Friends.

Mailed:
30 December 1963

Monthly Ecumenical Letters from Laboratories Of N-M-R

No. 63

DEADLINE FOR NEXT ISSUE
24 January 1964

Chemistry Department
Cornell University
Ithaca, New York

November 27, 1963

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

I would like to begin our subscription to MELLONMR by placing a position wanted item.

I have recently completed my Ph. D. studies at NYU where my dissertation was concerned to a large extent with solvent and asymmetry effects on NMR. I am currently a National Institutes of Health Post-Doctoral Fellow at Cornell working in Organic Chemistry.

I would like a position either in a university or a related research institute where there is some opportunity for teaching and where there is an opportunity to pursue Physical-Organic research geared to NMR and/or Mass Spec. I will be available in the Fall of 1964. I will be happy to forward a detailed resume to any interested parties.

Looking forward to our first copy of MELLONMR, I remain

Very truly yours,

George H. Wahl Jr.

George H. Wahl, Jr.

BY AIR MAIL

63-2

IMPERIAL CHEMICAL INDUSTRIES LIMITED
DYESTUFFS DIVISION

Telephone: Cheetham Hill 1411 (long distance)
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P.O. BOX 42
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MANCHESTER, 9
ENGLAND

Research Department.
Our ref. PL/PHY-5.
Your ref. Letter No.:

Dr.B.L.Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pennsylvania, U.S.A.

26th November 1963.

Dear Dr.Shapiro,

We are pleased to be put on your mailing list for MELLONMR. As promised in our last letter, we are now offering a few notes on N.M.R. laboratory techniques which may be of interest.

Air Conditioning

A few years ago we experimented with various air conditioning arrangements and eventually reached a system which gave good stability with a 40Mc/s Varian V-4300B spectrometer. A system based on this is giving excellent results with a recently installed HR-100 instrument. The basic principles are as follows:

(i) The magnet and the air conditioning unit are sited at opposite ends of the laboratory so that a considerable volume of air acts as a buffer. A baffle fitted over the air conditioner outlet breaks the airflow and prevents a direct blast towards the magnet.

(ii) The air conditioner is a water-cooled "Temkon" Series N made by Temperature Ltd., Fulham, London S.W.6 (also referred to by Page and Green, MELLONMR No.58, p. 28). The defrost relay is disconnected and no heater is used. The fan draws air continuously through a duct from an adjacent laboratory whose temperature is constant to within ± 3°C. (this is not critical).

(iii) On-off control is applied to the compressor of the "Temkon" by a mercury thermometer/thermostat with adjustable contact (J.C.Cowlishaw Ltd., London), through a thyratron-operated hot-wire relay (A.E.I., Type EA.4). The thermostat is mounted on the end of the magnet with a small fan drawing air over the bulb.

(iv) Air is exhausted from the laboratory through the V-2100B power supply to an extract duct with a booster fan at the exit.

(v) Venetian blinds are fitted to the double-glazed windows to keep out direct sunlight.

(vi) The air temperature at the magnet is continuously monitored by a sensitive recorder (Rustrak Model 133, 15-30°C., with Model 1334 probe).

Continued...

FROM I.C.I.Ltd., Dyestuffs Division, Hexagon House, Blackley, Manchester 9.

CONTINUATION: Sheet No. 2.

TO Dr.B.L.Shapiro,
Mellon Institute,
Pittsburgh 13.

Date

This system gives a cycle period of about 7 mins. with a peak-to-peak amplitude of about 1°C. at the magnet. This is found adequate to maintain a working field homogeneity for 12 to 24 hours on the HR-100 without shim coil adjustments. Small adjustments every few hours are needed to maintain optimum resolution.

Magnet Pole Insulation

Because the magnet coil faces and the preamplifier are considerable heat sources, the HR-100 is particularly susceptible to homogeneity loss owing to convection currents or draughts through the pole gap. We have fitted cylindrical aluminium covers in three pieces, backed by ¼" flexible polyurethane foam, which almost completely enclose the pole gap and are held on to the edges of the shim coil units by rubber bands. There are gaps for the probe and leads, and for inserting the sample. Fitting these brought a marked improvement in homogeneity stability.

Solution Filtering.

Filtering a small amount of solution to remove suspended solids may present difficulties when the amounts are small, and is in any case a tedious chore if gravity filtration is used. A quick and simple method is to push a fairly tight plug of cotton wool or glass wool into the middle of the empty N.M.R. sample tube, then pour in the solution and force it through the plug by whirling in a hand-operated centrifuge.

Yours sincerely,

J.K.Becconsall

J.K.Becconsall.

P. Coo.

P. Coo

P. Hampson.

P Hampson

63-4

WALTER REED ARMY INSTITUTE OF RESEARCH
WALTER REED ARMY MEDICAL CENTER
WASHINGTON 12, D.C.

IN REPLY REFER TO:

20 November 1963

NMR Identification of Isomeric Aminopropylthiosulfuric Acids

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

We would like to submit the following as an initial "subscription" to your excellent MELLONMR Newsletter. My colleague, Dr. Daniel L. Klayman, of the Department of Medicinal Chemistry of this Institute, has been interested in determining and distinguishing the isomeric Bunte salts I and II by physical means:

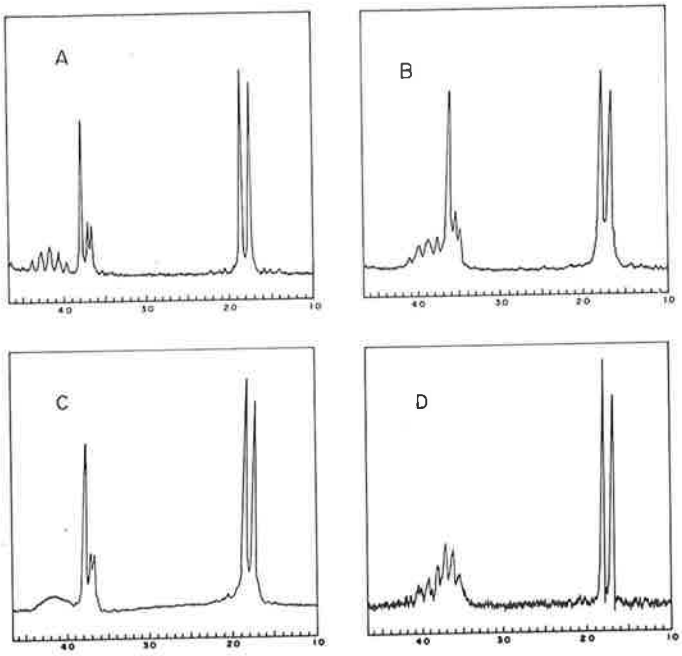
I $CH_3-\underset{SSO_3H}{\underset{|}{CH}}-CH_2-NH_2$ II $CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2-SSO_3H$

The A-60 spectra in D_2O solution are quite similar, the $\geq CH-CH_2$ group approximating to AB_2. At lower pH in water, however, the rate of protolysis of the NH_3+ protons is decreased so that one can observe the superimposed coupling of the NH_3+ protons to the CH or CH_2 protons depending on the isomer. Spectrum A goes to C and B to D on acidification and we can now assign the structures on the basis of intensity considerations. The B_2 protons (CH_2) of the primary amine shows the strong ca. 7 c.p.s. additional coupling from the NH_3+ protons in spectrum D, and so B and D represent I. Conversely, spectrum C shows additional coupling of the A proton and so represents structure II. Neutralization of the solution returns the spectra C and D to their original shapes.

We would be most grateful if you would send us any back issues of the Newsletter that you have available.

Sincerely,

James W. Lown, Ph. D.
Department of Biophysics



A-60 Spectra of 15% aqueous solutions. Scale in p.p.m. from T.M.S. as external reference.

UNION CARBIDE

UNION CARBIDE PLASTICS COMPANY

DIVISION OF UNION CARBIDE CORPORATION

RIVER ROAD, BOUND BROOK, N. J.

September 23, 1963

Practical Aspects of SH and OH Exchange

It is well known that OH hydrogens exchange (or can easily be induced to exchange) sufficiently rapidly that HCOH spin-spin splittings are obliterated. Anyone who has worked with mercaptans is aware, on the other hand, that somewhat more effort is required to promote equally rapid exchange of the SH proton. The literature connected with this phenomenon has recently been reviewed,[1] and it appears that under comparable circumstances, OH and SH exchange rates differ by several orders of magnitude. During the course of our work here we have come across a compound which exhibits qualitatively the various states of exchange: 3-mercapto-2, 2-dimethylpropan-1-ol (I). I'm presenting the effects of temperature and acid here with the hope that it will be of service to some of the readers in describing this type of phenomenon to neophytes.

HCOH splittings are not observed in samples of I, as they are normally examined. In order to slow the exchange sufficiently that the coupling effects are observed, it was necessary to treat a dilute (~ 2%) deuterochloroform solution of I by passing it over a short alumina column (Al_2O_3 packed in a medicine dropper) to remove the last traces of catalytic $H^{\oplus}$. This technique would appear to be generally useful for obtaining splitting patterns in samples which are sufficiently acidic to be exchange-decoupled. The patterns so obtained would, of course, have important structural implications.

HCSH coupling effects are quite apparent in the spectrum of a neat specimen of I. Some exchange effects are encountered on warming the sample. However, in this case it was necessary to add a trace of sulfuric acid (trace = touch wetted pipette to inside of NMR tube and shake) to the neat sample to bring about the full range of exchange effects within the available A-60 temperature range.

Figure 1 is a room temperature spectrum of a neat sample of I as received.[2] The peak assignments are obvious.

In the series of Figure 2, a 2% (by wt.) $CDCl_3$ solution of I, treated by the Al_2O_3 method, is examined at various temperatures. Note particularly the improved HCOH splitting pattern resolution as temperature is lowered, and the

variation of the chemical shift of the OH (hydrogen bonding effects). At -42°C., the OH and CH_2O chemical shifts become accidentally degenerate, and spin-spin splitting disappears from the spectrum.

In Figure 3, a neat, acidified sample of I is warmed. Note that while the coalescence temperature for the HCSH splitting is ~50°C., the coalescence temperature for the mergence of the OH and SH bands is ~75°C.

It has been stated [1] that the base catalyzed exchange of SH and OH are of comparable rate. Accordingly, it was found that 1 drop of an aliphatic amine (piperidine) produces the same effect on a neat specimen at room temperature as a trace of sulfuric acid at 133°C.

