

NMR

NEWSLETTER

NO. 326

NOVEMBER 1985

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FORTHCOMING NMR MEETINGS (Additional listings are solicited)

British Radiofrequency Spectroscopy Group - April 9-11, 1986; Oxford University, Oxford OX1 3QR England; see Newsletter No. 323, p. 23.

27th ENC - April 13-17, 1986; Hilton Hotel, Baltimore, Maryland; see Newsletter No. 323, p. 31.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

1986 Eastern Analytical Symposium - October 6-10, 1986; Hilton Hotel, New York; see Newsletter No. 325, p. 27.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed. Please make your wishes known.

All Newsletter Correspondence
 Should be Addressed to:

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

DEADLINE DATES

No. 328 (January) ---- 27 December 1985
 No. 329 (February) ---- 24 January 1986

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August 27, 1985

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843-3255

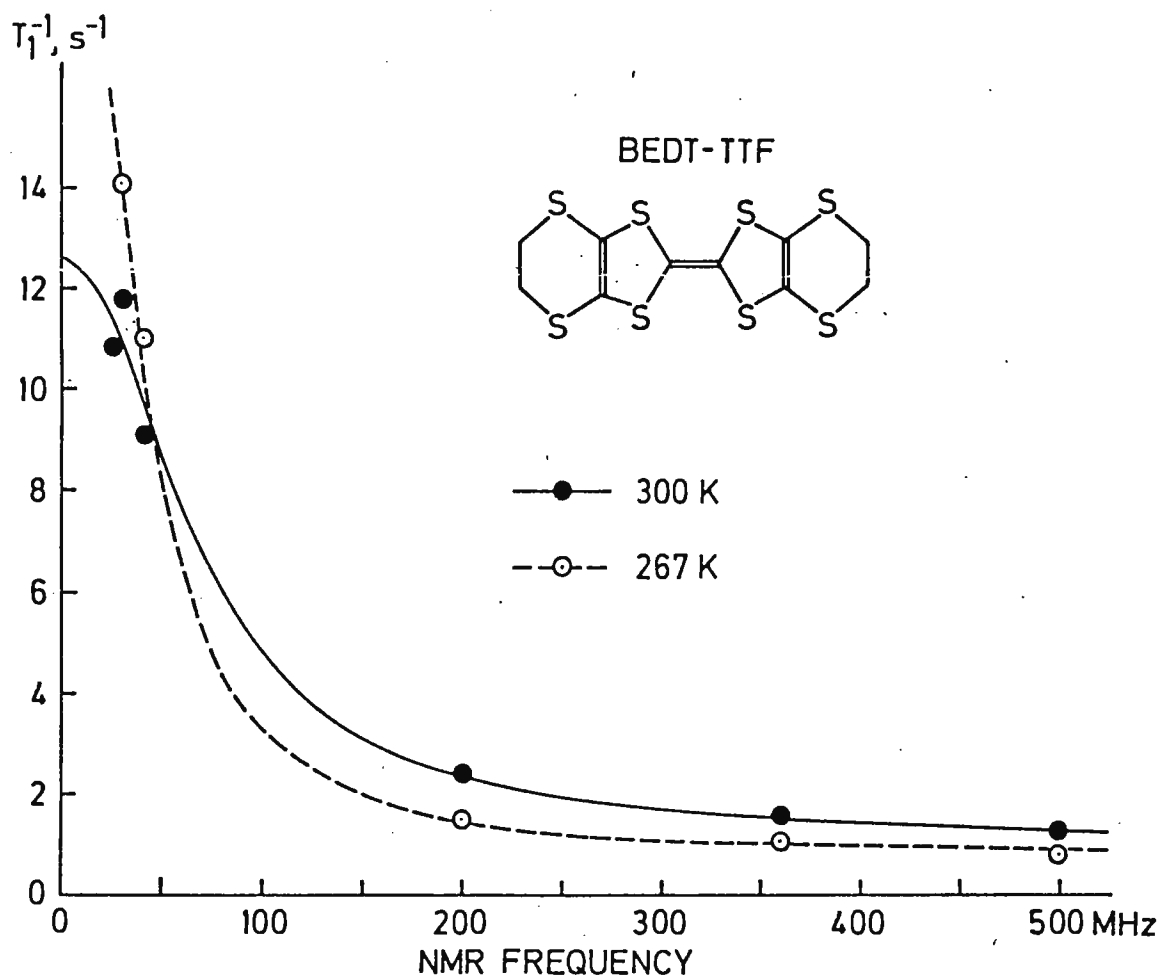
PROTON RELAXATION IN $(\text{BEDT-TTF})_2\text{I}_3$

Dear Professor Shapiro,

The existence of superconductivity has been reported in several quasi two-dimensional organic metals based on bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) with iodine. The triclinic β -modification of $(\text{BEDT-TTF})_2\text{I}_3$ has showed the highest transition temperature $T_c = 6-7$ K at atmospheric pressure among the organic superconductors and is therefore of special interest.

In metals with high conductivity, the hyperfine interaction of nuclear spins with conduction electrons provides an efficient relaxation mechanism for the nuclei. The corresponding relaxation rate T_1^{-1} is independent of the applied field and increases with temperature as described by the Korringa relation $T_1 \cdot T \cdot K^2 = \text{const.}$, with K being the Knight shift of nuclear resonance frequency. Indeed, such behavior was found in our experiments with β - $(\text{BEDT-TTF})_2\text{I}_3$ at temperatures below 170 K but in the range between 200 and 300 K, an additional relaxation pathway was detected in low fields. We believe that this mechanism is produced by proton-proton dipole interaction modulated by thermally activated transitions between two different conformational states of the packing-disorder generating end of the BEDT-TTF molecule. The accompanying figure shows the spectral density distribution of this

motion at 267 and 300 K. The temperature dependence of the correlation time τ_c is satisfactorily described by $\tau_c = 1.2 \cdot 10^{-12} \exp(2100/T)$ (about $1.3 \cdot 10^{-9}$ sec at room



temperature). The figure also indicates the field-independent electronic contribution together with an incomplete list of solid state NMR spectrometers currently in use in our lab.

Best regards,

E. Lippmaa
E. Lippmaa

M. Alla
M. Alla

A. Vainrub
A. Vainrub

I. Heinmaa
I. Heinmaa



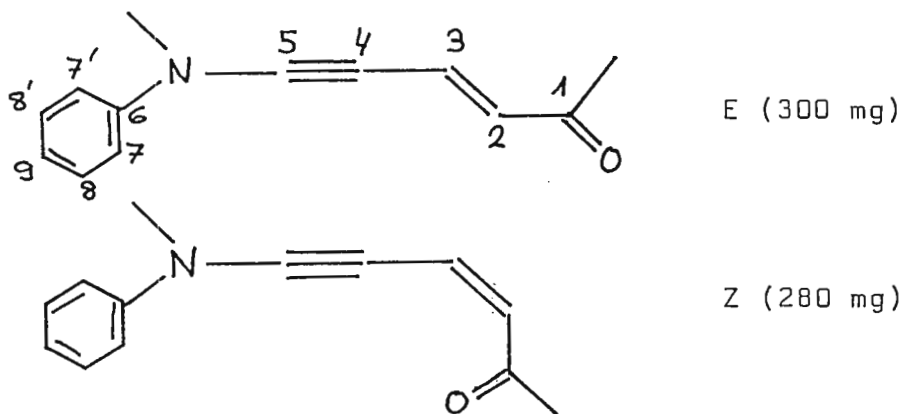
7. september 1985

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

Title: Carbon-Carbon Coupling Constants of two Push-Pull-Enins

Dear Barry

In order to fully characterize the compounds



with respect to bonding orders along the conjugated part of the molecule and with respect to substituent effects two INADEQUATE experiments were run on our BRUKER AM 400 WB system. To test the quality of the spectra (and of our new process controller) we focused our attention to the detection of one bond and long range couplings. As a typical example an expansion of the INADEQUATE

signals of carbon 4 is given below, which demonstrates the fairly good center peak suppression. Table 1 gives the values of the various $^nJ_{CC}$. The parameters for the INADEQ2.AUR pulse sequence (extended phase cycling) is given in Table 2.

Sincerely

Paul Bigler

P. Bigler

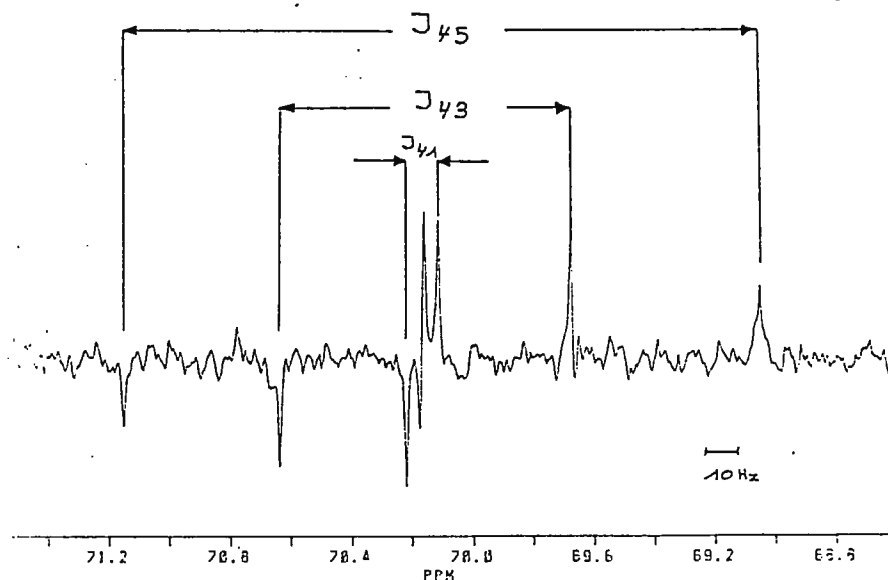


Fig. 1 (E-Isomer)

	E-Isomer			Z-Isomer		
C	$^1J_{CC}$	$^2J_{CC}$	$^3J_{CC}$	$^1J_{CC}$	$^2J_{CC}$	$^3J_{CC}$
1	77 (1-2)		10 (1-4)	77 (1-2)		3 (1-4)
2	77 (2-1) 73 (2-3)		4 (2-5)	77 (2-1) 73 (2-3)		3 (2-5)
3	73 (3-2) 90 (3-4)	17 (3-5)		73 (3-2) 97 (3-4)	10 (3-5)	
4	90 (4-3) 241 (4-5)		10 (4-1)	97 (4-3) 243 (4-5)		3 (4-1)
5	241 (5-4)	17 (5-3)	4 (5-2)	243 (5-4)	10 (5-3)	4 (5-2)
6	66 (6-7)		9 (6-9)	65 (6-7)	1 (6-8)	8 (6-9)
7	66 (7-6) 59 (7-8)		8 (7-8')	65 (7-6) 58 (7-8)		8 (7-8')
8	59 (8-7) 57 (8-9)		8 (8-7')	58 (8-7) 50 (8-9)	1 (8-6)	8 (8-7')
9	57 (9-8)		9 (9-6)	50 (9-8)		8 (9-6)

Tab. 1

300mg (E), 280mg (Z)
in 0.4 ml CDCl₃

SW: 10'640 Hz
AQ: 3.1 s
NS: 6784 (number of scans)
SI: 64K
WALTZ Decoupling (17H, P9: 110μs)
D1: 20s (relaxation delay)
D2: 0.035s (2N+1/4J_{CC})
DS: 4 (dummy scans)

accumulation time: 45h

Tab. 2



DEPARTMENT OF HEALTH & HUMAN SERVICES

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National Cancer Institute
Bethesda, Maryland 20205

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

October 8, 1985

Dear Barry:

Title: New NMR (MRI) T_1 Relaxation (Contrast) Agents

Many years ago I published some papers introducing $Gd(acac)_3$ as a T_1 relaxation agent for Carbon-13 NMR. Nowadays T_1 relaxation agents have been co-opted into medicine where NMR becomes MRI and paramagnetics altering proton T_1 values in vivo are called "MRI Contrast Agents".

