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Author Index
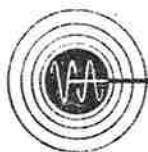
VARIAN associates

611 HANSEN WAY · PALO ALTO, CALIFORNIA · DAVENPORT 6-4000

November 22, 1961

Dr. Aksel A. Bothner-by
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Aksel:

We have recently run across an interesting example of the use of the shielding effect of the aromatic ring current to distinguish between two structural possibilities in an alkaloid interconversion problem sent to us by Dr. Neville Finch of the CIBA Laboratories, Summit, New Jersey. A compound arose which contained two methoxy groups and which could exist either as the essentially planar type of structure exemplified by yohimbine (Figure 1) or which could have the B and C rings joined in the spiro-fashion shown in Figure 2, in which case the plane of the aromatic ring would be perpendicular to the plane of the rest of the molecule.

Johnson and Bovey[1] have calculated the distribution of magnetic field around an aromatic ring as a function of the number of ring radii from the center of the ring along the axis perpendicular to the plane of the ring (Z) and radially in the plane of the ring (ρ). Dreiding models of the compounds in question were constructed and the values of Z and ρ for the estimated average position of the carbomethoxy group in each case were measured. For yohimbine, approximate values are $\rho = 5$, $Z = 1$. For the spiro-attachment of rings B and C, the approximate values are $\rho = 2$, $Z = 3.4$. From reference 1, one predicts that the carbomethoxy protons in yohimbine will be about 0.1 ppm less shielded than in a compound without an aromatic ring, while those in the compound shown in Figure 2 will be about 0.2 ppm more shielded.

Studies of a large number of model compounds have shown that the typical chemical shift for a carbomethoxy group is 3.67 ppm from $SiMe_4$. Yohimbine gives a peak at 3.79, less shielded by 0.12 ppm, while the unknown gives a peak at 3.52, 0.15 ppm more shielded than the typical unperturbed value. Thus, the structure shown in Figure 2 is confirmed.

From these results it can be seen that even when the protons being observed are 3.5 to 5 ring radii distant from the center of an aromatic ring, quite sizable effects can arise from the long-range shielding.

I am planning to submit a letter to the next issue of MELLONMR dealing with the use of various types of sample tubes in the A-60 spectrometer, as it appears that some misconceptions have arisen.

Sincerely yours,

James N. Shoolery

James N. Shoolery

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[1] J. Chem. Phys. 29, 1012 (1958).

Figure 1

Figure 2
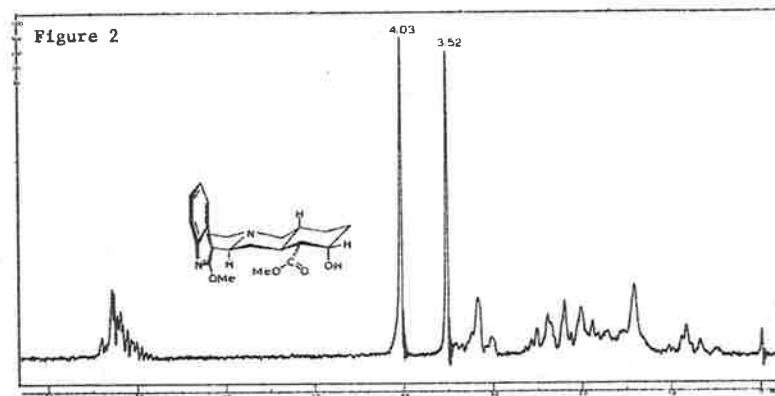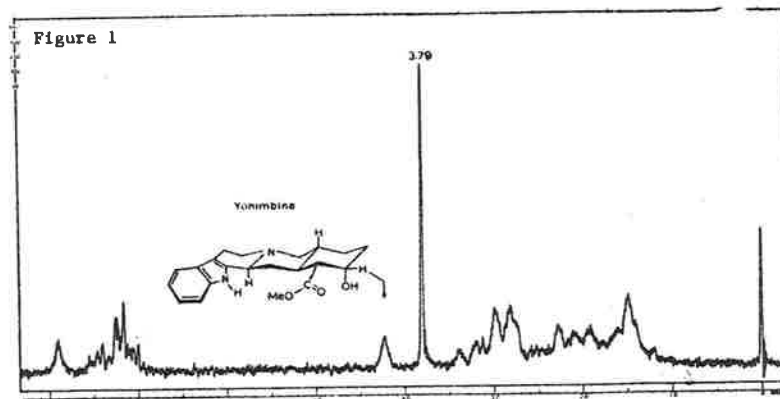
38-1

KARL-MARX-UNIVERSITÄT

PHYSIKALISCHES INSTITUT

Herrn
Dr.Aksel A. Bothner By
Mellon-Institut

P i t t s b u r g h 13 Pa

4400 Fifth Avenue

Dear Sir,

I would like to inform you of some of our works.

1. The dependence of the H-H spin coupling constants in hydrocarbons upon substituents

Using the formula published by Hiroike, it is possible to calculate the H-H coupling constants over 3 bonds in hydrocarbons by means of VB eigenfunctions in dependence on the coefficients of the ionic terms of the C-H bonds I_C. This has been practised on systems similar to ethane and ethylene, applying the VB functions of Karplus. The results thus yielded are somewhat to small compared to the experimental values, but they show the proper angular dependence. Multiplied by the factor 1.5, one gets the dependence upon the coefficient I_C approximatively like

$$J \text{ (ethyl)} = 6.59 - 4.2 \, I_C$$
$$J_{trans}(\text{vinyl}) = 18.3 - 13.5 \, I_C$$
$$J_{cis}(\text{vinyl}) = 13 - 10.5 \, I_C$$

On the other hand, the experiments give approximatively the following dependence on the electronegativity X of the substituents.

$$J \text{ (ethyl)} = 7.8 - 0.55 \, (X-2)$$
$$J_{trans}(\text{vinyl}) = 19 - 3.25 \, (X-2)$$
$$J_{cis}(\text{vinyl}) = 11.9 - 3.7 \, (X-2).$$

Comparing both terms, the relation $I_C \approx 0.3 \, (X-2)$ seems adequate.

2. Long range C^{13}-H coupling constants

By means of the VB eigenfunctions of Karplus for systems similar to ethane and ethylene $H_A-C_{A1} \quad C_{A2}-C_{B2} \quad C_{B1}-H_B$ the C^{13}-H coupling constants over 2 bonds may be calculated. This coupling constant has been evaluated for sp^{nb} hybridization of C_B as follows

$$J_{C^{13}-H} = J_{C_{B2}H} + \sum_{j=1}^{nb} J_{C_{B1}H_A} \, (\theta_j)$$

For systems similar to ethane, one obtains $J_C^{13} - C - H = -6.8\ldots -7.5$ cps according to the formula of Karplus and Anderson and $J_C^{13} - C - H = -4.4\ldots-5.1$ cps taking the formula of Hiroike. The experimental values of Karabatsos are lying between $|J| = 4.1$ and 5.6 cps.

