of $P(O)\emptyset_3$ and $P(S)\ \emptyset_3$. We would be pleased to hear about if anybody has done it.

CB

ζ_1 (according to LETCHER + VAN WAZER)



UNION CARBIDE CORPORATION

P. O. BOX 278, TARRYTOWN, N. Y. 10591

January 6, 1967

UNION CARBIDE
RESEARCH INSTITUTE

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

Dear Professor Shapiro:

The temperature gradient in the Varian THR insert has been used to make a direct measurement of the anisotropic part of the fluorine chemical shift in a molecule dissolved in a nematic liquid crystal solvent. Normally,[1] the measurement requires two experiments: 1) the isotropic chemical shift is obtained at high temperature, and 2) the chemical shift is measured in the anisotropic (nematic) phase. Since bulk susceptibilities are not available for the solvent (4,4'-di-n-hexyloxyazoxybenzene - HAB) at high temperature, the use of an external reference is questionable; an internal reference is preferable. The anisotropic contribution ($\Delta\sigma$) is taken to be the difference in chemical shifts between the isotropic and anisotropic measurements. For this procedure to be valid, the position of the internal reference signal must remain unchanged throughout both experiments. This requires 1) that the reference molecule experience no orientation in the liquid crystal solvent, and 2) that the chemical shift of the reference nuclei be unaffected by a phase change and independent of temperature within a given phase. The first condition is satisfied only if the reference molecule is a spherical top - for fluorine measurements, the perfluorinated analogue of methane, neopentane, tetramethylsilane (or any other spherical hydrocarbon) would be acceptable. CF_4 would be difficult to keep in liquid crystal solution at high temperature, and the other compounds do not seem to be readily available (See IIT-NMR Newsletter No. 91, p. 49).

We have taken advantage of a small temperature gradient in the Varian THR insert to make a direct measurement of $\Delta\sigma$ for fluorine in 1,3,5-trifluoro-2,4,6-tribromobenzene in HAB. Over a 1" length, there is a gradient of about 0.5°C, and, at 93°C, the sample at the bottom of the tube (about 10% of the volume in a 5mm O.D. thin-walled tube) is in the isotropic phase, while the remainder of the sample is in the nematic phase. The isotropic signal was easily observable, even with the isotropic region one centimeter below the receiver coil. The isotropic signal is a singlet upfield from the nematic triplet (see Fig. 1). In order to ensure uniformity of the external field, the magnet was cycled and shimmed (electrically) for a flat profile over the sample length (~ 0.75"). The "flatness" of the field was checked both before and after spectra were recorded, and the maximum gradient developed during several runs was 10 cps over the sample length. This is a small error for a fluorine shift anisotropy measurement. The results are close to those obtained with an external reference (C_6F_6), indicating a small bulk susceptibility effect:

$\Delta\sigma$ (by direct measurement) 354 ± 4 ppm.

$\Delta\sigma$ (by external reference) 349 ± 3 ppm.

$\Delta\sigma = \sigma_{\perp} - \sigma_{\parallel}$, where $\sigma_{\perp}$ and $\sigma_{\parallel}$ are the chemical shifts measured in directions perpendicular and parallel to the ring plane.

Since it should be possible to obtain a range of temperature gradients in the insert, this technique should be useful for a variety of nematic solutions.

With regard to the second requirement noted above, we are investigating the effect of a change of phase on the chemical shift, and temperature dependence in the nematic melt.

Sincerely yours,

Costantino S. Yannoni

CSY:nt

(1) A. Saupe, Z. für Naturforschung 19a, 161 (1964).

Figure 1

100-36

UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

DEPARTMENT OF CHEMISTRY

January 6, 1967

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

Dear Barry:

Since I will be going on leave next year, will you please transfer our subscription to Dr. Richard Newmark who submits the following material entitled: Proton Spin Relaxation in Metal-Liquid Ammonia Solutions.

Last year in John Waugh's laboratory at M.I.T., John Stephenson and I measured the proton spin-lattice relaxation time of potassium-ammonia solutions over a wide range of concentrations (2.10^{-4}M to 3M) and temperature (-74°C to +21°).[1] The relaxation time of the protons in the metal-ammonia solutions is reduced from that of pure ammonia due to dipole-dipole and/or hyperfine coupling with the electrons (or other paramagnetic species). Below 0.1 M, the relaxation rate increases as the potassium concentration is increased, and the rate is proportional to the paramagnetic susceptibility.[2] At about 0.1 M the relaxation rate levels off, and above .3 M decreases with further increases in potassium concentration. This decrease is attributed to the reduction in the electron correlation time as the solution becomes metallic. The pronounced decrease in the relaxation rate occurs at the same concentration as the great increase in the equivalent conductance.[3] The NMR results have been combined with Knight shift measurements,[4] Overhauser data[5], and the paramagnetic susceptibility to calculate the electron correlation time, τ. τ is 4×10^{-13} sec. for potassium concentrations under .1 M; above 1 M τ is less than 10^{-15} sec.

