



RICE UNIVERSITY

OVERHAUSER EFFECT AND NMR SPECTRA OF N-METHYL METHYLENIMINE

by

Chen-Fee Chang

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS

THESIS DIRECTOR'S SIGNATURE:

Robert Curl

Houston, Texas

May, 1966

ABSTRACT

Pure liquid samples of the simple but rather reactive species N-Methyl Methylenimine were studied at -60°C . The conventional NMR spectra and double resonance spectra were taken. The NMR constants and relative signs of three spin-spin coupling constants were determined. Absolute signs of the coupling constants were discussed.

ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. R. F. Curl Jr. for his patient guidance through my thesis work. I also thank Dr. W. R. Willcott for his considerable help in the use of his very fine spectrometer.

TABLE OF CONTENTS

I. INTRODUCTION.....1
II. THEORY.....3
III. EXPERIMENT.....7
IV. RESULT.....12
V. DISCUSSION.....18
VI. BIBLIOGRAPHY.....19

I INTRODUCTION

An unusually large proton spin-spin coupling constant was reported⁽¹⁾ for geminal proton coupling ($|J_{\text{HH}}|(\text{gem})=6.96 \sim 16.97$ cps.) in $\text{H}_2\text{C}=\text{N}-$ system. This is to be compared to the small values of $J_{\text{HH}}(\text{gem}) 0 \pm 3.5$ cps. in the $\text{CH}_2=$ groups of olefins.

The sign of $J_{\text{HH}}(\text{gem})$ in the olefins can be positive or negative⁽²⁾. $J_{\text{HH}}(\text{gem})$ in $\text{H}_2\text{C}=\text{N}-$ system was suggested to be negative without evidence.⁽¹⁾

It seems of interest for the study of molecular electronic structure to determine the sign and magnitude of proton spin-spin coupling constants which are transmitted via electron spins.

So far, reasonably accurate values of spin-spin coupling constants seem impossible to obtain from theoretical calculation except in the simplest cases. Experimental values of absolute and relative signs of coupling constants in $\text{H}_2\text{C}=\text{N}-$ system have not been reported.

Relative signs of spin-spin coupling constants can be decided by the Overhauser Effect. If the absolute sign of one of the coupling constants is known then the absolute signs of all coupling constants of the system may be determined.

It was the purpose of this investigation to approach the determination of the sign of $J_{\text{HH}}(\text{gem})$ coupling constant in the system $\text{H}_2\text{C}=\text{N}-$ through using the Overhauser Effect to determine the relative sign of spin-spin coupling constants of the $\text{H}_2\text{C}=\text{N}-\text{CH}_3$ molecule.

II THEORY

Originally Overhauser⁽³⁾ predicted that, if nuclear spin-lattice relaxation was governed principally by an interaction between nuclei and unpaired electron spins, $AI \cdot S$, then saturation of the electron resonance should lead to an increase in the nuclear polarization. The prediction was originally made for metals, but the principle can also operate in other paramagnetic substances.

Application of the Overhauser Effect to nuclear magnetic resonance became possible after a simple technique for obtaining proton double resonance spectra was developed.⁽⁴⁾ Since then the Overhauser effect has been used in double irradiation experiments to assign the NMR lines to possible transitions between energy levels. From the energy level pattern the relative signs of spin coupling constants may be determined.

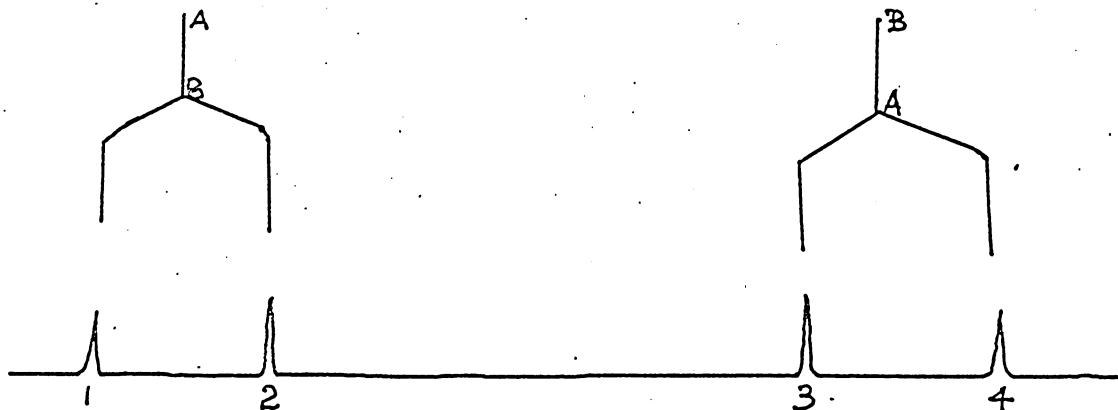
In proton double resonance spectra, the magnetic resonance of one group of hydrogen nuclei (Group A) may be observed by means of a radio-frequency field H_1 at frequency ω_1 , while a second group of hydrogen nuclei (Group X) is irradiated with a field H_2 at frequency ω_2 . Certain modifications in the spectral multiplet structure of group A result from the irradiation of group X if the multiplet structure is caused at least in part by spin coupling between the two groups of hydrogen atoms.

