Brian W. Sykes

Texas A & M University N - M - R Newsletter

No. 153
JUNE, 1971

Lambert, J. B.; Gosnell, J. L., Jr.
N,N'-Dichloro- and N,N'-Diformylpiperazine 1

Lunazzi, L.
Conformational Dependence of the Long-range Coupling in Ortho Substituted Thioanisoles 2

Greatbanks, D.
Tin Satellites and Solvent Reactions of Tributyl Tin Hydride 4

van Broekhoven, J.A.M.; Brackman, W.; Clague, A.D.H.
Benzene as Internal Reference and Lock Signal for ^{13}C NMR on Europium Complexes 5

Wilde, A. M.; Mathias, A.
Experiences with $Eu(DPM)_3$ 6

Kurland, R. J.
Request for Preprints; ^{13}C NMR Studies of Ligand Exchange in Metal Ion-β-Diketone Complexes with Pyridine 8

La Mar, G. N.
Quenching Nuclear Overhauser Effects in C-13 NMR 9

Colebrook, L. D.; Icli, S.
Line Follower Digitization of N.M.R. Spectra 12

Anteunis, M.
N.M.R. Spectra of 1.4:3.6-dianhydro-D-glucitol Mononitrates 14

Spragg, R. A.
Temperature Measurement with Methanol and Glycol Samples 16

Gutowsky, H. S.
Z Dependence of Coupling Constants between Directly Bonded Nuclei 18

Shindo, H.
Observations of CIDNP in Photo-Induced Reactions 20

Kaiser, R.
NMR Parameters of 2,3,5-trifluoro Dewar Benzene 23

Miller, J. M.
New Life for Old A-60 24

Kanekar, C. R.; Govil, G.
Contact Shifts and Metal-Nitrogen Bonds 26

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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Egan, R. S.
Uncertainties in the Analysis of AA'BB' Spectra 28

Gerig, J. T.
Spectrometer for Sale 30

Cooper, J. W.
Emission Lines in Pyridylalkyl Grignard Compounds; Fabri-Tek Becomes Nicolet 31

Green, R. D.
Ethylene Adsorbed on Zeolites 32

Holder, B.; Happe, J.; Maddux, A.; Ward, R.
Time and Frequency Domain Spectrometer 34

Cohn, M.
220 MHz. PMR Difference Spectroscopy for Proteins 37

Bernstein, H. J.
Specific Solvent Effects 40

Schaefer, T.
Exercises in Carrington and McLachlan: Query on Interest of Readers 42

Levy, G. C.; Cargioli, J. D.
Four Months with the XL-100-FT System 46

Tallon, W. A.; Block, R. E.; Brey, W. S., Jr.
Isotope Effects on Fluorine Chemical Shifts 48

Deadline Dates: No. 154: 5 July 1971
No. 155: 2 August 1971

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

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

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

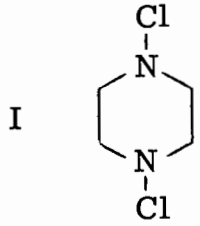
DEPARTMENT OF CHEMISTRY

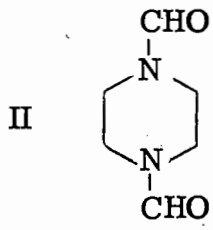
May 6, 1971

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

Dear Barry:

We have recently uncovered some interesting properties in the nmr spectra of N,N'-dichloro- and N,N'-diformylpiperazine (I and II).





At room temperature the spectrum of I is a singlet, indicating that both ring reversal and nitrogen inversion are fast. As the temperature is lowered, the spectrum passes through coalescence to produce an unsymmetrical spectrum by -40°. The equatorial-equatorial conformation can therefore be excluded, since it should produce a symmetrical AA'BB' spectrum. The axial-equatorial form, which improves on the electrostatic repulsion between dipoles and should give an ABCD, best explains the spectrum. Both reversal and inversion must be frozen out at -40°.

Above 100°, the diformyl compound also gives a singlet for the ring protons, indicating that ring reversal, nitrogen inversion, and N-CHO rotation are all fast. Because of amide resonance, inversion is probably fast at any temperature. At room temperature, separate spectra are observed for the syn and anti forms, so N-CHO rotation has been frozen out. A second coalescence phenomenon occurs below room temperature. By -100°, the syn form gives two AA'BB' spectra (one for each side of the ring) and the anti form one ABCD spectrum. All told, the spectrum is variable over a 240° range. These characteristics indicate that ring reversal has likewise been frozen out, the first example other than cyclohexenes for a molecule with two trigonal centers.

Sincerely,

Joseph B. Lambert

Jack L. Gosnell, Jr.

JBL/kc

Title: N,N'-Dichloro- and N,N'-Diformylpiperazine.
(to be published in Records of Chemical Progress)

153-2

Istituto di Chimica Organica e di Chimica Industriale
dell'Università di Bologna

li 29 . 4 . 1971

Viale Risorgimento, 4 - Tel. 42.18.80
c.a.p. 40136

Prof. B.L. SHAPIRO
Dept. of Chemistry
Texas A and M University
College Station

TEXAS 77843 - USA

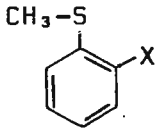
Title - Conformational dependence of the long-range coupling in ortho substituted thioanisoles.

Dear Doctor Shapiro,

thank you for your kind (blue) remind, here is the account of our most recent results.

We have been lately concerned in measuring the long range coupling (^5J) in ortho substituted thioanisoles in order to investigate the conformational dependence suggested by Goldstein and coworkers in the analogous anisoles (R.W.Crecely, K.W.McCracken, J.H.Goldstein, Tetrahedron 25, 877 (1969)).

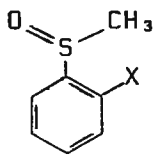
We observed indeed variation of ^5J with the size of the substituents as well as with the temperature: the corresponding relationships are shown in the figures a) and b) respectively. The results are consistent with the hypothesis that the greater is the population of the conformations "anti" (I), the greater is the coupling constant:



(I)

X =	$-CH_3$	-Cl	$-CMe_3$	-Br	-I	$-NO_2$
J =	0.13	0.17	0.25	0.31	0.36	0.43

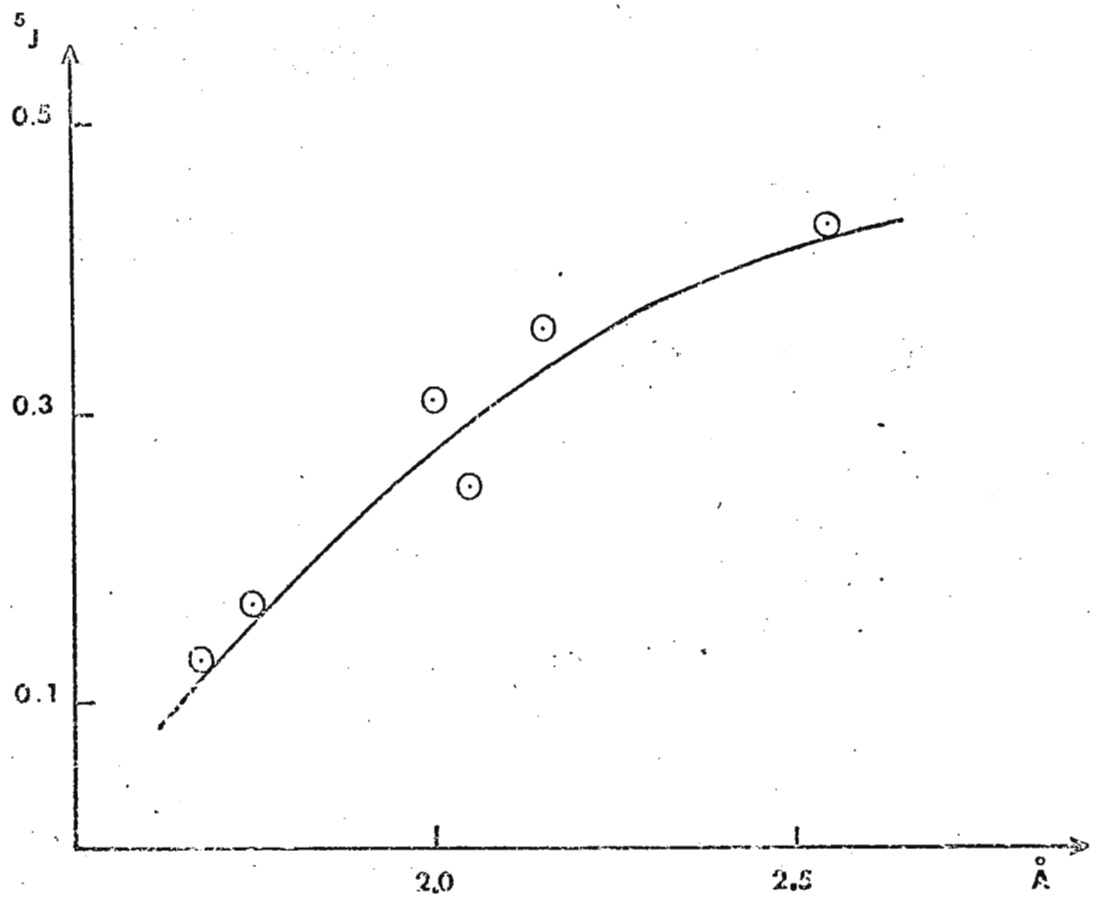
The lacking of any appreciable splitting in some of the corresponding sulphoxides and sulphones, where the ^5J should be expected to be even greater on a purely electronic point of view, (N.Van Meures, Spectrochim.Acta 19, 1965, 1963) seems to suggest that the latters mainly stay in conformations with the methyl group "syn" in respect to the bulky substituents;



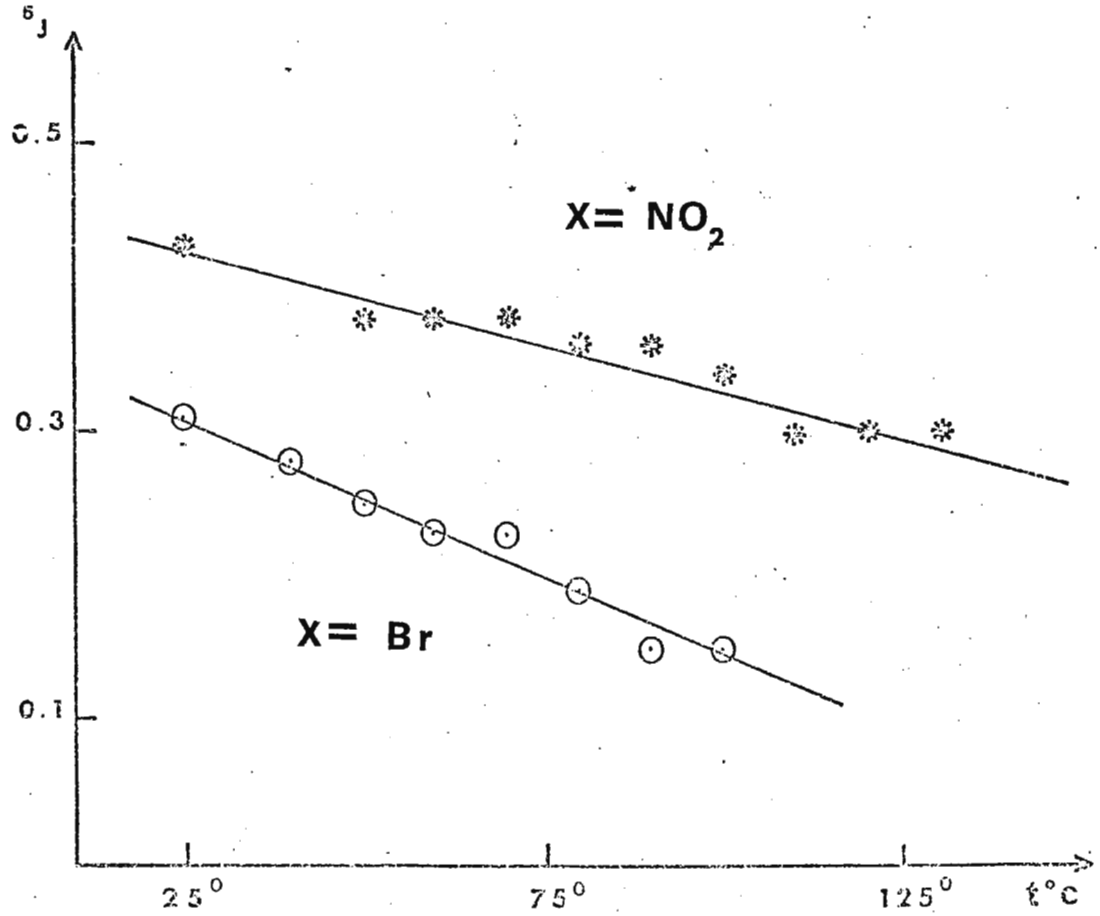
Best regards

(dr. L.Lunazzi)

a



b



153-4

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Pharmaceuticals Division

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

Your ref	Our ref	Tel ext	Date
	DG/KH		30th April, 1971.

