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The Infrared Spectra of 3,3-Dimethyldiazirine and 3,3-Dimethyl-d₀-diazirine

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The vapor and solid phase infrared spectra for 3,3-dimethyldiazirine and 3,3-dimethyl-d₆-diazirine have been observed in the 250-4000 cm⁻¹ region. Vibrational assignments have been made for all infrared active fundamentals for the protonated molecule, except the B_1 methyl torsion. Accidental degeneracy was observed in some vibrations, and band contours were, in general, rather poorly defined.

INTRODUCTION

The diazirine ring is unique in that it contains azo bonding in a strained three-membered ring and has become of considerable interest to chemists since the compound was prepared. Diazirine was first synthesized by Schmitz and Ohme (1), who also prepared several substituted diazirines (2), and by Graham (3). The infrared spectrum of diazirine was reported shortly thereafter (4), followed by the first infrared vibrational analysis of a substituted diazirine-diffuorodiazirine (5). We have recently begun a study of the infrared spectra of other substituted diazirines (6).

In making the assignments for 3,3-dimethyldiazirine, two basic difficulties were encountered, one of which was probably the result of the other. First, many of the fundamentals are almost degenerate as displayed by the many overlapping bands, particularly near 3000 cm⁻¹ where there are six C—H stretching fundamentals and near 1400 cm⁻¹ where there are six CH₃ deformation modes. Secondly, band contours were not distinct. In some instances, however, the latter were caused by the near degeneracy of some of the fundamentals. Attempts to obtain $\alpha\alpha\alpha$ dimethyl-d₃-diazirine in which some of these accidental degeneracies are absent resulted in varying degrees of deuterium substitution; however, 3,3-dimethyl-d₆-diazirine has been obtained. Standard group frequencies, assignments for other substituted diazirines and the shifts in the spectrum of the deuterated molecule were used in making the vibrational assignments for this molecule.

EXPERIMENTAL

3,3-Dimethyldiazirine was prepared by the method of Schmitz and Ohme (2) and 3,3-dimethyl-d₆-diazirine by a modification of this method (7). The

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samples were purified on a Beckman Megachrom Preparative Gas Chromatograph using four 12-ft. parallel columns packed with Apiezon J on firebrick at ambient temperature ($\sim 23^{\circ}$ C). The fractions were trapped at -126° C. Carbon dioxide and water, which were accumulated during purification, were removed by passing the samples through Ascarite and magnesium perchlorate.

All spectra were taken on a Beckman IR7 spectrophotometer in the spectral region 250–4000 cm⁻¹. Vapor phase spectra were obtained with varying pressures in a 10-cm cell. Solid phase spectra were obtained at 77°K using an Andonian dewar (8) fitted with cesium iodide windows and substrate. The observed frequencies were determined by interpolation between known frequencies of a calibrant gas recorded over the sample spectra (9).

DISCUSSION

In this paper, 3,3-dimethyldiazirine is treated as belonging to the symmetry group C_{2v} , and the molecule has 27 fundamental vibrations. There are nine vibrations in the a_1 species, five in a_2 , six in b_1 , and seven in b_2 . All fundamentals are infrared active except those of the a_2 species. The a_1 vibrations should exhibit type A-band contours, and the b_1 and b_2 vibrations should yield type C and type B bands, respectively. The P-R separations, as calculated by the method of



Fig. 1. Schematic of the 3,3-dimethyldiazirine molecule with the approximate orientation of the principal axes.

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Badger and Zumwalt (10), are the following: type A—20.6 cm⁻¹, type B—5.2 cm⁻¹, and type C—28.4 cm⁻¹. Well-defined band contours were observed in only a few bands.

Figure 1 is a schematic of the 3,3-dimethyldiazirine molecule with the approximate axes orientations. Parameters used in the calculations were C—C = 1.541 Å; C–H = 1.091 Å; \angle CCC = $111^{\circ}30'$; \angle HCH = 110° and those for the ring from microwave data for diazirine (11). The z-axis was chosen as the C_2 axis and the x-axis in the plane of the ring. The principal moments of inertia, using the parameters shown in the figure, were calculated (12) to be $I_a = 64.560$, $I_b = 96.834$, and $I_c = 133.824$ amu-Å². In 3,3-dimethyl-d₆-diazirine, the center of mass shifts farther away from the N atoms along the A-axis, and the principal moments are then $I_a = 79.581$, $I_b = 116.409$, and $I_c = 161.985$ amu-Å². Recent microwave spectral studies for the protonated molecule indicate the principal moment about the A axis as given here is somewhat small and about the B and C axes slightly large (13).

