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Vibrational Spectra and Structure of Tetramethyltetrazine

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The infrared spectra of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ have been studied from 4000 to 33 cm^{-1} in all three physical states. The Raman spectra of tetramethyltetrazine have been studied to within 30 cm^{-1} of the exciting line for the gaseous, liquid, and crystalline states. The initial infrared and Raman spectra recorded at liquid nitrogen temperatures correspond to the sample being in a supercooled liquid or glassy state; further annealing resulted in a crystalline state. A comparison between the infrared and Raman data obtained for the fluid and crystalline samples suggests that there are at least two conformations present in the fluid states but only one centrosymmetric conformer present in the crystalline state. A vibrational assignment is presented for tetramethyltetrazine and compared with data recently reported for similar molecules. The magnitude of the methyl internal rotational barrier was calculated to be 3.5 kcal/mol and the top-top coupling constant is estimated to be 0.3 kcal/mol. The N=N and N-N stretching modes were observed to be at significantly lower and higher frequencies, respectively, than might be expected which suggests the N=N double bond may be partially delocalized. A simple molecular orbital calculation is consistent with the experimental data since bond orders for the N=N and N-N groups were determined to be 1.72 and 1.44, respectively.

Introduction

Although hydrazine² exists as a single gauche (C_2) rotamer, two conformations have been identified for a number of hydrazine derivatives at ambient temperatures. For example, equilibrium mixtures of two isomeric forms of tetrafluorohydrazine,^{3a} methylhydrazine,^{3b} and *sym*-dimethylhydrazine⁴ have been characterized. However, the spectral data for *unsym*-dimethylhydrazine⁵ and tetramethylhydrazine⁶ can be explained on the basis of a single gauche structure in all three physical states. As an extension of these earlier studies, we have investigated the infrared and Raman spectra of tetramethyltetrazine $[(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2]$ in order to determine the symmetry of the molecule and whether or not more than a single structural form is present in the liquid and gaseous states. Since no previous vibrational study has been reported for tetramethyltetrazine, the vibrational spectra have been interpreted in detail.

The interesting low-frequency torsional fundamentals are expected in the region below 300 cm^{-1} and may be mixed with the low-frequency skeletal vibrations. It is noted that methyl torsional fundamentals typically give rise to the weakest bands in both the infrared and Raman spectra and, thus, identification of these modes may be concealed by the bands resulting from the more intense skeletal deformations.

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(1) 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.

(2) J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, **44**, 4238 (1966), and references therein.

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In addition, the low frequency associated with the torsional oscillations leads to a number of excited states being populated at ambient temperature which may result in a broadening of the respective bands in the fluid state. For these reasons, therefore, a study of the low-frequency spectrum at reduced temperatures may be helpful in assigning the $1 \leftarrow 0$ torsional transitions.

In an earlier study of the vibrational spectra of azomethane⁷ $[\text{CH}_3\text{N}=\text{NCH}_3]$, a surprisingly weak Raman line at 1574 cm^{-1} was assigned to the N=N stretching fundamental;⁸ however, the assignment of the 1574-cm^{-1} line to a skeletal mode was confirmed by a simultaneous investigation of azomethane- d_6 . It is anticipated that the double bond of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ may not be localized which suggests the frequencies assigned to the N=N and N-N groups will be significantly different than assignments previously proposed for the corresponding fundamentals in azomethane and tetramethylhydrazine.⁶

Experimental Section

The sample of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ was prepared by oxidizing commercial *unsym*-dimethylhydrazine with mercuric oxide.⁹ The product was vacuum distilled and the purity of the fraction collected at 56.5° and 51 Torr was verified by gas chromatography and nmr spectroscopy. The infrared spectra of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ between 4000 and 200 cm^{-1} were recorded with a Perkin-Elmer Model 621 spectrophotometer. A Beckman IR-11 spectrophotometer was utilized to record the infrared spectra between 33 and 300 cm^{-1} (see Figure 1). Both instruments were purged with dry air and calibrated with standard gases.¹⁰ For studies of the vapor phase, a 10-cm cell equipped with potassium bromide windows was used. In examining

