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Vibrational Spectra of Substituted Hydrazines. IV.[1] Raman and Far-Infrared Spectra and Structure of Tetramethylhydrazine

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The infrared spectra of gaseous and solid tetramethylhydrazine have been recorded from 33 to 4000 cm^{-1}. The corresponding Raman spectra of the gas, liquid, and solid have also been recorded and depolarization values have been measured. All spectra have been interpreted in detail and the normal vibrations have been characterized on the basis of the band contours, relative intensities, and depolarization values. A comparison of the infrared and Raman spectra of both the gaseous and solid states shows a one to one correspondence for all bands and it is concluded that the molecule is in the gauche form and has C_2 symmetry in all phases.

Introduction

In a recent series of investigations,[3-6] we have been trying to determine the factors which give rise to the various conformations found for the X_2Y_4 molecules where X is a group Va element and Y is a halogen, hydrogen, methyl, or perfluoromethyl group. For example hydrazine[3a] and tetrakis(trifluoromethyl)hydrazine[6] have been found to exist in a single form (gauche with C_2 symmetry) in all three physical states; however, a tetrafluorohydrazine[3b] has been found to be an equilibrium mixture of the gauche (C_2) and trans (C_{2h}) isomers of approximately equal amounts in the fluid states at ambient temperature. The factors which are expected to be the most important in determining the conformations of these X_2Y_4 molecules are the X-X bond length and the electronegativity of Y. The importance of the electronegativity factor can be demonstrated by considering the isomeric composition of the $P_2(CH_3)_4$ (40% trans) and P_2Cl_4 (95% trans) molecules.[3c,5] Since the P-P distance is expected to be nearly the same and the methyl group is about the same size as a chlorine atom, both the steric and exchange forces should be the same for these two compounds. However, the electronegativity of the methyl group (~2.0) is considerably smaller than that of the chlorine atom (3.0). Thus it appears that the increased electronegativity of the substituent favors the trans conformer.

Previous work[3c,4] has shown that an increased X-X bond length favors a greater percentage of the trans form. For example, $P_2(CH_3)_4$ was found[3] to be a 60-40% mixture of the gauche and trans isomers, respectively, whereas the $As_2(CH_3)_4$ was found[4] to have a 40-60% composition of the gauche and trans isomers, respectively. The only previous vibrational study[7] on tetramethylhydrazine was an infrared study from 4500 to 400 cm^{-1} of the gas, liquid, and solid. In order conclusively to determine the symmetry of these X_2Y_4 molecules, it is necessary[2] to compare the infrared and Raman data of the skeletal stretching and bending regions of the vibrational spectrum. Thus, a detailed investigation of the Raman spectrum as well as a study of the far-infrared spectral region is required for a confident symmetry determination of tetramethylhydrazine. In addition, we were interested in the frequencies for the methyl and skeletal N-N torsional modes.

Experimental Section

The sample of tetramethylhydrazine was obtained from the high-temperature pyrolysis of tetramethyltetrazine. The sample was carefully fractionated and its purity checked by gas chromatography. The boiling point of the sample was 73-74°. Sample authenticity was verified by comparison with an earlier infrared investigation and by its nmr spectrum.

The infrared spectra were recorded from 4000 to 250 cm^{-1} with a Perkin-Elmer Model 621 spectrophotometer. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry air. In the higher frequency region, the instrument was calibrated with standard gases.[8] The lower wave number region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.[9] The spectrum was recorded with the gaseous sample contained in a 20-cm cell equipped with CsI windows. The spectrum of the solid was obtained by condensing the sample on a CsI plate maintained at −190° with boiling nitrogen. Representative mid-infrared spectra are shown in Figure 1.

The Raman spectrophotometer[10] used was a Cary Model 82 equipped with an argon ion laser source. The Raman spectrum of the gas was measured at 25° in a standard Cary multipass gas cell using a CRL Model 53A argon ion laser source. The spectrum of the room-temperature liquid was taken with the sample sealed in a capillary tube. The spectrum of the solid sample (−90°) was obtained by using a cell which was similar in design to a far-infrared cell which was described earlier.[11] Depolarization measurements in the liquid phase were made by using the analyzer and the monochromator when making such measurements. Representative Raman spectra are illustrated in Figures 2 and 3.

The far-infrared spectrum was recorded from 33 to 590 cm^{-1} (see Figure 4) on a Beckman Model IR-11 spectrophotometer. The instrument was purged with dry nitrogen and calibrated with the frequencies reported for water vapor by Hall and Dowling.[9] For the spectrum of the gas phase in this frequency region, a Beckman variable-path-length cell equipped with polyethylene windows was used. The cell used for recording the spectrum of the solid at −190° has been described earlier.[11] The frequencies for all observed bands are expected to be accurate to ±2 cm^{-1}. These frequencies are listed in Table I with their relative intensities and proposed assignments.