For the C^{13}-H couplings separated by 3 bonds proper eigenfunctions have been established. Thus we will have following the formula of Hiroike for saturated systems $J_C^{13}-C-C-H = 4.2$ cps. Karabatsos' experimental values are lying between $|J| = 3.8$ and 5.8 cps.

These calculations are probably to bring out that the contact term represents a sufficient approximation to these coupling constants as well as to proton couplings.

3. The π contributions to the C^{13}-H couplings

Applying the theory of Karplus for the π contributions of proton couplings to C^{13}-H couplings, the following values for these contributions are obtained,

on 2 bonds from -1.6 to -2.3 cps
on 3 bonds form 0.4 to 5.4 cps
on 4 bonds from -0.6 to -1.7 cps.

These values are the result of the calculations for different positions of the π-electrons and for different assumed a_C^{13} values.

A detailed publication will appear in "Annalen der Physik".

Sincerely yours,

(J.Ranft)
Dipl.-Phys.

From Dr. R.E. Richards, F.R.S.

Lincoln College,

OXFORD.

16th November, 1961.

Dr. A.A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13,
Pa.,
U.S.A.

Dear Aksel,

I thought you might like to hear about some experiments which Mr. Herbison-Evans has been doing here at Oxford. The line widths of nitrogen nuclear resonance spectra are often determined by the spin lattice relaxation time of the nitrogen atom. This is affected mainly by the electric quadrupole coupling between the nitrogen and the electric field around it in the molecule. When the nitrogen atom is in symmetrical environments, as in the ammonium ion, the electric quadrupole coupling is small, the relaxation time is relatively long and narrow nuclear resonance lines are observed. When the electric field gradient is less symmetrical, as for example in amides, the quadrupole coupling is greater, the spin lattice relaxation time shorter and the line width broader. It occurred to us that these effects might be used to throw further light on the question of the mechanism of the protonation of amides. Infra-red evidence has been interpreted by many authors in terms of protonation on the nitrogen atom of amides, whereas the hydrogen nuclear resonance spectra have been interpreted in terms of protonation on the oxygen. If the addition of the proton occurs at the nitrogen atom, we would expect that the nitrogen would achieve a more symmetrical electrical environment, whereas if the proton is added onto the oxygen, the increased double bond character in the CN bond would cause the nitrogen to have a greater quadrupole coupling.

The spin lattice relaxation time of the nitrogen is inversely proportional to the square of the quadrupole coupling constant and also to the viscosity of the solution. If therefore we plot the nitrogen nuclear resonance line width as a measure of the inverse spin lattice relaxation time against the viscosity of the mixture, we should obtain a straight line. This plot for mixtures of dimethylformamide and glycerol does in fact turn out to be a straight line. Addition of strong acids, such as trifluoro acetic acid to dimethyl formamide, produce considerable changes in the viscosity and so we have plotted the nitrogen nuclear resonance line width in such mixtures against their viscosity. If the amide was protonated on the nitrogen atom we would expect the resulting plot to have a smaller slope than that for the amide and glycerol, whereas if protonation occurred on the oxygen then the plot would have a much steeper slope than that of the glycerol amide mixture. In fact the plot of line width against viscosity for dimethyl formamide trifluoro acetic acid mixtures rises very much more steeply than that for the glycerol amide mixtures, showing that the

quadrupole coupling constant is being increased by the addition of acid. This seems to us to provide strong additional support for the fact that these amides are protonated predominantly on the oxygen atom rather than on the nitrogen. The plot of line width against viscosity for the mixtures with acids is not linear except at very high acid concentrations because, of course, there is an equilibrium between amide, acid, and the protonated species. But the slope of the curve is so much steeper that there does not seem to us to be any ambiguity about it.

I should like to say how much we all appreciate receiving the Mellon News Letter and we find it most interesting.

With best regards,

Yours sincerely,

Rex Richards

Dr. A. A. Bothner-By
Mellon Institut
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Aksel:

Thanks for your offer of mentioning our collection of theoretical n.m.r. spectra in MELLONMR. Some time ago, we finally decided to calculate spectra for a considerable number of ABC and A_2B_2 cases so that we would have a reference file with which we could quickly compare observed spectra. There are a total of about 450 spectra of each group, with values of J/ν from 0-3. Several persons suggested that we should try to make this collection available to other chemists, and so we contacted Bill Benjamin and asked if he would be interested in publishing it. He was interested, and as a result, it will be published sometime next year.

Besides the above cases, the collection also includes, for reference, AB, AB_2, AB_3 and also A_2B_3 cases, the latter of which is restricted to those having all AB coupling constants equal. The spectra will appear in the form of ordered tables of frequencies and intensities, and also computor printouts of the actual spectra using a reasonable value for instrument resolving power. I think Bill Benjamin plans to send you a couple of examples of our spectra.

I am interested in your "super" n.m.r. program. I was thinking of trying to write one some time ago, but then heard from Moore at China Lake who said that he is working on such a program. Consequently, I have been happy to forget about this project.

While I am writing, I might mention that we have gotten the chemical shifts and spin coupling constants for cyclopropanecarboxylic acid. Using the following numbering,
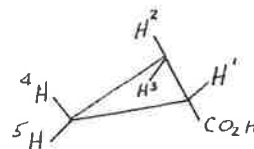
we find

$$\nu(1) = 505.4 \sec^{-1} \quad \nu(2) = 536.5 \quad \nu(3) = 541.7$$

(TMS = 600.0)

