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Newsletter

No. 155
AUGUST, 1971

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DEPARTMENT OF CHEMISTRY

TEL: (215) LA 5-1000

13 July 1971

Prof. B. L. Shapiro
Department of Chemistry
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Dear Barry:

Dr. Ilana Tamir came to Bryn Mawr from Notre Dame last September as the Huff Postdoctoral Fellow. One of the things she and I have done this year is a

Calculation of Exchange-Broadened NMR Spectra
AB Nuclear Magnetic Double Resonance

Last summer I had examined the effect of exchange on the AX NMDR spectra [J. Magn. Res. 4, 184 (1971)], and had uncovered two features of possible interest: at low rf power in the decoupling field, the A part of the AX spectrum (observe A, irradiate X) shows both positive- and negative-going lines. The double resonance spectrum is richer in structure for all rates of exchange up to $2\pi J$, and may provide, in some situations, a more facile measurement of the rate of exchange. At high rf power, only one (decoupled) line appears, whose intensity varies from positive to negative with the exchange rate, passing through zero for exchange rate = relaxation rate.

We endeavored to see if these same features could be detected and exploited in the strongly-coupled AB system as well.

The first can: the enclosed photographs show histograms of the AB double resonance spectrum (B nucleus to the right, A to the left) with the following parameters: shift= $J=10$, v_2 (2nd rf field) = 10, relaxation rate = 5, exchange rate = 0 (figure 1) and 5 (figure 2). Irradiation is at the resonance frequency of the B nucleus. The lines have been artificially broadened by increasing the relaxation rate to 5 because of the low resolution available using a histogram ("stick") plot.

The second feature from the AX calculations cannot be duplicated for AB systems, for, as v_2 is increased in an AB system, the A nucleus is perturbed as well as the B, and the clean separation of the two resonance frequencies cannot be

achieved. Consequently, there is not available the simple measurement of the ratio of exchange to relaxation rates that the AX system afforded.

The programming for these calculations is little different than what was reported earlier, save that special care must be exercised in the calculation of populations of energy levels to detect the apparent "crossing" of energy levels that some subroutines for matrix diagonalization (MATRIX) can generate.

Sincerely yours,

Jay

Jay Martin Anderson

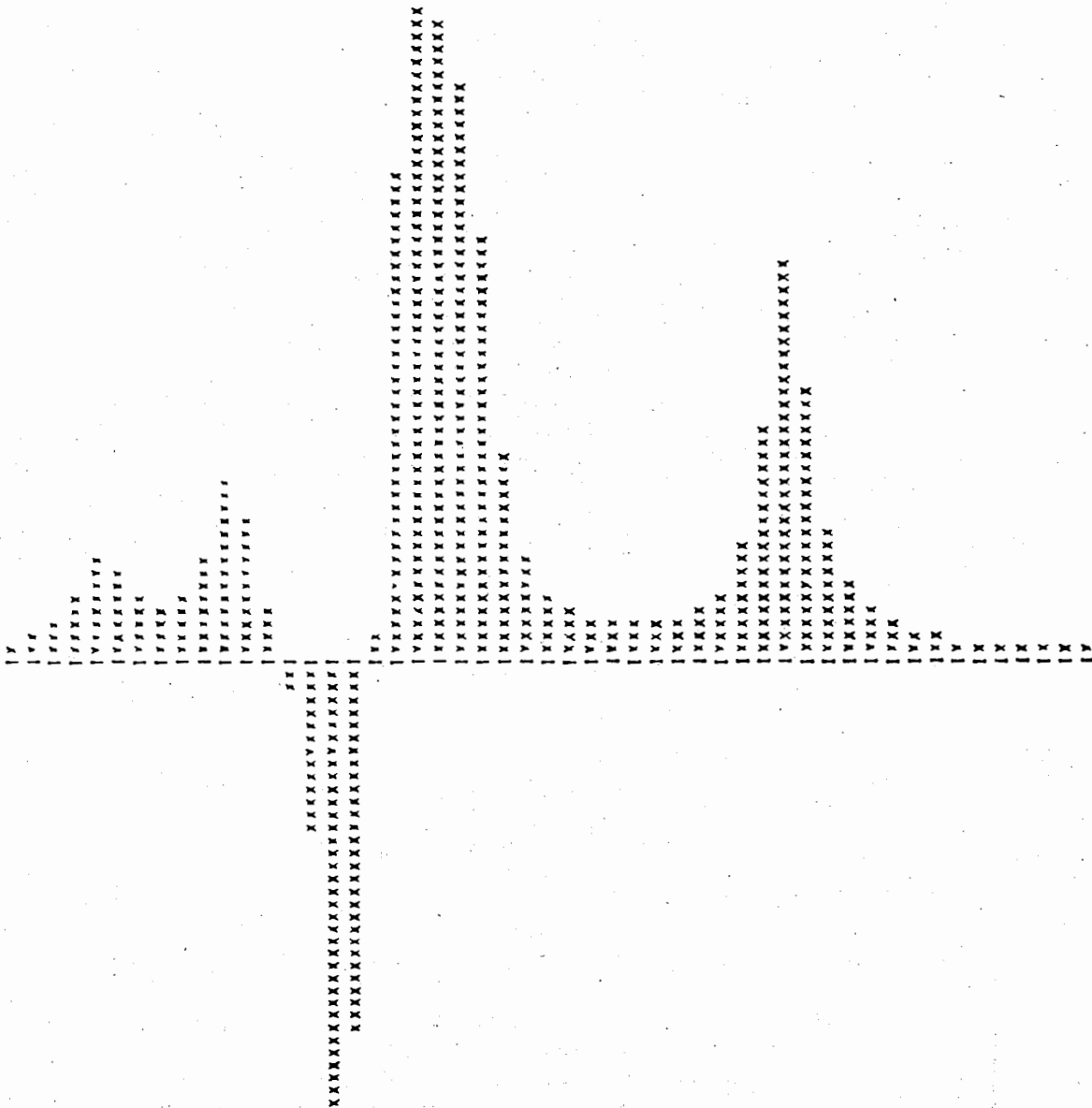


Fig. 1

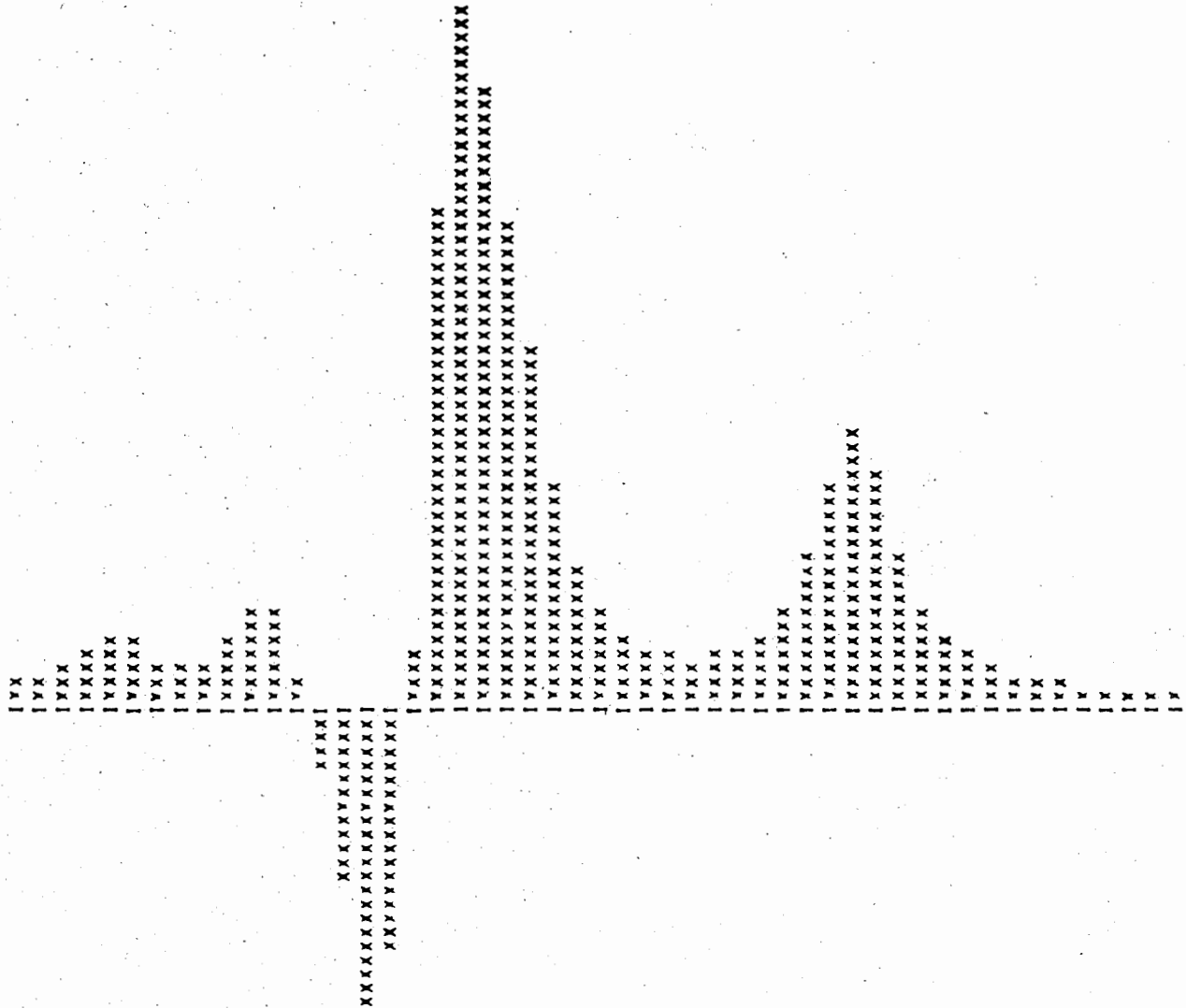


Fig. 3

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Department of Chemistry

July 7, 1971

Professor Bernard L. Shapiro
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DESPAIR or The Great Fluorine Shift Mystery

Dear Barry:

Fluorine chemical shifts are well known to respond in an extremely sensitive way to minute changes in molecular geometry; they could thus serve as a valuable tool in stereochemistry if it were not for the fact that we don't understand them. We have for some time been trying to do something about this situation by looking at asymmetric ethanes of the general formula RCF_2CXYZ (Table) and are just now beginning to see the light at the end of the tunnel. There are some other reasons why we decided to investigate model compounds of this kind, one of them being the possibility of applying a mathematical treatment of the Ruch - Ugi type to the time-averaged chemical shift differences, $\langle \Delta\phi \rangle$, between the diastereotopic geminal fluorines (for that reason the series includes all possible permutations of the five ligands H, F, Cl, Br, Ph for $R = Br$). For it is trivial to show that the quantity $\langle \Delta\phi \rangle$ must have precisely the same formal mathematical properties as the logarithm of the diastereomer ratio in asymmetric syntheses. However, the detailed computational verification of this part of the project still remains to be done.