1. A. Loewenstein and T. M. Conner, Ber. der Bunsengesellschaft 67, 280 (1963).

2. The sample of I was graciously supplied by Dr. G. L. Brode.

WFB:mjk

William F. Beach

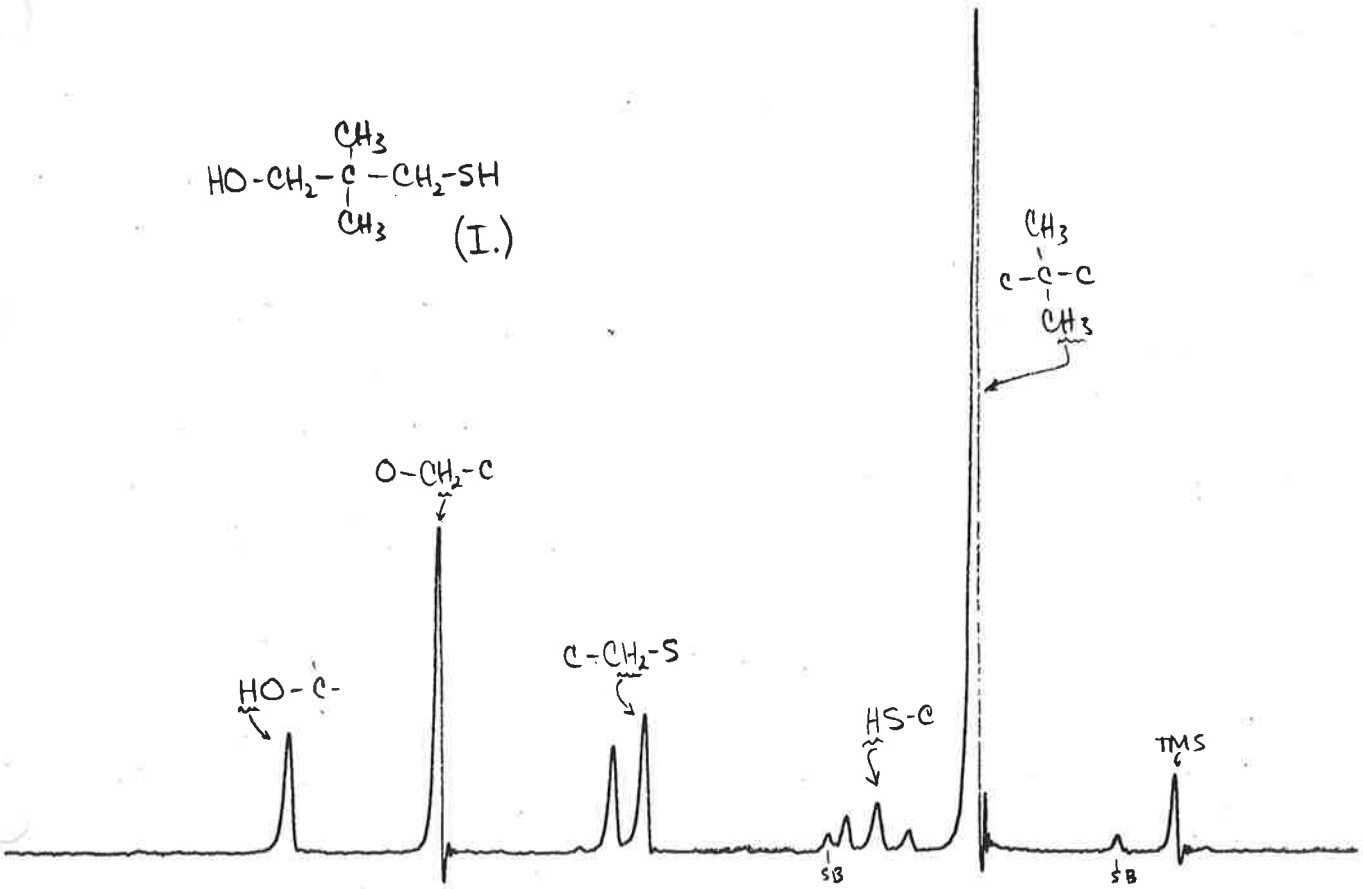


Figure 1

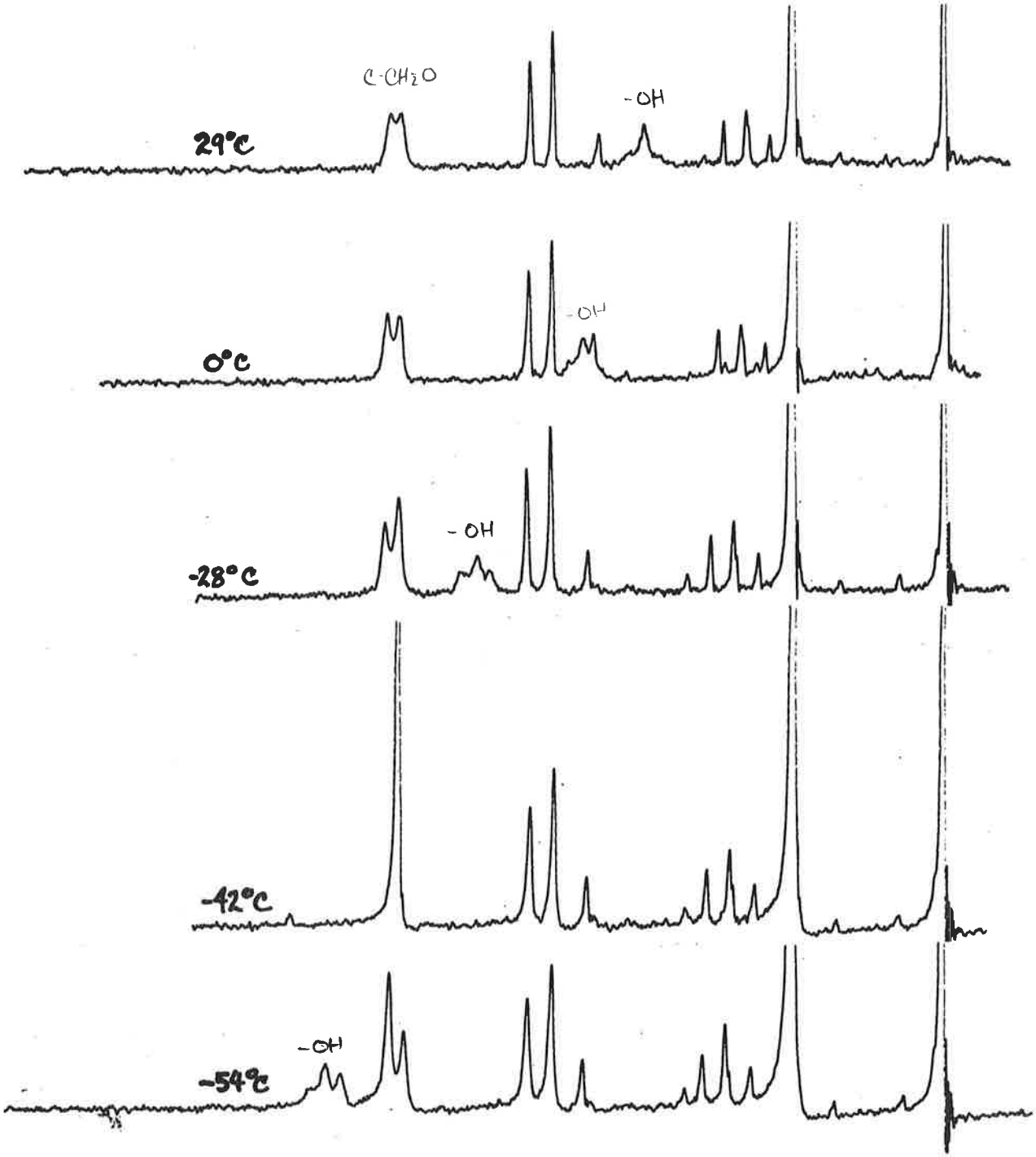


Figure 2

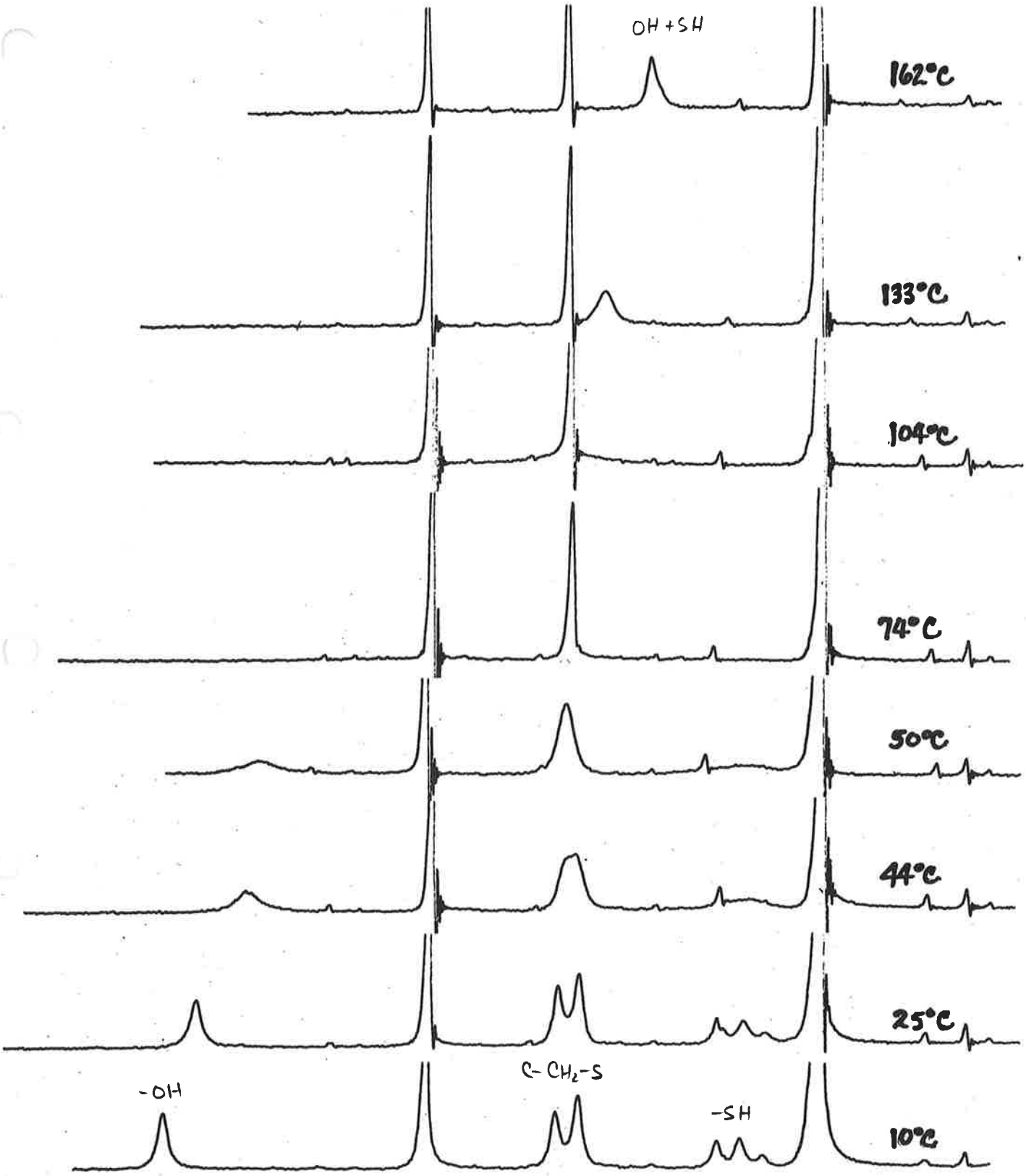


Figure 3

63-10

INDIANA UNIVERSITY
BLOOMINGTON, INDIANA, 47405

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

AREA CODE 812
TEL. NO.

November 22, 1963

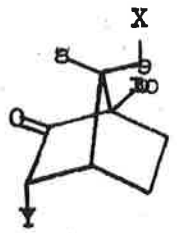
Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

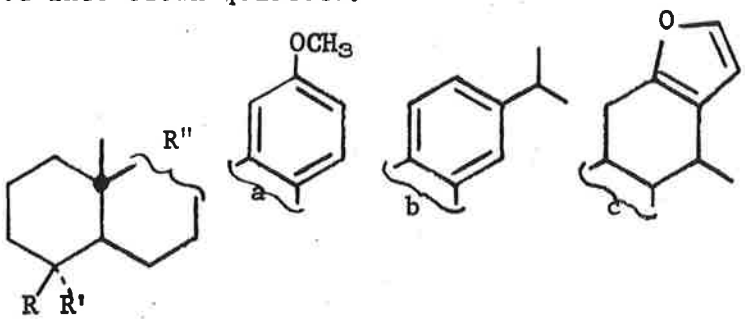
Stereospecific Long-Range H-H Couplings

Dear Barry:

I hope this letter will serve as an initial subscription fee for MELLONMR, perhaps procure for me such back issues as are available, and simultaneously provide some information of interest to your readers. It concerns some compounds in which we have observed stereospecific long-range couplings between protons connected only by single bonds, and may be useful to those concerned with the theory of such coupling.

One of the (non-equivalent) 9-CH_2 protons in 9-bromocamphor (Ia), 9-iodocamphor (Ib), and 3,9-dibromocamphor (Ic) is spin-coupled to one of the methyl groups with J≈1.0 c.p.s., the downfield half of the AB quartet appearing as a pair of quartets (Fig. 1). If the other 9-proton is likewise coupled to the methyl the magnitude of the coupling is much less, since the upfield half of the quartet consists of much narrower lines. We don't yet know which methyl group is involved, although we suspect C-8, but I hope that this question will soon be answered by deuterium labelling experiments which are in progress. It is interesting that the magnitude of the long-range coupling is somewhat dependent on the nature of the 9-substituent. Thus, while one of the 9-protons of the corresponding alcohol (Id) and p-toluenesulfonate (Ie) gives lines which are clearly broader than those from the other, their half widths are distinctly less than those from the bromide and iodide and they are not resolved into clean quartets.





Ia; X=Br,Y=H
b; X=I,Y=H
c; X=Br, Y=Br
d; X=OH, Y=H
e; $X=OSO_2C_6H_4CH_3$,Y=H

IIa; R=CHO, R'=CH_3,R''=a
b; R=CH_3,R'=CHO,R''=b
c; R=CHO,R'=CH_3,R''=c
d; R=CH_3,R'=CHO,R''=c

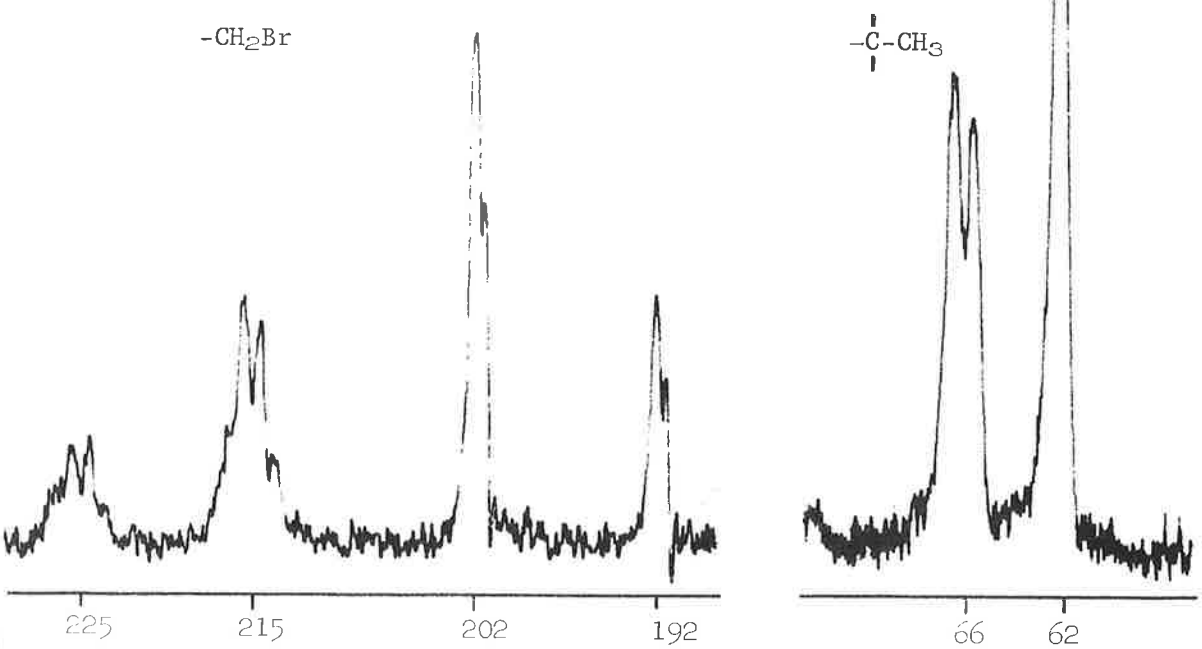
Our other example of stereospecific long-range coupling involves several diterpenoid aldehydes. The aldehyde proton resonance of O-methyl podocarpol (IIa) appears as a doublet (J=1.4 c.p.s.), while that of dehydroabietal (IIb) is a singlet. Similarly the C-4 epimeric pair vouacapenal (IIc) and vinhatical (IId) give a doublet and singlet resonance respectively for their aldehyde protons. In each case the axial aldehyde is long-range coupled whereas the equatorial one is not, and several other examples falling into the same pattern have been observed. It seems that the multiplicity of this peak may turn out to be a useful diagnostic in structure determinations. From the appearance of the multiplet (doublet) it seems that one proton is involved, and decoupling experiments locate that proton at a rather high field (68 ± 3 c.p.s. for IIa and 74 ± 3 c.p.s. for IIc). Again we have not yet ascertained which proton is involved, but soon hope to by deuterium labelling experiments.

Sincerely,

Walter L. Meyer
Assistant Professor
of Chemistry

rkw

Fig. 1 3,9-Dibromocamphor (Ic) in $CDCl_3$



63-12

JET PROPULSION LABORATORY *California Institute of Technology* • *4800 Oak Grove Drive, Pasadena, California*

27 November 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Recently Longone (Mellonmr, 61-14) made the comment "Anticipating less than optimum performance due to the hardware present in the V-6031 probe" etc., concerning the A-60 Variable Temperature probe. We have had one of these probes for some time and enclosed are some example spectra showing for CH_3CHO quartet at room probe temperature and -60°C. I think these spectra are indicative of the fact that the "hardware" doesn't perturb things very much. The low temperature spectra were obtained after about 15 minutes of -60° operation. I am curious about the performance other people are getting with this probe.

One very important item in the adjustment of this probe is the position in the magnet. We had some trouble at first until this adjustment was made while observing the quality of the field modulator signal at J-701 with a scope; if the 5 kc. signal is spiked and/or erractic then it is a good bet that the control sample is probably in a too inhomogeneous field. If one adjusts the probe position while the spectrometer is in "Adjust" one is optimizing the field at the sample position and the control sample may be in a quite inhomogeneous region. The manifestations of this situation or the borderline situation are not immediately obvious from the other simple tests one usually makes on the A-60, and this problem is best detected at J-701.