Results

Only the frequencies of the skeletal stretching and bending motions are expected to show significant variations with

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[1] Part III: J. R. Durig and W. C. Harris, *J. Chem. Phys.*, 55, 1735 (1971).

[2] Taken in part from the thesis of R. W. MacNamee to be submitted to the Department of Chemistry, University of South Carolina, in partial fulfillment of the Ph.D. degree.

[3] (a) F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, 47, 2104 (1967); (b) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, 48, 3216 (1968); (c) J. R. Durig and J. S. DiYorio, *Inorg. Chem.*, 8, 2796 (1969).

[4] J. R. Durig and J. M. Casper, *J. Chem. Phys.*, 55, 198 (1971).

[5] J. R. Durig, J. E. Saunders, and J. D. Odom, *J. Cryst. Mol. Struct.*, 2, 169 (1972).

[6] J. R. Durig, J. W. Thompson, and J. D. Witt, *Inorg. Chem.*, 11, 2477 (1972).

[7] D. C. McKean, *Spectrochim. Acta*, 10, 161 (1957).

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[9] R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, 47, 2454 (1967); 52, 1116 (1970).

[10] This instrument was purchased with funds from the National Science Foundation through Grant No. GP-28068.

[11] F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, 47, 2104 (1967).

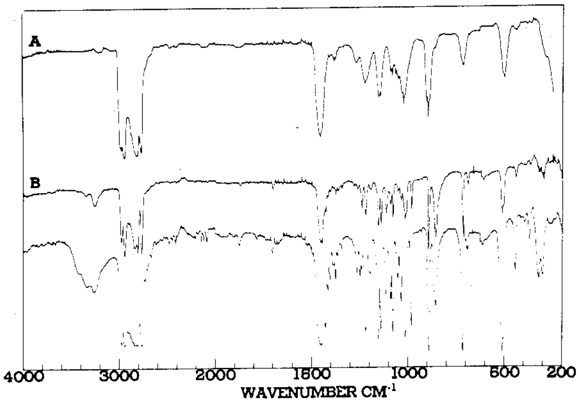

Figure 1. Infrared spectra of (A) gaseous $(CH_3)_2NN(CH_3)_2$ and (B) solid $(CH_3)_2NN(CH_3)_2$ recorded at liquid nitrogen temperature using a CsI support. Lower solid spectrum is of a heavier layer on the CsI support. Ordinate is in arbitrary units of absorbance.

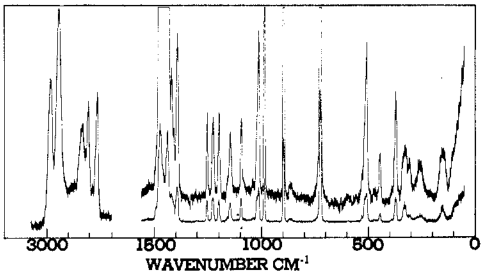

Figure 2. Raman spectra of solid $(CH_3)_2NN(CH_3)_2$ at liquid nitrogen temperature. Lower trace has gain reduced to show peak maxima. The gain for the region from 2700 to 3100 cm^{-1} has been reduced to half that of the upper trace for the 0–1600-cm^{-1} region. Ordinate is in arbitrary units of relative intensity.

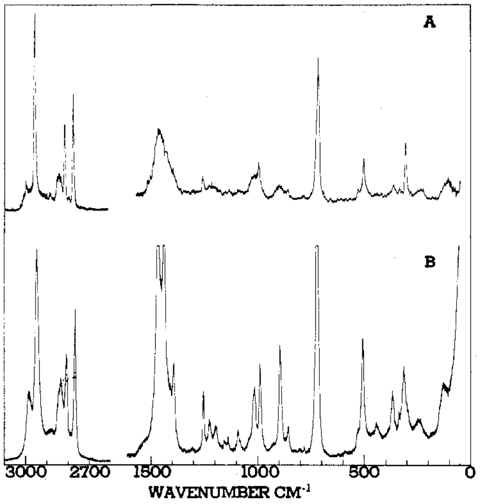

Figure 3. Raman spectra of (A) gaseous $(CH_3)_2NN(CH_3)_2$ at approximately 20 mm and (B) liquid $(CH_3)_2NN(CH_3)_2$ sealed in a capillary. The gain for the regions from 2700 to 3100 cm^{-1} has been reduced to half that of the 0–1600-cm^{-1} regions. Ordinate is in arbitrary units of relative intensity.