In the course of this work if was necessary to carry out extensive low-temperature studies. It was then that we became fully aware of the dark depths of the FSM. These shifts seem to defy all common sense!

No.	R	X	Y	Z	$\langle \Delta\phi \rangle_{\text{tot}}^{\text{LT}}$	$\langle \Delta\phi \rangle_{\text{int}}^{\text{LT}}$	$\langle \Delta\phi \rangle_{\text{rot}}^{\text{LT}}$	$\langle \Delta\phi \rangle_{\text{tot}}^{\text{RT}}$
1	Br	H	F	Cl	6.20	0.91	5.29	3.83
2	Br	H	F	Br	5.58	1.09	4.49	4.18
3	Br	H	Cl	Br	6.50	0.52	5.98	3.30
4	Br	H	F	Ph	3.14	0.64	2.50	1.73
5	Br	H	Cl	Ph	10.58	(-) 0.37	10.95	4.91
6	Br	H	Br	Ph				9.50
7	Br	F	Cl	Br	2.81	0.24	2.57	1.65
8	Br	F	Cl	Ph	0.00 ₅	0.38 ₃	(-) 0.37 ₈	0.46
9	Br	F	Br	Ph				1.95
10	Br	Cl	Br	Ph	0.95	0.33	0.62	< 0.4
11	Cl	H	Cl	Ph	7.34	(-) 0.30	7.64	3.13
12	Cl	H	Br	Ph	11.83	(-) 0.07	11.90	6.28
13	Cl	F	Cl	Ph	0.39	0.42	(-) 0.03	0.62
14	Cl	H	F	I	2.87	1.28	1.59	2.44

We have been desperately trying to find or invent some decent theory that would account for their erratic pattern. Without success. (If anybody can suggest an idea of what we ought to try, short of ab initio self-consistent perturbation calculations on optimized geometries, we should like to hear about it). In particular, electric field calculations of the type reported by Feeney et al. are self-contradictory when applied to these compounds and could in most cases not even qualitatively account for the trends. How we eventually managed to make all the assignments with the help of several empirical criteria and why we are reasonably confident that they are correct, is a long story which we will save for another occasion.

There is an additional aspect of this work deserving attention, namely the light it throws on the origin of the anisochronism of geminal groups in conformationally mobile systems. The relevant data (in ppm) are presented in the Table. In all but two cases we could detect all three conformers at low temperature (LT) (for 6 and 9 only two were significantly populated). If one succeeds in assigning all six geminal fluorine shifts one can easily calculate the intrinsic shift difference $\langle \Delta\phi \rangle_{\text{int}}$ and the term $\langle \Delta\phi \rangle_{\text{rot}}$, which depends on population differences, from Gutowsky's equation (including the absolute signs of these terms, not shown in the Table). The first to point this out was Raban, who used the low-temperature data of Newmark and Sederholm for 3 and 7 (the numbers have been redetermined by us). For comparison, the observed RT values are also listed.

Although, as could not reasonably be expected otherwise, the FSM extends to these data as well, the following general features are worth noticing. (1) The intrinsic term is in general by no means negligible. (2) Most importantly, the various terms may differ in relative sign. This fact, though seemingly obvious from Gutowsky's analysis, appears to have been universally missed by the workers in this field, giving rise to much muddled thinking. It may happen (e.g. 8) that the total time-averaged chemical shift difference becomes zero in spite of the fact that the intrinsic term is substantial. (3) As an interesting corollary, the absolute magnitude of $\langle \Delta\phi \rangle_{\text{tot}}$, which is of course all that can be extracted from time-averaged spectra, may not only decrease or increase monotonically on increase of the temperature, but may sometimes show a more complicated behavior, for instance decrease to zero and then increase again. (4) The intrinsic term should be strongly dependent on the degree of distortion of the individual conformers from idealized staggered geometry, although a rigorous analysis shows that the situation is in reality somewhat more complicated. This effect is visible in the series 4 \rightarrow 1 \rightarrow 2 \rightarrow 14.

Sincerely yours,

Gerhard

Gerhard Binsch

Robert D. Norris

Robert D. Norris

P.S. To stay in character: "Destitute Experimentalists in Search of a Plausible Acronym with which to Invigorate their Report" (no plagiarism of Nabokov intended).



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THE MICHAEL FARADAY LABORATORIES

DEPARTMENT OF CHEMISTRY

July 9, 1971

Area Code 815

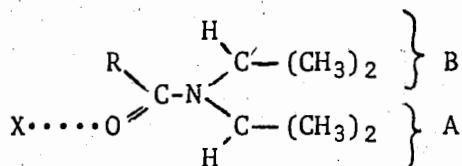
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Professor Bernard L. Shapiro
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Simultaneous Use of $\text{Eu}(\text{fod})_3$, $\text{Pr}(\text{fod})_3$ and Benzene Shifts for Amide
 Chemical Shift Assignments.

Dear Barry:

The hindered rotation about the central C-N bond in diisopropyl amides causes the appearance of two resonance peaks for the methine protons and two for the methyl protons at 0°C. in CCl_4 solution.



R = H or CH_3

X = $\text{Eu}(\text{fod})_3$ or
 $\text{Pr}(\text{fod})_3$

Frucht *et al.*¹ have unambiguously determined the assignment in diisopropylformamide (DIPF) in CDCl_3 solution using NOE and proton spin decoupling: methine A resonates to lower magnetic field than methine B and methyl A resonates to higher field than methyl B.

We have applied the lanthanide shift reagents², benzene solution studies, and spin decoupling to both DIPF and diisopropylacetamide (DIPA). One might guess that for each amide (a) benzene should shift the B proton peaks upfield faster³ than A, (b) $\text{Eu}(\text{fod})_3$ should shift the A proton peaks downfield faster than B, and (c) $\text{Pr}(\text{fod})_3$ should shift the A proton peaks upfield faster than B. Results (b) and (c) are expected because models show that for most conformations of the isopropyl groups, the Eu or Pr atom is closer in space to the A protons.⁴

The results of gradual addition of reagents to a CCl_4 solution of the amide at 0°C. are:

	DIPF	DIPA
Addition of benzene (All peaks move upfield)	Methines move apart Methyls move closer	Methines move closer Methyls move apart
Addition of $\text{Eu}(\text{fod})_3$ (All peaks move downfield)	Methines move apart Methyls move closer	Methine separation constant Methyls move apart
Addition of $\text{Pr}(\text{fod})_3$ (All peaks move upfield)	Methines move closer Methyls move apart	Methines move apart Methyls move closer

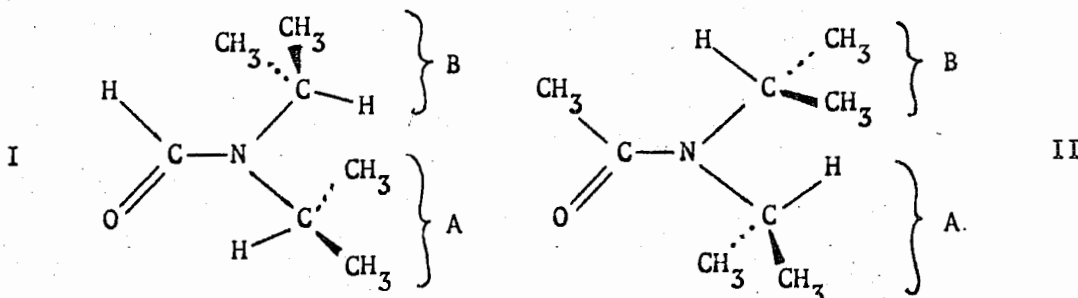
These results confirm the assignment of Frucht et al.¹ for DIPF and show that a chemical shift inversion occurs for DIPA: methine A resonates to higher field than methine B and methyl A resonates to lower field than methyl B.

For five-mole % solutions of the amides in CCl_4 at 0°C . the chemical shifts are (delta scale):

DIPF: methine A, 3.98; methine B, 3.68; methyl A, 1.27; methyl B, 1.29.

DIPA: methine A, 3.36; methine B, 3.90; methyl A, 1.31; methyl B, 1.20.

Steric effects probably cause the chemical shift inversion. Low temperature NMR studies show that DIPA possesses hindered rotation about the $\text{N}-\text{C}-\alpha$ bond (this effect was not observed in DIPF down to -60°C .)⁶ The most probable rotamers for DIPF and DIPA may be I and II. These are similar to



the C_1T_4 and C_3T_6 conformations for amide isopropyl groups⁶ in which the methine protons are about 30° out of the amide plane. The A methine proton of I and the B methine proton of II are in deshielding regions of the amide bond compared with the B methine proton of I and the A methine proton of II. Therefore, if the lifetimes of rotamers I and II are sufficiently long, the inversion of relative shielding between DIPF and DIPA is explained.

The interaction of the shift reagent with amides is being studied in more detail.

Sincerely,

Lori

Laurine L. Graham

1. M. Frucht, A. H. Lewin and F. A. Bovey, *Tetrahedron Lett.*, 3707 (1970).
2. $\text{Eu}(\text{fod})_3$ is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate, $\text{Eu}(\text{III})$.
3. W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970).
4. And the O-Eu-H internuclear angle is smaller than 35° . The shift of formyl or acetyl protons with $\text{Eu}(\text{fod})_3$ or $\text{Pr}(\text{fod})_3$ is more than twice as large as shifts for the N-alkyl protons, indicating the amide carbonyl oxygen as the site of interaction.
5. As well as for diisopropylpropionamide and diisopropylbutyramide, which were studied by benzene dilutions and spin decoupling.
6. T. H. Siddall, III, and W. E. Stewart, *J. Chem. Phys.*, **48**, 2928 (1968).

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Stockholm July 9, 1971

Professor Bernard Shapiro
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Water Internal Interface Effects

Dear Barry:

Barbro Maijgren of our group has for some time been looking into a few aqueous solute interaction problems. Here are some of her results.

In a $^{85}\text{Rb}^{79}\text{Br}$ /ethanol/ water mixture the width of the Rb resonance at constant ethanol concentration varies with the salt concentration as shown in Fig. 1.

A similar result for the Br resonance confirms this observation as do the results from observations on t-butanol included in Fig. 1. We are now investigating the influence of the concentration and type of the organic component. Fig. 2 shows the variation of the Rb and Br band widths at 1 M RbBr as functions of the concentration of the organic phase. The initial relative magnitudes of the line broadenings remain when viscosity effects are included.