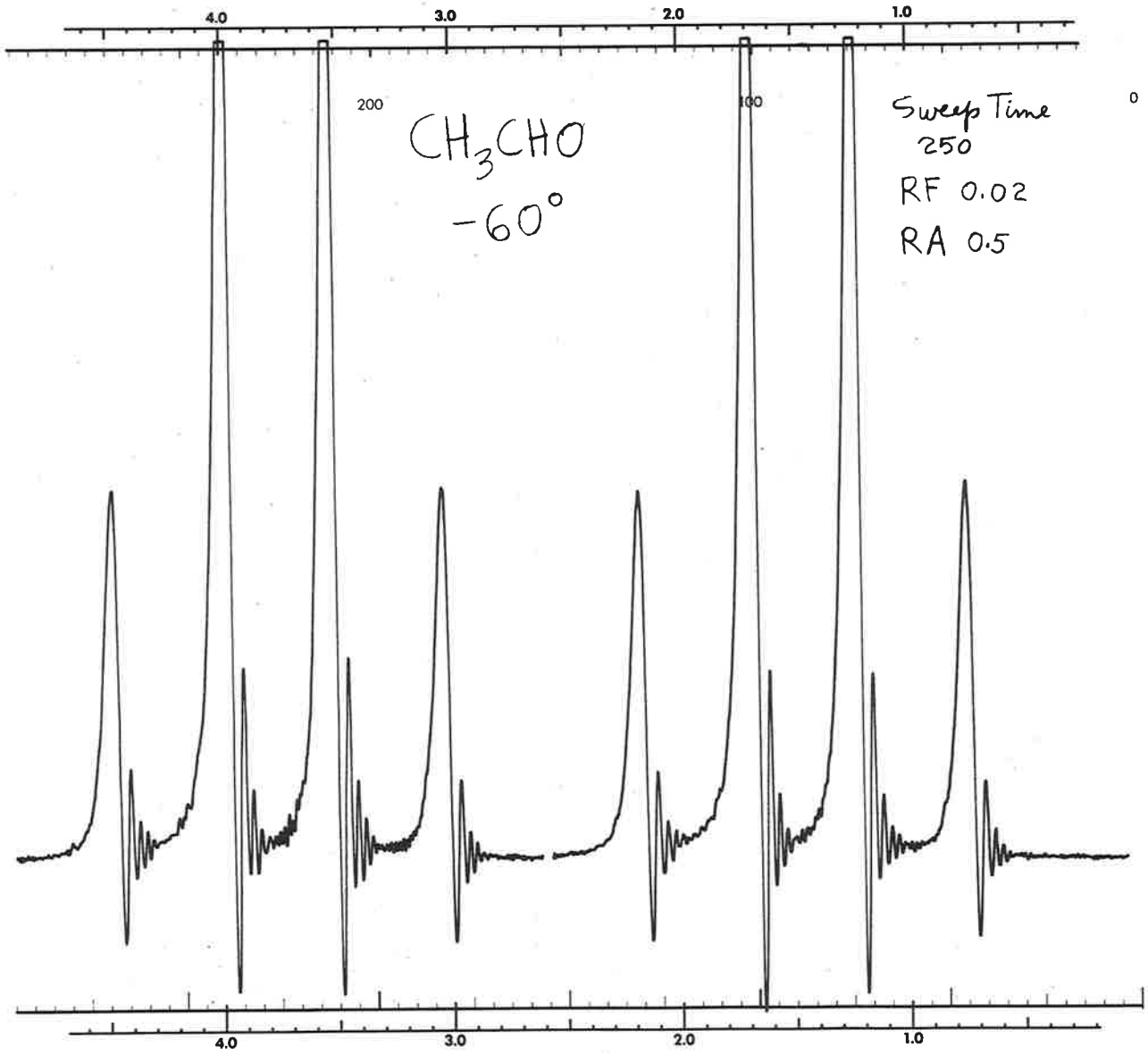
With best regards,

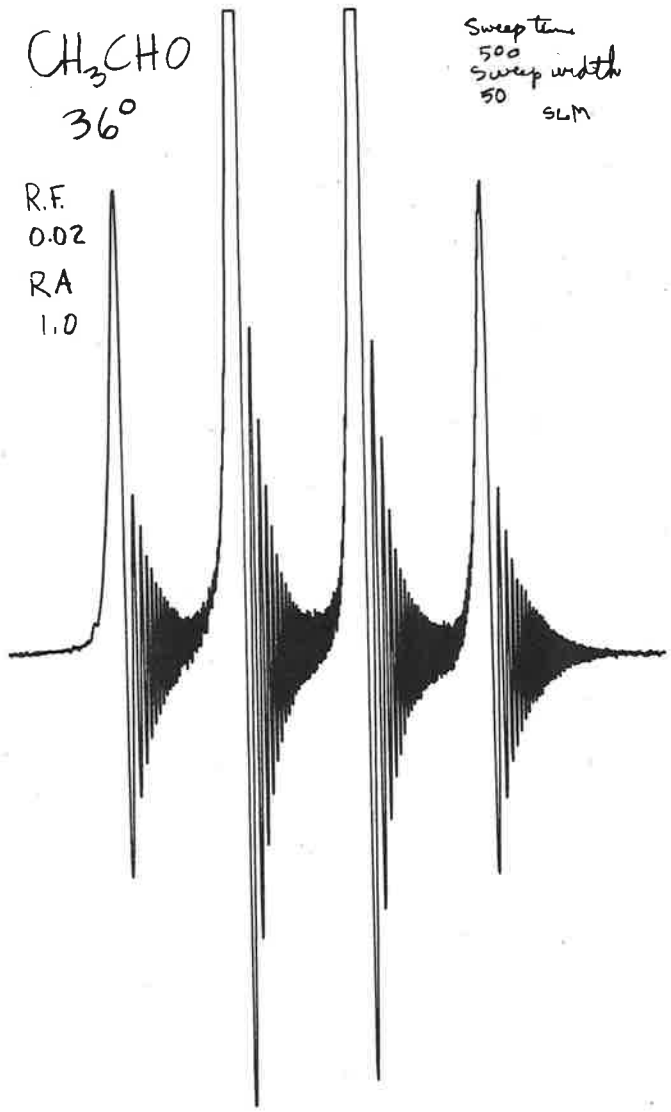
Stan

Stanley L. Manatt
Chemistry Section

SLM:jas
Enclosure
Air Mail

Telephone 354-4321 *Twx 213-449-2451*


4.0
3.0
2.0
1.0
200
100
0
CH_3CHO
-60°
Sweep Time
250
RF 0.02
RA 0.5


CH_3CHO
36°
Sweep time
500
Sweep width
50
SLM
R.F.
0.02
RA
1.0

63-14 UNIVERSITÉ DE STRASBOURG
Faculté des Sciences

INSTITUT DE CHIMIE

Téléphone 35.43.00

Boîte Postale 296

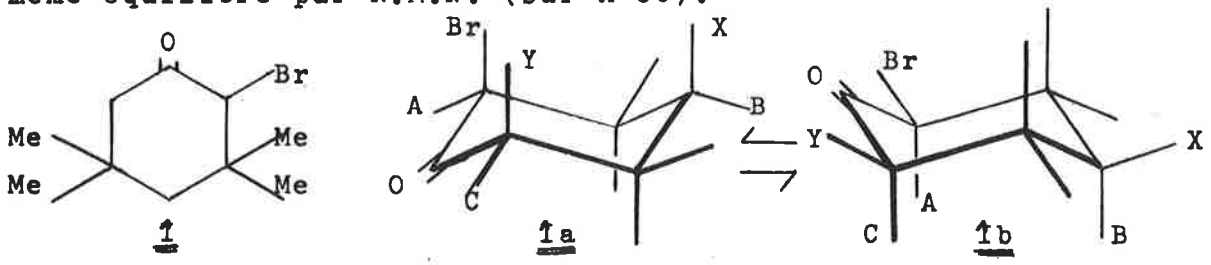
B.Waegell
F.Hemmert
G.Ourisson

Strasbourg, le 3 Décembre 1963
2, Rue Gœthe

Dr.B. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Shapiro,

Nous avons étudié, récemment, l'équilibre conformationnel qui existe dans les solutions de bromo-2 tétraméthyl-3,3,5,5 cyclohexanone 1, à l'aide des spectres I.R. et U.V., et des moments dipolaires (B.W. et G.O., Bull.Soc.Chim., 1963, pp. 495 et 496). Plus récemment, nous avons mis en évidence le même équilibre par R.M.N. (sur A-60).



DANS LES SOLVANTS PEU POLAIRES, comme CCl_4, le conformère 1a, à brome axial, prédomine. Le signal dû à H_A a la forme d'un triplet centré à 242 cps du TMS, attribué aux couplages:

$$^4J_{AB} = {}^4J_{AC} = 1{,}1 \text{ cps.}$$

Ces couplages sont possibles dans ce cas puisque les protons A et C, ainsi que A et B, présentent la "disposition en M"(ici, en W) nécessaire d'après Meinwald et Lewis.

En outre, les protons axiaux X et Y sont nettement différenciés des protons équatoriaux par suite de l'influence du groupe C-Br, exerçant favorablement son effet d'anisotropie diamagnétique. Les protons C et Y, ainsi que B et X, donnent ainsi des spectres caractéristiques de type AX (nomenclature évidemment un peu confuse, mais sans doute compréhensible...).

On observe alors $J_{CY} = J_{BX} = 13\text{-}14$ cps.

Mais, alors que les protons X et Y donnent les doublets normaux sans structure fine, les deux pics des protons B et C, dans le spectre AX ont chacun une structure fine de triplet; on a donc:

$$^4J_{AB} = {}^4J_{AC} = {}^4J_{BC} = 1{,}1 \text{ cps.}$$

DANS LES SOLVANTS POLAIRES tels que le benzonitrile, c'est le conformère 1b qui est prédominant. Le signal dû au proton A a alors la forme d'un singulet+: il n'y a plus de couplage à longue distance, le schéma en M n'étant plus réalisé. D'autre part, les protons B et X ne sont plus sous l'influence directe des groupements C=O et C-Br. Ils donnent donc un spectre AB (triplet avec bande centrale intense) ; les protons X et C donnent toujours un spectre AX.

Nous avons ici raisonné comme si les conformères 1a et 1b étaient dans chaque cas seuls présents. Il est certain qu'il faudrait dans une analyse plus précise tenir compte des populations relatives de ces deux conformères. Il est néanmoins remarquable que toutes les conséquences de l'équilibre conformationnel puissent être retrouvées sur ce système en utilisant une description aussi extrême.

Avec nos meilleures salutations

Guy Ourisson

+ légèrement élargi.

63-16

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Dr. H. Günther

KÖLN, Dec. 4, 63

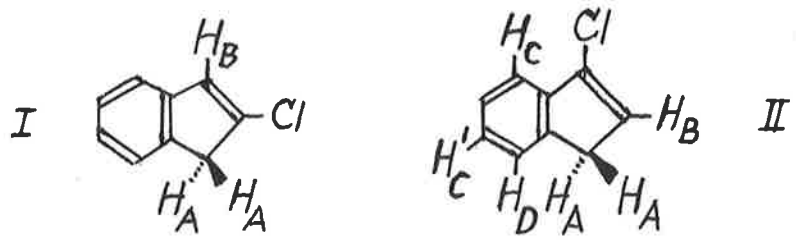
ZÜLPICHER STRASSE 47
TELEFON: 2024239

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Ave.
Pittsburgh 13, Pa., USA

NMR-spectra of Chloroindenes

Dear Barry,

In connection with some structure determination we were interested in the NMR-spectra of the two indene derivatives I and II:



Spectra were recorded in CCl_4 (30% v/v) with TMS (internal) and the following parameters obtained:

I	H_A	6.60	H_B	3.28	J_{AB}	1.7 cps
II	"	6.69 "	"	3.50 "	"	2.4 "

Assuming the two C-H_A-bonds 60° above or underneath the plane respectively, as indicated by models, the 1,3-coupling in I falls in the expected range (1). In II then, we have a pure gauche coupling, with 2.4 cps well under the limit of 3.9 cps for J_g predicted recently for propenes (2).

Longrange coupling: The CH_2-groups in both compounds as well as H_B in I show additional coupling with the aromatic protons. The doublet of the methylene group of II is shown on the enclosed figure at 50 cps sweep width and two sweep directions. Each component is split into apparently six lines (five clearly resolved), which could arise from a triplet of doublets. This would mean equal coupling by 0.5 cps to two aromatic hydrogens (H_C, H_C') and a smaller coupling of 0.2 cps to one (H_D). Longrange coup-

ling to two aromatic protons by 0.5 cps has been described for the CH_2-group of indene (3).

The lines of the H_B-triplet in I are further split too, but again it seems, that more than one aromatic proton is involved. We are looking at related compounds for cases which give similar effects.

Thanks for sending Mellon Letters to my new address. Regards to the Group,

truly yours,

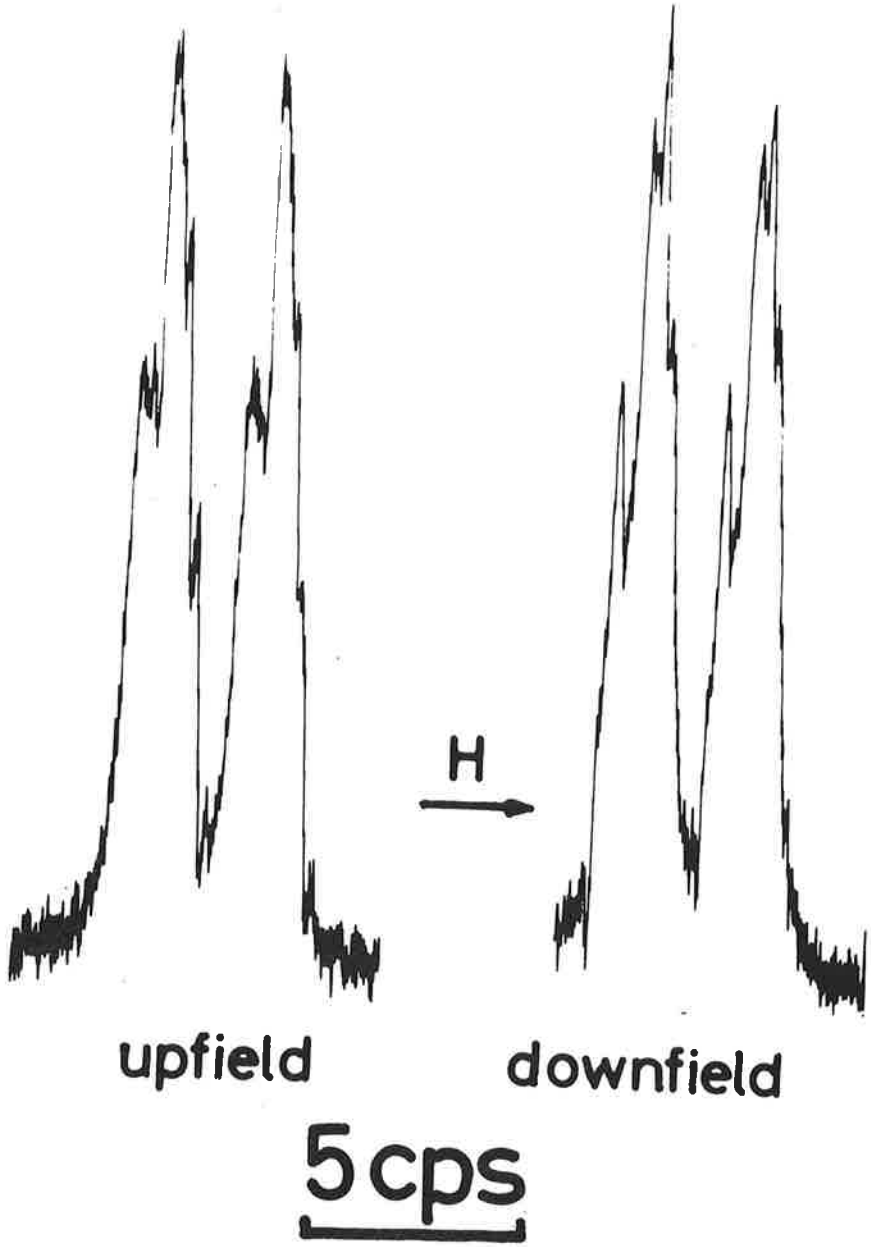
Dr. H. Günther Dr. H. Kiefer

(1) T.A. Wittstruck, S.K. Malhorta and H.J. Ringold, J. Amer. Chem. Soc. 85, 1699 (1963).

M. Karplus, ibid. 82, 4431 (1960).

(2) A.A. Bothner-By, C. Naar-Colin and H. Günther, ibid. 84, 2748 (1962).

(3) D.D. Elleman and S.L. Manatt, J. Chem. Phys. 36, 2346 (1962).


H
upfield
downfield
5 cps

BELL TELEPHONE LABORATORIES
INCORPORATED
MURRAY HILL, NEW JERSEY
TELEPHONE
AREA CODE 201
582-3000

A Conference on Magnetic Resonance in Biological Systems will be held July 20-22, 1964 at the House of the American Academy of Arts and Sciences in Boston, Massachusetts. The purpose of the conference is to provide an opportunity for discussion of NMR and ESR investigations of biological molecules and systems. Subjects will include radiation damage of nucleic acids, enzyme action, conformation studies of proteins and nucleic acids, light induced excited states, oxidation-reduction reactions, and paramagnetic metal ions in biological macromolecules.

Additional information can be obtained from R. G. Shulman, Bell Telephone Laboratories, Murray Hill, New Jersey.

J. DELMAU
63-20 Laboratoire de Spectroscopie Hertzienne
Institut de Physique Expérimentale
Boulevard d'Yvoy Genève (Suisse)

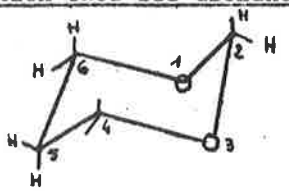
Genève, le 7 Novembre 1963

Docteur Shapiro
Mellon Institut
Pittsburgh 13 Pa
4400 Fifth Avenue

Cher Monsieur,

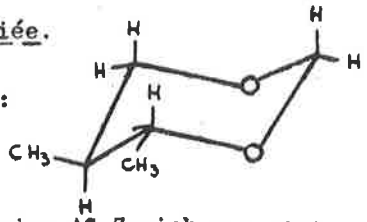
Faisant de la R.MN, je suis vivement interessé par le Bulletin d'Informations du Mellon Institut. Je serais heureux que ces quelques résultats me permettent de figurer parmi vos correspondants :

Equilibre dynamique entre isomères de conformation chez les dioxanes 1,3.



Nos études ont porté sur des dérivés substitués du Dioxane 1,3. Ces dérivés peuvent être répartis suivant trois catégories :

1°) Les composés à conformation nettement privilégiée.



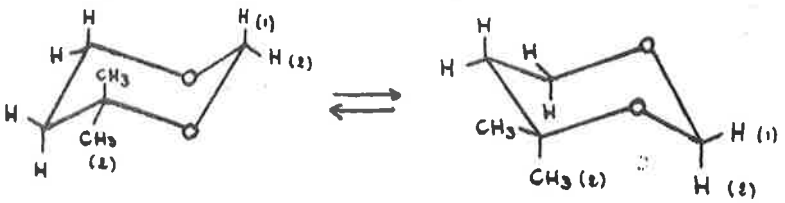
Le type en est le Diméthyl-trans-4,5-dioxane-1,3 : Les protons H_{2axial} et $H_{2équatorial}$ présentent un déplacement chimique δ = 23 C/s à 60 Mc/s (Spectre effectué sur A-60 par le Docteur Attilio Melera de Varian AG Zurich que nous remercions) et une constante de couplage J = 6,0 C/s dont la faible valeur est à remarquer.

Ces valeurs ont été vérifiées avec exactitude sur la totalité des produits de ce type que nous avons examinés.

2°) Composés en équilibre dynamique entre 2 conformations également probables

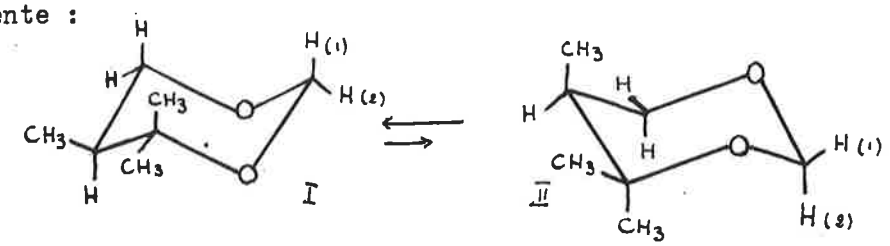
C'est le cas du Dioxane-1,3, du Diméthyl-4,4-dioxane-1,3 et du Diméthyl-5,5-Dioxane-1,3.

La résonance des 2 protons du groupe - O - CH_2 - O - est unique par suite de l'échange trés rapide entre les 2 formes



3°) Une catégorie de composés intermédiaires entre ces 2 extrêmes.

c'est en particulier le cas du Triméthyl-4,4,5 -dioxane-1,3. Pour ces composés J est inchangé et vaut toujours 6 cycles. Par contre, δ est ramené à 5,3C/s. Cette diminution de δ s'explique parfaitement en supposant qu'il y a équilibre dynamique entre 2 formes dont la probabilité d'existence est différente :



Le calcul donne 61,5% de forme I pour 38,5% de forme II.

Remarque: Le Méthyl-4-dioxane-1,3 présente un δ de 19,8 C/s, ce qui correspond suivant l'hypothèse précédente à un équilibre comportant 93% du produit avec méthyle équatorial et 7% avec méthyle axial. Cette valeur est à rapprocher de celle donnée par Eliel pour le Méthyl-cyclohexane: 95% du produit environ aurait le Méthyle en équatorial (1)

Recevez, cher Monsieur, l'expression de mes sentiments les meilleurs.

