Premas

Monthly
Ecumenical
Letters from
Laboratories
Of
N - M - R

No. 56

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DEADLINE FOR NEXT ISSUE
June 25, 1963
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THE SQUIBB INSTITUTE
FOR MEDICAL RESEARCH
NEW BRUNSWICK, N.J.

May 2, 1963

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

Dear Doctor Shapiro:

When a sample dissolved in chloroform is shaken with deuterium oxide, exchange of the amide proton occurs very slowly. In the presence of a base, such as triethylamine, the exchange occurs rapidly and quantitatively.

The sample is dissolved in 0.4 ml. deuterochloroform containing tetramethylsilane and the spectrum taken. The tube is removed, and 50 microliters of deuterium oxide and 5 microliters of triethylamine is added. The mixture is shaken several times and the tube is replaced in the probe.

The lower curve shows the chloroform spectrum of protected glycine while the upper curve shows the spectrum after base exchange of the amide proton. The -NH signal (4.45 tau) is absent in the upper curve and the methylene signal at 5.81 tau originally a doublet collapses to a singlet on exchange. In the upper curve, the signals for triethylamine and trace amounts of water are also seen.

Yours truly,

Allen I. Cohen

Allen I. Cohen
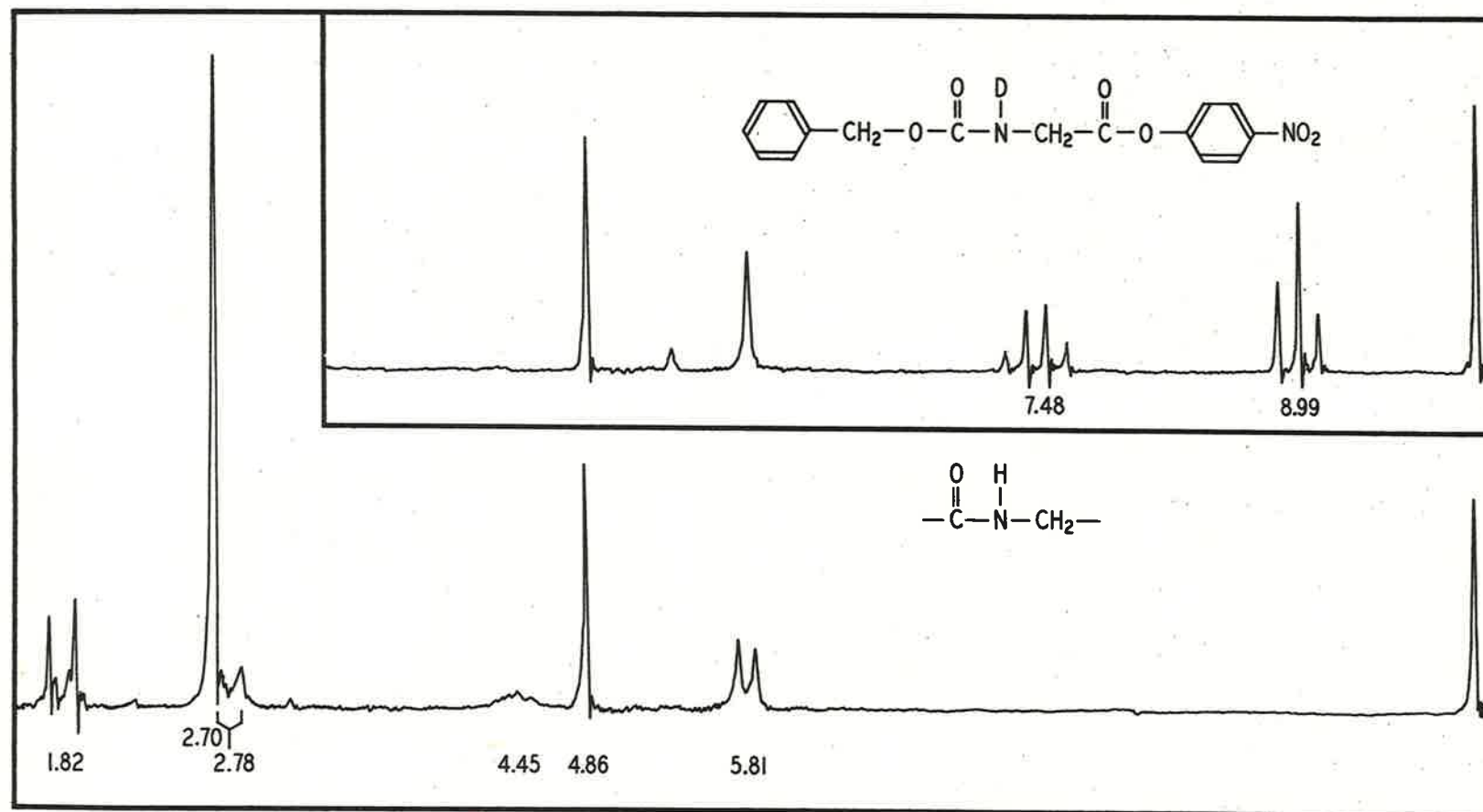
May 6, 1963

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

Dear Barry,

In an extension of work recently reported (J. Am. Chem. Soc., 85, 516 (1963)) on substituent effects in a saturated system we have analyzed the spectra of the following series of mono-substituted 1,1-dichlorocyclopropanes:

R= OAc   This system has been studied in hopes of answering some questions raised in our earlier bicyclo-
OCH$_3$ heptene series as well as shedding some light on
Br   the effect of ring strain on coupling constants.
∅
COOH   This particular system was chosen because 1) it has only three coupling protons, facilitating unambiguous analysis of the spectra, 2) it is rigid, thus eliminating changes in coupling constants due to changes in dihedral angle and 3) probably most important, only one substituent is changed in the system, facilitating comparison of spectra within the series.

The data for these compounds is presented in the Table. It will be noted in Fig. 1 that there is a roughly linear correlation between coupling constants and electronegativity of the substituent, in contrast to the findings of Graham and Rogers (J. Am. Chem. Soc., 84, 2249 1962) who concluded from their study of a non-homologous series of cyclopropane compounds that substituent effects were not important in the consideration of the proton-proton coupling constants. Hutton and Schaefer (Can. J. Chem., 41, (1963)) in a more recent study of coupling constants in the cyclopropane system concluded that substituent effects may be of some importance, but again they were not examining a homologous series of compounds, and thus could see no clear correlation.

In Fig. 2 we have plotted the internal chemical shift (in c.p.s. at 60 mc.) $\delta_x - \delta_A$ and $\delta_x - $_B vs. electronegativity. We are at a loss to explain the large deviations of some of the points.

From this work we conclude that coupling constants and internal chemical shifts are linear functions of the electronegativity of the substituent in the cyclopropane system.

R	J_{AX}	J_{BX}	J_{AE}	δ_A	δ_B	δ_X	Electronegativity[1]
OAc	5.4	8.0	-9.1	1.51	1.83	4.29	3.6
OCH$_3$[2]	5.3	8.4	-7.9	1.51	1.66	3.62	3.31
Br	6.6	9.4	-8.6	1.59	2.09	3.45	2.96
∅[3]	8.6	10.5	-7.3	1.74	1.85	2.80	2.75
COOH	6.8	11.0	-6.8	1.86	2.02	2.52	2.60

Sincerely,

Kenneth L. Williamson

Kenneth L. Williamson
Asst. Prof. Chemistry

1) As defined by Cavanaugh and Dailey, J. Chem. Phys. 34, 1099 (1961).
2) Data from Graham and Rogers, J. Am. Chem. Soc., 84, 2249 (1962).
3) Data from Reilly, Abstracts, 4th OCEANS, March 2, 1963.

Fig. 1

Fig. 2
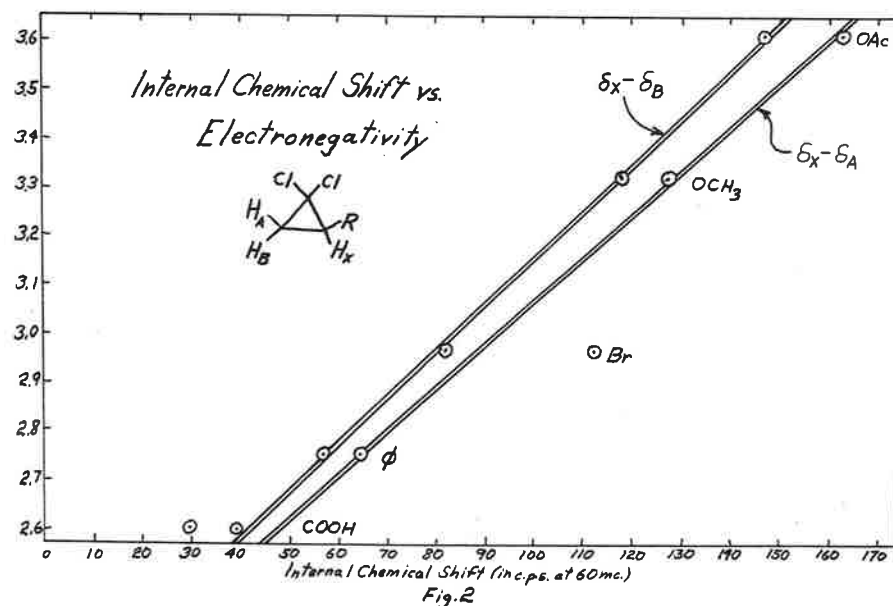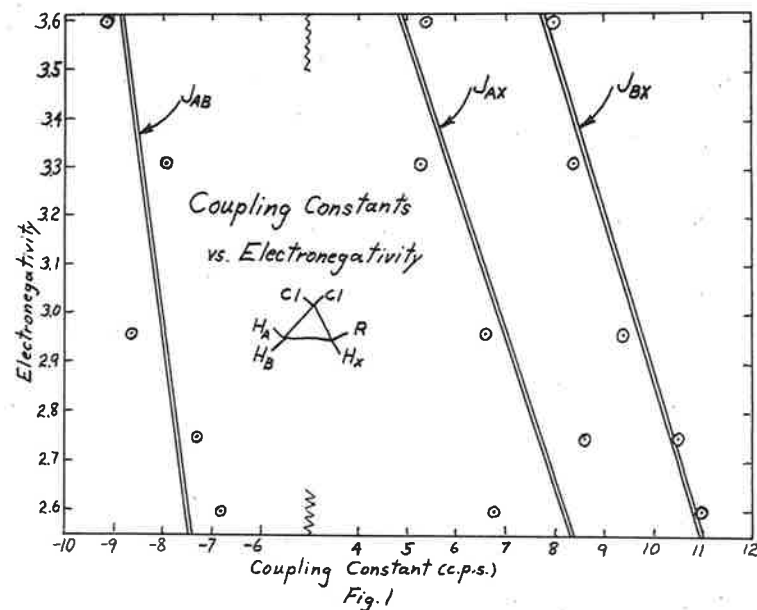
MOUNT HOLYOKE COLLEGE

SOUTH HADLEY, MASSACHUSETTS

DEPARTMENT OF CHEMISTRY
CARR LABORATORY

May 8, 1963

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

Dear Barry,

I feel I must take a stand in a little controversy raised in the last MELLON-M-R, namely the sign of the J_{HF}(gem) coupling constant. McLauchlan and Buckingham in #54 reported this coupling as having a negative sign, however this was questioned by Baldeschwieler and Barfield as well as Elleman, Manatt, and Pearce in #55 who would prefer to see a positive sign.

Elsewhere in this issue we have reported some work on couplings in a cyclopropane system in which it was shown that J_{HH}(gem) decreases algebraically with increasing electronegativity. This has previously been shown by us to be true for a bicycloheptene system (J.Am.Chem.Soc., 85, 516 (1963)) and by Schaefer for some ethylene compounds (Can.J.Chem. 40, 1 (1962)). Recently we have collected some data on mono-substituted epoxides and have shown that J_{HH}(gem) decreases algebraically as electronegativity increases. It has been shown that J_{HH}(gem) is positive in sign in the epoxides while in the systems mentioned above it is negative for the most part. It seems very logical to us that as one increases the electron withdrawing power of a substituent group on an atom, one would decrease the coupling between nuclei also bound to that atom. Therefore if one would assign to J_{HF}(gem) a negative sign (as reported by McLauchlan) then J_{HF}(gem) would decrease algebraically with increasing electronegativity of X in the CHF2X molecules studied by Arison, et al. (J.Chem.Soc., 1962, 3828), a behavior that would parallel the behavior in J_{HH}(gem).

It has been reported that J_{HH}(gem) can have both positive and negative signs. In MELLON-M-R #55 Ray Freeman demonstrated that $J(Cl3_{CH})$ can also have either sign. Undoubtedly the mixup in the J_{HF}(gem) sign has arisen through a comparison of two series of compounds between which a sign inversion has taken place.

Sincerely,

Kenneth L. Williamson
Ass't. Prof. of Chemistry

THE UNIVERSITY OF BIRMINGHAM

TELEPHONE: SELLY OAK 1301.

Department of Chemistry,
EDGBASTON,
BIRMINGHAM, 15.

9th May 1963.

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

Dear Dr. Shapiro,

Following upon Dr. Anet's recent contribution on cyclooctane, MELLONMR readers may be interested in some observations which Mr. Wyer and I have been making on its perfluoro analogue. The sample, provided by Prof. J.C. Tatlow, was examined in solution in CF_3Cl at 30.107 Mc/s. and the room temperature spectrum is a single sharp line ($\sim$ 2 c/s. width at half height) 120 p.p.m. upfield from the solvent signal, which is some 13 p.p.m. lower than the values for cyclic C_5F_{10} and C_6F_{12}. Lowering the temperature produces line broadening and, ultimately, splitting into a doublet with a separation of only 25.5 c/s., the coalescence temperature being $-50°C$. There is no indication of F—F geminal coupling, but if it is as large as in the other cyclic fluorocarbons the outer lines of the resulting AB quadruplet would be difficult to detect under these conditions. We hope to resolve this point by running at higher frequency when the J/d ratio will be more favourable. In the meantime we have treated it as an uncoupled system and, from both line-width and peak separation measurements, estimate the heat of activation for inversion as 6.6 Kcal/mole. and the entropy of activation ΔS^* as about -20 e.u.

We are also investigating the low temperature behaviour of a selection of highly fluorinated cyclohexanes.

Yours sincerely,

L.F. Thomas

Department of Chemistry,
Imperial College,
London, S.W.7.

9th May, 1963.

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

Dear Dr. Shapiro,

I expect this will arrive too late after your reminder to prevent
our missing a Newsletter, but perhaps it can get us back on the list.
I was interested to read Holm, Chakravorty and Dudek's letter in the J.A.C.S.
a few weeks ago, demonstrating the existence of discrete spectra for diastereo-
isomeric complexes, since I had also recently come across something similar
with cobaltous complexes of two amino acids.   The spectrum of [Co(D aspartate)$_2$]$^=$
is the same as that of [Co(L aspartate)$_2$]$^=$;   the extra line from the solution
containing both ligands comes from the complex, [Co(D aspartate. L aspartate)]$^=$;
the relative proportions of the three species in this mixed solution are about
25%, 25% and 50% respectively, assuming all lines areas have the same relation
to proton numbers.   With histidine, the relative proportions in the mixed
solution would seem to be, very roughly, 20% each of [Co(D Hist)$_2$] and
[Co(L Hist)$_2$], and 60% of [Co(D Hist. L Hist)].   The extra stability of the
mixed ligand complex is probably because it can have the most symmetrical
structure, with the 4 N atoms in a plane – the imidazole N's being <u>trans</u> to
each other – and above and below the plane a carboxyl group, which probably are
coordinated to the cobalt, but in any case are well out of each other's way.
To do this with 2D or 2L ligands, the imidazole groups have to be <u>cis</u> and then
they are rather close together;   alternatively the 4 nitrogens need not be in
a plane.   The <u>differences</u> in the line positions may arise partly because of
differences in the total extent of spread of unpaired electrons from the cobalt,
but also, presumably, because the steric interactions make the chelate rings
have different conformations in the two sorts of isomer, since there does seem
to be some relation between conformation and contact shifts in aliphatic ligands.