In any event, we synthesized a few new, seemingly stable, water soluble complexes of the Gadolinium(III) ion to investigate their effectiveness at influencing water T_1 values at pH 7. The data are graphed below.

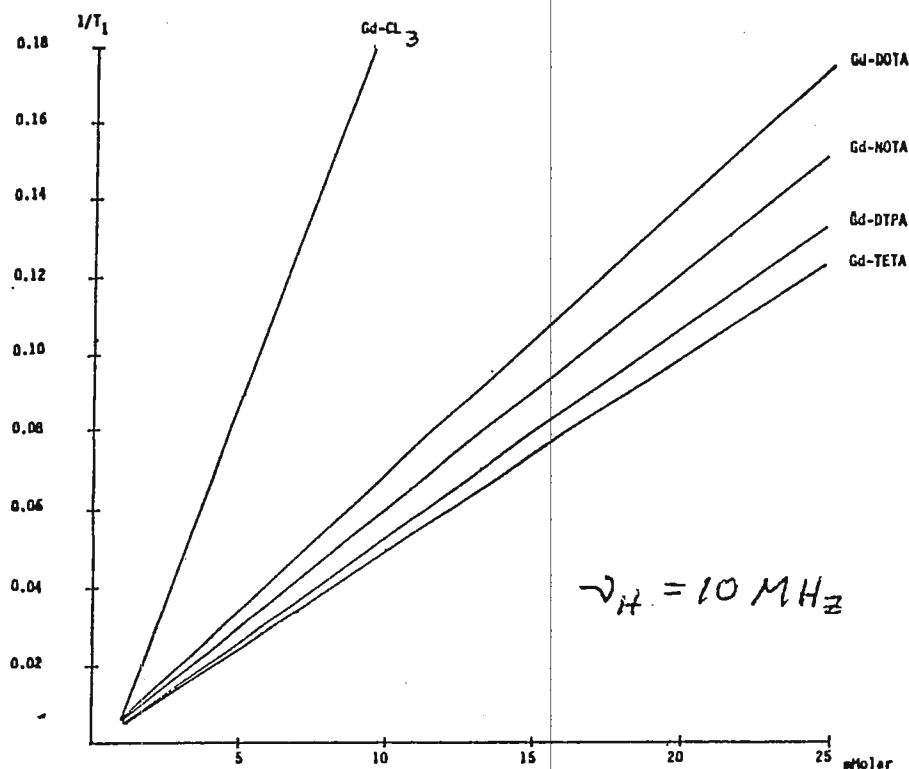
$Gd(DOTA)$ was chosen for some recently successful in vivo imaging studies. We are now pursuing the matter through the FDA.

Sincerely,

Otto A. Gansow, Chief
Inorganic Chemistry Section

Michael Magerstädt
Visiting Associate

Richard Knop, Matt Nägele
Medical Staff Fellows



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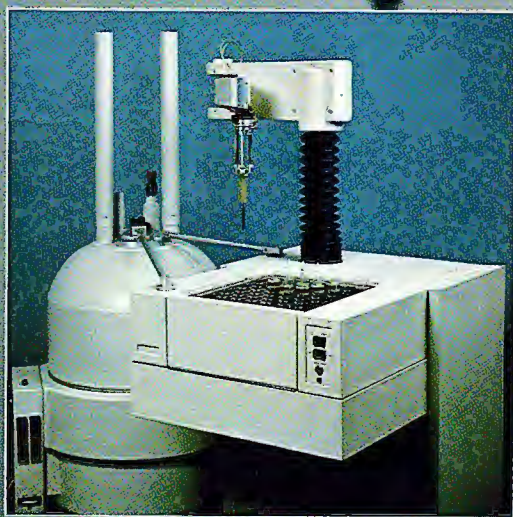


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PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY, ENGLAND.

Professor Barry Shapiro,
 Department of Chemistry,
 Texas A and M University,
 College Station, Texas.

BROADBAND DECOUPLING ACCORDING TO GARP

Dear Barry,

For most applications of carbon-13 spectroscopy, the WALTZ-16 broadband decoupling sequence (1,2) covers a suitable proton chemical shift range $2\Delta B_{\max}$ with a low setting of the radiofrequency intensity B_2^0 . This can be encapsulated in a figure of merit (Wang factor)

$$\mathcal{F} = 2\Delta B_{\max} / B_2^0$$

Typically \mathcal{F} is of the order of 2. Residual broadening or splitting of the carbon-13 resonances is small, of the order of 0.1 Hz, although proton-proton coupling can introduce additional broadening in some cases (3 - 5).

Occasionally however we would like much larger Wang factors, for example to observe protons with broadband decoupling of carbon-13 (6) or to broaden the range over which the homonuclear Hartmann-Hahn condition is satisfied (7). In return we might be prepared to accept larger residual splittings of the observed resonance, hiding these within the line broadening imposed by sensitivity enhancement or coarse frequency-domain digitization. This may be achieved either by tinkering with the WALTZ sequence itself (8 - 11) or by devising new sequences (12).

A new degree of freedom is introduced if the pulse flip angles are no longer constrained to be multiples of 90° ; this complicates the implementation of the decoupling sequence but this would be a small price to pay if a really large operating bandwidth is achieved without cooking the sample. Restricting the radiofrequency phases to just 0° and 180° ensures that the performance is quite insensitive to the accuracy of the phase shift (1,2). In the belief that B_2 spatial inhomogeneity is the downfall of many decoupling schemes, we have searched for a sequence that operates efficiently over a range of B_2 values near the nominal setting B_2^0 . We have allowed for the fact that the B_2 distribution is normally skewed towards values lower than nominal.

With these requirements, A.J. Shaka (12) has devised the sequence GARP-1 (Globally Optimized Alternating-phase Rectangular Pulses) which can be written as $G = R R \bar{R} \bar{R}$, where

R = 30.5	<u>55.2</u>	257.8	<u>268.3</u>	69.3	<u>62.2</u>	85.0	<u>91.8</u>	
134.5	<u>256.1</u>	66.4	<u>45.9</u>	25.5	<u>72.7</u>	119.5	<u>138.2</u>	
258.4	<u>64.9</u>	70.9	<u>77.2</u>	98.2	<u>133.6</u>	255.9	<u>65.6</u>	53.4

These flip angles are in degrees. A barred symbol represents phase inversion. Odd-ball flip angles are no particular problem when the sequence is implemented by software control of the pulse unit, but for a hardwired decoupler it would be useful to examine the sequence for some approximate common submultiple of all the flip angles so as to find an approximation to R that is easier to set up but which has comparable performance. Perhaps one of your readers might try this ?

For a formic acid test sample, Peter Barker has demonstrated that GARP-1 decouples effectively over a proton chemical shift range of 9.6 kHz for a radiofrequency level $\gamma B_2^0/2\pi = 2$ kHz. The carbon-13 lines were broadened to 1.5 Hz. This corresponds to a Wang factor $\mathcal{F} = 4.8$, which is what is predicted theoretically.

Peter has also explored just how low the decoupler level can be set while still giving acceptable carbon-13 spectra on a Varian XL-400 spectrometer. The sample was reserpine which has a proton chemical shift range of about 3.2 kHz (8 ppm). It proved possible to go as low as $\gamma B_2/2\pi = 700$ Hz. Cycling sidebands are then just becoming apparent in the flanks of the carbon-13 resonances (see Figure) since the cycling rate is very low. This appears to be the principal factor determining the minimum B_2 field.

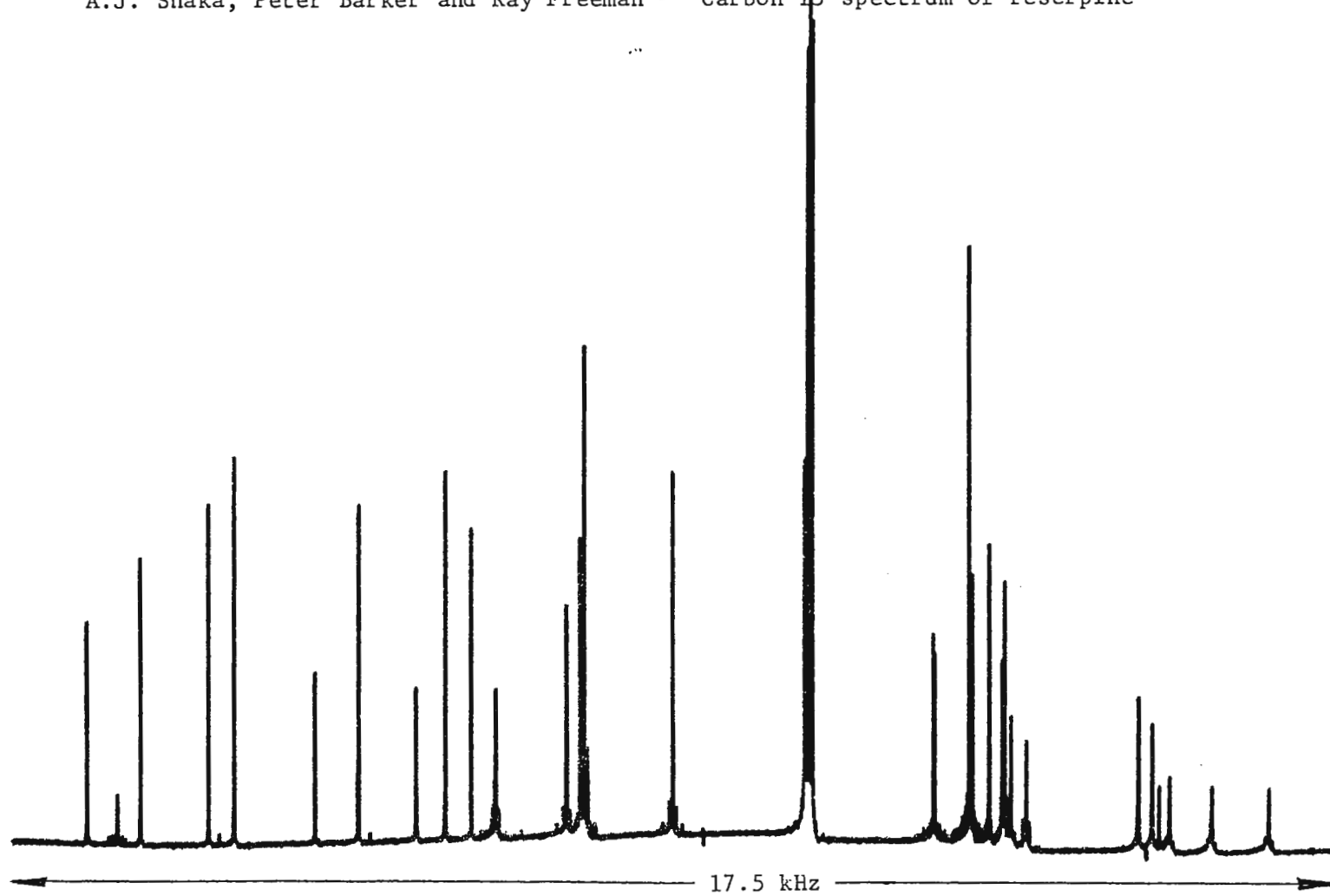
Yours sincerely

Ray

Ray Freeman

- (1) A.J.Shaka, J.Keeler, T.Frenkiel, R.Freeman, J.Magn.Reson. 52, 335 (1983).
- (2) A.J.Shaka, J.Keeler and R.Freeman, J. Magn. Reson. 53, 313 (1983).
- (3) T.Schaefer, K.Marfat and J.Peeling, private communication.
- (4) A.Allerhand, R.E.Addleman, D.Osman, M.Dohrenwend, J.Magn.Reson. (in press).
- (5) P.Barker, A.J.Shaka and R.Freeman, J. Magn. Reson. (in press).
- (6) D.Neuhaus, J.Keeler and R.Freeman, J. Magn. Reson. 61, 553 (1985).
- (7) D.G.Davis and A.Bax, J. Am. Chem. Soc. 107, 2820 (1985).
- (8) B.M.Fung, J. Magn. Reson. 59, 275 (1984).
- (9) B.M.Fung, J. Magn. Reson. 60, 424 (1984).
- (10) V.Sklenář and Z.Starčuk, Org. Magn. Reson. 22, 662 (1984).
- (11) V.Sklenář and Z.Starčuk, J. Magn. Reson. 62, 113 (1985).
- (12) A.J.Shaka, P.Barker and R.Freeman, J. Magn. Reson. 64, 547 (1985).