The difference in ethanol concentration dependence of

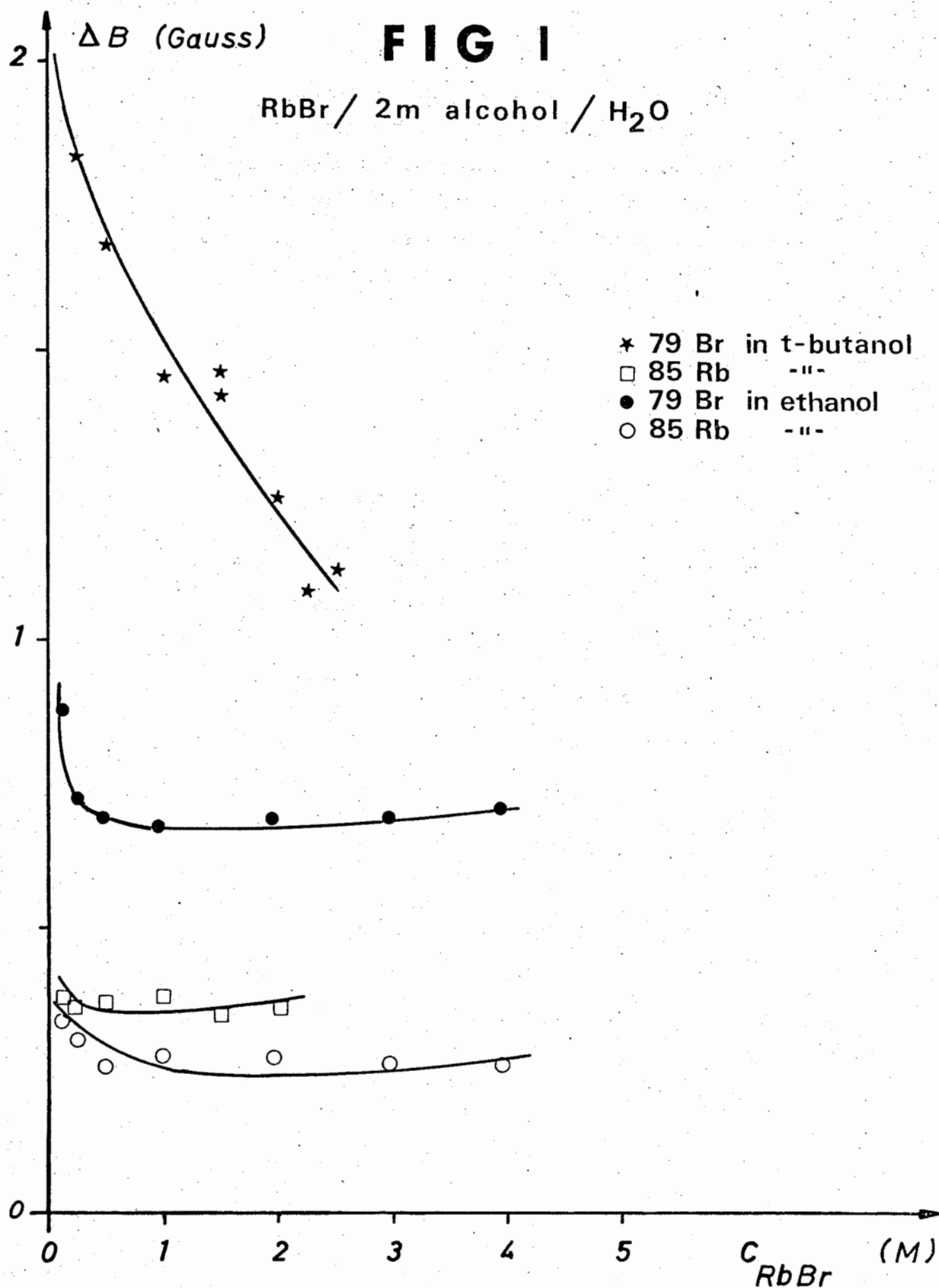
the Rb and Br signals is in rather satisfactory agreement with the ratio of the ionic polarizabilities, supporting the hypothesis of electric field gradients at the internal interface of the water lattice. You shall hear more about this in due course of time.

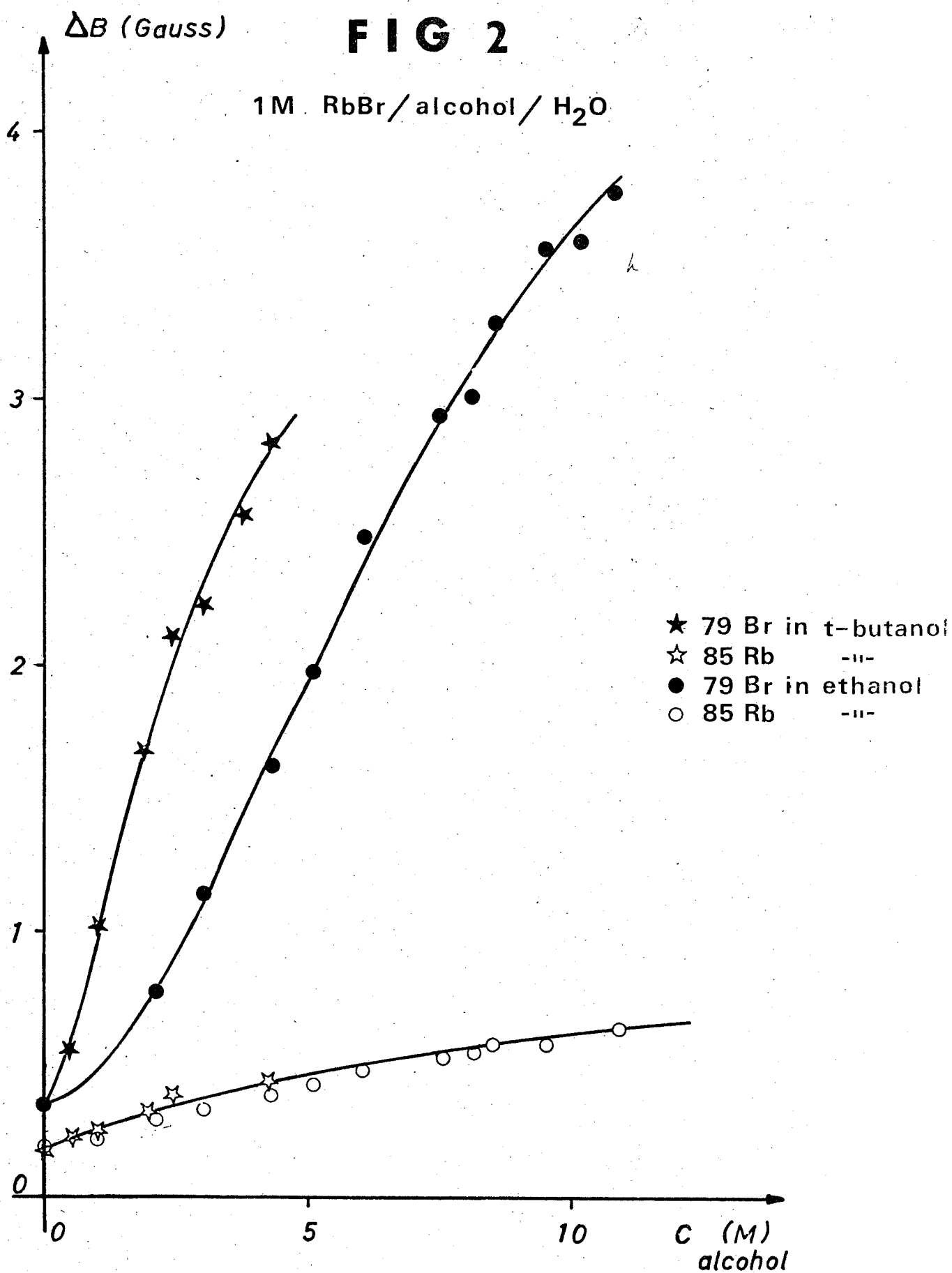
Regards,

Yours,

A handwritten signature in cursive script, appearing to read 'Erik'.

Erik Forslind







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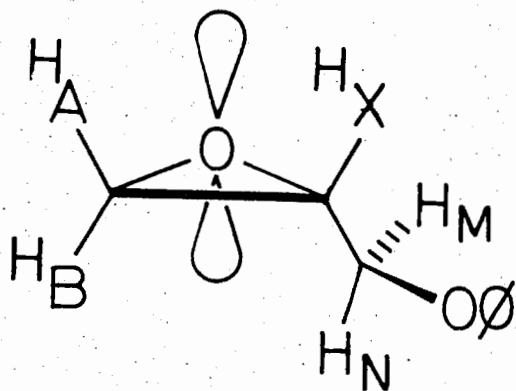
GENT, 12 July 1971
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Professor B.L. Shapiro
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Coupling values and relative signs in phenoxy propylene oxide

Dear Barry,

Recently we have analyzed the pmr spectra of some methylene substituted oxirane ^I compounds of which the most favourable case was phenoxypropylene oxide (see formula for



most probable conformation). With the aid of INDOR ^IH- {^IH} technique, peak attribution of the complicated X-part of the ABXMN spin system, and the evaluation of the signs of coupling constants involved were possible.

.../...



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.../...

The results were as follows :

$\delta(M) = 3.95$ $^2J(M,N) = -11.0$ Hz $^3J(N,X) = +5.05$ Hz
 $\delta(N) = 3.79$ $^2J(A,B) = +5.25$ Hz $^4J(B,M)$; $^4J(B,N)$ and $^4J(A,N)$
 $\delta(X) = 3.12$ $^3J(A,X) = +4.20$ Hz Small but real
 $\delta(A) = 2.65$ $^3J(B,X) = +2.40$ Hz $^4J(B,M)$ negative
 $\delta(B) = 2.51$ $^3J(M,X) = +3.80$ Hz

It is interesting to compare these values and especially their sign with previously published data ² on chloromethyl oxirane (Cl instead of O \emptyset), especially $^2J(M,N) = +11.7$, $^3J(M,X) = -4.0$, $^3J(N,X) = -6.6$, $^4J(A,N) = -0.1$: $^4J(B,M) = -0.2$ and $^4J(A,M) = +0.6$ Hz. Thus conflicting data with respect to the sign and the occurrence of a "classical" (planar zig-zag path) long-range (e.g. $^4J(A,M)$ not observed in the actual case) are found.

1. M. Anteunis, Chr. Van den Bossche and G. Verhegge ; O.M.R in press.

2. C. Reilly and J. Swalen ; J. Chem. Phys, 35², 1522(1961)

Prof. M. Anteunis

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Date 16 JUL 71

Dear Professor Shapiro,

NMR at Port Sunlight

The Solubilization of p-Xylene in SDS Micelles

Hydrogen Bonding and Molecular Motion in Simple Alcohol-Water Mixtures

Molecular Mobility in Lamellar Phase Liquid Crystals

In this laboratory NMR is used to investigate the properties of surfactant-water mixtures. Our instrumentation consists of two Brüker pulsed NMR spectrometers (BKR-322 and BKR-302), Perkin-Elmer high resolution spectrometers (40, 60 and 100 Mhz), a Varian PA-7 broad line spectrometer, and a home-made broad line spectrometer operating at 30 Mhz. These spectrometers are maintained, modified and updated by M L Bellis. Three recent NMR studies are summarized below.