Yours sincerely,

L. Pratt.

[Co (D Hist L Hist)]^0

Proton resonance spectra of cobaltous complexes
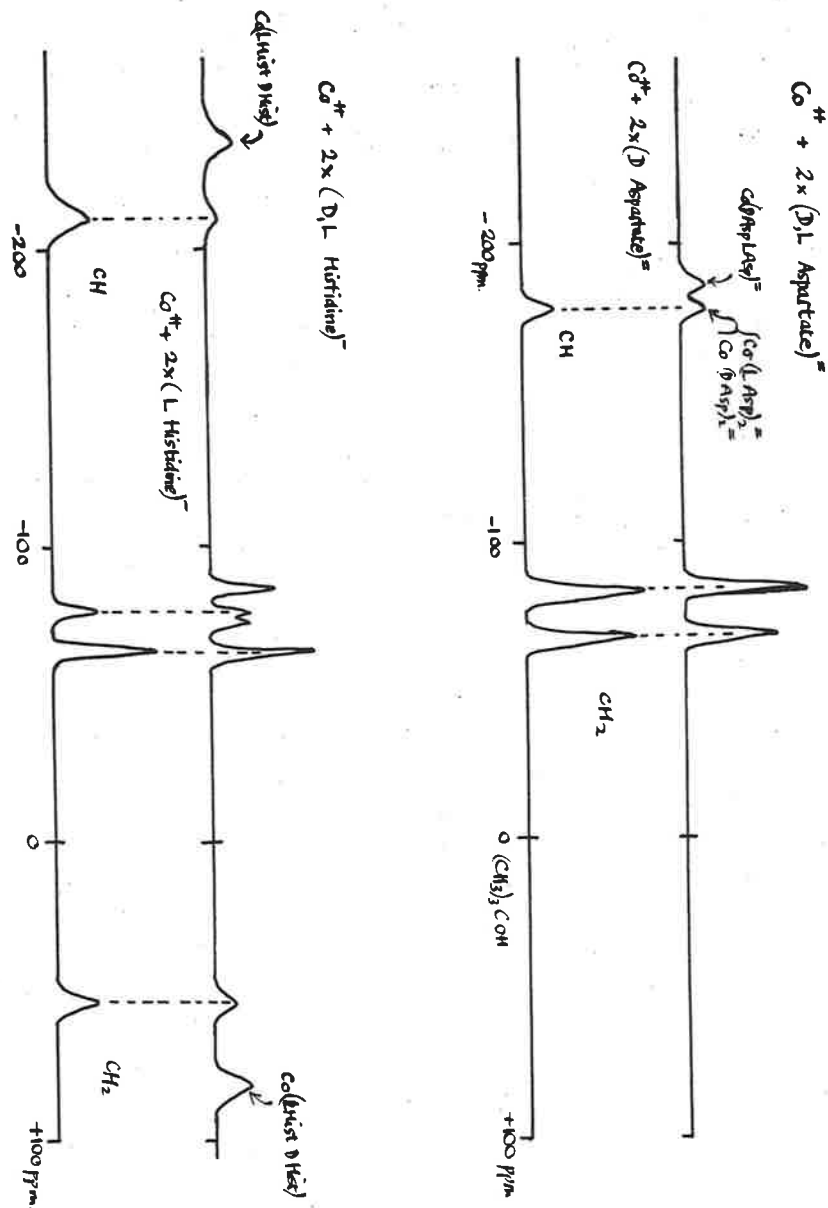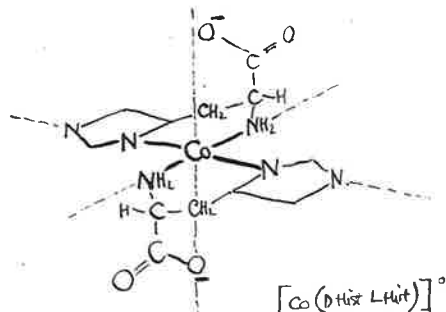
THE BRITISH **B**OAL **C**TILISA**U**TI**O**N **R**ESEAR**A**H ASSOCIATION

REGISTERED OFFICE:

RANDALLS ROAD
LEATHERHEAD, SURREY
TELEPHONE : LEATHERHEAD 4411
GRAMS : CURASSOC, LEATHERHEAD

YOUR REF:

OUR REF

WRL/SA

Dr. B. L. Shapiro,   11th April, 1963.
Mellon Institute,
4400 5th Avenue,
Pittsburgh 13,
Pennsylvania, U.S.A.

Dear Dr. Shapiro,

In connection with a recent NMR study of the hydrogen distribution in coals, we have continued our investigation of the broad-line spectra of organic solids. We wish to report the results of a few measurements on some methyl phenols.

The spectra of these compounds were recorded at liquid air temperature and the line-shape, expressed as the second moment, was calculated from the derivative form of the spectrum. The values found were as follows:

Compound	Second Moment (gauss^2)
o-Cresol	10.2 ± 0.5
2:3 xylenol	11.2 ± 0.3
3:5 xylenol	9.8 ± 0.2
5:6 xylenol	10.1 ± 0.4
Pseudocumenol	11.4 ± 0.6

It is known that the second moment of a large number of systems of aromatic and of (aromatic + phenolic) protons approximates to 10 gauss^2. This same value has also been found for the second moments of methyl-substituted aromatic systems provided that the methyl group is in a position where free rotation is possible, but restriction of rotation leads to an increase in the second moment. For example, the second moment of 1:8 dimethyl naphthalene is 17.5 gauss^2 and that of hexamethyl-benzene is 13.7 gauss^2.

- 2 -

In the case of the methyl phenols the second moment of 2:3 xylenol and pseudocumenol are appreciably higher than are to be expected for an aromatic system containing freely rotating methyl groups. However, when the methyl groups are not on adjacent ring sites only small deviations from a value of 10 gauss^2 are found. It appears that the presence of an OH group in an adjacent position on the ring influences the interaction of the neighbouring methyl group to some extent, since the second moment of 2:3 xylenol is significantly higher than that for o-xylene (9.8 gauss^2).

Since the contributions to the second moment from protons in aromatic groups, freely rotating methyl groups and phenolic groups are approximately 10 gauss^2 and the lone protons on tertiary aliphatic CH groups have a similar contribution, methylene protons (cyclohexane second moment 27.5 gauss^2) are the only protons likely to be present in coals in any significant quantity that possess a second moment appreciably different from 10 gauss^2. This makes it possible to use the second moment coals to estimate the fraction of the hydrogen present in the form of methylene.

If S_2 is the second moment of the coal, then the percentage of the total hydrogen in the form of methylene is given by:

$$\frac{S_2 - 10}{17.5} \times 100\%$$

Coals, which can usefully be characterised by their carbon contents (expressed on a dry mineral matter free basis), have second moments ranging from 18 gauss^2 for a high-volatile coal of 77% carbon to 12 gauss^2 for anthracite of 94% carbon. For this range of coal rank the methylene content changes from 46% for the coal of 77% carbon to 11% for the coal of 94% carbon. This is consistent with the observed decrease in the amount of aliphatic structures with increasing carbon content of the coals as shown by their infra-red spectra.

Yours sincerely,

W. R. Ladner.

W. R. Ladner.

INDIANA UNIVERSITY

BLOOMINGTON, INDIANA

May 30, 1963.

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

Dear Dr. Shapiro:

The proton spectrum of diborane has been recently obtained using a Varian model 4300B spectrometer operating at 60 Mc. High resolution was obtained only by tuning on the internal TMS in the samples. (Spinning the samples did not improve the resolution.)

The attached figure shows the proton n.m.r. spectra of 96% ^{10}B and isotopically normal diborane. Parts A and C show the complete spectrum for normal and ^{10}B diborane respectively. Parts B and D show the bridge proton regions expanded.

The bridge protons in normal diborane are split into a seven-lined multiplet by two ^{11}B's (Intensities should be 1,2,3,4,3,2,1). Each of these lines is further split into a quintet by coupling to the four terminal protons (B). This coupling cannot be seen when one looks at the terminal protons because of the broadness of the peaks.

The bridge proton region in the spectra of ^{10}B diborane (D) is complicated because the spin of ^{10}B is 3, and because the coupling of ^{10}B to protons is only $1/3$ that of ^{11}B. Thus the bridge proton region is overlapped and only the gross features of ^{10}B-H (bridge) and H(bridge)-H(terminal) coupling can be observed, though proton-proton coupling is clearly in evidence. Coupling through boron has been previously observed(1,2), but this is the first example of proton-proton coupling through boron. Other boron hydrides are presently being examined to see if proton-proton coupling can be observed. The values for the spectra are tabulated in the table.

Chemical Shifts and Coupling Constants for Diborane.

	BH$_2$			BHB			H$\cdot\cdot$H	
	δ	J		δ	J		J	
normal	-3.9$_3$[a]	135 c.p.s.		+0.5$_3$[a]	46.1 c.p.s.		7.0 c.p.s.	
96% ^{10}B	-3.9$_3$	44.5		+0.4$_3$	~15		~7	

(a) TMS = 0

Sincerely yours,

Donald F. Gaines,
Riley Schaeffer,
Fred Tebbe.
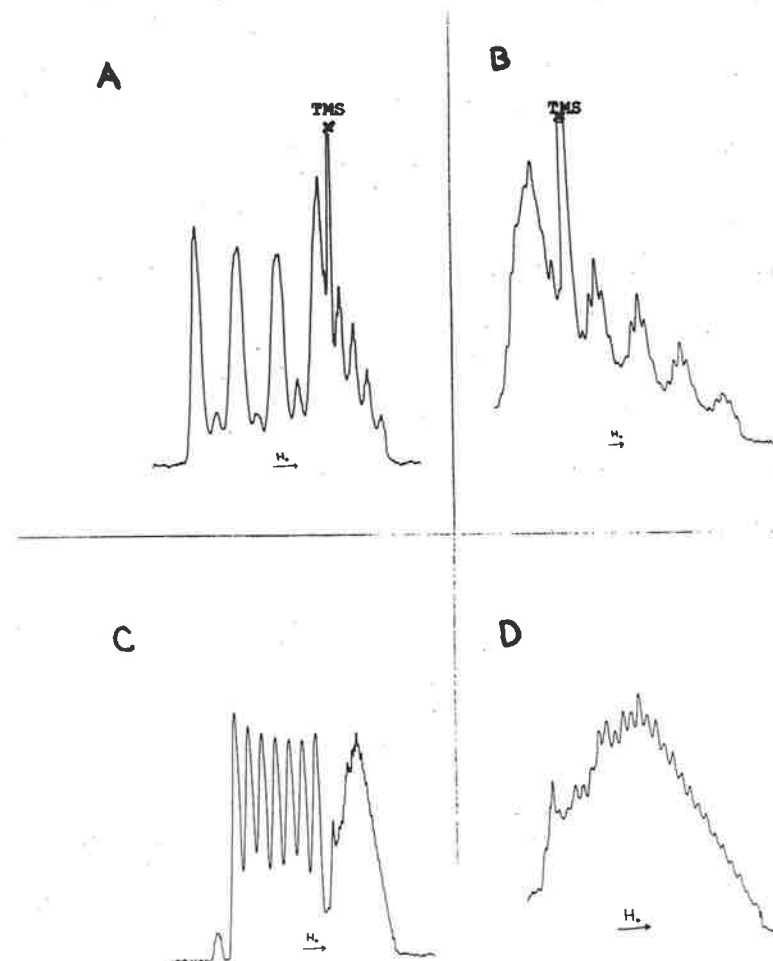
1) J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).
2) R. E. Mesmer and W. L. Jolly, J. Am. Chem. Soc., 84, 2039 (1962).

Nuclear Magnetic Resonance Group
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

Stockholm, May 10, 1963.

Cable address: Technology

SFn/BR

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

U S A

Dear Dr. Shapiro:

During the last few months we have, in collaboration with Bo Gestblom, performed a series of experiments which appear to offer a new possibility for the energy level assignment in nuclear spin systems. The principle of the method is to produce a transitory redistribution of the nuclear spin populations in an energy level system, either through transitory selective saturation or though selective population inversion by means of adiabatic fast passage.

Suppose this has been accomplished through strong irradiation of some chosen line for a time short compared to the relaxation times. Then if some part of the NMR spectrum is investigated within a time short compared to the nuclear relaxation times, lines having an energy level in common with one of the irradiated lines will display intensity changes which depend only on the population changes.
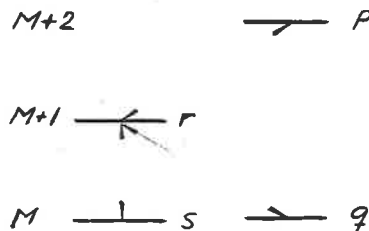
fig.1

For example if a nondegenerate transition $(r \leftrightarrow s)$ is strongly irradiated the population of the upper level (r) will be enhanced and that of the lower level (s) will be reduced in comparison to the undisturbed (Boltzman) distribution. Then the line corresponding to the transition $q \leftrightarrow r$ will be reduced in intensity while the intensity of the line corresponding to the transition $p \leftrightarrow r$ will be enhanced. Using the nomenclature of Freeman and Anderson (J.C.P. 37, 2053 (1962)), we may formulate the general rule that transitions with $\Lambda = 2$ will be enhanced in intensity and transitions with $\Lambda = 0$ will be reduced. With transitory

selective saturation the population of the irradiated levels r and s become equal and the intensity changes will amount to 50 % under optimum conditions. With population inversion through adiabatic fast passage the intensity changes will ideally be 100 %. With degenerate transition frequencies the population changes will be larger; they may however be deduced in the same simple manner.

In order to accomplish a transitory selective saturation the steady magnetic field and thus the energies of the various spin states should remain constant in time; the saturating rf.-field should be rapidly turned on and off immediately before the relevant part of the spectrum is investigated with a weak rf.-field by means of the frequency sweep method. Then, the transitorily saturated levels will all aquire the same averge population.

Population inversion by means of adiabatic fast passage can be carried out with a field sweep method and in this case the strong rf.-field is left on during the time when the magnetic field scans the line(s) to be irradiated (care must however be taken to turn off this strong rf.-field if some lines not to be irradiated, otherwise should be scanned during the time that the relevant part of the spectrum is investigated).

We will illustrate the potentialities of this method with a nice little example. Let us consider the case of a three-spin system (A B C) with one coupling (J_{AC}) experimentally equal to zero (we leave the choice of an upper limit to the reader). The schematic first order spectrum for this case is indicated at the bottom of Fig. 2, and in the upper part of this figure the energy level arrangements corresponding to equal and opposite signs of the two observable coupling constants are indicated. As is evident from these two level arrangements, strong irradiation of the lines A 1 and C 1 will reduce the intensity of the line B 1, the reduction being independent of the relative signs of the two couplings. However, if the line B 4 is also irradiated prior or simultaneously to the lines A 1 and C 1 the reduction of the line B 1 will be more pronounced if the coupling constants carry the same sign but unchanged if the coupling constants are of opposite sign. In this way we have shown that the two vicinal coupling constants in the side chain of cinnamaldehyde carry the same sign.

In conclusion we wish to express our sincere appreciation of your excellent bulletin and of the bibliography. An, perhaps sometimes overlooked, advantage of this bibliography is that it prevents works buried in some obscure European journal to pass completely unnoticed by our honourable American colleges.

