Mailed: Nov. 2, 1961

Monthly Ecumenical Letters from Laboratories Of N - M - R

No. 37

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

37-1

AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS
CHEMICAL THERMODYNAMIC PROPERTIES CENTER
Department of Chemistry
COLLEGE STATION, TEXAS

AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 44
MANUFACTURING CHEMISTS ASSOCIATION RESEARCH PROJECT

September 25, 1961

Air Mail

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

I wish to send some items of general interest from our new location:

Dr. Bruno J. Zwolinski is the Director of the two projects which constitute the Center. Contributions of nuclear magnetic resonance spectra to either project should be sent to this address.

As of the supplement under date of April 30, 1961, the number of valid sheets in the catalog of nuclear magnetic resonance spectra of the API Research Project 44 is 76. This supplement is being printed and will be distributed soon. These spectra are mostly of hydrocarbons.

The number of valid sheets in the catalog of the MCA Research Project will come to 92 with the supplement under date of June 30, 1961. This supplement will appear soon. These spectra are of phosphorus compounds and some miscellaneous compounds.

During the next 12 or 18 months, special attention and priority will be given by both projects to the issuance of nuclear magnetic resonance spectra. To strengthen the NMR catalogs we need the help of your group and that of other interested parties. Spectra from A-60 spectrometers are especially suited.

We will continue to issue spectra of good quality on any of the several acceptable scales until a firm decision has been made to abide by a single scale. Through Dr. Forrest S. Mortimer, who has recently held consultation with a number of agencies, and a summary report for the IUPAC, the Advisory Committee for the API Research Project 44 is especially alerted to any forthcoming developments. When such a decision has been made firm, the projects will issue a revised report for the NMR category.

The Department of Chemistry here at Texas A. and M. has an A-60 spectrometer on order. Some studies will be carried out on some API Research Hydrocarbons and also pure compounds to be provided by member laboratories of the MCA.

Bruno sends his best regards.

Very truly yours,

Alfred Danti

Alfred Danti
Associate Professor and Assistant Director
Spectral Program

AD/rsl

ELECTRON COUPLING OF NUCLEAR SPINS.

V. VIBRATIONAL EFFECTS IN CHX GROUPS.*

H. S. Gutowsky, V. D. Mochel,[1] and B. G. Somers[2]

Noyes Chemical Laboratory, University of Illinois

Urbana, Illinois

Previous calculations of the H—H coupling in CH_2 groups assumed a static H—C—H bond angle. It is shown here that, because the predicted angular dependence of the coupling is non-linear, the bond-bending vibrations should give an averaged value appreciably larger than that for the corresponding equilibrium, but static, angle. The contribution of excited vibrational states is very small and hence the averaged coupling constant is effectively temperature independent. There should be a small but detectable difference in the coupling constants for CH_2 and CHD groups because of the isotopic differences in vibrational amplitude. The available experimental coupling constants exhibit an apparently linear dependence upon the H—C—H angle, and careful measurements of the isotope effects could be useful in establishing whether or not there is any explicit curvature in the angular dependence, and thus whether the observed linearity is real or due to the neglect of substituent effects in the calculations. In any case, comparison between experiment and the predicted angular dependence suggests that too low of a value may have been used previously for one of the exchange integrals, $K(C_1,C_2)$ in the calculations for both the CH_2 and the HCCH groups. An attempt to detect an isotopic difference between the geminal H—F and D—F coupling in n-C_3F_7H and n-C_3F_7D gave negative results.

MONSANTO CHEMICAL COMPANY

PLASTICS DIVISION
SPRINGFIELD 2, MASSACHUSETTS
September 25, 1961

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

Possibly some MELLONMR readers may be interested in some programs I have written recently for the Bendix G-15 digital computer. The programs greatly facilitate the analysis of exchange-averaged Lorentzian-type doublets often encountered in NMR studies of rate phenomena. Each program may be used for doublets which are completely symmetric or asymmetric with respect to the intensity versus frequency surface.

The equations (4), (5) and (8) of Gutowsky and Holm[1] may be rewritten for the more general case of asymmetrical doublets as (1), (2) and (3), respectively. Parameters not defined here are the same as those used by Gutowsky and Holm.

(1) H.S. Gutowsky and C.H. Holm, J. Chem. Phys., 25, 1228 (1956).

The first program uses equation (1) for the generation of doublet shape functions for different rates of exchange averaging. As many as one-hundred shape functions corresponding to an equal number of equally-spaced values of the rate of averaging may be generated in one passage through the program. Each shape function consists of up to one-hundred different points, intensity versus frequency, equally spaced along the frequency coordinate. Example generations for an asymmetrical case are plotted in Figure 1.

A second program uses equations (1) and (2) for calculating the frequency positions and relative intensities of the maxima and central minimum for different rates of exchange averaging. As many as fifty sets of maxima and minimum frequencies and intensities corresponding to an equal number of equally-spaced values of the rate of averaging may be calculated in one passage through the program. The program may be used in all regions of exchange rates, i.e., before, during and after coalescence of the doublet components.

A third program uses equation (3) for calculating the effect of overlap on the apparent separation of any two Lorentzian lines in the absence of exchange averaging.

Complete copies of the programs are available to anyone who wants to use them.

Yours,

Jim Woodbrey

James C. Woodbrey

Enclosure (2)

37-2

$$\mathcal{V} = -\omega_1 M_o \cdot \frac{P\left[1 + \tau(p_B/T_{2A} + p_A/T_{2B})\right] + QR}{P^2 + R^2}, \quad \text{where} \tag{1}$$

$$P = \tau\left[(1/T_{2A}T_{2B}) - \Delta\omega^2 + (\delta\omega/2)^2\right] + p_A/T_{2A} + p_B/T_{2B} = S - \tau\Delta\omega^2 ,$$

$$Q = \tau\left[\Delta\omega - (\delta\omega/2)(p_A - p_B)\right] ,$$

$$R = \Delta\omega\left[1 + \tau(1/T_{2A} + 1/T_{2B})\right] + \tau(\delta\omega/2)(1/T_{2B} - 1/T_{2A}) + (\delta\omega/2)(p_A - p_B) ;$$

$$2\tau^2 A\Delta\omega^5 + 3\tau^2 B\Delta\omega^4 + 4\tau^2 C\Delta\omega^3 + (BD-AE)\Delta\omega^2 + 2(CD-AF)\Delta\omega + (CE-BF) = 0, \tag{2}$$

where $A = \tau^2(p_A/T_{2A} + p_B/T_{2B})$, $B = \tau^2\delta\omega(p_B/T_{2B} - p_A/T_{2A})$,

$$C = \tau(\delta\omega/2)^2\left[1 - (p_A - p_B)^2 + (A/\tau)\right] + (\tau/T_{2A}T_{2B})\left[1 + p_A^2 + p_B^2 + \tau(p_A/T_{2B} + p_B/T_{2A})\right] + \tau p_A p_B(1/T_{2A}^2 + 1/T_{2B}^2) + (A/\tau^2) ,$$

$$D = \left[1 + \tau(1/T_{2A} + 1/T_{2B})\right]^2 - 2\tau S ,$$

$$E = \delta\omega(D + 2\tau S)^{1/2} \cdot \left[p_A - p_B + \tau(1/T_{2B} - 1/T_{2A})\right] ,$$

$$F = S^2 + (E^2/4)(D + 2\tau S)^{-1} .$$

$$b_o(\delta\omega/2)^5 + b_1(\delta\omega/2)^4 + b_2(\delta\omega/2)^3 + b_3(\delta\omega/2)^2 + b_4(\delta\omega/2) + b_5 = 0 , \tag{3}$$

where $b_o = (p_A/T_{2A} - p_B/T_{2B})$, $b_1 = -3\Delta\omega_\infty(p_A/T_{2A} + p_B/T_{2B})$,

$$b_2 = 2\left[\Delta\omega_\infty^2 b_o + (1/T_{2A}T_{2B})(p_A/T_{2B} - p_B/T_{2A})\right] ,$$

$$b_3 = -2\Delta\omega_\infty\left[(\Delta\omega_\infty b_1/3) + (1/T_{2A}T_{2B})(p_A/T_{2B} + p_B/T_{2A})\right] ,$$

$$b_4 = (1/T_{2A}T_{2B})\left[p_A/T_{2B}^3 - p_B/T_{2A}^3 + 2\Delta\omega_\infty^2(p_B/T_{2A} - p_A/T_{2B})\right] - 3\Delta\omega_\infty^4 b_o ,$$

$$b_5 = (\Delta\omega_\infty/T_{2A}T_{2B})\left[(p_A/T_{2B}^3 + p_B/T_{2A}^3) + 2\Delta\omega_\infty^2(p_A/T_{2B} + p_B/T_{2A})\right] - (\Delta\omega_\infty^4 b_1/3) .$$

