Joseph B. Lambert

Mailed:
November 29, 1962

Monthly Ecumenical Letters from Laboratories Of N-M-R

No. 50

DEADLINE FOR NEXT ISSUE
December 28, 1962

Allied Chemical Corporation

GENERAL CHEMICAL DIVISION

RESEARCH LABORATORY • P. O. BOX 405 • MORRISTOWN, NEW JERSEY
JEFFERSON 8-8000

October 15, 1962

Dr. B. L. Shapiro
The Mellon Institute
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Recently we have had occasion to measure the ^{19}F chemical shifts of a number of compounds containing the N-F linkage. We were somewhat surprised to find that for liquid nitrosyl fluoride, F-N=O, at -70° ϕ = -479 p.p.m. relative to $CFCl_3$. This places nitrosyl fluoride well below F_2 (ϕ = -420 p.p.m.) on the ^{19}F chemical shift scale and, with the possible exception of UF_6 [Varian Technical Information Bulletin, 1, No. 3 (1955)], appears to be the lowest shift yet observed for ^{19}F.

That the N-F bond in nitrosyl fluoride is highly ionic is evident from several other observations: the abnormally long N-F bond length, the abnormally low force constant for the N-F stretching vibration and its chemical behavior as a fluoride ion donor. On the basis of the well known correlation between the ionic character of bonds to fluorine and chemical shifts, one might expect nitrosyl fluoride to have a slightly positive chemical shift.

The explanation of this result may be related to evidence obtained recently by Johnson and Bertin [J.Mol. Spectroscopy, 3, 683 (1959)], in a study of the chemiluminescence associated with the reaction between nitric oxide and fluorine, for the existence of a weakly-bound state of the nitrosyl fluoride molecule which lies approximately 2.4 e.v. above the ground state. In the valence-bond representation of this state a single electron is localized in a 2p orbital on fluorine. Residual orbital angular momentum resulting from the mixing of this state with the ground state in the applied magnetic field can account, at least qualitatively, for a large paramagnetic contribution to the shielding of the fluorine nucleus.

A quantitative estimate of this shielding, σ_p, can be made using the expression of Saika and Slichter [J. Chem. Phys., 22, 26 (1954)]. Taking ΔE_{Av} 2.4 e.v. and Pauling's estimate of the ionic character I = 0.50 and using values given by Saika and Slichter for the other parameters in their expression, we find $\Delta\sigma_p$ = -780 p.p.m. relative to free fluoride ion. This may be compared with the experimental value of -690 p.p.m. for the shift between nitrosyl fluoride and aqueous hydrogen fluoride.

Sincerely yours,

John R. Holmes
John R. Holmes
Research Chemist

Burch B. Stewart
Burch B. Stewart
Research Chemist

James S. MacKenzie
James S. MacKenzie
Manager-Special Projects

Koninklijke / Shell - Laboratorium, Amsterdam
Badhuisweg 3 Amsterdam-N.
Telefoon 61111

Amsterdam, 12th November 1962

Dear Dr. Shapiro,

An nmr investigation has been made of the systems anhydrous hydrogen fluoride/ethyl alcohol and anhydrous hydrogen fluoride/acetone, from which the dissociation of the acid can be deduced. The ion HF_2^- is found to possess remarkable magnetic properties.

The magnetic shielding of hydrogen in concentrated acid/water mixtures is dependent on the molar ratio of the components. This fact has been used[1,2] to interpret these systems; in particular one may thus determine the dissociation constant of the acid and the chemical shift of the H_3O^+ ion. The interpretation of the data is not always unambiguous and different authors arrive at different conclusions[3].

The nmr data of the systems HF/ethyl alcohol and HF/acetone can be handled in a straightforward manner. The spectrum of the former system shows apart from the ethyl group a combined signal of hydrogen in HF, HF_2^-, OH and OH_2^+, fused together by chemical exchange. The shielding of the CH_2 group in $C_2H_5OH_2^+$ is 1.1 ppm smaller than in C_2H_5OH (1.4 ppm for the methyl group in acetone). The concentration ratio $(C_2H_5OH_2^+)/(C_2H_5OH)$ and an estimate of the dissociation constant can be obtained from the chemical shift of the CH_2 group in an unambiguous manner (see Figure).

The behaviour of the fused line (see Figure) is interesting since it shows a pronounced maximum. This is obviously caused by the small magnetic shielding of $C_2H_5OH_2^+$ or $(CH_3)_2COH^+$ and HF_2^- ions. This is in agreement with the shift to low field of the solvent peak when H_2O or KF is added to HF.

The chemical shifts of H_3O^+, and $C_2H_5OH_2^+$ and $(CH_3)_2COH^+$ have been measured previously[4] so that the shift of the HF_2^- ion can be deduced. We consistently find a value of -22 ppm from C_6H_{12}, which is unusually low. It may be compared with chemical shifts of other ions in HF at -70°C (internal reference: C_6H_{12}):

HF	- 7.5 ppm	$H_2O.C_2H_5^+$	- 8.9 ppm
HF_2^-	- 22 "	$HO.C(CH_3)_2^+$	- 13.2 "
H_3O^+	- 9.4 "	H_2F^+	- 13 "

In the protonated species in the table the hydrogens carry a positive charge which will cause an additional shift to low field. The electron density on the hydrogen in the negatively charged FHF^- ion cannot be expected to be lower than the one in the HF molecule[5]. One possibility is that the small shielding is caused by second-order paramagnetism in the ion. Preliminary susceptibility measurements in KHF_2 single crystals have not revealed an anisotropy in the susceptibility larger than 10%. Moreover, the molar diamagnetic susceptibility value seems to conform to Pascal's rules.

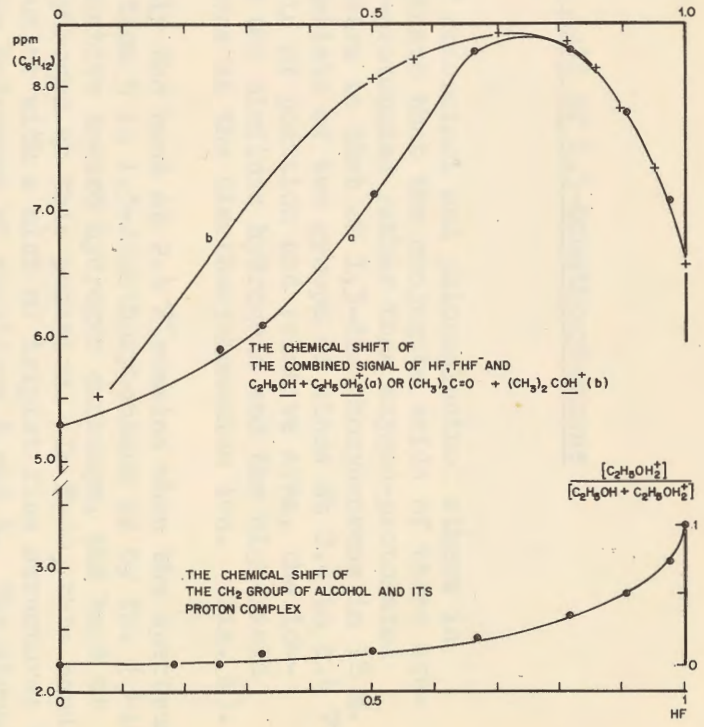
Qualitatively the smallness of the magnetic shielding is in line with the exceptionally small FHF distance of 2.26 Å.

In a solution of H_2O in HF (8.8 mole %) the fluorine resonance is shifted to low field over 335 c/s at 40 Mc/s. This again must be due to the HF_2^- ion and implies a fluorine shift of -23 ppm with respect to pure HF.

Yours sincerely,

E. L. Mackor C. MacLean

References
1 H.S.Gutowsky and A.Saika, J.Chem.Phys. 21 (1953) 1668.
2 G.C.Hood, O.Redlich and C.A.Reilly, J.Chem.Phys. 22 (1954) 2067 and 27 (1957) 1126.
3 R.J.Gillespie and R.F.M.White, Can.J.Chem. 38 (1960) 1371.
4 C.MacLean and E.L.Mackor, J.Chem.Phys. 34 (1961) 2207.
5 G.Bessis and S.Bratož, J.chim.phys. 57 (1960) 769.
E.Clementi, J.Chem.Phys. 34 (1961) 1468.



THE RELATIVE CONCENTRATION OF THE PROTON COMPLEX OF ETHYL ALCOHOL IS PLOTTED ON THE RIGHT-HAND SCALE OF THE LOWER GRAPH.

The Conjugate Acid of 1,3-Dimethoxybenzene

The proton NMR spectra of resorcinol and phloroglucinol ethers in concentrated mineral acids indicate that the conjugate acids of these substances are principally carbon-protonated rather than oxygen-protonated species. Typical of these spectra is that of 1,3-dimethoxybenzene in 18 M. sulfuric acid (Fig. 1). It consists of two groups of lines at 2.4 to 3.4 τ and 5.5 to 5.9 τ. On the basis of position and relative area, the low-field group can be assigned to the olefinic hydrogens and the high-field group, to the aliphatic hydrogens in the dimethoxyphenonium ion. (Fig. 1).

Of the olefinic group, only the band at 2.4 τ remains when the spectrum is taken in D_2SO_4. Since position 5 in 1,3-dimethoxybenzene is by far ($>10^6$) the aromatic position least reactive toward hydrogen exchange, the band at 2.4 τ can be assigned to the hydrogen at this position. In H_2SO_4 this band is an incompletely resolved doublet with a hint of triplet fine structure; this is the expected splitting by the hydrogens at positions 6 and 4. The signal from the hydrogen at position 2 should be unsplit whereas that from the hydrogen at position 6 should be a doublet. On this basis, the single line at 3.4 τ can be assigned to the 2-hydrogen and the doublet at 2.9 τ, to the 6-hydrogen. There are two methyl group resonances at 5.5 and 5.6 τ as is to be expected from the non-equivalent methoxyl groups in this unsymmetrical ion. Positive charge density in phenonium ions is known to be greatest at the position para to the protonation site, and the low-field line can be reasonably assigned to the methoxyl group at position 1. Since the line at 5.9 τ disappears in D_2SO_4 and since this is the only band with a relative area of two, it can be assigned to the methylene group at position 4.