The appearance of a double resonance spectrum depends on the manner in which it is obtained. (5)

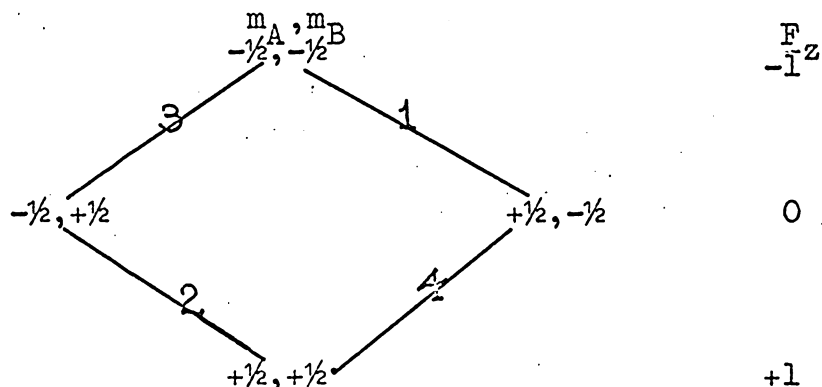
The modifications observed depend on the strength H_2 of the irradiation field. Three cases can be distinguished. (6)

- (1). $\gamma H_2 \gg 2\pi J$: strong perturbation of the multiplet structure. The details depend on the number of hydrogen atoms in groups A and X.
- (2). $2\pi J > \gamma H_2 \gg \frac{1}{T_1}$: formation of submultiplet. Each line of the multiplet splits into a number of components.
- (3). $\gamma^2 H_2^2 T_1 T_2 \sim 1$: nuclear Overhauser effect. The relative intensities of the multiplet lines change, because of a redistribution of the energy-level populations.

The quantitative aspects of the Overhauser effect have been discussed in numerous publications, a review and an extensive bibliography was given by Webb. (7) A detailed qualitative theory was discussed by Kaiser (5) using the system of AX_3 (8) as an example. We use a more simple system including only two non-equivalent protons AB as example to explain the Overhauser Effect.



The nuclear magnetic resonance spectra of the system is shown as Fig. 1. The energy level diagram for the weak-coupling approximation will be



F_z is total Z component of spin angular momentum. If number 4 line is weakly irradiated, the population of $+1/2, +1/2$ state decreases and $+1/2, -1/2$ state increases from the thermal equilibrium distribution. Because the population increase of the state $+1/2, -1/2$ the intensity of absorption line number 1 increases and the population decrease of state $+1/2, +1/2$ causes the intensity of line 2 to decrease. The line 3 is not affected.

Four general statements were derived by Kaiser.(5)

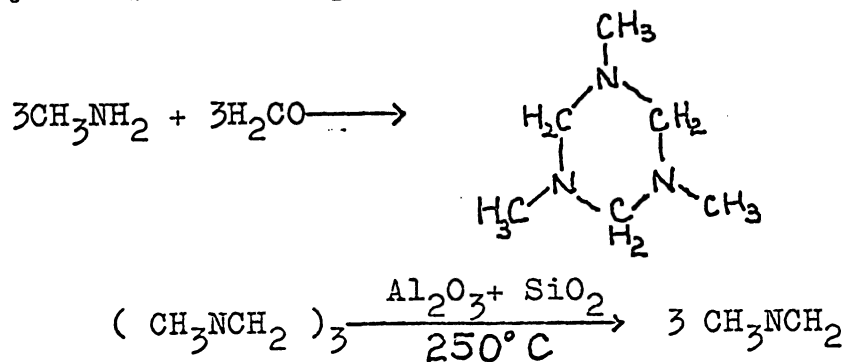
- (1). Irradiation of a transition affects only those transitions that have an energy level in common with it.
- (2). The changes of the relative intensities in the A multiplet resulting from irradiation of one line in the B multiplet are independent of the sign of the spin coupling constant J_{AB} .

(3). Irradiation of a "nondegenerate" line decreases the spectral intensity of "parallel" transitions and increases the spectral intensity of "series" transitions. A spectral line is "nondegenerate" if it corresponds to only one transition (which may have multiplicity greater than one) in the energy-level diagram. Two transitions are in "parallel" if they occur between the same F_z levels, they are in "series" if they have only one F_z level in common.

(4). The parallel-series relation is reciprocal, i.e., if irradiation of line L decreases the intensities of lines P and increases those of lines S, then irradiation of any one of the P lines decreases the intensity of L and irradiation of any one of the S lines increases the intensity of L.

III EXPERIMENTAL

N-Methyl Methylenimine was prepared following the procedure of J.L.Anderson⁽⁹⁾⁽¹⁰⁾ with the temperature of pyrolysis system changed to 250°-260°C.



In order to obtain pure N-Methyl Methylenimine in NMR sample tubing, the pyrolysis apparatus was designed as Fig.2