Surfactant molecules, which consist of a hydrophilic polar head group and a hydrophobic paraffin chain, aggregate in aqueous solution to form micelles above a certain concentration known as the critical micelle concentration (c.m.c.). These micellar solutions will dissolve ("solubilize") compounds with low water solubility. The solubilization of p-xylene in sodium dodecyl sulphate ($C_{12}H_{23}SO_4Na$) micelles has been studied by a high resolution technique utilizing the line broadening caused by paramagnetic counterions. It was found that the p-xylene cannot be considered to be solubilized at the centre of the micelle, but instead is distributed uniformly throughout the micellar interior. The correlation time for the interaction between the dissolved p-xylene and the ions studied (Mn^{++} , Gd^{+++} , Cu^{++}) was dominated by a single correlation time of approximately 6.5×10^{-11} seconds, which is probably due to the diffusional motion of the p-xylene within the micelle. (K K Fox, I D Robb and R Smith.)

The second contribution involves an investigation of the hydrogen bonding properties of water and the molecular mobility of water molecules. Chemical shifts have been measured for a series of short chain alcohols: ($MeOH \rightarrow Bu^nOH$, Pr^iOH , Bu^tOH) as a function of temperature and of their mixtures with water at

two temperatures, 273°K and 307°K. These experiments have been supplemented by measurements of relaxation rates (T_1^{-1} , T_2^{-1} for the hydroxyl protons at 273K and 298K.

The NMR chemical shifts and relaxation rates of hydroxyl protons in dilute aqueous solutions of alcohols can be explained in terms of the interactions of polar head groups and non polar alkyl groups with water. The effect of the head group on water structure, which gives rise to a low field shift, dominates over the effect of the alkyl groups which give rise to a high field shift at both 273°K and 307°K, but the effect of the alkyl group on water structure becomes relatively more important at 307°K. Both the alcoholic head groups and the alkyl groups increase the relaxation rate of water protons but, again, the behaviour is dominated by the effect of the head group on water structure. (J Oakes.)

Smectic liquid crystals (l.c.) are formed at certain concentrations in surfactant/water systems. One of the most common l.c. phase structures is the lamellar phase which consists of alternate layers of surfactant and water molecules. Studies of alkyl chain mobilities in these systems using E.S.R. spin probes have indicated that molecular motion increases with increasing distance from the head group⁽¹⁾. Spin lattice (T_1) relaxation rates are related to molecular mobility and the relative motions of different parts of the alkyl chains have been investigated by the measurement proton and fluorine T_1^{-1} values of a $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_{10}\text{CO}_2\text{Na}/\text{D}_2\text{O}$ lamellar phase sample. The relative T_1^{-1} values expected for no distribution of motions can be calculated using the formula for dipolar relaxation and the results are shown below:

Temperature	T_1^{-1} (proton)	T_1^{-1} (fluorine) (a)	T_1^{-1} fluorine (calc.)
40°C	3.0s ⁻¹	0.76s ⁻¹	0.64s ⁻¹

(a) Adjustment made for terminal CF_3 .

These results appear to indicate only a small (if any) distribution of rotational motions. Temperature variation and spin-spin relaxation measurements are consistent with these results. (G J T Tiddy.)

Papers on the above investigations will be submitted for publication shortly.

Reference

- (1) W L Hubbell and H M McConnell, J. Am. Chem. Soc., 93, 314 (1971)
J Seelig, J. Amer. Chem. Soc., 92, 3881, (1970)

Yours sincerely,

M. L. Bellis

L BELLIS

K Fox

K K FOX

J. Oakes

J OAKES

I D Robb

I D-ROBB

R. Smith

R SMITH

G J T Tiddy

G J T TIDDY

NORTH TEXAS STATE UNIVERSITY
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DEPARTMENT OF CHEMISTRY

July 15, 1971

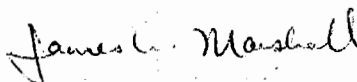
Dr. Bernard L. Shapiro
TAMNMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas

Dear Barry:

In the past several months, we have been synthesizing a series of monosubstituted benzene compounds and have studied their cmr and pmr patterns. These compounds, which include benzoic acid, methyl benzoate, benzoyl chloride, benzyl alcohol, benzonitrile, and toluene, were developed from the reaction of phenyl Grignard reagent with labeled carbon dioxide in a classical series of reaction steps. The art of synthesizing radioactive carbon-14 labeled compounds had previously been developed for many years, and thus the literature yielded procedures that we thought would be very useful. However, we found that the published procedures commonly involved the isolation of the labeled radioactive material by washing it out with natural abundance material. In the case of carbon-13 syntheses, this dilution technique was to be avoided, since a high percentage of labeled molecules was necessary to obtain the desired nmr spectral patterns. Hence, it was necessary to develop new techniques for the synthesis of carbon-13 labeled compounds; these techniques were worked out on a vacuum line system. Excellent yields for all reactions were thus obtained.

From the cmr spectra for these compounds, all carbon-carbon coupling constants involving the labeled carbon atom were obtained. In addition, the pmr spectra of some of the compounds (those whose protons have different chemical shifts: benzoic acid and methyl benzoate) were studied and all carbon-proton coupling constants involving the labeled carbon atom were obtained. Since the pmr spectra of benzoic acid and methyl benzoate are second-order, it was possible to deduce some of the relative signs of the long-range carbon-proton coupling constants.

Sincerely,



James L. Marshall
Assistant Professor of Chemistry

TITLE: CMR AND PMR STUDIES OF MONOSUBSTITUTED BENZENE COMPOUNDS

MONTECATINI EDISON S.p.A.

SEDE IN MILANO - CAPITALE L. 749.000.000.000 INTERAMENTE VERSATO

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Bollate, July 16, 1971

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Subject: Rotational isomers of $\text{CFCl}_2\cdot\text{CFCII}$

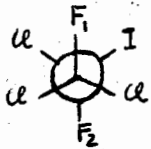

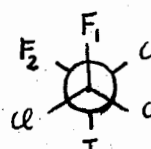
Dear Prof. Shapiro,

Thanks for your remainder. In connection with our work on rotational isomerism of fluoroethanes, we like to report the results obtained from the NMR spectra of $\text{CFCl}_2\cdot\text{CFCII}$ at low temperature. It is known that the vicinal couplings of the individual rotamers of substituted ethanes rarely can be directly measured even if observed at low temperature. The vicinal couplings of all individual rotamers could be measured, as far as we know, only for $\text{CF}_2\text{Br}\cdot\text{CFBrCl}$ (1,2) and $\text{CF}_2\text{Br}\cdot\text{CFBr}_2$ (3,4). Also $\text{CF}_2\text{Cl}\cdot\text{CFCII}$ (1) and $\text{CF}_2\text{I}\cdot\text{CFCI}_2$ (1) were "frozen down" at low temperature but only the vicinal couplings of one rotamer could be measured. To this poor list of successful studies of substituted ethanes we must add now the results obtained by us for $\text{CFCl}_2\cdot\text{CFCII}$. The spectrum of it at room temperature and at -90°C in CFCl_3 is reported in the attached figure. At room temperature, the band at low field ($-\text{CFCII}$) shows a more pronounced broadening than that at high field. This is due to a wider variation of rotamer chemical shifts for the fluorine of the $-\text{CFCII}$ group and to its incomplete averaging out at room temperature. At -90°C , the AB patterns of the three possible rotamers are clearly evidenced. The NMR parameters and the assignments given by us are collected below:

./...

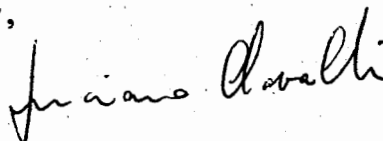
Bollate Research Center

Seguito al N. 1 del .7.71

	Temperature °C	Chemical shifts (ppm from CFC1 ₃)		Coupling Constant (c/s)
		F ₁	F ₂	
CFC1 ₂ ·CFC1I	28	65.21	63.20	-22.3
	-90	59.6	64.4	-19.5
	-90	68.8	63.5	-27.1
	-90	75.4	67.6	-22.0

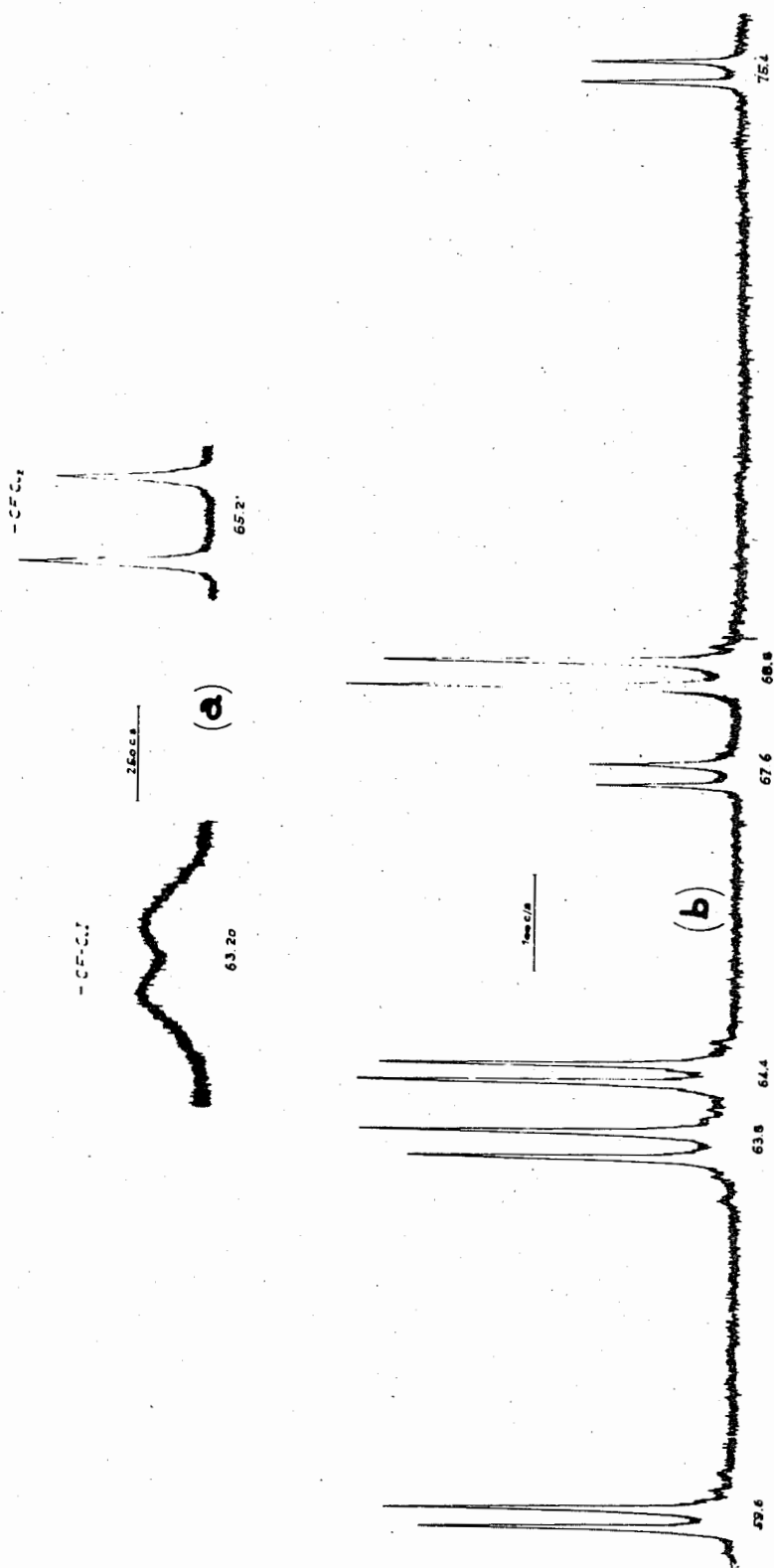
The three different rotamers have relative populations at -90°C in the ratio $x_I : x_{II} : x_{III} = 0.435 : 0.435 : 0.130$, corresponding to an enthalpy difference (neglecting entropy terms) equal to $\Delta(III-I) = \Delta(III-II) = 440 \text{ cal/m}$.

