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N-M-R Newsletter

No. 231

December, 1977

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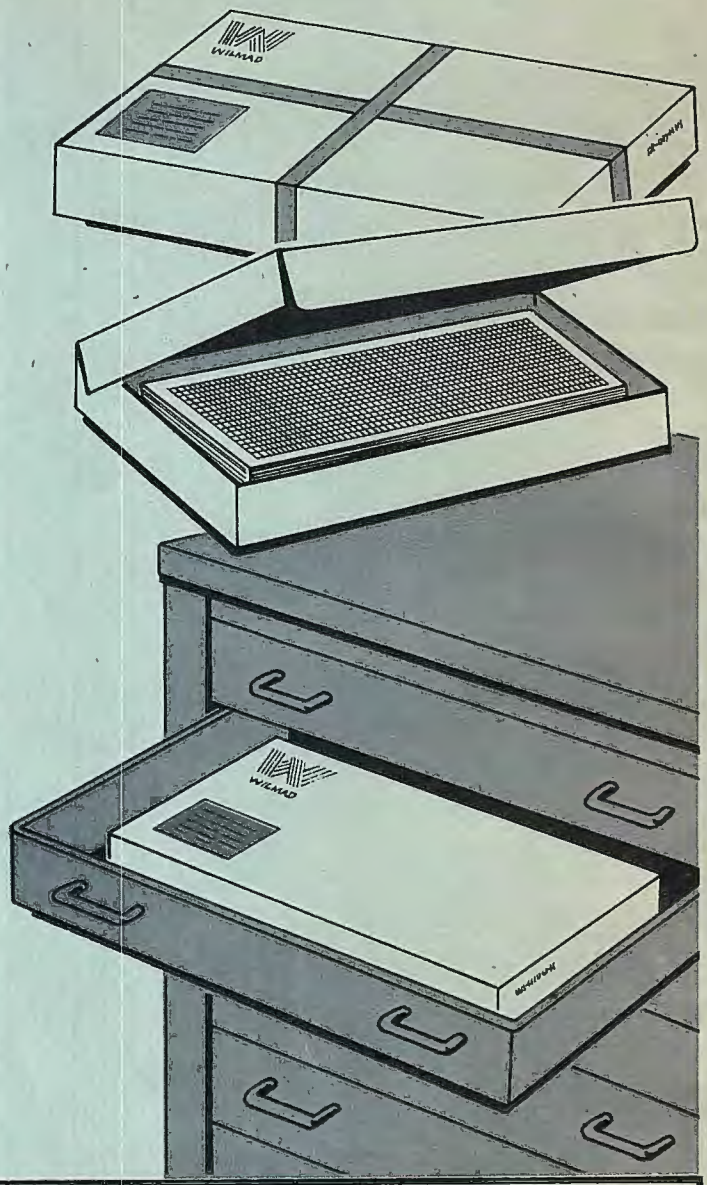

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DEADLINE DATES: No. 232: 3 January 1978
No. 233: 6 February 1978

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 231

LA JOLLA SYMPOSIUM ON

BIOLOGICAL APPLICATIONS OF NMR SPECTROSCOPY

bringing together investigators in the Southwestern United States

February 16-17, 1978

Recital Hall, Mandeville Center
University of California at San Diego
La Jolla, California

TENTATIVE PROGRAM

I. PEPTIDES/PROTEINS

John A. Rupley (U. of Arizona)
Victor J. Hruby (U. of Arizona)
Edward R. Birnbaum (N.M. State)
John H. Richards (Cal. Tech.)
Murray Goodman (U.C., San Diego)

II. MEMBRANES

Sunney I. Chan (Cal. Tech.)
Charles H. A. Seiter (U. of So. Cal.)
Edward A. Dratz (U.C., Santa Cruz)
Joel D. Morrisett (Baylor)
Edward A. Dennis (U.C., San Diego)

III. NUCLEIC ACIDS

Brian R. Reid (U.C., Riverside)
Ignacio Tinoco (U.C., San Diego - visiting)
Thomas W. Schleich (U.C., Santa Cruz)
Joseph V. Paukstelis (Kansas State)
David R. Kearns (U.C., San Diego)

IV. FUTURE DIRECTIONS

Frank A. L. Anet (U.C., Los Angeles)
John D. Roberts (Cal. Tech.)
James L. Sudmeier (U.C., Riverside)
Nathan O. Kaplan (U.C., San Diego)
Robert L. Vold (U.C., San Diego)

Sponsored by U.C.S.D. NMR Research Resource Center, a Biotechnology Resource supported by The National Institutes of Health. Program Committee: E. A. Dennis (Chairman), M. Goodman, N. O. Kaplan, D. R. Kearns, R. L. Vold, J. M. Wright.

REGISTRATION INFORMATION

All interested scientists and students are invited to attend. A registration fee of $25.00 is required and will include Symposium luncheons on February 16 and 17 and the Symposium dinner on February 16.

Registration information and fee should be received by January 18, 1978. Return the attached Registration Card or send name, affiliation, address and phone number to the Symposium Coordinator: Dr. John Wright, Department of Chemistry (B-014), U.C.S.D., La Jolla, CA 92093. Checks should be made payable to The La Jolla NMR Symposium. Inquiries about the conference should be directed to Dr. Wright (telephone: (714) 452-3049).

A limited number of motel accommodations will be available at The La Jolla Village Inn adjacent to the campus. These accommodations cannot be held past January 18, 1978, so RESERVATIONS MUST BE MADE BEFORE THAT DATE. Special Symposium rates are $18 single, $22 double. Reservations should be made directly with the motel by returning the attached Accommodations Card to, or writing: The La Jolla Village Inn, La Jolla Village Drive at Interstate 5, La Jolla, CA 92037. Indicate that you are attending the La Jolla NMR Symposium and request the special symposium rate. The motel offers free pickup and drop off at the San Diego Airport.

REGISTRATION: LA JOLLA SYMPOSIUM ON BIOLOGICAL APPLICATIONS OF NMR SPECTROSCOPY

NAME: _____

AFFILIATION _____

ADDRESS _____

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TELEPHONE _____

____$25 registration/meal payment enclosed.

RETURN BEFORE JANUARY 18, 1978, to:
Dr. John M. Wright
Department of Chemistry (B-014)
University of California, San Diego

ACCOMMODATIONS: LA JOLLA SYMPOSIUM ON BIOLOGICAL APPLICATIONS OF NMR SPECTROSCOPY

ARRIVAL DATE _____ ARRIVAL TIME _____

LENGTH OF STAY _____

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REMARKS: _____

NAME _____

ADDRESS _____

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RETURN BY JANUARY 18, 1978, to:
La Jolla Village Inn

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

November 22, 1977

Building 2, Room 122

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

Dear Barry:

IUPAC Recommendations on NMR Spectra

As you know, the International Union of Pure and Applied Chemistry (IUPAC) publishes recommendations for symbols and nomenclature for many areas of chemistry in its journal *Pure and Applied Chemistry*. The accompanying Recommendations on NMR were so published last year, but since *Pure and Applied Chemistry* is not the most widely read journal, I thought it would be useful to bring them to the attention of the NMR community, and IUPAC has now agreed to their reproduction here [from *Pure Appl. Chem.* 45, 219 (1976)].

In 1972 IUPAC published Recommendations for proton NMR spectra only, since the status of "other nuclei" was then ill-defined. The present recommendations complement the earlier ones and now apply to all nuclei. Like all IUPAC Recommendations, they were adopted only after publication of a provisional version and the consideration of all comments received over a two-year period. They are entirely compatible with the more detailed ASTM Recommendations that were circulated with the *Newsletter* a few months ago. Although these are regarded as "Final" Recommendations, in the sense that they are unlikely to be completely countermanded, no Recommendations in an active field of science are really final, since new developments require extensions and modifications. At present our Commission has no active NMR project, but we would welcome any comments or suggestions for extension of these Recommendations.

Sincerely,

Ted

Edwin D. Becker, Chairman
IUPAC Commission on Molecular
Structure and Spectroscopy

EDB:ell

Pure and Applied Chemistry 45, 219 (1976)

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY†

PRESENTATION OF NMR DATA FOR PUBLICATION IN CHEMICAL JOURNALS—B. CONVENTIONS RELATING TO SPECTRA FROM NUCLEI OTHER THAN PROTONS

(RECOMMENDATIONS 1975)

Section B constitutes the second part of the "Recommendations for the Presentation of NMR Data for Publication in Chemical Journals". Section A dealt with proton NMR spectra (*Pure Appl. Chem.* **29**, 627 (1972)). Although the present recommendations are directed toward nuclei other than protons, they are equally applicable to proton NMR.

(1) The nucleus giving rise to the spectrum should always be explicitly stated in full or in abbreviation, e.g. ^{10}B NMR spectrum (spoken: boron 10 NMR spectrum). The isotopic mass number should be stated except in cases where a single abundant isotope leads to a situation without ambiguity, e.g. NMR spectra from ^{19}F or ^{31}P.

Abbreviations such as PMR (for 'proton NMR' or 'phosphorus NMR') or CMR (for 'carbon NMR') are strongly discouraged.

(2) The dimensionless scale factor for chemical shifts should be 10^{-6}, i.e. parts per million, for which ppm is a convenient abbreviation. When large chemical shifts are given exactly, the radiofrequency of the standard substance should be reported with sufficient accuracy.

(3) The unit for spin–spin coupling constants should be hertz (cycles per second). The symbol for coupling constants is J. The coupling between two nuclei separated by n chemical bonds can be indicated by the left *super*script n, e.g. ^4J denotes the coupling constant between two nuclei separated by 4 chemical bonds. Right *sub*scripts may be used to give the symbols of the coupling nuclei, e.g. the coupling constant between the phosphorus nucleus and protons in trimethylphosphite, $P(OCH_3)_3$, would bear the symbol $^3J_{PH}$. Alternatively a notation of the type ^3J(PH) or $^3J(^{11}BH)$ may be used.

(4) The graphical presentation of spectra should show the frequency decreasing to the right (applied field increasing to the right), absorption increasing upwards, and the standard sweep direction should be from high to low frequency (low to high field). Solvent and impurity bands, and spinning side-bands, should be indicated as such.

(5) Whenever possible the dimensionless scale should be tied to an internal reference, which should be explicitly stated. The dimensionless scale should be defined as positive in the high frequency (low field) direction. The scale in parts per million should be termed the δ scale. A shift measured on this scale should be given as, for example, $\delta = 5.00$, not $\delta = 5.00$ ppm. If data from more than one nucleus are reported, the symbol δ should be used with the corresponding symbol of the element given in brackets, e.g. δ(C) or $\delta(^{11}B)$. The position of the nucleus in the structural formula could be denoted by an additional number following this symbol for the nucleus, e.g. δ(C-5) or $\delta(^{11}B\text{-}5)$.

(6) When the spectra are submitted for publication, additional information should include:

(a) A statement of how the spectrum was recorded, e.g. using the continuous wave (CW), pulse Fourier transform (pulse FT), or other technique. The number of spectra accumulated should be stated.

When a pulse FT technique is employed, both the duration of the pulse and the duration of a 90° pulse should be stated. These two pieces of data may be expressed in other forms, e.g. as the angle of reorientation of the magnetic vector and the duration of a 90° pulse.

(b) The name of the solvent used:

(c) The concentration of the solute.

(d) The name and concentration of the internal reference.

(e) The name of the external reference, if one is used.

(f) The diameter of the sample tube and whether or not it was rotated.

(g) The temperature of the sample.

(h) The approximate radio-frequency or magnetic field at which the measurements were made.

(i) If spectra are presented as diagrams there should be a graphical indication of the distance corresponding to a suitable range of Hz, so that fine structure spacings or widths of broad resonances can be estimated.

(k) Where relevant it should be stated whether oxygen has been removed from the sample.

(l) Other experimental information should be added where appropriate or necessary, e.g.

(i) in CW experiments the sweep rate and magnitude of the B_1 fields;‡

(ii) in double resonance experiments the magnitude of the irradiating field,‡ B_2, whether monochromatic or noise decoupling is used, and whether CW or pulsed operation is carried out;

(iii) in cases where the experimental data are processed by a computer, all relevant information about spectral width, filtering, apodization, deconvolution processes, number of data points, etc.

†*Titular Members*: N. Sheppard (Chairman), M. A. Elyashévich (Vice-Chairman), F. A. Miller (Secretary), E. D. Becker, J. H. Beynon, E. Fluck, A. Hadni, G. Zerbi, *Associate Members*: G. Herzberg, B. Jeżowska-Trzebiatowska, Y. Morino, S. Nagakura, C. N. R. Rao, Sir Harold Thompson, D. W. Turner.

‡In contrast to the previous recommendations concerned with proton spectra the more recently adopted symbol B is used for the magnetic induction (field).

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destinatario:

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

nostro riferimento: Department of Physical Chemistry data: Milano, October 27, 1977

Subject : RING INVERSION IN PHTHALAZINO[2,3-b] PHTHALAZINE-5,12(7H,14H)--DIONE (DIFTALONE)

Dear Prof. Shapiro,

we have studied the conformation in solution of diftalone, an antiinflammatory agent,[1-3] whose molecule consists of two symmetrical parts connected through the N-N bridge. Examination of the structure suggests the possibility of conformational inversion of the heterocyclic rings. In particular, assuming a fixed conformation for each of the two conjugated aromatic amide moieties, we hypothesize that this inversion involves the two bonds from each methylene group and the N-N bond. Thus, we have studied the exchange of the two geminal protons at C-7 and C-14 between the quasi-axial and quasi-equatorial orientations.

The ^1H NMR spectrum at 270 MHz in $CDCl_3$ at room temperature (fig.a) shows a sharp singlet for the two geminal protons, owing to a fast exchange. Low temperature experiments, using $CHCl_2F$ as a solvent (fig.b) show the coalescence at 193°K and 2 AB doublets (J = 14 Hz) at 153°K. The doublet at 4.80 δ is assigned to the quasi-axial proton and that at 5.98 δ to the quasi-equatorial one; they are in fact differently affected by the anisotropy of the carbonyl in peri position.

For determining the rate constant and the activation parameters, we have used the approximate relationship $Kc = \pi\left[(\nu_A - \nu_B)^2 + 6\, J_{AB}^2\right]/\sqrt{2}$, from which

$K_{193°}$ = 680 sec^{-1} K^{-1} is obtained. The introduction of this value into the Eyring equation $K = T \times const. \times e^{-\Delta G/RT}$, gives the value $\Delta G_{193°}$= 8.6 Kcal.mole $^{-1}$ for the free energy of activation of the inversion process.

Yours sincerely,

Ambrogio Ripamonti Edoardo Martinelli Gian Gualberto Gallo

References

1) E.Bellasio and E.Testa, Farmaco, Ed.Sci., 25 (1970) 305.

2) P.Schiatti, D.Selva, E.Arrigoni-Martelli, L.J.Lerner, A.Diena, A.Sardi and G.Maffii, Arzneim.Forsch., 24 (1974) 2003.

3) F.B.Nicolis, L.Schiatti, F.Porzio, A.Manzini, M.Marchetti and G.Acocella, Int.Clin.Pharmacol., 10 (1974) 239.

