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ILLINOIS INSTITUTE OF TECHNOLOGY
TECHNOLOGY CENTER
CHICAGO 16

Department of Chemistry

September 10, 1963

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

Dear Dr. Shapiro:

The 1,4-diynes constitute an unusual class of compounds. However, 5-phenylpenta-1,4-diyne shows normal 60 Mc acetylenic (triplet) and propargyl (doublet) proton resonances at -130.5 c.p.s and -199.5 c.p.s. respectively from TMS in the pure liquid. The compound is interesting in that it serves as an example of long-range spin-spin coupling observed in acetylenic hydrocarbons, for example by Professor Roberts and coworkers (J. Am. Chem. Soc., 84, 1582, 2004 (1962); Angew. Chem. internat. Edit., 2, 53 (1963)). We observe (using the notation of papers cited) $|J_{13}| = 2.9 \pm 0.2$ c.p.s. This value is quite large considering that coupling takes place through four chemical bonds, but is typical for acetylenes of this type.

Sincerely,

Sheldon H. Marcus

Sheldon H. Marcus

Hiroshi Taniguchi

Hiroshi Taniguchi

SM:mc

60-2

Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich

ZÜRICH,
Universitätstrasse
Tel. (051) 32 73 30

August 23, 1963

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

Dear Dr. Shapiro:

In high-resolution nmr-spectroscopy the question has arised whether the correspondence between the parameters of the hamiltonian:

$$(1) \qquad H = \sum_{i=1}^{n} \mathfrak{R}_i I_{iz} + \sum_{i<k} J_{ik} \vec{I}_i \vec{I}_k = Z + S$$

(Z = Zeeman term, S = spin-spin coupling term)

and the experimental spectrum is a one-to-one correspondence or not. This correspondence has been examined in the case of spin-½-particles.

The determination of the hamiltonian from the experimental spectrum is composed in a natural way of two parts. One of them deals with the correspondence between the experimental spectrum and the scheme of transitions. This correspondence has been examined by applying the theory of graphs and the following statement could be proved:

Statement 1

If one associates the absorption lines with the transitions in such a way that the intensity rules:

$$(2) \qquad \sum_i I_{ik}^{m-1} - \sum_j I_{kj}^{m} = 2m$$

m= magnetic quantum number

and the cycle conditions for the absorption frequencies:

$$(3) \qquad \begin{aligned} \nu_{ik}^{m} - \nu_{ip}^{m} &= \nu_{jp}^{m+1} - \nu_{kj}^{m+1} \\ \nu_{ik}^{m} - \nu_{ip}^{m} &= \nu_{jk}^{m} - \nu_{jp}^{m} \end{aligned}$$

are satisfied, there exist in general only two possible associations differing in the common sign of all frequencies.

Thereby ν_{ik}^{m} and I_{ik}^{m} denote frequency and intensity of an absorption line belonging to a transition of type $m \leftrightarrow m+1$.

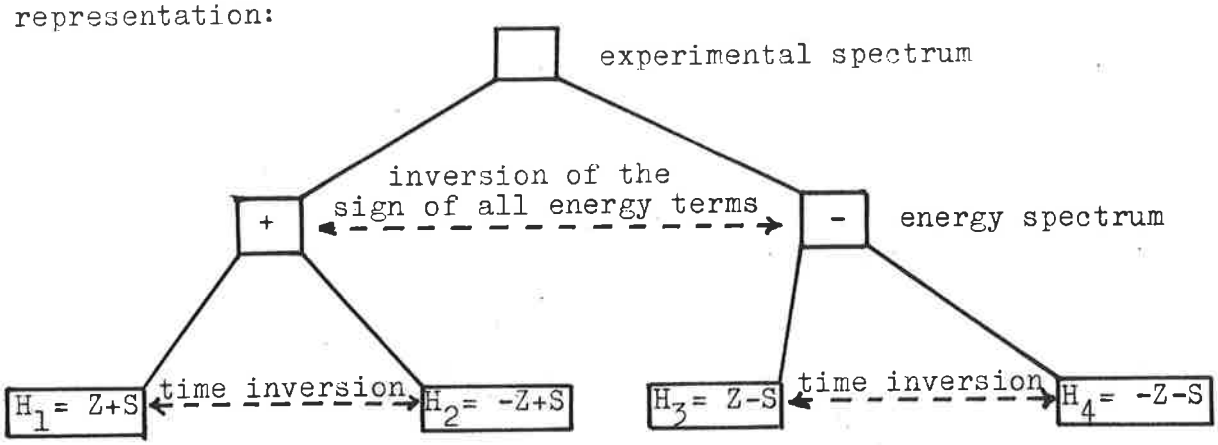
The number of independent equations is $2^n - 1$ for those of type (2) and $\binom{2n}{n-1} - 2^n + 1$ for those of type (3), where n means the number of protons, the system under consideration is composed of.

The second part consists in the determination of the hamiltonian from the energy spectrum. In this connection the following statement could be proved:

Statement 2

The only transformations which turn a hamiltonian of the form (1) again in a hamiltonian of this form possessing the same energy spectrum are the permutations of the protons and the time inversion.

Without regard to the permutations, there exist therefore in general only two hamiltonians which define the same energy spectrum. We can summarize the above statements with aid of the following graphical representation:



or in words:

Theorem

The usual method of calculating the (idealized) experimental spectrum is in general only in four ways invertable: The selective inversions of the sign of the Zeeman- and the spin-spin coupling term are the only transformations of the hamiltonian (1) which turn it in a hamiltonian defining the same spectrum as the operator (1).

The explicite proof of the above statements will be published in the Helvetica Physica Acta as soon as possible.

Sincerely yours

H. Kummer

H. Kummer

P.-D. Dr. W. von Philipsborn
Organisch-chemisches Institut
der Universität Zürich

Zurich, August 28, 1963

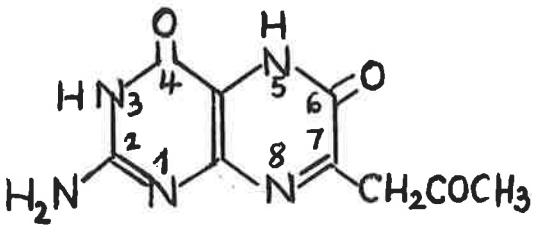
Dr. B. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh13, Pa.

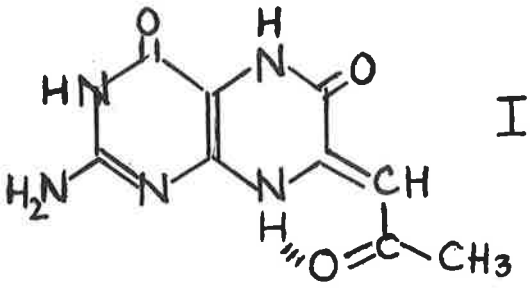
Dear Dr. Shapiro:

This is our second contribution to your excellent news letter. We are very sorry that you had to remind and finally punish us. A heavy teaching load is one of our excuses. Now we trust that you consider a few month without MelloNMR sufficient punishment and that you put us again on the mailing list.

The NMR-spectra of pteridines, a biologically important class of compounds have only very scarcely been investigated. We have now studied about 70 compounds in this series and wish to report some results in condensed form.[1] 2-amino-4-hydroxypteridines, the most important because naturally occurring pteridines are difficult to dissolve. We have found that CF_3COOH and conc. H_2SO_4 are suitable solvents and in some cases CD_3SOCD_3 may be used. Chemical shifts of relevant protons in the 2-amino-4-hydroxy-, 2-amino-4,6-dihydroxy- and 2-amino-4,7-dihydroxy-pteridine series are summarized in table 1. In the spectra of all compounds one observes a broad and temperature dependent peak for 2 protons between 7.7 and 8.8 ppm which must be assigned to the NH_2-group at C-2 as follows from the spectra of mono- and dialkylamino-derivatives. All the other NH protons at N-1, N-3, N-5 and N-8 exchange with CF_3COOH. From the chemical shift of the NH_2-protons in CF_3COOH, H_2SO_4 and CD_3SOCD_3 it can be concluded that protonation of all these compounds takes place in position 1 of the pyrimidine ring.

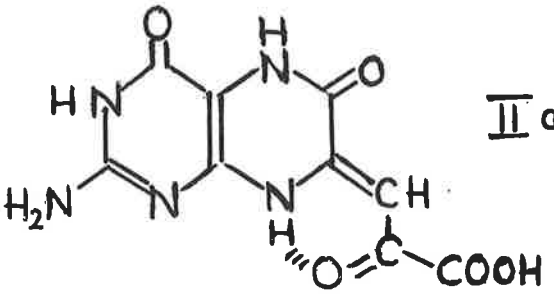
7-acetonylxanthopterine (I) and the red butterfly pigment (II) erythropterine do not show NH_2-absorption in acid. The spectra exhibit very sharp singlet vinylproton absorption. The spectra of I and II-methylester in CD_3SOCD_3 are shown in fig. 1 and 2.

I 



Ia

II 



IIa

The spectra are thus in full agreement with structures Ia and IIa. The very strong intramolecular hydrogen bond in CD_3SOCD_3 solution is nicely demonstrated by the chemical shift of the lowest field NH-absorptions and by the fact that these hydrogens do not easily exchange on addition of traces of CF_3COOH like all the other NH-protons. Since there is no coupling of the vinyl and methyl protons in I in both CF_3COOH and CD_3SOCD_3 solutions a possible enol structure[2] for the side chain can be ruled out. This also follows from other spectroscopic evidence.

Finally we would like to warn everybody not to use Varian's otherwise excellent microcells for CF_3COOH solutions. We found that they are more soluble than some of our pteridines and disintegrate after a few hours.

We shall very much appreciate some of the 1963 issues, if still available.

Sincerely yours,

W. v. Philipsborn

W. von Philipsborn

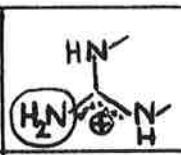
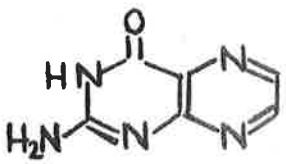
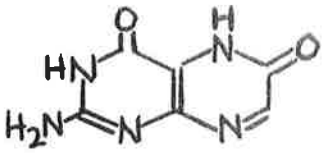
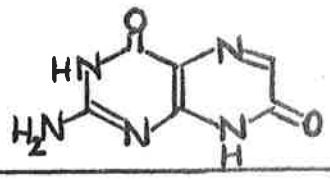
	Vinyl -H C-6, C-7	Methyl- C-6, C-7		N(1)-CH_3	N(3)-CH_3	N(8)-CH_3 N(5)-CH_3
I	8.90-9.10	2.88-2.90	8.50-8.75	4.15	3.79-3.86	--
II	8.55-8.70 9.27-9.35**)	2.78 3.05**)	7.95-8.25	--	3.73-3.87	4.20 [N(5)-CH_3]
III	8.25-8.37 8.57-8.65**)	2.82 3.02**)	7.70-8.10	--	3.72-3.86	3.72-3.86 [N(8)-CH_3]

table 1.

I = derivatives of 2-amino-4-hydroxypteridine 

II = -//- 2-amino-4,6-dihydroxypteridine 

III = -//- 2-amino-4,7-dihydroxypteridine 

*) If not otherwise specified chemical shifts are for CF_3COOH solutions (5-10%) in ppm relative to TMS as internal standard.

**) In conc. H_2SO_4 solution, TMS in CCl_4 as standard in a separate tube.

1) R. Mondelli & W. von Philipsborn, full paper will be published in Helv. chim. Acta.

2) W. Pfleiderer, Ber. deutsch. chem. Ges. 95, 2195 (1962).

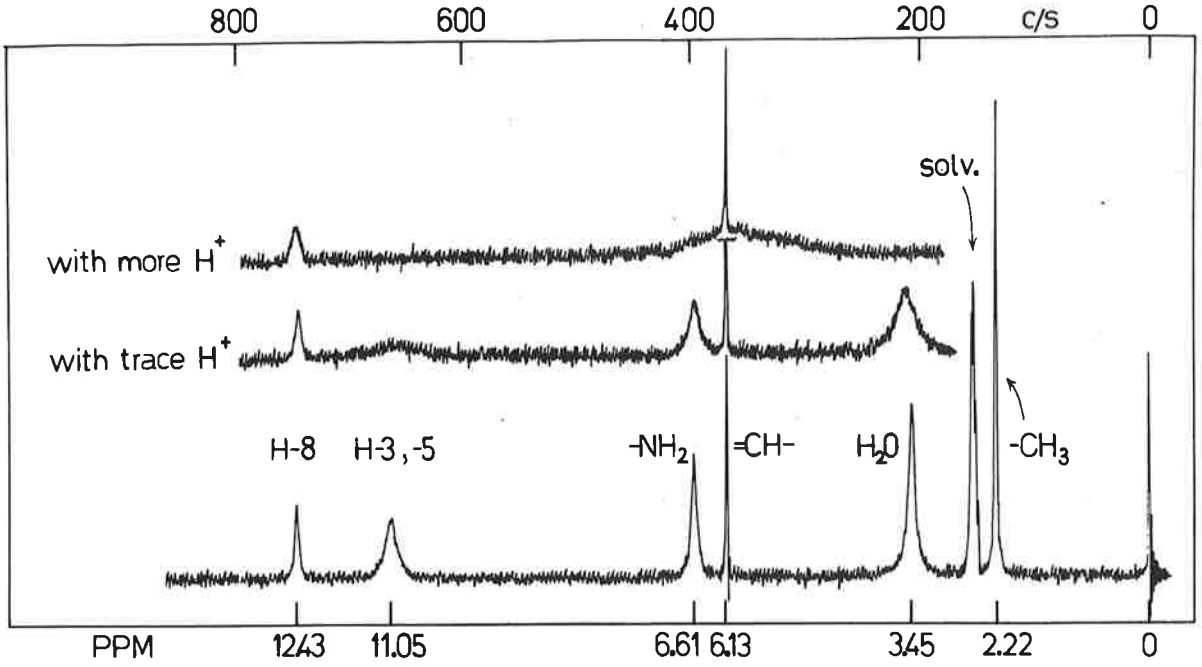

800
600
400
200
c/s
0
solv.
with more H+
with trace H+
H-8
H-3,-5
-NH2
=CH-
H2O
-CH3
PPM
12.43
11.05
6.61
6.13
3.45
2.22
0

fig. 1

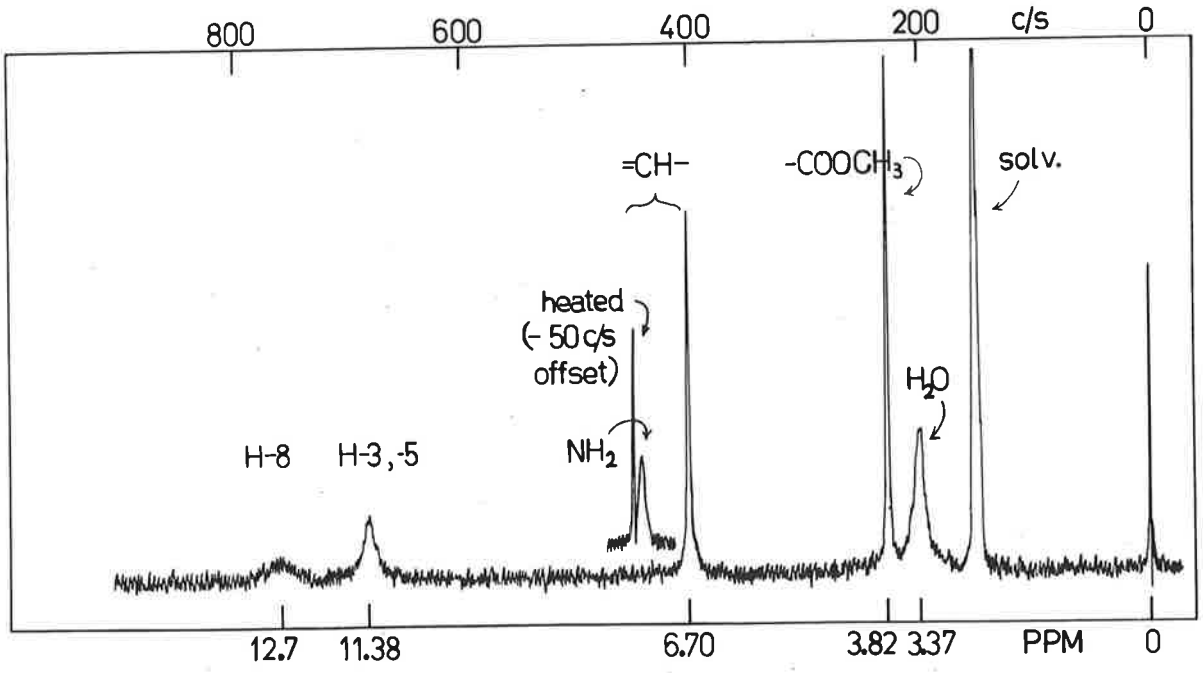

800
600
400
200
c/s
0
=CH-
-COOCH3
solv.
heated
(- 50 c/s
offset)
H2O
NH2
H-8
H-3,-5
12.7
11.38
6.70
3.82
3.37
PPM
0

fig. 2

60-8

CIBA Ltd.
Physical Laboratories
Basel, Switzerland

August 28, 1963

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

Dear Dr. Shapiro:

With the usual tardiness I should like to report on some observations concerning

6β-substituted steroids.

As is now well known the chemical shifts of the 18- and 19-hydrogen atoms (tertiary methyl groups) of steroids may easily be calculated. Each substituent at a certain position of the steroid frame makes a distinct contribution to their chemical shifts. Summing-up these contributions, provided they are known, one obtains the total chemical shift of the 18- and 19-hydrogen atoms. Until now it has been successfully assumed that the contributions to the chemical shift of the 19-hydrogen atoms of substituents at rings B, C and D are independent of the configuration at C-5, i.e. that for these substituents it does not matter if rings A and B are cis or trans linked.

Prompted by a paper of Y.Kawazoe, Y.Sato, M.Natsume, H.Hasegawa, T.Okamoto and K.Tsuda, Chem. and Pharm. Bulletin Pharm. Soc. Japan 10, 338 (1962), we have taken a second look at this problem. These authors found for 3,17-dioxo-6β-hydroxy-Δ^4-androstene and 3,20-dioxo-6β-hydroxy-Δ^4-pregnene and the respective acetoxy steroids smaller values for the additional chemical shifts of the 19-hydrogen atoms due to the 6β-substituents than we did [Helv. Chim. Acta 44, 1380 (1961)].

Therefore the PMR spectra of 15 6β-hydroxy- and 6β-acetoxy-steroids with 5α- or 5β-configuration or a double bond Δ^4 have been recorded and the additional chemical shifts due to the 6β-substituents have been determined. The result is surprising:

	19-H	
	cps*	ppm
6β-OH with 5α-steroids	13.5	0.225
6β-OH with 5β- or Δ^4-steroids	11.5	0.192
6β-OAc with 5α-steroids	11.0	0.183
6β-OAc with 5β- or Δ^4-steroids	5.5	0.092

*cps at 60 Mcps

Two possible explanations for these rather large differences are envisaged:

1. The 1,3-diaxial interaction between the C-19 methyl group and the 6β-substituent leads to different deformations of the rings according to the configuration at C-5.
2. The rotation of the hydroxy and acetoxy groups is hindered differently for the several configurations.

A repulsion between the C-19 methyl group and the 6β-substituent leads, in the case of 5α-configuration, to a conformation in which the substituent is eclipsed with the 4-CH_2 group while in the case of 5β-configuration it is eclipsed with the 5β-hydrogen atom, the latter being energetically favored. Therefore a deformation of ring B should be more easily possible for 5β-configuration. Symmetry considerations of the type discussed earlier (Helv. Chim. Acta, loc. cit. and Mellonmr Nr. 36) show the contribution of the 6β-substituent in the case of 5α-configuration to be of the "normal" magnitude, i.e. about equal to those of the 2β- and 4β-substituents. The 8β- and 11β-analogs are not exactly comparable as they experience a double 1,3-diaxial repulsion (due to the C-19 and C-18 methyl groups).

Nevertheless, we do not believe that the relatively big difference in the contributions of 6β-substituents is merely a consequence of the different ring deformations. If such deformations were so easily possible and if they could cause such large differences in the contributions of substituents, then much greater deviations between the calculated and the measured chemical shifts of the 18- and 19-hydrogen atoms would be expected than are actually found.

In a forthcoming paper (Helv. Chim. Acta, fasc. VI, 1963) on the chemical shifts of the 18- and 19-hydrogen atoms of 265 steroids and their dependence upon substituents the question of the different contributions of the 6β-substituents is discussed more comprehensively. The contributions due to identical functional groups in equivalent positions, i.e. in approximately the same steric relation to one of the tertiary methyl groups, are given and possible reasons for the variation of these contributions within sets of identical functional groups in equivalent positions are discussed.