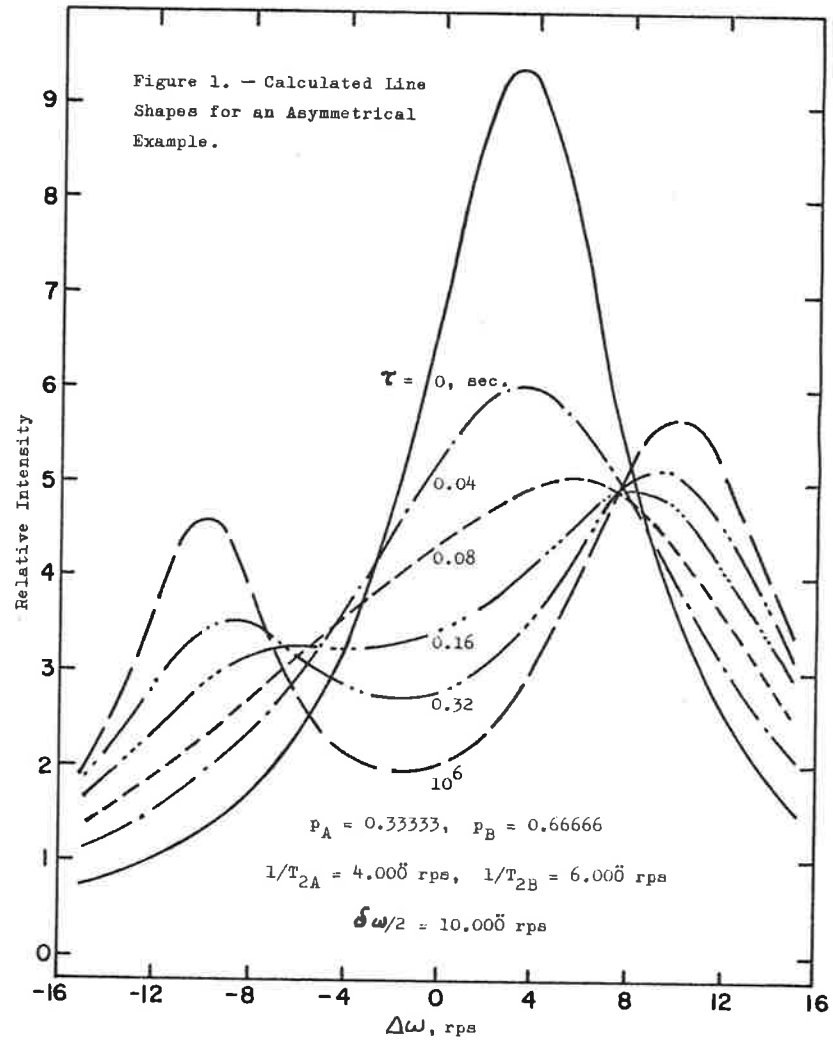

Figure 1. — Calculated Line Shapes for an Asymmetrical Example.

SHELL DEVELOPMENT COMPANY
A DIVISION OF SHELL OIL COMPANY
EMERYVILLE, CALIFORNIA

October 24, 1961

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

Dear Barrie:

As a contribution to MELLONMR I have two items which may be of interest to various NMR spectroscopists. One is an intensity sum which George Gioumousis and I have just proved. The other is the availability of our computer programs.

The general NMR intensity sum rule is

$$\sum_k I_{j_0 k} = \sum_i I_{j_0 i} + 2F_z(j_0) .$$

The sum on the left is the sum of the intensities of all the transitions to the state $j_0(\nu_{j_0 \leftarrow k})$, the sum on the right is the sum of intensities of all the transitions from the state $j_0(\nu_{i \leftarrow j_0})$, and the third term is twice the z component of the total spin of the state j_0. In the general sum rule the intensities are normalized so that the sum of the intensities of the whole spectrum is $N2^{(N-1)}$. The proof of this rule, based partly on the proof of the principle of spectroscopic stability and partly on the properties of spin operators, has been submitted to the Journal of Chemical Physics (preprints are available for interested readers).

This sum rule is a generalization of the specific sum rules for a three spin system given and proved by Castellano and Waugh (J. Chem. Phys. 34, 295 (1961)). A similar specific rum rule was also found for the four spin system (Reilly and Swalen, J. Chem. Phys. 34, 980 (1961)).

Reprint angef. 28.11.61

In regard to our computer programs, C. A. Reilly and I have just completed a number of modifications and have written instructions for users. The programs are applicable to three to eight spin systems. Computer controlled iteration to the "best parameters" is possible and the transitions are printed in an increasing order with their energy level ordering. The time for calculation on the IBM 7090 is less than a minute for a five spin or smaller system, about 2 minutes for a six spin system, about 3 to 5 minutes for a seven spin system, and about 10 to 15 minutes for an eight spin system. On an IBM 704 computer the times will be slightly longer.

The reproduction of the complete FORTRAN listings and cards and column binary cards for the IBM 7090 is being done and they will be available shortly. This material and additional information can be obtained by writing to me at the above address.

Sincerely,

Jerry

J. D. Swalen

JDS:jel

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

October 23, 1961

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

IN YOUR REPLY
REFER TO FILE NO.

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Aksel,

Here are some scraps of information which may be of interest to MELLONMR readers. Results obtained here on syn-anti isomerism in oximes prompted me to look for other compounds with carbon-nitrogen double bonds which might show this kind of isomerism. In symmetrical compounds of the type $R_2C{=}N$, the non-straightness of the bond angle at N may be reflected in the spectra by the appearance of two lines or bands for protons on the no longer equivalent R's.

I found this to be the case in some 2,4 dinitrophenylhydrazones. E.g. in the acetone-DNPH spectrum, there are two methyl peaks about 0.1 ppm apart, and in that of 3-pentanone-DNPH, two methylene quartets about 0.11 ppm apart are seen. The spectrum of formaldehyde-DNPH (in DMS; nitrobenzene also seems to be a good solvent for DNPH's) is still puzzling to me, as three more peaks appear than in the spectrum of 2,4 dinitrophenylhydrazine, and not two as one would expect. One possibility is that "formaldehyde-DNPH" does not correspond to the structure suggested by its name. At any rate, the results on the first two DNPH's make it advisable to look for syn-anti isomers in unsymmetrical DNPH's.

Another example is 2,6 dibromobenzoquinoneimine chloride. A saturated DMS solution (conc. unknown) gives a spectrum with two proton lines about 1/3 ppm apart.

Best wishes,

Ernest Lustig

37-4

HARVARD UNIVERSITY
DEPARTMENT OF CHEMISTRY

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

October 9, 1961

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

We have recently studied the two forms of N_2F_2 by F^{19}-$\{N^{14}\}$ nuclear magnetic double resonance. The preliminary results of this work will perhaps be of interest since they illustrate a rather nice application of the double resonance method, and indicate that the unstable isomer of N_2F_2 is probably a cis form.

It has been shown that there are two forms of N_2F_2, one form that is quite stable, and a second form that is rather reactive.[1] There seems to be general agreement that the stable form of N_2F_2 has a trans arrangement of the fluorine atoms.[2,3] However, there have been at least two structures proposed for the unstable isomer, a cis form, and a 1,1-difluoro structure.[2,3]

The F^{19} spectra of the trans, and unstable forms of N_2F_2 (40 Mc/s.) at room temperature in CCl_3F are shown in Figures 1 and 2. The trans spectrum consists of a simple triplet with the outer components broader than the central component. The spectrum of the unstable form, however, shows five lines. The spectra of both isomers at 56.4 Mc/s. are identical with the 40 Mc/s. spectra. The F^{19} and N^{14} chemical shifts measured for the two isomers are given below:

N_2F_2 Species	F^{19} Chem. Shift Rel. to CCl_3F	Rel. N^{14} Chem. Shift
Stable (trans)	-94.9 ppm	58.6 ppm
Unstable (cis)	-133.7 ppm	0 ppm

The N^{14} chemical shifts are obtained from the F^{19}-$\{N^{14}\}$ double resonance experiments described below.

For both the cis and trans structures of N_2F_2, the fluorines and nitrogens are not magnetically equivalent.[4] Thus the spectra of these isomers might be expected to be complicated examples of the $AA'XX'$ case, and the appearance of five resonances in the spectrum of the unstable form is not surprising. For a 1,1-difluoro structure, the spectrum would be of the ABX_2 type. For this structure, the complex multiplet pattern observed for the unstable form could only arise if the coupling of both nitrogen atoms with the fluorines was significant. An ABX_2 case, however, seems unlikely since the spectrum of the unstable isomer is the same at 40.0 and 56.4 Mc/s.

