

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM MARSH RICE UNIVERSITY, HOUSTON, TEXAS]

Infrared Spectrum of N-Methylenemethylamine¹

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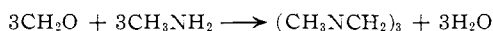
The infrared spectra of CH_3NCH_2 and CD_3NCH_2 have been obtained in the region of $4000\text{--}400\text{ cm.}^{-1}$ with the amine as pure solid as well as in an argon matrix. The fundamental vibrational frequencies have been assigned completely.

The preparation of N-methylenemethylamine was reported by Anderson² in 1956. He had obtained the amine as the principal product of the pyrolysis of hexahydro-1,3,5-trimethyl-s-triazine. The compound was reported to melt at -119° and polymerize rapidly near its boiling point, about -35° . In addition, an infrared absorption characteristic for the $\text{C}=\text{N}$ stretching at $6.02\ \mu$ was reported.

This compound represents the lowest known homolog of the Schiff bases, which are found to be stable only if part of larger conjugated molecules. It appeared therefore worthwhile to report a complete infrared study of this simplest Schiff base and attempt an assignment of its vibrational fundamentals. The microwave spectrum of this amine has already been investigated.³ From it the geometry of the molecule, its dipole moment, as well as the barrier of rotation of the methyl group, has been deduced.

Experimental

Preparation of Hexahydro-1,3,5-trimethyl-s-triazine.—Equivalent amounts of a 40% aqueous solution of formaldehyde and a 33% aqueous solution of methylamine were mixed at 0° .



Upon addition of solid KOH, the triazine was separated from the water. The triazine was dried over KOH and vacuum distilled; b.p. 62° at 17 mm.; yield 95%.

Preparation of N-Methylenemethylamine.—The procedure followed closely the method described by Anderson.² A U-tube was packed with Al_2O_3 fused with SiO_2 , ratio 1:1. The triazine was dropped slowly onto the bed of fused silica, which was maintained at $425\text{--}450^\circ$. The system was continuously evacuated to about 10^{-2} mm., and the pyrolysis product was collected in a trap at -196° . Unreacted trimer and possible traces of water were caught in an intermediate trap at -78° . The yields, while not measured, appeared good, close to 90%. Anderson² had reported a yield of 100%. It should be mentioned, however, that after several preparations the $\text{Al}_2\text{O}_3\text{--SiO}_2$ catalyst became ineffective and had to be renewed in order to give good yields.

Preparation of CD_3NCH_2 .—The preparation of $\text{CD}_3\text{--N}=\text{CH}_2$ was started with CD_3COOD (purchased from the Isomet Corp.). The tetradeuterioacetic acid was converted to CD_3NH_2 by a Schmidt reduction.⁴ CD_3COOD (7.3 g.) was mixed with 15 ml. of concentrated sulfuric acid. The mixture was covered with 30 ml. of chloroform, and, while stirring, 10 g. of sodium azide was added slowly. After stirring for 2 hr. more at 45° , the mixture was poured onto crushed ice and the chloroform was separated from it. The aqueous solution was made strongly alkaline, and the free amine was distilled off into hydrochloric acid giving $\text{CD}_3\text{NH}_3\text{Cl}$ at a yield of 60%. The hydrochloride of the amine was used directly in the preparation of the triazine.

Spectra.—All spectra were recorded with a Beckman IR-9 spectrophotometer in double beam operation over the range from 400 to 4000 cm.^{-1} . The sample to be investigated was deposited on a cold CsBr window in a cryostat described previously.⁵ The

temperature of the cold window was monitored with a copper-constantan thermocouple attached to the copper block holding the window. Spectra were obtained of the pure amine as a solid at -196° and, in addition, of the amine isolated in an argon matrix at 20°K .

In the matrix isolation experiments, the CsBr window was cooled with liquid hydrogen. The amine was evaporated onto the window out of a cold trap, maintained by an ethanol slush at -115° . Argon was leaked into the trap through a needle valve. The argon was permitted to mix with the amine during the 30-cm. path between trap and CsBr window. Unfortunately, it was not possible to control or determine the Ar-amine ratio this way. This ratio is estimated to be about 100:1 for the normal isotopic species and considerably less for the deuterated species. Experiments, in which it was attempted to mix definite amounts of argon and amine, failed because most of the amine trimerized before spray-on.

For the spectra of the pure solids, the same arrangement was used with the argon flow cut-off. Here the CsBr window was cooled with liquid nitrogen to -196° .

The deposits obtained were moderately opaque; however, sufficient energy was transmitted to obtain good spectra. At 400 cm.^{-1} 80% of the light was transmitted, while at 4000 cm.^{-1} the scattering increased and only 30 to 50% of the light was transmitted, depending on the quality of the deposit.