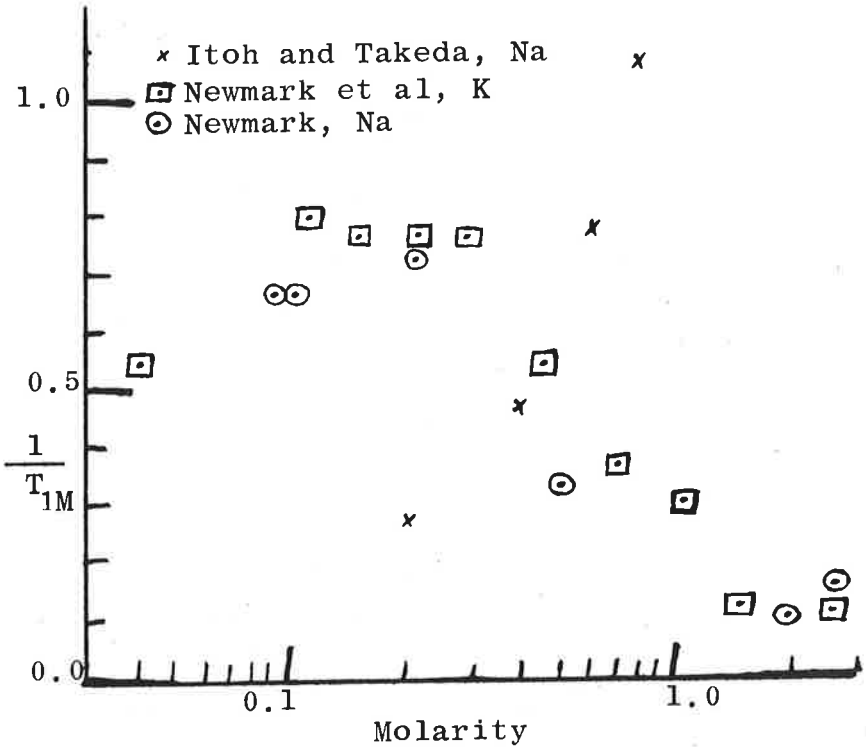
These results are considerably different than those of Itoh and Takeda for sodium-ammonia solutions. This discrepancy was very surprising in view of the similarity of the Knight shift,[7] paramagnetic susceptibility,[2] and conductivity[3] of the potassium and sodium solutions. Consequently, after arriving at the Univ. of Colorado, I have measured the proton spin lattice relaxation time for several moderately concentrated sodium-ammonia solutions at room temperature (no effort was made to analyze solutions below 0.1 M). The results are within experimental error of the earlier measurements on potassium, and substantially different from the data of Itoh and Takeda (see figure). I can offer no explanation for the different results; unfortunately, Itoh and

Takeda provide no experimental information in their note.

1. R. A. Newmark, J. C. Stephenson, and J. S. Waugh; submitted to J. Chem. Phys.
2. C. A. Hutchison, Jr. and R. C. Pastor, J. Chem. Phys. 21, 1959 (1953).
3. E. Arnold and A. Patterson, Jr. J. Chem. Phys. 41, 3089; (1964); C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc. 45, 2551 (1923).
4. T. R. Hughes, Jr., J. Chem. Phys. 38, 202 (1963).
5. T. R. Carver and C. P. Slichter, Phys. Rev. 102, 975 (1956).
6. J. Itoh and T. Takeda, J. Phys. Soc. Japan 18, 1560 (1963).
7. D. E. O'Reilly, J. Chem. Phys. 41, 3729 (1964).

Figure. Relaxation rate of the protons due to added metal in Na-NH_3 and K-NH_3 solutions at room temperature,

$$\frac{1}{T_{1M}} = \frac{1}{T_{1,exp}} - \frac{1}{T_{1,pure\ NH_3}}$$



Sincerely yours,

Melvin W. Hanna
Professor of Chemistry

Richard A. Newmark
Asst. Professor
of Chemistry

MH/RN:rs

100-38

University of Notre Dame
College of Science
Notre Dame, Indiana 46556

Department of Chemistry

January 9, 1967

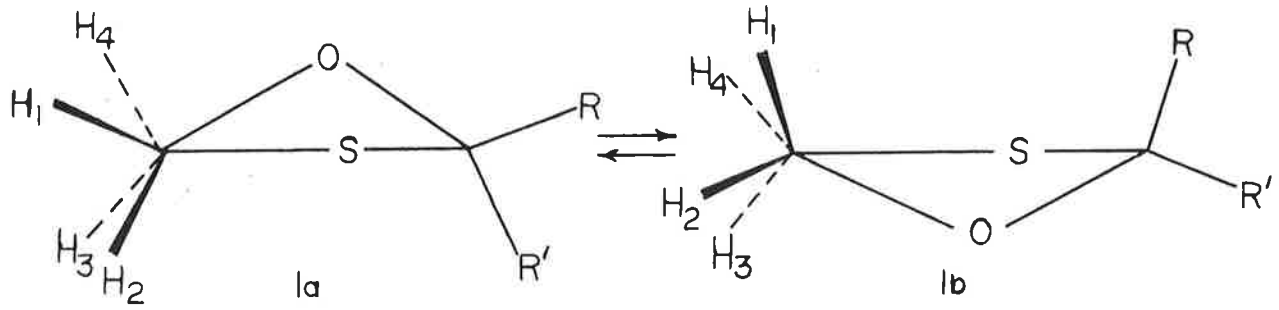
Dr. Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Conformational Analysis of the 2-Substituted Oxathiolane System and Analysis of Their NMR Spectra

The availability of a number of 2-substituted oxathiolanes led us to carry out a detailed analysis of their NMR spectra which in turn provided information as to the probable conformation of the oxathiolane ring and gave $-\Delta G$ values for substituents in the 2-position. We wish to outline a few of the conclusions we have arrived at.

The 4- and 5-hydrogens of the oxathiolane ring gave rise to spin systems from AA'XX' to ABXY to ABMX depending on the 2-substituent. The chemical shift and coupling constant data for a few selected compounds are given in Table 1. The conformation which is most consistent with the NMR data and by use of Dreiding models is an envelop form with the oxygen as the "flap" atom. The models indicate that the remaining four atoms lie in a single, fairly rigid plane. There is no evidence indicative of the presence of pseudorotation. The assignment of the respective hydrogens was arrived at by first assuming that the 5-hydrogen cis to the 2-substituent would prefer a pseudoequitorial position and should appear at lowest field. The remaining hydrogens were assigned by consideration of dihedral angles and coupling constants. It should be noticed that the pseudoaxial hydrogens on both methylenes appear at higher field than do their pseudoequitorial counterparts.



There are several interesting trends observable in the data appearing in Table 1. First of all, the average chemical shift of H_1 and H_2 for the parent compound (-234.77 Hz relative to TMS at 60 MHz) is substantially different than the corresponding averages of H_1 and H_2 in the 2-t-butyl (-239.20 Hz), 2-iso-propyl (-237.83 Hz), 2-ethyl (-238.34 Hz) and 2-methyl (-238.16 Hz) derivatives.