Yours sincerely,



L. Cavalli

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- 4) S.L. Manatt, D.D. Elleman, J. Am. Chem. Soc., 84, 1305, 1962





DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

Building 2, Room B2-02

July 19, 1971

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

Dear Barry:

^{15}N chemical shift in $\text{CH}_3^{15}\text{NO}_2$

As you know, I have been concerned about a scale for reporting nitrogen chemical shifts and was led to propose $(\text{CH}_3)_4\text{N}^+$ as a primary reference. The reasons for the choice have been given [J. Mag. Res. 4, 142 (1971)], but briefly are (1) $(\text{CH}_3)_4\text{N}^+$ has sharp lines for both ^{14}N and ^{15}N ; (2) the N--H coupling permits the use of $^1\text{H}\{\text{N}\}$ double resonance methods where desirable; and (3) the δ scale defined by this reference increases with increasing frequency, as does the ^1H scale based on TMS. Since nitromethane has also been suggested as a nitrogen reference, and many ^{14}N chemical shifts have been reported on this scale [e.g., Witanowski and Januszewski, J. Chem. Soc. B, 1062 (1967)], I thought it advisable to use our $^1\text{H}\{\text{N}\}$ double resonance methods to obtain accurate values for the ^{15}N resonance frequency of $\text{CH}_3^{15}\text{NO}_2$ in several solvents. We observed ^1H at 220 MHz and decoupled ^{15}N at 22.3 MHz. The results are as follows:

Solvent ^a	^1H chem. shift ^b	^{15}N frequency ^c	δ_{N} ^d
DMSO- d_6	972	22 300 922	338.2
D_2O	963	915	339.2
SO_2	946	866	336.1
CDCl_3	949	783	331.1
CDCl_3 (conc.) ^e	952	813	332.5
C_6D_6	646	793	----- ^f

a. Concentration 0.5% by volume ($\sim 0.1\text{M}$).

b. Hz at 220 MHz from internal TMS (or DSS, in D_2O).

c. Resonance frequency in field where ^1H of internal TMS resonates at exactly 220.000 MHz.

d. Chemical shift in ppm from $(\text{CH}_3)_4\text{N}^+\text{I}^-$.

e. Concentration $\sim 20\%$ by volume ($\sim 3.5\text{M}$).

f. $(\text{CH}_3)_4\text{N}^+\text{I}^-$ not studied in C_6D_6 .

Dr. Bernard L. Shapiro
July 19, 1971
Page 2

On the assumption that any solvent effects on TMS are negligible, the nitrogen chemical shift of $\text{CH}_3^{15}\text{NO}_2$ varies over a range of 6 ppm in these solvents, which is somewhat greater than the range of 2 ppm found previously for $(\text{CH}_3)_4\text{N}^+\text{I}^-$. Within that range, at least, data expressed with respect to nitromethane can now be put on the $(\text{CH}_3)_4\text{N}^+$ (TMA) scale.

Best wishes.

Sincerely,



Edwin D. Becker
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

P.S.: Computer retrieval of NMR Abstracts--Since you don't like blank space on these pages, I'll add a brief note on our progress in improving the coding system and computer program for data retrieval for the Preston NMR Abstracts. We are currently recoding many of the old abstracts to permit searching for specific nuclei, instead of the present group of "nuclei other than ^1H , ^{19}F , ^{31}P , ^{11}B and ^{13}C ," and are dividing some of the other categories as well. The new and much more detailed subject coding system will go into operation January 1, and our computer retrieval and printout programs will be modified by that time. I'll send more details in a few months.



Eidg. Technische Hochschule Zürich
Laboratorium
für Physikalische Chemie

8006 ZÜRICH,
Universitätstrasse 22
Tel. (051) 32 62 11

July 20, 1971

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

Another Step Towards a One Dollar NMR Spectrometer

Dear Barry,

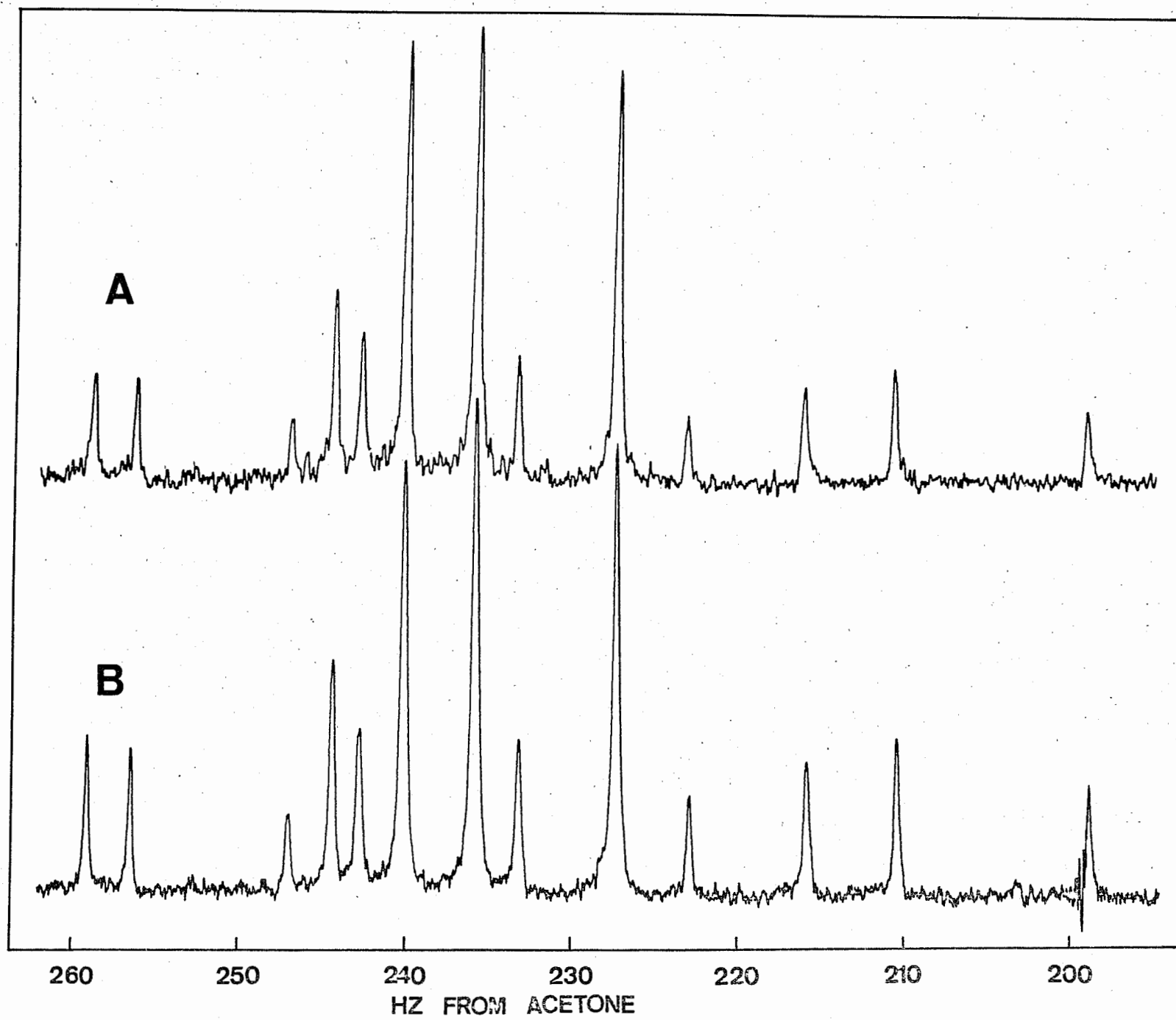
In my last letter, I mentioned a possibility for a simple, inexpensive Fourier spectrometer based on the direct observation of difference frequencies such that field-frequency stability is no more essential. But this spectrometer still requires a digital computer for the Fourier transformation of the free induction decays (J.Magn.Resonance 4, 280, 1971).

I would like to propose a further simplification replacing the digital computer by a simple phase-sensitive analog Fourier analyzer. This leads to what we call "difference frequency spectroscopy". The spin system is excited by a repetitive pulse sequence and the response demodulated in an envelope detector. The spectrum is determined point by point by means of the Fourier analyzer which essentially is a phase-sensitive detector whose reference frequency is swept through the range of expected difference frequencies. For phase-sensitive operation it is essential to synchronize the exciting pulse sequence to the reference frequency. Thus one is back to a single channel spectrometer which does not utilize the multiplex advantage of Fourier spectroscopy and has the same sensitivity as a conventional continuous wave experiment as is shown in the following figure. It represents two scans through the proton resonance spectrum of acrylonitrile using acetone as the strong reference peak: (A) difference frequency spectroscopy, (B) continuous wave spectroscopy, performed within the same total performance time, (A) without and (B) with field-frequency lock.

A more detailed description and analysis has been submitted for publication.

Sincerely yours

Richard R. Ernst
Richard R. Ernst



CLEMSON UNIVERSITY
CLEMSON, SOUTH CAROLINA 29631

DEPARTMENT OF
CHEMISTRY AND GEOLOGY

July 20, 1971

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

Aromatic Anisotropy; Theory and Practice
Dear Barry:

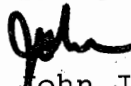
Thank you for the TAMUNMR reminder.

In connection with a study of barriers to rotation about carbon-carbon single bonds in cog-wheeled molecules we have had occasion to examine the magnetic anisotropy effect of aromatic rings in an effort to assign resonances. Our interests were in the shieldings experienced by various sensor groups in sectors perpendicular to aromatic rings.