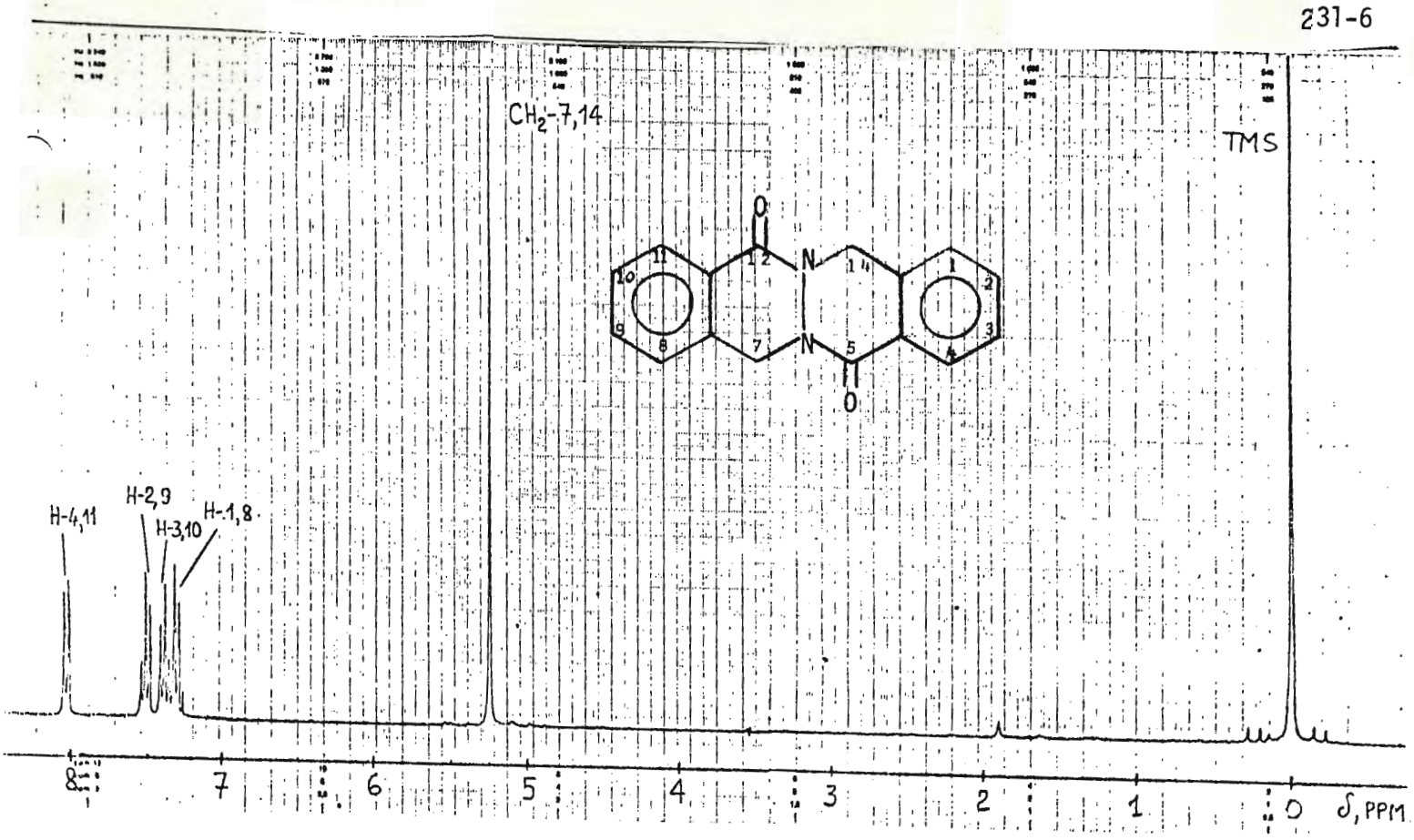


Fig. a - ^1H NMR spectrum of diftalone at 270 MHz in $CDCl_3$

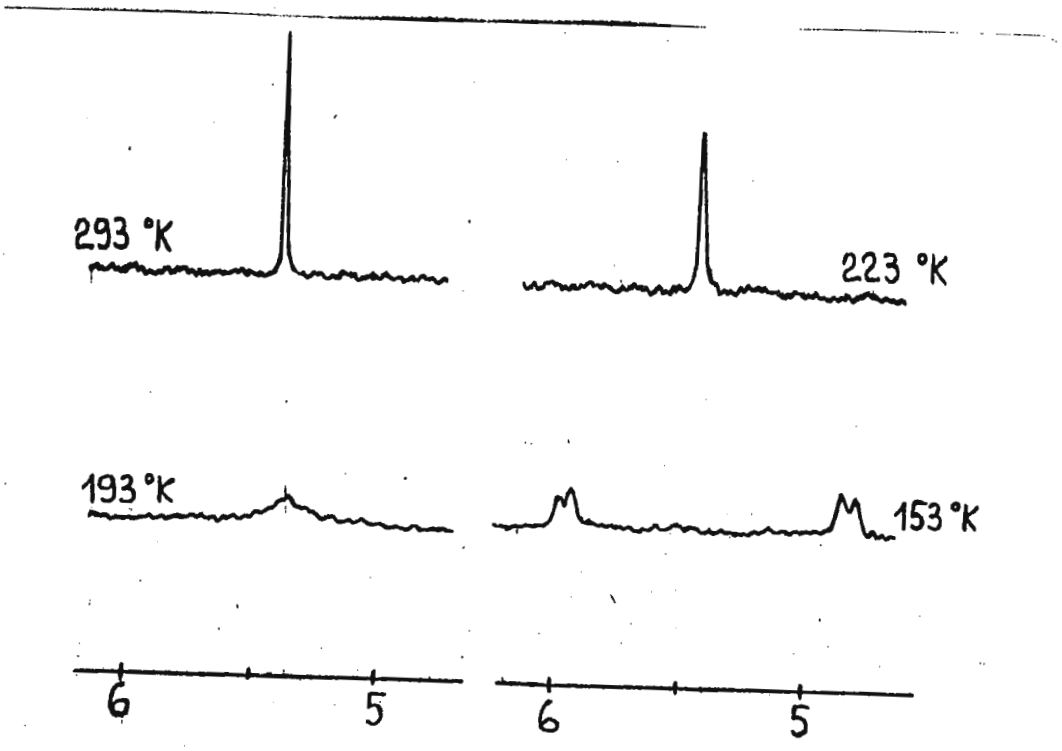
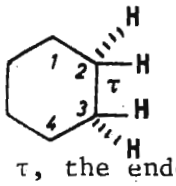


Fig. b - Methylene signal of diftalone in $CHCl_2F$ at various temperatures.

RIJKSUNIVERSITEIT GENT
LABORATORIUM
voor
ORGANISCHE CHEMIE

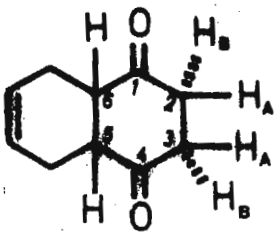
B-9000 GENT, August 23, 1977
KRIJGSLAAN 271 - S 4 Tel. 22 57 15
(België-Europa)

Dear Barry,

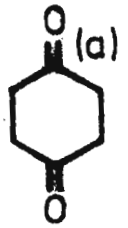


In a variety of hexacyclic systems the ratio R = J_{trans}/J_{cis} = $(J_{aa} + J_{ee})/(J_{ea} + J_{ae})$ can be related to τ, the endocyclic torsion angle 1-2-3-4, by the Lambert-Buys expression $\cos^2\tau = 3/(4R + 2)$.[1]

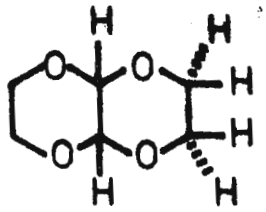
Recently we observed in I that the two principally distinct cis coupling constants J_{AA}, J_{BB} differ by almost 1 Hz. Of course, in the Lambert-Buys treat-



J_{AA} = 7.42 Hz
J_{BB} = 6.52 Hz } cis
J_{AB} = 7.70 Hz tr.
$^2J_{AB}$ = -17.9



J_{cis} = 6.23
$J_{tr.}$ = 8.05



I II III

	R	τ
II	1.29	49.7
I	1.18	48.1
	1.04	45.7

[a] Lambert; J.A.C.S. 89, 1836 (1967).

ment these two J_{cis} must be exactly equal, as is found e.g. in III.[2] The τ angle calculated from J^{tr}/J^{cis}_{AA} and J^{tr}/J^{cis}_{BB} are 45.7 and 48.1° respectively. The good agreement between these two angles is caused by the rapid change of R with respect to τ for $\tau \sim 45°$. The diketonic ring in I is thus calculated

to be slightly more flattened than the parent compound II. Also, in II, as in I, the diketonic ring assumes a boat conformation (large absolute value of ^2J).

It would be of interest to know what causes J_{AA} and J_{BB} to be different. The analysis of the spectrum does not tell whether a given cis coupling is J_{AA} or J_{BB}. Chemical correlation discloses that the less hindered A hydrogens undergo more rapidly a base-catalyzed H/D exchange than the B hydrogens. It is surprising that J_{AA} had increased more than J_{BB} (with respect to J^{cis} in II), although the B atoms are situated on the more sterically constrained inner face of I. As yet, we do not know why J_{AA} and J_{BB} are different. A problem is that the conformation of the remaining moiety of I remains unknown.

Yours sincerely,

D. Tavernier P. Vanhee M. Anteunis.

1. Lambert; Accounts Chem. Research, 4, 87 (1971).

2. Altona, Havinga; Tetrahedron, 22, 2275 (1966);
Frazer, Reyes-Zamora; Canad. J. Chem., 43, 3445 (1965).

ANNOUNCEMENT.

For Sale (Europe): Superconducting VARIAN HR300 ^{1}H-NMR spectrometer (including 620/i 24K computer and SC 8525-2 decoupler) working in frequency mode exclusively with Homo INDOR-DECOUPLING facilities. Or any spare part of this !

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DEPARTMENT OF CHEMISTRY

2 September, 1977

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

DISPERSION VERSUS ABSORPTION (DISPA):
A NEW ANALYSIS OF NMR LINE-BROADENING
MECHANISMS FOR HETEROGENEOUS SYSTEMS

Dear Barry,

In NMR, the usual spectral display is absorption (v-mode) versus frequency. However, Fourier transformation of a free induction decay provides convenient access to both absorption and dispersion (u-mode and v-mode) spectra, scaled by the same amplitude factor. We have recently noted that a plot of dispersion versus absorption (DISPA) gives a perfect semicircle for a single Lorentzian line, as shown in Figure 1 for an ordinary HDO signal from 99.7% D_2O. Moreover, for more complicated line shapes, the direction and magnitude of the displacement of an experimental DISPA curve from its reference semicircle (i.e., a semicircle centered on the abscissa, with diameter equal to maximum absorption peak height) can often serve to identify and distinguish between a variety of different line-broadening mechanisms, based on the spectra from a single F.I.D.

We have thus far examined theoretical (and in most cases, experimental) DISPA plots for: unresolved superposition of two Lorentzians of different chemical shift or different line width; Lorentzian line shapes which have been weighted by either a Gaussian distribution in chemical shift or log-Gaussian distributions in either relaxation time or correlation time; chemical exchange between two sites of different chemical shift or different line width; and phase-misadjusted spectra.

One case of immediate practical interest (detection of unresolved splittings) is shown in Fig. 2, which gives the DISPA plots for two peaks which are separated by various fractions of one line width. Fig. 3 gives an experimental example, based on the unresolved ^{19}F doublet (line width of each peak = 8.0 Hz, with a frequency separation of J_{HF} = 5.6 Hz) from 5-fluorouracil in D_2O.

We have found quite good agreement between theory and experiment for these and other test cases, and accurate phasing presents no problem in practice. We suggest that the DISPA plot should be useful in diagnosing line-broadening mechanisms for a large variety of inhomogeneously broad NMR lines. Theoretical and experimental examples have been submitted for publication.

Sincerely,

Alan G. Marshall

on behalf of

Alan G. Marshall and D. Christopher Roe
Department of Chemistry
University of British Columbia
Vancouver, B.C. V6T 1W5 CANADA

and Stephen H. Smallcombe
Analytical Instrument Div.
Varian Associates
611 Hansen Way
Palo Alto, CA 94303 U.S.A.

(Please credit to the account of A. G. Marshall.)

Figure 1.

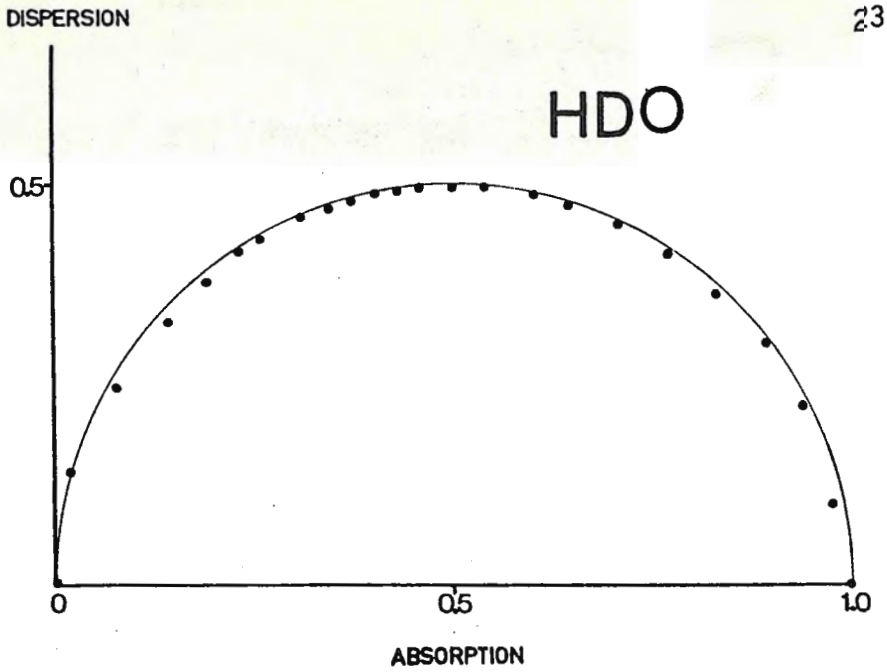


Figure 2.

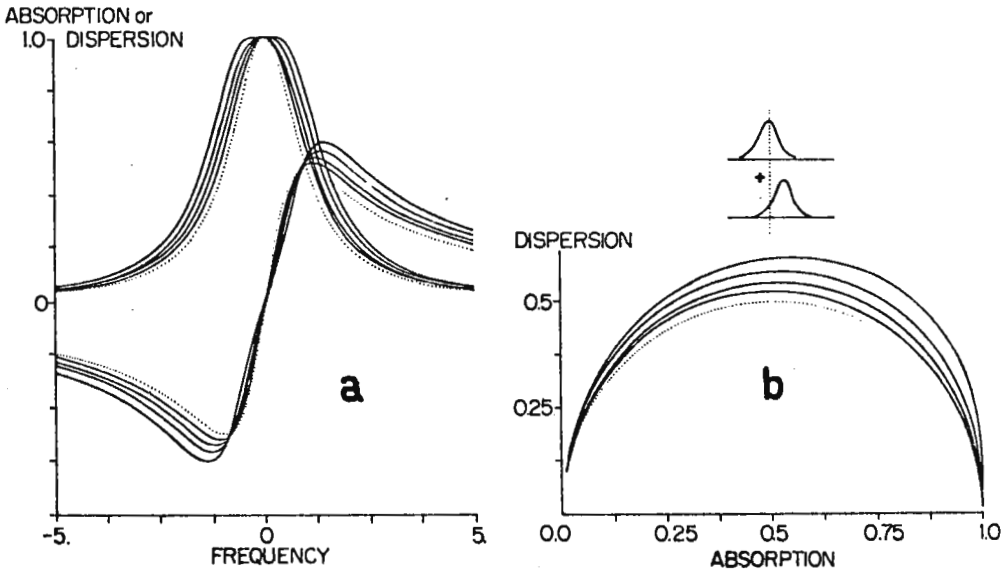
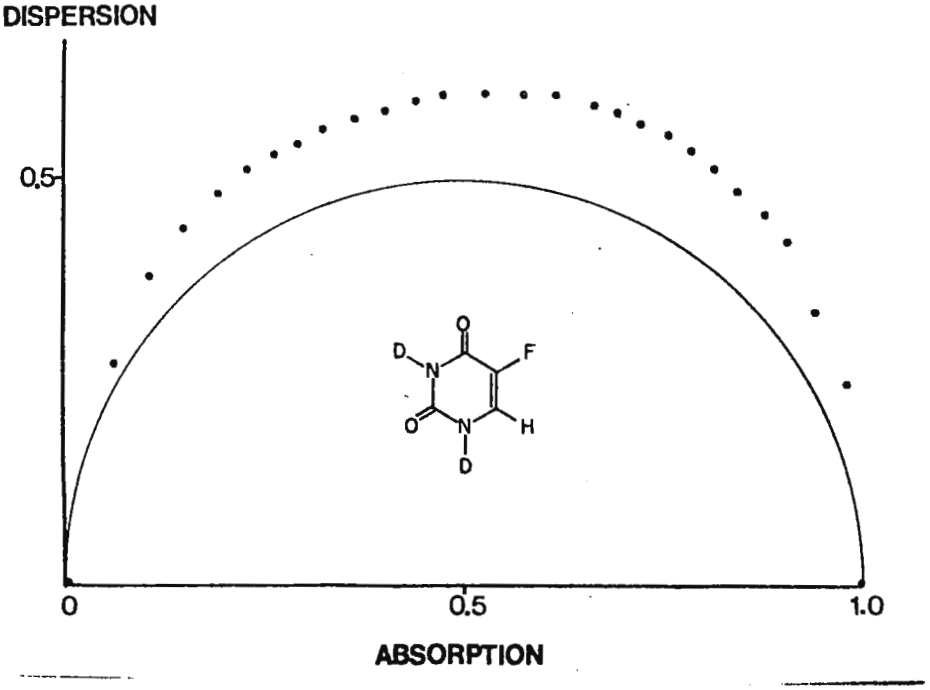


Figure 3.