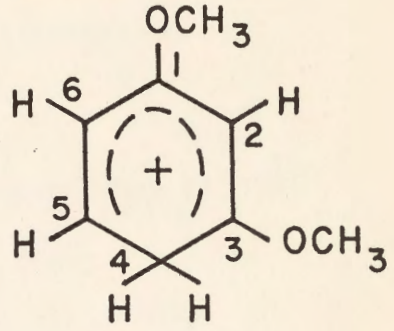
Lowering the concentration of sulfuric acid alters this spectrum. In progressively weaker acids the methylene and 6-hydrogen bands broaden and then disappear, the methoxyl bands broaden, merge, and then become a sharp single line, and the 5-hydrogen band loses its fine structure. These changes can be attributed to an increasing rate of exchange at the 4-and 6-positions. At slightly lower acid concentrations, the 2-hydrogen signal also broadens. This indicates that exchange at the 2-position is slower than exchange at the 4- and 6-positions at any given acidity. Exchange rates estimated in the usual way from these spectral changes are consistent with rates predicted from tritium exchange experiments done at lower acidities.

1. Line positions are with respect to tetramethyl silane and were measured using tetramethylammonium chloride (6.70 τ) as internal reference.

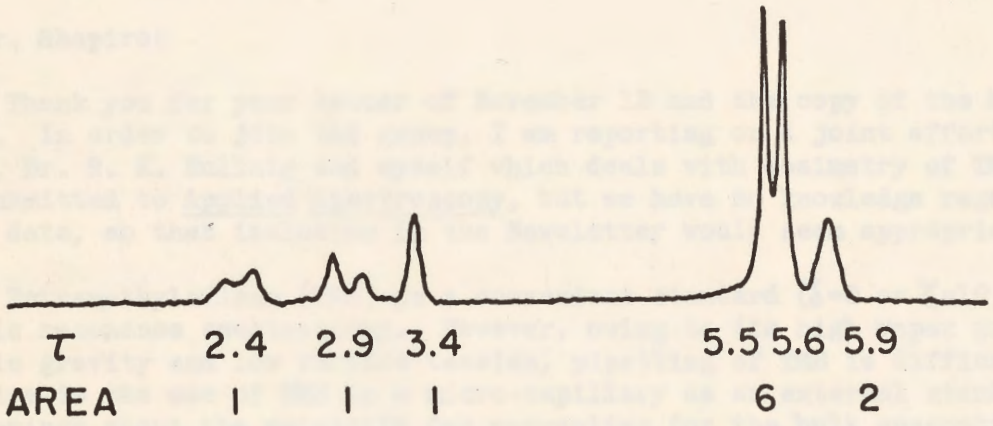
2. The shoulder on the up-field side of the 5.6 τ line is caused by methanol produced by gradual hydrolysis of dimethoxybenzene.

A. J. Kresge
Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois

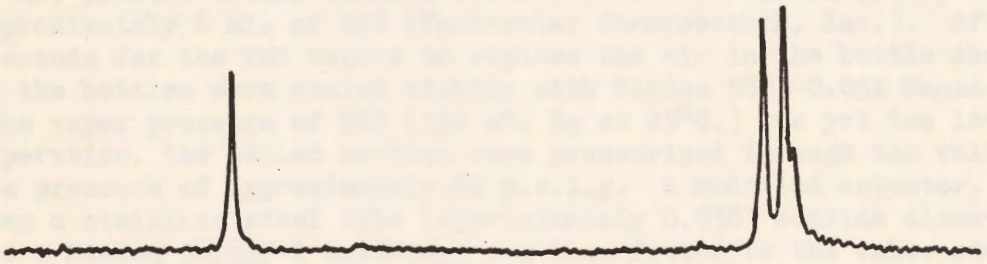
Y. Chiang
Union Carbide Research Institute, Tarrytown, New York



DMB IN 18 M. H_2SO_4



DMB IN 18 M. D_2SO_4



STERLING-WINTHROP RESEARCH INSTITUTE
A DIVISION OF STERLING DRUG INC.
RENSSELAER, NEW YORK

November 19, 1962

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Thank you for your letter of November 12 and the copy of the MELLONMR Newsletter. In order to join the group, I am reporting on a joint effort by Dr. W. G. Gorman, Dr. R. K. Kullnig and myself which deals with dosimetry of TMS. This has been submitted to Applied Spectroscopy, but we have no knowledge regarding publication date, so that inclusion in the Newsletter would seem appropriate.

Tetramethylsilane (TMS) is a convenient standard (δ=0 or τ=10) in nuclear magnetic resonance spectroscopy. However, owing to its high vapor pressure, its specific gravity and low surface tension, pipetting of TMS is difficult. The alternative is the use of TMS in a micro-capillary as an external standard. This again brings about the necessity for correcting for the bulk susceptibility, which differs from solution to solution.

Workers in the field have resorted to "doping" of solvents, but again the high partial pressure of TMS results in its rapid loss from the solvent. We have, therefore, sought means of adding reasonably reproducible amounts of TMS to individual solution samples of ca. 0.5 ml.

Pressurized vials of TMS were prepared in the following manner. Clean, dry, 10 ml. plastic coated aerosol bottles (Wheaton S-32-F1 clear) were filled with approximately 6 ml. of TMS (Peninsular Chemresearch, Inc.). After allowing a few seconds for the TMS vapors to replace the air in the bottle above the TMS liquid, the bottles were sealed tightly with Risdon 5883-0.05X Magna-Meter valves. Since the vapor pressure of TMS (700 mm. Hg at 25°C.) was yet too low for adequate valve operation, the sealed bottles were pressurized through the valve with nitrogen to a pressure of approximately 80 p.s.i.g. A modified actuator, prepared by attaching a stainless steel tube (approximately 0.058" outside diameter and 1.5" long) to a Risdon 5618EF-1 actuator; was then fitted to the valve stem. The actuator tube was bent downward, about 60° below horizontal, so that it could be readily inserted into an upright sample tube. Actuation of the valve then delivered a metered quantity of TMS through the actuator tube into the sample tube. With these units, an average of 60 $\pm$ 10 mg. of TMS can be discharged into the sample tube with each valve actuation.

After adding TMS to the tube, mixing by up-ending is rapid and the sample is ready for insertion into the probe.

We shall look forward to receiving this useful bulletin.

With best regards,

Sincerely yours,

F. C. Nachod

FCN/ga

F. C. Nachod

Battelle Memorial Institute

505 KING AVENUE COLUMBUS 1, OHIO

AREA CODE 614, TELEPHONE 299-3191

November 21, 1962

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Barry:

The M.E.L.L.O.N.M.R. readers, who do not have an IBM 7090 or comparable computer at their disposal, might be interested in the modifications which we have made in Freqint IV, with the aid of the Bendix people, so that we could use this program on our Bendix G-20 computer.

The basic difference in the two computers is that of storage - with our G-20 having about 8000 words which is only one-fourth the storage capacity of the 7090.

The first dimension statement in Freqint IV requires slightly more than 10,000 words. This alone precludes its use, in its present form on our G-20. More important than this, however, are the inherent differences between the two computers which would require some translation even though adequate storage was available.

In order to get Freqint IV to run on the Bendix G-20 version of Fortran, the following changes are required:

(1) Remove all 7090 control cards.

(2) Separate the subroutines and the main program.

(3) Insert Bendix Space System control cards and Bendix Fortran control cards in front of the subroutines and the main program. Exact instructions for this procedure are given in Bendix Manuals BPB-002 and BPB-004.

(4) Compile and load the subroutines onto a Bendix Systems tape.

(5) Compile and execute the main program which will call the subroutines from tape as required.

At this point one has the option of either having the compiled program punched on cards so that future runs will not require recompilation or of storing the compiled program on magnetic tape.

The Fortran program itself was not changed except for making the control card changes noted above and reducing the dimension statements to correspond to that of a four-spin system, so that our G-20 could handle the storage requirements.

In addition to the sample calculation furnished with the program, we have repeated the calculations of Reilly and Swalen, J. Chem. Phys., 32, 1378 (1960), and have obtained excellent agreement with the given results in both cases.

It should not be inferred that one is limited to four spins using this variation of Freqint IV with a Bendix G-20 computer. We see no reason why the general seven-spin system could not be solved by subdividing the calculation into several parts and treating each part as a separate problem.

I hope this will keep our subscription open.

Best personal regards,

Tom

Thomas F. Page, Jr.
Research Chemist
Molecular Spectroscopy

TFP:ajk

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

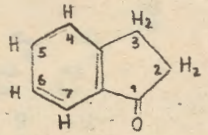
ADDRESS REPLY TO
NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

November 23, 1962

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Barry,

Let me report another example of a $-CH_2-CH_2-$ proton spectrum which could be analyzed quite completely. It is the aliphatic portion of the spectrum of 1-indanone. The low-field wing (see Fig. 1) whose fine structure is washed out by coupling with the benzene ring protons, presumably belongs to the 3-protons which are closer to the benzene ring than the 2-protons.



The analysis of the spectrum is based on the assumption that there is only one relative chemical shift between 2- and 3-protons, which in turn more or less implies that the five-membered ring is planar. The aliphatic protons constitute an A_2B_2 or A_2X_2 system whose A-part (3-proton lines) is perturbed by coupling with benzene ring protons. On account of recent developments, geminal and vicinal J's were taken to be of opposite signs. The assignment of lines expressible in closed form is shown in Fig. 2. The final fitting of the spectrum, especially for $|J'_{gem} + J''_{gem}|$ was done with the Frequint III program.

For the 60 mc spectrum, the resulting parameters are, in cps:

$1/2|\omega_3-\omega_4| = 16.0 \pm 1.5$

$J'_{gem} = \mp 15.5 \pm 1.5$ and $J''_{gem} = \mp 17.3 \pm 1.5$, subject to $|J'_{gem} - J''_{gem}| = 1.8$.

$J'_{23} = \pm 3.6 \pm 0.1$ and $J''_{23} = \pm 9.2 \pm 0.1$.

The relatively large uncertainty in the chemical shift is due to the fact that the center of the A_2B_2 spectrum is not accurately defined, because the two halves are not exactly superimposable. The high-field wing can be reproduced quite well within a 10% variation of the chemical shift.

The difference in sign of vicinal and geminal J's is now observed here in a spin system where the J_{gem}'s are between 'truly' equivalent protons. As can be seen from the two computed spectra (Fig. 2), the existence of this difference must be concluded not so much from the intensities, but from the line positions.

