

Mailed:

AUG 30 1960

M onthly
E cumenical
L etters from
L aboratories
O f
N - M - R
No. 23

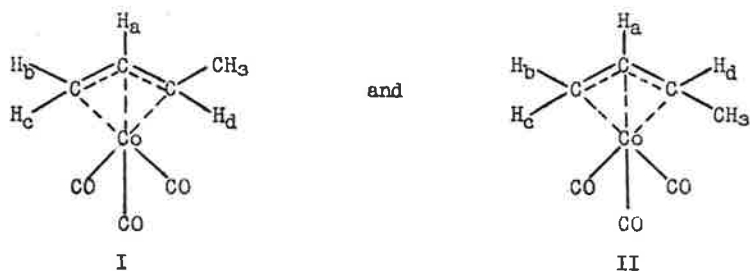
A monthly collection of informal private letters from laboratories of nmr.
Information contained herein is solely for the use of the reader. Quotation
is not permitted, except by direct arrangement with the author of the letter,
and the material quoted must be referred to as a "Private Communication."

NMR STUDY OF THE BUTADIENE-COBALT HYDROCARBONYL REACTION PRODUCTS

By D. W. Moore, H. B. Jonassen and T. B. Joyner

Michelson Laboratory, U. S. Naval Ordnance Test Station
China Lake, California

Proton magnetic resonance spectra of the two isomeric addition products of 1,3-butadiene with cobalt hydrocarbonyl, $\text{Co}(\text{CO})_4\text{H}$,¹ indicate the two following structures:



These compounds are formed by addition of the two starting materials at approximately -10°C . The reaction involves hydrogenation of a terminal methylene with simultaneous evolution of one molecule of carbon monoxide. Both isomers are mobile, wine-red liquids. They are unstable in air, and decompose slowly at room temperature even in vacuum.

The most significant results of the NMR study are the apparent equivalence of the two allenic carbon-carbon bonds and the approximate coplanarity of the five allenic proton positions. The indicated cobalt-carbon bonds are believed to represent overlap of three p-orbitals of the hydrocarbon with unoccupied orbitals of the cobalt. Three electrons of the ligand and one from the metal are presumed to occupy the resultant molecular orbitals. The compounds are diamagnetic.

These structural inferences have been drawn largely from the observed spin-coupling values of the two NMR spectra. Fig. 1 shows the 40 mc. spectrum of a sample which is ca. 95% pure isomer I. Pure isomer II was not available, but the spectrum of a sample containing ca. 65% of II is shown in Fig. 2. Measured spectral parameters are summarized in the following table:

Chemical Shift and Spin-Coupling Data

	Isomer I		Isomer II	
Chem. Shift*				
H_a	75.7 cps	+1.89 ppm.	66 cps	1.65
H_b	149.0	3.73	134	3.35
H_c	186.2	4.65	152	3.80
H_d	139.5	3.49	95	2.38
CH_3	201.2	5.03	218	5.45
Coupling Values				
J_{ab}		6.3 cps		7.1 cps
J_{ac}		10.5		12.3
J_{ad}		10.5		6.8
J_{bc}		<0.2		0.6
J_{bd}		<0.2		1.6
$J_{d-\text{Me}}$		6.5		7.0

*Shift measured relative to benzene as external standard using concentric tube technique.

We have interpreted the observed spectra as follows:

Isomer I

H_a - The doubled triplet structure arises from equal spin coupling with H_c and H_d and a weaker cis-coupling to H_b .

- H_b - The pair of lines assigned to H_c confirm the smaller coupling with H_a .
- H_c - This doublet shows the larger trans-coupling with H_a .
- H_d - Appears as a doubled quartet, the smaller up-field set being partly obscured by the H_b lines. A 60 mc. spectrum (for which we are indebted to Dr. John D. Roberts and his Caltech staff) shows this multiplet clearly resolved.
- CH_3 - The large high-field doublet confirms the spin interaction with H_d . A much smaller pair at higher field represents a trace of isomer II.

The absence of observable coupling between gem-protons H_b and H_c , is apparently explained in terms of the valence-bond treatment of Gutowsky, Karplus and Grant² in which the gem-coupling value is dependent upon the inter-proton bond angle, passing through zero at 125°. This would indicate that hybridization is very close to sp^2 for this terminal carbon.

Isomer II

- H_a - The low-field multiplet is again believed to be a doubled triplet, but with large and small J-values interchanged. Considerable overlap with the H_a group of isomer I distorts intensities, however.
- H_b - Group shows eight-fold multiplicity corresponding to H_a coupling, weak coupling to H_c , and long-range interaction with H_d .
- H_c - Strong coupling to H_a is confirmed, but partial overlap with one member of H_b (I) doublet obscures weak gem-coupling which appears as slight splitting of peak on right.

- H_d - Apparently a quintet with all lines doubled by long-range coupling to H_b . Quintet structure indicates coincidental equality of J-values with H_a and CH_3 .
- CH_3 - The 7-cps splitting is same as J_{ad} , confirming H_d multiplet assignment.

The data we have gathered indicate the structure of allylcobalt tricarbonyl, reported by Breslow and Heck,³ should be the symmetric structure indicated as II in the communication. Its NMR spectrum can be predicted from our data as follows:

- H_a - A triplet of triplets with J-values about 7 and 12 cps.
Area = 1.
- H_b - A 7-cps doublet at higher field than H_a perhaps showing weak splitting due to H_c . Area = 2.
- H_c - A 12-cps doublet at highest field. Area = 2.

Acknowledgments

We gratefully acknowledge the help received in discussions with Drs. Paul R. Shafer and Eric Nordlander of the Crellin Laboratory, California Institute of Technology.

References

- ¹ Aldridge, C. L., Jonassen, H. B. and Pulkkinen, E., Chem. and Ind., 1960, p. 374.
- ² Gutowsky, H. S., Karplus, M. and Grant, D. M., J. Chem. Phys., 1959, 31, 1278.
- ³ Breslow and Heck, J. Amer. chem. Soc., 1960, 82, 750.