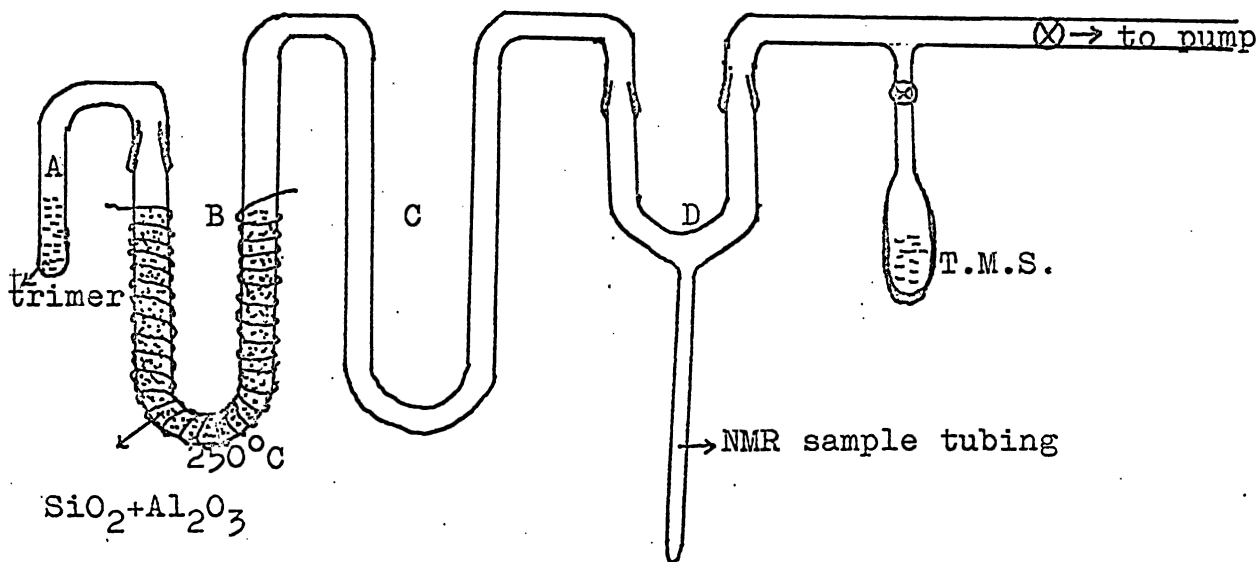


Fig. 2

Because the sample was very unstable and reacts with grease, no stopcock was used before it was trapped under liquid nitrogen temperature at D part.

The system was evacuated for thirty minutes then the C part was immersed in adry ice and acetone mixture to trap some impurity coming from the pyrolysis. The D part with NMR sample tubing was immersed in liquid nitrogen to trap the sample. The trmperature of A part which contained 1,3,5 trimethyl-hexahydrosymtriazine was raised gently by heating it with Bunsen burner. When enough sample was collected at D trap, the temperature of the polymer was cooled to -78°C to stop the pyrolysis. The pumping valve was then closed and tetramethylsilane was introduced to D trap. The temperature of D was raised from -195°C to -78°C so, both N-Methyl Methylenimine and TMS melted and flowed into the bottom of the NMR sample tube. The sample tube was sealed under vacuum and stored at liquid nitrogen temperature.

It was found necessary to pretreat the TMS by shaking it with aqueous NaHCO_3 to prevent catalysis of the polymerization.

Proton single and double resonance spectra of pure liquid $\text{CH}_3\text{N}=\text{CH}_2$ were taken at -60°C with Varian HA 100 machine operating at 100 MC.

conventional single resonance spectra.