Inspection of the available data on rigid molecules, e.g., paracyclophanes, metacyclophanes, and bicyclic systems, in connection with the Johnson-Bovey calculations (1,2) leads to a relatively unexpected result. In these geometrically well defined systems in plane monitor group (H and CH₃) shifts relative to appropriate standards are in substantial agreement with the Johnson-Bovey predictions, whereas out of plane monitor group shifts can be surprisingly lacking in agreement. A sampling of the available data are compiled in the Table. A part of the deviation can be attributed to steric compression as has been observed by Winstein et al. (3) in birdcage molecules. Granted even that the cyclophane systems are distorted aromatic molecules, which perhaps should not exhibit normal shieldings, the last entry in the Table exhibits a marked deviation between theory and practice. The magnitude of the discrepancy appears to be more severe the closer the approach of the monitor group to the adjacent aromatic system; see CH₃ (a) and CH₃ (b) of last entry in the Table.

We are presently compiling an "experimental" Johnson-Bovey curve and would be glad to receive any suggestions as to particular compounds or classes of compounds that might be employed for this purpose.

Sincerely yours,

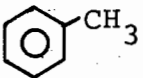
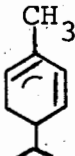
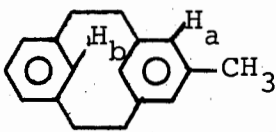
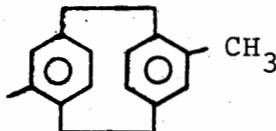
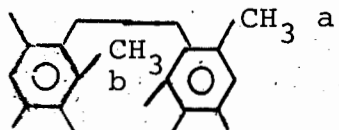
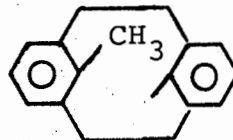
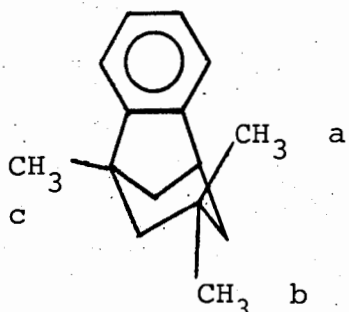


John Jacobus

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2. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, New York, 1965, p. 595 ff.
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4. D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., ibid., 82, 6302(1960).
5. H. J. Reich and D. J. Cram, ibid., 91, 3534(1969).
6. T. Sato, S. Akabori, S. Muto, and K. Hata, Tetrahedron, 24, 5557(1968).
7. B. L. Shapiro, M. J. Gattuso, and G. R. Sullivan, Tet. Letters, 223(1971)

TABLE

CALCULATED AND OBSERVED OUT-OF-PLANE CHEMICAL SHIFTS

COMPOUND	RELATIVE TO	AT γ	JOHNSON-BOVEY "CORRECTION"	CHEM. SHIFT		REF.
				CALCD.	OBS.	
		8.32	-0.8 ppm	7.52	7.66	1
	mesitylene H mesitylene CH ₃	3.356 7.778	H ^a -0.1 H ^b +3.6 CH ₃ -0.1	3.25 6.97 7.68	3.21 5.94 7.64	4
	toluene CH ₃	7.66	0.0	7.66	7.89	5
	toluene CH ₃	7.66	a) -0.1 b) +7.67	7.56 15.33	7.65 9.52	6
	toluene CH ₃	7.66	+7.67	15.33	9.44	4
	methylcyclohexane cumene	9.08 8.77	a) +2.6 b) +0.1 c) -0.4	11.7 9.2 8.4	10.15 9.16 8.70	7

JEOL

U.S.A., INCORPORATED • 235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016

INSTRUMENTS and APPLICATIONS CENTER • (201) 272-8820

TELEX NO. 13-8840

July 21, 1971

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

Greetings Barry:

FT NMR WORKSHOP ANNOUNCEMENT

I would like to announce a Fourier Transform NMR workshop which will be held here, in the JEOL Cranford Laboratory on November 8th, and 9th, 1971.

The first day of the workshop will include lectures by Dr. E. D. Becker from N.I.H. (introduction and general FT considerations), Dr. J. W. Cooper from Nicolet (Mini-computer and NMR-FT software and hardware applications), and myself (instrumentation and relaxation time applications). The second day will include practical laboratory experiments on our 25 MHz ^{13}C -FT and computer systems, as well as problem solving and question and answer sessions.

A modest fee (less than \$40.00) will be charged; anyone interested in further details should write to me at the above address.

Best regards,

JEOL U.S.A., INC.



Dr. T. C. Farrar
Dir. of Research & Development

TCF/rmh

P.S.

This workshop is just before the EAS Symposium to be held November 10, 11, and 12, in New York City. Anyone attending that Symposium (which includes a Thursday afternoon FT-NMR user's panel discussion) who wishes to visit our Cranford Laboratory, is invited to do so; some courtesy transportation facilities from New York to Cranford will be available.

The University of Oklahoma

620 Parrington Oval, Room 211

Norman, Oklahoma 73069

July 22, 1971

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

ABX SPECTRA OF DIELS-ALDER ADDUCTS OF HEXABROMOCYCLOPENTADIENE WITH MONOSUBSTITUTED ETHYLENES

Dear Dr. Shapiro,

Thank you for re-enrolling me as a TAMUNMR Newsletter subscriber. It's good to be back in the club.

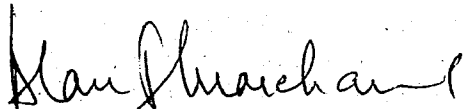
We have recently been investigating the reactivity of hexabromocyclopentadiene (I) as a Diels-Alder diene. Whereas the corresponding hexachlorinated compound is a well-behaved Diels-Alder diene, the behavior of compound I in this regard can best be described as recalcitrant.

Nevertheless, we have been successful in preparing a number of adducts of I with monosubstituted ethylenes, and we have calculated the nmr spectra of the resulting norbornenes, (3-spin systems). The chemical shifts and coupling constants which we have calculated for these adducts are reported on the left-hand side of the accompanying table; on the right side of this table we have included Williamson's results for the corresponding hexachlorinated norbornenes. Generally, spectra have been obtained for 10% w/w solutions of the solutes in CS₂. However, due to solubility problems, the hexabromonorbornene endo-5-carboxylic acid was measured as a 15% w/w solution in dimethylsulfoxide; the corresponding ester has been studied in both CS₂ and DMSO solvents for comparison.

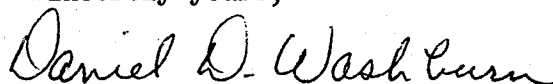
We see immediately from inspection of this table that the cumulative effects of the six bromines in system II vs. those of the six chlorine atoms in system III are negligible with regard to the calculated coupling constants. However, the chemical shifts in system II are uniformly greater than are the corresponding shifts in system III; evidently, the cumulative inductive-field-anisotropy effects of the Br's in II are overall net deshielding relative to the Cl's in III.

With the kind assistance of Dr. James C. Kauer at DuPont Central Research, we have succeeded in obtaining the adduct of I with ethylene itself; this reaction proceeds in good yield only at 3000 atm. and 125-150°C! We are now preparing deuterated analogs of bromonorbornanes derived from this adduct, and we will provide a detailed report of their nmr spectral characteristics in a future communication.

Sincerely yours,



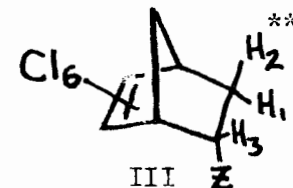
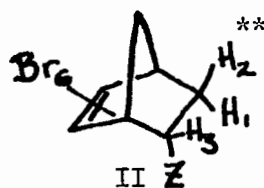
Alan P. Marchand
Associate Professor



Daniel D. Washburn



Department of
Chemistry



Z	OAc	Ph	COOH***	COOMe***	COOMe	CN	OAc	Ph	COOH	CN
$\delta(1)$	116.55	147.02	146.69	149.11	153.21	139.88	114	143	146	129
$\delta(2)$	185.05	179.24	164.89	166.93	163.78	179.38	177	172	163	162
$\delta(3)$	343.05	245.14	221.12	227.65	219.53	226.58	330	232	217	204
J_{12}	-13.31	-12.95	-12.54	-12.61	-12.43	-12.54	-13.3	-12.7	-12.6	-12.6
J_{13}	2.45	4.19	3.97	3.76	4.03	4.09	2.5	4.2	4.4	4.6
J_{23}	7.56	9.06	8.76	8.67	8.78	9.10	7.6	8.9	8.5	9.3

*K. L. Williamson, J. Amer. Chem. Soc., 85, 516 (1963).

**Values measured at 60 MHz. Probable error of each value never exceeded 0.08 Hz.

***Obtained as 15% w/w solution in DMSO. All other values reported in this table were obtained as 10% w/w solutions in CS₂.

UNIVERSITY OF HOUSTON
CULLEN BOULEVARD
HOUSTON, TEXAS 77004
UNITED STATES OF AMERICA

DEPARTMENT OF CHEMISTRY

July 22, 1971

NEWSLETTER

TITLE: Annotated Europium Bibliography

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

Dear Barry:

John Sapp is currently writing his Ph.D. dissertation and has decided to include an annotated lanthanide shift bibliography. We would be happy to share this when it is ready, about the middle of August, with any one of the newsletter readers. Simply drop us a reprint request card, or letter, or call.

Sincerely yours,

M. Robert Willcott
Associate Professor of Chemistry

MRW:mlg

DEPARTMENT OF THE AIR FORCE
AEROSPACE RESEARCH LABORATORIES (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433



23 July 1971

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

Review Article on Structural Aspects of Lanthanide Chemistry

Dear Dr. Shapiro:

The editor of Chemical Reviews has asked us to prepare a review article on structural aspects of lanthanide chemistry. In this review we will concentrate on x-ray studies of the structures of lanthanide compounds and we plan to devote some attention to lanthanide NMR shift reagents such as tris (2, 2, 6, 6-tetramethyl-3, 5-heptanedionato)europium(III), Eu(thd)₃, tris (1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-4, 6-octanedionato)europium(III), Eu(fod)₃, and other compounds.

We have almost completed our search of the literature and we would like to appeal to the readers of the NMR Newsletter to send us preprints or reprints of any work dealing with lanthanide NMR shift reagents. Please address correspondence to me at

Aerospace Research Laboratories
ARL/LJ
Wright-Patterson AFB, Ohio 45433

Thank you for your assistance.

Sincerely,

Robert E. Sievers

ROBERT E. SIEVERS
Principal Investigator
Apollo Lunar Analysis Project

Yale University

SCHOOL OF MEDICINE

NEW HAVEN, CONNECTICUT 06510

SECTION OF PHYSICAL SCIENCES

Position Open: ASSISTANT IN RESEARCH

Requirements: M.S. in chemistry, knowledge of electronics
and computer programming desired.