Table 1

R	R'	δ_{H_1}	δ_{H_2}	δ_{H_3}	δ_{H_4}	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
t-Bu	H	259.79	218.60	174.19	168.55	-9.03	2.21	5.77	5.02	9.92	-9.76
i-Pr	H	255.18	220.48	173.93	170.89	-8.85	2.85	5.93	5.62	9.40	-9.70
Et	H	254.98	221.70	177.76	173.75	-8.99	4.40	4.96	6.13	8.05	-9.95
Me	H	254.88	221.46	178.77	178.75	-9.09	4.67	4.69	7.23	7.21	-9.43
H	H	234.77	234.77	174.45	174.45	—	5.89	5.89	5.89	5.89	—
t-Bu	Me	254.88	234.98	175.51	167.83	-9.06	3.21	5.35	4.38	9.63	-9.86
Me	Me	243.41	243.41	180.97	180.97	—	5.80	5.80	5.80	5.80	—

Furthermore the average chemical shift decreases in going from the t-butyl to the methyl derivative. These effects are readily explained on the basis of long range shielding effects produced by the 2-alkyl group. Substitution of R=t-butyl for R=H in 1a, giving an equilibrium containing an estimated miminum of 99% of 1a, leads to calculated (McConnell Equation) average deshielding of 4.8 Hz compared to an observed value of 4.4 Hz. From our data it would appear that the long range shielding contributions of substituents in the 2-pseudoequitorial position do not vary as one goes from t-butyl to methyl.

The small decreases in the H_1-H_2 average in the 2-iso-propyl, 2-methyl and 2-methyl derivatives are due to long range shielding contributions due to the pseudoaxial alkyl groups in isomer 1b. The 2-pseudoaxial alkyl group shields H_1 but deshields H_2. Use of the McConnell Equation predicts a shielding of H_1 in the 2-t-butyl-2-methyl derivative of 1.5 Hz (observed 3.8 Hz); however this equation predicts a shielding of H_2 of 9.6 Hz whereas experimentally it is observed that H_2 is deshielded by 12.8 Hz. This is the only anomalous value encountered in calculating the effects on H_1, H_2, H_3, or H_4 in this system.

We have calculated the following values for the long range shielding constants for H_1: iso-propyl, 4.7 Hz; ethyl, 3.4 Hz; methyl, 3.8 Hz. The corresponding long range deshielding constants for H_2 are: iso-propyl, 15.7 Hz; ethyl, 11.3 Hz; and methyl, 12.8 Hz. The close similarity between the methyl and ethyl values are undoubtedly due to specific rotational conformations about the ethyl C-C bond.

Similar trends with H_3 and H_4 can be noted and qualitatively rationalized by use of the McConnell Equation.

We have calculated $-\Delta G$ values for the alkyl groups in the 2-position, making appropriate corrections in the extreme values for H_1 and H_2 due to the long range shielding effects of the respective alkyl groups. These values at 30° are: 2-iso-propyl, 1.17 kcal/mole; 2-ethyl, 1.15 kcal/mole; and 2-methyl, 1.13 kcal/mole.

We are currently preparing a full paper to describe in greater detail the above interpretations and interesting data covering other compounds in this series.

With best regards,

Daniel J. Pasto, Associate Professor of Chemistry
with T. Doyle and F. Klein

DJP:mm

HOFFMANN-LA ROCHE INC.

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January 10, 1967

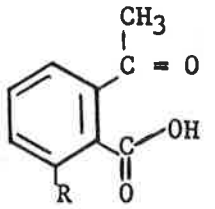
Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Professor Shapiro:

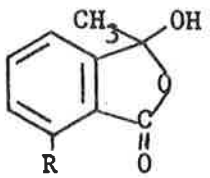
We would be grateful if you would add Hoffmann-La Roche, Inc. of Nutley, New Jersey to your mailing list of subscribers to IITNMR Newsletter and if you will consider the following as our contribution.

Ring-Chain Tautomerism of 2-Acetylbenzoic Acids

2-Acetylbenzoic acid (Ic) is of a class of compounds which could show ring-chain tautomerism, A⇌B. Jones[1] reported that the nmr spectrum of Ic in acetone-d_6



(A)



(B)

a) R = NH_2
b) R = OH
c) R = H
d) R = NO_2

I

indicated that Ic was partially if not wholly cyclic. Erley and coworkers[2] later reported that a single methyl peak at high field (δ 1.98 in $CDCl_3$) was evidence for the ring structure for Ic in chloroform or acetone-d_6. It was later suggested[3] that the single peak could result from a mixture of ring-chain tautomers in fast equilibrium, A⇌B, rather than a single tautomer (B). Analysis of ring-chain tautomerism gave a value of 79% ring tautomer, based upon a comparison of the chemical shift (δ 1.98) of Ic with those of its pseudo and normal esters (δ 1.83 and 2.53 respectively)[3].

We have found that the nmr spectrum of Ic in DMSO-d_6 solution showed the presence of both forms, A and B, with methyl bands located at δ 2.45 and 1.78 respectively. The former band is attributed to the chain form (A), since acetophenone showed a methyl singlet at δ 2.58; the latter band is assigned to the ring form (B). Relative intensities of these bands indicated for A and B a ratio of 1:2, and led to a weighted average chemical shift of δ 2.00. When a trace of hydrochloric acid was added to promote fast interconversion of tautomers, the two bands coalesced to a single band at δ 2.00. This value is in fair agreement with δ 1.98 for the methyl peak observed in $CDCl_3$ solution by Jones and coworkers. [2,3]

Hence the choice of solvent is important in demonstrating in a simple manner the existence of both tautomers. The spectra of Ic in different solvents are summarized in Table I. As in the case of chloroform, fast equilibration of tautomers occurred when certain solvents were used, and only a single methyl peak (column 4, entries 1 to 5) was observed. However, the remaining entries give the methyl peak positions of ring and of chain tautomers (columns 3 and 5), as well as the weighted average chemical shift observed when a trace of hydrochloric acid was added (column 4). The amount of ring tautomer found was in a range of 74 ± 7% (column 6). Interestingly, 2-acetyl-6-nitrobenzoic acid (Id) in DMSO-d_6 solution exists predominantly as the chain structure (A), while 2-acetyl-6-hydroxybenzoic acid (Ib) and 2-acetyl-6-aminobenzoic acid (Ia) exists predominantly as the ring structure (B). The corresponding δ values were 2.38 for Id versus 1.68 and 1.77 for Ib and Ia respectively.

Table I. Chemical shifts of methyl groups of 2-acetylbenzoic acid in different solvents.