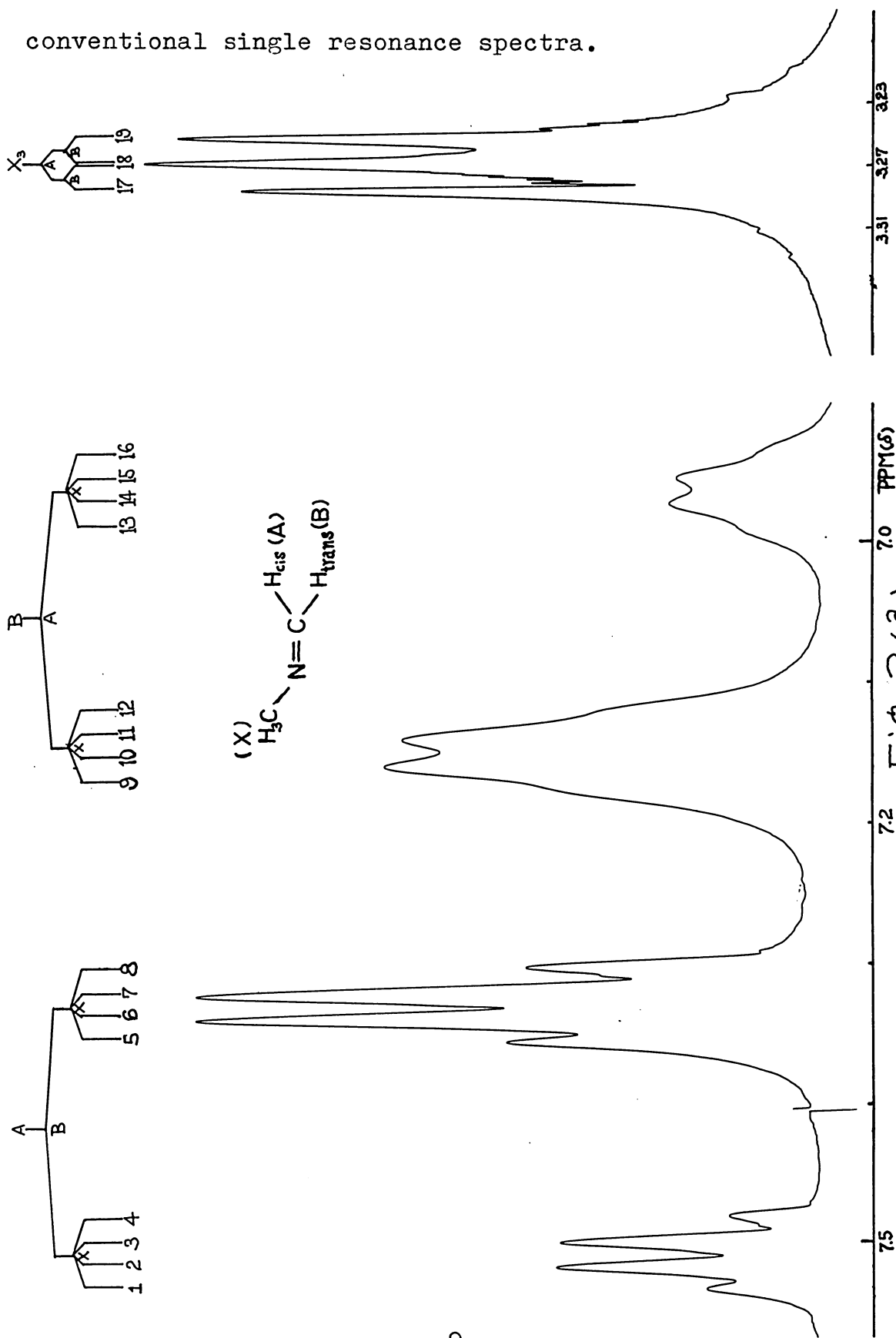
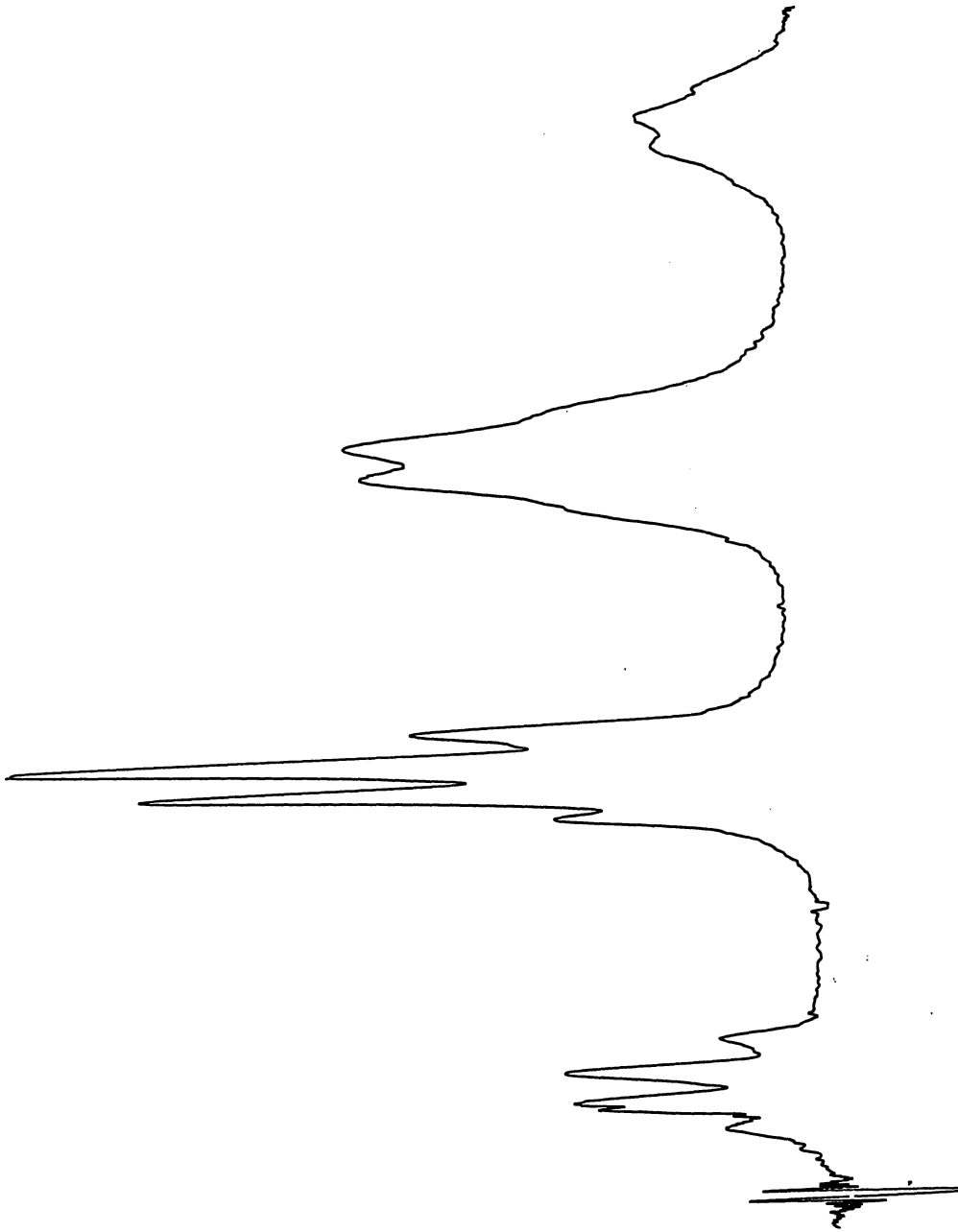