Duties: Engage in carbon-13 Fourier transform studies
of biologically important compounds and
further development of FT system, some service
work necessary.

Salary: \$6800-\$8500

Write: R.J. Cushley
Section of Physical Sciences
Yale University School of Medicine
333 Cedar Street
New Haven, Conn. 06510

Yale University
SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT 06510

SECTION OF PHYSICAL SCIENCES

28 July 1971

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

Dear Professor Shapiro,

Carbon-13 Fourier Transform Studies on the Biosynthetic Incorporation
of ^{13}C -labelled Acetate into Prodigiosin.

At this year's ENC meeting we described our IBM-1800 computer controlled Fourier transform system for ^{13}C , ^{31}P , and ^1H . The experimental system consists of a high resolution spectrometer modified for pulse-Fourier and directly interfaced to an IBM-1800 computer with 24K of 4 μsec core storage and numerous peripheral devices for data handling and data presentation. A high resolution Bruker HFX-3 nuclear induction spectrometer operating at 21.5 kilogauss is equipped with a B-SV2 power amplifier for proton noise decoupling and a Bruker 20 watt power amplifier for the excitation pulse. An internal field-frequency lock is provided at 84.7 MHz (^{19}F) or 90.0 MHz (^1H). The rf excitation pulse is created at mixers (HP 10514) which are gated by logic levels from an IBM Electronic Contact Operate (ECO) register. The whole system is completely computer controlled. Highlights include a 4K Fabri-Tek which has been digitally interfaced to the IBM 1800 and acts as an on-line, buffered CRT-plotter, a data clock utilizing the 2 MHz oscillator of the 1800 for completely synchronous co-addition of the free induction decay signals, and a computer-controlled active filter utilising Analog devices 4-pole Tchebyscheff filters # 9171, # 9172 designed to automatically select f_c 's according to the rate selection bits for the

data clock.

The full details of the FFT system should be appearing soon², and we should like to describe here some experiments using ^{13}C as a label in tracing a biosynthetic pathway. Recent studies have employed both ^{13}C -H satellite NMR spectroscopy³ and ^{13}C cw-NMR⁴ to assign biosynthetic labelling patterns. Fourier transform NMR, as used in this study, provides substantially greater sensitivity, which has allowed us to use ^{13}C single resonance spectra as an aid to assignment, and to work with small samples.

Prodigiosin (I), isolated from the bacterium *Serratia marcescens* is one of a series of bacterial secondary metabolites having in common an unusual system incorporating the methoxy-bipyrrole unit in a dipyrromethene structure⁵. There is special interest in the biosynthesis of the prodigiosins since it has been shown that they are formed by a route unrelated to porphyrin biosynthesis.

We have made a complete ^{13}C resonance assignment for prodigiosin hydrochloride (II). Figure A shows the proton noise-decoupled ^{13}C -FT spectrum of 1 molar II, with the ^{13}C -assignments. Conditions for determining the spectrum were: data set = 8K; rf pulse duration = 40 μsec ; receiver skip = 100 μsec^2 ; digitizing rate = 10 KHz; Tchebyscheff f_c = 4.8 KHz; scan time = 2.3 hours.

Nineteen peaks are shown with the C4 and C5 superimposed peaks being resolved by an off-resonance experiment. The magnitudes of the off-resonance residual splittings (J_r) for the A5, A4, A3, B4, C4, and 1" carbons were consistent with the ^{13}C -H couplings determined in the ^1H spectrum. The resonance frequencies of the seven tertiary carbons were confirmed by progressive saturation experiments, while frequencies of nine of the carbons bearing hydrogen (A5, A4, A3, B4, C4, 1", B3-OMe, C2-OMe,

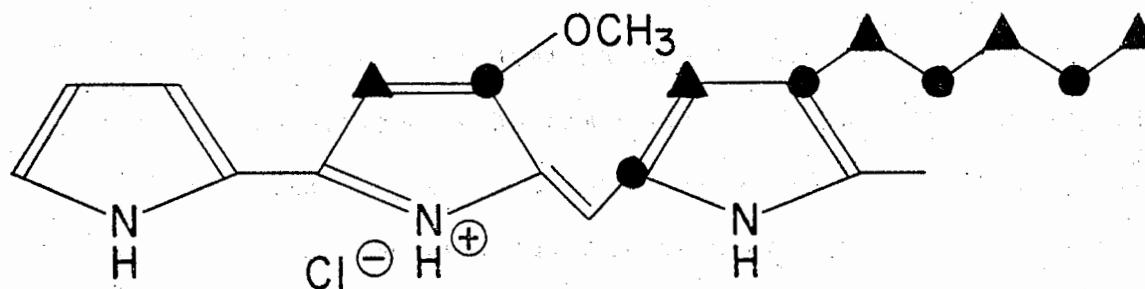
and 5') were confirmed by ^{13}C -INDOR.

In order to assign the tertiary centers at A2, B2, B5, B3, and C2, we resorted to single resonance and off-resonance experiments of N-deutero- and pentadeutero-N-deutero II as well as the use of pyrrole model compounds (including the mutant produced 3-methoxy-(5, 2')-bipyrrole-2-carboxaldehyde). Long-range ^{13}C - ^1H spin-coupling in the single resonance spectrum of N-deutero II clearly established positions B5 and C2 while a single resonance experiment on perdeutero II (positions A4 and 1" protonated) gave a sharp doublet (A2) and a broad multiplet (B2).

Of some interest are the disparate shifts for the B-ring carbons when compared to pyrrole (noise decoupled ^{13}C chemical shifts for pyrrole: $\text{C}_{2,5} = -40.24$ ppm ; $\text{C}_{3,4} = -30.10$ ppm from CHCl_3). We have also noted a marked upfield shift on carbons directly bonded to pyrrole. Thus C-1' of the amyl group appears to higher field than both C-2' and C-3' while the C2-Me resonance signal occurs at highest field.

The ^{13}C -FT spectrum of proton noise-decoupled 0.5 molar II, enriched with ^{13}C from 1- ^{13}C acetate is given in Figure B. Conditions were as in Figure A, scan time = 20 minutes. The level of primary incorporation at the 5 carbons indicated (about 8%) is sufficient to differentiate clearly the labelled positions from Overhauser enhanced resonances.

Figure C displays the ^{13}C -FT spectrum of 0.05 molar II enriched from 2- ^{13}C -acetate. Scan time was 6.7 hours. The labelling pattern of acetate incorporation into II is thus shown to be:



● 1- ^{13}C -acetate

▲ 2- ^{13}C -acetate

All the spectra shown in the Figures are phase corrected real spectra ². Chloroform solutions were contained in 10mm spinning tubes in which a 5 mm (Wilma Imperial) co-axial tube containing C_6F_6 was mounted for field-frequency locking to ^{19}F .

Sincerely yours,

Robert J. Cushley

Robert J. Cushley

Dennis R. Anderson

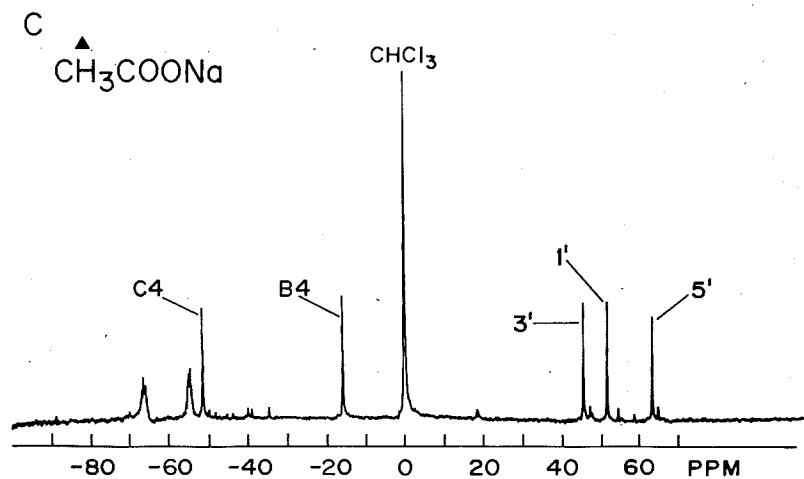
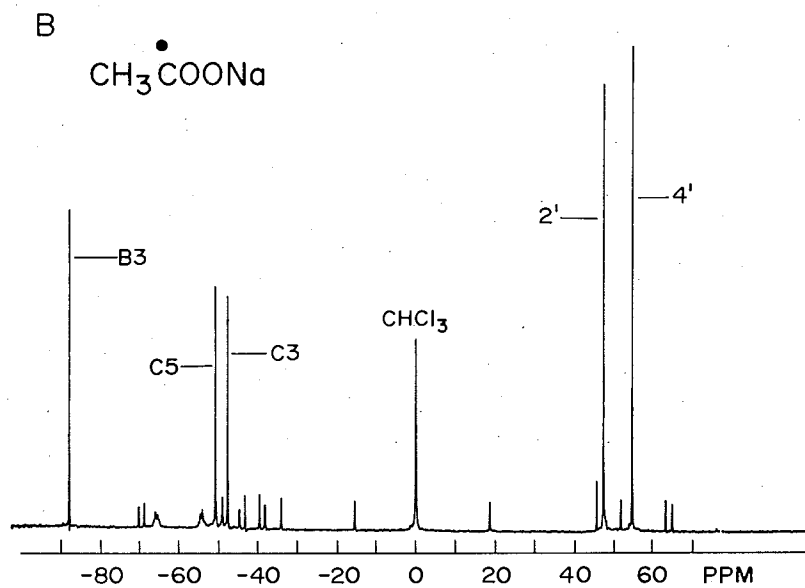
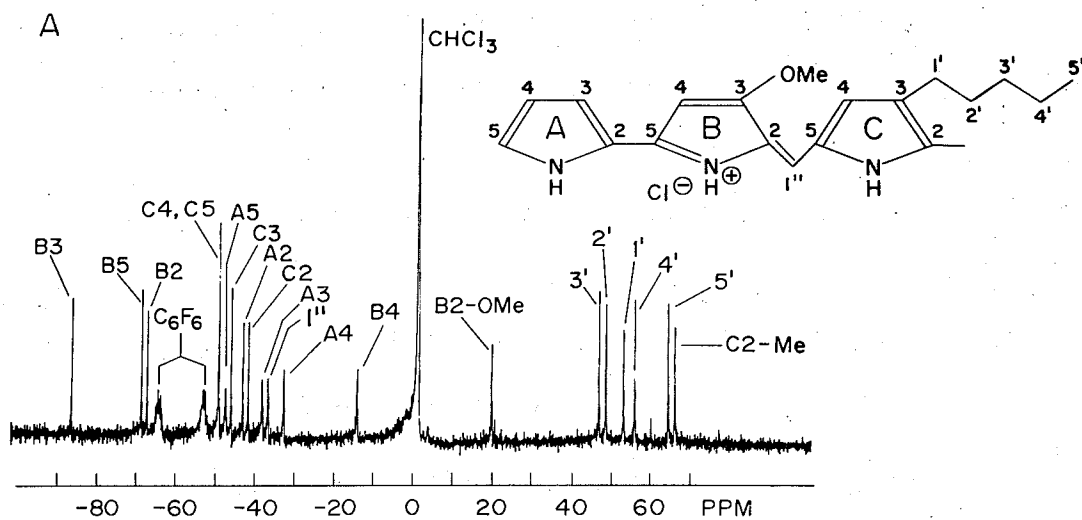
Dennis R. Anderson

Richard J. Sykes

Richard J. Sykes
(Department of Chemistry)

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STABILIMENTO PETROLCHIMICO
PORTO MARGHERA

Porto Marghera 21 June 1971

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ITALY

Corrections to TAMU NMR Newsletter #151, pages 25 and 30

Dear Professor Shapiro,

thanks for publishing our letters in the april number of Texas A & M U. NMR. Newsletter. We have noticed however an exchange between a page of the first letter and a page of the second letter. That is page 151-25 should go to the place of page 151-30 and viceversa; in fact page 151-25 regards the work on 1-2 dibromo-hexa-fluoropropane which is printed soon after and page 151-30 is the first page of the work on 2,4-dichloro-1-pentene which is printed first. Moreover in the cover of the magazine the names of the second author have been exchanged. The correct titles are

Gurato G.; Zenoni G.