Dear Professor Shapiro,

Tin Satellites and Solvent Reactions of Tributyl Tin Hydride

Tin satellites have been observed previously in the proton spectra of several methyl stannanes[1]. In this paper the satellites of ^{115}Sn (0.3% abundance) were not observed. We have had occasion to examine a sample of tributyl tin hydride $(CH_3CH_2CH_2CH_2)_3Sn\text{-}H$ and have observed in the 100 MHz spectrum of the neat liquid that $J_{^{119}Sn\text{-}H}$ = 1608 Hz, $J_{^{117}Sn\text{-}H}$ = 1536 Hz and $J_{^{115}Sn\text{-}H}$ = 1404 hz. These values bear a straight line relationship with μ, the magnetic moment of the isotopes as one would expect from the equation derived by Reeves and Wells $(J_{X\text{-}H}/\mu_X)^{\frac{1}{2}} = 0.676\ ZX + 8.0$ where Zx is the atomic number of the element X = C, Si, Sn and Pb. It is interesting to note that the J values we have observed are lower by ca. 130 hz than those observed for the methyl derivatives and as size of coupling is related to electronegativity, this difference is probably due to the different inductive effects of methyl and butyl groups.

The spectrum of tributyl tin hydride recorded in $CDCl_3$ as solvent showed a multiplet at 5.28δ assigned in the first instance to the hydride signal. This signal however showed no tin satellites and the multiplicity was 3 lines of equal intensity J = 1 Hz. It was realized that this signal was due to $CHDCl_2$ formed by a reaction between solute and solvent which was unexpected as tributyl tin hydride is used as a selective de-iodinating reagent. A similar reaction occurred using CCl_4 as solvent when $CHCl_3$ and CH_2Cl_2 were produced. With d_6 benzene as solvent, the expected septet was observed at 4.98δ (J = 2Hz) and on addition of a drop of CCl_4 the hydride signal slowly disappeared and varying amounts of $CHCl_3$, CH_2Cl_2 and CH_3Cl were observed.

Please credit this contribution to Dr. G.R. Bedord of these laboratories.

Yours sincerely,

D. GREATBANKS
Scientific Services Group

1. L.W. Reeves and E.J. Wells
Can.J.Chem., 41, 2698 (1963)

THE QUEEN'S AWARD TO INDUSTRY
1966 1967 1968 1969 1970

Koninklijke Shell - Laboratorium, Amsterdam
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TELEFOON (020) - 209111

Dear Professor Shapiro,

Benzene as internal reference and lock signal for ^{13}C NMR on europium complexes

The application of lanthanide-induced shifts in ^{13}C NMR, using a Varian HA 100 system, may be complicated by the occurrence of very strong spinning side bands when $^{13}CS_2$ is used as an external reference. The side bands are caused by field inhomogeneities in the paramagnetic sample due to the presence of the capillary containing the diamagnetic $^{13}CS_2$.

Since $^{13}CS_2$ is too expensive to be dissolved in the sample, we looked for another way to circumvent the side band problem.

An NMR tube with an ID of 8 mm, filled with benzene (natural abundance of ^{13}C) provides a ^{13}C signal strong enough to lock the radio frequency. As the $Eu(DPM)_3$ complex is very soluble in benzene in the presence of complexing agents (lone pair carriers), ^{13}C pseudo-contact shifts can be measured very conveniently when the protons are completely noise-decoupled. As an example we give the europium-induced ^{13}C and ^{1}H shifts in n-hexanol (molar ratio $Eu(DPM)_3$/hexanol 1:1)

	H−O−	CH_2−	CH_2−	CH_2−	CH_2−	CH_2−	CH_3	
^{13}C shift		44	10	7.4	4.4	2.6	1.0	ppm
^{1}H shift	81	21	13	8.7	4.2	2.6	1.4	ppm

Sincerely Yours,

Amsterdam, 7th April 1971

J.A.M. van Broekhoven

W. Brackman

A.D.H. Clague

153-6

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Dyestuffs Division

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

Your ref Our ref Research Department ARS/B4 Date 6th May, 1971

Dear Professor Shapiro,

EXPERIENCES WITH Eu $(DPM)_3$

Like many other laboratories, we were very interested in the early reports on the use of Tris-(dipivalomethanato)-Europium, Eu $(DPM)_3$, as an NMR shift reagent and we decided to investigate its usefulness in our own analytical problems. We examined first the usual range of simple reference compounds and found very useful selective downfield proton shifts for simple alcohols, amines, amides, ketones, ethers, esters and hetero-aromatic species such as pyridine and quinoline. Compounds containing nitro, azo, halide and urea groups appeared to be unaffected, however.

The largest shifts were found using CCl_4 or $CDCl_3$ as solvents. Shifts in d_6-DMSO were noticeably smaller, presumably because the Eu $(DPM)_3$ complexes with the small amount of water normally present in d_6-DMSO and to a lesser extent with the sample. The amount of Eu $(DPM)_3$ used was usually in the range 0.1 - 0.2 moles/mole of sample.

However, when we attempted to apply Eu $(DPM)_3$ as an aid in the solution of real problems, its usefulness was found to be less than we had hoped. The main type of problem involved the identification of unknown materials submitted to the NMR laboratory. When the normal 100 MHz spectrum was too complicated to yield a solution due to overlapped bands, the addition of Eu $(DPM)_3$ was tried. In the majority of cases, some shifts were found when small amounts of Eu $(DPM)_3$ were added, but these were too small to be

THE QUEEN'S AWARD TO INDUSTRY 1966 1968 1969

useful. Addition of larger amounts of Eu $(DPM)_3$ led to severe broadening of the spectra.

The sorts of materials examined included dyestuffs, antioxidants, brightening agents, dispersing agents and other industrial additives. Admittedly, the molecules involved are large and complicated and, in fact, it may be that it is the exchange of Eu $(DPM)_3$ between alternative sites in these large poly-functional species, that is responsible for the troublesome spectral broadening. We would be interested to hear of other people's experiences with the application of Eu $(DPM)_3$ to complex molecules.

Nevertheless, useful results were obtained in some cases so that we do not wish to give a too gloomy impression of the usefulness of Eu $(DPM)_3$. For example, the addition of Eu $(DPM)_3$ to mixtures of diamino-toluene isomers (important intermediates in poly-urethane foam manufacture) gave a series of methyl group proton peaks which were far better separated than in the original spectra so that the quantitative analysis of the isomeric components was facilitated. Also, our colleagues in other Divisions of this Company have had greater success with Eu $(DPM)_3$, in the steroid field, for example.

Yours sincerely,

Margaret Wilde Alan Mathias.

A.M.WILDE. A.MATHIAS.

AMW/AM/LG.

State University of New York at Buffalo

153-8

DEPARTMENT OF CHEMISTRY

FACULTY OF NATURAL SCIENCES AND MATHEMATICS

May 8, 1971

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

TITLE: Request for Preprints; ^{13}C NMR Studies of Ligand Exchange in Metal Ion-β-Diketone Complexes with Pyridine.

Dear Barry:

Bruce McGarvey and I are preparing a chapter on "heteronuclear" nmr studies of paramagnetic systems (i.e., other than pmr); we would be grateful for any preprints on this subject that TAMU readers might care to send us in the next few months.

Dr. James Cooper and I have been studying paramagnetic carbon-13 shifts of pyridine in the systems: bis(β-diketonato) M(II) in mixed pyridine--chloroform solvents; here the metal, M, may be Cu, Ni or Co and the substituents at the 2,4 positions of the β-diketonate moiety may be CH_3, CF_3 or phenyl. Our preliminary results indicate that the rate constants for exchange between solvent and complexed pyridine decrease as the total electron withdrawing power of the 2,4 β-diketone substituents increase, i.e., as the Lewis acid strength of the metal in the β-diketone complex increases. This result and rough values for the reaction orders suggest that the mechanism for pyridine ligand exchange is primarily dissociative, in accord with pmr studies of similar systems (1). Another feature of our observations (one which is probably obvious on a priori grounds to most, if not all of the TAMU readers) is the possibility of different exchange behavior for the proton and carbon-13 nmr spectra of a given system. For example, the carbon-13 spectra of bis(β-diketonato)(Cu(II)--pyridine systems correspond to the slow exchange limit, while under the same conditions of temperature and concentrations the proton nmr spectra exhibit fast exchange behavior.

According to what the organic chemists here (who are the ultimate jury) tell me, the JEOL MH-100 has been performing within specifications since it was installed about four weeks ago. I should add that it was necessary to install a regulator on our tap-water line to the JEOL magnet cooling unit, in order to prevent frequent magnet shut-offs due to wildly fluctuating mains water pressure (we are close to Niagara Falls, you know). I'll be happy to supply details to those of the readership that are interested.

Sincerely,

Bob

Robert J. Kurland, Associate Professor

(1) R. W. Kluiber, F. Thaller, R. A. Low, and W. DeW. Horrocks, Jr. Inorg. Chem. 9, 2592 (1970).

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SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY

BERKELEY, CALIFORNIA 94720

May 10, 1971

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

Quenching Nuclear Overhauser Effects in C-13 NMR

Dear Barry:

Please consider this contribution as my downpayment for a subscription to your newsletter. As of September, 1971, I will be initiating a research program in nmr at the University of California campus at Davis, and will therefore no longer have access to Charlie Reilly's copy.

We have been interested in the nuclear Overhauser effect, NOE, in decoupled C-13 spectra, more specifically, in methods to suppress the NOE in order to obtain true intensities without having to rely on undecoupled spectra. Our initial attempts using free radicals, [J.Am.Chem.Soc. 93, 1040 (1971)], indicated that the NOE in p-dioxane can be suppressed by the addition of as little as 25 mM di-tert-butyl nitroxide. We have since extended this work to include a number of paramagnetic transition metal ions, of which several are considerably more efficient than the free radical, as shown in Fig. 1. Spectra were recorded on the Bruker HFX-90, using 10 mm spinning tubes, and a F-19 lock, (C_6F_6) capillary). Since the limiting intensities at high concentrations are essentially the same whether free radicals or metal ions are used, it appears that the NOE may be quantitatively eliminated. In Fig. 2, we illustrate the effect of Mn^{+2} on the C-13 linewidths, which shows that this limiting intensity is achieved at concentrations below where linebroadening becomes serious.

The exact relationship between this limiting intensity in Fig. 1 and the intensity in the undecoupled spectrum is being investigated currently.

Sincerely yours,

Gerd

Gerd N. La Mar
Department of Chemistry
University of California
Davis, California 95616