231-11

BRUKER Instruments, Inc.
MANNING PARK
BILLERICA, MASSACHUSETTS 01821
(617) 272-9250

1 November 1977

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

Dear Dr. Shapiro:

Re: Positions Available

BRUKER is looking for a chemist/physicist having a strong background in solid state and/or high resolution N.M.R. A working knowledge of electronics and computer programming is desirable. This person would be expected to spend an initial period working at Bruker-Physik in Karlsruhe, West Germany. After this time he would continue with a challenging position at our growing facility in the Boston area.

This position would involve a wide range of responsibilities in the scientific and instrumental aspects of N.M.R.

Please send resumes to Don Ware at the above address.

Yours faithfully,

Bruker Instruments, Inc.

Don Ware
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WP-200

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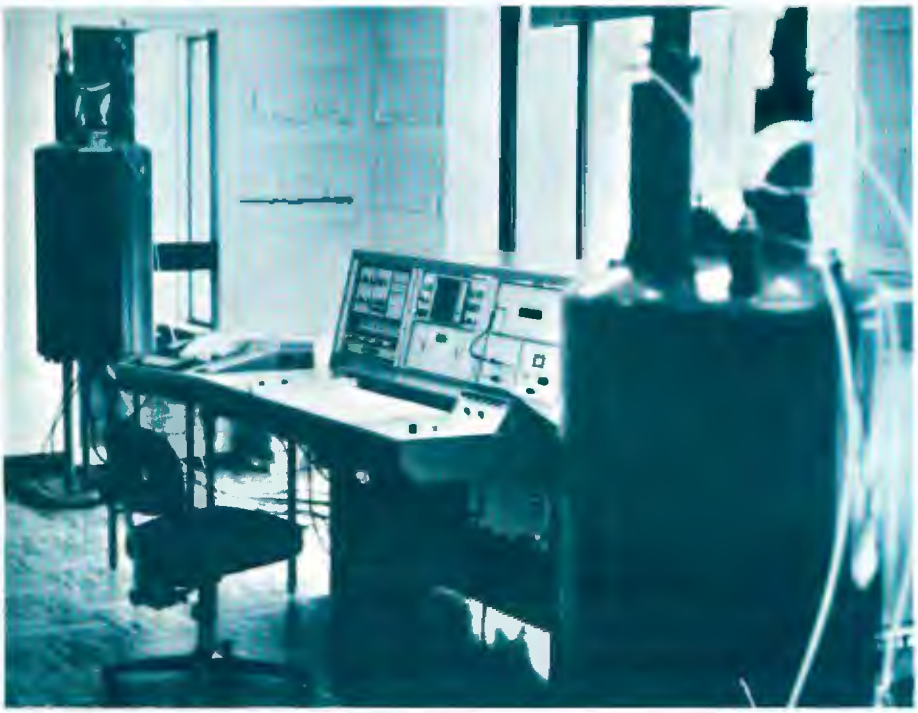

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November 17th, 1977

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

^{13}C chemical shift assignments of the carbonyl groups in Penicillins and Cephalosporins. ^{13}C and ^{15}N study of enamide systems.

Dear Barry,

we would like very much to arrive once in time with our contribution, i.e. before the arrival of your multicolored reminders.

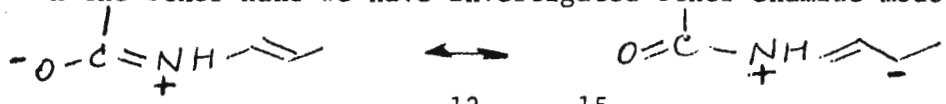
When we became involved in a ^{13}C study of penicillins and cephalosporins (1), we realized that the frequency assignments of the three carbonyl carbons present in the molecules was not an easy task. We succeeded in these assignments uniquely by proton SFSD and "gated" decoupling. SFSD experiments were performed with very low decoupling power since the couplings present are long-range and therefore small. In some cases, when this method was unsuccessful, the long-range interactions or the multiplicity of the signals have been used.

We were surprised to find the same shift for the β-lactam carbonyl carbon of Δ^3-cephalosporins I-III (biologically active) and Δ^2-cephalosporin IV (inactive), since the IR ν_{CO} stretching frequency suggested an increase in the bond order of the C=O bond for Δ^3- vs Δ^2-cephalosporins.

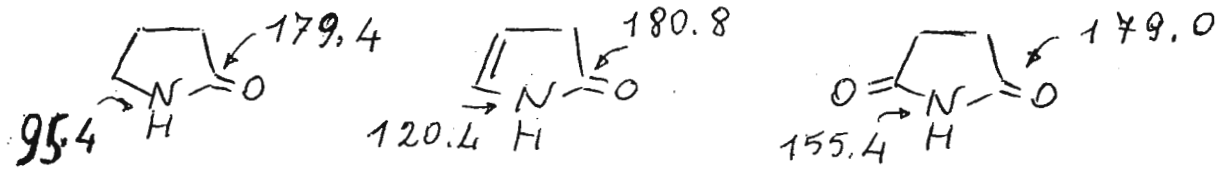
As it is generally accepted (2) that the inhibition of the amide resonance, owing to the delocalization of the nitrogen lone pair on the double bond, is the major determining factor in differentiating the activity of these antibiotics, the NMR results appear particularly interesting. In fact the mechanism of the antibacterial activity should involve

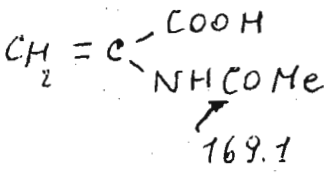
a nucleophilic attack at the β- lactam carbonyl carbon by the enzyme. Now, the presence of the conjugated double bond in Δ^3-cephalosporins (active) is believed (2) to increase to positive charge on that carbon, leaving it more susceptible to the nucleophilic attack. But the similar values of the β-lactam ^{13}C shifts found for Δ^3- and Δ^2-cephalosporins indicate that the charge density at the carbonyl carbon in both systems are approximately the same; thus the above interpretation is not supported by the NMR results.

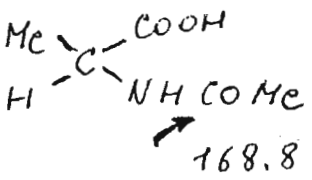
On the other hand we have investigated other enamide model systems(3):



in order to check whether the ^{13}C and ^{15}N (4) chemical shifts show the same behavior as in Δ^3-cephalosporins and thus to question the accepted concept that the possibility of enamine conjugation does necessarily inhibit the amide resonance.



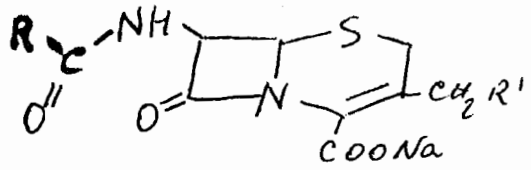


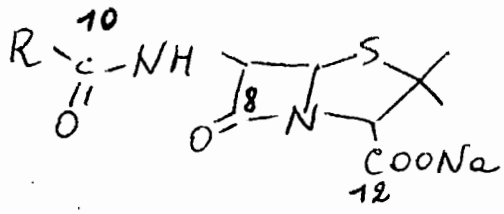


^{15}N under measure

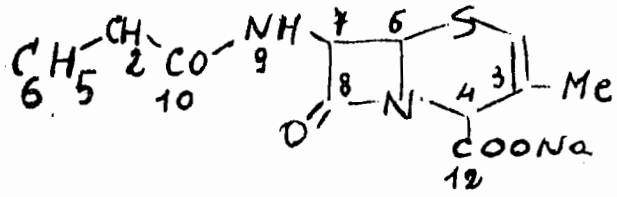
These preliminary results show that the invariance of the carbonyl carbon shift and the large down field effect on the nitrogen seem to be general for these systems. Thus, not to mention the inductive effects (which are often underestimated), we believe that the existence of enamine type delocalization involving the lone pair of the amide nitrogen may not affect the situation at the carbonyl, but only that at the nitrogen; since the electron availability at the nitrogen atom is such to supply the electron density demand by the adjacent π-bond.

(1) R.Mondelli, P.Ventura,J.C.S. Perk II in press.
(2) E.H.Flynn, Cephalosporins Penicillins, Acad. press 1972.
(3) G.Fronza, R.Mondelli, E.W.Randall, J.C.S. Perk II in press.
(4) For N-15 of cephalosporins, seeR.Lichter,D.E.Dorman, J.Org.Chem.41,582(1977).





I	$R = PhCH_2$	$R' = H$	V	$R = PhCH_2$	
II	$R = PhCH_2$	OAc	VI	$PhOCH_2$	
III	$R = PhCHNH_2$	H	VII	$PhCHNH_2$	



IV

^{13}C chemical shift assignments for the carbonyl carbons[a]

	β-lact	COONa	CONH		β-lact	COONa	CONH
I	165.3	170.9	176.3	V	175.3	174.7	174.1
II	165.6	169.2	176.1	VI	174.8	174.6	171.4
III	164.9	170.9	176.3	VII	175.5	175.4	176.3
IV	166.4	175.2	176.0				

C-H long-range coupling constants

	$^3J_{C_8H_4}$	$^3J_{C_8H_6}$	$^2J_{C_8H_7}$	$^3J_{C_{10}H_7}$	$^2J_{C_{10}H_{11}}$[b]	$^2J_{C_{12}H_4}$
I	—	6.5[c]	6.0[c]	2.5	6.5	—
II	—	6.0	6.0	3.0	6.5	—
III	—	6.5[c]	5.5[c]	4.0[d]	4.0[d]	—
IV	5.0	5.0	5.0	3.0	7.0	6.5
V	5.0	= 16.0[e]		2.0	6.5	4.0
VI	5.0	= 15.5[e]		2.0	3.8	4.5
VII	5.0	= 12.0[e]		[f]	[f]	4.0

a) (ppm) in D_2O (0.8 M); b) for I-III, V and VI, average values of two couplings; c) values within horizontal lines may be reversed; d) values deduced from the width of the signal; e) only the sum of the Js could be measured; f) not determined.

best greetings, sincerely yours

R. Mondelli

31-19

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DEPARTMENT OF CHEMISTRY

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

27th September, 1977.

Dear Professor Shapiro,

Deuterium Isotope Effects Upon Peptide Carbonyl ^{13}C Resonances

The six peptide carbonyl ^{13}C resonances of viomycin are well resolved and for a solution in 50:50 H_2O/D_2O at pH 1.45 yield the spectrum shown. Feeney et al[1] have demonstrated the existence of a two bond deuterium isotope effect -NH(D)-CO-, and we now point out the existence of a three bond effect -CO-CH-NH(D)-. This effect is very small but can be of use:-

resonance	a	b	c	d	e	f	
two bond	0.06_8	0.07_6	0.07_9	0.08_1	0.07_4	0.06_8	p.p.m.[2]
three bond		0.01_9	0.01_9		0.02_8	0.01_9	p.p.m.[2]

We had independently assigned resonance a to C10, and of the remaining five carbonyls only C28 cannot show a three bond isotope effect and so resonance d must be due to C28.

The proton spectrum shows that exchange of the different amide protons with the solvent occurs at distinct pH's. Therefore we have a method for assigning the carbonyl ^{13}C resonances (providing the ^{1}H amide region can be assigned) by observing the pH dependent collapse of their isotope splittings. In fact this confirmed the assignments a (C10) and d (C28), and gave the assignments e (C17), and f (C21).

Please credit this contribution to Ed Randall's account.

Yours sincerely,

Geoff Hawkes.

Dr. G.E. Hawkes

90.5 MHz ^{13}C spectrum (WH-360), run in collaboration with Dr. W.E. Hull of Bruker Physik AG.

1. J. Feeney, P. Partington and G.C.K. Roberts, Mol. Magn. Resonance, 1974, 13, 268.

2. The digital resolution in the spectrum is 0.003 p.p.m.

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

NATIONAL HEART, LUNG, AND BLOOD INSTITUTE

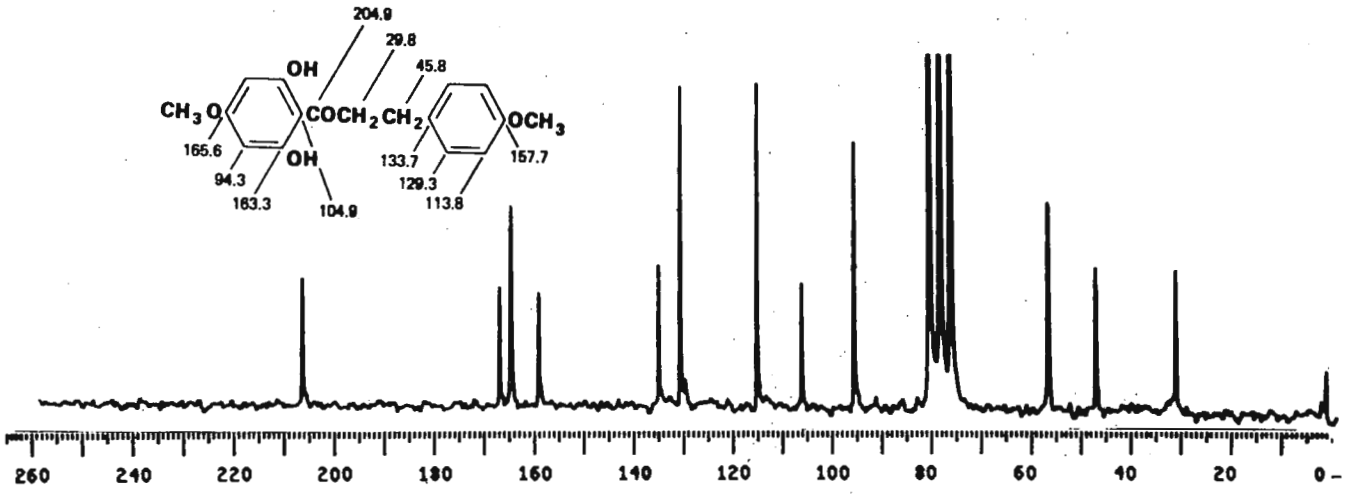
October 12, 1977

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

Dear Barry,

A Dihydrochalcone Structure from ^{13}C NMR

Recently a sample from the tropical silver fern, Pityrogramma Calomelanos (L) Link (Gymnogrammaceae) provided an unusual opportunity to establish a fairly complex structure directly from the ^{13}C nmr, without extensive reference to closely related materials. The molecular formula, $C_{17}H_{18}O_5$,



suggested a couple of aromatic rings, while the fact that there are only eight peaks between 170 and 90 ppm shows some symmetry. The spectrum obtained using a 60-sec interval between pulses provided peaks in this region with the approximate intensities of 1:2:1:1:2:2:1:2, consistent with two aromatic rings, each with a two-fold axis of symmetry. A chemical shift of 94.3 ppm is unusual for an aromatic carbon, but fits the phloroglucinol system, with three oxygen substitutes contributing

cumulative upfield shifts to ortho and para carbons. Assigning a methoxyl the position para to the carbonyl retains the required symmetry and accounts for the peaks at 165.6(1C) and 163.3(2C). The remaining resonances fit the anisyl ethyl system nicely--the methoxyl at 56 ppm is a doublet when spread out. Recent publications on flavonoids provide structures and assignments closely enough related to support these deductions, which are consistent with ^1H nmr and mass spec observations.