The J_{gem}'s, although not equal, are compatible with the data presented and the predictions made by Barfield and Grant (MELLONMR 48): J_{gem}'s for protons with one adjacent π-bond fall in the neighborhood of -14.5 ± 1 cps.

An assignment of the J_{23}'s can be ventured with the aid of Karplus' expression for J_{vic}'s. With the assumption of eclipsed cis-protons and tetrahedral bond angles on the aliphatic carbons, one obtains for

$$\frac{J_{cis}}{J_{trans}} = \frac{9.15}{3.65} \approx \frac{A_1\cos^2\phi_{cis}}{A_2\cos^2\phi_{trans}} \approx \frac{A_1}{A_2 \cdot 0.3}$$

whence $A_2 = 1.3\ A_1$, quite in accord with previous observations that the branch for $\pi > \phi > \pi/2$ is steeper than that for $\pi/2 > \phi > 0$.

I trust that this contribution will renew my subscription to MELLONMR which vivat, crescat et floreat. The same to you!

Best regards,

Ernest

Ernest Lustig

Fig. 1. Aliphatic Bands of 1-Indanone Spectrum (20% CS_2 Solution)

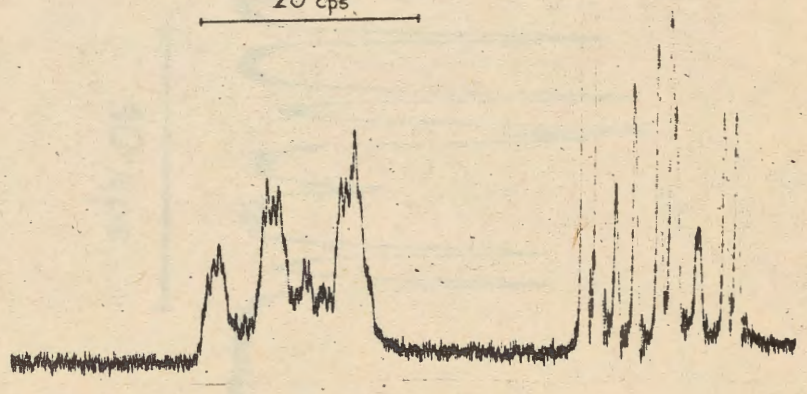
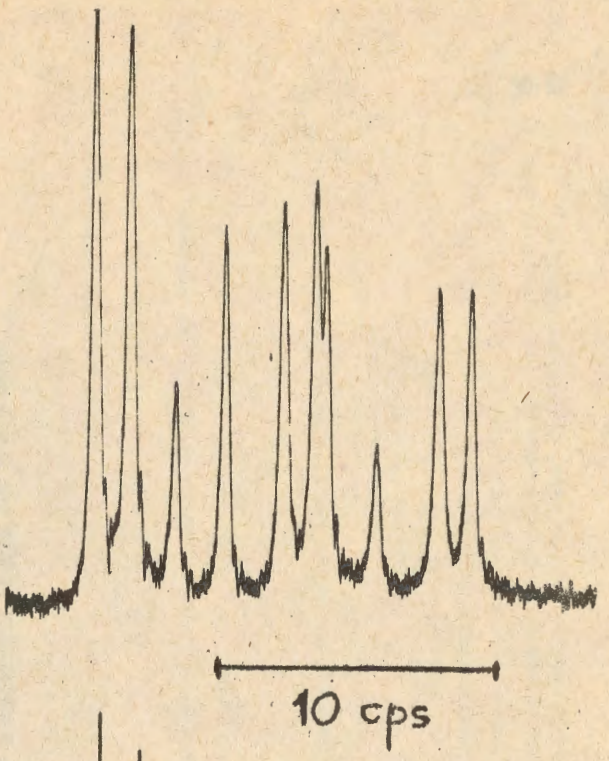


Figure 2.

a) Observed Spectrum (20% CS_2 Solution)



b) Computed for $|\omega_2-\omega_3|$ = 31.0 cps

J'_{gem} = -15.5 cps J'_{23} = +9.15 cps

J''_{gem} = -17.3 cps J''_{23} = +3.65 cps

c) Computed for $|\omega_2-\omega_3|$ = 31.0 cps

J'_{gem} = +15.5 cps J'_{23} = +9.15 cps

J''_{gem} = +17.3 cps J''_{23} = +3.65 cps

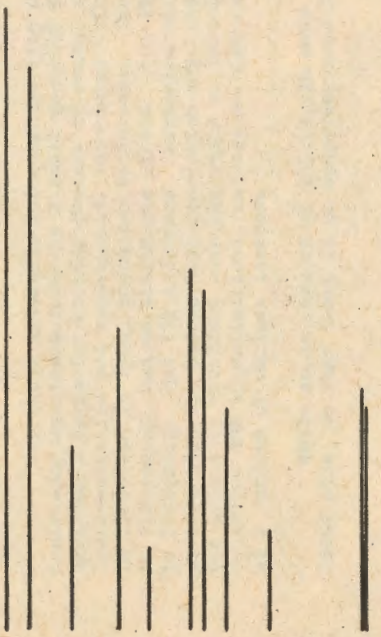


Fig. 2. High-field Band of Aliphatic Portion of 1-Indanone Spectrum

4TH OCEANS

ANNOUNCEMENT

The Fourth Omnibus Conference on the Experimental Aspects of Nuclear-magnetic-resonance Spectroscopy (4th OCEANS) will be held at Mellon Institute in Pittsburgh, Pennsylvania, on Thursday, Friday, and Saturday, February 28 to March 2, 1963. (The up-front addition of "Omnibus" to last year's conference name has resulted in the puckered title, OCEANS, easier both to say and to write; the urge to call this the Winter Mellon Festival has been thus far resisted.)

The program, as outlined on the accompanying sheets, will consist of twelve 90 minute sessions, presided over by NMR spectroscopists of world renown, and covering practically every phase of experimental NMR.

4th OCEANS has been purposely scheduled to immediately precede the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (PCACAS), which will be held March 4 to 8. The considerable number and variety of NMR papers to be presented at PCACAS have been specially arranged for Monday, March 4, as a convenience for persons wishing to attend both OCEANS and PCACAS.

For those presently unacquainted with OCEANS, this conference was inaugurated by a small group of NMR spectroscopists desiring a forum for keeping abreast of recent advances in instrumentation and experimental techniques. The first meeting, in Cleveland in 1960, attracted 44 persons. The 1961 meeting, in Pittsburgh, had an attendance of 118. The 1962 meeting, also in Pittsburgh, had 150 attendees. Beginning with a strong predilection for proton high-resolution NMR, the scope of OCEANS has gradually broadened over the years to include pulse and broadline NMR investigations, as well as high-resolution studies of a variety of nuclear isotopes.

While an attendance of 150 is, in many respects, an ideal size, so that there is no desperate need for OCEANS to

continue to expand numerically, still it is to be hoped that no interested NMR experimentalist will miss 4th OCEANS because of lack of knowledge of its existence. Hence, this announcement in MelloNMR. Communication being a fragile web, readily ruptured under the best of circumstances, your cooperation in spreading the word to your brethren will be very much appreciated.

Thank you.

The 4th OCEANS Committee

Dr. A. L. Allred
Dr. P. C. Lauterbur
Dr. T. F. Page, Jr.
Dr. J. N. Shoolery
Dr. C. W. Wilson, III, Chairman

P.S. Please do not overlook the accompanying sheet, which solicits contributed papers for 4th OCEANS.

4th OCEANS Program

Thursday, February 28, 1963

Morning

A-1 "New Broadline NMR Techniques, Problems and Applications"

Chairman: Dr. D. I. Bolef
Westinghouse Research Labs.
Pittsburgh, Pa.

A-2 "NMR in Solids Other Than Polymers"

Chairman: Dr. T. J. Rowland
Department of Metallurgy
University of Illinois, Urbana, Ill.

Afternoon

A-3 "NMR in Polymers (General)"

Chairman: Dr. D. W. McCall
Bell Telephone Labs.
Murray Hill, N. J.

A-4 "New NMR Applications; Overflow Papers and Miscellany"

Chairman: Dr. R. S. Codrington
Varian Associates,
Palo Alto, California

Friday, March 1, 1963

Morning

B-1 "NMR Instrumentation: Shortcomings and Maintenance"

Chairman: Dr. T. J. Flautt
Proctor & Gamble Miami Valley Labs.
Cincinnati, Ohio

B-2 "New Developments in NMR Instrumentation"

Chairman: Dr. E. B. Baker
The Dow Chemical Company
Midland, Michigan

4th OCEANS Program (Continued)

Afternoon

B-3 "High Resolution NMR in Polymers"

Chairman: Dr. F. A. Bovey
Bell Telephone Labs.
Murray Hill, N. J.

B-4 "NMR Relaxation Phenomena; Overflow Papers and Miscellany"

Chairman: Dr. S. Meiboom
Bell Telephone Labs.
Murray Hill, N. J.

Saturday, March 2, 1963

Morning

C-1 "Double Resonance"

Chairman: Dr. J. B. Baldeschwieler
Chemistry Dept.
Harvard University

C-2 "Non-H^1 NMR Spectra and Special Techniques"

Chairman: Dr. P. C. Lauterbur
as of Feb. 1, 1963 { Dept. of Chemistry
State Univ. of New York, Stony Brook, L.I., N.Y.
until Feb. 1, 1963 { Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Afternoon

C-3 "A-60 Type Instruments and Quantitative NMR Measurements"

Chairman: Dr. B. L. Shapiro
Mellon Institute
Pittsburgh, Pa.

C-4 "NMR Spectral Analysis; Overflow Papers and Miscellany"

Chairman: Dr. C. A. Reilly
Shell Development Company
Emeryville, California

Notes: 1) Each session lasts 90 minutes.

2) There are no simultaneous sessions.

3) The fourth and final session each day may be used in part to resume discussions cut short in earlier sessions.

4TH OMNIBUS CONFERENCE ON THE EXPERIMENTAL ASPECTS OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

To be held at: Mellon Institute, Pittsburgh, Pennsylvania
February 28 through March 2, 1963

Call For Contributed Papers

While invited papers recruited by the twelve session chairmen will comprise the major portion of the 4th OCEANS program, a substantial number of contributed papers are desired to insure the informality, the diversity of interest, the breadth of participation, and the timely pertinence of reports

that have characterized these conferences in the three previous years.

