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N-M-R
Newsletter

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FEBRUARY, 1969

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Deadline Dates: No. 126: 3 March 1969
No. 127: 1 April 1969

All Newsletter correspondence, etc., should be addressed to:

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

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

17 January 1969

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

Dear Barry:

Determination of Magnetic Susceptibility of Dilute Solutions

We recently had occasion to determine the magnetic susceptibilities of dilute solutions of complexes of paramagnetic transition metal ions in H_2O. The classical Gouy method gave uncertain results because we had to have large amounts of excess ligand and our magnet is not a large one. The largest magnets in most departments are in nuclear magnetic resonance spectrometers and we referred again to the technique suggested by D. S. Evans in J. Chem. Soc., 2003 (1959).

The technique as described by Evans consists of putting an inert reference compound in the solution and comparing its chemical shift with the same reference in solution in a capillary. In our hands, at least, this configuration always gave rise to spinning side bands which sharply limited the usefulness of the method.

Our department has recently obtained a Hitachi Perkin-Elmer R-20 instrument which is of the external reference frequency sweep type. Mr. T. Phil Pitner and Dr. Peter J. Morris working in our laboratory prepared two separate sample tubes, each containing solution and reference compound but only one containing the metal ion complex. The relative positions of the reference peak in each tube were determined by using a frequency counter connected directly to the sweep oscillator. The susceptibility can then be determined from the difference in resonance positions of the reference peaks in the usual way. The mass susceptibility of a standard solution of nickel chloride was measured as 34.4 in good agreement with the literature value of 34.2.

Sincerely yours,

Bruce

R. Bruce Martin
Professor and Chairman

UNION CARBIDE CORPORATION
P. O. BOX 278, TARRYTOWN, N. Y. 10591

UNION CARBIDE
RESEARCH INSTITUTE

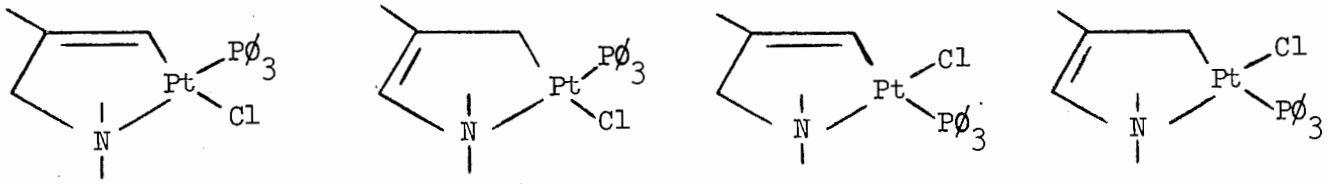
January 8, 1969

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

^{1}H-{^{31}P} and ^{1}H-{^{195}Pt} Double Resonance Experiments

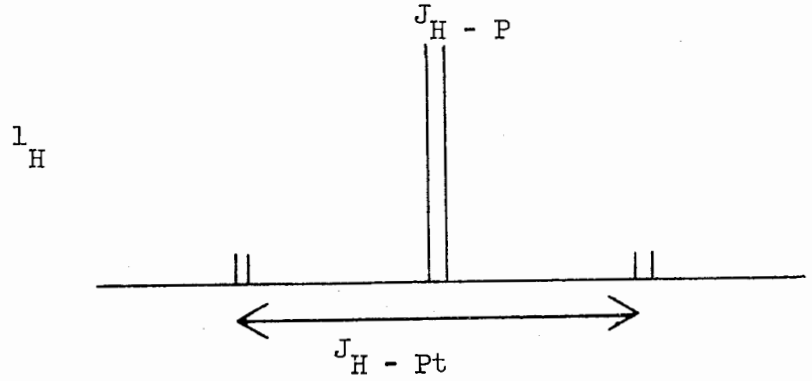
Dear Barry:

Nuclear spin couplings between metals and directly bonded ligand atoms are often diagnostic of structure in coordination complexes. Thus, Pidcock, Richards and Venanzi[1] have inferred that large $d\pi$ - $d\pi$ contributions to the bonding cause stronger couplings of ^{195}Pt to ^{31}P when the π-bonding ligands are in a cis arrangement. These couplings are apparent only in the ^{31}P or ^{195}Pt spectra, the observation of which is hampered by low sensitivity and, in our case, the lack of specialized equipment. Double resonance techniques, therefore, seem particularly well suited to these problems whenever the ligands contain protons which also couple to the ^{31}P and/or ^{195}Pt atoms. A case in point is the complex between N,N-dimethyl methallylamine, triphenylphospine, and $PtCl_2$, which can have either of the four structures shown below:[2]

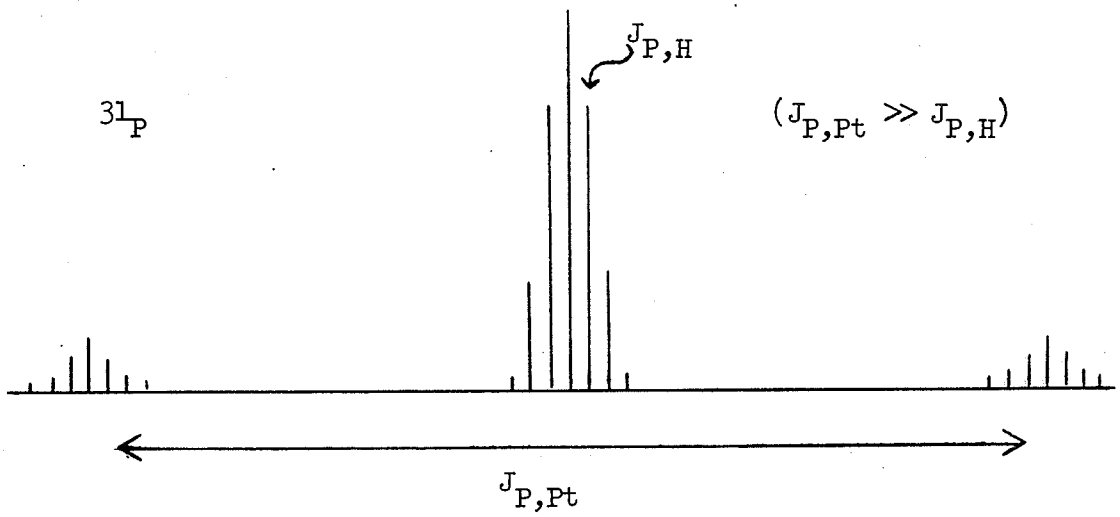


I II III IV

The proton magnetic resonance spectrum of the N-methyl groups has the appearance shown schematically below, the outer four lines being due to the ~ 30% of species containing the magnetic ^{195}Pt nucleus (spin = 1/2), and the



inner pair of lines due to the remaining nonmagnetic natural isotopes of platinum. From this, and ignoring couplings of other protons to phosphorus, we can infer the appearance of the ^{31}P spectrum to be as shown below, the spacing between the outer septets being the unknown coupling between ^{31}P and



^{195}Pt. If this coupling is of the same order as the ^{1}H - ^{31}P coupling, the ^{31}P septets will overlap.

It is convenient to consider the three sets of closely spaced patterns in each figure above as arising from ^{1}H - ^{31}P couplings in three distinct species; (1) species containing ^{195}Pt spins in the + 1/2 configuration; (2) species containing nonmagnetic Pt, and (3) species containing ^{195}Pt in the - 1/2 configuration. The order listed may be that of increasing or decreasing frequency depending on the sign of the coupling of each nucleus to ^{195}Pt. So long as the patterns are well resolved, it is possible to decouple ^{1}H from ^{31}P in each species separately. The results of such an experiment are shown in Figure 1, where it is seen that separate ^{31}P irradiating frequencies collapse each small doublet in the ^{1}H spectrum at the values summarized in Table I.

Table I

Double Resonance Frequencies in Magnetic Field Required to Produce ^{1}H Resonance in TMS at 59.998315 MHz.

Pattern (Fig. 1)	Center frequency of ^{1}H pattern collapsed	^{31}P irradiating frequency (MHz)
A	59.998510	24.290273
B	59.998496	24.288156
C	59.998482	24.286013

The splitting of the outer irradiating lines gives the value of the ^{31}P coupling as 4260 Hz, and the fact that the perturbing and observing frequencies follow the same sequence determines that ^{195}Pt couplings to both ^{1}H and ^{31}P have the same sign.

The decoupling frequency for the center pattern serves to measure the ^{31}P chemical shift. This is most conveniently referred to the tetramethylsilane reference by taking the ratio of ^{31}P decoupling frequency to that of the protons in TMS in the magnetic field required to produce resonance in the latter. A corresponding measurement of the known[3] ^{31}P shift in diethyl hydrogen phosphite provides a reference point between the proton and phosphorus chemical shift scales, permitting us to express the ^{31}P shift in the ^{195}Pt complex in more conventional terms.

	^{31}P center freq.	^{1}H in TMS	ν_P/ν_H	difference (ppm)	δ (ppm) 85% ext. H_3PO_4
Complex	24.288156	59.998315	0.40481397	-7.8	-15.3
$(EtO)_2PHO$	24.287973	59.998332	0.40481080	--	- 7.5[3]

The proton resonance spectrum favors structures I or III on the basis that the methylene protons are coupled to both ^{31}P and ^{195}Pt by the same amount as the N-methyl protons, this implying that the number and type of intervening chemical bonds is the same. The large ^{195}Pt - ^{31}P coupling implies that the two ligands capable of π-bonding to platinum are cis to each other, as in structure I.

In two later experiments, we "parked" the spectrometer on each of the two highest frequency N-methyl satellite lines and swept a perturbing RF field through the ^{195}Pt spectrum. This revealed four broad bands corresponding to ^{195}Pt couplings to ^{31}P ($J \sim 4200$ Hz) and to the vinyl proton ($J \sim 128$ Hz), and enabled us to determine that the coupling of the N-methyl protons to ^{31}P has the same sign as the coupling of ^{31}P to ^{195}Pt, and hence as the N-methyl protons to ^{195}Pt. The ^{195}Pt shift relative to ^{1}H in TMS is 0.21407227; unfortunately, we had no other ^{195}Pt compounds around in which to compare shifts.

Happy New Year!

Sincerely,

E. B. Whipple

EBW:srp

References:

1. A Pidcock, R. E. Richards, and L. M. Venanzi, Proc. Chem. Soc., 184, 1962.

2. Provided by Dr. Jonathan M. Kliegman, Chemicals and Plastics Research Laboratory, South Charleston.

3. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance, Pergamon Press, 1966, Vol. 2, p. 1053.

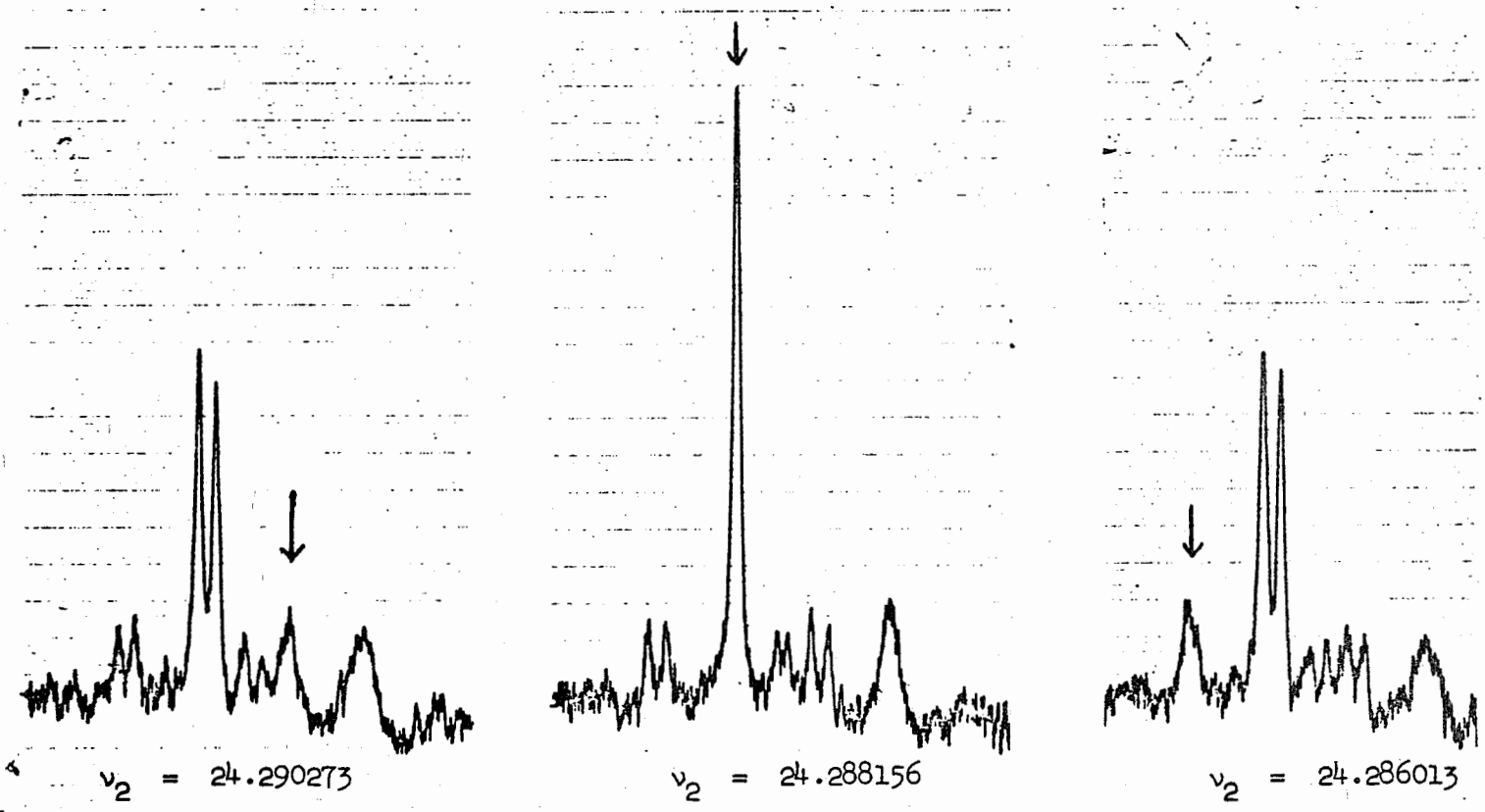


Figure 1 - N-Methyl proton resonances successively perturbed by ^{31}P irradiating frequencies.

CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN
INSTITUT FÜR ORGANISCHE CHEMIE
Dr. Rudolf Knorr

8000 MÜNCHEN 2, Jan. 13, 1969
Karlstr. 23 - Tel. ~~55 79 36~~ 5902-247

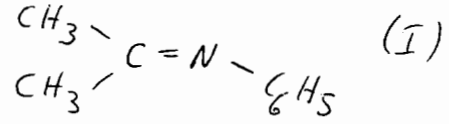
Professor Bernard L. Shapiro
Texas A&M University
College of Science
College Station, Texas 77843

Dear Professor Shapiro,

1) N-Isopropylidene Aniline
2) Attempted Extension of the Marquardt-Ferguson Program

Please accept my apologies for sending my contribution so late.

1) Last summer we started looking at energy barriers of the cis-trans isomerisation of simple azomethins by complete lineshape analysis. For the first, though not very convenient example we chose N-isopropylidene aniline I (1).



(I)

The parameters of activation have been reported (2) for I ($\Delta\nu$ of the CH_3 groups 25.5 Hz at 60 MHz) in diphenyl ether: $\Delta G^{\neq}$ 20.3, E_a 22.3±2.0 kcal/mole, log A 14.9±1.0. We find essentially the same values in two other solvents (diphenyl and 1,2-dichlorobenzene) and the coalescence points at about 130°.
A serious drawback of the lineshape analysis in this case is the relatively rapid formation of decomposition product(s) whose peaks interfere strongly with the CH_3 signals used for the τ-determination. The uncertainty in τ-values may, therefore, be up to about 20%. Because of the necessity of doing the measurements as quickly as possible, the error in the (corrected) temperatures was estimated to about 1°.
Parameters of activation were calculated using the most reliable τ-values according to Arrhenius (E_a, log A) and Eyring ($\Delta G^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$, transmission coefficient = 1). Because of the very large error limits, no safe conclusions can be drawn for this system, but it may be significant that the points obtained in these two solvents of very different polarity have almost the same regression line. The relevant data are collected in the table.
Considering the difficulties indicated, the use of several other methods of analysis (1) (3) is certainly difficult.

2) We tried to extend the Marquardt and Ferguson program to a maximum of 8 groups of magnetically non-equivalent spins, for use at an IBM 360/50 computer. Although a lot of space can still be saved in NMRXT and other subroutines, the peculiar method of

Solvent (T range used)	Coal. point	$\Delta\nu$ Hz (60 MHz)	E_a kcal/ mole	log A	$\Delta G_{12}^{\neq}$, kcal/ mole	$\Delta H^{\neq}$ kcal/ mole	$\Delta S^{\neq}$ e.u.
Diphenyl 119.5-137°	~130°	27.5	24 ± 6	15 ± 3	20	22 ± 6	4 ±14
1,2-Dichlorobenzene 118-138°	~129°	24.7	20 ± 5	13 ± 3	20	19 ± 5	-3 ±13

error calculation inherent in the program would require a lot of tape or disk handling during execution time because of storage problems. At this point we found ourselves saved by the 'ad' of C.W.Haigh's most elegant new program (4), LAME, which we are currently extending (more groups, direct plotting) and adapting to IBM facilities.

Yours sincerely,

Rudolf Knorr.

(1) R.Kuhn and H.Schretzmann, Chem.Ber. 90, 557 (1957)

(2) D.Wurmb-Gerlich, F.Vögtle, A.Mannschreck, and H.A.Staab, Liebigs Ann.Chem. 708, 36 (1967); compare also Tetrah.Letters 1965, 697.

(3) H.G.Schmid, H.Friebolin, S.Kabuß, and R.Mecke, Spectrochimica Acta 22, 623 (1966)

(4) TAMUNMR-Newsletters, 121-54

THE UNIVERSITY OF UTAH

SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

January 14, 1969

Comment on Dr. Lustig's Suggestion About NMR Computer Programs

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

Dear Barry,

I would like to strongly endorse Ernest Lustig's suggestion (TAMUNMR 123-50) that an annotated list of NMR computer programs be compiled. A great deal of effort is wasted by people in different locations writing similar programs. However, the problems of maintaining useful, up-to-date and self-explanatory listings should not be underestimated. The amount of "minor" variation needed to cover the wide range of modern computers is quite formidable. As many of TAMUNMR's British readers may be aware, we have been trying for the last year (with the aid of Science Research Council money) to build up a library of NMR computer programs at the University of East Anglia, Norwich (take little notice of the heading to this letter - I'm on Sabbatical Leave in Salt Lake City until the end of May). We have the rather specific aim of putting the programs on library tapes at the Atlas computer at Chilton, Berks., which may be used by all British universities. We have got off to a rather slower start than we had hoped and currently have available only LAOCOON III and UEA NMR (a spectral analysis program using magnetic equivalence factoring), in two "sizes" each (e.g. a 4-spin and a 7-spin LAOCOON version). We are certainly happy to interchange ideas with any other group. Those interested should write to:

Mr. J. Stokes
School of Chemical Sciences
University of East Anglia
Norwich NOR 88C
England

I would like to add that we envisage the following programs:

(1) Spectral analysis (as already mentioned)
(2) Liquid crystal spectral analysis
(3) Double resonance spectral analysis
(4) Band-shapes for spectra of systems undergoing rate processes (a variety of systems needed)
(5) Spectra of systems involving relaxing quadrupolar nuclei
(6) Band-shape calculations for spin systems with intramolecular dipole-dipole relaxation

There are also, of course, related quantum mechanical programs for the calculation of coupling constants and chemical shifts by MO or VB methods which may be required, as well as minor ones for least-squares fitting of data, etc. Incidentally, we already have quite a bit of information about the uses British University NMR spectroscopists make of computers, from a questionnaire sent out about a year ago.

Would anyone like to add to the above list of desirable programs?

Yours sincerely,

Robin

Robin K. Harris

RKH:fjc

125-10

Dr. L. Pohl
im Hause

E. MERCK · DARMSTADT
AKTIENGESELLSCHAFT

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Professor B. L. Shapiro
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Ihre Zeichen	Ihr Schreiben vom	Hausruf	Unsere Zeichen	Datum
		2784	Dr.Pl/MH	14. Jan. 1969

Betr.: "Cyclosilan-d_{18}", eine Lock-Substanz bis + 200°C

Sehr geehrter Herr Professor Shapiro!

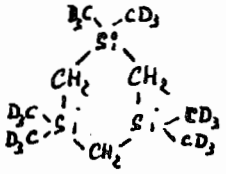
In den TAMU-NMR-Letters 119-4 berichtet W.L. Budde von der Anwendung des Tris(trimethylsilyl)amin als Standard und Lock-Substanz für NMR-Messungen im Temperaturbereich bis + 200°C. Im Gegensatz zu anderen bisher üblichen Standardsubstanzen wie Hexamethyldisilan, Hexamethyldisilazan oder Hexamethyldisiloxan besitzt es den Vorteil, bis + 200°C ein stabiles Locksignal zu liefern, ist aber leider polar, so daß unterschiedliche Wechselwirkungen mit dem Lösungsmittel und der gelösten Substanz auftreten können. Auf Grund der chemischen Verschiebung von σ = 0,229 ppm erlaubt es weiterhin keine ungestörten Messungen zwischen σ = 0 und 1 ppm, was besonders bei Steroiden und Dreiringsystemen nachteilig ist, die in diesem Bereich häufig wichtige Resonanzsignale aufweisen.

E. MERCK · DARMSTADT
AKTIENGESELLSCHAFT

125-11
LUFTPOST

Empfänger Prof. B.L. Shapiro Unsere Zeichen Dr.Pl/MH Tag 14.1.69 Blatt 2

Wir verwenden für Messungen im Temperaturbereich bis + 200°C das 1,3,5-Hexakis(trideuteromethyl)1,3,5-trisila-cyclohexan,



das wir kurz "Cyclosilan-d_{18}" nennen, eine Flüssigkeit, die in den meisten organischen Lösungsmitteln, die für Arbeiten bei erhöhter Temperatur in Frage kommen, gut löslich ist, wie z.B. Pyridin-d_5, Tetrachloräthan-d_2, Dimethylformamid-d_7 , Tetramethylharnstoff-d_{12}, Dekalin-d_{18}, Hexachloraceton, Hexachlorbutadien und HexamethylPhosphorsäuretriamid-d_{18}. Die Verbindung siedet unzersetzt bei + 208°C, besitzt bei σ = - 0,327 ppm ein scharfes Resonanzsignal mit einer Halbwertsbreite von 0,5 Hz und liefert einen stabilen Lock zwischen - 100°C und + 200°C. Sie erlaubt also die Aufnahme ungestörter NMR-Spektren von σ = 0 ppm an feldabwärts. Bei normaler oder tiefer Temperatur kann Cyclosilan-d_{18} natürlich auch in Verbindung mit TMS als Nullpunktsignal verwendet werden.

Mit freundlichem Gruß

Ihr L. Pohl

Dr. Ludwig Pohl

CASE WESTERN RESERVE UNIVERSITY • CLEVELAND, OHIO 44106

January 15, 1969

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

Dear Barry:

TITLE: RELIABLE TACTICITIES BY NMR NOT SO RELIABLE

It is customary in my contributions to the Newsletter to begin by apologizing for being late and needing to be reminded, and this case is no different. My excuse this time is that I have just recently joined the academic world, and the transition was a little more time consuming than I had anticipated. If any of the Newsletter readers are in the Cleveland area, I would be delighted to have them drop in and see my new home.

We have had a continuing interest in the applications of NMR techniques to the elucidation of polymer structures. As all readers who are interested in polymers know, NMR is generally regarded as the standard technique for measuring tacticity in polymer systems. This implies high reliability of the results obtained, and we should like to inject here that caution must be employed. This can be illustrated in some work that we have done jointly with Jim Harwood at the University of Akron.

Phenyl methacrylate, o-biphenyl methacrylate, p-biphenyl methacrylate, α-naphthyl methacrylate, β-naphthyl methacrylate, benzyl methacrylate, and 2-phenylethyl methacrylates were polymerized by free radical techniques in a series of solvents at several temperatures. The NMR spectra of the polymers were obtained. The resolution of the α-methyl and methylene resonance regions were only adequate to permit qualitative stereoregular determinations. Then the polymers were converted into the corresponding polymethyl methacrylates by transisterification. The NMR spectra of these polymers were then obtained and the pertinent resonance areas were well enough resolved to permit quantitative stereoregularity determinations. Yokata and Ishii (J. Polymer Sci. 3B, 771, (1965)) has suggested that poly-2-phenylethyl methacrylate has an unusally high syndiotactic structure and our results on the parent polymer tend to agree with theirs. However, if one examines the spectra of the transisterified polymer, an entirely different picture is seen; the structure is much less syndiotactic than originally believed, and even less syndiotactic than conventional polymethyl methacrylates. In fact, the polymers derived from the methacrylates with the bulky ester groups were found to be more random in structure than those derived from less hindered monomers only when examining the transisterified polymer spectra. The spectra of the

parent polymers indicated higher syndio contents. The point is then, that the NMR measurements of tacticity are reliable on polymethacrylate systems in which the ester is either a methyl or a very simple alkyl group, and if a bulky ester group is involved, then it probably would be desirable and wise to transisterify this to the methyl ester for purposes of tacticity measurements of NMR.

Representative results obtained for the above mentioned polymerization conducted at 60°C are given below. Sigma is defined as the fraction of isotactic diads present and ∴ 1-σ is the fraction of syndiotactic diads present.

Monomer	Polymerization Solvent	1-σ
Phenyl Methacrylate	Bulk	0.228
Phenyl Methacrylate	methyl Benzoate	0.175
o-Biphenyl "	Bulk	0.243
p-Biphenyl "	"	0.190
α-Naphthyl "	"	0.226
β-Naphthyl "	Benzene	0.283
Benzyl "	Bulk	0.226
2-Phenylethyl "	"	0.283
Methyl "		0.30

We hope to publish these results in greater detail with a more meaningful discussion in the near future.

Sincerely,

Bill

William M. Ritchey

Associate Professor

UNIVERSITY OF CALIFORNIA, DAVIS

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

SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

January 17, 1969

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

Title: TMS as an Internal Standard for ^{13}C Magnetic Resonance.

Dear Barry,

Sorry that I again challenged the diverse spectrum of colors of your reminder stationery. Enclosed is contribution of our penitent research group. The work was done primarily by Mark Bacon.

Some of our work on experimental and instrumental techniques has centered upon the application of internal-lock methods to less-receptive nuclei.[1,2] A related problem is the proper choice of reference compounds, and we have been exploring internal references which can also provide adequate internal lock signals. The availability of proton-decoupling capabilities (we are using a Varian V-3512-1) widens the choice of potentially useful species. Since most proton work employs TMS as the internal reference, we have been studying the use of TMS as both a ^{13}C reference and lock signal, and are initiating analogous ^{29}Si experiments with ^{29}Si-labelled TMS. The aim is to relate all ^{1}H, ^{13}C, and ^{29}Si chemical shifts to a proton TMS reference (see reference 3 for this general type of approach to ^{13}C shieldings).