Yours very truly,

Bob

R. J. Highet
Laboratory of Chemistry

J. V. Bardouille
Department of Chemistry
The University of Guyana
Georgetown, Guyana

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DEPARTMENT OF CHEMISTRY

concordia university

October 28, 1977

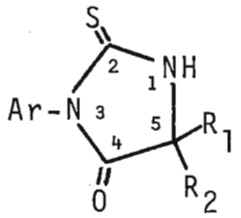
Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843
U.S.A.

^{13}C SPECTRA OF 3-ARYL-2-THIOHYDANTOINS

Dear Barry:

I apologize for the tardiness of this contribution to the newsletter.

For a while now, we have been determining the ^{13}C spectra of some nitrogen containing heterocycles. These include 3-aryl-2-thiohydantoins



where R_1 = H, CH_3; R_2 = H, CH_3, C_6H_5, and Ar = phenyl, o-tolyl, 2,3-dimethylphenyl, α- or β-naphthyl, o-halophenyl, 2-methyl-4-nitrophenyl, or 2-methyl-4-methoxyphenyl.

The principal chemical shift ranges (DMSO solutions, ppm) are as follows:

Dr. B.L. Shapiro October 28, 1977

C-2 (thiocarbonyl)	178.1 - 183.6
C-4 (carbonyl)	171.7 - 178.2
C-5 (unsubstituted)	49.2 - 49.5
C-5 (monomethyl substituted)	54.9 - 55.5
C-5 (dimethyl substituted)	59.3 - 61.6
Methyl (C-5)	15.3 - 17.3
Dimethyl (C-5)	22.7 - 25.3

The thiocarbonyl (C-2) and carbonyl (C-4) carbon signals show upfield and downfield shifts, respectively, upon introduction of methyl groups at C-5. However, the magnitude of these shifts is strongly dependent upon the nature of the substitution on the aryl group. Introduction of methyl groups at C-5 causes the expected downfield shifts on the C-5 carbon signal, the magnitude of the shifts again being dependent on the nature of the aryl group.

The chemical shifts of carbon atoms in, or substituted on, the hetero ring are sensitive to changes in substitution of the aryl group. Both electronegativity and steric effects of aryl group substituents appear to be important. Changes in the size of ortho substituents are likely to affect the dihedral angles between the two rings.

The data also suggest that changes in the extent of solvation of the carbonyl and thiocarbonyl groups resulting from changes in substitution patterns cause chemical shift changes. The thiocarbonyl (C-2) signal shows a marked solvent dependence.

Many of these compounds show the splitting of signals which results from slow rotation about the aryl C-N bond. Thus, all the compounds which have enantiomeric rotational isomers and which have a gem dimethyl group at C-5 show two C-5 methyl signals. Similarly, all C-5 monomethyl compounds which have diastereomeric rotational isomers show two C-5 methyl signals.

In principal, the C-2, C-4, and C-5 signals in those compounds having diastereomeric rotational isomers should also be split into two components. However, such splitting was observed only for the C-4 signals and then only in a few cases.

Best regards.

Yours sincerely,

L.D. Colebrook

M.A. Khadim

LDC,MK/ac

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DEPARTMENT OF CHEMISTRY, B-014
LA JOLLA, CALIFORNIA 92093

28 October 1977

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

Re: NUCLEAR RELAXATION AND VIBRATIONAL AVERAGES

Dear Barry:

Since vibrational motion is normally much more rapid than molecular reorientation in liquids, relaxation Hamiltonian operators used to describe the latter should first be vibrationally averaged. For ^{13}C-H dipolar relaxation, this fact implies that the appropriate "length" to use in the usual formula for dipolar relaxation is

$$r_{eff} = \langle \tfrac{1}{2}(3\cos^2\beta - 1)/r_{CH}^3 \rangle^{-\frac{1}{3}} = r_e + \langle \Delta z \rangle + \frac{2}{r_e}\{\langle \Delta x^2 \rangle - \langle \Delta z^2 \rangle\} \qquad (1)$$

Here β is the instantaneous angle between the CH vector and its equilibrium position (along a C_3 axis for this special case), r_e is the equilibrium bond length, $\langle \Delta x^2 \rangle$ and $\langle \Delta z^2 \rangle$ are harmonic oscillator mean square displacements, and $\langle \Delta z \rangle$ is an anharmonic correction. Diehl and co-workers[1] have pointed out that this r_{eff} is appropriate for use with dipolar coupling constants in liquid crystals.

Neglect of vibrational averaging can lead to large uncertainties in estimating correlation times from relaxation rate measurements. In chloroform, for example, the ratio r_{eff}/r_e is 1.123/1.1 = 1.0209 and use of r_e instead of r_{eff} would lead to ~13% low values for the correlation time.

Similar remarks apply to using relaxation rates for estimation of quadrupole coupling constants. For example, the familiar procedure of determining (e^2qQ/h) from measurements of ^2H and ^{13}C relaxation in appropriately isotopically substituted derivatives requires knowledge of r_{eff}^3. It follows that the uncertainty in (e^2qQ/h) is ~3 times larger than the uncertainty in r_{eff}, and that neglect of vibrational averaging can lead to apparent values for (e^2qQ/h) which are ~10% too large.

Since relaxation rates can, in favorable cases, be measured with accuracy approaching 1-2%, uncertainties of the magnitude noted above are annoying. They can be avoided if mean square displacements are available for the vibrations in question, if one believes that the procedure of using mean square displacements is correct!

At present we are not entirely convinced on this point. Bending and stretching normal modes are, after all, supposed to be independent motions and it is not clear to us whether a normal mode analysis of the vibrational problem would lead to Eq. (1). We would certainly appreciate enlightening comments on this matter.

Finally, we hope that the above will suffice to restore our subscription. The efficacy of your pink notice is matched only by the blizzard of local paperwork.

Sincerely,

Bob & Gitte

Robert L. and Regitze R. Vold

RL&RRV:mh

1. P. Diehl, S. Sykora, W. Niederberger and E. E. Burnell, J. Magn. Reson. 14, 260 (1974).

THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W.
Department of Organic Chemistry

2nd November, 1977

Professor B. Shapiro,
Department of Chemistry,
Texas A&M University,
COLLEGE STATION,
Texas 77843, U.S.A.

Dear Professor Shapiro,

Subject: SOME SUBSTITUENT EFFECTS ON ^{13}C-NMR SPECTRA OF LACTONES

Some years ago, Drs R.N. Johnson, J.B. Lowry, and myself reported on the synthesis and p.m.r. spectra of various butyro- and valerolactones, and derived conformational conclusions on these compounds in solution (1). Except in a few favourable cases, detailed analyses of the spectra to obtain the desired ring-proton vicinal coupling constants could be carried out only when gem-dimethyl and phenyl or other non-coupling substituents were present.

For ^{13}C-n.m.r. spectra, the currently more interesting parameters are substituent effects on chemical shifts and, as a result of the synthesis by Dr. Devinder Singh of all the gem-dimethylbutyro- and valerolactones, all (except 4-phenylvalerolactone, which has resisted various synthetic approaches) the phenyl-lactones, we are able to present the reference values in Tables 1 and 2. Broadly, the phenyl substituent shifts the resonance of the C atom to which it is attached downfield by 18-21 p.p.m., comparable with the effect (17.6 p.p.m.) in cyclohexane, but only by 12-13 p.p.m. if the phenylated C atom is attached to oxygen. The gem-dimethyl effects are more variable (5-16 p.p.m.) but all are much larger than that for cyclohexane (3 p.p.m.), and are perhaps enhanced slightly at the C atom attached to oxygen. These opposite effects may occur because the electon-attracting phenyl group calls the polarizability of the oxygen atom into play whereas the gem-dimethyl groups do not. We make no suggestion at present as to why the gem-dimethyl substituent effect at C2 (adjacent to the carbonyl group) is 5-8 p.p.m. less than at other positions; the 2-phenyl substituent-effect is not affected in this way.

For the gem-dimethylphenylbutyrolactones also synthesised by Dr. Singh, the substituent effects in Table 1 are roughly additive except at C3 for which there are discrepancies of up to 14 p.p.m. For the gem-dimethylphenylvalerolactones (resynthesized and studied here by Dr. A.I.R. Burfitt), additivity of the substituent effects in Table 2 occurs for only about 30% of the resonances, and we are still looking for some order in the results.

We thank Dr. David Doddrell and Mr. Peter Barron, of Griffith University, for measuring many of the spectra required for this study.

Yours sincerely,

N.V. Riggs

N.V. Riggs
Professor of Organic Chemistry

Table 1: SOME SUBSTITUENT EFFECTS[A] ON ^{13}C-NMR SPECTRA OF BUTYROLACTONE

	C1[B]	C2	C3	C4
PARENT[A]	177.9	27.7	22.2	68.6
2-Ph	-0.5	+17.7	+9.2	-2.1
3-Ph	-1.5	+7.8	+18.7	+5.3
4-Ph	-0.9	+3.2	+6.7	+13.2
2,2-diMe	-1.0	+9.4	+2.5	+11.0
3,3-diMe	-1.3	+15.0	+14.3	+10.5
4,4-diMe	-1.3	+6.8	+7.1	+15.9

Table 2: SOME SUBSTITUENT EFFECTS[A] ON ^{13}C-NMR SPECTRA OF VALEROLACTONE

	C1[B]	C2	C3	C4	C5
PARENT[A]	171.2	29.9	19.1	22.3	69.3
2-Ph	+6.9	+21.0	+11.3	+22.1	+6.4
3-Ph	+0.2	+11.3	+19.9	+12.8	-7.0
5-Ph	+0.3	+0.4	-0.8	+6.9	+12.1
2,2-diMe	+5.1	+5.0	+6.1	-1.6	+1.1
3,3-diMe	-0.4	+14.1	+10.6	+13.5	-3.1
4,4-diMe	+2.1	-0.6	+14.4	+11.7	+2.5
5,5-diMe	+0.4	+3.8	-2.4	+6.7	+13.0

[A]Values given for parent compounds are in p.p.m. downfield from TMS, those for substituted compounds in p.p.m. downfield from corresponding signal for parent.

[B]C1 is carbonyl C.

(1) Tetrahedron Letters, 1964, 2911-17; 1967, 5113-17, 5119-22. Aust. J. Chem., 1971, 24, 1643-58, 1659-66.

University of East Anglia

From Dr. R. K. Harris
Dr. K. J. Packer

School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ, ENGLAND
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR NORWICH

4th November, 1977

Dear Barry,

HIGH-RESOLUTION NMR OF THE SOLID STATE - PART 2

In response to your pink letter, we would like to describe progress with our home-built cross-polarisation spectrometer. We cannot claim any great novelties, since we are treading in the footsteps of others, but we are quite excited about the possible applications of the techniques. After some frustrating experiences with a double-coil system we changed over to the single-coil circuitry as described by Vaughan et al[1]. We are very pleased with the results, which represent a gain in S/N of ca. 3 over our previous best. We have also been able to improve the computing side of the spectrometer system by purchasing a Diablo disc accessory and a Hewlett-Packard Display Station (which is really fun to play with). Magic-angle spinning has been instituted using the simple design of Schaefer, Stejskal and Buchdahl[2], and the attached figure shows the results of 16 minutes spectrometer time on the "standard" PMMA machined sample, using phase-alternated pulse sequences. There is still an annoying baseline problem which we are having difficulty tracing, but we feel we are in a position to commence applications work now-and there are plenty of experiments we want to try. This year our joint research group on this project consists of 6½ people, so we hope to be able to report plenty of results before very long.