Yours sincerely

Ragnar A. Hoffman

Sture Forsén

The University of Sydney

SYDNEY, N.S.W.

TELEPHONE: MW 0522.

IN REPLY PLEASE QUOTE: AVR:ik

Department of Organic Chemistry,
16th May, 1963.

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

Coupling Constants in Cyclobutanes

The discussion below gives coupling constants for two cyclobutane compounds and is relevant to the previous MELLONMR letters by Lustig (45-6) and by Cox and Flanagan (48-8).

1. 3,4-Dichlorocyclobutane-1,2-dicarboxylic Acid.

The isomer studied has the stereochemistry shown. The NMR spectrum was taken in pyridine solution and the ring protons give an A_2X_2 pattern.
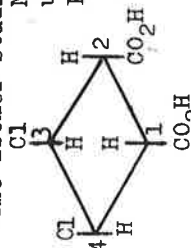
H-1, H-2 at $\delta 4.18$ ppm; H-3, H-4 at $\delta 5.46$ ppm.
$J_{A,A'} = 6.3$ cps: vicinal cis coupling = $J_{1,2}$ or $J_{3,4}$
$J_{X,X'} = 10.6$ cps: vicinal cis coupling = $J_{3,4}$ or $J_{1,2}$
$J_{A,X} = J_{A',X'} = 5.9$ cps: vicinal trans coupling = $J_{1,4} = J_{2,3}$
$J_{A,X'} = J_{A',X} = -1.5$ cps; trans diagonal coupling = $J_{1,3} = J_{2,4}$

2. 3,4-Dibromocyclobutane-1,2-dicarboxylic Acid.

The isomer studied has the stereochemistry shown. The spectrum consists of four separate triplets a, b, c, d

$J_{AB} \cdot J_{BC} > 0$ $J_{AB} \cdot J_{BC} < 0$
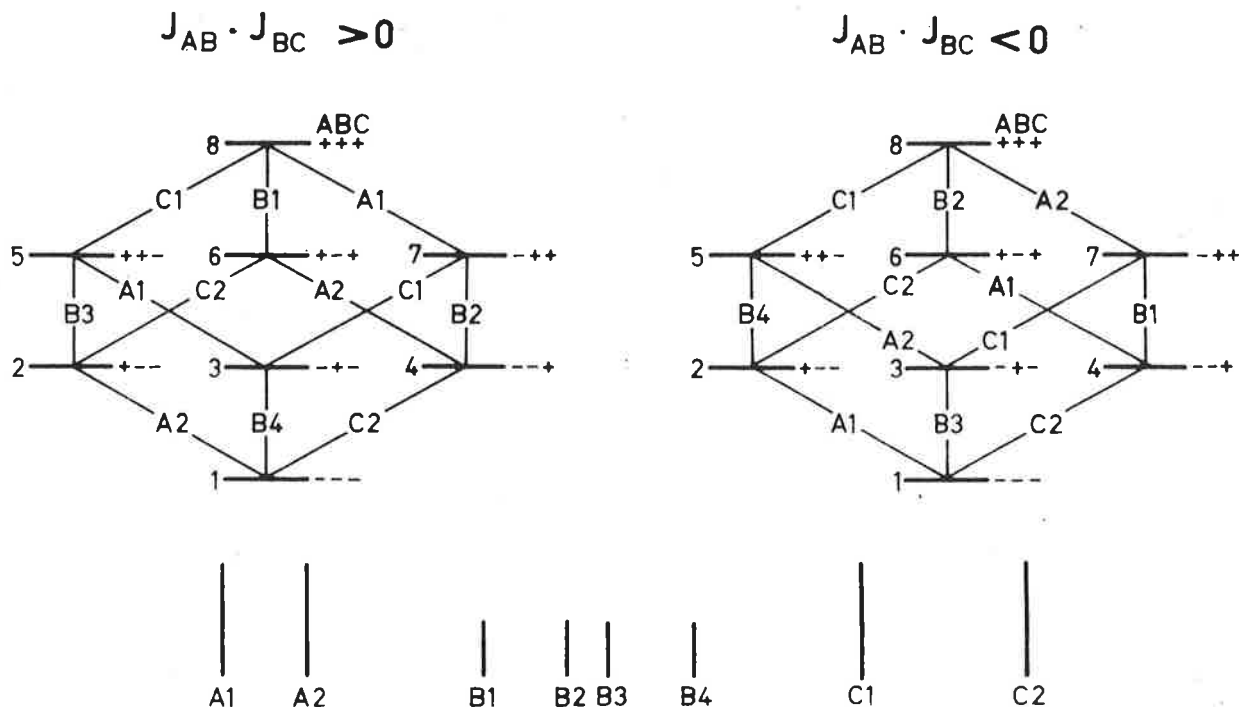
fig.2

at δ 5.79, 5.16, 4.45 and 4.04 ppm respectively. The triplets arise because each proton is strongly coupled to its two neighbours on the adjacent carbons with a constant of the same magnitude. In addition, the branches of triplets <u>b</u> and <u>d</u> are each doubled by splitting of 0.5 cps, so that proton <u>b</u> is diagonally opposite proton <u>d</u>. Therefore the protons corresponding to triplets <u>a</u>, <u>b</u>, <u>c</u>, <u>d</u> are consecutively around the ring in that order. This assignment is confirmed by decoupling experiments, and direct measurement from an expanded trace gives the coupling constants below. However we do not feel the analysis permits a clear distinction between the assignment of signals to protons as in I or II. If anyone reading this is confident that the chemical shifts will distinguish I from II, then I would be glad to hear from them.

I   II
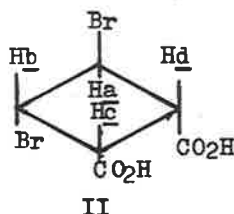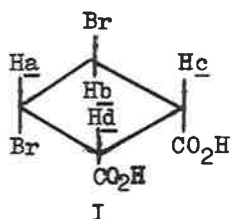
$J_{a,b}$ = 8.7 cps

$J_{a,d}$ = 8.7 cps

$J_{b,c}$ = 8.7 cps

$J_{c,d}$ = 9.2 cps

$J_{b,d}$ = $\pm$0.5 cps

$J_{a,c}$ = 0.0 cps

In either case the four main couplings $J_{a,b}$, $J_{a,d}$, $J_{b,c}$ and $J_{c,d}$ represent two vicinal <u>cis</u> and two vicinal <u>trans</u> couplings yet they all have practically the same magnitude.

The stereochemical configurations of the dichlorodiacid and the dibromodiacid are based on the chemical shifts of the ring protons, and on the dipole moments of the corresponding anhydrides. It is obvious that the Karplus equation could not have been used to deduce the stereo-

chemistry from the coupling constants. How much this is due to puckering of the ring and bond angles by the bulky substituents, to the state of hybridization of the carbon atom, or to a fundamental blind spot in the theory, is beyond the capacity of practising empiricists like myself to determine. I propose instead the first Law of Microsociology: "Whereas people are either squares or delinquents, cyclobutanes are both".

The compounds studied above are degradation products of the dihalides formed by chlorination and by bromination of cyclooctatetraene. The intriguing conclusion is that the chlorination yields a <u>cis</u>-dichloride and the bromination a <u>trans</u>-dibromide. A full paper, including photographs of the spectra and some wild mechanistic speculation is in press with Tetrahedron. My associate perpetrators are Vlasios Georgian (Tufts University) and Roy Johnson (Varian Associates).

Yours sincerely,

Alea. Robertson

A. V. Robertson.

PROFESSOR DR. F. BOHLMANN
ORGANISCH-CHEMISCHES INSTITUT
TECHNISCHE UNIVERSITÄT BERLIN

Berlin-Charlottenburg 2, den   11.5.63
Straße des 17. Juni Nr. 115
Fernruf: 32 51 81/252

Dr. B. L. Shapiro

4400 Fifth Avenue
Pittsburgh 13, Pa.
USA

Dear Dr. Shapiro,

to-day we have two contributions concerning spectra of acetylenic compounds. Although our English is not the best one we prefer using it, since we believe many of the participants will understand our bad English better than our good German.

1) On the linear relation between the screening constants in some acetylenic compounds and their corresponding methyl derivatives.

D r e n t h and L o e w e n s t e i n[1] have plotted the chemical shift of the acetylenic protons of compounds Y-C≡CH against the shielding differences of the methyl and methylene groups of the corresponding ethyl compounds Y-CH$_2$CH$_3$. This shielding difference was correlated by D a i l e y and S h o o l e r y[2] to the elektronegativity of Y, and therefore D r e n t h and L o e w e n s t e i n took it as a measure of the I-Effect of the Y substituent.

As shown in that graph of D r e n t h and L o e w e n s t e i n the linearity between the electronegativity of Y and the screening constant of the acetylenic proton is not quite good because of the different M-effects

of the Y substituents.

We found that there is a very exact linearity if one selects only close related compounds. Plotting, for instance, the τ-values of the acetylenic protons of the carbonyl compounds H-C≡C-COX (X = H, Me, OMe, OEt) against the τ-values of the methyl groups of the corresponding CH$_3$COX compounds - the latters being taken as a measure of the electronegativity of -COX[3] - one finds all points lying exactly on a straight line (see fig. 1) according to the following equatation:

$$\tau_{(\equiv C-H)} = \tau_{(-CH_3)} \cdot 2.901 - 16.134 \text{ ppm}$$
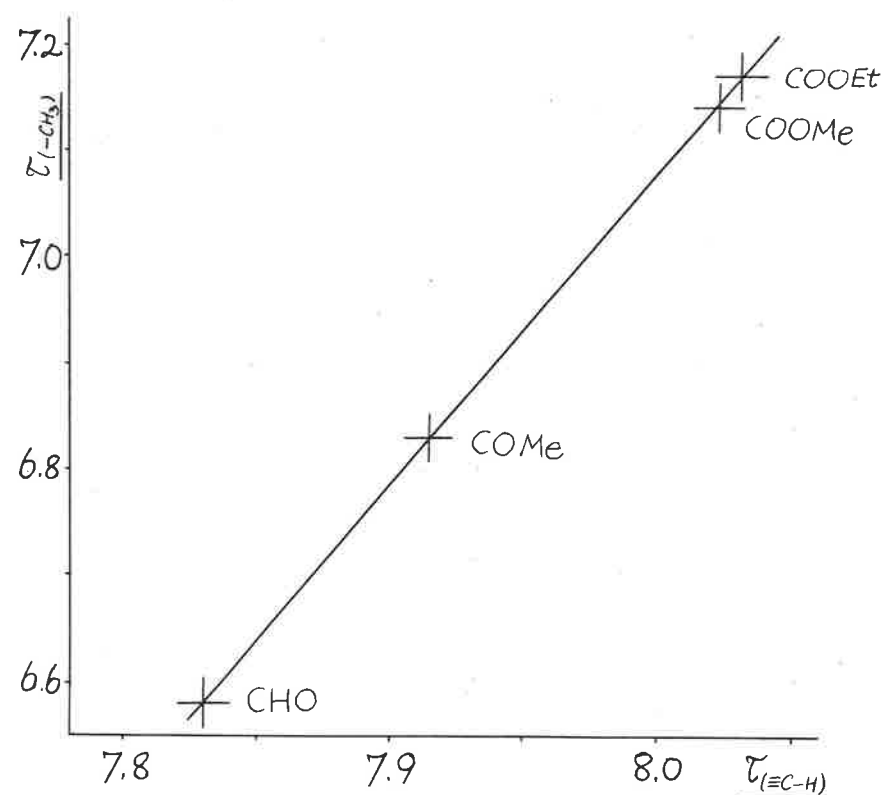
fig. 1   values see next page!

1) Rec. trav. chim. Pays-Bas 81, 635 (1962)
2) J. Am. Chem. Soc. 77, 3977 (1955)
3) Cavanaugh and Dailey, J. Chem. Phys. 34, 1099 (1961)

X =	CH$_3$COX	HC≡C-COX
H	7.83[5]	6.58
Me	7.915[4]	6.83[5]
OMe	8.024	7.14
OEt	8.032	7.17

By the way, we found the τ-value of propiol aldehyde given by K r e e v o y , C h a r m a n and V i n a r d[6] (8.11 ppm) being in disagreement with the fact that acceptor substituents commonly are lowering the frequency of acetylenic protons. Since the deviation from the hour one (6.53 ppm) is nearly 100 Hz we believe that there will be a mis-calculation in the work of those authors.

2) On the dependence of the acetylenic proton's shielding on the number
of conjugated carbon-carbon triple bonds.

As shown in tab. 1 the replacement of one triple bond by two or three ones in aliphatic hydrocarbons with no conjugation with double bonds has no considerable effect on the shielding of the acetylenic proton.

tab. 1 τ-values of acetylenes

CH$_3$-C≡CH	8.20[1]	(CH$_3$)$_3$C-C≡CH	8.125
CH$_3$-(C≡C)$_2$H	8.12	(CH$_3$)$_3$C-(C≡C)$_2$H	8.125
		(CH$_3$)$_3$C-(C≡C)$_3$H	8.07

In contrast, in the phenyl conjugated series (see tab. 2) the shielding of the acetylenic hydrogen increases by an amount of 0.57 ppm if the number of triple bonds increases from one to two. Going from two to three there is a further diamagnetic shift towards higher fields by 0.23 ppm.

4) G.V.D. Tiers, J. Phys. Chem. 62, 1151 (1958)
5) taken from H. Conroy in Advances in Organic Chemistry, Vol. II, 265(1960)
6) J. Am. Chem. Soc. 83, 1978 (1961)

tab. 2 τ-values of phenylconjugated acetylenes

Ph-C≡CH	7.125[2]
Ph-(C≡C)$_2$H	7.70
Ph-(C≡C)$_3$H	7.93

Increasing the number of triple bonds in the phenyl conjugated series, one can expect a diamagnetic shift caused by the decreasing of the deshielding effect of the aromatic ring arising from the increasing distance of the acetylenic hydrogen.

Calculation after J o h n s o n and B o v e y[3] yields values for the deshielding effect of the benzene ring anisotropy (-0.226; -0.063; -0.026 ppm) the differences of which (0.16 and 0.04 ppm, resp.) are considerably lower than the observed ones (0.57 and 0.23 ppm, resp.), thus indicating that the increasing of the hydrogen's distance cannot be the essential origin of these large diamagnetic shifts we have observed.

This is confirmed further by the fact that there is a similar effect in the series of compounds in which the triple bond system is conjugated with one double bond, e. g., butenyne (τ = 7.08 ppm)[4] and cyclohexen(1)-yl(1)-butadiyne (τ = 7.70 ppm).

In contrast to D r e n t h and L o e w e n s t e i n[5] and to Cook and D a n y l u k[2], we believe there must be assumed some not negligible interaction between the aromatic ring and the conjugated acetylenic bonds. Doing this one might expect any parallelism of the screening constant and the reactivity of the compound in question. For this reason we have plotted the "first" half-value period of the oxydative coupling reaction of some phenyl conjugated acetylenic compounds against their τ-values (see the graph on the next page).

1) J. Mol. Spectr. 5, 110 (1960)
2) Tetrahedron 19, 177 (1963)
3) J. Chem. Phys. 29, 1012 (1958)
4) J. Am. Chem. Soc. 83, 1979 (1961); ibid., 84, 2009 (1962)
5) Rec. trav. chim. Pays-Bas 81, 635 (1962)

This reaction which yields $(R-C{\equiv}C-)_2$ from $R-C{\equiv}C-H$ is carried out in presence of a large excess of couprous and cupric chloride in acid solution (ethanolamine hydrochloride in methanol) and is found to be a second order one.