In order to characterize ^{13}C as an internal reference, a set of experiments was carried out on a series of solutions with TMS (natural abundance) in 20% solutions, by volume, and a variety of solvents. The experiments were carried out in a manner which permitted proton-referencing, as follows: In all of the experiments the TMS protons were decoupled at a constant frequency, the frequency at which the protons in pure TMS were decoupled in a predetermined, convenient field for which the ^{13}C signal could be readily observed at about 25.1 MHz (known exactly); this condition insured that the effective field experienced by the protons was constant for all experiments. Then, to the extent that the internal chemical shifts of the TMS protons are independent of solvent, the frequency for which the TMS ^{13}C resonated in each solvent gave a direct measure of the solvent dependence of the ^{13}C chemical shift of TMS. Of course, the contributions to shielding differences associated with bulk susceptibilities are automatically removed from consideration in the usual advantageous manner fundamental to internal referencing. The results of such experiments are shown in Table I, where it is seen that the solvent dependence of the "internal" ^{13}C shielding of TMS is within about 1.7 ppm, a rather small range considering the 500-600 ppm range

of ^{13}C shieldings due to molecular structural differences,[4,5] and the appreciable (~15 ppm) solvent effects found in some cases.[4]

The sensitivity of the internal TMS proton shielding to solvent changes was neglected in outlining the methods above; we are engaged in obtaining very precise data on this point, so that whatever small corrections need be applied can be made accurately.

Sincerely,

Gary

Gary E. Maciel
Associate Professor
of Chemistry

GEM:sb

References:

1. I.I.T. NMR Newsletter, No. 98, 34 (1966).

2. I.I.T. NMR Newsletter, No. 105, 33 (1967).

3. E. G. Paul and D. M. Grant, J. Am. Chem. Soc., 86, 2977 (1964).

4. G. E. Maciel and J. J. Natterstad, J. Chem. Phys., 42, 2752 (1965).

5. O. W. Howarth and R. J. Lynch, Mol. Phys., 15, 431 (1968).

Table I. Internal ^{13}C Chemical Shifts of TMS Relative to the Field of Resonance for TMS Protons at 99.972279 MHz.

Solvent	man, Hz[a]	anal, Hz[b]	δrel, ppm[c]
Tetramethylsilane	1634.9	2621.0	0
Tetramethylsilane	1634.2	2620.9	0*
CH_3OH	1633.7	2633.8	12.9 Hz = 0.513 ppm*
CH_3CN	1571.1	2635.8	14.9 Hz = 0.593 ppm*
CH_3CN	1571.3	2635.6	14.7 Hz = 0.585 ppm*
CH_3CH_2CN	1630.7	2622.4	1.5 Hz = 0.059 ppm*
CH_3I	1609.7	2592.9	-28.0 Hz = -1.11 ppm*
CH_3CH_2I	1639.5	2617.3	- 3.7 Hz = -0.147 ppm
CH_2Cl_2	1620.8	2616.5	- 4.4 Hz = -0.175 ppm*
$CHCl_3$	1620.5	2607.5	-13.4 Hz = -0.533 ppm*
CCl_4	1621.4	2600.5	-20.5 Hz = -0.816 ppm
$(CH_3)_2CO$	1638.7	2624.7	3.7 Hz = 0.147 ppm
$(CH_3)_2CO$	1639.9	2623.1	2.2 Hz = 0.088 ppm*
dioxane	1627.5	2619.1	- 1.8 Hz = -0.072 ppm*
Tetrahydrofuran	1628.3	2624.6	3.7 Hz = 0.147 ppm*
Cyclohexane	1628.6	2623.3	2.3 Hz = 0.092 ppm
Cyclohexane	1629.2	2623.0	2.1 Hz = 0.084 ppm*
n-hexane	1632.0	2625.6	4.7 Hz = 0.187 ppm*
C_6H_6	1637.4	2613.8	- 7.2 Hz = -0.286 ppm
C_6H_6	1637.5	2613.5	- 7.4 Hz = -0.294 ppm*
CS_2	1619.0	2599.6	-21.4 Hz = -.852 ppm
n-heptane	1631.1	2622.0	1.1 Hz = 0.049 ppm

a. Audiofrequency of upper-sideband ^{13}C signal on which a $H^{13}CO_2H$ (external capillary) is locked. b. Audiofrequency of lower-sideband TMS ^{13}C signal. c. Internal ^{13}C shift with respect to pure TMS, calculated from b. *The starred relative shifts were obtained with the centerband frequency of 25.140651.8 MHz; the unstarred shifts were obtained with a 25.140651.0 MHz centerband.

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January 15, 1969

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

Are J's strictly proportional to γ's?

Dear Barry:

A proportionality between J and γ is widely used to "measure" otherwise undetectable coupling constants by isotopic substitution. However, several reasons might be given why a small deviation is possible, e.g. for light nuclei the nuclear motion and for heavy nuclei the well-known nuclear-volume effect. Murrell et.al. have given (TAMU NMR 120-58) such an example. We thought it wise to investigate a one-bond coupling where a theoretical interpretation seems easier to do along the lines of Z. Naturforschung 22a, 1458 (1967). We found the following splittings by either H or H-{Si} resonance:

SiH_3J: 239.5 ± 0.1 Hz

SiH_2DJ: 239.2 ± 0.1 and $238.4 \pm 0.6 \cdot \gamma_D/\gamma_H$ Hz

Using a Varian-spectrometer and a GR-synthesizer which were both locked to the standard frequency of a hp-counter we do not expect any systematic error in these measurements. The question which still bothers us is the finite relaxation time of the nuclei. Are these long enough that we can interpret our data as $^1J_{Si-H}$ coupling constants?

We would appreciate any comment on this question.

Best wishes,

Christian Schumann

Herbert Dreeskamp

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Dr. H. Günther

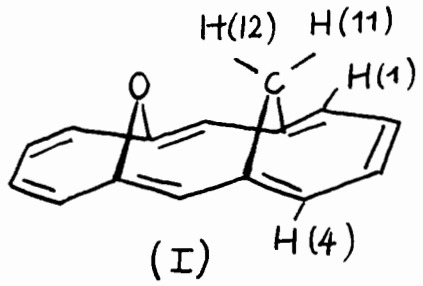
5 KÖLN, January 14, 1969
ZÜLPICHER STRASSE 47
TELEFON: 2024 2239

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

STERIC EFFECTS ON PROTON CHEMICAL SHIFTS

Dear Dr. Shapiro:

In the course of our investigations of substituent effects in the n.m.r. spectra of aromatic compounds we came upon an interesting effect. The two protons H(11) and H(12) of the methylene-bridge in 1.6-methano-8.13-oxido-[14]annulene [1] (I) have considerably different chemical shifts, even though calculations of the ring current-effect suggest that the absorption frequencies of H(11) and H(12) should be similar. A double resonance experiment allowed the assignment of the two protons in the AB-system (fig. 1). Irradiation at the resonance frequency of H(1) and H(4) (fig. 1b) eliminated the long range coupling (triplet-splitting) of the A-part. Assuming that an M-mechanism is most favourable for a long range coupling, the following frequencies are obtained: τ_{11} = 11.40 ppm, τ_{12} = 9.08 ppm.



(I)

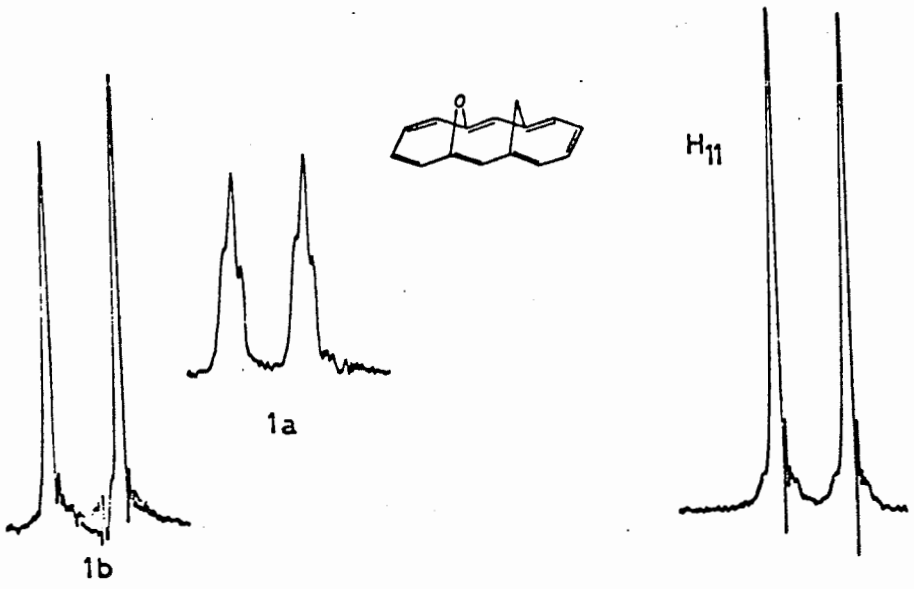
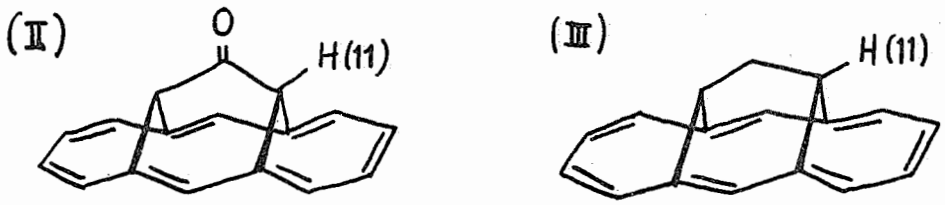


fig. 1

Two compounds present themselves for comparison: 16-oxo-1.6; 8.13-propano-[14]annulene [2] (II) and 1.6; 8.13-propano-[14]annulene [2] (III). The effect of the ketogroup on the proton resonance in II can be evaluated



τ_{11} = 10.87 ppm; τ_{corr} = 11.27 ppm τ_{11} = 11.15 ppm [3]

from model compounds of similar stereochemistry to be about -0.4 ppm, thus the resonance frequency of an undisturbed proton 11 (or 12) in I is 11.27 ppm. This was confirmed indeed some weeks ago by the spectrum of the hydrocarbon III.

On the basis of an average value of 11.2 ppm, which we would expect as resonance frequency of the two bridge protons, we find that proton 11 is shifted upfield by 0.2 ppm, while proton 12 is deshielded by about 2 ppm. This is in good agreement with the suggestion of Winstein and Anet [4] that the free electron pair of oxygen pushes the electron from H(12) to H(11), thereby decreasing the electron density and the chemical shift at proton 12 and increasing them slightly at proton 11 (cf. fig 2). Regardless of whether or not this explanation is right, the observed effect in our compound is of the same magnitude, and seems to result from the unique geometry of the proton overlapping with the free electron pair of the oxygen. Similar observations, by the way, were made by Battiste and Brennan [5].

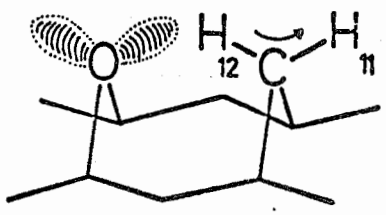


fig. 2

Sincerely yours,

Wolfgang Hans Günther

(W. Bremser) [6] (H. Günther)

[1] U. Haberland, Ph.D. Thesis, Köln (1968)
[2] A. Vogel and E. Vogel, unpublished results
[3] A. Vogel, private communication
[4] S. Winstein, P. Carter, F.A.L. Anet, A.J.R. Brown, J.Amer.Chem.Soc. 87, 5247 (1965)
[5] M.A. Battiste, M.E. Brennan, Tetrahedron Letters 1966, 5857
[6] Present address: Department of Chemistry, California Institute of Technology, Pasadena, Calif. 91109

THE UNIVERSITY OF UTAH

SALT LAKE CITY 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

January 14, 1969

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

NMR and SI

Dear Barry,

Now that the majority (?) of the scientific world has decided that it is desirable to change over to a fully coherent set of units, and has chosen the Système International (SI), it is up to scientists to look into the problems involved in their specialized areas. No doubt there are many groups doing this for NMR, but we would like put forward some of our own ideas on the subject.

NMR is fortunate in that the principal parameters used (shielding constants and coupling constants) are unaffected by the change to SI. Theoretical expressions for these parameters (such as Lamb's formula for diamagnetic shielding or Ramsey's expressions for the three contributions to J) need alteration by the factor $\mu_0/4\pi$ where μ_0 is the permeability constant ($4\pi \times 10^{-7}$ kg m $s^{-2}A^{-2}$), but this is relatively trivial. There are, however, two features which need stressing:

(a) The NMR spectroscopist is used to using the symbol H for "magnetic field", implying, for instance, that the energy of a dipole in the field is $\underline{\mu}.\underline{H}$. This is strictly incorrect, since the relevant field property is the magnetic induction field (≡ magnetic flux density), which physicists give the symbol B. The NMR spectroscopist confuses the issue by using "gauss" as the unit - this is the correct unit for B in the c.g.s. system, whereas the "oersted" is the correct unit for H. This confusion is trivial in c.g.s. since H and B are equal numerically; however, in SI they differ by $4\pi \times 10^{-7}$. We suggest that NMR spectroscopists become used to writing B rather than H, and to using the SI unit the tesla (1 T ≡ 10^4 gauss). There is no hardship in this change.

(b) Secondly, the units for the reduced coupling constant need to be considered. In the c.g.s. system, where no allowance is made for a separate electromagnetic "dimension", the reduced coupling constant

K, as defined by Pople and Santry was in cm^{-3}. However, magnetic quantities were implicit in the definition. To our minds it is best to retain the Pople-Santry definition in that K is the coupling energy expressed in terms of nuclear magnetic moments as:

$$U_{jk} = K_{jk} \mu_j \mu_k$$

This also retains the relationship:

$$K_{jk} = \frac{J_{jk}}{\hbar} \left(\frac{\gamma_j}{2\pi}\right)^{-1} \left(\frac{\gamma_k}{2\pi}\right)^{-1}$$

Thus in the SI system K appears in newton ampere^2 metre^{-3} (N A^2 m^{-3}). This unit is very conveniently related to the Pople-Santry c.g.s. unit -- 1 N A^2 m^{-3} ≡ 10 cm^{-3}. Admittedly, it does not allow the straight forward change $cm^{-3} \rightarrow m^{-3}$, but there are other examples where the value of $\mu_0/4\pi$ must be explicit in SI. The important fact is that the simplicity of definition is retained.