Accordingly, any interested NMR spectroscopist is hereby urged to submit a 10 minute contributed paper on any novel instrumentation or technique for the advancement of: (1) experimental measurements, (2) spectrometer maintenance, operation or calibration, (3) associated computations, (4) spectral interpretation, or (5) sample preparation.

To facilitate coordinating the program while keeping the door open for even last minute developments, the deadline for acceptance of contributed papers will be in two parts:

I. Prior to January 15, 1963, a specific and informative title of the intended paper is due. This will assist placement in the most appropriate conference session.

II. Prior to February 12, 1963, a 200 to 1000 word abstract or preprint of the paper is due. This should be neatly typewritten, suitable for photographic reproduction, and on not more than four 8-1/2 x 11 pages, including figures and tables. Such abstracts will be assembled, reproduced and multilithed for distribution at the conference.

The appropriate documents relating to contributed papers must be in the hands of the undersigned on or before the stipulated deadline dates in order to appear on the announced program.

Chas. W. Wilson III

Chas. W. Wilson, III, Chairman
Fourth OCEANS Committee
Research and Development Dept.
Union Carbide Chemicals Co.
South Charleston (3), W. Va.

RÉPUBLIQUE FRANÇAISE
PREMIER MINISTRE
COMMISSARIAT A L'ÉNERGIE ATOMIQUE

CENTRE D'ÉTUDES NUCLÉAIRES DE GRENOBLE
CHEMIN DES MARTYRS - GRENOBLE (ISÈRE)

ADRESSER LA CORRESPONDANCE :
BOITE POSTALE 269 - GRENOBLE

TÉL. 87-59-11 ET LA SUITE

M. B.L. SHAPIRO
Mellon Institute
4400 Fifth Avenue
PITTSBURGH 13

RÉFÉRENCE A RAPPELER : G/ MEL - 2

VOTRE RÉF. :

VOTRE LETTRE DU

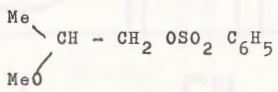
GRENOBLE, LE 3 Octobre 1962

NON EQUIVALENCE OF PROTONS OF A METHYLENE AT ROOM TEMPERATURE

F. Csakvary., D. Gagnaire. ; Laboratoire COP

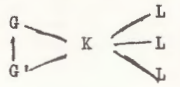
Cher Dr. Bothner-By,

Nous voudrions vous faire part ici, du résumé d'un article que nous sommes en train de publier (1) et qui met en evidence un empêchement de la libre rotation autour d'une liaison C-C à température ambiante. L'exemple étudié est le méthoxy-2 propanol-1 benzene sulfonate :



Le spectre du produit pur (sans solvant) montre le groupement méthoxy découplé ainsi que le groupement benzène, plus le spectre de protons couplés $CH_3 - CH - CH_2 -$

Nous avons étudié ce spectre, du type :

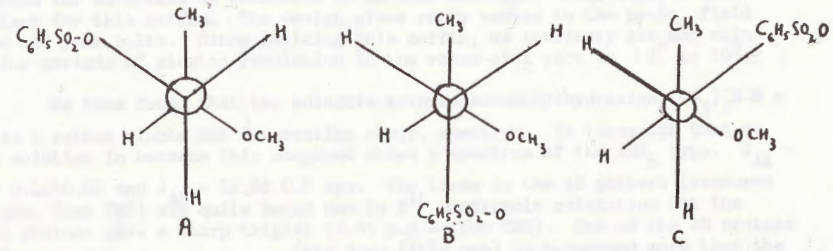


(couplages indiqués par les traits)

en developpant dans ce cas particulier (par ordre de grandeur du couplage) le traitement proposé par Pople (2). On met alors en évidence son ambiguité possible, la non équivalence des protons du groupement $-CH_2-$.

La construction d'un modèle permet de conclure à la necessité d'une entrave à la libre rotation, probablement par association entre les groupes C_6H_5. Ce phénomène disparait en solution dans CCl_4 (solution à 25 %) mais a été observé en étudiant le spectre de ce corps en solution dans le nitrotoluène (on observe dans ce cas la formation d'un complexe de transfert de charge, coloré, entre le benzène sulfonate et le solvant). Ceci permet de penser à une association de groupements benzènes qui génerait la libre rotation du groupement $\left[\begin{matrix}Me\\MeO\end{matrix}\!\!>\!CH\right]-\left[CH_2-OSO_2-\varphi\right]$.

Il devient alors possible d'attribuer une probabilité de présence aux 3 configurations suivantes :



On trouve, en utilisant l'expression donnée par Karplus (3) les probabilités suivantes : pour (A) 50 % ; pour (B) 0 ; pour (C) 50 %.

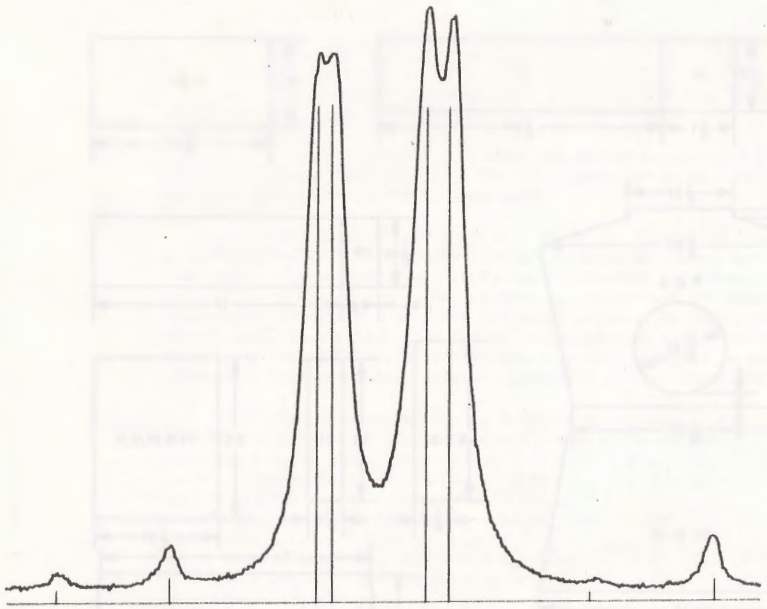
(1) Csakvary et Gagnaire : NMR et Stéréochimie, I (sous presse) J.Chim.Phys.
(2) Pople et Schaeffer : Molec. Phys. 3, (1960), 547.
(3) Karplus : J. Chem. Phys. 30, (1959), 11.
Voir aussi H.S. Gütowsky, G.G. Belford, P.E. McMAHON. J. Chem. Phys. (1962) 36. 3353.

Sincèrement votre,

F. Csakvary, D. Gagnaire,

Figure jointe : resonance des protons du CH2 avec le spectre theorique correspondant

50-13



Résonance du groupe CH_2 et spectre théorique

JET PROPULSION LABORATORY *California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California*

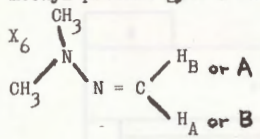
31 October 1962

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Barry:

At the last Mellon NMR meeting we described a "Styrofoam" coffin which we constructed around our magnet. Because we have had a number of requests for a description of this coffin, I thought that perhaps MELLON-M-R readers might be interested. We have found this to be much more satisfactory insulation than wooden boxes, pieces of plastic, shower curtains and the like. The price for materials is estimated to be less than $40. Fig. 1 and 2 show the plans for this coffin. The design gives ready access to the probe, field trimer and yoke bolts. Since building this coffin, we routinely get and maintain for periods of minutes resolution in the range of 1 part in 10^8 to 10^9.

We have found that the molecule methylenedimethylhydrazine $(CH_3)_2N\text{-}N = CH_2$ has a rather simple but interesting n.m.r. spectrum. It turns out that as a ~5% solution in benzene this compound shows a spectrum of the ABX_6 type. $J_{AX} = J_{BX} = 0.44 \pm 0.02$ and $J_{AB} = 12.0 \pm 0.2$ cps. The lines in the AB pattern (centered 5.98 ppm. from TMS) are quite broad due to N^{14} quadrupole relaxation but the methyl protons give a sharp triplet (2.55 p.p.m from TMS). One of the AB protons (the down field one) is broadened more than the other. The geminal proton coupling constant is rather large in magnitude for the $=C\begin{smallmatrix}H\\H\end{smallmatrix}$ type.



$J_{AB}^{\pm}$; $J_{AX}^{\mp}$; $J_{BX}^{\mp}$

I think that the long-range coupling observed here is the first one ever found through two nitrogen atoms! Double resonance studies showed the long range couplings to be of different sign than the geminal coupling.

Sincerely,

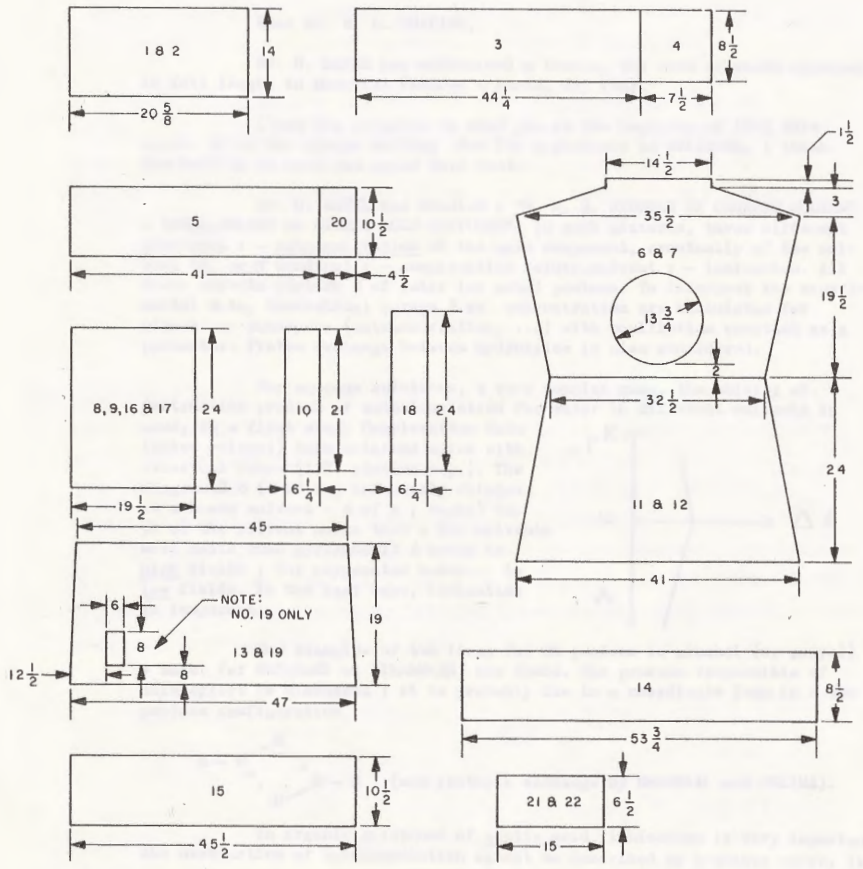
JET PROPULSION LABORATORY

Stan
Claude D Pearce

Stanley L. Manatt
Claude D. Pearce

SLM/CDP:jas
Air Mail

Sylvan 0-6811 Murray 1-3661 Twx 7486u



ALL DIMENSIONS IN inches

NOTE:

A - MATERIAL, 3 in. STYROFOAM

B - ASSEMBLED WITH 1/4 in. WOODEN DOWLES

C - ALL SEAMS COVERED WITH 2 IN. MASKING TAPE

FIG 2

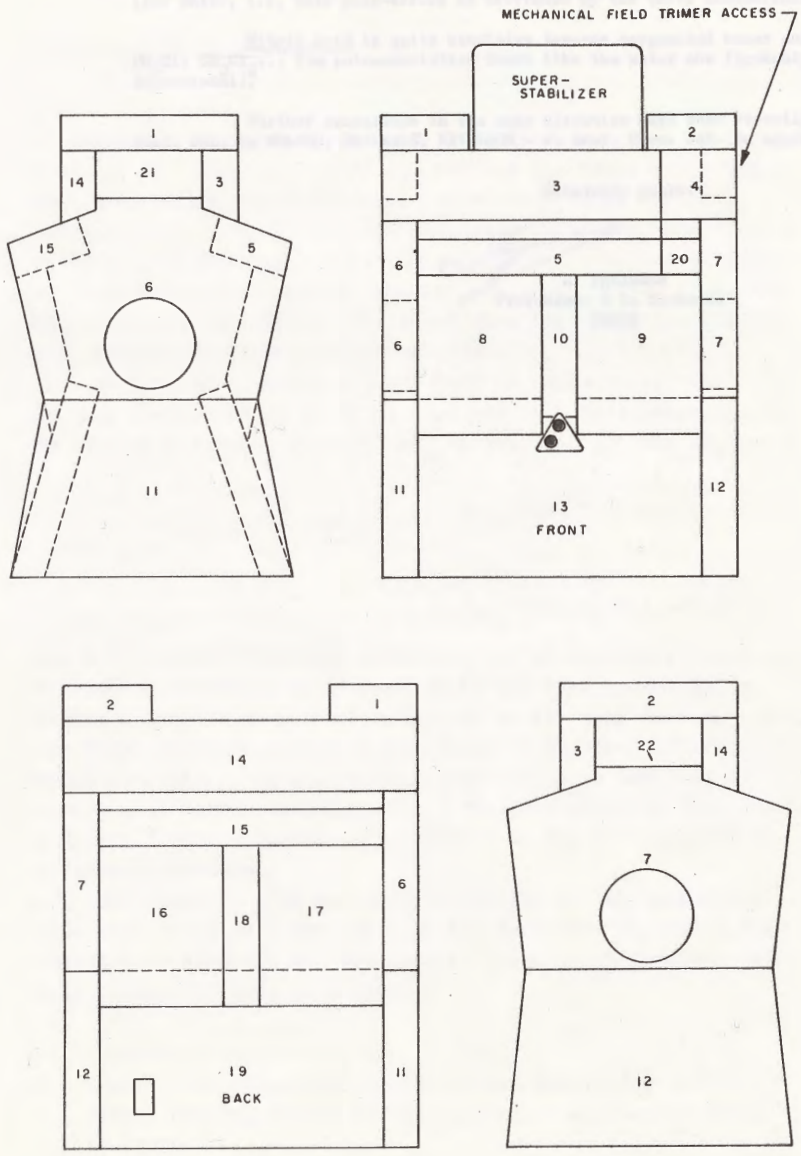


FIG 1

LABORATOIRE DE SPECTROSCOPIE HERTZIENNE
ANNEXE DU
LABORATOIRE DE RECHERCHES PHYSIQUES A LA SORBONNE
1, RUE VICTOR COUSIN, PARIS-V•

620/RF/MNF

PARIS, LE 12 novembre 1962
ODéon 24-15 POSTE 484

Dr. B. L. SHAPIRO
MELLON INSTITUTE
4400 Fifth Avenue
PITTSBURGH 13
Pennsylvanie
U. S. A.

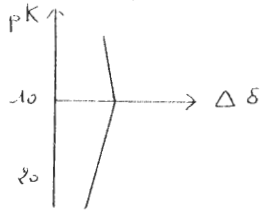
Dear Dr. B. L. SHAPIRO,

Dr. G. MAVEL has maintained a thesis, the text of which appeared in full length in Memorial Poudres - Paris, 43, 1961.

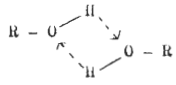
I had the occasion to send you at the begining of 1962 this paper. As we are always waiting for its appearance in MELLONMR, I think the best is to send you again this text.

Dr. G. MAVEL had studied : "N. M. R. STUDIES OF ORGANIC SOLVENT + WATER, ACETIC OR NITRIC ACID MIXTURES". In such mixtures, three different phenomena : - autoassociation of the main component, eventually of the solvent (H. or π bonding) ; - complexation solute.solvent ; - ionization. All these effects perturb δ of water (or acid) protons. To interpret the experimental data, theoretical curves δ vs. concentration are calculated for elementary phenomena (autoassociation, ...) with equilibrium constant as a parameter. Proton exchange between hydroxyles is also considered.

For aqueous solutions, a very complex case, the unicity of destruction process of autoassociation for water in different solvents is used, in a first step. Complexation data (water solvent) then obtained agree with classical ideas (I.R. studies esp.). The diagram Δ δ (δ of w ; infinetely diluted in a basic solvent - δ of w ; vapor) vs. pK of the solvent shows that ; for solvents more basic than pyridine Δ δ moves to high fields ; for oxygenated bases... to low fields. In the last case, ionization is inoperant.



New examples of two lines for OH protons in alcohol (or polyol) + water (cf WEIMBERG et ZIMMERMAN) are found. The process responsible of this effect is discussed ; it is probably due to a coordinate jump in a two protons configuration



(see isotopic exchange by BRODSKII and SULIMA).

In organic solutions of acetic acid, ionization is very important ; the destruction of autoassociation cannot be described by a unique curve, it

is strongly dependant of complexation solute - solvent. The linear and cyclic kind of polymerization of ac. acid is probably the origin of such an occurence (for water, i.e, this side-effect is decreased by the three dimensional array)

Nitric acid is quite sensitive towards oxygenated bases and even CH_3Cl, CH_2Cl_2... Its autoassociation looks like the water one (probably three dimensional).

Further researches in the same direction have been recently published, esp. by HOLMES, DAINKARD, KIVELSON - J. Amer. Chem. Soc. to appear.

Sincerely yours.

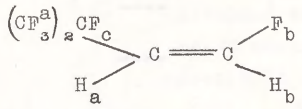
R. FREYMANN
Professeur à la Sorbonne
PARIS

50-16

^{19}F Coupling Constants in Alkenes

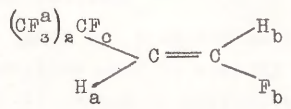
by N. Boden, J.W. Emsley, J. Feeney and L.H. Sutcliffe.
Donnan Chemical Laboratories, Liverpool University.

We have measured the ^1H and ^{19}F resonance spectra of the fluorinated alkene (I) obtained at 56.4 Mc/s : the chemical shifts and coupling constants extracted from a first order analysis of the spectra are given in the table. The molecule



(I)

was confirmed to be the cis isomer by the presence in the ^1H spectrum of a J_{HH} splitting 5.9 c/s characteristic of cis H-H coupling in olefinic systems[1]. In vinyl fluoride[2], the value of J_{HH} cis is 4.7 c/s. On this basis $J_{H_aF_b}$ (=36.9 c/s) can be assigned unambiguously to the trans H-F coupling constant. Usually this type of assignment cannot be made without appealing to some other physical technique to establish the isomeric form. A preliminary investigation of the trans isomer (II) has also been made and a value for the J_{HF}cis



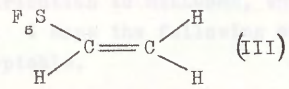
(II)

$J_{H_aF_b}$ = 16.2 c/s
$J_{H_bF_c}$ ~ 0 c/s
$J_{F_bF_c}$ = 5.5 c/s

coupling constant obtained (16.2 c/s).
Comparing our values of J_{HF} trans and J_{HF} cis with those previously reported strongly suggests that the former is always larger than the latter. A similar conclusion can be reached from the work

of Banwell and Sheppard[2] who made a detailed analysis of vinyl fluoride but their values of J_{HF} cis and J_{HF} trans (20.1 and 52.4 c/s respectively) are much larger than those normally encountered. Considering now the coupling between the fluorine nucleus (F_c) attached to the tertiary carbon atom and a hydrogen or fluorine nucleus on the terminal ethylenic carbon atom, the cis F-F coupling constant is larger than the trans whereas for H-F coupling the situation is reversed.

We have also examined the ^{19}F and ^1H spectra of vinyl sulphur pentafluoride (III) at 40.0 and 56.4 Mc/s respectively as part of a general study of SF_5 derivatives[3]. The SF_5 group



(III)

J_{HF_B} gem = 6.1 c/s
J_{HF_B} cis ~ 0 c/s
J_{HF_B} trans= 2.3 c/s.

has a tetragonal pyramidal structure and is therefore comprised of four magnetically equivalent basal fluorine nuclei and a single apical fluorine nucleus giving an AB_4 spin system. Only the basal fluorine nuclei couple with the hydrogen nuclei in the vinyl fragment. Again, the J_{HF} trans coupling constant is numerically larger than J_{HF} cis. The generality of this finding suggests that any spatial contribution to the H-F coupling is of minor importance.

Obviously, a good molecule to include in the comparison made here is $CF_3CH = CH_2$: we have not been able to obtain this compound so we would be delighted if anyone could provide us with either NMR data or a sample.