Sincerely yours,

Zürcher

R. F. Zürcher

60-10

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

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

August 29, 1963

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

Re: Two New Diagonalizing Operators

Dear Barry:

We would like to describe a way of evaluating the effects of certain exponential operators[1] and then a way of using these operators to diagonalize two specific Hamiltonians. We are curious to see if anyone else finds these techniques of interest.

The rotation operators $\exp(i I_x \theta)$, $\exp(i I_y \theta)$, and $\exp(i I_z \theta)$ can be used to diagonalize some Hamiltonians encountered in NMR. For example, Anderson and Freeman[2] have employed a similarity transformation by $\exp(i I_{y(x)} \theta)$ to handle a double resonance Hamiltonain. More generally, the

$$\mathcal{H}_z = AI_x + BI_y + CI_z \qquad (1)$$

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1. C. P. Slichter, "Principles of Magnetic Resonance", Harper & Row (1963), p. 23.

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2. W. A. Anderson and R. Freeman, J. Chem Phys., 37, 85 (1962).

Hamiltonian (1) is made diagonal on the I_z basis set via a transformation by $\exp(i I_y \phi) \times \exp(i I_z \theta)$ when $\theta = \tan^{-1}(B/A)$ and $\phi = \tan^{-1}\left(\frac{\sqrt{A^2+B^2}}{C}\right)$. Unfortunately, this trick with rotation operators won't work for more complicated Hamiltonians such as those for a quadrupolar nucleus exposed to a non-zero electric field gradient or for an AB system.

For two special cases, however, the Hamiltonain c a n be diagonalized by using a more general form of these rotation operators: $\exp(i\mathcal{O}\theta)$, where $\mathcal{O}$ is any Hermitian operator. Unless $\mathcal{O}$ is Hermitian, the inverse of $\exp(+i\mathcal{O}\theta)$ will not be $\exp(-i\mathcal{O}\theta)$. To find the effect of a transformation by $\exp(i\mathcal{O}\theta)$, successive derivatives of the transformed operand are taken -- just as is done to calculate the effect of the rotation operators.[1] These derivatives in turn involve commutators of $\mathcal{O}$ with various angular momentum operators. The important point to note is this: for a given spin basis set, only a limited number of possible operators exist that can arise for a given commutator. For example, consider $[I_+J_+, I_+J_-] = I_+[J_+,J_-]I_+ = I_+^2[J_+,J_-]$. Now, on the ½-½ basis set, I_+^2 is a null matrix, so that this particular commutator on this particular basis set equals zero instead of $2 I_+^2 J_z$.

The way to take advantage of such simplifications for a single-spin basis set is to express all operators as combinations of "irreducible tensor components" T_q^k where k is the rank of the tensor and q denotes the component $(q = -k, -k+1, \ldots +k)$. On a spin-one basis set, $T_{+2}^2 = \frac{1}{2} I_+^2$, $T_{-2}^2 = \frac{1}{2} I_-^2$, and $T_0^2 = \frac{1}{\sqrt{6}}\{3I_z^2 - 2\}$ [3]. These tensors are used because their commutators are readily calculable from a formula

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3. E. Ambler, J. C. Eisenstein, and J. F. Schooley, J. Math Phys., 3, 118 (1962).

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given by Judd[4] in terms of 3-j and

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4. B. R. Judd, "Operator Techniques in Atomic Spectroscopy", McGraw-Hill (1963), p. 102 and p. 157.

6-j symbols:

$$[T^{k_1}_{q_1}, T^{k_2}_{q_2}] = \sum_{k_3,q_3} (-1)^{2I-q_3}\left((-1)^{k_1+k_2+k_3}-1\right)\sqrt{2k_1+1}\sqrt{2k_2+1}\sqrt{2k_3+1} \times \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix} \begin{Bmatrix} k_1 & k_2 & k_3 \\ I & I & I \end{Bmatrix} T^{k_3}_{q_3} \qquad (2)$$

where the underlined expression is the 3-j symbol and the expression in curly brackets is the 6-j symbol. Note that the commutator depends on I, the spin angular momentum. These 3-j and 6-j symbols automatically take care of the fact that only a limited number of operators need be considered for a given basis set. An example of the restrictions imposed by formula (2) is the fact that the 6-j symbol is always zero for $k \geq 2I+1$, so tensors of rank higher than $2I$ need not be considered. The transformations in Table IA were calculated by taking derivatives of the transformed operands and then by simplifying with the commutation formula. From these results it can be seen that the quadrupole Hamiltonian

$$\mathcal{H}_Q = AI_z^2 + B(I_x^2 - I_y^2) + C \qquad (3a)$$

or in tensor notation

$$\mathcal{H}_Q = \alpha T_0^2 + \beta(T_2^2 + T_{-2}^2) \qquad (3b)$$

is diagonalized on the spin-one basis set by transformation with the operator $\exp\left(i_x \frac{T_2^2 - T_{-2}^2}{i} \frac{\pi}{4}\right)$, which is independent of A and B and C or α and β.

To handle the more complicated case of an AB system, which involves two spins, the would-be diagonalizer must resort to double tensors $W^{A}_{a}{}^{B}_{b}$, where the W's are just shorthand notation for terms like $I_z J_z$, $I_+ J_-$, etc. Table II

TABLE IA

$\mathcal{O}$	operand $\mathcal{M}$	transformed operand	basis set 1
$\frac{T^2_2 - T^2_{-2}}{mi}$	T^2_0	T^2_0	
$\frac{T^2_2 - T^2_{-2}}{mi}$	$T^2_2 + T^2_{-2}$	$(T^2_2 + T^2_{-2})\cos(\frac{2\theta}{m})$ $+\sqrt{2}\,T'_0 \sin(\frac{2\theta}{m})$	

TABLE IB

$\mathcal{O}$	operand $\mathcal{M}$	transformed operand	basis set $1/2 - 1/2$
$\frac{W^{11}_{1-1} - W^{11}_{-11}}{i}$	W^{11}_{00}	W^{11}_{00}	
$\frac{W^{11}_{1-1} - W^{11}_{-11}}{i}$	$W^{11}_{1-1} + W^{11}_{-11}$	$(W^{11}_{1-1} + W^{11}_{-11})\cos 2\theta$ $+ (W^{10}_{00} - W^{01}_{00})\sin 2\theta$	
$\frac{W^{11}_{1-1} - W^{11}_{-11}}{i}$	W^{10}_{00}	$-\frac{1}{2}(W^{11}_{1-1} + W^{11}_{-11})\sin 2\theta$ $+\frac{1}{2}(W^{10}_{00} - W^{01}_{00})\cos 2\theta$ $-\frac{1}{2}(W^{10}_{00} - W^{01}_{00}) + W^{10}_{00}$	
$\frac{W^{11}_{1-1} - W^{11}_{-11}}{i}$	W^{01}_{00}	$+\frac{1}{2}(W^{11}_{1-1} + W^{11}_{-11})\sin 2\theta$ $-\frac{1}{2}(W^{10}_{00} - W^{01}_{00})\cos 2\theta$ $+\frac{1}{2}(W^{10}_{00} - W^{01}_{00}) + W^{01}_{00}$	

When the operand $\mathcal{M}$ in the second column is operated on the left by $\exp(i\mathcal{O}\theta)$ and simultaneously on the right by $\exp(-i\mathcal{O}\theta)$, the result is the transformed operand given in the third column. m is any real constant, not zero.

TABLE II

Translation of double tensors W^{AB}_{ab} on the ½-½ basis set into equivalent expressions as the products of angular momentum operators.

A	a	B	b	operator representation
1	1	1	1	$+I_+J_+$
1	1	1	0	$-\sqrt{2}\,I_+J_z$
1	1	1	-1	$-I_+J_-$
1	0	1	1	$-\sqrt{2}\,I_zJ_+$
1	0	1	0	$+2I_zJ_z$
1	0	1	-1	$+\sqrt{2}\,I_zJ_-$
1	-1	1	1	$-I_-J_+$
1	-1	1	0	$+\sqrt{2}\,I_-J_z$
1	-1	1	-1	$+I_-J_-$
0	0	1	1	$-\frac{1}{\sqrt{2}}J_+$
0	0	1	0	$+J_z$
0	0	1	-1	$+\frac{1}{\sqrt{2}}J_-$
1	1	0	0	$-\frac{1}{\sqrt{2}}I_+$
1	0	0	0	$+I_z$
1	-1	0	0	$+\frac{1}{\sqrt{2}}I_-$

translates these W's on the ½-½ basis set into regular operator language. From a commutation formula similar to (2)[4], the transformations listed in Table IB were calculated. By use of these tabulated relations, it can be seen that the Hamiltonian $\mathcal{H}_{AB}$ for an AB system

$$\mathcal{H}_{AB} = AW_{00}^{10} + BW_{00}^{01} + \frac{J}{2}W_{00}^{11} - \frac{J}{2}(W_{1-1}^{11} + W_{-11}^{11}) \qquad (4)$$

on the ½-½ basis set is diagonalized by the operator $\exp(i \times \frac{W_{1-1}^{11} - W_{-11}^{11}}{i} \times \phi)$ when $2\phi = \tan^{-1}(\frac{J}{B-A})$.

Right now these generalized rotation operators don't appear very practical. Perhaps they could be used to make more convenient some first order perturbation calculations: perform the transformation on the perturbing operator and take diagonal matrix elements on the I_z or $I_z J_z$ basis set. Anyhow, we think they're interesting.

Yours very truly,

Richard H. Albert

John D. Baldeschwieler

/ms

60-16

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY

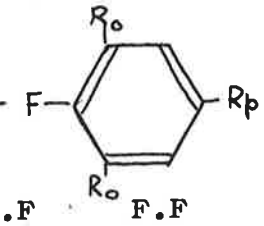
Chemistry Department,
GLASGOW, C.1
TELEPHONE : BELL 4400

2nd September, 1963.

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

Dear Barry,

In collaboration with Dr. D. W. A. Sharp and Mr. J. Winfield we have recently run F^{19} spectra of several highly substituted chlorofluorobenzenes (e.g. C_6ClF_5, $C_6Cl_2F_4$ isomers, $C_6Cl_3F_3$ isomers). The chemical shifts and coupling constants are broadly in agreement with other peoples figures and can be summarised:-

Chemical shifts in 

R_o	F.F	F.F	F.Cl	F.Cl	Cl.Cl	Cl.Cl
R_p	F	Cl	F	Cl	F	Cl
ϕ	161.5	155.5	138.2	133.2	116.4	112.6
No. of examples	3	4	4	5	4	2
Range of values (p.p.m.)	1.7	1.5	5.0	5.6	4.1	0.1

Notes

$\phi \equiv$ p.p.m from CCl_3F as internal standard.
Spectra were run on 30% solution in CCl_4 on a Perkin Elmer instrument at 37.65 Mc/s.

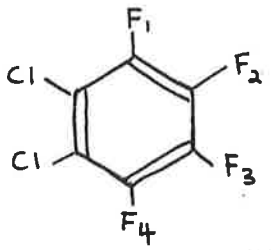
The predominant effect of ortho and para substituents is noticed. The nature of meta substituents had very little effect.

The effects of OH and H as substituents in the ortho and para positions resembled those of F and Cl respectively (to within 1 p.p.m.).

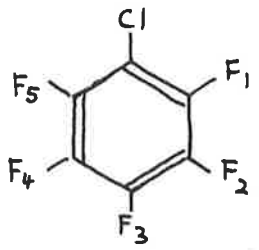
F^{19} - F^{19} Coupling constants

	ortho	meta	para	
Average	20.4	2.3	8.4	c.p.s.
No. of Examples	11	11	7	
Range of values	2.0	4.6	3.4	c.p.s.

Two compounds which had second order spectra were C_6ClF_5 and o-$C_6Cl_2F_4$. From these spectra we got the results:-



$J_{12} = \pm 20.5$; $J_{13} = \mp 2.5$;
$|J_{23}| = 19.1$; $|J_{14}| = 7.4$ c.p.s



$J_{12} = \pm 20.7$; $|J_{23}| = 19.6$
$|J_{13}| = \sim 1.0$; $|J_{15}| = 5.3$
$J_{14} = \mp 6.4$; $|J_{24}| = 2.0$ c.p.s.

The signs of J para and J meta are thus opposite to that of J ortho, confirming Evans' findings by the double resonance approach [Mol.Phys. 6, 179 (1963)]. I wonder whether J meta always has an opposite sign to that of J ortho, we had some very small meta couplings of indeterminate sign and it is possible the values lie either side of zero (any comments?).

Yours sincerely,

Peter Bladon.

Peter Bladon.

60-18

UNIVERSITY OF FLORIDA
GAINESVILLE

DEPARTMENT OF CHEMISTRY

September 3, 1963

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

Dear Barry:

I trust the following material on recent work in our laboratories will serve to extend our subscription to your very valuable Newsletter. Rather than present material at length, it has seemed appropriate to give some information concerning papers which are being submitted and we hope eventually will be published.

NUCLEAR MAGNETIC RESONANCE STUDIES OF ADSORPTION OF THORIUM OXIDE, Wallace S. Brey, Jr., and Kenneth D. Lawson. To be submitted to J. Phy. Chem. Preprints are available.

Abstract and Introduction: Nuclear magnetic resonance line widths and relaxation times have been measured for water, methyl alcohol, ethyl alcohol, and butylamine adsorbed on thorium oxide. The source of the thorium oxide and the conditions of its activation influence the relaxation times of the adsorbate. Temperature dependence studies of the relaxation times of adsorbed water permit an estimate of the activation energy for the motions producing relaxation of the adsorbed molecules. Similar studies of the organic molecules lead to a quite different sort of information: it is possible to see in the line width thermal transitions corresponding to the successive loss of motional freedom of various parts of the molecule. Line width behavior seems also to be related to the ratio of molecular diameter to pore size.

A number of measurements have been reported in the literature of line widths or relaxation times for various systems. However, it has not been in general possible to differentiate between the behavior of various portions of the adsorbed molecule. For hydrogen atoms, the usual range of chemical shifts is 500 to 1000 cycles at 60 megacycles, and the line widths of interest are of the order of several hundred to several thousand cycles, so that the absorption peaks of nuclei of different chemical shifts overlap one another. Furthermore, not much attention has been paid to the relationship between the history and structure of the adsorbent and the n.m.r. parameters of adsorbates on its surface.

In the present work, temperature dependence studies have led to results which can only be interpreted in terms of varying behaviors of different parts of the adsorbate molecule. Line width measurements for methanol, ethanol, and n-butylamine adsorbed on thorium oxide, carried out over the range from room temperature down to -100° C. show that restriction of motion of part of the molecule, presumably the polar group attached to the surface, occurs not far below room temperature, while a narrow absorption band continues to appear at very much lower temperature. The latter must be associated with persistence of the free motion of the alkyl portions of the molecules at the lower temperatures.

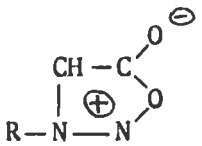
Samples of thorium oxide prepared by dehydration of the hydroxide have also been compared with those obtained by thermal decomposition of the solid oxalate. As it will be shown below, not only does this difference in origin make a considerable difference in the behavior of the adsorbate, but also conditions of activation of the material from any one source, such as the temperature, modify the n.m.r. behavior of the adsorbate.

CHEMICAL SHIFTS AND TEMPERATURE DEPENDENCE OF SPIN-SPIN COUPLING CONSTANTS OF FLUOROPROPENES. Kermit C. Ramey and Wallace S. Brey, Jr. To be submitted to J. Chem. Phys.

Abstract: NMR spectral parameters of the compounds CF_2=CFY in which Y is CF_3, CF_2Cl, CF_2Br, CF_2I, or COF have been measured at room temperature and spin-spin coupling constants in four of these molecules have been investigated in the range of temperature from -100° to +100° C. Some aspects of the temperature dependence of the coupling constants can be related to changing equilibria between cis-trans or rotational isomers, but there is an intrinsic temperature dependence, aside from these effects, which is attributed to excitation of molecular vibrations. Particular J values which change magnitude in one direction with increasing temperature are found to change magnitude in the opposite direction in regular fashion as one goes through the series of halogen-substituted compounds from fluorine to iodine. Chemical shifts observed at room temperature are discussed in terms of the effects of substituents.

HYDROGEN CHEMICAL SHIFTS OF 3-ALKYL AND 3-PHENYL SYDNONES. K. D. Lawson, Wallace S. Brey, Jr., and L. B. Kier. Submitted to J. Am. Chem. Soc. Preprints are available.

Abstract: The sydnone ring system is an unusual one, for it can not be represented satisfactorily by any canonical structure which does not place formal charges somewhere in the ring. The conventional formulation of a 3-substituted sydnone is:



The chemical and spectroscopic properties of molecules containing the sydnone ring have been interpreted to indicate a six-electron aromatic system, delocalized over the five atoms of the ring. Proton resonance spectra of five 3-alkyl sydnones and 3-phenyl sydnone have been determined in acetone and in chloroform solution. The ring hydrogen chemical shifts in chloroform solution are strongly concentration-dependent in a manner which indicates that the chloroform solvent is breaking down aggregates of solute molecules. The resonances of the hydrogens in the substituent group which are alpha to the sydnone ring fall strikingly far downfield, indicating an unshielding by the aromatic ring current as well as by the electronegative effect of the nitrogen atom in the ring.

Cordially yours,

Wallace S. Brey, Jr.

Wallace S. Brey, Jr.
Associate Professor of Chemistry

R-12003-CRL

60-20

E. I. du Pont de Nemours & Company
INCORPORATED
Carothers Research Laboratory
Experimental Station
Wilmington, Delaware

Textile Fibers Department

September 6, 1963

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

Dear Dr. Shapiro:

We have recently investigated the behavior of polycrystalline succinonitrile at temperatures below the melting point using wide line NMR. Early dielectric constant and other measurements had indicated a rotational transition in solid $(CNCH_2)_2$, but at the same time they had underscored its peculiarity. The transition occurs at about 230°C, and it was thought to be probably a combination of intermolecular and intramolecular rotations. Below this temperature the solid exists entirely in the C_2 (gauche) rather than C_{2h} (trans) configuration.

Spectra were recorded on a Varian DP-60 spectrometer at 15.9 $Mc/_s$ using a gas-flow type cryostat. At low temperatures the spectrum is a doublet characteristic of close-lying pairs of nuclei. The IBM 7090 at the University of Maryland Computer Center was programmed and experimental second moments calculated.

The second moment has a value of17.7 $gauss^2$ and remains constant up to 229°K, at which point it drops to 0.7 $gauss^2$. The low temperature value is in good agreement with the theoretical second moment, although it cannot be used to establish the low-temperature configuration of the molecules. The sharp drop in second moment at 229°K indicates the onset of rotation in agreement with infrared and other observations. In addition, the NMR data clearly indicate that the transition is a general isotropic reorientation involving the whole molecule and not a simple rotation or oscillation about the C-C bond. X-ray results have shown

that the crystal lattice is too small to accommodate freely rotating succinonitrile molecules; therefore, the rotation is probably not completely free, but as it has been suggested, coupled to the rotation of neighboring molecules with two rotating molecules in a cell penetrating into their mutual rotation ranges.

There is a further reduction in second moment between 240° and 280°K. This is explained by postulating self-diffusion in the crystal lattice. This is corroborated by the close agreement between the lattice energy and the calculated energy required to form a vacancy in the lattice by removal of one molecule and the activation energy required to move an adjacent molecule into this vacancy.

This work was done at the University of Maryland, and it will appear shortly in J. Chem. Phys. in greater detail.

I have recently joined the Du Pont Company Experimental Station, and I will appreciate receiving my copies of the NMR newsletter here.

Sincerely yours,

NYLON TECHNICAL DIVISION

Leon Petrakis

Leon Petrakis

LP:mb

60-22

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

6 September 1963

Proton NMR Studies of CHDO and CH_2O[1]*

B. L. Shapiro, R. M. Kopchik and S. J. Ebersole

We have measured $|J_{HD}|$ in CHDO[2] in various solvents, and from the values so obtained, have deduced[3] the corresponding $|J_{HH}|$ in CH_2O. We have also measured the chemical shifts of CHDO and CH_2O in the various solvents and the differences between these shifts. Our results are summarized in Table I.

To the best of our knowledge, these are by far the largest $|J_{HD}|$(gem) and $|J_{HH}|$(gem) values which have been reported. In fact, they appear to be the largest H-D and H-H couplings known with the exception of the value obtained for the HD molecule[4]. Analogous, even larger solvent dependences of $|J_{HH}|$(gem)'s have also been observed in other systems[1,5].

Also noteworthy are the $\Delta\tau$'s observed[6], other reported values[7] being $\leq 0.017 \pm 0.002$ ppm per D-for-H substitution.

A fuller account and discussion of these and other aspects of the spectra will appear in due course.

---

*Submitted for publication in J. Chem. Phys.