A.J. Shaka, Peter Barker and Ray Freeman -- Carbon-13 spectrum of reserpine



RÉSONANCE MAGNÉTIQUE NUCLÉAIRE
ET RÉACTIVITÉ CHIMIQUE
UA - CNRS N° 472The History of one of the Most Expensive
Barometers and Daters in the World !

Dear Barry,

It was really nice to meet you in CAMBRIDGE (UK) for the NMR DG meeting after such a number of years of epistolary relationship !

In the course of our study of site-specific natural isotope fractionation by ^2H -NMR we have observed two amazing climatological effects in the deuterium spectra of the two main wine components, i.e. water and ethanol.

The first effect, which is related to the field drift, is quite trivial (Fig. 1) but it encouraged us to develop in cooperation with Brüker-France, a new kind of barometer for the moneyed classes (*). Indeed, we observed a very significant correlation between field drift and atmospheric pressure since at that time we did not use a locking device. Incidentally, this climatological effect had also a climatic interest because we were able to run ^2H spectra during stormy or rainy weather only, when atmospheric pressure was low and helium consumption high. Therefore we had plenty of time left in the summer to enjoy the Atlantic beaches during the sunny days !

But considering that performance of the group was quite low, we convinced ourselves to fit our specific ^2H probe with a ^{19}F locking device in order to increase our productivity. This system happened to be quite gratifying since it permitted us to observe a climatological effect on ^2H spectra from wine and cognac samples (Fig. 2).

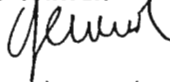
Then using data bases containing the meteorological parameters of various regions and different years, and SNIF data bases, our computer expert system called SNIFFER is now able to detect the year of the sample under study.

Since nowadays the atmospheric natural radioactivity is no longer perturbed by the artificial one, the ^{14}C dating method becomes less and less useful for short term dating of wines (on the other hand, long term dating of wines is useless since the wines are now drunk quite young and, except for testing the Egyptian mummies libations, it seems not necessary now to date wines older than 20 years old).

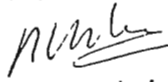
Thus with respect to the radioactive ^{14}C method, stable isotope SNIF-NMR could be a useful alternative for dating wines, brandies, fruit juice ... and, generally speaking, natural products containing water and glucides.

Sincerely,

G.J. MARTIN



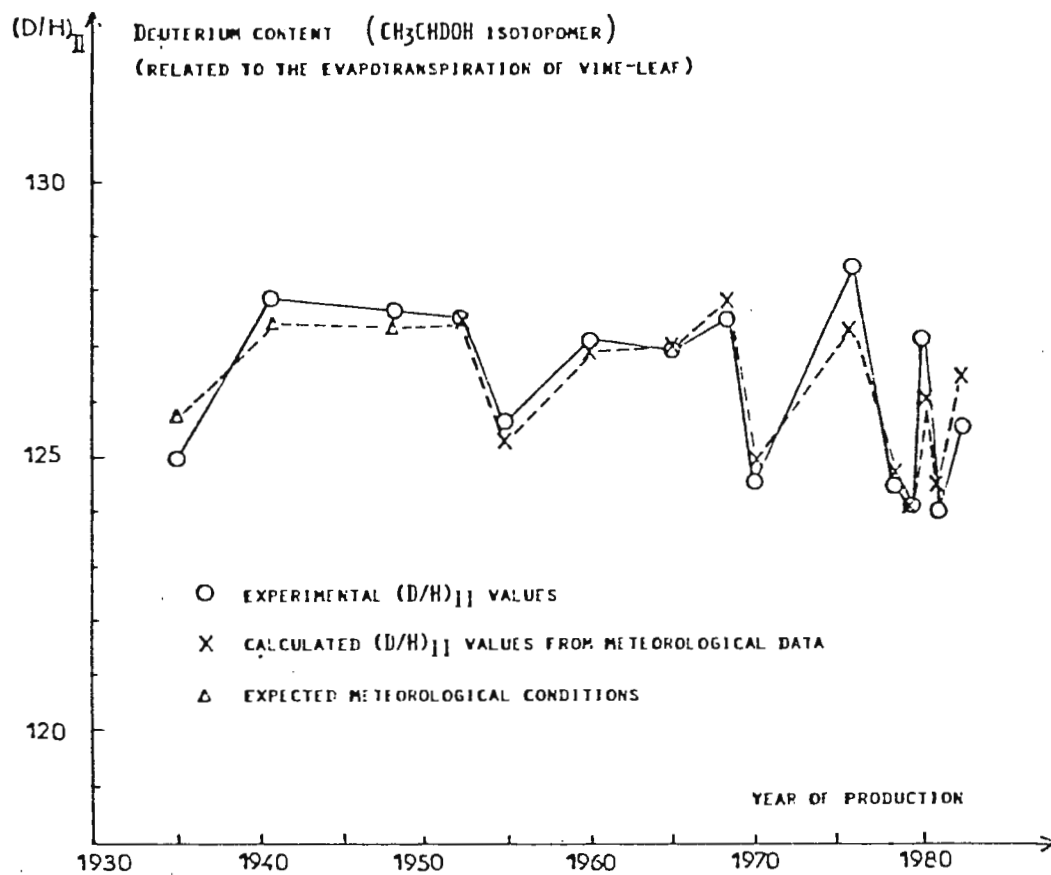
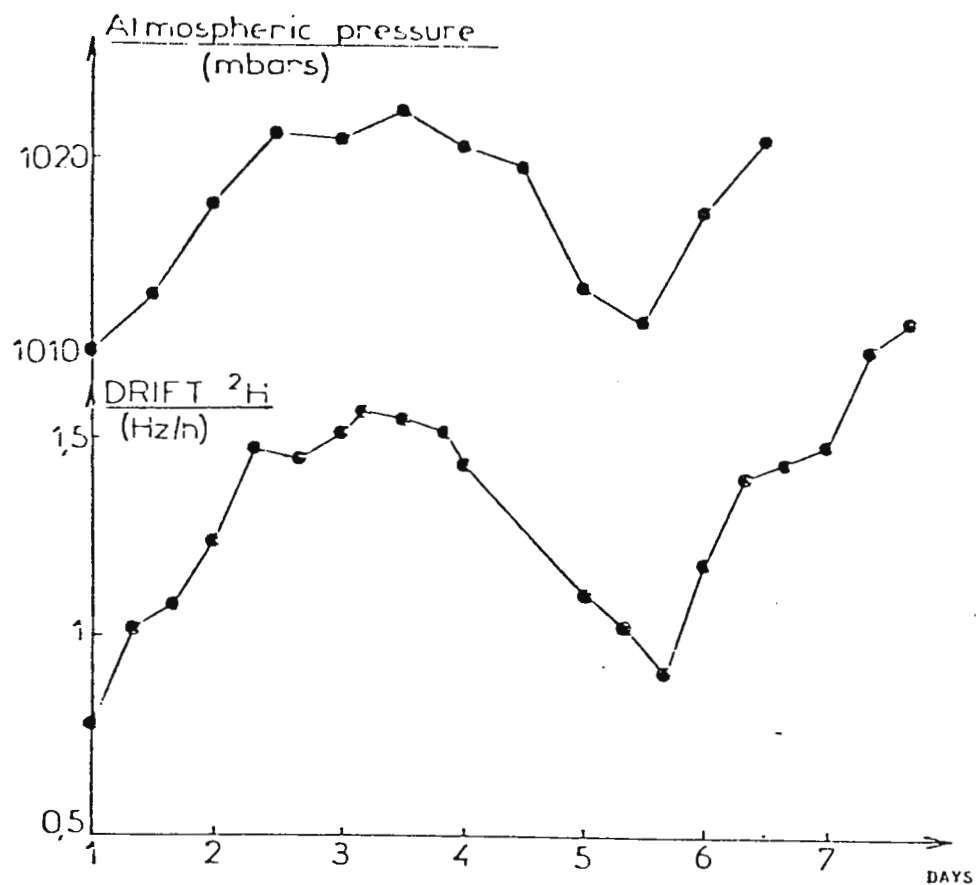
M.L. FILLEUX



M.L. MARTIN



(*) For this use as a barometer, a 5% discount can certainly be discussed with Brüker by the less affluent ones.



Department of Chemistry
University of Denver
Denver, CO 80208
303-871-2980

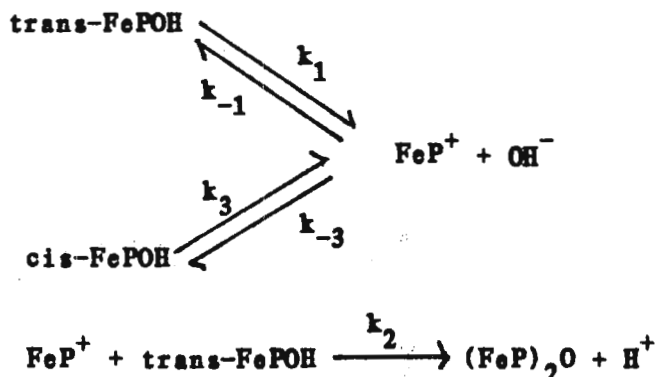
October 19, 1985

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

Re: Kinetics of Dimerization of ortho-substituted Iron Tetraphenylporphyrin Hydroxides

Dear Barry:

The rate of formation of oxo-bridged dimer from iron tetraphenylporphyrin hydroxide ($\text{Fe}(\text{TPP})\text{OH}$) in fluid solution is sufficiently slow that it can be monitored by ^1H NMR as a function of time at room temperature. While preparing a series of iron porphyrins with substituents on the ortho position of one phenyl ring we found that the rates of dimerization were dependent on the substituent. We examined the kinetics for 2 alkyl substituents, ethyl and nonyl, and 3 substituents with $\text{O}-(\text{CH}_2)_n\text{C}=\text{ONH}$ -tert-butyl for $n = 1, 2, \text{ or } 4$. In these monosubstituted porphyrins the hydroxide ligand can be on the same side of the porphyrin plane as the ortho substituent (cis isomer) or on the opposite side of the plane (trans isomer). The data were consistent with a two-step mechanism.



In the first step the hydroxide dissociates from an iron porphyrin, either cis or trans. That porphyrin then reacts with a trans isomer to form the oxo-bridged dimer. The rate of dissociation of hydroxide from the cis isomers was 7 to 70 times slower than from the trans isomers. The larger differences between the cis and trans isomers were found for the longer chain substituents. As the number of CH_2 groups between the ether oxygen and the amide increased, the population of the cis isomer increased. For the ether substituent with $n = 4$, the iron porphyrin hydroxide was about 98% cis isomer. These results indicate substantial stabilization of the hydroxide by interaction with the nearby substituent in the cis isomer.

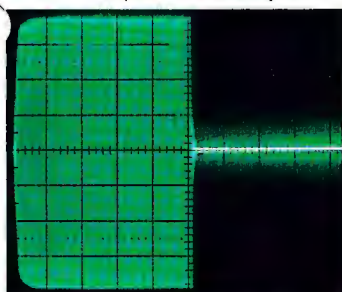
Sincerely,


Gareth R. Eaton
Professor

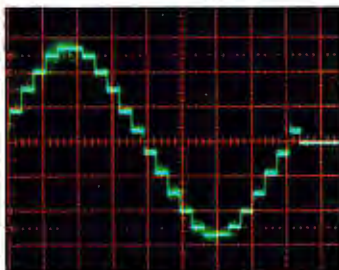
Sandra S. Eaton
Associate Professor

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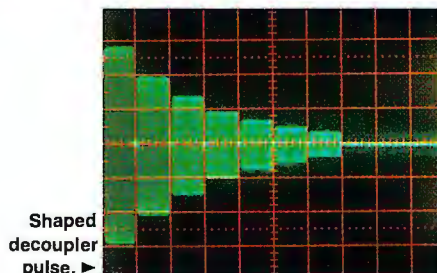
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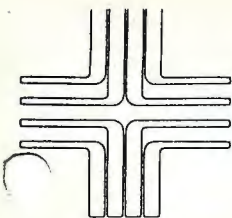
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Department of Radiology

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We are currently conducting research in the following areas: fluorine imaging, cardiac imaging and spectroscopy, image reconstruction, coil design and contrast agents. Many new projects are planned for the coming year.