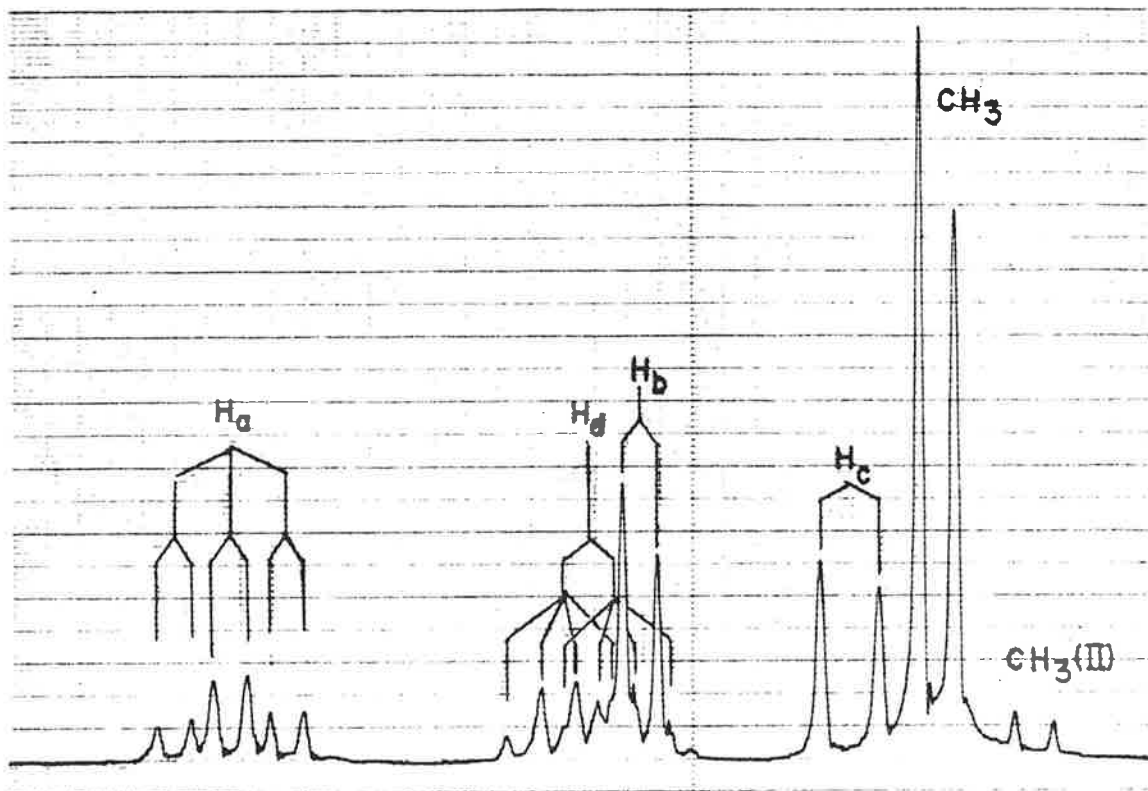
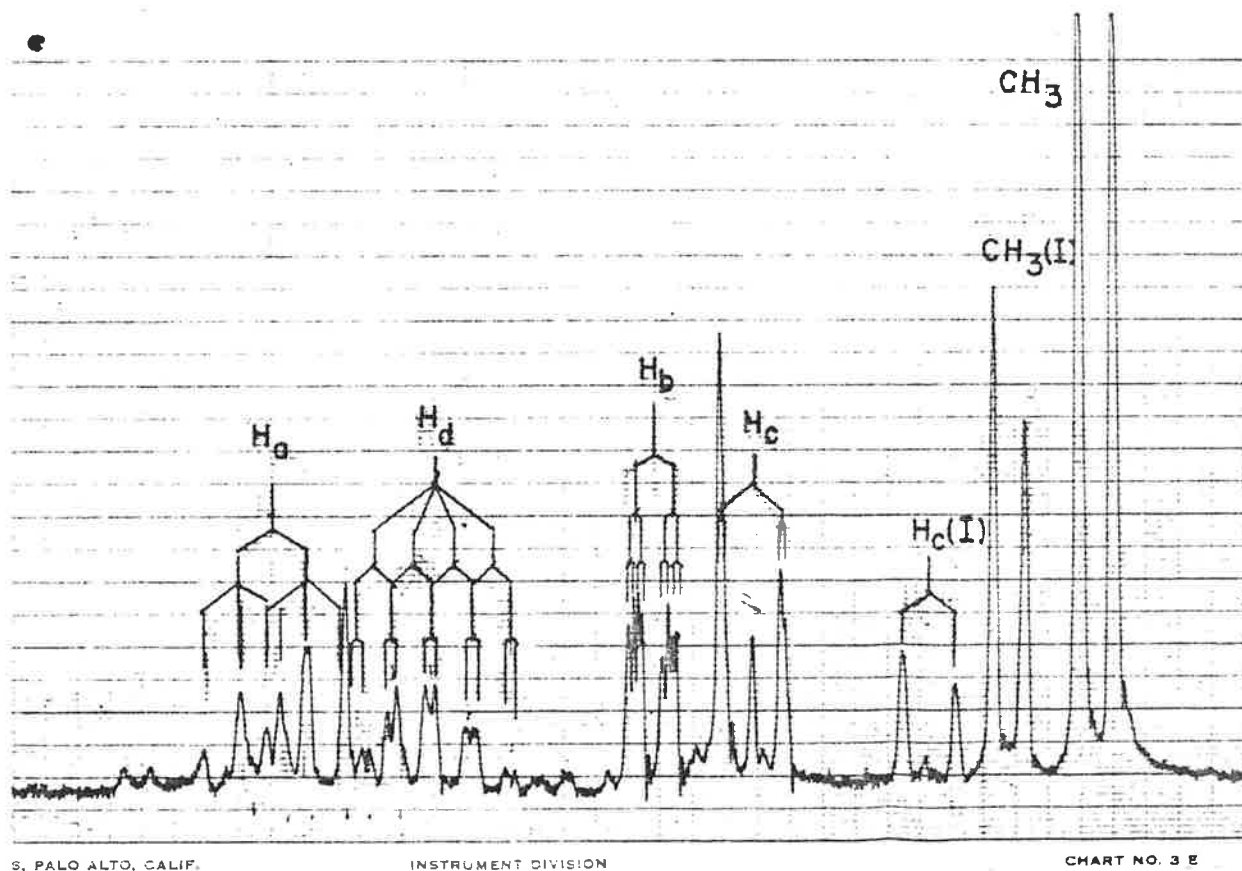


Fig. 1. 40 mc. NMR spectrum, methylallenylcobalt tricarbonyl, isomer I.



S. PALO ALTO, CALIF.

INSTRUMENT DIVISION

CHART NO. 3 E

Fig. 2. 40 mc. NMR spectrum, methylallenylcobalt tricarbonyl, isomer II.

10 August, 1960

DEPARTMENT OF CHEMISTRY

Dr. Aksel A. Bothner By,
Mellon Institute,
4400 5th Ave.,
Pittsburgh 13 Pa,
U. S. A.

Dear Aksel,

In view of the letter by Claeson Androes and Calvin, we should like to summarise the results of some studies we have been making on saturated six membered ring compounds, some of which will appear in the August issue of Can. J. Chem. (1) We have concluded from a detailed study of several systems and a survey of many, that providing there are no large locking groups, saturated six membered rings can be resolved into two chair forms at temperatures of about -50° to -80°C by the proton resonance method.

Our interests have been mainly in the population studies of two isomers in equilibrium, but as a by product we have obtained the approximate energy barriers for conversion from the so called 'Coalescence Temperature' (2). In general the substitution of a group in the ring produces broad peaks for the adjacent proton with very little observable structure (at 40 Mc.) due to many coupling constants to chemically shifted protons. It is the proton resonance of this adjacent proton which gives the information on populations since it will split into two components at low temperature which overlap a little in the tails. Relative intensity measurements will give us populations to a high degree of internal consistency by various recording techniques and under a range of magnetic field sweep rates. The method we have used is certainly superior to various indirect methods so far suggested (3) (4).