$$J(1,2) = 8.0 \quad J(1,3) = 4.6 \quad J(2,3) = -4.3$$

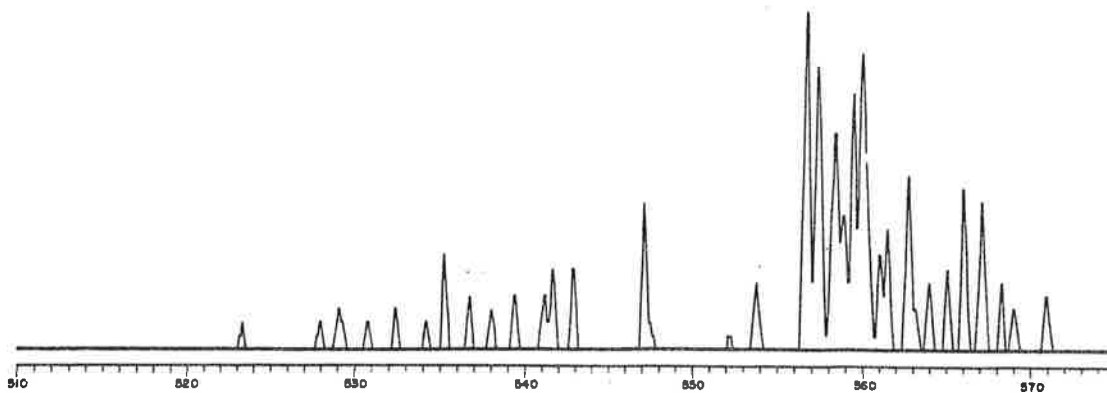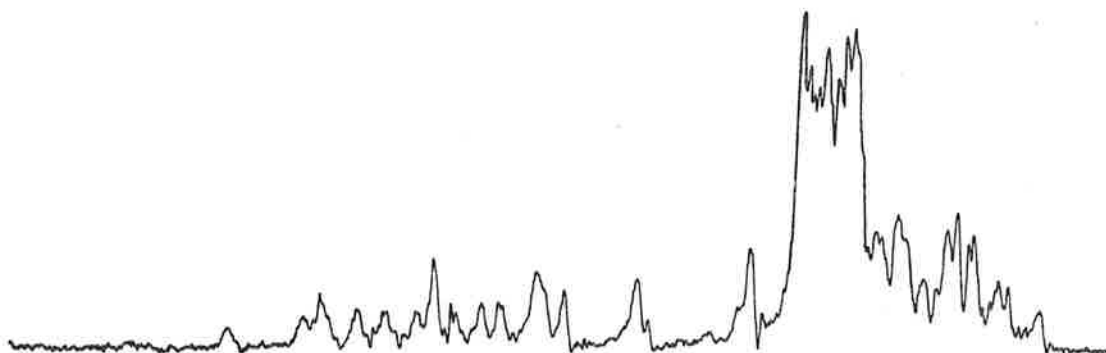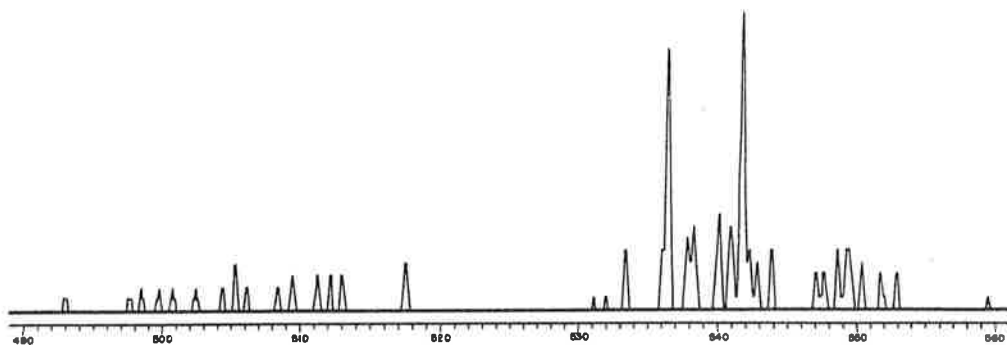$$J(2,4) = 11.0 \quad J(2,5) = 7.5$$

These parameters gave a good fit at both 40 and 60 mc. (see the enclosed figures), and it was not possible to get agreement with the spectrum of the acid or of its α-deutero derivative if $J(2,3)$ were chosen to have the same sign as the other coupling constants.
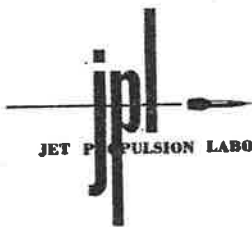
Sincerely,

Kenneth B. Wiberg

November 10, 1961

Dr. Aksel A. Bothner-By
Assistant Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

We have been doing some more work with our proton-proton spin decoupler. After seeing Freeman's very interesting recent MELLONMR letter on the determination of relative signs of spin coupling constants, we have given his technique a try. It's really amazing how easy it works!

We have been able to show what all the relative signs of the coupling constants are in the five membered ring of indene. J_{AK} and J_{KX} have the same sign while the sign of J_{AX} is different from the latter two. We have submitted a paper on indene to the Journal of Chemical Physics. Some of the spectra we obtained are shown below.
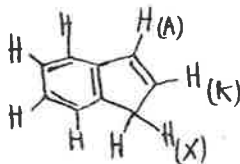
The following set of parameters fit the five membered-ring protons excellently:

$J_{AK} = 15.58 \pm 0.02$ cps $\delta_A = 399.60 \pm 0.80$ cps
$J_{AX} = -1.90 \pm 0.02$ $\delta_K = 368.37 \pm 0.80$ } relative to TMS
$J_{KX} = 12.02 \pm 0.02$ $\delta_X = 179.51 \pm 0.20$

As can be seen from the spectra, there is a long-range coupling of 0.59 ± 0.02 between the A proton and one of the aromatic ring protons. There are additional long-range couplings between the X_2 protons and aromatic ring protons as shown.

Snyder and Roberts have recently looked at 1-chlorobutadiene-1,2 and the relative signs were bothering them. We had them up one day for a demonstration and we determined that J_{AB} and J_{BX} have different signs as shown by the spectra below.
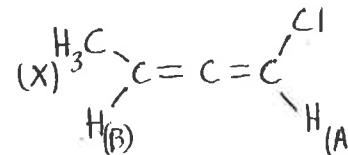
We enjoy reading MELLONMR letters very much. We would like to know if it is possible to obtain back issues. The first one we received was #29. We would be willing to pay.

There have been some comments in recent months on filing systems for NMR spectra. We would like to remark (with tongue in cheek) that the most important components in our filing system are an adequately sized waste basket and a pair of sharp scissors.