A recorder trace of the vapor phase spectrum of 3,3-dimethyldiazirine is shown in Fig. 2. A small quantity of water vapor is responsible for the many sharp, low intensity lines in the 1600–1900 cm⁻¹ region. The absorption at 200



Fig. 2. The vapor phase infrared spectrum of 3,3-dimethyldiazirine. Spectrum A was obtained with ~ 200 mm, pressure and spectrum B with 31 mm.



FIG. 3. The vapor phase infrared spectrum of 3,3-dimethyl-d₆-diazirine. Spectrum A was obtained with 150 mm. pressure and spectrum B with 38 mm.

 $\rm cm^{-1}$ is due to the cesium iodide cell windows and fore prism. Figure 3 is the vapor phase spectrum of 3,3-dimethyl-d₆-diazirine. The many low intensity lines in the 1400–1800 cm⁻¹ region indicate the presence of some water vapor in this sample, also.

Table I lists the gas and solid phase frequencies and the suggested assignments of 3,3-dimethyldiazirine. Table II contains the gas and solid phase frequencies and the suggested assignments for 3,3-dimethyl-d₆-diazirine. Although these assignments are in line with the expected frequency shifts

TABLE I

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C	as	Solic	1	
cm ⁻¹	Relative intensity	cm ⁻¹	Relative intensity	Assignment
356	w	-	-	ν ₁₉
369.6	w-m	-	-	ν ₂₇
433	vs	438	m-s	ν ₉
738	w	-	-	ν_8
788.1	m	769	m-s	ν ₁₈
958.5	w	965	w	^v 26
987.6	m	993	w	ν ₇
~ 1110	w	1098	w	^ν 17
1136	w	1126	w	ν_6
-	-	1155	w	$v_8 + v_9 = 1171 \text{ (gas)}$
1249	vs	1235, 1243	vs	V ₂₅
-	vs	1376 ?	w-m	^ν 24
1391.1	vs	1383	vs	ν ₅
1431	m	1435	m	ν ₂₃
1458	vs	1449	vs	ν_4
1469.6	vs	1464	s	v_{16}
-	-	1528	s	$v_8 + v_{18} = 1526 \text{ (gas)}$

Observed Gas and Solid Phase Vibrational Frequencies, Relative Intensities, and Assignments for 3, 3-Dimethyldiazirine

^aw = weak, m = medium, s = strong, vs = very strong, w-m = weak to medium, and m-s = medium to strong intensities.

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TABLE I (Concluded)

Gas		Solid		<u>.</u>	
cm ⁻¹	Relative intensity ^a	cm ⁻¹	Relative intensity	Assignment	
1564.4	vs	-	-	$2\nu_{18}$	
1603.3	vs	1586	vs	ν ₃	
1701	m	-	-	$v_8 + v_{26} = 1696$	
2107	w	-	-	$\nu_6 + \nu_7 = 2123$	
2208	w	-	-	$v_{25} + v_{26} = 2207$	
2345	w	-	-	$v_{24} + v_{26} = 2347$	
2381	w	-	-	$\nu_6 + \nu_{25} = 2385$	
2448	w	-	-	$v_7 + v_{16} = 2457$	
2643	w	-	-	$v_5 + v_{25} = 2640$	
2756	m	-	-	$2\nu_{24} = 2778$?	
2831	m	-	-	$v_4 + v_5 = 2849$	
-	-	2867	w	?	
2892	s	2894	w	$v_4 + v_{23} = 2889$	
2933	VS	2930, 2942	m	ν ₂ , ν ₂₂	
2960.2	vs	2958, 2971	m	^ν 15	
2995	vs	2988, 299 7	m	ν ₁ , ν ₂₁	
3040	w	-	-	$v_3 + v_{16} = 3055$	
3345	w	-	-	$2\nu_4 + \nu_9 = 3349$	

Observed Gas and Solid Phase Vibrational Frequencies, Relative Intensities, and Assignments for 3, 3-Dimethyldiazirine

^aw = weak, m = medium, s = strong, vs = very strong, w-m = weak to medium, and m-s = medium to strong intensities.

