# Texas A & M University N-M-R Newsletter

No. 256

January, 1980

R. Wasylishen
ADAMANTANE: $^{13}C$ and $^{2}H$ Spin-Lattice Relaxation Results . . . . . 1

R. L. Vold and R. R. Vold
Nuclear Relaxation and Vibrational Averages . 5

E. Santoro, G. Bragato and F. Corda
$^{1}H$ NMR of Some Tetrasubstituted Cyclopropanes . . . . . 7

G. E. Pollard
Trimethylphosphite Stability . . . . . .10

J. A. G. Drake, D. W. Jones and H. Pakdel
H-H Couplings and $^{1}H$ Solvent Shifts in Fluorenes . . . . . .11

P. A. Hart
Degassing Samples for Cylindrical Insert Tubes. . . . . .13

G. J. Bene
Recent and Forthcoming Publications; Joint ISMAR - Ampere Int. Conf. on Magnetic Resonance, Delft (Netherlands), 25-30 August 1980. . . . . .14

A. A. Chalmers
Assignment of $^{13}C$-$^{13}C$ Couplings with Dante .17

J. L. Marshall
Effect of the Orientation of a Terminal Substituent on Vicinal C-13 C-13 Couplings .19

J. A. B. Lohman and C. MacLean
Solvent Effect on the Anisotrophy in the Diamagnetic Susceptibility . . . . .21

W. Boenigk and G. Hägele
Programs CYMTRY, CYBER, and CYMPLOT for the Analysis of NMR Spectra. . . . . .23

J. Feeney and G. C. K. Roberts
Photo-CIDNP Studies of Surface Accessibility of Aromatic Residues in Dihydrofolate Reductase and its Complexes with Ligands . . .25

H. Günther and H. Fischer
WH-400 Experience - Cycloheptatriene Carboxaldehyde. . . . . .29

R. Lenkinski
Lanthanide Complexes of Bleomycin . . . . .31

R. S. Matthews and A. Royston
90MHz Decoupling Amplifier. . . . . .33

N. Sheppard
Equipment Wanted . . . . . .34

M. A. R. Smith
Industrial Postdoctoral Fellowship in Nuclear Magnetic Resonance. . . . . .35

R. A. Byrd and I. C. P. Smith
Research Associate Position in Biophysical NMR .36

G. E. Maciel
21st ENC, Tallahassee, Florida, March 16-20, 1980. . . . . .37

K. Sweet
Positions Available . . . . . .38

B. L. Shapiro
TAMU NMR Newsletter - Back Issues Available . .39

## TAMU NMR NEWSLETTER - ADVERTISERS


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Varian Instrument Division - see p. 2
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| DEADLINE DATES: | No. 257 | 4 February 1980 |
|---|---|---|
| | No. 258 | 3 March 1980 |

All Newsletter Correspondence, Etc., Should be Addressed To:


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


## AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 256


Bene, G. J.....14
Boenigk, W.....23
Bragato, G..... 7
Byrd, R. A.....36
Chalmers, A. A.....17
Corda, F..... 7
Drake, J. A. G.....11
Feeney, J.....25
Fischer, H.....29
Günther, H.....29
Hägele, G.....23
Hart, P. A.....13
Jones, D. W.....11
Lenkinski, R.....31
Lohman, J. A. B.....21
Maciel, G. E.....37
MacLean, C.....21
Marshall, J. L.....19
Matthews, R. S.....33
Pakdel, H.....11
Pollard, G. E.....10
Roberts, G. C. K.....25
Royston, A.....33
Santoro, E..... 7
Shapiro, B. L.....39
Sheppard, N.....34
Smith, I. C. P.....36
Smith, M. A. R.....35
Sweet, K.....38
Vold, R. L..... 5
Vold, R. R..... 5
Wasylishen, R..... 1

THE UNIVERSITY OF WINNIPEG
WINNIPEG, CANADA R3B 2E9

December 13, 1979

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

Dear Barry:

ADAMANTANE: $^{13}C$ and $^{2}H$ Spin-Lattice Relaxation Results

During the past two years we have studied the $^{13}C$ nmr of several plastic cyrstals. Because adamantane plays a central role in both experimental and theoretical studies of orientational disorder in crystals we felt that readers might be interested in the results of a $^{13}C$ and $^{2}H$ nmr study of $C_{10}H_{16}$ and $C_{10}D_{16}$ respectively. Rotational jump times for phase I as a function of 1/T are given in figure 1 (squares, $^{13}C$ results for $C_{10}H_{16}$; circles, $^{2}H$ results for $C_{10}D_{16}$). For comparison, the results of a detailed $^{1}H$ nmr study by Resing (1) are given (broken line). Agreement between the $\tau$'s calculated from the $^{13}C$ data are in good agreement with those obtained by Resing. The $\tau$'s of $C_{10}D_{16}$ are systematically a little longer than those of $C_{10}H_{16}$ but the observed differences are within the uncertainties in the experimental data and $e^2qQ/h$ and $r_{CH}$.

It is interesting to point out that at temperatures immediately below the solid I, solid II phase transition (208.6 K for $C_{10}H_{16}$) both the methylene and methine $^{13}C$ resonances are still resolvable on a Varian CFT-20 and that the $^{13}C$ $T_1$'s increase with decreasing temperature indicating that one is on the right hand side of the $T_1$ min. ( $\tau > 10$ ns ). Calculated $\tau$'s from the limited data that we have for phase II also agree well with the results given in ref. 1.

Yours sincerely,

Rod Wasylishen

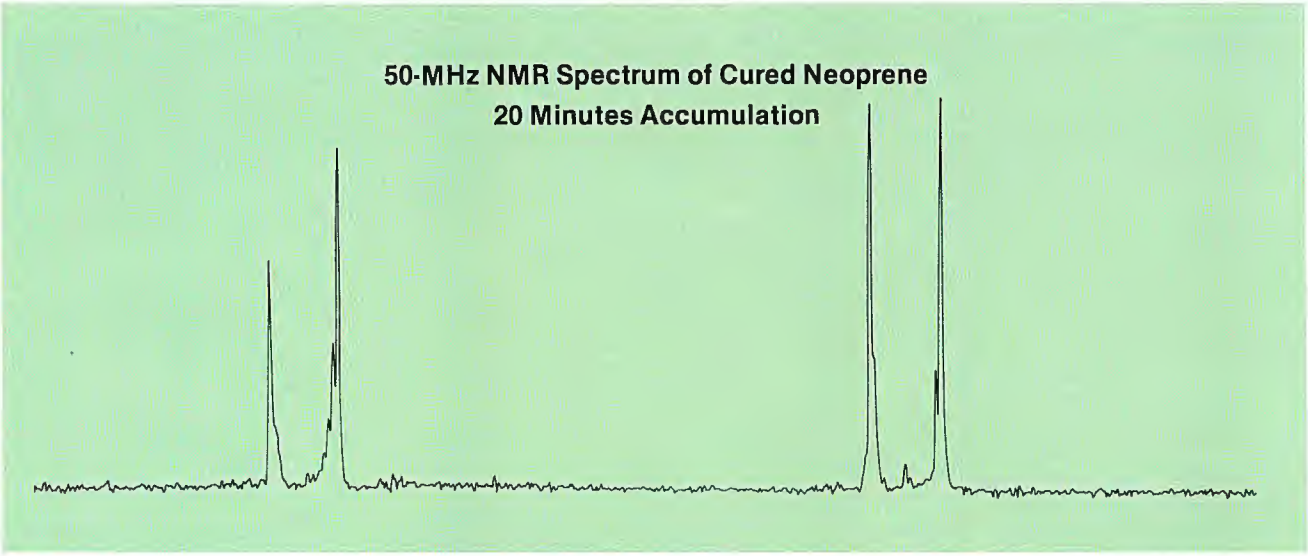
Rod Wasylishen
Department of Chemistry

RW/nl

1. H. A. Resing, Molecular Crystals and Liquid Crystals 9, 101 (1969).

# If you can't observe solids as readily as liquids on your superconducting FT NMR...

# ...you just don't have an XL-200!




*$^{13}C$ spectrum of cured neoprene with carbon black* in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the fine structure. The width of the plot is 10 KHz. *Sample courtesy of E.I. Du Pont de Nemours and Company*

With the new $^{13}C$ solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 superconducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; generate your own convenient macro-commands; create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband accessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including $^{13}C$) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.

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For immediate assistance contact: 611 Hansen Way, Palo Alto, CA 94303 • Florham Park, NJ (201) 822-3700 • Park Ridge, IL (312) 825-7772
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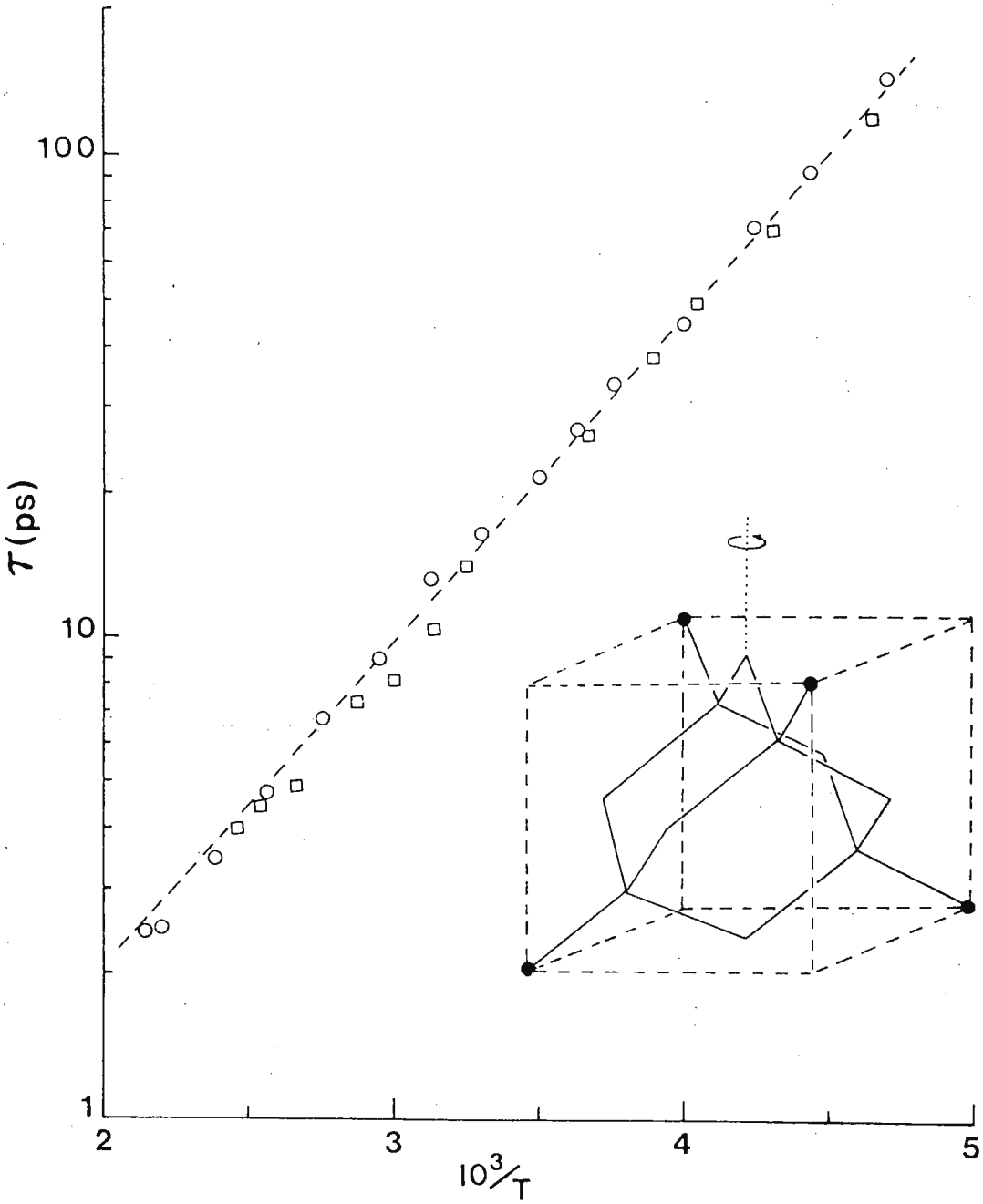
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DEPARTMENT OF CHEMISTRY, B-014
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December 5, 1979

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

Re: NUCLEAR RELAXATION AND VIBRATIONAL AVERAGES

Dear Barry,

We're sorry to be tardy with our contribution, but since you switched from pink to yellow paper the threats don't seem quite so ominous...the words "FINAL ULTIMATUM" nevertheless retain a certain vibrant ring, so here goes:

In TAMUNMR 231-25 (1) we suggested that the proper effective distance to use with nuclear relaxation formulae is

$$r_{eff} = r_e + \langle \Delta z \rangle + \frac{2}{r_e}\left(\frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2} - \langle \Delta z^2 \rangle\right) \qquad (1)$$

(Actually, we considered a molecule with $C_{2v}$ symmetry so that $\langle \Delta x^2 \rangle = \langle \Delta y^2 \rangle$. Eq. (1) had been derived previously by Diehl and coworkers (2) in connection with liquid crystal work). Eq. (1) takes into account the contributions to r from vibrational motion.