With best wishes,

Yours sincerely,

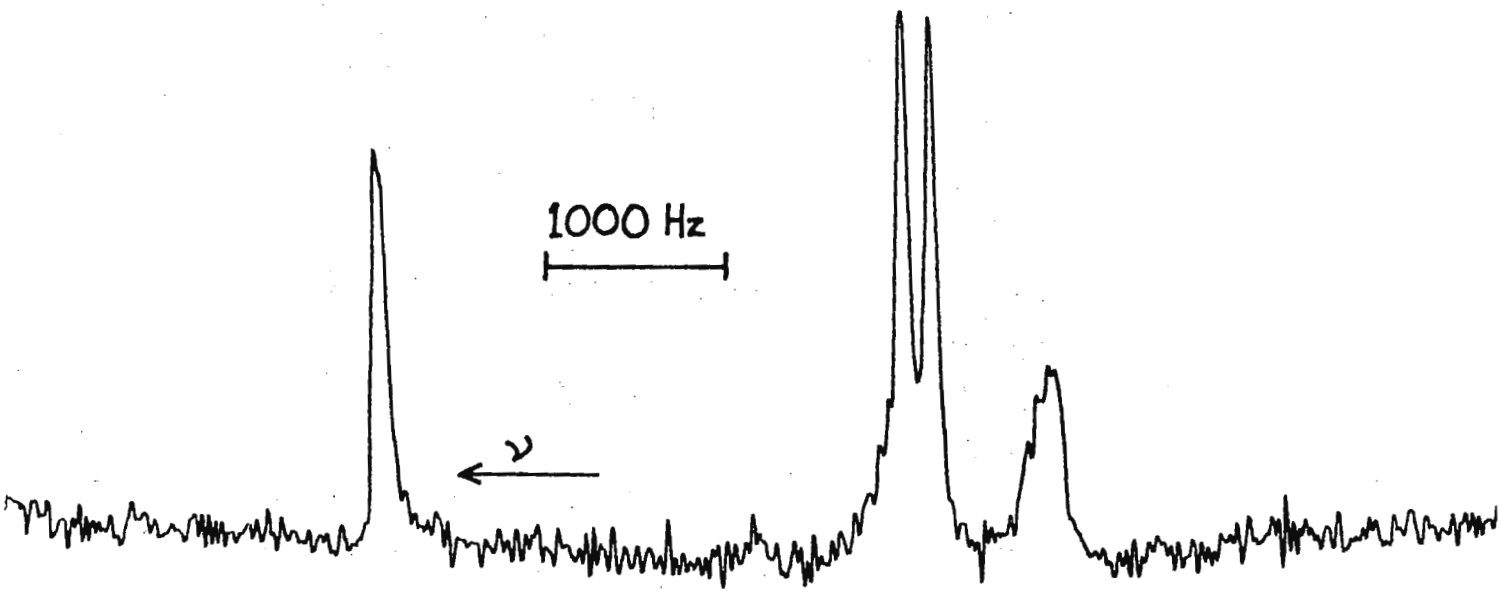
Robin Ken

R. K. Harris K. J. Packer

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

1. M. E. Stoll, A. J. Vega and R. W. Vaughan, Rev. Sci. Instrum. 48, 800 (1977).

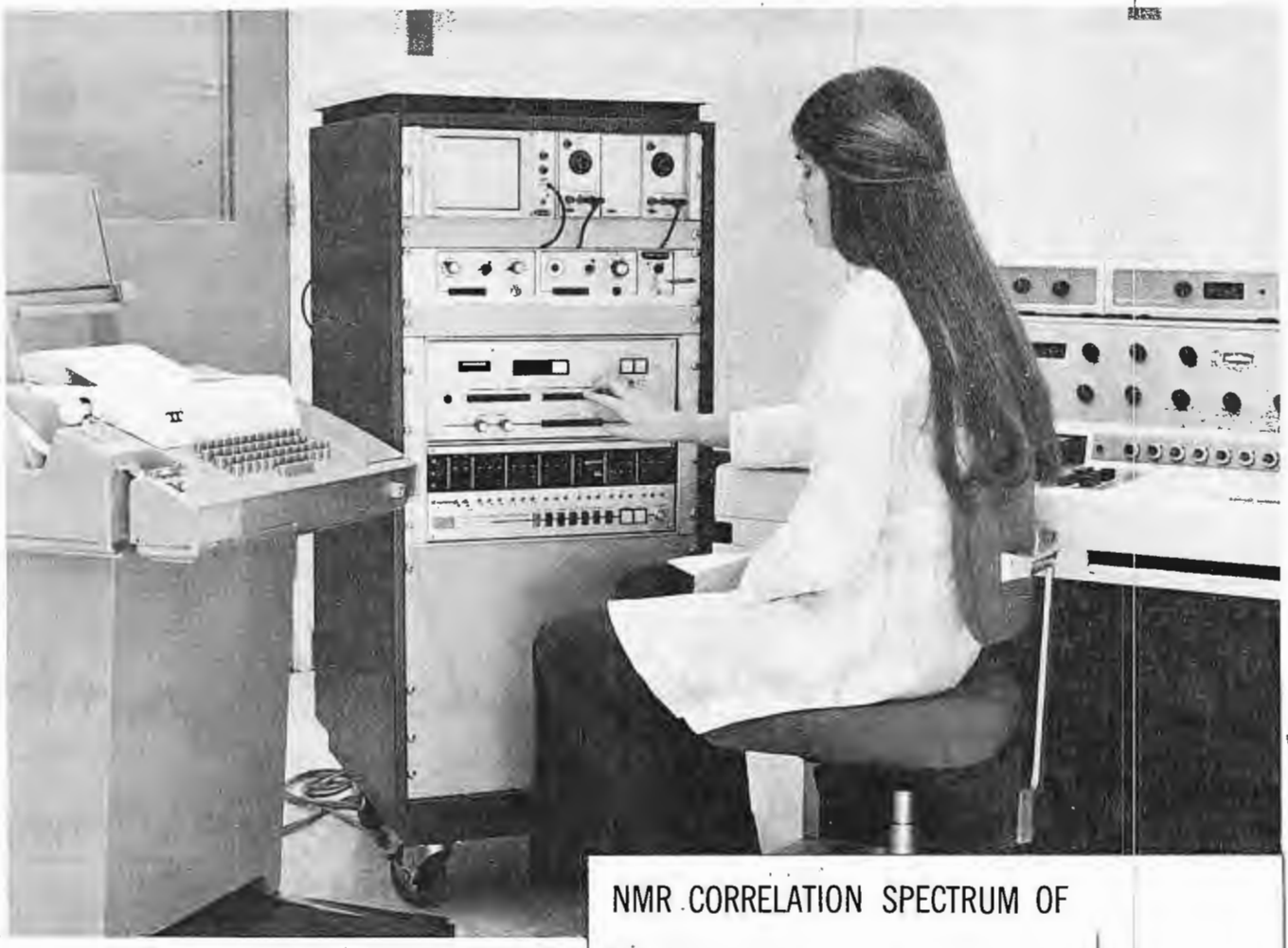
2. J. Schaefer, E. O. Stejskal and R. Buchdahl. Macromolecules 10. 384 (1977).



22·6 MHz ^{13}C-{^{1}H} (dipolar-decoupled) NMR SPECTRUM
of SOLID POLY(METHYLMETHACRYLATE)
with magic-angle spinning (~ 3 kHz)

cross-polarization contact time 3 ms
recycle delay time 1 s (single contact)
1000 cycles
1 K points acquired ; zero-filled to 4 K
dwell time 64 μs

APPROACH THE SPEED AND SENSITIVITY OF PULSE FT-NMR ON YOUR CW SPECTROMETER USING A NICOLET NMR-80 DATA SYSTEM FOR RAPID SCAN CORRELATION NMR SPECTROSCOPY



Rapid scan correlation NMR spectroscopy offers these advantages over CW techniques:

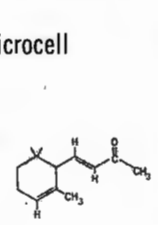
1) Greater sensitivity per unit time,
2) Greater sample throughput per unit time, and
3) The ability to follow fast reactions and produce meaningful data.

Rapid scan correlation NMR spectroscopy offers these advantages over pulsed techniques:

1) Power distribution over spectrum is exactly square and independent of sweep width.
2) Large solvent resonances can be avoided by sweeping only a small part of the total spectrum.
3) Resolution is increased because the final spectrum occupies all of data memory.

NMR CORRELATION SPECTRUM OF

50 μg ∝-ionone in spherical microcell
128 scans, 11 sec. per scan
TOTAL TIME 23 min.
Signal/Noise (Peak to Peak) of methyl peaks = 36:1



This spectrum of 50 micrograms of ∝-ionone was obtained by correlation NMR in 23 minutes. Normal CW averaging techniques would require over 4 hours.

For more information on the Nicolet NMR-80 data system for rapid scan correlation NMR spectroscopy please write or phone.

NICOLET INSTRUMENT CORPORATION
5225 Verona Road
Madison, Wisconsin 53711
Telephone: 608/271-3333

Photo and spectrum supplied by Varian Instrument Division, Palo Alto, CA.

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129
817-926-2461

Department of Chemistry

November 4, 1977

Dear Barry:

In his theoretical derivation of the relation between solution viscosity and dielectric relaxation Debye stipulated that the viscosity referred to was an experimentally inaccessible microviscosity. Given the possibilities of solute-solute, solute-solvent, and solute-solvent interactions the use of an experimental translational kinetic viscosity for dielectric or NMR relaxation studies will certainly be safer for studies of one solute in differing concentrations in one solvent. Dr. Allerhand (TAMUNMR 229) is correct; I (TAMUNMR 227) did not understand that the cholesteryl chloride determinations of he and his colleagues were in a varied series of solvents. This was pointed out to me by another but not in time to alter my statements in Vol. 227. Let my apology take the form of two papers and a review chapter, all in press, each of which acknowledges the value or the contributions made in his ground-breaking paper.

I don't regret having made the measurements on cholesteryl chloride since they were not a repeat of anyone's work and did lead to the realization that such relaxation measurements could be used to assess steroid aggregation. To add something new to this discussion, it is doubtful that chemical shift measurements can be used for a similar purpose - the case in point being the recent observation by Fendler and Rosenthal (TAMUNMR 221) that the chemical shifts of the carbons in methyl cholate move upfield with increasing concentration in deuterochloroform.

The chemical shifts of several of the carbons of methyl cholate are given here against TMS as an internal standard and as a function of concentration at 35°.

C	0.25M	0.33M	0.5M	0.83M	1M
3	71.92	71.95	71.94	71.90	71.82
12	73.07	73.13	73.10	73.01	73.01
21	17.36	17.34	17.34	17.32	17.34
18	12.49	12.49	12.49	12.49	12.49
$CDCl_3$ (center)	77.07	77.11	77.20	77.21	77.28

The insensitivity of the methyl cholate chemical shifts to concentration is evident. What is also evident is a downfield shift of the $CDCl_3$. This suggests that they were using the $CDCl_3$ as their internal standard and actually measuring the hydrogen bonding of the solvent to the steroid.

Best regards,

Bill

William B. Smith

bw

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INSTITUTE OF ORGANIC CHEMISTRY
KARLSTRASSE 23

GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

November 7, 1977

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

Direct Analysis of Very Intricate Nmr spectra

Dear Barry:

We'd like to have you meet DAVIN the First, who, though in strict fact being only a computer program, has, since first seeing the light of day as a tottering infant 27 months ago, now, after exposure to much hardship and painful experiences during adolescence, attained a state of maturity, though not yet perfection, and in the course of the hardening process acquired some character traits of a veritable personality, such as pride, independence, unpredictability, arrogance, but fortunately also dependability and efficiency; so we thought he deserved a pronounceable acronym.

DAVIN1 was engendered in the hope that he might eventually manage to analyze unsaturated steady-state NMR spectra automatically for chemical shifts, isotropic coupling constants, exchange rates, relaxation parameters and even impurity peaks under the following constraints: (1) The full information content of a spectrum should be used, *i.e.* the total bandshape. (2) His performance should not depend on any preconceived notions about the parameters, *i.e.* he should be capable of starting from random numbers. (3) No trial calculations and no assignments of lines or energy levels should be necessary. (4) For static spectra the only additional piece of information (beyond the digitized bandshape) to be supplied by the human operator should be the theoretical model, *i.e.* the type of spin system. (5) Extensive overlap of peaks or noise should be no obstacles. (6) The error output should give an objective representation of the true information content of the spectrum. (7) DAVIN1 should know when he has ended up in a false local minimum and should be capable of extricating himself without external intervention.

The crux of the matter is the last problem; once a satisfactory solution for it has been found, the rest is comparatively trivial. And in this context it proved crucial to adopt the right attitude. Most past attempts along similar lines have been based on the explicit or implicit hope that such pathological behavior might, with luck and by exploiting empirical knowledge and intuition to the utmost, be the exception, but it is obvious that just the opposite must be true if one insists on condition 2: The probability of not getting trapped in false local minima without special tricks is so minute that one may as well forget about it. To have recognized this fact clearly at the very inception of our work one of us owes much to Peter Diehl, who in a private lecture on the occasion of a visit to Basel in December 1974 supplied some of the essential physical and mathematical insights. Part of the work of Diehl's group has in the meantime been published (*JMR* 19, 67 (1975); *OMR* 8, 638 (1976)). Superficially, our own approach looks very different: we do not make use of integral transforms or of expansions into basis functions. But as we shall show in the paper which we hope to write in the near future, Diehl's method is in fact reducible to ours (albeit not the other way around). Incidentally, Diehl's method remains decidedly superior in those cases where only part of the spectral information is used, especially when this information consists of a large body of discrete line frequencies for spectra of oriented molecules; so anybody wishing to tackle such problems should by all means stick to Diehl's procedure.

We elaborate on four of DAVIN's peculiarities. *Pride*: We sometimes try to help him by starting with educated guesses of the parameters, but he is wont to proudly reject the offer. The first thing he does is to switch the nuclear labels, so that everything becomes completely garbled again, and then approaches the global minimum from an entirely unexpected direction. But just when you begin to get used to this characteristic and suspect that it might somehow be built into his chromosomes, he surprises you the next time around by gracefully accepting good advice and heading for the global minimum like a shot; that's his *unpredictability*.

To illustrate his *dependability* we show (Figure) four static ABCD spectra synthesized from parameter sets obtained by a random number generator. Each spectrum was selected as a target spectrum and in each case we started with the parameter sets corresponding to the remaining three spectra. The results are collected in the success-failure matrix $\underset{\sim}{S}$ shown below. It just so happens that there are no negative off-diagonal elements in this particular case. The integers indicate the number of "grand cycles" (to be explained in our paper) needed to find the correct solution. An objective evaluation of DAVINS's performance will have to await the feedback from a few colleagues whom we intend to ask to independently try him on tough cases.

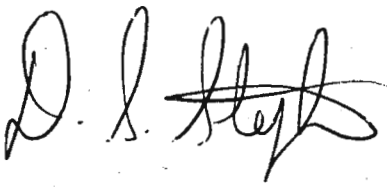
$$\underset{\sim}{S} =$$

0	2	2	1
2	0	2	2
2	1	0	1
3	3	2	0

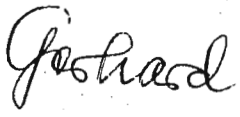
These examples also give an idea of DAVIN's *efficiency*: 2-4 minutes of CPU time on a CDC CYBER 175 were needed in each case. We have not yet found the time to optimize the code. We may or may not do a little along these lines before making DAVIN1 available to the general public through QCPE. Other people are then welcome and encouraged to work on improvements.

In closing we offer a piece of frivolous advice to NMR spectroscopists short of research money. The next time you have to buy an NMR instrument, order one without a recorder; you don't need that part any more unless, of course, you insist on being so old-fashioned as still wanting to *see* your spectra.

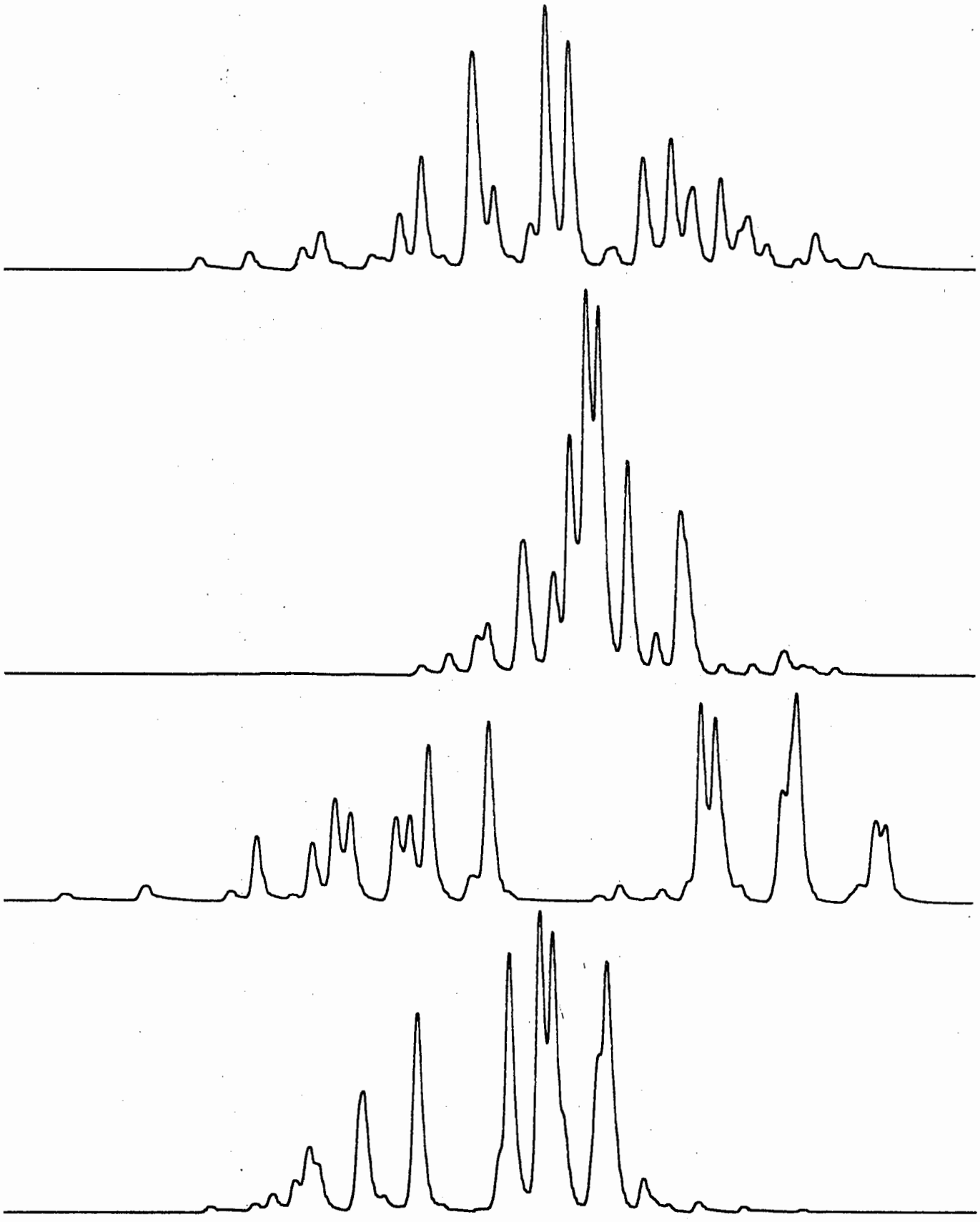
Sincerely yours,



David S. Stephenson



Gerhard Binsch



Figure

231-37

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TELEX 31679 MONTEDIS

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

Proton chemical shifts in sulphuric acid of some oxygenated products

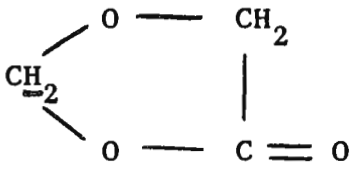
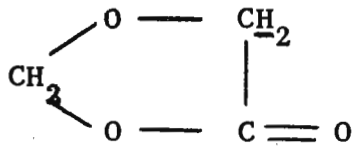
Dear Prof. Shapiro,

One of the methods of industrial production of ethylene glycol is the carbonylation of formaldehyde to glycolic acid, followed by hydrogenation. During a study of the carbonylation reaction in sulphuric acid, we followed it with ^1H n.m.r. Since sulphuric acid, used as a solvent, is a medium with peculiar interactions solute - solvent, it was necessary to establish some correlation between chemical shift and structure in order to identify the reaction species of the system $CH_2O - CO - H_2SO_4$. Then we prepared some of the possible reaction products and run the spectra in 100% sulphuric acid with HMDS as external reference. Table I collects the observed chemical shifts. The corresponding values in $CDCl_3$ are about 0.5 ÷ 1.5 p.p.m. at higher field; this is normally attributed to the strong acidity of the medium which promotes the formation of protonated ionic species[1]. In some molecules two sites are allowed for the protonation: the ether and the carboxyl groups. The observed chemical shifts can help us to decide which is the preferred site. However we must take into account the possibility of medium effects.
One procedure uses the intramolecular shift between two groups (e.g. CH_2 and CH_3 of the same molecule). In the cases where this is possible the values of the intramolecular shift observed in $CDCl_3$ and H_2SO_4 support the hypothesis that the preferred site for the protonation is the ether one.
This is in agreement with the greater donicity[2] of the oxygen in the ether group compared to the carboxyl group.

