Illinois Institute of Technology

N-M-R Newsletter

No. 66
MARCH, 1964

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Deadline Date for Next Issue: April 20, 1964

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

Illinois
Institute of
Technology

N-M-R
Newsletter

POLICIES AND PRACTICAL CONSIDERATIONS

1. Policy: The IIT NMR Newsletter (née MELLONMR) is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its surpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything.". (This is usually followed by the mental reservation "that won't land us in jail".) No editorial functions are performed. The IIT NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in.

As suitable subjects for contributions, we have suggested the following:

1. Reproductions of particularly interesting spectra or parts of spectra.
2. Measurements and calculations of same.
3. Theoretical considerations and interpretations.
4. Novel experimental methods and techniques.
5. Complete or partial mysteries.
6. Comments on material appearing in earlier letters.
7. Requests for help in locating odd or rare compounds.
8. Announcements of forthcoming meetings, colloquia, symposia, books, etc. Also "Preprints Available".
9. Notices of "Positions Available" or "Situations Wanted".
10. Wild theories (this category added at the request of Dr. Ray Freeman).
11. Anything else which you feel your co-workers in the field might find interesting - even mild polemics.

Foreign participants should not feel obliged to render their contributions in English.

2. Bibliography: The titles and references appearing in the "Bibliography" section are merely those which the NMR people at Mellon Institute come across in their perusal of the literature. (Even though the undersigned and the Newsletter have moved, the Bibliography will continue to be provided through the courtesy of the NMR group at Mellon Institute.) No claims for completeness are made and we once again invite all participants to send in references and titles which we have missed for inclusion in a subsequent issue. This invitation is extended particularly to foreign, and most especially foreign-language, journals, since this is where the NMR searching is most apt to be late at best and also incomplete at worst.

Since there appears to be no simple, objective way of deciding on the inclusion of some NMR-containing references and the exclusion of others, the Bibliography will continue to list (in alphabetical order of journal name) all references found which contain any NMR data, spectra or other "hard" information. The bibliography is printed on only one side of the page, so each reader can take scissors in hand and do his own custom editing.

3. Subscriptions: We will continue to send out the IIT NMR Newsletter without charge although we would be grateful for the cooperation of all participants as outlined in the section below on "Practical Considerations". We are willing to send your issue by air-mail if you are willing to pay the rather formidable air-mail postage; rates and ground rules on request.

Participation is the prime requisite for receiving the IIT NMR Newsletter; in order to receive the Newsletter, you must make at least occasional contributions to its contents. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution, you will receive a "reminder letter". If no contribution is then forthcoming ten months after your last contribution, you will receive the "ultimatum letter", and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending in a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of 9 per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

(cont'd.)

PLEASE NOTE: A subject of considerable interest and concern to several present and potential IIT NMR Newsletter participants - as well as to ourselves - is whether the IIT NMR Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that an IIT NMR Newsletter contribution should not duplicate, summarize or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the IIT NMR Newsletter account. On the other hand, let it be emphasized firmly that if the appearance in a journal is several months away - as is frequently the case - a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the IIT NMR Newsletter fulfills one of the very functions which we feel this Newsletter can provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the IIT NMR Newsletter audience before they could read it elsewhere.

4. Brevity: Brevity is good - see the section on Practical Considerations.

5. Public Quotation: Public quotation in print or in a talk is expressly forbidden, and reference to the IIT NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the IIT NMR Newsletter it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted (and abide by) the statements of policy and practical considerations.

6. Practical Considerations: (a) All contributions to the IIT NMR Newsletter should be sent to the attention of the undersigned and will always be included in the next issue if received before about the 20th of the month. (The actual deadline date appears on the cover of the previous issue.)

(b) Contributions should be on the minimum number of 8-1/2 x 11" (21 x 27.5 cm) pages, printed on one side only, with at least 3/4" (2 cm) margins on all sides. Black ink, typing, drawings, etc., on white paper are good, grey or blue ink, typing, etc., on anything are ghastly - i.e., high contrast is essential.

Since reproductions of various kinds do not themselves reproduce too well, contributors are urged to submit their originals to us and we will be happy to return these if requested.

(c) Please provide short titles of all the topics of your contributions, as this will ensure accuracy (and lessen our work) in preparing the title-page index.

(d) Please try to avoid sending in manuscripts, theses, books, etc., and asking us to be your consciences in selecting what should and shouldn't go into the Newsletter.

(e) Brevity is getting more and more golden as our mailing list increases. Single spacing is almost as good as brevity and in general, you will help us keep our costs down to a reasonable level by sending in as much material as you wish, but by planning it to fill the minimum integral number of pages. This will help cut the costs of both reproduction and mailing.

7. Suggestions: They are always welcome.

B.L. Shapiro 19/3/64

Address for all contributions and inquiries:
Associate Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Nuclear Magnetic Resonance Study of Iodine Complexes

by

Anthony Fratiello*

Bell Telephone Laboratories

Murray Hill, New Jersey

Abstract

A nuclear magnetic resonance study of iodine in several organic solvents, varying in the nature of functional groups and heterogeneous atoms present in the molecule, was carried out. In many cases, primarily systems involving nitro-compounds, benzene, and substituted benzenes, the complexing between iodine and solvent was not intensive enough to perturb the proton chemical shifts of the latter. Large shift displacements were observed using other solvents, primarily amines and other nitrogen containing compounds. In these cases, the presence of selective proton shifts gave some indication as to the site of the interaction. An attempt was made to interpret the observed shifts in terms of electron density changes accompanying the formation of an iodine-solvent complex.

(Preprints available)

*Present address: Department of Chemistry, California State College at Los Angeles, Los Angeles 32, California

66-2

KAMcL/DMT

Department of Scientific and Industrial Research
NATIONAL PHYSICAL LABORATORY
TEDDINGTON, Middlesex
Telegrams: Physics, Teddington Telephone: TEDdington Lock 3222, *ext.* 813

Please address any reply to
THE DIRECTOR
and quote: BP.24/7/013
Your reference:

BASIC PHYSICS DIVISION

10th February, 1964

Dear Barry,

Firstly let me express the feelings of all your readers by saying how glad I am that your invaluable newsletter is continuing from its new address.

Reading of the beautiful work carried out on liquid crystal systems by Englert and Saupe has spurred David Buckingham and I to attempt to discover new methods of orienting molecules which produce larger effects than our original electric field technique. I hope to say something about them all at the Pittsburgh meeting but in the meantime shall tell you of the most successful method which, I believe, enables a considerable extension in the size and type of molecule which can be aligned.

Many broad-line N.M.R. studies have been made on clathrate compounds. In particular urea clathrates have been studied in some detail and their crystal structure is well known. It appears that urea will occlude almost any length of straight-chain hydrocarbon derivative but that the crystal structure changes with chain length. Molecules less than 5 C atoms in length enable urea to adopt its cage structure whilst larger molecules produce a structure which includes long channels of molecular dimensions. It occurred to us that the guest molecule might diffuse reasonably freely in these channels and in fact at least one broad line study has shown signals due to the guests which are sharp compared with the detector ~~modulation~~ band width.

To cut a long story short our experiments suggest that small molecules are mobile, but oriented, even in the cage type of structure. The simplest system is urea crystallised directly from methanol. The urea crystallises in the form of long platelets, growth beingfastest along the C-axis. The spectrum I include shows the result of spinning the crystal about this axis. The result is a complex spectrum since the dipole-dipole interactions are large compared with the chemical shift.

I hope to have it sorted out in time for Pittsburgh where I look forward to seeing you.

With best wishes,

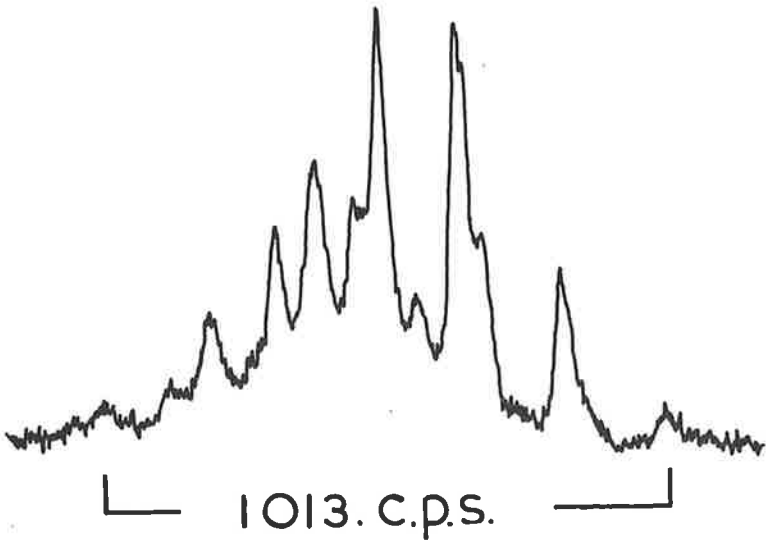
Yours,

K. A. McLauchlan

Assoc. Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago 16,
Illinois,
U.S.A.

CH_3OH in urea.

single crystal spun approx.
parallel to c-axis.



Polycrystalline sample spun
approx. // to c-axes.

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UNIVERSITÉ DE GENÈVE
INSTITUT DE PHYSIQUE EXPÉRIMENTALE
BOULEVARD D'YVOY

GJB/cp

Genève, le 14 février 1964

Dr. B. L. Shapiro
Mellon Institute

4400 Fifth Avenue
Pittsburgh 13, Pa.

U. S. A.

Cher Dr. Shapiro,

Dans l'espoir que cette contribution me permettra de figurer dans la liste de distribution de "Mellon NMR", je me permets de vous donner ci-dessous le résumé de deux publications soumises ces jours derniers pour publication et qui émanent de mon laboratoire. Elles se rapportent essentiellement à l'observation de spectres de RMN haute résolution dans le champ magnétique terrestre et à l'interprétation des résultats obtenus.

1) Résonance magnétique nucléaire de composés organophosphorés dans le champ magnétique terrestre - couplages $P^{31} - H^1$ par Eugène Duval, Institut de Physique Expérimentale de l'Université de Genève (Suisse). (Soumis pour publication - Revue de l'Institut Français du Pétrole - Paris- France) (Février 1964).