We hope there might be general agreement on this usage. Comments are invited.

Yours sincerely,

Robin Harris

Robin K. Harris

Ruth Lynden-Bell

Ruth M. Lynden-Bell

RKH:fjc

P.S. This letter is sent as from the University of Utah because one of us (R.K.H.) is on sabbatical leave there. Our home addresses are: (R.K.H.) School of Chemical Sciences, University of East Anglia, Norwich, England. (R.M.L-B.) The Chemical Laboratory, University of Sussex, Brighton, England.

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
NORTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
1815 NORTH UNIVERSITY STREET
PEORIA, ILLINOIS 61604

January 20, 1969

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

Modification of the HA-100 Lock Box for Front Panel
Control of Scope and Counter Display

Dear Professor Shapiro:

We have found three variations in operation to be highly useful in our research: (1) DC Monitor of lock signal, originally suggested by Dr. Roy Johnson of Varian, which requires installation of a 1 megohm resistor at pin P of the AC AMP and Ø DET card going to the high end of a grounded 2 mfd condenser. The signal from the junction of the resistor and condenser is DC proportional to the lock signal and can be applied to the scope to monitor low lock signals. (2) Our method of using a computer (CAT) and a function generator with the HA system, ITTNMRN-117-14, involves removing the SWEEP OSCILLATOR TUNED NET card from the Lock Box and applying the external sweep frequency from the function generator to J1307 on the back of the Lock Box (SWEEP OUT). (3) Counter Monitor of Spinning Rate, suggested by van der Haak and Spaargaren, TAMUNMRN-121-1, entails counting the signal from J314 of the Transmitter, V4311.

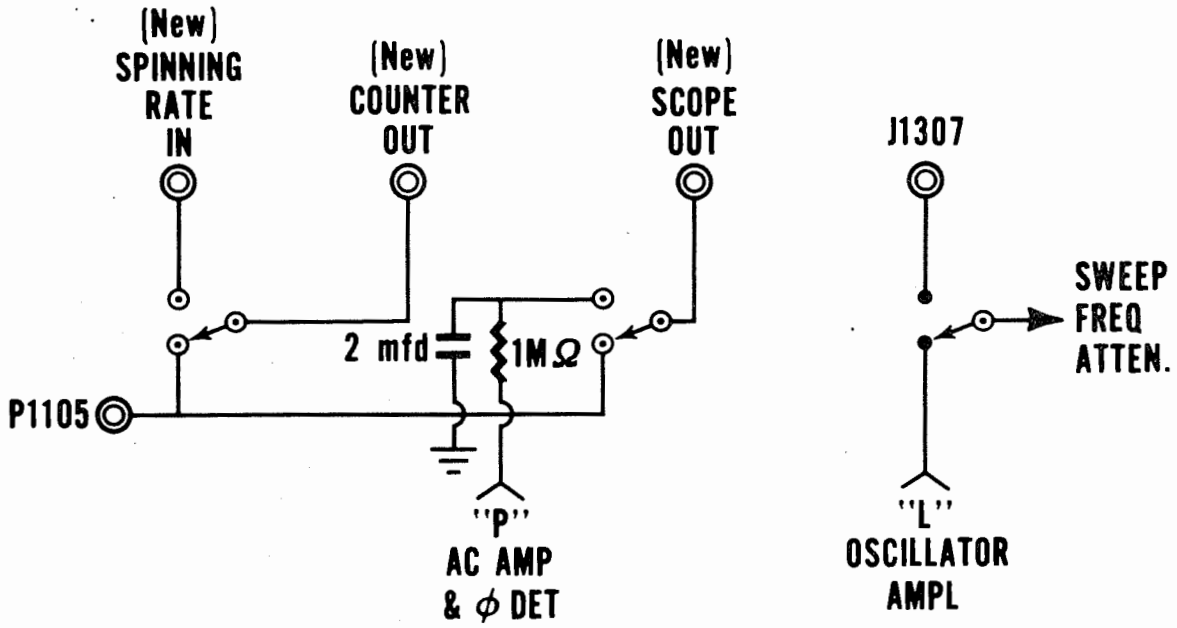
Each of these variations requires movement of cables and/or cards and generates a fixed mode of operation until the cables/cards are again moved. This makes operation tedious and requires repeated trips around to the back of the console to generate a new function. We have accomplished these three functions with three switches mounted on the Lock Box just above the words "INTERNAL REFERENCE". (See schematic.)

The first switch from left to right (last in point of time of our installation) selects the signal being counted. In the down position the counter displays the count of the function selected by the SIGNAL MONITOR switch and the counter is in a normal configuration. In the up position the signal from J314 is counted which is the Spinning Rate, and this is the only signal applied to the counter regardless of the setting of SIGNAL MONITOR switch or the DC MONITOR switch. This switch is labeled SPINNING RATE MONITOR.

The second switch is the DC MONITOR switch. This switch selects the signal to be displayed on the scope. In the down position the function selected by the SIGNAL MONITOR switch is displayed. In the up position the DC signal from the AC AMP and Ø DET card is displayed on the scope enabling precise adjustment of homogeneity especially at the low levels of lock signal that we prefer. In the up position this is the only signal displayed on the scope regardless of the setting of the SIGNAL MONITOR switch and the SPINNING RATE MONITOR switch.

The third switch is the EXTERNAL SWEEP switch. The down position selects the sweep frequency generated at the SWEEP OSCILLATOR TUNED NET card and applies it to the SWEEP FREQUENCY attenuator of the Lock Box in the normal manner. The up position selects an external sweep frequency from the SWEEP OUT jack, J1307, on the back of the Lock Box, and applies this to the SWEEP FREQUENCY attenuator.

It should be pointed out that all switches must be in the down position to operate in the HR or SCAN mode. In SPINNING RATE MONITOR mode no "X" signal is applied to the scope from Linear Sweep box. In DC MONITOR excessive capacity is introduced in the scope signal and over-filtering is observed.



C. A. Glass, Chemist
Physical-Chemical Properties
Investigations
Cereal Properties Laboratory

David Weisleder, Chemist
Physical-Chemical Properties
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125-24 Dr. W. Brügel i.Fa.
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Ludwigshafen am Rhein, Girokonto 51/82

Prof. Dr. B.L. Shapiro

Department of Chemistry
Texas A & M University

College Station, Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Telex	67 Ludwigshafen am Rhein
		Dr.Brü/Fa	(0621) 60...	464...	16. 1. 1969

Betreff Report on HR-220; NMR parameter of 1.2-disubstituted naphthalenes

Sehr geehrter Herr Professor Shapiro!

Verzeihen Sie, bitte, daß eine Mahnung des fälligen Beitrags zu TAMU-NMR-Newsletter notwendig geworden ist; ich beeile mich aber, der Aufforderung zu folgen, um meine Subskription nicht zu gefährden.

Wie Sie schon wissen, verfügt das NMR-Labor im Rahmen des Hauptlaboratoriums der BASF seit etwas mehr als 1 Jahr über ein Varian HR-220 mit supraleitendem Solenoid. Das Instrument hat sich in dieser Zeit hervorragend bewährt, so daß man die Kollegen von Varian Ass. dazu nur beglückwünschen kann. Das Spektrometer hat uns bei der schnellen Lösung zahlreicher Probleme geholfen, die wir mit Geräten des 60- oder 100-MHz-Typs überhaupt nicht oder nur mit großem Arbeits- und Zeitaufwand hätten erreichen können. Sein Betrieb und seine Bedienung haben sich als viel einfacher und weniger problematisch erwiesen, als ursprünglich befürchtet. Anfällig ist das HR-220 verständlicherweise gegen Änderungen der magnetischen Umgebung. Auch schnell verlaufende Druckänderungen der über dem flüssigen Helium liegenden Atmosphäre und Erschütterungen können zu Störausschlägen führen. Ein kritischer Punkt ist außerdem die Rotation des Meßröhrchens, an die viel höhere Ansprüche zu stellen sind als bei 100-MHz-Spektrometern. Die Leistungsfähigkeit des HR-220 sei mit ein paar Zahlen belegt: erzielbare Linienhalbwertsbreite bei Acetaldehyd 0.6 Hz, Signal-Rausch-Verhältnis (1%ige Äthylbenzollösung, übliche Bedingungen) etwa 70:1. Störend wirken sich im Spektrum die leider unvermeidlichen 1. und 2. Rotationsseitenbänder aus, wobei das 1. Rotationsseitenband eine Intensität von etwa 3 bis 5% des Zentralbandes hat. Die Integration des Spektrums kann daher problematisch sein.

Betreff

Für den Einsatz des HR-220 mit dem Ziel, aus dem Spektrum genaue Werte der NMR-Parameter zu entnehmen, muß man bedenken, daß seine Wirkung hauptsächlich in einer Verkleinerung des Kopplungsfaktors $J/\nu_0\delta$ beruht, daß aber kleine Kopplungsaufspaltungen infolge der erzielbaren Linienhalbwertsbreite (die häufig bei 1 Hz oder darüber liegt) nicht gesehen werden können. Während man also chemical-shift-Werte sehr gut aus dem 220-MHz-Spektrum entnehmen kann, muß man vor allem bei kleinen Werten von Kopplungskonstanten vorsichtig sein. Die aus einem 220-MHz-Spektrum entnommenen Werte sollten daher grundsätzlich nur als erste Annäherung für die exakte mathematische Analyse des zugehörigen 60- oder 100-MHz-Spektrums sein.

Mit der Verfügbarkeit des HR-220 in unserem Laboratorium habe ich auch wieder meine Arbeiten über die Analyse der Spektren von monosubstituierten und 1.2-disubstituierten Naphthalinen aufgenommen. Ich habe darüber schon früher berichtet (MELLO-NMR-Newsletter No. 59, August 1963 und 8. European Congress on Molecular Spectroscopy, Kopenhagen 1965). Auch bei Benutzung mit dem HR-220 gewonnener Ausgangsdaten ist die Lösung der 6- und 7-Spin-Probleme ein hartes Brot. Ich füge eine Tabelle für die NMR-Parameter von 1.2-disubstituierten Naphthalinen bei, die die Verhältnisse illustriert. Gegenübergestellt sind die Analysenergebnisse für das 220- und das 60-MHz-Spektrum. Dabei wurde für 220 MHz der nicht substituierte Ring als 4-Spin-Problem gerechnet, während das AB-System des substituierten Ringes unmittelbar aus dem Spektrum entnommen ist. Für 60 MHz wurde das vollständige 6-Spin-Problem gerechnet. Für alle Rechnungen wurde das Programm LAOCOON II bzw. LAOCN 3 benutzt. In der letzten Spalte ist der "Anpassungsfehler" in Hz angegeben, d.h. der RMS-Fehler der gerechneten gegen die gemessenen Linienlagen. Zur Anpassung wurden im 220-MHz-Spektrum etwa 30 Übergänge bei etwa 20 beobachteten Linien, im 60-MHz-Spektrum etwa 380 Übergänge bei etwa 50 unterscheidbaren Spektrallinien verwendet. Die Ausmessung geschah jeweils nur an einem Spektrogramm. Die Anpassung durch Iteration wurde abgebrochen, sobald der Anpassungsfehler die Größenordnung des Meßfehlers der Linienlage erreichte. Demzufolge ist die 2. Dezimale in den Kopplungskonstanten aus dem 60-MHz-Spektrum auf keinen Fall mehr signifikant. Man erkennt die gute Übereinstimmung der chemical-shift-Werte aus beiden Spektren - die auftretenden Unterschiede sind teilweise mit Sicherheit auf Temperatureinflüsse zurückzuführen (HR-220: 17°C)-; bei den Kopplungskonstanten treten dagegen teilweise sehr beachtliche Unterschiede auf.

Mit freundlichen Grüßen

Ihr

W. Brügel

(Dr. W. Brügel)

R_1	R_2	ν_o	H_3	H_4	H_5	H_6	H_7	H_8	J_{34}
Cl	Cl	220	7.44	7.63	7.774	7.494	7.577	8.232	8.7
		60	7.466	7.645	7.755	7.501	7.583	8.249	8.86
Cl	OH	220	7.24	7.67	7.753	7.367	7.544	8.035	8.8
		60	7.243	7.673	7.759	7.373	7.552	8.058	8.80
Cl	OCH_3	220	7.23	7.73	7.757	7.367	7.536	8.200	9.0
		60	7.268	7.752	7.776	7.407	7.566	8.246	9.13
Br	OH	220	7.23	7.61	7.749	7.358	7.534	8.026	8.7
		60	7.209	7.607	7.690	7.301	7.487	7.945	8.69
Br	NH_2	220	6.95	7.58	7.665	7.274	7.500	8.033	8.6
		60	6.955	7.606	7.700	7.278	7.531	8.084	8.67
Br	$NHCOCH_3$	220	7.76	7.93	7.956	7.564	7.659	8.180	8.7
		60	7.747	7.949	7.969	7.570	7.697	8.177	9.02
NO_2	NH_2	220	7.20	7.86	7.777	7.342	7.589	8.530	9.3
		60	7.193	7.862	7.760	7.342	7.585	8.539	9.02

NMR-Parameter von 1.2-disubstituierten Naphthalinen. 10% in $CDCl_3$ (für 1-Br-2-$NHCOCH_3$: DMSO-d_6), innerer Standard TMS. Werte der chemischen Verschiebung in ppm positiv nach kleinerem Feld, Werte der Kopplungskonstanten und des "Anpassungsfehlers" Δ in Hz.