Results and Interpretation

Traces of the spectra obtained are shown in Fig. 1. The similarity of the matrix and pure solid spectra indicates that there are no strong intermolecular interactions in the solid at the temperature of liquid nitrogen.

N-Methylenemethylamine in its most symmetric arrangement has only a plane of symmetry and belongs to point group C_s ; therefore, all 18 fundamentals are expected to be infrared active. Twelve of the fundamentals are symmetric with respect to the plane of symmetry, species A' , and six are antisymmetric, species A'' . The assignment of the different fundamentals is greatly aided by a close analogy, which can be drawn between the vibrational spectrum of N-methylenemethylamine and that of propylene. For the latter, detailed assignments are on hand.⁶ Nevertheless, a number of uncertainties remained with respect to the differentiation of methyl and methylenic hydrogen motions. The spectra of the trideuterated species resolved this difficulty and only ambiguities persist in the assignment of the weak CH_3 deformation modes.

There can be little doubt about the assignment of the methylenic hydrogen stretchings ν_1 and ν_3 for the asymmetric and symmetric mode, respectively. The unexpected third strong band in the 2800-cm.^{-1} region in the spectrum of the deuterated amine is readily understood as caused by Fermi resonance of the combination $\nu_5 + \nu_3$ with ν_3 . The assignment of the hydrogen stretches of the methyl group is also straightforward. However, one cannot tell directly which of

(1) Supported by Grants C-092 and C-071 from the Robert A. Welch Foundation.

(2) J. L. Anderson, U. S. Patent 2,729,679, Jan., 1956.

(3) K. V. L. N. Sastry and R. F. Curl, Jr., *J. Chem. Phys.*, **41**, 77 (1964).

(4) H. Wolff, "Organic Reactions," Vol. 3, p. 307.

(5) A. Snelson and K. S. Pitzer, *J. Phys. Chem.*, **67**, 882 (1963). The high-temperature Knudsen cell attachment to the cryostat was not used.

(6) (a) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Princeton, N. J., p. 354; (b) J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Std.*, **37**, 163 (1946); (c) R. C. Lord and P. Venkateswarlu, *J. Opt. Soc. Am.*, **43**, 1079 (1953).

the two higher frequencies belongs to species A' and A'', respectively, since in the matrix and solid information obtainable from the contours of the bands is lost. In analogy to propylene, the higher frequency was assigned to species A''. One difference between the assignment of the hydrogen stretchings of the amine and of propylene deserves mentioning; that is, the two asymmetric modes of the methyl hydrogens are obtained at higher frequency than the symmetric stretch of the methylenic hydrogens, as proven clearly by the spectrum of the deuterated amine. Possibly the assignment of the hydrogen stretching modes in propylene needs revision in this point.

The bending modes of the methylene group are given clearly by the pronounced bands at about 1465 cm.^{-1} for ν_6 , 1220 cm.^{-1} for ν_9 , and 1025 cm.^{-1} (matrix) and 1060 cm.^{-1} (solid) for ν_{16} , all of which are not shifted significantly in the spectrum of the deuterated compound. The splitting of ν_8 in the solid is interesting; this is likely a crystal effect and is observed also for ν_8 , ν_{10} , and ν_{17} . The assignment of the different deformation modes of the methyl group remains somewhat ambiguous. The bands observed for the protonated and deuterated amine in the region of the methyl deformation modes, 1400 and 1000 cm.^{-1} , respectively, could be explained consistently only if it is assumed that the strong CH_2 rocking mode, ν_{16} , covers the asymmetric methyl deformation mode, ν_7 , in the spectrum of the deuterated species. This assumption is supported by the broad appearance of ν_{16} in the spectrum of the deuterated amine.

The assignments of the $\text{C}=\text{N}$ and $\text{C}-\text{N}$ stretching modes, ν_5 and ν_{11} , are definite. In fact, there are two strong bands in the region of 940 cm.^{-1} where the $\text{C}-\text{N}$ stretch is expected. This splitting is reasonably explained as a Fermi resonance of ν_{11} with $2 \times \nu_{17}$.⁷ The methyl wagging and the methylene rocking modes can be assigned with certainty. Clear is also the twisting mode, ν_{17} , of the methylene group. The

$\text{C}=\text{N}$ bending frequency appears to be just at the lower limit of our observation. In the pure solid of the protonated species an absorption at 400 cm.^{-1} , corresponding to ν_{12} , is observed, while in the other spectra this band must have been shifted somewhat to lower frequency. There is a weak band, observed in the spectrum of the deuterated species at 754 cm.^{-1} , which could be explained as $2 \times \nu_{12}$, giving for ν_{12} about 380 , which appears reasonable.