[1]Part II of the series "NMR Spectral Studies of sp^2-type CH_2 Systems", for Part I, see B. L. Shapiro, S. J. Ebersole and R. M. Kopchik, J. Mol. Spectry., In Press.

[2]Prepared by pyrolysis of eu-$(CHDO)_n$, supplied by Merck, Sharp and Dohme of Canada, Ltd.

[3]Using the relationship $|J_{HH}| = \frac{\gamma H}{\gamma D}|J_{HD}| = 6.5144|J_{HD}|$. The value of γ_H/γ_D used is that derived from B. Smaller, E. Yasaitis and H. L. Anderson, Phys. Rev., 81, 896 (1951).

[4]H. Y. Carr and E. M. Purcell, Phys. Rev., 88, 415 (1952).

[5]J. H. Goldstein, J. Mol. Spectry., In Press.

[6]The apparently real solvent dependence of $\Delta\tau$ is intriguing, but not as yet to be taken as firmly established.

[7](a) G. V. D. Tiers, J. Chem. Phys., 29, 963 (1958).
(b) H. S. Gutowsky, J. Chem. Phys., 31, 1683 (1959).
(c) G. S. Reddy and J. H. Goldstein, J. Mol. Spectry., 8, 475 (1962).

TABLE I. NMR Spectral Data[†] on CHDO and CH_2O

Solvent	$\lvert J_{HD} \rvert$[a] (c/s)	$\lvert J_{HH} \rvert$[b] (c/s)	τ^{c}_{CHDO}	τ_{CH_2O}	$\Delta\tau$[d] (ppm)
Tetramethylsilane	6.52	42.42	0.427	0.398	0.029
Tetrahydrofuran	6.26	40.70	0.440	0.417	0.023
Acetonitrile	6.18	40.22	0.417	0.391	0.026

[†] All data obtained on dilute (< 5%) solutions, using a carefully calibrated Varian Associates A-60 NMR spectrometer operating at 60 mc/sec. Sample temperature 37 ± 1°C.

[a] P.E.: ± 0.02 c/s.

[b] Calculated as described in Ref. 3; P.E.: ± 0.13 cps.

[c] Chemical shift on the τ-scale. See G. V. D. Tiers, J. Phys. Chem., 62, 1151 (1958). P.E.: ± 0.001.

[d] P.E.: 0.002 ppm or less.

Monthly Ecumenical Letters from Laboratories Of N-M-R

60-24

Eidg. Technische Hochschule
Laboratorium
für Organische Chemie
Zürich

ZÜRICH, August 31, 1963
Universitätstr. 6
Tel. (051) 32 73 30

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

Dear Dr. Shapiro:

We have recently investigated a group of metabolites from Actinomyces called rifamycins. Extensive degradative and spectroscopic studies lead eventually to the unusual structure I for rifamycin S. In the n.m.r. spectrum of this compound (Figure 1) 4 doublets a-d ($J \sim 7$ cps) corresponding to four CH_3-(CH)-groups (C-31; C-32; C-33 and C-34) are easily recognizable. Noteworthy is the position of two of these doublets at $\delta = 0{,}22$ and $0{,}67$ ppm (Varian A 60, $CDCl_3$). The occurrence of the methyl proton signals at such high magnetic fields is evidently due to the long range shielding of methyl protons located above the plane of the naphthoquinone nucleus by the magnetic field of aromatic π-electrons. This shielding becomes much stronger when the compound is reduced to the naphthalene derivative II. The signal of the one of the methyl groups in the n.m.r. spectrum of II lies at $\delta = -0\,59$ ppm and can be easily overlooked in routine work. Similar results have been obtained in the course of our work with many other derivatives of rifamycins.

The unusual position of the methyl protons at high magnetic fields helped considerably to recognize at a very early stage of our work that the aromatic system in rifamycins must be bridged by a long aliphatic chain, as in cyclophanes [cf. J.S. Waugh and R.W. Fessenden, JACS 79, 846 (1957)] and other so called ansa-compounds.

Dr. B.L. Shapiro August 31, 1963

When the aliphatic bridge in rifamycins is open on one side, as in degradation product III, the signals of all four CH_3-(CH)-groups (Figure 3) almost coincide and have the normal δ-value around 1.

We think that these results may be of interest not only to natural product chemists who use n.m.r. as a tool for structure elucidation, but that they also deserve further study with simpler model compounds.

With apologies for delay in "paying" our subscription and with best personal regards,

Sincerely yours,

W. v. Oppolzer V. Prelog

W. v. Oppolzer and V. Prelog

60-26

Figure 1

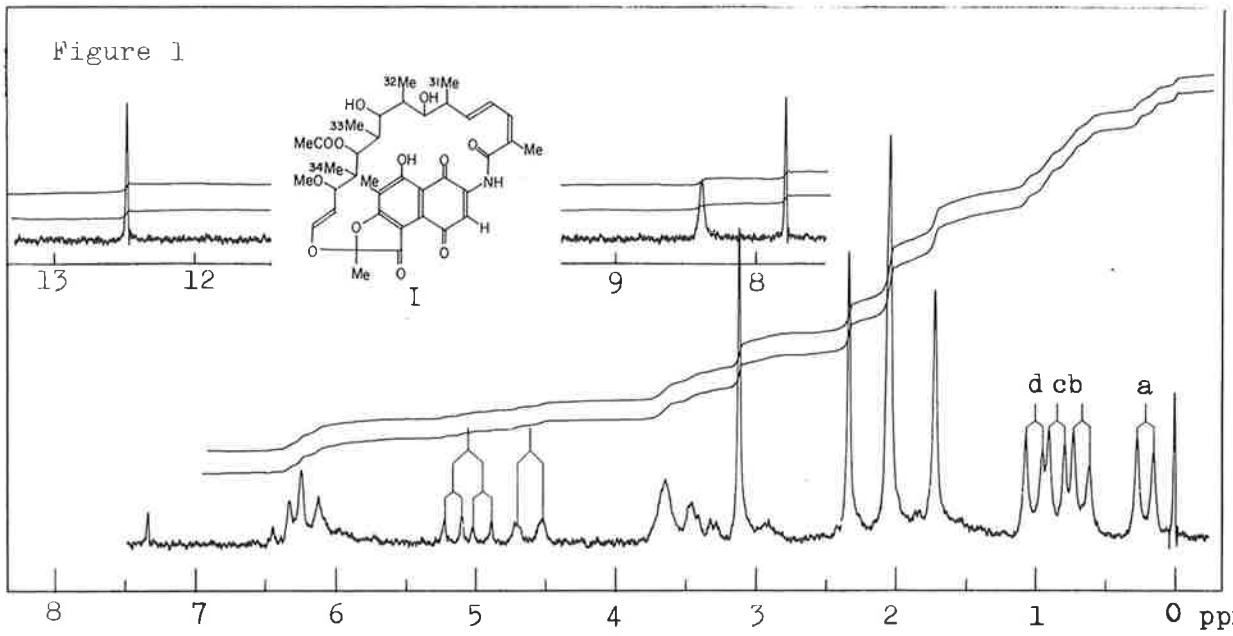


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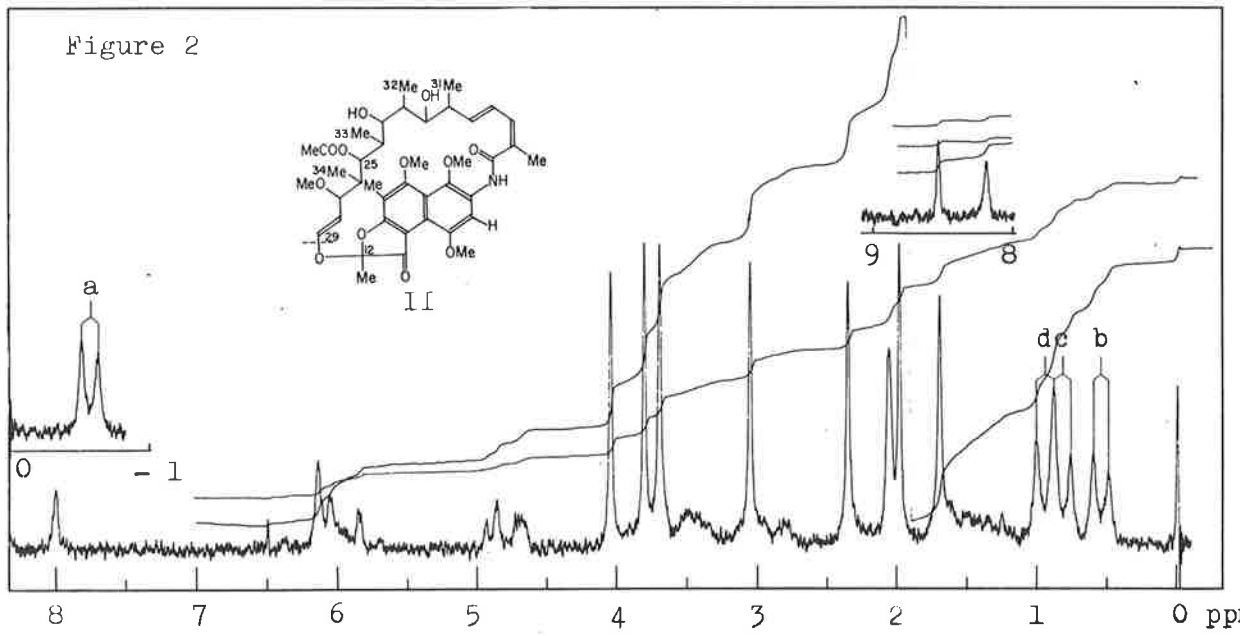
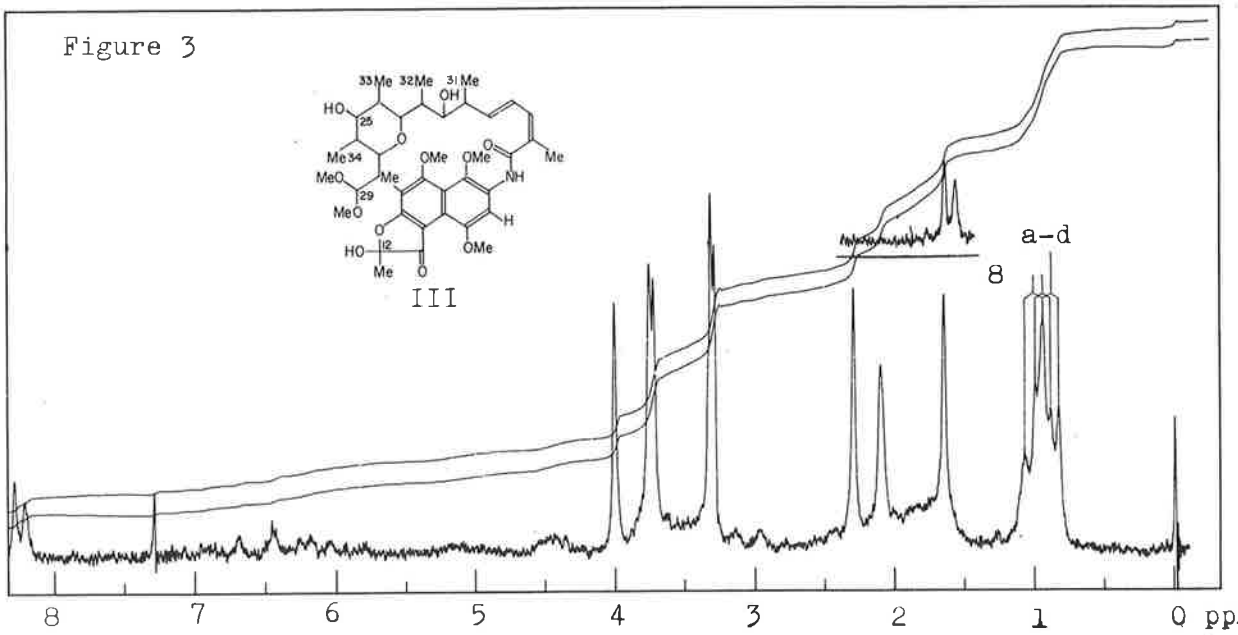
Figure 2



II

Figure 3



III

INSTITUT FÜR ELEKTROWERKSTOFFE

GEMEINNÜTZIGES FORSCHUNGSINSTITUT DER FRAUNHOFER-GESELLSCHAFT

INSTITUTSDIREKTOR:
PROF. DR. R. MECKE

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

FERNRUF NR. 5514
FREIBURG I. BR.
ECKERSTRASSE 4

Ihre Zeichen | Ihre Nachricht vom | Unser Zeichen

High-resolution NMR-Spectra of Orientated Molecules.

Since about three years we have been interested in the proton magnetic resonance (PMR) spectra of liquid crystals, especially of the so-called nematic type[1]. We have obtained some interesting results which we should like to discuss here briefly.
In the nematic phase the long-shaped molecules are aligned essentially parallel to each other. This direction is the optical axis of the anisotropic melt, turning parallel to the external magnetic field in NMR experiments. Despite their ordering, the molecules are highly mobile(no regular arrangement of the centers of the molecules, low viscosity), and therefore the intermolecular direct dipole-dipole interaction is reduced practically to zero as in isotropic liquids. On the other hand, the reduction of the intramolecular dipole-dipole interaction is less complete because of the molecular orientation. The reorientation of the molecules, however, is at least in some cases very rapid as can be shown from dielectric measurements with p-azoxyanisole[2] (PAA; $R\text{-}O\text{-}C_6H_4\text{-}\underset{O}{N}{=}N\text{-}C_6H_4\text{-}O\text{-}R$, $R=CH_3$; mp. 117°C, clearing point 136°C). We expected therefore that the PMR-spectrum of this compound in the nematic phase should consist of a large number of sharp lines.
The spectrum of PAA has been extensively studied by several authors[3] and has been described as a broad diffuse triplet. In contrast to these earlier observations we have found a very detailed fine structure of the signal of the nematic phase in agreement with our expectation (fig.1). With improved resolution even more details are to be expected.
If the methyl groups are replaced by larger groups ($R= C_nH_{2n+1}$, n=2 to 7) the spectra become more and more quasi-continuous due to the strongly increasing number of lines.
A very sharp line superimposed on a much broader signal has been observed in the spectra of nematic p-butoxybenzoic acid ($C_4H_9OC_6H_4CO_2H$) and similar compounds. The sharp line is assigned to the acidic protons rapidly exchanging between different molecules.
Upon heating above the clearing point (isotropic phase) all compounds gave normal high-resolution spectra with chemical

shifts and J-couplings close to those observed in solutions. We have extended our PMR investigations to solutions of organic molecules (not possessing liquid crystalline properties) in nematic phases. By this matrix method a partial orientation of the dissolved molecules can be achieved, the degree of ordering being much higher than that attainable in electric fields (Mc Lauchlan and Waugh, MELLONMR 54).
Using normal high-resolution technique we have taken spectra of "isolated" n-spin systems (n=1 to 6), some examples are given in fig.2. and 3. The spectra consist of sharp lines (some cps) with an overall splitting up to several kcps, depending on the number of interacting protons, internuclear distances and the orientation and degree of ordering of the molecules. The broad signal of the nematic matrix is lost in the background.
The following applications are possible:

1) Measurement of relative internuclear distances.
2) Determination of arrangement and degree of ordering; study of the intermolecular forces.
3) Measurement of the anisotropy of the chemical shift, including isotropic contributions of neighbouring groups.
4) Determination of the absolute sign and perhaps of the anisotropic part of the indirect spin-spin-coupling.
5) Investigation of the quadrupole interactions.

Some of our results may be mentioned here:

1) Benzene, dissolved in the nematic melt of 4.4-di-n-hexyloxy-azoxybenzene (R= C_6H_{13}): Degree of ordering (depending on concentration and temperature) $S=\langle 3\cos^2\Theta - 1\rangle / 2 = -0.099$ (Θ = $\sphericalangle$ C_6-axis and optical axis)
   Chemical shift: 420.7 $\pm$ 0.4 cps (nematic) below TMS
   432.1 $\pm$ 0.3 cps (isotropic) " "
   The anisotropy of the screening constant turns out to be $\Delta\sigma = \sigma_z - \frac{1}{2}(\sigma_x + \sigma_y) = -2.88 \cdot 10^{-6}$ (z-axis parallel C_6)
   The J-coupling is observable in the spectrum of the nematic solution in spite of the strong direct dipole-dipole interaction.
2) 1.3.5-Trichloro-benzene in the same nematic matrix:
   $S = -0.14$; $\Delta\sigma = -5.0 \cdot 10^{-6}$
   The anisotropy is considerably stronger because of the influence of the chlorine atoms.
3) We have also investigated the spectra of tetrachloro-substituted anisoles and of 2.3.5.6-tetrachloro-toluene. For the latter compound we obtained for the ratio of proton distances : $r(H_4-H_{CH_3}) / r(H_{CH_3}-H_{CH_3}) = 3.225 \pm 0.025$

Finally we should like to point out that solutions of stable free radicals in nematic melts are very easily obtained in small concentrations sufficient for ESR-experiments. This might be of interest to those, who would like to investigate the anisotropic part of the nucleus-electron spin-spin interaction.

Sincerely yours,

Alfred Saupe Gerhard Englert

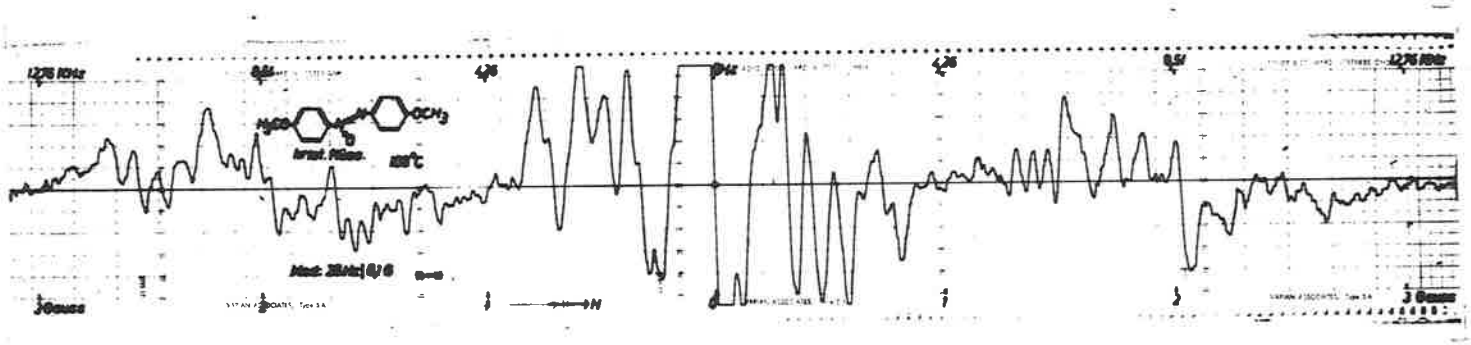


Fig.1. p-azoxyanisol, spectrum of the nematic phase(derivative curve).

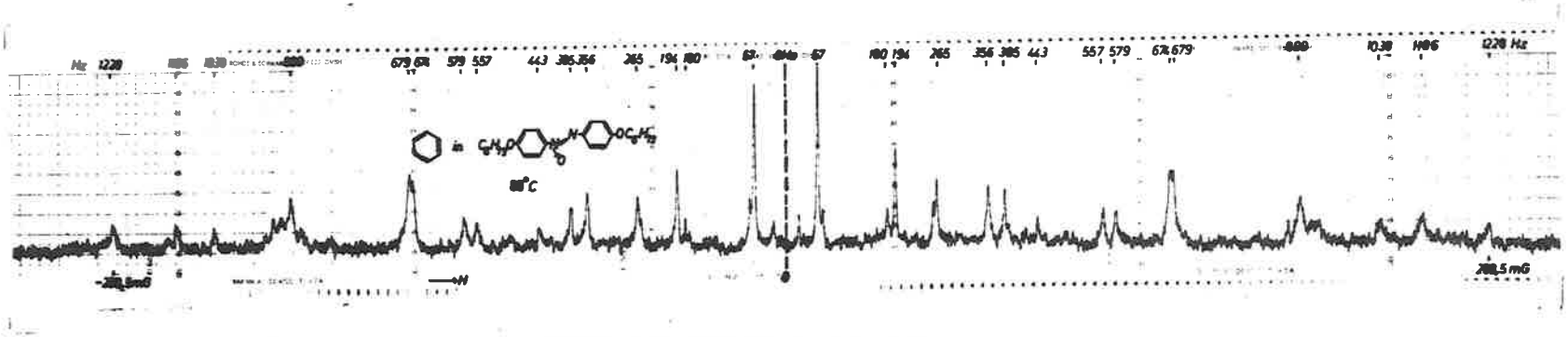


Fig.2. benzene, spectrum in nematic solution.