Résumé

Les spectres R. M. N. du triéthyl phosphate [1] et du triéthyl phosphite [2] obtenus avec le spectromètre construit par Monsieur Hochstrasser, fonctionnant dans le champ magnétique terrestre nous ont permis de mesurer les constantes de couplage J_{PCH_2} et J_{PCH_3} pour les deux substances avec une précision dépassant $\pm$ 0,05 C/S, et de déterminer les signes relatifs de ces constantes.

Une théorie du couplage spin noyau - spin noyau [3], via les couplages spin-noyau - spin électron (Fermi) et spin électron - spin électron (covalence et Hund), nous permet une interprétation [4] telle qu'en première approximation, on puisse dire que la constante de couplage entre deux noyaux est égale à la somme de deux contributions dont l'une est due aux liaisons formant la chaîne

moléculaire, et l'autre à la liaison partielle entre les atomes auxquels appartiennent les deux noyaux interagissant. La première sera positive si les deux noyaux sont séparés par un nombre d'atomes nul ou pair, négative s'ils sont séparés par un nombre impair d'atomes. La deuxième contribution sera toujours positive, la liaison partielle directe étant de nature covalente.

Les résultats suivants sont à rapprocher de ceux donnés pour le triéthyl phosphine et l'ion tétraéthyl phosphonium:

1) Triéthyl phosphate $O = P(OCH_2CH_3)^3$

$J_{PCH_2} = \pm 8,4$ C/S $\quad J_{PCH_3} = \pm 0,84$ C/S

2) Triéthyl phosphite $P(OCH_2CH_3)^3$

$J_{PCH_2} = \pm 7,9$, $\quad J_{PCH_3} = F\ 0,55$

Reférences:

1) Béné, Duval, Finaz, Hochstrasser C. R. 256, 2365 (1963)
2) Béné, Duval, Finaz, Hochstrasser et Koïdé. Physics letters 7, 34 1963
3) Duval et Koïdé - soumis pour publication Physics Letters
4) Koidé et Duval - soumis pour publication J. Chem. Phys.
5) P. T. Narasimhan et M. T. Rogers J. Chem. Phys. 34, 1049 (1961)
6) John E. Lancaster - Communication au Mellon Institut le 31 octobre 1963

2) Long Range Spin-Spin Interaction between Nuclei in the Saturated Compounds - S. Koïdé and E. Duval - Institute of Physics, University of Geneva, Switzerland.

The importance of the intra-atomic Hund coupling between electron spins is emphasized to account for the general features of the electron coupled interaction between nuclear spins seperated by several atoms. This seems to be quite consistent with the experimental results, especially with the appearance of the negative coupling constants in many of the long range cases. By using the simple covalent bond method, the effect of the Hund coupling on the coupling constant between nuclear spins is expressed in terms of the various exchange integrals between adjacent electron orbitals for the cases of one, two, and three intervening atoms.

Soumis pour publication au Journal of Chemical Physics - février 1964.

Croyez, cher Dr. Shapiro, à mes meilleurs sentiments.

Prof. ~~G.~~ J. Béné

66-6

IOWA STATE UNIVERSITY
of Science and Technology
AMES, IOWA

Department of Chemistry

25 February 1964

Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Dr. Shapiro:

I should like to make a comment concerning the additional Fortran statements, suggested by C. A. Reilly (MelloNMR No. 62), which were to be inserted in the subroutine BEQUIV, offered by A. Douglas (MelloNMR No. 59).

The purpose of these statements was to maintain the coupling between magnetically equivalent protons at zero. These statements are indeed necessary for most systems. However, with A_2B_2 systems, the magnetic equivalence of the two pairs of protons does not mean that J_{aa} and J_{bb} are zero. For the A_2B_2 system, and also for any others in which the preceeding statement is true, these additional computer instructions are not desired and will in fact cause the iterative program NMRIT to give incorrect answers. Additional control instructions, so that the computer may decide for itself whether or not an A_2B_2 is being computed, are desired.

Sincerely yours,
L.B. Rodewald
L. B. Rodewald

LBR:kab

cc: Dr. Reilly

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

March 6, 1964

Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Barry,

I have a copy of a letter from L. B. Rodewald of Iowa State University concerning a flaw in BEQUIV. This flaw was also called to my attention earlier by A. Douglas, who indicated he would inform MELLONMR (or is it now officially IIT NN?) readers accordingly. Since he has not done so, the revised part of the listing is given in the box below.

```
12    NN = N - 1
      DO 14 I = 1, NN
      JI = I + 1
      DO 14 J = JI, N
      IF(AB(I,J,1)) 14, 13, 14
13    AA(I,J) = 0.0
14    CONTINUE
      DO 10 I = 1, NN
         etc.
```

This small change will take care of both magnetic and symmetric equivalence. I have been using it quite successfully for some time now. However, one has to be careful that the starting parameters (even the very small, non-zero, ones) are given values that accurately reflect the symmetry of the problem.

Sincerely yours,

Charlie

C. A. Reilly

66-8

The Standard Oil Company
(An Ohio Corporation)
Research Department
4440 Warrensville Center Road
Cleveland 28, Ohio

E. C. HUGHES
VICE PRESIDENT

March 2, 1964

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

You will find enclosed a call for papers for the Third National Meeting of the Society of Applied Spectroscopy, which will be held in Cleveland this fall. I wonder if you could include as much of this as you consider practical in the News Letter. It's worth noting, if it isn't mentioned on the program sheets, that there will be a session on electron spin which will be under the general chairmanship of Larry Piette of Varian and a session on NMR under the chairmanship of Professor Max Rogers of Michigan State.

Many thanks.

Sincerely,

W. M. Ritchey

WMR/jem

The Third National Meeting
Society for Applied Spectroscopy

SEPTEMBER 28 - OCTOBER 2, 1964
SHERATON-CLEVELAND HOTEL/CLEVELAND, OHIO

Newsletter No. 2

THE PROGRAM

All phases of **EMISSION** and **ABSORPTION** spectroscopy and **X-RAY FLUORESCENCE** will be represented in the program. In addition **SPECIAL SYMPOSIA** will be held in the following areas:

Spectroscopy of gases at high temperatures.
Applications of spectroscopy in astronomy.
Molecular spectroscopy.
Spectroscopy of the Solid State.
Mass spectroscopy.
Nuclear magnetic resonance.
Analytical Absorption Spectroscopy:
- Medical and Biological applications
- Polymers
- Organometallic and inorganic systems
- Group frequencies

Analytical Emission Spectroscopy:
- New techniques
- Instrumentation
- Health physics

The program will include invited papers in these areas. Keynote speakers will include the following:

Speaker	Subject
W. J. Potts Dow Chemical Company	Group Frequencies
J. J. Nassau Case Inst. of Technology	Spectroscopy in Astronomy
Isidore Adler U.S. Dept. of Interior	X-ray & Microprobe Techniques
R. H. Tourin Warner and Swasey	Spectroscopy of Plasma Jets and Electric Arcs

Additional keynote speakers and topics will be announced later.

Submission of Papers

Original papers on all phases of spectroscopy are invited. Details concerning procedure to be followed appear on page 2.

SARAH H. DEGENKOLB
Co-Chairman
U. S. STEEL CORP.

L. E. ZEEB
Co-Chairman
141 FOURTH AVENUE
BEREA, OHIO

DR. ERNEST YEAGER
Program Chairman
DEPT. OF CHEMISTRY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO 44106

JOHN A. WYMAN
Exhibit Chairman
137 S. PROSPECT STREET
MEDINA, OHIO

66-10

The Third National Meeting
Society for Applied Spectroscopy

SEPTEMBER 28 - OCTOBER 2, 1964
SHERATON-CLEVELAND HOTEL/CLEVELAND, OHIO

Regulations for Contributed Papers

1. Correspondence regarding papers should be directed to:

   Dr. Ernest Yeager, Program Chairman
   Department of Chemistry
   Western Reserve University
   Cleveland, Ohio 44106

2. Deadline for receipt of titles and short abstracts: May 1, 1964.

3. A brief abstract, in triplicate, of not more than 150 words for use in the program should be submitted. Please use attached abstract form for original copy and include two carbon copies on plain white paper. Receipt of paper will be acknowledged.

4. On the abstract form, please indicate the following:
   a. The title of the paper.
   b. The names of the author(s), the company or university in whose laboratories the work was done, and address. If the present address of any author is different, both addresses should be given.
   c. In the case of multiple authors, the name of the person who will present the paper should be distinctly indicated by underlining.
   d. The section of the program to which the author believes the paper should be assigned. (Example: Emission Spectroscopy, X-ray Fluorescence, etc.)

5. With the exception of the special symposia, the presentation time will be 15 minutes followed by a 5-minute discussion period.

6. A booklet of condensed papers or extended abstracts will be prepared. All authors will be requested to submit an extended abstract or summary of not more than 750 words on or before June 15, 1964. Further information concerning the submission of the extended abstract will be sent to authors after receipt of the title and short abstract. Complete manuscripts are not required.

7. Submission of the paper will be considered a representation that the paper has not been presented previously or published elsewhere. Subsequent submission of the paper for publication in Applied Spectroscopy is encouraged but not required.

SARAH H. DEGENKOLB
Co-Chairman
U. S. STEEL CORP.

L. E. ZEEB
Co-Chairman
141 FOURTH AVENUE
BEREA, OHIO

DR. ERNEST YEAGER
Program Chairman
DEPT. OF CHEMISTRY
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CLEVELAND, OHIO 44106

JOHN A. WYMAN
Exhibit Chairman
137 S. PROSPECT STREET
MEDINA, OHIO

The Third National Meeting
Society for Applied Spectroscopy

SEPTEMBER 28 - OCTOBER 2, 1964
SHERATON-CLEVELAND HOTEL/CLEVELAND, OHIO

Exhibitors Attention!