Further evidence against the ABX_2 assignment of the spectrum of the unstable isomer is provided by F^{19}-$\{N^{14}\}$ double resonance studies. In these experiments, the F^{19} resonances were observed with the weak radio frequency field $\vec{H}_1$, while the sample was irradiated with a strong field $\vec{H}_2$ at about the N^{14} resonance frequency, ν_{oN}. The analysis of double resonance spectra in the region of intermediate amplitudes of $\vec{H}_2$ has been described in detail.[5] If the double resonance spectra are recorded by sweeping the magnetic field with constant ω_1 and ω_2, the observed resonance will be symmetric when $\omega_2/2\pi = \nu_{oN}$, if both nitrogens have the same resonance frequency, $\nu_{oN} = \nu_{oN'}$. When $\omega_2/2\pi$ is not equal to ν_{oN}, the double resonance spectrum usually does not have a symmetric appearance. However, for $\omega_2/2\pi = \nu_{oN} + \Delta\omega_2/2\pi$, the trace will be the mirror image of the trace for $\omega_2/2\pi = \nu_{oN} - \Delta\omega_2/2\pi$. These readily observed qualitative regularities of the double resonance spectrum will not occur if $\nu_{oN} \neq \nu_{oN'}$.

The double resonance spectra of trans and unstable N_2F_2 for a series of values of $\Delta\omega_2/2\pi$ are shown in Figures 3 and 4. Since both nitrogen atoms must contribute to the multiplet structure of the unstable

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form if the 1,1-difluoro structure is proposed, these results indicate that $\nu_{oN} = \nu_{oN'}$ for the unstable form. The above evidence, in addition to N^{14} resonance studies, indicates that a 1,1-difluoro structure for N_2F_2 is quite improbable.

The N^{14} chemical shifts for the two N_2F_2 isomers can be readily determined to an accuracy of $\pm$ 5 c/s. from the qualitative appearance of the double resonance spectra as a function of $\omega_2/2\pi$.[6] Since the double resonance experiments are performed in the field H_o appropriate for the F^{19} resonance at 40 Mc/s., the N^{14} resonance frequencies of cis and trans N_2F_2 are measured at somewhat different values of H_o. The relative N^{14} chemical shifts between the two isomers are readily corrected for this effect.

Calculations to indicate a possible assignment of the structure of the spectra of these two isomers are currently in progress.

One of us (C. B. Colburn) would like to ask if this contribution could be accepted as a down payment on a regular subscription to MelloNMR.

Yours very truly,

John D. Baldeschwieler

Joseph H. Noggle

Charles B. Colburn

Charles B. Colburn
Rohm and Haas Company
Redstone Arsenal Research Division
Huntsville, Alabama

JDB:br

References:

1 C.B. Colburn, F.A. Johnson, A. Kennedy, K. McCallum, L.C. Metzger, and C.O. Parker, JACS, 81, 6397 (1959).

2 R.H. Sanborn, J.C.P., 33, 1855 (1960).

3 R. Ettinger, F.A. Johnson, and C.B. Colburn, J.C.P., 34, 2187 (1961).

4 J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. (1959), p. 116.

5 J.D. Baldeschwieler, J.C.P. (in Press).

6 J.D. Baldeschwieler and E.W. Randall, Proc. Chem. Soc., 303 (1961).

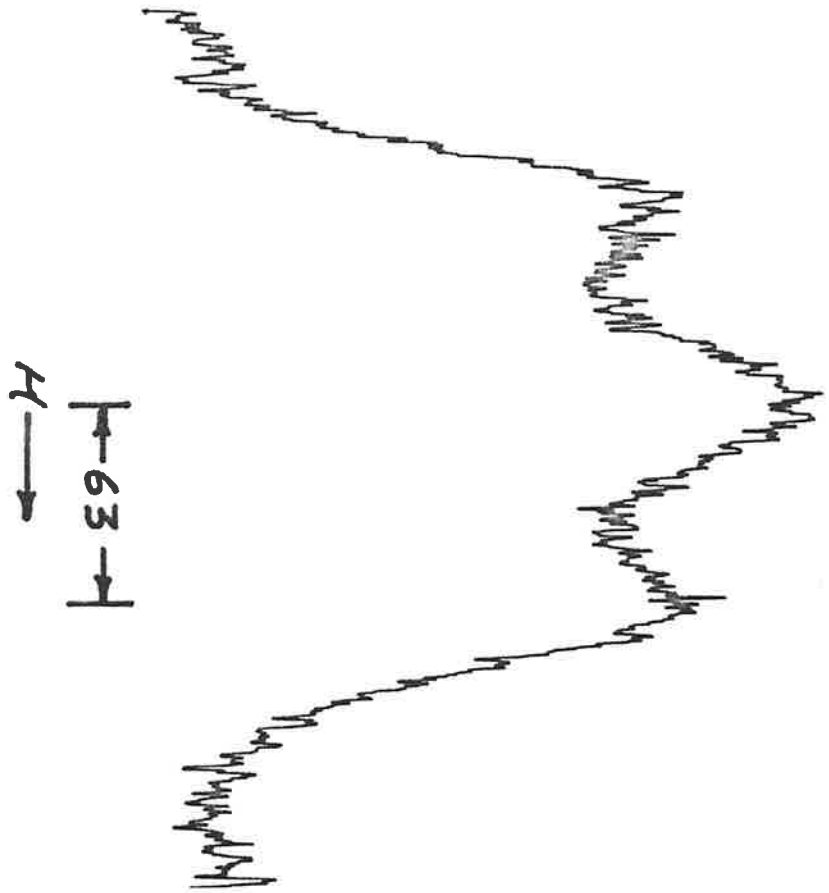


FIGURE 1 TRANS

37-6

FIGURE 2

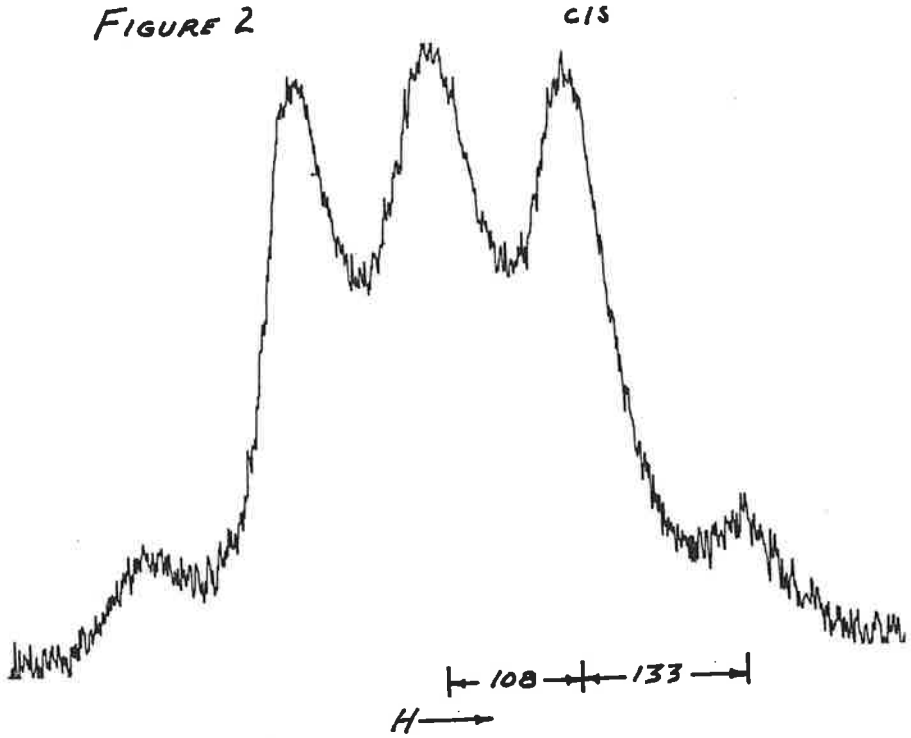


FIGURE 3 TRANS

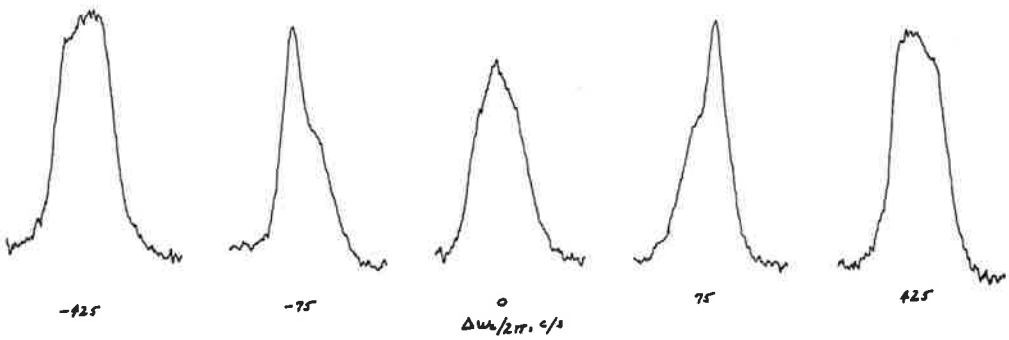
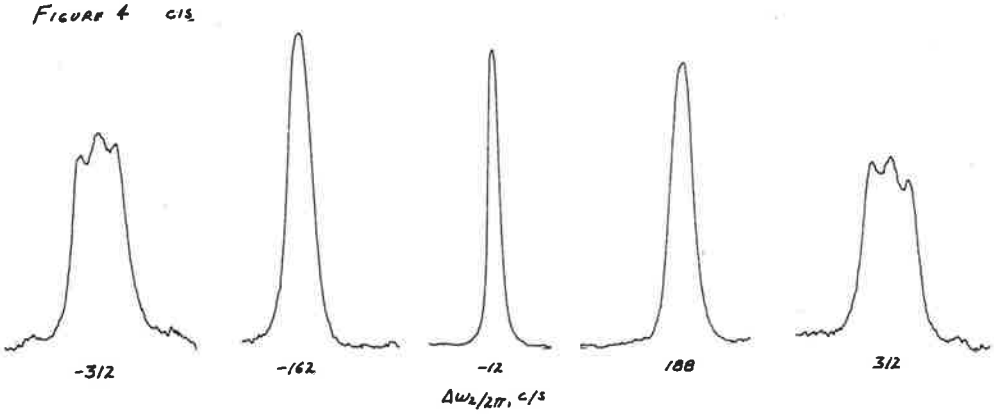