Interested candidates should send their curriculum vita to me at the address above.

Sincerely,

Joel F. Martin, Ph.D.
Assistant Professor

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Téléphone (021) 44 42 50

Switzerland

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

25th September 1985

Dear Dr Shapiro,

Effects of T_2 relaxation on coherence transfer

Artefacts in 2D spectroscopy have always been a favourite source of inspiration. Recently, we have discovered a new variety which have come to be known as "forbidden cross-peaks".

In p-quantum filtered correlation spectra (pQF-COSY) (1), we thought that we should obtain greatly simplified spectra due to the restrictions imposed by coherence transfer selection rules (2). These rules, which were derived on the assumption that T_2 relaxation can be safely neglected, imply for example that in AX_3 systems it should be impossible to transfer single-quantum coherence belonging to one of the X spins into multiple-quantum coherence involving more than one X spin. In pQF-COSY with $p = 3$ or 4, this would imply that AX_3 groups cannot give rise to any cross-peaks. If such peaks appear, one might be tempted to conclude that one deals with more complex systems.

The partial 4QF-COSY spectrum in Fig.1b shows however that the AX_3 system of alanine in basic pancreatic trypsin inhibitor (BPTI) does in fact give rise to a sizeable cross-peak. We have been able to rationalize the multiplet structure and the peculiar peak-shape of the "forbidden" signals by noting that each component of the doublet of the X-region of an AX_3 system is in fact fivefold degenerate, and that the transverse relaxation of degenerate single-quantum coherences is multiexponential, as described by Redfield's equations.

These relaxation effects also have implications for double- and triple quantum spectra. In the latter, we have found signals

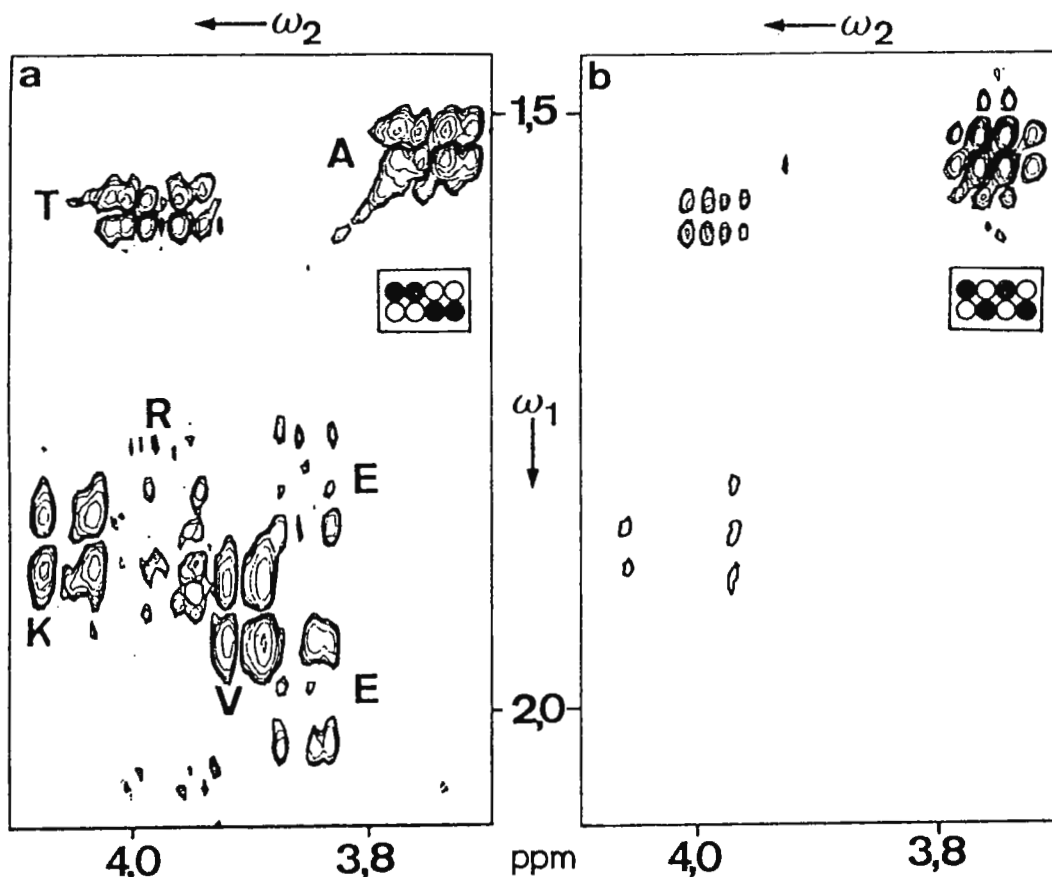


Fig.1 Phase-sensitive 2QF-COSY (a) and 4QF-COSY spectra (b) of BPTI. In (b), the signals due to alanine (A) and threonine (T) would vanish if it were not for multiexponential T_2 relaxation.

due to AX_3 groups at $\omega_1 = 3\Omega_X$ or $2\Omega_X + \Omega_A$ and $\omega_2 = \Omega_X$. Even the singlet of $\epsilon\text{-CH}_3$ of Met-52 in BPTI gives rise to a triple-quantum signal at $\omega_1 = 3\Omega_A$. The lineshapes of these forbidden peaks may give new insight into molecular motion.

Yours sincerely

Geoffrey Bodenhausen

Geoffrey Bodenhausen

Richard R. Ernst

Richard R. Ernst

Norbert Müller

Norbert Müller

Kurt Wüthrich

Kurt Wüthrich

P.S. Please credit this contribution to G.B.'s new account.

(1) U.Piantini, O.W.Sørensen and R.R.Ernst, JACS 104, 6800 (1982).

(2) L.Braunschweiler, G.Bodenhausen and R.R.Ernst,

Molec. Phys. 48, 535 (1983).

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October 14, 1985

A Case of Degenerate
Interconversion(!)

Prof. Bernard SHAPIRO
TAMU NMR NEWSLETTER
Department of Chemistry
Texas A & M University
College Station TX 77843
U.S.A.

Dear Professeur Shapiro,

As compared to the case of benzimidazole, interconversion of the two degenerated prototropic structures of parent compound 2-acetybenzimidazole, can be slowed down by the chelation process involving carbonyl group and labile hydrogen (figure 1).

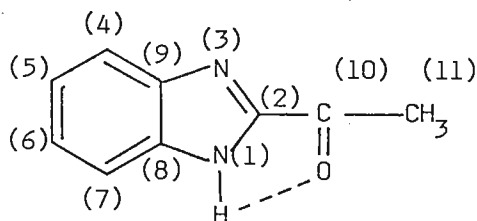


Figure 1.

At 310° K, in DMSO-d₆ solution, the asymmetry of the absorptions of the aromatic area in proton and carbon-13 NMR spectra (figure 2) confirms the hypothesis of a slow exchange situation. Peaks of carbons 5 and 6 coalesce at 340° K, at this temperature, the energy barrier can be estimated by absolute rates theory to be equal to 76 kJ/mole.

When calculated from cristallographic date and correlation times obtained from T1 of protonated carbons, predicted dipolar longitudinal relaxation times for quaternary carbons 8 and 9 in a chelated but "frozen" structure are markedly distinct ; they are equal to 15.4 s and 33.5 s respectively whereas the measured ones, obtained from amplitudes of individual peaks (IRFT) and NOE measurements, are identical and equal to 21 s (table 1).

At the temperature of the experiments (310°K), a residence time of ca 0.2 s in each site is estimated from the activation energy and is thus two orders of magnitude shorter than the relaxation times.

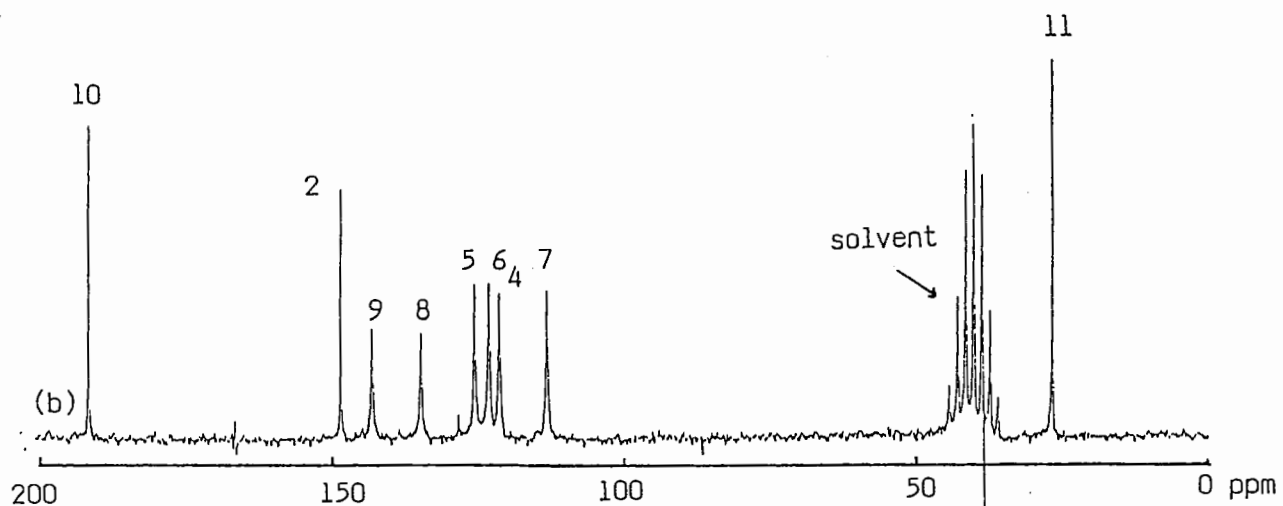
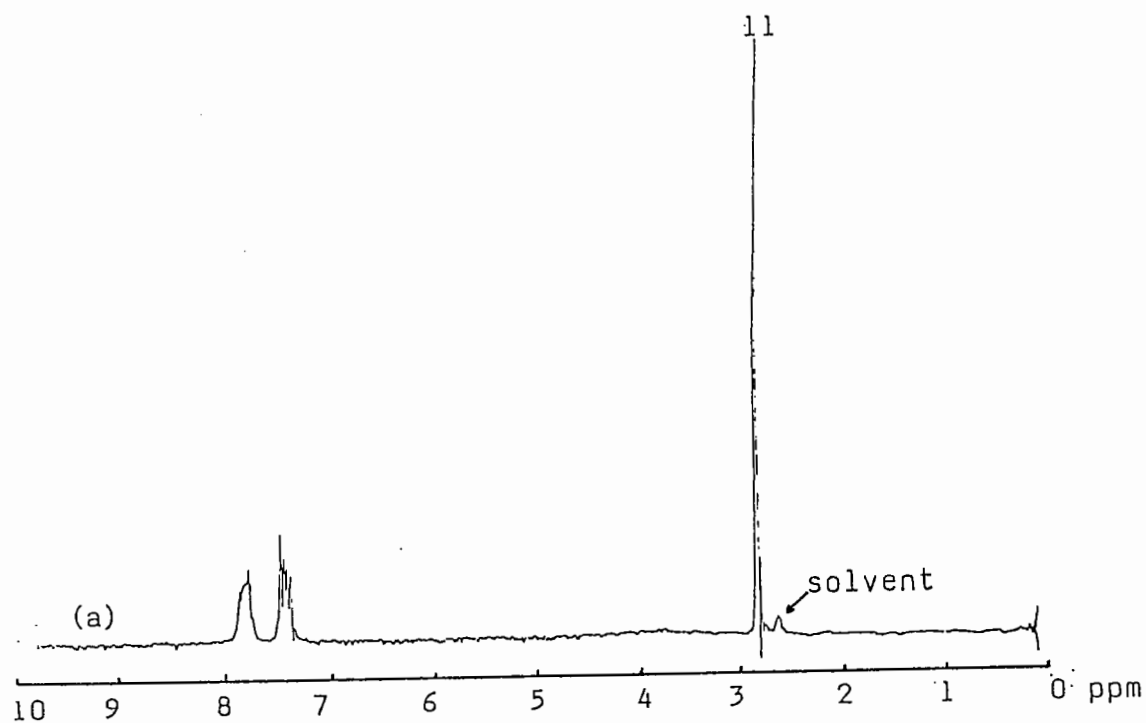


Figure 2: (a) proton NMR spectrum of 2-acetylbenzimidazole (100 MHz).
(b) carbon-13 NMR spectrum of 2-acetylbenzimidazole (15.08 MHz).