Claudette Barbier Jean Delmau

(1) E.L. Eliel and M Rerick. J.Am.Chem.Soc. 82, 1367 (1960)

63-22

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

DEPARTMENT OF CHEMISTRY

December 9, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Readers of MELLONMR may be interested in the plans for the Fifth Experimental NMR Conference (successor to 4th OCEANS). It will be held on Friday and Saturday, 28 and 29 February, 1964, at Mellon Institute. As in past years, the Conference will be devoted to new developments in advanced instrumentation and experimental techniques; it does not compete with Workshops and courses offering an introduction to this field.

Although sessions will consist largely of invited papers, contribute papers are welcome and should be sent to the appropriate Session Chairman or to the Chairman of the Conference. The Sessions and their chairmen are as follows: Superconducting Magnets (D. D. Elleman), Relaxation Experiments (D. C. Douglass), Instrumentation Maintenance, Repair, Modification and Operation (F. A. Nelson and M. M. Crutchfield), Electric Field Experiments (J. S. Waugh), Double Resonance (R. Freeman), Signal Enhancement (J. D. Baldeschwieler), Spectral Analysis (C. A. Reilly).

Additional information may be obtained from the enclosed instructions or by writing to me. Prompt expression of interest is desirable; it may be necessary to limit attendance because of restricted physical facilities.

Yours truly,

Paul

Paul C. Lauterbur
Associate Professor
Chairman, Fifth ENC

PCL:jv

enclosure

FIFTH EXPERIMENTAL NMR CONFERENCE

Instructions for Speakers and Contributors

I. Lengths of invited and contributed papers will be assigned by Session Chairmen so as to leave ample time for discussion in each 90 minute session.

II. Abstracts and supplementary material (figures, tables, etc.) in no case exceeding 6 pages should be sent, by February 1, to:

Dr. A. A. Bothner-By
ENC Arrangements
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

They will be printed and distributed to the conferees. Additional material, either too long or too late to have been printed, may be reproduced by the author and arrangements will be made to distribute it at the Conference. A distribution center will also be provided for commercial material of possible interest to the conferees. Authors are urged to submit detailed abstracts and drawings, schematics, spectra, etc., if at all possible. Participants in past conferences have found such a printed record to be quite valuable. In addition, the presentation of undigestible masses of data, complicated schematics, etc. on slides or blackboard is obviated, saving time and easing communication.

III. Abstracts and details of post-deadline papers and of contributions not accepted for formal presentation will be printed in a Supplementary Program and may be discussed at any appropriate session if time permits. The deadline and length limitation are the same as for contributed papers.

IV. Projectors for 3-1/2 x 4 inch and 2 x 2 inch slides will be available at all sessions. Unusual requirements of any sort should be transmitted to the Session Chairman.

63-24

DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
FOOD AND DRUG ADMINISTRATION
WASHINGTON 25, D.C.

December 16, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Ave.
Pittsburgh 13, Pa.

Dear Barry:

With apologies I submit a correction to my contribution in MELLONMR 57, 49-51(1963). The first two formulas on the second page of my letter should read:

$$3(J_{cis} + J_{trans}) = (\omega_2-\omega_1) + (\omega_4-\omega_3$$

$$2\delta^2 = (\omega_3-\omega_1)^2 + (\omega_4-\omega_2)^2 - 9/2\ (J_{cis} + J_{trans})^2$$

Please insert these corrections in the next MELLONMR issue.

Best regards.

Sincerely yours,

Ernest

Ernest Lustig
Chemist
Division of Food
Bureau of Biological & Physical Sciences

THE ROCKEFELLER INSTITUTE

A Graduate University and Research Center

NEW YORK 21, NEW YORK

December 12, 1963

Messrs. Bothner-By and Shapiro
The Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pa.

Dear Aksel and Barry:

I attach the abstracts of four articles recently submitted for publication of which a very limited number of preprints is available. They are entitled "The Role of Multiple Quantum Transitions in NMR: A three-spin system," "The Magnetic Shielding of a nucleus by a neighboring atom," "The Fermi-contact contribution to the Proton-deuteron Coupling Constant in HD," and "Comments on Orbital Hybridization." The first of these will appear in J. Chem, Phys., the second has been submitted to J. Chem. Phys. and the third submitted to the Phys. Rev. The last of these, in view of its armchair-scientist and nontraditional aspects, as well as its potential significance, might not be considered publishable and therefore the preprint might turn out to provided its entire circulation. I hope not, but who knows?

I would like to take this opportunity to expound some of my prejudices. (1) We do not know as much about chemical shifts as we think we do; (2) We do not know as much about coupling constants as we think we do; yet (3) we go on blithely using our worn-out concepts to make still more correlations and rationalizations without trying to understand what is wrong with our model, or why our model does give good results when it does. NMR can be a wonderful probe into molecular structure, if we only would use it critically!

To be specific:

(1) We say regularly that protons from hydrogens on sp^2 hybridized carbons resonate to lower field than those on sp^3 carbons <u>because of the hybridization on the carbon</u>. Those on sp hybridized carbons should come at still lower field, but one accepts Pople's explanation of the "high-frequency" contribution to σ, an argument that could be applied (with modification) to the shielding in ethylene as well as in acetylene. Has anyone ever tried to

THE ROCKEFELLER INSTITUTE

A Graduate University and Research Center

NEW YORK 21, NEW YORK

estimate the shielding at a proton in an sp^3, sp^2 and sp carbon bond using the same screening parameters and ionic character for all these? I did once, a couple of years ago, and found a variance of only $\sim$ 0.2 ppm in the Lamb-term contributions. (Perhaps Guy and his coworkers are about to do a proper calculation now.) What this showed me was that the hybridization itself has no effect on the shielding -- certainly not of the order of 1 ppm. What has the effect? Probably different screening parameters and ionic characters, because, after all, forgetting hybridization, a double-bonded carbon has a single weakly shared π-electron rather than the strongly shared σ-electron in a single bond. This can, of course, change the screening and ionic character without affecting the hybridization. In fact, I believe that all three types of bond are essentially sp hybridized. Then, too, at this short distance the exact structure on the carbon is significant . . . The long-range shielding of a substituent group is generally treated in the dipole approximation despite the seemingly absurd results so obtained. The crudest possible observation on this problem -- the distance at which this approximation is valid for Slater wave functions is calculated -- is made in my paper "The magnetic shielding of a nucleus by a neighboring atom."

(2) We say that ^{13}C-H coupling constants depend on "s-character" in a simple way, and then find the C-H bond in formyl fluoride to be s-p. Is there no such thing as self-consistency in this game, or do we throw all exceptions into the bucket of "bent-bonds"? A significant deviation of a single point from a curve should not only involve a rationalization of that point's deviation, but rather the re-evaluation of the validity of the curve itself, or at least one must be convinced that the arguments rationalizing this single point are in applicable to the other points as well. Another example: everyone believes that Fermi-contact contributions to J's must be positive, despite McLachlan's questioning the procedure, since his comments were answered by Karplus, who said, in effect, that because we believe these J's to be positive then the principle contribution to J comes from the lowest excited state whose contribution is positive. (Karplus actually uses the reverse of this, but it amounts to the same thing.) I've been talking for some time

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about J in HD being negative (which no one believed); for example, when I talked about it at the Gordon conference. Yet now that there is experimental evidence that the C-F J is negative, one can argue, as does Pople, that in this case the other low-lying excited states can mix, etc. Since we know very little about excited states past the first, even for H_2, no less for the C-H bond, what are we really driving at by these rationalizations? Similar arguments hold for the attempted improvements (Karplus, Jardetsky) of the "Karplus-curve" for ^4J's since these are still examples which do not fit. Furthermore, it is supposedly well known since the 1940's that the valence bond theory does not give good results -- see also my Mellonmr note of early this year on this subject. Cannot we be satisfied with experimental correlations and realize that an organic molecule is a terribly complicated thing, and scarcely subject to decimal-place correlations in terms of qualitative parameters such as electronegativity?

I hope that I have not offended anybody's sensibilities, but I feel that one of the great uses of Mellonmr is for an occasional sounding off. Although I'm not convinced that my "prejudices" will evoke much discussion, I would certainly be willing to answer specific "comments" or "criticisms" on their content.

Best regards,

Sincerely,

Jeremy

Jeremy I. Musher

JIM/sm

Comments on Orbital Hybridization

Jeremy I. Musher
The Rockefeller Institute, New York 21, N.Y.

ABSTRACT

It is observed that the existence of rare gas molecules contradicts the traditional chemical picture of orthogonal atomic hybrid orbitals. It is also shown that the present interpretation of C^{13}-H NMR coupling constants is ambiguous and does not constitute an experimental verification of the usual sp^3, etc. hybridization of carbon atoms.

Magnetic Shielding of a Nucleus by a Neighboring Atom

Jeremy I. Musher
The Rockefeller Institute, New York 21, New York

ABSTRACT

The Lamb term of the magnetic shielding of a nucleus in calculated for an electron on a neighboring atom in as s- or a p-state using Slater atomic wave functions. This exact calculation is presented in order to illustrate the radial dependence of long-range nuclear magnetic shielding and to point out explicitly for these wave functions the distance at which the dipole approximation introduces only a negligible error.

Fermi-Contact Contribution to the Proton-deuteron Coupling Constant in HD

Jeremy I. Musher

Department of Chemistry, Harvard University*
Cambridge 38, Massachusetts
and
The Rockefeller Institute†, New York 21, N.Y.

ABSTRACT

The Fermi-contact contribution to the proton-deuteron coupling constant in HD is calculated for the Coulson-MO ground state wave function. A new approximate procedure for performing perturbation theory calculations on simple ψ_o's is used which enables most of this part of J_F to be obtained in closed form. The result is $J_F = -29.5$ cps with +3.0 cps coming from the one-electron term and the remainder the two-electron term. This J_F is opposite in sign to the results of previous calculations. The discrepancy is attributed to the arbitrariness of the previous procedures either as to the form of variational trial function or to the choice of the arbitrary "average energy." The validity of the procedure can only be absolutely determined by comparison of the result obtained with that of experiment.

* This research was supported in part by a fellowship from the Division of General Medical Sciences, Public Health Service and by support extended Harvard University by the Office of Naval Research.

† Present address

The Role of Multiple Quantum Transitions in N. M. R.: A Three-Spin System*

J. I. Musher
The Weizmann Institute of Science†, Rehovot, Israel
and The Rockefeller Institute‡, New York 21, N. Y.

ABSTRACT

The double and triple quantum (DQ and TQ) transitions in molecules containing 3 weakly coupled nuclei of spin 1/2 are examined theoretically and experimentally. Owing to the rapid growth and saturation of these transitions with increasing rf, it is practicable to observe each individual resonance only within a limited rf range. Based on the theory of Yatsiv, expressions at a given $T_1 = T_2$ are computed for the rf fields at which the various MQ absorption signals will attain their maxima and the intensity of these absorptions relative to the maximum intensity for SQ signals. It is pointed out that the usual MQ signal measured in liquids has a linewidth almost equal to that of a SQ signal, since a considerable saturation of the former is necessary for its easy observation. A frequency shift only significant for high-rf MQ signals is also computed. The DQ spectrum of a camphor derivative containing 3 weakly coupled protons is examined and the experimental results for the observable peaks agree rather well with the theory. The geminal J is opposite in sign to the vicinal J's.

---

* For preliminary report see Bull. Am. Phys. Soc. II8, 35 (1963).

† Guest scientist (spring semester 1962)

‡ Present address

NUCLEAR MAGNETIC

NMR Specialties

RESONANCE SPECIALTIES
INCORPORATED

145 Greensburg Road
New Kensington, Pa.
Area Code 412
337-7727

December 20, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Barry:

In connection with a research program on phosphonitrile ring systems, I had occasion to perform a decoupling experiment on the A-60. The results of this experiment, performed on di-n-monomethylamino-tetra-n-dimethylamino-triphosphonitrile, are shown on the attached spectra. Before irradiation the methyl resonance appears as a doublet broadened by additional coupling. On irradiation of the phosphorous at 24.28 Mc., the doublet is observed as two singlets at $\tau = 7.35$ and 7.46. This observation is consistent with our proposed structure.

To confirm the fact that decoupling had occurred, we also performed several other experiments. The attached spectra show the methyl doublet of trimethyl phosphite collapsing to a singlet upon irradiation at 24.28 Mc.

I have also submitted a block diagram to illustrate the basic method used to achieve the desired irradiation.

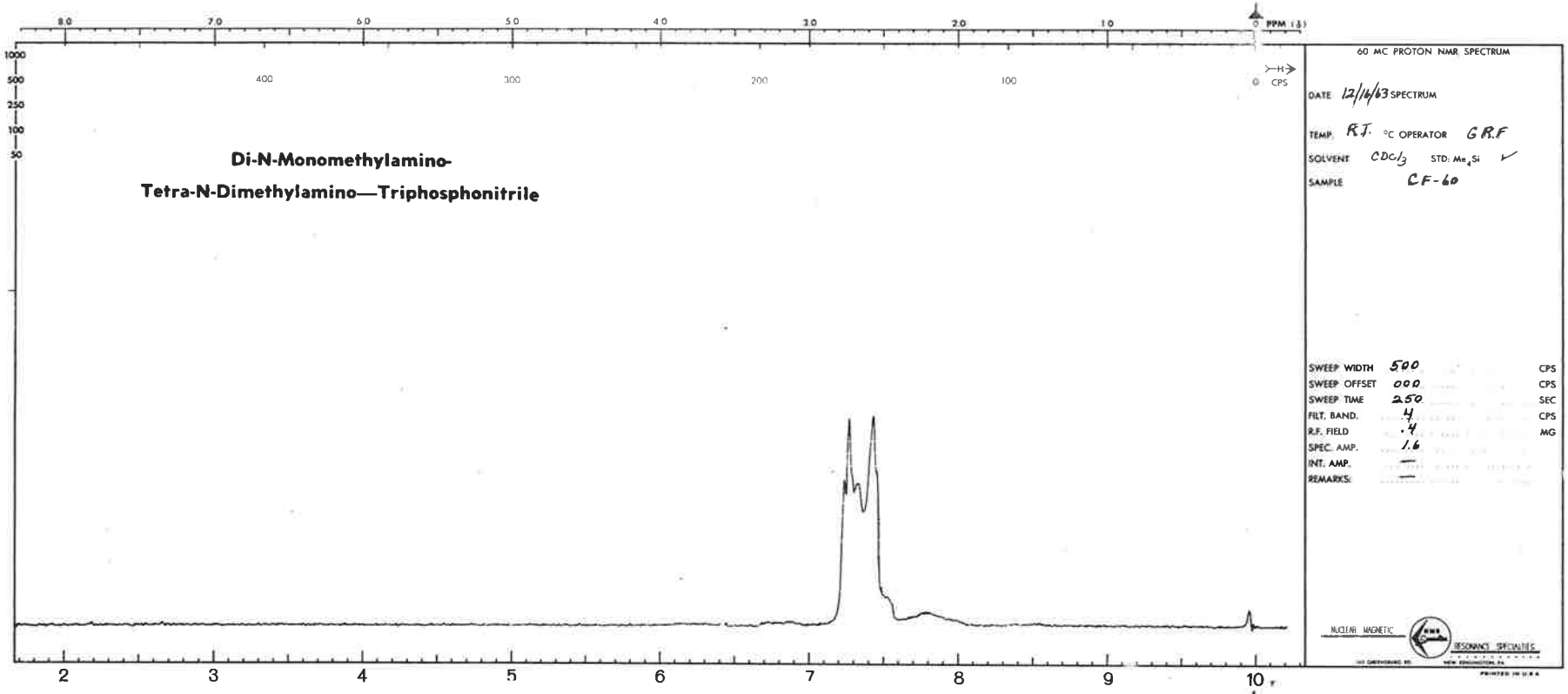
We wish to thank the Armstrong Cork Fellowship at Mellon Institute, specifically Dr. I. I. Bezman and Mr. C. T. Ford, for supplying us with the phosphontrile sample.