EFFECT OF METAL IONS ON C-13 INTENSITY OF PROTON DECOUPLED p-DIOXANE

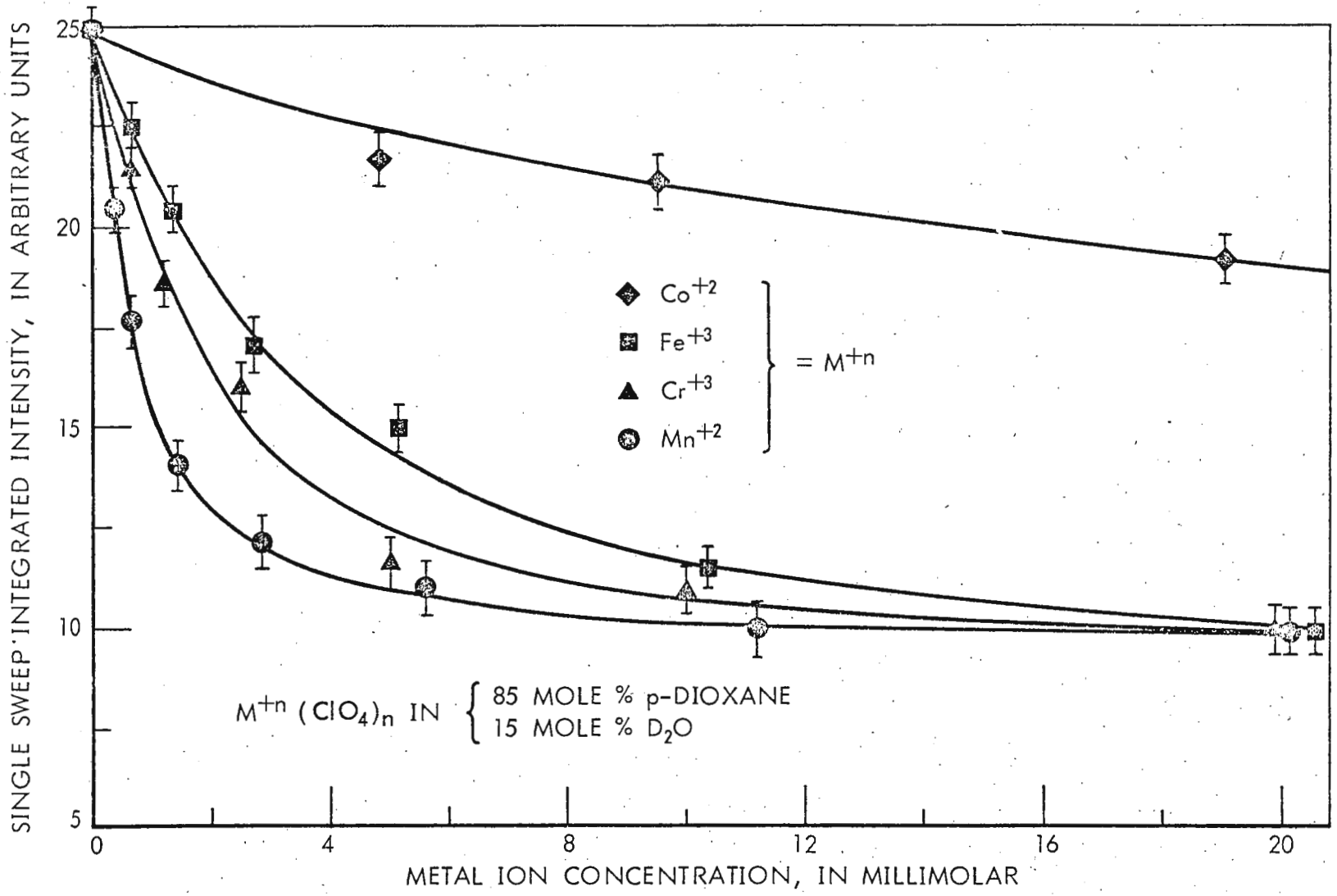
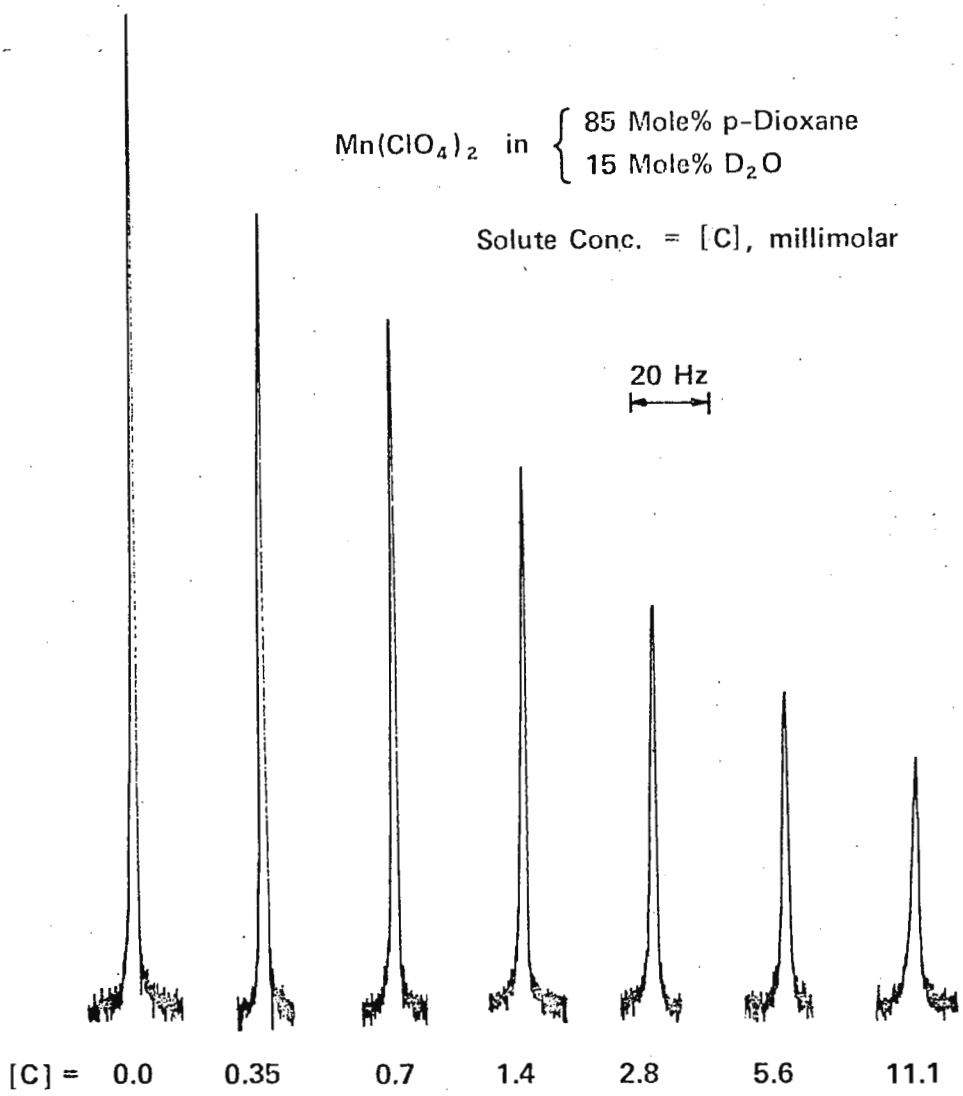


Fig. 1

Fig. 2


$Mn(ClO_4)_2$ in { 85 Mole% p-Dioxane / 15 Mole% D_2O
Solute Conc. = [C], millimolar
20 Hz
[C] = 0.0 0.35 0.7 1.4 2.8 5.6 11.1

SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

May 12, 1971

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

Dear Barry,

Line Follower Digitization of n.m.r. Spectra

One of the problems involved in complete n.m.r. line shape analysis by computer fitting is that of getting the spectra into the computer in suitable digital form. An approach we have taken is to use a combination of Hewlett-Packard F-3B Line Follower, H-P 7001AM X-Y recorder, and H-P 2114B computer to digitize directly from recorded spectra. The computer drives the X-axis sweep of the recorder through an 8 bit DA converter while the line follower head follows the spectral trace (recorded in black ink) and a voltage proportional to the spectral intensity is supplied to the AD converter from the Y-axis slide wire. The computer moves the recorder arm across the spectrum in 250 increments, storing a digitized intensity for each step. Before the run is started the line follower head is adjusted successively to the left and right limits of the portion of the spectrum to be scanned, using the recorder zero and gain controls, and the two frequency limits are entered into the computer. On output, the computer calculates the frequency corresponding to each intensity.

The main programme is written in Fortran, and the subroutines which drive the recorder, effect digitization, and provide a variable delay to control the scanning rate, are written in Assembler. Since a line follower cannot cope with steep curves, there is provision in the programme for interrupting the sweep through the computer switch register so that the spectrum can be scanned a point at a time under operator control. In this mode, the line follower head may be moved by hand back to the curve if this has been lost, before the intensity is digitized. There is also provision for aborting a scan through the computer switch register.

The computer outputs up to 251 (the number is selectable) baseline corrected intensity-frequency data pairs on the typewriter, and also punches them on paper tape. Another Fortran programme has been written for the 2114B to process the paper tapes at a later stage. This programme writes the digital information on magnetic tape together with the required control parameters for the non-linear regression programme we use for fitting a computed spectrum to the digitized spectrum. The operator must type in the initial guesses for the parameters and specify which parameters (if any) are to be held constant. All other aspects of the magnetic tape preparation are under programme control. The data on magnetic tape are then processed on the CDC 3300 in the Computing Centre.

To check on how well the sequence of operations works, we calculated some spectra using the 2114B and plotted them with the 7001AM X-Y recorder. These were then digitized using the line follower, transferred from paper tape to magnetic tape, and fitted by the CDC 3300. For example, a two site, zero coupling, spectrum was calculated with the following parameters: lifetimes- 0.080 and 0.100 secs; chemical shifts- 8.00 and 17.00 Hz; line width- 1.0 Hz; and plotted over a 0.0 to 25.0 Hz range (256 points). This spectrum was digitized twice (51 points) and fitted twice. The starting values given to the CDC 3300 were: lifetimes- 0.1 and 0.05 secs; chemical shifts- 6.0 and 16.0 Hz; line width- 1.0 Hz. The line width parameter was held constant in this case. The values of the parameters returned by the CDC 3300 for the best fit spectra were as follows (second run in brackets) :
lifetimes- 0.07986 (0.08010), 0.09981 (0.10001); chemical shifts- 7.9813 (7.9701), 17.0083 (16.9780).

The line follower can cope with average amounts of noise on real spectra. For very noisy spectra, it may be desirable to record in coloured ink, which the line follower cannot detect, and eyeball a best curve through the centre of the noise in black ink or pencil. The line follower will then digitize the super-imposed trace.

Best regards,

Yours sincerely,

Laurie

L. D. Colebrook
S. Icli

RIJKSUNIVERSITEIT GENT

LABORATORIUM
voor
ORGANISCHE CHEMIE

STATE UNIV. of GENT
ORGANIC CHEM. DEPT.
LAB. for NMR SPECTROSCOPY
Prof. M. ANTEUNIS
Krijgslaan 271 — GENT B — 9000
BELGIUM

B-9000 GENT, May 13th 1971.
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(België - Europa)

Assoc. Prof. B. L. SHAPIRO,
TAMRU Newsletters,
Texas A and M University,
College Station,

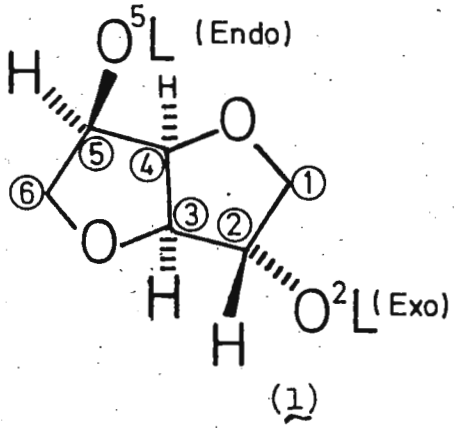
TEXAS 77843. U.S.A.

Dear Barry,

N.m.r. Spectra of 1.4:3.6-dianhydro-D-glucitol mononitrates.

I have lately had the occasion to look to the nmr spectra of 2-exo- and 5-endo-1.4:3.6-dianhydro-D-glucitol mononitrates (1, $^2L = ONO_2$ (exo); $^5L = ONO_2$ (endo)). The following nmr data could be extracted :

2-exo-isomer :



(1)

	$CDCl_3$	Pyr		$CDCl_3$	Pyr
δ(H1)	4.14	4.24	J(1,2)	5.0	*
δ(H1')	4.14	4.10	$^2J(1)$	-	11.4
δ(H2)	5.39	5.47	J(2,3)	~0.3	~0
δ(H3)	4.57	4.58	J(3,4)	~4.5	~4.0
δ(H4)	4.65	4.64	J(4.5)	~5.0	~5.7
δ(H5)	4.33	4.39			
δ(H6)	3.65	3.79	J(5,6)	5.5	6.5
δ(H6')	3.91	3.91	J(5,6')	5.5	5.0
			$^2J(6)$	9.6	8.8

* Anisochronous in pyridine J(1,2) = 4.3 J(1',2) = 1.0

.../...

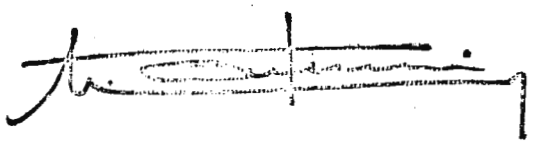
5-endo-isomer :

	$CDCl_3$	Pyr		$CDCl_3$	Pyr
δ(H1) =	3.92	4.12	J(1,2) =	5.0	*
δ(H1') =	3.92	4.02	^{2}J(1) =	-	9.3
δ(H2) =	4.35	4.54	J(2,3) =	$\sim$0	$\sim$0
δ(H3) =	4.39	4.59	J(3,4) =	$\sim$5.1	$\sim$5.6
δ(H4) =	4.98	5.12	J(4.5) =	$\sim$5.3	$\sim$5.8
δ(H5) =	5.34	5.41			
δ(H6) =	3.87	3.83	J(5,6) =	5.5	5.6
δ(H6') =	3.98	3.97	J(5,6') =	3.2	2.5
			^{2}J(6) =	11.6	11.3

* Anisochronous in pyridine J(1,2) = 1.0 J(1',2) = 3.5

The difference in ^{2}J(6) between the exo resp. endo isomer is typical and might be brought in connection with conformational behaviour [1] because changes in ^{2}J in such systems are related with σ(C-H) and adjacent p(O) interactions [2].
Also the solvent induced shifts are interesting. For the exo-isomer no appreciable deshielding (0/0.08 ppm) occurs in pyridine, but for the endo-isomer typical deshielding is noticed for H-1, H-2 and H-3 only (0.1/0.25 ppm). Obviously an endo-OH group already involved in strong H-bond ($\Delta\nu(OH_{free} - OH_{intra}) = 148cm^{-1}$ for < 0.005 M CCl_4 solutions) can't hardly participate with inter H-bridge association, while the exo-O_2H does form solute-solvent complexes ($\Delta\nu(OH_{free} - OH_{intra}) = 82\ cm^{-1}$ in CCl_4) e.g. with π-electron rich participants.

Yours sincerely,



Prof. M. Anteunis.

[1] M. Anteunis and T. Rosseel; in preparation.

[2] M. Anteunis; Bull.Soc.Chim.Belges 75, 413 (1966).
M. Anteunis, G. Swaelens, P. Dirinck and F. De Ketelaere-Anteunis; Bull.Soc.Chim.Belges; in press.
M. Anteunis, J. Gelan and G. Swaelens; Tetrahedron; in press.

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

13th May, 1971

Dear Dr. Shapiro,

Temperature measurement with methanol and glycol samples

The methanol and glycol peak separations will undoubtedly continue to be used widely for temperature measurement in NMR. Therefore it was distressing that 1970 should have brought us calibration curves differing by more than 10° at some points (1,2). (A peak separation of 2.25 ppm for methanol corresponds to 216°K (1) or 228°K (2).)

Even if the calibration curves can be agreed upon there remains the problem, common to all methods, of ensuring reproducibility of the conditions between establishing a calibration and recording the spectrum. One source of error is the variation in heat losses with different samples. To overcome this the temperature control system must respond to changes in the sample temperature, rather than establishing the temperature of the gas stream before it reaches the sample.