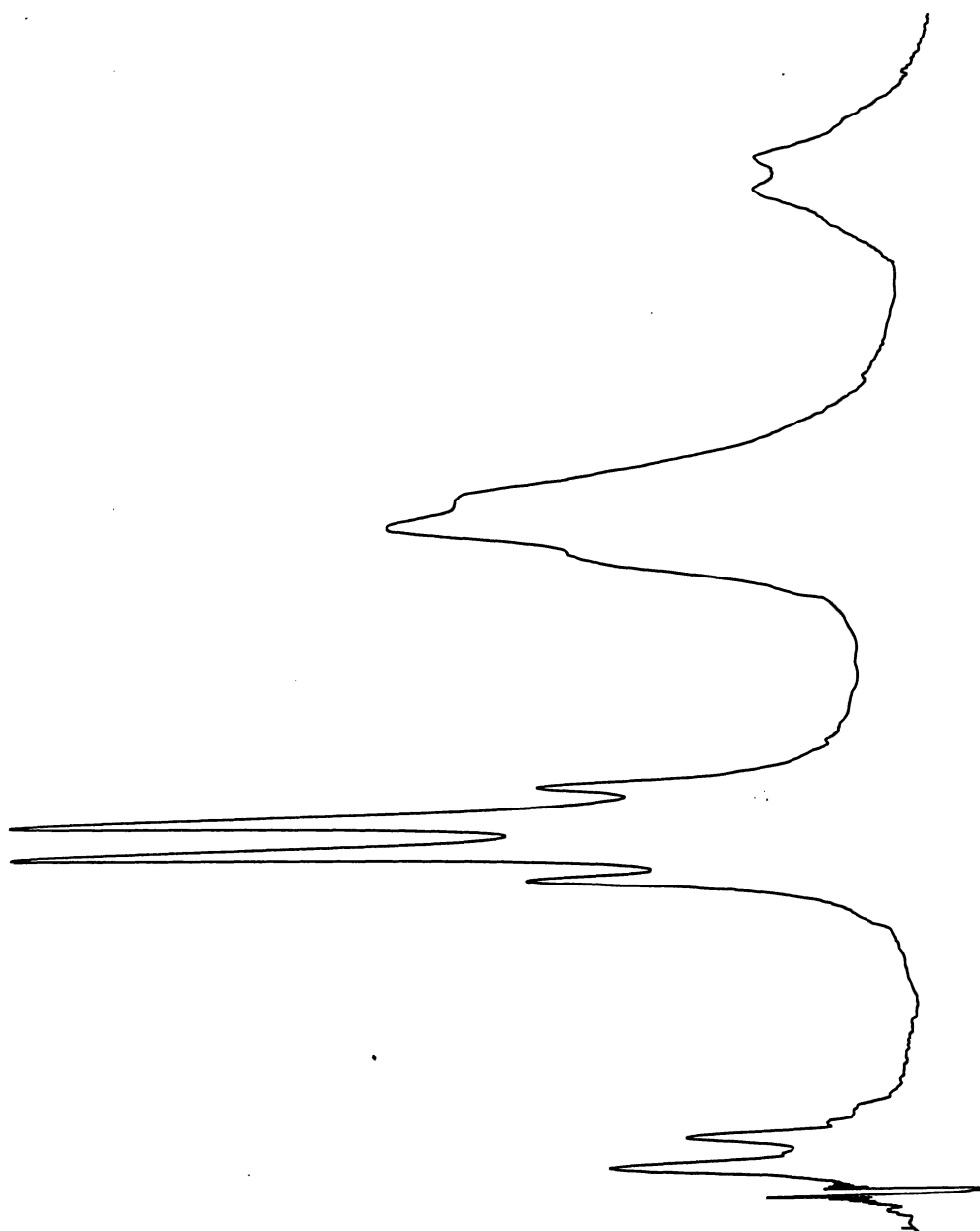
Fig 3(a)

Fig. 3b



double resonance spectra with line 17 weakly irradiated.

Fig. 3c



double resonance spectra with line 19 weakly irradiated.

IV. RESULTS

Figure 3a shows conventional field-sweep spectrum of N-MethylMethylenimine and its interpretation. The line widths of the resonances of both the CH₂ protons are unusually large, especially the two quadruplets appearing in high-field are widely broadened. B. L. Shapiro, S. J. Ebersole and R. M. Kopchik⁽¹¹⁾ assigned the broad resonances to the H_{trans}, the proton trans to the methyl group. The line broadening has its origin in incomplete quadrupole washing out of J_{H_{cis}-C-N} and J_{H_{trans}-C-N} (the latter coupling is evidently larger than the former.)

A good approximation to the usual constants is obtained from a first order interpretation of an ABX₃ case. The values were refined by iterating to a converged solution with the computer program of Reilly and Swalen.⁽¹²⁾ The chemical shifts in ppm. from T.M.S. as zero are X=3.20, B=6.95, and A=7.24. The coupling constants are |J_{AB}^(gem)| = 16.32 and |J_{AX}| ≈ |J_{BX}| = 1.57 cps.

Figure 3b was taken with line 17 weakly irradiated. It shows the intensities of lines 7,8,15,16, were increased and the intensities of lines 5,6,13,14 were decreased. The lines 1,2,3,4,9,10,11,12 were not changed.

Figure 3c was taken with line 19 weakly irradiated, the intensities of lines 1,2,9,10, were increased and 3,4,

11,12 were decreased. The lines 5,6,7,8,13,14,15,16 were not changed.

The energy level diagram is illustrated in Figure 4,5,6,7 and is marked in the notation (m_A, m_X, m_B) for the weak-coupling approximation. The assignment of spectral lines to transitions between energy levels depends on the relative signs of the three spin coupling constants. Four different combinations are possible.

Case 1: $J_{AB}=(+)$, $J_{AX}=(+)$, $J_{BX}=(+)$.