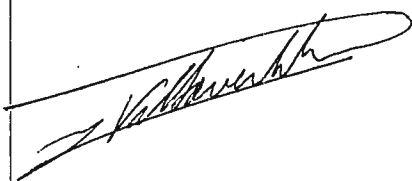
In this situation of fast exchange in terms of relaxation rates, one can calculate, for carbons 5 and 6, a mean and common relaxation time equal to 21 s which corresponds perfectly to the observed values (table 1).

Table 1 : Measured T_1 and NOE factors, experimental and predicted T_1^{DD} of 2-acetylbenzimidazole ($\tau_c = 8.53 \cdot 10^{-11}$ s).

	T_1 (s)	η	$T_1^{DD}_{meas}$ (s)	$T_1^{DD}_{calc}$ (s)
C8	8.99	0.86	20.8	15.4
C9	9.11	0.86	21.1	33.5

This particular case exemplifies the limit of applicability of relaxation parameters to structure investigation when chemical exchange takes place.

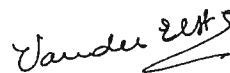
Sincerely,



Prof. Y. VAN HAVERBEKE



Dr. R.N. MULLER



Dr. L. VANDER ELST

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1969: Introduction of Fourier transform techniques for NMR.

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1983: Entrance into NMR Imaging (MRI) and in-vivo spectroscopy.

1984: Introduction of fiberoptics data link for high-speed data transfer and ultra-fast array processors for FT applications in IR and NMR.

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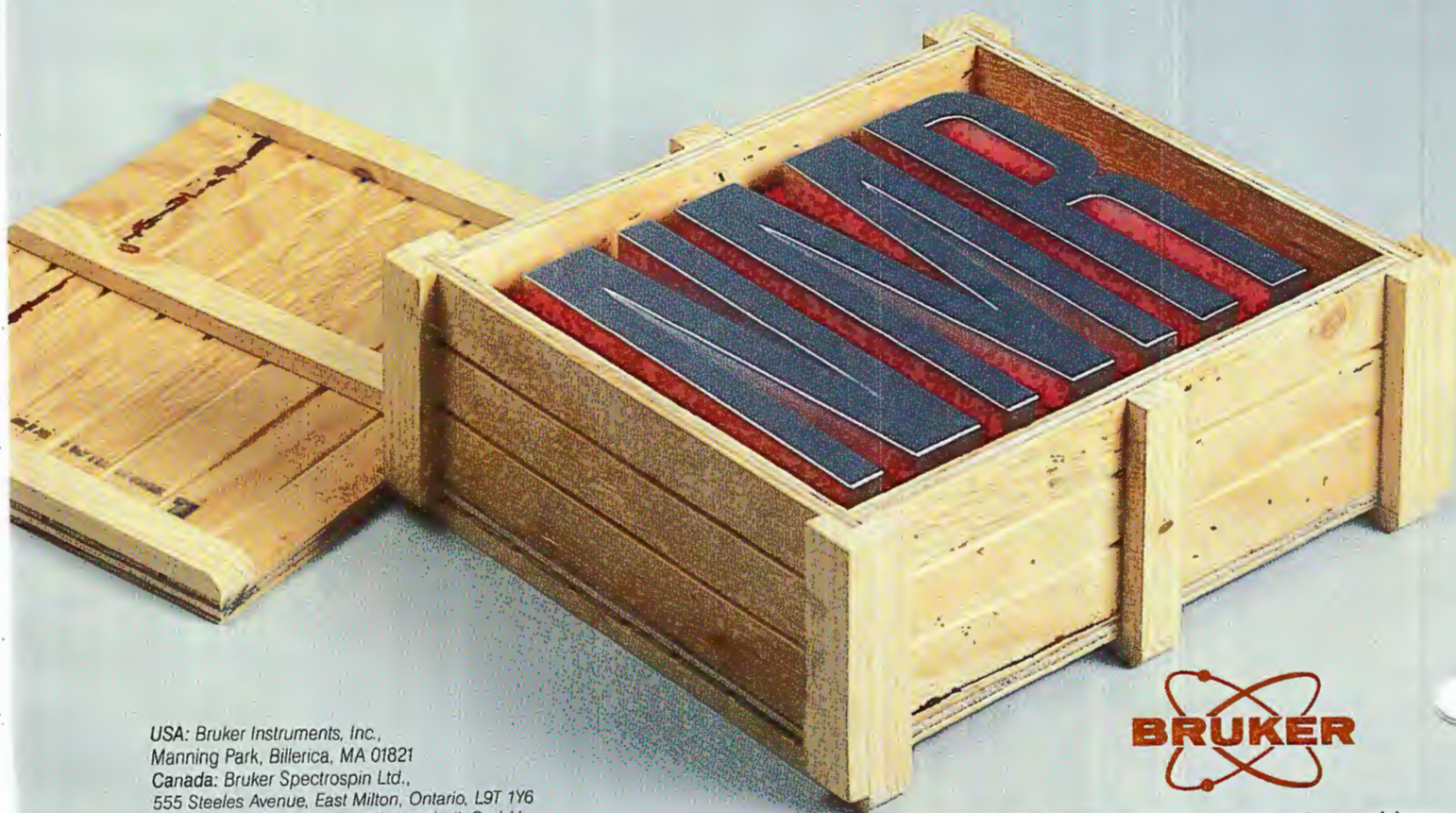
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IN REPLY REFER TO:

6120-638:ANG:mbr
26 September 1985

Professor Bernard L. Shapiro
TAMU NMR Newsletter
Chemistry Department
Texas A & M University
College Station, Texas 77843-3255

Postdoctoral and Visiting Scientist Programs at NRL

Dear Barry,

The Naval Research Laboratory has programs for both postdoctoral research fellows and visiting scientists.

There are two postdoctoral programs at NRL: the National Research Council (NRC) associateship and the Office of Naval Technology (ONT) fellowship, administered through the American Society for Engineering Education (ASEE). Each program selects applicants on a competitive basis. A relocation and professional travel allowances are provided. An immutable requirement is that the applicant be a U.S. citizen.

The NRC appointment is for two years; the stipend is expected to be \$26.3 K. A third year of contractual support from the Office of Naval Research may be available for NRC associates who continue research at an academic institution. There are two selection cycles yearly with deadlines of 15 January and 15 April 1986. Applications are available from:

Associateship Office, JH 608
National Research Council
2101 Constitution Avenue, N.W.
Washington, D.C. 20418
(202) 334-2760

The ONT program is newer and smaller than the NRC program. ONT appointment is for one year, renewable for a second and possibly third year. The ONT stipends start at \$29K. There are four award cycles with deadlines of 1 January, 1 April, 1 July and 1 October 1986. For applicant's packages, contact:

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The Laboratory has a program for visiting faculty members on sabbatical or leave, under the provisions of the Inter-governmental Personnel Act (IPA). Depending on the circumstances, supplemental or full support may be available. An IPA agreement may cover any period from a few months to two years. Allowances are provided for moving expenses and travel to scientific meetings. There is also an ASEE summer fellow program which brings university faculty to NRL for a 10 week period.

Within the Polymer Diagnostics Section we address a wide range of problems through magnetic resonance. Present efforts and interests include: adsorbed molecules, intercalated species in graphites; NMR imaging in solids; mechanical properties of polymers; hydro-dynamics of polymers in solution; NMR and ESR in phospholipids.

Please encourage anyone interested to contact me or my fellow research advisors directly and informally.

A. N. Garroway (202) 767-2323
H. A. Resing -2025
C. F. Poranski, Jr. -2488

Your assistance in publicizing these postdoctoral and visiting scientist programs is greatly appreciated.

Sincerely,

AI

A. N. Garroway, Head
Polymer Diagnostics Section
Code 6122
Polymeric Materials Branch
Chemistry Division

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Division of Natural Sciences—II

Santa Cruz, California 95064

October 18, 1985

Floppy Disk Drive Service

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

Dear Barry:

JEOL FX-100 users who are configured to the Standard PERSCI Model #270 Floppy Disk Drive are well aware of the difficulties in getting maintenance service on the disk drive, insofar as PERSCI, Inc. has been incorporated by EF Industries of California and JEOL no longer stocks or maintains the PERSCI disk drive.

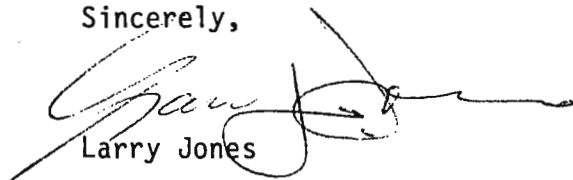
In our desperation to get our disk drive repaired it became apparent that only one vendor, other than EF Industries, was in the business of PERSCI disk drive repair and alignment. There may be others, but we couldn't locate them either through JEOL or EF Industries.

Computer Performance, a division of Pulse Tech., 11366 Amalgam Way, Suite C, Rancho Cordova CA 95670, (916) 638-3357, will up-grade, repair and align the Standard Model #270 PERSCI disk drive at a most reasonable cost, with exceptional turn-around time. In our case we were on-line with the FX-100 within three days.

We highly recommend that interested floppy disk drive users check out this alternative to EF Industries.

Please credit this letter to the account of Jim Loo.

Sincerely,


Larry Jones

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

27 September 1985

Dear Barry,

RUBIDIUM - POOR MAN'S POTASSIUM?

We have been continuing our work on ^{23}Na and ^{39}K nmr as a means of measuring Na^+ and K^+ fluxes through membranes. ^{39}K is not the easiest nucleus to observe. Its low frequency and sensitivity mean that we can't see it on our own WP80 and that a high field instrument is needed. We therefore turned to Rubidium.

Rb^+ is very similar in its chemistry to K^+ , much more so than Na^+ is to K^+ as can be seen from the table below, taken from Cotton & Wilkinson.

	Na^+	K^+	Rb^+
Crystal radii pm	95	133	148
Hydration radii pm	276	232	228
Hydration energy (kcal mole ⁻¹)	97	77	70

^{87}Rb is also readily observable coming at slightly higher frequency than ^{23}Na with about half the sensitivity.

The tripolyphosphate shift reagent that works well for $^{23}\text{Na}^+$ and for $^{39}\text{K}^+$ was tried on Rubidium but the shifts obtainable were considerably smaller than for Na^+ or K^+ and the line broadenings much greater. The line broadening, therefore, seemed to us to be the parameter to go for. A relaxation time difference between intracellular and extracellular $^{87}\text{Rb}^+$ is potentially as useful as a chemical shift difference.

So far we have broadened $^{87}\text{Rb}^+$ from ca 100 Hz in the absence of added reagent to ca 400 Hz with the $\text{Dy}(\text{PPP})_2^-$ reagent and to 600 Hz when Mn^{2+} or Cu^{2+} tripolyphosphates are used as paramagnetic agents. This is now getting into a useful difference and will undoubtedly lead us into further interesting areas.

Rubidium might be a poor nmr spectroscopist's potassium. You save at least £0.25m on the cost of your spectrometer! Alas, it is a rich chemist's metal because its salts are typically 60 times as expensive. Still, for your quarter of a million pounds you could buy 250kg of Rubidium Chloride!! More than enough to last?