1 Entry	2 Solvent	3 Ring	4 Averaged	5 Chain	6 % Ring Tautomer
1	Chloroform-d_1		1.98		
2	Methylene-d_2 chloride		1.93		
3	Acetonitrile-d_3		1.86		
4	Methanol-d_4		1.98		
5	Tetramethylene-d_8 sulfone		1.92		
6	Dimethyl-d_6 sulfoxide	1.78	2.00	2.45	67
7	Dimethylformamide-d_7	1.86	2.01	2.52	77
8	Tetramethylurea-d_{12}	1.80	1.95	2.45	77
9	Tetrahydrofuran-d_8	1.78	1.92	2.42	78
10	Monoglyme-d_{10}	1.78	1.92	2.40	78
11	p-Dioxane-d_8	1.78	1.91	2.43	80
12	Diethyl-d_{10} ether	1.77	1.89	2.38	80
13	Acetone-d_6	1.82	1.93	2.41	81

References:

1) P. R. Jones, Chem. Rev., 63 461 (1963) cited unpublished results of P. R. Jones and G. Berchtold.

2) D. S. Erley, W. J. Potts, P. R. Jones and P. J. Desio, Chem. and Ind., 1915 (1964).

3) P. R. Jones and P. J. Desio, J. Org. Chem., 30 4293 (1965).

Yours sincerely,

TW/RGP:cs

Thomas Williams

Ross G. Pitcher

HOOKER CHEMICAL CORPORATION

Niagara Falls, New York 14302

January 6, 1967

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

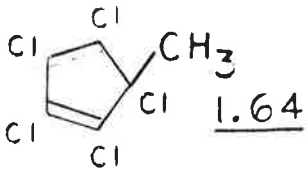
P.m.r. characterization of some polychlorocyclopentadienes and hexachloronorbornenes.

Dear Dr. Shapiro:

Investigating the effect of halogen substituents on hydrogen in the n.m.r. and infrared spectra of sterically rigid systems, we determined the spectral characteristics of several derivatives of hexachlorocyclopentadiene.

Some of our results, which illustrate the interactions and which could be helpful in various structural assignments, are given below:

1. The effect of multiple chlorine substituents and unsaturation on the methyl protons in the various positions of the cyclopentadiene ring is shown in the following examples (δ ,p.p.m.).



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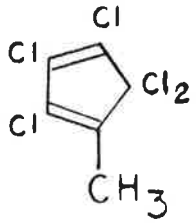

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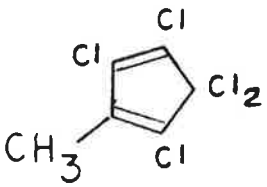
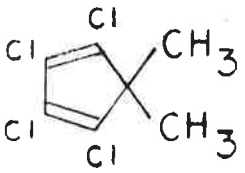
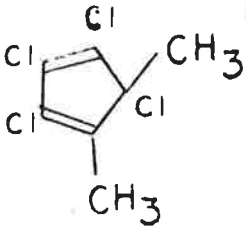


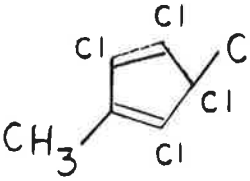
1.97



1.18

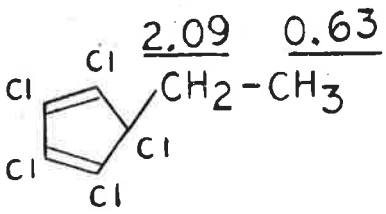


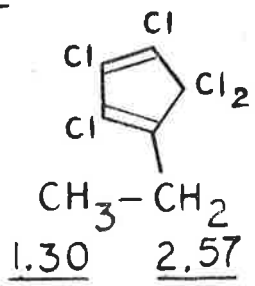
1.55
1.97

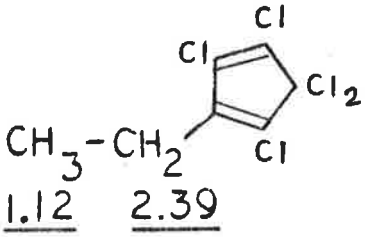


1.58
1.92

A similar relationship was found to exist in the ethyl and isopropyl series also, e.g.,

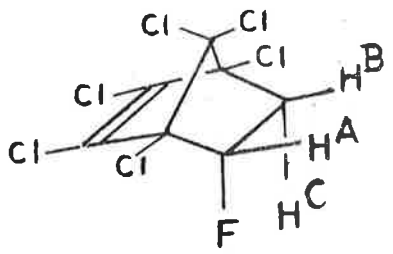






The large difference between the chemical shifts of the methyl groups in the last series of compounds is probably the result of the anisotropy of the unsaturation.

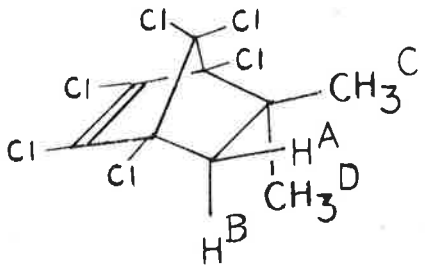
2. The n.m.r. analysis of the adduct of hexachlorocyclopentadiene and vinyl fluoride, I (m.p. 118-120°), yielded information on the dependence of H-F coupling on bond angles in a rigid system. The results suggest a relationship between J_{HF} (vic) and dihedral angle similar to the one predicted by Karplus and confirmed in hydrocarbon systems. We noted that Dr. Ken Williamson described in the November issue of the Newsletter the vicinal HF coupling constants of I. Due to the active interest in analogous structures, we wish to complete the n.m.r. picture of I and to report all of the proton n.m.r. data (determined on an HA-100 spectrometer, as 10% (w/v) solution in $CDCl_3$, and coupling constants obtained from scans of 50 Hz width):



δ_{H^A}	5.37 p.p.m.	J_{H^AF}	54.10 Hz	$J_{H^AH^B}$	7.17 Hz
δ_{H^B}	2.92 p.p.m.	J_{H^BF}	12.36 Hz	$J_{H^BH^C}$	13.46 Hz
δ_{H^C}	2.18 p.p.m.	J_{H^CF}	25.10 Hz	$J_{H^CH^A}$	1.81 Hz

B.L. Shapiro

3. In the Diels-Alder adducts of hexachlorocyclopentadiene and various vinyl compounds, one of the methylene hydrogens is considerably less shielded than its geminal partner (e.g., vide supra). The deshielded proton is assigned the exo position and the effect is attributed to the proximity of the bridge chlorine atoms. To test the deshielding effect on a larger substituent we determined the proton characteristics of an adduct with geminal dimethyl substituents II (m.p. 167-169°).