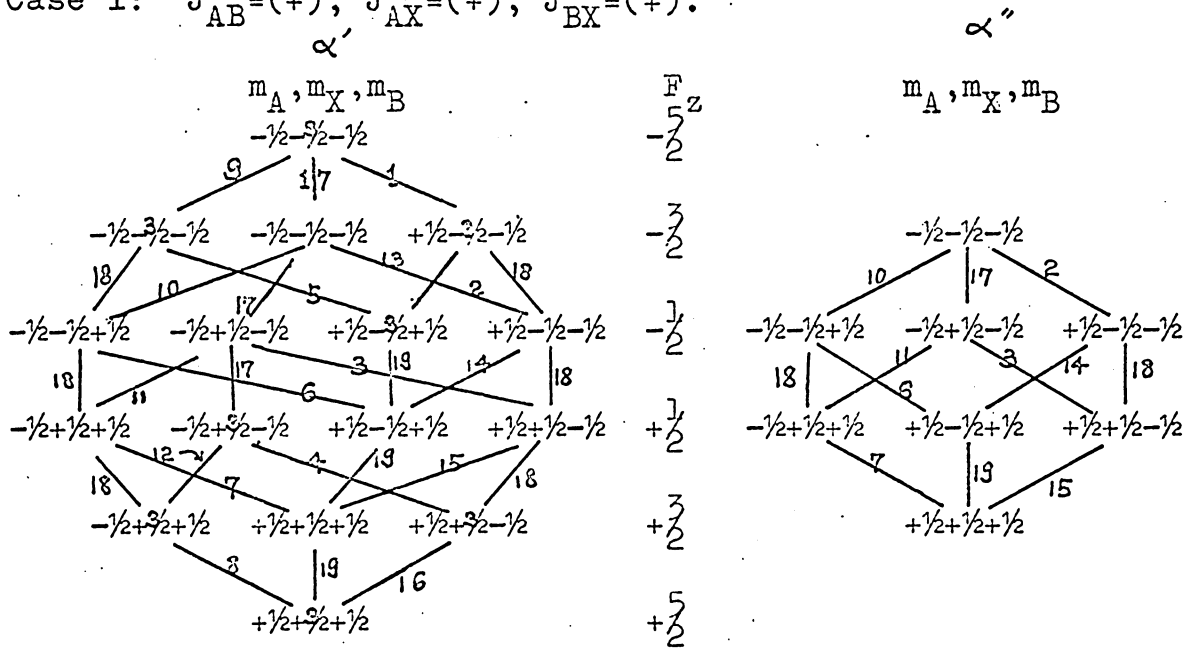


Fig. 4

Case 2 ; $J_{AB}=(+)$, $J_{AX}=(+)$, $J_{BX}=(-)$.

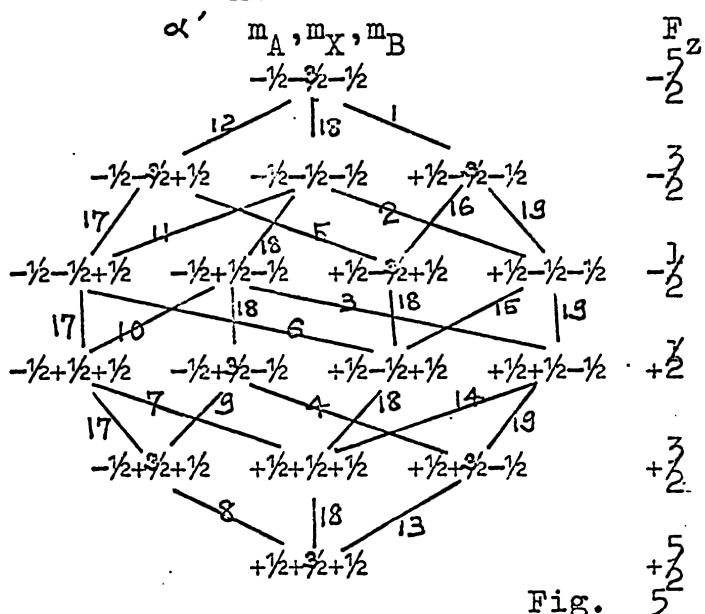
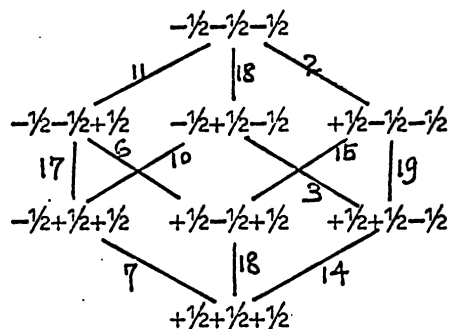


Fig. 5

α'' m_A, m_X, m_B



Case 3 : $J_{AB}=(+)$, $J_{AX}=(-)$, $J_{BX}=(+)$.