NMR Spectrum of 1,2-dibromo-hexa-fluoropropane.

Gurato G.; Rigo A.

NMR Spectrum of 2,4-dichloro-1-pentene and of 2,4-dichloro-1-pentene-1-d₁

In addition in the cover in correspondence of reference of page 30 the word 2,4-dichloro-1-pentene should be substituted with 2,4-dichloro-1-pentene.-

We shall be very grateful if you will kindly publish these variations.

Thanks for your attention

Faithfully yours

(Giorgio Gurato)

Giorgio Gurato

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Prof. H. Günther

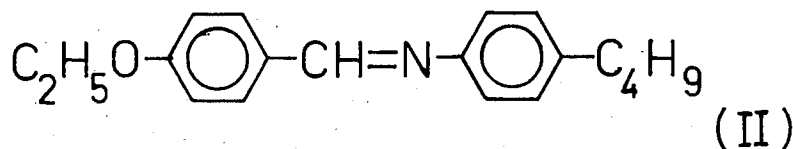
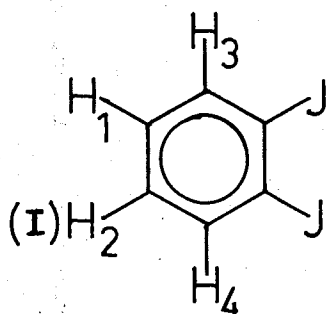
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ZÜLPICHER STRASSE 47
TELEFON: 470 3283

Herrn
Prof. Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
USA

- N M R in nematic solvents -

Dear Barry,

recently we have been interested in some of the experimental aspects of "liquid crystal nmr spectroscopy" of small molecules. To check the accuracy of line measurements we chose to study o-diodobenzene (I) dissolved in the phase (II). With our HA-100 spectrometer, the following results were obtained for 19 lines



of the AA'BB'-system of I:

- 1) HR-mode operation, side band calibration using TMS signal:
halfwidth 5 Hz; rms error ± 0.75 Hz (8 spectra)
- 2) HA-mode operation, lock signal TMS, side band calibration:
halfwidth 3 Hz; rms error ± 0.48 Hz (10 spectra)
- 3) HA-mode operation, lock signal TMS, direct line measurement
(using recorder by setting pen on top of each peak):
halfwidth 3 Hz; rms error ± 0.26 Hz (6 measurements).

The analysis of the three sets of spectra, using indirect coupling constants as reported¹ and the program LAOCOONOR² yielded the following dipolar coupling constants (all data in Hz):

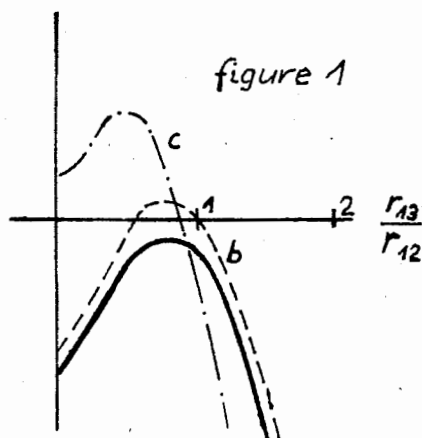
	D_{12}	D_{13}	D_{14}	D_{34}	rms error
1)	-424.27	-432.38	-82.54	-54.42	± 0.51
2)	-421.40	-430.00	-82.17	-54.15	± 0.46
3)	-421.34	-429.96	-82.15	-54.00	± 0.34

From these three sets only 2) and 3) are comparable, since all experimental conditions were constant. For set 1) the rf-power was changed, leading to small changes in temperature, orientation, and consequently different D_{ij} -values.

The crucial test for the three sets of data was now to calculate the molecular geometry as far as the protons of I are concerned. Here, however, we found difficulties. Our program "YMODI" did not converge. The reason for this behaviour became clear, as we plotted the equation

$$D_{13} \left(\frac{r_{13}}{r_{12}} \right)^5 - D_{14} \left[\left(\frac{D_{12}}{D_{34}} \right)^{\frac{1}{3}} + \left(\frac{r_{13}}{r_{12}} \right)^2 \right]^{\frac{5}{2}} + D_{12} \left(\frac{D_{12}}{D_{34}} \right)^{\frac{1}{3}} = 0$$

given by Diehl³ against the ratio r_{13}/r_{12} . As one can see (figure 1), there is no solution, unless D_{14} is changed slightly (curve b). Then, however, two solutions are possible. Normal cases, as o-dichlorobenzene, which we measured also, give well defined solutions as shown by curve c. The reason for this peculiar behaviour of I is not yet clear. It may be due to the experimental errors in the D_{ij} -values. Another possibility seems to us, that the molecule may be distorted. Our assumption of regular geometry and planarity, used for the calculations, may then be invalid.



Schmickler (modified)
H. Schmickler J.B. Pawliczek

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Relaxation with " T_2 " Longer Than " T_1 "

For two like nuclei of spin one-half, Redfield's equations of motion may be used to obtain the following "Bloch equations" for the transverse magnetizations:

$$\dot{M}_a = i\Omega M_a - R_{aa} M_a - R_{ab} M_b$$

$$\dot{M}_b = i\Omega M_b - R_{bb} M_b - R_{ba} M_a$$

Here a and b refer to respective nuclei with chemical shift 2Ω rad/sec. The four relaxation rates R_{aa} , R_{bb} , R_{ab} , and R_{ba} , are obtained from the usual expressions in terms of spectral densities and matrix elements of the relaxation Hamiltonian. For dipole-dipole interactions between two spins, we find

$$R_{aa} = R_{bb} = 2R_{ab} = 2R_{ba} = \frac{\gamma^4 h^2}{r^6} \tau_d$$

where r is the (fixed) distance between the spins, which are assumed to undergo random isotropic rotational diffusion with correlation time τ_d .

The equations of motion appear similar to Bloch equations modified to include chemical exchange, except for a change in sign of the effective "exchange rate" R_{ab} . Solution of these equations subject to the boundary conditions of a non-selective Carr-Purcell experiment proceeds exactly like that for chemical exchange and yields the result

$$R_2 = \frac{\gamma^4 h^2}{r^6} \tau_d \left[1 + \frac{\sin \Omega \tau_{cp}}{2\Omega \tau_{cp}} \right]$$

where R_2 is the apparent relaxation rate and τ_{cp} is the spacing between successive 180° pulses.

In the small pulse spacing limit, $\Omega\tau_{cp} \ll 1$, neither M_a nor M_b precess very far in the xy plane before being refocussed, so despite their chemical shift they relax as "like" spins, with

$$\lim_{\tau_{cp} \rightarrow 0} R_2 = \frac{3}{2} \frac{\gamma^4 h^2}{r^6} \tau d$$

In the large pulse spacing limit, the chemical shift "has time" to develop large precession angles between pulses, and the spins relax as if they are "unlike",

$$\lim_{\tau_{cp} \rightarrow \infty} R_2 = \frac{\gamma^4 h^2}{r^6} \tau d$$

The equations of motion for M_a and M_b also describe spin lattice relaxation, if terms in Ω are dropped and M_a and M_b refer to the differences between the instantaneous longitudinal magnetizations and their thermal equilibrium values. Thus after a non-selective 90° or 180° pulse, the sum $(M_a + M_b)$ returns to equilibrium at a rate

$$R_1 = \frac{3}{2} \frac{\gamma^4 h^2}{r^6} \tau d$$

This is expected since neither Z component of magnetization precesses; both are perturbed equally by the initial pulse, they behave as "like" spins. But we have the novel inequality

$$R_2 \leq R_1$$

Although the equations for two spins with only intramolecular dipole dipole interactions do not strictly apply, an equimolar mixture of chloroform and benzene may exhibit effects of transverse "cross relaxation", particularly in view of the hydrogen bonded complex. Figure 1 shows early attempts of Dr. Sai On Chan and myself to observe R_2 as a function of pulse spacing for this solution.

The diamonds represent R_2 for pure benzene and the circles, R_2 for the equimolar benzene/chloroform. For pulse spacings less than about

60 msec, R_2 of the mixture is indeed less than R_1 , moreover, the periodic oscillations in R_2 as a function of pulse spacing correspond closely in frequency to those predicted from $\sin \tau_{cp} \Omega$ where Ω is $\pi \times 33 \text{ H}_z$ (measured with a Varian T-60 and converted to the given value for 55 MHz , our operating frequency).

The general upward drift in R_2 with increasing pulse spacing has us puzzled, T_2^* was found to be 35 msec so diffusion is negligible. Our Varian HR60 magnet is not locked, perhaps field drifts or fluctuations could be responsible. Does anyone have for sale a used V4311 rf unit for 9.1 MHz operation in a Deuterium lock system?

Yours truly,

Robert L. Vold

Robert L. Vold
Chemistry Department
University of California-San Diego

RLV/bh

1. *G. L. Sutowsky, R. L. Vold and E. J. Wells J. Chem. Phys. 43, 4107 (1965)*

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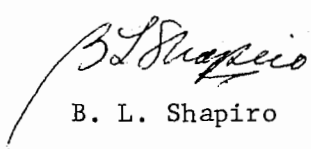
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Department of
CHEMISTRY

2 August 1971

NMR Spectroscopist Available

I have just been informed of the availability of an excellent NMR spectroscopist with 15 years experience in the field, including all the usual computer applications of NMR. The individual in question has a strong physical chemistry background, and considerable experience in the other common branches of spectroscopy in addition to NMR. Anyone interested in the possibility of making a position available to this man is invited to contact me at (713) 845-6944.


B. L. Shapiro

2



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