1. Schaefer, Can.J.Chem., 40, 1, (1962).
2. Banwell and Sheppard, Proc.Roy.Soc., A263, 136, (1961).
3. Boden, Emsley, Feeney and Sutcliffe, Trans.Faraday Soc., in press.

Coupling Constants	From ^{1}H Spectrum	From ^{19}F Spectrum
$J_{H_aH_b}$	5.9 ± 0.1 c/s	---- c/s
$J_{H_bF_c}$	2.1 ± 0.1	2.1 ± 0.1
$J_{H_bF_b}$	77.2 ± 0.2	77.3 ± 0.1
$J_{H_bF_a}$	~0	----
$J_{H_aF_a}$	0.62 ± 0.07	----
$J_{H_aF_c}$	22.8 ± 0.3	22.7 ± 0.5
$J_{H_aF_b}$	36.9 ± 0.2	37.0 ± 0.2
$J_{F_aF_c}$	----	7.6 ± 0.3
$J_{F_bF_c}$	----	31.0 ± 0.3
$J_{F_aF_b}$	----	5.8 ± 0.2

Chemical Shifts.

τ_{H_a} = 5.10 ± 0.01; τ_{H_b} = 3.40 ± 0.01 ppm

δ_{F_a} = 1.82 ± 0.01; δ_{F_b} = 32.6 ± 0.3; δ_{F_c} = 108.9 ± 0.9 ppm from CF_3OOH external reference: positive shifts are to high fields of the reference signal.

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

(Faculty of Technology in the University of Manchester.)

MANCHESTER 1 · TELEPHONE CENTRAL 3266

Department of Chemistry

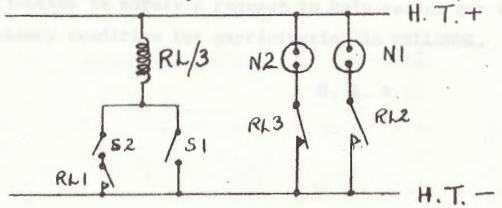
7th November, 1962.

Dr. B. L. Shapiro,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, 13,
Pennsylvania,
U. S. A.

Dear Barry,

Please accept my apologies for the delay in sending my contribution to MELLONMR, which we find very interesting and useful. I hope the following small items of information will be acceptable.

1. We have fitted a Slow Sweep Direction Indicator to our AEI Spectrometer. The indicator shows (a) the direction of the current sweep, and (b) the direction last swept when the sweep toggle switch is in the OFF position. Perhaps we are more forgetful than other operators (or perhaps more visitors interrupt our operation) but, with this device, we find we lose the signal less frequently. The modification is extremely simple and is basically as follows. Clearly, it may be fitted to any instrument.



RL/3 is a three contact relay. The contacts are: RL1 and RL2, normally open; RL3, normally closed.
S1, S2 are spare contacts on the INCREASE-OFF-DECREASE toggle switch on the Slow Sweep Unit.
N1, N2 are neon indicators mounted on the INCREASE and DECREASE sides, respectively, of the toggle switch.
The sequence of changes is as follows:

Toggle position	S1	S2	Neon lit
Increase	Closed	Closed	N1
Off (following Increase)	Open	Closed	N1
Decrease	Open	Open	N2
Off (following Decrease)	Open	Closed	N2

arranged according to spare contacts available

2. We are currently investigating the disymmetry of the X absorption in ABCX, ABCDX, A_2B_2X systems. Such dissymmetry must arise whenever Hamiltonian sub-matrices of higher order than 2 are involved. I may be wrong but I suspect that this expectation has not been sufficiently emphasised previously. Some people may therefore be under the misapprehension that absorption due to a nucleus or a group of chemically-equivalent nuclei, isolated in chemical shift from all others, should be symmetrical despite other complexities.

3. Is there not a strong case now for an examination of the symbolism used to specify the type of magnetic system?
(a) If we are to persist with the Pople, Bernstein and Schneider symbolism (ABX, A_2B_2 etc.) - and personally I am not convinced that we necessarily should- could we have some standardisation on the letters to be used for third and subsequent chemical shift regions. Unfortunately, Reilly

and Swalen have monopolised K and L for other purposes, so presumably we will have to manage without these (except for the special purpose).
(b) May we also be uniform about the significance of primed letters. Do these signify magnetic inequivalence or accidentally equal chemical shifts?

Kind regards,

Yours sincerely,

J. Lee

A Reminder to Contributors Who Send In Copies of Their Contributions

Contributors who send in 200 copies of each page of their contribution are reminded that if the contribution consists of more than one page, these pages should not be gathered or stapled. Gathering, etc., makes our collation procedure much longer and hence more expensive. Contributors are also reminded that to be of use for us, the 200 copies must be on 8-1/2" x 11" paper. Finally, it might be repeated that the providing of 200 copies of a contribution is merely a request to help reduce our costs, and is in no way a necessary condition for participation in MELLONMR.

B. L. S.

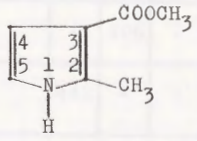
Dr. C. von Planta
Dr. A. Furlenmeier
Dr. B. Vaterlaus
c/o F. Hoffmann-La Roche & Co.
Limited Company
B a s l e / Switzerland

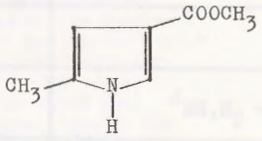
Basle, November 8, 1962

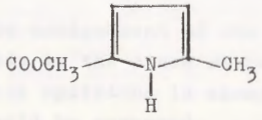
Dr. B.L. Shapiro
Mellon Institute
4400 Fifth Avenue
PITTSBURGH 13, Pennsylvania

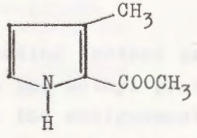
Dear Dr. Shapiro:

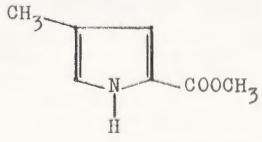
We have studied the NMR spectra of the 6 possible isomers of methyl-carbomethoxy-pyrrols in $CDCl_3$ solution of the same concentration (10 % of weight).

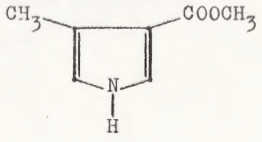
1. 

2. 

3. 

4. 

5. 

6. 

The signals of the ring protons (2-5) are split due to spin spin interaction of the ring protons with themselves and with the NH proton giving an ABX spectrum for the 3 proton system. The analysis of the spectrum is impossible because of the quadropole broadening of the NH signal which does not allow the determination of the AX and BX coupling constants. Therefore we prepared the corresponding acids which were soluble in a 1n solution of NaOD in D_2O. In this solution the NH protons are decoupled from the ring protons by chemical exchange and the analysis of the corresponding AB spectrum is straightforward revealing the coupling constants of the ring protons of the acids. If we assume that these coupling constants are the same in the methyl esters, we obtain from their spectra approximately the coupling constants of the NH protons with the ring protons but only of those which are in a position on the ring where the signal is not further split by long range spin spin interaction with the methyl protons.

The following two tables give the chemical shifts of the methyl groups and the spin spin coupling constants J (cps) of the ring protons.

Chemical shifts of the methyl signals

on cps from TMS at 60 Mcps.

compounds No.	cps
1	150
2	134
3	137
4	141
5	126
6	138

Chemical shifts and spin spin coupling constants

of the ring proton signals in cps.

compound No.	H_2	H_3	H_4	H_5	$J_{H,H}$	J_{NH,H_x}
1	-	-	394	394	not measurable	$J_{NH,H_5} = J_{NH,H_4} = 2.5$
2	438	-	378	-	2	$J_{NH,H_2} = 3$
3	-	356	411	-	3.5	$J_{NH,H_4} = 2.5$
4	-	-	365	409	2.5	$J_{NH,H_5} = 2.5$
5	-	406	-	403	1	-
6	442	-	-	392	2	$J_{NH,H_2} = 3.5$

The assignement of the signals to the corresponding protons can be made in the cases where one signal is split by the methyl protons. This splitting is absent in case 1 and 5 where the assignement could be reversed.

We thought this information might be of interest to chemists working in the field of natural products and thank you kindly for sending us Mellon MR.

Yours very truly,

C. H. Plattner

G. Fuhrmann

V. v. Balaban

Research Department
F. HOFFMANN-LA ROCHE & CO.
Limited Company

Pa/ar

50-21

THE UNIVERSITY OF TEXAS
AUSTIN 12

THE PLANT RESEARCH INSTITUTE

November 15, 1962

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

I want to present some NMR results which were obtained while I was associated with Dr. Andre S. Dreiding at the University of Zurich.

We were interested in determining the number of exchangeable hydrogens in certain natural products. The compounds were dissolved in deuterotrifluoroacetic acid and the deuterium-for-hydrogen exchange reaction followed by NMR. Deuterotrifluoroacetic acid was easily prepared in better than 95% deuterated form from trifluoroacetic anhydride and deuterium oxide. No special handling precautions were necessary to preserve above 90% deuterium purity in the acid during numerous exposures to the atmosphere. The results obtained with 2-methylcyclohexanone in deuterotrifluoroacetic acid are presented to illustrate the effectiveness of this method.

In a typical experiment, 2-methylcyclohexanone (36 mg.) was sealed (using a plastic cap and wax) into an NMR tube with 2 g. of deuterotrifluoroacetic acid (95% D). 2-Methylcyclohexanone contains 3 protons alpha to the keto group which in the process of exchanging produced about 10% trifluoroacetic acid in an average NMR sample of the deutero acid. The trifluoroacetic acid ($\sim$15%) present after equilibrium had been reached prevented total exchange. In spectrum (1) of 2-methylcyclohexanone in trifluoroacetic acid the doublet (3 H's) (J=6.5 cps) centered at τ 8.91 was assigned to the methyl group; the broad peak ($\sim$3 H's) at τ 7.49 was assigned to the three hydrogens alpha to the keto group and the multiplet ($\sim$ 6 H's) between 8.07 and 8.21 τ was assigned to the remaining methylene hydrogens. Spectra (2), (3) and (4) show the results obtained after the 2-methylcyclohexanone-deuterotrifluoroacetic acid mixture was allowed to stand at 25° in a sealed NMR tube for 18 minutes, 25 minutes, and 8 hours respectively. As the hydrogen at C-2 exchanged for deuterium the methyl group doublet dissappeared and a singlet appeared at τ 8.91. Simultaneously the broad peak at τ 7.49 decreased in intensity.