"First" half value period means that time in which the concentration of $R-C{\equiv}CH$ has reached just one half of the value of the standard beginning concentration.

Although the linearity cuould be a better one it is shown that there is any dependence of magnetic screening and reactivity of acetylenic bonds. This could be interpreted easily in terms of the charge density at the most external triple bond.

All the spectra were scanned using a Varaian A 60 spectrometer in 1-molar solution in CCl_4. Tetramethylsilane was taken as internal reference. The scanning rate was 0.1 Hz/Sec.

<div style="text-align:center">

Sincerely yours

F. Dolle

</div>

P.S. We would enjoy obtaining the former issues as complete as possible.

Graph axes: horizontal axis $\log t_{\frac{1}{2}}$ [t in min] (values 2.0, 2.5, 3.0, 3.5, 4.0, 4.5); vertical axis $\tau_{(R-C{\equiv}CH)}$ (values 6.8, 7.0, 7.2, 7.4, 7.6, 7.8).

Data points: $p-NO_2-Ph-$, $Ph-$, $p-CH_3O-Ph-$, $Ph-C{\equiv}C-$, $Ph(C{\equiv}C)_2-$

τ - values of phenyl substituted monoäcetylenes are taken from ref. 2)
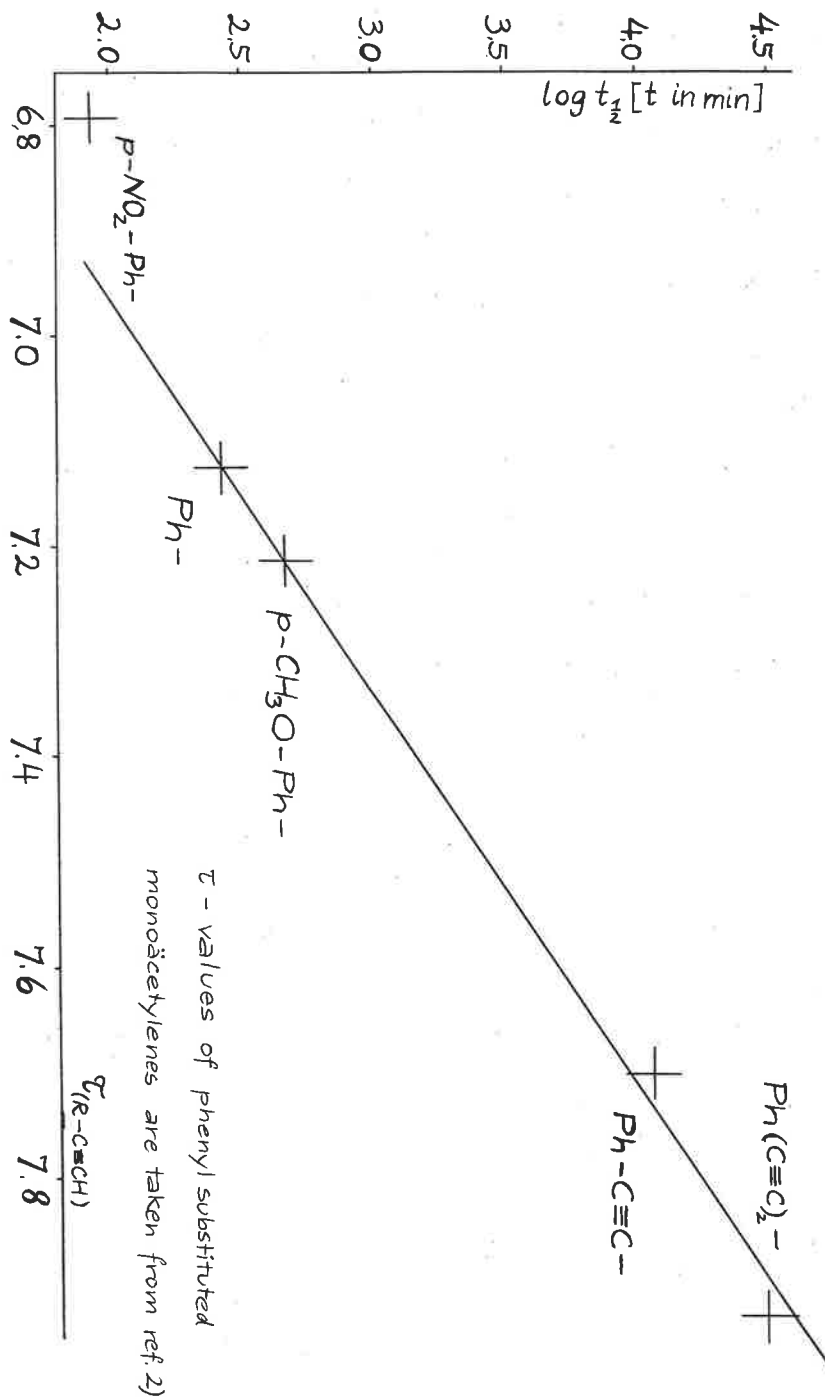
QUEEN MARY COLLEGE
(UNIVERSITY OF LONDON)
MILE END ROAD · E·1
TELEPHONE · ADVANCE 4811
Department of Chemistry

14th May, 1963

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

Dear Barry,

The research of the N.M.R. group here has blossomed considerably in several widely different area. I shall try to summarise the results briefly.

1. ^{19}F spectra of pentafluorophenyl* derivatives, C_6F_5X (Tony Bourn and Duncan Gillies)

As a result of the synthesis of a number of pentafluorophenylmetal compounds by Drs. A.G. Massey and F.G.A. Stone and their coworkers and the availability of several fluoroaromatic compounds, we have been able to make fairly comprehensive ^{19}F n.m.r. studies.

The chemical shifts of the ortho-fluorine atoms appear to be influenced by the presence of unoccupied lowlying orbitals in the group X. The work is an exact parallel of the perfluoroalkyl study of Pitcher, Buckingham and Stone (J. Chem. Phys., 1962, 36, 124). When X is a heavy atom, e.g. in C_6F_5I as opposed to C_6F_5Cl, or contains a metal with lowlying d orbitals, e.g. in $C_6F_5Mn(CO)_5$ versus $(C_6F_5)_2SnMe_2$, the ortho-fluorine resonance is moved to low field. The effect should also be present, of course, in ortho-substituted monofluorobenzenes, and indeed the presence of an unexplained shift to low field has been recognised (see Pople, Schneider, Bernstein, p.325) although so far not adequately explained. We are considering the meta and para-shifts in the light of recent theories of electron densities (J. Chem. Phys., 1963, 38, 374 and 381).

The J_{FF}'s show interesting variations with substituent X, and we are investigating the J_{HF}'s in such molecules as for similar variations.
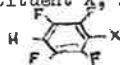
There are some intriguing long-range couplings: e.g., between CH_3 and ortho F's in $(C_6F_5)_2SnMe_2(0.35$ c/s.) and C_6F_5OMe (1.05 c/s.), and between the CF_3 and the para-fluorine in $C_6F_5CF_3$ (1.4 c/s.).

* Known to be initiated as 'phufyl', since the CF_3 group has been termed the 'mufyl' group.

over/

Dr. B.L. Shapiro   -2-   14th May, 1963

2. Tetraethyl derivatives of Group III and IV Elements (Dr. Massey and Derek Shaw)

There are spin-spin effects between protons and the central atoms evident in the proton spectra of Et_4B^-, Et_4N^+ and Et_4As^+ (c.f. Lancaster and Neglia, Mellonmr, No. 43, 19) and in Me_4B^- and Me_4As^+. The results are $J(B^{11}CH_2) = 4.0$ c/s.; $B^{11}CH_3 = 3.0$; $N^{14}CH_2 \sim 0$; $N^{14}CH_3 = 1.7$ (negotiated with Lancaster and Neglia); $As^{75}CH_2 < As^{75}CH_3$. Boron thus resembles fluorine with respect to the relative size of the short- and long-range couplings.

The appearance of the proton spectrum for Et_4As^+ depends upon the solvent. Only in solvents of high polarity are spin-spin effects (other than J_{HH}) evident. In other solvents we conclude that ion-pair formation allows rapid relaxation of the quadrupolar nucleus. Mr. Chuck has noticed similar effects on spin multiplets in the ethyl-pyridinium salts, as well as ion-pair influences on the chemical shifts (c.f. Gideon Fraenkel's work on anilinium salts).

3. $H\{H\}$ and relative signs of J's in N^{15}-amides (Tony Bourn)

We have looked at the cases:
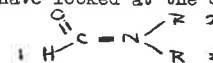
R 2 = R 3 = H;   I
R 2 = R 3 = Me;   III
R 2 = Me, R 3 = H;   II

The relative signs and magnitudes of the couplings are

	In I	II	III	
J (N1)	∓ 16.3	∓ 15.5	∓ 15.6	Set 1
J (N2)	∓ 86.5	± 1.2	± 1.2	
J (N3)	∓ 90.0	∓ 92.6	± 1.1	
J (12)	± 13.4	∓ 0.8	0.9†	
J (23)	A ± 2.8	± 4.8 B	0	Set 2
J (13)	± 1.7*	± 1.9	0.4†	

We hope to do $H\{N^{15}\}$ or $N^{15}\{H\}$ to link these two sets

* Tentative relative sign compared with J_{12} and J_{13} in block A.
† Signs unknown

Signs in block B relative to block A have been deduced assuming sign of J_{13} is the same in both A and B

Yours sincerely,

Ed Randall

Ed Randall

EWR/JLC

56-14

15th May, 1963

Dear Barry,

The case against wiggles

It occasionally happens that the feasibility of an experiment hinges almost entirely on the resolving power of the NMR spectrometer. Such was the case in a recent experiment of ours (described in the note that follows this) and it led us to re-examine the factors that determine the observed line-width. Throughout the $3\frac{1}{2}$ year history of our own DP60 we have usually been able to whittle the lines down to a width of about 0.4 cps (full width at half height) but not much better, and one gets the impression that other spectrometers tend to exhibit a similar "hard core" of line width that is proof against any amount of fiddling with shim coil controls. It does seem a little bit surprising that this should be simply a field inhomogeneity effect.

Let us assume that power broadening by saturation has been avoided, and that properly degassed solutions of low viscosity have been employed so that the true natural line-width $(\pi T_2)^{-1}$ is less than the instrumental width.

Radiation damping may rear its ugly head (see Mellon 55, 31) but requires that the particular line in question be so strong that its absorption is no longer a negligible fraction of the driving radiofrequency level. When there are many lines in the spectrum, or when dilute solutions are used, broadening by this mechanism should be negligible.

Field or frequency instability could conceivably give rise to broadened lines, but a fast acting field-frequency controller should cure this difficulty. Our own set-up feeds an error signal from a strong line in the spectrum to the flux stabilizer and at the same time pulls the rf crystal frequency to counteract rapid fluctuations.

One possible explanation of this line width 'barrier' is that the slow passage requirement becomes very difficult to fulfill for very sharp lines. The required condition is that the time taken to sweep through the line should be long compared

/with

Dr. B. L. Shapiro,
Mellon Institute,
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with the inverse line width (i.e. halving the line width would require a fourfold decrease in sweep rate). If this rather stringent condition is not met, then the broadening of the natural line may exceed the field inhomogeneity broadening. Jacobsohn and Wangsness (Phys. Rev. 73, 942, 1948) have calculated the line shapes to be expected for sweep rates comparable with the inverse line width. One may deduce that a line 0.2 cps wide would require a sweep rate of the order of 4 cps/minute to avoid appreciable broadening (and incidentally there is then very little ringing after the line). This is so slow as to necessitate some kind of field-frequency controller.

Some evidence for this view-point is provided by recording part of the spectrum of 3-bromothiophene-2-aldehyde at two different sweep rates. The upper trace recorded by sweeping the radiofrequency at 12 cps/minute, the lower trace at 3 cps/minute with a compensating fourfold reduction in chart speed. Resolution was improved by almost a factor 2, giving a line-width of <0.2 cps. Even sharper lines were obtained at lower sweep rates but then changes in field homogeneity with time become appreciable. Fortunately the continuous oscilloscope display of the error signal used in the control loop allows adjustments to be made to the Y gradient control while the spectrum is actually being recorded.

Yours sincerely,

Ray Freeman

Ray Freeman.

(The case against wiggles)

a

b

c ps

Dear Barry,

The case for tickling twice

It would be interesting from the theoretical point of view to be able to relate the signs of long-range proton spin coupling constants to couplings of known sign. To do this by the spin-decoupling method requires the two protons to be part of a triangle of nuclei (AMX) where all three couplings produce observable splittings in the spectrum (e.g. J_{AM} may be related to J_{AX} by washing out J_{AX}). Unfortunately it often happens that one of the couplings is so small that it produces no detectable splitting at all; this is somewhat to be expected if one is trying to relate a five-bond coupling to a vicinal coupling because the third coupling is necessarily long-range itself. A typical example is 3-bromothiophene-2-aldehyde ($|J_{AX}| < 0.2$ cps, $|J_{MX}| = 1.1$ cps, $|J_{AM}| = 5.2$ cps) of which the 60 Mc/s spectrum is shown below.
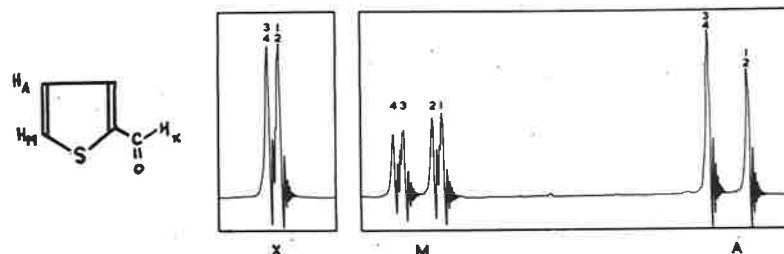
This problem can not be circumvented by a simple tickling experiment because if J_{AX} is less than the line width, irradiation of an X line does not split an A line. The general rule in a tickling experiment is that transitions are split if they share an energy level with the irradiated line; we must therefore refer to the energy level diagram (shown here for all coupling constants positive).
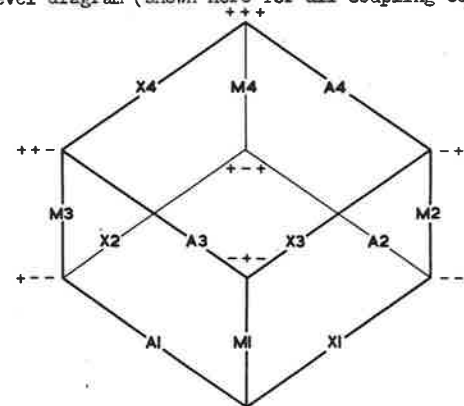
NATIONAL PHYSICAL LABORATORY

For $J_{AX} = 0$ each X line and each A line is in fact composed of two degenerate transitions. Irradiation of an X line (e.g. transitions X1 and X2) necessarily perturbs both upper and lower levels of A1 and A2 equally and in a coherent fashion with the result that no net effect is observed.

One way of lifting this troublesome degeneracy is by the tickling experiment itself. Irradiation of any one M transition would split just one transition of each degenerate pair, making each A and X line a 1:2:1 triplet. For example, consideration of the energy level diagram shows that irradiation of M1 would split A1, A3, X1 and X3, but would leave A2, A4, X2 and X4 only very slightly affected. In practice $|J_{LX}|$ is so small that even a weak H_2 perturbs line M2 to some extent, and this generates a weak satellite line on one side of A2 and A4 (see Fig. 2b).