Yours very truly,

Stanley L. Manatt
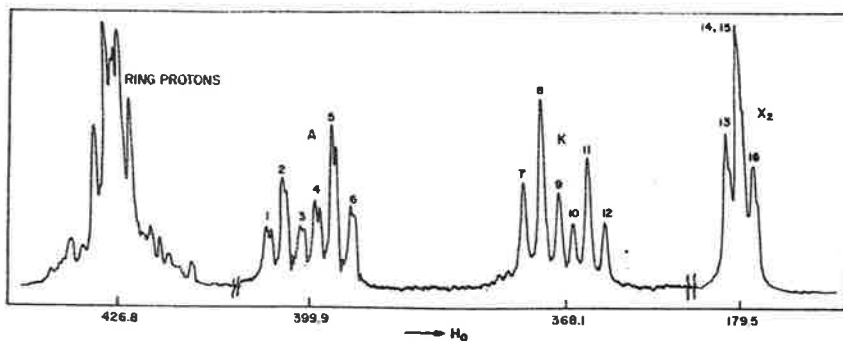
Daniel D. Elleman

SLM:DDE:ch

Fig. 1. The 60 Mc/sec NMR spectrum of indene. The A and K regions were run at twice the gain of the aromatic ring protons and the X_2 region.
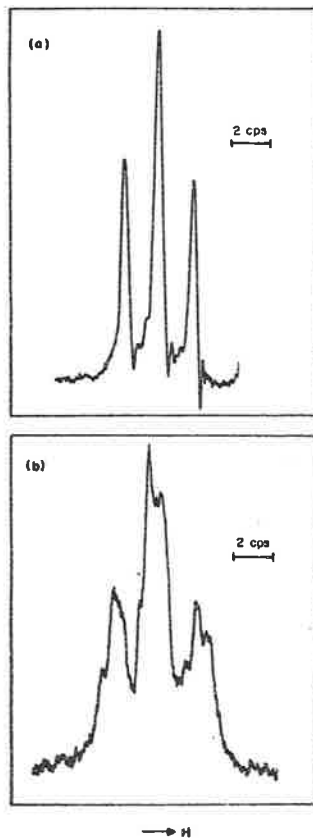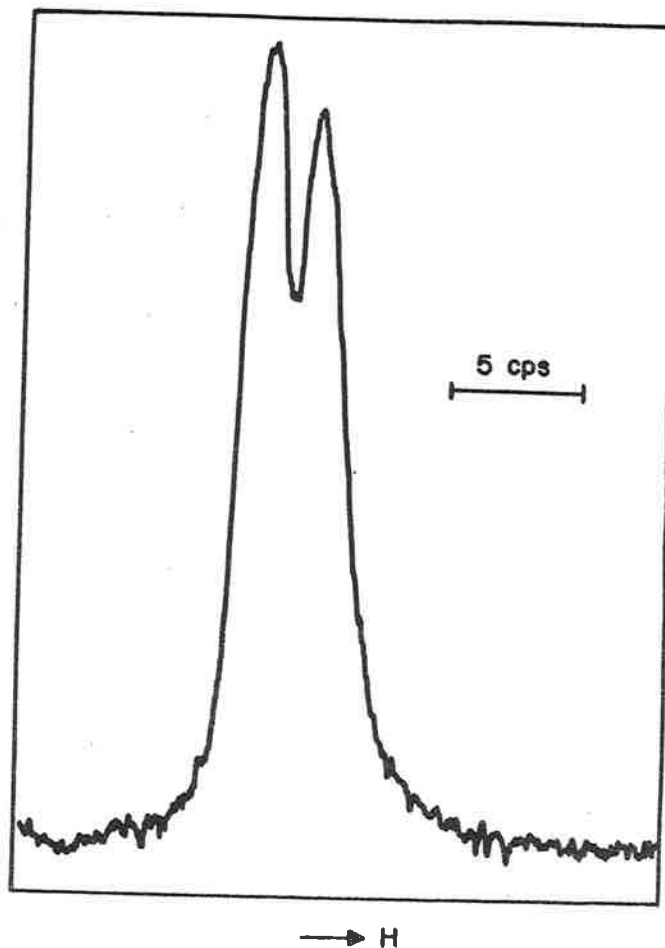

Fig. 2.

The X_2 region of the spectrum: a, double irradiation of the aromatic ring protons, $\gamma H_1/2\pi$ about 21 cps.; b, normal high-resolution spectrum of the X_2 region at a slightly slower sweep rate showing the structure due to long-range coupling with the aromatic protons.