FIGURE 4 CIS



THE UPJOHN COMPANY

FINE PHARMACEUTICALS SINCE 1886

KALAMAZOO, MICHIGAN

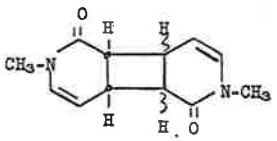
October 20, 1961

SCIENTIFIC ADMINISTRATION
301 HENRIETTA STREET

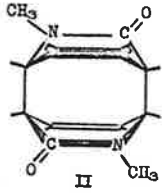
Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

We recently studied a photodimer, which we believed to be I, in an effort to discover the geometry of the ring fusions. The surprising results may be of interest to readers of MELLONMR. The NMR spectrum forced us to the conclusion that the dimer was actually the novel tricyclic octadiene, II.



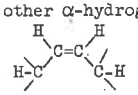
I



II

The N.M.R. spectrum of the dimer (Figure 1) showed three types of hydrogens of relative abundances 4, 4, and 6, from area measurements, based on the dimeric empirical formula. The least shielded multiplets centered at 399 and 374 are in the region ordinarily assigned to olefinic hydrogens with additional unshielding groups nearby. Closer examination discloses that it is an AB multiplet

(doublet of doublets) with two additional splits. The large asymmetric split (J = 8 cps.) indicates cis-olefinic hydrogens. The symmetrical second split (J = 6.5 cps.) is by an atom in the intermediate group and indicates the presence of a hydrogen atom α to the double bond having a dihedral angle of 0 or 180 degrees. Since both olefinic hydrogens are split thus, similar α-hydrogens are required on each side. The nature of the third split (J = 1.5 cps. symmetrical) indicates that this partner (also of the intermediate group) is the other α-hydrogen coupled through the double bond, thereby suggesting the system



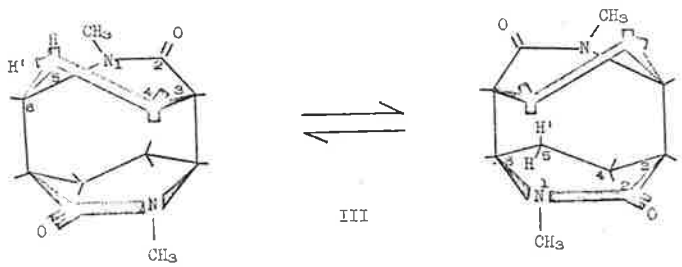
The intermediate multiplets at 241 and 217 cps. are also of the AB pattern with two additional symmetrical splits. The large asymmetric split (J = 9.5 cps.) is indicative of an interaction of similar adjacent hydrogens having a dihedral angle of 0 or 180 degrees. The two remaining symmetrical splits are the counterparts of those described above, and they require that these four AB type hydrogens all be α to the olefinic hydrogens, thus necessitating the 1,5-cycloöctadiene formulation.

The presence of two equivalent N-methyl groups is confirmed by the sharp singlet at 168 cps.

The N-methyl amide residues must be attached to the 1,5-cycloöctadiene in a head-to-tail arrangement. The two adjacent tertiary hydrogens are now coplanar yet environmentally different, fulfilling the requirement for splitting, and the transoid conformation gives the compound the symmetry required by the N.M.R. spectrum and the dipole moment.

This structure gained additional support from the N.M.R. spectrum of the tetrahydro derivative, III (m.p. 284-285°). Three types of hydrogen absorptions

27-8



III

in an abundance of 4, 6, and 8 are present (cf. Figure II). The two tertiary hydrogen absorptions centered at 230.5 and 185.5 cps. are still a doublet of doublets (J = 10.5 cps.) but have additional splitting of each line into symmetrical triplets (J = 3 cps.) by the new methylene groups. This confirms that these tertiary hydrogen atoms were α to the double bond in the photodimer and further identifies this coupling in Figure I.

The N-methyl line has shifted to lower field because of the removal of the double bond with its diamagnetic anisotropy. The new ring methylenes show an absorption at 116 cps. which lacks the usual distinction between hydrogens in the axial and equatorial conformations. The formation of symmetrical triplets (J = 3 cps.) is of interest because it indicates that the coupling to both methylene hydrogens which have different conformations is identical and that the dihedral angles are about 45°.

The situation was clarified when a Dreiding Stereomodel was constructed and the molecule was observed to undergo very facile ring interconversion between two boat forms of the two six-membered rings. The third form, with the

ring fusions in the flagstaff positions, is highly strained and is the transition state between the other two. It is of interest to observe that the two forms (cf. Structure III) are mirror images after rotation of one through 180°. During this process, the equatorial hydrogens become axial and vice-versa (see III), the net effect averaging the methylene hydrogens (only one absorption frequency) and the dihedral angle to about 45° as required.

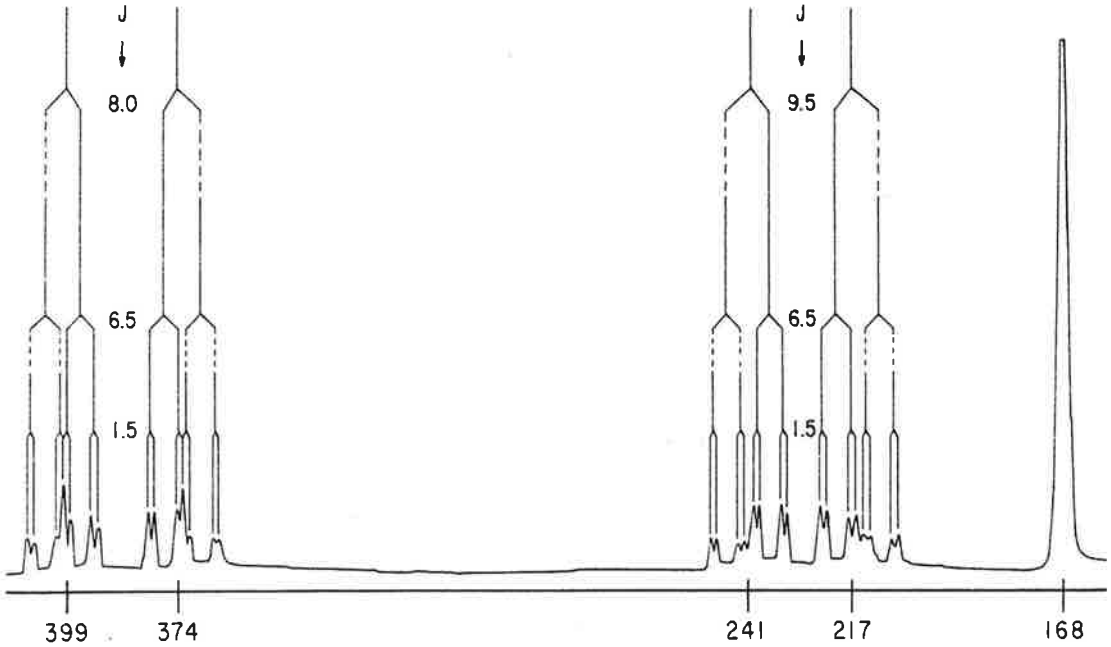
We certainly appreciate the fine job you are doing with MEILONMR and hope that we may continue to receive these letters.