If a third radiofrequency field H_3 is now set on the central line of one of the X triplets (say X2 in the high-field triplet) and if the perturbation of the other components of this triplet (X1) is kept very small by making $H_2 > H_3$, then a very small splitting of all the components of one of the A triplets should be observed. For like signs of J_{AM} and J_{MX} this will be the high-field triplet (A1 and A2), for opposite signs, the low-field triplet. In practice magnet field inhomogeneity affects proton-proton tickling experiments, causing some doublets to be abnormally sharp and others abnormally broad, so the small splitting is only resolved for the central line A2 but not for the outer lines A1 as seen in Fig. 2c, but it is clear that the low-field A triplet is unaffected.

J_{AM} would be expected to have the same sign as ortho benzene couplings which have been shown to be positive (McLauchlan, Mellon 54), indicating that the five-bond coupling to the aldehydic proton is also positive.

One of the headaches of such an experiment is to know how to propitiate those deities that control magnet performance and resolution (see preceding note), because interpretation of the tiple resonance spectrum is only straightforward if the splitting $\gamma H_3/2\pi$ is a small perturbation compared with $\gamma H_2/2\pi$, which in turn must be small compared with $J_{MX} = 1.1$ cps. The experiment has nevertheless proved quite feasible, and we feel it may one day emerge as a general method of finding the signs of long-range coupling constants.

We acknowledge the generosity of Drs. Hoffman and Gestblom in providing the sample of bromothiophene aldehyde, even while they were attacking the problem of the sign of the long-range coupling by another technique.

Yours sincerely,

A.D. Cohen   Ray Freeman   Keith McLauchlan   D.H. Whiffen

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

*?

Figure 2
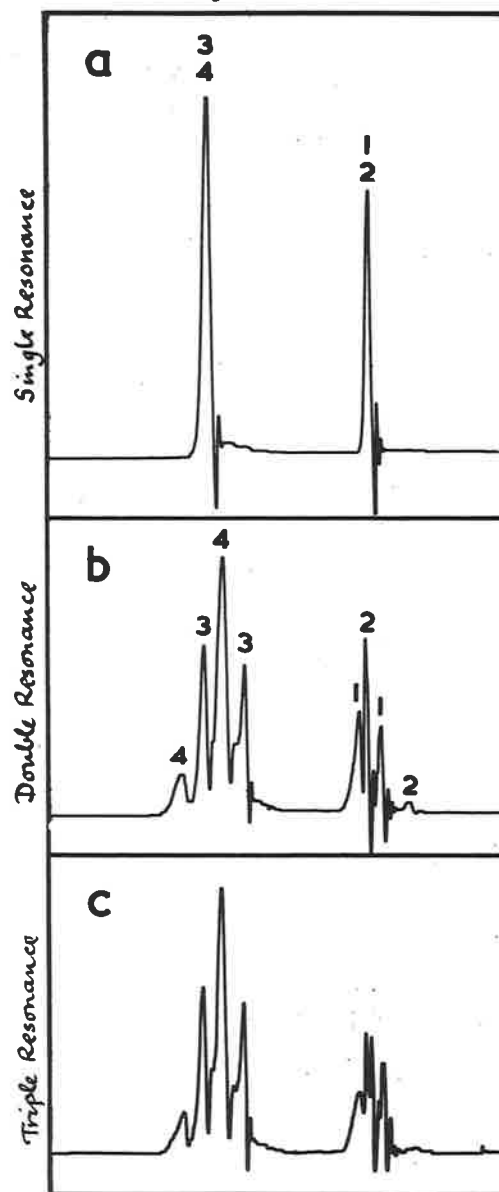
15th May 1963

Dear Dr. Shapiro,

With the increasing use of N.M.R. in organic structure deter-
mination it is important that the dangers inherent in its use be
realised. One case has been pointed out[1]. A blatant case of
building on unsound conclusions is the paper by Gatlin and Davis[2];
these authors "prove" that deoxycytosine exists in the hydroxy-
form and discuss at length the biological implications. Their
data are seriously in error[3].

Accidental coincidence of chemical shifts provides another
pitfall. We recently considered the nitration of quinoxaline I –
reported to yield the 5,6-dinitrocompound II.[4] This appeared an
unusual orientation for the product. The evidence for it was the

I   II   III   IV   V
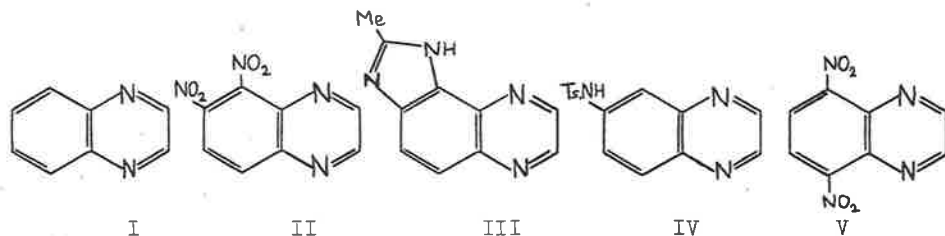
reductive ring closure to III[4] and also the independent formation[5]
of III starting from the nitration of 6-tosylaminoquinoxaline IV.

However, it seemed to us possible that the dinitro compound
could be the 5,8-isomer V, and that the reduction ring closure
could be explained by a quinoxaline ring opening and reclosure
mechanism. Two sharp peaks at τ 0.63 and 1.30 in the dinitro
compound appeared to confirm this view. Luckily, we obtained a
dipole moment which proved II to be correct. The chemical shifts
of the protons in the 7- and 8-positions of this compound are
evidently sensibly identical.

Until the use of the tetramethyl ammonium ion[6,7] and methane-
sulphonic acid[8] as internal reference standards for work in
concentrated sulphuric acid had been generally accepted, we had
been using tetramethylsilane which appeared to be slightly soluble
in sulphuric acid.[9] We have now shown that tetramethylsilane is

-2-

immiscible with sulphuric acid, but on shaking reacts to give
methane and trimethylsilyl sulphate. In chloroform solution
the τ value of trimethylsilyl sulphate is 9.59 p.p.m. and in
sulphuric acid 9.44 p.p.m., using 6.80 p.p.m. as the τ value
for tetramethyl ammonium ion in sulphuric acid as suggested
by Tiers[7]. This means that previous measurements[8] of chemical
shifts in sulphuric acid solution using what was thought to have
been tetramethylsilane as an internal standard should be reduced
by 0:56 p.p.m.

We thank Professor Harold Hart for discussion.

Yours sincerely,

A. R. Katritzky, R. E. Reavill

1. A. R. Katritzky and A. J. Waring, Chem. and Ind., 695 (1962).
2. L. Gatlin and J. C. Davis, J. Amer. Chem. Soc., 84, 4464 (1962).
3. H. T. Miles, J. Amer. Chem. Soc., 85, 1007 (1963).
4. M. J. S. Dewar and P. M. Maitland, J. Chem. Soc., 1957, 2521.
5. F. H. Case and J. A. Brennan, J. Amer. Chem. Soc., 1959, 81,
    6297.
6. A. J. Kresge and Y. Chiang, M.E.L.L.O.N.M.R., 50, (1962), 3.
7. G. van D. Tiers, Personal Communication to Professor
    Harold Hart.
8. H. Hart and P. A. Law, J. Amer. Chem. Soc., 1962, 84, 2462.
9. A. R. Katritzky and R. E. Reavill, J. Chem. Soc., 1963, 753.

May 16, 1963

Dr. Bernard L. Shapiro
Mellon Institute
Pittsburgh 13, Pa.

On the NMR Spectra of Ethyl Glycinate and
Methyl Hydroxyprolinate

Dear Barry:

At the recent 4th OCEANS Conference, we presented a paper on the use of metal ions in NMR spectral interpretation of amino acid esters. In the Abstract of the 4th OCEANS, the spectra of ethyl glycylglycinate and ethyl cysteinate are given. We would like to submit the results on ethyl glycinate and methyl hydroxyprolinate as our contribution to MelloNMR.

Fig. 1 shows the spectra of ethyl glycinate, EG, in the absence and presence of 10^{-4} M cupric chloride and 0.5 M cadmium chloride. Solutions were prepared in 99.8 % heavy water and contained 0.5 M ester and 0.25 M NaOD. Benzene was used as the external reference. EG gives a relatively simple spectrum and therefore serves to illustrate the effects of paramagnetic and diamagnetic metal ions. The CH_2 group of the glycyl residue lies between the coordination sites (the amino and carbonyl oxygen groups) while protons from the ethyl group are situated away from the coordination sites. Therefore one would expect the former proton signal at 2.76 p.p.m. to experience a greater effect of the metal ions. This is shown to be true. In the presence of Cu(II) only the signal at 2.76 is broadened to the extent that it becomes unobservable. Furthermore, the effect of cadmium chloride on the downfield chemical shift of the 2.76 p.p.m. signal is seen to be greater than that of the 5.22 or 2.70 p.p.m. signal. The effects of the paramagnetic cupric and diamagnetic cadmium ions can be used as aid in interpretation of more complex spectra.

As an example, Fig. 2 gives the spectra of methyl hydroxyprolinate, MHP, in the absence and presence of cadmium chloride and cupric chloride. In the absence of metal ions, the following signals are observed: a low field multiplet at 2.08 p.p.m., a singlet at 2.67, and multiplets at 3.23 and 4.25 p.p.m.

The effect of cadmium chloride on the downfield chemical shift of the 2.08 p.p.m. multiplet (from 2.08 to 1.75) is seen to be greater than on other signals. Since the coordination sites are the NH and carbonyl oxygen groups, one would expect the effect to be greater on the CH which is situated in between these two groups. The multiplet at 2.08 p.p.m. therefore is ascribed to the CH proton. This assignment is confirmed by adding cupric chloride. Here the signal at 2.08 is broadened to a greater extent than other signals. The multiplet at 3.23 p.p.m. in the absence of metal ion is seen to yield a singlet at 3.15 and a broadened multiplet in the presence of 10^{-3} M cupric chloride. The latter is ascribed to the CH_2 adjacent to the –NH group which is a coordination site. The singlet at 3.15 p.p.m. is methyl alcohol, an impurity.

The above study has therefore indicated the usefulness of metal ions as aid in spectral interpretation. Diamagnetic metal ions, such as Cd(II), cause downfield shifts of the NMR frequencies of the ligands, the extent of the shift depending upon the proximity of the protons to the binding sites. Paramagnetic ions cause a selective broadening of the lines of protons sufficiently near the binding sites.

The spectra of Fig. 1 and 2 were obtained at Dr. Edwin D. Becker's laboratory at the National Institutes of Health. The A-60 at Duquesne University has been in operation for two months and we expect that our next contribution to MelloNMR will come from results using our own spectrometer.

Sincerely yours

Norman C. Li

Norman C. Li

Raj Mathur

Raj Mathur

Fig. 2
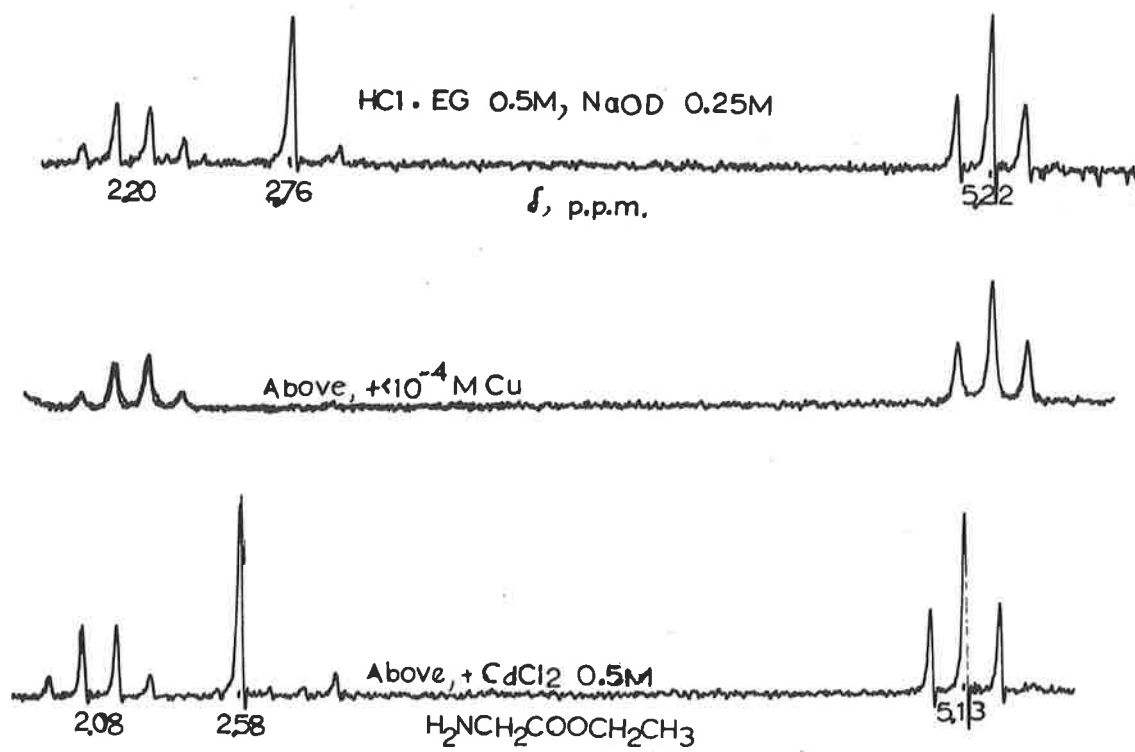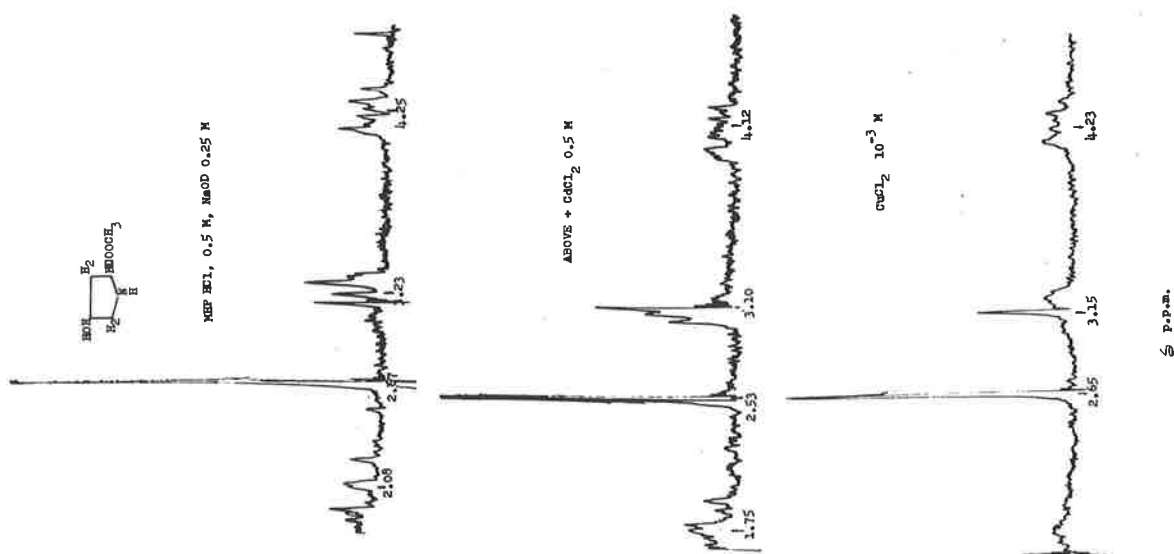
Fig. 1

P.D. Dr. P. Diehl

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 – TEL. 430422
VORSTEHER: PROF. DR. P. HUBER

Basle, May 7, 1963

Dear Barry,

Here is a short MELLONMR contribution on a subject which,
I suppose, should be made generally known:

These are the "facts": I have, some time ago, observed
that a wrong value for the constant $\partial H/\partial D$ has found
its way into literature. The " correct" value is
$6,51440074 \pm 0,00000112$[1] and not 6,55. The wrong value
can be traced back to about 1959 and has since been
used several times e.g. in order to calculate J_{HH} from J_{HD}.
In this case, the mistake is well within the experimental
errors, although it causes a systematic increase of J_{HH} by
about 0,1 cps. If on the other hand J_{HF} is compared with
J_{DF}, the mistake may be of the order of 1 cps.