Ga	s	Sc	olid	
cm ¹	Relative intensity	cm ^{- l}	Relative intensity	Assignment"
_		308	W	ν_{19}
389	s	400	m	$ u_{ij}$
660	W			ν_{s}
		731	W.	ν_{26}
748.5	m	753	W	ν_{18}
818	W.			ν_{1}
971	m	962	w	V 17
1053.0	8	1047	s	${m u}_{ m ii}$
		1042	s	ν_{24}
-		1056	8	$\boldsymbol{\nu}_{5}$
1060.9	s	1058	я	$ u_{16}$, $ u_{23}$
1123	m			ν_{4}
1271	VS	1268	vs	ν_{25}
1482	W	-		impurity
1588	vs	1578	vs	<i>V</i> 3
2075	m			$2\nu_{24} = 2084 \text{ (solid)}$
2134	s			$m{v}_2$, $m{v}_{22}$
2220.1	vs	2220	W	ν_{15}
2235	VS	2236	w	ν_{1} , ν_{21}
2936.4	m			impurity

TABLE II

Observed Gas and Solid Phase Vibrational Frequencies, Relative Intensities, and Assignments for 3,3-Dimethyl-ds-diazirine

Assignment with reference to 3,3-dimethyldiazirine molecule.

for the isotopic molecule, in some regions in the spectrum alternate assignments are also feasible. An approximate description of the vibrations in the appropriate symmetry species for each molecule and the frequencies assigned to these vibrations are given in Table III.

C-H STRETCHING VIBRATIONS

There are six fundamental C—H stretching vibrations in the 3,3 dimethyldiazirine molecule. Two each belong to the a_1 and b_2 species and one each to the a_2 and b_1 species. Only five are observed in the infrared spectrum.

In both of the methyl substituted diazirines studied previously the C -H stretching vibrations of the methyl group occurred in the 2940–3005 cm⁻¹ region (6). Of the three bands observed in the 3,3-dimethyldiazirine spectrum, only the 2960.2 cm⁻¹ band is well defined with the 2933 and 2995 cm⁻¹ bands appearing only as shoulders.

The spectrum of 3,3-dimethyl-d₆-diazirine reveals four fairly strong bands at 2235, 2220.1, 2134, and 2075 cm⁻¹. A weak-medium band is observed at 2936.4 cm⁻¹ which appears to be due to a small inpurity.

TABLE III

Species	Approximate description	(CH ₃) ₂ CN ₂	(CD ₃) ₂ CN ₂
a ₁	nCH ₃ stretch ^a	2995	2235
	$sCH_3 stretch^b$	2933	2134
	NN stretch	[1586] ^c	1588
	nCH ₃ deformation	1458	1123
	sCH_3 deformation	1391.1	[1056]
	CN stretch	1136	[1047]
	ÇH ₃ fock	987.6	818
	CC stretch	738	660
	CCC deformation	433	389
ъ	nCH ₃ stretch	2960.2	2220.1
	nCH ₃ deformation	1469.6	1060.9[1058
	CH3 rock	1110	971
	CN stretch	788. 1	748.5
	CCC wag	356	-
	CH3 torsion	-	-
^ь 2	nCH ₃ stretch	(2995) ^d	(2235)
_	sCH ₃ stretch	(2933)	(2134)
	nCH ₃ deformation	1431	[(1058)]
	sCH ₃ deformation	(1391, 1)	[1042]

Fundamental Frequency Assignments (cm⁻¹) for 3,3-Dimethyldiazirine and 3,3-Dimethyl-d₆-diazirine

TABLE III (Concluded)

Fundamental Frequency Assignments (cm⁻¹) for 3, 3-Dimethyldiazirine and 3, 3-Dimethyl- d_2 -diazirine

Species	Approximate description	(CH ₃) ₂ CN ₂	(CD ₃) ₂ CN ₂	
	CC stretch	1249	1271.9	
	CH ₃ rock	958	[731]	
	CCC rock	369 . 6	-	

 $a_{n \text{ and }}^{b}$ s refer to nonsymmetric and symmetric vibrations, respectively.