R_1	R_2	J_{45}	J_{48}	J_{56}	J_{57}	J_{58}	J_{67}	J_{68}	J_{78}	Δ
Cl	Cl	- 0.48	- 0.88	8.4 8.96	0.9 2.12	0.1 0.71	6.9 6.75	0.9 1.16	8.6 8.75	0.15 0.29
Cl	OH	- 0.36	- 0.76	8.5 8.58	1.5 1.48	0.0 0.08	7.0 7.28	1.1 1.08	8.7 8.68	0.21 0.26
Cl	OCH_3	- 0.39	- 0.79	7.6 9.19	1.2 0.87	0.0 0.11	7.0 6.79	1.3 0.99	8.3 8.79	0.23 0.27
Br	OH	- 0.46	- 0.86	8.6 8.24	1.4 1.44	0.0 0.29	7.0 6.95	1.5 1.54	8.7 9.19	0.23 0.25
Br	NH_2	- 0.31	- 0.71	8.3 7.35	1.3 1.35	0.1 0.50	6.9 7.40	1.3 1.35	7.9 9.43	0.47 0.28
Br	$NHCOCH_3$	- 0.21	- 0.61	8.4 7.62	0.9 1.12	0.0 0.12	7.0 7.12	1.2 1.12	8.9 9.32	0.19 0.26
NO_2	NH_2	- 0.24	- 0.64	8.2 8.25	1.3 1.10	0.1 0.00	6.9 6.90	1.3 1.10	8.8 9.00	0.31 0.24

UNIVERSITY OF ILLINOIS
Department of
CHEMISTRY AND CHEMICAL ENGINEERING
URBANA
61801

The William Albert Noyes Laboratory

January 21, 1969

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

Dear Barry:

As an overdue payment of my subscription to the TAMU NMR Newsletter you may be willing to accept the abstract of some work which Cynthia Jameson and I are finishing up on "Another Look at the Coupling of Directly Bonded Nuclei."

The indirect coupling constant J_{AB} has been observed for the magnetic nuclei in fifty different pairs of directly bonded A-B atoms. A synopsis is given of the reported values along with the corresponding reduced constant $K_{AB} = (2\pi/h\gamma_A\gamma_B)J_{AB}$ which depends only on the molecular electronic structure. There are three nuclei, N = ^1H, ^{13}C and ^{19}F for which K_{XN} is now known for fifteen or more different nuclei X, enough that trends are visible in the dependence of K_{XN} upon the position of X in the periodic table. The sign of K_{XN} (positive for H_2) changes across the table somewhere between Groups V and VI, the sense of the change for N = ^{19}F being the reverse of that for N = ^1H and ^{13}C. Furthermore, there is a marked increase in the magnitude of K_{XN} with increasing nuclear charge of atom X in each Group, <u>for negative as well as positive coupling constants</u>.

The significance of these observed trends is considered. The Ramsey theory for the electron coupling of the nuclear spins includes orbital, spin-dipolar, and contact contributions. For directly bonded atoms, the orbital contribution is zero unless there is multiple bonding, the tendency for which decreases with increasing Z in a given Group. The spin-dipolar contribution increases with increasing Z; however, it is positive and the values calculated are an order of magnitude smaller than those found experimentally for K_{AB}. A model is presented attributing the observed trends to the contact contribution, which depends upon the nature of the bonding orbitals employed by each atom in the bond. If both atoms employ ns orbitals in the bond, the direct contact interaction term, which is positive, dominates. The bonding of Group VII and, to a lesser degree, Group VI atoms employs primarily p orbitals. In such atoms the contact interaction is indirect, involving polarization of the core s electrons

and a change in sign of the term. The contact term with inclusion of such core polarization effects provides a model consistent with the data available.

The model is used to predict the signs, in some cases also the magnitudes, of several coupling constants not yet observed. For example, in NF_3, OF_2, and F_2, we expect K_{NF} to be negative, K_{FF} positive and K_{OF} probably positive. A number of features are discussed including the coupling in highly-ionic bonds such as the Rb, Cs and H fluorides, and the relationship of the model to nuclear hyperfine interactions in atoms and ions with unpaired spins and in organic free radicals.

With best regards,

H. S. Gutowsky
Head of Department

cc: Cynthia J. Jameson

CALIFORNIA STATE COLLEGE AT LOS ANGELES

Department of Chemistry

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)

January 21, 1969

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

PMR Ion-Pairing Study of Ga^{3+} Halide Solutions

Dear Barry:

We have been extending our low temperature, proton magnetic resonance technique to coordination number studies of a variety of diamagnetic cations in aqueous solution. The latest systems completed are the nitrate solutions of Sc(III), Y(III), and Th(IV). A manuscript describing these results is available if anyone is interested.

Since this method permits the direct observation of cation hydration shells, quantitative estimates of anion effects, that is, contact or inner sphere ion-pairing, can be readily made. For example, in Table I are listed the hydration numbers for Ga^{3+} in water-acetone solutions of the chloride, bromide, and iodide salts of this ion. These results were obtained by determining the areas of the signals arising from bulk and complexed water molecules. It can be seen that as acetone is added to the aqueous solution, water molecules are successively replaced by the halide ions, this process occurring most readily in the chloride solutions. At low water concentrations, such as that represented in Fig. 1, multiple signals arising from differently hydrated Ga^{3+} ions are observed. In addition to indicating an ion-pairing tendency decreasing in the order $Cl^- > Br^- > I^-$, the data also provide evidence for the existence of tetrahedral Ga^{3+} complexes. Our preliminary measurements indicate that this phenomenan is prevalent in solutions of many different ions, including Be^{2+} and In^{3+}. A preprint describing the Ga^{3+} results is available.

Sincerely,

Tony
Anthony Fratiello

Robert Lee
Robert Lee

Ronald C Schuster
Ronald Schuster

TABLE I

Ga^{3+} Hydration Numbers in Water-Acetone Solutions of $GaCl_3$, $GaBr_3$ and GaI_3

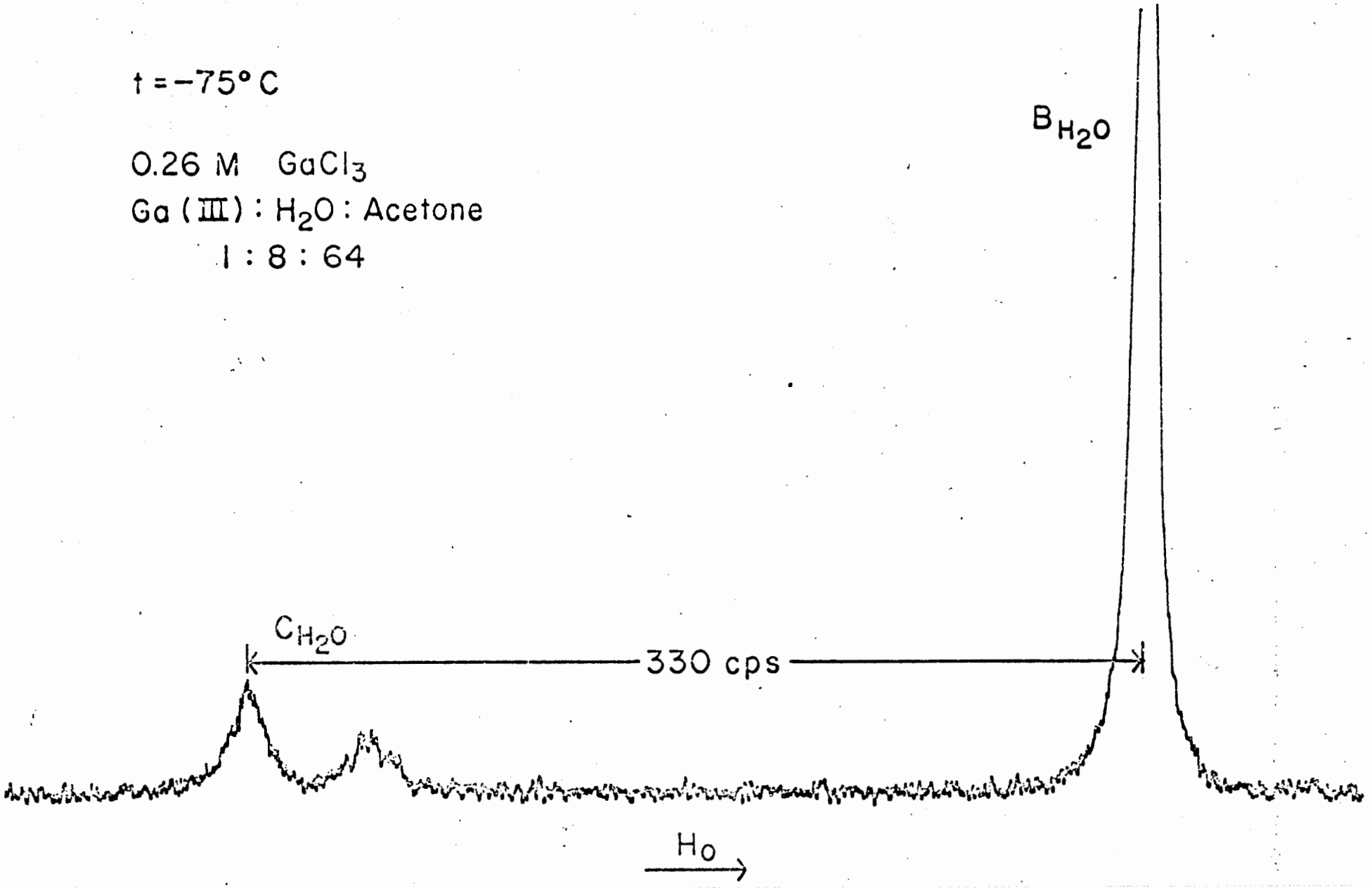
Ga^{3+}:H_2O:Acetone (mole ratios)	$\mathcal{E}$ (25°C)	Ga^{3+} Hydration Numbers					
		$GaCl_3$		$GaBr_3$		GaI_3	
		Molarity	Hy. No.	Molarity	Hy. No.	Molarity	Hy. No.
1:40:6.5	55	0.70	5.2 ±..2	0.71	6.2 ±0.2	(freezes)	
1:30:6.5	55	0.94	4.42±0.03	0.93	6.2 ±0.2	0.94	6.2 ±0.2
1:20:7.1	43	1.01	3.11±0.02	1.07	4.84±0.05	1.16	5.74±0.03
1:15:7.5	41	1.14	2.78±0.06	1.16	3.36±0.05	1.20	4.60±0.05
1:15:11	37	0.89	2.55±0.09	0.93	3.55±0.25	1.00	4.51±0.10
1:15:15	32	0.77	2.12±0.16	0.71	3.43±0.02	0.79	4.63±0.05
1:15:22	28	0.50	1.55±0.10	0.53	3.22±0.05	0.55	4.56±0.07
1:8:64	20	0.21	1.47±0.10	0.27	1.64±0.10	0.21	2.46±0.10

t = −75° C

0.26 M $GaCl_3$

Ga (III) : H_2O : Acetone

1 : 8 : 64



UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

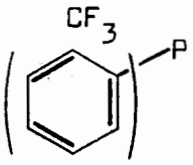
23 January 1969

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

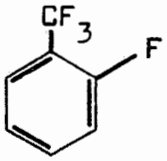
Dear Dr. Shapiro:

Recently we synthesized (o-$CF_3\phi)_3P$, (m-$CF_3\phi)_3P$, (p-$CF_3\phi)_3P$, and some related compounds. We were not able to detect any P-F coupling in the meta- and para-substituted compounds ($J_{PF} \leq 1$ Hz), but in the ortho-substituted compound, J_{PF} = 55 Hz. This compound (I) is very similar to 2-fluoro-

(I)



(II)



benzotrifluoride (II) which has a surprisingly large F-F coupling constant (13 Hz). The coupling in (II) and related compounds has received much study over the last decade[1,2,3] and both the magnitude and the temperature dependence of J_{FF} have been explained on the basis of the "through space" mechanism being dominant in these compounds. In view of the structural similarity of (I) and (II) and the fifty-fold difference in J_{PF} between (I) and the meta- and para-substituted compounds, it is reasonable to conclude that the "through space" mechanism is dominant in (I) as well. The temperature dependence of J_{PF} in (I) is similar to that of J_{FF} in (II), supporting this conclusion. In view of the magnitude of J_{PF}, it appears likely that "through space" coupling is important for most nuclei which are separated by a distance on the order of the sum of the van der Waal's radii or less.

Sincerely yours,

Gerald Ray Miller

A.W. Yankowsky

S.O. Grim

1. R.E. Richards & T. Schaefer
Trans. Far. Soc. 54, 1447 (1958)

2. H.S. Gutowsky & V.D. Mochel
J. Chem. Phys. 39, 1195 (1963)

3. J. Jonas, L. Borowski, & H.S. Gutowsky
J. Chem. Phys. 47, 2441 (1967)
and papers cited therein

TITLE: "Through space" P-F coupling

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

January 22, 1969

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

Dear Barry:

Fluorine nmr Thermometer

Tim Johnson and I have been measuring temperature dependent fluorine spectra and found a need for a thermometer usable in the range -40 to +100°. A mixture containing 2 volume percent $CFCl_2CFCl_2$ in $CF_3C_2Cl_3$ turns out to be satisfactory. Both materials are available from Peninsular Chemresearch, Inc. Each gives a single peak in the above temperature range, and the separation in ppm obeys

$$T(^{\circ}C) = 555.0 - 86.30\ \delta$$

We are submitting a short note to J. Phys. Chem. which gives more details and a few preprints are available, but I expect that it will not appear for about half a year, and the results, while not terribly original in principle, are so useful that I think they're appropriate for inclusion in the newsletter.

Since I have the better part of a page left, let me register a vote against the current subscription policy.

In the orderly pursuit of a research program, fragmentary or preliminary results which are really worthy of widespread dissemination are produced occasionally, but surely it is unrealistic to suppose that this will occur according to a schedule imposed from Pittsburgh, Chicago, or College Station. The present policy not only implies the contrary but also seems to be based on the questionable premise that a fat newsletter is ipso facto better than a thin one. Consequently, too many authors are confessing more or less openly that their offering represents a premature or not especially interesting contribution, sent in only to keep a subscription in force. For my part, I should much prefer to receive a trimmed-down newsletter containing only material which its authors felt moved to submit because they considered it too valuable to do otherwise.

If experience shows that the newsletter indeed can be kept alive only through the use of pink slips, blue slips, and other devices which must cause you no little expense and inconvenience, then it would be as well to let it die. My own belief is that abolition of the present policy would make the newsletter thinner, but not less valuable.