Yours sincerely,

Peter

P.D. Dr. P. Diehl

[1] B. Smaller, E.L. Yasaitis and H.L. Anderson,
Phys. Review 80,137,1950.

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

24 May 1963

Concerning Indexes for MELLONMR

Both Subject and Author indexes for MELLONMR are being prepared
for distribution in the near future. The purpose of this notice is to
solicit help from any MELLONMR participant who may in fact already have
prepared any such complete or partial indexes. If so, we would appreciate
very much receiving a copy of such an index for incorporation in the version
which is being prepared. Any index, however incomplete or whatever its
format, would be of considerable assistance. We can, of course, return
an original if necessary.

B. L. Shapiro

Monthly

Ecumenical

Letters from

Laboratories

Of

N - M - R

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

A Home-made Pen Holder and Ink Reservoir for the A-60

For reasons of esthetics, permanency and ease of reproduction (photographic or other), we have been using black ink (K & E 3015E) in our A-60 pens. Despite careful house-keeping procedures, we have been unable to keep the pens supplied by Varian in working condition for long enough periods; clogging was frequent and cleaning either failed or caused cracking of the plastic. We have therefore designed and built a home-made pen holder which we have been using with complete satisfaction for several months.

A view of this holder is seen in Figure 1, and details of both the holder and ink reservoir are shown in Figures 2 and 3. The pen holder was machined from Hysol 6000 C-8 cast epoxy resin (from Hysol Corporation, Inc., Olean, N. Y.). It takes about a morning's work to make one of these pen holders, the final fitting being done conveniently using a small triangular file. We have subsequently made a duplicate as a spare, but have had no occasion to use it.

The ink reservoir is made of Teflon. We have also used such a reservoir and pen in the Varian G-10 recorder associated with our HR-60, with excellent results over a long period.

The pens are standard, inexpensive Leroy lettering pens (K & E 61-0070); we normally use the -00 size with the cleaning pin in. Clogging very seldom occurs and is almost always curable with a wet finger tip. Ultimately, the pen-point wears away, but replacement is fast, easy - and cheap. We have also used the -0 and the -000 pen sizes with equal success. All three sizes give spectra which reproduce well by either the Oxalid or Xerox process. The pens track well on Varian chart paper; not perfectly, but easily as well as the Varian pens.

J. J. Burke
J. A. Lorenc
B. L. Shapiro
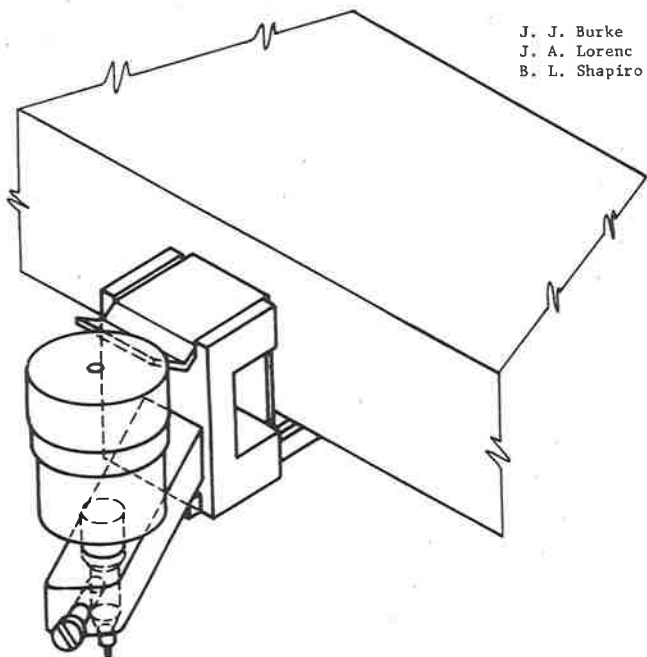
Fig. 1
Recording Pen Assembly

Fig. 2
Pen Holder Details
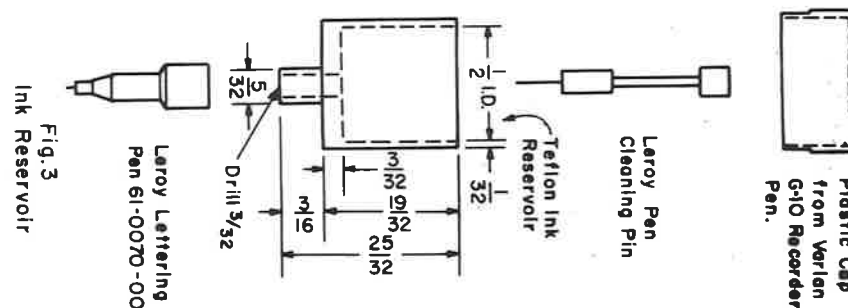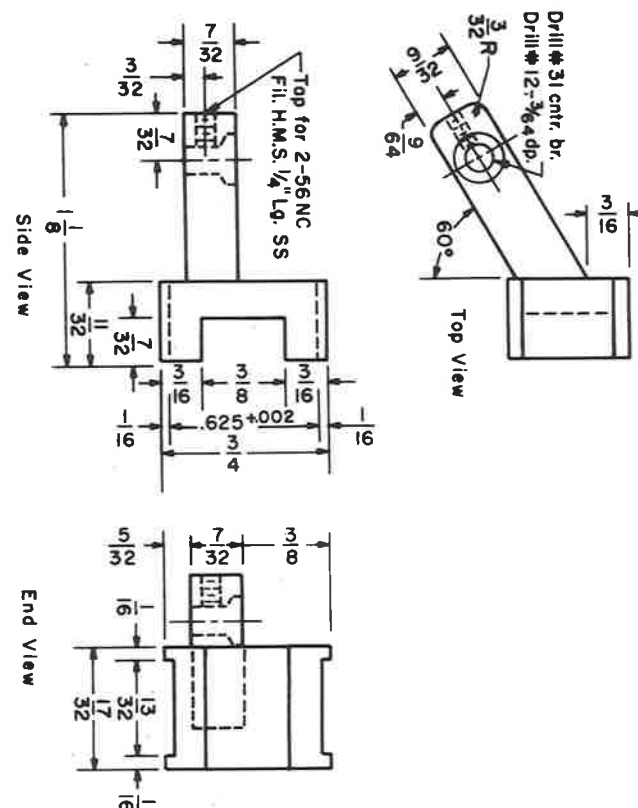
Fig. 3
Ink Reservoir

22nd May, 1963.

Dr. B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13, Pa.,
U.S.A.

Dear Barry,

We are very keen to renew our subscription to the exceedingly valuable M.E.L.L.O.N.M.R. and apologise for the delay. We hope that our present 'double-barrelled' contribution will give some compensation for this.

Calculations on Dipolar Coupling (R.M. L-B)

In calculations of coupling constants it is usually assumed that only the contact term is important. Although this is probably true for interproton coupling there is no reason why it should be so for couplings involving C^{13}. We think that the most probable explanation for the anomalous long range C^{13}-H coupling in acetylenes and for the bromine effect observed by Dr. Lauterbur on the C^{13}-C-H coupling in substituted ethylenes is either the dipolar J(2) or the orbital J(1) contribution.

We made an unsuccessful attempt to calculate the magnitude of J(2) for acetylene. We used a molecular orbital wave function (McClean, J.C.P., 32, 1595) and instead of using the ground state wave function and an average energy approximation, we calculated the second order perturbation correction due to each of the excited states in which one electron is promoted to an antibonding orbital made of 2s and 2p carbon and 1s hydrogen orbitals. The energy of this triplet state was taken to be the sum of the orbital energies.

Assuming the orbitals can be expressed as linear combinations of atomic orbitals all the integrals of the

Dr. B.L. Shapiro   2.   22nd May, 1963

dipolar interaction can be performed analytically (except for one which is expressed in terms of the exponential integral).

We found (1) that the dipolar interaction of nucleus A with an electron in an atomic orbital centred on nucleus B was surprisingly large and for the carbon atoms in acetylene larger than the interaction with an electron in an A.O. centred on nucleus A. This indicates that in, for example, vinyl bromide, interaction with the electrons on the bromine atom may well be important.

(2) All the terms were critically dependent on the internuclear distance.

(3) The largest contribution did not come from the excitation $\pi_3 \to \pi_u^*$ (the lowest excitation). The contributions were relatively insensitive to ΔE.

(4) The largest terms (of opposite sign) arose from the excitations $\sigma_g \to \sigma_u^*$ and $\sigma_u \to \sigma_u^*$ where the "overlap" terms $\langle \phi_N(k) | \mathcal{H}_{Nk} | \phi_{N'}(k) \rangle$ did not cancel.

(5) The extent to which these terms cancel depends critically on the coefficients of the A.O.'s in the M.O.'s, which we do not think are known with sufficiently accuracy to provide meaningful results.

Long-Range Couplings of Protons

The other (N.S.), with several colleagues, has been studying the NMR spectra of the natural product molecules eleutherin and isoeleutherin which have the formulae given below as proved by synthesis.
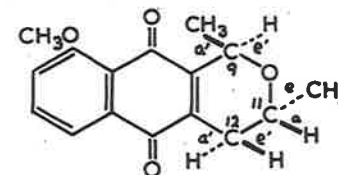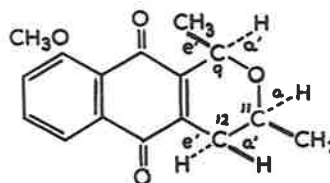
The combination of the magnitudes of the long range $J_{9,12}$ and vicinal $J_{12,11}$ coupling constants enabled a very detailed check to be made on the structures and also conformations of the partially saturated rings.   The vicinal $J_{12,11}$ coupling constants show which of the two CH_2 hydrogen nuclei is pseudo-axial and which pseudo-equatorial and this in turn allows the assignment of the 'long-range' $J_{9,12}$ couplings.   These come out as

$J_{a'a'} = 3.5$ $J_{a'e'} = 2.9$ c/s (from eleutherin)

and $J_{e'a'} = 2.0$ $J_{e'e'} < 1$ c/s (from isoeleutherin).

This stereochemically-sensitive pattern of long-range couplings may prove to be very useful in other molecules and very satisfactorily confirms the expectation based on the $\sigma - \pi$ configuration interaction mechanism that $J_{a'a'} > J_{a'e'} \rightleftharpoons J_{e'a'} > J_{e'e'}$.

This brings me to the more general topic of long-range proton-proton coupling constants.   I made some comments on this at the Boulder meeting last year, and these were written down and amplified in a paper Dr. Banwell and I presented at the Faraday Society Discussion on NMR (Discussion No. 34, 1962, p.115).   My own opinion is that after one has eliminated those long-range couplings which can be accounted for on Karplus' very successful $\sigma - \pi$ configuration interaction mechanism (either on grounds of the expected stereospecific variations - as in the examples given in the last paragraph - or on grounds that C=C-H $\rightarrow$ C=C-CH$_3$ substitution does not change the value of the long-range coupling by much as suggested by Hoffman and Gronowitz in MelloNMR No. 51 and their earlier papers) there remains a set of residuals that conform reasonably to a pattern.   Bhacca and Freeman (MelloNMR No. 47) suggest that the long-range 5-bond coupling which usually goes with our suggested 'straightest' planar zig-zag conformation

rather than

for example, can be correlated with the
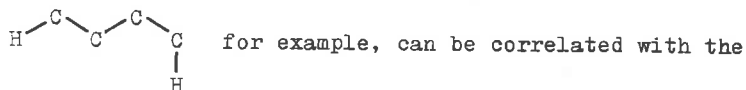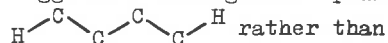
possibility of resonance structures of the type

in most cases (as unsaturated molecules are involved).   Banwell and I have ourselves put more emphasis on the fact that many long-range 4-bond couplings in saturated molecules are also highly stereospecific and correspond to the planar zig-zag path

.
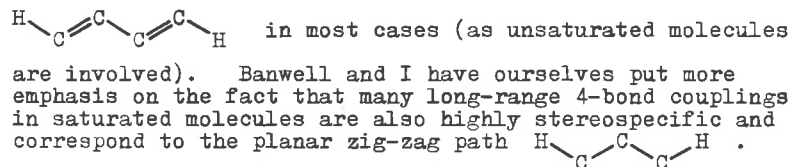
The best examples are taken from rigid ring systems such as Anet's spectra[1] of Camphane-diols and Hall and Hough's 1:3 diequatorial couplings in sugars with chair conformations.[2] The hypothesis is also consistent with Davis and Roberts[3] trans CH_3-C-C-H couplings in substituted ethanes; however in another case of the latter sort Bothner-By and Naar-Colin[4] have concluded that the long-range coupling involves a gauche CH_3-C-C-H group.   Our hunch is that the 4-bond (in saturated molecules) and 5-bond (in unsaturated molecules) long-range couplings have common origin in a σ -bond stereospecific coupling mechanism which simply extends and renders more selective the trans > gauche situation [or cis] in vicinal couplings.   Eyring and colleagues have suggested that such 'straight' paths may correspond to configurations of particular stability.