We show a few spectra and quote a few representative results. Figure 1 shows complete spectra of chloro and bromo cyclohexane, sweeping left to right from low to high field. The narrow resonance at high field is tetramethyl silane standard and the solvent in this case is CS_2 . Side bands on the internal standard calibrate spectra. For the sake of brevity, complete assignments will not be given since they are in most cases obvious. The temperatures and spectra are Fig. 1 (a) bromocyclohexane 55 mole % CS_2 , 28°C . (b) chlorocyclohexane 55 mole % CS_2 , 28°C . (c). Spectrum of bromocyclohexane at -104.5°C in same solution (d) spectrum of chlorocyclohexane in the same solution at -91°C . Figure 2. shows the 'Adjacent' $-\text{CH}_2-$ proton signal in the two compounds at low temperatures from which we obtain populations. (a) bromo cyclohexane at -88°C (b) bromo cyclohexane at -97°C (c) chlorocyclohexane at -92.5°C .

1. L. W. Reeves and K. O. Strömme
Can. J. Chem. August 1960
2. J. A. Poppe, W. G. Schneider and H. J. Bernstein
High Resolution Nuclear Magnetic Resonance
McGraw Hill 1959 Chapter 10.
3. E. L. Eliel
Chem. and Ind. p568 (1959).
4. S. Brownstein and R. Miller
J. Org. Chem. 24 p1886 (1959)
5. B. S. Gutowsky and A. Saika
J. Chem. Phys. 21 p1688 (1953)

- 2 -

Figure 3 shows results for 1,2 trans disubstituted cyclohexanes. 3(a) shows adjacent proton signal in 1,2 dibromo cyclohexane with chemical shift referenced against hexamethyl disiloxane. 3(b) (c) and (d) show appearance at successively lower temperatures and 3(c) is a selected spectrum for the corresponding 1,2 dichloro compound at low temperature.

Figure 4 shows the results of a solvent and concentration study for 1,2 trans dibromo cyclohexane. The points Δ represent concentration in CS_2 and the points \circ represent concentration in a more polar solvent acetone. The abscissa correspond to mole % of dibromocyclohexane and ordinates represent % axial-axial bromine form in the equilibrium. It can be seen that there is very little effect of concentration in CS_2 but dilution in acetone favours the form with higher dipole moment i.e. the ee form.

Figure 5 shows an example similar to that of Claeson, Androes and Calvin namely a hetero alicyclic ring compound, NN' dimethyl piperazine. 5(a) shows the room temperature spectrum the low field peak is due to the ring methylene protons the high field peak represents the N methyl groups. Even at room temperature broadening of the low field peak is detectable and it broadens very rapidly as the temperature is lowered until at -48°C as represented in Figure 5(e) the narrow methyl peak remains but in place of the single methylene peak we have a typical A_2B_2 case. We have a partial analysis of the spectrum at low temperatures in spite of the overlap. Without going into our interpretations of these and other studies we quote a table which summarises work on the compounds mentioned here. Populations quoted refer to temperature region -70 to -120°C although we also have the populations at room temperature from the averaged chemical shifts (5); they are not quoted.

Yours sincerely,

Leonard W. Reeves
Knut O. Strömme

Leonard W. Reeves,
Knut O. Strömme

LWR:avh

P.S. The authors would be grateful if a reader could locate or supply any of the following compounds:

Fluorocyclohexane, 1,2 trans difluorocyclohexane,
1,4 trans difluorocyclohexane, perfluorocyclohexane
or 4 trans dichloro and 1,4 transdibromo cyclohexane.

F

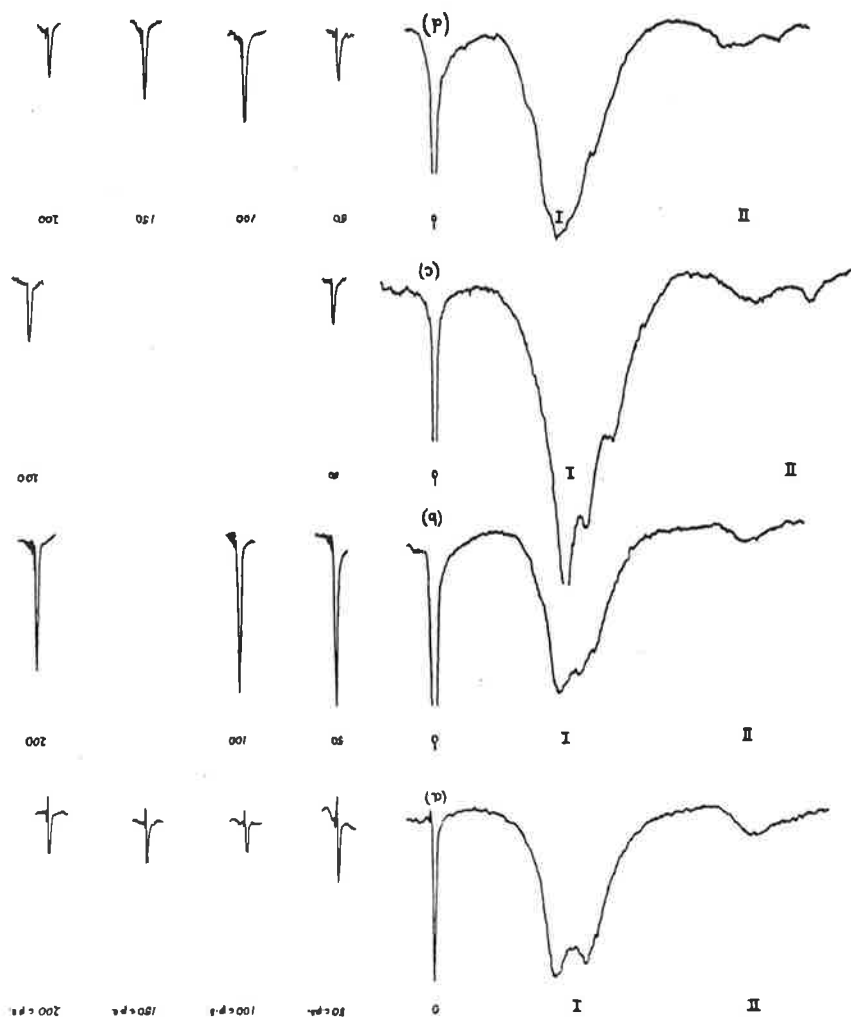
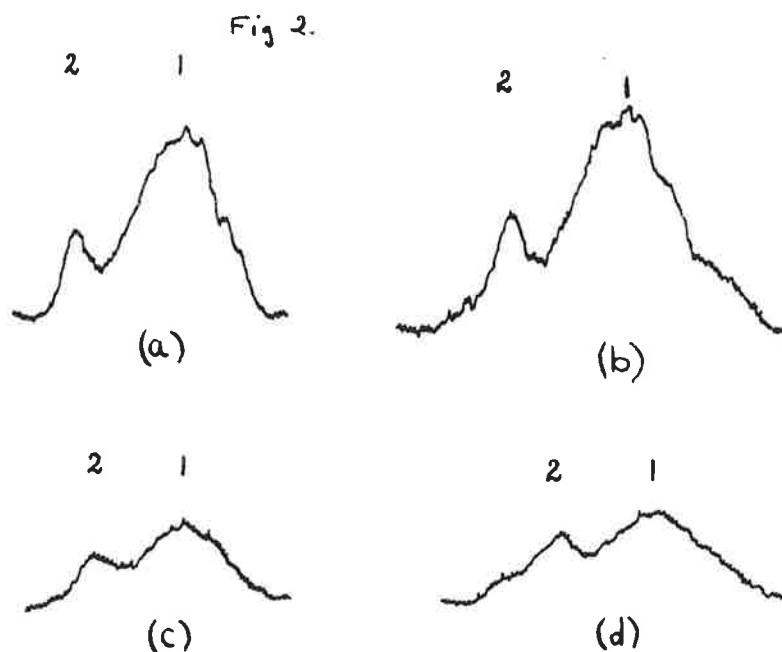