References

1) On liquid crystals see: G.W.Gray,"Molecular Structure and the Properties of Liquid Crystals", Academic Press, London-New York 1962;G.H.Brown and W.G.Shaw,Chem.Rev. 57,1049,(1957)
2) W.Maier and G.Meier,Z.Naturforsch.16a, 12000,(1961).
3) See for example: P.L.Jain,J.C.Lee and R.D.Spence, J.Chem.Phys.23, 878,(1955);H.Lippmann,Ann.d.Phys. 2,287,(1958);K.H.Weber,Ann.d.Phys.3,1,(1959).

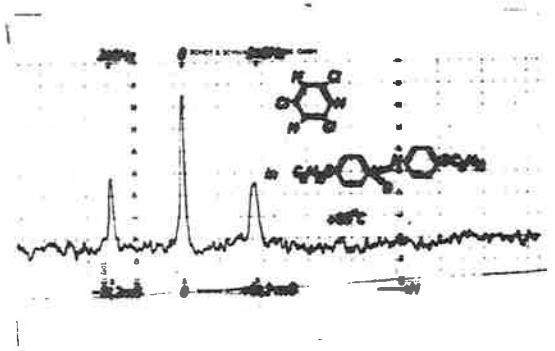


Fig.3. 1.3.5-trichlor-benzene, spectrum in nematic solution.

60-30

National Chemical Research Laboratory
of the South African Council for Scientific and Industrial Research

CSIR

Telegrams NAVORSCHEM Telephone 74-6011

PO Box 395
Pretoria

Our file Our letter Your file Your letter

4 NMR

AIR MAIL

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

10 SEP 1963

Dear Dr. Shapiro,

pH-Dependence of Coupling Constants in Aspartic Acid

In the course of an investigation of the NMR-spectra of certain α-amino acids, we found a strong pH-dependence of the coupling constants[1]. A detailed study of aspartic acid showed a direct relation between the geminal coupling constant and the degree of dissociation of the amino group. Using the dissociation constant[2]

$$\frac{[RNH_2] \cdot [H^+]}{[RNH_3^+]} = 9.842$$

[with $R = (CO_2^-)\text{-}CH_2\text{-}CH(CO_2^-)$], we calculated the percentage of RNH_2 at a given pH and plotted the coupling constants against these values (Figure 1). The relationship is almost linear. The deviation from linearity may well be due to systematic errors in the correction of the pH-values as the pH, as well as the Na^+ concentration, were rather high.

An interpretation of these findings may be attempted in the light of Barfield and Grant's recent calculations of the angle dependence of the π-electron enhancement of geminal coupling constants.[3] Aspartic acid anhydride with a planar five-ring structure has a geminal coupling constant of 18.0 c/sec[4]. The π-electron contribution should be 4.5 c/sec giving a basic value of 13.5 c/sec. The lowest value (at high pH) measured for aspartic acid is 15.2 c/sec with a relative increase of 1.7 c/sec which corresponds roughly with the average enhancement by a freely rotating β-π-electron. Decreasing the pH means increasing the cationic form of the aspartic acid (RNH_3^+) allowing for electrostatic interaction between amino group and β-carboxyl group favouring a locked position of the carboxyl group with an increased π-electron contribution to the geminal

coupling /...

coupling constant by maximal 3.9 c/sec compared with the basic value.

As nice as this sounds, serine and cystine with no β-π-electrons in respect to the methylene group also show an increase of the geminal coupling constant with decreasing pH which cannot be explained on the same basis.

Yours sincerely,

K. Pachler
RESEARCH OFFICER
CHEMICAL PHYSICS GROUP
NATIONAL CHEMICAL RESEARCH LABORATORY

c.c. Dr. Herbstein
Dr. Abraham

KP/CV

REFERENCES

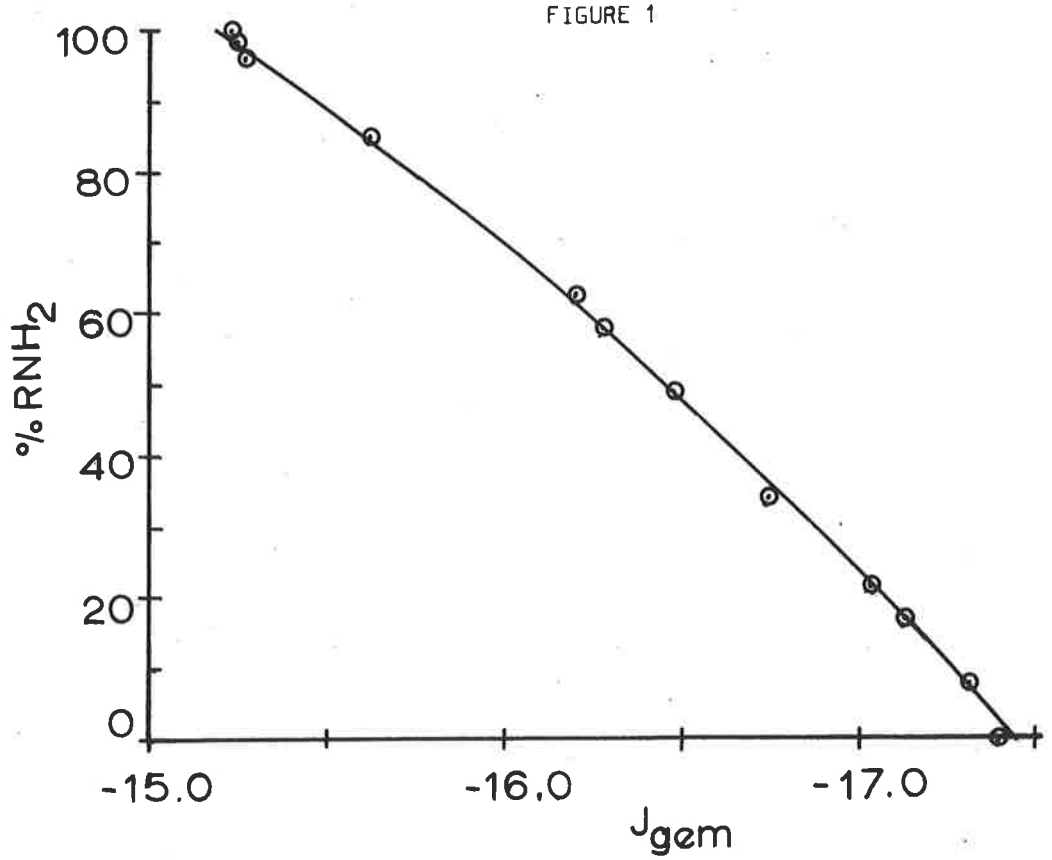
(1) K. Pachler, Mellon 50, Spectrochim. Acta (in print).

(2) A.C. Batchelder, C.L.A. Schmidt, J. Phys. Chem. 44, 893 (1940).

(3) M. Barfield, D.M. Grant, J. Am. Chem. Soc. 85, 1899 (1963).

(4) R.E. Lundin, Mellon 32.

FIGURE 1



60-32

NEW YORK UNIVERSITY
UNIVERSITY HEIGHTS, NEW YORK 53, N.Y.

DEPARTMENT OF CHEMISTRY

TELEPHONE: LUDLOW 4-0700

9/16/63

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

Dear Dr. Shapiro:

We would like to add some further observations to our previous letter in MELLONMR No. 57.

(1) The apparent singlets of the dimethylthiepin If in carbon tetrachloride and of the diketone IIIe in deuteriochloroform are not resolved[1] even at 100 Mc.! Other solvents which give apparent singlets (peak width at half-height: 1.5-2.1 c.p.s., 60 Mc.) for those two compounds: carbon disulfide, pyridine, nitrobenzene. The unique position of benzene is heavily underscored by these additional findings. In the same vein, the separation of diastereomeric oxepin (b-series) and azepine (c-series) proton resonances $\Delta\tau$ (leaving aside cases of magnetic equivalence due to conformational interconversion) increases with dielectric constant <u>except</u> for benzene solutions in which $\Delta\tau$ is abnormally small. Conversely, in the thiepins (f-series) $\Delta\tau$ appears to decrease with increasing dielectric constant <u>except</u> again for the benzene solutions which exhibit the largest values of $\Delta\tau$ (for If, the <u>only</u> measurable values!). This behavior can no doubt be related to the large diamagnetic anisotropy of benzene molecules in suitable orientations[2], but the complete ineffectiveness of the other solvents in revealing the AB pattern of If and IIe is really rather startling. Our studies are continuing and we shall report to MELLONMR again.

(2) Concerning the average position of the diastereomeric methylene protons $\bar{\tau}$ $(= (\tau_A + \tau_B)/2)$, we note that (a) $\bar{\tau}$ has its lowest value in pyridine solutions, (b) $\bar{\tau}$ of the b- and c-series has its highest values in carbon disulfide solutions, whereas $\bar{\tau}$ of the e- and f-series has its

highest values in benzene solutions. Furthermore, $\bar{\tau}$ of the I-series is invariably higher than $\bar{\tau}$ of the II- and III-series (for a given X and a given solvent) and, with a few exceptions, $\bar{\tau}$ of the II-series is similarly higher than $\bar{\tau}$ of the III series. We interpret these results in terms of shielding by the distal benzene ring and conclude that, for a given X, the biphenyl angle of torsion θ decreases in the order I > II > III. We have completely independent evidence of the same order in the u.v. spectra, which, for a given X, show a progressive red shift of the conjugation band, in the order λ_{max} I < II < III. This change in angle within each "horizontal series" (i.e. the three oxepins) is of course not revealed by the Dreiding models, which only respond to gross changes in angle strain and bond stretching, but which are insensitive to torsional and nonbonded strain.

(3) The J_{AB} values are characteristic for each horizontal series, as shown in the Table. For any one compound in each series, J_{AB} is solvent-independent. This result is in sharp contrast with the findings of Snyder[4] who has claimed a solvent dependence of diastereomeric methylene proton coupling constants in non-rigid systems. Within each series, compounds III have J_{AB} values which are larger than those of the corresponding compounds I by 0.3-0.4 c.p.s. These results may be rationalized as follows: the characteristic range of values reflects the nature of the substituent attached to the methylene carbon (e.g. oxygen or sulfur) while the small variation within each range reflects the change in θ, which may in turn affect the magnitude of the HCH angle[3].

(4) In the series of dimethylbiphenyls I, the C-methyl proton signal is a sensitive function of θ. In the Figure are plotted (circles) the methyl proton τ-values against the values of θ calculated from normal molecular dimensions. For $\theta = 90°$ the τ-value of 2,2',6,6'-tetramethylbiphenyl (τ 8.12) was selected. A theoretical estimate of the change in shielding values with geometry[5] (curve, Figure) fits the semi-experimental points rather well, and the τ-value of 7.75 found for 9,10-dihydro-4,5-dimethylphenanthrene, which is a good deal above the calculated value of 7.48, suggests out-of-plane bending and extra shielding of the methyl groups.

Nevertheless it must be pointed out that the general usefulness of the function plotted in the Figure is severely limited, as revealed by the fact that 4-methylbiphenyl, 2-methylbiphenyl and 2,2'-dimethylbiphenyl, with estimated (from u.v.) θ-values of 0°, 58° and 70°, have τ-values of 7.62, 7.72 and 7.92, respectively. This is not really surprising in view of the crudeness of our theoretical treatment.

(5) Kurland has reported in MELLONMR No. 59 that E_{act}-values for the racemization of oxepin IIb and thiepin IIf are 9.6 ± 0.6 and 16.2 ± 0.3 kcal./mole, respectively, and that these n.m.r.-derived activation energies agree rather well with those estimated by halving our calculated E_{act}-values for III (11 and 18.5 kcal./mole, respectively). Actually the agreement is even better than that, since for IIb and IIf proper we had calculated 9 and 17 kcal./mole, respectively! However, we are the first to admit that this agreement is probably largely fortuitous: so many assumptions had to be plugged into our computations that we must be dealing with much cancellation of errors. - We thank Dr. Kurland for stimulating discussions.

Sincerely yours,

Kurt Mislow

Kurt Mislow

George H. Wahl, Jr.

George H. Wahl, Jr.

KM:GD

P.S. I am aghast at finding a letter to MELLONMR referred to in the open literature[6], and I believe that a clarification would be in order.

Kurt Mislow

Kurt Mislow

CLARIFICATION (?):

Aksel Bothner-By and I are also both aghast at finding a reference to MELLONMR in the open literature. Despite our repeated requests, warnings, statements, etc. about this, every once in a while a felony of this kind occurs - and not always by individuals outside of or on the periphery of the MELLONMR family. In each case which we come across (including that to which you refer), we write a pointed letter to the individual concerned giving him The Word. So far, we have at least had no repeat offenders and there have been less than a half dozen instances all together in nearly five years, so we have been fairly successful in this. MELLONMR participants can help this situation by not only observing the rules themselves, but also by trying to make sure that all those who come in contact with their particular copy of MELLONMR are aware of those rules.

Barry Shapiro

Footnotes

(1) The measurements were kindly performed by Dr. N. S. Bhacca, Varian Associates, Palo Alto, Calif.

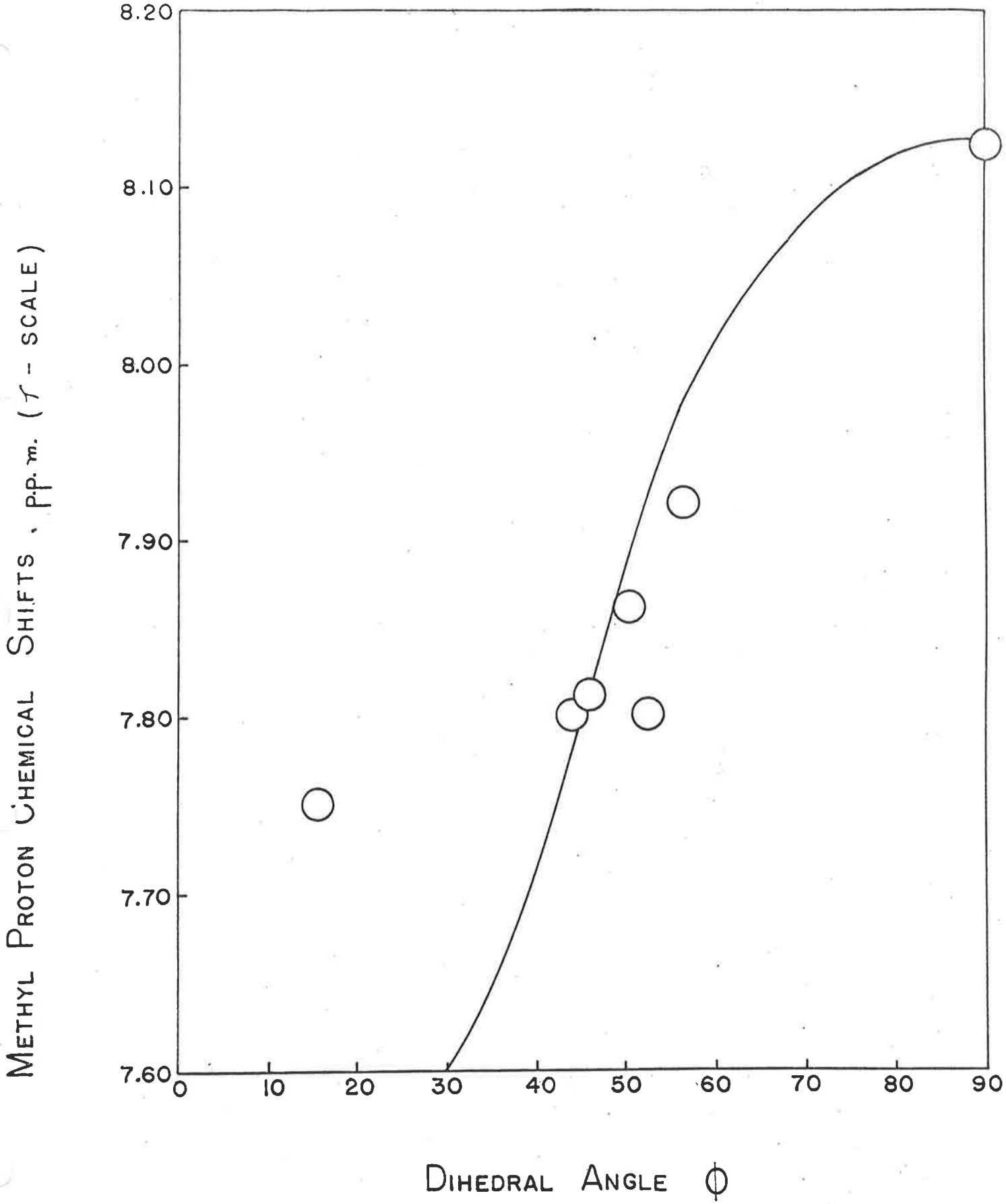
(2) A. A. Bothner-By and R. E. Glick, J. Chem. Phys., 26, 1651 (1957) and subsequent papers by W. H. Schneider and others.

(3) H. S. Gutowsky, M. Karplus and D.M. Grant, J. Chem. Phys., 31, 1278 (1959); H. J. Bernstein and N. Sheppard, ibid.,37, 3012 (1962).

(4) E. I. Snyder, J. Am. Chem. Soc., 85, 2624 (1963). We are grateful to Dr. Snyder for informing us of his results prior to publication.

(5) J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc., 79, 846 (1957); C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958). In the present computations an "average proton" was taken at the midpoint of the triangle defined by the three methyl protons.

(6) J. M. Conia and J. Salaün, Tetrahedron Letters,No. 18, 1175 (1963).


8.20
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METHYL PROTON CHEMICAL SHIFTS, P.P.M. (τ - SCALE)
DIHEDRAL ANGLE Φ

60-38

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
LOS ANGELES 24, CALIFORNIA 90024

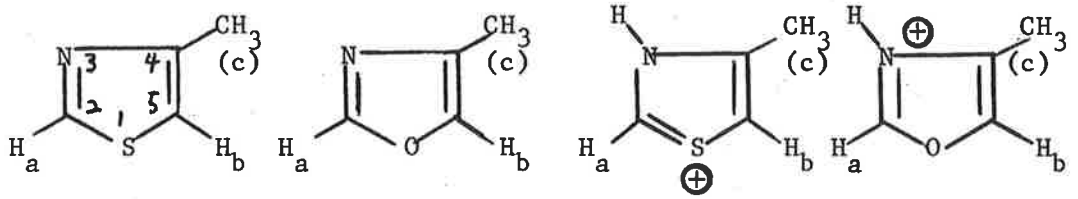
September 3, 1963

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

Dear Dr. Shapiro:

In connection with a comparison that we are making between oxazole and thiazole and between oxazolium ions and thiazolium ions because of the importance of the thiazole system in biological catalysis, we have noted some interesting H-H and C^{13}-H coupling constants which are tabulated below.

Compound	Solvent	J_{ab}	J_{bc}	J_{ac}	$J_{c^{13}-H_a}$	$J_{c^{13}-H_b}$
A	neat	1.86	1.00	0.28	209	187
B	neat	1.01	1.28	0.45	231	209
C	CF_3CO_2H	2.39	0.69		218	200
D	CF_3CO_2H		1.15		247	224



A B C D

Note that although J_{ab} is larger in the thiazole, J_{ac} is larger in the oxazole. This long range coupling constant was resolved for both A and B and although our values may be slightly inaccurate, there's no question but that J_{ac} is larger in B. The large C^{13}-H coupling constants, especially for the 2-hydrogens, are of considerable interest because of the unusual acidity of thiazolium ions.[1] The results suggest that oxazolium ions should be even more acidic than thiazolium ions and our preliminary results

September 3, 1963

on rates of exchange of the 2-hydrogen indicate that this is correct.

Although thiazolium ions, C, have customarily been written with the positive charge on nitrogen, our M. O. results (using a variety of models for the participation of sulfur in the pi system of thiazole) and those of Pullman[2] indicate that the majority of the charge in the ring is on sulfur and structure C is a more appropriate single representation of the structure. Qualitative reasoning based on electronegativities suggests the same conclusion.

Walter B. Miller III

Walter B. Miller

Paul Haake

Paul Haake

References:

1. Breslow, J. Amer. Chem. Soc., 79, 1762 (1958)

2. Pullman and Spanjaard, Biochem. Biophys. Acta., 46, 576 (1960)

PH:lh

60-40

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Your Ref.

Our Ref. RES/DTT/KBS

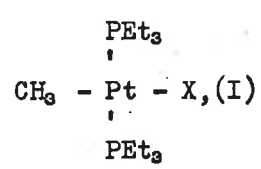
12th September, 1963

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

Dear Dr Shapiro,

Spectra of Platinum-alkyls

During our study of the N.M.R. spectra of square-planar platinum-alkyls, we have noticed that the Pt-H coupling constants depend on the group present in the trans-position. For example, in the compound



this coupling constant increases from 48 to 71 when changing X from Br to CN. When CN is substituted for Br in I the signal moves upfield from 9.03 to 9.19 τ. Initial indications are that the coupling constant increases as the "trans-effect"[1] of the trans-substituent increases; in addition the position of the resonance moves upfield. Relevant results, obtained using a Varian A60 instrument, are summarised in the following table :

FROM: D.T. Thompson.