δ_{H^A}	2.50 p.p.m.	δ_{H^B}	1.97 p.p.m.	J_{AB}	12.3 Hz
δ_{H^C}	1.50 p.p.m	δ_{H^D}	1.03 p.p.m.		

The effect, as anticipated, is similar to the one observed with the geminal methylene hydrogens, and its magnitude is also comparable ($\Delta\delta$ 0.47 vs. 0.53 p.p.m.).

Sincerely,

Victor Mark

Victor Mark
Research Associate

VM/sak

100-46

PROFESSOR OF ORGANIC CHEMISTRY
W. D. OLLIS

TELEPHONE 78555 EXT. 315

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SHEFFIELD 10

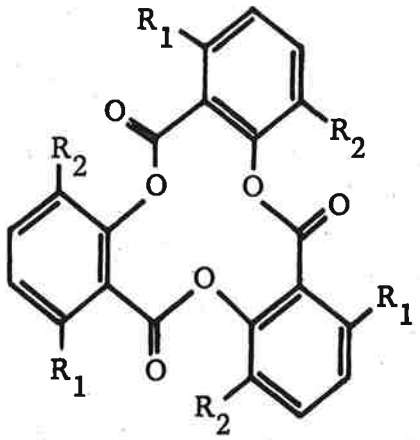
3rd January, 1967

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

Dear Barry,

Conformational Behaviour of Tri-o-carvacrotide

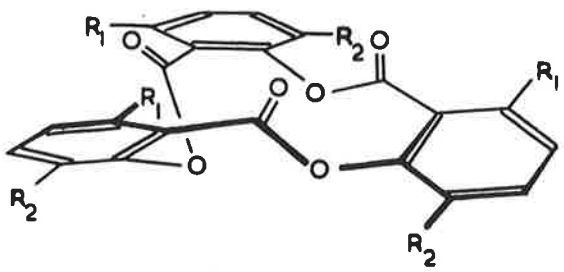
Recently we published a preliminary communication (Chem.Comm., 1966, 402) on the conformational behaviour of tri-o-thymotide (I) and we should now like to report our results on a similar investigation of the isomeric macrocycle, tri-o-carvacrotide (II).



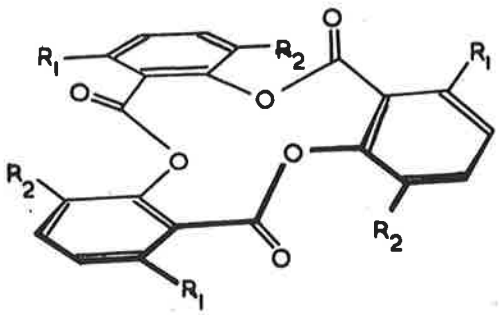
Tri-o-thymotide (I) $R_1 = Me$; $R_2 = CHMe_2$

Tri-o-carvacrotide (II) $R_1 = CHMe_2$; $R_2 = Me$

We recognised tri-o-thymotide some fifteen years ago and among its interesting properties were the formation of a large number of clathrate compounds with many different solvents, and its ability to exhibit the phenomenon of spontaneous resolution. This meant that the conformation adopted by tri-o-thymotide in the solid state must be chiral and our more recent studies were prompted by the possibility of using the isopropyl groups of the tri-o-thymotide molecule as a probe of its chirality in solution. The NMR spectrum of tri-o-thymotide clearly showed a non-equivalence of its isopropyl methyl groups, but the situation was complicated by the fact that tri-o-thymotide could take up two conformations in solution. These were called the propeller (III) and helical (IV) conformations to describe the arrangements adopted by the component benzene rings. As we have discussed in our preliminary communication, both the propeller and helical conformations are chiral so that the two methyl groups of each isopropyl group are diastereoisomeric by internal comparison (Mislow, "Introduction to Stereochemistry", W.A. Benjamin, 1965; see also IITNN, 94 - 8). Thus, in principle, tri-o-thymotide could show, under conditions of slow inversion, signals due to eight types of isopropyl methyl groups associated with the propeller conformation ($3Me_A$ and $3Me_B$) and the helical conformation (Me_C, Me_D, Me_E, Me_F, Me_G, and Me_H). Due to apparent chemical shift equivalence, signals due to each type of methyl group were not separately observed, but a detailed line shape analysis of the NMR spectra of tri-o-thymotide is now almost completed and we hope to report this shortly.



Propeller conformation
(III) R_1 = Me; R_2 = R = $CHMe_2$
(V) R_1 = $CHMe_2$; R_2 = Me



Helical conformation
(IV) R_1 = Me; R_2 = $CHMe_2$
(VI) R_1 = $CHMe_2$; R_2 = Me

Thus our analysis of the NMR spectrum of tri-o-thymotide was initially bedevilled by the consequences of chemical shift equivalence, so you can imagine our delight when the NMR spectrum of tri-o-carvacrotide was determined. This clearly showed (see Figure) signals which could be assigned with certainty to three non-equivalent aromatic methyl groups (Me_A, Me_B, and Me_C) of the helical conformation (VI) and one methyl singlet to be assigned to three equivalent aromatic methyl groups of the propeller conformation (V). The Figure summarises the experimental information and extrapolation from the rate constants for methyl site exchange between Me_A, Me_B, Me_C, and Me_D for tri-o-carvacrotide (II) gave the rate constants for the conformational changes (propeller ⟶ helix, helix ⟶ propeller, and helix ⟶ enantiomeric helix) from which the activation parameters given in the Table were determined. The rate constants for methyl site exchange were determined by detailed comparison of computed and observed line shapes. The computation of line shapes was achieved using a Mercury Autocode programme based directly upon the McConnell equations (J.Chem.Phys., 1958, 28, 430).

TABLE. Activation parameters for the conformational changes of tri-o-carvacrotide (IV) in pyridine solution

Process	E_a [a] kcal/mole	$\log_{10}A$ [a,b]	$\Delta G_o^{\ddagger}$ [a] kcal/mole
Propeller ⟶ Helix	22.8 ± 1.5	14.5 ± 1.0	20.6 ± 0.2
Helix ⟶ Propeller	22.8 ± 1.5	14.7 ± 1.0	20.3 ± 0.2
Helix ⟶ Enantiomeric helix	21.4 ± 1.3	15.9 ± 1.0	17.6 ± 0.2

[a] The errors quoted refer to 90% confidence limits.