changes in molecular structure. All of the carbon-hydrogen motions except the methyl torsions fall above 1000 cm^{-1} and the frequencies of the skeletal motions are all expected to fall below 1050 cm^{-1} and should be distinguishable from the C-H vibrations. An inspection of the Raman spectrum of solid tetramethylhydrazine (see Figure 2) shows eleven distinct lines between 300 and 1050 cm^{-1}. This is exactly the number of lines expected for the skeletal modes, exclusive of the methyl and N-N torsions, when the molecule has C_2 symmetry. If the molecule were in the trans form, then one expects only six Raman lines in this spectral region. In addition, one finds an excellent correspondence between the infrared and Raman bands in the solid; thus the rule of mutual exclusion is not operative and the molecule has C_2 symmetry in the solid. It should be noted that all of the bands found in the solid are also present in the liquid phase. Thus, there are no bands observed in the solid whose origin can be attributed to low site symmetry or to the correlation field. Similarly, there are no bands in the liquid which disappear with solidification as would be expected if the molecules existed in more than one form in the fluid states. Although the Raman spectrum of the gas shows the pronounced Q branches for the symmetric modes the most clearly, the broad lines of the antisymmetric modes can still be identified. Thus, on the basis of the Raman spectrum alone, it can be concluded that the tetramethylhydrazine exists in only one isomer form in the gas, liquid, and solid states and that this form is the gauche with C_2 symmetry.

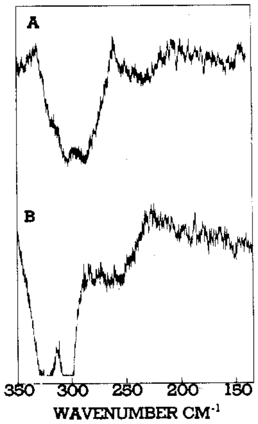

Figure 4. Far-infrared spectra of (A) gaseous $(CH_3)_2NN(CH_3)_2$ recorded in a cell of 10-m path length and (B) solid $(CH_3)_2NN(CH_3)_2$ recorded at liquid nitrogen temperature on a silicon support. Ordinate is in arbitrary units of absorbance.

Vibrational Assignment

McKean[7] has proposed assignments for most of the observed infrared bands, but his frequency range was limited to 400 cm^{-1} and above; therefore, assignments have been previously given for most of the carbon-hydrogen motions and the skeletal stretching modes, but the low-frequency bending and torsional modes have not been assigned. Therefore, the assignments for these low-frequency modes will be discussed first and then the differences in assignment of some of the higher frequency bands which was necessitated by the depolarization data will be pointed out.

The N-N torsion is observed at 114 cm^{-1} in the Raman spectrum of the gas but shifts to 132 cm^{-1} with liquefaction and then to 150 cm^{-1} with solidification. This frequency does not differ significantly from the 123 cm^{-1} found for the corresponding mode in N_2F_4. The four CH_3 torsional modes appear as broad bands at 238 cm^{-1} in both the infrared and Raman spectra of the gas; again, a significant shift was observed for this band with solidification.

The six NC_2 bending modes are assigned on the basis of the observed depolarization ratios along with the consideration of the reported frequencies (425 cm^{-1}, e mode; 366 cm^{-1}, a_1 mode) for the NC_3 bending modes of trimethylamine.[12] The e mode should correlate with the NC_2 deformations and twists whereas the a_1 mode correlates with the NC_2 wag.[13]

[12] G. Dellepiane and G. Zerbi, *J. Chem. Phys.*, **48**, 3573 (1968).

[13] A. B. Harvey and M. K. Wilson, *J. Chem. Phys.*, **44**, 3535 (1966).

Table I. Raman and Infrared Frequencies (cm^{-1}) of Tetramethylhydrazine[a]