The rate of exchange of the C-2 hydrogen was followed by the increase in the 8.91 τ singlet. The overall exchange was determined by comparing

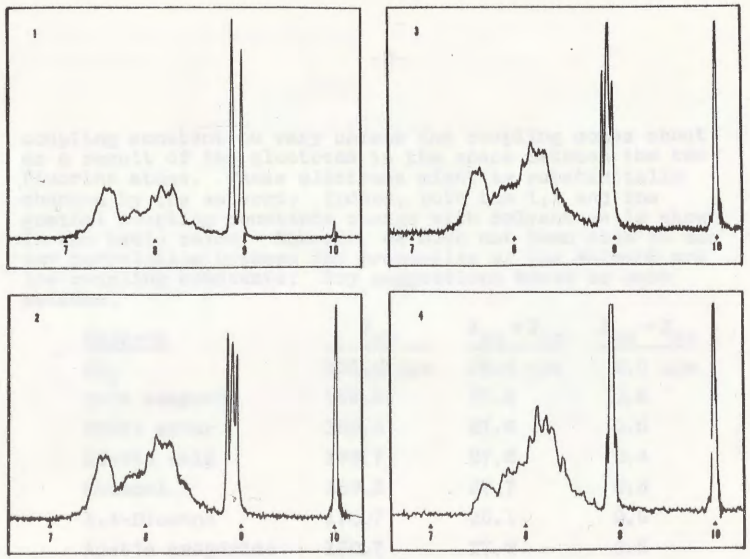


Figure I. NMR spectra of 2-methylcyclohexanone in CF_3CO_2H (1) and in CF_3CO_2D after 18 minutes (2), 25 minutes (3) and 8 hours (4). The τ-scale is used with tetramethylsilane as an internal reference.

the integrations of the continuously decreasing area resulting from the ring hydrogens with the integration of the constant area from the methyl group. The total exchange rate was further checked by integrating the continuously increasing trifluoroacetic acid peak (not shown in the spectra in Figure I). The two methods gave similar results. It was difficult to determine accurately the ratio of the exchange rates at the two alpha positions, but examination of spectrum (3) showed, as expected, that exchange was much more rapid at C-2 than at C-6. The broad peak at τ 7.49 had decreased in intensity by 0.8 H's after 25 minutes and by 2.2 H's (75% of theoritical) after 8 hours.

Most of the spectra were determined on a Varian A-60 spectrometer. The technique described above was found to be useful when applied to other ketones.

Sincerely,

Tom J. Mabry

Tom J. Mabry
Research Chemist

TJM:fmw

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA

November 19, 1962

Dr. Bernard Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Sorry that you had to remind me to contribute to MELLONMR. I certainly appreciate my subscription and should not be so remiss about paying my "dues."

We have been doing several things in this laboratory during the last few months, but we really have nothing in a nearly completed form. Therefore, this can only be a progress report.

We were interested in Sutcliffe's NMR spectrum of CF_3CFICF_2Cl. Since rotation about the 2,3 carbon-carbon bond does not give three identical minima in the potential energy curve, we expect the CF_3 to CF_2Cl coupling constants to vary with temperature. By making very accurate measurements of these coupling constants as a function of temperature, we hope to do some curve fitting, a la Gutowsky, and find the differences in the energies of the three minima as well as the 1,3 coupling constants as a function of the 2,3 dihedral angle assuming rapid rotation about the 1,2 carbon-carbon bond. Here we are looking to see if the coupling constant between fluorine atoms which are close together in space is large compared to the one between fluorine atoms that are far apart, in defense of coupling through space. Along this line, the recent MELLONMR letter from Brey, Ramey, and Lawson scared us somewhat. We are therefore planning to investigate their hypothesis that the coupling constants cannot be calculated as just a time weighted average over the three minima, but the average must be taken over all dihedral angles.

Again concerning coupling through space, we have some data on CF_2Br-$CFBrCl$ which is somewhat puzzling. As this compound is dissolved in various solvents, we expected the 1,2 coupling constants to change due to changes in the energies of the potential minima resulting from dipole-dipole interactions with the solvent. However, we did not expect bond distances and angles to vary with the solvent, and hence we did not expect the geminal

coupling constant to vary unless the coupling comes about as a result of the electrons in the space between the two fluorine atoms. These electrons might be substantially changed by the solvent. Indeed, both the 1,2 and the geminal coupling constants change with solvent as is shown in the table below. However, we have not been able to see any correlation between the properties of the solvent and the coupling constants. Any suggestions would be most welcome.

Solvent	J_{ab}	$J_{ax}+J_{bx}$	$J_{ax}-J_{bx}$
CS_2	165.0 cps	28.4 cps	0.5 cps
Pure compound	166.6	27.6	0.5
Ethyl ether	169.3	27.6	0.5
Acetic acid	169.7	27.8	0.4
Ethanol	169.8	27.7	0.6
1,4-Dioxane	170.7	28.1	0.5
Acetic anhydride	170.7	27.9	0.5
Methanol	170.9	27.6	0.6
Acetonitrile	171.2	27.8	0.6
Actone	171.5	27.8	0.6

Finally, we have been spending a fair amount of time writing some computer programs. We have made modifications of Reilly's program which he mentioned in MELLONMR 49. These involved modifying his program to run a Cal-comp plotter hook up to a 1401 in the manner recommended by IBM rather than the manner recommended by Cal-comp. As he indicated, we will be happy to send these programs to anyone wishing them. We are also attempting to write programs to calculate the spectra of exchanging molecules taking into consideration spin-spin coupling constants. i.e., a quantumechanical calculation rather than one based on the Block equations. So far, we have the program working for three, two-spin molecules interchanging among themselves. We plan to expand this program so that it will take care of up to five or six spins in two or three exchanging molecules.

One last comment, I do not believe that the recent paper by Mannatt, et al. in which they have found the trans-fluorine-fluorine coupling constant in $CFBr_2$-$CFBr_2$ to be non-zero demolishes our ideas on through space coupling. We still believe that the main contribution to fluorine-fluorine coupling constants come about as a result of electrons, other

than the ones in the sigma chemical bonds, which exist in the space between the two fluorine atoms. In the case of the above mentioned compound, we believe that the non-zero trans coupling constant is brought about as a result of the huge bromine atoms which are contributing many electrons through which the fluorines could couple in the trans configuration.

Sincerely,

C. H. Sederholm

CH:nm

M onthly
E cumenical
L etters from
L aboratories
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N - M - R

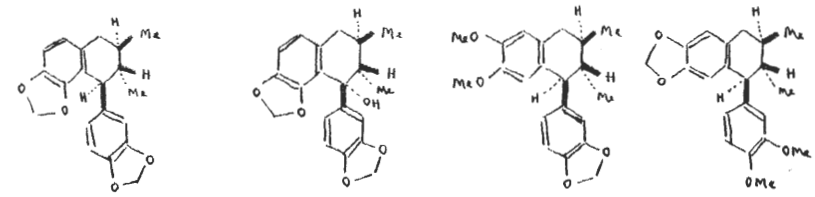
A monthly collection of informal private letters from laboratories of nmr. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication."

Summary

Lignans from Myristica Otoba.

By R. Wallace, A. L. Porte and R. Hodges.

Proton magnetic resonance studies have been made on otobain, hydroxy-otobain and on iso-otobain, three lignans obtained from Myristica Otoba, and their structures have been shown to be I, II and III or IV respectively.



I II III IV

The proton magnetic resonance spectrum of iso-otobain does not distinguish between structures III and IV, but IV is known from other, chemical, evidence to be the structure of another compound, galcatin. Hence iso-otobain is III. The conformations of the molecules and the configurations at the asymmetric centres have been obtained from the spectra.

The proton magnetic resonance spectrum of galcatin has been examined. It confirms structure IV for this compound. Hence the conformations and configurations of the otobain series of lignans have been related to those of the galcatin series.

The Department of Chemistry, The University, Glasgow, W.2., Scotland.

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Prof. dr L. J. Oosterhoff

nr.:

onderwerp:

Dr. B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pennsylvania
U.S.A.

Leiden, November 21, 1962

Dear Dr. Shapiro,

We are very grateful receiving M.E.L.L.O.N.M.R.; apart from the contributions, the bibliography is very valuable.

The beginning of our nmr story is a bit sad: a Dutch firm offered to construct a 30mc spectrometer for us, but did not succeed satisfactory up till now.
"Many be called, but few chosen", seems to be the appropriate device for these experiments. Yet we are still hopeful.

Some time ago we bought a Varian A-60. The instrument is used for both routine and research work. One of the fields people of our theoretical department are working in, is that of charge distribution in certain aromatic compounds and the corresponding ions. Nmr proves to be a very valuable tool in this research.

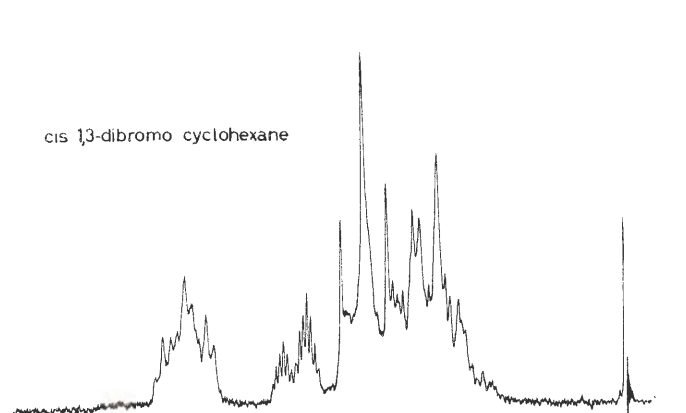
Recently we investigated, together with Mr. H.M. van Dort, all isomers of dichloro-, dibromo-, and chloro bromo cyclohexane by nmr. The main purpose was to get certainty about the conformations of the trans-1,3- and cis-1,3 compounds. This work forms part of an investigation into the conformations of cyclohexane derivatives directed by Professor Havinga. It will be included the thesis which Mr. van Dort is writing. He also prepared the substances and studied them in many other aspects as well.
The trans-1,3 compounds showed the expected triplets for the protons on C2. (mean value of J_{vic} = 5.5 cps)
The spectrum of one of the cis-1,3 compounds is shown in the figure. The spectra confirm the idea that the e-e (halogen) conformation is the only one occurring. The protons on C2 will give rise to a AB quartet (J_{gem} = 12.5 cps) the lower part of which, distinguishble in the spectrum, is attributed to the equatorial C2 proton.
Coupling between this proton and the axial protons on C1 and C3 (J= 3.9 cps) and a long range coupling (J= 1.9 cps) with one pair of the protons on C4 and C6 would explain the observed septuplets.