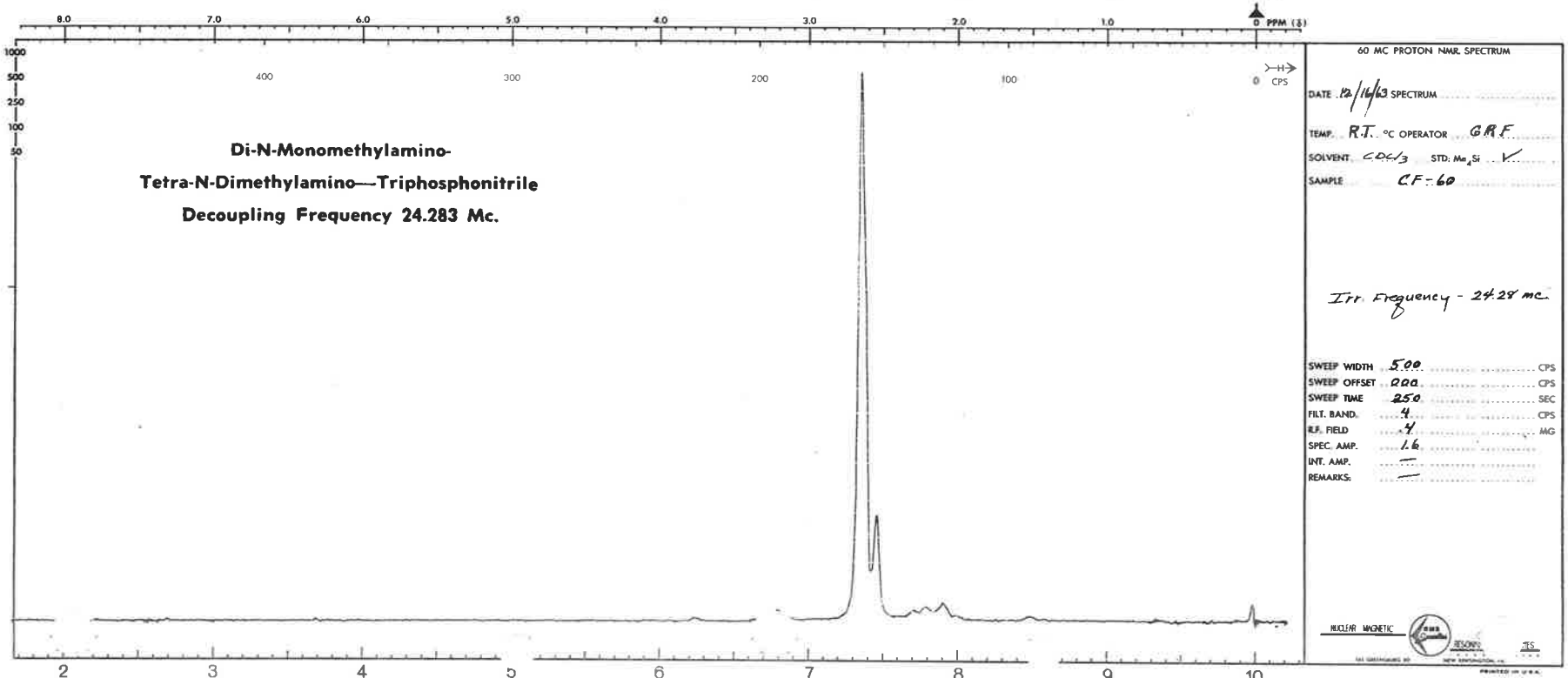
Sincerely,

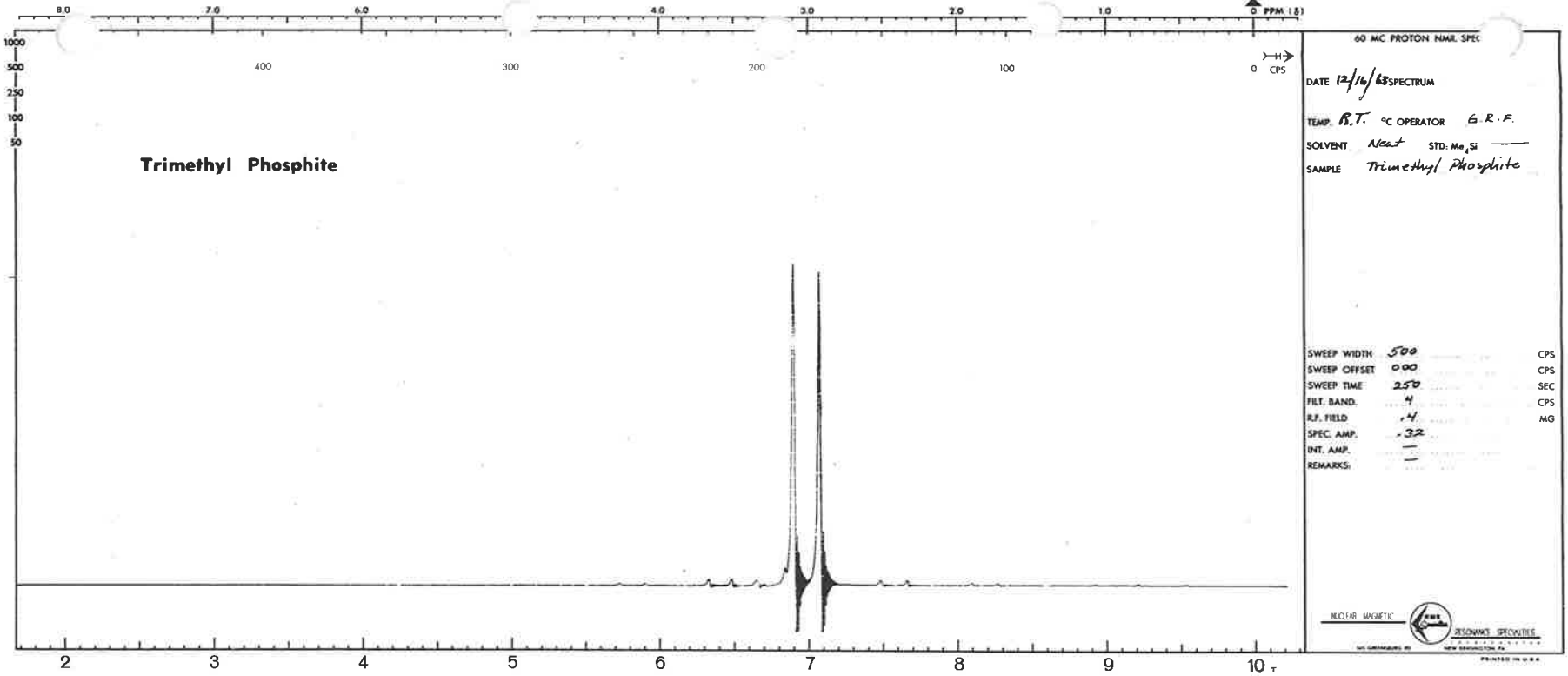
Frank E. Dickson
Executive Vice-President

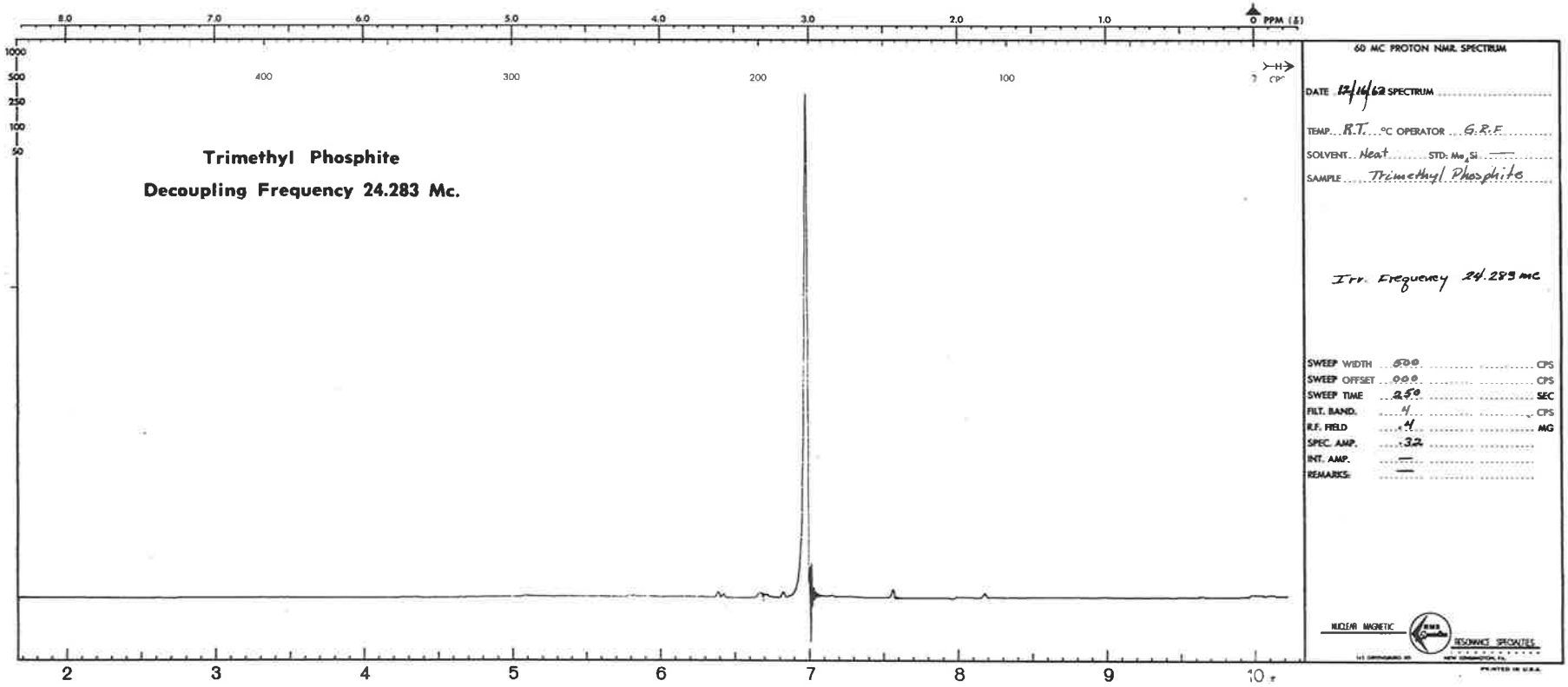
FED/ams

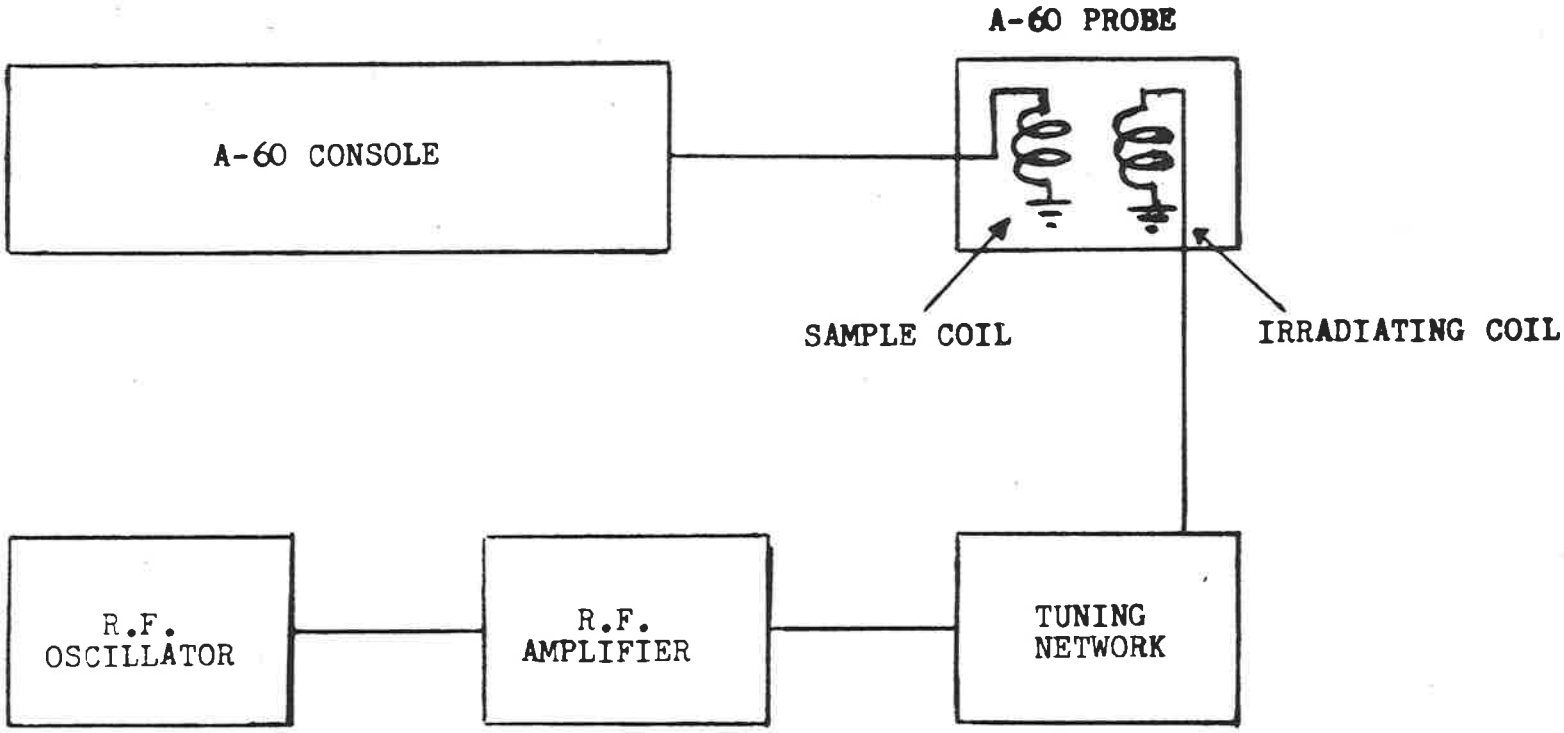
Enclosures - 3


Di-N-Monomethylamino-
Tetra-N-Dimethylamino—Triphosphonitrile
60 MC PROTON NMR SPECTRUM
DATE 12/16/63 SPECTRUM
TEMP. R.T. °C OPERATOR G.R.F
SOLVENT CDCl3 STD: Me4Si ✓
SAMPLE CF-60
SWEEP WIDTH 500 CPS
SWEEP OFFSET 000 CPS
SWEEP TIME 250 SEC
FILT. BAND. 4 CPS
R.F. FIELD .4 MG
SPEC. AMP. 1.6
INT. AMP. —
REMARKS: —
NUCLEAR MAGNETIC RESONANCE SPECIALTIES


Di-N-Monomethylamino-
Tetra-N-Dimethylamino—Triphosphonitrile
Decoupling Frequency 24.283 Mc.
60 MC PROTON NMR SPECTRUM
DATE 12/16/63 SPECTRUM
TEMP. R.T. °C OPERATOR G.R.F
SOLVENT CDCl3 STD: Me4Si ✓
SAMPLE CF-60
Irr. Frequency - 24.28 mc.
SWEEP WIDTH 500 CPS
SWEEP OFFSET 000 CPS
SWEEP TIME 250 SEC
FILT. BAND. 4 CPS
R.F. FIELD .4 MG
SPEC. AMP. 1.6
INT. AMP. —
REMARKS: —
NUCLEAR MAGNETIC RESONANCE


Trimethyl Phosphite
60 MC PROTON NMR. SPEC
DATE 12/16/62 SPECTRUM
TEMP. R.T. °C OPERATOR G.R.F.
SOLVENT Neat STD: Me4Si —
SAMPLE Trimethyl Phosphite
SWEEP WIDTH 500 CPS
SWEEP OFFSET 000 CPS
SWEEP TIME 250 SEC
FILT. BAND. 4 CPS
R.F. FIELD .4 MG
SPEC. AMP. .32
INT. AMP. —
REMARKS: —
NUCLEAR MAGNETIC RESONANCE SPECIALTIES


Trimethyl Phosphite
Decoupling Frequency 24.283 Mc.
60 MC PROTON NMR. SPECTRUM
DATE 12/16/62 SPECTRUM
TEMP. R.T. °C OPERATOR G.R.F.
SOLVENT Neat STD: Me4Si —
SAMPLE Trimethyl Phosphite
Irr. Frequency 24.283 mc
SWEEP WIDTH 500 CPS
SWEEP OFFSET 000 CPS
SWEEP TIME 250 SEC
FILT. BAND. 4 CPS
R.F. FIELD .4 MG
SPEC. AMP. .32
INT. AMP. —
REMARKS: —
NUCLEAR MAGNETIC RESONANCE SPECIALTIES



BLOCK DIAGRAM
A-60 DECOUPLING TECHNIQUE

POLAROID CORPORATION

CAMBRIDGE 39, MASSACHUSETTS

RESEARCH DIVISION, 730 MAIN STREET

UNIVERSITY 4-6000

December 20, 1963

Dr. Barry L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

EXCHANGE OF AROMATIC PROTONS IN NAPHTHOLS

Dear Barry:

We are currently observing the exchange of the aromatic hydrogens in some hydroxylated naphthalene derivatives with D_2O, using our A-60, and would like to present some preliminary results. Unless otherwise stated, the experiments reported here were performed by dissolving one equivalent of the aromatic compound in 0.6 Molal NaOD in 50 vol.% D_2O-dioxane, the tube sealed under nitrogen.

Under these basic conditions 2-naphthol exchanges its 1-hydrogen with a half-life at 29° of about 2 hours. None of the other ring protons showed evidence of exchanging even after 120 hours.

With a very similar half-life 8-amino-2-naphthol also shows exchange only of its 1-hydrogen. When only two-thirds of an equivalent of NaOD was present the exchange was very much slower, only about 25% having taken place after 3 days.

In 7-amino-1-naphthol only the 2-hydrogen was found to exchange, with a half-life of about 6-7 days. When only 0.8 equivalents of NaOD was present it was not possible to observe any exchange after 3 days.

With 1,7-dihydroxynaphthalene and 1.2 moles of NaOD, both the 2- and 8-hydrogens exchange with similar half-lives of about 2 days. Phenol itself shows no observable exchange with NaOD after 16 days.

