#### NOTES

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Received July 6, 1966

# Proton Magnetic Resonance Spectrum and Nuclear Overhauser Effects of N-Methylmethylenimine<sup>†</sup>

The molecule,  $CH_3 - N = CH_2$ , is the simplest Schiff base which can be obtained. The properties of this molecule have been described (1-3). This work describes the proton magnetic resonance spectrum of this  $ABX_3$  system. In addition to determination of the magnitudes of the coupling constants and chemical shifts, the relative signs of the coupling constants were determined by study of the nuclear Overhauser effect.

N-methylmethylenimine was prepared by the procedure described by Andersen (1) the only modification being that the temperature of the pyrolysis system was reduced to 260°C from 450°C.

<sup>\*</sup> National Science Foundation Undergraduate Research Participant.

<sup>&</sup>lt;sup>†</sup> This work supported by grants C-071, E-183, and A-088 of The Robert A. Welch Foundation and by Public Health Service Training Grant No. T1-GM942 from National Institute of General Medical Science.

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FIG. 1 (a). Conventional single resonance spectrum of  $CH_3NCH_2$  (neat with 20% TMS) at  $-60^{\circ}C$ . (b) Double resonance spectrum with line 17 weakly irradiated. The zero beat to low field is spurious. (c) Double resonance spectrum with line 19 weakly irradiated. The zero beat on line 1 is spurious.



Fig. 1(b)



FIG. 1(c)

 $3CH_{3}NH_{2} + 3H_{2}CO \rightarrow (CH_{3}NCH_{2})_{3}$   $(CH_{3}NCH_{2})_{3} \xrightarrow{Al_{3}O_{4} + SiO_{3}}{250^{\circ} \sim 260^{\circ}C} 3CH_{3} - N = C$ 

Because the sample was very unstable and appeared to react with grease, no stopcock was used before it was trapped at liquid nitrogen temperature. The  $Al_2O_3$  and  $SiO_2$  in the pyrolysis system must be fresh, otherwise some small contamination from the used pyrolysis system caused the sample to polymerize even at dry ice temperature. It was also found necessary to pretreat the tetramethylsilane, used as an internal reference, by shaking it with NaHCO<sub>3</sub> to prevent catalysis of the polymerization. The NMR sample tube containing the sample was degassed and was sealed under vacuum.

Proton single and double resonance spectra of pure liquid  $CH_3$ —N= $CH_2$  with 20% TMS were taken at  $-60^{\circ}C$  with Varian HA 100 machine operating at 100 Mc/sec. The spectra are shown in Fig. 1.

#### RESULTS

Figure 1a shows the conventional frequency-sweep spectrum of N-methyl methylenimine and its interpretation. The line widths of the resonances of both the CH<sub>2</sub> protons are unusually large, especially the two quadruplets appearing at high-field are widely broadened. Shapiro, Ebersole, and Kopchik (4) 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  $J_{\rm HN}(cis)$  and  $J_{\rm HN}(trans)$ . [The latter coupling is evidently larger than the former (4).]

A good approximation to the usual constants is obtained from the first-order interpretation of an  $ABX_3$  case. The values were refined by iterating to a converged solution on a digital computer. The chemical shifts in ppm from TMS as zero are X = 3.274, B = 7.094, and A = 7.3985. The coupling constants are  $|J_{AB}|(gem) = 17.5$  and  $|J_{AX}| = |J_{BX}| = 1.61$ cps.



FIG. 2. Schematic energy-level diagram and transition assignment for N-methyl methylenimine. The energy levels are marked in the notation  $(m_A, m_X, m_B)$  for the weak coupling approximation;  $F_z$  is total Z component of spin angular momentum.

Figure 1b 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. A qualitative analysis of intensity changes in Overhauser experiments has been given by Kaiser (5). There are four permutations of the relative signs of the coupling constants in CH<sub>3</sub>NCH<sub>2</sub>. The set,  $J_{AB} = (-)$ ,  $J_{AX} = (+)$ , and and  $J_{BX} = (+)$  or  $J_{AB} = (+)$ ,  $J_{AX} = (-)$ , and  $J_{BX} = (-)$ , is the correct one.

The assignment of spectral lines to transitions between energy levels according to the  $J_{AB}(gem) = (-), J_{AX} = (+)$ , and  $J_{BX} = (+)$  is shown in Fig. 2. A single experiment is sufficient to determine the relative signs of the three coupling constants. The double resonance spectrum in Fig. 1c with line 19 weakly irradiated gives a check. It showed 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.

#### DISCUSSION

The results obtained agree quite well with previous studies of similar systems. For example, the geminal couplings  $J_{\rm HH}$  (gem) for the neat liquid of  $\rm CH_2=N-C(\rm CH_3)_3$  and  $\rm CH_2=N-C(\rm CH_3)_2C(\rm CH_3)_3$  were found to be 16.52 and 16.97 cps. respectively (6).

There are no closely analogous examples to help decide the absolute sign of any coupling constants in this molecule. If



can be compared to

where  $J_{24} = J_{34} = (-)$ , and  $J_{23} = (+)$  (7), then  $J_{AX} = J_{BX} = (-)$  and  $J_{AB} = (+)$ . This agrees with the theoretical prediction of Gutowsky, Karplus, and Grant (8) that the geminal coupling constant will be positive if the <HCH angle is 100°-125°.

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## Chemiluminescent Emission Spectrum of Germanium Dichloride<sup>†</sup>

Using a diffusion flame technique that has been described previously (1-4), we have observed the chemiluminescent emission from flames of GeCl<sub>4</sub>, GeBr<sub>4</sub>, and GeI<sub>4</sub> burning in potassium vapor. GeCl<sub>4</sub> gives a bright blue flame, GeBr<sub>4</sub> a bright green, and GeI<sub>4</sub> a bright orange flame. Argon is used as the carrier gas, and a total pressure of about 10 torr is used in all experiments. Flame spectra have been recorded with the aid of a Jarrell-Ash f/6.3 plane grating, 0.75-meter spectrograph, using exposures of about 2 hours duration.

The flame spectrum of GeCl<sub>4</sub> consists of a group of closely spaced, diffuse bands (Figure 1) in the region 4900-4100 Å, with what seems to be an underlying continuum. The bands strongly resemble those of SnCl<sub>2</sub>, emitted by a flame of SnCl<sub>4</sub> (1). GeBr<sub>4</sub> yields what appears to be a genuine continuum in the region, 5200-4400 Å. We have not yet obtained a spectrum of the GeI<sub>4</sub> flame because of difficulties with flame stability.



FIG. 1. Emission spectrum of  $GeCl_2$ . Several transitions have been labeled with their assigned quantum numbers. A listing of all the observed bands appears in Table I.

A Deslandres scheme for a triatomic molecule is quite successful when applied to the band spectrum emitted by the GeCl<sub>4</sub> flame. Thus it seems virtually certain that the emission is due to GeCl<sub>2</sub>. Our measurements on the bands, which are typically uncertain by about 5 cm<sup>-1</sup>, are summarized in Table I together with the quantum numbers assigned to the bands. Wave numbers followed by a question mark are less certain than the others. It will be noted that we have assigned  $v_3'' = 0$  for all the bands, which is merely an indication that  $v_3''$  seems to be the same for all bands observed; i.e., all the bands can be accounted for in terms of two quantum numbers for the upper state and two for the lower state.

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Received August 27, 1966

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<sup>&</sup>lt;sup>†</sup>Work supported by a grant from the National Science Foundation.