Fig. 3. The X_2 region of the spectrum of indene with double irradiation of the A proton, $\gamma H_1/2\pi$ about 21 cps.
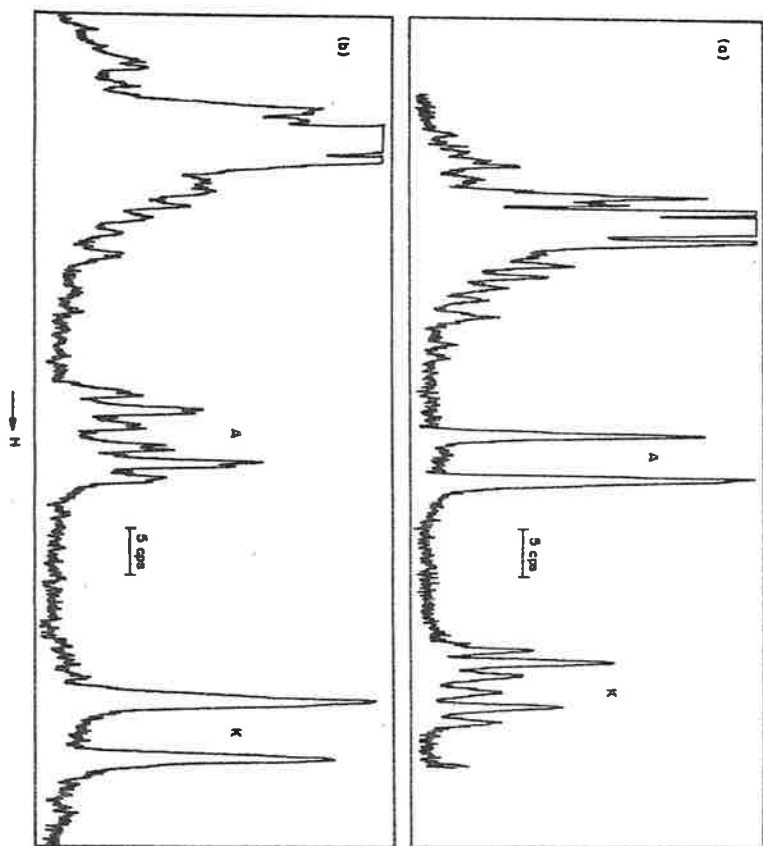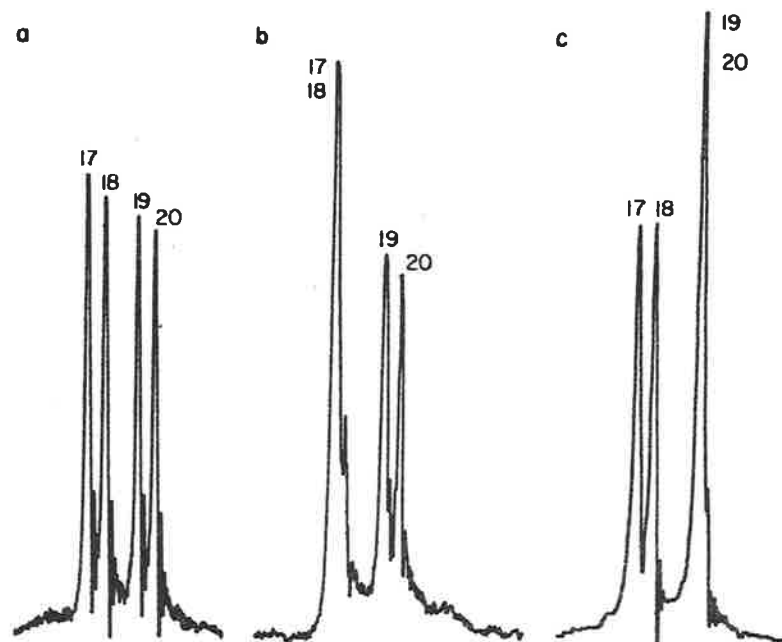
Fig. 4. Strong irradiation of the X_2 protons, $\gamma H_1/2\pi$ about 21 cps: a, while observing the A-region; b, while observing the K-region. Sweep rate of b slower than a.
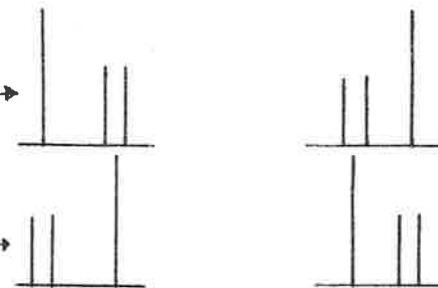
Fig. 5.--Methyl protons of 1-chlorobutadiene-1,2: a, undecoupled phase detected; b, decoupled phase detected with $\underline{\Omega} = 245.0$ cps. $\underline{\gamma H_1}/2\pi = 8.9$ cps.; c, decoupled phase detected with $\underline{\Omega} = 258.0$ cps., $\underline{\gamma H_1}/2\pi = 8.9$ cps. In all cases increasing field is to the right.
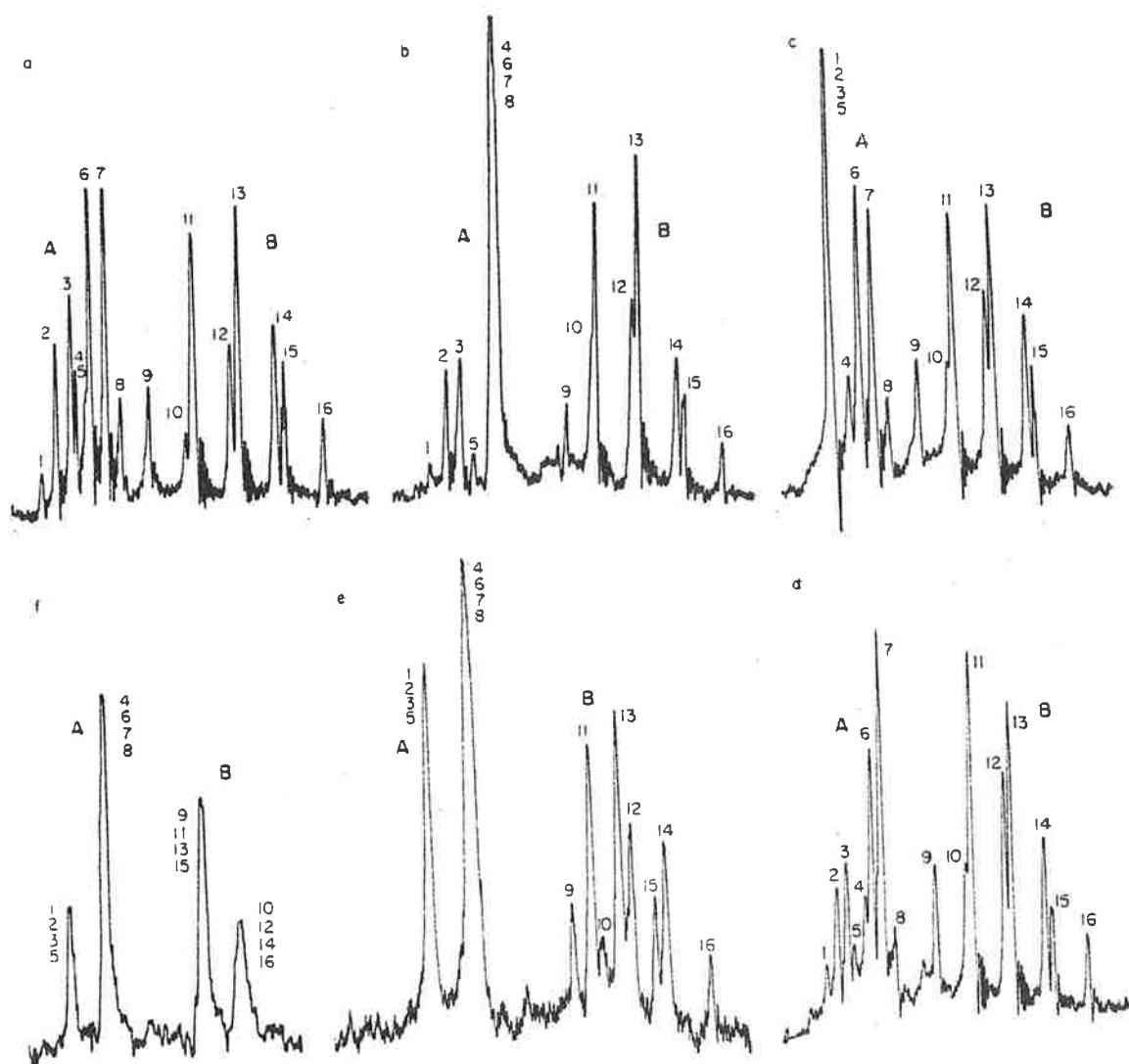
Fig. 6.--Allenic proton region: a, undecoupled phase detected; b, decoupled phase detected with $\Omega = 245.0$ cps., $\gamma H_1/2\pi = 8.9$ cps.; c, decoupled phase detected with $\Omega = 258.0$ cps., $\gamma H_1/2\pi = 8.9$ cps.; d, decoupled phase detected with $\Omega = 251.5$ cps., $\gamma H_1/2\pi = 8.9$ cps.; e, A proton completely decoupled from X_3 protons, $\Omega = 250.5$, $\gamma H_1/2\pi = 45$ cps.; f, AB region completely decoupled from X_3 protons, $\gamma H_1/2\pi = 112$ cps. In all cases increasing field is to the right.

Department of Scientific and Industrial Research

NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

Telegrams: Physics, Teddington   Telephone: TEDdington Lock 3222, ext. 199

BASIC PHYSICS DIVISION

Please address any reply to
THE DIRECTOR
and quote: BP.5/6/01
Your reference:

31st October, 1961.

Dear Professor Bothner-By,

A negative long-range coupling?

We felt we had to follow the latest n-m-r fashion and go hunting for long-range couplings in saturated systems. Guided by the work of Roberts et al (1) we found one that appears to be most probably negative into the bargain, while the n-m-r spectrum exhibits some interesting solvent effects. The substance is 2:3 dibromobutyric acid which has two asymmetric carbon atoms and therefore two possible diastereoisomers. These have different melting points so that we know that the molecule investigated has the structure illustrated below. We have considered it as a substituted ethane, and from the value of J_{AB} it is clear that of the three possible rotational isomers (rapid exchange) this form predominates:
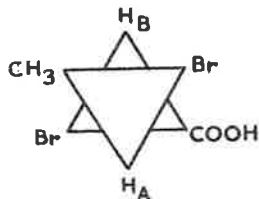
On dissolving this substance in various solvents, we were surprised to find that the form of the spectra observed varied considerably with solvent; two examples are shown in the figure (the COOH proton does not couple to the others and its resonance has been omitted). It soon became clear when the spectra were analysed as ABX_2 systems (2) that this was due entirely to a preferential solvent shift of H_A with respect to H_B accentuated by the fact that δ_{AB} is very small.

SOLVENT	AB SHIFT
Benzene	+ 3.0 c/s
Chloroform	+ 0.6 c/s
Acetonitrile	− 0.9 c/s
Acetone	− 1.5 c/s
Dioxan	− 2.7 c/s

/A

Professor Bothner-By   31st October, 1961.