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Table I. Infrared Spectra of Tetramethyltetrazine^a

ν, cm^{-1}					Assignment
Gas	Liquid	Glass	Solid annealed		
3070 sh, vw					
3003 m	2996 s	3001 m	3004 vs		CH ₃ str
2967 s	2959	2965 s	2969 vs		CH ₃ str
2861 s	2853 s	2861 s	2893 s		CH ₃ str
2833 sh, m	2820 sh, m	2823 m	2827 s		CH ₃ str
2802 m	2796 m	2794 m	2975 vs		CH ₃ str
1468 m	1467 s	1470 m	1470 m		CH ₃ def
			1458 sh, w		CH ₃ def
			1452 sh, m		CH ₃ def
	1440 sh, s	1447 sh, m	1447 m		CH ₃ def
			1417 w		1000 + 420 = 1420
	1396 w	1397 w	1397 w		CH ₃ sym def
1275 m	1273 m	1267 s	1267 s		CH ₃ rock
1246 m	1238 m	1236 s	1236 m		CH ₃ rock
1140 m	1137 m	1151 s	1151 s		NC ₂ str
1091 vw	1091 w	1096 w	1096 m		CH ₃ rock
1046 sh, vw	1046 vw	1057 w			
1034 sh, w	1034 m	1034 m	1039 m		CH ₃ rock
1006 s	998 s	1000 vs	1000 s		N-C ₂ str
897 w	895 m	895 m			Isomer II
823 w	819 m	821 m	821 s		N-N str
592 m	591 s	592 s	587 s		NC ₂ def
480 vw	478 m	490 w	478 m		N=N-N bond and NC ₂ wag
445 vw	445 m	452 w			Isomer II
		417 w			NC ₂ rock
		374 w	420 vw		Isomer II
317 vw		332 w	330		N=N torsion
			268 vw		CH ₃ torsion
226 vw			248 vw		CH ₃ torsion
162			177 w		N-NC ₂ torsion

^a Abbreviations used: m, medium; s, strong; w, weak; v, very; sh, shoulder.

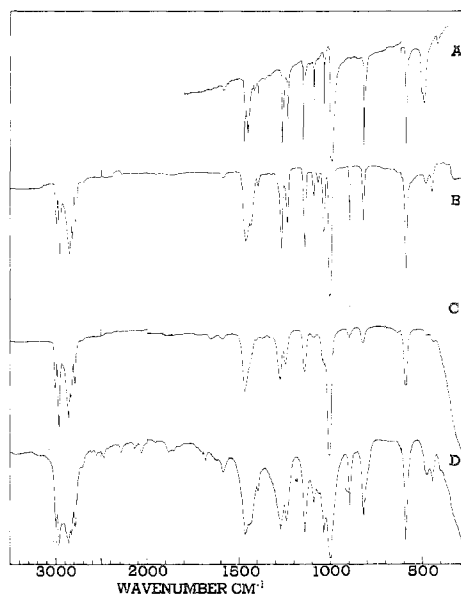


Figure 1. Infrared spectra of tetramethyltetrazine: A, annealed solid at -195° ; B, glass at 195° ; C, gas; D, liquid.

the low-temperature spectra, the sample was slowly sublimed onto either a cesium iodide or a silicon support maintained at liquid nitrogen temperatures. The sample was slowly annealed until no further spectra changes were observed. Survey scans for the infrared spectra of gaseous and solid tetramethyltetrazine may be seen in Figure 1. The reported frequencies are believed accurate to $\pm 2 \text{ cm}^{-1}$.

The Raman spectra of tetramethyltetrazine were recorded on both Cary Model 82¹¹ and Jarell-Ash 500¹² spectrometers equipped

with CRL argon ion lasers. The 5145-A line was used and the laser power was varied from 500mW to 5W depending upon the physical state under investigation. Whereas a simple capillary tube was employed to obtain the spectrum of liquid tetramethyltetrazine, a standard Cary gas cell with the multipass optics was utilized to study gaseous $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$. The spectrum of solid $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ was recorded by subliming the sample onto a standard cold cell maintained at liquid nitrogen temperatures. The Raman spectra of tetramethyltetrazine may be seen in Figure 2.