Very truly yours,

George Slomp
Forrest MacKellar
Leo A. Paquette

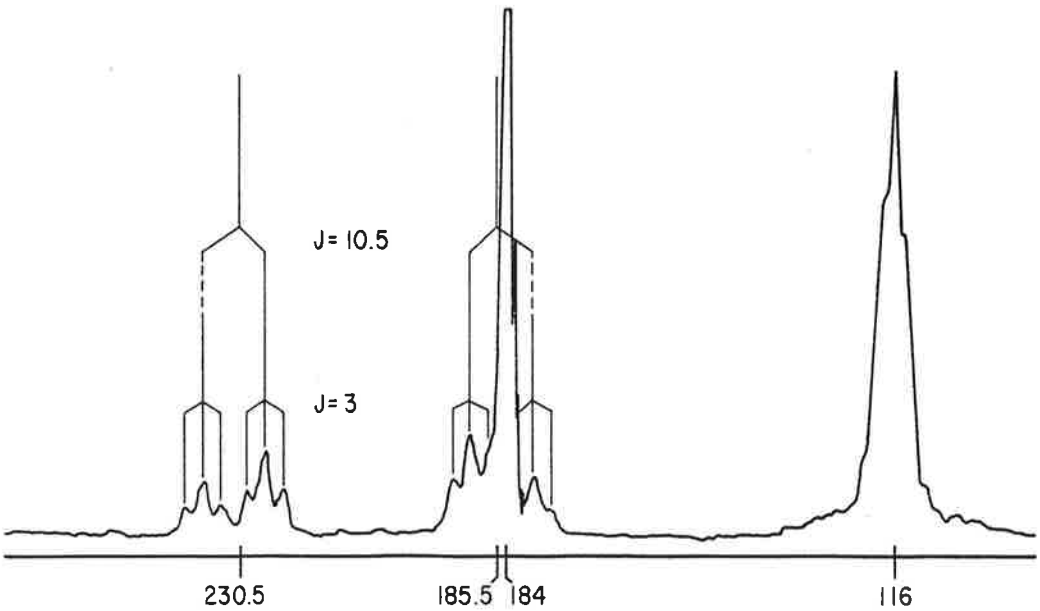
37-9

Figure I. N.M.R. Spectrum of Photodimer of N-Methyl-2-pyridone



cps., at 60 mc., from TMS, in $CDCl_3$

Figure II. N.M.R. Spectrum of Tetrahydro Derivative



cps., at 60 mc., from TMS, in $CDCl_3$

UNIVERSITÉ D'OTTAWA
FACULTÉ DES SCIENCES PURES ET APPLIQUÉES

UNIVERSITY OF OTTAWA
FACULTY OF PURE AND APPLIED SCIENCE

OTTAWA 2, CANADA

DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

October 19th, 1961.

Dr. A.A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.,
U.S.A.

Dear Dr. Bothner-By,

May I say that I greatly appreciate receiving MELLON-M-R. I am including in this letter summaries of some of our current work in n.m.r.

(a) Cyclic 2,3-disubstituted butanes.

The spectra of the acetonides (2,2,4,5-tetramethyl dioxolanes) and cyclic carbonates of meso and dl 2,3-butanediol have been analyzed as $X_3AA'X'_3$ systems by the method previously used (Proc. Chem. Soc., 327 (1959)) and the following coupling constants (in cps.) have been obtained.

	$J_{AA'}$	J_{AX}	$J^*_{AX'}$
meso-2,3-butanediol cyclic carbonate (cis)	7.35	6.55	-0.15
dl-2,3-butanediol cyclic carbonate (trans)	7.20	6.10	-0.10
cis-2,2,4,5-tetramethyl dioxolane	5.85	6.30	-0.25
trans-2,2,4,5-tetramethyl dioxolane	8.35	5.90	-0.15

* Assuming J_{AX} to be positive

In all these compounds the 1:3 coupling constant $J_{AX'}$ has a finite value of opposite sign to J_{AX}.

(b) Spectra of compounds containing $\overset{C}{C}\!>\!CHCH_3$ groups.

It was observed in our laboratory that the methyl band of the alkaloid lycodine and its derivatives was either unsplit, or a poor doublet of very small splitting (F.A.L. Anet and V. Rao, Tetrahedron Letters No. 20, 9 (1960)), although in either case the band was broad. The chemical evidence showed that the grouping $\begin{matrix}-CH_2\\-CH_2\end{matrix}\!>\!CH\text{-}CH_3$ was present. Similar apparently small (or even zero) "coupling constants" have been found by J.I. Musher in the dimethylcyclohexanes (Spectrochimica Acta, 16, 835 (1960)) and by G. Slomp and B.R. McGavrey in some 6-methyl steroids (J. Am. Chem. Soc., 81, 2200 (1959)) for which no explanation was given. In all these cases the tertiary proton adjacent to the methyl group can be expected to be only slightly chemically shifted from, but strongly coupled to neighbouring CH_2 or CH groups. It is important to realize that in such cases the observed splitting of the methyl band may give a quite misleading idea of the coupling constant. This is true even if the chemical shift between the methyl group and adjacent proton is large and the methyl group is only coupled to the adjacent proton. A paper elaborating this point and containing a number of examples will appear in Can. J. Chem. (Nov.). In most cases a correct analysis of the spectrum would be very difficult. Deuteration in specific positions can make the analysis simple. Thus 2,2,6,6-tetradeuterio-1-methylcyclohexane has a $>\!CHCH_3$ grouping that can be analyzed, to a very good approximation, as an AB_3 system. The CH_3CH coupling constant (6.8 cps.) has thus been obtained and is considerably larger than the splitting (not the coupling constant!) (4.7 cps.) of the methyl band (at 60 Mc/sec.) of 1-methylcyclohexane. The point made here has of course much wider implications than the specific subject mentioned above.

Of course the term "coupling constant" should not be used merely to indicate the separation of two lines or the splitting of a band unless analysis indicates that these are indeed equal to the coupling constant.

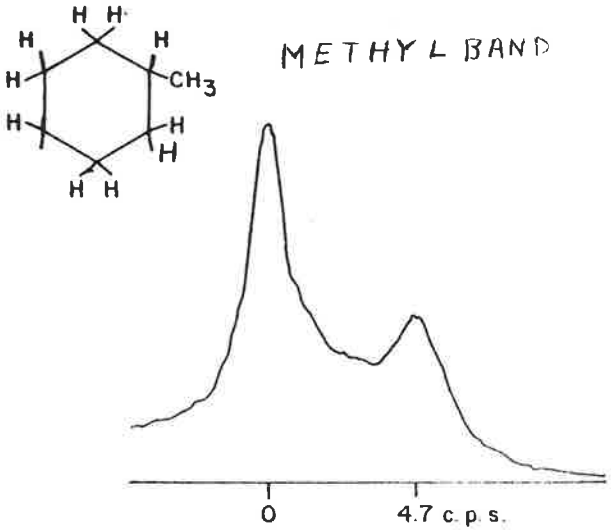
Yours sincerely,

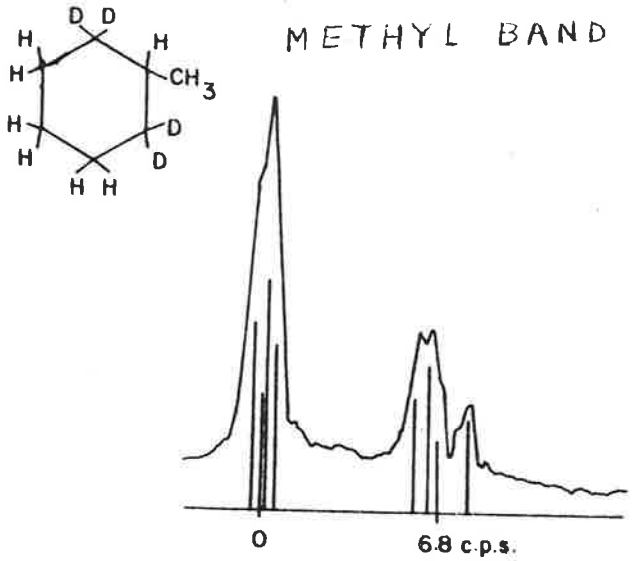
F.A.L. Anet

FALA/cb

F.A.L. Anet.

37-11





Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

6th Oct., 1961

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By

We have interest in expanding the Bloembergen's theory on nuclear relaxation to a multi-spin system. As you know, the relaxation times are calculated by regarding the dipole-dipole interactions as a time dependent perturbation, where the Brownian motions are treated classically and incorporated in the transition probabilities through a certain correlation function $K(\tau)$. In Bloembergen's treatment the correlation function is assumed to be given by

$$K(\tau) = K(0)\exp(-|\tau|/\tau_c),$$

where τ_c is the correlation time. The assumption is justified in the light of Debye's theory on the dielectric relaxation, in which the molecule is treated as a small sphere. However, by the study of dielectric relaxation, many substances which do not obey the Debye's theory have been found. It means that the correlation function is not characterized by a single correlation time. The same circumstance may be expected in the nuclear magnetic relaxation, especially, in the resonance of high polymers.

The discrepancy between the Debye's theory and the experiments may be attributed to the anisotropic Brownian motions, because the rotational and translational Brownian motions depend strongly on the molecular shape as well as the viscosity of liquid. The Brownian motions of an ellipsoid were investigated from a theoretical view point by Perrin, who also gave a theory of dielectric relaxation based on this anisotropic motions. The Perrin's theory is applicable to the substances which can not be treated by the Debye's

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theory. It is, therefore, hoped to calculate the magnetic relaxation times by using the Perrin's theory.

The calculation is characteristic in the following two points: 1) the translational Brownian motions which do not affect the dielectric relaxation should be considered; the translational Brownian motions depend on the rotational Brownian motions but the latters do not depend on the formers, and 2) the correlations between different interatomic vectors should not be neglected. Detailed explanation will not be given here; it is very complicated. We will, however, show the effect of the anisotropic motion, taking the three-spin system of acrylic acid as an example.