^cbrackets indicate solid phase frequency.

^dparentheses indicate this fundamental is accidentally degenerate with another in the table.

In acetone, Cossee and Schactschneider (14) observed only three bands in this region of the spectrum which appeared to be due to fundamentals. To the higher frequency (3020 cm⁻¹) they assigned the a_1 and b_2 nonsymmetric CH₃ stretching, to the 2973 cm⁻¹ band the b_1 nonsymmetric CH₃ stretching, and to the 2926 cm⁻¹ band the a_1 and b_2 symmetric CH₃ stretching vibrations. The dimethyl sulfoxide spectrum reveals only two bands in this region: at 2973 and 2908 cm⁻¹ (15). The nonsymmetric, a_1 , b_1 , and b_2 , CH₃ stretching vibration was assigned to 2973 cm⁻¹ and the symmetric a_1 and b_2 CH₃ stretching to 2908 cm⁻¹.

The band at 2960.2 cm⁻¹ in the 3,3-dimethyldiazirine spectrum has type-*C* contour and appears to be analogous to the 2220.1 cm⁻¹ band in the spectrum of the deuterated molecule. We assign this band to the b_1 nonsymmetric CH₃ stretching vibration. The band at 2995 cm⁻¹ is observed only as a shoulder on the 2960.2 cm⁻¹ band, but probably contains both the a_1 and b_2 nonsymmetric CH₃ stretching vibrations. They appear to be contained in the rather broad band at 2235 cm⁻¹ in the spectrum of the deuterated molecule. We assign the a_1 and b_2 symmetric CH₃ stretching vibrations to the 2933 cm⁻¹ band. These vibrations are contained in either the single, rather broad band at 2134 cm⁻¹ or in the broad band, which contains the a_1 and b_2 nonsymmetric CH₃ stretching modes, at 2235 cm⁻¹. We assign them to the band at 2134 cm⁻¹.

The vapor phase band at 2892 cm⁻¹ appears to be an overtone of 1458.0 cm⁻¹ which may be shifted slightly, to lower frequencies, by Fermi resonance with the a_1 component of the 2933 cm⁻¹ band. There appears to be appreciable interaction in this region as observed also in the band at 2830.6 cm⁻¹.

CH₃ Deformations

The six CH₃ deformation vibrations of 3,3-dimethyldiazirine are divided, according to group theory, into two each in the a_1 and b_2 species and one each in the a_2 and b_1 species. Only five are infrared active.

In 1,1-dimethylcyclopropane, the symmetric a_1 and b_1 vibrations have been assigned to 1385 and 1380 cm⁻¹, respectively, and the nonsymmetric a_1 at 1460 cm⁻¹ and b_1 and b_2 at 1465 cm⁻¹ (16). Methylchlorodiazirine revealed the two nonsymmetric deformations at 1443 and 1463 cm⁻¹ with the symmetric one occurring at 1390 cm⁻¹. In methylbromodiazirine they were observed at 1437, 1453, and 1385 cm⁻¹, respectively (6).

In the 3,3-dimethyldiazirine spectrum four bands are observed: 1391.1, 1431, 1458, and 1469.6 cm⁻¹. The band at 1391.1 cm⁻¹ has some characteristics of both type-A and type-B bands with a minimum absorption at 1389.1 cm⁻¹ and a maximum at 1391.1 cm⁻¹.

These bands are expected to shift considerably in the 3,3-dimethyl-d₆-diazirine spectrum and should occur near 1100 cm⁻¹. Three bands are observed in this region in the vapor phase spectrum at 1053.0, 1060.9, and 1123 cm⁻¹. Four bands are observed in the solid phase spectrum at 1042.3, 1047.4, 1055.5, and 1058.5 cm⁻¹. Since very little evidence of splitting is exhibited elsewhere in the spectrum, the four are believed to be due to fundamentals.