Results

In previous studies it has been demonstrated that the skeletal stretching and bending frequencies of group Va molecules are sensitive conformational probes. Thus, we compared the room-temperature spectra of tetramethyltetrazine with the spectra obtained for the crystalline sample in order to determine if more than a single conformation is present in the fluid states (see Figures 1 and 2). The transitions observed in the low-frequency infrared and Raman spectra are summarized in Tables I and II. It is apparent that the conformation giving rise to the spectra of the annealed sample has a center of inversion in view of the mutual exclusion between the infrared and Raman frequencies and it is likely the symmetry of this conformer is C_{2h} . In the spectra of the fluid states, however, a number of additional facts are observed in the region below 1100 cm^{-1} which are believed to originate from a second conformer with either C_1 or C_2 symmetry. The agreement between the frequencies of the infrared and Raman bands for the different physical states suggests the centrosymmetric conformation is also present at ambient temperatures.

There are no bands in the low-frequency spectra of crystalline tetramethyltetrazine whose origin can be attributed to low site symmetry or to the correlation field. Thus a vibrational assignment for the trans conformer will be out-

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Table II. Raman Spectra of Tetramethyltetrazine^a

Liquid	$\Delta\nu, \text{cm}^{-1}$		Assignment
	Glass ^b	Solid annealed	
3001 s, dp	3005 vs	3004 vs	CH ₃ antisym str (B _g)
2965 vs, p	2969 vs	2969 vs	CH ₃ antisym str (A _g)
2880 s, dp(?)	2892 s	2893 s	CH ₃ antisym str (B _g)
2860 s, p	2868 vs	2870 s	CH ₃ sym str (A _g)
2822 s, p	2827 s	2827 s	2 × 1418 = 2836 Fermi resonance with CH ₃ str motions
2779 s, p	2779 m	2795 m	} CH ₃ sym str (A _g)
		2781 s	
		1488 vs	898 + 593 = 1491
1475 vs, p	1472 vs	1476 vs	} N=N str (A _g)
		1472 vs	
		1458 m	
1442 s, p	1445 s	1445 s	CH ₃ antisym def
1418 vs	1421 s	1429 m	} CH ₃ def
		1423 m	
1395 w, dp	1396 m	1402 m	} CH ₃ sym def
		1396 m	
1292 s, dp	1295 w	1297 w	NC ₂ str (B _g)
		1271 vw	1289 w
1250 w	1250	1251 w	CH ₃ rock
1142 s, p	1147 vs	1151 s	NC ₂ str (A _g)
		1125 vw	
1090 m	1100 w	1102 w	CH ₃ rock
		1070 vw	
		1066 vw	
1036 w, p	1036 w	1037 w	CH ₃ rock
895 vs, p	896 s	898 m	N-N str (A _g)
		824 w	
587 w, p	590 w	593 w	NC ₂ def (A _g)
517 w, p	520 vw		C ₁ , C ₂ , or isomer II
464 m, p	468 m		C ₁ , C ₂ , or isomer II
377 m, p	395 m	398 s	N=N-N bend (A _g)
		364 w	
339 m	339 w	367 m	NC ₂ wag (B _g)
		342 w	
		254 w	CH ₃ torsion
	241 w, sh	235 w	CH ₃ torsion
199 m, p	218 w	222 vs	N-NC ₂ torsion
145 m, p	170 w		Isomer II
		127 vw	Lattice mode
		110 w	Lattice mode
		69 s	Lattice mode
		37 m	Lattice mode

^a Abbreviations used: m, medium; s, strong; w, weak; v, very; sh, shoulder; dp, depolarized; p, polarized. ^b Two very weak lines at 1000 and 370 cm⁻¹ were omitted from this column.