In TAMUNMR 244-11 (3), the authors suggest that Eq. (1) is incorrect, and present another equation which is obtained by computing $\langle 1/r^6 \rangle$. Their procedure is <u>not correct for relaxation</u>. The correlation functions which govern relaxation involve an ensemble average $\langle \mathcal{H}_{ij}(t)\mathcal{H}_{ij}^*(t+\tau)\rangle$, where $\mathcal{H}_{ij}(t)$ is a matrix element of the relaxation Hamiltonian (eg. the dipole-dipole Hamiltonian). Vibration is generally much faster than rotation and for times $\tau$ which are longer than a vibrational relaxation time, the vibrational motion implicit in $\mathcal{H}_{ij}(t)$ is uncorrelated with that in $\mathcal{H}_{ij}^*(t+\tau)$. It follows that the vibrational averages of $\mathcal{H}_{ij}(t)$ and $\mathcal{H}_{ij}^*(t+\tau)$ should be performed separately, and the results subsequently combined to construct the rotational correlation function. This procedure yields dipolar spectral densities which are of the form

$$J_{abcd}(\omega) = 0.3\, D_{ab}D_{cd}\int_0^\infty g_{rot}(\tau)\exp(-i\omega\tau)d\tau \qquad (2)$$

Here $r_{ab}$ is the instantaneous internuclear vector and $\beta_{ab}$ is the angle between this vector and its equilibrium, molecule fixed position. According

to Eq. (2) the spectral density for an autocorrelation term ab=cd is proportional to $D_{ab}^2$, and if one uses the procedure of Diehl and coworkers (2) to evaluate $D_{ab}$, the dipolar relaxation rate is proportional to $^1/r_{eff}^6$ where $r_{eff}$ is given by Eq. (1). This is not at all the same as $\langle {}^1/_r{}^6 \rangle$.

It is worth noting that the dipolar coupling constants appearing in Eq. (2) are directly measurable from liquid crystal splittings, uncorrected for vibrational averages. For example, in 1,2,3-trichlorobenzene (4) $D_{16}/D_{12}$ = 1756.88/598.65 = 2.9347. According to Eq. (2) this same ratio should be obtained by comparing the $C_6$-$H_1$ dipolar relaxation rate with $J_{1212}$ from proton relaxation data (spins are labelled here as in Fig. 2 of Ref. (4)). Using our relaxation data (5) for 1,2,3-trichlorobenzene in $CS_2$ solvent we find $(0.3R_1(C6\text{-}H1)/J_{1212})^{\frac{1}{2}} = 2.92 \pm 0.04$.

If equilibrium internuclear distances are used to compute the interaction strength ratio, the resulting value 3.0957 is too large by 5.4%. Since correlation times depend on the square of the interaction strength, we conclude that neglect of vibrational averaging for 1,2,3-trichlorobenzene would involve errors of ∿11% in determining effective correlation times. Dill and Allerhand (6) pointed out that such errors are further magnified by nonlinear relations between $T_1$ and rotational correlation times for proteins.

Sincerely,

Bob & Gitte

Robert L. Vold and Regitze R. Vold

RL&RRV/sh

References

1. R.L. & R.R. Vold, TAMUNMR Newsletter 231-25 (1977).
2. P. Diehl, S. Sykora, W. Niederburger and E.E. Burnell, J. Magn. Reson. 14, 260 (1974).
3. P. Diehl, TAMUNMR Newsletter 244-11 (1978).
4. P. Diehl and H. Bösiger, J. Magn. Reson. 35, 367 (1979).
5. R.L. Vold, R.R. Vold and D. Canet, J. Chem. Phys. 66, 1202 (1977).
6. K. Dill and A. Allerhand, J. Am. Chem. Soc. 101, 4376 (1979).

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Prof. B.L. Shapiro
Texas A.& M. University
College of Science
College Station, TEXAS 77843

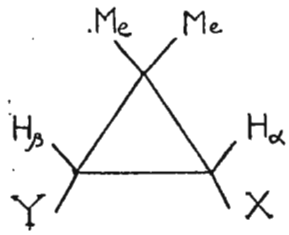
VS. RIF.

NS. RIF. ac/

TITLE: $^1$H n.m.r. of some tetrasubstituted cyclopropanes

Dear Prof. Shapiro,

Recently we had the opportunity to examine the $^1$H n.m.r. spectra of the following tetrasubstituted cyclopropanes:[1)]




$Y = F_3C-CF=CH_\gamma-$

$X = -COOH, -COCl$

Since there are two sites of configurational isomerism, the double bond and the ring, we have the possibility of four isomers for each product. We have been able to determine the spectral parameters of each isomer by means of the n.m.r. spectra of mixtures of different isomeric composition and some decoupling experiments. In fact the n.m.r. spectra of these compounds are fairly easy to evaluate and contain enough information to determine all types of coupling constants directly. Table 1 collects the data obtained in the two solvents $CDCl_3$ and $C_6D_6$.

Proton $H_\beta$ is easily identified since its AB resonance lines are splitted by the adjacent vinyl hydrogen $H_\gamma$. Furtherly the $H_\beta$ (and $H_\gamma$) resonances are broader ($\Delta\nu_{1/2} \sim$ 2-3Hz) than $H_\alpha$ resonance lines ( $\Delta\nu_{1/2} <$ 1Hz) as a consequence of long range coupling with fluorine. The stereochemistry on the cyclopropane ring can be deduced since the cis vicinal hydrogens (with a 0° dihedral angle) will give a large coupling constant whereas the trans vicinal hydrogens (with a 145° dihedral angle) will give a relative small coupling constant. The values observed

8 and 5 Hz are typical for the cyclopropane ring[2]. The stereoisomerism on the double bond can be assigned considering the coupling constant $J_{H_\gamma F}$ which will be large in the trans configuration and small in the cis configuration[3]. The strong magnetic anisotropy associated with the COOH, COCl groups in cyclopropanes, is reflected by the fact that the cis vicinal hydrogens are shifted at lower field than the corresponding trans vicinal hydrogens. Similarly the low field methyl is assigned to the cis position. Particularly interesting are the shifts induced by benzene, which can also be correlated with the stereochemistry. The solvent shift in carbonyl substituted cyclopropanes, $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$, is generally more positive for the hydrogen or methyl in a trans position to the COOH, COCl groups[2,4]. The values found are in agreement with this conclusion.
On the same bases we can explain the low field resonance and the large $\Delta$ effect of the $H_\gamma$ proton when it is in the cisoid and transoid position to the X group respectively. These shifts can be of diagnostic value for the assignment of stereochemistry in similar compounds.

Yours sincereley

E. Santoro G. Bragato F. Corda


References

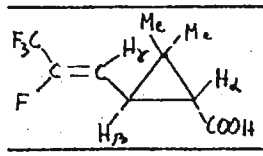
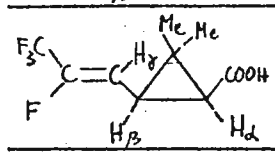
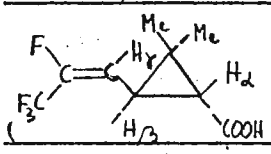
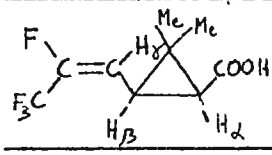
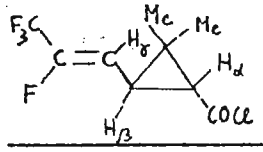
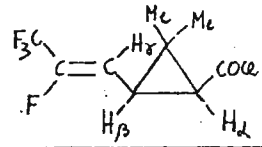
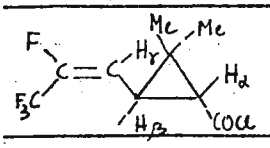
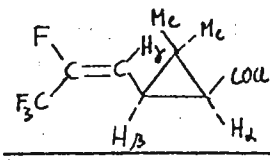
1) Synthesized by the "Centro Ricerche Antiparassitari" DIAG, Montedison, U.K. Patent Appl. G B 2015519A

2) H. Booth in "Progress in NMR spectroscopy" vol. 5, edit. by J.W. Emsley, J. Feeney and L.H. Sutcliffe, Pergamon Press (Oxford 1969), p. 149

3) N.F. Chamberlain "The practice of NMR spectroscopy", Plenum Press (New York 1974), p. 322

4) D.W. Boykin, A.B. Turner and R.E. Lutz "Tetrah." Lett. 9, 817 (1967).