Band contours are not well resolved, and exact assignment of the nonsymmetric deformations is rather difficult. We assign the b_2 vibration to 1431 cm⁻¹ and the a_1 and b_1 modes to the bands at 1458 and 1469.6 cm⁻¹, respectively. These bands appear to shift to (1058), 1123, and 1060.9 cm⁻¹, in the order given, in the 3,3-dimethyl-d₆-diazirine spectrum. The two symmetric deformation vibrations are undoubtedly contained in the band at 1391. 1 cm⁻¹. They appear to be shifted to 1056 and 1042 cm⁻¹ in the solid phase spectrum of the deuterated molecule. The broad band at 1482 cm⁻¹ (± 10) in the 3,3-dimethyl-d₆-diazirine spectrum appears to be an impurity.

SKELETAL VIBRATIONS

There are nine vibrations associated with the two methyl carbon atoms and the diazirine ring. In species a_1 , these consist of the N=N, symmetric C—C and C—N stretching modes and the CCC scissoring vibration. In the b_1 species, there are two: the antisymmetric C—N stretch and a CCC wag. The vibrations in the b_2 species are the antisymmetric C—C stretch and a CCC rocking vibration. The a_2 mode, which is a CCC torsion against the ring, is infrared inactive. Considerable mixing is observed in some of the modes. This is especially observed in the b_2 C—C stretching and CH₃ deformation modes.

The vibration expected to have the highest frequency of this group is the N=N stretch. Ettinger (4) observed two strong, equally intense bands at 1626 and 1604 cm⁻¹ in the infrared spectrum of diazirine. The 1604 cm⁻¹ band was

assigned as an overtone which was in Fermi resonance with the fundamental, assigned at 1626 cm⁻¹. In the electronic spectrum the fundamental was observed at 1606 cm⁻¹ (17). In methylchlorodiazirine, this vibration was observed at 1573.4 cm⁻¹ and in methylbromodiazirine at 1571.3 cm⁻¹ (6).

The 3,3-dimethyldiazirine spectrum reveals two strong bands in this region at 1603.3 and 1564.4 cm⁻¹. Both bands have approximately equal intensity, and since only one fundamental should be observed in this region, one of the bands should be due to an overtone or combination, which appears to be in Fermi resonance with the fundamental and is thereby sharing intensity. In the spectrum of the deuterated molecule, a single band is observed at 1588 cm⁻¹.

We assign the N=N stretching vibration to the 1603.3 cm⁻¹ band and the 1564.4 cm⁻¹ band to an overtone of the antisymmetric b_1 CN stretching vibration (788.1 cm⁻¹). If the 1564.4 cm⁻¹ band is indeed an overtone of 788.1 cm⁻¹, it is shifted 12 cm⁻¹ from the calculated frequency, and a similar shift for the 1603.3 cm⁻¹ band would put the unperturbed fundamental at 1591 cm⁻¹. This is supported somewhat by observing the shift in the 1588 cm⁻¹ vapor phase band of the deuterated molecule to 1578 cm⁻¹ in the solid phase spectrum. If the fundamental is at approximately 1591 cm⁻¹, by comparison, it should shift to 1581 cm⁻¹. The single strong band at 1586 cm⁻¹ shows a shift of only 5 cm⁻¹, but such a shift is in the direction of that observed in the deuterated molecule.

Alternately, since the only experimental evidence for Fermi resonance is the unusual intensities of these two bands in the infrared vapor spectrum, the assignment is somewhat questionable. The intensities can be explained as a combination of a low frequency a_2 vibration with one of the b_1 or b_2 species. If one of the a_2 vibrations appears near 250 cm⁻¹, then strong intensities of its combination bands may occur. Also the solid spectrum and the electronic spectrum of 3,3-dimethyldiazirine show no evidence for Fermi resonance of these two bands.

The antisymmetric C–C stretching vibration has been observed in acetone at 1218 cm⁻¹ (14) and is expected to have a somewhat similar frequency in this molecule. We observe a very strong band at 1249 cm⁻¹. This band is assigned to the b_2 antisymmetric C–C stretching vibration. There appears to be strong mixing of this mode and the CH₃ deformation as evidenced by a shift in this band to 1271.9 cm⁻¹ in the vapor phase spectrum of 3,3-dimethyl-d₆-diazirine, while the deformation bands appear near 1100 cm⁻¹ (18).