Fig 1.



Compound	Concentration mole %	Solvent	Equilibrium	% of one form*	Energy Barrier from Coalescence Temperature, in cals.
Chlorocyclo- hexane	54.5	CS ₂	Cl _{ax} ⇌ Cl _{eq}	77% Cl _{eq}	10,850
Bromocyclo- hexane	55.4	CS ₂	Br _{ax} ⇌ Br _{eq}	82% Br _{eq}	10,850
1.2 trans dichloro cyclohexane	40.0	CS ₂	$\left\{ \begin{array}{l} \text{Cl}_a\text{Cl}_a \rightleftharpoons \\ \text{Cl}_e\text{Cl}_e \end{array} \right.$	35% Cl _a Cl _a	11,950
	29.0	cyclohexane		33% Cl _a Cl _a	11,950
1.2 trans dibromo cyclohexane	28.0	CS ₂	$\left\{ \begin{array}{l} \text{Br}_a\text{Br}_a \rightleftharpoons \\ \text{Br}_e\text{Br}_e \end{array} \right.$	70.9 Br _a Br _a	11,850
	53.0	CS ₂		71.6 " "	"
	69.0	CS ₂		70.2 " "	"
	21.0	acetone		49.9 " "	—
	34.0	acetone		54.2 " "	—
	59.0	acetone		61.3 " "	—
	73.0	acetone	" "	64.0 "	—
NN' dimethyl piperazine	40.0	CS ₂	2 identical chair forms	Trivial case	12,000

*Accuracy of results to $\pm 1.5\%$ of the figure quoted.

Fig 3

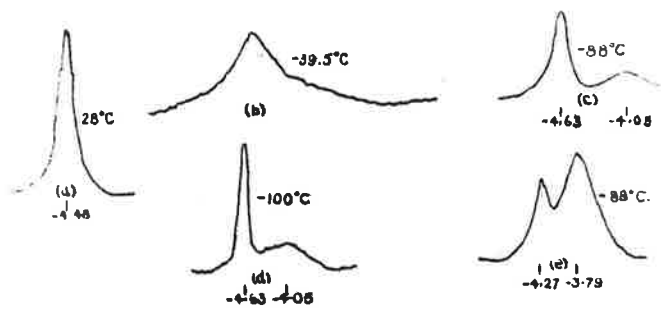


Fig 4

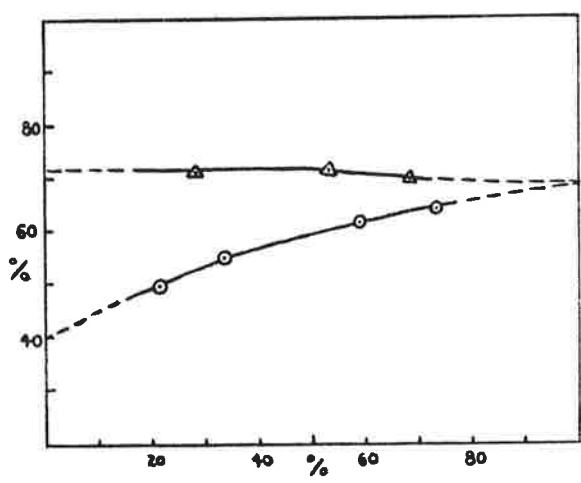
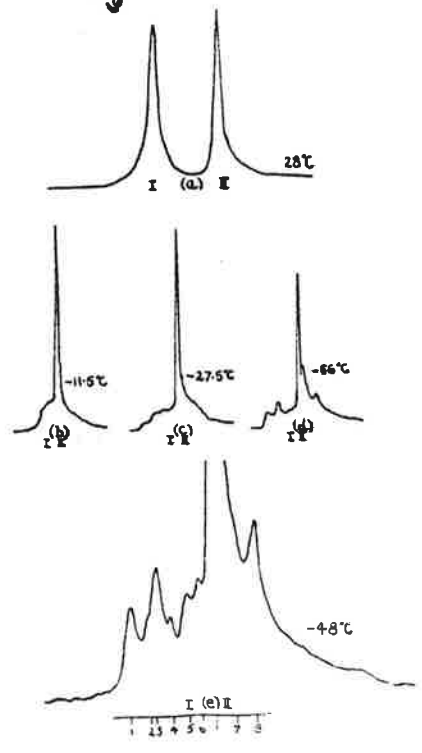


Fig 5



THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER CAMPUS STATION
ROCHESTER 20, NEW YORK

DEPARTMENT OF CHEMISTRY

8 August, 1960

Dr. Barry Shapiro
Mellon Institute
440 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry,

Here is my subscription to your *MELLONMR*, which I have found most informative and instructive.

Dr. Robert Autrey and I have recently investigated the proton magnetic resonance spectrum at 60 Mc of phloroglucinol. It has frequently been suggested (see Noller, *CHEMISTRY OF ORGANIC COMPOUNDS*, p. 503, for example) that phloroglucinol exists in tautomeric equilibrium between the keto and the enol forms. It gives a blue-violet color with ferric chloride and reacts with diazomethane to form a trimethyl ether, characteristic of enols; it also reacts with ammonia and with hydroxylamine in a manner characteristic of a ketone. Its reaction with methyl iodide is also characteristic of a triketone, rather than of the aromatic structure (see Noller, p. 504).

We attempted to investigate this equilibrium with NMR, which would permit the observation of isotopic exchange if the rate of equilibration were slow, and would allow an estimate to be made of the mean life of a ring proton if the reaction were fast. If appreciable concentrations of the keto form were present, one might either find two separate CH proton peaks or perhaps a broadening of a single CH peak.