This is achieved in the R12 system by turning the gas stream back through an outer annulus past the temperature sensor after it has passed the sample. (The variable temperature accessory for the Models R12A and R12B NMR spectrometer has recently been announced). Thermal contact between the returning gas and the sensor provides compensation for varying heat leakage from the sample. Using this system we find excellent agreement between temperatures measured with a calibrated Pt resistance and those obtained from the calibration curves of Van Geet (1) in the range 223° to 423°K.

Measurement of the peak separations for glycol is rather inconvenient since the peaks are too close to use one for locking. Using an external reference is not to be recommended as this leads to radial temperature gradients and hence temperature differences between measurement and calibration samples. We have measured the peak separation for glycol containing 5% w/w DSS as an internal reference and find that the separation is 0.017 ppm less than that of neat glycol throughout the range 330° to 430°K.

../..

Directors: C. W. Nimitz, Jr. (U.S.A.), A. R. Gilson, M.B.E., M.A. (Managing), M. A. Ford, Ph.D., J. M. Beharrell

Dr. B.L. Shapiro,
Texas A & M University.

13th May, 1971

Please credit this to John Arthur's subscription.

Yours sincerely,

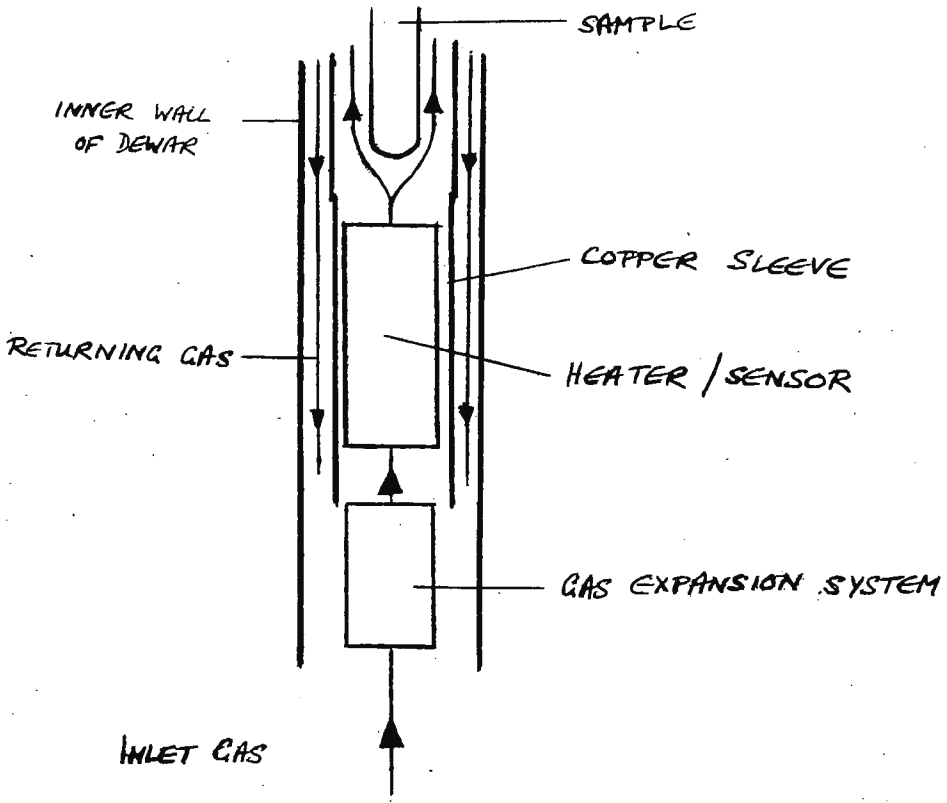
R A Spragg

R.A. Spragg
(NMR Applications Laboratory)

1. A.L. Van Geet. Anal Chem. 42,679, (1970)

2. O. Yamamoto and M. Yanagisawa, Anal. Chem. 42, 1462, (1970)

GAS CIRCULATION OF R12 (SCHEMATIC)



RAS/EMP

UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *Urbana, Illinois 61801*

School of Chemical Sciences

Department of Chemistry

May 14, 1971

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

Dear Barry:

We've continued our interest in the "Z Dependence of Coupling Constants between Directly Bonded Nuclei." The most recent endeavor along these lines in our group has been that of Don K. Dalling, who has looked further at the Z dependence of the electron spin density $|s_X(0)|^2$ at the nuclei of the isolated atoms. A paper describing the results has been submitted to the Journal of Chemical Physics.

The most direct and accurate way to determine $|s_X(0)|^2$ is from atomic beam measurements or optical hyperfine structure of gaseous atoms in $^2S_{1/2}$ states. However, such experimental data are available for only a few of the elements, so of necessity we took a less direct approach. Spectroscopic term values are known for most atoms from their optical spectra, and several methods have been proposed for estimating the electron spin density at the nucleus from such data. We tested two such methods by using them to calculate $|s_X(0)|^2$ for the alkali metals and comparing the results with the spin densities from atomic beam experiments.

Breit many years ago [Phys. Rev., 42, 348 (1932)] developed an equation for $|s_X(0)|^2$ which uses spectroscopic term values and which is exact for Coulombi fields. Howevers, an s-electron is often in the vicinity of the nucleus and the finite nuclear size leads to a non-Coulombic field, for which allowance must be made.

The first approach we tried is an empirical correction based on the rate of change of electronic energy with the principal quantum number of the excited electron [Fermi and Segré, Z. Physik, 82, 729 (1933)]. The rate of change may be calculated from the experimental $^2S_{1/2}$ spectral term values [Crawford and Schawlow, Phys. Rev., 76, 1310 (1949)] which are available for most atoms of interest. However, this procedure gives values of the spin density which are too large for small Z_X and too small for large Z_X, in comparison with spin densitites from atomic beam measurements of hyperfine splitting atoms in Group I.

Therefore, we turned to a second type of correction derived by Goudsmit in calculating nuclear moments from hyperfine splitting factors for atoms with a lone outer s electron. The correction [Phys. Rev., 43, 636 (1933] is designed to treat relativistic effects, and leads to appreciably better agreement with experiment for the Group I atoms. This method was employed to calculate spin densities at the nucleus of most of the main group elements and the results were used to study the reduced internuclear coupling constant K_{XN}.

It is concluded that K_{XN} for a series of isoelectronic, isostructural compounds varies as $Z_X^{\varkappa}$, where $\varkappa$ is the relativistic correction, which ranges from 1.0 to about 2.5 depending on Z_X. The theoretical results are compared with experimental data for symmetrical compounds with bonds of the type XF, XH, and XC, and apparent core polarization contributions to K_{XN} are noted. The directly bonded coupling constant between ^{73}Ge and ^{13}C has been measured in tetramethylgermane; it is 18.7 ± 0.9 Hz.

We hope this will keep me on your mailing list for a while, or restore me to it if I've been too slow.

Best regards,

H. S. Gutowsky
Head of Department

HSG:cfh

c Don K. Dalling

JEOL

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May 20, 1971

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

Dear Professor Shapiro:

Observations of CIDNP in Photo-Induced Reactions

It is known that emission and/or enhanced NMR signals are often observed during rather rapid radical reactions, and what we call CIDNP (Chemically Induced Dynamic Nuclear Polarization) are often observed. This interesting phenomenon is important in relation to the dynamics and mechanism of radical reactions.

One difficulty in the NMR observation of CIDNP in photo-induced reactions is how intense UV light can be applied to the sample in the NMR probe. The light source (high-pressure-mercury 500W arc lamp) is mounted about 40 cm from above the magnet. The light is focused and guided into the probe through a hole (diameter 13 mm). It is then reflected from the aluminum mirror attached within the probe and arrives at the sample through a vacuum Dewar quartz tube (used for variable temperature work). To be used effectively, the light is again reflected through the sample by a coated aluminum mirror on the outside of the Dewar quartz tube. This is shown schematically in Fig. 1.

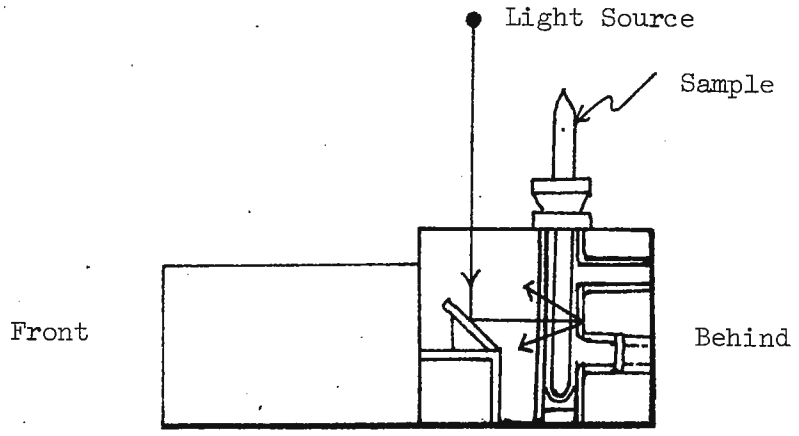
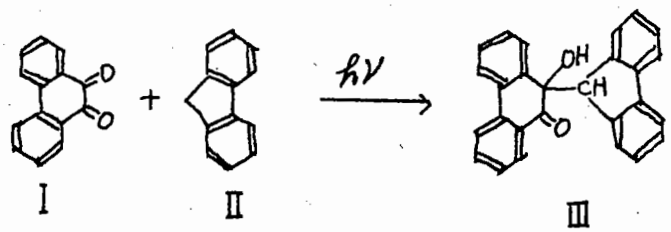


Fig. 1: Sketch of the pathway of the light to the sample in NMR probe.

Furthermore, all the glass in the commercial probe equipment was replaced by quartz so that the intensity of UV light is as great as possible; the intensity at the sample was measured with a photodiode.

By using the method described above, a strongly enhanced NMR singlet line was observed in the hydrogen abstraction reaction of phenanthraquinone (I) with fluorene (II) in benzene.



I II III

This singlet line is assigned to the methine proton of the 1.2-adduct (III) which appears about 45 Hz downfield from the methylene protons of fluorene. The time variation of the intensities of the singlet line was obtained at 70° C by field scanning with 1Hz saw-tooth wave as shown in Fig. 2.

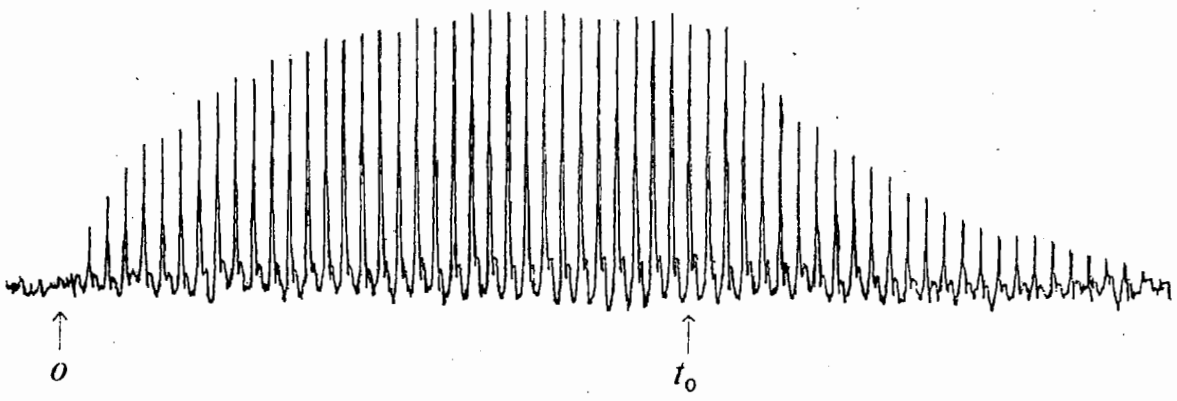


Fig. 2: Time dependence of the signal intensity of the methine protons of the 1.2-adduct (III). All signals are 1 sec apart.

The signal intensity increases exponentially just after the application of light at t=o, and then establishes its steady-state polarization. When the irradiation is turned off at $t=t_o$ of the peaks in Fig. 2., the signal again decays exponentially, but with a different time constant.

continued.....

This envelope of the peaks in Fig. 2 can be described by two relaxation times. They are 6.6 and 9.4 sec for irradiation and no-irradiation, respectively. The difference between these two relaxation times is general, and seems to be due to the existence of certain magnetic species present during the irradiation. Other kinetic information is also available from the envelope curve.

The details of this work will be submitted for publication in Bul. Chem. Soc. Japan.

Sincerely yours,

H. Shindo

Heisaburo Shindo

HS/rmh

DEPARTMENT OF PHYSICS

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.
Canada

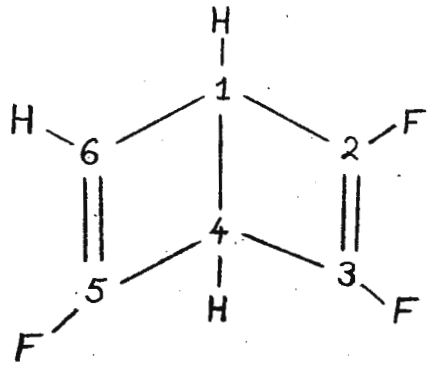
Prof. B.L. Shapiro,
Department of Chemistry,
College Station,
Texas A & M University,
Texas 77843

May 24, 1971

NMR Parameters of 2,3,5-trifluoro Dewar benzene

Dear Barry:

Several months ago, our photochemists prepared several trifluoro-Dewar-benzenes. They are unstable at room temperature (the Dewar benzenes) but one NMR sample spent most of its idle time in liquid nitrogen, and I could play with it while visiting Prof. L. Reeves' laboratory at the University of Waterloo. Hydrogen and fluorine spectra were recorded at 100 MHz and 56.4 MHz, respectively. They are first order but look somewhat complicated at first because several of the $6 \times 2^5 = 192$ lines coincide due to an accidental near equality of several coupling constants. The molecule and its NMR parameters are



	1	2	3	4	5	6
1	3.88	10.8	5.1	2.8	5.4	0.4
2		44.36	8.1	5.1	13.2	.5
3			42.70	11.1	.6	4.1
4				3.37	11.5	.5
5					75.71	10.0
6						5.45

The numbers on the diagonal of the Table are the chemical shifts in ppm to low field, from TMS for hydrogen and from hexafluorobenzene for fluorine. The numbers off the diagonal are the absolute values of the spin coupling constants in Hz. Some of your readers may be interested in adding these parameters to the list for similar compounds recently published by L. Cavalli (J. Chem. Soc. B 1970, 1616). The value J(23) = 8.1 Hz seems large in comparison with 1 to 4 Hz commonly found in these compounds.