Exhibition booths are on the same floor as, and adjacent to, the meeting rooms. Choice space is still available. For requirements and information contact:

Mr. John A. Wyman
Exhibit Chairman
137 S. Prospect Street
Medina, Ohio
Phone: Area Code 216 PArk 2-1501

The growing list of exhibitors includes:

Beckman Instruments
General Electric X-Ray
Harshaw Chemical Company
National Carbon Company
National Spectrographic Laboratories
Perkin-Elmer Corp.
Phillips Electronic Instruments
Picker X-Ray Corp.
Siemens America, Inc.
Spex Industries, Inc.
Ultra Carbon Corp.
Wilks Scientific Corp.

Free coffee will be available in the exhibit area.

SARAH H. DEGENKOLB
Co-Chairman
U. S. STEEL CORP.

L. E. ZEEB
Co-Chairman
141 FOURTH AVENUE
BEREA, OHIO

DR. ERNEST YEAGER
Program Chairman
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JOHN A. WYMAN
Exhibit Chairman
137 S. PROSPECT STREET
MEDINA, OHIO

66-12

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA
19010

DEPARTMENT OF CHEMISTRY

5 March 1964

Prof. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Prof. Shapiro:

I should like briefly to outline a calculation examining the effect of nuclear relaxation on the symmetry of NMR spectra. Previous work has developed a theorem for when an NMR spectrum, neglecting relaxation, is symmetric [1,2,3]. This theorem is based on the commutation properties of the spin Hamiltonian with a spin inversion operator, λ.

Similarly, the symmetry of spectra with the effect of relaxation included depends on the commutation properties of the relaxation operator with λ. It is found that relaxation does not destroy spectral symmetry if there is but one dominant relaxation mechanism, or if there are two dominant relaxation mechanisms with the same commutation properties with λ. However, if two relaxation mechanisms have different commutation rules with λ, have the same rank of spatial dependence, and are of nearly equal magnitude, the presence of cross-correlation terms [4] in the relaxation matrix elements destroys the symmetry of the spectrum. In particular, T_2 for the transition $i \rightarrow j$ is not equal to T_2 for the otherwise symmetric transition $\lambda i \rightarrow \lambda j$, so that these two lines have different widths or different saturation factors.

The use of this asymmetry to determine the absolute sign of a spin-spin coupling constant is proposed. The cross-correlation between the dipole-dipole relaxation operator and the quadrupole relaxation operator is a case in point. A molecule with a high-spin nucleus coupled to a low-spin (1/2) nucleus known to have reasonably equal magnitudes for e^2qQ and $\gamma_1\gamma_2/r_{12}^3$ (the magnitudes of the qudrupole and dipole-dipole relaxation operators) would be appropriate. Like David going

forth to do battle with Goliath, the author, who hasn't access to high-resolution NMR facilities, invites the suggestion of molecules and experiments to test this analysis (e.g., the D-NMR of HD?).

Preprints giving details of the calculation, and listings of 1620 Fortran II programs used in the calculation will soon be available to those interested.

Sincerely yours,

Jay Martin Anderson

Jay Martin Anderson

References:
1. J. M. A. and J. D. Baldeschwieler, J. Chem. Phys. 37, 39 (1962).
2. J. M. A. and J. D. B., J. Chem. Phys. 38, 570 (1963).
3. R. Ernst and J. M. A., J. Chem. Phys. (to be published).
4. For notation, etc., see Noggle, Kuhlmann and Baldeschwieler, IIT/NMR Newsletter 65, pg. 65-2; J. D. Baldeschwieler, J. Chem. Phys. 40, 459 (1964).

66-14

CANISIUS COLLEGE
BUFFALO 8, NEW YORK

DEPARTMENT OF CHEMISTRY

February 26, 1964

Dr. Bernard L. Shapiro
Associate Professor of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr. Shapiro:

Although I am not due yet for another contribution to the newsletter, I would like to call attention to some new work I have done.

In my last letter I cited our use of arsenic trichloride as an N.M.R. solvent for polymers. There are some polymers which this solvent will not dissolve but molten $SbCl_3$ will. We have found that 50% by weight of $SbCl_3$ will dissolve in arsenic trichloride to give a liquid at room temperature with good solvent properties.

As an example, the spectra of Dupont's polymer H is presented. This polymer would not dissolve in arsenic trichloride but does go into the mixture quite well. The assignments of the signals are as follows:

The lowest field signal is an acidic H, the next is the aromatic rings of the polymer and the highest field signal is H_2O.

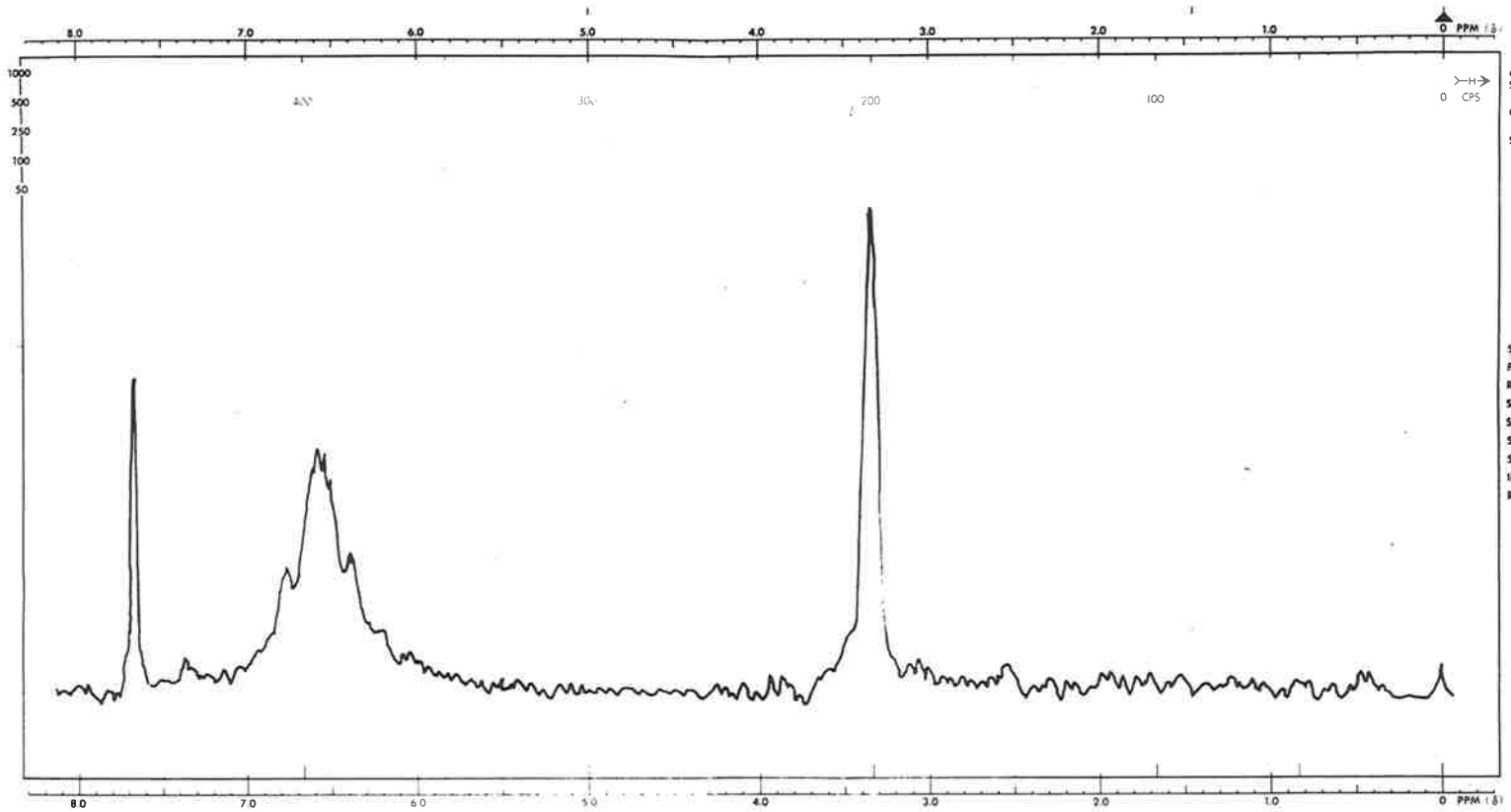
The mixed solvent can also be used for I.R. as it is fairly transparent in the 2 - 12 micron region.

Sincerely,

Herman A. Szymanski

Dr. Herman A. Szymanski
Chairman
Department of Chemistry

Has/am



60 MC NMR
SPECTRUM NO

OPERATOR DATE

SAMPLE H-FILM

SOLVENT: $AsCl_3/SbCl_3$ 1:1
FILTER BANDWIDTH: 0.4 cps
R. F. FIELD: 1.0 mG
SWEEP TIME: 250 sec
SWEEP WIDTH: 500 cps
SWEEP OFFSET: 0 cps
SPECTRUM AMP: 160
INTEGRAL AMP: OFF
REMARKS:

VARIAN associates
PALO ALTO, CALIFORNIA
INSTRUMENT DIVISION

CHART 5-60A

66-16

Division of Physical Chemistry
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

Cable address: Technology

March 6, 1964.

EF,LOA/MH

NUCLEAR MAGNETIC RESONANCE GROUP
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70 SWEDEN

Associate Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center

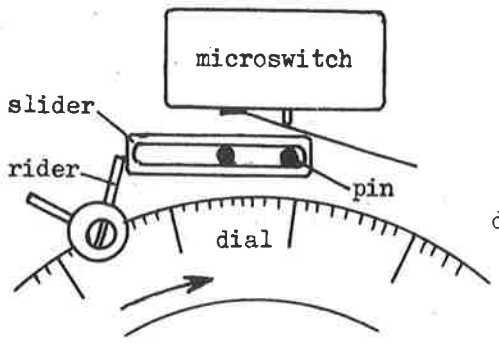
CHICAGO 16, Illinois
USA

Dear Dr. Shapiro:

Thank you for the reminder. We are sorry and will try to contribute to the MELLONMR more regularly in the future.

Although the Newsletter mostly contains high resolution topics, we hope there are still some readers who would be interested in some devices which we have used in our wide line work.