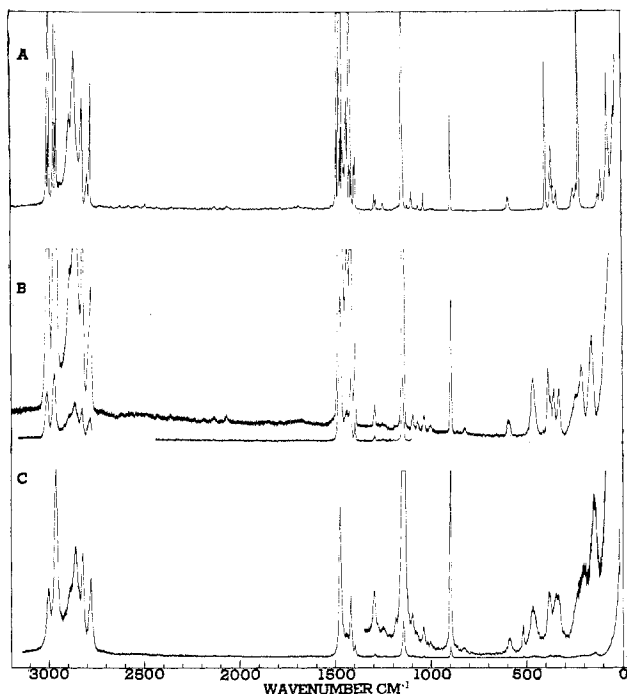


Figure 2. Raman spectra of tetramethyltetrazine: A, annealed solid at -195°C; B, solid glass at -195°C; C, liquid.

lined in the following section and the transitions associated with the second rotational isomer will simply be summarized in the appropriate tables. It should be noted that changes in the vibrational spectra of tetramethyltetrazine might be attributed to bands arising from impurities as well as changes in conformation. The former possibility was eliminated by permitting the annealed sample to liquefy whereupon the bands originating from the second conformation reappeared. Subsequently, the vapor-phase spectrum of this same sample was measured and supported the conformational interpretation of the spectral variations. Assignment of a "doublet component" in the fluid phase to a difference tone can be rejected on the basis of the relative band intensities.

Vibrational Assignment

Under C_{2h} symmetry the fundamental vibrations of $(\text{CH}_3)_2\text{-NN}=\text{NN}(\text{CH}_3)_2$ belong to the following irreducible representations: $15 A_g + 12 B_g + 13 A_u + 14 B_u$. The gerade (g) and ungerade (u) subscripts specify which of the normal modes are Raman or infrared active, respectively. Theoretically, the CH₃ motions should give rise to 36 of the fundamental modes, whereas the remaining 18 vibrations originate from motions of the skeletal framework. Since isotopic derivatives were not available, the vibrational assignment necessarily proceeds from arguments based upon group frequencies and relative infrared and Raman band intensities. In

particular, the assignments we propose for $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)$ will be compared with the vibrational descriptions previously suggested for $\text{CH}_3\text{N}=\text{NCH}_3$,⁷ $(\text{CH}_3)_2\text{NNH}_2$, and $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$.⁶

The four NC_2 stretching fundamentals of $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$ were assigned to bands at 896, 986, 1012, and 1015 cm^{-1} , respectively.⁶ In the present study of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ there is little question that the intense Raman line at 1151 cm^{-1} results primarily from the symmetric NC_2 stretching vibration. The B_g NC_2 valence vibration is tentatively assigned to the weak line at 1297 cm^{-1} in the spectrum of the solid sample. A similar frequency was previously assigned to the antisymmetric CC_2 stretching fundamental in isobutene¹³ (1271 cm^{-1}) and acetone¹⁴ (1229 cm^{-1}). The two infrared-active NC_2 stretching motions have been assigned to bands at 1151 and 1000 cm^{-1} , respectively. Although the assignments proposed for $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ appear consistent with earlier studies and with arguments based upon band intensities, a detailed investigation of the "methyl- d_{12} " system is required in order to distinguish more accurately the fundamentals resulting from skeletal stretchings and methyl bendings.