The a_1 symmetric C—C stretching vibration was observed in acetone at 779 cm⁻¹ (14), and a candidate for this vibration in the 3,3-dimethyldiazirine spectrum is the weak band at 738 cm⁻¹. Band contours are not well defined, but this band shifts to 660 cm⁻¹ in the spectrum of the deuterated molecule. The 738 cm⁻¹ band is then assigned to the a_1 symmetric C—C stretching mode.

The symmetric C—N stretching mode should have type A band contour and the antisymmetric type B. The symmetric vibration has been observed at a frequency (991–1282 cm⁻¹) somewhat higher than the antisymmetric (807–

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1091 cm⁻¹) in the vibrational assignments for all previously analyzed diazirines. The vapor phase spectrum of 3,3-dimethyldiazirine reveals a rather broad band at 1136 cm⁻¹ which occurs in the expected spectral region and is assigned to the a_1 symmetric C—N stretching vibration. This band has apparently shifted in 3,3-dimethyl-d₆-diazirine to near 1050 cm⁻¹ where a number of bands appear. We have assigned it to the solid phase band at 1047 cm⁻¹.

A potential candidate for the antisymmetric C—N stretch is the type-C band at 788.1 cm⁻¹. This band shifts to 748.5 cm⁻¹ in the 3,3-dimethyl-d₆-diazirine spectrum. The 788.1 cm⁻¹ band occurs only slightly below the region where this vibration is observed in other diazirines, has the proper band contour, and is assigned to this vibration.

The four remaining modes included in skeletal vibrations involve primarily the three carbon atoms and are expected to occur at fairly low frequencies. A strong, rather broad band is observed at 433 cm⁻¹ and a medium to weak band at 369.6 cm⁻¹ which appears to overlap a band at approximately 356 cm⁻¹. The spectrum of the deuterated molecule reveals a strong band at 389 cm⁻¹ and some indication of a very weak band slightly above 300 cm⁻¹.

Since the CCC scissoring vibration is expected to have the higher frequency, we assign it to the 433 cm⁻¹ band and rather arbitrarily assign the CCC wagging and CCC rocking to 369.6 and 356 cm⁻¹, respectively.

CH₃ Rocking and Torsions

There are four CH₃ rocking vibrations in 3,3-dimethyl-diazirine and two CH₃ torsional modes, with one of each belonging to the a_2 species, and therefore infrared inactive. The other torsional mode is expected to occur at a frequency somewhat below the region under consideration. The three infrared active CH₃ rocking vibrations are divided into one each in the a_1 , b_1 , and b_2 species.

Three bands have not been assigned: 958.4, 987.6, and ~1110 cm⁻¹. The 958.5 band is observed on the side of the 987.6 cm⁻¹ band but is sufficiently resolved for its existence to be certain. The band at approximately 1110 cm⁻¹ is badly overlapped with the 1136 cm⁻¹ band, but the solid phase spectrum reveals a weak, but sharp, band at 1098 cm⁻¹ which is apparently the 1110 cm⁻¹ vapor phase band. The 1110 cm⁻¹ band appears to shift to 971 cm⁻¹, the 987.5 cm⁻¹ band to 818 cm⁻¹, and the 958 cm⁻¹ band to the solid phase band at 731 cm⁻¹ in the 3,3-dimethyl-d₆-diazirine spectrum.

In the spectrum of acetone (14), the a_1 , b_1 , and b_2 vibrations were observed at 1067, 1098, and 896 cm⁻¹, respectively. In 1,1-dimethylcyclopropane, the a_1 and b_1 vibrations were observed at 928 and 970 cm⁻¹ (16). The three unassigned bands in the 3,3-dimethyldiazirine spectrum are in the region consistent with these assignments and show significant shifts in the spectrum of the deuterated species. They are, therefore, assigned to the CH₃ rocking vibrations: the a_1 to 987.6 cm⁻¹, b_1 to 1098 cm⁻¹, and b_2 to 958 cm⁻¹.

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