In summary, the sodium salts of 2-naphthol and 8-amino-2-naphthol exchange only the 1-hydrogen at an appreciable rate, and this some 70-80 times faster than 7-amino-1-naphtol exchanges its 2-hydrogen; both are much more rapid than NaOPh.

We have been able to assign many of the bands and coupling constants for these compounds and will be happy to make these known to anyone interested. Although this work is obviously far from complete, and conclusions would be premature, we hope that this communication may be of some interest. We wish to express our appreciation to Dr. Daniel Ross for his suggestions and synthetic work important to this problem.

With best regards,

Patricia C. Morrison Ronald F. W. Cieciuch

(Mrs.) Patricia C. Morrison Ronald F. W. Cieciuch

63-36 Physikalisch-Chemisches und Elektrochemisches
Institut der Technischen Hochschule München
Direktor: Em. o. Prof. Dr. G. Scheibe

8 München 2,
Arcisstraße 21
Telefon: 55 92 / 351

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13 , Pa

Sehr geehrter Herr Dr. Shapiro !

Es wurden Kernresonanzspektren einfacher Cyaninfarbstoffe untersucht.
Die Protonenresonanz der Kettenchromophore von Dimethyl= amino-propenyliden-dimethylammoniumperchlorat (I) und Dimethylamino-pentadienyliden-dimethylammoniumperchlorat (II) ist vom AX_2 bzw. A_2X_2Y-Typ.
Ein Dublett der Protonen in α -Stellung der Cyaninkette von (I) (0,5 m in D_2O) liegt bei $\delta_\alpha = 7{,}4_9$ ppm , ein Triplett der ß-Protonen bei $\delta_\beta = 5{,}1_9$ ppm (TMS 4 Mol % in CCl_4 ext.).
Bei (II) (0,1 m in CD_3COCD_3) erscheinen ein Dublett der α -Protonen bei $\delta_\alpha = 7{,}1_7$ ppm , ein Quartett der Protonen in ß-Stellung der Cyaninkette bei $\delta_\beta = 5{,}3_3$ ppm und ein Triplett der γ-Protonen bei $\delta_\gamma = 7{,}0$ ppm (TMS 4 Mol % in CCl_4 ext.) . $J_{\alpha\beta} = 11{,}8$ Hz , $J_{\beta\gamma}$ - 12,7 Hz . [1]
Im Grundzustand liegt all Transkonfiguration vor . [2]

Bei Normaltemperatur in neutralem Medium geben die Methyl= gruppen der Auxochrome bei beiden Verbindungen Anlaß zu je= weils zwei gleichstarken Signalen bei δ_{CH_3} (I) $3{,}2_3$ und

$3{,}0_3$ ppm (in D_2O 0,5 m) , bzw. δ_{CH_3} (II) $2{,}7_9$ und $2{,}5_9$ ppm (in $CD_3CO\,CD_3$ 0,1 m) .
Diese Aufspaltung der Methylsignale ist temperaturabhängig und geht in etwa linear mit der Feldstärke (bei (I) in $HCCl_3$ $11{,}7_5$ Hz bei 60 MHz , 4,4 Hz bei 25 MHz) . Solange neutrales Medium vorliegt , ist sie weitgehend unabhängig vom Lösungsmittel . Fremdionenzusatz bleibt ohne Einfluß auf die Größe der Aufspaltung.

Die experimentellen Befunde sind als gehinderte , innere Rotation der $N(CH_3)_2$ Gruppen um die $N\cdots C_\alpha$ Bindung zu deuten,[1,4] wie sie bei Carbonylverbindungen von Gutowsky , Philips u.a. [3] beschrieben worden ist. Sie ist säurekatalysiert , wie alle cis-trans-Umlagerungen.
Die Höhe der Energiebarriere E_a der Drehung um die $N\cdots C_\alpha$ Bindung kann nach Gutowsky et al. [3] für (I) in Benzophenon zu 17 Kcal/M (bei T_2 = 0,227 sec/rad) , für (II) im gleichen Lösungsmittel zu 10 Kcal/M (bei T_2 = 0,274 sec/rad) , für Dimethylamino-heptatrienyliden-dimethylammoniumperchlorat zu 7 Kcal/M (bei T_2 = 0,227 sec/rad) abgeschätzt werden.
Mit wachsender Kettenlänge nimmt E_a und $T_{Koll.}$ ab. Dimethylamino-heptatrienyliden-dimethylammoniumperchlorat zeigt bei Normal= temperatur nur mehr ein Methylsignal.
Säurezusatz erniedrigt die Aktivierungsenergie der Rückorientierung bei (I) . 0,11 Vol % H_2SO_4 in einer wäßrigen Lösung von (I) (0,2 mMol / ml) verringert E_a auf 8 Kcal / M.
Das NMR-Spektrum der Kettenprotonen wird dabei nicht geändert, d.h. die Transverknüpfung der Cyaninkette bleibt erhalten. Jedoch tritt ein Protonenaustausch der H-Atome in ß-Stellung der Cyaninkette ein, der in schwerem Wasser als Lösungsmittel bei Säurezusätzen von etwa

0,1 Vol % D_2SO_4 so langsam erfolgt, daß die Kinetik untersucht werden kann.

Mit freundlichen Grüßen

V. Seiffer

H. Zimmermann

Lit.

1) Scheibe et al. Ber. Bunsenges. für phys.Chem. 67 560 (1963)

2) Scheibe Chimia 15 10 (1961) s.Lit.Hinw.

3) Gutowsky J.Chem.Phys. 25 1228 (1956) s.Lit.Hinw.

4) Hammond, Neuman J.Phys.Chem. 67 1655 , 1659 (1963)

THE UNIVERSITY OF WESTERN ONTARIO
UNIVERSITY COLLEGE
OF ARTS AND SCIENCE

DEPARTMENT OF CHEMISTRY

LONDON, CANADA

December 19, 1963.

Dr. B. L. Shapiro,
Mellon Institute,
4400 Fifth Ave.,
Pittsburgh 13, Pa.
U.S.A.

Dear Barry,

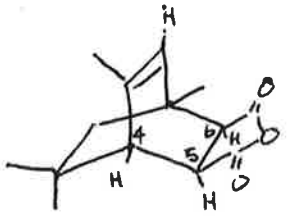
I apologize for the fact that you had to send a reminder about the lapsed "subscription" and I hope that the following bits of news may be amusing or interesting to some of the readers of MELLONMR.

C^{13} NMR: Our study of aromatic carbonyl compounds is nearing completion and one interesting feature appears to be a correlation of carbonyl chemical shifts with the degree of planarity in conjugated systems. An examination of the data for some seventy aromatic ketones indicates that substituent effects in the meta- or para-positions are very small but in the ortho-position marked low field shifts are found which appear to be proportional the size of the substituent. This suggests that the major factor contributing to the carbonyl shift is the extent of conjugation between the carbonyl group and the aromatic ring and a correlation of the carbonyl shift with angle of twist, θ, assuming a $\cos^2 \theta$ relation, provides a self-consistent set of values for θ which agree with simple steric considerations. The results may be compared with estimates of θ obtained from UV and dipole moment data and this is illustrated by a few of the results in the table. Other factors contributing to the low field shift in the hindered cases appear to be of minor importance and our results indicate that suitable "corrections" may be made. For example, the "ortho effect" of methyl groups on aromatic rings has been noted previously by Lauterbur and ourselves and allowance for this 1 p.p.m. difference alters the θ values only slightly as shown in the table. Extension of this approach to other systems appears possible, although introducing additional complications which may require corrections. For example, in the series $X-C_6H_4-COR$, where R is Me, Et, i-Pr or t-Bu, the effect of the different alkyl groups on the carbonyl carbon must be considered and the results for the two series, MeCOR and RCOR, provide the necessary data. (Incidentally, the general survey of the C^{13} spectra of carbonyl compounds which Paul Lauterbur and I have been working on for so long should be submitted for publication shortly. We hope it will appear in Can. J. Chem.)

Double Resonance Work: We have been using heteronuclear spin decoupling to aid in the analysis of certain ABCX spectra where A,B,C = H,X=F. Since the ABCX spectrum is the superposition of two ABC patterns and the decoupled spectrum is another ABC pattern with the same H-H couplings, there are three patterns which can be used to complete the spectral analysis. Dr. J. D. Talman of the Mathematics department wrote a program to do this based on Waugh and Castellano's approach but requiring only one set of E's as input data. The other possible sets are generated and all possible solutions computed. Then one selects e set of parameters which best fit all three patterns. In addition, an error analysis program has been completed recently by Dr. Talman. A typical case is illustrated by the accompanying figure, the limits shown are those given by the error analysis. Heteronuclear spin decoupling, $H^1-(P^{31})$, to determine P^{31} chemical shifts has been examined and I am

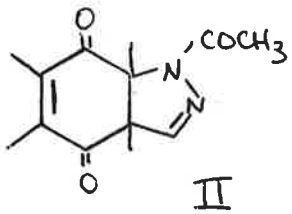
surprised that organic chemists have not made use of this method, since it allows P^{31} shift data to be measured on small quantities (just sufficient for the proton spectrum, of course) and one can obtain data to within 0.5 p.p.m. very readily. I have used our older spin decoupler (with a VFO) for this work, but the use of the SSB Unit would improve the precision.

An example of some homonuclear spin decoupling experiments is shown in the second figure. This compound (I) is one of a series of bicyclo [2.2.2] octane derivatives we have been studying and these spectra clearly show the coupling between the vinyl and the bridgehead protons which is confirmed by decoupling. I have used our NMR Specialties HD-60 unit for these spectra and the particular side band and its frequency for each trace are indicated. Spectrum D shows the effect of changing the SB (from upper to lower) during a scan in order to decouple two multiplets. The small change in the base-line occurred when the side band was changed. To conserve space in this drawing traces at two different amplitudes were used for A.



I

Miscellaneous notes - Some longer range couplings have been found recently which may be of interest to some readers. (a) Proton-proton coupling of 1.35 ± 0.1 c/s between methyl groups on the double bond in Cpd. II (supplied by Dr. W. C. Howell of this department) was found. It is interesting that these methyls are equivalent in the parent, non-acetylated, pyrazoline. (b) Examples of P^{31}-H couplings of the type P-O-C-C-H have been observed for phosphorus esters, employed in the decoupling work mentioned above, having the structure $(EtO)_2P(X)YC_6Cl_5$ where X=O,O,S and S with Y=O,S,O, and S, respectively. The methyl protons show a splitting of 1 ± 0.1 c/s.



II

I hope these items warrant a renewal of my subscription to the newsletter.

Sincerely,

Jake

J. B. Stothers
Assistant Professor

JBS:vl

Estimates of θ for some Ortho-Substituted Acetophenones by Various Methods

Substituent(s)	Method of Estimation		
	C^{13} NMR (corr.)*	UV Spectra (1)	Dipole Moment (1)
2-Me	24° (28°)	40°	34°
2,4-Me_2	21° (25°)	24°	-
2,5-Me_2	21° (25°)	35°	46°
2,6-Me_2	44° (50°)	55°	-
2,4,6-Me_3	46° (51°)	63°**	62°
2,3,5,6-Me_4	51° (57°)	-	-
2-Et	25°	-	-
2-i-Pr	29°	-	-
2-t-Bu‡	51°	-	-
2-MeO	17°	-	-
2-Cl	22°	30° (2)	-
2-Br	24°	-	-
2-I	29°	-	-
2,6-Et_2	44°	-	-
2,4,6-i-Pr_3	50°	-	-
Isobutryophenone	19°	-	-
Pivalophenone	33°	34°	-

* Data in parentheses have been corrected for "ortho" effect of methyl group(s).

‡ Using the data for 2,5-di-t-butyl acetophenone

** The value 67° has also been reported (1).

(1) E. A. Brande and F. Sondheimer. J. Chem. Soc. 3754 (1955).

(2) W. F. Forbes. Can. J. Chem. 38, 1104 (1960).

SPECTRA of
63-42

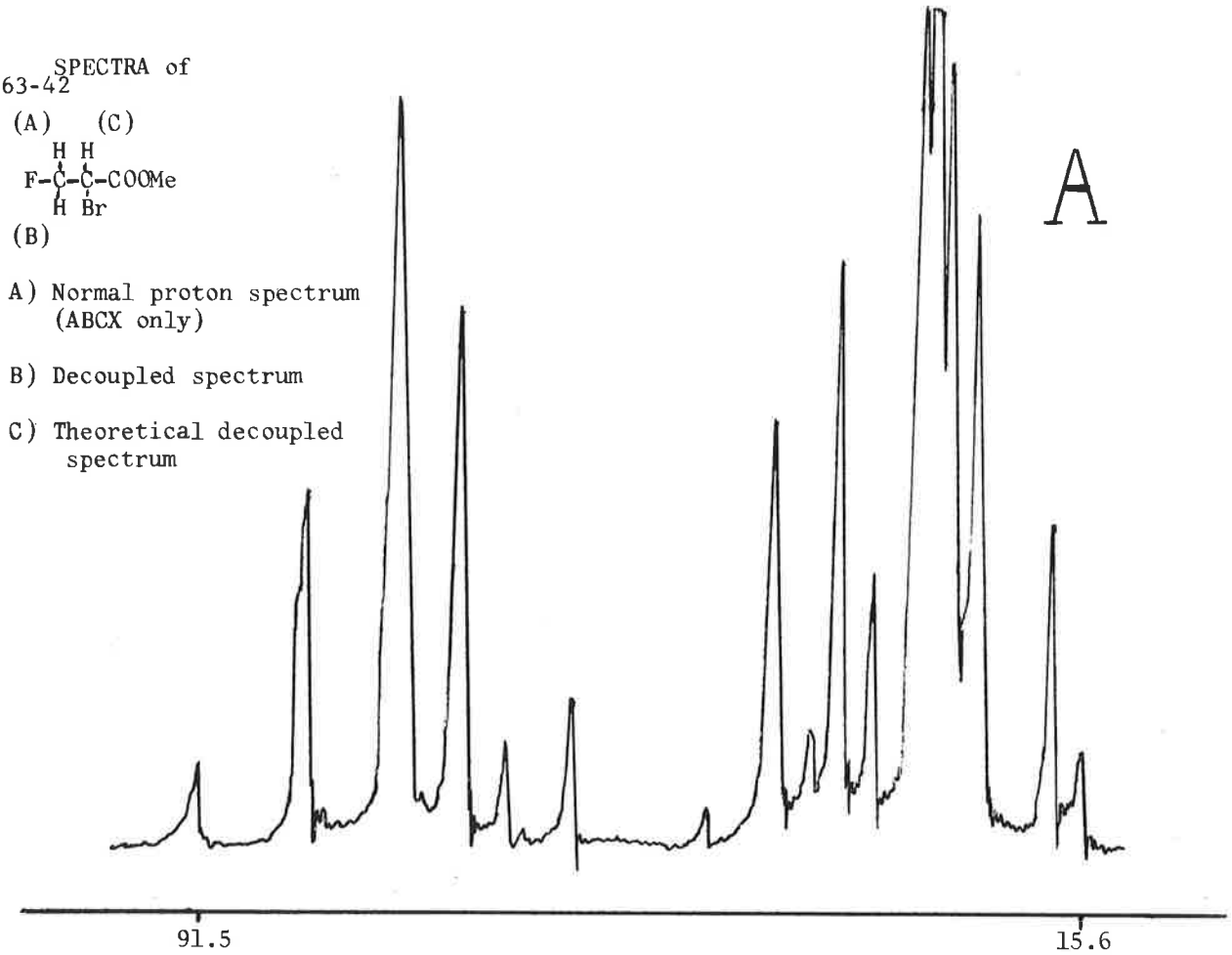
(A) (C)

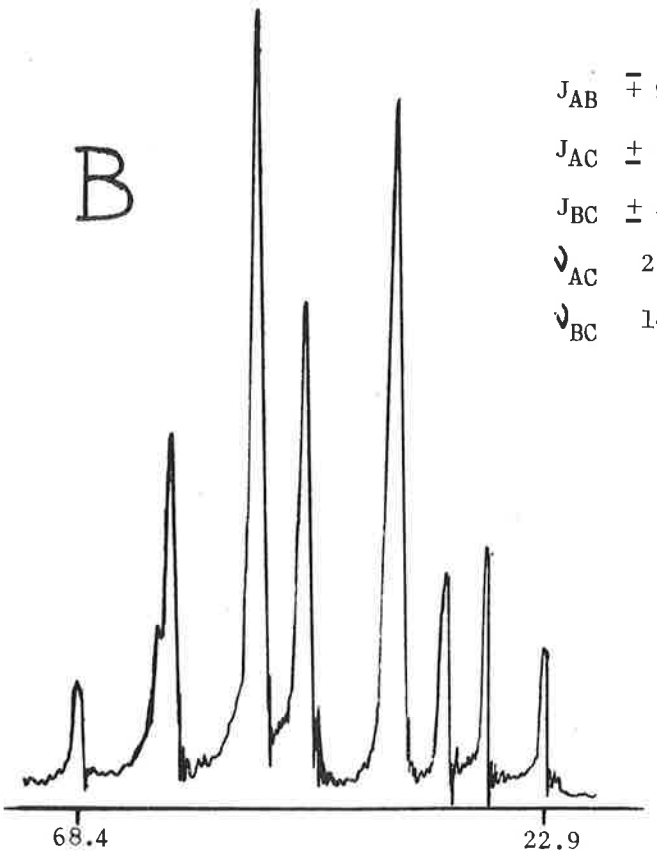
(B)