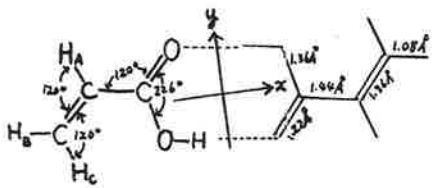
Acrylic acid has a dimeric structure below 130°C, and if the structure is assumed as the figure, the ratio of the rotational diffusion constant around the principal axes, x, y, and z, will be approximately given by $D_x = 1.77D$ and $D_y = D_z = 0.61D$, where the constants are measured with a proper unit D. In order to see the anisotropic effect, you can consider, a spectral density,

$$J_{ijkl}(\omega) = g_{ij} g_{kl} \, j_{ijkl}(\omega),$$

and

$$g_{ij} = \hbar \gamma^2 r_{ij}^{-3};$$

the transition probabilities of the relaxation are proportional to the spectral density. This spectral density is caused because of the existence



of a certain correlation between two vectors r_{ij} and r_{kl}; the two vectors may or may not be equivalent one. It is noticed here, that $j_{ijkl}(\omega)$ is independent of the interatomic distances; it depend only on the direction of the interatomic vectors.

If the Brownian motion is isotropic (we will discuss here only the effect of the rotational motion), you can expect

$$j_{ABAB} : j_{BCBC} : j_{CACA} = 1 : 1 : 1,$$

on the other hand, the ratios become

$$= 1.2 : 1.0 : 1.5$$

for anisotropic motion. And also $j_{BACA} : j_{CBAB} : j_{ACBC}$ 0.37: -0.5: 0.04 for isotropic motion, and 0.47: -0.17: 0.36 for anisotropic motion.

We can define a potential force of nuclear relaxation at a particular position in the molecule by the following way: for example, for the position of the proton A, it is defined as $\psi_A = j_{ABAB} + j_{ACAC} + j_{ABAC}$. This value is proportional to the spectral density of fluctuating field at the position A, provided that the interatomic distances, r_{AB} and r_{AC}, have a unit length. Thus the potential forces are

$$\psi_A : \psi_B : \psi_C = 2.74 : 1.00 : 2.08 \quad \text{for isotropic rotation}$$

and

$$= 2.25 : 1.00 : 1.72 \quad \text{for anisotropic rotation.}$$

These values of the potential forces give a measure for an effect of anisotropic Brownian motion, from which it will be supposed that the nuclear relaxation may be used as a method useful to investigate the molecular structure.

Yours sincerely

Hiroshi Shimizu

Hiroshi Shimizu

Shizuo Fujiwara

Shizuo Fujiwara

37-13

CABLE ADDRESS "RESEARCH"

IN YOUR REPLY PLEASE QUOTE

FILE No.

NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF PURE CHEMISTRY

OTTAWA 2, October 12, 1961

Dr. Axsel A. Bothner-By,
Mellon Institute,
440 Fifth Avenue,
Pittsburgh 13, Pennsylvania

Dear Axsel:

I am sending you some information on gem hydrogen coupling constants in CH_3X compounds which may be of interest to M.E.L.L.O.N.M.R. readers. The spacings were obtained for the CH_2DX compounds with a Varian spectrometer operating at 40 M c/s. The separations were measured by wiggle beat and side band techniques and the results given in the Table are the averages from six measurements. The HH coupling constants were obtained from

$$J_{HH} = \frac{\mu_H}{\mu_D} \cdot \frac{I_D}{I_H} \times J_{HD} = 6.55\ J_{HD}$$

so that an error of 0.05 c/s in J_{HD} is about ±0.4 c/s in J_{HH}. Using the values of J_{HH} in the Table, the HCH angles obtained from the theoretical curve of Gutowsky, Karplus and Grant are compared with the experimental values obtained from complete microwave structure determinations. The agreement is seen to be quite satisfactory except perhaps for CH_3F and CH_3OH.

Best regards,

Yours sincerely,

Harold

H.J. Bernstein

HJB/rt

Compound	J^*_{HD}	J_{HH}	HCH[a]	HCH[b]
CH_2DF	1.47	9.6	112.5	110.7
CH_2DCl	1.66	10.8	111.5	111.2
CH_2DBr	1.57	10.2	112.0	112.0
CH_2DI	1.41	9.2	113.0	112.2
CH_2DOH	1.66	10.8	111.5	109.1[c]
CH_2DCCl_3	2.00	13.0	109.8	
CHD_2CCl_3	2.00	13.0	109.8	

[a] Values calculated from theory of Gutowsky, Karplus and Grant, J. Chem. Phys. 31, 1278 (1959). An error of ±0.4 c/s in J_{HH} corresponds to about ±0.5 degrees.

[b] C.C. Costain, J. Chem. Phys. 29, 864 (1958).

[c] See S. Mizushima and T. Shimanouchi, Am. Rev. Phys. Chem. 7, 450 (1956).

* The experimental error is ±0.05 c/s.

37-14

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THE RESEARCH LABORATORY · ZÜRICH 8
KLAUSSTRASSE 43 · TELEPHONE 051/472420

Zurich, October 5th, 1961

Dr. Bothner-By
Director of Research
MELLON INSTITUTE
4400 Fifth Avenue

Pittsburgh 13, Pa

U.S.A.

Dear Dr. Bothner-By,

Your reminder has reached our laboratories thus obliging us to send you a tip as to a method we are using to calibrate the A-60 frequency scale. It is much more rapid for use in the field than the system of using an audio oscillator synchronised to the power line frequency.

We use a sample of 5% chloroform in carbon tetrachloride (or 2% Benzene in the same solvent) with TMS added. The separation between the two lines being 436 cps.

Our procedure is simple and goes like this:

(1) First we make certain that the zero adjustment remains constant when one switches between all the various sweep width settings from 50 to 1000. If they are not constant, then we loosen the sprocket which drives the recorder chain and rotate that sprocket on its shaft until we obtain the desired constant zero setting for all sweep widths. It is usually necessary to rotate the sprocket only about 40 degrees.

(2) Secondly we calibrate the sweep offset control, for this is the control which we will use in principle to calibrate all of the other settings. So we carefully set the TMS line at zero on the 50 cycle sweep width, then insert 436 cycles of offset and run the recorder again to see if the chloroform line is superimposed on the zero. If it is not, we adjust the "minus 1 volt adjust" until the desired super position is obtained.

(3) Having made the above adjustment we then proceed to the adjustment of the 500 cycle offset adjustment. We switch to "50 cycle sweep width (-500 offset)" and we insert 500 cycles of offset on the sweep offset control. This should bring the TMS line back to zero again, and we adjust the "-500 cycle adjustment" until this condition is obtained.

. / .

KLYSTRONS, TRAVELING WAVE TUBES, BACKWARD WAVE OSCILLATORS, LINEAR ACCELERATORS, MICROWAVE SYSTEM COMPONENTS,
R.F. SPECTROMETERS, MAGNETS, MAGNETOMETERS, STALOS, POWER AMPLIFIERS, GRAPHIC RECORDERS,
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(4) We then proceed to the adjustment of the sweep widths for each of the five settings using the sweep offset control to cause lines to fall at the left-hand edge of the chart paper. We assume that the offset readings introduced on the offset control are correct and adjust the individual sweep width adjustments until the lines fall properly at the left-hand edges of the paper.

As for the A-60 we too have discovered that the resolution stability is sensitive to room temperature fluctuations (our instrument is not in an air conditioned room) but we can operate it and get an excellent resolution by simply avoiding strong air drafts. We put the instrument on "Stand-By" position at night then first thing in the morning we switch back to "Operate" with the air spinner on (the spinning air is on all the time during the day); after a ½ hour the instrument is mostly equilibrated and a small readjustment of the fine Y gradient and curvature control allows us to split the first line of the ethanol quartet. (We own a precious ethanol sample which can be split well; an easier check is actually given by the acetaldehyde quartet although it is more difficult to adjust the resolution and especially the curvature, by means of this sample than it is by means of the first line of the ethanol quartet).

Sincerely yours,

Attilio Melera
Research Chemist
Varian A.-G.

James D. Ramsay
Manager - Varian
Service Center

AM:tb

37-15

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

6 October 1961

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

Dear Barry:

In a recent communication Baldeschwieler and Randall, (Proc. Chem. Soc. 1961, 303) have drawn attention to the accuracy with which ^{14}N chemical shifts can be measured by the double resonance technique. For such precise values to be of use, it is necessary to have an internal reference with a line position invariance of the same order as tetramethylsilane (T.M.S.), the internal reference employed in proton spectroscopy. Drs. D. W. Turner and J. A. Glassel of our department have just constructed an ancillary instrument for our Varian spectrometer which makes it possible to use T.M.S. as the internal reference for ^{14}N chemical shifts.