[b] Rate constants and A values are based upon sec^{-1} units.

It is clear that our understanding of the conformational behaviour of tri-o-thymotide (I) has been placed upon a much firmer basis by the results for tri-o-carvacrotide (II). Following our use of the NMR

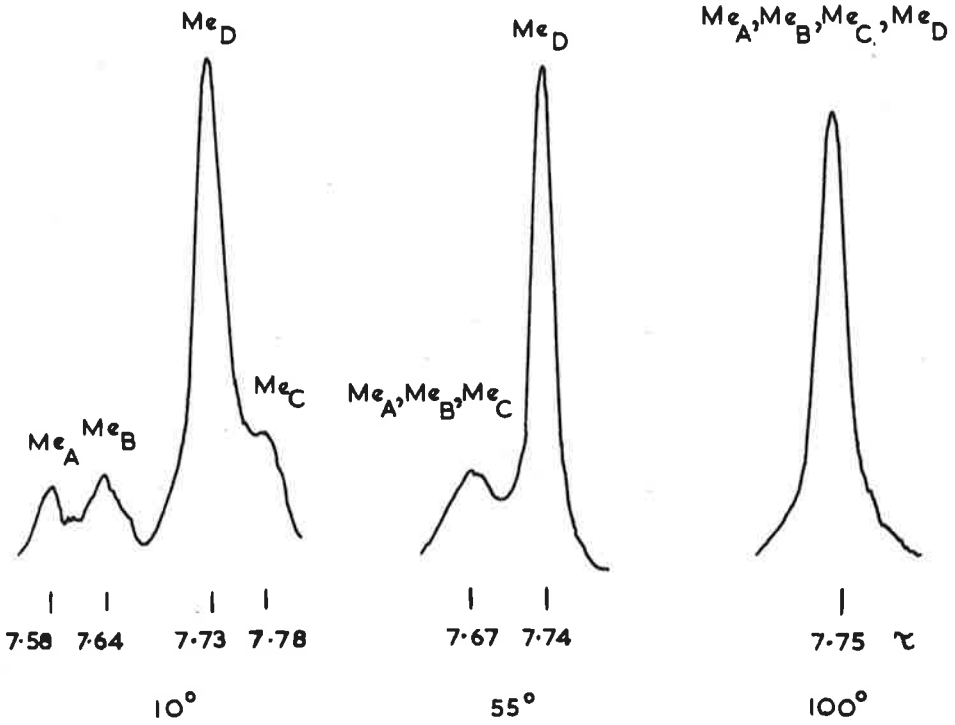


FIGURE. Nuclear magnetic resonance spectrum due to the aromatic methyl groups of tri-o-carvacrotide (II). The spectra were determined in pyridine solution at the indicated temperatures.

characteristics of the isopropyl group as a probe for chirality in tri-o-thymotide, several related studies have been described. These include the very interesting study of a transformation product of fuerstione (von Philipsborn and Conti, IITNN, 96 - 23; Conti, Eugster, and von Philipsborn, Helv.Chim.Acta, 1966, 49, 2867), and Mannschreck's recent report on the inversion behaviour of an isopropyl-diaziridine (IITNN, 97 - 54).

Greetings to you and your research group for 1967,

Yours sincerely,

A. P. Downing W. D. Ollis I. O. Sutherland

A. P. DOWNING W. D. OLLIS I. O. SUTHERLAND

Institut für Physikalische Chemie
der Rhein.-Westf. Techn. Hochschule
Aachen, Direktor Prof. Dr. U. Franck

Zur Messung der Amplitude des HF-Feldes durch das Kernresonanz-experiment.

Folgende Bezeichnungen werden benutzt:
H_0: Feldstärke des Gleichfeldes ($\omega_0 = -\gamma H_0$)
ω und ω_1 : Kreisfrequenz bzw. die Amplitude des HF-Feldes ($\omega_1 = -\gamma H_1$),
$\Delta\omega = \omega_0 - \omega$ und
Ω und ω_s: Kreisfrequenz bzw. Amplitude des NF-Störfeldes in Richtung des Feldes H_0.

Die Blochschen Gleichungen im rotierenden Koordinatensystem lauten:

$$\left.\begin{aligned} \dot{u} &= \Delta\omega\, v - u/T_2 \\ \dot{v} &= -\Delta\omega\, u - v/T_2 - \omega_1 w \\ \dot{w} &= \omega_1 v - (w-1)/T_1 \end{aligned}\right\} \qquad (1)$$

Unter den Voraussetzungen:

$$\chi = \frac{\omega_s}{\Omega} \ll 1 \qquad (2)$$

$$\alpha = 1/\Omega T_1 \ll 1 \qquad (3)$$

$$\beta = 1/\Omega T_2 \ll 1 \qquad (4)$$

$$|\delta - 1| = \left|\frac{\omega_{eff}}{\Omega} - 1\right| \ll 1 \qquad (5)$$

worin $\omega_{eff} = \gamma H_{eff} = \sqrt{\Delta\omega^2 + \omega_1^2}$ (6)

ist, und die Richtung des effektiven Feldes durch

$$\operatorname{tg}\varphi = \frac{\omega_1}{\Delta\omega} \qquad (7)$$

gegeben ist, erhält man für die Blochschen Gleichungen im Koordinatensystem, dessen eine Achse mit der Achse des effektiven Feldes zusammen-

fällt, die Beziehungen:

$$\dot{u}' = -v + (1-\delta-\chi\cos\varphi\cos\tilde{\tau})v - (\alpha+\beta+(\alpha-\beta)\sin^2\varphi)u' + (\alpha-\beta)\sin\varphi\cos\varphi w' - \alpha\sin\varphi \tag{8a}$$

$$\dot{v} = u' - (1-\delta-\chi\cos\varphi\cos\tilde{\tau})u' - \beta v + \chi\sin\varphi\cos\tilde{\tau}w' \tag{8b}$$

$$\dot{w}' = -\chi\sin\varphi\cos\tilde{\tau}\cdot v + (\alpha-\beta)\sin\varphi\cos\varphi u' - (\alpha+\beta - (\alpha-\beta)\sin\varphi)w' + \alpha\cos\varphi \tag{8c}$$