I am much obliged to Prof. Reeves for the use of his spectrometers.

Sincerely yours,

Reinhold

R. Kaiser

Department of Chemistry

BROCK University

St. Catharines, Ontario

Glenridge Campus
684-7201 Ext. 317

May 20, 1971.

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

Dear Dr. Shapiro,

NEW LIFE FOR OLD A-60

Steve Hartman received his "blue notice" two weeks ago, just as he was leaving to get married, so I'm sending this off to be credited to his subscription.

We have just finished, with the help of Mike Cotton of Varian, replacing one of the coils of our A-60 magnet, which had suddenly shorted to the cooling coils, which is perhaps not surprising in view of its age (~ 9 years). We were successful in re-shimming the magnet and getting the machine back in excess of specification (0·6 Hz and 5:1 S/N spec for our old machine), i.e. we are back routinely doing 0·3 Hz resolution and 15:1 S/N. I have had it up to 0·2 Hz resolution and 40:1 S/N with slight effort, although this is after modifications which we have made.

The three-week shut down of the machine awaiting the magnet coil was more serious than the problem of the magnet. It took us four days (and 15 new tubes) to get the electronics working to our satisfaction, perhaps not surprising, since we have not had any electronic down time since June, 1970.

A-60 users please note that the tubes in the transmitter and field modulator can be temperamental. Of several new tubes, all testing in excess of spec on a tube tester, often one will be so microphonic as not to work in the A-60.

. . . 2

I've also obtained INDOR spectra with our HD-60 heteronuclear decoupler attached to the A-60 and this will be a topic of a future communication when I have some meaningful data.

Yours sincerely,

Jack M. Miller,
Associate Professor

JMM:csd

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

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May 21, 1971

Re: Contact Shifts and Metal-Nitrogen Bonds

Dear Professor Shapiro,

Dr. C. L. Khetrapal had submitted a contribution to your newsletter on behalf of the High Resolution NMR Group of our Institute. He is at present in U. S. A. To continue the group's contribution we give below a brief account of one of our activities.

We have recently undertaken extensive investigations on the studies of metal-ligand bonding in systems which are prototype of metal-enzyme and metal-nucleic acid interactions using NMR contact shifts. As a first step to this aim, we have investigated the NMR contact shifts in systems of the type $Ni(dtp)_2L_2$ where dtp = diethyldithiophosphate and L is a saturated amine like n-propylamine, piperidine etc. or an aromatic base like pyridine, picoline, etc. When L is a saturated amine, the reaction leads to the formation of both 1:1 and 1:2 adducts. The formation constants and absolute values of contact shifts have been estimated in these complexes by a least squares analysis of the observed spectra, which are time averages of the free ligand and the complex. With aromatic amines,

...2

the formation constants are fairly large for 1:2 complexes and stable $Ni(dtp)_2L_2$ complexes could be isolated. In latter systems, analysis of the absolute contact shifts in the light of INDO calculations has shown that the spin delocalisation from metal ion to the base involves not only the highest filled ligand orbitals of σ symmetry but also the low lying π orbitals. A short account of this work is in press and a limited number of preprints are available for distribution.

Yours sincerely,

(C. R. Kanekar) (G. Govil)

ABBOTT LABORATORIES, SCIENTIFIC DIVISIONS

NORTH CHICAGO, ILLINOIS 60064

May 24, 1971

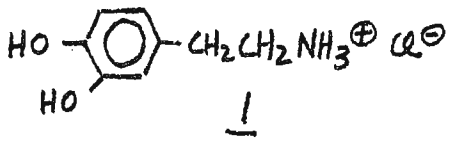
Professor Bernard L. Shapiro
Texas A and M University
Department of Chemistry
College Station, Texas 77843

Dear Dr. Shapiro:

UNCERTAINTIES IN THE ANALYSIS OF AA'BB' SPECTRA

We have recently been using the iterative version of LAOCN3 in the analysis of a number of AA'BB' spectra. Upon beginning such problems we are plagued by an uneasy feeling that this time we will fall into the trap that others have encountered and not recognize a false minima in the iterations or not recognize a deceptively simple case and misinterpret the results. The careful analysis of the ABC case by Abraham and Castellano (1) has emphasized the potential dangers.

Abraham and Pachler (2) have cautioned that deceptively simple 10 line AA'BB' spectrum result when $|L| << |K|$, a condition generally present in the case of 1,2-disubstituted ethanes, the spectrum cannot be readily analyzed to obtain K and only $|M|$ can be determined. We have encountered this circumstance in the analysis of the nmr spectrum of a D_2O solution of dopamine hydrochloride (1).



1

Although this phenomenon is well documented in the literature, for emphasis we list calculated transition frequencies for such a system when N, L, and M remain constant while K is varied. It should be noted that only three transitions vary with a three-fold increase of K and the largest change is only 0.09 Hz.

When iterative computer techniques were used to analyze such a spectrum and the magnitudes of the geminal couplings were treated as variables, unreasonable values were obtained, both anomalously large or small, even though the calculations smoothly minimized to solutions with RMS errors of 0.032 or less after 3 - 4 iterations. However, the calculated value of $|M|$ was always in excellent agreement with the value measured directly from the spectrum.

This problem has been recognized in the analysis of the spectra acetylcholine and isologs (3,4,5) as well as in the spectrum of histamine (6).

Calculated Transition Frequencies for an AA'BB' Spin System when N = 14.0, L = -2.0, $|M| = 0.9$, $\delta\gamma = 19.0$, and K is variable.

When K = -24.3 $J_A = -12.6$, $J_B = -11.7$	When K = -44.3 $J_A = -22.6$, $J_B = -21.7$	When K = -64.3 $J_A = -32.6$, $J_B = -31.7$
12.36	12.24	12.27
13.25	13.25	13.25
17.48	17.48	17.48
18.38	18.38	18.38
19.67	19.67	19.67
19.75	19.77	19.78
20.57	20.57	20.57
20.75	20.73	20.72
25.85	25.84	25.84
27.25	27.25	27.25

A second indeterminacy is encountered in the analysis of AA'BB' spectra concerning the sign of L which has been shown by Abraham and Pachler (2) to be diagnostic of the preferred conformer. Methods involving solvent effects and electronegativity have been used to determine this parameter. In our study of dopamine hydrochloride we have used the temperature dependence of the vicinal couplings to determine the sign. Gutowsky and others (7) previously attempted this method with 1,2-disubstituted ethanes without success; however, instrumentation improvements have been made since 1962 (c.f. footnote 25 in reference 7). Since the analysis is long and involved, no discussion will be made here; however, preprints are available for those interested.

The conclusion reached from our study was that the trans conformer of dopamine hydrochloride is energetically preferred in D_2O solution with a population of 0.43 ± 0.05 mole fraction over a 60° temperature range. The experimental results show a small increase in the trans population with an increase in temperature, contrary to what would be expected from the Boltzman law.

Sincerely,

Richard S. Egan
nmr lab, D-408

vc

(1). R.J. Abraham and S. Castellano, J. Chem. Soc., 49 (1970).
(2). R.J. Abraham and K.G.R. Pachler, Mol. Phys., 7, 165 (1964).
(3). C.C.J. Culvenor and N.S. Ham, Chem. Comm., 537 (1966).
(4). C.C.J. Culvenor and N.S. Ham, Chem. Comm., 1242 (1970).
(5). R.J. Cushley and H.G. Mautner, Tetrahedron, 26, 2151 (1970).
(6). A.F. Casy, R.R. Ison, and N.S. Ham, Chem. Comm., 1343 (1970).
(7). H.S. Gutowsky, G.G. Belford and P.E. McMahon, J. Chem. Phys., 36, 3353 (1962).

153-30

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

May 21, 1971

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

"SPECTROMETER FOR SALE"

Dear Barry:

We are offering for sale our Bruker 321S pulsed n.m.r. spectrometer at a reasonable price. This is a variable frequency instrument that currently can be operated in the 16-62 MHz. range and includes a Schomandl synthesizer and Tektronix storage scope. It is about 1.5 years old. Interested parties should contact the undersigned.

Sincerely yours,

Tom

J. T. Gerig
Assistant Professor

JTG:rt

NICOLET INSTRUMENT CORPORATION

May 25, 1971

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

Emission Lines in Pyridylalkyl Grignard Compounds
Fabri-Tek Becomes Nicolet

Dear Barry:

Moving here from the East has temporarily interrupted my nmr research, although I do expect to initiate a research effort here in the near future.

You might note that the company name here, formerly Fabri-Tek Instruments, is now Nicolet Instrument Corporation, although our products, signal averaging and FFT devices designed for nmr, remain unchanged.

While examining the room temperature spectrum of 2-(4-pyridyl)-2 methylpropylmagnesium bromide in THF, I found sporadic evidence for CIDNP: an emission line at 3.7τ. This may shed some light on the nature of this Grignard reagent in THF, but since this work is in a very early stage, I don't feel speculation is appropriate. Hopefully, in another nine months, I'll be able to contribute something more concrete.

Sincerely,

James W. Cooper

James W. Cooper
Chemistry Applications Manager

JWC:rg

UNIVERSITI MALAYA

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Department of Chemistry
University of Malaya
Kuala Lumpur
Malaysia.
24 May 1971.

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

Ethylene Adsorbed on Zeolites

Dear Dr Shapiro:

While at the University of East Anglia, Norwich, U.K. recently, Dr T. A. Egerton and I had the opportunity to study the N.M.R. spectrum of ethylene adsorbed onto the surfaces of various dehydrated zeolites (molecular sieves). "High resolution" N.M.R. spectroscopy has not yet been applied to studies of adsorbed molecules very much, although the experiments are not difficult to perform.

At low coverages of ethylene on Ca exchanged Y zeolite, the linewidth was found to be much greater than on the Na form of the same zeolite. This difference is accounted for by adsorption at Ca ion sites, although the mechanism of the broadening is not understood. At higher coverages of ethylene, the linewidths tend to a common value of something less than 200 Hz at 100 MHz. This peak is found at about 4.3 p.p.m. downfield from external TMS.

However, at very high coverages of ethylene on Ca exchanged zeolite, a second peak appears at about 0.5 p.p.m. below TMS. When the sample is allowed to stand, this second peak grows in intensity at the expense of the original one. This behaviour is shown in the figure. In fact, although this is not obvious from the figure, yet another peak, very broad, is growing simultaneously. We have assigned the peak at 0.5 p.p.m. to the methyl and methylene resonances of oligomers of ethylene, and the very broad peak to polyethylene.