TABLE 1. Chemical shifts* (δ scale) and coupling constants (Hz) of some tetrasubstituted cyclopropanes.

| | $H_\alpha$ | $H_\beta$ | $H_\gamma$ | $Me_{cis}$*** | $Me_{tr}$*** | $J_{H_\alpha H_\beta}$ | $J_{H_\beta H_\gamma}$ | $J_{H_\gamma F}$ | Solv. |
|---|---|---|---|---|---|---|---|---|---|
|  | $1.3_3$ | $2.2_5$ | $4.9_0$ | $1.0_1$ | $0.6_2$ | $5.3$ | $9.7$ | $32.0$ | $C_6D_6$ |
| | $1.6_7$ | $2.3_6$ | $5.2_7$ | $1.3_0$ | $1.1_6$ | $5.3$ | $9.8$ | $32.0$ | $CDCl_3$ |
| | $0.3_4$ | $0.1_1$ | $0.3_7$ | $0.2_9$ | $0.5_4$ | | | | Δ |
|  | $1.5_7$ | $1.8_4$ | $6.0_8$ | $0.9_4$ | $0.7_1$ | $8.3$ | $9.7$ | $33.2$ | $C_6D_6$ |
| | $1.8_9$ | $2.2_0$ | $5.9_9$ | $1.2_5 \leftrightarrow$ | $1.2_3$** | $8.3$ | $9.8$ | $32.9$ | $CDCl_3$ |
| | $0.3_2$ | $0.3_6$ | $-0.0_9$ | $0.3_1$ | $0.5_2$ | | | | Δ |
|  | $1.2_6$ | $2.2_5$ | $4.9_2$ | $1.0_1$ | $0.6_2$ | $5.3$ | $9.0$ | $19.6$ | $C_6D_6$ |
| | $1.5_8$ | $(2.3_6)$ | $5.4_3$ | $1.2_8 \leftrightarrow$ | $1.1_5$** | $5.3$ | $9.7$ | $19.7$ | $CDCl_3$ |
| | $0.3_2$ | $0.1_1$ | $0.5_1$ | $0.2_7$ | $0.5_3$ | | | | Δ |
|  | $1.5_3$ | $1.8_4$ | $6.0_9$ | $0.9_4$ | $0.7_1$ | $8.3$ | $9.0$ | $21.2$ | $C_6D_6$ |
| | $1.8_4$ | $(2.2_0)$ | $6.1_4$ | $1.2_8 \leftrightarrow$ | $1.2_3$** | $8.5$ | $10.0$ | $21.6$ | $CDCl_3$ |
| | $0.3_1$ | $0.3_6$ | $0.0_5$ | $0.3_4$ | $0.5_2$ | | | | Δ |
|  | $1.7_8$ | $2.2_3$ | $4.8_1$ | $0.9_0$ | $0.6_0$ | $5.2$ | $9.0$ | $31.1$ | $C_6D_6$ |
| | $2.2_5$ | $2.3_8$ | $5.2_7$ | $1.3_3 +$ | $1.2_5$ | $5.1$ | $9.3$ | $31.1$ | $CDCl_3$ |
| | $0.4_7$ | $0.1_5$ | $0.4_5$ | $\sim 0.4_3$ | $\sim 0.6_5$ | | | | Δ |
|  | $2.0_1$ | $1.8_8$ | $5.7_3$ | $0.8_1$ | $0.6_7$ | $8.0$ | $9.0$ | $32.5$ | $C_6D_6$ |
| | $(2.3_8+2.5_8)$ | | $5.7_7$ | $1.3_3+1.2_5$ | | – | $8.6$ | $32.3$ | $CDCl_3$ |
| | — | — | $0.0_4$ | $\sim 0.5_2$ | $\sim 0.5_8$ | | | | Δ |
|  | $1.7_0$ | $2.2_3$ | $4.8_3$ | $0.9_0$ | $0.6_0$ | $5.2$ | $8.0$ | $19.6$ | $C_6D_6$ |
| | $2.1_8$ | $(2.3_8)$ | $5.4_2$ | $1.3_3+1.2_5$ | | $5.1$ | $8.6$ | $19.0$ | $CDCl_3$ |
| | $0.4_8$ | $0.1$ | $0.5_9$ | $\sim 0.4$ | $\sim 0.7$ | | | | Δ |
|  | $1.9_9$ | $(1.8_8)$ | $5.7_2$ | $0.8_1$ | $0.6_7$ | $8.0$ | $8.0$ | $20.0$ | $C_6D_6$ |
| | $(2.3_8+2.5_8)$ | | $5.8_8$ | $1.3_3+1.2_5$ | | – | $8.5$ | $20.2$ | $CDCl_3$ |
| | — | — | $0.1_6$ | $\sim 0.4$ | $\sim 0.6$ | | | | Δ |

(*) The chemical shifts are slightly concentration dependent. The data reported are obtained at a concentration of about 10%.

(**) The assignment con be reversed

(***) Cis, trans to the COOH, COCl groups.

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BIOLOGICAL SCIENCES RESEARCH CENTER

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

Dear Barry:

Re: Trimethylphosphite Stability

The warning from S. L. Patt[1] about purity of trimethylphosphite used as a phosphorus sensitivity standard for $^{31}P$ NMR is appropriate. The trimethylphosphite degrades into several components.

$$(CH_3O)_2\overset{O}{P}H, \quad (CH_3O)_3\overset{O}{P}, \quad (CH_3O)_2\overset{O}{P}CH_3, \quad (CH_3O)_2\overset{O}{P}OH, \quad \text{etc.}$$

Our experience shows that the best storage conditions are in Pyrex glass bottles or Erlenmeyer flasks with glass stoppers, well sealed to prevent evaporation losses. However, even under the best circumstances, the product can unexplainedly begin to generate the above compounds. These impurities are detected at relatively low levels ($\approx$ 1%) by $^1H$ NMR or infrared spectroscopy.

Please credit this contribution to Dr. C. A. Reilly's subscription.

Sincerely,

SHELL DEVELOPMENT COMPANY

G E Pollard

G. E. Pollard
Spectroscopist

1) S. L. Patt, TAMU NMR Newsletter No. 254-38.

UNIVERSITY OF BRADFORD

Bradford West Yorkshire BD7 1DP England
Telephone Bradford 33466 (STD Code 0274)
Telex 51309 UNIBFD G

School of Studies in Chemistry

Please quote ref

7th December, 1979.

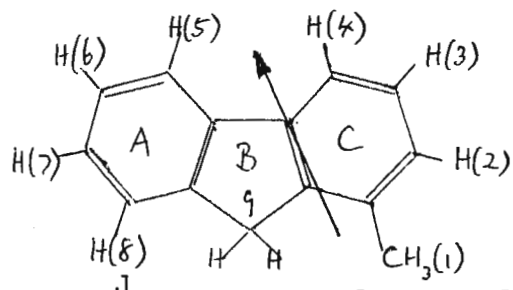
Professor B.L. Shapiro, TAMUNMR Newsletter,
Department of Chemistry, Texas A & M University,
College Station,
TEXAS 77843.
U.S.A.

Dear Professor Shapiro,

H-H Couplings and $^1$H Solvent Shifts in Fluorenes

Overlapping ABCD and ABC spin systems of the aromatic $^1$H resonances in the 220 MHz $^1$H NMR spectra of 1-methylfluorene(I) in $CS_2$ and $CDCl_3$ solutions have been analysed by J.A.G.D. (now at School of Home and Institutional Studies, The Polytechnic, Leeds LS1 38E, England) with the aid of $CH_3$- and $CH_2$-decoupled spectra. $^1$H-$^1$H ortho-coupling constants in rings A and B

I




differ very little and $^J$H...H are mostly very close to the corresponding values (Table 1) in fluorene (II)[1] and fluorene-9-one (III)[2]. However $^1$H shifts in the fluorene nucleus change appreciably with nature, concentration and temperature of solvent and with substitution; shifts for chloroform solutions of I, II, and III are compared in Table 2. Table 2 also shows that the changes in $^1$H shift $\Delta\delta$, when the solvent is changed from $CDCl_3$ to $CS_2$, are in the sequence H(5)∿H(4)>H(2)∿H(3)>H(8)∿H(6)∿H(7)>$CH_2$>>$CH_3$. In each solvent, dilution shifts are biggest (apart from the $CHCl_3$ in $CDCl_3$ solution) for $CH_3$(1) and next biggest for H(8) and $CH_2$(9), i.e. all on one side of the molecule. Possibly an enhanced chloroform-induced molecular dipole (approximately in the direction of the arrow) influences the sequence of solvent shifts in I, while in chloroform solution there may be some loose solute-solute association between pairs of perpendicular molecules, in which the $CH_2$ of one approaches ring B of the other.

Table 1. $^{J}H$, H in I, II, and III.

| J/Hz | 1,2 | 1,3 | 1,4 | 2,3 | 6,7 | 2,4 | 5,7 | 3,4 | 5,6 | 8,$CH_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 7.7 | 1.1 | 0.7 | 7.5 | 7.4 | 1.0 | 1.1 | 7.6 | 7.6 | 0.8 |
| II[1] | 7.6 | 1.0 | 0.8 | 7.6 | | 1.1 | | 7.5 | | 0.9 |
| III[2] | 7.4 | 1.1 | 0.7 | 7.5 | | 1.0 | | 7.5 | | - |

Table 2. $^{1}H$ shifts, δ/p.p.m., for chloroform solutions

| δ/p.p.m. | $CH_3$(1) | H(2) | H(3) | H(4) | H(5) | H(6) | H(7) | H(8) | $CH_2$(9) |
|---|---|---|---|---|---|---|---|---|---|
| I | - | 7.13 | 7.31 | 7.64 | 7.78 | 7.37 | 7.30 | 7.56 | 3.80 |
| II[1] | 7.53 | 7.29 | 7.37 | 7.79 | 7.79 | 7.37 | 7.29 | 7.53 | 3.91 |
| III[2] | 7.67 | 7.30 | 7.49 | 7.53 | 7.53 | 7.49 | 7.30 | 7.67 | - |
| δΔ for I ($CDCl_3$ -$CS_2$) | 0.04 | 0.15 | 0.15 | 0.19 | 0.19 | 0.14 | 0.14 | 0.14 | 0.12 |

Yours sincerely,

John Drake — J.A.G. Drake

Denny Jones — D.W. Jones

Hooshang Pakdel — H. Pakdel

1. K.D. Bartle and D.W. Jones, J. Mol.Structure, 1, 131 (1967)

2. J.A.G. Drake and D.W. Jones, Spectrochim Acta A, in the press.

256-13

University of Wisconsin Madison

CENTER FOR HEALTH SCIENCES
School of Pharmacy
425 North Charter Street
Madison, Wisconsin 53706
Telephone: 608/262-1416

December 5, 1979

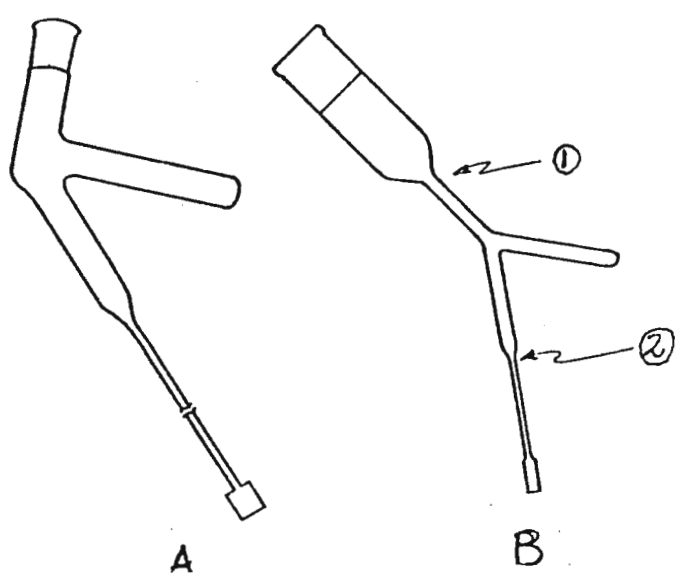
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Dear Barry:

Degassing Samples For Cylindrical Insert Tubes

In many cases $T_1$ and NOE measurements require carefully degassed samples. I have found that multiple freeze-pump-thaw cycles at high vacuum give the best results. Single coil pulsed instruments require that the samples for $T_1$ measurements, be constrained to the coil space and that condition is best met by using the various cylindrical or spherical sample containers that can be inserted into a standard tube and positioned within the receiver coil space. It is impossible to degass aqueous solutions contained in these tubes by the freeze-thaw method, thus I have devised an indirect technique. Shown below are two drawings of two devices that accomplish the desired degassing procedure nicely.