We would in any case much appreciate hearing of further examples that either reinforce or weaken our hypothesis. In the case of a

coupling where the Karplus $\sigma - \pi$ mechanism predicts a zero coupling constant, the present hypothesis would still allow a finite coupling (although not appreciably for

)

With best regards,

1. Can.J.Chem., 1961. 39, 789.
2. Proc.Chem.Soc., 1962, 382.
3. J.Amer.Chem.Soc., 1962, 84, 2252.
4. J.Amer.Chem.Soc., 1962, 84. 743.
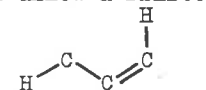
Yours sincerely,

Ruth M Lynden-Bell

Norman Sheppard

N. Sheppard   R.M. Lynden-Bell

"Gem. Dithiols"
B. Magnusson
Acta Chem. Scand. 17, 273 (1963)

"Long-range Proton Spin Couplings in Thieno [3,2-b] thiophene"
B. Gestblom
Acta Chem. Scand. 17, 280 (1963)

"Hydrogen Nuclear Magnetic Resonance Chemical Shift Correlations in Halogen Derivatives of Benzene and Alkyl Benzenes"
F. C. Stehling
Anal. Chem. 35, 773 (1963)

"Alkaloidal Constituents of Crotalaria Fulva Roxb., Fulvine and its N-Oxide"
R. Schoental
Australian J. Chem. 16, 233 (1963)

"Alkaloids of Crotalaria Crispata F. Muell. ex Benth., The Structures of Crispatine and Fulvine"
C. C. J. Culvenor and L. W. Smith
Australian J. Chem. 16, 239 (1963)

"The Major Alkaloid of Pultenaea Altissima F. Muell. ex Benth., N(b)N(b)-Dimethyl-1-Tryptophan Methyl Ester"
J. S. Fitzgerald
Australian J. Chem. 16, 246 (1963)

"Degradation of Carbohydrates. IV. Formation of Cis-unsaturated Hexosones"
E. F. L. J. Anet
Australian J. Chem. 16, 270 (1963)

"The Formation of the 6,8-Dihydrodipyrido[1,2-c:2',1'-e] [1,3,6]Oxadiazepidi-inium Cation in the Reaction of 2,2'-Bipyridyl with Methylene Sulphate"
I. C. Calder, W. H. F. Sasse and T. McL. Spotswood
Australian J. Chem. 16, 289 (1963)

"The Chemistry of the Western Australian Rutaceae. III. The Alkaloids of Boronia Ternata Endl."
A. M. Duffield and P. R. Jefferies
Australian J. Chem. 16, 292 (1963)

"Nuclear Magnetic Resonance of Eu151 and Eu153 in Ferromagnetic EuS.
E. L. Boyd
Bull. Am. Phys. Soc. 8, 439 (1963)

"Intramolecular Interaction between Hydroxl Group and π-Electrons. XVIII. Proton Magnetic Resonance Spectra of Aryldimethylcarbinols and Related Compounds"
M. Ôki and H. Iwamura
Bull. Chem. Soc. Japan 36, 1 (1963)

"Synthesis of 1-Oxaazulan-2-imine Derivatives from Tropone"
T. Nozoe, T. Mukai and T. Suzuki
Bull. Chem. Soc. Japan 36, 38 (1963)

"Proton Magnetic Resonance Spectra of Some Thenyl Derivatives"
K. Takahashi, T. Sone, Y. Matsuki and G. Hazato
Bull. Chem. Soc. Japan 36, 108 (1963)

"Le β-gurjunène. Identification avec le calarène"
J. Streith, P. Pesnelle et G. Ourisson
Bull. Soc. Chim. France 518 (1963)

"Spectres de Résonance Magnétique Nucléaire de Certains Alcaloïdes de la Série de la Morphine; Étude de la Conformation du Cycle C"
T. Rull
Bull. Soc. Chim. France 586 (1963)

"Structure de la ψ-Akuammigine et de la Picraline:Alcaloïdes du Picralime nitida Stapf (Apocynacées), (6e Mémoire). Application de la Spectrographie de Masse aux Problèmes de Détermination de Structure et de Stéréochimie (Partie XXVIII)"
L. Olivier, J. Levy, J. Le Men, M.M. Janot, C. Djerassi, H. Budzikiewicz, J. M. Wilson, L. J. Durham
Bull. Soc. Chim. France 646 (1963)

"Alkylaluminum Hydride Trimethylamine Complexes"
F. M. Peters, B. Bartocha and A. J. Bilbo
Can. J. Chem. 41, 1051 (1963)

"The Stereochemistry of Maleopimaric Acid and the Long Range Shielding Effect of the Olefinic Bond"
W. A. Ayer and C. E. McDonald and J. B. Stothers
Can. J. Chem. 41, 1113 (1963)

"The Nuclear Magnetic Resonance Spectrum of Sodium Methylcyclopentadienide"
S. McLean and P. Haynes
Can. J. Chem. 41, 1231 (1963)

"Observations on Alkylboranes"
C. A. Lutz and D. M. Ritter
Can. J. Chem. 41, 1344 (1963)

"Some Reactions of Organoaluminum Compounds with Nitrogen-Containing Bases"
N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr. and D. W. Moore
Can. J. Chem. 41, 1359 (1963)

"Synthese von Diketolactonen mittlerer Ringgrösse"
J. Falbe und F. Korte
Chem. Ber. 96, 919 (1963)

"Chemistry of Catharanthine: Evidence for a Novel and Remarkable Acid Rearrangement"
J. P. Kutney, J. Trotter, T. Tabata, A. Kerigan and N. Camerman
Chem. Ind. 648 (1963)

" Planar Sulphur d-Orbital Overlap with Unshared Electron Pairs"
T. G. Traylor
Chem. Ind. 649 (1963)

"Nuclear Magnetic Resonance Study of a New Flavonoid"
D. H. S. Horn and J. A. Lamberton
Chem. Ind. 691 (1963)

"Bis (Alkyne)-Mercuric Ion Complexes"
W. L. Budde and R. E. Dessy
Chem. Ind. 735 (1963)

"A Nuclear Magnetic Resonance Spectral Examination of the Interaction between Trimethylamine and 1,3,5-Trinitrobenzene"
P. R. Hammond
Chem. Ind. 737 (1963)

"Réaction diénique des bases de Mannich du phénol et synthèse de chromannes 2-substitués."
J. Brugidou et H. Christol
Compt. Rend. 256, 3149 (1963)

"Résonance Nucléaire. -- Variation Adiabatique de la Température de Spin par Modulation du Champ Local."
M. Goldman
Compt. Rend. 256, 3643 (1963)

"Résonance Magnétique Nucléaire. -- Observation de Transitions Induites par un Champ Radiofréquence Parallèle au Champ Statique."
H. Benoit et J. Pommier
Compt. Rend. 256, 3647 (1963)

"Resonance Magnetique Nucleaire. -- Étude de l'Association de l'Éthyl-3 Pentanol-3 en Solution dans le Tétrachlorure de Carbone."
J. Martin
Compt. Rend. 256, 3651 (1963)

"Résonance Magnétique Nucléaire. -- Étude des Régimes Transitoires de la Polarisation Dynamique dans les Liquides."
A. P. Legrand, J. Auvray et J. Uebersfeld
Compt. Rend. 256, 3655 (1963)

"Preparation and Reactions of some Tetracyanocyclopropanes"
F. Freeman
Dissertation Abstr. 23, 3631 (1963)

"Synthesis and Stereochemistry of 2-Pyrazolines"
M. J. Michelson
Dissertation Abstr. 23, 3636 (1963)

"Studies in Molecular Structure: I. The Microwave Spectrum and Molecular Structure of Malononitrile-D2. II. C13 Splittings in Fluorine Magnetic Resonance Spectra."
D. T. Carr
Dissertation Abstr. 23, 3643 (1963)

"Macro Rings. XXV. Fate of Carbonium Ions Held in π-Clouds of Benzene Rings"
D. J. Cram and M. Goldstein
J. Am. Chem. Soc. 85, 1063 (1963)

"Macro Rings. XXVI. [2.2] Paracyclophanyl as a Neighboring Group"
D. J. Cram and L. A. Singer
J. Am. Chem. Soc. 85, 1075 (1963)

"Macro Rings. XXVII. Transannular Substituent Effects in π-π-Complexes of Paracyclophanes"
L. A. Singer and D. J. Cram
J. Am. Chem. Soc. 85, 1080 (1963)

"Macro Rings. XXVIII. Structure-Reactivity-N.m.r. Spectra Relationships in the [1.n]Paracyclophanes"
D. J. Cram and L. A. Singer
J. Am. Chem. Soc. 85, 1084 (1963)

"Macro Rings. XXIX. Stereochemistry of a 1,6-Cycloaddition Reaction"
D. J. Cram, C. K. Dalton and G. R. Knox
J. Am. Chem. Soc. 85, 1088 (1963)

"The Anthrasteroid Rearrangement. X. Elucidation of the Stereochemistry of the C/D Ring Fusion from Chemical Transformation and N.m.r. Data."
J. A. Steele, L. A. Cohen and E. Mosettig
J. Am. Chem. Soc. 85, 1134 (1963)

"Two Unusual Reactions Encountered during the Devious Hydrolysis of 3,3-Dimethyl-1,1,2,2,-tetracyanocyclopropane to the Corresponding Tetracarboxylic Acid"
H. Hart and F. Freeman
J. Am. Chem. Soc. 85, 1161 (1963)

"The Molecular Structure and Electronic Spectrum of [8] Paracyclophane. A New Synthetic Method for the Preparation of Strained Large Rings"
N. L. Allinger, L. A. Freiberg, R. B. Hermann and M. A. Miller
J. Am. Chem. Soc. 85, 1171 (1963)

"Synthesis of the New 3,4-Dihydro-2-H-naphtho[1,2-b]pyran-6-yl Phosphate from Vitamin K"
A. F. Wagner, P. E. Wittreich, B. Arison, N. R. Trenner and K. Folkers
J. Am. Chem. Soc. 85, 1178 (1963)

"Exchange Reactions in Group II Organometallic Systems"
R. E. Dessy, F. Kaplan, G. R. Coe and R. M. Salinger
J. Am. Chem. Soc. 85, 1191 (1963)

"A Note on Steric Isotope Effects. Conformational Kinetic Isotope Effects in the Racemization of 9,10-Dihydro-4,5-Dimethylphenanthrene"
K. Mislow, R. Graeve, A. J. Gordon and G. H. Wahl, Jr.
J. Am. Chem. Soc. 85, 1199 (1963)

"Carbethoxynitrene"
W. Lwowski, T. J. Maricich and T. W. Mattingly, Jr.
J. Am. Chem. Soc. 85, 1200 (1963)

"Burnamicine, A Cryptopine-Like Analog of Corynantheol"
M. F. Bartlett and W. I. Taylor
J. Am. Chem. Soc. 85, 1203 (1963)

"Ring Inversion in Cyclooctane"
F. A. L. Anet and J. S. Hartman
J. Am. Chem. Soc. 85, 1204 (1963)

"The Reactions of Sulfur Atoms. II. Sulfur Atom Insertion in Carbon-Hydrogen Bonds. The Formation of Cyclopropyl Mercaptan in the Reaction with Cyclopropane"
A. R. Knight, O. P. Strausz and H. E. Gunning
J. Am. Chem. Soc. 85, 1207 (1963)

"Electrophilic Substition and Other Reactions of Diazocyclopentadiene"
D. J. Cram and R. D. Partos
J. Am. Chem. Soc. 85, 1273 (1963)

"Carbon-13 Nuclear Magnetic Resonance Spectra of Olefins and Other Hydrocarbons"
R. A. Friedel and H. L. Retcofsky
J. Am. Chem. Soc. 85, 1300 (1963)

"F19 Chemical Shifts of the Sulfur Pentafluoride, Trifluoromethoxy, Trifluoromethylthio and Trifluoromethylsulfonyl Groups in Aromatic Compounds"
D. R. Eaton and W. A. Sheppard
J. Am. Chem. Soc. 85, 1310 (1963)

"The Decarboxylation of β-Ketoacids: A Study of the Decarboxylation of 1-Carboxybicyclo[3,3,1] nonane Derivatives"
J. P. Ferris and N. C. Miller
J. Am. Chem. Soc. 85, 1325 (1963)

"Stable Carbonium Ions. IV. Secondary and Tertiary Alkyl and Aralkyl Oxocarbonium Hexafluoroantimonates. Formation and Identification of the Trimethylcarbonium Ion by Decarbonylation of the tert-Butyl Oxocarbonium Ion"
G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien and E. B. Baker
J. Am. Chem. Soc. 85, 1328 (1963)

"Some Charge-Transfer Salts of 1,2,3,4,5-Pentacarbomethoxycyclopentadienyl Anion"
E. Le Goff and R. B. LaCount
J. Am. Chem. Soc. 85, 1354 (1963)

"Alkylation of Aromatic Hydrocarbons by Alkyllithium Reagents"
J. A. Dixon and D. H. Fishman
J. Am. Chem. Soc. 85, 1356 (1963)

"The Synthesis and Characterization of Nitronic Esters"
N. Kornblum and R. A. Brown
J. Am. Chem. Soc. 85, 1359 (1963)

"The Mechanism of a Diels-Alder Reaction"
S. Seltzer
J. Am. Chem. Soc. 85, 1360 (1963)

"The Isolation of a Pentacyclic Triterpenoid Alcohol from a Protozoan"
F. B. Mallory, J. T. Gordon and R. L. Conner
J. Am. Chem. Soc. 85, 1362 (1963)

"Magnetic Susceptibility of Diatomic Molecules"
M. Karplus and H. J. Kolker
J. Chem. Phys. 38, 1263 (1963)

"Molecular Orbital Theory of Diamagnetic Polarization.
III. Anisotropic Properties of the Carbonate and Nitrate
Ions"
J. A. Pople
J. Chem. Phys. 38, 1276 (1963)

"Ring Currents in Pentacyclic Hydrocarbons"
J. D. Memory
J. Chem. Phys. 38, 1341 (1963)

"C^{13} Nuclear Magnetic Resonance Spectroscopy. III. Iodo-
benzene and Methyliodobenzenes"
P. C. Lauterbur
J. Chem. Phys. 38, 1406 (1963)

"C^{13} Nuclear Magnetic Resonance Spectroscopy. IV. Aniline,
N,N-Dimethylaniline, and their Methyl Derivatives: Steric
Inhibition of Conjugation"
P. C. Lauterbur
J. Chem. Phys. 38, 1415 (1963)

"C^{13} Nuclear Magnetic Resonance Spectroscopy. V. Nitro-
benzene and Methylnitrobenzenes: Steric Inhibition of
Conjugation"
P. C. Lauterbur
J. Chem. Phys. 38, 1432 (1963)

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

"Medium Effects in NMR. III. Fluorine Resonance in Gases"
L. Petrakis and H. J. Bernstein
J. Chem. Phys. 38, 1562 (1963)

"Nuclear Magnetic Resonance Studies of Electron Transfer
between Tris(2,2'-dipyridyl) osmium(II) and (III) Ions,
between Bis(cyclopentadienyl)iron(II) and (III) Ions, and
between Tris(1,10-phenanthroline)iron(II) and (III) Ions"
M. W. Dietrich and A. C. Wahl
J. Chem. Phys. 38, 1591 (1963)

"Fast-Exchange Width of Nuclear Magnetic Resonance Spectra"
S. Alexander
J. Chem. Phys. 38, 1787 (1963)

"NMR Studies of Hydrated Sodium Tetraborate Minerals. I.
Boron-Oxygen Polyion in Borax and Tincalconite"
J. D. Cuthbert and H. E. Petch
J. Chem. Phys. 38, 1912 (1963)

"Model for the Electronic Structure of Metal Tungsten
Bronzes"
A. R. Mackintosh
J. Chem. Phys. 38, 1991 (1963)

"Cyclo-octatriene and Related Complexes of Iron and Cobalt"
W. McFarlane, L. Pratt and G. Wilkinson
J. Chem. Soc. 2162 (1963)

"The Chemistry of Boron. Part V. New Methods for the Prep-
aration of Ethyl- and n-Propyl-diboranes"
L. H. Long and M. G. H. Wallbridge
J. Chem. Soc. 2181 (1963)

"A Possible Structure for Eremolactone, a New Type of Diter-
pene"
A. J. Birch, J. Grimshaw and J. P. Turnbull
J. Chem. Soc. 2412 (1963)

"The Chemistry of Cedrelone"
R. Hodges, S. G. McGeachin and R. A. Raphael
J. Chem. Soc. 2515 (1963)

"^{13}C-H Spin-Spin Splitting in the Nuclear Magnetic Resonance
Spectra of the Methyl Esters of Some Inorganic Oxyacids"
P. R. Hammond
J. Chem. Soc. 2565 (1963)

"Some New Forms of Regrouping of Arbuzov. XIV. Investiga-
tion of the Addition Products of Trialkyl Phosphites and
Diacetyl by Physical Methods"
V. A. Kukhtin, K. M. Kirillova, R. R. Shagidullin, Y. Y.
Samilov, N. A. Lyazina and N. F. Rakova
J. Gen. Chem. U.S.S.R. 32, 2020 (1962)

"Syntheses with the Help of Free Hydroxyl Radicals III. The
Reaction of Alkyl Acetates with Hydroxyl Radicals"
G. A. Razuvaev and L. S. Boguslavskaya
J. Gen. Chem. USSR 32, 2288 (1962)

"Stereochemistry of the Interaction of Enantiomeric 1,3-
Dioxolane Analogs of Muscarone with Cholinergic Receptors"
B. Belleau and J. Puranen
Med. Chem. 6, 325 (1963)