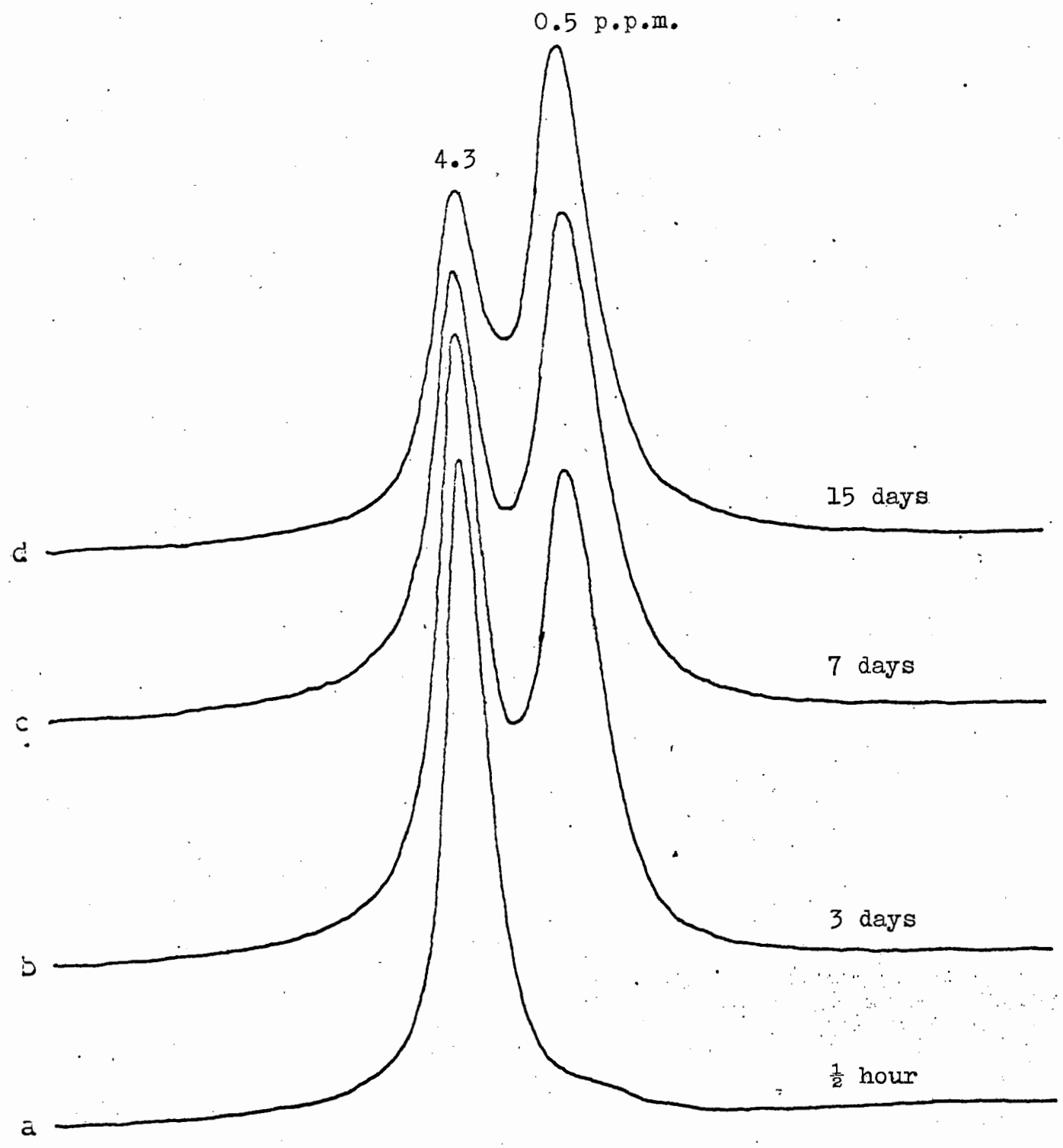
Such polymerisation on these types of zeolites appears to have been unknown in past, although the time scale is obviously not of commercial interest. This behaviour was not observed on the Na zeolite, indicating that the calcium ions are responsible for the polymerisation. Interestingly, however, the extra peaks do not appear at lower ethylene coverages, even though most of the ethylene is adsorbed onto the calcium ions. We can only speculate that the hydroxyl groups, which are formed as a consequence of hydrolysis of residual water molecules by the calcium ions, are the active centres.

A fuller report of this work has been submitted for publication.

Yours sincerely,

R D Green

R. D. Green



Short Title: Ethylene Adsorbed on Zeolites.

UNIVERSITY OF CALIFORNIA

LWRENCE RADIATION LABORATORY
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May 25, 1971

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

Dear Barry:

Time and Frequency Domain Spectrometer

I thought for my contribution this time I would bring you up to date on the status of our spectrometer development. You may remember we reported at the 10th ENC on our development of an all solid-state multinuclei frequency-swept high resolution spectrometer operating from 2-60 MHz using a pair of frequency synthesizers for r.f. sources. The addition of a rather elaborate time base and pulse sequence generator has permitted us to construct a dual purpose time-domain (i.e. pulsed nmr) and frequency domain nmr spectrometer of considerable versitility.

The heart of the system is a time base and pulse sequence generator (TB-PSG) which supplies all of the time-share gate signals, pulse widths, time delays, etc., in both the time and frequency domains. Driven by the 1 MHz crystal oscillator of the frequency synthesizer driver, the TB-PSG internally consists of one free-running time base, 2 resetable time bases, and about a dozen presetable counters (3-4 digit thumbwheels). These presetable counters serve as pulse width controllers, receiver gates, adjustable time delays, and period generators. Some of these presetable counters are dedicated (such as $\frac{\pi}{2}$ pulse width) while others have optional purposes. All of them, however, have their inputs and/or outputs available at a front panel pin matrix board so that they can be interconnected in a variety of configurations including nesting feedback loops. The enclosed example (Figure 1.) is a T_1 measurement of a ^{13}C resonance in 6% ^{13}C enriched methyl iodide taken with a single pulse sequence in the time domain. The pulse sequence was:

$$\pi,\ d_1,\ \frac{\pi}{2},\ R,\ -\frac{\pi}{2},\ d_1,\ \frac{\pi}{2},\ R,\ -\frac{\pi}{2},\ d_1\ - - -$$

where, in addition to the usual meaning of π, $\frac{\pi}{2}$, $-\frac{\pi}{2}$, the delay between sampling is d_1 and the receiver gate is open for an appropriate time at R. The sub-sequence, $\pi/2$, R, $-\pi/2$, brings the magnetization from the z axis to the x axis, reads its length and returns it to the z axis.

Our list of isotopes which have been examined by this spectrometer continues to grow and now includes H^1, H^2, Li^6, Li^7, C^{13}, F^{19}, Na^{23}, Si^{29}, P^{31}, Cl^{35}, K^{39}, Br^{79}, Br^{81}, Rb^{85}, Cs^{133}, Hg^{199} and Tl^{205}. If any readers desire more explicit details of our operating conditions for these isotopes, I will be glad to supply such information.

Sincerely,

Bert Holder

Bert Holder (subscription credit)
James Happe
Al Maddux
Raymond Ward

BH:ob

Bert Holder
Lawrence Radiation Laboratory
May 25, 1971

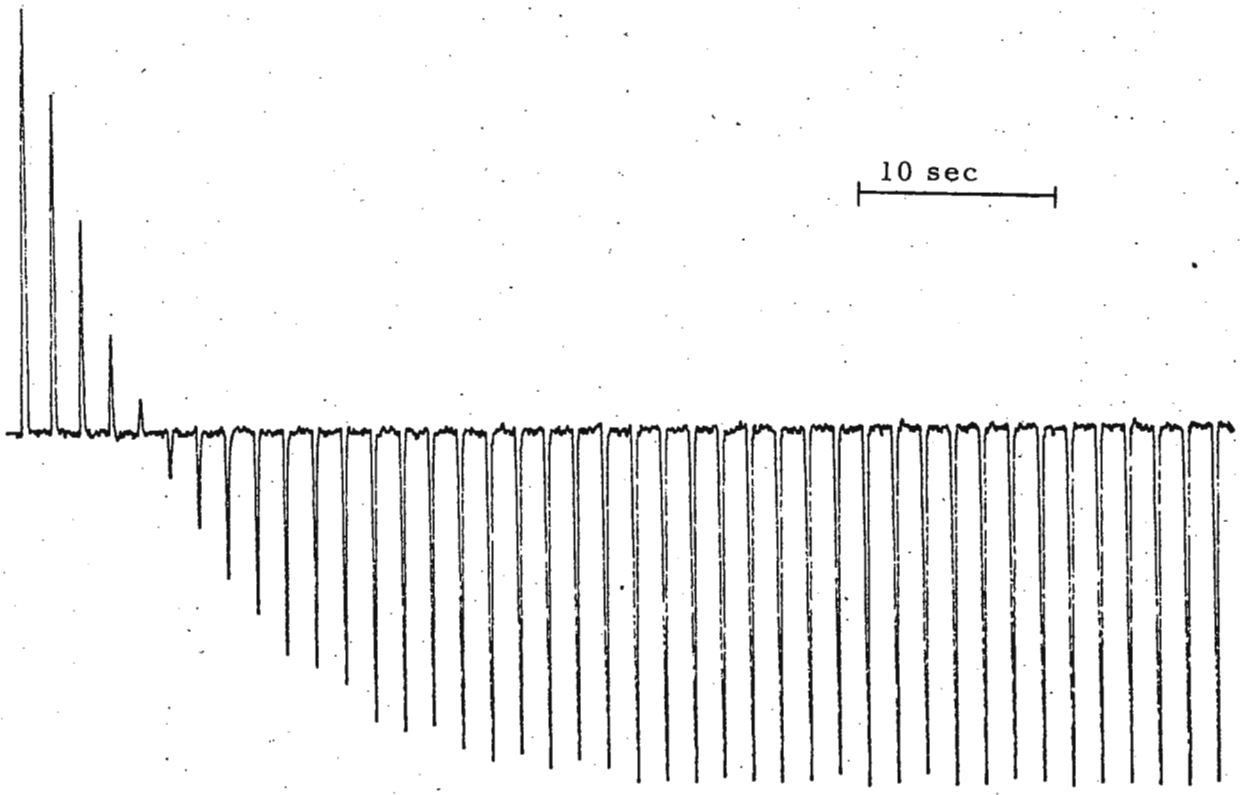

Figure 1. T_1 of one line of the ^{13}C quartet of 6% enriched ^{13}C methyl iodide at 15.087 MHz. by multiple pulse method. T_1 approximately 7 seconds.

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The School of Medicine

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May 25, 1971

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

Dear Professor Shapiro:

220 MHz PMR Difference Spectroscopy for Proteins

King and Bradbury (1) have shown that the resonances of C-4 protons of histidine of the protein, bovine pancreatic ribonuclease (M. W. = 12,640), which normally fall under an envelope of aromatic amino acid residues in the pmr spectrum can be located and revealed by a difference spectrum between two pH values. We have recently extended this technique to the pmr of another protein, rabbit muscle pyruvate kinase, (M. W. = 237,000, presumably 4 identical subunits) by recording the difference of the spectra in the presence and absence of substrate and cations. The ions K^+ and Mg^{++} are obligatory for the functional activity of the protein and it has been shown (2) that the addition of these ions induces a conformational change in the structure of the protein.

In figure 1, curve A shows the low field spectrum of pyruvate kinase in buffer and curve B shows the same region of the spectrum in the presence of K^+, Mg^{++} and one of the substrates phosphoenolpyruvate. The spectra were scanned on a Varian 220 MHz instrument at 20 Hz/sec at 18°C and the subtraction was done with a CAT; curves C and D are the difference spectra between spectrum B and A determined in two experiments. Although we cannot assign the resonances to specific amino acids until much more information is available on the structure of

this protein, the result is gratifying in that resonances with line widths of the order of 10 cycles are easily discernible in a molecule of molecular weight of approximately a quarter of a million. Furthermore from spectra not shown in the figure, the conformational change indicated by the shift of the three protein lines between 6.9 and 8.0 ppm result from the addition of the ions alone and the protein peaks which appear further downfield, below 8 ppm result from the addition of phosphoenolpyruvate.

With best regards,

Sincerely yours,

Mildred Cohn

Mildred Cohn

MC/la

---

1. King, N. L. R. and Bradbury, J. H.,Nature 229, 404 (1971).

2. Kayne, F. J. and Suelter, C. H., J. Am. Chem. Soc. 87, 897 (1965).

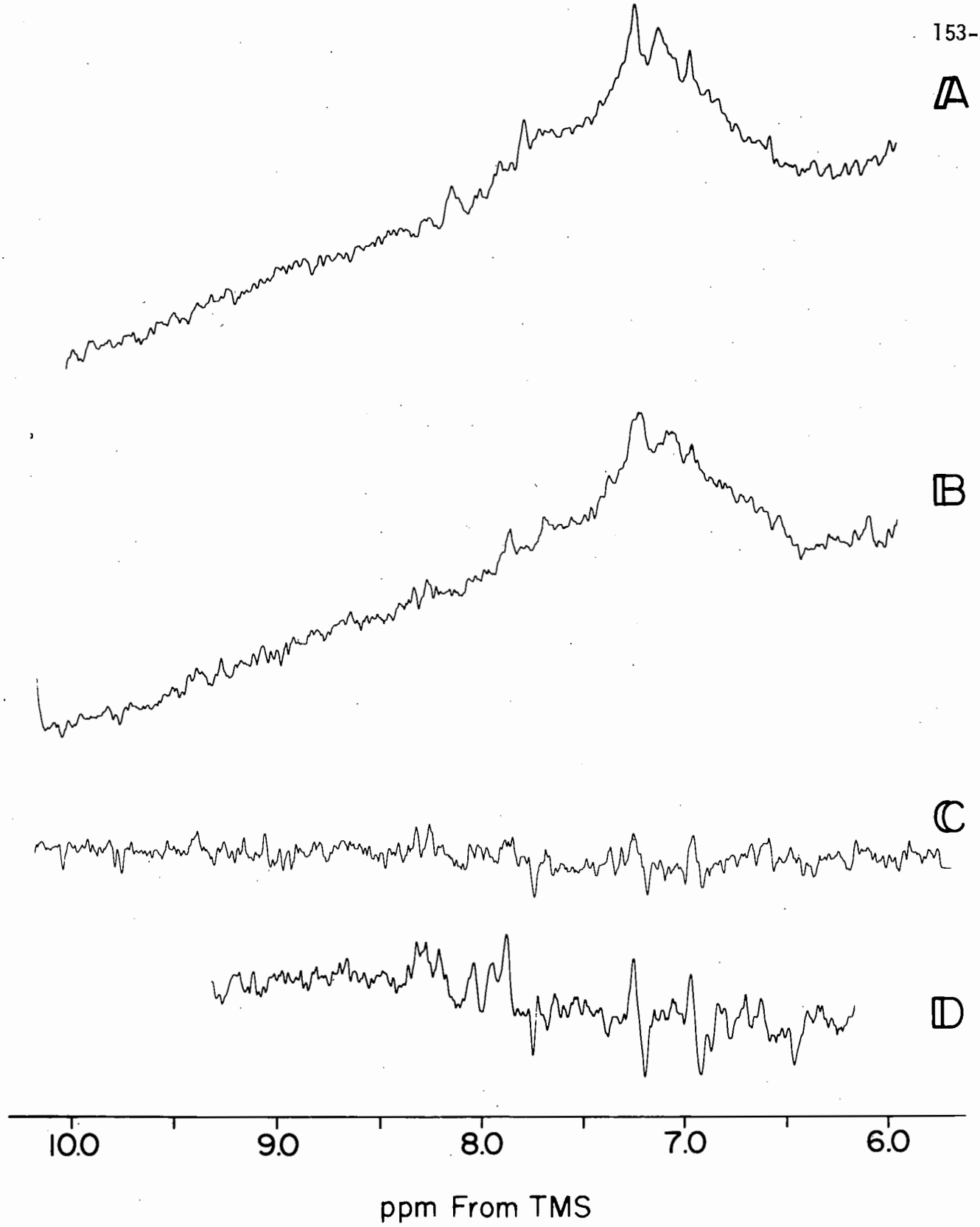

Figure 1. 220 MHz pmr spectrum of rabbit muscle pyruvate kinase, 100 mg/ml in 5mM $(CH_3)_4$ N^+-phosphate buffer, 20mM $(CH_3)_4N$-Cl, pH 7.8. Curve (A), no additions, 25 scans. Curve (B), additional components: 0.1M KCl; $MgCl_2$, 7mM; phosphoenolpyruvate, 2mM; 25 scans. Curve (C), difference between (B) and (A), 25 scans; Curve (D), difference between (B) and (A), 75 scans.