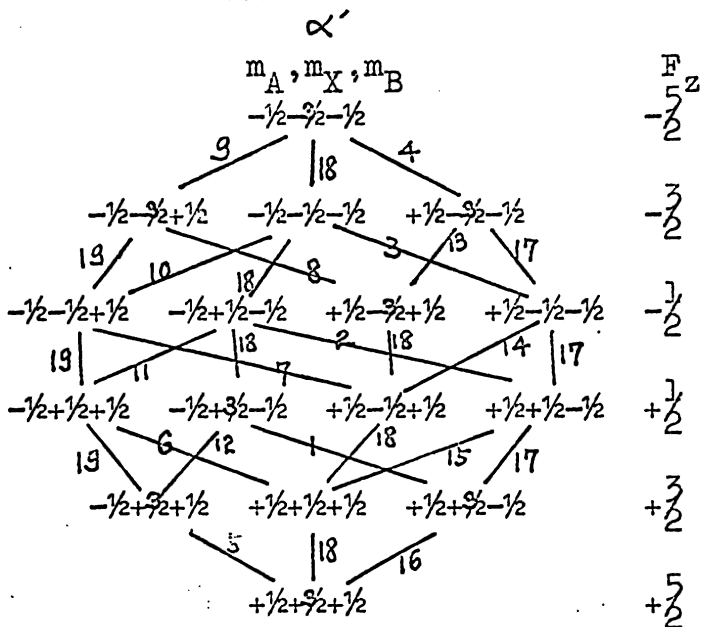
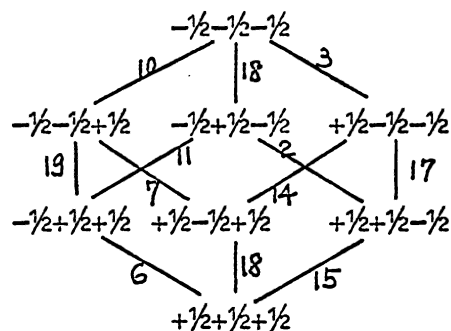


Fig. 6

α'' m_A, m_X, m_B



Case 4 : $J_{AB}=(-)$, $J_{AX}=(+)$, $J_{BX}=(+)$.

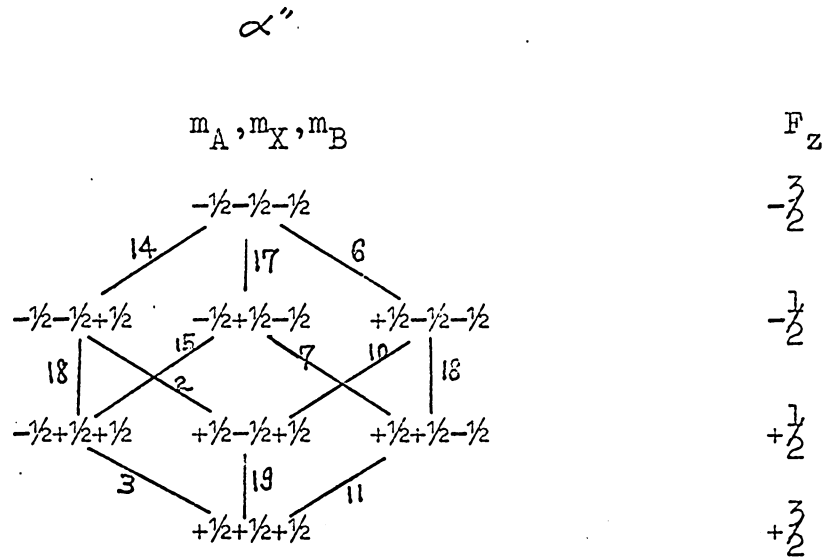
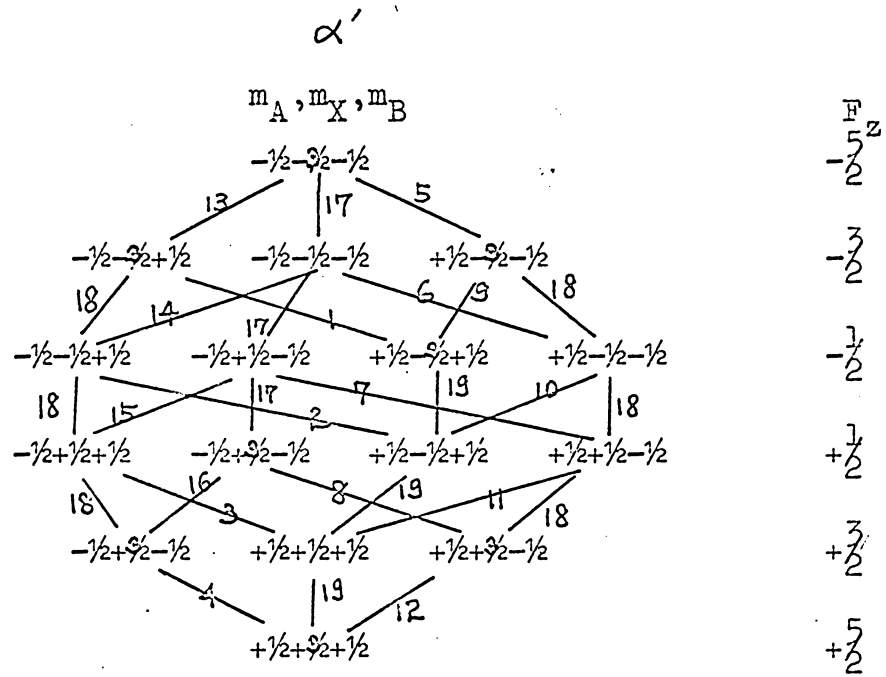


Fig. 7

The prediction of intensity changes from, the Overhauser Effect by irradiating number 17 and 19 lines in each case was shown in Table 1.