Yours sincerely

E. Santoro, M. Tampieri

TABLE 1 - Proton chemical shift (δ scale, ext. ref. HMDS) in 100% sulphuric acid.

p.p.m. *	
6.1_6 (5.5_2)	
6.0_3	$(CH_2O)_n$
6.0_3 (4.5_8)	$CH_3O-CH_2-OCH_3$
5.9_8 (4.7_0)	$CH_3OOC-CH_2O-CH_2-OCH_3$
5.5_7	$HOOC-CH_2-O\,SO_3H$
5.4_7 + 5.5_1	$HOOC-(CH_2-OOC)_n-CH_2OH$
5.4_2	$HOOC-CH_2-OH$
5.3_5 (4.1_7)	$CH_3OOC-CH_2OH$
5.1_0	$HOOC-CH_2-O-CH_2COOH$
5.0_7 (4.2_1)	
5.0_7 (4.1_7)	$CH_3OOC-CH_2-OCH_3$
5.0_7 (4.1_7)	$CH_3OOC-CH_2-O-CH_2-OCH_3$
4.4_8 (3.4_5)	CH_3OH
4.4_5 (3.4_0)	$CH_3O-CH_2-COOCH_3$
" "	$CH_3O-CH_2O-CH_2-\ COOCH_3$
" "	$CH_3O-CH_2-OCH_3$
4.4_1 (3.7_5)	$CH_3OOC-CH_2OCH_2OCH_3$
4.4_1 (3.7_8)	$CH_3OOC-CH_2OCH_3$
" "	$CH_3OOC-CH_2OH$
3.0_6 (2.1_0)	CH_3COOH

* The values within the parenthesis are the chemical shift measured in $CDCl_3$ (int. ref. TMS).

1) R.J. Gillespie and T.E. Peel, "Adv. in Phys. Org. Chem." Vol. 9 Pag. 1, Edited by V. Gold, Acad. Press N.Y. (1971).

2) V. Gutmann "Chem. Tech." 255 (1975)

McGill University
Department of Chemistry
Pulp and Paper Building

November 11, 1977.

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

Dear Dr. Shapiro:

The choice of a reference, or field-frequency lock, compound for p.m.r. spectra of D_2O solutions presents some difficulties. A commonly used internal standard is DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate), but because this compound gives peaks in the region of 0.5-3.0 p.p.m., related perdeuterio compounds are being marketed as alternatives. In either case, if the sample is to be recovered, this type of reference compound becomes a contaminant that may not be removed easily. On the other hand, if a TMS capillary is used, it is difficult to maintain a stable lock at temperatures above 60°C because of the high volatility of TMS.

In this laboratory, we routinely use tetramethyltin (TMT) in a capillary as an external reference with D_2O solutions. Because of its relatively high b.p. (78°C), TMT provides a stable lock at higher temperatures than attainable with TMS. In addition to this advantage, however, it turns out that the observed chemical shifts for compounds in D_2O are very close to those obtained with internal DSS whereas, characteristically, a capillary of TMS produces a large downfield displacement. This is shown for dioxane and methanol in the Table below, and analogous data for higher molecular weight compounds can be cited.

Postal address: 3420 University Street, Montreal, PQ, Canada H3A 2A7

Professor B.L. Shapiro November 11, 1977

	Dioxane		CH_3OH		
	in D_2O	in $CDCl_3$	in D_2O	in $CDCl_3$	in $(CD_3)_2CO$
int. DSS	3.70 p.p.m.	--	3.33	--	--
int. TMS	--	3.66	--	3.41	3.32
ext. TMS	4.14	4.13	3.72	3.81	3.15
ext. TMT	3.67	3.64	3.24	3.33	2.66

With $CDCl_3$ as a solvent, one occasionally finds that the introduction of sufficient TMT for a strong lock, causes precipitation of the sample. Here, again, the TMT capillary is useful because of the virtual coincidence of observed chemical shifts relative to the external TMT as compared with internal TMS (Table).

Presumably, the close correspondence in chemical shifts between external TMT and internal DDS in D_2O, or TMS in $CDCl_3$, is a consequence of an almost exact balance between chemical shift and bulk diamagnetic susceptibility differences. This is suggested also by the fact that quite different results are obtained with a solvent such as hexadeuteroacetone (Table). That is, the volume magnetic susceptibilities of water and chloroform are approximately the same, whereas that of acetone is much lower.

Yours sincerely,

N. Cyr
R. Simoneau
S. Katz
A.S. Perlin

ASP/ce

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

November 15, 1977

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

Dear Barry:

Broadband Multi-Nuclei Operation on the FT-80

We've now had some time to explore the possibilities of the broadband accessory for the FT-80. The device uses a PRD synthesizer to generate an LO frequency 2.25 MHz below the nominal observe frequency. After mixing with the phase-selectable 2.25 MHz reference frequency, the observe frequency is routed through a broadband power amplifier and to the probe. Howard Hill and John Lautermilch have developed a tunable probe covering the range of 5-35 MHz, allowing observation of any nucleus from ^{14}N through ^{31}P. Tuning is accomplished in a single meter and one variable tuning capacitor. Their new design has allowed sensitivity to match dedicated single frequency probes across the frequency range, i.e., ^{31}P ~100:1 for 10% trimethylphosphite, ^{13}C ~150:1 90% ethylbenzene and ^{17}O ~50:1 25% D_2O. Protons and fluorine also have been run, with excellent resolution in the same probe (fig. 1, 30% ODCB). It's been fun looking at ~20 nuclei, including some "least" common nuclei such as ^{33}S (fig. 2) and ^{55}Mn (fig. 3). In the latter case, crown-ether solubilization of $KMnO_4$ in benzene can be studied conveniently via the ^{55}Mn resonance when the complexation of the K^+ leaves the MnO_4^- in solution, experiencing a 15.2 ppm deshielding, a linebroadening of a factor of 6, and a reduction of T_1 to ~4 ms. At the suggestion of Jaques Reuben I looked at the ^{17}O NMR of $Fe(CO)_5$ (fig. 4). The good sensitivity and remarkably narrow line should interest the metal carbonyl chemists since it should also be the case in other metal carbonyls even in less symmetric environments.

Jim Shoolery has been active in exploring the utility of deuterium and lithium NMR. He's particularly interested in the use of ^2H chemical shifts as accurate input data for simulations of complex second order proton spectra. See you at ENC.

Sincerely yours,

George A. Gray, Manager
NMR Applications Laboratory
Instrument Division

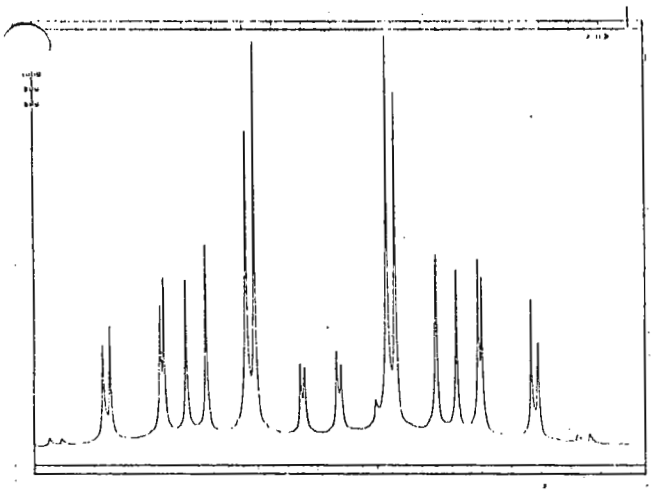


Fig. 1. 30% ODCB ^{1}H Observe. 16 sec AT, 19 Transients. 40 Hz Plot, 10 mm Tube. FT-80

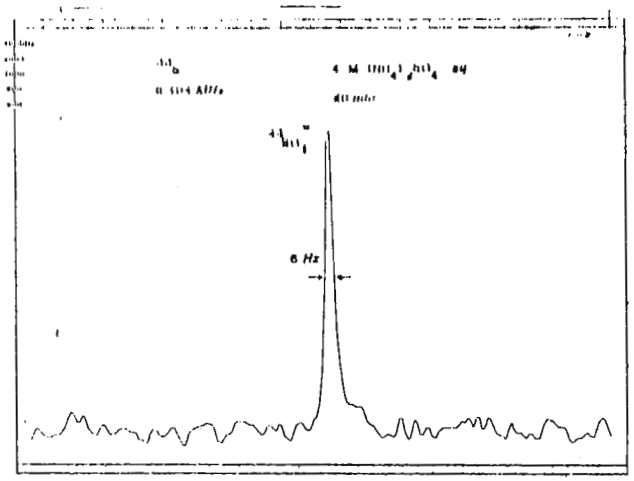


Fig. 2. ^{33}S Observe. 10 mm Tube. D_2O Internal Lock.

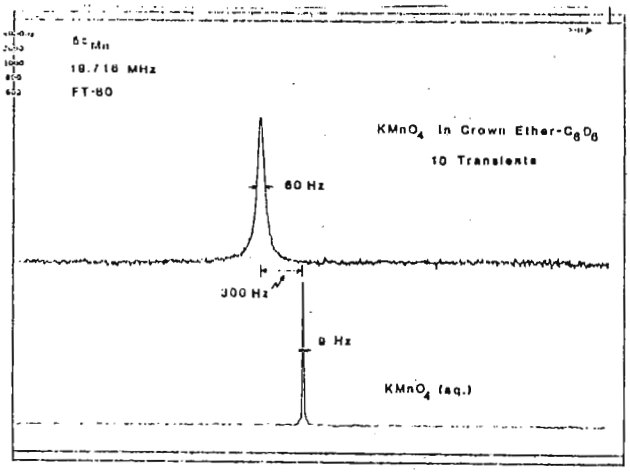


Fig. 3. ^{55}Mn Observe. 10 mm Tube

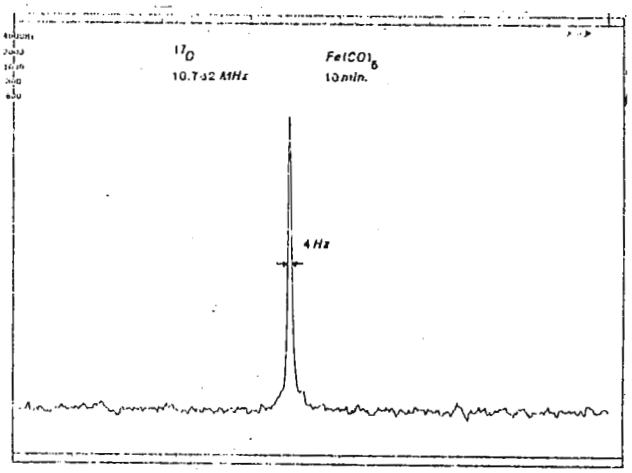


Fig. 4. ^{17}O Observe. 10% C_6D_6 Lock.

ABBOTT

231-43

Scientific Division

Abbott Laboratories
North Chicago, Illinois 60064

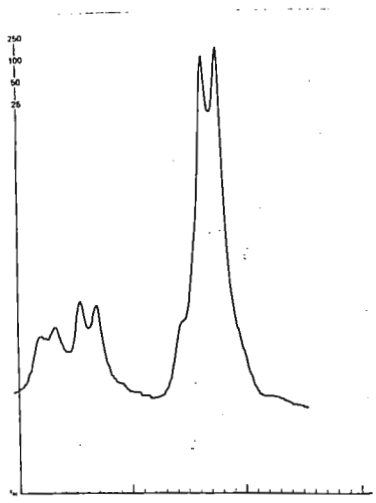
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Neighboring Group Effects in PMR of Glucans

Dear Barry,

PMR has been widely applied in the determination of the anomeric composition of polysaccharides. Recent publications have outlined results obtained with starches (1,2) and dextrans or glucans (3,4) whose PMR typically demonstrate separate anomeric proton resonances for each of the α-D linkages present.

Dental caries producing strains of Streptococcus mutans elaborate extracellular glucans which have been chemically characterized as "highly branched" - that is, contain a high proportion of α-D (1→3) linkages compared to the α-D (1→6) linkages which generally predominate. PMR studies of these compounds have been conducted in a 9:1 DMSO-d6:D_2O mixture for improved solubility and give rise to 100 MHz spectra as shown in the figure. Spectra recorded at 270 MHz confirm that four separate anomeric resonances are present - a major resonance at 4.75 ppm with a partially obscured minor resonance at 4.80 ppm both in the chemical shift range associated with α-D (1→6) linkages and two lower field resonances at 5.00 and 5.09 ppm arising from non-α-D (1→6) linkages. This multiplicity of resonances was an unusual observation and led to additional studies to determine its origin.



CMR studies conducted by Dr. Ian C.P. Smith at the NRC in Ottawa clearly revealed that only α-D (1→6) and α-D (1→3) linkages were present thereby eliminating other linkages as the source of the additional peaks. This led to the supposition that the doubling arises from a neighboring group effect - α-D (1→3) linkages adjacent to α-D (1→3) or α D (1→6) for one pair, and α-D (1→6) linkages adjacent to α-D (1→3) or α-D (1→6) for the other pair with the latter condition likely associated with the major peak.

This supposition was confirmed and specific resonance assignments were possible when such a glucan was treated with Worthington dextranase which specifically cleaves α-D (1→6) linkages and the products of that treatment were examined by PMR. The enzy-

matic hydrolysis was performed by Dr. B.L. Lamberts, Naval Dental Research Institute, Great Lakes, IL. The water insoluble residue which remained after treatment contained 90% or more α-D (1→3) linkages and its PMR exhibited only the 5.09 ppm resonance thereby assigning this resonance to α-D (1→3) adjacent to α-D (1→3) linkages. The PMR of the water soluble material present in the supernatant revealed major resonances at 5.00 and 4.80 ppm assignable to α-D (1→3) adjacent to α-D (1→6) and α-D (1→6) adjacent to α-D (1→3) linkages, respectively. The 4.75 ppm resonance associated with α-D (1→6) adjacent to α-D (1→6) linkages is very much reduced as would be expected after dextranase treatment.

A recent publication (5) has reported a similar effect in Lichenin, a polysaccharide containing β-D (1→4) and β-D (1→3) linkages. However, this is the first report of such a neighboring group effect in glucans and it offers an important new insight into the structure of these compounds. Full details of these studies will be presented in a forthcoming publication.

(1) G.G. Burch and M.S.A. Kheiri, Carbohyd. Res., 16, 215 (1971).

(2) W.N. Pasika and L.H. Cragg, Can. J. Chem., 41, 293 (1963).

(3) T. Usui et. al., Carbohyd. Res., 33, 105 (1974).

(4) R.L. Sidebotham, Advan. Carbohyd. Chem., 30, 371 (1974).

(5) G. Gagnaire et. al., Tetrahedion Lett., 3953 (1975).