It was anticipated that the symmetrical N-N stretching motion would give rise to the most intense feature in the Raman spectrum below 1100 cm^{-1} . In $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$, for example, the N-N valence vibration was assigned⁶ to the intense Raman line at 721 cm^{-1} . Inspection of Figure 2, therefore, leads to the assignment of the 898- cm^{-1} line to the N-N symmetric stretching of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$. The corresponding infrared N-N stretching fundamental, ν_{40} , is assigned to the band at 821 cm^{-1} (see Figure 1). It is noted that the in-phase N-N stretching motion is observed in the absorption spectrum of the second conformer which exists in the fluid states (see Figure 1). The 895- cm^{-1} infrared band disappears in the spectrum of crystalline $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$, which is in accord with the principle of mutual exclusion, which appears to dictate the transitions for the spectra recorded of the crystalline sample. In addition, the out-of-phase N-N stretching motion is Raman active for the liquid-state conformation and was observed at 824 cm^{-1} (see Figure 2).

The 3 A_g + 1 B_g + 1 A_u + 3 B_u skeletal bending modes of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ have been assigned to bands between 300 and 600 cm^{-1} , respectively, in accord with earlier studies.⁴⁻⁷ Although all eight skeletal deformations are symmetry allowed for the second conformer, only six lines were resolved for the spectra of the fluid states which is not particularly surprising in view of the anticipated overlap of fundamentals in this spectral region. Thus, the Raman lines centered at 593, 398, and 342 cm^{-1} have been attributed to the 3 A_g skeletal deformations of the centrosymmetric conformation, and the band at 367 cm^{-1} has been attributed to the 1 B_g mode (see Table II). Similar frequencies have also been proposed for the corresponding infrared-active skeletal modes and have been summarized in Table I.

There are three additional Raman lines between 127 and 300 cm^{-1} of crystalline $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ which have yet to be assigned. The intense 222- cm^{-1} line appears to have shifted from 199 cm^{-1} (see Figure 2) upon crystallization and has been ascribed to the B_g N- NC_2 torsion. A frequency of 114 cm^{-1} has previously been assigned⁶ to the

N- NC_2 torsional mode in $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$ which supports the present description. The A_u N- NC_2 torsional frequency has been assigned to the band in the absorption spectrum of crystalline $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ centered at 177 cm^{-1} (see Figure 1). It should probably be noted that both N- NC_2 torsional fundamentals are symmetry allowed in the spectrum of the fluid states and are observed at 145 and 226 cm^{-1} , respectively. The two remaining low-frequency Raman shifts, centered at 254 and 235 cm^{-1} are believed to originate from the A_g and B_g methyl torsional oscillations. This assignment for the methyl torsions of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ is supported by a recent study in which the B_2 and A_2 methyl torsions of isobutene were assigned to Raman lines at 239 and 209 cm^{-1} , respectively.¹⁵ Similar frequencies were also resolved for the two infrared-active torsions (see Table I). In view of the relatively large separation between the tops on opposite ends of the molecule, the harmonic approximation applicable for molecules with two methyl rotors has been utilized to calculate the barrier heights.¹⁶ Thus, the methyl torsional barrier has been determined to be 3.5 kcal/mol ($^{2/9}$ K) and the top-top coupling constant is estimated to be 0.3 kcal/mol ($^{-2/9}$ L). It should be emphasized that this calculation is based upon the transitions measured in the Raman spectrum of crystalline $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$.

The A_u N=N torsional mode for the crystalline state is active only in the infrared spectrum and has been assigned to the band centered at 330 cm^{-1} . This assignment is supported by the previous assignment of the A_u N=N torsional mode of azomethane to the 312- cm^{-1} band.⁷ It is noted that this fundamental is extensively mixed with other low-frequency a_u modes.