The twisting motion of the methyl group is expected to be considerably below 400 cm.^{-1} , the lower range of our instrument. Fortunately, it was possible to obtain in the solid spectrum of the normal species a band at 704 cm.^{-1} , which can be understood as a combination band of $\nu_{18} + \nu_{17}$, giving for ν_{18} about 205 cm.^{-1} . From the barrier of rotation of the methyl group, determined from the microwave spectrum,⁸

(7) It was pointed out to us by one of the referees that the explanation of this doublet as Fermi resonance appears not quite satisfactory. Especially in the case of the solid hydrogen compound, $2 \times \nu_{17}$ is considerably above the ν_{11} doublet. However, there seems to be no alternative; no other band, which is not shifted strongly upon deuteration, is expected in the region of ν_{11} . It is observed that just ν_{16} and ν_{17} are shifted strongly to higher frequency in the solid, indicating a strong intermolecular interaction for the A' modes of the CH_2 group. This could be taken as an indication that ν_{17} is quite anharmonic in the solid.

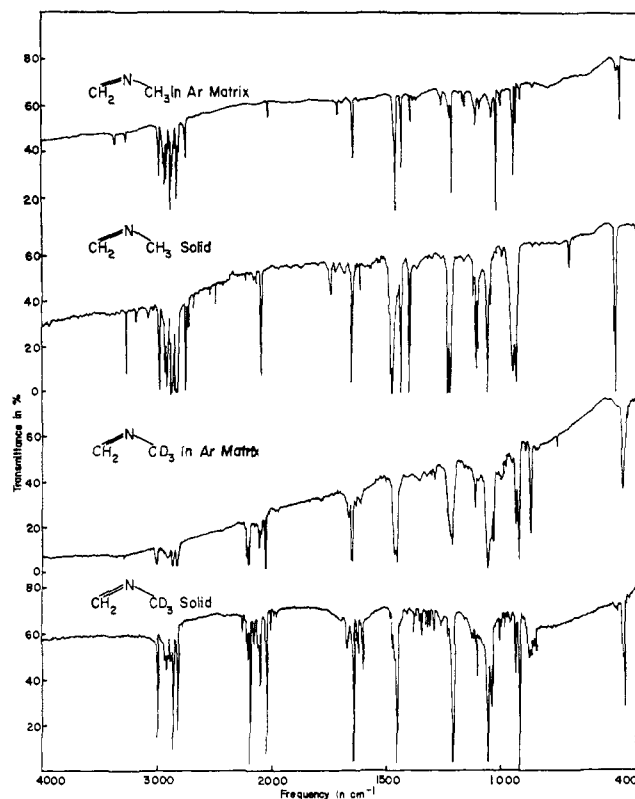


Fig. 1.—Infrared absorption spectra of normal and trideuterated N-methylenemethylamine as solid at -196° and in an argon matrix at 20°K .

ν_{18} is computed to be 193.5 cm.^{-1} , a gratifying agreement. For the trideuterated compound 158.7 cm.^{-1} is obtained for ν_{18} from the microwave data. Unfortunately, no clear band could be found at about 615 cm.^{-1} , corresponding to a combination of ν_{18} and ν_{17}

TABLE I
ASSIGNMENT OF VIBRATIONAL FUNDAMENTALS

			Matrix		Solid	
			H	D	H	D
ν_1	A'	CH_2 asym. stretch	3005	3012	3009	3010
ν_2	A'	CH_3 asym. stretch	2930	2212	2940	2198
ν_3	A'	CH_2 sym. stretch	2894	2882	2896	2875
ν_4	A'	CH_3 sym. stretch	2768	2066	2774	2055
ν_5	A'	$\text{C}=\text{N}$ stretch	1658	1652	1657	1649
ν_6	A'	CH_2 scissor	1467	1454	1477	1458
ν_7	A'	AH_3 asym. deform.	1472	1111	1485	1107
ν_8	A'	CH_3 sym. deform.	1399	1038	1407	1038
ν_9	A'	CH_2 rocking	1218	1214	1234	1217
ν_{10}	A'	CH_3 wagging	1098	867	1108	872
ν_{11}	A'	$\text{C}-\text{N}$ stretch	948	931	954	932
			938	919	939	918
ν_{12}	A'	$\text{C}=\text{N}$ bend	400	(380)	400	(380)
ν_{13}	A''	CH_3 asym. stretch	2957	2221	2957	2220
ν_{14}	A''	CH_3 asym. deform.	1439	1060	1439	1065
ν_{15}	A''	CH_3 wagging	1045	845	1049	843
ν_{16}	A''	CH_2 rocking	1023	1055 ^a	1062	1061
ν_{17}	A''	CH_2 twist	478	460	501	462
					497	457
ν_{18}	A''	CH_3 twist	(205)	(160)	(205)	(160)

^a Probably this band is higher for the deuterated species because the $\text{Ar}-\text{CH}_3\text{NCH}_2$ ratio is lower for the CD_3NCH_2 spectrum than for the CH_3NCH_2 spectrum.

in the spectra of the trideuterated compound, but it is believed that 160 cm.^{-1} is close to where ν_{18} could be found. The final assignment is shown in Table I.