Sincerely,

Rich

Richard S. Egan, Ph.D.
Structural Chemistry Section

UNITED STATES DEPARTMENT OF ENERGY
PITTSBURGH ENERGY RESEARCH CENTER
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

The Carbon Aromaticity Problem in Coal Research

The carbon aromaticity ($f_a = C_{ar}/C$) has been one of the most elusive chemical structure parameters in coal research. f_a Values for Pittsburgh Coal as a function of time (well, not really! - actually as a function of experimental technique) are presented in the upper left figure on the accompanying page. The plot illustrates the present state of confusion; note that some of the values differ by such large amounts, that they reflect essentially qualitative disagreements.

Recent developments in NMR instrumentation and techniques have greatly improved the situation with regard to coals and coal-derived materials. For the sake of discussion, it is convenient to classify these materials as follows: (1) those soluble in solvents suitable for direct studies by ^{13}C NMR, (2) those soluble in conventional ^{1}H NMR solvents, and (3) those materials which are essentially insoluble in any solvent.

Materials such as carbonization oils and carbon disulfide extracts of coals can be examined directly by correlation mode or FT ^{13}C NMR. If one is willing to take the time to do the experiments properly, unambiguous f_a values can be obtained. f_a Values for CS_2 extracts of selected coals are plotted in the figure at the upper right. We are convinced that many published ^{13}C NMR f_a values for coal-derived materials are low because sufficiently long time delays between pulses were not allowed.

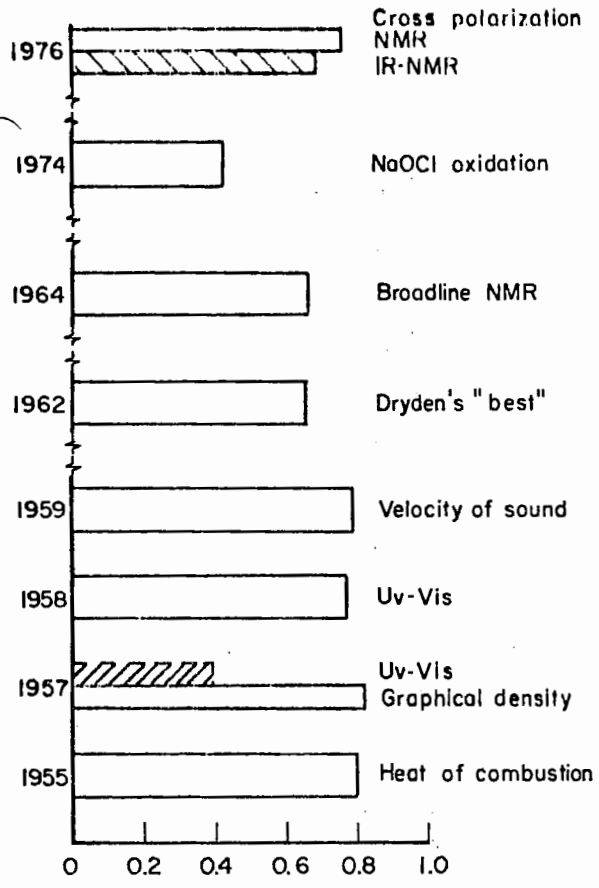
A number of coal-derived materials are soluble in solvents suitable for ^{1}H NMR studies, but not suitable for ^{13}C NMR studies. For these materials we rely upon the Brown and Ladner method (Fuel, 48, 21, 1969). The usefulness of the method can be deduced from the figure in the lower left which compares Brown and Ladner-type f_a' values for the CS_2 soluble portions of a large variety of materials from coal with the corresponding f_a values obtained by correlation-mode ^{13}C NMR. f_a Values for pyridine extracts of coal (upper right) have been determined by this method.

For solid samples, such as whole coals or their petrographic components, we have found that the cross-polarization ^{13}C NMR technique gives reliable f_a values. Results for vitrains from selected coals are plotted in the upper right figure; representative CP NMR spectra of macerals from Hernshaw hvAb coal are shown in the lower right figure. Our confidence in the quantitative reliability of the CP technique stems from a study of soluble fractions from coal in which we found good agreement between the CP f_a values on the solid samples and the correlation mode values on the same samples in solution.

Herb

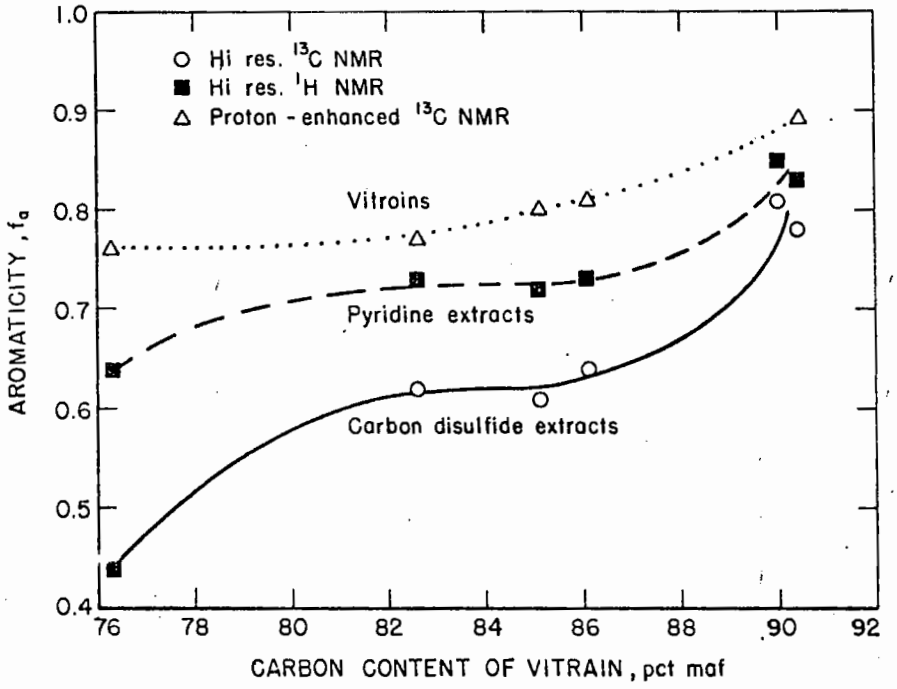
H. L. Retcofsky
Chief
Molecular Spectroscopy Branch

November 16, 1977



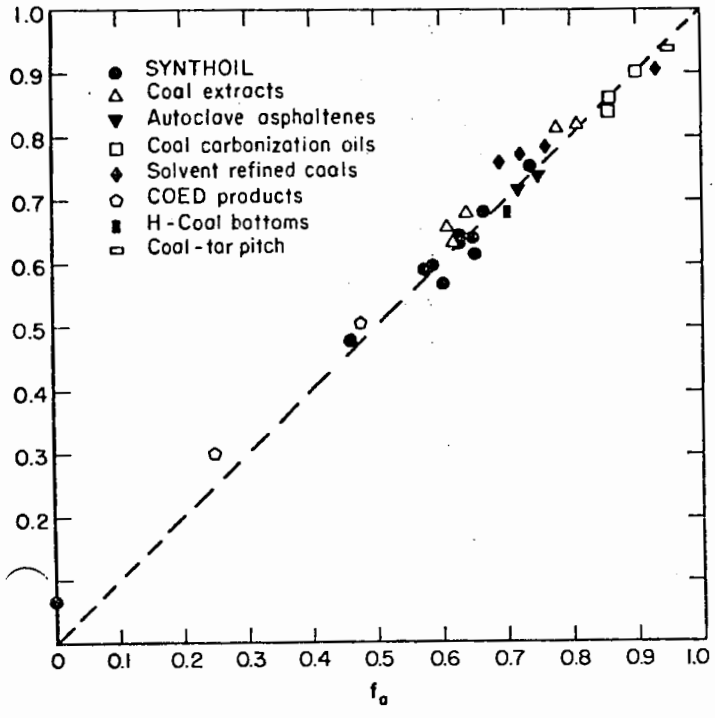
Carbon aromaticities for 82.6 % C coal

L-14827



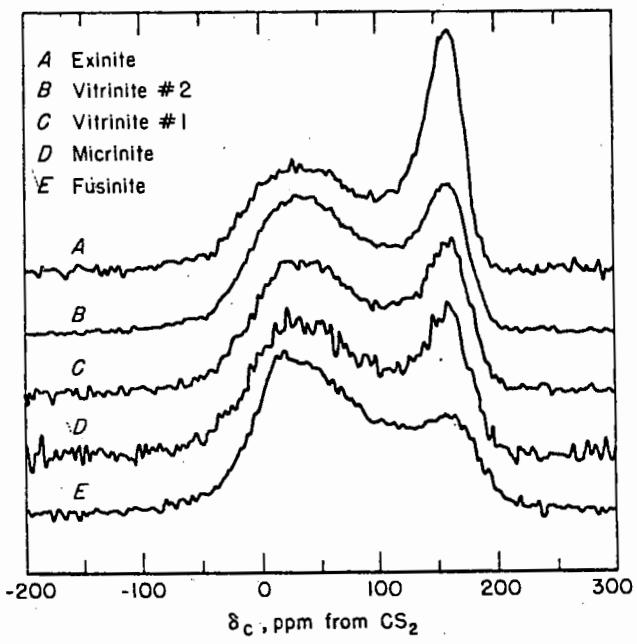
Aromaticities of coals and coal extracts.

6-16-76 L-14916



Comparison of proton and carbon-13 aromaticities for materials derived from coal.

6-16-76 L-14917



Cross polarization ^{13}C NMR spectra of macerals from Hernshaw coal.

9-7-77 L-15581

231-47

Dr. W. Bremser o/o
BASF Aktiengesellschaft
Hauptlaboratorium

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

Texas 77843

U S A

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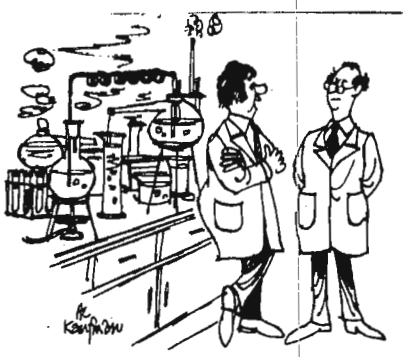
		WHE-WBr/Dg	(0621) 60- 8401	464-	18.11.77

Betreff

Dear Barry,

Systematics of coupling constant registers

Harald Günther made a very valid point in his recent contribution [1] where he demonstrated that the classical description of coupling constants only by means of the elemental composition of and the distance between the interacting nuclei is not sufficient to classify larger numbers of coupling constants. Hybridisation and bond character as well as changes in electron density by electronegative substituents should be taken into account.



"Why be systematic? Most great discoveries have been made by accident."

In our ^{13}C-NMR-data collection we use the HOSE-substructural codes [2] to describe the environment of the coupling carbon atoms. The registers are inverted to either the numerical value of the coupling constants or the structural characteristics. The latter is illustrated in the accompanying printout of a file of 6000 C-X-coupling constants (a separate file of similar size and arrangement exists for C-H-couplings). The first column contains the "classical" descriptor arranged with increasing number of bonds and aliphabetical order of the coupling partner. Then the substructural codes

g.-Nr. 9030210

Betreff

characterising type and bonding of the α-, β-, and γ-substituents follow. They are arranged according to the priority rules defining the numerical value of the code. Last criterion for the order is the size of the coupling constants. The entries on the rigth hand side lead to the corresponding references and atom numbers in the data collection.

The register of coupling constants presented in this example prooved to be very helpful reference material in everyday spectroscopic work of elucidating or verifying chemical structures and assigning resonances.

Best regards,

Wolfgang

W. Bremser

1) H.Günther, TAMU-NMR 220-22

2) Hierachiaally Ordered Spherical Representation of Environment

	*C*C(*C,*C/*C,*&/*&C)	0.4	14908-0-06	14907-0-12	14907-0-06	5690-1-05
	*C*C(*C,*C/*C,*&/*&C)	0.3	14906-0-06	14906-0-12		
5J(C,F)	*C*C*C(*C*C,*C,*C/*CF,*	1.5	3445-0-10	3445-0-10	3445-0-10	
	*C*C*C(*C*C,*C,*C/*C,*C,	0.7	3426-0-10	3426-0-10	3426-0-10	
	*C*CC(*C,*C,FFF/*C,*:	1.0	3420-0-01	3420-0-01	3420-0-01	3420-0-04
			3420-0-04			
	*C*C(*C*C,*CC/*C*C,*C,*:	1.5	4760-0-05			
	*C*C(*C*C,*CC/*C*C,*C,*:	1.2	4761-0-05	3446-0-05		
	*C*C(*C*C,*C/*C*C,*CF,*	1.0	3444-0-08	3444-0-08	3444-0-08	
	*C*C(*C*C,*C/*C*C,*C,*&	1.2	3447-0-05	3424-2-05	3424-3-05	
	*C*C(*C*C,*C/*C*C,*C,*&	1.0	3448-0-05	3448-0-05	3448-0-05	
	*C*C(*C*C,*C/*C*C,*C,*&	0.1	3424-1-05			
	*C*C(*CC,*C/*C*C,FFF,	5.9	3444-0-06			
	*C*C(*CC,*C/*C*C,FFF,	0.5	3448-0-07			
	*C*C(*CC,*C/*C,=OC,*C*&	0.7	4760-0-07			
	*C*C(*CC,*C/*C,C,*C*&/*	0.6	4761-0-07			
	*C*C(*CC,*C/*C,FFF,*C	1.0	3445-0-06			
	*C*C(*CC,*C/*C,FFF,*C	0.9	3446-0-07			
	*C*C(*CC,*C/*C,FFF,*:	1.2	3419-0-06	3419-0-06	3419-0-06	3419-0-04
			3419-0-04			
	*C*C(*C,*C/*C*C,*&/*C*:	1.7	3435-0-06			
	*C*C(*C,*C/*C*C,*&/*C*:	1.2	3424-0-07			
	*C*C(*C,*C/*C*C,*&/*C*:	0.9	3424-3-07			
	*C*C(*C,*C/*C*C,*&/*C*:	0.7	3424-2-07			
	*C*C(*C,*C/*C*C,*&/*C*:	0.3	3443-0-06			
	*C*C(*C,*C/*C*C,*&/*C*:	0.1	3424-1-07	362-2-06		
	*C*C(*C,*C/*C,*&/*&C)	1.3	634-1-04	634-1-04	634-1-04	
	CFFF(*C*C,,,/*C*C,*C,	0.3	3444-0-11			
5J(C,HG)	*C*C(*C,*C/*C,*&/*&C)	32.0	1463-0-12	1463-0-05		
6J(C,C)	*C*C(*C*C,*C/*C*C,*C,*C*	0.3	1412-0-05			
	*C*C(*C,*C/*C*C,*C*&/*C	0.8	1142-0-07			
	*C*C(*C,*C/*C*C,*C*&/*C	0.7	1143-0-07			
6J(C,F)	=C(C/*C*C/*C,*C)	1.9	3423-0-08			
	*C*CC(*C,*C,=OC/*C*C,*&	2.6	4760-0-06			
	*C*CC(*C,*C,C/*C*C,*&,=	2.7	4761-0-06			
	*C*CF(*C,*C,/*C*C,*&/*	3.1	3441-0-06	3441-0-02		
	*C*C(*CC,*C/*C,FFF,*C	3.2	3447-0-06			
	*C*C(*CF,*C/*C*C,,*&/*	2.6	3438-0-02			
	*C*C(*CF,*C/*C,,*C*&/*	5.2	3442-0-06	3442-0-03		
	*C*C(*C,*C/*C*C,*&C/*C*	2.5	3448-0-06			
	*C*C(*C,*C/*C*C,*&F/*C	3.0	3439-0-03			
	*C*C(*C,*C/*C*C,*&/*C*:	2.8	3424-0-06			
	*C*C(*C,*C/*C*C,*&/*C*:	2.7	3424-2-06			
	*C*C(*C,*C/*C*C,*&/*C*:	2.5	3424-3-06	3424-1-06		

231-49 University of Illinois at Urbana-Champaign

School of Chemical Sciences
Urbana, Illinois 61801

November 18, 1977

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

Dear Professor Shapiro:

ASSIGNMENT OF ^{13}CO RESONANCES IN $H_2Os_2(CO)_{10}$ USING T_1 DATA

The ^{13}C spectrum of 40% C-13 enriched $H_2Os_3(CO)_{10}$ at room temperature consists of four lines with peak heights in the ratio of 1:1:1:2 as listed in Table 1. The spectrum is consistent with the previously proposed and recently confirmed[1] structure shown in Fig. 1. In the figure, A, B, C, D represent CO groups, the same letter meaning magnetically equivalent groups.