Raman			Infrared		
Gas	Liquid	Solid	Gas	Solid	Assignment
2997 w, dp	2986 vs, p	2986	2998 s	2978 vs	
2959 vs, p	2952 vvs, p	2949	2965 vs	2943 vs	
2844 m, p	2832 vs, p	2835 b	2832 s	2842 s	CH_3 str
2807 vs, p	2808 vvs	2808		2806 s	
2776 vs, p	2772 vvs, p	2766	2787 s	2765 s	
1460 m, b, dp	1470 vs, dp	1473			CH_3 antisym def
			1462 vs, sh	1458 vs	CH_3 antisym def
	1441 vs, dp	1440	1450 vs	1449 vs	CH_3 antisym def
		1422			CH_3 sym def
		1409	1411 w	1406 w	CH_3 sym def
1395 w, dp	1396 m	1393	1388 w	1393 w	CH_3 sym def
				1267 w	896 + 372 = 1268
1262 vw, p	1250 m, p	1256	1258 w	1251 m	CH_3 rock + NC_2 antisym str
1228 vw, dp	1224 w, dp	1227	1220 w	1223 s	CH_3 rock
	1196 w, dp	1199	1195 w, sh	1196 m	CH_3 rock
1162 vw, dp	1153 vw, dp	1161	1149 s	1157 s	CH_3 rock
1122 vw, dp	1137 vw	1147	1139 s	1143 s	CH_3 rock
				1116 m	896 + 250 = 1146?
	1094 vw, dp	1095	1087 w	1092 m	CH_3 rock
		1084	1078 w	1082 s	CH_3 rock
			1054 w	1054 w	721 + 326 = 1047
		1042		1037 m	CH_3 rock
			1020 s	1015 s	NC_2 antisym str
1012 vw	1012 m, dp	1014		1012 s	NC_2 antisym str
999 vw, p	986 m, p	987	988 sh	986 s	NC_2 sym str
905 vw, dp	895 m, dp	899	891 s	896 s	NC_2 sym str
860 vw, p	866 vw	861	860 sh	860 m	509 + 372 = 881
720 s, p	720 s, p	725	712 m	721 s	N-N str
				693	372 + 326 = 698
				515 s	NC_2 def (b)
504 m, p	506 m, p	507	505 m	509 s	NC_2 def (a)
	442 vw, dp	444	438 w	445 m	NC_2 twist (b)
	380 vvw, sh	387 sh		390 vw	250 + 141 = 391
363 vw, p	368 w, p	372		372 w	NC_2 twist (a)
308 m, p	320 w, p	328	303 m	326 m	NC_2 wag (a)
		304	288 m	303 m	NC_2 wag (b)
238 vw	245 vw	260	238 w	250 w	CH_3 torsion
114 vw, b	132 w, dp	150	116 w	141 w	N-N torsion

[a] Abbreviations used: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; b, broad; p, polarized; dp, depolarized; sh, shoulder; a and b refer to symmetry species.

An inspection of the Raman and infrared spectra of the solid in the 300-500-cm^{-1} region shows five pronounced bands at 304, 328, 372, 444, and 507 cm^{-1} using Raman frequencies of the solid. The Raman frequencies of the liquid (320, 368, and 506 cm^{-1}) corresponding to the 328-, 372-, and 507-cm^{-1} bands in the Raman spectrum of the solid were found to be polarized and are thus assigned to the in-phase NC_2 wag, twist, and deformation, respectively, of "a" symmetry, whereas the 304- and 444-cm^{-1} bands in the Raman spectrum of the solid correspond to the NC_2 wag and twist, respectively, of b symmetry. The NC_2 deformation of b symmetry clearly appears at 515 cm^{-1} in the infrared spectrum of the solid. This band is assigned to a fundamental rather than to factor group splitting of the 509-cm^{-1} band, since no other intramolecular mode showed any splitting. A weak band near 390 cm^{-1} in the infrared spectrum of the solid appears to be a combination of the torsional modes.

The N-N stretch is confidently assigned to the strong polarized Raman line at 720 cm^{-1} in the gas and the liquid. Three of the four NC_2 stretching modes are readily assigned to the Raman lines at 895, 986, and 1012 cm^{-1} in the liquid. The 986-cm^{-1} band had been previously assigned as a CH_3 rocking mode of b symmetry, but the polarization data clearly indicate that it belongs to a vibration of symmetry species a and the relative Raman intensity is consistent with an N-C stretching mode. The assignment for the other N-C stretch is rather arbitrary, since no other band shows up strongly in this region, but since it is expected to have a frequency near 1000 cm^{-1}, the strong infrared band at 1020 cm^{-1} in the gas is assigned to the other antisymmetric NC_2 stretch. It has been shown[12] that the NC antisymmetric stretch in trimethylamine is strongly coupled with the CH_3 rocking modes so the relatively strong polarized Raman band at 1250 cm^{-1} in the liquid is expected to have significant contribution from this motion.

Eight CH_3 rocking modes are expected between 1000 and 1250 cm^{-1} but the vibrations of a symmetry are expected to give nearly depolarized lines for this motion so it is not possible to distinguish between the CH_3 rocks of a and b symmetry. The Raman spectrum has this number of lines in this region which have not been previously assigned and they are chosen as fundamentals. The two additional infrared bands for the solid in this same spectral range are assumed to be combination or overtones. Three of the four CH_3 symmetric deformations were observed, but the eight CH_3 antisymmetric deformations appear bunched as three lines. The CH stretching region is complicated with possible overtones of the CH_3 deformations in Fermi resonance with these fundamentals and assignment of individual lines to the two different symmetry species was not possible.