To obtain a final check on the assignment of the fundamentals of the normal and trideuterated compound, the ratios for the product rule were calculated for both species A' and A'' . The moments of inertia around the three principal axes needed for this computation were obtained from the microwave data.³ The values are in atomic mass units times \AA^2 .

$$I_A = 9.633 \quad I_B = 47.389 \quad I_C = 53.831$$

$$I_A = 12.795 \quad I_B = 55.613 \quad I_C = 62.031$$

for normal and trideuterated amine, respectively.

The computed values of the product rule are 0.203 and 0.323 for species A' and A'' . The corresponding values obtained from the frequencies observed are 0.227 and 0.346 for the matrix spectra and for the pure solid 0.215 and 0.321, respectively. The agreement, especially for the solid is quite good, indicating that there are no gross inconsistencies in the assignment. The somewhat high values for the matrix spectra are attributed to the fact that, in the case of the spectrum of the deuterated species in the matrix, the amine concentration must have been high. This is reflected also in the broader lines observed in this spectrum.

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Binding Regions in Polyatomic Molecules and Electron Density Distributions

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The concept of a binding region as developed by Berlin² is extended to polyatomic molecules. Various electron density distributions for the water molecule are examined to determine whether or not they concentrate charge density in the binding region, a necessary requirement for the attainment of electrostatic equilibrium. This is accomplished by plotting the difference in density ($\Delta\rho$) between a proposed molecular density distribution and one obtained from the original atomic densities located with the same molecular geometry. The latter distribution does not concentrate sufficient charge density in the binding region to balance the nuclear forces of repulsion, and thus the sign of $\Delta\rho$ in the binding region provides a test of proposed density distributions. In this manner, limits may be placed on the form of an acceptable density distribution for the water molecule. It is found that the lone-pair orbitals must possess close to sp hybridization and that the bonds to the hydrogen atoms must be "bent" and of almost pure $2p$ character. It is also shown that the lone-pair density plays an essential role in binding the protons in the water molecule.

In 1950 Berlin² introduced the valuable concept of dividing the space in a homonuclear diatomic molecule into binding and antibinding regions. Electron density placed in the region between the two nuclei (the binding region) exerts forces on the nuclei drawing them together, while electron density placed behind either nucleus (the antibinding region) exerts unequal forces on the nuclei and leads to the separation of the molecule into atoms. These two spatial regions are separated by two surfaces (see Fig. 1a) which pass through the nuclei and which have the property that any negative charge density placed on these surfaces exerts an equal force along the bond axis on both nuclei. These boundary curves thus represent positions from which electron density neither increases nor decreases the internuclear distance. It is worth stressing that the concept of a binding region is a rigorous one, being a direct result of the Hellmann-Feynman³ theorem. This theorem states that the force on any nucleus in a molecule is the sum of the electrostatic forces due to the other nuclei and to the electron charge distribution treated as a continuous charge density by classical methods.

Charge density must be concentrated in the binding region to achieve electrostatic equilibrium. Thus a knowledge of the binding region for a polyatomic molecule would be useful in that various charge distributions could be tested to determine whether or not

they do indeed concentrate charge density in this region. The backbone of the density distribution for a molecule composed of atoms from the first two periods will be in terms of the $1s$ orbital for the hydrogen atom, and the $1s$, $2s$, and $2p$ orbitals for the other atoms present. Since so much of the chemist's reasoning and theories of electronic structure are couched in terms of the $1s$, $2s$, and $2p$ orbitals, it is important to know the limiting forms of the best possible description of a density in terms of these orbitals. It is the purpose of the present method to provide these limiting density distributions.

To construct the binding region for the water molecule, which we choose to illustrate the procedure, we first consider the case of a heteronuclear diatomic molecule. There will be a point on the internuclear axis at a distance r behind the nucleus of smaller charge at which an element of negative charge density will exert equal forces on both nuclei, *i.e.*, $Z_A/(R+r)^2 = Z_B/r^2$ for some value of r when $Z_A > Z_B$ and R is the bond length. This is illustrated in Fig. 1b. Thus for a heteronuclear diatomic molecule, one boundary surface curls back onto itself to form an enclosed region, while the boundary surface through the nucleus of greater charge opens up and approaches a straight line perpendicular to the bond axis. This has been pointed out by Hirschfelder, *et al.*, who also give the equations for the boundary curves.⁴ For an O-H

(1) A. P. Sloan Research Fellow.

(2) T. Berlin, *J. Chem. Phys.*, **19**, 214 (1951).

(3) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(4) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 935.