A) Normal proton spectrum (ABCX only)

B) Decoupled spectrum

C) Theoretical decoupled spectrum





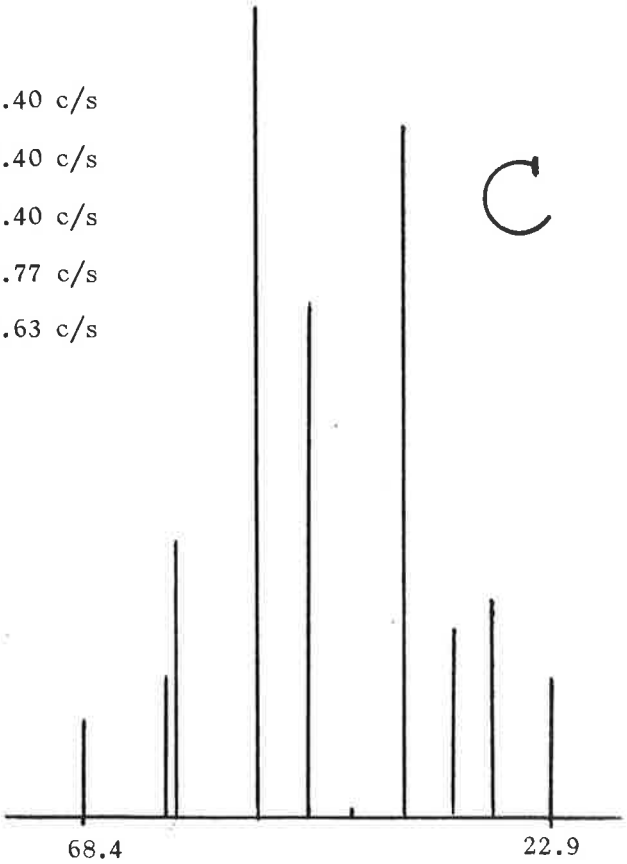
J_{AB} $\mp$ 9.46 $\pm$ 0.40 c/s

J_{AC} $\pm$ 8.31 $\pm$ 0.40 c/s

J_{BC} $\pm$ 5.65 $\pm$ 0.40 c/s

ν_{AC} 26.73 $\pm$ 0.77 c/s

ν_{BC} 14.07 $\pm$ 0.63 c/s



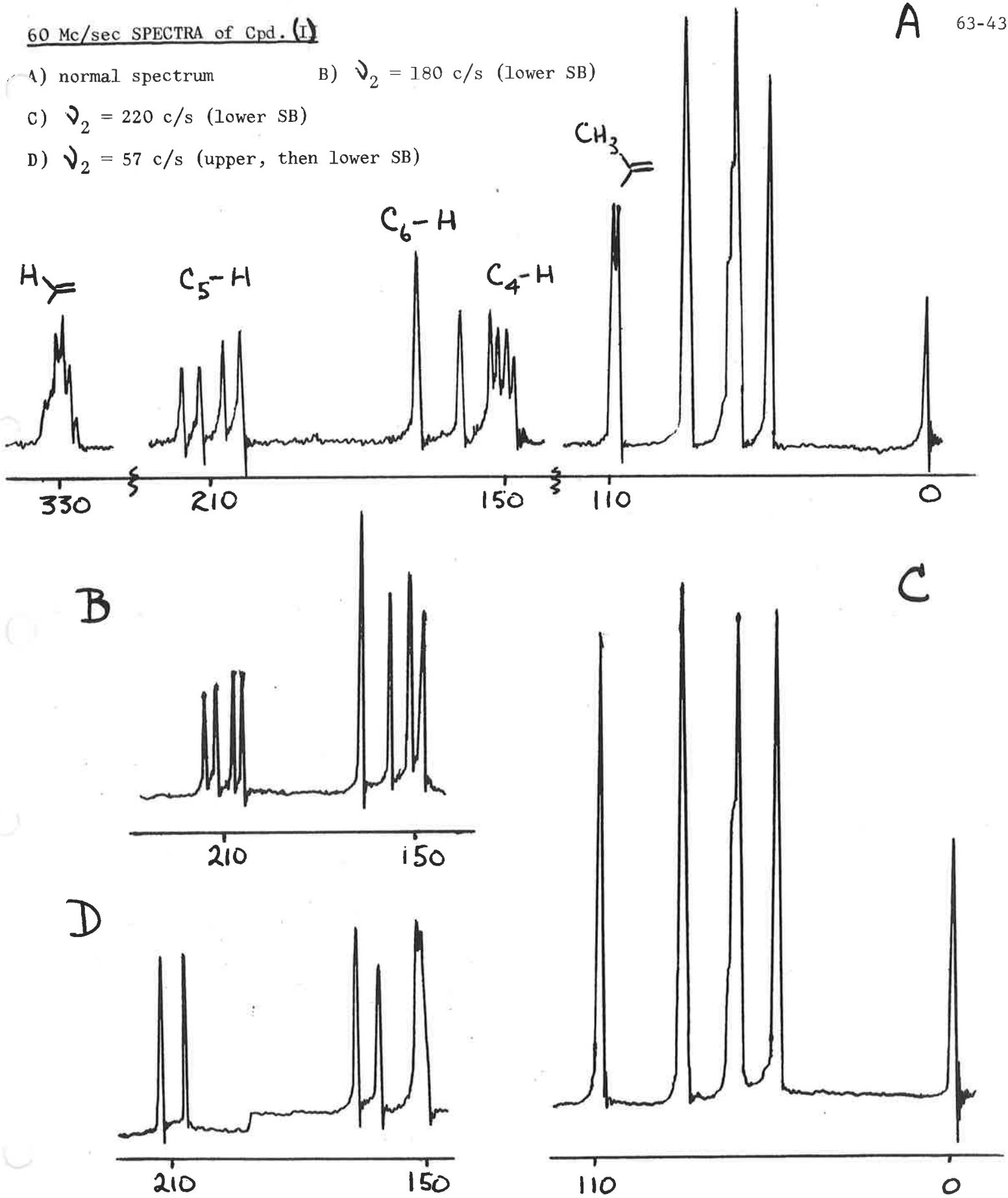
60 Mc/sec SPECTRA of Cpd. (I)

A) normal spectrum

B) ν_2 = 180 c/s (lower SB)

C) ν_2 = 220 c/s (lower SB)

D) ν_2 = 57 c/s (upper, then lower SB)



"Hydrogen Bonding and Stereospecific Long-range Spin Coupling in 3-Nitro- and 5-Nitrosalicylaldehyde"
S. Forsén and B. Akermark
Acta Chem. Scand. 17, 1712 (1963)

"A New Method for the Study of Moderately Rapid Chemical Exchange Rates Employing Nuclear Magnetic Double Resonance"
S. Forsén and R. A. Hoffman
Acta Chem. Scand. 17, 1787 (1963)

"Kernresonanzmessungen an Deuterierten Monoderivaten des Benzols; Chemische Verschiebung der meta-Protonen"
F. Langenbucher, R. Mecke und E. D. Schmid
Ann. Chem. 669, 11 (1963)

"Zur Linienbreite der Kernresonanz an ausgedehnten Proben im inhomogenen Magnetfeld"
G. Richter und A. E. Schwind
Ann. Phys. 11, 405 (1963)

"On the Preparation of Some Iodine-Substituted Thiophenes and Bithienyls"
S. Gronowitz and V. Vilks
Arkiv Kemi 21, 191 (1963)

"Optically Active Bithienyls. IV. On the Synthesis of 2,2′-Dicarboxy-4,4′-Dinitro-3,3′-Bithienyl"
S. Gronowitz and K. Dahlgren
Arkiv Kemi 21, 201 (1963)

"Unsaturated γ-Thiolactones. III. Preparation and Tautomeric Structure of Some Methyl-, Bromo- and Methoxy-Substituted Thiolene-2-ones"
A.-B. Hörnfeldt and S. Gronowitz
Arkiv Kemi 21, 239 (1963)

"On the Structures of the Thiophene Analogues of Phthalaldehydic Acid"
S. Gronowitz, A. Biezais and B. Mathiasson
Arkiv Kemi 21, 265 (1963)

"Mechanisms of Steroid Oxidation by Microorganisms. IV. Seco Intermediates"
K. C. Wang and C. J. Sih
Biochem. 2, 1238 (1963)

"Isolation and Characterization of Human Urinary Metabolites of Aldosterone. IV. The Synthesis and Stereochemistry of Two Bicyclic Acetal Metabolites"
W. G. Kelly, L. Bandi and S. Lieberman
Biochem. 2, 1243 (1963)

"Activated Hydrogens in Compounds Related to Thiamine"
W. Hafferi, H. Lundin and L. L. Ingraham
Biochem. 2, 1298 (1963)

"Caractérisation de la L-Thréo-β-Hydroxyleucine. A Partir de Deutzia Gracilis"
J. Jadot, J. Casimir et F. Alderweireldt
Biochim. Biophys. Acta 78, 500 (1963)

"An Investigation of the Structure of Chemical Compounds by Means of Nuclear Magnetic Resonance Spectra. 2. The Determination of the Structure and Confirmation of a Number of Substituted Cyclopentenones"
V. F. Bystrov, T. E. Pozdnyakov, A. N. Elizarova and A. A. Akhrem
Bull. Acad. Sci. USSR, Div. Chem. Sci. (English Transl.) 58 (1963)

"NMR Relaxation Times of Pt^{195} in Pt-Au Alloys"
M. Weger and C. Froidevaux
Bull. Am. Phys. Soc. 8, 591 (1963)

"Core-Induced Negative NMR Frequency Shift in Pt-Au Solid Solutions"
C. Froidevaux
Bull. Am. Phys. Soc. 8, 591 (1963)

"Nuclear Magnetic Resonance in a Cadmium Single Crystal"
H. E. Schone
Bull. Am. Phys. Soc. 8, 592 (1963)

"Transient NMR Study of the Conduction Band of Metallic Na_xWO_3"
A. T. Fromhold, Jr. and A. Narath
Bull. Am. Phys. Soc. 8, 592 (1963)

"Observation of the Br^{79} and Br^{81} Nuclear Resonances in Ferromagnetic $CrBr_3$"
S. D. Senturia, F. Heller and G. B. Benedek
Bull. Am. Phys. Soc. 8, 592 (1963)

"Étude par Résonance Magnétique Nucléaire du Proton de Composés Organo Phosphorés: X. Étude de la Cinétique de l'Alcoolyse de la Tris-diméthylamino Phosphine"
R. Bargada, G. Martin et G. Mavel
Bull. Soc. Chim. France 2154 (1963)

"Résonance Magnétique Nucléaire de Certains Alcaloïdes de la Série de la Morphine: Étude du Cycle B (2e partie)"
T. Hüll et D. Gagnaire
Bull. Soc. Chim. France 2189 (1963)

"Étude des Constituants Neutres du Cistus Labdaniferus"
C. Tabacik-Wlotzka, M. Mousseron et A. Chafai
Bull. Soc. Chim. France 2299 (1963)

"Stéréochimie dans la Série de l'Acide Agathique"
S. Bory, M. Pétizon et P. Laszlo
Bull. Soc. Chim. France 2310 (1963)

"Alcaloïdes Stéroïdiques, XXII. Structure de l'α-Hydroxyconessine."
R. Goutarel, C. Conreur et J. Parello
Bull. Soc. Chim. France 2401 (1963)

"Role du Solvant dans la Transposition de Favorsky"
A. Guademer, J. Parello, A. Skrobek et B. Tchoubar
Bull. Soc. Chim. France 2405 (1963)

"Étude des Molécules Polycycliques Cancérogenes par la Résonance Magnétique Nucléaire. I. Examen de 6 Dérivés Monométhyles du Benzo-1,2 Anthracène"
P. Durand, J. Parello, N. P. Buu-Hoï et L. Alais
Bull. Soc. Chim. France 2438 (1963)

"Couplages des Protons d'un Méthyle à Travers Cinq Liaisons en Résonance Magnétique Nucléaire: Éthers Vinyliques Hétérocycliques"
D. Gagnaire et E. Payo-Subiza
Bull. Soc. Chim. France 2623 (1963)

"Die Konfiguration der Glykosidbundgen in Erythromycin und Magnamycin"
W. Hofheinz und H. Grisebach
Chem. Ber. 96, 2867 (1963)

"Über den Mechanismus der sÄurekatalysierten Kondensationsreaktionen der Hydroxy-Flavans und Hydroxy-flavanole-(3)"
K. Weinges, Y. Naya und F. Toribio
Chem. Ber. 96, 2870 (1963)

"Über Nitroso-3.4-dimethyl-pyrazolon-(5) und zwei daraus darstellbare ,,Bispyrazolone"
R. Hüttel und A. Authaler
Chem. Ber. 96, 2879 (1963)

"Rhodosamin, Isolierung, Konstitution und Konfiguration"
H. Brockmann, E. Spohler und T. Waehneldt
Chem. Ber. 96, 2925 (1963)

"Die Reaktion von Tetrakis(dimethylamino)-Äthylen mit Lewis-Säuren"
N. Wiberg und J. W. Buchler
Chem. Ber. 96, 3000 (1963)

"The Resin Acids of Ricinocarpus Stylosus"
C. A. Henrick and P. R. Jefferies
Chem. Ind. 1801 (1963)

"Two Minor Diterpenoid Constituents of Ricinocarpus Stylosus"
C. A. Henrick and P. R. Jefferies
Chem. Ind. 1802 (1963)

"Aromatin and Aromaticin, New Sesquiterpene Lactones Isolated from Helenium Aromaticum"
J. Romo, P. Joseph-Nathan and Fernando Diaz A.
Chem. Ind. 1839 (1963)

"Cimicine and Cimididine: Lactonic Alkaloids of the Aspidospermine Skelatel Type"
M. P. Cava, S. K. Talapatra, P. Yates, M. Rosenberger, A. G. Szabo, B. Douglas, R. F. Raffauf, E. C. Shoop and J. A. Weisbach
Chem. Ind. 1875 (1963)

"Condensations d'Aldéhydes α-Éthyléniques en Milieu Hetérogène. I. Condensation du Méthyl-2 Pentenal sur les Aldéhydes para et Ortho-Méthylcinnamiques. II. Condensation de l'α-phénylcrotonal sur les Aldéhydes de Formule R—CH=CH—CHO"
J.-J. Godfroid
Compt. Rend. 257, 2296 (1963)

"Étude en Résonance Magnétique Nucléaire des Molécules H_2 et HD à l'État Gazeux"
E. Bayan, G. Widenlocher et M. Chaigneau
Compt. Rend. 257, 2455 (1963)

"Remarques sur la Teneur en Scopolétine des Cultures de Tissus de Tabac Anergiés Sains et Infectés par le Virus de la Mosaïque du Tabac"
P. Benveniste, L. Hirth, S. Munavalli et G. Ourisson
Compt. Rend. 257, 2704 (1963)

"The Location of the Ring C Hydroxyl Group in Fusidic Acid"
D. Arigoni, W. von Daehne, W. O. Godtfredsen, A. Marquet and A. Melera
Experientia 19, 521 (1963)

"Nuclear Magnetic Resonance with Stochastic High-Frequency Fields"
R. R. Ernst and H. Primas
Helv. Phys. Acta 36, 583 (1963)

"Indirect Spin Coupling in NiAS Type Magnetic Compounds"
K. P. Sinha, M. K. Sinha and U. N. Upadhyaya
Indian J. Phys. 37, 417 (1963)

"A New Series of Organoboranes. II. The Chlorination of 1,2-Dicarbaclovododecaborane(12)"
H. Schroeder, T. L. Heying and J. R. Reiner
Inorg. Chem. 2, 1092 (1963)

"Further Studies of the Tetraborane Carbonyl B_4H_8CO"
J. R. Spielman and A. B. Burg
Inorg. Chem. 2, 1139 (1963)

"A Displacement Study and Proton Nuclear Magnetic Resonance Investigation of the Relative Base Strengths of the Dimethylaminophosphines with Triethylborane"
R. R. Holmes and R. P. Carter, Jr.
Inorg. Chem. 2, 1146 (1963)

"Principles of Phosphorus Chemistry. XIV. Interchanges in Esters of Monophosphorus Acids"
K. Moedritzer, G. M. Burch, J. R. Van Wazer and H. K. Hofmeister
Inorg. Chem. 2, 1152 (1963)

"The Configurations of Yellow and Red Trichlorotris-(diethyl sulfide)-iridium (III)"
G. B. Kauffman, J. Hua-Fan Tsai, R. C. Fay and C. K. Jørgensen
Inorg. Chem. 2, 1233 (1963)

"Reactions of Triethylaluminum, Diethylaluminum Chloride, and Ethylaluminum Dichloride with Dimethyl-, Trimethyl-, and Tetramethylhydrazines"
D. F. Clemens, W. S. Brey, Jr. and H. H. Sisler
Inorg. Chem. 2, 1251 (1963)