Best wishes,

Yours sincerely,

Frank

Dr F G Riddell

Tim

T E Southon

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NE-L5 Yellow	505-PS	60MHz: Routine analysis, quality control. Not compatible with vortex plugs and coaxial inner cells.	178	2.40	2.30	2.20
			203	2.60	2.50	2.40
NE-M5 Green	507-PP	90-100 MHz: General research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	3.85	3.75	3.65
			203	4.35	4.25	4.15
NE-H5 Blue	528-PP	220-360 MHz: Research, FT applications. A superior sample tube for ultimate resolution and sensitivity. Compatible with vortex plugs and coaxial inner cells.	178	6.65	6.55	6.45
			203	7.15	7.05	6.95

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			203	8.25	8.00	7.50
NE-M10	513-5PP	90-100 MHz: General research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	12.25	11.75	11.00
			203	13.00	12.50	11.75
NE-H10	513-7PP	100 MHz and up: Research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	14.25	13.75	13.00
			203	15.00	14.50	13.75

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University of Delaware

DEPARTMENT OF CHEMISTRY
NEWARK, DELAWARE 19716

October 10, 1985

Professor B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843-3255

Solid-State ^{13}C NMR at Delaware

Dear Barry:

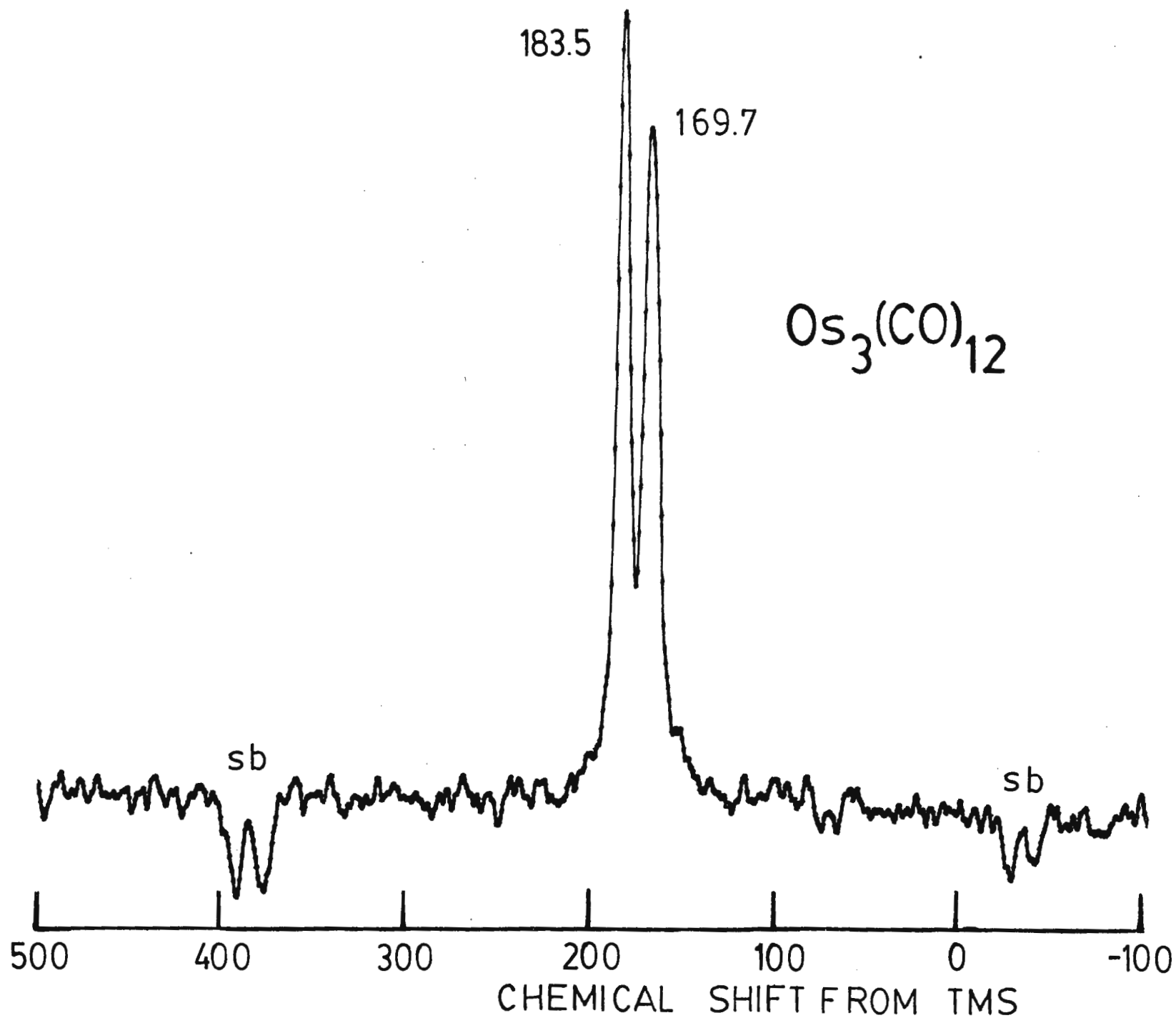
How quickly the months fly! We have been doing ^1H solid-state line-narrowing NMR for some time with our home-built spectrometer. However, recently we have been modifying it to perform the CP/MAS experiment on carbon nuclei. After a great many frustrations, our group has been able to carry out the C-13 experiment at 14.18 MHz. Perhaps others have experienced the same frustration which arose out of the fact that our PDP11 computer broadcasts near that frequency. We found that we had to use triax cable for all connections between the power amplifier, the probe and the receiver. This seemed to shield the rf sections from the offending computer's emissions.

The enclosed spectrum is that of $\text{Os}_3(\text{CO})_{12}$ in the crystalline state at room temperature. The sample has been enriched to 30% in C-13 and there is no decoupling or cross-polarization. With a relaxation delay of 2 minutes and a 5-microsecond 90° pulse, we can achieve a reasonable signal-to-noise ratio in about an hour. The sample was spun at 2950 Hz, although we can typically spin in excess of 4000 Hz in the Doty probe with ease. At the rate, spinning sidebands are visible due to the large anisotropy of the chemical shift. The shifts match (within 1 ppm) those in a liquid-state C-13 spectrum taken at 10°C . At room temperature in solution, the spectrum is a singlet due to rapid exchange between axial and equatorial positions. We are studying complexes like this in the solid state and as they are deposited on the surface of an oxide support. We still have to optimize the carbon spectrometry, but it is clear that solid-state carbon NMR will play a crucial role in determining the structures of catalytically active surface species.

Yours truly,

Cecil

Cecil Dybowski
Associate Professor
of Chemistry





Buenos Aires, october 10,1985.

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

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

Hardware Development

Dear prof. Shapiro:

I am proud to announce that our home built,C.W.,High Resolution,multinuclear 100 MHz NMR spectrometer is now operational.

The instrument was built around a Varian 12" 2.35 T electromagnet and two Schomandl frequency synthesisers.It has three SSB transmitters:one for f_0 ,the lock frequency;one for f_1 ,the observing frequency and one for f_2 ,the perturbing frequency.

It has three receivers: one for f_0 with two detectors in quadrature,one for the lock and the other for the homogeneity control.Two receivers in quadrature for f_1 to improve S/N ratio.

We also built the probes.With the standard 5 mm probe we can get good ^1H and ^{19}F spectra,locking either on ^1H or ^{19}F .The resolution is as good as can be expected from the high resolution magnet,thanks to the courtesy of Jim Schoolery from Varian's and Hp.Kellerhals from Bruker, who kindly supplied us with the special,zero magnetic susceptibility wire essential for the receiving coil.

We currently use Correlation Spectroscopy to improve S/N but with our actual analog frequency sweep it is difficult to accumulate more than,say,ten spectra.We are working now on a digital sweeper which,we hope, will allow us much bigger accumulations.

Our next task will be do develop a "switchable" receiver for F.T.Spectroscopy.We have already the power amplifier and the on line computer (a Nicolet NMR 812).We began already building the 10 mm,spinning probe for ^{13}C and eventually ^{31}P .We assume this will take us the whole of next year.

We are now currently working in the determination of the signs of HH, FH and FF spin-spin coupling constants.

Yours, sincerely

V.J.Kowalewski.

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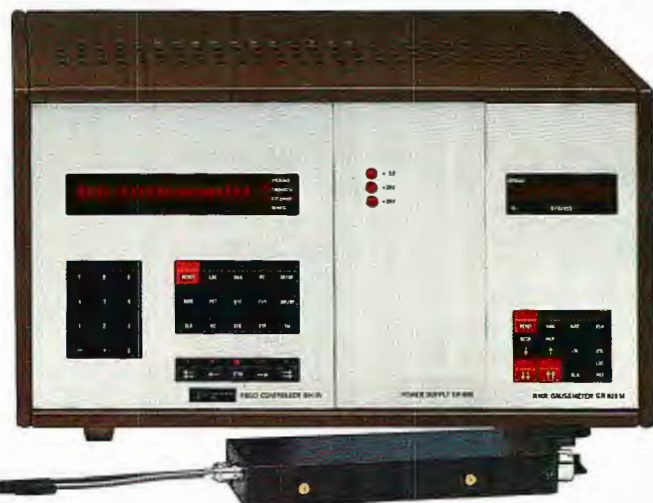
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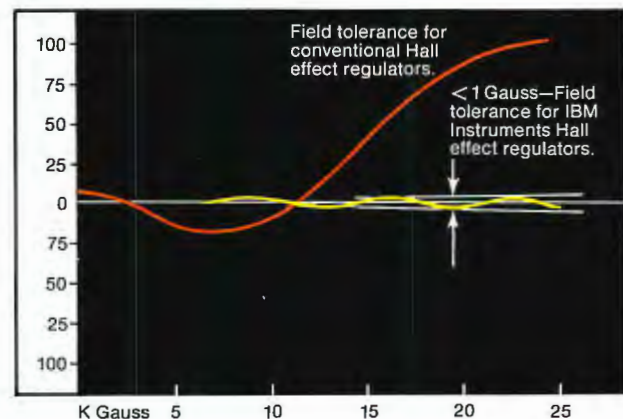
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October 15, 1985

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

Dear Professor Shapiro:

Re: WALTZin' Fluorine: Broad Band Fluorine Decoupling Using an X-Nucleus
Decoupler and Composite Sequences

Simplification of carbon spectra can be accomplished by broad band heteronuclear decoupling. The traditional noise or phase modulated broad band decoupling scheme requires 2 to 5 watts of power to decouple protons. The power required with this technique results in sample heating and, for nuclei such as fluorine, in possible probe damage. The introduction of composite decoupling schemes (MLEV, WALTZ, etc.) has alleviated many of the problems typical of the traditional broadband decoupling technique (1).


Decoupling fluorine always presents a challenge. Taking into account the broad chemical shift range of fluorine (300 ppm), the power requirements for effective fluorine decoupling in the traditional broad band scheme require as much as a ten fold increase in power over that required for protons; hence sample heating and probe break down are potential problems.

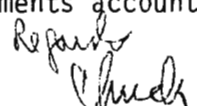
We have utilized a WALTZ composite decoupling scheme with only 10 watts of power to effectively decouple fluorine over a chemical shift range of 29,000 Hz. The spectra were acquired on an IBM Instruments NR 270/AF NMR spectrometer equipped with a BSV-3 X-Nucleus decoupler and a fluorine amplifier at a frequency of 254.14 MHz.

The figure shows for the perfluorinated compound the following carbon spectra:

a) Fluorine coupled (no decoupling); b) Fluorine decoupled using traditional phase modulation (25 watts) on the BSV-3 and c) Fluorine decoupled using WALTZ decoupling (10 watts) on the BSV-3. The improved decoupling bandwidth with WALTZ is evident.