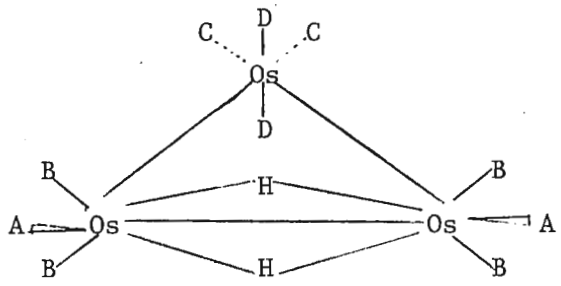


Fig. 1

Table 1

Resonance	Shift*	T_1(sec)
B	174.6	63
A	176.2	69
C	181.2	112
D	182.1	89

*Shift in ppm relative to TMS

Professor B. L. Shapiro
November 18, 1977

The A and B resonances were easily identified on the basis of chemical shifts and peak heights. Identification of C and D resonances was initially made[2] using chemical shifts and the observation of a small ^{13}C-H coupling. Since the angular dependence of J ^{13}C-H in this system is unknown, we sought to use T_1 data to verify this identification. The recent X-ray investigation of $H_2Os_3(CO)_{10}$ shows the angle D-Os-D is 167°, inclined toward the hydrogens, while the C-Os-C angle is 98° and inclined away from the hydrogens. Assuming similar rates for CO group rotation, the relaxation for the D carbons should be shorter than for the C carbons. On this evidence we assign the C resonance to the line at 181.2 ppm and the D resonance to the line at 182.1 ppm.

1. M. R. Churchill, J. F. Hollander, and J. P. Hutchinson, Inorg. Chem., 16, 2697 (1977).

2. J. R. Shapley, unpublished results.

Sincerely yours,

Stephen E. Ulrich

Stephen E. Ulrich

John R. Shapley

John R. Shapley

dfc

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

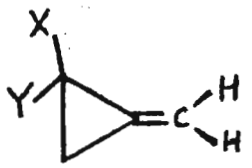
November 22, 1977

The University of Sydney
DEPARTMENT OF ORGANIC CHEMISTRY
N.S.W. 2006

Dear Barry,

GEMINAL COUPLING CONSTANTS IN EXOCYCLIC METHYLENE GROUPS

We have observed a long time ago[1] that the above coupling constants appear to vary with the size of the ring. Systematic investigations, carried out mainly by Dr. R. J. Spear, confirm this (see Fig. 1) and also show that substituent effects may be superimposed upon the ring-size effect. We also have some data for α-methylenecycloalkanones, which show a similar , but less well-defined trend. On the basis of rather scarce structural data, it is tempting to rationalize the ring-size effect in terms of the variation in the H-C-H angles , as the coupling constants follow the relationship predicted by Pople[2]. However, methylenecyclopropanes do not follow the trend as the geminal olefinic coupling constants vary from +1.19 Hz [for X=Y=Me, sign established by tickling] to (-)2.2 Hz [for X=Y=CN[3], sign inferred by us on the basis of data for other compounds] and take on the full range of values in between with varying X,Y and solvent.



With best regards
yours sincerely

Sev Sternhell

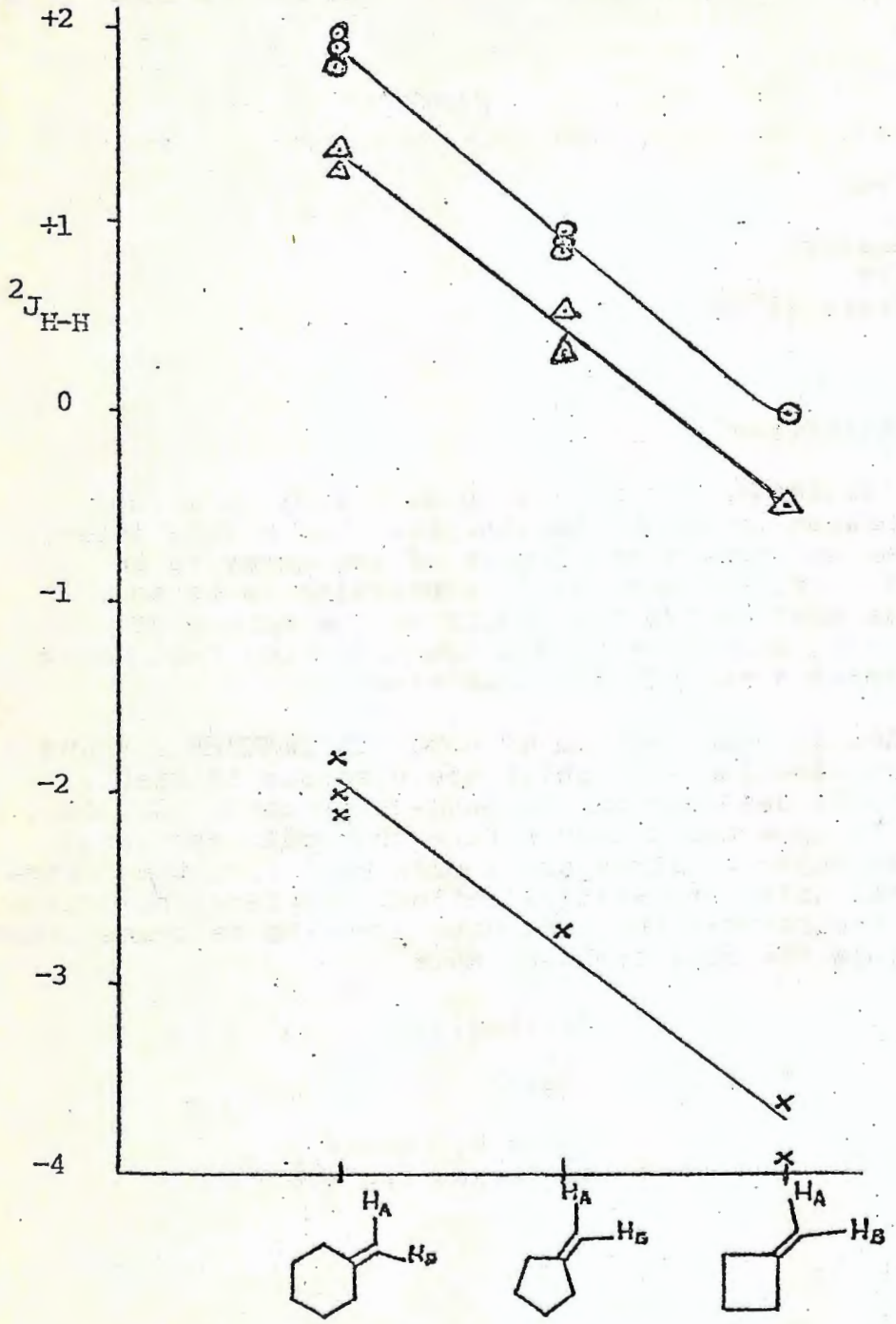
S. Sternhell

1 Jackman and Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry", Pergamon 1969, p. 279; Newsoroff and Sternhell, Aust. J. Chem., 25, 1669 (1972).

2 Maciel, McIver, Ostlund and Pople, J. Am. Chem. Soc., 92, 4151 (1970).

3 Ciganek, J. Am. Chem. Soc., 88, 1979 (1966).

Fig. 1 A plot of $^2J_{H-H}$ against size of the attached ring for series of exocyclic methylene compounds (see footnotes)



⊙—— Alkyl substituted methylenecycloalkanes.

△—— 2,3-Benzomethylenecycloalkanes.

×—— α-Methylene cyclic ethers.

231-53

DEPARTMENT OF CHEMISTRY TUFTS UNIVERSITY MEDFORD, MASSACHUSETTS 02155

November 9, 1977

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

Dear Barry:

"Sinusoidal Congestion"

Dr. J. A. den Hollander's comments on sine look-up methods in TAMUNMR 228 attribute to me the implication that a sine look-up table must always be one-fourth the length of the array to be Fourier transformed. If, in fact, no interpolation is to be performed, the table must be 1/8 the length of the number of points in a real array, since during the transform the real array is treated as a complex array of half that size.

However, I meant to point out in my notes in TAMUNMR 215 and 226 that quite short sine look-up tables are possible if simple linear interpolation is used during the look-up process. Simple interpolation of this type has the advantage that only one table is used and that two adjacent sines are looked up. Then the interpolation is performed using one multiplication. In fact, however, interpolation only occurs when the real data array to be transformed is longer than 8 times the sine look-up table.

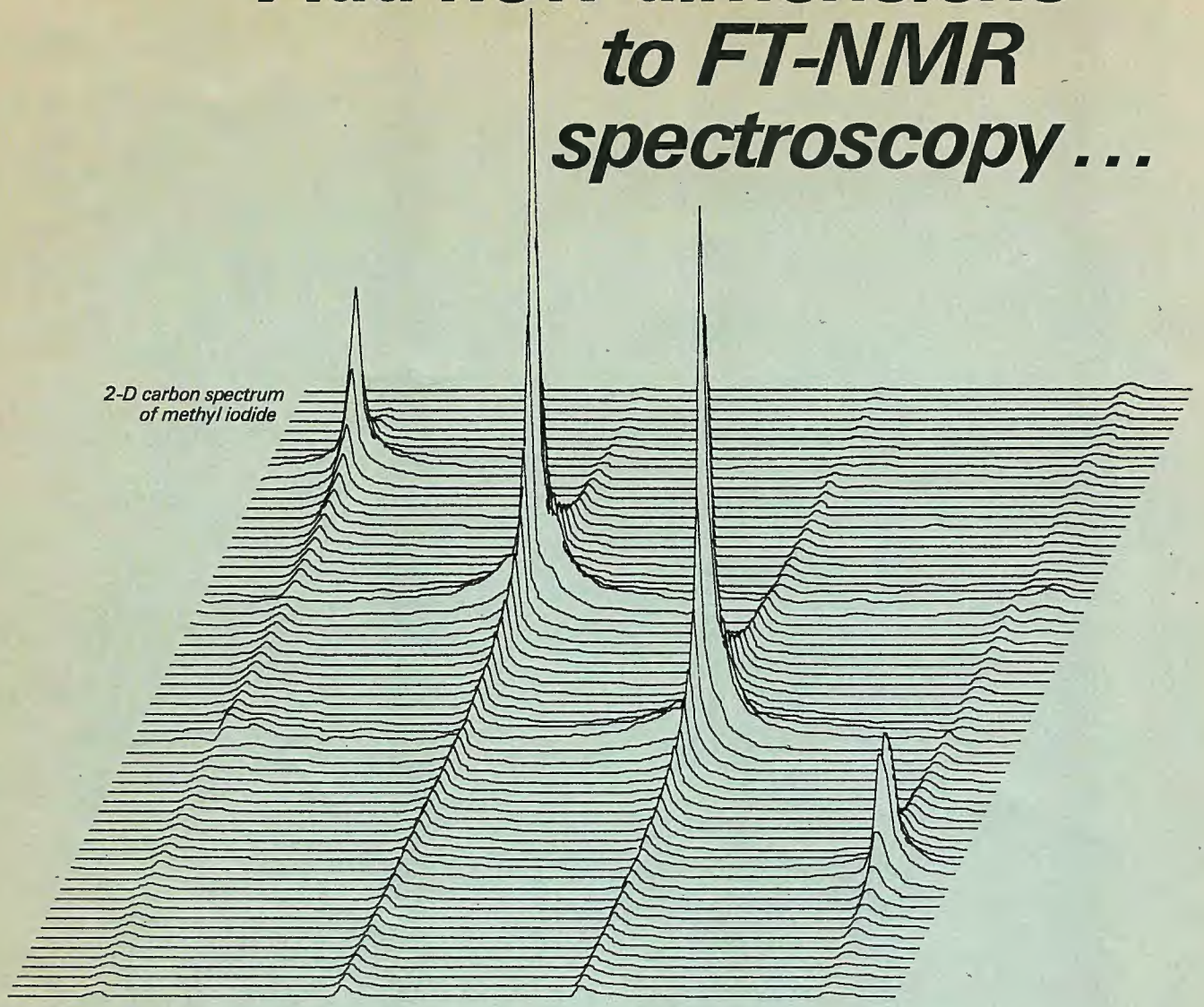
Sincerely,

Jim

James W. Cooper
Assistant Professor

JWC/nmc

Add new dimensions to FT-NMR spectroscopy . . .



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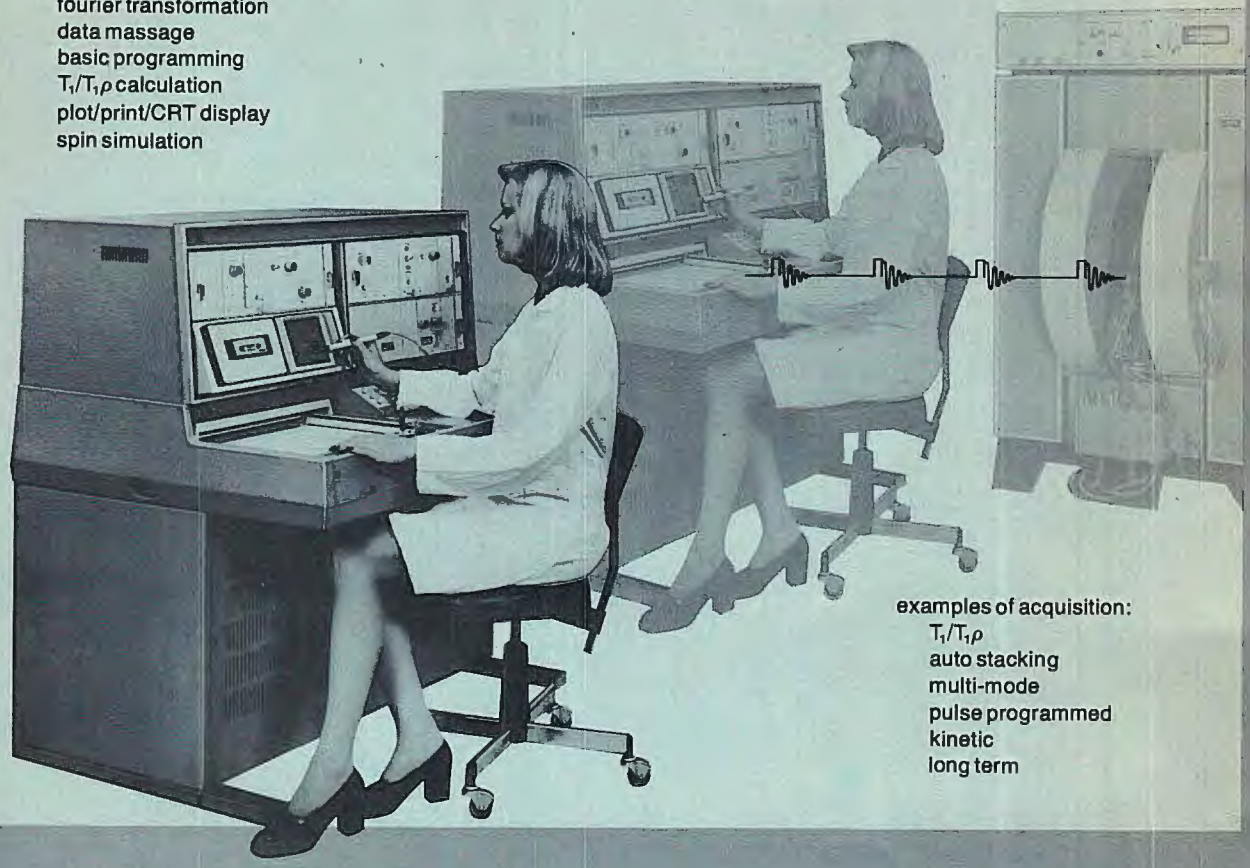
- $T_1/T_1\rho$ calculation
- plot/print/CRT display
- spin simulation



examples of acquisition:
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