Drawing A corresponds to the device used for 10 mm inserts. The 10 mm insert is fused to one leg, the sample is placed in the other and attachment to a high vacuum manifold is made via the standard taper joint that also serves as a bearing. When the sample has been degassed in the usual way, the thawed sample (still under vacuum) is simply poured into the insert by rotating the apparatus on the bearing. The neck of the insert is then fused at an appropriate spot, sealing the sample and removing the insert. Drawing B corresponds to the device used for 5 mm inserts. In this case, after the degassing procedure and while the sample is still frozen and under vacuum, the smaller diameter tube is fused at 1 , the sample is thawed and poured into the insert and the neck of the insert is fused at 2 . The smaller scale device is more difficult to make and use but both work very well once the techniques have been mastered.




Sincerely yours,

Phil

Phillip A. Hart, Professor

**DÉPARTEMENT DE PHYSIQUE DE LA MATIÈRE CONDENSÉE**

32, boulevard d'Yvoy CH-1211 GENÈVE 4

UNIVERSITÉ DE GENÈVE
SECTION DE PHYSIQUE
TÉLÉPHONE (022) 21 93 55

V/RÉF.

N/RÉF. GJB/ek

Professeur B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science
College Station Texas
77843 U.S.A.

Recent and Forthcoming Publications; Joint ISMAR - Ampere Int. Conf. on Magnetic Resonance, Delft (Netherlands), 25-30 August 1980

Genève, le 17 décembre 1979

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 6 décembre 1979.

Notre groupe a continué de s'intéresser à l'emploi du magnétisme nucléaire dans le champ magnétique terrestre en vue du diagnostic médical.
Nos efforts ont porté sur les temps de relaxation $T_1$ et $T_2$ dans des fluides physiologiques humains, animaux ainsi que sur l'identification in situ de fluides physiologiques sains ou pathologiques

Publications récentes : (ou en cours d'impression)
(on peut obtenir tirés à part ou preprints)

1) "Etude de phénomènes biologiques dynamiques par relaxation nucléaire dans le champ terrestre"

(avec E. HILTBRAND, B. BORCARD et P. MAGNIN)

ABSTRACT : The short time necessary to determine $T_2$ of a fluid by the HP 9845A computer makes it possible to follow the evolution of such a fluid. We can follow :
- in vitro : the coagulation of the milk
- in situ : the increase of the temperature in the stomach of drunken cold water.

2) "Identification in situ de fluides physiologiques humains par mesure des temps de relaxation"

(avec P. MAGNIN, B. BORCARD et E. HILTBRAND)

ABSTRACT : For the in situ identification of human physiological fluids (or drunk fluids) it is necessary to distinguish the signal of the investigated fluid from that of other present tissues. A method has been divised by

means of which such a discrimination is automatically done by a computer (HP 9845A). The method has been applied to the study of urin in the bladder.

(en cours de publication - Helvetica Physica Acta (1979))

3) "Diagnosis of the presence of meconium in amniotic fluid by proton spin relaxation dispersion"

(avec B. BORCARD, E. HILTBRAND, P. MAGNIN, V. GRAF et F. Noack)

ABSTRACT : Dispersion curves of the longitudinal relaxation $T_1$ of protons in healthy amniotic fluid and in a meconium solution are distinct at low Larmor frequencies ($\nu_o$ < 100 kHz). We are thus able to distinguish these fluids by $T_1$ measurements in this range.

(soumis pour publication:
Français : Comptes Rendus de l'Académie des Sciences
Anglais : Lettres du Journal of Physics)

Mises au point d'ensemble en cours de publication:

1) "Foundations and preliminary results on medical diagnosis by nuclear magnetism"

Chapter in vol. 49 (1979) of the series "Advances in electronics and electron physics". - Academic Press (New York)

2) "Nuclear magnetism of liquid systems in the earth field range"

ABSTRACT : In this paper we review the used techniques and the main results obtained by nuclear magnetism in the low field range. After a brief survey of the characteristics of nuclear magnetism in low fields, the experimental techniques are described: obtaining constant and homogeneous fields, resonance experiments and pulse techniques (free precession and spin echoes). The most important results include: studies of line-width and shape in the liquid state, some features on the interaction between electromagnetic field and nuclear moments (spin echoes, non-resonant excitation) and a new possible investigation of microscopic structure and dynamics in the liguid state (indirect spin-spin interaction and dispersion of relaxation times).

(Physics Reports)

Prochains meeting du "Groupement Ampère" :

Joint ISMAR - Ampère Int. Conf. on Magnetic Resonance

XXI Ampere Congress

Delft (Netherlands)
25 - 30 August 1980

c/o K.l.v.l., 23 Prinsessegracht. The Hague

Adresse pour information :

Prof. J. Smidt
Lab. voor Technische Natuurkunde
Lorentzweg - 1 DELFT
The Netherlands

Avec mes sentiments très cordiaux

Prof. G.-J. BENE

256-17

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Please address all correspondence to the Director

Our ref. 600/400/94/1 Your ref.

Prof. B.L. Shapiro
Texas A & M University
COLLEGE STATION
Texas 77843
USA

10. DEC. 1979

Dear Prof. Shapiro

ASSIGNMENT OF $^{13}C$-$^{13}C$ COUPLINGS WITH DANTE

Like others we have had fun with the selective excitation generated by Morris and Freeman's DANTE (Devilish AcroNym Transcending Explanation) and since we have a considerable commitment to the study of $^{13}C$ labelling of metabolites it seemed valuable to see if the method could be used to unravel $^{13}C$-$^{13}C$ couplings in PND spectra of doubly labelled species. We are not equipped with an additional frequency synthesiser to do this in the rare event that the coupled unit cannot be assigned from the magnitude of the coupling.

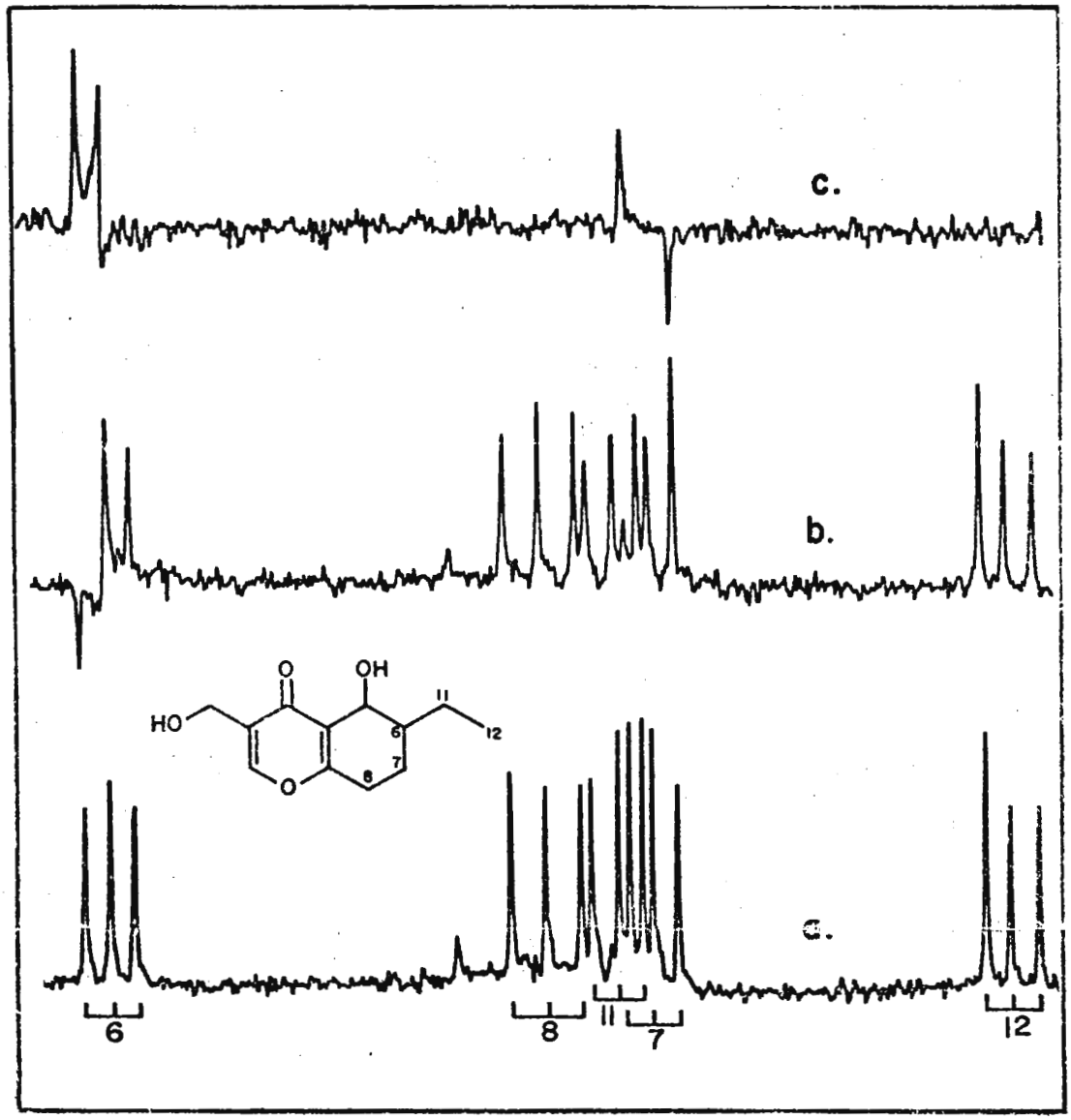
Diplosporin derived for [1,2 $^{13}C$]acetate gave the PND spectrum shown in Fig. a. Aiming the DANTE excitation at the lowest field line of $C_6$ with a cumulative pulse angle of $\pi$ and following up with a non-selective sampling pulse of $\pi/6$ gave spectrum fig. b. A clearer picture of the intensity changes in the coupled $C_7$ is shown in Fig. c, where alternate transients with and without DANTE have been subtracted from and added to memory. Some may prefer Fig. c inverted but the computer felt that the difference was arbitrary.

As you may know Klaus Pachler is now with E. Merck, Postfach 4119, Darmstadt, W. Germany, so would you credit this to Dr Wessels account.

Yours sincerely

A A Chalmers

A.A. Chalmers
CHIEF RESEARCH OFFICER


c.
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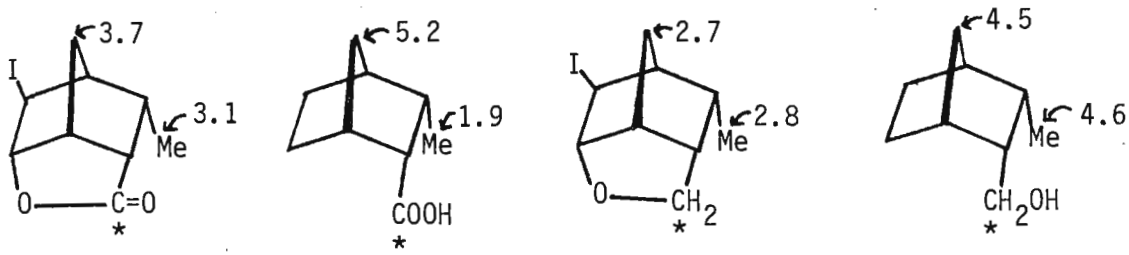
North Texas State University
Denton, Texas 76203
Department of Chemistry

December 15, 1979

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

Dear Barry:

One of the questions raised in attempting to use $^{13}C$-$^{13}C$ coupling constants in conformational analysis is: What effect does the orientation of a terminal substituent have on the value of J(CC)? The compounds below were studied in an attempt to answer the question.