A positive shift indicates that line A is at a lower field than line B. For all the solvents the coupling constants fall within the ranges $|J_{AB}|$ = 10.7 ±0.1 c/s, J_{AX} = ±6.8 ±0.1 c/s, J_{BX} = ∓ 0.35 ±0.1 c/s, so that in fact the preferential solvent shifts are here turned to good advantage in that they provide several independent analyses of the high resolution spectrum of a single compound, adding weight to the conclusion that J_{BX} (an interaction over four chemical bonds) is of opposite sign from J_{AX} and thus presumably (3) negative. The theoretical spectra are fitted to the experimental traces in the figure. Two gain settings have been used to illustrate the fitting of both strong and weak lines.

Yours sincerely,

Klaus Pachler

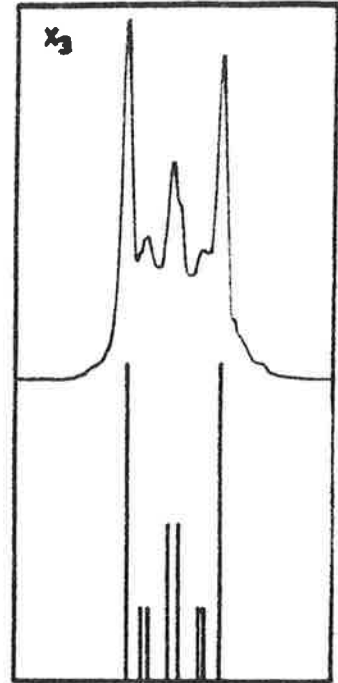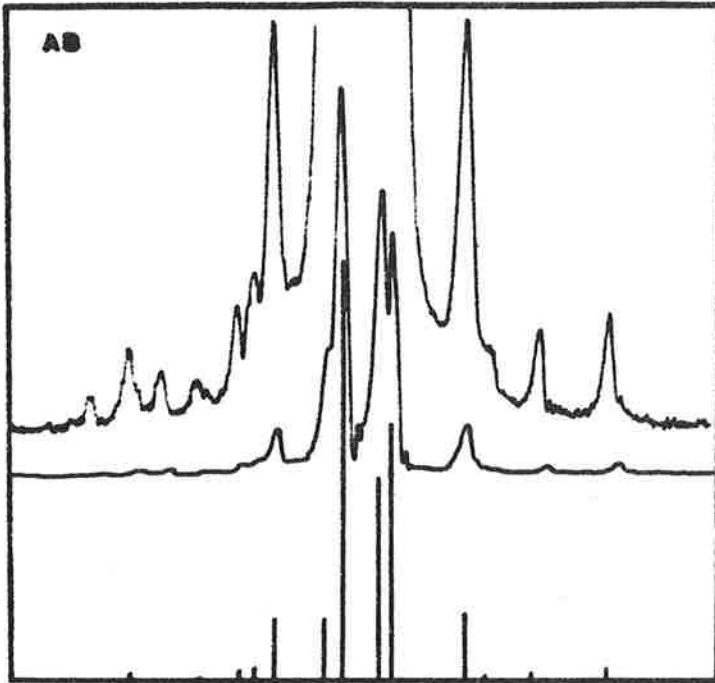*Ray Freeman*

K. Pachler
R. Freeman
Basic Physics Division

(1) Davis Lutz and Roberts - J.A.C.S., **83**, 246 (1961).

(2) Pople and Schaefer - Mol. Phys., **3**, 547 (1960).
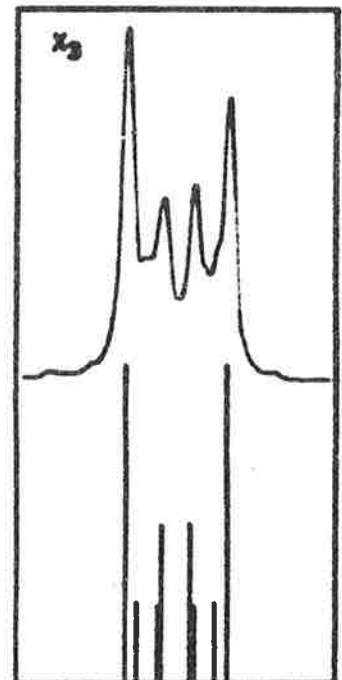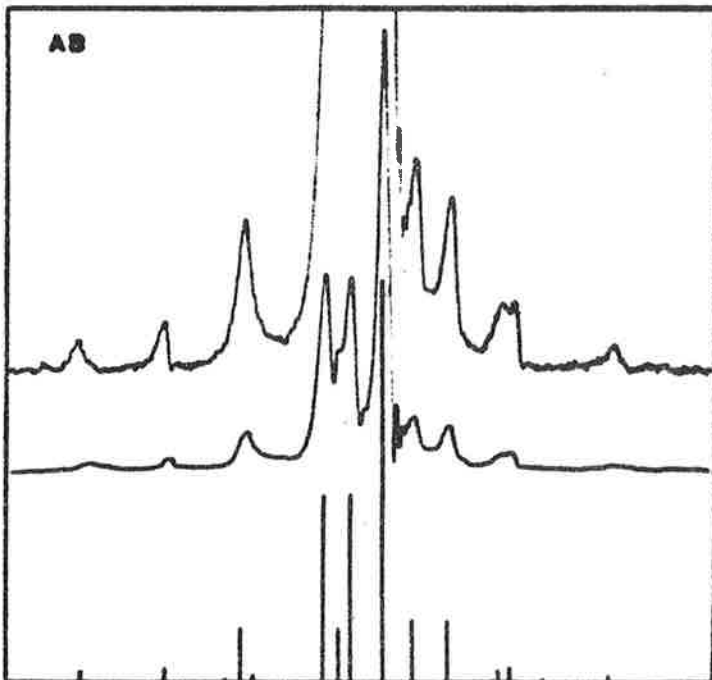
(3) But see Mellon 35, Kaplan and Roberts.

Dr. A.A. Bothner-By,
Director of Research,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa,
U.S.A.

2:3 DIBROMOBUTYRIC ACID IN ACETONE

IN BENZENE

PACHLER (CONTINUED)

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE.
TELEPHONE 58491.

30 October, 1961.

Dr. Aksel A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pa., U.S.A.

Dear Aksel,

I should like to offer as my belated M.E.L.L.O.N.M.R. subscription some recent work that Mrs. R.M. Lynden-Bell and I have been doing on the spectra of the simple hydrocarbons ethane, ethylene and acetylene. Because all the hydrogen atoms of these molecules are chemically equivalent, and because ^{12}C is non-magnetic, the normal hydrogen spectrum of each molecule consists of a single sharp line, and the only information to be derived from it is the chemical shift of the hydrogen. However, if one or both of the carbon atoms are replaced by magnetic ^{13}C then one gets much more complicated spectra which require a considerable effort for their full analysis. From their analysis one can, however, obtain a great deal of additional information about the magnitude of HH, $H^{13}C$ and $^{13}C\ ^{13}C$ coupling constants. Mrs. Lynden-Bell has prepared each of these hydrocarbons with one and with two ^{13}C atoms (or rather she has prepared mixtures of these isotopic molecules which are of suitable concentration in the species desired). The analyses of the proton spectra give the results for the coupling constants in c/s shown in the Table, where they are compared with values derived theoretically from various sources, mainly Karplus and his colleagues.