CONTINUATION: SHEET No. 2

TO: Dr B.L. Shapiro.

DATE: 12.9.63

Compound	Central triplet of methyl resonance (τ)	J_{PH} (c/sec.)	J_{PtH} (c/sec.)
$Me-Pt(PEt_3)_2-Br$	9.03	6.5	48
$Me-Pt(PEt_3)_2-Cl$	9.00	6.5	48
$Me-Pt(PEt_3)_2-CH_3$	9.11	7.0	62
$Me-Pt(PEt_3)_2-CN$	9.19	6.5	71

Yours sincerely,

David T. Thompson

(D.T. Thompson)

[1]See, e.g., (i) Chatt, Duncanson, and Venanzi, J., 1955, 4456.
(ii) Chernyaev, Ann. Inst. Platine, U.S.S.R., 1926, 4, 243; 1927, 5, 118.

60-42

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

(Faculty of Technology in the University of Manchester.)

MANCHESTER 1 · TELEPHONE CENTRAL 3266

Department of Chemistry

Dr. J. Lee
Mr. J. Dyer

16th September, 1963.

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

Dear Barry,

^{1}H spectra of stannylamines.

We have been investigating the 60 Mc/s ^{1}H spectra of compounds containing a Sn-N bond. The results of our spectral analysis are given in Table 1. With one exception (as indicated in the Table), the materials were studied as neat liquids. Some of these were rather impure, but there was no difficulty in recognising the impurity bands. Below are some of the significant features in the results.

A. Chemical Shifts

1. In group I, the Sn-CH_3 shielding order is $NMe_2 > N(H)\emptyset > N\emptyset_2$. This is sensibly interpreted in terms of (a) the order of positive inductive effect (electron donation: $Me_2 > \emptyset$, $H > \emptyset_2$, and (b) the possibility of delocalisation of nitrogen lone-pair electrons into the aromatic π-system. Either mechanism which facilitates electron transfer to the nitrogen substituents would (i) assist the inductive transfer Sn → N, and (ii) diminish any possibility of a migration of the nitrogen lone pair into an $Np\pi$ - $Snd\pi$ orbital.

2. A comparison of the average shieldings for phenyl attached to nitrogen and to tin (groups I and II) shows a higher value for the former. This is probably associated with the possibility of nitrogen lone-pair delocalisation and the absence of an analogous situation with Sn - $\emptyset$.

contd/

B. Coupling Constants

1. J_{CH} is slightly greater in a methyl group bonded to nitrogen than in one bonded to tin. This is compatible with (a) greater electron attraction from CH_3 by the more electronegative nitrogen (especially if this atom may reduce its π-electron density by donation to N - Sn) causing an increased s character in the carbon hybrids used for C - H bonding, and (b) a higher steric effect with Sn causing a reduction of $\widehat{HCH}$, i.e. a decreased s character of the hybrids.
2. ^{117}Sn - H and ^{119}Sn - H coupling constants are not quite in the ratio of magnetogyric ratios ($\gamma 117/\gamma 119 = 0.9556$) indicating a coupling constant isotope effect.
3. Sn - H couplings, Sn - N - CH_3, may be compared with "corresponding" values in ^{29}Si - N - CH_3 and ^{31}P - N - CH_3 systems. This comparison, made for both the coupling constants as such and "nuclear-free" coupling constants (to use Norman Sheppard's nomenclature - MELLONMR No. 25, P11) is given in Table 2. Whichever form we adopt, an increase with increasing atomic number of the hetero-atom is indicated.

Yours sincerely,

J. Lewis

J. D Dyer

Table 2.

X - NCH_3

X	J_{X-H}	J_{X-H} H X
^{29}Si	*	*
^{31}P	~14	~35
^{117}Sn	35-44	98-124
^{119}Sn	36-46	97-123

* Not previously reported but probably very small since $J_{^{29}Si - CH_3} \sim 6$c/s

Table 1.

		CHEMICAL SHIFTS [c] (τ VALUES)						COUPLING CONSTANTS (c/s)							
								Sn–H						^{13}C–H	
								$Sn\overset{\frown}{-}CH_3$			$Sn\overset{\frown}{-}N\overset{\frown}{-}CH_3$			NCH_3	$SnCH_3$
		MeSn	Me_2N	ØN [f]	ØSn [f]	HN	b	^{117}Sn	^{119}Sn	a	^{117}Sn	^{119}Sn	a		
I	$Me_3SnNØ_2$	9·76		3·13				55·5	58·3	0·991					131·0
I	$Me_3SnN(H)Ø$	9·79		3·29		7·22		56·8	59·0	0·993					130·9
I	Me_3SnNMe_2	9·83	7·43					54·8	57·8	0·990	e	e		129·3	125·8
II	$Ø_3SnNMe_2$ [d]		7·85		2·62			d	d		d	d		d	
II	$Ø_2Sn(NMe_2)_2$		7·10		2·61						43·5	44·9	0·994	133·6	
II	$ØSn(NMe_2)_3$		7·18		2·62						44·0	45·7	0·993	132·0	
	$^{n}Bu_3SnNMe_2$		7·35				9·08,8·78				35·0	36·5	0·992	127	
	$^{n}Bu_2Sn(NMe_2)_2$		7·30				9·07,8·78				e	e		e	
	$^{n}BuSn(NMe_2)_3$		7·32				9·08,8·75				e	e		e	

a. Ratio of coupling constant $^{117}Sn/^{119}Sn$.
b. Butyl absorption; complex structure but two main regions, one with greater intensity than other; first figure gives position of most intense region, second figure gives "average position of whole absorption.
c. ± 0·03
d. In CCl_4 solution; τ -values may need "solvent correction"; solution too dilute for observation of satellites.
e. Satellites not observed.
f. Phenyl absorption complex and not yet analysed.

Koninklijke Shell-Laboratorium, Amsterdam
BADHUISWEG 3 AMSTERDAM-N.
TELEFOON (020)-6 11 11

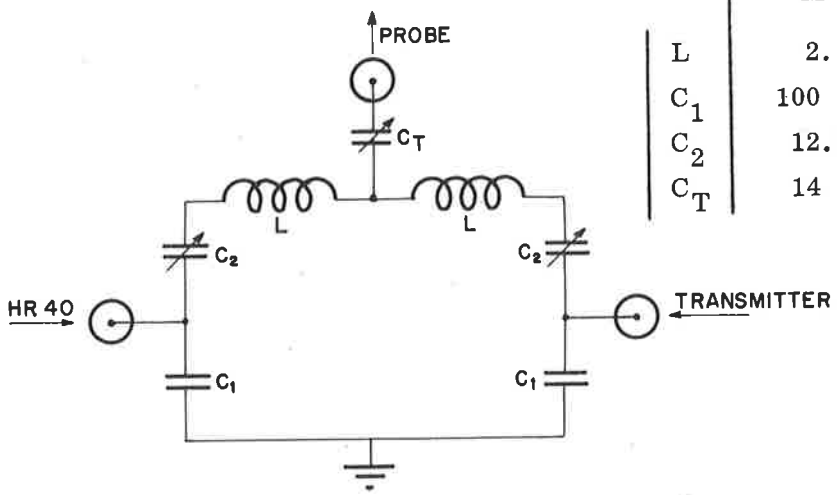
20th September 1963

Dear Dr. Shapiro,

In connection with our work on nuclear relaxation in HF [1] an apparatus has been constructed for spin decoupling of hydrogen and fluorine. The spin coupling constant in HF (521 c/s) required the stirring field to be large (>450 mØ). For Mellonmr readers who are interested in proton-fluorine decoupling we give the following details.

Our spin decoupler is used in conjunction with the Varian HR 40 instrument. The stirring frequencies (42.5 M c/s or 37.6 M c/s) are obtained by tripling crystal-controlled oscillators. The crystals have been shunted by small capacitors (40 pF) to allow frequency variation over 20 kc/s.

The Varian nmr probe can be used in these experiments, provided some minor modifications are made. The transmitting coil in the probe is normally connected to two small capacitors. These should be removed and the coil should be directly connected to the power input plug P 100, which in its turn is plugged to a matching box. Three of these matching boxes are in use: for stirring at 42.5 M c/s and at 37.6 M c/s, respectively, and the third one for normal high-resolution work. In the last case the matching box contains the above-mentioned capacitors only. The two other matching boxes contain the following circuitry, which has resonance peaks both at the measuring (40 M c/s) and the stirring frequency (37.6 or 42.5 M c/s).



	40 and 37.6 M c/s	40 and 42.5 M c/s
L	2.1 µH	2.0 µH
C_1	100 pF	100 pF
C_2	12.5 pF	12 pF
C_T	14 pF	12 pF

The inductances (L) are made of 10 to 15 turns of copper wire ("Povin" 0.25 mm enamelled) on a 7-mm rod. By stretching the coil one can adjust L to the correct value. The variable capacitors C_T and C_2 are of the flat ceramic type (3-15 pF).

The amplifying stages in the transmitter are conventional. The power tube is type PE 1/100. The maximum attainable stirring field has a peak amplitude of about 700 mØ.

When doing quantitative Overhauser experiments one should be certain that the characteristics of the receiver are not modified by leakage of the r.f. power of the transmitter. Although the circuits are highly selective this has proved to be impossible at high power levels unless the spectra are recorded using a nearly perfect probe balance. Base-line independence of the amount of stirring power can thus be obtained and its influence on the receiver is eliminated. This can be checked by adding to the sample an internal or external reference.

Fig.1 displays the broadened doublet of HF; the chemical exchange is relatively slow. Stirring the fluorine makes the spectrum collapse into one single line and it is expected that an Overhauser effect will be observed. The exchange rate is too small to have any influence on the magnitude of the Overhauser effect. This is in accordance with the ratio of 3/2 of the integrals of the spectra.

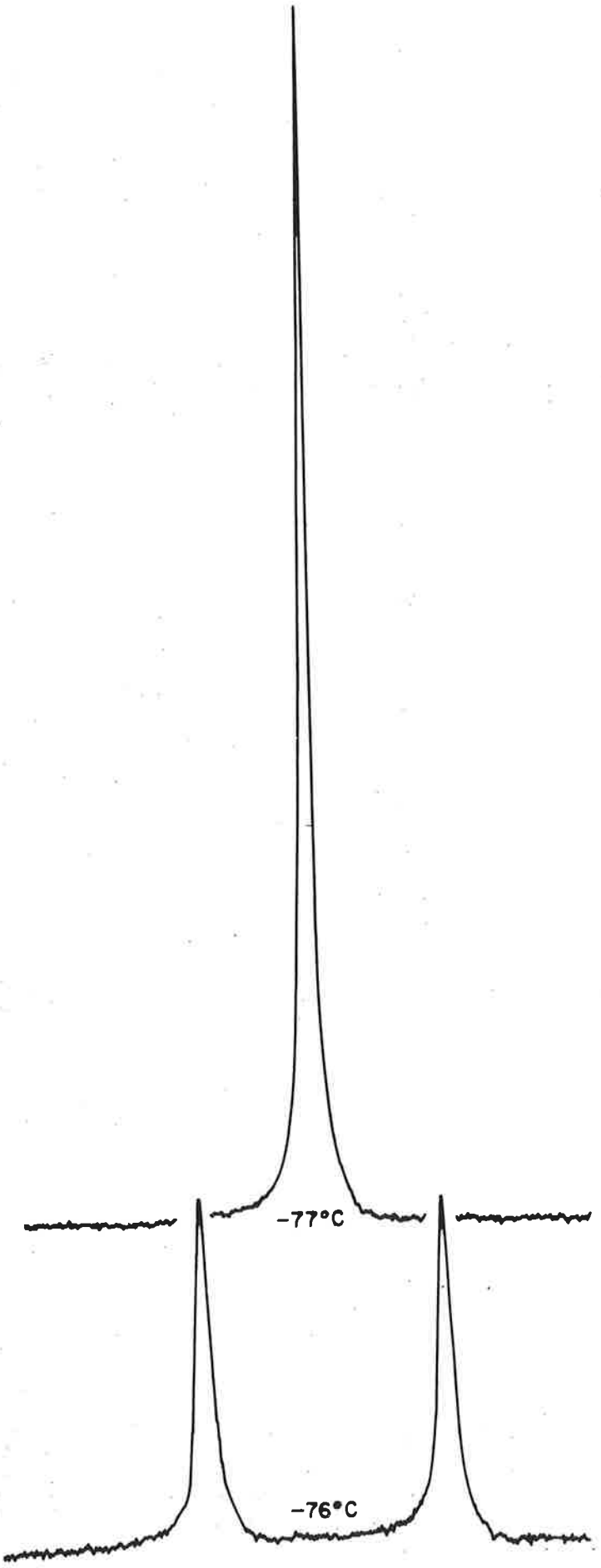
The line widths of the components of the doublet are determined by lifetime-limiting exchange reactions. This cause of line broadening is removed by double resonance as can be seen from the smaller line width in the collapsed spectrum.

Yours sincerely,

I.A.M. Hesselmann C. MacLean

Reference

1. C.MacLean and E.L.Mackor, Colloque Ampère, Eindhoven 1962 (North Holland Publishing Company, Amsterdam)



SPECTRUM OF HF WITH AND WITHOUT STIRRING

DRAWN Te
DWG. 63.08.1096

JAP/DMT

60-48

Department of Scientific and Industrial Research
NATIONAL PHYSICAL LABORATORY
TEDDINGTON, Middlesex
Telegrams: Physics, Teddington Telephone: TEDdington Lock 3222, *ext.* 767
BASIC PHYSICS DIVISION

Please address any reply to
THE DIRECTOR
and quote: BP.A.P.4
Your reference:

20th September, 1963

Dear Barry,

Molecular Orbital Theory of Nuclear Spin Coupling Constants

We believe we have made some progress in the theory of coupling constants between directly bonded atoms which may interest MELLONMR readers.

We consider reduced coupling constants K_{AB} defined as $(2\pi/\hbar\,\gamma_A\,\gamma_B)\,J_{AB}$ where J_{AB} is in c/s and γ_A, γ_B are the nuclear magnetogyric ratios. These K-constants (units cm^{-3}) are independent of the nuclear isotope and may reasonably be compared along a series of related atoms. According to McConnell's molecular orbital theory of spin coupling[1], the contact contribution to K_{AB} is given by

$$K_{AB}(\text{cont}) = (64\pi^2/9)\beta^2\,({}^3\Delta E)^{-1}\,S_A^2(0)\,S_B^2(0)\,P^2_{S_A S_B} \qquad (1)$$

where ${}^3\Delta E$ is a mean triplet state excitation energy, $P_{S_A S_B}$ is the molecular orbital bond order between the valence S atomic orbitals S_A and S_B, and $S_A(0)$, $S_B(0)$ are the values of these orbitals at the respective nuclei. According to eqn (1), the contact contribution is positive. However, if the theory is developed without the approximation of using a mean excitation energy (this is an important refinement), (1) has to be replaced by

$$K_{AB}(\text{cont}) = -(256\pi^2/9)\,\beta^2\,S_A^2(0)\,S_B^2(0)\sum_i^{\text{occ}}\sum_j^{\text{unocc}}\left({}^3\Delta E_{i\to j}\right)^{-1} C_{iS_A}C_{iS_B}C_{jS_A}C_{jS_B} \qquad (2)$$

where ${}^3\Delta E_{i\to j}$ is the excitation energy to the triplet state in which an electron is removed from the occupied molecular orbital ψ_i and placed in the unoccupied one ψ_j. C_{iS_A} is the LCAO coefficient of the atomic S-orbital S_A in the molecular orbital ψ_i and the double summation covers all such triplet excited states.

If all the excitation energies ${}^3\Delta E_{i\to j}$ are equal, (2) reduces to (1) and K_{AB} (cont) is positive. But if they differ widely, the sum in eqn (2) may have either sign. This modification is particularly important if either of the atoms is fluorine, for the 2S-atomic orbital is then very low in energy. Consider hydrogen fluoride, for example. The valence σ-molecular orbitals can be constructed from the hydrogen 1s function (h), the fluorine 2p-function (p) and the fluorine 2s-function (s). The energy level diagram is then roughly:

ψ_3 —— p − h + [s]

ψ_2 —— p + h − [s]

HF:

ψ_1 —— s + [h]

contd....

Because of the low energy of s, to a first approximation ψ_1 is constructed purely from the fluorine 2s-function, which has something of the character of an inner shell. The other two molecular orbitals ψ_2 and ψ_3 are bonding and antibonding combinations of fluorine 2p and hydrogen 1s. To a higher approximation, some h is mixed with s to give ψ_1 a little bonding character and, at the same time, ψ_2 and ψ_3 acquire some s to give them some antibonding character between h and s (although ψ_2 remains overall bonding between h and p). These general characteristics of the MO's are confirmed by more detailed LCAO calculations and by Ransils accurate SCF work[2]. Since both ψ_2 and ψ_3 involve h and s with opposite signs, the contribution of the lowest triplet excitation $\psi_2 \rightarrow \psi_3$ to K_{HF} (cont) is negative. Further, the energy of the excitation $\psi_1 \rightarrow \psi_3$ is much larger, so the theory predicts that the 2,3 term is dominant and that $K_{HF} < 0$, other non-contact contributions being relatively small. A similar argument applies to K_{CF} (where there is experimental evidence for a negative sign[3]), the only modification being the replacement of the hydrogen 1s atomic orbital by a carbon tetrahedral hybrid.

We have applied equation (2) to the coupling constants between atoms directly connected by single bonds with reasonable quantitative success. Our (rather tentative) prediction of signs (for K_{AB}) is:

	H	B	C	N	O	F
H	+	+	+	+	?	-
B		+	+	+	+	?
C			+	+	?	-
N				+	?	-
O					?	-
F						-

References

1. McConnell H.M. J. Chem. Phys. 24, 460 (1956)
2. Ransil B.J. Rev. Mol. Phys. 32, 239 (1960)
3. Tiers G.V.D. J. Amer. Chem. Soc. 84, 3972 (1962)

Yours sincerely,

D. P. Santry

John Pople

D. P. Santry

J. A. Pople

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

60-50

NUCLEAR MAGNETIC RESONANCE SPECIALTIES
INCORPORATED

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

September 24, 1963

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

Dear Barry:

In our letter of March 22, 1963, which appeared in Mellonmr No. 54, we offered engineering data for an A-60 Cooling System. We now are submitting specifications and parts lists to Mellonmr in the hope that this information will be of use to other A-60 owners.

A unit of this type has been operational in our laboratory for several months, and we have found it to be most satisfactory.

Sincerely,

Frank E. Dickson
Executive Vice-President

FED/ck

Enc.

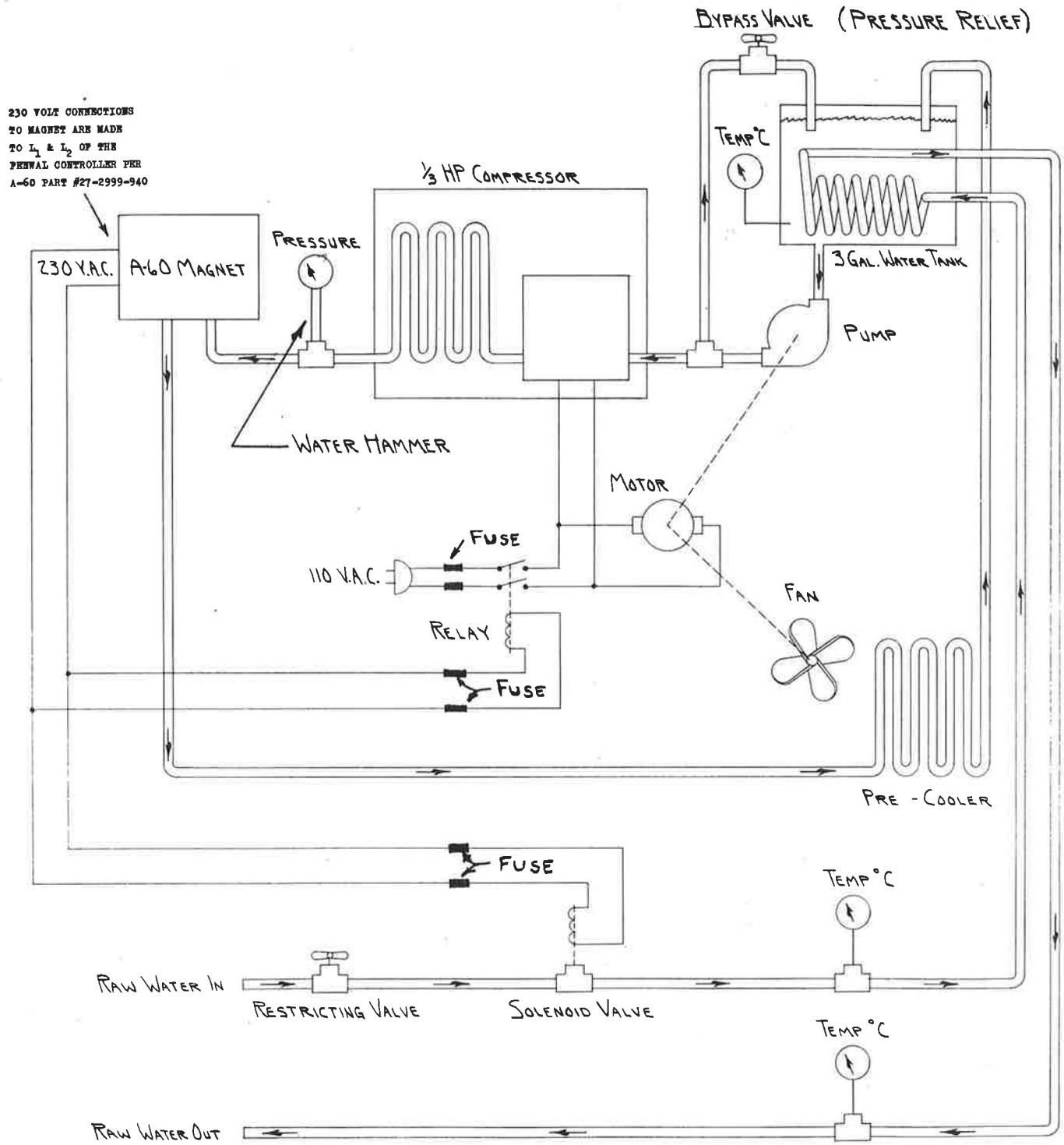
P.S. Note that in the attached graph, indicating the performance of the cooler, the upper line is the "magnet out" and the center one is "magnet in". I had hoped that, in reproduction, the red circles on the "magnet in" points would drop out; but our conscientious printer made every effort to get them in.