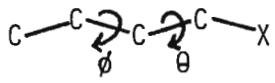

1 2 3 4

(The asterisk designates the $^{13}C$ label; the numbers are the couplings (in Hz) to the labeled carbon)

For the cis couplings, comparison of the couplings to the methyl group in 1 and 2 indicates that when the plane of the carboxyl group is rotated orthogonal to the plane of the coupling C-C-C-C linkage, the coupling increases; comparison of the couplings to the methyl group in 3 and 4 indicates that as the -OH substituent is rotated orthogonal to the C-C-C-C linkage, the coupling decreases.

For the trans couplings, coupling to the 7 position in 1 and 2 suggests the coupling decreases when the carboxyl group is rotated coplanar with the C-C-C-C linkage; the corresponding values in 3 and 4 again suggest the coupling decreases when the -OH group is rotated coplanar (and cisoid) with the C-C-C-C group.

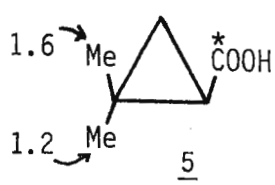
The above observations are consistent with INDO-FPT calculations. For the group



where ø and θ are respectively the dihedral angles of the C-C-C-C group and the C-C-C-X group (X = -OH for the alcohol, =O for the carboxylic acid), the calculated values are:

| ø,° | θ,° | J(alcohol) | J(acid) |
|---|---|---|---|
| 0 | 30 | 4.12 | 1.72 |
| 0 | 90 | 6.40 | 3.14 |
| 0 | 180 | 6.70 | 1.93 |
| 180 | 0 | 4.06 | 5.70 |
| 180 | 60 | 4.38 | |
| 180 | 90 | 4.88 | 5.36 |
| 180 | 120 | 5.28 | |
| 180 | 180 | 5.02 | 5.80 |

The cis couplings in 2 and 4 parallel the analogous couplings in the cyclopropane compounds 5 and 6, respectively. It is difficult, however, to arrive at other synthetically possible compounds with θ ≈ 90°. Any ideas?

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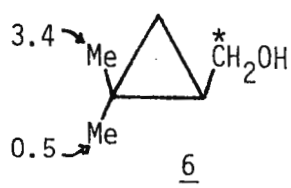



6

Many thanks are due to Mike Barfield and Steve Walter of the University of Arizona for obtaining the C-13 nmr spectra of 3-6.

Sincerely,

J. L. Marshall

Title: Effect of the orientation of a terminal substituent on vicinal C-13 C-13 couplings

256-21

VRIJE UNIVERSITEIT

VAKGROEP FYSISCHE CHEMIE
SUBFACULTEIT DER SCHEIKUNDE

1081 hv amsterdam
de boelelaan 1083
telefoon 020 - 548

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

| uw kenmerk | uw brief van | ons kenmerk | datum | bijlage(n) |
|---|---|---|---|---|
| | | JABL/CM/IS | December 17, 1979 | |

onderwerp

TITLE: Solvent Effect on the Anisotrophy in the Diamagnetic Susceptibility

Dear professor Shapiro,

Last year we reported a new alignment effect in high resolution NMR spectra (1). It results from the interaction of a strong magnetic field with the magnetic moment it induces in magnetically anisotropic molecules. The partial orientation was detected via the quadrupolar line splittings in $^2H$ spectra of aromatic molecules (2,3).

From the line splittings the value for the anisotropy in the magnetic susceptibility may be deduced and we performed experiments in various solvents (diethylether, carbondisulfide, n-butane) and at different concentrations ($10^{-1}$ - $10^{-3}$ - molar) in order to study a possible solvent effect upon this quantity. No effects have been detected up to recently (4).

Last month however we were enabled to do some experiments on the Bruker WM 500 spectrometer of Bruker Analytische Messtechnik GmbH in Karlsruhe, operating at 11.7 Tesla.

The main object of this study was to check the magnetic field dependence of the line splittings which is theoretically predicted to be quadratic. The results were satisfactorily conform this prediction.

With respect to the solvent effect upon the susceptibility anisotropy a new feature came about in the 76.77 Mhz $^2H$ spectrum of nitrobenzene-$d_5$. In the spectrum of the pure compound splittings were detected of 1.2 Hz (para) and 0.9 Hz (ortho, meta). In a solution of 30% nitrobenzene in ether the para splitting was reduced to 0,7 Hz whereas no splittings could be resolved in the ortho- and meta-signals.

It is our intention to do a more systematic study of this rather drastic effect in the near future.

Sincerely,

Joost A.B. Lohman
Bruker Spectrospin N.V.
P.O. Box 88
1530 AB WORMER
The Netherlands

C. MacLean
Chemical Laboratory
Free University
De Boelelaan 1083
1081 HV AMSTERDAM
The Netherlands

REFERENCES

(1) J.A.B. Lohman and C. MacLean, TAMU NMR newsletter, 245, 3 (1979)

(2) J.A.B. Lohman and C. MacLean, Chem. Phys., 35, 269 (1978)

(3) J.A.B. Lohman and C. MacLean, Chem. Phys. Letters 58, 483 (1978)

(4) J.A.B. Lohman and C. MacLean, Mol. Phys., 38, 1255 (1979)

**Winfried Boenigk and**
Prof. Dr. Gerhard Hägele
Institut für Anorganische
und Strukturchemie

4000 Düsseldorf, 17.12.79
Universitätsstraße 1
Tel. 0211-311-2288

to
Prof. B. Shapiro
Dept. of Chemistry
Texas A&M University
College Station
Texas 77843 U. S. A.

TITLE: Programs CYMTRY, CYBER, and CYMPLOT for the Analysis of NMR Spectra

Dear Professor Shapiro,

in TAMU NMR Newsletter No. 248 we reported about our ALL- FORTRAN version of SYMTRY, a computer program which allows the calculation of nmr spectra of symmetric molecules based on spin systems consisting of single spins I= 1/2. We finished very recently our studies on composite particles and here we wish to present the results. We developed a program CYMTRY which takes into account general symmetry for chemical equivalence and in addition hereto magnetical equivalence in composite particles. Two versions are tested till now. A 60 bit word CYBER adapted program tackles up to 10 composite particles with total spins up to 15/2. Another version dealing with 48 bit words up to 7 composite particles and total spins up to 15/2 is running on a TELEFUNKEN computer. The latter program includes CALCOMP plotting facilities and is named CYMPLOT. Our programs were tested in a systematic manner. One example applying $C_3$- symmetry is given with the calculation of an $[AX_3]_3$ system, using Acrivos' early mesitylene studies given in Mol. Phys. 5,1 (1962). Theory and programming of CYMTRY and CYMPLOT closely follow the techniques we described in our paper on SYMTRY, J. Magn. Res. 26, 505 (1977). The spin-functions are conveniently stored as integer variables in order to apply symmetry operations in form of bit- manipulations. This method guarantees efficiency and speed in calculations. Further details will be given in near future.

Best wishes for a Happy New Year

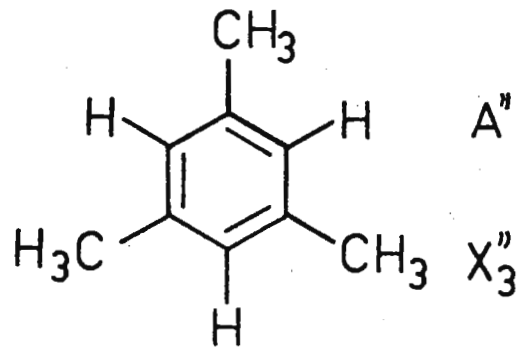
Winfried Boenigk

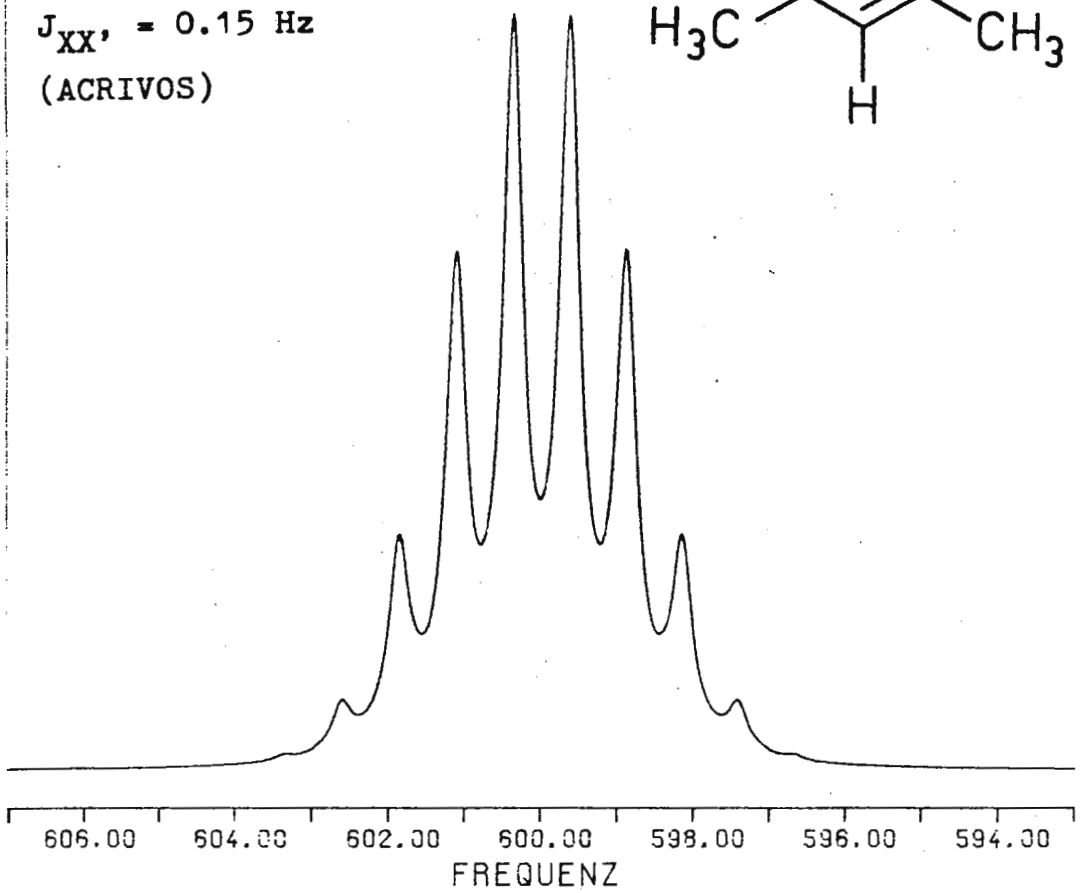
Winfried Boenigk

G Hägele

Gerhard Hägele

$J_{AA'}$ = 2.20 Hz
$J_{AX}$ = 0.89 Hz
$J_{AX'}$ = 0.45 Hz
$J_{XX'}$ = 0.15 Hz
(ACRIVOS)