The final skeletal fundamental to be assigned is the N=N stretching motion. In earlier studies of azomethane⁷ and 1-pyrazoline,⁸ bands at 1574 and 1552 cm^{-1} were assigned to the N=N valence vibrations, respectively. Whereas one might predict intense Raman lines to result from an N=N stretching fundamental, the lines attributed to the N=N motion in previous studies have been relatively weak. It should be reiterated that the assignment of the 1574- cm^{-1} line to the N=N stretch for $\text{CH}_3\text{N}=\text{NCH}_3$ was confirmed by a simultaneous study of $\text{CD}_3\text{N}=\text{NCD}_3$. In the Raman spectrum of liquid $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$, the intense line at 1475 cm^{-1} appears to be the most likely candidate for the N=N stretch, since no other Raman lines were observed between 1470 and 2700 cm^{-1} in the fluid state, and the band at 1488 cm^{-1} in the annealed solid can be assigned as a combination between the N=N stretch and the N- C_2 deformation. This is a surprisingly low frequency for an N=N stretching fundamental and it is also considerably more intense than Raman lines previously observed for the N=N linkage. It might be noted that in view of the proximity of the A_g and B_g methyl deformations, the 1470- cm^{-1} line is likely to be a mixture of the N=N valence vibration and the CH_3 deformations.

Assignments for the CH_3 fundamentals are summarized in Tables I and II and are based upon the observed relative band intensities and group frequency correlations. Thus, the CH_3 stretching fundamentals are assigned to bands between 2800 and 3000 cm^{-1} . The additional spectral features observed in this region are believed to be overtones or combination bands in Fermi resonance with the CH_3 stretching fundamen-

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tals. The methyl deformations have likewise been assigned to bands between 1390 and 1470 cm^{-1} in accord with the earlier studies of $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$ and $\text{CH}_3\text{N}=\text{NCH}_3$. The remaining CH_3 bending modes are assigned to bands between 1000 and 1300 cm^{-1} and are likely to be mixed with the skeletal stretching modes also assigned to this spectral region. An assignment of the methyl torsional modes to bands below 275 cm^{-1} has previously been discussed and the complete vibrational assignment for $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$, based upon the crystalline spectra, is given in Tables I and II.

Discussion

The observation of significant frequency perturbations between bands assigned to specific skeletal fundamentals of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ and assignments previously established for the corresponding motions in similar molecules suggest the N=N double bond of tetramethyltetrazine may not be isolated. For example, the N=N stretching mode in $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ is approximately 100 cm^{-1} lower than the analogous motion in $\text{CH}_3\text{N}=\text{NCH}_3$. In addition, the N-N valence vibrations of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ are on the order of 150 cm^{-1} higher than the corresponding fundamental for $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$. A simple Huckel molecular orbital calculation leads to bond orders of 1.44 and 1.72 for the "N-N" and "N=N" linkages of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$, respectively. Thus, the molecular orbital description of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ reflects the observed vibrational frequency variations between the "model" systems, $\text{CH}_3\text{N}=\text{NCH}_3$ and $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$, and tetramethyltetrazine in terms of a delocalized π system.

As noted previously both the in-phase and out-of-phase N-N stretching frequencies are observed in the spectra of the fluid states at 898 and 821 cm^{-1} , respectively. If the sample is rapidly cooled to liquid nitrogen temperatures, there is no measurable intensity alteration between the 898- and 821- cm^{-1} bands. After the sample has been annealed, however, the 898- cm^{-1} band disappears and the conformation stable in the crystalline state has a center of symmetry. It should also be noted that there are several additional bands which clearly display mutual exclusion between

the infrared and Raman frequencies for solid tetramethyltetrazine.

Conclusions

The vibrational spectra of $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ have been measured in all three physical states. It is concluded that the conformer present in the solid state has a center of symmetry (C_{2h}) since the principal of mutual exclusion is operative. In addition to the centrosymmetric conformer present in the crystalline state, we have suggested that a second conformer with either C_1 or C_2 symmetry is also present in the fluid states. A detailed vibrational assignment has been proposed for the low-temperature conformer based upon group frequency correlations and relative infrared and Raman band intensities. The corresponding assignments for the liquid state have also been tabulated. The frequencies for the N=N and N-N stretching modes were significantly lower and higher than would be predicted for a molecule in which the above groups were isolated. These experimental observations suggest a delocalization of the π -electron system which is in agreement with the bond orders calculated for the N-N (1.44) and N=N (1.72) groups from simple molecular orbital theory. Finally the internal rotational barrier of the methyl groups was calculated to be 3.5 kcal/mol which is in excellent agreement with the 3.4-kcal/mol barrier previously deduced for $\text{N}_2(\text{CH}_3)_4$.

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