With best regards,

Sincerely,

Norbert Muller

NM:ma

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

27 January 1969

Professor Norbert Muller
Department of Chemistry
Purdue University
Lafayette, Indiana 47907

TAMU NMR NEWSLETTER SUBSCRIPTION POLICY

Dear Nobby:

Thank you for your Newsletter contribution of January 22. I am always pleased to have comments on the operation of the Newsletter even when, as in this case, I think they are unrealistic. I would be indeed happy if you would let me know how one should arrange to have only important contributions in the Newsletter, since if it works for the Newsletter we may be able to make our fortune selling the mechanism to editors of journals, grant funding agencies, etc. Seriously, no one has yet presented me or anyone with a scheme whereby publications which appear linearly with time can be properly phased with results, which tend to occur non-linearly with time. I am afraid I resent the implication that we have 'imposed a schedule' on the productivity of your research group. Let me recall to your attention the following facts: (a) a contribution at least once every nine or ten months is a minimum requirement, not a maximum one. Surely most participants have something - sometimes large, sometimes small - to convey to our colleagues at least this often; (b) the use of colored notices is not an expense and an inconvenience relative to not using them. This semi-mechanized approach seems to work well without involving very much of my time or making the recipients of these notices feel like they are being singled out; (c) participating in, and hence receiving, the Newsletter is optional, not mandatory. I have long felt that this is the major advantage of this Newsletter, since if it really should die, as you suggest, it will do so by the participants simply failing to send in a contribution. In fact, I have had many expressions of appreciation for the little colored reminders, people being as busy and time moving as rapidly as is generally the case.

Other things being equal (you can always quibble if this is so), a fat Newsletter is ipso facto better than a thin one; dull, trivial or not especially interesting contributions to some may make exciting, significant and important reading to others. I still feel that the let-the-chips-fall-where-they-may policy is the best one, and when the ratio of wheat to chaff tends to zero, the declining membership list or its completely changed character (which isn't happening) will give me the word.

By the way, your Fluorine NMR Thermometer seems to be very useful, and like a rather appropriate Newsletter contribution. I also note with a little amusement that you did submit it, social-protest season notwithstanding. Your further comments - serious or otherwise - on the Newsletter subscription policy will be welcomed indeed, since I do not mean to imply that the system is anywhere near perfect or ideal. I will be happy to hear comments from others about the Newsletter subscription policy, especially if these comments suggest workable alternatives.

With all best regards,

Sincerely,

Barney

Bernard L. Shapiro
Professor

BLS/jc

UNIVERSITY OF SASKATCHEWAN REGINA CAMPUS

DEPARTMENT OF BIOLOGY REGINA, SASKATCHEWAN

January 22, 1969

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

Dear Dr. Shapiro:

What is the definition of chemical shift δ ?

If one disregards for one moment the textbook argument that field scanning is mathematically equivalent to frequency scanning, it can be shown that the numerical value of the chemical shift δ depends on the kind of experimental set-up.

In a constant frequency, field scan experiment on two nuclei of the same γ but different shielding, one has the resonance conditions.

$$\nu_o = \gamma H_o^A(1 - \sigma_A) \qquad (1) \quad \text{and} \quad \nu_o = \gamma H_o^B(1 - \sigma_B) \qquad (2)$$

In this case δ should be defined in terms of magnetic fields i.e. with dimension gauss/gauss;

$$\delta_{AB} = \frac{H_o^A - H_o^B}{\nu_o/\gamma} \qquad (3)$$

but certainly not as $(H_o^A - H_o^B)/H_o$ since H_o is a variable. Neither does one want H_o^{ref} in the denominator; this would make the definition of δ (as well as its numerical value) dependent upon the choice of reference signal. Our definition (3) avoids these problems.

From (1), (2) and (3) it follows that $\delta_{AB} = \frac{1}{1 - \sigma_A} -$

$$\frac{1}{1 - \sigma_B} \approx (\sigma_A - \sigma_B)(1 + \sigma_A + \sigma_B) \qquad (4)$$

In the constant field, frequency scan experiment we have $\nu_o^A = \gamma H_o(1 - \sigma_A)$ (5) and $\nu_o^B = \gamma H_o(1 - \sigma_B)$ (6). Now δ should have the dimension of sec^{-1}/sec^{-1} and be defined as

$$\delta^*_{AB} = \frac{\nu_o^A - \nu_o^B}{\gamma H_o} \qquad (7)$$

not as $(\nu_o^A - \nu_o^B)/\nu_o$!!)

which, in combination with (5) and (6) reduces to

$$\delta^*_{AB} = -\sigma_A + \sigma_B \qquad (8)$$

It is seen therefore that δ_{AB} and δ^*_{AB} differ (apart from the sign) by a factor $(1 + \sigma_A + \sigma_B)$.
Admittedly the difference is very small in ^1H spectroscopy (1×10^{-4} ppm), but it becomes sizeable in ^{19}F and ^{31}P spectroscopy (up to about 0.05 ppm) and may be rather large for nuclei such as ^{119}Sn (ranging from 0 to 2.5 ppm). In the latter two cases the effect seems open to experimental verification.

Things start getting complicated when both kinds of scanning are employed in the same experiment (as in certain heterogeneous decoupling experiments). And what to think of the δ's measured on A-60's and A-56's, where both frequency and field fluctuate some 100 ppm (be it in harmonious concordance) on top of which a genuine field scan is superimposed?

Yours ~~sincerely~~,

F. H. A. Rummens D.Sc.
Associate Professor of Chemistry

FHAR/smr

MONTECATINI EDISON S.p.A.

SEDE IN MILANO - CAPITALE L. 749.000.000.000 INTERAMENTE VERSATO

CENTRO RICERCHE DI BOLLATE

Bollate, Jan. 23, 1969

Si prega indirizzare la risposta a:
MONTECATINI EDISON S.p.A.
Centro Ricerche di Bollate
Via S. Pietro 50
20021 - BOLLATE (Milano)

Our Ref.: 553/LC/sd

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

Subject: The F^{19} NMR spectrum of para-bonded hexafluorobenzene ("Dewar" isomer)

Dear Prof. Shapiro,

the recent communication of Dr. Kaiser (TAMU - NMR - No. 124/2) on the analysis of the "Dewar" isomer of perfluorobenzene prompts us to send you our results on the NMR analysis of the same product. As already announced in a precedent issue of the Newsletter (IIT - NMR - No. 106/40), we succeeded in the AA'XX'X"X"' analysis.
The following NMR parameters were obtained:

$\phi^{\mathbb{X}}_A = 191.0$	$J_{AX} = \pm 9.92^a$ c/s	$J_{AA} = \mp 9.36$ c/s
$\phi^{\mathbb{X}}_X = 122.8$	$J'_{AX} = \mp 7.12^a$ "	$J_{XX} = \pm 0.10$ "
		$J'_{XX} = \pm 14.03^b$ "
		$J''_{XX} = \mp 3.01^b$ "

which appear to be in good agreement with those of Dr. Kaiser. The pairs of values a) and b) cannot be distinguished by the analysis. The assignment of the coupling constants as shown in Fig. 1, where the C_6F_6 "Dewar" molecule with the labelling used is reported, follows from the results of several substituted derivatives of the perfluoro-Dewar benzene.
Experimental and calculated spectra (56.4 Mc/s) of vinylic fluorines (Fig. 2) and of bridge fluorines (Fig. 3) are hereby attached.
The work has been accepted for publication and it will soon appear in J.Chem.Soc., B.