WC-60

PARTS LIST

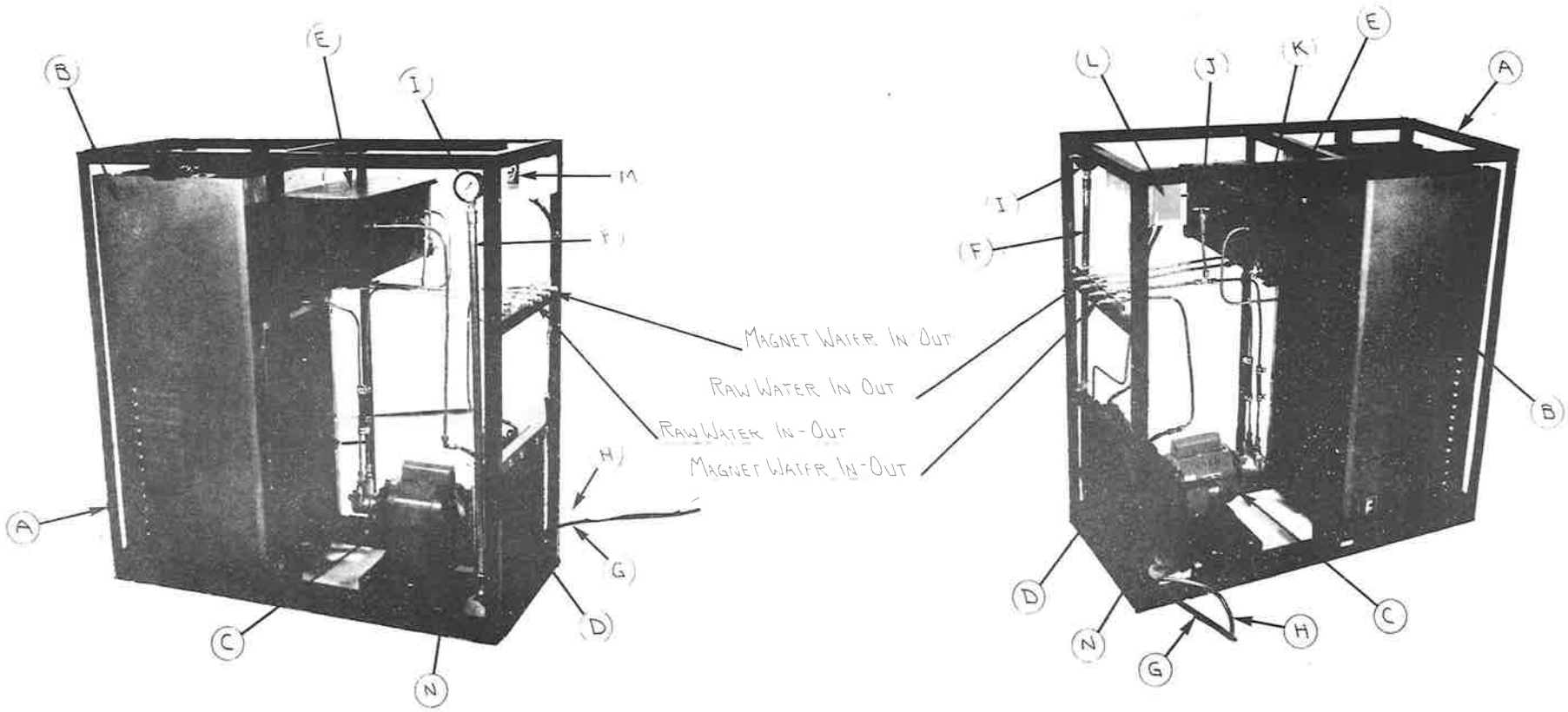
Drawing Reference	Part Description	Manufacturing Data	N.M.R. Specialties Part No.
A	Steel Frame	See Drawing (Frame may be bolted or welded	WC-101
B	Water Cooler	Sunroc NM3B NHI or Marchase MCA33-H6	WC-102
C	Pump	Tuthill WF-60 or Aurora B6319612 B32-AB	WC-103
C	Motor	Westinghouse, Type FHT 1/3 hp, rpm. 1725	WC-104
D	Pre-cooler	Marchase, 4 Pass (all copper)	WC-105
E	Water Tank	Copper Sheet, 15-1/2" x 8-1/2" x 6-1/2", 16 oz. (per sq. ft.)	WC-106
F	Water Hammer	Copper Pipe, 1/2" (length about 30")	WC-107
G	Power Cable	Belden 17408-S, 8' Belden 17410-S, 10'	WC-108
H	Relay Power Cable	Belden 8461, 15'	WC-109
I	Pressure Gauge	U.S. Gauge 98CB - 60 psi.	WC-110
J	Bypass Valve	Sherman #597 or equivalent	WC-111
K	Drain Valve	Copper or bronze	WC-112
L	Control Relay	Potter Brumfield PR7AY, DPST 230 V.A.C.	WC-113
M	Fuse Block	Bussman, one each 3742, two each 3743	WC-114
M	Fuse	Fusetron, 2 each FNM 20	WC-115
N	Fan	8", 32° pitch, 525 cfm, 1500 rpm.	WC-116
	Rubber Feet	Fisher Rubber Stoppers #12	WC-117
	Pump Mount	For Tuthill WF60 Pump - Tuthill OL81C Foot Mount	WC-118
	Copper Pipe	Soft 3/8"	WC-119
	Solenoid Valve	Hayes Mfg. 2155-2161	WC-120
	Thermometer	Rochester 1250	WC-121
	Raw Water Coil	Soft Copper Water Tube, 1/4" 20 - 4" coils	WC-122

Approximate Parts Cost:- $550.00

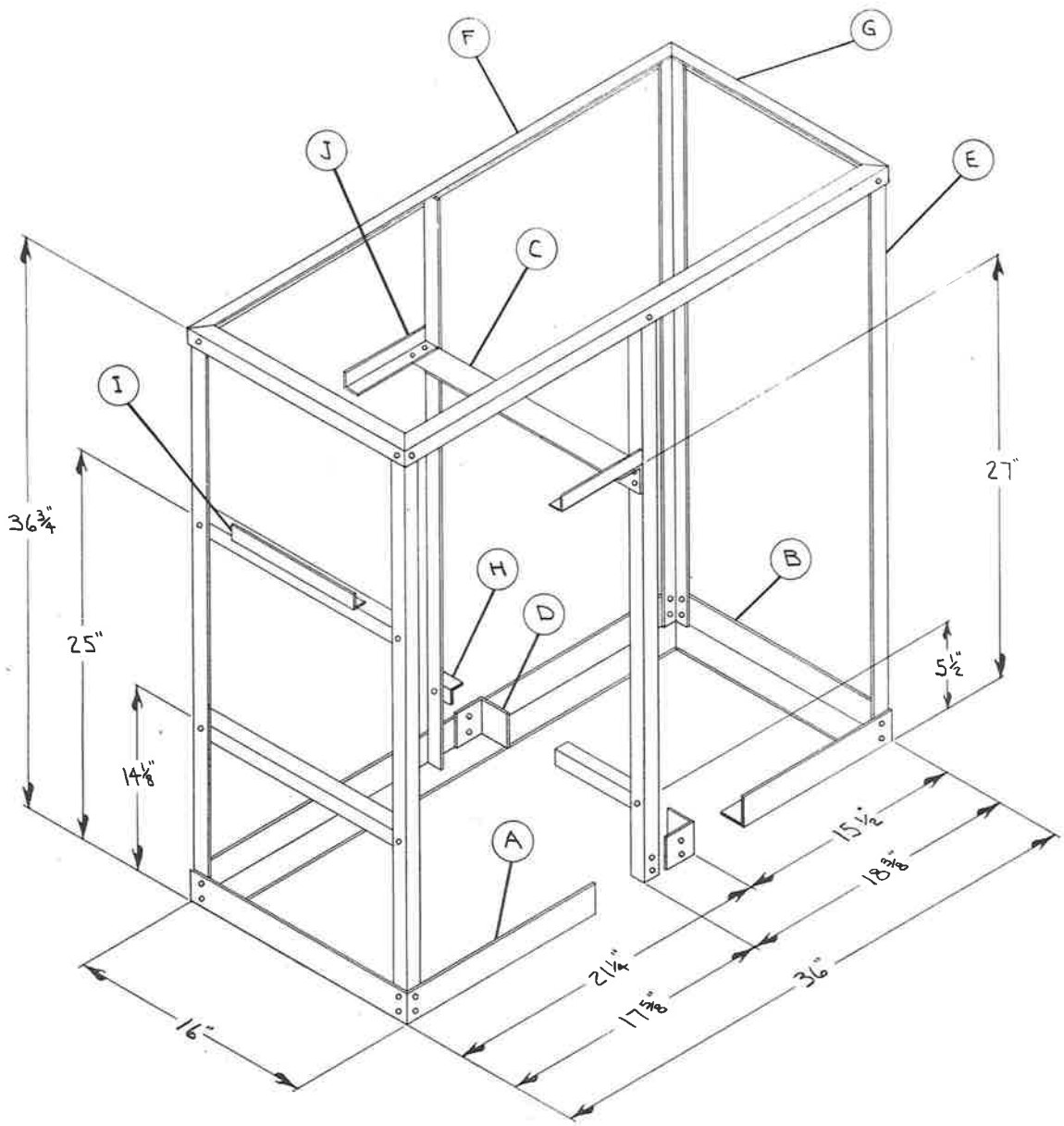


OPERATIONAL DATA

MAGNET TEMP. IN	30° C ± ½° C
MAGNET TEMP. OUT	41° C ± 1° C
CIRCUIT PRESSURE	45 PSI ± 5PSI
FLOW	.6 GAL./MINUTE
AMBIENT	70° F



(A) WELDED FRAME
(B) COOLER
(C) MOTOR-PUMP
(D) PRE-COOLER
(E) STORAGE TANK
(F) WATER HAMMER
(G) POWER CABLE
(H) MAGNET CONTROL CABLE
(I) PRESSURE GAUGE
(J) BYPASS VALVE
(K) DRAIN VALVE
(L) CONTROL RELAY
(M) FUSE BLOCK
(N) FAN



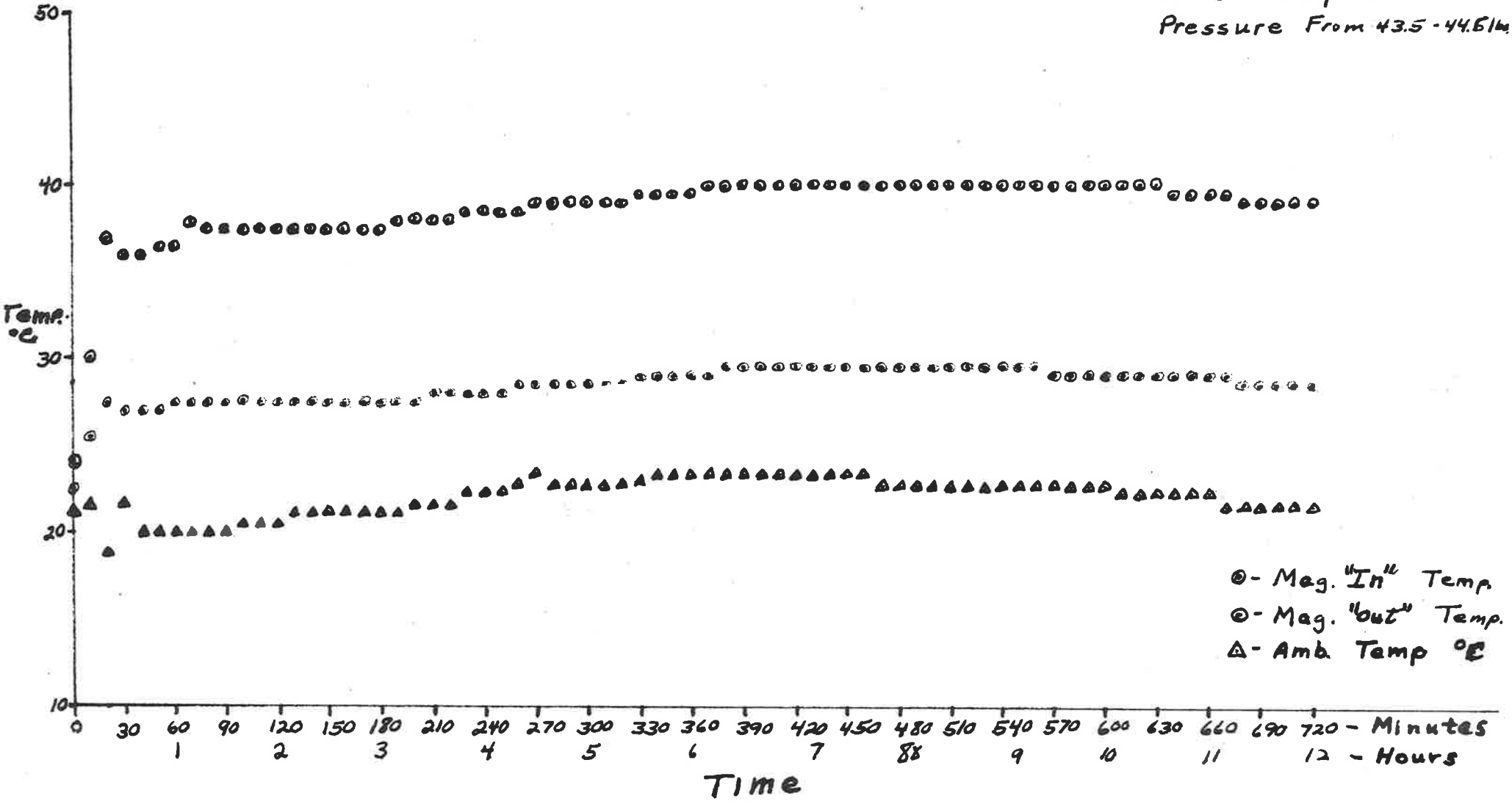
A	2 Ls	2" × 2" × ⅛" × 3'-0"
B	2 Ls	2" × 2" × ⅛" × 1'-4"
C	1 L	2" × 2" × ⅛" × 1'-3¾"
D	2 Ls	2" × 2" × ⅛" × 0'-2"
E	6 Ls	1" × 1" × ⅛" × 3'-0½"
F	2 Ls	1" × 1" × ⅛" × 3'-0"
G	2 Ls	1" × 1" × ⅛" × 1'-4"
H	3 Ls	1" × 1" × ⅛" × 1'-3½"
I	1 L	1" × 1" × ⅛" × 0'-9"
J	2 Ls	1" × 1" × ⅛" × 0'-6"

NOTES

ALL HOLES TO BE $\frac{7}{32}$" DIA. (#11 DRILL) FOR #10-32 NC BOLTS.

IF FACILITIES PERMIT, ANGLES SHOULD BE WELDED NOT BOLTED FOR A MORE RIGID FRAME.

WC - 60 Test
Date 8/4/63
Inst. 246
Raw Water - None
Test Mag. Varian A-60
Unit Complete
Pressure From 43.5 - 44.6 lbs



60-56

MELLON INSTITUTE

4400 FIFTH AVENUE

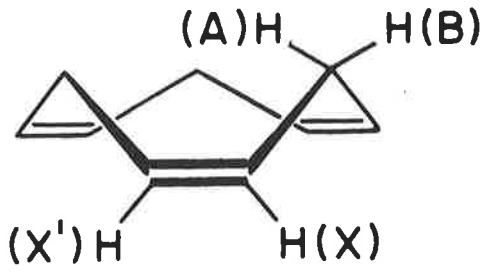
PITTSBURGH 13, PA.

24 September 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania, 15213

Dear Barry:

Recently we reported the synthesis and properties of cis,cis,cis-1,4,7-cyclononatriene (I).[1] We would like to present the results of proton-proton spin decoupling experiments which provide the proof of structure and conformation.



I

The undecoupled and composite decoupled spectra of I taken at low temperature (ca. -40°C) are shown in Figure I. The methylene pattern at 6.05 τ (Fig. 1a) is assigned to the inner methylene protons (H_A in I). A Dreiding molecular model of I (normal bond distances and angles) clearly shows that any two nuclei of the inner methylene protons would be much closer (ca. 1.6Å) than two hydrogen van der Waal radii (2.4Å). We believe that this considerable compression of the inner proton electronic orbitals would have caused a redistribution of their electron densities in such a way as to reduce the net shielding associated with these protons.[2] This phenomenon would account for their chemical shift at lower field. The observed chemical shift may also be due, in part, to the anisotropy of the double bonds. However, we cannot determine the contribution of this effect, while on the other hand, the magnitude of this shift is consistent with the molecular geometry and other downfield shifts which have been attributed to steric effects[3]. The undecoupled and decoupled spectra of I taken at high temperature (ca. 80°C) are shown in Fig. 2.