Table 1

Case 1: $J_{AB}(+), J_{AX}(+), J_{BX}(+)$ or $J_{AB}(-), J_{AX}(-), J_{BX}(-)$.

line # irrad.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
17	-	-	+	+	0	0	0	0	-	-	+	+	0	0	0	0
19	0	0	0	0	+	+	-	-	0	0	0	0	+	+	-	-

Case 2: $J_{AB}(+), J_{AX}(+), J_{BX}(-)$ or $J_{AB}(-), J_{AX}(-), J_{BX}(+)$.

line # irrad.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
17	0	0	0	0	-	-	+	+	-	-	+	+	0	0	0	0
19	+	+	-	-	0	0	0	0	0	0	0	0	+	+	-	-

Case 3: $J_{AB}(+), J_{AX}(-), J_{BX}(+)$ or $J_{AB}(-), J_{AX}(+), J_{BX}(-)$.

line # irrad.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
17	-	-	+	+	0	0	0	0	0	0	0	0	-	-	+	+
19	0	0	0	0	+	+	-	-	+	+	-	-	0	0	0	0

Case 4: $J_{AB}(-), J_{AX}(+), J_{BX}(+)$ or $J_{AB}(+), J_{AX}(-), J_{BX}(-)$.

line # irrad.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
17	0	0	0	0	-	-	+	+	0	0	0	0	-	-	+	+
19	+	+	-	-	0	0	0	0	+	+	-	-	0	0	0	0

"+" means intensity increases, "-" means intensity decreases and "0" means no affect.

Case 4 was chosen, for example, to explain the construction of Table 1.

When line 17 was weakly irradiated, in α' part, the population of $-\frac{1}{2}, +\frac{3}{2}, -\frac{1}{2}$ decreased and $-\frac{1}{2}, -\frac{3}{2}, -\frac{1}{2}$ increased, states of $-\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}$ and $-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$ did not change (this statement supposes that the probabilities per unit time for a given state to make upward and downward transitions are the same. The supposition is reasonable, because the $\frac{uH}{kT} \approx 10^{-5}$ is so small comparing to one) These population changes caused the intensities of lines 8,16(series) to increase and the intensities of lines 5,13(parallel) to decrease. In α'' part the populations of states $-\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}$ decreases and $-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$ increases, causing the intensities of lines 7,15 (series) to increase and the intensities of lines 6,14 (parallel) to decrease. Results of irradiating line 19 are explained in a similar way.

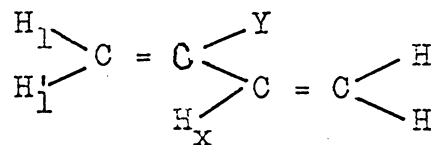
A single experiment is sufficient to determine the relative signs of the three coupling constants.

Comparing the experimental result in Fig. 3 to Table 1 obviously Case 4 in table 1 is the correct one, J_{AB} has different sign from J_{AX} and J_{BX} .

V DISCUSSION

The results obtained agree quite well with previous studies of similar systems. For example, the geminal couplings $J_{HH}(\text{gem})$ for the neat liquids of $\text{CH}_2=\text{N}-\text{C}(\text{CH}_3)_3$ and $\text{CH}_2=\text{N}-\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$ were found to be 16.52 and 16.97 cps. respectively. (1)

The values of (H,H) coupling constants for substituted 1,3 butadienes were summarized and discussed in terms of σ - and π -contributions by A.A.Bothner-By and R.K. Harris. (13) If their conclusion, that substitution at the position of Y of 1,3 butadiene with a highly electronegative atom or group, changes $J_{H_1H_X}$ and $J_{H'_1H_X}$ from negative values gradually to positive values,



is acceptable, then J_{AX} and J_{BX} in the $\text{CH}_2=\text{N}-\text{CH}_3$ molecule should be $J_{AX} \approx J_{BX} = + 1.57$ cps. and $J_{AB}(\text{gem}) = - 16.32$ cps. The negative sign of J_{AB} is as the suggested previously by Shapiro, et. al. (1)

VI BIBLIOGRAPHY

1. B.L.Shapiro, S.J.Ebersole, G.J.Karabatsos, F.M.Vane and S.L.Manatt, J.Am.Chem.Soc., 85, 4041(1963).
2. (a). C.N.Banwell, A.D.Cohen, N.Sheppard, and J.J. Turner, Proc.Chem.Soc. , 266 (1959). (b). E.B. Whipple, J.H.Goldstein and L.Mandell, J.Am.Chem.Soc. 82, 3010 (1960). (c). R.T.Hobgood Jr. and J.H. Goldstein. , J.Mol. Spectry. 12,76 (1964).
3. A.W.Overhauser, Phys. Rev. 91, 476 (1953).
4. R.Kaiser, Rev.Sci. Instr. , 31, 963 (1960).
5. R.Kaiser, J.Chem.Phys. , 39, 2435 (1963).
6. W.A.Anderson and R.Freeman, J.Chem.Phys. ,37,85(1962).
7. R.H.Webb, Am.J.Phys. ,29,428 (1961).
8. J.A.Pople, W.G.Schneider, and H.J.Bernstein,"High Resolution Nuclear Magnetic Resonance" McGraw-Hill Book Company, Inc. New York, 1959.
9. J.L.Anderson, U.S. Patent 2729679 (January,1956).
10. K.V.L.N.Sastry and R.F.Curl Jr. J.Chem.Phys. 41, 77 (1964).
11. B.L.Shapiro, S.J.Ebersole and R.M.Kopchik, J.Mol. Spectry. , 11,326 (1963).
12. C.A.Reilly and J.D.Swalen , J.Chem.Phys., 37, 21(1962).
13. A.A.Bothner-By and R.K.Harris, J.Am.Chem.Soc. ,87, 3451 (1965).