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

Dear Barry,

Specific Solvent Effects

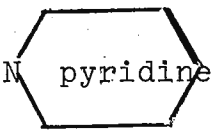
While Dr. A.A. Grey# was a postdoctoral Fellow with me ['66-'68] he obtained infinite dilution data for $(CH_3)_3C{\equiv}C{-}H$ in a variety of solvents. Some of his results are given below for the $C(CH_3)_3$ protons as well as for $\equiv C{-}H$:-

Solvent	$\delta C(CH_3)_3$	$\delta \equiv C{-}H$
TMS	335.0	299.0
C_6H_6	361.6	316.2
C_5H_5N	364.2	266.1

The chemical shifts are in Hz measured from benzene as external standard and are corrected for bulk susceptibility of the solvents.

It is clear that benzene and pyridine behave in similar fashions when "seen" by the alkyl protons. In both solvents the signal has been moved to high field from that in TMS and by about equal amounts. The alkyne proton in C_6H_6behaves in a similar manner, its signal moving to high field in benzene solution. The alkyne proton in pyridine however has a signal at lower field than in TMS and suggests that the orientation of pyridine with respect to the $\equiv C{-}H$ group is as shown in Fig. 1a

.... P. 2.

$(CH_3)_3C-C\equiv C-H$ .....  1a

whereas in benzene it is as shown in Fig. 1b

$(CH_3)_3C-C\equiv C-H$ 1b

The hydrogen bond shift in pyridine may be estimated as follows.

We shall assume the anisotropy effect of benzene on $\delta\equiv C-H$ is given by $\delta^{benzene}_{\equiv CH} - \delta^{TMS}_{\equiv C-H} = 17.2$, also that

$$\delta^{pyridine}_{\equiv CH} - \delta^{TMS}_{\equiv CH} = -8.6^{*} + \text{H bondshift} = -32.9 \text{ cps.}$$

Thus the hydrogen bond shift is -24.3 cps.

This value for the hydrogen bond shift evaluated in this way is only very approximate.

Best wishes,

Sincerely,

Harold

Harold J. Bernstein.

#Present address: Ontario Research Foundation, Sheridan Park, Toronto.

*This is one half the anisotropy effect in benzene but with opposite sign since the ring current for the orientation in Fig. 1a gives a low field shift of half the magnitude of that in Fig. 1b which is a high field shift.

153-42

The University of Manitoba

Department of Chemistry
Winnipeg 19, Manitoba, Canada

May 31, 1971

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

Dear Barry:

Short Title: Exercises in Carrington and McLachlan: Query on interest of readers.

During the past two years various clever students and I have worked about 100 of the some 120 exercises in 'Introduction to Magnetic Resonance' in detail. By detail, I mean, for example, that the first two problems in Chapter 5 have been worked so that decent senior undergraduates can follow the development, which takes about 25 pages of work: one uses Slichter's approach, of course, but supplements the treatment at points of difficulty.

On the other hand there are also problems which a first year student can handle. As an example, I enclose a copy of the solution to a very simple problem (the seventh in the seventh in the revelation) as worked by George Wollner. The almost silly detail is meant for first year students, strong on logic and new math, but weak on what we "old ones" think of as elementary algebra and trig.

There may be a number of your readers who would find the solutions useful. To put these 100 or more problems into reproducible form would take time not normally at my disposal. However, I have a sabbatical in 1971-72 and could spend a month or two on this since it would also be useful for my teaching work. If your readers were really interested they would presumably be willing to pay, say, fifteen dollars for a copy. I invite queries and if a sufficient number show an interest, I shall do the donkey work.

All the best, from,

Ted Schaefer

TS:lg
Encl.

7. The two β-proton couplings of the adipic acid radical $COOH-CH-(CH_2)_3-COOH$ whose isotropic parts are +112 Mc/s and +74 Mc/s demonstrate that the two β-protons are not magnetically equivalent, both having large contact hyperfine interactions varying with the angle θ between the plane of the C-C and C-H bonds and the axis of the p_z orbital. The two β-protons must lie at different angles θ and the $CH-CH_2$ bond must be twisted by an angle ϕ.

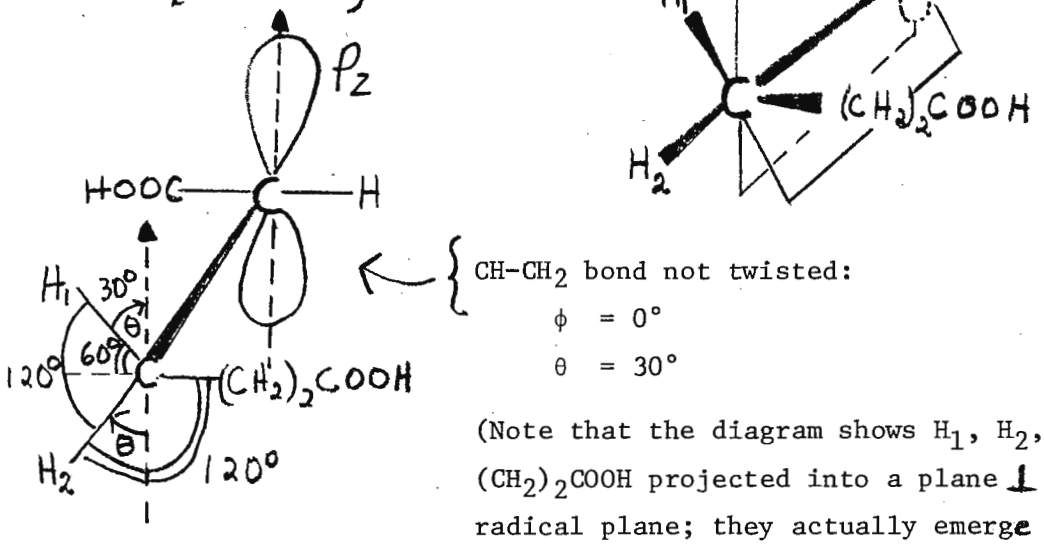
The two β-protons may be distinguished; β-proton H_1 has a larger interaction (+112 Mc/s) than β-proton H_2 (+74 Mc/s) since the projection of $C-H_1$ is more nearly perpendicular to the radical plane than the projection of $C-H_2$.

The twisting of the $CH-CH_2$ bond may be estimated from consideration of the diagrams below and the empirical relationship

$$A = B_o + B_2 \cos^2\theta$$

where A is the contact hyperfine interaction coupling constant, and B_o and B_2 are constants with $B_o \ll B_2$. In general, B_o = 0 to +10 Mc/s.

θ = angle between the H_1-C-C plane and the axis of the p_z orbital.

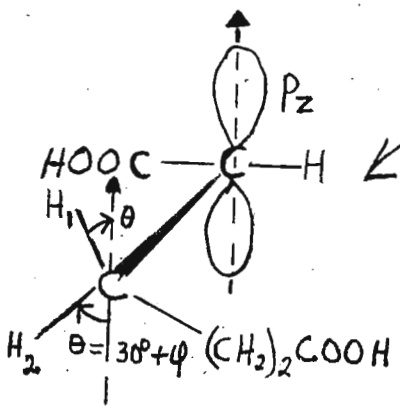


$CH-CH_2$ bond not twisted:

$\phi = 0°$

$\theta = 30°$

(Note that the diagram shows H_1, H_2, and $(CH_2)_2COOH$ projected into a plane ⊥ to the radical plane; they actually emerge from the plane of the paper while H and COOH on the α-carbon are actually behind the plane of the paper).



{ $CH-CH_2$ bond twisted:
For H_1 (a = +112 Mc/s), $\theta = 30° - \phi$
For H_2 (a = +74 Mc/s), $\theta = 30° + \phi$

Assuming $B_o = 0$ Mc/s:

$$A = B_2 \cos^2 \theta$$

For H_1 (A = +112 Mc/s):

$$+112 = B_2 \cos^2 (30° - \phi) \qquad \ldots\ldots 1$$

For H_2 (A = +74 Mc/s):

$$+74 = B_2 \cos^2 (30° + \phi) \qquad \ldots\ldots 2$$

Equations 1 and 2 may be solved simultaneously to yield values of B_2 and ϕ:

$$112 = B \cos^2(30° - \phi)$$
$$= B[\cos 30° \cos \phi + \sin 30° \sin \phi]^2$$
$$= B[\cos^2 30° \cos^2 \phi + 2 \cos 30° \cos \phi \sin 30° \sin \phi + \sin^2 30° \sin^2 \phi]$$
$$74\left(\frac{112}{B}\right) = 74 \cos^2 30° \cos^2 \phi + 148 \cos 30° \cos \phi \sin 30° \sin \phi + 74 \sin^2 30° \sin^2 \phi.$$

$$74 = B \cos^2 (30° + \phi)$$
$$74 = B[\cos 30° \cos \phi - \sin 30° \sin \phi]^2$$
$$= B[\cos^2 30° \cos^2 \phi - 2 \cos 30° \cos \phi \sin 30° \sin \phi + \sin^2 30° \sin^2 \phi]$$
$$112\left(\frac{74}{B}\right) = 112 \cos^2 30° \cos^2 \phi - 224 \cos 30° \cos \phi \sin 30° \sin \phi + 112 \sin^2 30° \sin^2 \phi.$$

$$112\left(\frac{74}{B}\right) - 74\left(\frac{112}{B}\right) = 112 \cos^2 30° \cos^2 \phi - 224 \cos 30° \cos \phi \sin 30° \sin \phi$$
$$+112 \sin^2 30° \sin^2 \phi - [74 \cos^2 30° \cos^2 \phi$$
$$+148 \cos 30° \cos \phi \sin 30° \sin \phi + 74 \sin^2 30° \sin^2 \phi]$$
$$= 0$$

$$38\cos^2 30°\cos\phi - 372\cos 30°\cos\phi \sin 30° \sin\phi + 38\sin^2 30° \sin^2\phi = 0$$

$$38\left(\sqrt{3}/2\right)^2\cos^2\phi - 372\left(\sqrt{3}/2\right)\cos\phi(1/2)\sin\phi + 38(1/2)^2\sin^2\phi = 0$$

$$\frac{38(3)}{4}\cos^2\phi - \frac{372\sqrt{3}}{4}\cos\phi\sin\phi + \frac{38}{4}\sin^2\phi = 0$$

$$3\cos^2\phi - \frac{372\ 3}{38}\cos\phi\sin\phi + \sin^2\phi = 0$$

Dividing through by $\cos^2\phi$:

$$3 - \frac{372\sqrt{3}}{38}\frac{\sin\phi}{\cos\phi} + \frac{\sin^2\phi}{\cos^2\phi} = 0$$

Now $\frac{\sin\phi}{\cos\phi} = \tan\phi$:

$$\tan^2\phi - \frac{372\ 3}{38}\tan\phi + 3 = 0$$

$$\tan^2\phi - 16.96\tan\phi + 3 = 0$$

$$\tan\phi = \frac{-(-16.96) \pm \sqrt{(-16.96)^2 - 4(1)(3)}}{2}$$

$$= \frac{16.96}{2} + \frac{\sqrt{275.64}}{2}$$

$$= 8.48 \pm {}^{16.60}/_{2}$$

$$= 8.48 \pm 8.30$$

$$= 0.18,\ 16.78$$

$$\phi = 10.2;\ 86.6°$$

$\phi = 86.6°$ would give a negative angle for $\theta = (30° - \phi)$, so $\phi = 10.2°$ is chosen as the angle of twist.

The value of the constant B_2 may now be calculated as well:

$$112 = B_2\cos^2(30° - \phi)$$
$$= B_2\cos^2(30° - 10.2°)$$
$$= B_2\cos^2(19.8°)$$
$$= B_2(0.941)^2$$
$$= B_2(0.885)$$
$$B_2 = \frac{112}{0.885}$$
$$= 126.6$$
$$= 127\ \text{Mc/s}$$

or

$$74 = B_2\cos^2(30° + \phi)$$
$$= B_2\cos^2(30° + 10.2°)$$
$$= B_2\cos^2(40.2°)$$
$$= B_2(0.764)^2$$
$$= B_2(0.584)$$
$$B_2 = \frac{74}{0.584}$$
$$= 126.7$$
$$= 127\ \text{Mc/s}$$

If B_o is taken as large as 10 Mc/s, as for the $CH_3CH(COOH)$ radical in section 7.9, one obtains θ = angle of twist = 12° and B_2 = 113 Mc/s.