You will see that for acetylene and ethylene we have experimentally determined the magnitudes (and some of the relative signs) of the coupling constants between all pairs of nuclei in the molecule. For ethane, ^{13}C substitution does not suffice to determine the J_{HH} coupling between hydrogen on the same carbon; isotopic hydrogen substitution will be necessary to obtain the value of this parameter.

The most unexpected experimental values are for J_{CC} and the long-range J_{CH} in acetylene. In the case of J_{CC}, of course, many terms additional to the contact term could be of importance. It may be that in both cases the special magnetic properties of the cylindrically symmetrical π -type orbitals are responsible for the discrepancies. For the J_{HH} coupling constants, i.e. J_{cis} and J_{trans} of ethylene and J_{HH} for ethane, (= $\frac{1}{3}(2J_{gauche} + J_{trans})$) it is seen that the theoretical values are consistently too ~~high~~ low by a factor of about 2. However, the ratio J^{cis}/J^{trans} is in good agreement with theory.

Yours sincerely,

N. Sheppard.

38-11

Inter-nuclear Coupling Constants of C$_2$ Hydrocarbons in c/s

	J$_{CC}$(exp.)	J$_{CC}$(theory)	J$_{CH}$(exp.)	J$_{CH}$(theory)	J$_{HH}$(exp.)	J$_{HH}$(theory)*
Acetylene	171.6	138	$\begin{cases}249.0 \\ +49.3\end{cases}$	251	9.55	~+7 (~+11.6)
Ethylene	67.6	61 (76)	$\begin{cases}156.4 \\ -2.4\end{cases}$	167 (158)	$\begin{cases}19.1(\text{trans}) \\ +11.7(\text{cis}) \\ +2.5(\text{gem})\end{cases}$	$\begin{cases}+11.9\ (13.4) \\ +6.1\ (7.6) \\ +\ 5\end{cases}$
Ethane	34.4	–+	$\begin{cases}125.3 \\ -4.5\end{cases}$	–+	8.0	+4.2

+ The theoretical values of J$_{CC}$ and the large J$_{CH}$ coupling constants were calculated from the experimental values for ethane assuming the contact term to be the only one of importance and that this is determined solely by the degree of s character of the carbon atom(s) (Shoolery, J.Chem.Phys. 1959, 31, 1427). The s character of the carbon atoms of ethane, ethylene and acetylene are assumed to be $\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$ respectively, except that the alternative values of the coupling constants given in brackets for ethylene were derived from s values of the carbon of 0.315 for the CH bonds and 0.37 for the CC bond which are more consistent with the molecular geometry.

* The values in brackets for J$_{HH}$(theor) are the values obtained by adding π contributions (Karplus, J.C.P. 1960, 33, 1842) to the σ contributions which are listed without brackets (Karplus, J.C.P. 1959, 30, 11 for ethylene and ethane; Gutowsky, Karplus and Grant, J.C.P. 1959, 31, 1278 for J(gem) of ethylene; Karplus, Anderson, Farrar and Gutowsky, J.C.P. 1957, 27, 597, for acetylene).
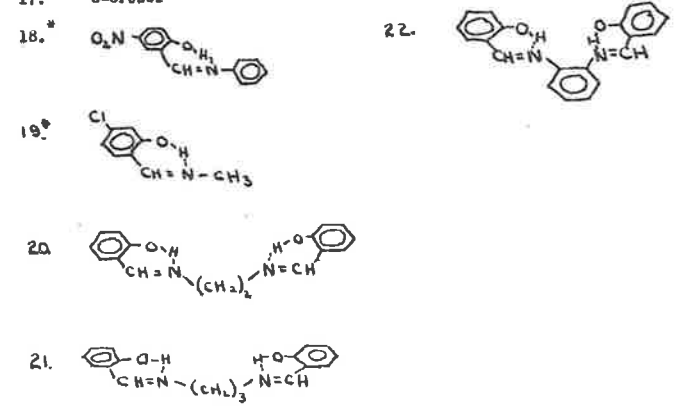
THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

1 November, 1961

Dr. A. A. Bothner By,
   Mellon Institute,
   Pittsburgh 13, Pa.,
   U.S.A.

Dear Aksel,

We have recently made a study of intra-molecular hydrogen bonds by the proton resonance method. The first part consisted in an extension of a previous correlation between chemical shift change $\Delta\sigma_{OH}$ and –O-H stretching frequency change $\Delta\gamma_{OH}$ on formation of an intramolecular hydrogen bond of type –O-H– – – Y. (Can. J. Chem. 38. p1249 (1960)). We have now measured 34 compounds under the conditions specified in the reference and these include 5 membered chelated rings with O-H– – – O, O-H– – Cl, O-H– – Br, O-H– – – I, O-H – – –S and O-H – – – F, 6 membered chelated rings with O-H – – O=, O-H·O.OHN= and the 6½ membered ring O-H – – – H. The final correlation is attached in figure 1 and a list of compounds referring to the numbered compounds is appended in a table.

In weak intramolecular hydrogen bonds such as those formed by the ortho-halo-phenols, the infinite dilution chemical shift of the –O-H proton reflects the cis-trans populations of the –O-H group in a non polar solvent.

$$\delta_{M_\infty} = \chi_{cis}\, \delta_{cis} + (1 - x_{cis})\delta_{trans} \qquad (1)$$

If we assume $\Delta S = 0$ in the cis-trans conversion, then both a temperature dependence of the cis/trans population ratio's and the population ratio at one temperature gives a value of ΔH, for formation of the intra-molecular hydrogen bond.

A measured 'δ_{M_∞}' at infinite dilution can be extrapolated at low temperatures to give a trial value of δ_{cis}. Since the equilibrium constant is given by:-

$$K_1 = \frac{(\delta_{M_\infty} - \delta_{cis})}{(\delta_{trans} - \delta_M)} = \frac{[trans]}{[cis]}$$

then by using 3 temperatures or more we can determine δ_{trans}, δ_{cis} and K_1. Figure 2 illustrates data for O-bromo phenol in CS$_2$ against internal cyclohexane reference at approximately 5,4,3,2 and 1 mole % at 6 temperatures. Figure 3 shows the values of δ_{M_∞} plotted against temperature for this

compound. We assume that δ_{cis} and δ_{trans} are temperature invariant. In Table I we list the relevant parameters for O chloro O- bromo and O-iodo-phenol. There was no evidence of hydrogen bonding in O-fluoro phenol. The data is consistent except that δ_{trans} seems too much to high field. It is extremely sensitive to the δ_{cis}, trial choice of δ_{cis}, because K_1 is small, but ΔH_f is quite insensitive to these parameters and is consistent to ± 150 cals for a given compound in all cases.