$[AX_3]_3$ A-Part

$X_3$

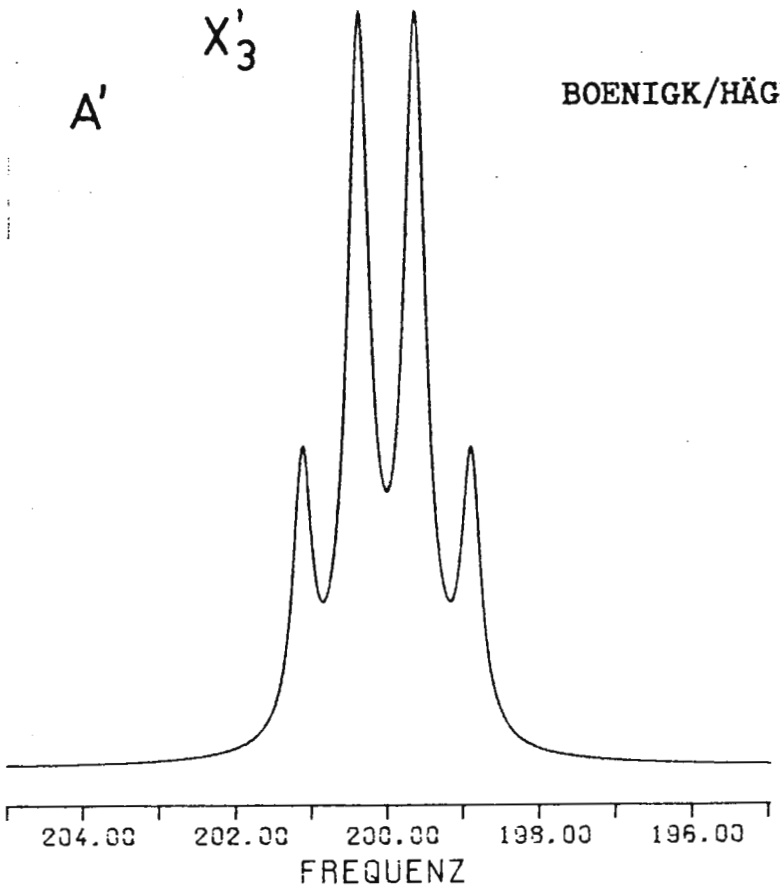
A

A'

$X'_3$

$\delta_A$ = 6.747 ppm
$\delta_X$ = 2.232 ppm

BOENIGK/HÄGELE




$[AX_3]_3$ X-Part

256-25

MRC
Medical Research Council

National Institute for Medical Research
The Ridgeway, Mill Hill
London NW7 1AA

telegrams Natinmed LondonNW7
telex 922666(MRCNAT G)
telephone 01-959 3666

reference

21st November 1979.

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

Dear Barry,

Photo-CIDNP studies of surface accessibility of aromatic residues in dihydrofolate reductase and its complexes with ligands

In collaboration with Robert Kaptein (Groningen University) we have recently carried out some photo CIDNP experiments on complexes of dihydrofolate reductase. Kaptein[1,2] has shown that histidine, tyrosine or tryptophan residues which are on the surface of a protein and accessible to a flavin dye in the solution can be detected in such experiments. A brief illumination with a laser excites the dye to its triplet state: the excited dye then reacts reversibly with any accessible histidine, tyrosine or tryptophan residue leading to transient radical formation and subsequent polarisation of some of their nuclei resulting in large changes in signal intensity. These changes can best be observed by examining difference spectra between a normal spectrum ('dark' spectrum) and one obtained immediately after illumination with the laser ('light' spectrum). In the aromatic region of these difference spectra an accessible histidine gives absorption lines for the C2 and C4 protons, a tyrosine gives emission lines for the C3',C5' protons and a tryptophan gives absorption lines for the C2, C4 and C6 protons.

In photo CIDNP experiments on L.casei dihydrofolate reductase (in the presence of 0.2 mM lumiflavin dye) we observe that four of the seven histidines and at least one of the four tryptophan residues are accessible to the dye. One of the five tyrosines is slightly accessible. Of the accessible histidine residues, one (His F) becomes inaccessible on the binding of p-aminobenzoyl glutamate (PABG) or ligands such as folate and methotrexate which contain the PABG moiety: His F has been assigned to His 28 which is known to bind directly to the PABG γ-carboxylate anion (Matthews[3], 1978). Another histidine, (His 64) interacts directly with the adenine ring of $NADP^+$ and this histidine (His C = His 64) becomes inaccessible in the complex of the enzyme with $NADP^+$. This is shown in the CIDNP spectrum, given in Figure 1a: the positions of the histidine C2 signals in the dark spectrum are also indicated. Addition of trimethoprim (Figure 1b) or folate (Figure 1c) to the enzyme.$NADP^+$ complex increases the accessibility of His A. In addition, the binding of several ligands, notably trimethoprim, increases the accessibility of a tryptophan residue. Such increases in accessibility provide clear evidence for ligand induced conformational changes in dihydrofolate reductase.

All the experiments were carried out on a Bruker WH360 spectrometer in Dr. Kaptein's laboratory at the University of Groningen.

Yours sincerely,

Jim Feeney  Gordon Roberts

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# NMR ≡ Bruker

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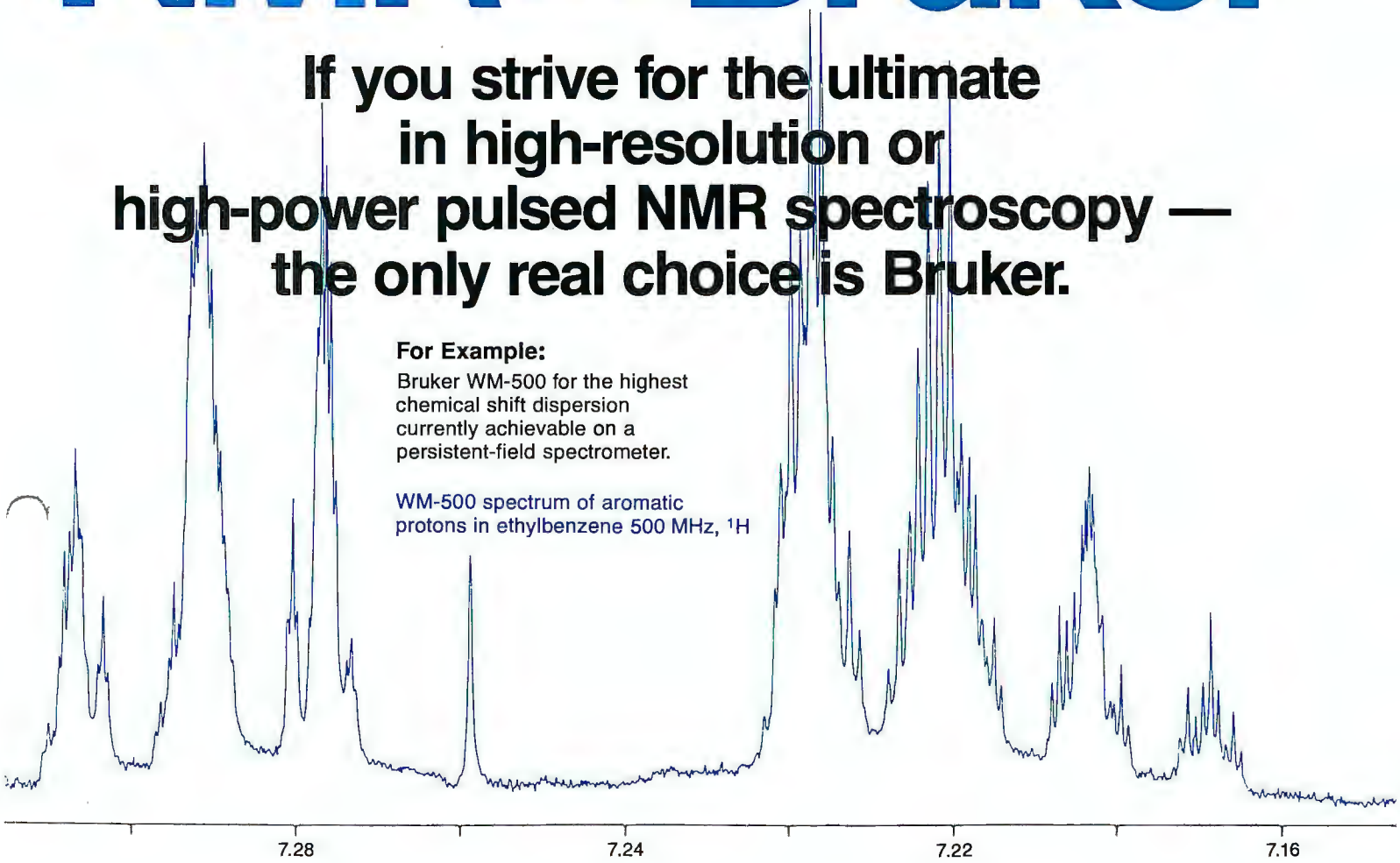


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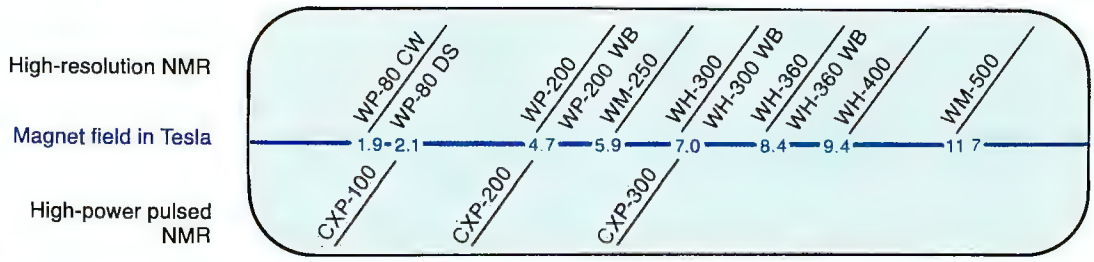


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(415) 941-3804

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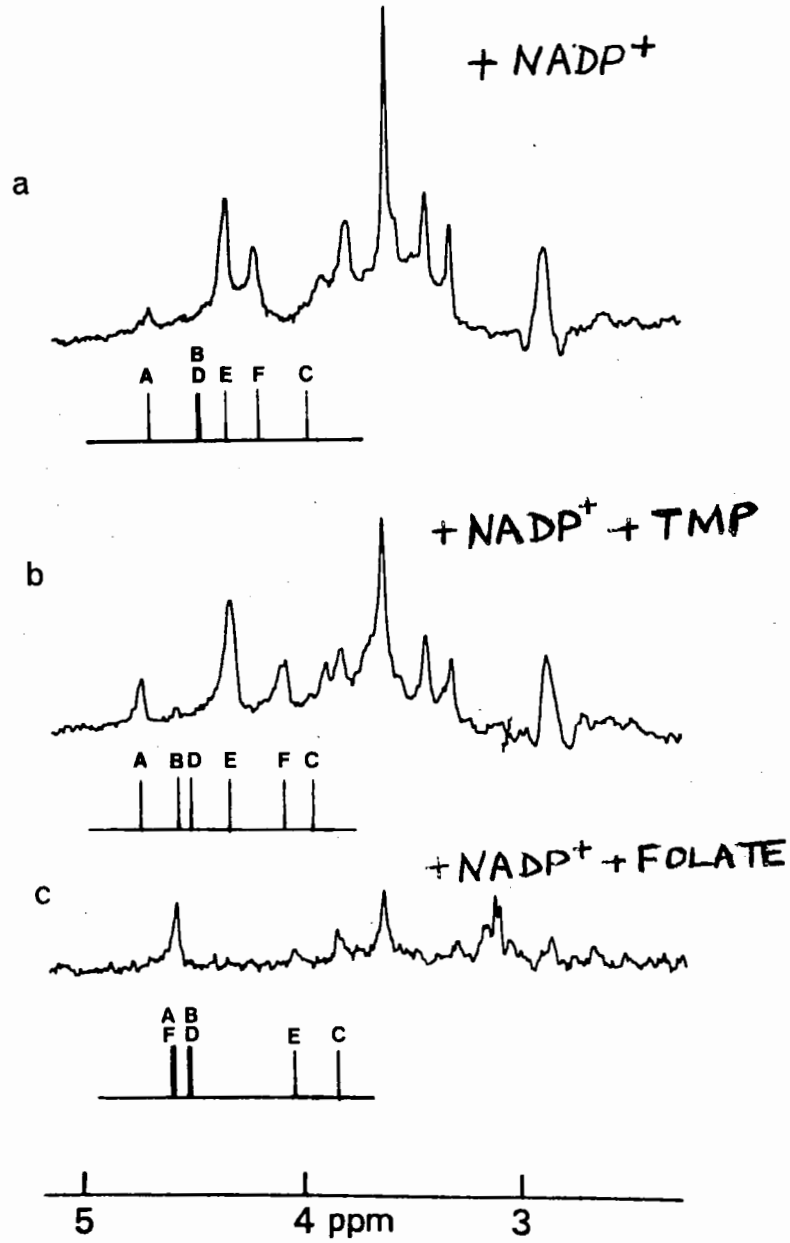
(301) 762-4440