"Direct Analysis of nmr Spectra"
D. R. Whitman
J. Mol. Spectr. 10, 250 (1963)

"Fluorine NMR Spectroscopy--Studies of ^{13}C Satellite Spectra"
R. K. Harris
J. Mol. Spectr. 10, 309 (1963)

"Macrocyclic Diterpenes Isolated from Tobacco. α-and β-3,8,13-
Duvatriene-1,5-diols"
R. L. Rowland and D. L. Roberts
J. Org. Chem. 28, 1165 (1963)

"Vinyl Proton Abstraction during Metalation of α-Olefins"
C. D. Broaddus, T. J. Logan and T. J. Flautt
J. Org. Chem. 28, 1174 (1963)

"The Reaction of Chloroacetaldehyde with Cyanide Ion in Aque-
ous Medium"
R. M. Nowak
J. Org. Chem. 28, 1182 (1963)

"Synthetic Studies on C-19 Oxygenated Pregnanes"
J. F. Bagli, P. F. Morand and R. Gaudry
J. Org. Chem. 28, 1207 (1963)

"The Synthesis and N.m.r. Spectra of Some Tetracyanocyclopro-
panes"
H. Hart and F. Freeman
J. Org. Chem. 28, 1220 (1963)

"Organic Sulfur Compounds. IX. Addition of Diethyldithio-
phosphoric Acid to Dienes"
A. A. Oswald, K. Griesbaum and B. E. Hudson, Jr.
J. Org. Chem. 28, 1262 (1963)

"The Effect of Solvent upon the N.m.r. Spectra of N-Methyl-
amides. I. Solvent-Solute Complex Formation between
Amides and Aromatic Solvents"
R. M. Moriarty
J. Org. Chem. 28, 1296 (1963)

"The Chemistry of Pyridine. II. The Reaction of 1-Alkoxy-
picolinium Salts with Mercaptide and Thiophenoxide Ions"
L. Bauer and L. A. Gardella
J. Org. Chem. 28, 1323 (1963)

"The Reaction of cis-2,6 -Dibromo-4,4-dimethylcyclohexanone
with Sodium Acetate in Acetic Acid, a New Elimination-Re-
arrangement Reaction"
F. G. Bordwell and K. M. Wellman
J. Org. Chem. 28, 1347 (1963)

"Debromination of N,N-Diethylcinnamamide Dibromide"
A. J. Speziale and C. C. Tung
J. Org. Chem. 28, 1353 (1963)

"The Reaction of Diketene with Glycine"
S. Garratt and D. Shemin
J. Org. Chem. 28, 1372 (1963)

"Preparation of 4,5-Dihydrooxepine and 1,2-Divinylethylene
Oxide"
R. A. Braun
J. Org. Chem. 28, 1383 (1963)

"Steroids. CCXXXII. One-step Rearrangement of 17α-Methyl-
Δ1,4,6- androstatrien-17-ol-3-one to an 18-Norequilenin
Derivative"
S. Kaufmann
J. Org. Chem. 28, 1390 (1963)

"Rearrangement of 2-Cyano-3-t-butyl-1-indenone"
E. Campaigne and D. R. Maulding
J. Org. Chem. 28, 1391 (1963)

"Methylation of Benzimidazole and Benzothiazole Carboxaldoximes"
E. J. Poziomek, R. H. Poirier, R. D. Morin and T. F. Page, Jr.
J. Org. Chem. 28, 1411 (1963)

"Bridged Polycyclic Compounds. XXII. The Carbenoid De-
composition of Nortricyclenone p-Toluenesulfonylhydrazone"
S. J. Cristol and J. K. Harrington
J. Org. Chem. 28, 1413 (1963)

"The Monoaddition of Phenylsilane to Cyclic Polyolefins"
R. E. Bailey, D. S. Tutas and R. West
J. Org. Chem. 28, 1417 (1963)

"The Anomalous Behavior of m-Trifluoromethylnitrosobenzene
Dimer"
L. A. Errede and H. R. Davis
J. Org. Chem. 28, 1430 (1963)

"Nuclear Magnetic Resonance Spectra of Some Substituted
Methanes"
S. G. Frankiss
J. Phys. Chem. 67, 752 (1963)

"N. M. R. Spectra of Silicon Hydride Derivatives: II.
Chemical Shifts in Some Simple Derivatives"
E. A. V. Ebsworth and J. J. Turner
J. Phys. Chem. 67, 805 (1963)

"N. M. R. Studies of Hydrogen Bonding. I. Binary Mixtures of
Chloroform and Nitrogen Bases"
P. J. Berkeley, Jr. and M. W. Hanna
J. Phys. Chem. 67, 846 (1963)

"Fluorine N.M.R. Spectroscopy. XI. CCl_2F-CCl_2F; Proof of
Opposite Signs for $J(C^{13}F)$ and $J(C^{13}CF)$ by Spin Decoupling"
G. V. D. Tiers
J. Phys. Chem. 67, 928 (1963)

"Long Range Spin-Spin Splittings in 4-Vinylidenecyclopentene"
M. W. Hanna and J. K. Harrington
J. Phys. Chem. 67, 940 (1963)

"Formation and Exchange Rates of Some Complexes of Boron
Fluoride with Amines and Ethers"
S. Brownstein, A. M. Eastham and G. A. Latremouille
J. Phys. Chem. 67, 1028 (1963)

"Detection of Oxygen-17 n.m.r. in Solid MgO"
J. A. Jackson
J. Phys. Chem. Solids 24, 591 (1963)

"Nuclear Magnetic Resonance in Ferromagnetic Mn_4N and Mn_5Ge_3"
T. Hihara, Y. Kōi and Akira Tsujimura
J. Phys. Soc. Japan 18, 454 (1963)

"Nuclear Magnetic Resonance in Antiferromagnetic α-Mn Metal"
J. Itoh, Y. Masuda, K. Asayama and S. Kobayashi
J. Phys. Soc. Japan 18, 455 (1963)

"Nuclear Magnetic Resonance of Cu-Ni Alloys"
K. Asayama, S. Kobayashi and J. Itoh
J. Phys. Soc. Japan 18, 458 (1963)

"Molecular Motion in Polyethylene. III"
D. W. McCall and E. W. Anderson
J. Polymer Sci. A1, 1175 (1963)

"NMR Study of Molecular Chain Structure of Polyvinylidene
Fluoride"
C. W. Wilson, III
J. Polymer Sci. A1, 1305 (1963)

"Self-Diffusion and Nuclear Relaxation in Polyisobutylene"
D. W. McCall, D. C. Douglass and E. W. Anderson
J. Polymer Sci. A1, 1709 (1963)

"Colloid Chemical Properties of Ampholytic Surfactants.
II. The Critical Micelle Concentration and Micellar
Weight of Octylbetaine"
K. Tori and T. Nakagawa
Kolloid Z. u. Z. Polymere 188, 47 (1963)

"Beitrag zur Deutung des Infrarotspektrums von Nylon 6,6"
G. Heidemann und H. Zahn
Makromol. Chem. 62, 123 (1963)

"Magnetic Anisotropy of the Nitro Group Studied by Nuclear
Magnetic Resonance"
I. Yamaguchi
Mol. Phys. 6, 105 (1963)

"Solvent Effects on the Nuclear Magnetic Resonance Spectra
of Aromatic Amines"
H. Suhr
Mol. Phys. 6, 153 (1963)

"The Relative Signs of Fluorine N.M.R. Spin Coupling Con-
stants in Aromatic Compounds"
D. F. Evans
Mol. Phys. 6, 179 (1963)

"Beiträge zur Chemie der Silicium--Stickstoff-Verbindungen,
19.Mitt.: Silylsubstituierte Hydroxylamine"
U. Wannagat und J. Pump
Monatsh. Chem. 94, 141 (1963)

"Structure of Chorismic Acid, a New Intermediate in Aromatic
Biosynthesis"
F. Gibson and L. M. Jackman
Nature 198, 388 (1963)

"The Use of Methyldichlorosilane for Determining the Resolu-
   tion of NMR Spectrometers"
A. V. Kessenikh
Opt. Spectr. (USSR) 14, 168 (1963)

"Proton Spin Relaxation in Liquid Hydrogen Chloride and Hydro-
   gen Bromide"
K. Krynicki and J. G. Powles
Phys. Letters 4, 260 (1963)

"Temperature Dependence of Spin-Lattice Relaxation in Alkali
   Halides"
M. J. Weber
Phys. Rev. 130, 1 (1963)

"Covalency Effects in KNiF$_3$. I. Nuclear Magnetic Resonance
   Studies"
R. G. Shulman and S. Sugano
Phys. Rev. 130, 506 (1963)

"Covalency Effects in KNiF$_3$. II. Optical Studies"
K. Knox, R. G. Shulman and S. Sugano
Phys. Rev. 130, 512 (1963)

"Covalency Effects in KNiF$_3$. III. Theoretical Studies"
S. Sugano and R. G. Shulman
Phys. Rev. 130, 517 (1963)

"Relaxation Time Measurements in Ruby by a dc Magnetization
   Technique"
S. Y. Feng and N. Bloembergen
Phys. Rev. 130, 531 (1963)

"Spin Temperature in Nuclear Double Resonance"
F. M. Lurie and C. P. Slichter
Phys. Rev. Letters 10, 403 (1963)

"On the Structure of Phycaron"
W. H. L. Hackeng, H. Copier and C. A. Salemink
Rec. Trav. Chim. 82, 322 (1963)

"Syntezy Monoenowe. II. O Mechaniźmie Kondensacji
   Azodwukarboksylanu Etylu Z Połaczeniami Olefinowymi"
"Monoenic Syntheses. II. The Mechanism of Ethyl Azodi-
   carboxylate Condensation with Olefins"
O. Achmatowicz and O. Achmatowicz (Jr)
Roczniki Chem. 37, 317 & 330 (1963)

"The Structure of Bruceol"
A. M. Duffield, P. R. Jefferies, E. N. Maslen and A. I. M. Rae
Tetrahedron 19, 593 (1963)

"Studies on the Alkaloids of Securinega Virosa Pax. Et Hoffm.
   I. Structure of Virosecurinine"
T. Nakano, T. H. Yang and S. Terao
Tetrahedron 19, 609 (1963)

"Sesquiterpenoids --III. The Constitution and Stereochem-
   istry of Valdiviolide, Fuegin, Winterin and Futronolide"
H. H. Appel, R. P. M. Bond and K. H. Overton
Tetrahedron 19, 635 (1963)

"Heartwood Constituents of Sciadopitys Verticillata Sieb. et
   Zucc. -- I. The Constitution of Sciadin"
M. Sumimoto
Tetrahedron 19, 643 (1963)

"Celebixanthone: A Combined Chemical and Crystallographic
   Structure Proof"
G. H. Stout, V. F. Stout and M. J. Welsh
Tetrahedron 19, 667 (1963)

"The Structure of Munetone"
C. S. Barnes, J. L. Occolowitz, N. L. Dutta, P. M. Nair,
   P. S. Phadke and K. Venkataraman
Tetrahedron Letters 281 (1963)

"The Structure of Lunarine"
P. Potier, J. LeMen, M-M. Janot, P. Bladon, A. G. Brown,
   and C. S. Wilson
Tetrahedron Letters 293 (1963)

"Rapid Allylic Rearrangements in 2-Halo-3-Hydroxy-2,4-Di-
   methylcyclobutenones"
D. G. Farnum, M. A. T. Heybey and B. Webster
Tetrahedron Letters 307 (1963)

"Cyanomaclurin"
P. M. Nair and K. Venkataraman
Tetrahedron Letters 317 (1963)

"A New Carbon-Carbon Condensation Via Cyclic Oxyphosphoranes.
   Tartaric Acids from α-Ketoesters"
F. Ramirez, N. B. Desai and N. Ramanathan
Tetrahedron Letters 323 (1963)

"Phlebiarubrone, A Basidiomycete Pigment Related to Poly-
   poric Acid"
T. C. McMorris and M. Anchel
Tetrahedron Letters 335 (1963)

"Fluorine-19 Resonance in Monofluoro Aromatic Compounds"
M. J. S. Dewar, R. C. Fahey and P. J. Grisdale
Tetrahedron Letters 343 (1963)

"Photolysis of Vinyl Benzoates"
M. Feldkimel-Gorodetsky and Y. Mazur
Tetrahedron Letters 369 (1963)

"The Structure of Tecomanine"
G. Jones, H. M. Fales and W. C. Wildman
Tetrahedron Letters 397 (1963)

"Synthesis of a Degradation Product of Cephalosporin C and
   Related Sulfur-Containing α-Tetronic Acids"
E. Galantay, A. Szabo and J. Fried
Tetrahedron Letters 415 (1963)

"The Constitution of Morellin"
G. Kartha, G. N. Ramachandran, H. B. Bhat, P. M. Nair,
   V. K. V. Raghavan and K. Venkataraman
Tetrahedron Letters 459 (1963)

"Glutarimide Antibiotics. Part III. The Determination of the
   Stereochemistry of the Methyl Groups of Cycloheximide iso-
   mers by Nuclear Magnetic Resonance Spectroscopy"
F. Johnson and N. A. Starkovsky
Tetrahedron Letters 1173 (1962)

"Studies on Securinine and Allosecurinine"
I. Satoda, M. Murayama, J. Tsuji and E. Yoshii
Tetrahedron Letters 1199 (1962)

"Free Radical Additions to Squalene"
R. Breslow, E. Barrett and E. Mohacsi
Tetrahedron Letters 1207 (1962)

"Structures et Configurations de Pentenediones-1,5 Dérivées
   de Sels de Pyrylium"
G. Rio et Y. Fellion
Tetrahedron Letters 1213 (1962)

"An NMR Study of the Reaction of Furan with Maleic Anhydride
   and Maleic Acid"
F. A. L. Anet
Tetrahedron Letters 1219 (1962)

"Structure of the Alleged Diels-Alder Adduct from 2,3-Dimethyl-
   Quinoxaline and Maleic Anhydride"
E. C. Taylor and E. S. Hand
Tetrahedron Letters 1225 (1962)

"The Stereochemistry of Panaxadiol"
S. Shibata, O. Tanaka, M. Nagai and T. Ishii
Tetrahedron Letters 1239 (1962)

"The Reactions of Steroidal Alcohols with 2-Chloro-1,1,2-
   Trifluorotriethylamine"
L.H. Knox, E. Velarde, S. Berger, D. Cuadriello and A.D. Cross
Tetrahedron Letters 1249 (1962)

"Configurational Stability at the Carbon-Nitrogen Double Bond"
D. Y. Curtin and C. G. McCarty
Tetrahedron Letters 1269 (1962)

"The 17α-Hydroxylation of Cardiac Aglycones. Conversion of
   the Cardenolide to the Cortisone Side-Chain"
N. Danieli, Y. Mazur and F. Sondheimer
Tetrahedron Letters 1281 (1962)

"Bildung siliciumorganischer Verbindungen. XVIII. Zur
   Konstitution des $Si_2C_6H_{16}$ aus der Pyrolyse des $Si(CH_3)_4$"
G. Fritz, W. Kemmerling, G. Sonntag, H. J. Becher,
   E. A. V. Ebsworth und J. Grobe
Z. Anorg. Allg. Chem. 321, 10 (1963)

"Organosilyläthylendiaminverbindungen. I. Die Reaktionen
   der Methylchlorsilane und $SiCl_4$ mit N,N'-Bis-(trimethylsilyl)-
   äthylendiamin"
D. Kummer and E. G. Rochow
Z. Anorg. Allg. Chem. 321, 21 (1963)

"Einige Anwendungen der Kernresonanz-Spektroskopie in der
   Organischen Chemie"
A. R. Katritzky
Z. Chem. 3, 81 (1963)