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RESEARCH AND DEVELOPMENT CENTER

May 28, 1971

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

"4 MONTHS WITH THE XL-100-FT SYSTEM"

Dear Barry:

We are now starting our fifth month of Fourier operation with the Varian XL-100-FT System.

Our system is the first installed in a customer laboratory in the U.S. (International #1 was installed two weeks earlier at NRC, Canada). The General Electric system currently consists of an XL-100-15 with a VFT-100 Fourier transform package. Initial operation has been for ^{1}H and ^{13}C nuclei.

Overall operation of the system has been excellent, with no major difficulties noted. Fourier downtime during the first four months has been under three days (a 5V power supply failed). Ease of operation of the software has been responsible for a large instrument throughput.

Sensitivity enhancement has exceeded promises for ^{13}C NMR but has lagged somewhat for ^{1}H observation. For ^{13}C, we typically observe a 10-15 fold increase in sensitivity, corresponding to time savings of 100-225, compared to CW experiments (10-20Hz/sec., 5000Hz sweeps). ^{1}H NMR FT experiments result in 3-4 times the sensitivity of 4Hz/sec CW experiments (1,000Hz sweeps).

GENERAL ELECTRIC

"4 MONTHS WITH THE XL-100-FT SYSTEM"

The General Electric system currently acquires 4K data points, yielding 2K output points in the phase corrected real spectrum. In July/August we will double our available data channels to achieve higher effective resolution with wide spectral widths. At that time, we are adding a magnetic tape unit to our system (linc tape, Computer Operations, Beltsville, Maryland). We will then also add computerized CW operation, replacing conventional time averaging with a C-1024 CAT with the Varian 620-i (16K).

Sincerely yours,

George Levy

Dr. George C. Levy
Materials Characterization Operation

Joseph D. Cargioli

Joseph D. Cargioli
Materials Characterization Operation

GCL:JDC:pf

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

DEPARTMENT OF CHEMISTRY

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

June 2, 1971

Isotope Effects on Fluorine Chemical Shifts

Dear Barry:

As a result of a search for a good fluorine reference and also of the measurement of one- and two-bond coupling constants between carbon-13 and fluorine, we have recently become interested in the effects of changing isotopic mass on fluorine chemical shifts. One-bond effects of this type have been reasonably well studied, but much less has been reported for two-bond effects. The behavior observed for the resonance of a fluorine atom attached to a carbon atom also bearing three chlorines was illustrated in a letter from Derek Shaw in your issue of August, 1970.

A good illustration of how the two-bond chlorine isotope effect may be applied to confirmation of assignments of resonances in fluorine compound is illustrated in the two attached spectra, for the terminal groups in the molecule $CFCl_2CF_2CFClBr$. In the group with only one chlorine, each peak in the spin-spin multiplet appears as two, with an intensity ratio close to the expected 3/1. When two chlorines are present, there appear three components, present in the ratio of about 9/6/1 for the 35-35, 35-37 and 37-37 mass combinations, respectively.

In ethanes and propanes, the first substitution of a chlorine of mass 37 for one of mass 35 produces an upfield shift which is about 0.6 Hz at 94 MHz at room temperature and increases to about 0.8 Hz at -100°C. The magnitude of the shift seems to be independent of the solvent. Because of the low intensity of the 37-37 peak in a $CFCl_2$ group, it is not possible to locate its position quite so well, but the shift from the major peak seems to be just about twice that for the 35-37 peak. In the substituted methyl groups of some 2-propanones, the 35-35 to 35-37 difference is only about 0.4 Hz.

It seems significant that the two-bond effect of substituting carbon-13 for carbon-12 is an increase in shielding (decrease in resonance frequency), parallel to the upfield shift observed in the two-bond chlorine effect and in the one-bond carbon effect. We append a table of some one- and two-bond coupling constants, expressed in Hz, and some one- and two-bond isotope shifts ($-\Delta\phi^1$ and $-\Delta\phi^2$), expressed in ppm. While the one-bond isotope shifts show a regular variation from CF_3 to CF_2Cl to $CFCl_2$, there is not an obvious pattern for the two-bond shifts.

Gutowsky discussed deuterium isotope effects in terms of an electrostatic model [J. Chem. Phys. 31, 1683 (1959)] in which the nucleus undergoing change in mass is viewed as a center of positive charge which unshields the

atom of which the resonance is examined. The nucleus of smaller mass can approach more closely because of the greater asymmetry in its vibration resulting from a larger zero-point energy, and thus produces a greater downfield shift. To explain the temperature dependence, one might then presume that the smaller interval between vibrational levels for the system of greater mass causes excited levels to be more extensively populated as the temperature is raised. The vibrational amplitudes are greater in excited states and the resulting closer approach of the two nuclei should lead to greater unshielding by the heavier isotope. In many of the ethanes and propanes which are unsymmetrically substituted, there are temperature dependences of the chemical shifts resulting from changes in conformational equilibria, and of course there may always be medium effects. However, it is satisfying to note that in the molecule $CF_2Cl\text{-}CCl_3$, increasing temperature shifts all the resonances to lower fields, moving the resonance in the heavier isotopomer farther to low field than that of the lighter one.

Cordially yours,

William A. Tallon

William A. Tallon

Ronald B Block

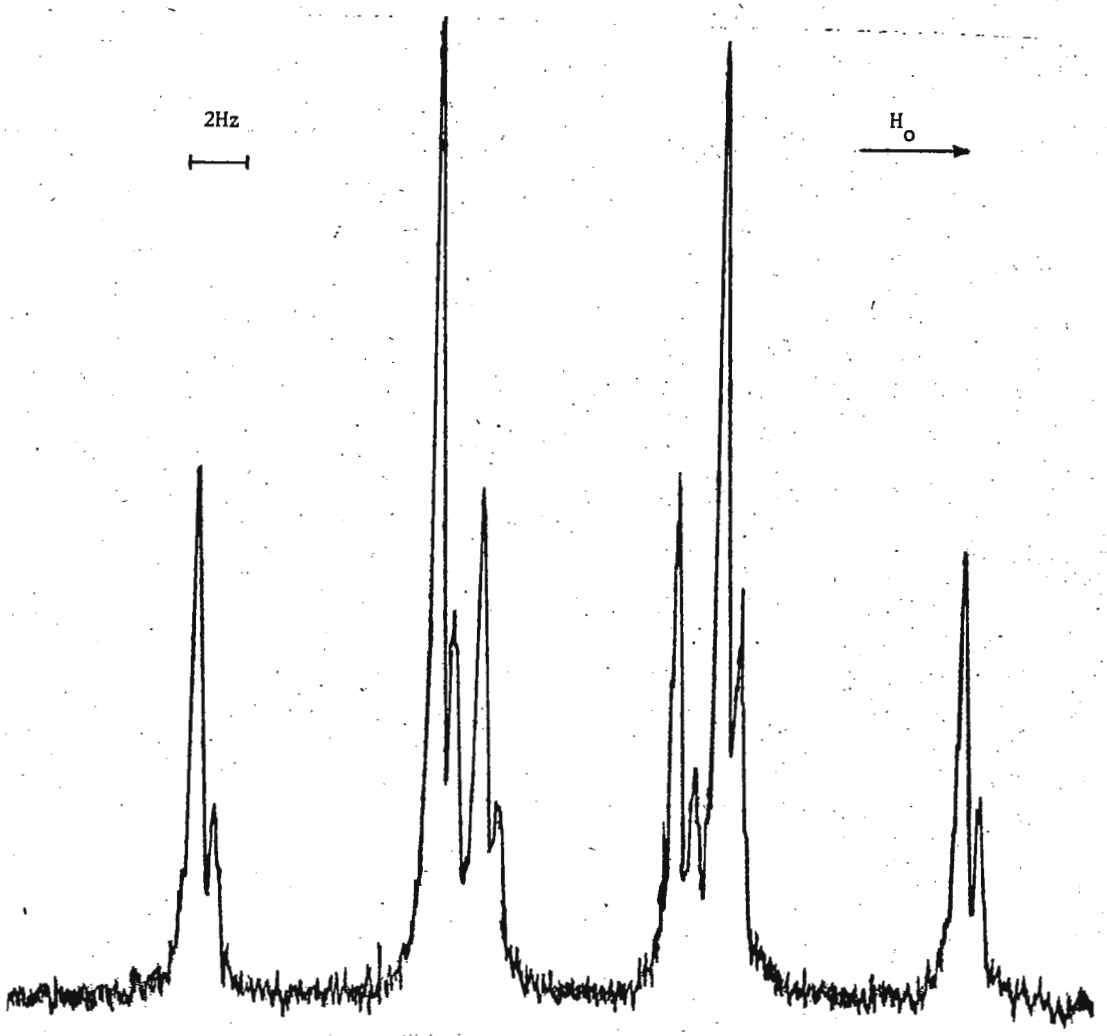
Ronald B Block

Wallace

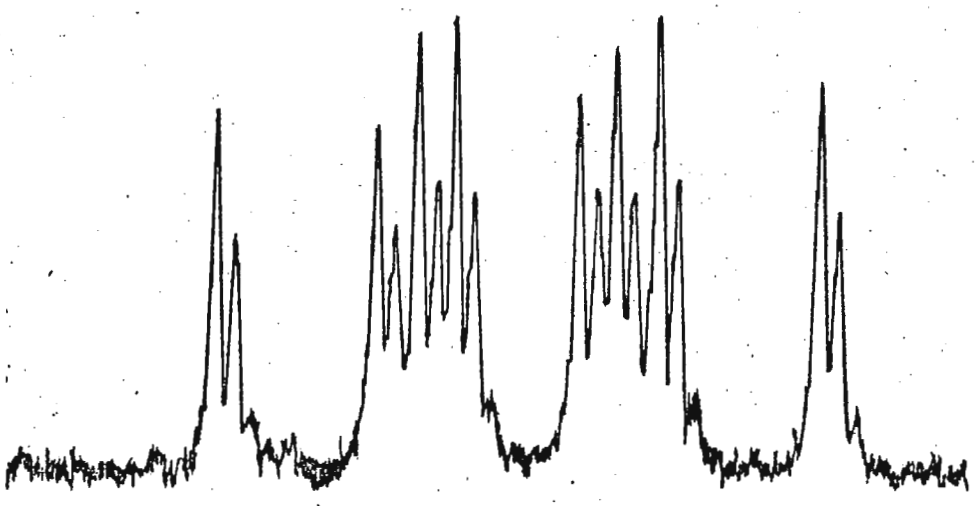
Wallace S. Brey, Jr.

WSB/ewh

COMPOUND	$^1J_{CF}$	$-\Delta\phi^1$	$^2J_{CF}$	$-\Delta\phi^2$	COMPOUND	$^1J_{CF}$	$-\Delta\phi^1$	$^2J_{CF}$	$-\Delta\phi^2$
CF_3CH_2OH	277.3	0.124	35.1	0.015	CF_2ClCCl_2H	295.2	0.136	35.7	0.015
CF_3CH_2Br	273.6	0.129	38.0	0.014	CF_2ClCCl_3	300.9	0.136	34.8	0.012
CF_3CH_2I	273.6	0.125	35.8	0.014	$CF_2ClCFCl_2$	300.6	0.141	38.0	0.014
CF_3CFICF_3	284.4	-	36.9	0.012	CF_2BrCF_2Br	312.3	0.135	38.9	0.007
$CF_3CF_2CH_2I$	285.7	0.123	37.8	0.015	$CFCl_2CCl_3$	309.1	0.160	34.3	-
CF_3CCl_2H	278.5	0.122	41.0	0.014	$CFCl_2CFCl_2$	308.2	0.157	35.2	0.014
CF_3CCl_3	282.3	0.124	43.0	0.012	$CFCl_2CF_2Cl$	305.6	0.157	44.0	0.020
					$CFCl_2CCl_2H$	301.4	0.164	-	-



$CFClBr-$



$CFCl_2-$

in

$CFCl_2CF_2CFClBr$

Author Index - TAMU NMR Newsletter No. 153

Anteunis, M.	14	Holder, B.	34
Bernstein, H. J.	40	Icli, S.	12
Block, R. E.	48	Kaiser, R.	23
Brackman, W.	5	Kanekar, C. R.	26
Brey, W. S., Jr.	48	Kurland, R. J.	8
van Broekhoven, J.A.M.	5	La Mar, G. N.	9
Cargioli, J. D.	46	Lambert, J. B.	1
Clague, A.D.H.	5	Levy, G. C.	46
Cohn, M.	37	Lunazzi, L.	2
Colebrook, L. D.	12	Maddux, A.	34
Cooper, J. W.	31	Mathias, A.	6
Egan, R. S.	28	Miller, J. M.	24
Gerig, J. T.	30	Schaefer, T.	42
Gosnell, J. L., Jr.	1	Shindo, H.	20
Govil, G.	26	Spragg, R. A.	16
Greatbanks, D.	4	Tallon, W. A.	48
Green, R. D.	32	Ward, R.	34
Gutowsky, H. S.	18	Wilde, A. M.	6
Happe, J.	34		

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