1603 Darwin Court, Wheaton, IL 60187
(312) 668-4441

1 Kaptein, R. (1978) 'NMR Spectroscopy in Molecular Biology' p.211 Editor, B. Pullman. D. Reidel Publishing Company.

2 Kaptein, R., Dijkstra, K., Muller, F., Van Schagen, C.G., and Visser, A.J.W.S. (1978) J. Mag. Res., 31, 171.

3 Matthews, D.A. (1979) Biochemistry 18, 1602.



Gesamthochschule Siegen
Fachbereich 8, Organische Chemie II
Prof. Dr. H. Günther

5900 Siegen 21, den Dec. 18, 1979
Adolf-Reichwein-Straße
Fernruf 0271/740 – 1
Nebenstelle 4390, 4400

Gesamthochschule Siegen, Postfach 21 02 09, 5900 Siegen 21

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

WH-400 Experience - Cycloheptatriene Carboxaldehyde

Dear Barry,

after nearly 5 months of practical experience with our new WH-400 spectrometer we find little to critisize. The sensitivity of the instrument is marvellous, rendering $^{1}$H-NMR on mg- or less samples a matter of minutes, even including $^{13}$C-satellite spectra. Similarly, $^{13}$C usually requires not more than 200-500 transients for sufficient S/N ratio. The line shape is very satisfactory, halfwidth 0.06-0.08 Hz both for $^{1}$H and $^{13}$C and fairly narrow at the bottom. The low temperature unit works fine, and as a first result we unravelled the dynamic behaviour of cycloheptatriene carboxaldehyde (see fig. 1; Angew. Chem., in print). Of course, the determination of the correct sample temperature is still difficult, and from the various approaches suggested we used the determination of the freezing and melting points of a number of solvents.

As a warning, however, we would like to point out that extensive low-temperature work, especially with short cooling and warming-up periods, might damage the probehead. Apparently the correct adjustment of the r.f. coils is affected. As a result, the resolution is greatly diminished. Our first probehead, therefore, has recently been replaced.

Helium consumption is low with 20-25 l every 3-4 weeks. Since we still lack the electronic helium-level meter, a more correct number will have to be determined later.

Season's greetings and best wishes for 1980!

Sincerely yours,

Horst Günther  H. Fischer

H. Günther  H. Fischer

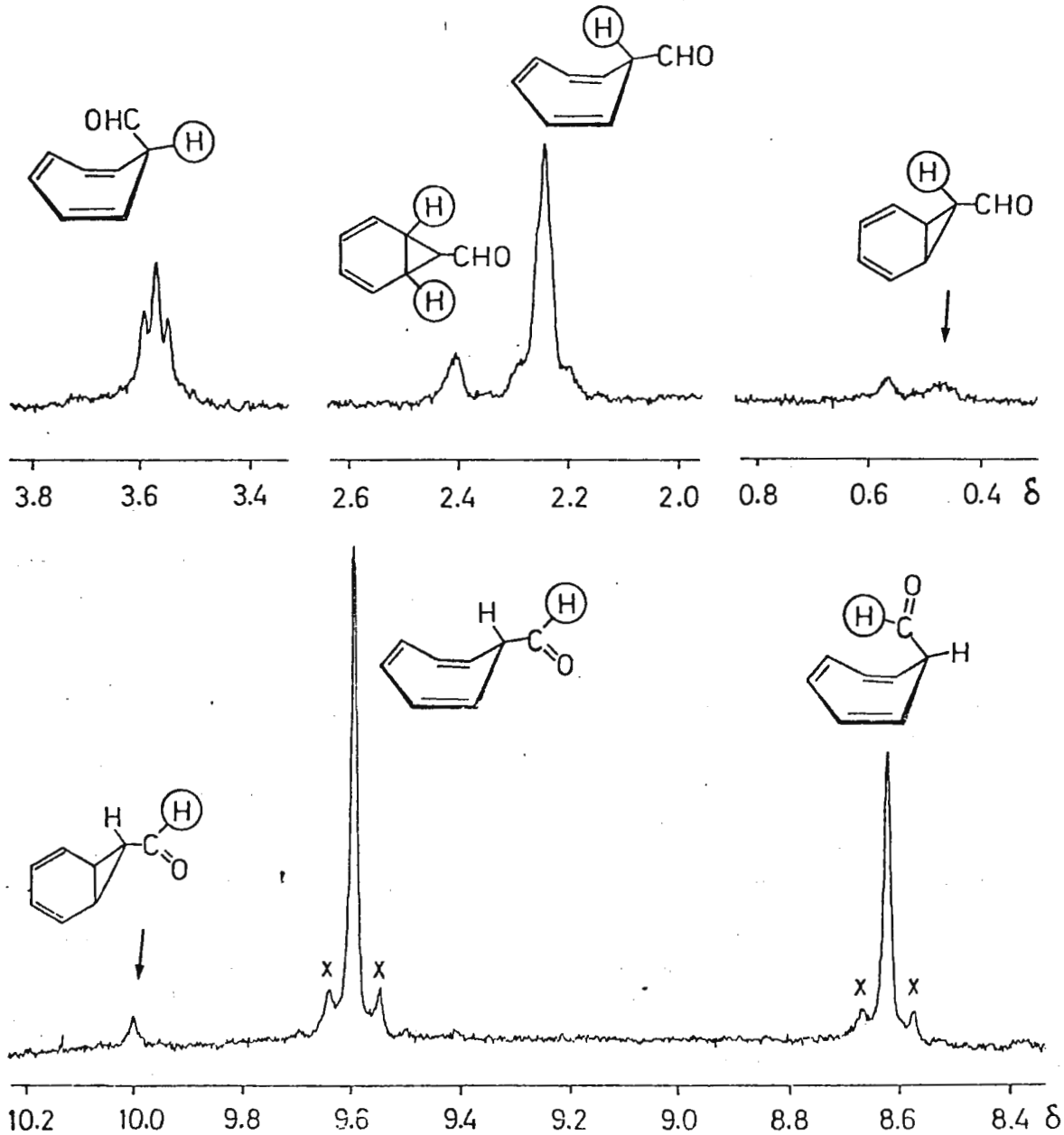



*Fig. 1* $^{1}H$*-n.m.r. spectrum of cycloheptatriene carboxaldehyde at -152 °C in* $CD_2Cl_2$*/vinylchloride (1:2) at 400.16 MHz; δ-values in ppm refer to TMS; x rotational side bands. At this temperature both the norcaradiene-cycloheptatriene valence tautomerism and the ring inversion of the triene aldehyde are slow on the n.m.r. time scale. Three isomers can be identified: triene exo- and endo-aldehyde and norcaradiene exo-aldehyde. The valence tautomerism is frozen out at -100 °C. Below this temperature, new line broadening is observed for the triene signals until finally the signals for the two conformational isomers endo- and exo-triene aldehyde emerge.*

The University of Alabama in Birmingham
Comprehensive Cancer Center
205/934-5696

Dec. 19,1979

Barry Shapiro
Texas A and M University
College Station TX 77843

Lanthanide Complexes Of Bleomycin

Dear Barry,

In the course of monitoring the interactions of bleomycin, which is an antitumor agent, with the trivalent lanthanide ions in aqueous solution, we stumbled across an interesting phenomenon. We discovered that while the $Pr^{3+}$-bleomycin complex was in fast exchange on the proton NMR chemical shift time scale, the $Yb^{3+}$ complex was in slow exchange. We subsequently have measured the formation constants for a number of lanthanide complexes of the antibiotic (see figure 1 for its structure). These constants were determined from fluorescence experiments involving $Tb^{3+}$. The formation constants vary with the ionic radius of the metal ion as shown in figure 2. Note that there is ca three orders of magnitude difference between the formation constants obtained for $Pr^{3+}$ and for $Yb^{3+}$. Since the rate constant for metal ligation is very nearly equal down the series for a number of ligands, we suggest that the lifetimes of the bleomycin complexes vary dramatically down the series. If this explanation is correct, the $Yb^{3+}$ complex has a lifetime that is around $10^3$ times longer than the $Pr^{3+}$ complex.

I add parenthetically that the proton NMR experiments were performed on our Bruker WH-400 spectrometer. We are routinely obtaining ca 110:1 s/n for 0.1% ethylbenzene for protons (5mm) and ca 110:1 on the ASTM standard sample for $^{13}C$ (10 mm). Proton resolution as measured on 10% ODCB is routinely about 0.1 Hz.