Es bedeuten:

$$u' + iw' = e^{i\varphi}(u+iw) \tag{9a}$$

$$\tilde{\tau} = \Omega t \tag{9b}$$

$$\dot{u}' = \frac{du'}{d\tilde{\tau}} \tag{9c}$$

Die Lösung der Gleichungen (8a-c) in nullter Näherung lauten:

$$v_0 + iu_0' = A'e^{-i\tilde{\tau}} \quad ; \quad w_0' = B \tag{10a}$$

(10b)

Die Konstanten $A' = A_1' + iA_2'$ und B werden nach dem Vorschlag von K. U. VLADIMIRSKII so bestimmt, daß in erster Näherung keine Glieder linear in $\tilde{\tau}$ vorkommen, unter dieser Bedingung erhält man für:

$$A' = \frac{\pm \chi/2 \sin\varphi\cos\varphi\left(\frac{1}{\beta} + \frac{(\alpha-\beta)}{\alpha\beta^2}\sin^2\varphi\right)}{1 + S' + (\Delta\Omega)^2 T_2'^2} \tag{11}$$

$$S' = \left[(\alpha-\beta)^2 + \frac{\chi^2}{4}\right]\frac{\sin^2\varphi}{\alpha\beta} + \left[\left(\frac{1}{4\beta} - \frac{1}{\alpha}\right)(\alpha-\beta) + \frac{\chi^2}{2\alpha\beta}\right]\left(\frac{\alpha-\beta}{\beta}\sin^4\varphi - \frac{(\alpha-\beta)^2}{\alpha}\sin^6\varphi\right) \tag{12}$$

$$T_2'^2 = T_2^2\left(1 - \frac{\alpha-\beta}{\alpha}\sin^2\varphi\right) \tag{13}$$

$$\Delta\Omega = \Omega - \omega_{eff} \tag{14}$$

Dann gibt A_1' das Absorptionssignal an, wenn die Phasenlage entsprechend $\phi(\omega) = 0$ und $\phi(\Omega) = \pi/2$ eingestellt ist.

S' ist der Sättigungsterm. Da aber $\alpha \approx \beta$ und $\sin\varphi < 0{,}5$, ist nur

der erste Term in der Summe für die Sättigung wesentlich. Für kleine Winkel φ hat das Absorptionssignal im u, v, w System die Form:

$$A_1 = \pm \frac{\frac{\omega_1}{\omega_{eff}} \omega_s T_2 \left[1 + \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \frac{T_2}{2\omega_{eff}} \omega_1^2\right]}{1 + \omega_1^2 T_1 T_2 \left[\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^2 + \frac{\omega_s^2}{4}\right] \frac{1}{\omega_{eff}^2} + \Delta\omega^2 T_2^2 \left[1 - \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \frac{T_1}{\omega_{eff}^2} \omega_1^2\right]} \qquad (15)$$

Das Vorzeichen hängt davon ab, ob $\Delta\omega$ positiv oder negativ ist. Man erkennt aus Gleichung (12), daß die Sättigung durch den Korrekturfaktor herabgesetzt wird. Im Nenner von A_1 wird T_2 vergrößert. Die einzige Variable ist ω_{eff} $(\Delta\omega)$. Damit wird S' und T_2 frequenzabhängig. Wir erhalten keine Lorentzkurven mehr. Man kann aber aus der Signalform, die durch A_1 dargestellt wird, optimale Meßbedingungen ermitteln.

Abschließend sei bemerkt, daß nach ANDERSON die Feldstärke ω_1 des HF-Feldes aus den Resonanzlagen für das effektive Feld

$\omega_{eff} = \gamma H_{eff} = \sqrt{(\Delta\omega)^2 + \omega_1^2}$ bestimmt wird.

Mit besten Grüßen

Ihre

Roland Mosfeld

Literatur:

NMR and EPR-Spectroscopy, Anderson, p. 176.
K. V. Vladimirskii: Soc. Phys. JETP 6, 413 (1958).
W. A. Anderson: Phys. Rev. 102, 151 (1956).

RCO Chemical Company

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Research Division
Research & Development Center--Philadelphia

100-53

January 6, 1967

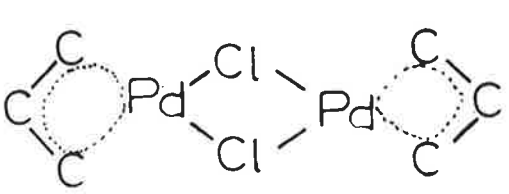
Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

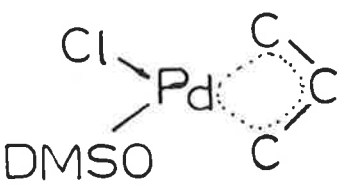
Intermediates in the Conversion of π-into σ-Allylic Palladium(II) Complexes

Recent reports[1,2] on the temperature dependence of nuclear magnetic resonance spectra of several systems consisting of allylpalladium(II) chloride and various ligands including dimethylsulfoxide, triphenylphosphine, and triphenylarsine have shown that a number of equilibrations are involved in the conversion of π-to σ-complexes.

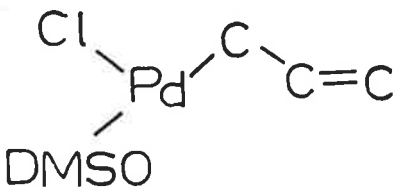
Additional information concerning the allylic equilibrations has been obtained from concentration studies used in conjunction with the temperature dependence of the NMR spectra. For the systems, allyl, methallyl, and crotylpalladium(II) chloride in solution in $CDCl_3$ to which has been added one mole of DMSO-d_6/mole of Pd, the NMR spectra suggest two π-structures are present at low and intermediate temperatures and a σ-structure seems to be indicated at elevated temperatures[2]. The low temperature species was postulated to be II which was involved in another equilibration, that of ligand exchange[1,2]. The temperature dependence of the NMR spectra for various concentrations of DMSO-d_6 suggests the following equilibrations, where the dominant species are: I at low temperatures, II at intermediate, and III at elevated temperatures. Structure III is based primarily upon the equivalence of the terminal protons which may result from: (1) the equilibration II $\rightleftharpoons$ III and the process may or may not involve the addition of a second mole of DMSO-d_6, (2) a head-over-tail process involving only structure III, or (3) a combination 1 and 2.