In neutral solutions in acetone and deuterium oxide there is no evidence of any methylene resonance; the ring proton resonance occurs at 229 cps below acetone, and the line is very sharp. The ring proton line of phloroglucinol in D_2O remained unchanged in area for four hours, although the OH resonance was absent (as expected) due to rapid exchange. Addition of traces of sulfuric and hydrochloric acids to acetone solutions of phloroglucinol left the ring proton resonance unchanged, as did addition of large amounts of glacial acetic acid. Sodium hydroxide, sodium carbonate, and larger amounts of mineral acid catalyzed the exchange.

Solutions of phloroglucinol in concentrated sulfuric acid

-2-

gave a single sharp peak 306 cps up-field from the sulfuric acid signal and a single broad peak of about the same area at 440 cps up-field from sulfuric acid. These solutions were saturated with phloroglucinol trihydrate.

These results appear to indicate that no keto-enol tautomerization occurs in phloroglucinol, and that recourse must be had to other intermediates to account for the reactions undergone by this molecule. Additional work is being done to see if the species present in concentrated sulfuric acid can be positively identified.

Sincerely yours,

David J. Wilson

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
 DEPARTMENT OF CHEMISTRY
 CAMBRIDGE 39, MASSACHUSETTS

July 28, 1960.

Dr. Aksel A. Bothner-By,
 Mellon Institute,
 Pittsburgh, Penna.

Dear Aksel:

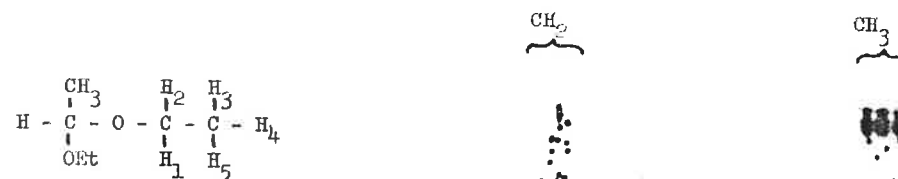
We recently contributed to MELLONMR a statement that your IBM 704 program had been modified and extended to make possible displays of computed high resolution spectra of a type that facilitated the comparison between calculation and experiment. We inadvertently neglected to submit a sample of the results which can be obtained in this way. The following example is now enclosed for the amusement of your readers.

The spectrum is one obtained on the way to fitting the observed spectrum of the two equivalent ethyl groups in acetal, in which the methylene groups contain hydrogens which are not equivalent by virtue of their environment with respect to internal rotation. The chemical shifts and coupling constants are given in the figure, and are almost but not quite correct at 40 Mc. The upper spectrum is of the whole ethyl group, and is not very useful because of the relatively low resolution of the computer display. The lower part of the figure is a picture of the CH₂ part of the spectrum blown up to occupy most of the display. The component line width, range of frequencies displayed, and vertical amplification are at the control of the computer operator.

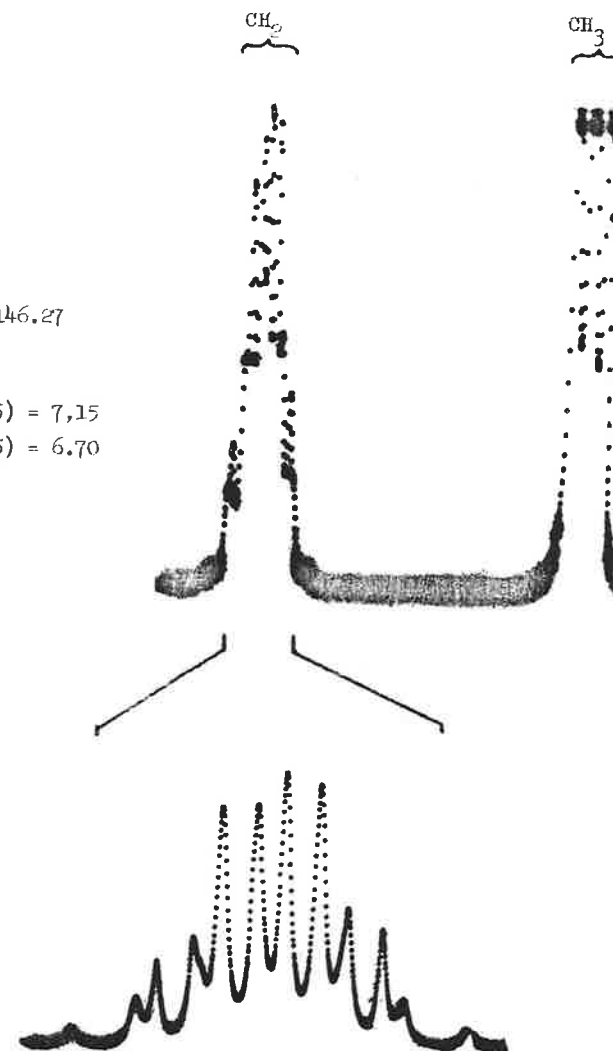
I hope this material will convey the nature of our computer output more graphically than the remarks we sent you earlier. As I remarked last time, copies of the complete program are available to anyone who wants to use it.

Yours very sincerely,

John S. Waugh
 John S. Waugh



$$\begin{aligned}
 \nu_0 \delta_1 &= 1000.00 \\
 \nu_0 \delta_2 &= 1009.15 \\
 \nu_0 \delta_3 &= \nu_0 \delta_4 = \nu_0 \delta_5 = 1146.27 \\
 A(1,2) &= 9.20 \\
 A(1,3) &= A(1,4) = A(1,5) = 7.15 \\
 A(2,3) &= A(2,4) = A(2,5) = 6.70 \\
 \text{all other } A(i,j) &= 0
 \end{aligned}$$



NMR STUDIES OF HYDROGEN BONDING

II. ALCOHOLS

by Jeff C. Davis, Jr., Kenneth S. Pitzer, and O.N.R. Rao

Department of Chemistry and Lawrence Radiation Laboratory,
University of California, Berkeley

(1) Present address: Department of Chemistry, The University of Texas,
Austin 12, Texas.

The proton magnetic resonance spectra of methanol, ethanol, i-propanol, and t-butanol in CCl_4 and ethanol in benzene have been studied at 60 Mcps in the temperature range 20° - 60° C.

Hydrogen bonding in alcohol solutions has been a favorite subject of nmr, IR, dielectric, and other methods of study.² The observed nmr shifts of the hydroxyl proton have been variously interpreted in terms of a monomer-dimer equilibrium³ and a monomer-polymer equilibrium.⁴

In brief, the shifts observed in this study covering a wide range of temperatures and concentrations indicate that:

(a) When the hydroxyl shift is extrapolated smoothly to infinite dilution (lowest concentrations measured were about 0.005 mole fraction) curves are obtained which, for all the alcohols, have a finite slope. At the higher temperatures, straight-line extrapolations were possible. The finite values of the slopes at infinite dilution indicate that a monomer-dimer equilibrium is present.

(b) The monomer shifts obtained by these extrapolations were, within a few cps, temperature independent.