Sincerely yours,

Bob

Robert Lenkinski

Comprehensive Cancer Center

Structure of bleomycin

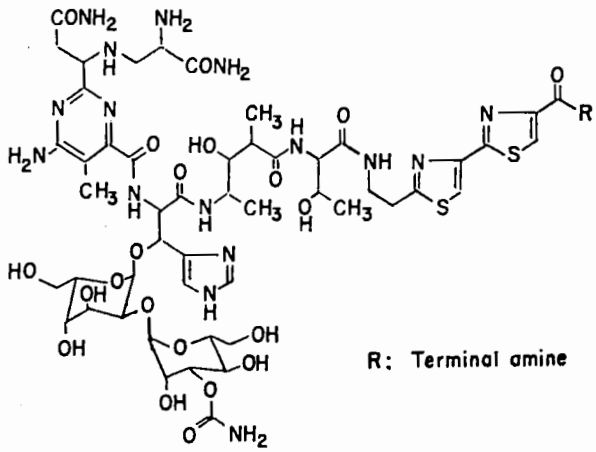
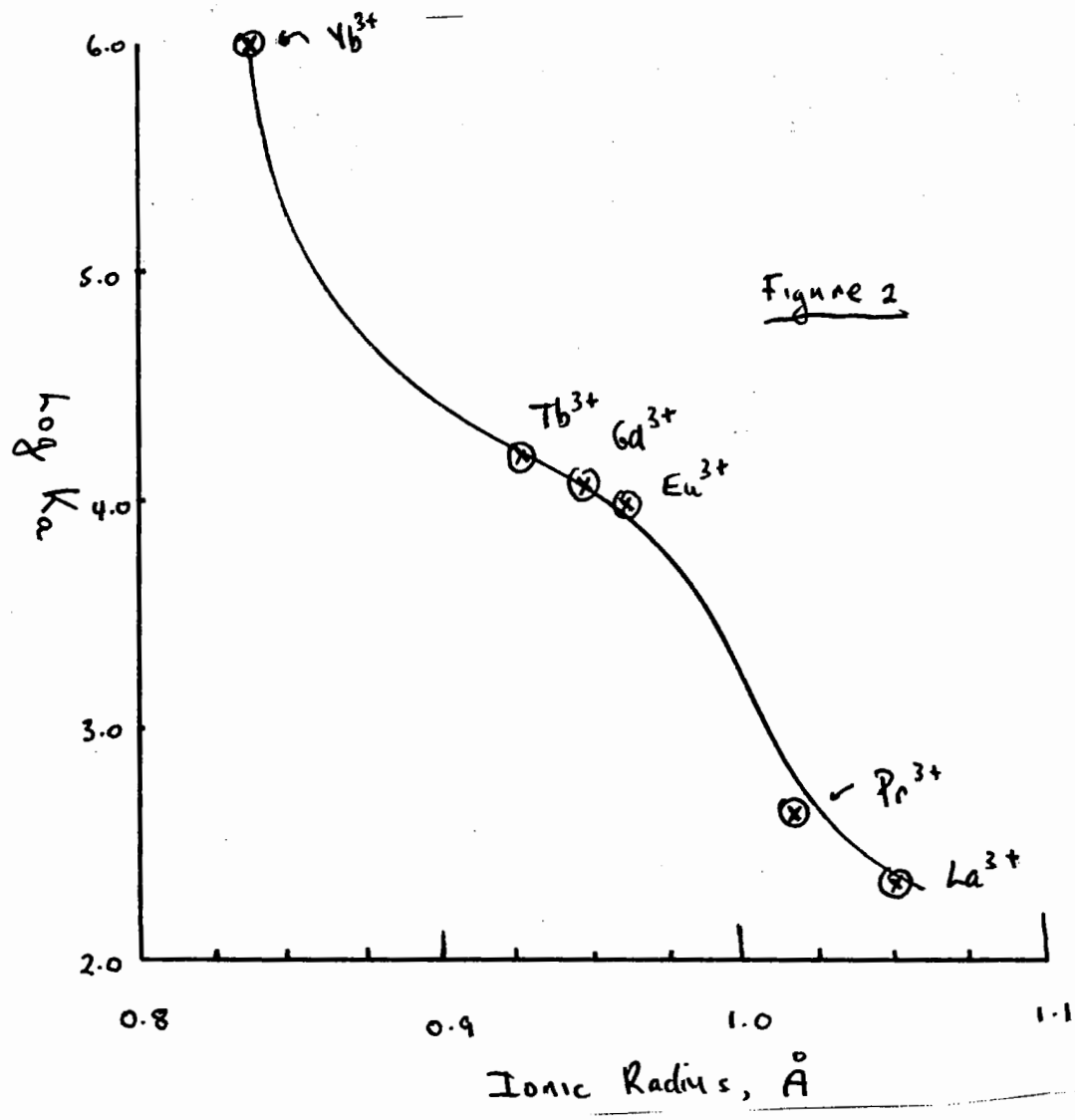



**Figure 1.** The primary structure of the bleomycin antibiotics. In the $A_2$ congener R is $-HNCH_2CH_2CH_2S^+(CH_3)_2$; in the $B_2$ congener R is $-HNCH_2CH_2CH_2CH_2N(H)C(NH_2)_2^+$.



University of Durham Department of Chemistry

Science Laboratories, South Road, Durham, DH1 3LE
Telephone: Durham 64971 (STD code 0385)

18th December, 1979.

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

90MHz Decoupling Amplifier

Dear Professor Shapiro,

Yet again we need a reminder to send a contribution.

For the past two years we have been using a Mallard BGY33 VHF amplifier module as a transmitter for proton and fluorine and proton FT spectroscopy, as well as for proton noise decoupling. This amplifier, which is intended for mobile communication equipment, gives about 20W in the 80-108 MHz region from a 2V input. It is very stable and much cheaper ($150) than any other commercial amplifiers. If it is used for decoupling it needs a 1.5°C/W heatsink and a 12.5V/5A power supply.

Yours faithfully,

RS Matthews Tony Royston

R.S. Matthews & A. Royston.

**University of East Anglia**

From Professor N. Sheppard FRS

School of Chemical Sciences
University of East Anglia,
Norwich NR4 7TJ

Telephone Norwich (0603) 56161
Telegraphic Address UEANOR NORWICH

18th December 1979

Dear Barry,

Although I am no longer a registered contributor to the TAMNMR Newsletter, I wonder if you would be prepared to publish this letter?

We are interested in buying a second hand Varian V 4415 probe, preferably, but not essentially, for work in the 7 to 15 MHz region.

Would anyone interested in selling me such equipment please write to me at the above address.

With best regards,

Yours sincerely,

Norman

N. Sheppard

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

BRUKER SPECTROSPIN (CANADA) LTD.

INDUSTRIAL POSTDOCTORAL FELLOWSHIP

IN NUCLEAR MAGNETIC RESONANCE

Applications are invited from eligible candidates for the above position. The appointment will be initially for one year with the possibility of a one year extension.

The appointee will find his duties divided into two areas. The first will be located at our laboratory in Mississauga, where we are equipped with WP 80 and WM 250 multinuclear spectrometers, and will involve day to day communication with customers on application problems in nmr, assistance during demonstrations, etc. The second will be located at the NRC laboratories in Ottawa where in conjunction with Dr. I.C.P. Smith we intend to develop and refine the methods (magic angle spinning and high power decoupling) currently used to effect narrowing of the nmr resonance lines of solid samples at high magnetic fields, particularly in gels and related materials. Dr. Smith's laboratory is equipped with a CXP 300 cryospectrometer.

Applicants should be thoroughly familiar with the technique of nmr in both the so called 'high resolution' and 'high power' disciplines. A proven ability in developmental aspects of the field will be a distinct advantage.

It is envisioned that on termination of the fellowship, satisfactory performance would lead to a permanent appointment with the Bruker group of companies.

Interested candidates should write to:-

Dr. M.A.R. Smith,
General Manager,
Bruker Spectrospin (Canada) Ltd.,
2410 Dunwin Drive, Unit 4,
Mississauga, Ontario.
L5L 1J9.

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

File Référence

December 28, 1979

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77840
U.S.A.

RESEARCH ASSOCIATE POSITION IN BIOPHYSICAL NMR

Dear Barry:

In the Molecular Biophysics Group we expect to have a post-doctoral Research Associate position available as of April 1, 1980. We are looking for someone with a sound background in NMR, and experience (or at least interest) in spectrometer modification. This position will involve NMR ($^{2}H$, $^{13}C$, $^{31}P$) studies of whole cells and membranes, and the improvement of our NMR spectrometers.

The spectrometers comprise: a high power, high and low resolution, Bruker CXP-300; a wide bore, high power, home-built 200MHz spectrometer for the study of solids (including cross-polarization, magic angle spinning); a much-modified, Varian XL-100; a Varian CFT-20, $^{13}C$-only.

The position is renewable for up to five years, and has an annual stipend of $19,343 or more, depending on experience, plus fringe benefits such as hospital insurance, pension plan etc., as well as return travel expenses for the successful candidate and spouse.

Applicants should write to either of us immediately with copies of their curricula vitae, and request that two letters of recommendation be forwarded to us.

Wishing you and all our colleagues a happy and successful 1980,

Yours sincerely,

Andy
R.A. Byrd

Ian
Ian C.P. Smith

RAB/ICPS:dp

Ottawa, Canada
K1A 0R6

256-37

# ENC Inc.

**Twenty-first Experimental Nuclear Magnetic Resonance Spectroscopy Conference**

**Tallahassee, Florida, March 16-20, 1980**

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**ENC Inc.**

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21st ENC

January 2, 1980

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

Dear Barry:

The 21st ENC will be held in Tallahassee Florida, March 16-20, 1980. Anyone wishing to attend who has not recieved registration materials and information should write to Prof. A.A. Bothner-By, Department of Chemistry, Carnegie-Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213. Here is the tentative program.

| | Morning | Afternoon | Evening |
|---|---|---|---|
| Monday | Cross Polarization and Magic-angle Spinning. (Chairman: E. Stejskal) E. Stejskal, D.L. VanderHart, W.S. Veeman, C.A. Fyfe, S.J. Opella | Poster Session (Chairman: J. Frye) | Multiple Pulse Line Narrowing Techniques. (Chairman: B. Gerstein) B. Gerstein, D. Carlson C. Dybowski, W.K. Rhim |
| Tuesday | Refocussing and 2-Dimensional Techniques. (Chairman: L. Hall) L. Hall, R. Freeman, R. Ernst, G. Bodenhausen, R. Vold | Developments in High Resolution Techniques for Liquids. (Chairman: L.F. Johnson) J.S. Waugh, G. Morris, W. Moniz, D. Traficante, J. Dallas<br><br>Quadrupolar Nuclei. (Chairman: R. Bryant) R. Bryant, M. Bloom, H. Speiss | |
| Wednesday | New Avenues in NMR Applications. (Chairman: P.M. Henrichs) K. Wuthrich, J. Jonas, J.J.H. Ackerman, C.S. Yannoni, A. Vega, H. Resing | Poster Session Chairman: J. Frye Department of Chemistry, Colorado State University, Fort Collins, CO 80523 (Abstract for Poster should be one 8½"x 11" page). | NMR Imaging. (Chairman: P.C. Lauterbur) P.C. Lauterbur, D. Hoult, J. Hutchison, W. Moore |
| Thursday | Progress in Very High Field Spectrometers. (Chairman: F. Anet) F. Anet, J. Dadok, M. Sauzade, R. Wheatley, L. Neuringer, D. Reuben, W.E. Hull<br><br>Probe Design for Superconducting Magnets (Chairman: B.L. Hawkins) D. Hoult, P.D. Ellis, G.C. Levy, D.W. Alderman | | |

Sincerely,

Gary

Gary E. Maciel
Chairman, 21st ENC

NICOLET TECHNOLOGY CORPORATION
(formerly Transform Technology Inc.)
145 East Dana Street ▪ Mountain View, California 94041 ▪ Phone: 415/969-2076

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**TEXAS A&M UNIVERSITY**
DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843

7 January 1980

TAMU NMR NEWSLETTER - BACK ISSUES AVAILABLE

In the twin hopes that some of our readers may wish to make their collection of TAMU NMR Newsletter issues more complete, and also help us with our storage problem, we would like to announce the availability of back issues of the Newsletter as follows:

| Issues Available | Prices |
|---|---|
| Oct. 1978 - Sept. 1979 | $50/yr* |
| Oct. 1977 - Sept. 1978 | $40/yr* |
| 1970 - Sept. 1977 | $30/yr* |

Single issues, as available (no academic or personal discounts):

| | |
|---|---|
| Oct. 1978 - Sept. 1979 | $4.25/ea |
| Oct. 1977 - Sept. 1978 | $3.50/ea |
| Sept. 1977 and earlier | $2.50/ea |

* The normal 50% discount for personal and academic subscribers will apply. Orders for three or more years qualify for a special package price; inquire, if interested.

The above prices are net U.S. funds. Pre-payment with your order is required. Please make checks payable to Texas A&M University. All prices are post-paid at surface printed matter rates. If you desire first class mail delivery, you will be charged for the extra mailing costs.

The above prices are good until July 1, 1980.

B. L. Shapiro

BLS/ks

# NT-Series Fourier Transform Superconductive Magnet NMR Spectrometers

The NT-Series has been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, the NT-Series represents a *completely modular approach* to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

*Outstanding NT-Series features include these:*

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The multiple-technique NT-Series spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

*Some of these are:*

- **High-resolution studies of solids with Waugh-Pines cross-polarization and magic-angle spinning**
- **High-sensitivity wide-bore $^{13}C$ studies of high molecular weight polymers.**
- **Automated $T_1$ and $T_2$ measurements.**
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- **Temperature-programmed experiments.**
- **$^{31}P$ experiments on living organs.**

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## System Features

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- Module Performance Indicator Lights
- Comprehensive Auto Stacking
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- Floppy; MH Disc Storage
- 50KHz Spectral Width
- CPU Expansion to 65K

JEOL

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