In one type of spectra with very low signal-to-noise ratio we try to add out the noise by repeating the spectra many times. This takes time, but we can let the spectrograph do it overnight by the following simple device. A rider is mounted on the "scan fine" outer dial on the Varian scanning unit in such a position that when the spectrum is completed it will move a slider which is guided by two pins. The slider actuates a microswitch that is connected to an additional setting of the scanning direction switch. The microswitch is connected to each motor and, depending on the position of the switch, current is fed either to the forward or to the reverse motor. When the scanning direction is changed the slider holds the microswitch in its new position while the rider moves away. Another rider will move the slider back again when the spectrum has been completed in the reverse direction, and the switch feeds the current to the forward motor.



If during this scanning back and forth a very strong signal has to be passed, which cannot be recorded with the same spectrometer settings as for the remainder of the spectrum, we have made the spectrograph change the settings in the following way. When with rising signal amplitude the pen

recorder (Leeds & Northrup Speedomax) goes out of scale, limit switches activated by the pen carriage at each end of the scale control a time relay which starts to run and at the same time feeds a second relay operating on the output control unit. Connections to the "amplitude coarse" and the "response" switches assure the right settings for the recording of the strong signal when the relay is activated. When the time, to which the time relay has been preset and which is long enough to permit the passage of the strong signal, has elapsed, the relay on the output control unit is inactivated and the settings appropriate for the recording of the small signal are again restored.

For another type of wide line spectra we analyze the band shape with the aid of a computer and therefore need digital information about the spectrum. We have built a machine which consists essentially of a driving roll for the recorder paper and a slide on which is mounted a hair-cross moving perpendicularly to the paper feed direction. The motion of the slide, when the hair-cross is brought to follow the trace, operates a rack and pinion rotating a multiturn potentiometer fed by a stabilized voltage, the output of which over its sliding contact is measured by a digital voltmeter. When a lever is pressed to turn the roll and feed the paper a certain preset stretch, a signal is given to a tape punch which is connected to the digital voltmeter punching its reading. The hair-cross is now moved to coincide with the curve at the new point and the procedure is repeated until the whole curve has been punched on to the tape, which can be fed directly into a computer.

Yours sincerely,

Erik Forslind Lars-Olov Andersson

Erik Forslind Lars-Olov Andersson

66-18

UNIVERSITY OF ILLINOIS

THE WILLIAM ALBERT NOYES LABORATORY

March 10, 1964

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

In order to help balance out the preponderance of high resolution NMR covered in the NMR Newsletter, and also to ring in something on the sorely neglected electrical quadrupole, I would like to give you a summary of some broad-line NMR work which Clive Coogan (CSIRO, Melbourne, Australia) and I have just finished writing up. The work is concerned with the nature of the phase transition in NaCN.

In particular, the Na^{23} nuclear magnetic resonance absorption has been observed in the cubic phase of polycrystalline NaCN between about 15°C and 170°C, but could not be detected in the orthorhombic phase which forms below 10.5°C. The observed line shape and its second moment S are compatible with a model in which $S = S_d + S_{q_o} + S_q(T)$, where S_d and S_{q_o} are temperature independent terms, $S_d \cong 0.39G^2$ resulting from magnetic dipolar interactions of the "rigid lattice" of Na^+ ions and $S_{q_o} \cong 0.16G^2$ from first order nuclear quadrupole interactions with field gradients produced by lattice defects. $S_q(T)$ is a quadrupole broadening term which decreases exponentially from $\sim 13G^2$ at 10.5°C to near zero at 170°C.

We attribute the electric field gradients involved in $S_q(T)$ to the electric dipoles of the CN^- ions, and the temperature dependence, to the averaging out of the gradients by thermally activated reorientations of the CN^- ions. The reorientations are deemed responsible for the existence of a cubic phase.

By treating them as a random walk problem, we obtained algebraic expressions by means of which an activation energy of 6 kcal/mole is calculated from the experimental $S_q(T)$, and 5×10^8 cps at 10°C and 10^{10} cps at 150°C are estimated for ν_j, the CN^- reorientational jump frequency. The nucleation of the cubic to orthorhombic phase transition is related to ν_j.

The next time I pay my subscription I will try to use "coin of the realm".

With best regards,

H. S. Gutowsky

HSG:jah

66-20

STATE UNIVERSITY OF NEW YORK
AT STONY BROOK
STONY BROOK, LONG ISLAND, NEW YORK

DEPARTMENT OF CHEMISTRY

March 11, 1964

Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

Please apply this note to the subscription account of either of us to

W itty
I IT
N MR
D ehiscences

or whatever MELLONMR is to be called in its Chicago incarnation.

We have completed the first phase of a study of the NMR spectra of cyclic alkanes and related compounds. Our data on the hydrocarbons are best summarized by the attached Figure. Aside from the strikingly high shieldings of both carbon and hydrogen nuclei in cyclopropane, the most notable new features are the transition in the proton shieldings at C_{11} and the large fluctuations in the carbon shieldings in the C_8-C_{15} region. These we cannot explain, although various correlations might be pointed out.

An interesting model can be constructed to account for the cyclopropane data, however. If we measure both of the shifts from the dotted line in the Figure (for the central methylene groups in n-alkanes up to $C_{32}H_{66}$), and apply the ring current model recently used by several people, it is found that the observed ratio of the carbon shift to that of the protons is given by a ring current 1.10 Å in radius, outside the carbon nuclei. The observed values of the shifts are then obtained by assuming a 3.5 electron current. The same model yields a value for the diamagnetic susceptibility in fairly good agreement with the experimental one (again relative to "normal" methylene groups). Whether such a model corresponds very closely to the real cyclopropane ring is, of course, still quite an open question.

Yours truly,

John J. Burke
Mellon Institute

Paul

PCL:jv

Paul C. Lauterbur
State University of
New York at Stony Brook

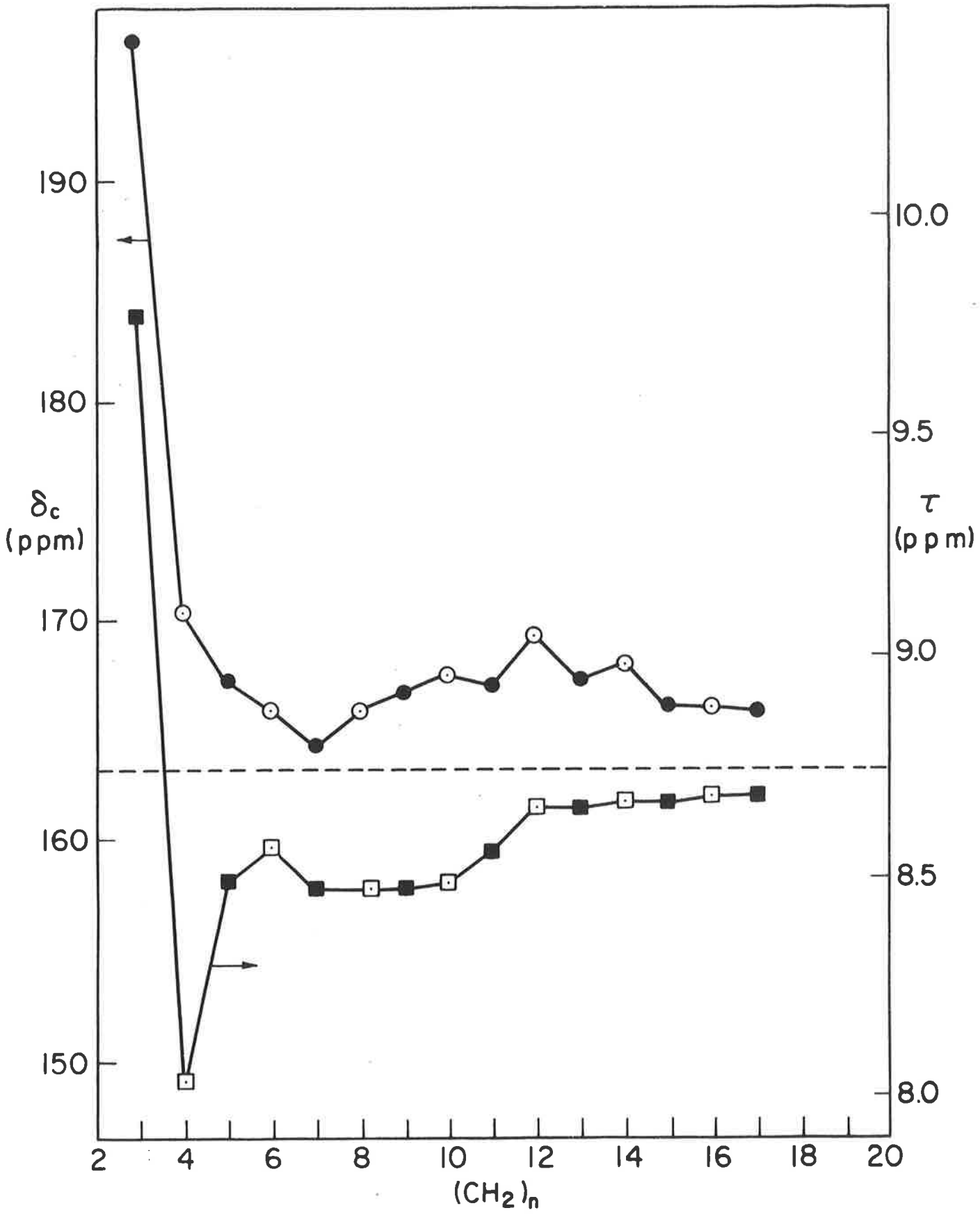


Fig. 1. Nuclear Magnetic shieldings in cycloalkanes. Carbon (○,●), hydrogen (□,■). Central CH_2 groups in long-chain n-alkanes. Carbon and hydrogen (— — —).

66-22

UNIVERSITY OF ILLINOIS
Department of
CHEMISTRY AND CHEMICAL ENGINEERING
URBANA
61803

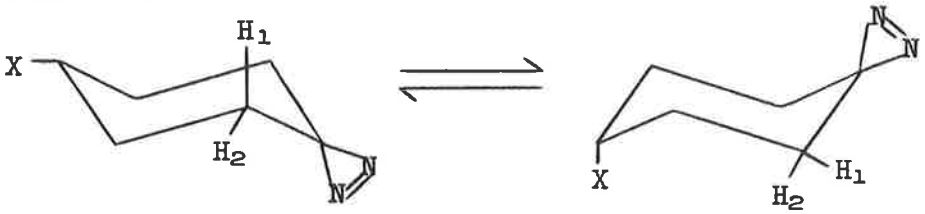
The William Albert Noyes Laboratory

March 9, 1964

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

Some time ago Jack Uebel and I mentioned in a letter to MELLONMR (53, 20) our observation of a very large chemical shift difference between the axial- and equatorial-protons on the α-methylenes of a pentamethylenediazirine derivative. We have found this large difference (of about 1.4-1.5 ppm.) to be quite general and have exploited it in the determination of conformational equilibria in cyclohexane derivatives in a modification of the method due to Eliel.