(c) The monomer shift of ethanol in benzene was essentially identical (relative to the ethanol methyl peak) with that in CCl_4 . This would indicate that there was no strong interaction of the monomer OH with benzene, at least not an interaction which affects the shift of the OH proton. This may indicate our interpretation of the carboxylic acid shifts⁵ is in error although such interactions should certainly be smaller for the less polar alcohols.

(d) The order of increasing monomer shielding was found to be i-propanol, t-butanol, ethanol, methanol. Shifts for the first two were, however, within 2 cps of one another and the i-propanol extrapolation was uncertain. Apparently the monomer shift is not a direct function of the "polarity" of the OH proton.

Since data were collected at several temperatures an attempt was made to estimate additional thermodynamic information. Assuming only a monomer-dimer equilibrium at the lowest concentrations it can be shown⁶ that

$$\left(\frac{\partial \delta}{\partial X}\right)_{X=0} = 2K_2(\delta_D - \delta_M)$$

2.

where X is the mole fraction of alcohol. The dimer shift δ_D cannot be obtained directly because of the presence of higher polymers. However, assuming both δ_M and δ_D to be independent of temperature (there is no evidence that δ_D is constant except that for the carboxylic acids the calculated dimer shifts did not vary excessively) it should be possible to estimate ΔH of dimerization from the slope of a plot of the log of the limiting slope vs. reciprocal temperature. In figure 1 are shown the resulting graphs of $\log(\partial \delta / \partial X)_{X=0}$ vs. $1/T$. It is seen that reasonably good straight lines can be drawn, perhaps justifying the assumption that δ_D is constant. The calculated enthalpies of dimerization were -9.4 ± 2 , -7.6 ± 2 , -7.3 ± 3 , and -4.4 ± 2 kcal. mole⁻¹ for methanol, ethanol, i-propanol, and t-butanol in CCl_4 and -5.1 ± 1 kcal. mole⁻¹ for ethanol in benzene. Since both open and cyclic dimers may be possible in these systems these apparent enthalpies may not be the true heats of association for a particular species. There is evidence from dielectric data that there are only open dimers in the ethanol-benzene solutions and hence the true ΔH of dimerization may be assumed to be about 5 kcal. mole⁻¹. (for ethanol in benzene)

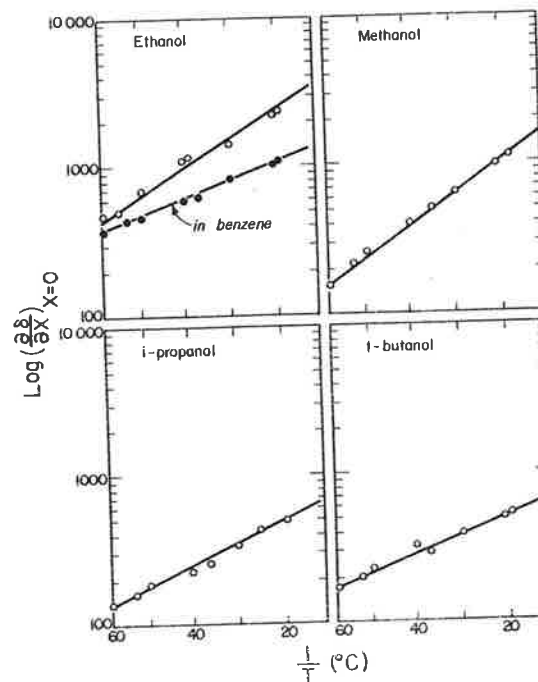


Figure 1. Effect of Temperature on Limiting Slopes of Hydroxyl Shifts vs. Conc. Curves for Alcohols in Carbon Tetrachloride

An attempt was also made to estimate δ_D , K_2 , and an average polymer shift by correlating infra-red measurements with the nmr data. The IR

3.

intensities obtained by Liddel and Becker⁷ for methanol, ethanol, and t-butanol at several concentrations and temperatures in CCl_4 were analyzed as suggested by Becker, et. al.³ and the results indicate strongly that δ_2 is at least approximately temperature independent in the range studied. However, the IR data do not cover the higher concentrations sufficiently to be sure of polymer shifts and the errors involved in both IR and nmr measurements at very low concentrations reduced the precision of the calculation considerably. The IR results of Liddel and Becker for ethanol also do not agree entirely with the work of Grunwald and Coburn,⁸ and the possibility of both cyclic and open dimers reduces the significance of these calculations somewhat. It is interesting to note that our nmr measurements for ΔH correspond closely with those obtained by Liddel and Becker from IR data.⁷

Saunders and Hynes⁴ have approached the analysis of alcohol shifts by assuming a monomer-polymer shift and fitting the experimental data with a calculated curve to obtain from best fit a polymer shift, monomer shift, and equilibrium constant. Following their procedure a good fit was obtained for ethanol only for a monomer-tetramer system with a tetramer shift -240 cps below the methyl peak and an association constant in mole fraction units of about 10^4 . Since there is considerable evidence, however, that a dimer species is present in this system an attempt was also made to fit the data with a monomer-dimer-polymer equilibrium. The monomer shift (28.5 cps), dimer shift (-30 cps) and dimerization constant (11.0) were obtained from the analysis of our nmr shifts and Liddel and Becker's IR data. The best fits obtained are shown in Figure 3. The pentamer curve, as an example, was fit with a pentamer shift of -270 cps and an association constant of 1×10^5 . Clearly, consideration of the monomer-dimer equilibrium drastically affects the interpretation in terms of higher polymers. It seems doubtful that such is to be gained by expressing the equilibrium mixture of several polymers by a single "average" polymer.

Further work is in progress with alcohol systems in which polymers larger than the dimer are absent in an attempt to elucidate both the nmr and IR interpretations. One important factor yet to be studied adequately is the effect of impurities such as dissolved oxygen, acid, etc., on the shifts of these systems. Agreement between various investigators has not been close despite the usual precautions of sample preparation. Certainly the interpretation of the results is seriously affected by such differences.

(2) Pimentel and McGlellan, "Hydrogen Bond", Freeman, 1960

(3) Becker, Liddel, and Shoolery, J. Mol. Spec. 2, 1 (1958)

(4) Saunders and Hynes, J. Chem. Phys. 29, 1319 (1958)

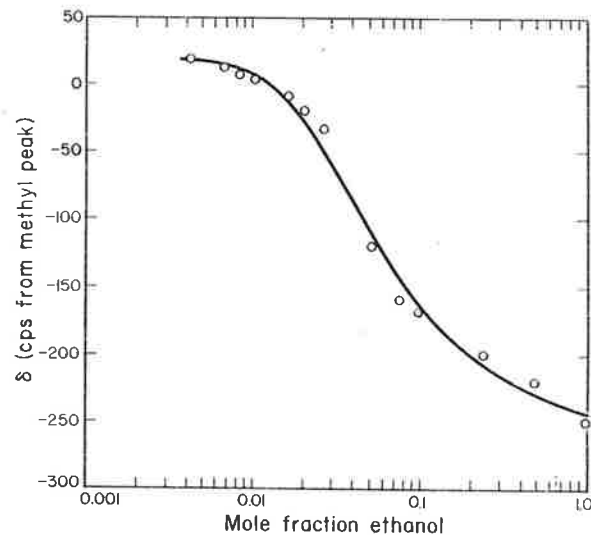
(5) Davis and Fitzer, MELLONIR #21, p.9 (J. Phys. Chem. in press)

(6) Huggins, Pimentel, and Shoolery, J. Phys. Chem. 60, 1311 (1956)

(7) Liddel and Becker, Spec. Acta 10, 10 (1957)

(8) Coburn and Grunwald, JACS 80, 1318 (1958)

4.