These observations demonstrate that the structure and conformation of cis,cis,cis-1,4,7-cyclonoatriene are that represented by I. The arguments that lead to this conclusion are as follows: a) in the low temperature spectra, the AB quartet of the decoupled methylene protons verifies that there is only one type of methylene hydrogen pair (the magnitude of J_{AB}, 12.4 c.p.s., is in

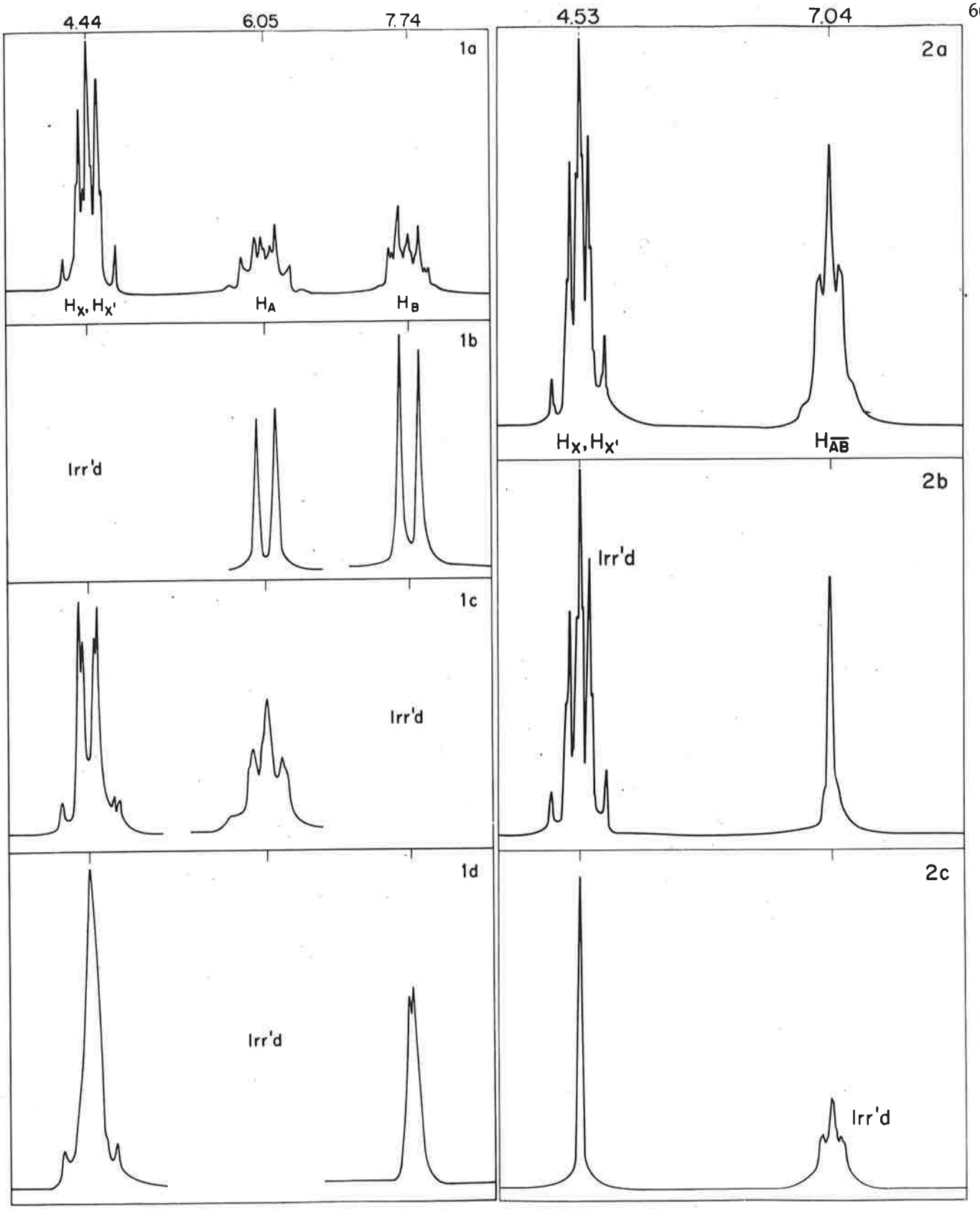


FIG. 1

Low Temperature N.m.r. Spectra of I

FIG. 2

High Temperature N.m.r. Spectra of I

agreement with known aliphatic geminal coupling constants) and thus eliminates the alternative conformation, the saddle;[1b] b) in the high temperature decoupled spectra, (Figure 2b, 2c) the single sharp peaks prove the magnetic equivalence of the olefinic protons and that of the methylene protons; c) the decidedly different H_X, H_X' patterns observed at low temperature when each type of methylene proton is irradiated in turn, substantiates the magnetic equivalence of the olefinic protons and d) the narrow irradiating frequency range (ca. 5 c.p.s. at the strongest irradiating field employed) required for complete decoupling of H_A and H_X, H_X' protons further attests to the equivalence of the olefinic protons.

It is also evident from the decoupled spectra that $|J_{AX}|$ is greater than $|J_{BX}|$. The previous assignment of H_A and H_B, based on steric considerations, is supported by this result. If one assumes that the dependence of the olefin-aliphatic coupling constants is given qualitatively by a curve such as that of H. Conroy,[4] one can say that dihedral angles for H_A-C-C-H_X less than ca. 135° and for H_B-C-C-H_X less than ca. 20° would be required if $|J_{AX}|$ were to be less than $|J_{BX}|$. The dihedral angles estimated from a Dreiding molecular model are ca. 165° for H_A-C-C-H_X and ca. 45° for H_B-C-C-H_X. The actual dihedral angles in the molecule are probably less than these; however it is unlikely that they are less than 135° for H_A-C-C-H_X and 20° for H_B-C-C-H_X.

A. A. Bothner-By et al.[5] have presented data which allow for a determination of the vicinal olefin-aliphatic coupling constants for trans and gauche arrangements. Values of 11.6 c.p.s. for J_{trans} and 3.7 c.p.s. for J_{gauche} were cited. The curve,[4] calculated for aliphatic vicinal H-H couplings, would predict 11 and 2 c.p.s. for J_{trans} and J_{gauche}, respectively.

Yours sincerely,

Karl

KGU:hb K. G. Untch

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1. (a) K. G. Untch, J. Am. Chem. Soc., 85, 345 (1963).
(b) K. G. Untch and R. J. Kurland, ibid., 85, 346 (1963).

2. (a) A. D. Buckingham and J. A. Pople, Proc. Camb. Phil. Soc., 53, 262 (1957).
(b) A. D. Buckingham, Can. J. Chem., 38, 300 (1960).

3. S. Gordon and B. P. Dailey, J. Chem. Phys., 34, 1084 (1961) and C. MacLean and E. L. Mackor, Mol. Phys., 3, 223 (1960).

4. H. Conroy in "Advances in Organic Chemistry", Vol. II, Interscience Publishers, Inc., New York, N.Y., 1960, p. 311.

5. A. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc., 83, 231 (1961); A. A. Bothner-By, C. Naar-Colin and H. Günther, ibid., 84, 2748 (1962).

60-59

THE UNIVERSITY OF MANCHESTER,

DEPARTMENT OF CHEMISTRY,

MANCHESTER, 13.

TELEPHONE: ARDWICK 3333

23rd September, 1963.

KHW/MC.

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

Dear Dr. Shapiro,

Following the letters by Muller and Rose in M.E.L.L.O.N.M.R. nos. 52 and 55 (concerning the association of carboxylic acids in donor solvents) Dr. Allen suggested that I measure molecular weight data on such solutions.

This was accomplished using the Mechrolab Vapour Pressure Osmometer Model 301A. Solutions of benzoic acid in various donor solvents at concentrations up to 0.2M - the maximum possible with this instrument - were studied. Benzoic acid was chosen in preference to acetic acid, since current infra-red investigations lead us to believe that acetic acid behaves somewhat anomalously in its association compared with other carboxylic acids.

Up to 0.2M in solution in acetone and in tetrahydrofuran, the benzoic acid showed no detectable association - the molecular weight of monomeric benzoic acid being obtained throughout. Thus, over this concentration range, complexing of the monomeric acid with these typically donor solvents occurs to a much greater extent than self-association of the acid.

/The

The "controversial" statement by Allen and Caldin[1] quoted by Muller and Rose was only intended to refer to the range of concentrations normally used in molecular weight determinations from colligative properties - up to about 0.2M - and these osmometry results bear out the statement over this concentration range. At higher concentrations of acid, the dimerisation equilibrium competes more effectively with, and eventually predominates over, the monomer-solvation equilibrium.

The N.M.R. results quoted by Muller and Rose[2,3] were at relatively high concentrations, (between 0.3M and pure acid) and over this concentration range it is highly likely that the observed concentration dependence of chemical shift is basically due to the dimerisation of the acid. At lower concentrations where the extent of dimerisation is relatively small, the chemical exchange between the acid proton and water present is an additional factor which causes strong concentration dependence of the chemical shift.

Yours sincerely,

Kenneth H. Webb

(Kenneth H. Webb.)

1. G. Allen and E.F. Caldin, Quart.Revs. 7, 278 (1953).

2. C.M. Huggins, G.C. Pimentel and J.N. Shoolery, J.Phys.Chem. 60, 1311 (1956).

3. L.W. Reeves, Trans.Farad.Soc., 55, 1684 (1959).

"Identification of Triisobutylene and Tetraisobutylene Isomers by a Combination of Gas Chromatography and Nuclear Magnetic Resonance Techniques"
S. A. Francis and E. D. Archer
Anal. Chem. 35, 1363 (1963)

"Analysis of C_7 Olefins by a Combination of Gas Chromatography and Nuclear Magnetic Resonance Spectrometry"
E. D. Archer, J. H. Shively and S. A. Francis
Anal. Chem. 35, 1369 (1963)

"Photoisomericierung von 1.3-Cyclohexadienen. II."
H. Prinzbach und J. H. Hartenstein
Angew. Chem. 75, 639 (1963)

"Darstellung von Pyrazoleninen und ihre Photolyse zu Cyclopropenen"
G. L. Closs und W. Böll
Angew. Chem. 75, 640 (1963)

"Synthese und Eigenschaften von Tricyclo[3.3.2.$0^{4,6}$]deca-2.7.9-trien (Bullvalen)"
G. Schröder
Angew. Chem. 75,722 (1963)

"Darstellung von 5-Aminozuckern und Deren Umwandlung in Pyridinderivate"
R. Paulsen
Ann. Chem. 665, 166 (1963)

"Nuclear Spin and Dipole Moment of Cd^{115}"
F. Byron, R. Novick, B. Perry and E. Saloman
Bull. Am. Phys. Soc. 8, 463 (1963)

"Nuclear Magnetic Resonance of As^{75} in Ferroelectric KH_2AsO_4"
J. L. Bjorkstam
Bull. Am. Phys. Soc. 8, 464 (1963)

"Deuteron-Spin Relaxation in Deuterated Modifications of Methane"
G. A. De Wit and M. Bloom
Bull. Am. Phys. Soc. 8, 467 (1963)

"Nuclear-Spin Relaxation Times in H_2 Gas at Low Pressures"
W. N. Hardy
Bull. Am. Phys. Soc. 8, 467 (1963)

"Nuclear Magnetic Resonance of Oxygen-17 in MnO and CoO"
D. E. O'Reilly and T. Tsang
Bull. Am. Phys. Soc. 8, 468 (1963)

"The Electron Density Distributions in Hydride Molecules. III. Hydrogen Fluoride"
R. F. W. Bader and G. A. Jones
Can. J. Chem. 41, 2251 (1963)

"Heterocyclic Steroids. II. Preparation and N.M.R. Spectra of 17,17-Dialkyl-13(14)-Unsaturated Steroids"
E. Caspi and D. M. Piatak
Can. J. Chem. 41, 2294 (1963)

"Cyclohexane Compounds. IV. Nuclear Magnetic Resonance Spectra of some Derivatives of the Stereoisomeric 3-Amino-1,2-Cyclohexanediols"
F. A. L. Anet, R. A. B. Bannard and L. D. Hall
Can. J. Chem. 41, 2331 (1963)

"Ring-Proton Chemical Shifts of Some Substituted Anilines in Carbon Tetrachloride and Trifluoroacetic Acid"
W. F. Reynolds and T. Schaefer
Can. J. Chem. 41, 2339 (1963)

"Extractives from Populus Tremuloides Heartwood. The Triterpene Alcohols"
R. A. Abramovitch and R. G. Micetich
Can. J. Chem. 41, 2362 (1963)

"Reactions of Phenyl-Substituted Heterocyclic Compounds. IV. Bromination of 2-Phenyl-1,2,3,2H-Triazole"
B. M. Lynch
Can. J. Chem. 41, 2380 (1963)

"The Dimer of Bromotrifluoroethylene"
W. R. Cullen and Pritam Singh
Can. J. Chem. 41, 2397 (1963)

"Spectroscopie Hertzienne. -- Détection Optique de la Résonance Magnétique par Modulation de l'effet Faraday Paramagnétique Transversal à la Fréquence de Larmor"
J. Manuel et C. Cohen-Tannoudji
Compt. Rend. 257, 413 (1963)

"Résonance Magnétique Nucléaire.-- Étude de la position de la Raie de Résonance Nucléaire de Carbures Saturés en Phase Gazeuse"
E. Dayan et G. Widenlocher
Compt. Rend. 257, 883 (1963)

"Trends in the Chemistry of the Group IV-B Elements"
N. A. Matwiyoff
Dissertation Abstr. 24, 502 (1963)

"Studies of Organotin Compounds"
G. L. Morgan
Dissertation Abstr. 24, 502 (1963)

"A Study of the Oxidation of Gossypol with Hydrogen Peroxide in Alkaline Aqueous Solution"
L. B. Farmer
Dissertation Abstr. 24, 510 (1963)

"Electric and Magnetic Interactions in Molecules"
H. J. Kolker
Dissertation Abstr. 24, 536 (1963)

"Nuclear Relaxation in Solutions of Free Radicals"
J. M.-J. C. Tai
Dissertation Abstr. 24, 541 (1963)

"Overhauser Effect in Metallic Sodium"
J. F. Reichert
Dissertation Abstr. 24, 794 (1963)

"Dynamic Nuclear Orientation and Spin-Lattice Relaxation of Co^{59}"
W. P. Unruh
Dissertation Abstr. 24, 800 (1963)

"Zur Kenntnis ätherischer Öle. 2. Mitteilung. Die Struktur der sogenannten «Linalooloxide» "
D. Felix, A. Melera, J. Seibl und E. sz. Kovats
Helv. Chim. Acta 46, 1513 (1963)

"Photochemische Reaktionen. 22. Mitteilung. UV.-Bestrahlung von 11-Oxo-Steroiden III. Zur Beeinflussung der (11→19)-Cyclisation durch sterische Faktoren"
J. Iriarte, K. Schaffner und O. Jeger
Helv. Chim. Acta 46, 1599 (1963)

"Zur Struktur des Betanidins. 6. Mitteilung. Über die Konstitution des Randenfarbstoffes Betanin"
H. Wyler, T. J. Mabry und A. S. Dreiding
Helv. Chim. Acta 46, 1745 (1963)

"6-Vinylfulven"
M. Neuenschwander, D. Meuche und H. Schaltegger
Helv. Chim. Acta 46, 1760 (1963)

"Pronuciferin, ein Benzylisochinolin-Alkaloid mit para-Cyclohexadienon-Gruppierung"
K. Bernauer
Helv. Chim. Acta 46, 1783 (1963)

"Über die Verrucarine und Roridine. 3. Mitteilung. Struktur von Verrucarol"
J. Gutzwiller und Ch. Tamm
Helv. Chim. Acta 46, 1786 (1963)

"Odeur et constitution XXI. Synthèses d'aldéhydes β-éthyléniques cis. II"
M. Winter
Helv. Chim. Acta 46, 1792 (1963)

"Über die Inhaltstoffe von Zizyphus oenoplia MILL. 1. Mitteilung: Isolierung der Inhaltstoffe"
E. L. Ménard, J. M. Müller, A. F. Thomas, S. S. Bhatnagar und N. J. Dastoor
Helv. Chim. Acta 46, 1801 (1963)

"The Mechanism of the Base-Initiated Dehydrohalogenation and Rearrangement of 1,1-Diaryl-2-bromoethylenes in t-Butyl Alcohol"
W. M. Jones and R. Damico
J. Am. Chem. Soc. 85, 2273 (1963)

"Thiabenzenes. IV. 1- and 2-Thianaphthalenes and 10-Thiaanthracenes. Evidence for Cyclic Conjugation"
C. C. Price, M. Hori, T. Parasaran and M. Polk
J. Am. Chem. Soc. 85, 2278 (1963)

"The Formation of a 1,3,6-Cyclooctatriene by 1,4-Radical Addition to Cyclooctatetraene and its Intramolecular Isomerization to a Bicyclo[4.2.0]octa-2,4-diene"
J. L. Kice and T. S. Cantrell
J. Am. Chem. Soc. 85, 2298 (1963)

"Metal Salts and Complexes of Dialkoxyphosphonylacetylmethanide Ions"
F. A. Cotton and R. A. Schunn
J. Am. Chem. Soc. 85, 2394 (1963)

"Structure and Rearrangement of Neutral Phenylketene Dimer"
J. E. Baldwin and J. D. Roberts
J. Am. Chem. Soc. 85, 2414 (1963)

"Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. II. Unsubstituted 1,4-Dien-3-ones"
P. J. Kropp and W. F. Erman
J. Am. Chem. Soc. 85, 2456 (1963)

"Some Aspects of the Chemistry of Cyclopolyphosphines"
W. A. Henderson, Jr., M. Epstein and F. S. Seichter
J. Am. Chem. Soc. 85, 2462 (1963)

"The Stereochemistry of the Heteroyohimbine Alkaloids"
M. Shamma and J. M. Richey
J. Am. Chem. Soc. 85, 2507 (1963)

"The Steric Course of Mitrosyl Halide Addition to Norbornene and Norbornadiene"
J. Meinwald, Y. C. Meinwald and T. N. Baker, III
J. Am. Chem. Soc. 85, 2513 (1963)

"Long-Range Spin-Spin Couplings in the Nuclear Magnetic Resonance Spectra of Some Bicyclo[2.2.1]heptanes"
J. Meinwald and Y. C. Meinwald
J. Am. Chem. Soc. 85, 2514 (1963)

"Trialkyl Phosphites: Novel Ring-Opening Reactions with Dimethylketene Dimers"
W. G. Bentrude and E. R. Witt
J. Am. Chem. Soc. 85, 2522 (1963)

"Acid- and Base-Catalyzed Hydrogen Exchange in Methyl-Substituted Indoles"
B. C. Challis and F. A. Long
J. Am. Chem. Soc. 85, 2524 (1963)

"Electrochemical Syntheses. The Methoxylation of Dimethoxybenzenes to Quinone Ketals and the Ring Fission of 1,2-Dimethoxybenzene to Hexamethyl cis,cis-Orthomuconate"
B. Belleau and N. L. Weinberg
J. Am. Chem. Soc. 85, 2525 (1963)

"Metal Nitrosyl Derivatives with Bridging Nitrosyl Groups"
R. B. King and M. B. Bisnette
J. Am. Chem. Soc. 85, 2527 (1963)

"Bicyclobutane"
D. M. Lemal, F. Menger and G. W. Clark
J. Am. Chem. Soc. 85, 2529 (1963)

"Electronic Interactions in Biradicals. 1. Reversible Bond Formation"
E. A. Chandross and R. Kreilick
J. Am. Chem. Soc. 85, 2530 (1963)

"The Synthesis and Properties of Homotropone"
J. D. Holmes and R. Pettit
J. Am. Chem. Soc. 85, 2531 (1963)

"The Structure of Streptonigrin"
K. V. Rao, K. Biemann and R. B. Woodward
J. Am. Chem. Soc. 85, 2532 (1963)

"Studies of the Cycloheptatriene-Norcaradiene Isomerism in Some Novel Steroids"
L. H. Knox, E. Velarde and A. D. Cross
J. Am. Chem. Soc. 85, 2533 (1963)

"Use of Carbon-13-Proton Coupling Constants in the Assignment of Proton Signals in the N.m.r. Spectrum of S-Methyl Thioacetate"
R. L. Middaugh and R. S. Drago
J. Am. Chem. Soc. 85, 2575 (1963)

"New Aromatic Anions. V. The Synthesis of Diketocyclobutenediol and its Conversion to Octahydroxycyclobutane"
R. West, H. Y. Niu and M. Ito
J. Am. Chem. Soc. 85, 2584 (1963)

"Photoisomerizations in the α-Tropolone Series: The Mechanistic Path of the α-Tropolone Methyl Ether to Methyl 4-Oxo-2-cyclopentenylacetate Conversion"
W. G. Dauben, K. Koch, S. L. Smith and O. L. Chapman
J. Am. Chem. Soc. 85, 2616 (1963)

"Studies in Magnetic Nonequivalence. N.m.r. Spectra of Two-Spin and Two-Spin-Group Systems"
E. I. Snyder
J. Am. Chem. Soc. 85, 2624 (1963)

"Spectrometric Studies of Carbonyl-Hydrogen Interactions in Different Steric Environments"
W. W. Brandt
J. Am. Chem. Soc. 85, 2628 (1963)

"Two Nitriles Derived from 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl Bromide. A 2-Cyano-2-methyl-1,3-dioxolane Derivative"
B. Coxon and H. G. Fletcher, Jr.
J. Am. Chem. Soc. 85, 2637 (1963)

"The Relative Signs of Phosphorus-Proton Nuclear Magnetic Resonance Coupling Constants"
S. L. Manatt, G. L. Juvinall, D. D. Elleman
J. Am. Chem. Soc. 85, 2664 (1963)

"Relative Signs of the ^{31}P-^{1}H and ^{31}P-C-^{1}H Nuclear Magnetic Resonance Coupling Constants"
G. M. Whitesides, J. L. Beauchamp, J. D. Roberts
J. Am. Chem. Soc. 85, 2665 (1963)

"The Preparation of Dihalomethyl Derivatives of Carbon, Silicon, and Germanium by the Action of Phenyl(trihalomethyl) mercurials on C-H, Si-H, and Ge-H Linkages"
D. Seyferth and J. M. Burlitch
J. Am. Chem. Soc. 85, 2667 (1963)

"Chemical Applications of Sensitivity Enhancement in Nuclear Magnetic Resonance and Electron Spin Resonance"
L. C. Allen and L. F. Johnson
J. Am. Chem. Soc. 85, 2668 (1963)

"Geometrical Isomerism about a Carbon-Sulfur Double Bond"
J. F. King and T. Durst
J. Am. Chem. Soc. 85, 2676 (1963)

"The Hydrolysis of Five-Membered Cyclic Phosphotriesters to Cyclic Phosphodiesters"
F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson and E. M. Banas
J. Am. Chem. Soc. 85, 2681 (1963)

"Nuclear Pure Quadrupole Relaxation and Its Temperature Dependence in Solids"
D. E. Woessner and H. S. Gutowsky
J. Chem. Phys. 39, 440 (1963)