The large chemical shift difference can be accurately measured by spin-decoupling techniques, observing the collapse of the upfield multiplet related to the predominantly equatorial H_2. The shielding of this proton, attributed to the magnetic anisotropy of the diazirine ring, shifts it upfield into a region of the spectrum free of interference from signals of other groups of protons.

A study of the temperature dependence of the H_1-H_2 chemical shift difference for the case X=CH_3 provided data from which thermodynamic parameters for the equilibrium were calculated: ΔH = -1.91±0.04 kcal./mole; ΔS = -0.42±0.14 e.u.; ΔF (30°) = -1.78±0.06 kcal./mole. These values are in good agreement with those obtained for the difference in equatorial-methyl and axial-methyl cyclohexane derivatives by other methods.

The method is easily applied and is being extended to the quantitative evaluation of the conformational preferences (Y values) for other substituents on six-membered rings.

Yours,

J. C. Martin
Associate Professor of
Organic Chemistry

JCM:dsi

Southern Research Institute

2000 NINTH AVENUE SOUTH
BIRMINGHAM 5, ALABAMA

March 13, 1964

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois

Dear Dr. Shapiro:

Sometimes we have discovered the presence of ferromagnetic impurities suspended in an NMR sample solution after the solution has been placed in the sample tube. Where sample is limited and/or solvent very expensive, we have found that sometimes the impurities may be removed with minimum loss of solution in the following way:

A micro magnetic stirring bar (teflon-coated) is introduced into the sample tube. This microbar may be manipulated by another magnet held outside the tube to regulate contact with the solution and to remove the microbar from the solution.

These microbars may be purchased from Laboratory Plasticware Fabricators, Kansas City 41, Missouri. We use size No. 119, 1/2" x 1/8", which fits nicely into 5mm sample tubes, and which cost about $2.00 each.

I hope that this procedure may be of some use to other NMR workers, and that sending it along will entitle me to a place on the mailing list of your newsletter which I would like very much to receive.

Sincerely yours,

Martha C. Thorpe

Martha C. Thorpe
Associate Chemist

mct pb

66-24

DEPARTMENT OF CHEMISTRY

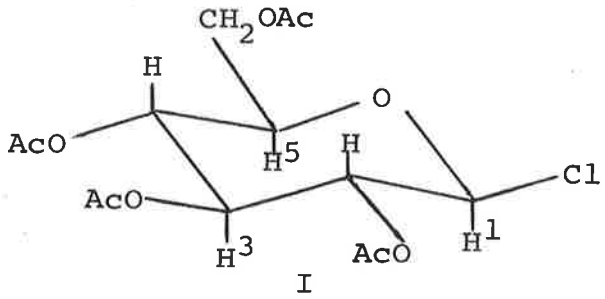
EDMONTON, ALBERTA
CANADA

March 10, 1964.

Dear Dr. Shapiro,

Strong, Specific Deshielding by Chloride Ion

In the course of an investigation of the anomerization of tetra-O-acetyl-β-D-glucopyranosyl chloride (I) by tetraethylammonium chloride in acetonitrile, we found that the chemical shifts of protons 1, 3 and 5 were strongly dependent on chloride ion concentration. Table I shows the downfield



I

shift, on changing the total chloride ion concentration from 0 to 1.0 M., of about 0.8 p.p.m. for H^1, 0.2 p.p.m. for H^3 and 0.6 p.p.m. for H^5. Figure 1 illustrates the phenomena. Note that the other protons are virtually unaffected, which vindicates the hopeful assumption that internal TMS is a suitable reference in this system.

TABLE I

Chemical Shifts (τ Scale) vs. Concentrations of β-Chloride (I) and Tetraethylammonium Chloride.

Concentrations, mole l^{-1}		Chemical Shifts		
I	Et_4NCl	τ_1	τ_3	τ_5
0.10	0.00	4.500		
0.10	0.05	4.424		
0.10	0.10	4.364		
0.10	0.20	4.248		
0.10	0.40	4.076		
0.10	0.60	3.929		
0.10	0.80	3.804		
0.10	0.90	3.782		
0.10	1.00	3.736		
0.10	1.20	3.650		
0.10	1.40	3.604		
0.50	0.00	4.492	4.76	6.04
0.50	0.20	4.289	4.71	5.9
0.50	0.40	4.115	4.68	5.8
0.50	0.60	3.975	4.63	5.7
0.50	0.80	3.858	4.62	5.56
0.50	1.00	3.746	4.59	5.43

Figure 1

N.m.r. spectra of tetra-O-acetyl-β-D-glucopyranosyl chloride (I) in acetonitrile at 100 Mc.p.s.

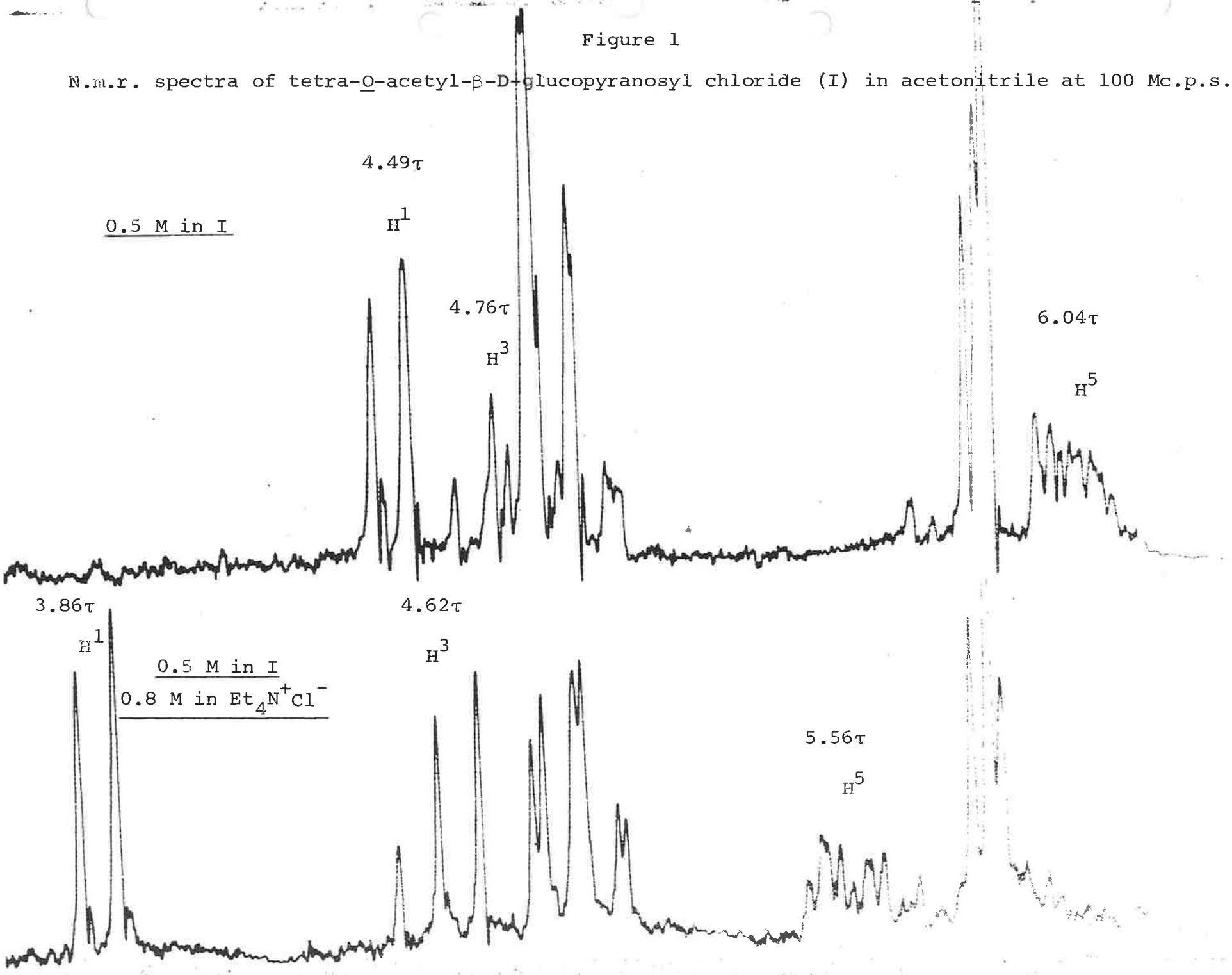
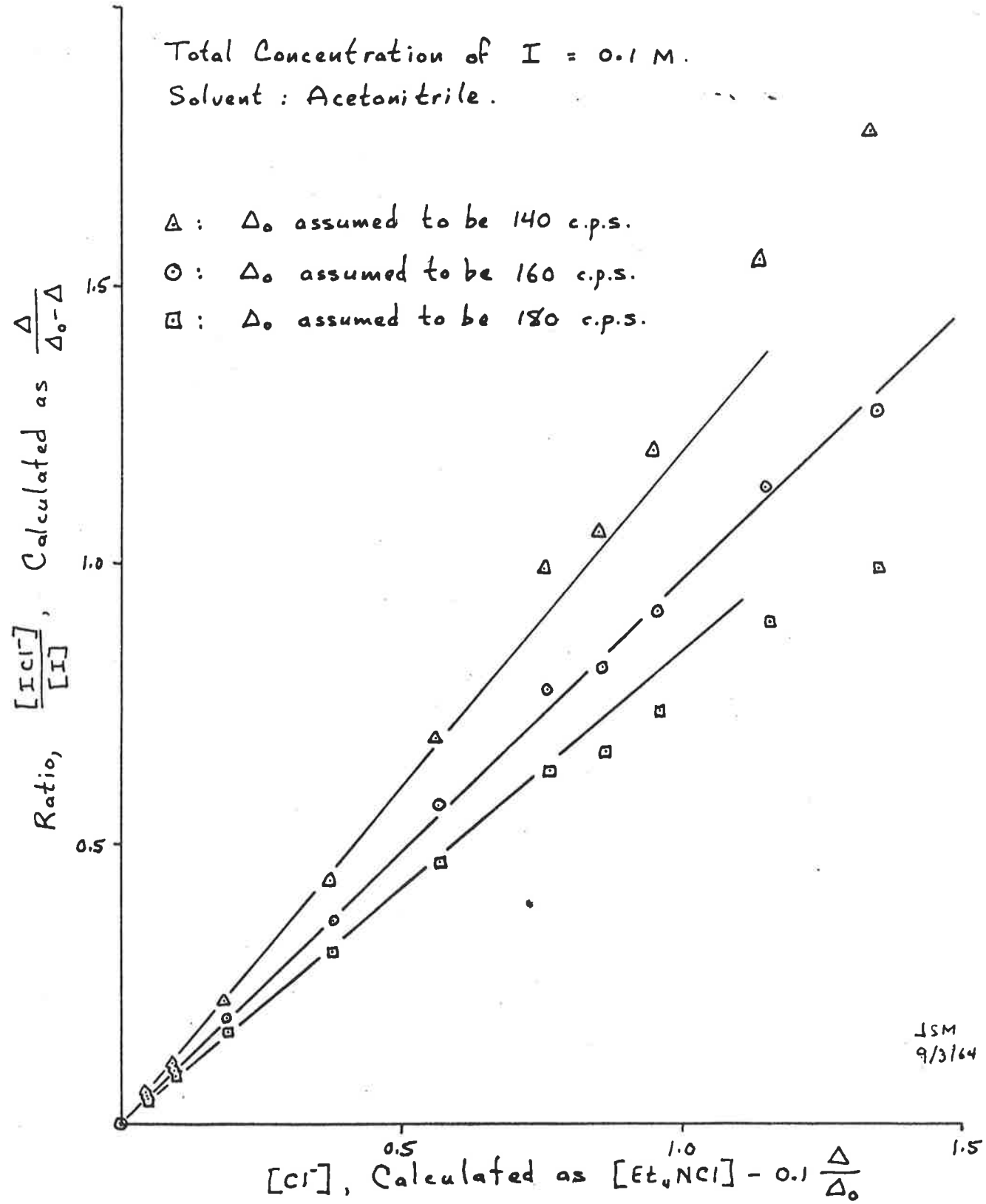