4. Fit of Data for Monomer-Tetramer System

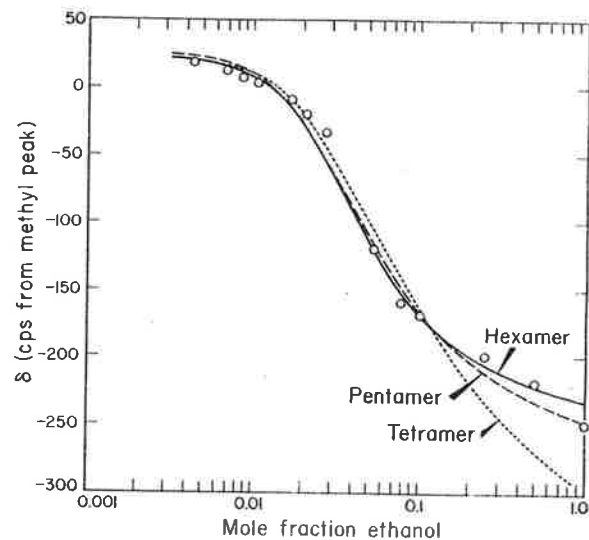


Figure 3. Fit of Data for Monomer-Dimer-Polymer Equilibria

ZÜRICH, July 30, 1960
 Universitätsstrasse
 Tel. (051) 32 73 30

Laboratorium
 für physikalische Chemie
 Eidg. Technische Hochschule
 Zürich

H. Primas

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

Dear Aksel,

In spite of the great progress in the numerical analysis of nmr spectra we feel that any deeper analytical insight into the structure of nmr spectra would be valuable. From the theoretical point of view the so called "direct method" (1) has many advantages over the conventional method of analysing nmr spectra. Some time ago we developed a general approximation method in this direct formalism. The general theory will be published soon (2) but this first part will not yet contain any specific applications to problems of nmr spectroscopy. Your readers of MELLONMR may perhaps be interested in some preliminary results of the application of this method to the analysis of nmr spectra.

It can be shown that there is an unitary transformation which transform the original spin-Hamiltonian H

$$H = \sum_j \Omega_j I_{jz} + \sum_{j < k} J_{jk} (\vec{I}_j \cdot \vec{I}_k)$$

(for sake of simplicity we assume here that the spin is 1/2 and that there is no degeneracy, i.e. the symmetry group should be C₁)

to the level shift representation

$$\tilde{H} = \sum_j \tilde{\Omega}_j I_{jz} + \sum_{j < k} \tilde{J}_{jk} I_{jz} I_{kz} + \sum_{j < k < l} \tilde{K}_{jkl} I_{jz} I_{kz} I_{lz} + \dots$$

If the operator of this unitary transform is known the calculation of the intensities and resonance frequencies is simple, especially with the direct method. The following sum rules - first exemplified by Fessenden and Waugh (3) - holds generally:

$$\sum_j \tilde{\Omega}_j = \sum_j \Omega_j$$

$$\sum_{j < k} \tilde{J}_{jk} = \sum_{j < k} J_{jk} \quad \text{etc.}$$

There are several approximation methods for this unitary transformation to the level shift representation that are much more general and powerful than the usual perturbation theory. I will just discuss shortly our first approximation method: the two particle approximation of the nmr many-body problem. It fulfils the following conditions:

- For the special case of very weak couplings ($J_{jk}/\Delta_{jk} \ll 1$) the n-th order of the two particle approximation reduces to the n-th order of the conventional perturbation theory.
- If all but one arbitrarily chosen J_{jk} are set to zero, the two particle approximation gives in first order the exact result. All terms of higher order vanish in this case,
- In any order of the two particle approximation there is no spurious coupling between uncoupled spins.

The last condition is by no means trivial, most known cluster developments (e.g. the Brückner theory of atomic nuclei) do not fulfil it, (mathematically it means that the development of the unitary operator must be unitary and a Lie function in any order).

In this two-particle approximation the scalars $\tilde{\Omega}_j$, \tilde{J}_{jk} , \tilde{K}_{jkm} are given by

$$\tilde{\Omega}_j = \Omega_j + \sum_{k \neq j} K_{jk} + \frac{1}{4} \sum_{r \neq j} \left\{ J_{jr}^2 \sum_{s \neq r} (K_{sj} - K_{sr}) \right\} + \text{terms of fourth and higher order}$$

$$\tilde{J}_{jk} = J_{jk} - \frac{1}{4} J_{jk} \sum_{r \neq j, k} (J_{jr}^2 + J_{kr}^2) + \frac{1}{4} \sum_{r \neq j, k} (J_{jr}^2 J_{kr} + J_{kr}^2 J_{jr}) + \frac{1}{2} \Delta_{jk} J_{jk} \sum_{r \neq j, k} J_{jr} J_{kr} + \text{terms of fourth and higher order}$$

$$K_{jkm} = 0 + \text{terms of fourth and higher order}$$

We have used the following abbreviations:

5.9.1963:

$$\Delta_{jk} \equiv \Omega_j - \Omega_k, \quad f_{jk} \equiv J_{jk} / \Delta_{jk}, \quad \vartheta_{jk} \equiv \tan^{-1} f_{jk}, \quad f_{jk} \equiv \frac{1}{2J_{jk}} \left\{ \sqrt{1 + f_{jk}^2} - 1 \right\}$$

$0 \leq \vartheta_{jk} \leq \pi/2$ $0 \leq f_{jk} \leq 1/2$

$$\Omega_j = \Omega_j + \sum_{k \neq j} f_{jk} J_{jk} + \frac{1}{4} \sum_{r \neq j} \left\{ \vartheta_{jr}^2 \sum_{\substack{s \neq j \\ s \neq k}} (f_{sj} J_{sj} - f_{sr} J_{sr}) \right\} + \dots$$

$$J_{jk} = J_{jk} + \frac{1}{4} \sum_{\substack{r \neq j \\ r \neq k}} \left\{ \vartheta_{jr}^2 (J_{rk} - J_{jk}) + \vartheta_{kr}^2 (J_{jr} - J_{jk}) \right\} + \frac{1}{2} \Delta_{jk} \vartheta_{jk} \sum_{\substack{r \neq j \\ r \neq k}} \vartheta_{jr} \vartheta_{kr} + \dots$$

$$K_{jk\ell} = 0 + \text{terms of fourth + higher order.}$$

$$\begin{aligned} \Delta_{jk} &= -\Delta_{kj} = \Omega_j - \Omega_k \\ \tilde{J}_{jk} &= -\tilde{J}_{kj} = \tan^{-1}(J_{jk}/\Delta_{jk}) \\ \kappa_{jk} &= -\kappa_{kj} = \frac{1}{2} \Delta_{jk} \left\{ +\sqrt{1 + J_{jk}^2/\Delta_{jk}^2} - 1 \right\} \end{aligned}$$