Discussion

The barrier to internal rotation around the N-N bond for $N_2(CH_3)_4$ appears to be quite similar to the value obtained[14]

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(14) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, 31, 1129 (1959).

for N_2F_4. Since all four methyl torsions appear to fall at about the same frequency, it is possible to calculate an "average" barrier assuming negligible top-top coupling. On the basis of the Mathieu equation, a periodic methyl torsional barrier of 3.4 kcal/mol is calculated from the 238-cm^{-1} band. This value is in excellent agreement with the 3.3-kcal/mol barrier obtained for the methyl torsional barrier in 1,2-dimethylhydrazine[15] but considerably lower than the 4.69-kcal/mol value for 1,1-dimethylhydrazine[16] although the latter value was for the solid state. In general, the barrier increases significantly with the addition of more methyl groups on the same nitrogen (see Table II). This trend does not appear to hold for this tetramethyl-substituted hydrazine. A possible explanation for this seemingly low barrier might be given in terms of the CNN angle which is expected to be significantly larger for this substituted hydrazine compared to the similar angle in the disubstituted hydrazines because of steric factors.

Although several substituted diphosphine compounds have been found to crystallize with the molecules in the trans configuration,[5,17,18] a similar result does not occur for the hydrazines. For example, tetramethyldiphosphine is approximately 60% gauche isomer at room temperature, but in the crystal the molecule has the trans structure.[17] From the one to one correspondence between the infrared and Raman frequencies in the solid state, it is quite clear that this hydrazine molecule retains the C_2 configuration in the solid. The relative energies for the trans and gauche isomers of substituted hydrazines appear to be considerably larger than the corresponding quantities for the diphosphines, since only tetrafluorohydrazine has been found to have an appreciable concentration of the trans isomer at room temperature.

Table II. Some Barriers to Internal Rotation about C-N Bonds

Molecule	Barrier, kcal/mol	Ref	Molecule	Barrier, kcal/mol	Ref
CH_3NH_2	1.98	*a*	$(CH_3)_2NNH_2$	4.69 (solid)	*e*
$(CH_3)_2NH$	3.28	*b*	$(CH_3)_3N$	4.41	*f*
CH_3NHNH_2	3.67	*c*	$(CH_3)_2NN(CH_3)_2$	3.3	*g*
$CH_3NHNHCH_3$	3.34	*d*			

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Registry No. $(CH_3)_2NN(CH_3)_2$, 6415-12-9.

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(18) Y. C. Yeung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

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Vibrational Spectrum of Bis(trifluoromethyl) Trioxide

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The infrared spectrum of solid $(CF_3)_2O_3$ and the Raman spectrum of gas, liquid, and solid $(CF_3)_2O_3$ have been measured in the fundamental region. A new vibrational assignment is proposed in which the symmetric O-O stretch of the triatomic O_3 bridge is located at 875 cm^{-1}, considerably higher than previously reported. This value is very similar to the value of 890 cm^{-1} for the O-O stretch in CF_3OOCF_3 and indicates a similarity in the O-O bond order in the two molecules. The high intensity of the 875-cm^{-1} band demonstrates the usefulness of Raman spectroscopy in the detection of O-O stretching vibrations.

Introduction

The infrared spectrum of gaseous CF_3OOOCF_3 has recently been reported.[1] The spectrum was assigned on the assumption that the molecule possessed only trivial C_1 symmetry. In view of the surprising stability of this substance, the vibrational frequencies of the trioxide skeleton are of particular interest. The symmetric and antisymmetric O-O-O stretching frequencies were assigned[1] to strong infrared bands at 773 and 897 cm^{-1}, respectively.

More recently, the structures of $(CF_3)_2O$, $(CF_3)_2O_2$, and $(CF_3)_2O_3$ were investigated by electron diffraction.[2] An O-O bond length of about 1.5 Å and an O-O-O of 120° was found for the trioxide. This bond length corresponds to an O-O single bond as found, for example, in hydrogen peroxide, HOOH. Durig and Wertz[3] have examined the infrared and Raman spectra of CF_3OOCF_3. They assigned the strongest Raman band in the spectrum at 886 cm^{-1} to the O-O stretching vibration. Because of the large polarizability change associated with symmetric motions of this type, Raman spectroscopy is particularly well

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