It is interesting to note that the shape of δ_M vs concentration is linear out to 4 mole %. (See fig. 2). We consider this to be due to the formation of a cis-trans dimer species. Assuming this to be the case, then providing we assume that in the cis-trans dimer the proton on the cis molecule is not perturbed appreciably from that on the cis-monomer molecule we can derive a K_2 for dimer formation.

$$K_2 = \frac{A}{a} \frac{(1 + 2K_1)}{K_1} \qquad (2)$$

a = total moles of phenol as monomer.
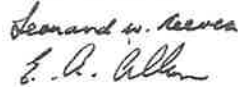
M_s = moles of solvent

where $(a + M_s) = 1$ (3)

$$A = \left[\frac{(\delta_{M_0} - \delta_{M_\infty})}{(\delta_{T_D} - \delta_T) + (\delta_{M_0} - \delta_M)} \right] \qquad (4)$$

M_c = chemical shift of -O-H proton at concentration c > o

T_D = chemical shift of -O-H proton in trans molecule in dimer form.

K_2 is obtained in mole fraction units. From the correlation mentioned earlier a value of $(\delta_{T_D} - \delta_T)$ of 320 c.p.s. at 40 Mc. is appropriate for an O-H -- O hydrogen bond. A plot of log K_2 vs $\frac{1}{T}$ enables us to evaluate ΔH_f of the intermolecular hydrogen bond. This experimental value, if the analysis is valid at all, should give a heat of formation appropriate for an O-H -- O hydrogen bond and the value obtained should be independent of the halo phenol studied. We obtain 5827 cals mole^{-1}, 5585 and 5606 cals mole^{-1} from O chloro, bromo and iodo phenol results respectively.

I trust that this has not been too lengthy a contribution.

Yours sincerely,

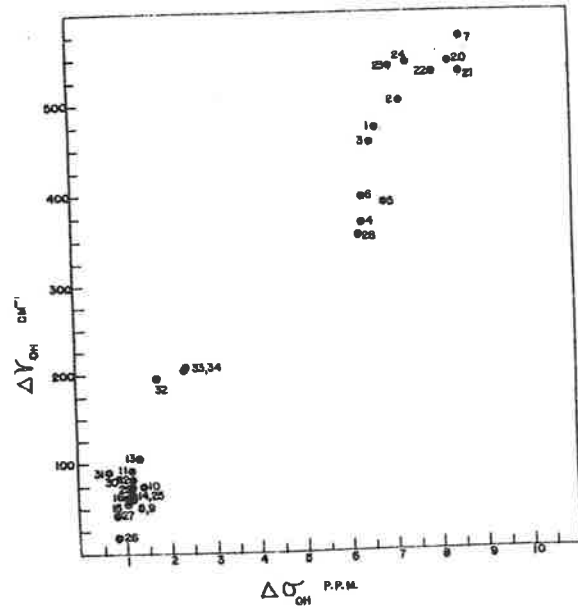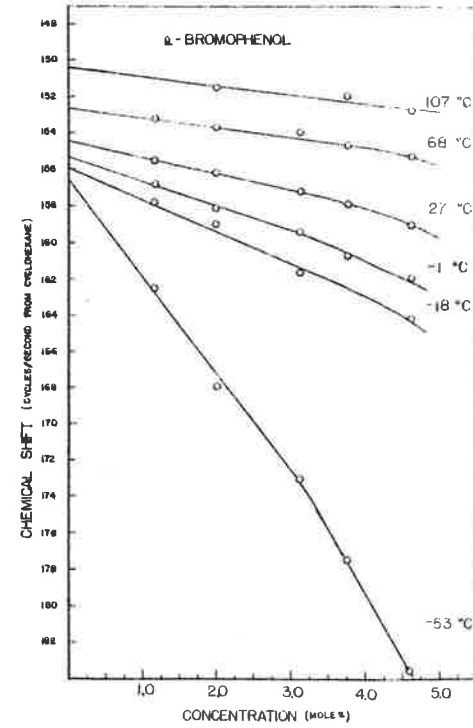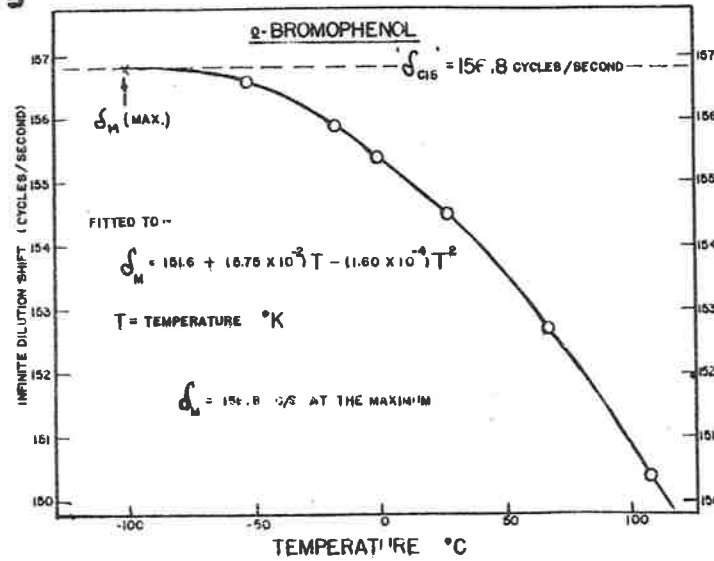*Leonard W. Reeves*

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Figure 1

The change in chemical shift ' δ_{OH} ' and the frequency shift of the -O-H ' δ_{OH} ' stretching band in 34 compounds. The numbered points on the figure refer to the numbered compounds below.

Table of Compounds

1.	Salicylaldehyde	23.	1-Nitro, -2 Naphthol
2.	5-Nitrosalicylaldehyde	24.	2,4-Dinitro-1-naphthol
3.	5-Bromosalicylaldehyde	25.	2,5-Dichlorophenol
4.	o-Nitrophenol	26.	o-Fluorophenol
5.	2,4-Dinitrophenol	27.	o-Phenylphenol
6.	Methyl Salicylate	28.	4-Chloro-2 nitrophenol
7.	o-Bromo Benzoic Acid	29.	2-Bromo-4 phenylphenol
8.	o-Chlorophenol	30.	1-Bromo-2 naphthol
9.	2,4-Dichloro Phenol	31.	2,4-Dibromo-1-naphthol
10.	2,4,6 Trichlorophenol	32.	o-(Methyl Thio) phenol
11.	o-Bromophenol	33.	2-Methyl-6 (Methyl Thio) phenol
12.	2,4-Dibromophenol	34.	o-(Isopropylthio) phenol
13.	o-Iodophenol		
14.	o-Mehoxy phenol		
15.	2,6 Dimethoxy phenol		
16.	o-allylphenol		
17.	o-Cresol		

18. *

19. *

20.

21.

22.

* The values of $\Delta\gamma_{OH}$ were not obtainable because of overlap with the -C-H stretching frequencies. The chemical shifts δ_{OH} are 9.42 p.p.m. and 8.47 respectively.

TABLE I

Phenol	ΔH_f	K_1 at 25°C	δ_{cis}	$(\delta_{cis} - \delta_T)$
O Chloro-	2356 c.m.$^{-1}$	1/56	-159.5 c.p.s.	193.5 c.p.s.
O Bromo-	2141	1/38	-157.2	105.3
O-Iodo-	1651	1/19	-148.9	64.0

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Fig. 1.

Fig. 2

Fig. 3

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