The spectrum resembles that of cyclohexane-1,3 diol described by Finegold and Kwart (J. Org. Chem., 27, 2361 (1962)), however they did not mention any multiplicity for the C2 protons.
Cooling down of the cis-1,3 compounds (-105°C) did not change the spectrum.
The low temperature spectra were recorded at the Shell Laboratories at Amsterdam.

Yours sincerely,

A.H. Huizer

Th.J. Sekuur



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Zürich

ZÜRICH,
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November 22, 1962

Dr. B.L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13 Pa.

Dear Dr. Shapiro:

In my last letter I had derived some new relations between the products νI (ν = resonance frequency, I the corresponding intensity) of a proton resonance spectrum. If we denote the sum of those products, belonging to the transition $m \to m+1$ by S^m, then the relations (6) of my last letter are of the form:

$$S^{m-1} + S^{-(m+1)} = S^m + S^{-m} \tag{1}$$

The relations are a consequence of the following two equations:

$$2Z = \left[\left[H,F_+\right],F_-\right] \tag{2}$$

$$Tr_m(Z) + Tr_{-m}(Z) = 0 \tag{3}$$

(I hope you will excuse me for having forgotten to write the factor 2 on the left side of equation (2), i. e. (4) in my last letter.) If we replace the equation (5) by the more general one:

$$Tr_m(Z) = \frac{m}{n+2m}\left(\frac{n}{m-1} - 2\right) Tr_{m-1}(Z) \qquad n = \text{number of protons} \tag{4}$$

which holds for the partial traces of Z, we can derive in the same way as in the last letter a more general system of equations of type (1):

$$n(2m-1)\,S^{m-1} = m(n-2(m-1))\,S^{m-2} + (m-1)(n+2m)\,S^m \tag{5}$$

n-1 among these equations are independent.

Now I had promised to show, that the equation (2) allows to base a numerical analysis of nmr-spectra on it. Some monts ago Reilly and Swalen (1) have published an iterative procedure to calculate the constants of the Hamiltonian in proton resonance spectroscopy. This procedure demands an approximative Hamiltonian H_0. But exactly for finding such an approximative Hamiltonian

equation (2) is well suited. If we express the equation in the eigenbasis of the Hamiltonian, we see that we can calculate the matrix elements of Z in this basis from the frequencies and the matrix elements of F_-:

$$f_{ij}^{m-1} \equiv \langle m-1,i \mid F_- \mid m,j \rangle \tag{6}$$

which are strongly related to the intensities:

$$(f_{ij}^{m-1})^2 = I_{ij}^{m-1} \tag{7}$$

Therefore, to get the matrix elements f_{ij}^{m-1} from the intensities, we have only to determine the signs of the quantities $\sqrt{I_{ij}^{m-1}}$. It could be proved that if we choose the signs so that the equations:

$$\sum_\varrho f_{i\varrho}^m f_{j\varrho}^m = \sum_k f_{ki}^{m-1} f_{kj}^{m-1} \tag{8}$$

which are consequencies of the operator equation:

$$\left[F_+,F_-\right] = 2F_3 \tag{9}$$

are satisfied, the choice of the signs is unique. Once we have found the matrix $(Z)_\Psi$ of Z in the eigenbasis $\{\Psi^m\}$ of the Hamiltonian, we pick out the submatrix $(Z)_\Psi^{-n/2+1}$, which belongs to the magnetic quantum number $m = -\frac{n}{2} + 1$. Now we diagonalize this n x n-matrix:

$$\tilde{U}\ (Z)_\Psi^{-n/2+1}\ U = (Z)_\Phi^{-n/2+1} \tag{10}$$

If all the chemical shifts are different from each other, the matrix U is uniquely determined apart from the signs of the column-vectors, which we choose so that:

$$(\Phi_\iota^{-n/2+1},\ F_+\Psi^{-n/2}) > 0 \tag{11}$$

With the matrix U, defined in that way, we transform the sub-hamiltonian $(H)_\Psi^{-n/2+1} = (\delta_{ik}E_k^{-n/2+1})$ (herein the $E_k^{-n/2+1}$'s mean the energieterms belonging to the quantum number $m = -\frac{n}{2} + 1$), according to:

$$\tilde{U}\ (H)_\Psi^{-n/2+1}\ U = (H)_\Phi^{-n/2+1} \tag{12}$$

Approximative values for the chemical shifts we get in a simple way from the eigenvalues $(Z)_\Phi^{-n/2+1}$ of Z, and the off-diagonal elements of $(H)_\Phi^{-n/2+1}$ represent without regard to a factor 2 approximative values for the coupling constants.

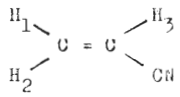
From these remarks we see that equation (2) is able to give us a first approximation for the Reilly-Swalen procedure, the accuracy of which is dependent on the precision of the intensity measurement.

If we take account of the fact, that the matrix elements f^m_{ik} are not independent, but satisfy certain relations, we can improve the experimental values with the help of the least square approximation. Qualratic relations of the mentioned type we can derive from the operator equation (9) (e.g. the intensity relations!) and from:

$$(13) \qquad \left[\left[H,F_+\right],F_+\right] = 0$$

In the case of a threeproton-system the fifteen matrix elements of F_- in the eigenbasis of the Hamiltonian are bounded by a system of at least thirteen independent quadratic equations (which of course also involves the frequencies).
If we take account of this fact by applying the least square approximation, our method gives a very good first approximation for the Reilly-Swalen procedure as the following example demonstrates: We have analyzed the spectrum of a 1:1 solution of acrylonitrile in CCl_4. Our method gave the following approximative values for the constants of the Hamiltonian, which still depend slightly on the experimental intensities.

Chemical shifts (ppm)	Coupling constants (cps)
$\delta_1 = 0.3326$	$A_{12} = 0.887$
$\delta_2 = 0.2105$	$A_{13} = 11.528$
$\delta_3 = 0.7075$	$A_{23} = 18.176$



This values have been subjected to the Reilly-Swalen procedure and the following values, which depend now only on the frequencies, were obtained:

Chemical shifts (ppm)	Coupling constants (cps)
$\delta_1 = 0.3333$	$A_{12} = 1.04$
$\delta_2 = 0.2093$	$A_{13} = 11.71$
$\delta_3 = 0.7080$	$A_{23} = 17.88$

As J. Waugh (2) has done, we have referred our chemical shifts to the first line in the spectrum, the intensity of which is essentially different from zero. But precaution must be token if one wants to compare the numerical values with those of Waugh. Only the differences of the chemical shifts and of course the coupling constants have a meaning independent on the field strength. Besides it is probably that the solvent effect has also a certain influence. Further details about this subject will soon be published.

fours sincerely

H. Kummer

H. Kummer

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(2) S. Castellano and J.S. Waugh, JCP 34, 295 (1961)

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Dr. B.L. Shapiro,
The Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13, Pa,
U.S.A.

Dear Dr. Shapiro,

N.M.R. of Amino Acids

We have started a detailed study of high resolution nuclear magnetic resonance spectra of some α-amino acids in alkaline solution. Previous investigations[1,2,3] were mainly concerned with chemical shifts and solvent effects. No attention was paid to the fine structure of the spectra partly due to the fact that trifluoroacetic acid has been used as a solvent. Amino acids in strongly acetic media exist as cation.

$$R - CH\begin{matrix}\diagup NH_3^+ \\ \diagdown CO_2H\end{matrix}$$

giving complex splitting patterns due to couplings with the hydrogens at the nitrogen.

We used approximately 2 mol.% solutions of α-amino acids in $D_2O + NaOD$, the pH being high enough to ensure that the amino acid exists in its anionic form

$$R - CH\begin{matrix}\diagup NH_2 \\ \diagdown CO_2^-\end{matrix}$$

The hydrogens of the amino group exchange readily. Amino acids of the type

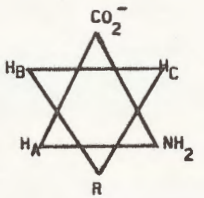
$$R - CH_2 - CH\begin{matrix}\diagup NH_2 \\ \diagdown CO_2^-\end{matrix}$$

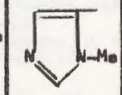
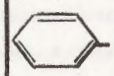
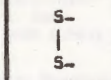
with no hydrogens on the γ-carbon thus give ABC-type spectra as the α-carbon is asymmetric and the β-hydrogens are non-equivalent due to different populations of the rotational isomers and the magnetic anisotropy of the carboxyl group.

The spectra were run on a Varian A-60 instrument and analysed by means of an IBM 704 programme for the direct analysis of ABC-spectra. This computer programme follows in principle the procedure outlined by W. Brügel, Th. Ankel, and F. Krückeberg[4] and gives solutions for all possible sign combinations.

Those assignments with the two vicinal couplings of opposite sign could be rejected immediately because of intensity differences. In all spectra which were sufficiently different from the ABX-type, the comparison of measured and calculated intensities favoured the solution with the geminal coupling of opposite sign to the vicinal couplings. When combination lines were observed, they confirmed this assignment. It seems as if the opposite signs of geminal and vicinal couplings in saturated systems may be accepted as a general rule.[5,6,7,8,9,10]

Our results are combined in the following table, and the figure shows the probable assignment of the protons looking down the C_α-C_β-bond.



Compound	R	$\nu_A - \nu_B$ (cps)	$\nu_B - \nu_C$ (cps)	J_{AB} (cps)	J_{AC} (cps)	J_{BC} (cps)
Histidine		33.2	9.9	±5.16	±7.87	∓14.83
1 Methyl-histidine		31.2	7.4	±6.02	±7.25	∓15.29
Phenylalanine		28.9	12.7	±5.47	±7.78	∓13.66
Asparagine	NH_2–CO–	55.2	13.9	±4.91	±8.90	∓14.86
Aspartic acid	HOOC–	55.6	19.7	±4.14	±9.66	∓15.52
Cystine		26.9	12.8	±4.81	±7.66	∓13.70

Yours sincerely,

Klaus Pachler

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

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