In principle, our method involves the production of a decoupling R.F. signal, the frequency of which is locked to the proton (56.4 Mc/s) oscillator through a series of division and multiplication stages so designed that the final frequency lies close to that of the ^{14}N resonance. A final audio-modulation permits the adjustment of the decoupling frequency to the exact ^{14}N resonance frequency.

The relation of the resonance frequencies of ^{14}N and ^{1}H is $\nu_N = 13\nu_H/180 \pm 1$ kc./s. The basic crystal frequency of our 56.4 Mc/s. oscillator is $\nu_H/4$ which on division by 3,3, and 5 becomes $\nu_H/180$. The 13th harmonic of this has the desired frequency. Modulation over ca. 2 kc/s. with a supressed carrier modulator followed by power amplification then produces a signal suitable for irraditing ^{14}N. The figure, which shows the spectrum of the $-\overset{+}{N}H_3$ protons of the methylammonium ion as a function of the modulation frequency, indicates that the ^{14}N resonance can be located to within ± 1 c/s.

In general, measurements are made in organic solvents containing T.M.S. and the ^{14}N chemical shift can then be expressed as:

$$\delta_N = 10^6 \left[(180\nu_N/13 - \nu_{T.M.S.}\right] / \nu_{T.M.S.}$$
$$= 10^6 \left[180\nu_{mod}/13 - \Delta\right] / \nu_{T.M.S.}$$

where ν_{mod} is the audio-modulation frequency and Δ is the chemical shift (c/s) of the decoupled proton referred to T.M.S., Δ being positive for protons less shielded than those of T.M.S.

This technique could readily be adapted to the study of ^{2}H, ^{7}Li, ^{11}B, ^{10}B, ^{13}C, ^{19}F, and ^{31}P.

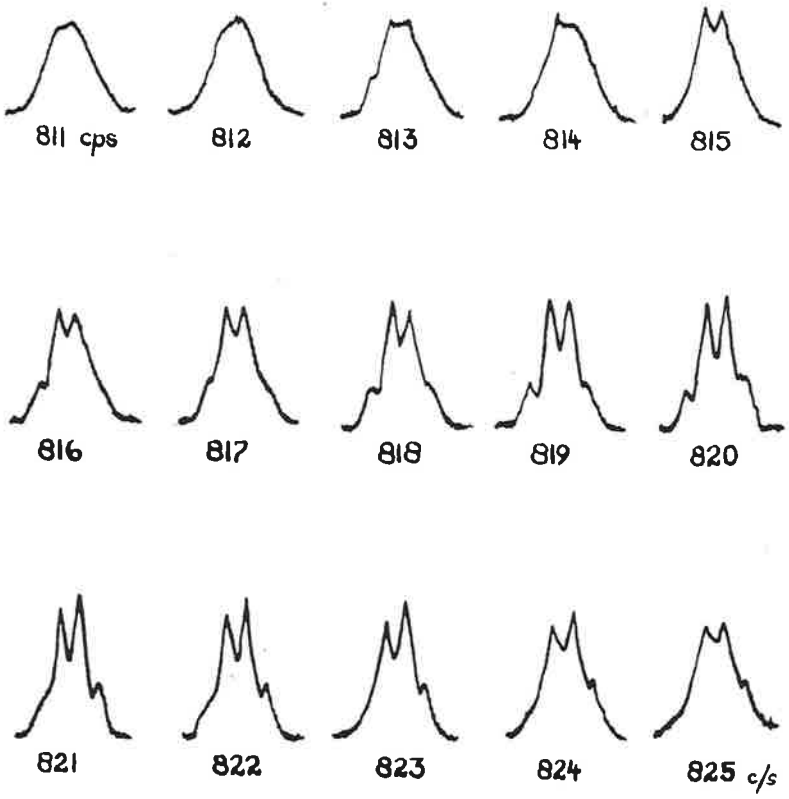
I would like to take this opportunity of telling you how much I am enjoying my visit to the Mellon Institute. I greatly appreciate having the opportunity to partake in such important matters as discussions on the future of NMR, viewing the World Series, bridge, chess, etc., etc.

With best wishes,

Yours sincerely,

Lloyd M. Jackman
Department of Organic Chemistry
Imperial College of Science and Technology
London, S.W. 7, ENGLAND

37-16



CHEMISTRY DEPARTMENT
THE UNIVERSITY
GLASGOW, W.2
TEL: [redacted]

4th October, 1961.

Dr. Aksel A. Bothner-By,
Director of Research,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13,
Pa., U.S.A.

Dear Dr. Bothner-By,

I must begin this letter by apologising to you for not writing much sooner than this. The reason is not because I have not had anything to write about but rather the reverse; I have too much and am not quite sure where to begin.

We have now had an A.E.I. high-resolution n.m.r. spectrometer for just over a month, and at the moment are equipped to operate, at room temperatures, at frequencies of 40 Mc./s. and 60 Mc./s. In the near future we should be equipped for operation over a range of temperatures and we hope, in addition, to add other frequency units. The apparatus is working rather well, the field stability and homogeneity is maintained with only a few minor adjustments each morning; we can attain a routine resolution of somewhere between 0·5 and 1 cycle; and we have already helped in clearing up a number of molecular structural problems.

I hope sometime to get round to writing to you about this work. Meanwhile, perhaps M.E.L.L.O.N.M.R. readers might be interested in the enclosed summaries of broad-line investigations into two of the "hydrates" of uranium trioxide. I became involved in these whilst working with Professor Gutowsky and continued with them after returning to Glasgow last October. The full account has just been sent off to J. Chem. Phys.

Many thanks for sending your bulletin. It is very much appreciated.

With best wishes,

Andrew.

Andrew L. Porte

37-17

PROTON MAGNETIC RESONANCE STUDIES OF POLYCRYSTALLINE SAMPLES OF SOME HYDRATES OF URANIUM OXIDES. I. β-$UO_3 2H_2O$.

A.L. Porte

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

H.S. Gutowsky

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

and

J.E. Boggs

Department of Chemistry, University of Texas, Austin, Texas.

The broad-line proton magnetic resonance spectra of polycrystalline samples of the compound formulated empirically as β-$UO_3 2H_2O$ have been investigated in the temperature range 77-350°K. The second moment of the absorption spectrum at 77°K indicates that some of the protons in the crystal are not present in water of crystallisation and an analysis of the derivative line shape function of this same spectrum shows that the compound is the trihydrate of pyrouranic acid, $U_2O_5(OH)_2 \cdot 3H_2O$. The chemical properties of the compound are accounted for on the basis of this formula.

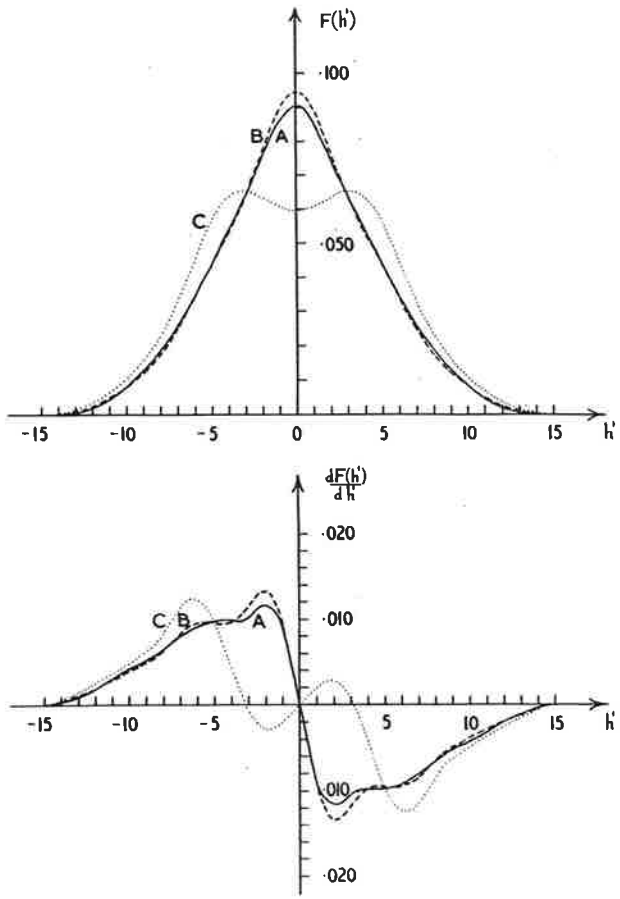


Fig. 1.

Fig. 1. Proton magnetic resonance spectrum of polycrystalline β-$UO_3 2H_2O$ at 77°K. Observed (—) and calculated (- - - ; ····) normalised absorption, F(h'), and derivative, dF(h')/dh', curves. h' is the displacement, in gauss, of the applied magnetic field from the value, 6324 gauss, at the centre of the absorption.

Curves B can be shown to be those expected for $U_2O_5(OH)_2 \cdot 3H_2O$, whilst curves C can be shown to be those expected for $UO_3 \cdot 2H_2O$.

39-83

PROTON MAGNETIC RESONANCE STUDIES OF POLYCRYSTALLINE SAMPLES OF SOME HYDRATES OF URANIUM OXIDES. II. β-UO_3H_2O.