FIGURE 2. $\frac{[\text{Complex}]}{[\text{p-chloride}]}$ vs. $[Cl^-]$.



The α-anomer of I, which has the Cl in the axial position, shows no comparable shifts, and thus it was concluded that I can form a fairly stable complex with the chloride ion, involving H^1, H^3 and H^5. This would be in accord with the strongly nucleophilic behaviour of chloride ion in this solvent.

The chemical shift data for H^1 in Table I have been interpreted in terms of a rapid reversible reaction according to the equation,

$$I + Cl^- \rightleftharpoons I \cdot Cl^-$$

This requires a linear dependence of the ratio of complexed to free β-chloride on free chloride ion concentration according to the equilibrium relation,

$$\frac{[I \cdot Cl^-]}{[I]} = K\,[Cl^-]$$

The ratio on the left hand side is equal to $\Delta/(\Delta_o - \Delta)$, where Δ is the observed mean shift of H^1 from the uncomplexed value at $[Cl^-] = 0$, and Δ_o is the corresponding shift for the pure complex. This latter value cannot be observed directly. It was inferred to be 160 ± 10 c.p.s. at 100 Mc.p.s., since this value gave the best linear plot in Figure 2. The equilibrium constant, K, is thus about 1.0.

The magnitude of the downfield shift of the three affected protons in the complex can be accounted for approximately in terms of an electrostatic model such as Buckingham's, if the bare chloride ion is about 2.5 to 3 Å from these protons.

This highly specific interaction has also been observed in methyl β-D-glucopyranoside tetraacetate. The nature of the solvent is important, as well as the anion. Bromide ion produces a smaller but significant effect; perchlorate none at all. This specific effect of unsolvated anions is receiving further attention.

Sincerely yours,

R.U. Lemieux, J.S. Martin and Jun'ichi Hayami

Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, Illinois 60616, U. S. A.

RUL: ma

66-28

GENERAL ELECTRIC COMPANY

RICHLAND, WASHINGTON 99352 . . . . AREA CODE 509, TELEPHONE 942-1111

HANFORD ATOMIC PRODUCTS OPERATION

HANFORD LABORATORIES

March 9, 1964

Dr. Bernard L. Shapiro
Editor, MELLON-M-R
Department of Chemistry
Illinois Institute of Technology
Technical Center
Chicago 16, Illinois

Dear Barry,

SOLVENT EFFECTS IN BENZENE SOLUTIONS OF β-DICARBONYLS

We would like to report an interesting solvent effect found in the course of some NMR studies at Michigan State University[1,2] on benzene solutions of β-dicarbonyl compounds of the acyclic variety. These compounds exist as tautomers in the following equilibrium:

$$\underset{\text{(keto)}}{RCOCHR'COR''} \longrightarrow \underset{\text{(enol)}}{RC(OH)=CR'COR''}, \qquad (1)$$

where R" is a halogen, an alkyl or alkoxy group, and R, R' may be a halogen, an alkyl or phenyl group.

Chemical shifts for most protons of the β-dicarbonyls occur at higher applied magnetic field on dilution in benzene as a result of the usual ring current effect. However, the enol OH resonance peak is shifted downfield as much as 45 cps at infinite dilution for a series of compounds variously substituted with electron-donating and electron-withdrawing groups. Exceptions to this unusual effect include trifluoro- and hexafluoroacetylacetone. Table I includes chemical shifts for several such compounds at infinite dilution in benzene.

These effects may be explained in terms of a model which suggests a particular orientation of benzene with the β-dicarbonyl molecule. Thus in the proposed complex for acetylacetone shown in Figure 1 the more positive end of the molecule (acetyl methyls) lies above the plane of the ring in the region of greatest π-electron density, whereas the more negative carbonyl groups tend to avoid this region. A comparison of the observed chemical shift values with those calculated from the table of Johnson and

(1) J.L. Burdett, Ph.D. Thesis, Michigan State University, 1963.

(2) J.L. Burdett and M.T. Rogers, submitted for publication.

GENERAL ELECTRIC

Bovey[3] for protons in the vicinity of a benzene ring results in good agreement with experiment if the proposed complex consists of two molecules of benzene for one molecule of the β-dicarbonyl. Since the highly electronegative CF_3 group would not be attracted to the π-electron region of the benzene molecule, trifluoro- and hexafluoroacteylacetone would not be expected to form a stable complex with this configuration. Similar association complexes of benzene with polar molecules have been proposed by Hatton and Richards[4], Schneider[5], and LaPlanche and Rogers[6].

More detailed studies of solvent effects in β-dicarbonyls[1,7] and NMR studies of the pure β-dicarbonyls[1,2,7] may be found elsewhere.

One of the authors (JLB) would like to be added to the mailing list (General Electric Company, Hanford Laboratories, Richland, Washington) with this as an initial contribution.

Sincerely yours,

Jane L. Burdett

Max T. Rogers

JLB:bt

(3) C.E. Johnson, Jr. and F.A. Bovey, J. Chem. Phys., 29, 1012 (1958)

(4) J.V. Hatton and R.E. Richards, Mol. Phys., 3, 253 (1960)

(5) W.G. Schneider, J. Phys. Chem., 66, 2653 (1962)

(6) L. LaPlanche and M.T. Rogers, J. Am. Chem. Soc. 85, 3728 (1963); 86, 337 (1964).

(7) J.L. Burdett and M.T. Rogers, J. Am. Chem. Soc., in press.

GENERAL ELECTRIC

Table I. Chemical Shifts of the Proton Groups of β-Diketones and β-Ketoesters in Benzene at Infinite Dilution*

Compound	Ethyl		Acetyl					
	CH_3	CH_2	CH_3^e	CH_3^k	α-H^k	α-H^e	OH^e	Other
Acetylacetone	-	-	25	33	50	39	-45	-
α-Chloroacetylacetone	-	-	25	29	39	-	-29	-
Hexafluoroacetylacetone	-	-	-	-	-	40	+37	-
Trifluoroacetylacetone	-	-	57	54	-	46	+27	-
α-Methylacetylacetone	-	-	24	29	47	-	-34	20^k α-Me 32^e α-Me
Ethyl acetoacetate	19^k 21^e	16^k 14^e	25	31	35	8	-35	-
Ethyl α-chloroacetoacetate	30^k 27^e	30^k 26^e	21	32	43	-	-25	-
Ethyl trifluoroacetoacetate	30^k 32^e	31^k 33^e	-	-	47	24	-10	-
Ethyl α-methylacetoacetate	23	18	-	24	28	-	-39	8 α-Me

*Chemical shifts are in cps relative to the pure compound, and are recorded on the Varian A-60 spectrometer.

k = keto, e = enol tautomer.