The "three spin" term K_{jkm} gives a nonvanishing value only by interaction of four nuclei (in our approximation: in the fourth order) and may be expected to be exceedingly small for reasonable high fields. Up to the third order of the two-particle approximation the nmr spectrum of any molecule without symmetry with N nuclei of spin 1/2 consists therefore of following lines:

- a) the "two-particle" lines with the resonance frequencies

$$\tilde{\Omega}_j \pm \tilde{J}_{j1} \pm \tilde{J}_{j2} \pm \dots \pm \tilde{J}_{jN}$$

- b) the combination lines with the resonance frequencies

$$(\tilde{\Omega}_{j_1} + \dots + \tilde{\Omega}_{j_m}) - (\tilde{\Omega}_{j_{m+1}} + \dots + \tilde{\Omega}_{j_{2m-1}})$$

The fourth order term would further contain:

- a) corrections to the third order values of $\tilde{\Omega}_j$ and \tilde{J}_{jk} in the fourth power of the development parameter, e.g. terms

like $\tilde{J}_{12}^2 \tilde{J}_{13}^2$ or $\kappa_{12} \tilde{J}_{23}^2 \kappa_{31}$ etc.

Pure two-particle terms like

$$\tilde{J}_{12}^4 \text{ or } \kappa_{12}^4$$

never occur.

- b) There will be a further splitting due to the "three spin" operator $K_{jkm} I_{jz} I_{kz} I_{mz}$. This is the result of the simultaneous interaction of four nuclei (absent in three spin systems).

This method gives excellent results at any field strength if always two strong coupled nuclei are separated by only weak couplings. Notice that contrary to the conventional perturbation theory above expressions are not divergent at zero field strength. If there are

adjacent strong couplings the results are at least as good as a third order perturbation theory. In order to check the results for the worst case, we calculated the strong coupled three spin systems analysed by Fessenden and Waugh (3) *). For the vinyl group of styrene ($\Delta_{12} \hat{=} -0,980$ ppm, $\Delta_{23} \hat{=} -0,520$ ppm, $\Delta_{31} \hat{=} +1,500$ ppm, $J_{12} = 17,800$ Hz, $J_{23} = 1,200$ Hz, $J_{31} = 11,300$ Hz) we found in the third order of the two-particle approximation:

	40 Mc/s	25 Mc/s	16 Mc/s	10 Mc/s	0 Mc/s
$\tilde{\Omega}_2 - \tilde{\Omega}_1$ exact	43,53	31.99	23.86	18.91	11.20
approx.	43,49	30.90	24.29	20.50	8.76
$\tilde{\Omega}_3 - \tilde{\Omega}_2$ exact	19.42	11.35	7.43	7.14	11.20
approx.	19.44	11.02	5.70	2.02	-0.79
$\tilde{\Omega}_3 - \tilde{\Omega}_1$ exact	63.03	43.34	31.29	26.06	22.39
approx.	62.93	41.92	29.99	22.53	7.97
\tilde{J}_{12} exact	17.72	17.48	16.26	13.41	7.91
approx.	17.74	17.65	17.38	16.75	3.55
\tilde{J}_{21} exact	1.82	2.51	3.48	4.62	7.91
approx.	1.85	2.66	4.04	6.21	17.67
\tilde{J}_{31} exact	10.76	10.31	10.56	12.26	14.89
approx.	10.71	9.99	8.88	7.34	9.08

(values for $\tilde{\Omega}$'s are in ppm, values for \tilde{J} 's in cps)

For this case a two-particle approximation is of course not very appropriate. Nevertheless the results are always essentially better than a third order perturbation theory although not at all exciting at low fields. In order to fill this gap (adjacent strong coupling at low fields) we started a similar cluster development that should give good results in the low field regions. Expressions for the intensities, cluster expansions for molecules with symmetries and higher spins will be published later.

Yours sincerely
Hans Primas
 Hans Primas

- (1) Helv. Phys. Acta 31, 413 (1958), Spectrochimica Acta 14, 17 (1959)
 (2) "Das Mehrteilchenproblem der magnetischen Kernresonanzspektroskopie", "I. Clusterentwicklung der Korrelationsfunktion". Will probably be published in Helv. Phys. Acta.
 (3) R.W. Fessenden, J.S. Waugh, JCP 31, 996 (1959)

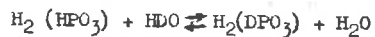
*) I am indebted to Professor J.S. Waugh for making available details of his calculations of this three spin systems.

NMR - Study of the Deuteration process in Phosphorous and Hypophosphorous acids

F. Diehl*, Basic Physics Division, National Physical Laboratory, Teddington, Middlesex, England.

We recently have studied isotope-effects in NMR-spectra of phosphorous acids. During the course of this work we had to investigate the deuteration of these acids. We found that N.M.R. is a very suitable method for studying exchange-reactions in the "minute-range" even in cases where the exchange takes place in consecutive steps.

In fig. A we observe the ~~time~~ independence of the D-resonance due to the exchange;



The resonance shown is one half of the P-D doublet. We find a half time for this exchange (1 gr. H_3PO_3 + 1cc D_2O) of $\tau_{\frac{1}{2}} = 190 \pm 20$ min, compared to $\tau_{\frac{1}{2}} = 204$ min. obtained recently by means of Raman spectra. (1)

The deuteration of hypophosphorous acid is shown in fig. B. The spectrum given is one half of the P-H doublet. It consists of a superposition of a single line due to the molecule $H(H_2PO_2)$ and a triplet due to the molecule $H(HDPO_2)$, the H- resonance being split by a spin-spin interactions

J_{HD} .

Looking at D-resonance of the same exchange (one half of the P-D doublet; fig.C) one recognises a superposition of a single line $[H(D_2PO_2)]$ and a doublet $[H(HDPO_2)]$ due to the spin-spin interaction J_{HD} .

Measuring the areas of lines as a function of time one can easily separate the exchange into two consecutive first order reactions and obtain the four rate constants involved. (X)



The fact, that the triplet in fig. C is not exactly on top of the single line can be explained by isotope effects on chemical shifts and on spin-coupling constants. (2)

(2) These isotope effects will be published elsewhere.

* On leave from the Physical Institute of the University of Basle, Switzerland

(1) R. Bruce Martin, J. Amer. Chem. Soc. 81, 1542, (1959)

(X) At an acid concentration of 1.66 moles litre⁻¹ they are of the order of 5.10⁻² litres mole⁻¹ hour⁻¹.