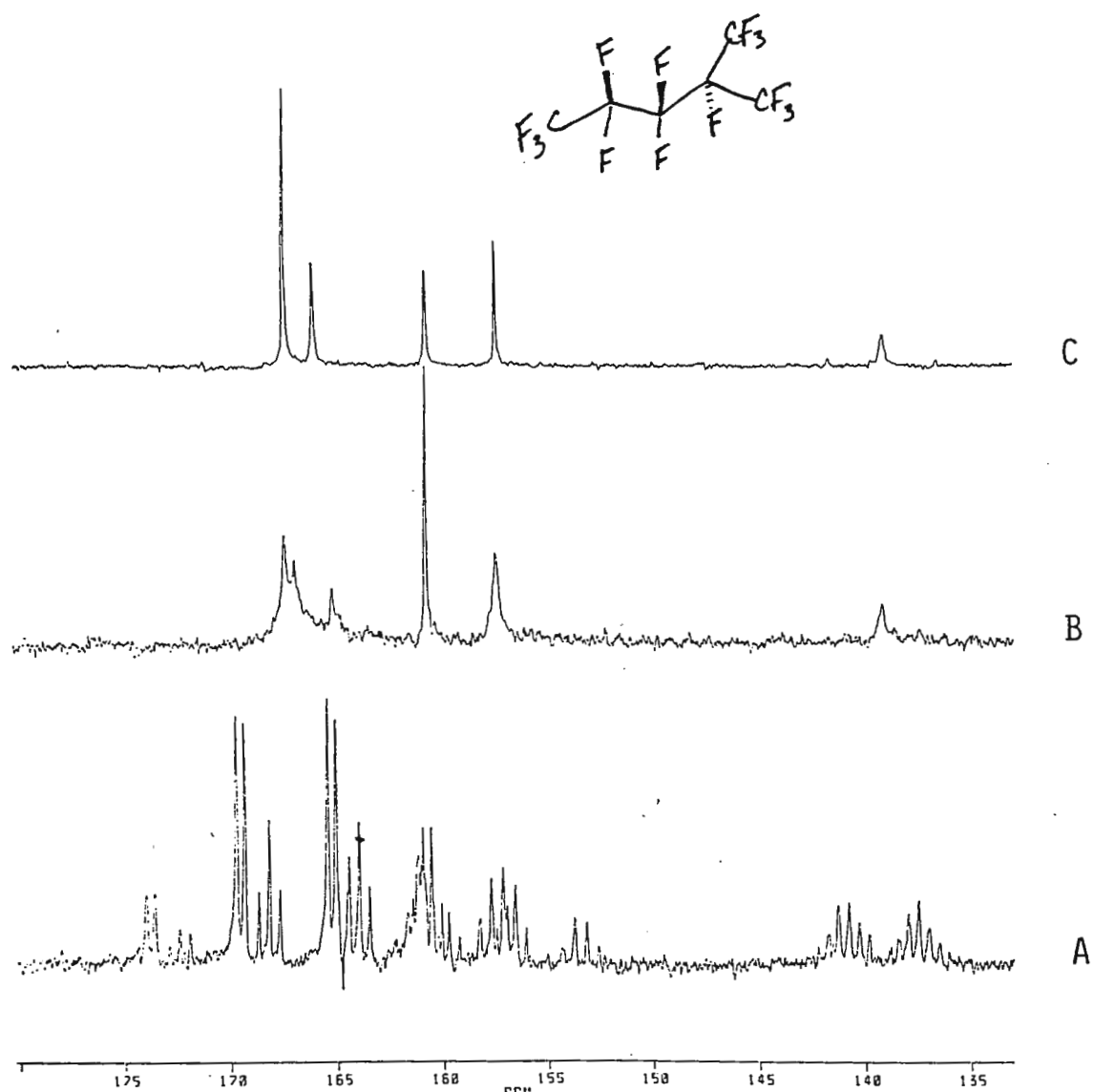
Please credit the IBM Instruments account of Charles Wade.


Mark O'Neil-Johnson
IBM Instruments, Inc.


Charles Wade
IBM Instruments, Inc.


Tom Kestner
3M

1. M. H. Levit, et al. J.Mag.Res. 43, 502 (1981);
2. A. J. Shaka, et al. J.Mag.Res. 53, 313 (1983) and references therein.



- A Fluorine coupled carbon spectrum
- B Partial broad band decoupled carbon spectrum
- C WALTZ fluorine decoupled carbon spectrum



October 24, 1985

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

Dear Barry,

Subject: Ceramic Spinners for CXP

The December 1984 issue of TAMU Newsletter published a letter concerning MAS spinners manufactured from toughend Zirconia (Nilcra PSZ).

We recently started using these spinners in our Bruker CXPl00. They were supplied with Kel-F end caps without flutes and, as advertised, gave absolutely no signal in the ^{13}C spectrum. However, on our system we were unable to reach spinning speeds in excess of ~2200 Hz. At any higher speed, the increased mass of these spinners was quite evident.

We have a bench-top stator assembly in which we spin some samples before placing them in the MAS probe. When these spinners JUMPED from the stator, they would knock the lid off the assembly. However, when end caps with flutes were used, the spinning speed approached 3500 Hz--quite acceptable for a ^{13}C frequency of 25.18 MHz, and the spinners stopped jumping out of our bench-top stator assembly.

In our hand, these spinners (with flutes) are the best spinners we have used to date in our Bruker system--especially when one considers the large internal volume.

See you at the ENC...

Very truly yours,

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

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

JMH-PMH:jah

J. Michael Hewitt, P. Mark Henrichs
Chemistry Division
Research Laboratories



Scripps Clinic and Research Foundation

10666 North Torrey Pines Road
La Jolla, California 92037

Research Institute of Scripps Clinic
Department of Molecular Biology

October 11, 1985

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

"Inverse" Heteronuclear Experiments on a
Bruker AM500 Spectrometer

Dear Dr. Shapiro:

In our studies of peptide and protein structure we have become interested in applying heteronuclear multiple quantum techniques with observation of the proton magnetization (1). Such experiments are not possible in the standard configuration of most Bruker spectrometers unless an X-nucleus decoupler is available. With minor modifications, however, it is possible to pulse both X-nucleus and protons (using the proton decoupling channel) and observe the proton signal. We briefly describe here the changes made to our AM500 spectrometer which is equipped with the digital phase-shifting hardware.

It is necessary to derive the 6MHz IF receiver reference frequency from the F2 transmitter board instead of the F1 board. The required circuit had already been laid out on our original F2 board, but with no components installed. Bruker supplied us with a replacement board fitted with the necessary components. Patch-boxes are inserted in the cables to the F1 and F2 boards so that cables V (168.766MHz input signal) and R (6.17MHz IF output) can be rerouted into F2 instead of F1. It is also necessary to install a three-pole-double-throw switch in the BSV-6 amplifier unit such that the control voltages (0 or 25V) for relays RL1, RL2, RL3 in the rf mixing unit 2 and RL5 can be overridden and set to 25V. This causes the output BU5 to be 506MHz. To run an inverse experiment, the spectrometer is set up as for a conventional heteronuclear experiment, except that the proton preamp is selected, the decoupler output is connected to the transmitter input of the preamp housing, and the F1 transmitter cable is connected directly to the X-nucleus coil of the probe. The center of the proton spectral window is determined by O2.

With this set-up there is a software modification which would be highly desirable. The phase-shifts of the F1 and F2 frequencies are those of the last F1 and F2 pulses applied. Because the receiver reference frequency is normally derived from F1, the software resets the phase of F1 to a constant value just prior to triggering the digitizer. Unfortunately there is no such facility for the F2 channel; thus, at some point between the end of the last desired proton (decoupler) pulse and the triggering of the data acquisition it is necessary to issue a short F2 pulse of a constant phase (0.2 usec is the minimum allowed by software) in order that the receiver reference frequency will be of constant phase. Hopefully, future software up-dates will allow the phase of F2 to be changed without the necessity of issuing a pulse.

Yours sincerely,

Mark Rance

Mark Rance

Peter Wright

Peter E. Wright

(1) L. Muller, J. Am. Chem. Soc., 101, 4481-4484 (1979).

MR/st

POST DOCTORAL FELLOWSHIP

NMR IMAGING AND IN-VIVO SPECTROSCOPY

UNIVERSITY OF ALBERTA

Applications are invited from persons with NMR experience and who have (or expect to receive) a Ph.D. for a Post Doctoral Fellowship in the in-vivo NMR facility at the University of Alberta. Ideally candidates would also be familiar with some hardware aspects of Bruker spectrometers.

The facility includes both a 2T clinical unit and a smaller (40 cm bore) 2.35T system for animal studies. Each of these NMR systems is employed on research programmes in both imaging and in-vivo spectroscopy.

The appointment will be for one year, initially, with the possibility of renewal and the salary will be in the range of \$21,800 to \$26,345 (Canadian). The laboratory environment is non-smoking.

The University of Alberta is an equal opportunity employer and preference will be given to Canadian citizens or landed immigrants.

Applications, including the names of two referees should be sent to:

Dr. Peter S. Allen
Department of Applied Sciences in Medicine
10-102 Clinical Sciences Building
University of Alberta
Edmonton, Alberta, CANADA
T6G 2G3



The Ohio State University

Department of Chemistry

140 West 18th Avenue
Columbus, Ohio 43210-1173

Phone 614-422-2251

Professor Gideon Fraenkel

614 422-4210 office

614 422-4100 lab

TELEX 810 48217 15

October 16, 1985

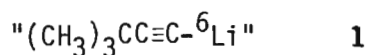
Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Fine Structure in ${}^6\text{Li}$ NMR

Dear Barry,

In response to the dreaded pink sheet I would like to propose that long term contributors deserve some special dispensation from TAMUNMR such as less frequent contributions, a discount for the Newsletter, or perhaps a medal. *

Here goes anyway - Lithium t-butyl acetylide, **1**, is a species



which exhibits all the variegated behavior of typical organolithium compounds but unlike most of them is very stable. The acetylide is insoluble in hydrocarbon but dissolves readily in cyclopentane in the presence of an equivalent of t-butyllithium. Carbon-13 NMR at 100° of a sample of acetylide- ${}^6\text{Li}$ and t-Bu- ${}^6\text{Li}$, 1:1, in cyclopentane gave rise to two overlapping heptets for the C_2Li carbons of t-butyllithium. Neither of these center at the t-Bu-Li shift and thus must represent new species. The heptet multiplicity comes from three ${}^6\text{Li}$'s coupled to each C_2 ($J=5.9$ and 5.8 Hz) (of what was t-Bu- ${}^6\text{Li}$) in a tetramer. There are thus two mixed tetramers which differ in the alkynyl/t-Bu ratio, probably one 1/3, the other 2/2. Lithium-6 NMR at -100° shows two sharp lines (1 Hz) of almost equal intensity, separated by 1.9 ppm. On warming this sample above -100° the original doublet is replaced by a symmetrical multiplet of five lines. By -20° the two original lines undergo signal averaging while the shape of the now more intense new resonance remains unchanged, see figures at bottom of letter. I am puzzled by the symmetrical shape of this new resonance. It implies either some unique symmetrical structure with nonequivalent lithiums and/or some ${}^6\text{Li}$ - ${}^6\text{Li}$ coupling. Such couplings are expected from theory to be quite small. This leads to the other possibility that the multiplet comes from some oriented polymeric "RLi" super-cluster and the splitting comes from dipolar coupling. We are doing the obvious experiments, for example using 50% ${}^7\text{Li}$ 50% ${}^6\text{Li}$, and obtaining NMR data at different fields. Suggestions as to the origin of our ${}^6\text{Li}$ fine structure will be welcomed.

There is a Postdoctoral position in my group for someone who will work on both preparation of organolithium compounds and the study of their structures and dynamic behavior using the methods of NMR line-shape analysis. This may include some work on the mapping of ion pairs.

For a long time it has been suspected that temperature gradients in NMR samples significantly degrade resolution and altogether give rise to uninterpretable line-shapes especially when the line shape is dependent on the

* Gideon - see bottom of page 42.

temperature. We also know that running in VT mode at 40° gives much better data than simply using the probe at room temperature. Now Adam Allerhand has elegantly confirmed all this with precise temperature control. I hope that manufacturers of NMR equipment will follow suit and finally come out with simple, easy to use, properly thermostatted probes, -150° to +250°.