I

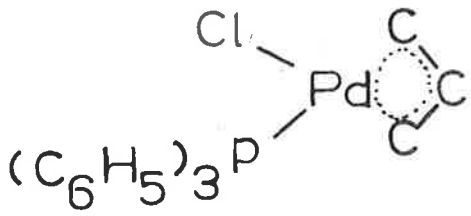


II



III

For the systems consisting of allyl, methallyl, and crotylpalladium(II) chloride in solution in $CDCl_3$ to which has been added one mole or less of $(C_6H_5)_3P$, the NMR spectra suggest that the equilibrations are different from those for the DMSO systems. In Fig. 1, is shown the temperature dependence of the NMR spectrum of allylpalladium(II) chloride to which has been added one-half mole of $(C_6H_5)_3P$/mole of Pd. At -40°C, the spectrum exhibits sharp resonances for I and IV.



IV

As the temperature is increased the resonances for IV first broaden then coalesce into a broad band centered at τ, 6.4. The spectra indicate that the equilibrations of IV do not involve the dimer I below 50°C, although they do interact at higher temperatures. For the methallylpalladium(II) chloride system to which has been added one mole or less of $(C_6H_5)_3P$, the temperature dependence of the spectra shows the two cis and the two trans protons equilibrating and again the process does not appear to involve the dimer. Still another equilibration is observed for the system consisting of allylpalladium(II) chloride to which has been added one mole of $(C_6H_5)_3P$. As the temperature is increased from -40°, the resonances for the CH_2 protons cis to the $(C_6H_5)_3P$ ligand first broaden then coalesce while those for the trans protons remain relatively sharp. Clearly a number of equilibrations are involved and they appear to be quite sensitive to not only the basicity of the ligands, but also to the substituents upon the allyl groups. Additional work on the equilibrations of allylic systems with a variety of ligands is in progress.

References

(1) G.L.Statton and K.C.Ramey, J.Am.Chem.Soc., 88, 1327 (1966).

(2) K.C.Ramey and G.L.Statton, J.Am.Chem.Soc., 88, 4387 (1966).

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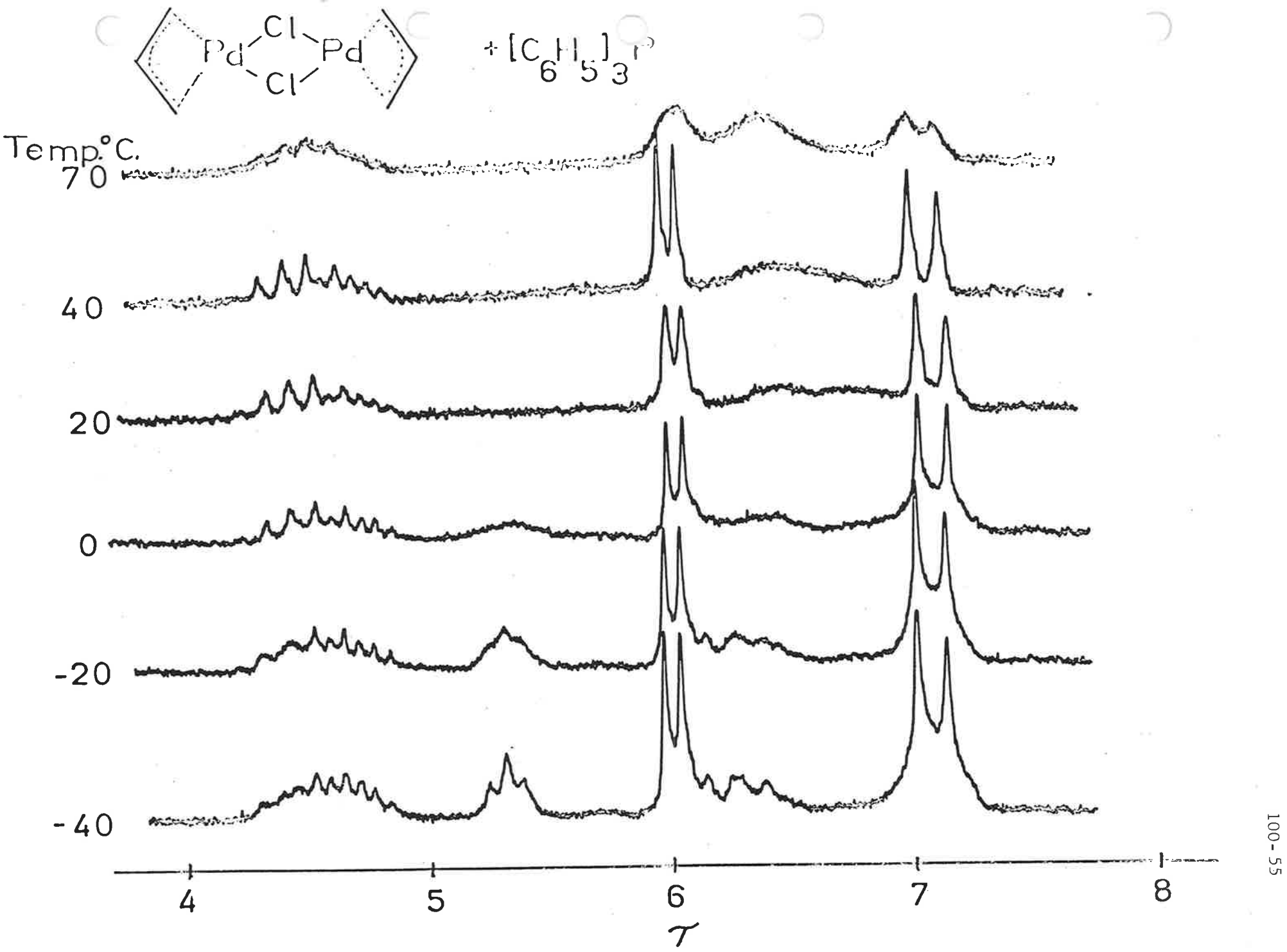

Fig. 1. Temperature dependence of the n.m.r. spectrum of allylpalladium(II) chloride in solution in $CDCl_3$ — ½ mole of (ϕ_3P/ mole of Pd.