A.L. PORTE

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

H.S. GUTOWSKY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois.

and

J.E. BOGGS

Department of Chemistry, University of Texas, Austin, Texas.

The broad-line proton magnetic resonance spectra of polycrystalline samples of the compound formulated empirically as β-UO_3H_2O have been examined in the temperature range 77-370°K. Analysis of the spectrum at 77°K shows that the compound is uranyl hydroxide $UO_2(OH)_2$. The inter-relationships between the different phases in the uranium trioxide - water system which involved the β- modification of the "uranium trioxide hydrates" are discussed.

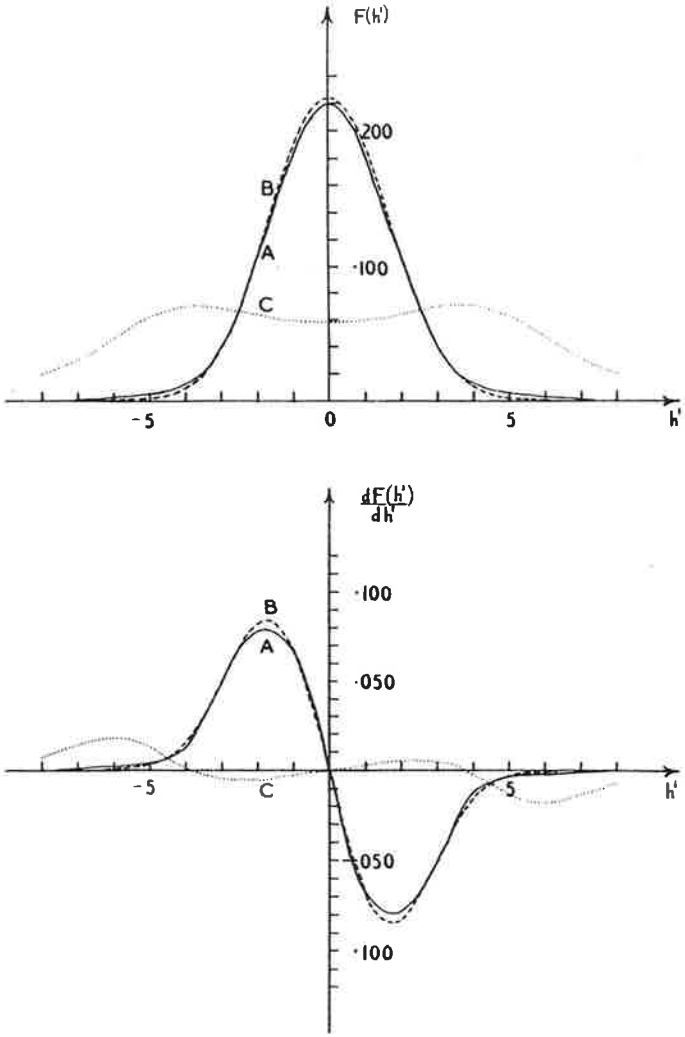


Fig. 2.

Fig. 2. Proton magnetic resonance spectrum of polycrystalline β-UO_3H_2O at 77°K. Observed (—) and calculated (- - - ; ····) normalised absorption, F(h'), and derivative, dF(h')/dh', curves. h' is the displacement, in gauss, of the applied magnetic field from the value, 6324 gauss, at the centre of the absorption.

Curves B can be shown to be those expected for $UO_2(OH)_2$. Curves C can be shown to be those expected for $UO_3.H_2O$.

INSTITUTE OF CHEMISTRY
UNIVERSITY OF UPPSALA
UPPSALA
SWEDEN

October 4, 1961

Dr. A.A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.
U.S.A.

Dear Dr. Bothner-By:

We think it is high time for us to tell you something about our present activities. We have recently completed a study on the NMR-spectra of substituted pyrroles. Such a study is somewhat more complicated than that of thiophenes and furans, due to the presence of the N-hydrogen, which as Abraham and Bernstein have shown, couples to the α- and β-hydrogens. We have found that these couplings are easily eliminated through base-catalysed (piperidine) prototropy. Thus fig. 1 shows the rather simple (40 Mc/s) spectrum of 2-pyrrolealdehyde which may be compared with that published by Abraham and Bernstein (Can. J. Chem. 39, 905 (1961). Another example is furnished by fig. 2a and b, which clearly reveal the great simplification obtained by this "chemical decoupling". We have also found that the base-concentration necessary to obtain decoupling depends upon the electronic effects of the substitutents in the expected way. Together with B. Gestblom we are about to investigate quantitatively the kinetics of the prototropy in pyrroles.

Full papers on the NMR-spectra of pyrroles have been submitted for publication in Arkiv Kemi.

In connection with our general program on the NMR-spectra of heteroaromatic compounds we are continuing our studies in the pyrimidine series.

We are also studying the NMR-spectra of some simple furans and have obtained some results which may be worth mentioning. Since the relay of the mesomeric effect of a substituent to the 4-position in thiophenes presumably involves resonance structures having decetts on the sulphur (Arkiv Kemi 16, 539 (1960)) one would predict that no mesomeric effect appears in the chemical shifts of the 4-hydrogen in 3-substituted furans. Characteristic differences between the chemical shifts of 3-substituted furans and the corresponding thiophenes have also been observed, but it appears that the shift of the 4-hydrogens in furans in some way also depends on mesomeric effects. In the 2-substituted furans the ratio δ_3/δ_5 is much larger than in the corresponding thiophenes in agreement with the lesser aromaticity of furan.

Best wishes for continued success with MELLONMR

Yours sincerely

Salo Gronowitz

Salo Gronowitz

Ragnar A. Hoffman

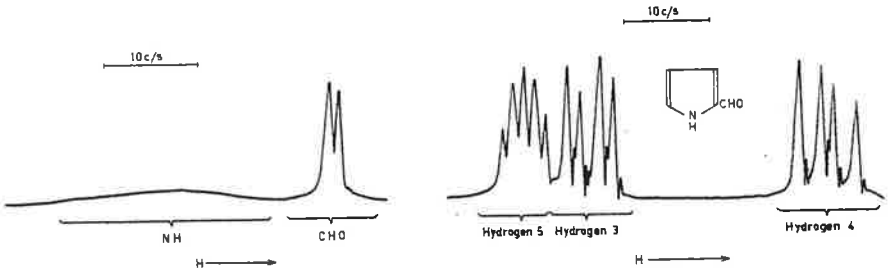
Ragnar A. Hoffman

37-20

37-21

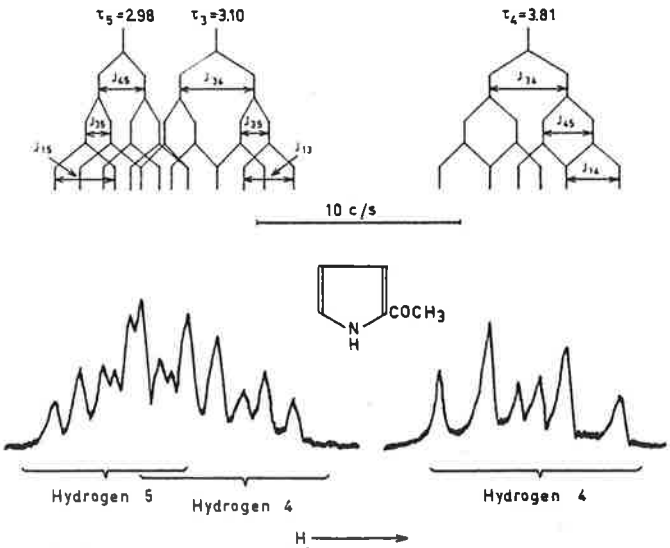
KEMISKA INSTITUTIONEN
UPPSALA UNIVERSITET
UPPSALA
TEL.: VÄXEL 594 80

Fig. 1



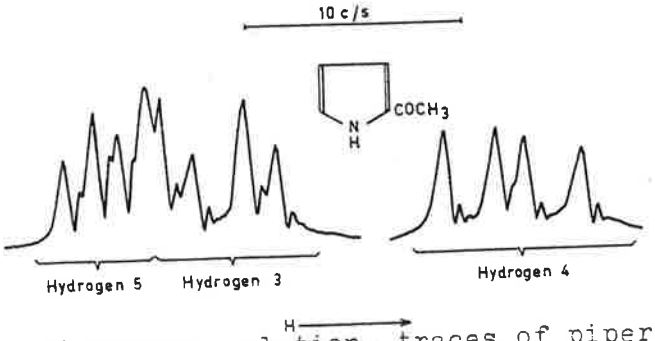
34% dioxane solution containing traces of piperidine.

Fig. 2a



25% dioxane solution

Fig. 2b



29% dioxane solution, traces of piperidine.

EDITOR'S CORNER

Apologies for the late arrival of MELLONMR this time. The assistant editor and circulation manager was in bed with the flu.

* * *

DEADLINE FOR NEXT ISSUE - MONDAY, NOV. 27.

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