Luciano Cavalli
Montecatini Edison S.p.A.
Centro Ricerche Bollate-Milano, Italy

Giorgio Rigatti
Istituto di Chimica Fisica
Università di Padova

92/14

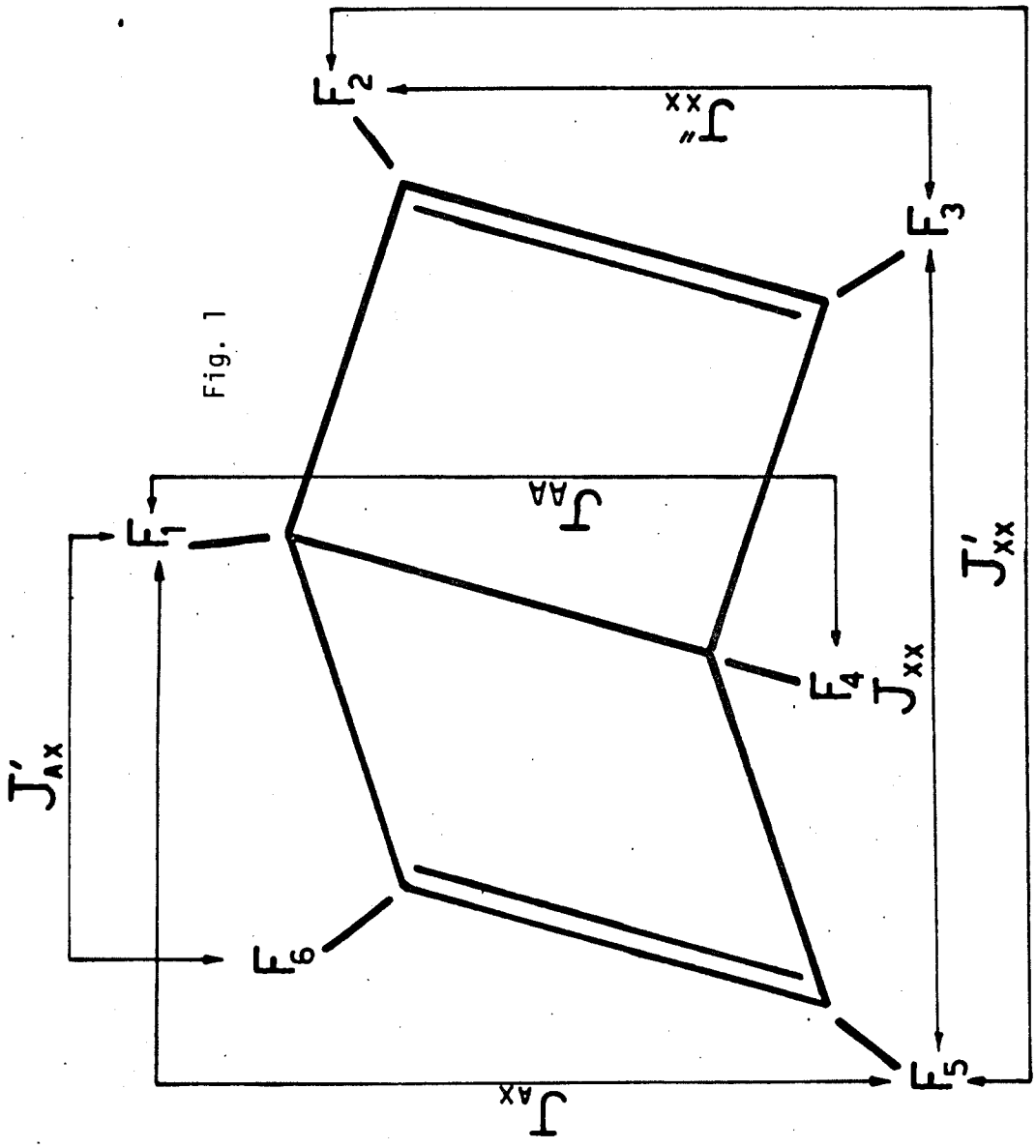


Fig. 1

Fig. 2

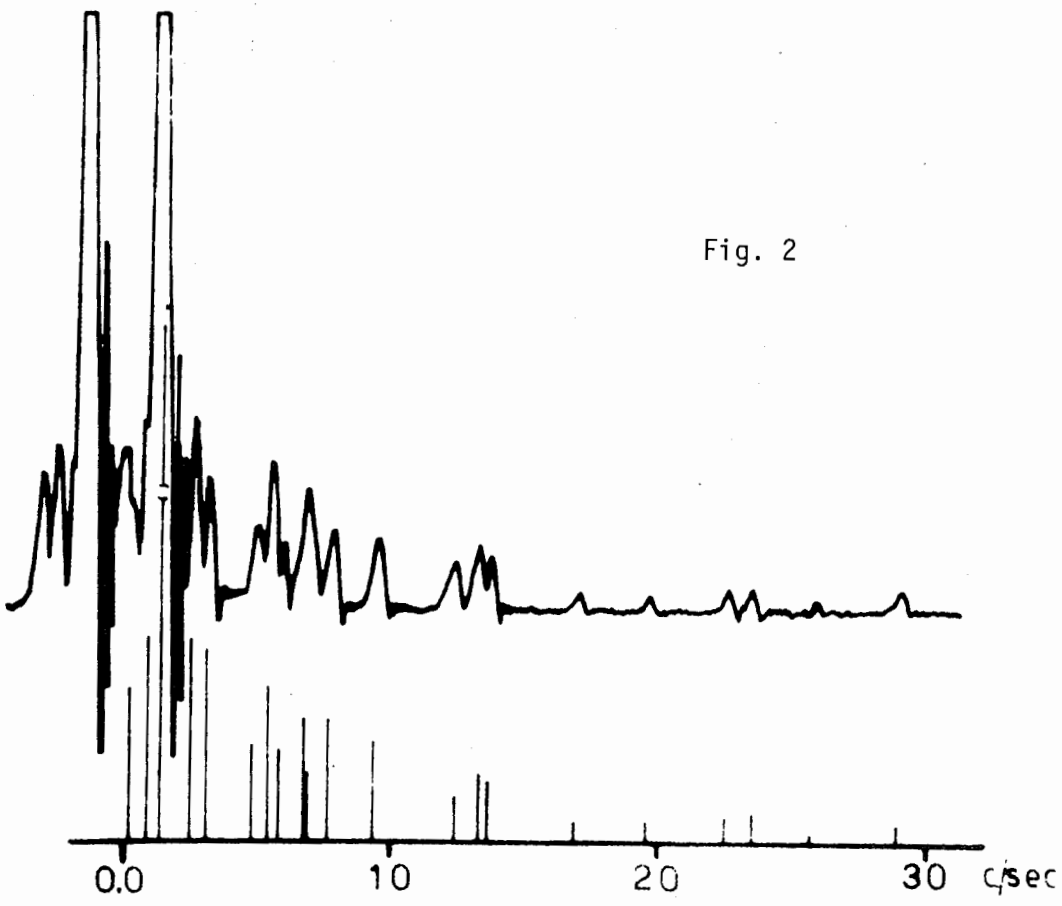
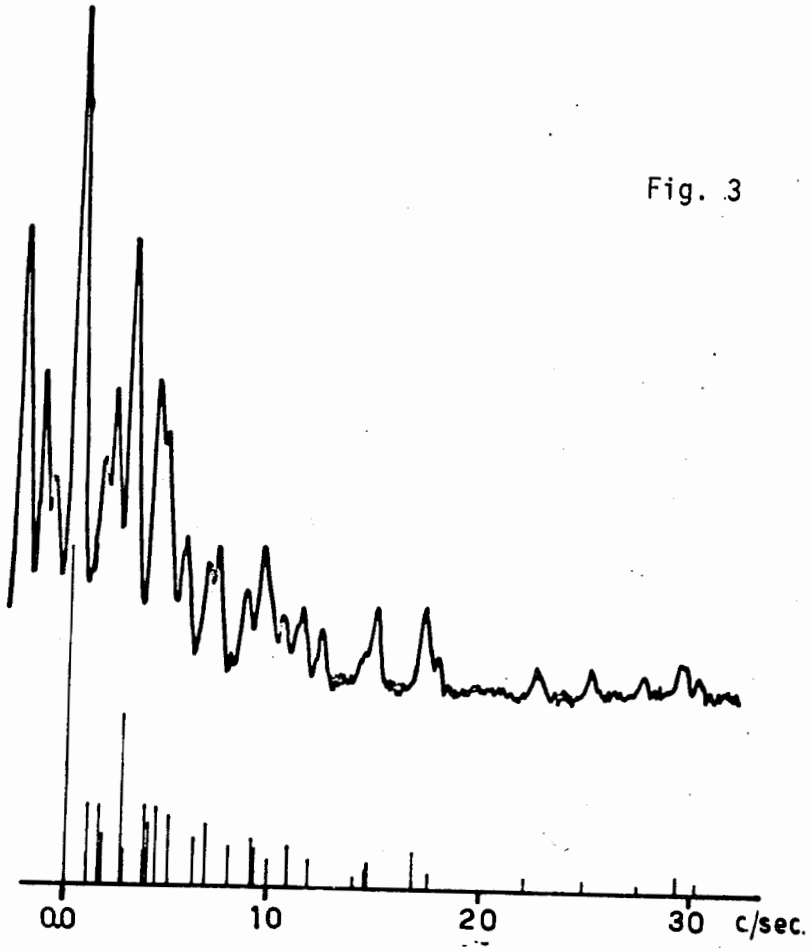


Fig. 3



INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN UNIVERSITÄT BRAUNSCHWEIG

PROF. DR. PHIL., DR. MED. h. c. H. H. INHOFFEN
(Dr. Jochen Ullrich)

33 BRAUNSCHWEIG
SCHLEINITZSTRASSE
Tel. T.U. 4781
Durchwahl Institut 4782225
Vorwahl 0531

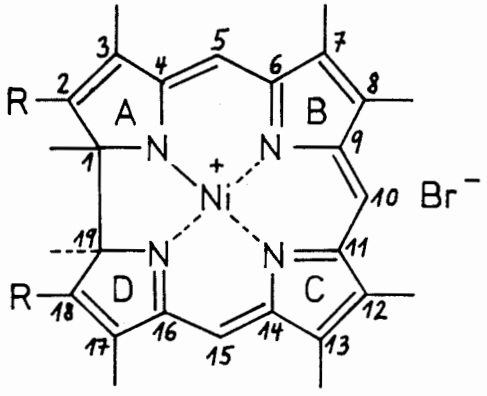
9. Januar 1969

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

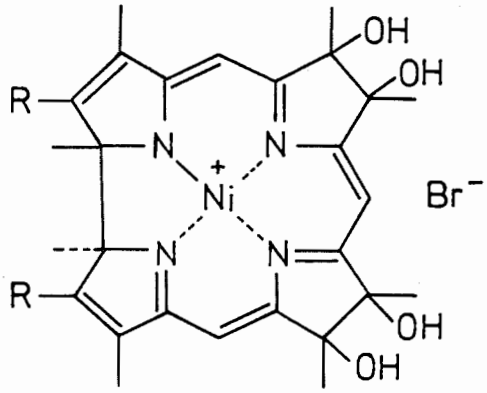
Sehr geehrter Herr Professor Shapiro!

Konstitutionszuordnung an Umwandlungsprodukten von Tetradehydrocorrin-Nickelkomplexen.

Bei der Umsetzung der Tetradehydrocorrin-Nickelkomplexe 1a und 1b mit Osmiumtetroxid (1, 8 Mol) wurden als Hauptprodukte die Tetrahydroxy-Verbindungen 2a und 2b erhalten.



1



2

a) R = CH_3; b) R = H

Die Strukturzuordnung für 2a und 2b ließ sich auf Grund der Kernresonanzspektren treffen. Einmal unterliegen die Signale der 1, 19-Methylgruppen keiner wesentlichen Verschiebung im Vergleich mit den entsprechenden Signalen von 1a und 1b (Tab. 1), während diese Wasserstoffatome in Corrin-

Derivaten (1, 2) zu tieferen Feldstärken ($\delta > 1$) verschoben sind. Zum anderen zeigt das Spektrum von 2b die Verschiebung von vier Methylgruppen zu höheren Feldstärken (1, 60 δ), was nur bei Hydroxylierung der Ringe B und C der Fall sein kann.

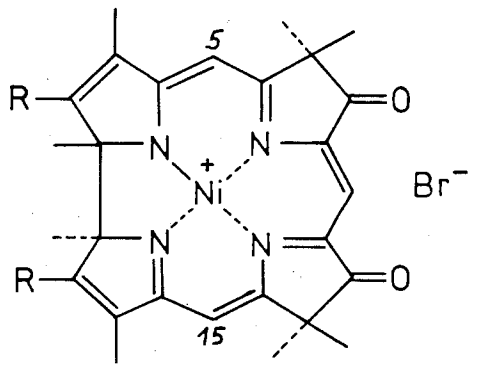
Da die cis-Hydroxylierung an beiden Seiten der Molekülebene möglich ist, handelt es sich bei den Verbindungen 2a und b um Gemische von diastereomeren Racematen, was sich durch Aufspaltung der einzelnen Signale in den Kernresonanzspektren bemerkbar macht.

TABELLE 1 (Lsgm. $CDCl_3$, Werte in δ)

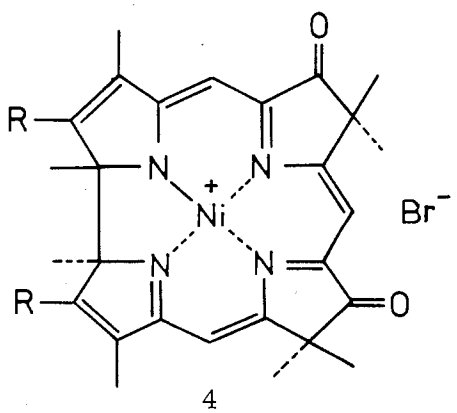
Protonen	1a	1b	2a+)	2b
1, 19-CH_3	0, 62	0, 78	0, 80 (unscharf)	0, 65 (unscharf)
7, 8, 12, 13-CH_3	2, 58	2, 60	1, 88; 1, 95	1, 60 (aufgesp.)
3, 17-CH_3				2, 34
2, 18-CH_3	2, 52		2, 30; 2, 37	
2, 18-H		8, 37		7, 32
5, 15-H	7, 41	7, 42	6, 61; 6, 64	6, 77 (aufgesp.)
10-H	7, 47	7, 52	6, 94; 6, 96	7, 20 (" ")

+) Dieser Substanz wurde zum Lösen Deuteropyridin zugesetzt.

Die Pinakolumlagerung von 2a und b führte jeweils zu zwei isomeren Gemini-diketonen, nämlich 3a und b sowie 4a und b



3



4

a) R = CH_3; b) R = H

Die beiden Isomeren ließen sich im Kernresonanzspektrum leicht unterscheiden, da das eine symmetrisch, das andere unsymmetrisch strukturiert ist. Die Symmetrie der Verbindungen 3a und b zeigt sich im Auftreten nur eines scharfen Singuletts für die 1, 19-CH_3-Gruppen, zweier Singuletts gleicher Intensität für die geminalen CH_3-Gruppen und zweier scharfer Signale im Intensitätsverhältnis 2:1 für die Methinwasserstoffatome, wobei die den geminalen Methylgruppen benachbarten 5, 15-Wasserstoffatome zu höheren Feldstärken verschoben sind gegenüber den analogen Wasserstoffatomen in 1a und b (Tab. 2).

TABELLE 2 (Lsgm. $CDCl_3$; Werte in δ)

Protonen	3a	3b	4a	4b
1, 19-CH_3	0, 80	0, 88	0, 77; 0, 82	0, 83; 0, 87
gem.-CH_3	1, 63; 1, 69	1, 63; 1, 69	1, 57; 1, 60; 1, 63; 1, 69	1, 59; 1, 63; 1, 67
3, 17-CH_3	2, 46	2, 52	2, 34	2, 44; 2, 48
2, 18-CH_3			2, 44	
2, 18-H		8, 40		8, 40; 8, 49
5-H	7, 22	7, 15	7, 35	7, 40
15-H			7, 17	7, 06
10-H	7, 69	7, 77	7, 19	7, 25

Demgegenüber sind in 4a und b die Signale der geminalen und der 1, 19-Methylgruppen aufgespalten und für die Methinwasserstoffatome erhält man drei Signale gleicher Intensität.

LITERATUR

1) A. Eschenmoser, R. Scheffold, E. Bertele, M. Pesaro u. H. Gschwend, Proceedings of the Royal Society (A) 288, 306 (1965).

2) R. Grigg, A. W. Johnson u. P. van den Broek, Chem. Comm. 1967, 502

Mit vorzüglicher Hochachtung
Ihr

J. Ulrich

THE UNIVERSITY OF TENNESSEE
KNOXVILLE 37916
DEPARTMENT OF CHEMISTRY

Prof. B.L.Shapiro
Texas A&M University
Dept. of Chemistry
CollegeStation, Texas 77843

January 27,1969

CHEMICAL SHIFTS IN 1-IODOALKENES

Dear Barry,

In 1966 , Pascual,Meier and Simon[1] have demonstrated that the chemical shifts of the olefinic protons in polysubstituted alkenes can be reproduced to a surprising degree of accuracy by the use of additive substituent parameters (Z values). More recently[2] , Prof. Simon's groups in Zurich and our group in Sydney have extended this work and produced a table of Z values for 43 functional groups. In further work[3] we explored the deviations from additivity in certain classes of compounds. In most instances , we were able to postulate reasonable explanations for the deviations , but 1-iodoalkenes defy our inganuity.

The data for compounds (1)-(4) are derived from reliable published sources[4]. The remaining data are a by-product of the studies carried out by Mr.Addy Pross in Sydney and refer to 100 MHz spectra of ca 5% solutions in CCl_4.

With the exception of compounds (1),(2),(3) and (11) , the assignments are based principally on the relative magnitudes of long-range coupling constants and therefore alternative assignments cannot be excluded. It can be seen that the alternative Z values derived from compounds with terminal methylene groups , i.e. (4),(5) and (6) are not unreasonable , and , in fact, an argument could be made for reversing the assignments in (6) for the sake of consistency. However, in the isomeric 2-iodobutenes ,(7) and (8), and in the isomeric 2-iodo-4-phanylbutenes ,(9) and (10) , one of the Z values in each pair must be abnormally small. We cannot rationaliza this result and point out that other features of the NMR spectra of (2)-(4) are also not entirely straightforward[4]. Clearly, caution is necessary in the use of the additive shielding increments[1-3] with 1-iodoalkenes.

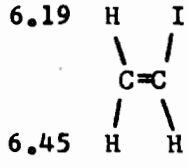
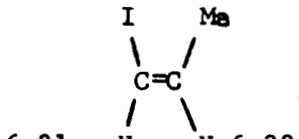
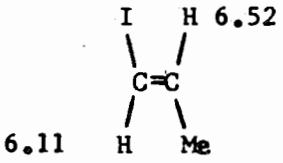
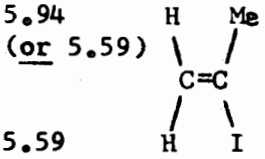
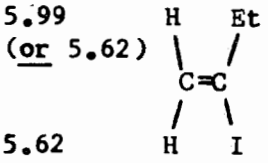
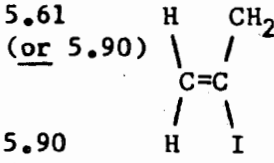
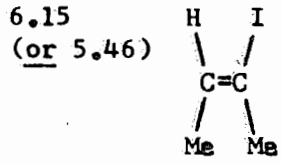
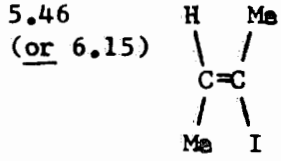
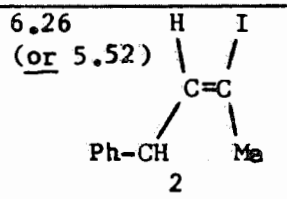
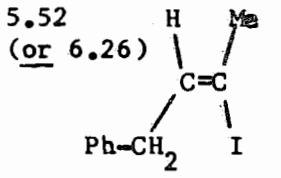
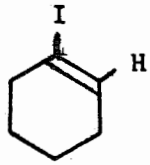
With best regards
yours sincerely

(Sev Sternhell)

Note: Please credit this contribution to my SYDNEY address and continue to send the Newsletter there. I shall stay at the University of Tennessee only until July 1st 1969 as a Visiting Professor.