"Deuteron Magnetic Resonance Study of Barium Chlorate Monohydrate"
T. Chiba
J. Chem. Phys. 39, 947 (1963)

"Electron Coupling of Nuclear Spins. VII. J_{FF} for 2-Fluorobenzotrifluorides"
H. S. Gutowsky and V. D. Mochel
J. Chem. Phys. 39, 1195 (1963)

"Polymer NMR Spectroscopy. X. The Use of H^1-H^1 Spin Decoupling in the Elucidation of Polymer Structure"
F. A. Bovey, E. W. Anderson and D. C. Douglass
J. Chem. Phys. 39, 1199 (1963)

"Isotropic NMR Shifts in Pyridine-Type Bases Complexed with Paramagnetic Ni^{II} and Co^{II} Acetylacetonates"
J. A. Happe and R. L. Ward
J. Chem. Phys. 39, 1211 (1963)

"NMR Studies of Hydrated Sodium Tetraborate Minerals. II. Na^{23} Sites in Borax and Tincalconite"
J. D. Cuthbert and H. E. Petch
J. Chem. Phys. 39, 1247 (1963)

"Nuclear Spin-Spin Coupling Involving Heavy Nuclei. The Coupling between Hg^{199} and H^1 Nuclei in CH_3HgX and CH_3 CH_2HgX Compounds"
J. V. Hatton and W. G. Schneider and W. Siebrand
J. Chem. Phys. 39, 1330 (1963)

"Proton NMR Chemical Shifts of Hydronium and Hydroxyl Ions"
A. J. Kresge
J. Chem. Phys. 39, 1360 (1963)

"An Infrared and Nuclear Magnetic Resonance Study of the Nature of Ethylenediaminetetra-acetic Acid and Some Related Substances in Solution: Hydrogen Bonding in α-Aminopolycarboxylic Acid Systems"
D. Chapman, D. R. Lloyd and R. H. Prince
J. Chem. Soc. 3645 (1963)

"The Constitutions of the Cucurbitacins"
W. T. DeKock, P. R. Enslin, K. B. Norton, D. H. R. Barton, B. Sklarz and A. A. Bothner-By
J. Chem. Soc. 3828 (1963)

"A Nuclear Magnetic Resonance Study of cis-trans-Isomerism in 2-Methylpent-2-enyl Thiolacetate"
B. K. Tidd
J. Chem. Soc. 3909 (1963)

"Synthetic Studies in the Diterpene Series"
D. Nasipuri
J. Indian Chem. Soc. 40, 407 (1963)

"The Tumor-Enhancing and Irritant Principles from Croton tiglium L."
B. L. Van Duuren, E. Arroyo and L. Orris
J. Med. Chem. 6, 616 (1963)

"Synthesis of 1,1-Dimethyl-trans-decalin-10-carboxylic Acid"
W. L. Meyer and A. S. Levinson
J. Org. Chem. 28, 2184 (1963)

"Stereoisomeric 3β,17β-Dihydroxyandrostan-16-ylacetic Acids"
P. Kurath, W. Cole, J. Tadanier, M. Freifelder, G. R. Stone and E. V. Schuber
J. Org. Chem. 28, 2189 (1963)

"The Alkaloids of Cephalotaxus drupacea and Cephalotaxus fortunei"
W. W. Paudler, G. I. Kerley and J. McKay
J. Org. Chem. 28, 2194 (1963)

"Reactions of the Dibromocarbene Adducts of Bicyclo[2.2.1]heptene and Bicyclo[2.2.1]heptadiene"
W. R. Moore, W. R. Moser and J. E. LaPrade
J. Org. Chem. 28, 2200 (1963)

"Addition Products of Dichlorocarbene to Norbornylene and Norbornadiene and Their Rearrangements"
R. C. DeSelms and C. M. Combs
J. Org. Chem. 28, 2206 (1963)

"Reactions Related to the Addition of Dichlorocarbene to Norbornylene"
E. Bergman
J. Org. Chem. 28, 2210 (1963)

"Ring Expansion of 2-Alkyl-1-indanones to Isocarbostyril Derivatives"
E. J. Moriconi, F. J. Creegan, C. K. Donovan and F. A. Spano
J. Org. Chem. 28, 2215 (1963)

"Steroids with Functional Sulfur Groups. III. The Reaction of Some Thiocyano Steroids"
I. Kitagawa, Y. Ueda, T. Kawasaki and E. Mosettig
J. Org. Chem. 28, 2228 (1963)

"Structural Determination of cis- and trans-1,3-Dibromocyclohexane"
B. Franzus and B. E. Hudson, Jr.
J. Org. Chem. 28, 2238 (1963)

"Polycyclic Musks. I. Acyl- and Dinitropolyalkyltetralin Derivatives"
T. F. Wood, W. M. Easter, Jr., M. S. Carpenter and J. Angiolini
J. Org. Chem. 28, 2248 (1963)

"The Pyrolysis of Hexachlorocyclopentadiene"
E. T. McBee, W. L. Dilling and H. P. Braendlin
J. Org. Chem. 28, 2255 (1963)

"The Stereochemistry of the Neber Rearrangement"
H. O. House and W. F. Berkowitz
J. Org. Chem. 28, 2271 (1963)

"The Products of the Reactions of Sodium t-Butylmercaptide with Vinyl Chloride, Vinylidene Chloride, and cis- and trans-Dichloroethylenes"
J. Flynn, Jr., V. V. Badiger and W. E. Truce
J. Org. Chem. 28, 2298 (1963)

"The Conformational Preference of Sulfur in Hemithioketals"
M. P. Mertes
J. Org. Chem. 28, 2320 (1963)

"Addition of Grignard Reagents to 1,3-Dimesitoylbenzene"
R. C. Fuson and R. J. Sauer
J. Org. Chem. 28, 2323 (1963)

"2,4-Dinitrophenylhydrazones. IV. The Reactions of Vinyl Ketones and β-Alkoxy Ketones. The Formation of Substituted 6-Nitrobenzotriazole Oxides"
H. J. Shine, L.-T. Fang, N. E. Mallory, N. F. Chamberlain and F. Stehling
J. Org. Chem. 28, 2326 (1963)

"Organic Sulfur Compounds. XI. Amine-Hydroperoxide Complexes as Intermediates in the Co-oxidation of Thiols with 2,5-Dimethyl-2,4-hexadiene"
A. A. Oswald, K. Griesbaum and B. E. Hudson, Jr.
J. Org. Chem. 28, 2351 (1963)

"Organic Sulfur Compounds. XII. Factors Determining a 1,2- vs. 1,4-Mechanism of Radical Reactions of Conjugated Diolefins. Co-oxidation with Thiols by Oxygen"
A. A. Oswald, K. Griesbaum and B. E. Hudson, Jr.
J. Org. Chem. 28, 2355 (1963)

"Imidazoimidazoles. I. The Reaction of Ureas with Glyoxal Tetrahydroimidazo[4,5-d]imidazole-2,5-diones"
J. Nematollahi and R. Ketcham
J. Org. Chem. 28, 2378 (1963)

"A Synthesis of Quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (Quadricyclene) via Photochemical Decomposition of 6,7-Diazaquadricyclo[3.2.1.$1^{3,6}$.$0^{2,4}$]non-6-ene"
R. M. Moriarty
J. Org. Chem. 28, 2385 (1963)

"Terpenoids. LIII. Demonstration of Ring Conformational Changes in Triterpenes of the β-Amyrin Class Isolated from Stryphnodendron coriaceum"
B. Tursch, E. Tursch, I. T. Harrison, G. B. C. T. DeC. B. Da Silva, H. J. Monteiro, B. Gilbert, W. B. Mors and C. Djerassi
J. Org. Chem. 28, 2390 (1963)

"The Synthesis of 1,8-Diphenylnaphthalene"
H. O. House, R. W. Magin and H. W. Thompson
J. Org. Chem. 28, 2403 (1963)

"Reduction of Azabicyclic Ketones"
H. O. House, N. C. Müller, C. G. Pitt and P. P. Wickham
J. Org. Chem. 28, 2407 (1963)

"The Synthesis and Reactions of N,N'-Dicarbalkoxy-N,N'-dialkoxyhydrazines and Some Observations on Carbalkoxylium Ions"
R. J. Crawford and R. Reap
J. Org. Chem. 28, 2419 (1963)

"Steroid Epoxy Ketones. II. 2,3-Oxygenated Steroids from 1α,2α-Oxidocholestan-3-one"
W. Reusch and R. LeMahieu
J. Org. Chem. 28, 2443 (1963)

"The Synthesis of Δ^5-Cholestene-3β,19-diol via the 3,5-Cyclosterol Rearrangement. A Novel Route to 19-Nor Sterols"
R. M. Moriarty and T. D. D'Silva
J. Org. Chem. 28, 2445 (1963)

"The Preparation of Chloromethyl Vinyl Ketones"
R. F. Hudson and P. A. Chopard
J. Org. Chem. 28, 2446 (1963)

"Comments on N.m.r. Spectra of Some Optically Active Dimethylcyclohexenes"
G. V. Smith and P. J. Trotter
J. Org. Chem. 28, 2450 (1963)

"Synthesis and Identification of Dispiro[5.1.5.1]tetradecane"
P. F. Donovan, S. A. Liebman and S. D. Koch
J. Org. Chem. 28, 2451 (1963)

"Acetylenic Amines. VI. Amides of Secondary Acetylenic Amines"
N. R. Easton and R. D. Dillard
J. Org. Chem. 28, 2465 (1963)

"Solvent Effects on the Claisen Rearrangement of β-Methylallyl Phenyl Ether"
A. T. Shulgin and A. W. Baker
J. Org. Chem. 28, 2468 (1963)

"3-Thietanone 1,1-Dioxide"
R. H. Hasek, P. G. Gott, R. H. Meen and J. C. Martin
J. Org. Chem. 28, 2496 (1963)

"Nuclear Magnetic Resonance of Alumina Containing Transition Metals"
D. E. O'Reilly and C. P. Poole, Jr.
J. Phys. Chem. 67, 1762 (1963)

"Bridge Proton-Terminal Proton Coupling in Diborane"
D. F. Gaines, R. Schaeffer and F. Tebbe
J. Phys. Chem. 67, 1937 (1963)

"Proton Magnetic Resonance of the Silver Perchlorate-Dioxane Complex $AgClO_4 \cdot 3C_4H_8O_2$"
A. Kawamori
J. Phys. Soc. Japan 18, 1218 (1963)

"Polymerization of Alicyclic Epoxides with Aluminum Alkyl Catalysts"
R. Bacskai
J. Polymer Sci. A1, 2777 (1963)

"Effects of High Energy Irradiation on Polypropylene"
S. E. Chappell, J. A. Sauer and A. E. Woodward
J. Polymer Sci. A1, 2805 (1963)

"Proton Magnetic Resonance in Natural Rubber: Comparison with Dielectric Measurements"
H. Kusumoto and H. S. Gutowsky
J. Polymer Sci. A1, 2905 (1963)

"Stereoregular Polymers of Methyl, iso-Butyl and tert-Butyl Vinyl Ethers"
R. J. Kern, J. J. Hawkins and J. D. Calfee
Makromol. Chem. 66, 126 (1963)

"Nuclear Magnetic Resonance in Ferromagnetic Mn_5Ge_3 at Low Temperatures"
R. F. Jackson, R. G. Scurlock, D. B. Utton and T. H. Wilmshurst
Phys. Letters 6, 39 (1963)

"Magnetic Susceptibilities and Nuclear Magnetic Resonance Measurements in V-Fe Alloys"
D. J. Lam, D. O. Van Ostenburg, M. V. Nevitt, H. D. Trapp and D. W. Pracht
Phys. Rev. 131, 1428 (1963)

"Nuclear Magnetic Resonance Study of Al^{27} in NiAl"
J. A. Seitchik and R. H. Walmsley
Phys. Rev. 131, 1473 (1963)

"Correlation Effect on the Nuclear Magnetic Resonance Linewidth in Magnetic Materials"
P. Pincus
Phys. Rev. 131, 1530 (1963)

"Diffusion Narrowing of Nuclear Magnetic Resonance Linewidth of F^{19} in $CaF_2:Sm^{2+}$"
W. J. Veigele and A. W. Bevan, Jr.
Phys. Rev. 131, 1585 (1963)

"Nuclear Magnetic Relaxation by Hindered Rotations"
R. DeMicheli, L. Giulotto and G. F. Nardelli
Phys. Rev. 131, 1619 (1963)

"Nuclear Magnetic Resonance Studies of Polymers. III. Chemical Reactions in a Solution of Poly-(γ-Benzyl Glutamate) in Trifluoroacetic Acid"
M. V. Volkenstein, A. I. Kol'tsov and J. Marshall
Polymer Sci. U.S.S.R. 4, 286 (1963)

"Isomeric Equilibrium Among Methylcyclopentadiene Isomers"
V. A. Mironov, E. V. Sobolev and A. N. Elizarova
Proc. Acad. Sci. USSR. Chem. Sect. (English Transl.) 146,898 (1962)

"Structure of Amorphigenin, the Aglycone of the First Natural Rotenoid Glycoside"
L. Crombie and R. Peace
Proc. Chem. Soc. 246 (1963)

"The Synthesis of a New Fragmentation Product of a Cephalosporanic Acid Derivative"
S. H. Eggers, T. R. Emerson, V. V. Kane and G. Lowe
Proc. Chem. Soc. 248 (1963)

"Mechanism for Self-Diffusion in Ice."
L. Onsager and L. K. Runnels
Proc. Nat. Acad. Sci. U.S. 50, 208 (1963)

"Nuclear Magnetic Resonance in Metals under Anomalous Skin Effect Conditions"
P. S. Allen and E. F. W. Seymour
Proc. Phys. Soc. 82, 174 (1963)

"The Width of Nuclear Magnetic Resonance Rotary Saturation Lines"
S. Clough, K. W. Gray and I. R. McDonald
Proc. Phys. Soc. 82, 182 (1963)

"Nuclear Spin-Lattice Relaxation in Ferro- and Antiferromagnetic Materials"
L. L. Buishvili
Soviet Phys. - Solid State (English Transl.) 5, 166 (1963)

"Resonance Absorption by Band Carriers in InSb"
Yu. A. Bratashevskii, A. A. Galkin and Yu. M. Ivanchenko
Soviet Phys. - Solid State (English Transl.) 5, 260 (1963)

"Spin-Lattice Relaxation of Yb^{3+} in CdF_2"
P. P. Pashinin and A. M. Prokhorov
Soviet Phys. - Solid State (English Transl.) 5, 261 (1963)

"Second Moment of the Nuclear Resonance Line for Spin 5/2 Nuclei"
I. Biryukov and I. Berson
Soviet Phys. Solid State (English Transl.) 5, 364 (1963)

"Theory of Magnetic Resonance Saturation in Ionic Crystals"
B. N. Provotorov
Soviet Phys. Solid State (English Transl.) 5, 411 (1963)

"Theory of the Paramagnetic Spin-Lattice Relaxation in Crystals with Ions in the S State. One-Phonon Processes"
A. M. Leushin
Soviet Phys. Solid State (English Transl.) 5, 440 (1963)

"Theory of Two-Quantum Magnetoacoustic Transitions"
A. R. Kessel' and U. Kh. Kopvillem
Soviet Phys. Solid State (English Transl.) 5, 485 (1963)

"The Stereochemical Configuration of the Cyclooctatetraene Dihalides"
V. Georgian, L. Georgian and A. V. Robertson
Tetrahedron 19, 1219 (1963)

"The Reaction Between Pyridazine and Maleic Anhydride"
R. C. Cookson and N. S. Isaacs
Tetrahedron 19, 1237 (1963)

"Studies on the Constituents of Umbelliferae Plants. VII. Structure of Ligustilide 2"
H. Mitsuhashi and U. Nagai
Tetrahedron 19,1277 (1963)

"Estafiatin, A New Sesquiterpene Lactone Isolated From Artemisia Mexicana (Willd)"
F. Sánchez-Viesca and J. Romo
Tetrahedron 19, 1285 (1963)

"Hawaiian Plant Studies . IX. The Alkaloids of Platydesma Campanulata Mann"
F. Werny and P. J. Scheuer
Tetrahedron 19, 1293 (1963)

"Mutarotation of a D-Glucurone Derivative"
F. P. Johnson and H. V. Riggs
Tetrahedron Letters 1023 (1963)

"The Tautomeric Structure of Deoxycytidine"
T. L. V. Ulbricht
Tetrahedron Letters 1027 (1963)

"A Non-Conjugated 1,3-Diene"
H. Wynberg, A. De Groot and D. W. Davies
Tetrahedron Letters 1083 (1963)

"The Stereochemistry of Atisine. A Chemical Correlation of Atisine and the Resin Acids"
W. A. Ayer, C. E. McDonald and G. G. Iverach
Tetrahedron Letters 1095 (1963)

"A Novel Rearrangement Catalyzed by a Grignard Reagent"
S. O. Winthrop
Tetrahedron Letters 1113 (1963)

"On the Reaction of Cyclopentadienylsodium and Epichlorohydrin"
K. Bangert and V. Boekelheide
Tetrahedron Letters 1119 (1963)

"The Structure of Arborescin"
R. B. Bates, Z. Cěkan, V. Procházka and V. Herout
Tetrahedron Letters 1127 (1963)

"π-Cyclopentadienyl-π-Cycloheptatrienyl Derivatives of Chromium and Molybdenum"
R. B. King and M. B. Bisnette
Tetrahedron Letters 1137 (1963)

"Conversion of Indones to Quinoline and Isoquinoline Derivatives. III. Schmidt Reaction with 2,3-Diphenylindone and Similar Compounds"
A. Marsili
Tetrahedron Letters 1143 (1963)

"Effect of Symmetry on C^{19} N.M.R. Shifts in Steroids"
E. R. Malinowski, M. S. Manhas, G. H. Müller and A. K. Bose
Tetrahedron Letters 1161 (1963)

"Mecanisme de la Transposition de Favorski de la Bromo-2 Cyclobutanone"
J. M. Conia et J. Salaün
Tetrahedron Letters 1175 (1963)

"Tetrachlorocyclopropene and Hexachlorocyclopropane from Pentachlorocyclopropane"
S. W. Tobey and R. West
Tetrahedron Letters 1179 (1963)

"On the Structure of the Indole Grignard Reagent"
M. G. Reinecke, H. W. Johnson and J. F. Sebastian
Tetrahedron Letters 1183 (1963)

"Thia-Aromaten. IX. Dithiafulvalene"
A. Lüttringhaus, E. Futterer und H. Prinzbach
Tetrahedron Letters 1209 (1963)

"The Conformations of the Cis and Trans-1,2-Cyclohexanediols and Certain of their Derivatives"
R. U. Lemieux and J. W. Lown
Tetrahedron Letters 1229 (1963)

"An Intramolecular Diels-Alder Reaction. A Simple Synthesis of Y-Apopicropodophyllin"
L. H. Klemm and K. W. Gopinath
Tetrahedron Letters 1243 (1963)

"The Structure of Kryptocapsin"
L. Cholnoky, J. Szabolcs, R. D. G. Cooper and B. C. L. Weedon
Tetrahedron Letters 1257 (1963)

"A Novel Benzenoid Steroid"
C. F. Hammer, D. S. Savage, J. B. Thomson and R. Stevenson
Tetrahedron Letters 1261 (1963)

"Nuclear Magnetic Resonance Studies of Silicon Hydrides and Derivatives. Part 3. Chemical Shifts and Spin-Spin Coupling Constants in Monomethylsilyl Compounds"
E. A. V. Ebsworth and S. G. Frankiss
Trans. Faraday Soc. 59, 1518 (1963)

"Nuclear Spin-Lattice Relaxation in Polyethylene Glycols"
G. Allen, T. M. Connor and H. Pursey
Trans. Faraday Soc. 59, 1525 (1963)

Methacrylsäuremethylester-eisentetracarbonyl und Vinylacetat-eisentetracarbonyl"
E. Koerner von Gustorf, M.-J. Jun und G. O. Schenck
Z. Naturforsch. 18b, 503 (1963)

"Über Aromatenkomplexe von Metallen LXXI. Cyclopentadienyl-benzol-mono-kohlenoxyd-Kationkomplexe des Molybdäns und Wolframs"
E. O. Fischer und F. J. Kohl
Z. Naturforsch. 18b, 504 (1963)

"Cyclopentadienyltrimethylplatinum (IV)"
S. D. Robinson and B. L. Shaw
Z. Naturforsch. 18b, 507 (1963)

"Kernmagnetische Messungen an einem linearen Polyäthylen. I. Spin-Gitter-Relaxationzeit T_1 und Linienform"
U. Haeberlen, R. Hausser und F. Noack
Z. Naturforsch. 18a, 689 (1963)

"Die Protonenrelaxation in konzentrierten wässrigen Lösungen von Magnesiumsulfat"
U. Lindner und H. Pfeifer
Z. Naturforsch. 18a, 773 (1963)