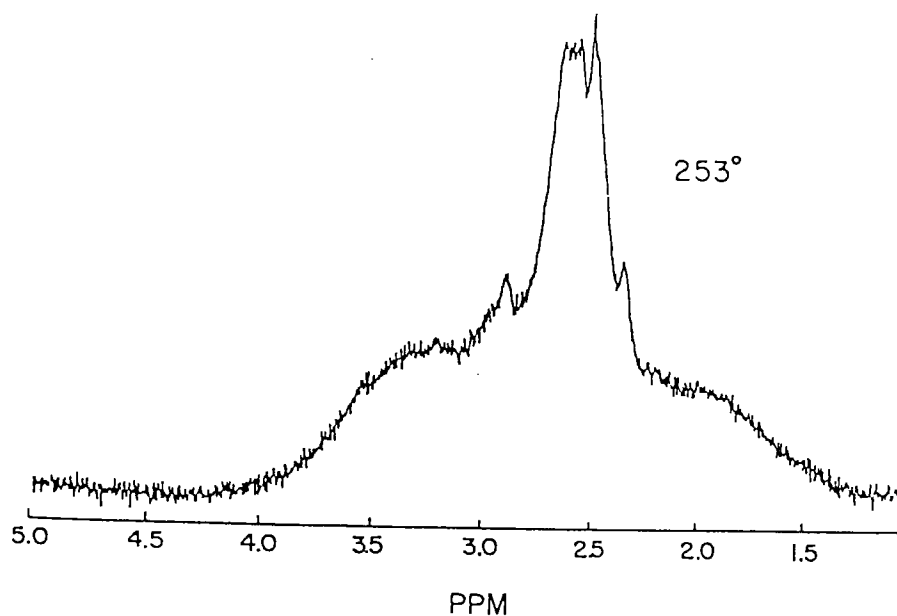
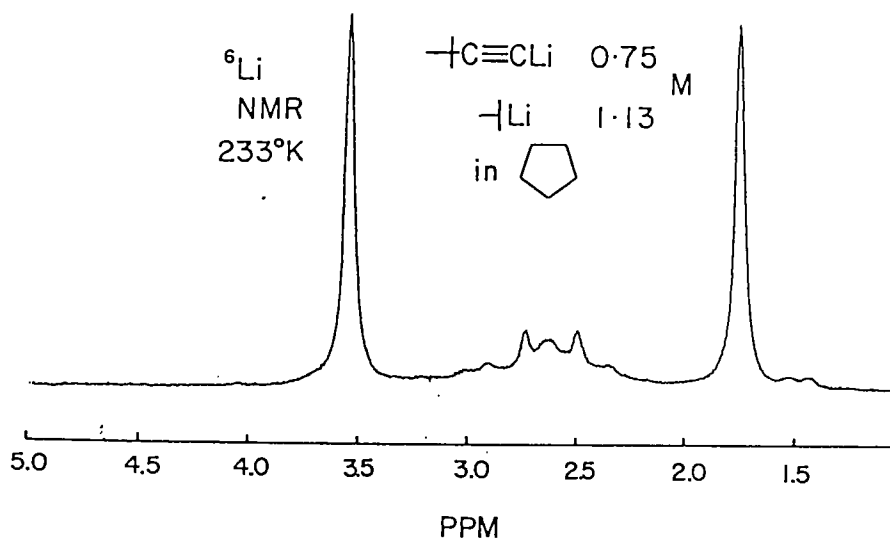
With best regards.

Yours sincerely,

Gideon

Gideon Fraenkel
Professor of Chemistry

1s





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October 3, 1985

Dr. B. L. Shapiro
Texas A&M Nmr Newsletter
College of Science
College Station, TX 77843

Dear Barry:

"Parallel Data Transfer --New Software Release"

One of the projects I've been working on in the past year is a parallel data transfer scheme to send data from our spectrometer (Aspect) computers to the 9000 workstation. This gives a substantial improvement in data transfer rate and allows you to send data from within DISNMR using a user-module command in both the foreground and in automation. This is now an available product from IBM Instruments.

Nmr and epr workstation customers should note that release 2.0 of NMR1D, NMR2D and EPR for the S/9000 is now available. They should contact their local marketing representative or us here at IBM Instruments for information on how to obtain these upgraded software packages.

Best regards,

A handwritten signature in cursive script that reads 'Jim Cooper'.

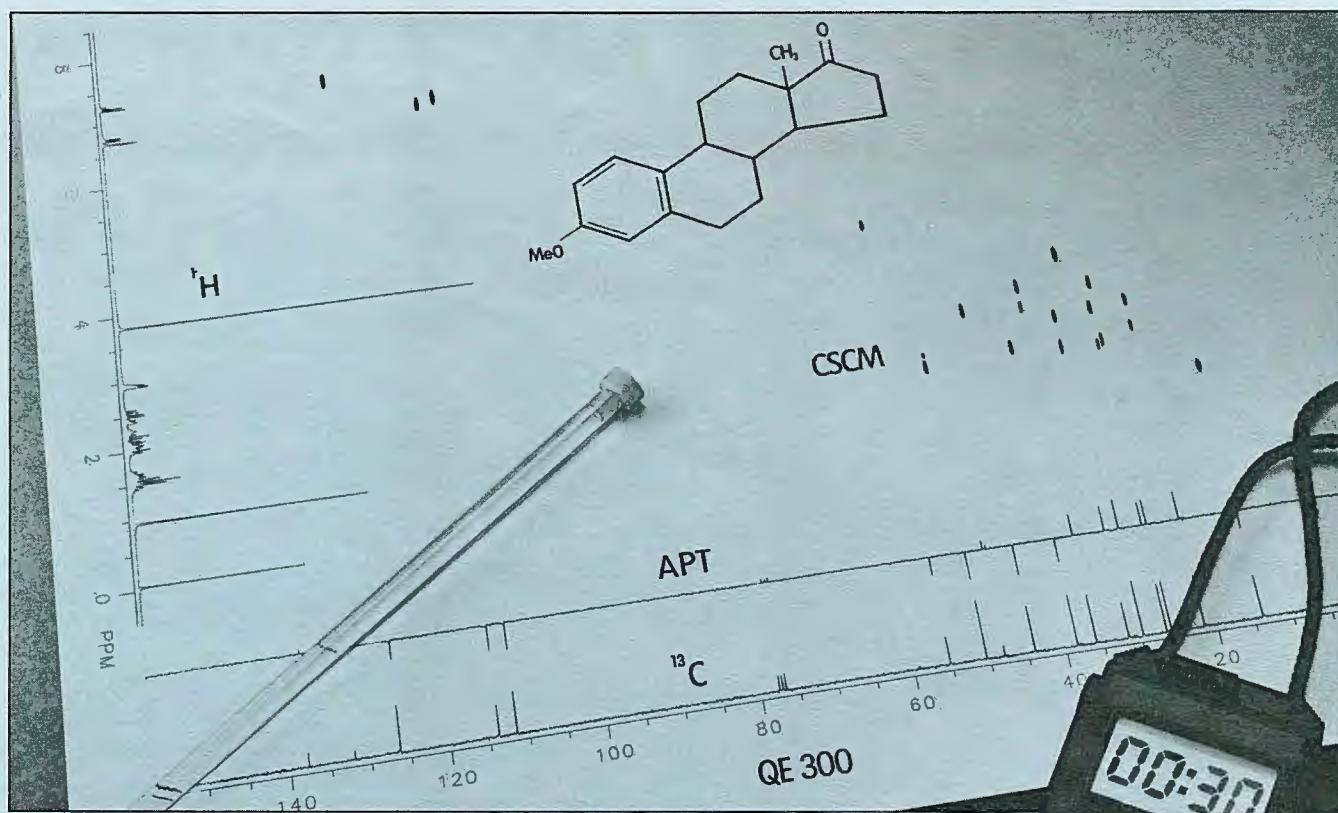
James W. Cooper



Attention Gideon Fraenkel:

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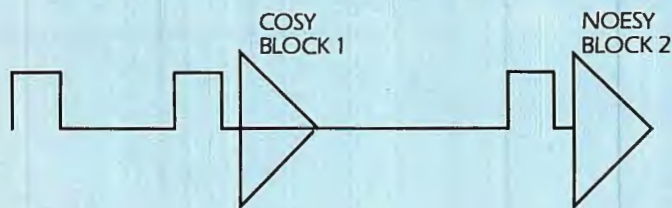
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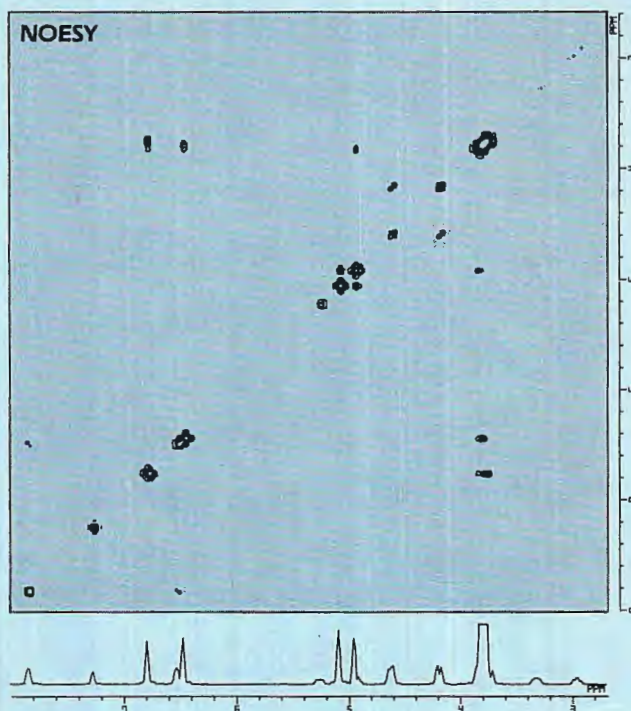
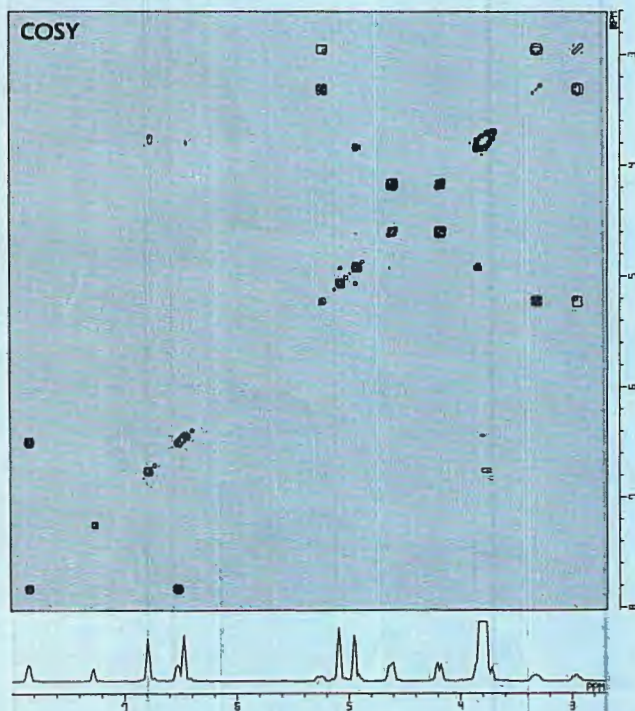
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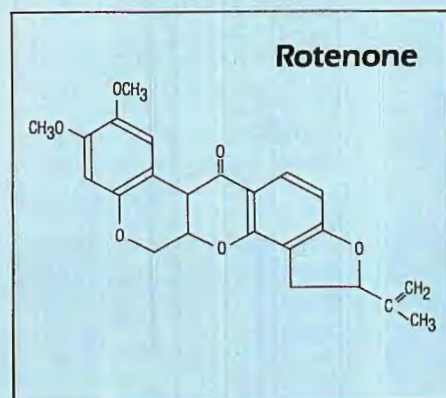


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*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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