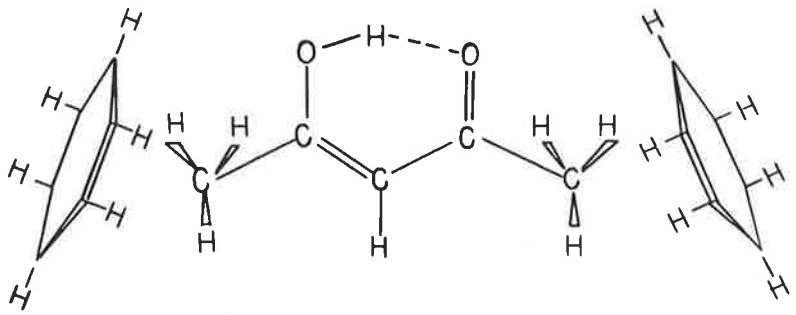


Figure 1. Complex of Benzene with Acetylacetone

LABORATORIUM FÜR PHYSIKALISCHE
CHEMIE UND ELEKTROCHEMIE DER
TECHNISCHEN HOCHSCHULE, STUTTGART

STUTTGART N
Wiederholdstraße 15
Telefon 29 97 83 93

Dr. H. Dreeskamp

March 12, 1964

Re.: Comments on hetero nuclear Spin coupling

Dear Dr. Shaprio:

In a recent publication (1) I drew attention to a remarkable regularity of the values of X-H coupling constants in XH_4 compounds (X=C,Si,Ge,Sn,Pb). Adopting the opinion that the Fermi-contact term dominates the coupling mechanism, the coupling constant is a product of essentially 3 factors: A containing the constants of the magnetic properties of the nuclei, B the density of the binding electrons at the nuclei and C properties of the electronic wave function i.e. besides Δ E the M-O "bond order"-(2) or the V-B "deviation of perfect pairing" (3). Since the "normalized coupling constant" $J'=J/A$ (I suggest to retain the units of [cps] for this quantity) correlates well with the density of valence electrons from atomic spectral data[1], I think this factor C is essentially constant in these compound and further all J' are positive. In $X(CH_3)_4$ compounds a similar correlation has been given earlier[4], and a correlation of J_{X-C-H}/J_{X-H} with J_{C-H} given and interpreted as due to a variation of the factor C in the methyl compounds. In a footnote to Fig.3 of (1) it was stated that an opposite sign of J_{X-C-H} to J_{X-H} has been found for Sn and Si compounds. I would like to sketch the line of reasoning that lead to this statement:

In their extensive study of Sn $H_i(CH_3)_{4-i}$ compounds Flitcraft and Kaesz[5] gave the coupling constants which are plotted in Fig.1. Interpreting the variation in J-values as due to "hybridization" at the Sn nucleus if follows a constancy of

$$\sum J = i J_{X-H} + (4-i)\frac{J_{X-H}(XH_4)}{J_{X-C-H}(XMe_4)} J_{X-C-H}$$

which is remarkably well obeyed. The same was found to be true in the analogous Si-compounds Fig.2. Further, using the H-H decoupling facilities of the

Varian-Integrator an opposite sign of J_{Si-H} to J_{Si-C-H} was established for $SiH_i(CH_3)_{4-i}$ (i=1,2,3) and for $Sn\,H(CH_3)_3$. I think it safe to extrapolate to i=0 and 4 and accept J'_{X-H} as positive and J'_{X-C-H} as negative. Still along the same - gratifyingly simple - line of reasoning [as done for J_{C-C} in (1)] the J_{Pb-C} in $Pb(CH_3)_4$ is predicted to be +600 cps. Working with substance of isotopes in natural abundance and the Nucl. Mag.Res.Spec. C^{13} Spin Decoupler this coupling was found to be $J_{Pb-C}=+380\pm50$ cps, [assuming J'_{Pb-C-H} to be negative]. Fig.3 summarizes the nomalized coupling constants J'. Values for X-H are divided by a factor of 4, to take care of the fact that the H is engaged in only one bond against four for the rest of the plot. Please feel free to use the term hybridisation here.

A suggestion as to nomenclature: Might it still be possible to retain the term "coupling unit" (6) [c.u] for J_{X-H}? A remarkable variety of coupling constants expressed in [c.u] show a very simple pattern, only a few I have demonstrated above.

(1) H.Dreeskamp, Zeitschr.f.Naturf. 19a 139 (1964)

(2) H.M.McConnell, J.Chem.Phys. 24 460 (1956)

(3) M.Karplus, J.Chem.Phys. 30 11 (1959)

(4) H.Dreeskamp, Z.Phys.Chem. N.F. 38 121 (1963)
G.W.Smith, J.Chem.Phys. 39 2031 (1963)

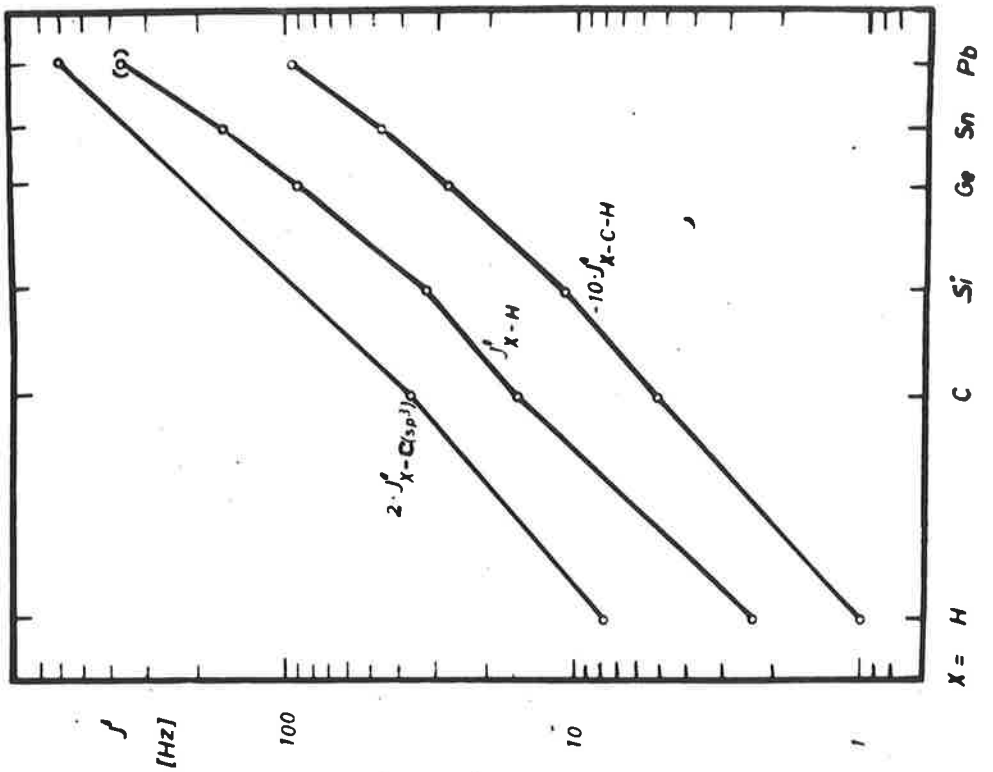
(5) N.Flitcroft and H.D.Kaesz, JACS 85 1377 (1963)

(6) R.M.Lynden-Bell and N.Sheppard,
Proc.Roy.Soc.London A269 385 (1962)

Very truly yours,

H. Dreeskamp

Fig. 3



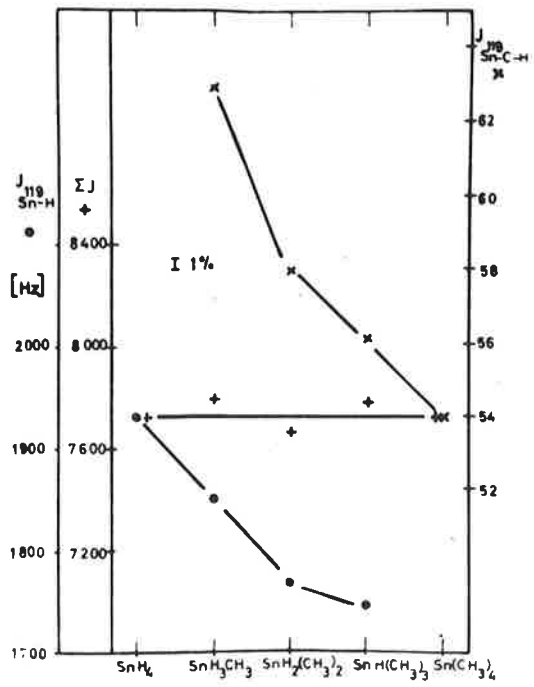


Fig. 1

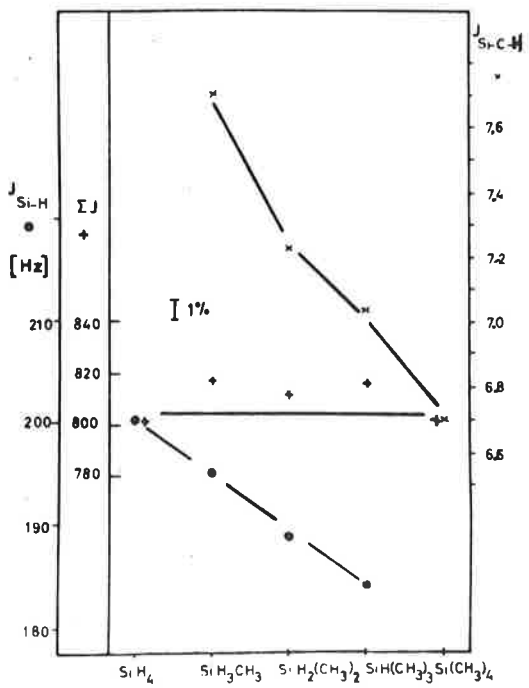


Fig. 2

66-34

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

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

March 5, 1964

Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

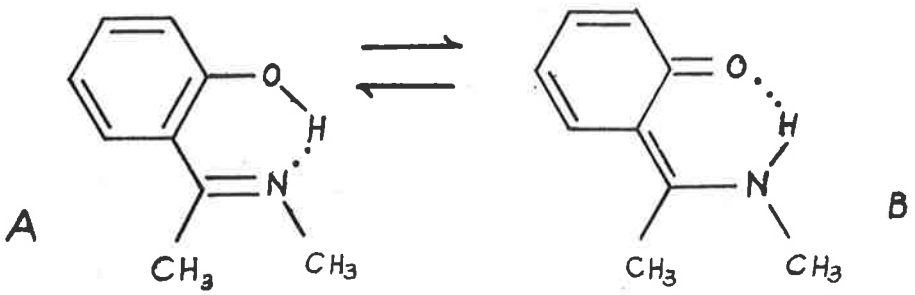
Thank you for your subscription reminder. As usual, I have a pot pourri of comments, which I hope will be of interest to your readers and will fulfill my obligation.