"Nuclear Magnetic Resonance Spectra and Stereochemistry of Propenylmercury Compounds"
D. Moy, M. Emerson and J. P. Oliver
Inorg. Chem. 2, 1261 (1963)

"Further Nuclear Magnetic Resonance and Electron Paramagnetic Resonance Studies on the System $N_2F_4 \rightleftharpoons 2NF_2$"
R. Ettinger and C. B. Colburn
Inorg. Chem. 2, 1311 (1963)

"The Structure of Neocarborane"
H. Schroeder and G. D. Vickers
Inorg. Chem. 2, 1317 (1963)

"Studies of Boron-Nitrogen Compounds. VI. Chemical Properties of the Isomers of 1,3,5-Trimethylcycloborazane"
D. F. Gaines and R. Schaeffer
J. Am. Chem. Soc. 85, 3592 (1963)

"Structural Studies by Nuclear Magnetic Resonance. V. Phenylhydrazones"
G. J. Karabatsos and R. A. Taller
J. Am. Chem. Soc. 85, 3624 (1963)

"A Detailed Analysis of the 7-Norbornadienyl Carbonium Ion Nuclear Magnetic Resonance Spectrum"
P. R. Story, L. C. Snyder, D. C. Douglas, E. W. Anderson and R. L. Kornegay
J. Am. Chem. Soc. 85, 3630 (1963)

"Electrophilic Addition to Olefins. III. The Stereochemistry of Addition of Deuterium Bromide to 1-Phenylpropene"
M. J. S. Dewar and R. C. Fahey
J. Am. Chem. Soc. 85, 3645 (1963)

"Specific Solvation in Binary Solvent Mixtures. III. The Solvolysis of o-, m-, and p- Methyl and Nitrobenzyl Chlorides in Ethanol-Water Mixtures"
J. B. Hyne and R. Wills
J. Am. Chem. Soc. 85, 3650 (1963)

"The Total Synthesis of (±)-Thujopsene"
W. G. Dauben and A. C. Ashcraft
J. Am. Chem. Soc. 85, 3673 (1963)

"A 100-Mc. Nuclear Magnetic Resonance and Nuclear Magnetic Double Resonance Study of Puromycin"
L. F. Johnson and N. S. Shacca
J. Am. Chem. Soc. 85, 3700 (1963)

"The Isolation and Characterization of $B_{20}H_{19}^{-3}$ and $B_{20}H_{18}^{-4}$ Ions"
M. F. Hawthorne, R. L. Pilling, P. F. Stokely and P. M. Garrett
J. Am. Chem. Soc. 85, 3704 (1963)

"A New Noncyclic Butadiene Oligomer: trans-3-Methylhepta-1,4,6-triene"
S. Otsuka, T. Kikuchi and T. Taketomi
J. Am. Chem. Soc. 85, 3709 (1963)

"Conformational Studies of Cyclobutane Systems"
J. B. Lambert and J. D. Roberts
J. Am. Chem. Soc. 85, 3710 (1963)

"On the Stereochemistry of Homoenolization"
A. Nickon, J. H. Hammons, J. L. Lambert and R. O. Williams
J. Am. Chem. Soc. 85, 3713 (1963)

"Isomerization of Cyclononatrienes"
J. W. H. Watthey and S. Winstein
J. Am. Chem. Soc. 85, 3715 (1963)

"Anorganische und Allgemeine Chemie in Einzeldarstellungen. Band V. Die Kernmagnetische Resonanz und Ihre Anwendung in der Anorganischen Chemie. By E. Fluck; Springer-Verlag, 1963.
Reviewed by A. A. Bothner-By
J. Am. Chem. Soc. 85, 3720 (1963)

"Configurations in Unsymmetrically N,N-Disubstituted Amides"
L. A. LaPlanche and M. T. Rogers
J. Am. Chem. Soc. 85, 3728 (1963)

"New Cyclopentadienyl Complexes of Rhodium"
R. J. Angelici and E. O. Fischer
J. Am. Chem. Soc. 85, 3733 (1963)

"A Nuclear Magnetic Resonance Study of Structures of Cobalt (II)-Histidine Complexes"
C. C. McDonald and W. D. Phillips
J. Am. Chem. Soc. 85, 3736 (1963)

"Proximity Effects. XXXV. Stereospecific Synthesis and Acetolysis of cis- and trans-5-Methylcyclooctyl Tosylates"
A. C. Cope and D. M. Gale
J. Am. Chem. Soc. 85, 3743 (1963)

"Proximity Effects. XXXVI. Solvolysis of Deuterium-Labeled Cyclooctyl Brosylate"
A. C. Cope and D. M. Gale
J. Am. Chem. Soc. 85, 3747 (1963)

"Carbon-Carbon Bond Fission in Cyclopropanes. II. The Acid-Promoted Opening of the Three-Membered Ring in 2,3-Methano-trans-decalin"
R. T. LaLonde and M. A. Tobias
J. Am. Chem. Soc. 85, 3771 (1963)

"The Photochemistry of α-Keto Acids and α-Keto Esters. I. Photolysis of Pyruvic Acid and Benzoylformic Acid"
P. A. Leermakers and G. F. Vesley
J. Am. Chem. Soc. 85, 3776 (1963)

"Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. III. An Example of Steric Control"
P. J. Kropp
J. Am. Chem. Soc. 85, 3779 (1963)

"Synthetic Transformation of Natural Products. I. 1-Methylene-2,10-methano-5,5,9-trimethyldecahydronaphthalene"
G. Brieger
J. Am. Chem. Soc. 85,3783 (1963)

"Synthesis of 1,9-cis-Diacetoxy-$\Delta^{5,10}$-octalone-6; Stereochemical Course of the Robinson Annelation Reaction"
T. A. Spencer, K. K. Schmiegel and K. L. Williamson
J. Am. Chem. Soc. 85, 3785 (1963)

Synthesis of the New 5-Phosphomethyl-6-chromanyl Acetate of Vitamin $K_{1(20)}$ by a Novel Cyclization Reaction"
A. F. Wagner, A. Lusi, R. E. Erickson, B. Arison, N. R. Trenner and K. Folkers
J. Am. Chem. Soc. 85, 3793 (1963)

"The Base-Induced Pyrolysis of Tosylhydrazones of α, β-Unsaturated Aldehydes and Ketones. A Convenient Synthesis of Some Alkylcyclopropenes"
G. L. Closs, L. E. Closs and W. A. Böll
J. Am. Chem. Soc. 85, 3796 (1963)

"Nuclear Magnetic Resonance Spectra and Molecular Association of Chlorophylls a and b, Methyl Chlorophyllides, Pheophytins, and Methyl Pheoporbides"
G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas and H. H. Strain
J. Am. Chem. Soc. 85, 3809 (1963)

"Synthesis of Dihydrooxadiazinones and Study of Geometrical Isomerism in α-Ketol Carbethoxyhydrazones"
M. Rosenblum, V. Nayak, S. K. DasGupta and A. Longroy
J. Am. Chem. Soc. 85, 3874 (1963)

"The Reactions of Phosphorus Compounds. VIII. Kinetics and Mechanism of the Wittig Reaction"
A. J. Speziale and D. E. Bissing
J. Am. Chem. Soc. 85, 3878 (1963)

"Aroylation at the Terminal Methyl Group of a 1,3,5-Triketone to Form a 1,3,5,7-Tektraketone"
M. L. Miles, T. M. Harris and C. R. Hauser
J. Am. Chem. Soc. 85, 3884 (1963)

"Structural Studies by Nuclear Magnetic Resonance. VI. The Stereospecificity of Coupling between Protons Separated by Five Bonds and Conformations of Some Aromatic Aldehydes"
G. J. Karabatsos, and F. M. Vane
J. Am. Chem. Soc. 85, 3886 (1963)

"Reactions of Organolithium Compounds and Diphenylacetylene"
J. E. Mulvaney, Z. G. Gardlund and S. I. Gardlund
J. Am. Chem. Soc. 85, 3897 (1963)

"Solvent Effects on the C^{13} Chemical Shift of the Carbonyl Group of Acetone"
G. E. Maciel and G. C. Ruben
J. Am. Chem. Soc. 85, 3903 (1963)

"Photoisomerization of Pyrazolenines and Formation of 7,7-Dimethylbicyclo[4.1.0]heptene-Δ-1,6"
G. L. Closs and W. A. Böll
J. Am. Chem. Soc. 85, 3904 (1963)

"Use of the Nuclear Overhauser Effect in the Analysis of High-Resolution Nuclear Magnetic Resonance Spectra"
R. Kaiser
J. Chem. Phys. 39, 2435 (1963)

"Magnetic Resonance of Mn^{2+}-Doped LiF Crystals"
T. T. Chang, W. H. Tanttila and J. S. Wells
J. Chem. Phys. 39, 2453 (1963)

"Computation of Unique NMR Parameters for ABC Systems with the Aid of C^{13}-H Satellite Spectra"
R. T. Hobgood, Jr., R. E. Mayo and J. H. Goldstein
J. Chem. Phys. 39, 2501 (1963)

"Sulfur and Silicon Isotope Effects in Fluorine Nuclear Magnetic Resonance Spectroscopy"
R. J. Gillespie and J. W. Quail
J. Chem. Phys. 39, 2555 (1963)

"Nuclear Magnetic Shielding Constants and X-Ray Atomic Scattering Factors for Two-, Three-, and Four-Electron Systems by Means of Analytic Hartree-Fock Wavefunctions"
M. L. Rustgi and P. Tiwari
J. Chem. Phys. 39, 2590 (1963)

"Nuclear Magnetic Relaxation and Diffusion in Liquid SF_6"
W. R. Hackleman and P. S. Hubbard
J. Chem. Phys. 39, 2688 (1963)

"Proton Relaxation in Deuterated Solutions of Asphalt"
E. R. Poindexter
J. Chem. Phys. 39, 2772 (1963)

"Temperature Dependences of Nuclear-Transfer and Spin-Relaxation Phenomena of Water Adsorbed on Silica Gel"
D. E. Woessner
J. Chem. Phys. 39, 2783 (1963)

"Valence-Bond Theory of Resonance: Aniline, Phenol, and Fluorobenzene"
J. C. Schug
J. Chem. Phys. 39, 2798 (1963)

"Study of Moderately Rapid Chemical Exchange Reactions by Means of Nuclear Magnetic Double Resonance"
S. Forsén and R. A. Hoffman
J. Chem. Phys. 39, 2892 (1963)

"Motion of the H_2O Molecule in Barium Chlorate Monohydrate"
J. W. McGrath and A. A. Silvidi
J. Chem. Phys. 39, 3017 (1963)

"Pure Quadrupole Resonance Spectra of Trialkylboranes"
P. Love
J. Chem. Phys. 39, 3044 (1963)

"NMR Studies of Phase Transitions. I. NaSH"
C. K. Coogan, G. G. Belford and H. S. Gutowsky
J. Chem. Phys. 39, 3061 (1963)

"Time-Weighted-Average Approximation in the NMR Spectrum of $CF_2BrCFBrCl$"
R. A. Newmark and C. H. Sederholm
J. Chem. Phys. 39, 3131 (1963)

"Proton NMR Studies of CHDO and CH_2O"
B. L. Shapiro, R. M. Kopchik and S. J. Ebersole
J. Chem. Phys. 39, 3154 (1963)

"Comments on the Orientation of the Proton-Proton Vectors of Water in Tutton's Salts"
D. H. Templeton, A. Zalkin and T. N. Margulis
J. Chem. Phys. 39, 3155 (1963)

"Erratum: High-Resolution NMR Spectrum of 1,2-Benzanthracene" [J. Chem. Phys. 38, 1453 (1963)]
J. D. Memory and T. B. Cobb
J. Chem. Phys. 39, 3155 (1963)

"Volume Magnetic Susceptibility Measurements by NMR"
D. C. Douglass and A. Fratello
J. Chem. Phys. 39, 3161 (1963)

"NMR Study of Hydrogen Bonding between Chloroform and Dimethyl Sulfoxide, Ethylene, and Propylene Carbonates"
A. L. McClellan, S. W. Nicksic, and J. C. Cuffy
J. Mol. Spectroscopy 11, 340 (1963)

"Nuclear Spin-Lattice Relaxation in Liquids"
P. K. Sharma and S. K. Joshi
Phys. Rev. 132, 1431 (1963)

"Nuclear Susceptibility of Solid Helium-3"
A. L. Thomson, H. Meyer and P. N. Dheer
Phys. Rev. 132, 1455 (1963)

"Knight Shifts and Linewidths of the Pb^{207} Nuclear Magnetic Resonance in Lead-Indium Alloys"
R. J. Snodgrass and L. H. Bennett
Phys. Rev. 132, 1465 (1963)

"Nuclear Magnetic Resonance Line Shapes Resulting from the Combined Effects of Nuclear Quadrupole and Anisotropic Shift Interactions"
W. H. Jones, Jr., T. P. Graham and R. G. Barnes
Phys. Rev. 132, 1898 (1963)

"The Anisotropy of the NMR in Copper Sheets"
K. Tompa and F. Tóth
Phys. Stat. Sol. 3, 2051 (1963)

"Hyperfine Splittings in Aromatic Radicals"
M. Karplus
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 207 (1962)

"Hyperconjugation in Proton Hyperfine Interaction"
S. Aono
Proc. Intern. Symp. Mol. Struct. & Spectroscopy . Tokyo. D 209 (1962)

"NMR Studies of Conformational Equilibria in Substituted Ethanes"
H. S. Gutowsky
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 212 (1962)

"Structure and Motion of Water Molecules of Hydration in Crystals by Deuteron Magnetic Resonance"
T. Chiba
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 213 (1962)

"Double Resonance and Relaxation in High Resolution Proton Resonance"
Y. Kakiuchi, M. Matsouka and K. Mizuno
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 214 (1962)

"Proton Resonance in DNP-Amino Acid"
S. Fukiwara, Y. Arata, N. Hayakawa and H. Momoi
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 216 (1962)

"Simple Molecular Orbital Study on the Ring Current Methods of the Porphine Skeleton"
G. Hazato
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 217 (1962)

"Nuclear Magnetic Resonance of Trapped Molecules"
H. Nakajima
Proc. Intern. Symp. Mol. Struct. & Spectroscopy. Tokyo, D 219 (1962)

"Fluorine Electron Nuclear Double Resonance (ENDOR) in Calcium Fluoride"
J. M. Baker and J. P. Hurrell
Proc. Phys. Soc. 82, 742 (1963)

"A Variation Principle in the Quantum Theory of Irreversible Processes"
H. Nakano
Proc. Phys. Soc. 82, 757 (1963)

"The Formation of Cyclols from N-Hydroxyacyllactams"
R. G. Griot and A. J. Frey
Tetrahedron 19, 1661 (1963)

"The Stereospecific Cyclolization of N-(α-Hydroxyacyl)-Phenylalanyl- Proline Lactams"
H. Ott, A. J. Frey and A. Hofmann
Tetrahedron 19, 1675 (1963)

"1,2-Dihydroquinoline Studies -- I. The Structure of the Arylamine-Acetone Condensation Products"
C. C. Tung
Tetrahedron 19, 1685 (1963)

"Reassignment of Structures of the Dihydro-v-Tetrazines"
D. Y. Curtin and N. E. Alexandrou
Tetrahedron 19, 1697 (1963)

"Sulphur Substitution Compounds of Aminosugars. VI. The Synthesis of 2-Amino-2,3-Dideoxy-3-Mercapto-p-Allose Derivatives Through Thiazoline Intermediates"
W. M. Zubeckendorf and W. A. Bonner
Tetrahedron 19, 1721 (1963)

"Resonance Magnetique Nucleaire De Produits Naturels. VI, Triterpenes Dérivés de la Bétuline"
J. M. Lehn and A. Vystrcil
Tetrahedron 19, 1733 (1963)

"Triterpenoid Compounds. VI. The Constitution of Melaleucic Acid -- II"
C. S. Chopra, M. W. Fuller, K. J. L. Thieberg, D. C. Shaw, and D. E. White, G. H. Hall and E. N. Maslen
Tetrahedron Letters 1847 (1963)

"Long Range Shielding by the Epoxide Ring."
P. R. Jefferies, R. S. Rosich and D. E. White
Tetrahedron Letters 1853 (1963)

"Lichtinduzierte Decarbonylierung Gelöster Ketone Bei Raumtemperatur"
G. Quinkert, K. Opitz, W. W. Wiersdorff und J. Weinlich
Tetrahedron Letters 1863 (1963)

"The Degenerate Cope Rearrangement of Tricyclo $[3.3.1.0^{4,6}]$ Nona-2, 7-Diene-9-One"
J. B. Lambert
Tetrahedron Letters 1901 (1963)

"Kernresonanzabsorption und Lumineszenzeigenschaften von Fe^{57} in ZnS-Phosphoren"
K. Luchner und J. Dietl
Z. Phys. 176, 261 (1963)

"Bestimmung der Anordnung der Wasserstoffatome in Natriumdithionatdihydrat, $Na_2S_2O_6 \cdot 2H_2O$ durch Untersuchung des kernmagnetischen Resonanzspektrums der Protonen in Einkristallen"
I. Berthold und A. Weiss
Z. Physik. Chem. 36, 140 (1963)