REFERENCES: [1]Pascual,Meier and Simon, Helv. 49,164 (1966); [2]Matter,Pascual,Pretsch, Pross,Simon and Sternhell , Tetrahedron, in press ; [3]Idem, submitted to Tetrahedron; [4]Mayo and Goldstein, J.Mol.Spec., 14,173 (1964) , Hruska,McBride and Schaefer,Canad. J.Chem., 45,1081 (1967).

THE UNIVERSITY OF TENNESSEE
KNOXVILLE 37916
DEPARTMENT OF CHEMISTRY

1		Z_{gem}=1.23 Z_{cis}=0.94 Z_{trans}=1.20
2		Z_{gem}=1.34 Z_{trans}=0.59
3		Z_{gem}=1.08 Z_{cis}=0.82
4		Z_{cis}=0.62 or 0.97 Z_{trans}=0.91 or 0.56
5		Z_{cis}=0.65 or 1.02 Z_{trans}=0.96 or 0.59
6		Z_{cis}=0.93 or 0.64 Z_{trans}=0.58 or 0.87
7		Z_{cis}= 0.73 or 0.04
8		Z_{trans}=-0.02 or 0.67
9		Z_{cis}= 0.84 or 0.10
10		Z_{trans}=0.04 or 0.78
11	 6.33 Alternatively, the chemical shift of the olefinic protons of cyclohexene (5.59) , can be subtracted from 6.33 to give Z_{cis}=0.74	Z_{cis}=0.67

The shielding substituents (Z values)[1] for iodine were derived by simple subtraction using the π^2 values : For alkyl: Z_{gem}=0.45, Z_{cis}= -0.22 , Z_{trans}= -0.28 ppm. For alkyl-ring: Z_{gem}=0.69 , Z_{trans}= -0.28ppm. Base value : 5.25 ppm.

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
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Department of
CHEMISTRY

1 February 1969

NBS NMR Data Generation and Compilation Program

About one year ago, the National Bureau of Standards (NBS), through its Office of Standard Reference Data (OSRD), undertook to foster a program of NMR data generation and compilation. The nature and orientation of this program was guided in large measure by the report of an ad hoc committee (of the National Research Council) meeting* held in Washington under the auspices of the NRC Office of Critical Tables. It is important to re-emphasize the point made elsewhere that the orientation given to this program by the committee report was a general and a flexible one, and the NBS has adopted the most benevolent possible viewpoint toward the recommendations of this report. Subject to the usual budgetary considerations, this program can go forward in whatever directions are deemed desirable by the NMR community.

With regard to proton NMR, the program is now going forward, beginning primarily with a state-of-the-art evaluation phase. General announcements of the nature and scope of this work will be forthcoming shortly, as will our plans for fluorine NMR.

In its report, the committee urged that no matter how stringent budgetary factors might be, it is important that at least some attention be given at the earliest possible moment to problems of nuclei other than protons and fluorine. The burden of the present announcement, then, is to announce and solicit participation in the first steps in this direction.

^{13}C and ^{31}P NMR Spectroscopy

Consultation with some of the committee members indicated that ^{13}C and ^{31}P were the two nuclei most appropriate for receiving initial attention. What (if anything!) this NBS program can or should do for workers interested in either of these nuclei remains to be defined. It is therefore the purpose of this announcement to solicit opinions from those interested. These opinions should be relayed to the undersigned, in whatever form is most convenient.

There is one particular aspect of ^{13}C NMR which several people have indicated to me is worthy of special attention at the present time. The Atomic Energy Commission may be in a position to provide the public with enriched ^{13}C materials in the not-too-distant future, and a contact at the AEC has indicated a willingness to have AEC efforts in this direction influenced by opinions of those doing or interested in doing ^{13}C NMR

(Continued)

spectroscopy. One possibility which has been raised is to hold a one-day meeting (place to be chosen when the list of potential attendees is known; time - probably late spring of this year) to discuss enriched ^{13}C materials and such other problems as may interest those gathered. If the interest warrants, part of this day could also be devoted to problems of interest to ^{31}P NMR spectroscopists, since there seems to be a substantial overlap between our primitive lists of ^{13}C and ^{31}P workers.

Thus anyone interested in making his views on either of the above two nuclei known is invited to indicate this interest to the undersigned. It should be emphasized again that this NBS program can deal with virtually any aspect of NMR spectroscopy in which enough interest exists, and we are not restricted merely to gathering and compiling spectral data.

Bernard L. Shapiro
Chairman, Advisory Committee
on NMR Spectroscopy

*NMR attendees at this meeting: E. D. Becker, F. A. Bovey, E. G. Brame, W. S. Brey, S. M. Castellano, T. C. Farrar, R. B. Johannesen, L. F. Johnson, S. L. Manatt, B. L. Shapiro, G. Slomp, J. B. Stothers.

DOW CORNING

January 29, 1969

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

Dear Dr. Shapiro:

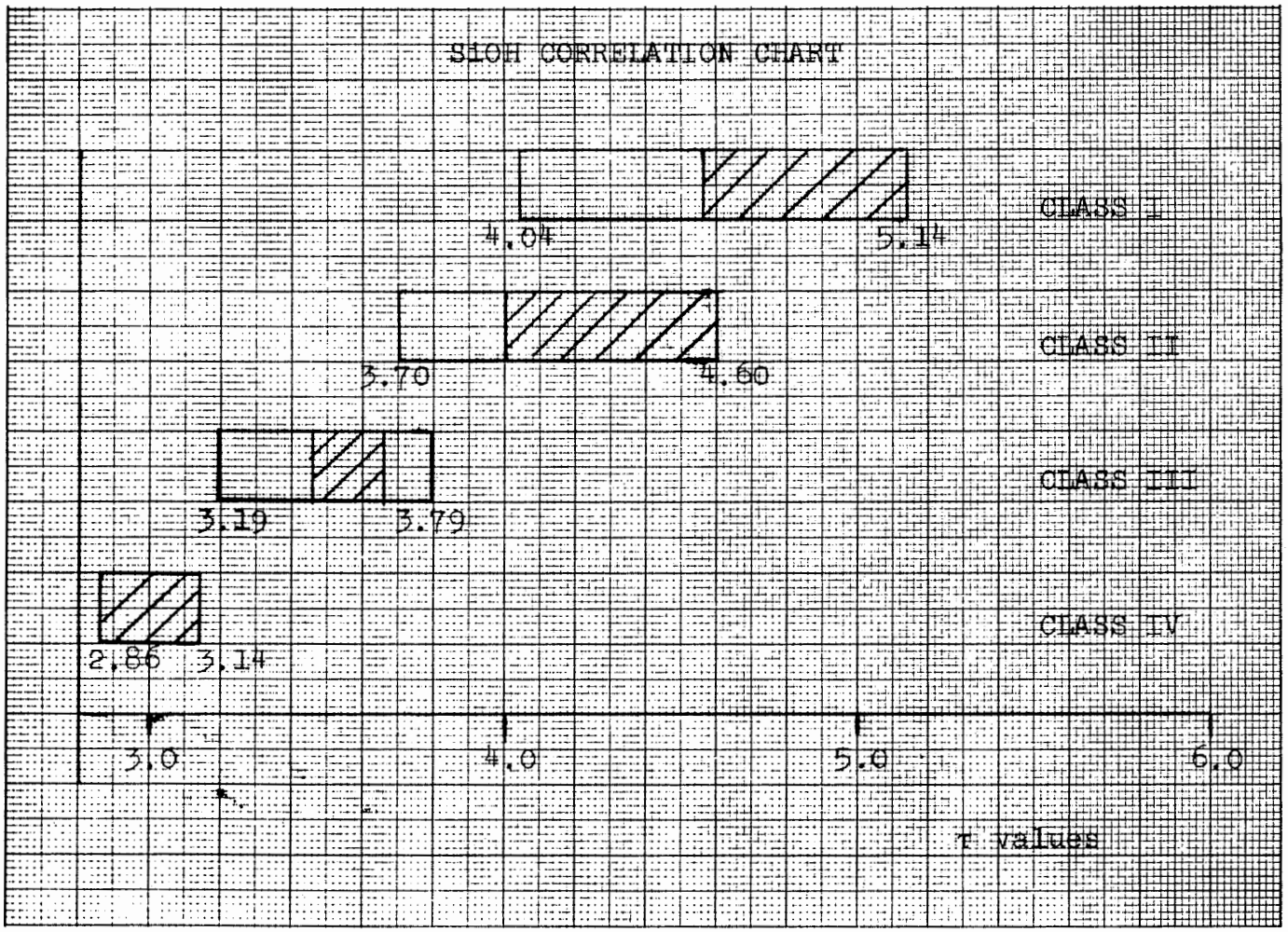
Re: Correlation chart for SiOH τ values

We would like to present a correlation chart for SiOH ^{1}H NMR τ values which we have found useful for structure determination. The spectra were obtained on the A-60 in DMSO as 10 vol. % solutions. The extreme range of τ values was estimated for each class of compounds by use of the additivity rule. Although τ values for protons close to silicon do not obey the additivity rule (1), the deviations are such that application of this rule will lead to an overestimate of the range of τ values. This means that although only twenty-three selected compounds (2) were used in this chart, the shift range will include the shifts of any member of the class. Deviations may occur, however, if solutions are not sufficiently dilute to suppress self association (3) in DMSO or when the alkyl group possesses an active hydrogen which may exchange with the SiOH or a highly polar moiety in a favorable position to form an intramolecular hydrogen bond. Among R groups, vinyl causes the furthest downfield shift and tertiary carbon alkyls cause the furthest upfield shift of the SiOH.

The barred areas in the correlation chart illustrate the observed shift range for each class while the larger rectangles illustrate the estimated shift range for each class.

CLASS I : R_3SiOH
CLASS II : R_2ASiOH; R_2BSiOH
CLASS III: RB_2SiOH; $RABSiOH$; BA_2SiOH
CLASS IV : AB_2SiOH; B_3SiOH

R = Alkyl, cyclopropyl, vinyl, benzyl, allyl
A = OH, H
B = Phenyl, CH_2Cl



Very truly yours,

Dwight E. Williams

Dwight E. Williams

Gary Ronk

(1) Unpublished observations on large number of SiMe, $SiCH_2X$, SiH compounds.

(2) All compounds were synthesized in the laboratories of Dow Corning, chiefly by Jim Hampton and coworkers.

(3) J. F. Hampton et al, Inorg. Chem. 4, 1659 (1965).

gb

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THE OHIO STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY
140 W. 18TH AVENUE
COLUMBUS, OHIO 43210

1969 January 29

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

Justification of Linearity of Carbon-13 Shift with Charge

Dear Barry:

In view of the present interest in carbon-13 nmr, I would like to describe some calculations of shifts in azines(reactive to benzene) and to show that one can account for all the shift as well as the linearity of C-13 shift with charge.

The main contribution to these shifts comes from the paramagnetic term σ_p, in Ramsay's equation. With Pople's approximations, this comes out to be $\chi < r^{-3} >$ where the susceptibility, χ, is a function of coefficients from MO's and inverse excitation energies and $< r^{-3} >$ is proportional to the charge on the atom in question.

Using appropriate σ and π wavefunctions, we evaluated σ_p by means of the following increasingly approximate methods:

(1) straight from Ramsay's equation, using overlap and the Gaussian Transform method (Karplus-Kern-Shavitt) to evaluate the multicenter integrals; (2) Pople's formula, ignoring overlap and multicenter integrals, with excited states, σ and π electrons; (3) same as (2) but with average energy approximation, (4) same as (3) with non-polar σ-bonds. These methods were used in conjunction with several sets of wavefunctions-extended Huckel, CNDO-2, SCF + Del Ré, omega + Del Ré, matching the level of approximation of σ_p with that of the wavefunction. When we did this, the following results were obtained. Benzene came out the same way however we did the calculation (265 ± 3 ppm). On the other hand, the calculated azine shifts are incredibly sensitive to both method and wavefunction. The agreement of theory and experiment is terrible for case (1), excellent for case (2), when we use Jaffe's CNDO-2 wavefunctions (see table), and then declines again with the simpler methods and wavefunctions.

Method (2), in conjunction with Jaffe's wavefunction, accounts for all of the shift. Furthermore, the observed shifts are proportional to total charge, $\sigma + \pi$, on carbon, the constant being 158 ppm/electron.

For the other calculations, the shifts are always smaller in magnitude than the observed ones, though they follow the correct qualitative variations. Still, even the unsatisfactory calculated shifts are proportional to the total charge on carbon.

The shift, with respect to benzene $\Delta\sigma_p$ is given by $\Delta\chi < r^{-3} > + \chi\Delta < r^{-3} > + \Delta\chi\Delta < r^{-3} >$. The last term can probably be neglected. From the above mentioned results, it would appear that $\Delta\chi$ and $\Delta < r^{-3} >$ are proportional to each other. Each is linear with the total charge, the constants being 75 and 80 pmm/electron for the $\Delta\chi$ and $\Delta < r^{-3} >$ plots respectively. The reasons behind this proportionality are still not clear, but I don't think it is fortuitous.

What we have learned here is that it is critical to have a wavefunction which gives the correct smaller excitation energies, $n \rightarrow \pi^*$, and which takes account of polar σ-bonds.

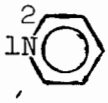
With best wishes,

Sincerely yours,

Gideon

Gideon Fraenkel
Associate Professor of Chemistry

Azines, calculated and observed[1-3] shifts with respect to benzene.

		2	3	4	5
	obs	-20.31	+ 2.04	- 6.51	
	calc	-21.72	+ 4.20	- 7.71	
	obs	-16.3			
	calc	-16.8			
	obs		-21.03		
	calc		-24.		
	obs	-38.69		-28.46	- 0.79
	calc	-30.5		-28.9	+ 6.1

1. P. C. Lauterbur, J. Chem. Phys., 43, 360(1965).
2. R. G. Pugmire and D. M. Grant, J. Am. Chem. Soc., 90, 697(1960).
3. A. Mathias and V. M. S. Gil, Tetrahedron Letters, 3163 (1965).

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