Re: Dr. Abraham's query (IITNMR No. 65), one of the service engineers from Varian has taken A-60 Variable Temperature probes many times to -100° C (with both the customers knowledge and risk). The temperature can be kept below -60° for only about 15 minutes since the control sample eventually will freeze. To attain low temperatures, the "nitrogen" line between the dewar and the probe is made as short as possible. In use, the system is allowed to soak a while (set to -30 or so) until the inlet lines are thoroughly cool. If all is well, one can drop quickly to -60 and then to -80 or better.

The following comments are well known to the older ones, but may save the newer NMR'ers some grief. If trouble is experienced in obtaining resolution with a probe, check the various parts for iron. For example, a Varian service engineer recently found a sheet iron hinge on our magnet probe cover (for a while we thought we had the most thermally sensitive system in existence). The best yet was finding a ferromagnetic shield on a probe cable. I gather that a few iron (or steel) screws in a probe body is commonplace.

By the way, we've had no trouble with locating either of our variable temperature probes in the magnet gap. We just set them in the center and adjust the shim controls and all is usually well. As a precaution we pound our hands bloody shaking the air bubble (which cannot be seen in the variable temp. probe) back up. If the 5 KC becomes unstable after a few temperature cycles (above and below room temperature), pull the probe out of the gap and pound the bubble back into place (the optimum force is that just short of breaking the probe).

Dr. Emily Dudek and I have some work on N^{15} substituted Schiff Bases in progress. The most interesting finding is with:



At low temperatures ($CDCl_3$ soln, -30°), the "hydroxyl" signal is a 30 cps doublet, suggesting that this results from the presence of about 1/3 or form B. At room temperature, the acidic proton resonance is about 8 cps wide, here the equilibrium favors tautomer A (the expected one). To eliminate any chance of "through space" couplings, the UV spectra were checked as a function of temperature. In $CHCl_3$ soln., a weak band at 390 m increases in intensity as the temperature is lowered, thus corroborating the p.m.r. results.

The hydrogen bonding studies of 2-carbamoyldimedone and related compounds is being sent to the Journal.

Congratulations on your new position, I hope the family is well settled in their new home.

Yours truly,

Gerald Dudek
Research Associate

66-36

March 16, 1964

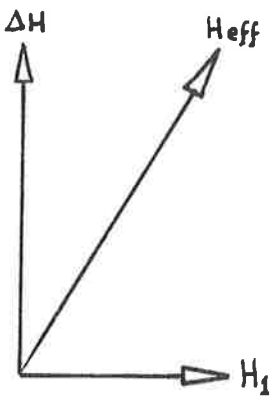
Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

Bloch-Siegert Shifts

We might logically extend the use of this term to cover a whole set of situations where small displacements of an NMR signal may be attributed to the effect of a strong, off-resonance radiofrequency field. The original effect was of course described in a very early paper by F. Bloch and A. Siegert, Phys. Rev. 57, 522 (1940). This note is merely a collection of old and new examples of the phenomenon and an attempt to apply a very simple pictorial description to fit them all.

Let us consider a transition that is offset by an amount ΔH gauss from a strong oscillatory field H_1 gauss (rotating component), and transform to a frame of reference that is rotating about the direction of the applied static field H_o at the frequency of the rf field and in the sense of the nuclear precession. The nuclei experience an effective field, H_{eff}, given by the condition



$$H_{eff}^2 = \Delta H^2 + H_1^2 \qquad (1)$$

The transition frequency will suffer a small displacement S which, if $\Delta H \gg H_1$ will be given by the approximate condition

$$S = \left(\frac{\gamma}{2\pi}\right)\left(H_{eff} - \Delta H\right) \approx \tfrac{1}{2}\left(\frac{\gamma}{2\pi}\right) H_1^2 / \Delta H \quad \text{cps} \qquad (2)$$

This simple expression can be used to calculate "Bloch-Siegert shifts" in many situations.

(1) The Bloch-Siegert Effect Itself

When a linearly oscillating rf field ($2H_1$) is employed in an NMR experiment it is thought of as two rotating components of opposite senses. The component that rotates in the sense of the nuclear precession excites the resonance--but the other component is responsible for a small shift. In this case the offset ΔH is $2H_o$ and the NMR line is shifted downfield by

$$S = \tfrac{1}{4}\left(\frac{\gamma}{2\pi}\right) H_1^2 / H_o \quad \text{cps} \qquad (3)$$

(2) Shifts of Modulation Sidebands

Modulation of H_o or the spectrometer radiofrequency generates sideband responses, and these are slightly shifted by the presence of the strong centerband rf field H_1. If the modulation frequency is ν_m cps, the Larmor condition is fulfilled by

$$\left(\frac{\gamma}{2\pi}\right) H_{eff} = \nu_m \qquad \text{cps} \qquad (4)$$

Two different experiments must be distinguished:

(a) Field sweep. If the sideband response is examined by sweeping the applied field H_o, it will appear at a distance $\gamma\Delta H/2\pi$ from the centerband resonance; that is, less than ν_m by the correction,

$$S \approx \tfrac{1}{2}\left(\frac{\gamma}{2\pi}\right) H_1^2/\Delta H \approx \tfrac{1}{2}\left(\frac{\gamma}{2\pi}\right)^2 H_1^2/\nu_m \qquad \text{cps} \qquad (5)$$

This is of course the experiment commonly employed to calibrate H_1.

(b) Frequency sweep. If the applied field H_o is held constant and the sideband response recorded by sweeping ν_m, it will appear further from the centerband resonance than the offset $\gamma\Delta H/2\pi$ by the same correction S.

In systems that use another sideband response, ν_m^*, for example from tetramethylsilane, as an error signal for field-frequency control, there are two opposed corrections which must be applied when relating the signal frequency to TMS,

$$S \approx \tfrac{1}{2}\left(\frac{\gamma}{2\pi}\right)^2 H_1^2 \left[(\nu_m)^{-1} - (\nu_m^*)^{-1} \right] \qquad \text{cps} \qquad (6)$$

(3) Spin Decoupling

When the strong rf field (which is now usually called H_2) is used to perturb one group of nuclei (X) while the resonance of a second group of nuclei (A) is recorded, there is a displacement S of the A resonance, which therefore affects the condition for optimum separation of the two rf fields in a field sweep experiment. For ~~the~~ first-order spectra $\gamma\Delta H/2\pi$ is approximately equal to the chemical shift $\nu_A - \nu_X$.

$$S = \tfrac{1}{2}\left(\frac{\gamma}{2\pi}\right)^2 H_2^2 / (\nu_A - \nu_X) \qquad \text{cps} \qquad (7)$$

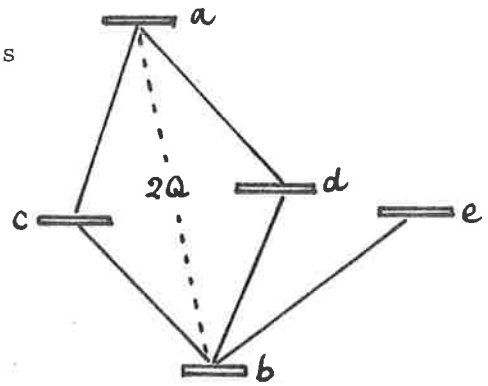
However another effect intervenes, for the "optimum decoupling" condition involves a slight offset of the strong rf field from exact resonance for the X nuclei, towards the A resonance, a correction which is approximately twice that shown above and in the opposite sense (see Mellon Newsletter 43, 10).

(4) Shifts of Double-Quantum Lines

Application of strong rf fields to complex nuclear spin systems may be thought of as distorting the energy level diagram, since each transition experiences not the constant applied field H_o but an effective field H_{eff} determined by the offset ΔH from the strong oscillatory field H_1. A further complication in strongly coupled spectra is that the rf field only perturbs a transition in proportion to the matrix element λ for that transition; as a result H_1^2 is always associated with the transition intensity λ^2 ($\lambda^2 \rightarrow 1$ for first order spectra).

The detection of double-quantum lines involves the application of unusually large rf fields and the consequent shifts of energy levels can appreciably shift the

double-quantum line itself. Consider a double-quantum transition of frequency Q. Its Bloch-Siegert shift may be calculated as the sum of all the possible perturbations of the levels a and b, that is a summation over all the transitions that terminate on levels a and b. Note that a shift R cps of a given transition frequency becomes a shift R/2 cps of one of the energy levels and only R/4 cps in the observed double-quantum frequency Q. Hence



$$S = \frac{1}{8}\left(\frac{\gamma}{2\pi}\right) H_1^2 \sum_i \left(\lambda_i^2 / \Delta H_i\right) \quad \text{cps} \qquad (8)$$

It is of interest to note that pairs of transitions such as a → c and c → b have the same offset ΔH, and in the first-order limit contribute equal and opposite terms to the summation. For a two-spin system the shift is necessarily zero. Reported shifts of double-quantum lines have usually been of the order of a few tenths of a cps.

(5) Shifts of Combination Lines

(a) Combination lines that have a weak relative intensity λ^2 can be detected in a double resonance "tickling" experiment providing the irradiating rf field H_2 is strong enough to produce an observable splitting of a second transition that has an energy level in common with the combination line. Since the splitting is given by $\gamma H_2 \lambda / 2\pi$ cps, and λ is very small for a weak combination line, H_2 will appreciably distort the energy level diagram and the combination line will be shifted. This is now a normal $\Delta m = 1$ transition, so a perturbation of one of the energy levels affects the combination line frequency directly, with the result that the summation for the shift is just twice that shown in Eq. 8. Shifts as high as 1 cps have been observed in practice.

(b) The saturation parameter for a transition in a strongly coupled system is

$$(\gamma H_1)^2 \lambda^2 T_1 T_2 \qquad (9)$$

One may therefore enhance the relative intensity of a weak combination line in a single resonance experiment by increasing H_1 above the optimum setting for strong lines. This compensation for the small value of λ^2 is obtained at the expense of applying an unusually strong rf field, which can distort the energy level diagram and cause a shift of the frequency of the combination line. Taking the argument to the extreme, any NMR line should show (extremely small) shifts due to this type of generalized Bloch-Siegert effect.

Sincerely yours,

Ray Freeman

Ray Freeman
Analytical Instrument Research

RF:iw

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