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by

J. Dage, D. L. Snively and V. A. Walters

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Infrared Spectrum of Gaseous 3-Pyrroline and Pyrrolidine and Overtone Spectrum of 3-Pyrroline

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Abstract

The infrared absorption spectra of gaseous 3-pyrroline and pyrrolidine are presented. These spectra are compared to pyrrole and previous work on liquid pyrrolidine. Also presented is the vibrational overtone spectrum of 3-pyrroline. Three vibrational overtone progressions are identified: the olefinic C-H stretch, the aliphatic C-H stretch and the N-H stretch. The olefinic stretches are well separated from the other absorptions, while the other C-H and N-H absorptions are overlapped.

Introduction

The infrared absorption spectra of pyrrolidine and 3-pyrroline (see Figure 1 for the molecular structures along with pyrrole) are presented in this work. The vibrational spectra of these cyclic amines is of interest in the investigation of intramolecular vibrational coupling, and hence, the distribution of internal energies at high levels of excitation. This work is part of a larger study of the complete vibrational analysis of the N-H oscillator focusing on the spectra of pyrrole¹, pyrrolidine¹ and pyrroline (included here for the first time) up to 17,000 cm⁻¹ excitation.

The vibrational spectra of cyclic amines also bears information on molecular conformation. In particular the equilibrium between the lone pair axial or equatorial species has been studied^{2,3} with regard to piperidine and its derivatives. The first overtone of the N-H stretch for several piperidines and related compounds, including pyrrolidine, was investigated² to search for conformational evidence. Two peaks appeared in the pyrrolidine N-H overtone spectrum; the higher energy peak was assigned to the equatorial N-H and the lower to the axial. The spectral intensities of these two bands indicate that both axial and equatorial conformers are present in about equal concentrations in the gas phase.

Experimental

The pyrrolidine used for analysis was obtained commercially with 99% purity, while 3-pyrroline was obtained at 75% purity with the 25% impurity being pyrrolidine. Gaseous spectra of both compounds were obtained on a Nicolet 20DX FTIR. Analysis parameters were optimized for 1 cm^{-1} resolution and 100 background/sample scans were obtained and ratioed. Samples of gaseous pyrroline and pyrrolidine were transferred via the vacuum line into a 10 cm glass absorption cell fitted with KBr windows. The N-H stretch for these compounds is very weak. It was necessary to record the spectrum of pyrrolidine at 12 torr pressure in a 9.75 m multipass cell on a Cignus 100 Mattson FTIR in order to observe the N-H stretch. Liquid spectra were obtained on a Mattson Galaxy 6020. A 10 cm liquid quartz cell was used to record the CCl_4 dilution spectra. Dilutions as high as 1:1000 by volume were used.

Pure 3-pyrroline was obtained by GC preparation on a Varian 920 with an 8 ft by 3/8 in Carbowax 4000 10% Chromosorb W acid washed column. The resulting sample was 99% pure by GC determination and filled the IR cell to 15 torr. In addition the 3-pyrroline spectrum was obtained by a subtraction from the impure sample, which contained about 25% pyrrolidine. A 4 torr pure pyrrolidine spectrum was subtracted from a 4 torr impure 3-pyrroline spectrum. A second pyrrolidine spectrum was then taken at 20 torr pressure to be used for comparison with the 3-pyrroline and pyrrole.

The vibrational overtone spectra were recorded by laser intracavity photoacoustic spectroscopy. The experimental setup has been described previously¹.

Results

The infrared spectra of pyrrolidine and 3-pyrroline are shown in Figures 2 and 3, respectively. Peak wavenumbers for these two compounds along with those of pyrrole are listed in Table 1 with corresponding bands arranged in a horizontal fashion. Each band contour shape is classified as A, B or C and the peak intensity in absorbance. The peak absorption wavenumbers were taken as the sharp Q-branch (labeled with a Q) or the center of the band contour if no Q branch was visible.

The overtone spectrum of 3-pyrroline is displayed in Figure 4 and the transition wavenumbers are tabulated in Table 2. The data was collected over four different dye gain curves. The intensity scale on Figure 4 is a relative scale and changes from dye to dye.

Discussion

Peak assignments for the C-H stretching region in pyrrolidine can be made by comparison to 3-pyrroline (Figure 2) and pyrrolidine- α,α' -d₄⁴. The peaks at 2818 and 2980 cm^{-1} appear to

be the α -C-H stretch since in the α -CD₂ compound the high energy peak intensity decreases, and the low energy band almost disappears. In the α,α' -CD₄ compound the high and low energy peaks have completely disappeared⁴.

The peaks at 2970 and 2884 cm⁻¹ in the pyrrolidine spectrum (Figure 2) are tentatively assigned to the β -C-H stretch. In the α,α' -CD₄ compound these peaks remained with no decrease in intensity. Furthermore, in the 3-pyrroline spectrum (Figure 3) there was a drastic intensity decrease at the higher energy end of the region where these peaks were expected, while the intensity at the lower energy end seemed to not change.

The peak at 3084 cm⁻¹ in the 3-pyrroline spectrum is probably caused by the olefinic stretch. The peak at 2870 cm⁻¹ is most likely caused by the α -C-H stretch in 3-pyrroline. The intensity of the peak is about the same as that of the lower energy α -C-H in pyrrolidine; however, the peaks to higher energy in the 3-pyrroline all decreased in intensity in comparison with the pyrrolidine spectrum.

The N-H stretch absorption in pyrrolidine occurs between 3300 and 3400 cm⁻¹. The band contour appears to be two overlapping transitions: one broad and structureless and one with four pronounced Q branches. This fundamental band contour is repeated in the first, second and third N-H overtone contours which we have recorded¹. Following the discussion of Baldock and Katritzky², the higher energy structureless band arises from the equatorial N-H oscillator and the lower energy structured band arises from the axial N-H. Krueger and Jan found similar results for liquid pyrrolidine diluted in CCl₄. They suggested that the conformation with N-H equatorial is favored (main band at 3362 cm⁻¹) over the conformation with the N-H axial (shoulder at 3320 cm⁻¹). The N-H stretching region in our gaseous spectrum displays a broad peak overlapping a second absorption with several sharp bands at 3324, 3329, 3335 and 3342 cm⁻¹ clearly due to rotational structure. In order to check for a possible conformation switch between the gas and liquid, a series of liquid spectra from pure pyrrolidine to a 1:1000 dilution in CCl₄ were collected. The N-H stretching frequency shifts by 93 cm⁻¹ toward higher energy in the gaseous state, but there is no change in relative peak intensities of the 3362 and 3320 cm⁻¹ band even at high dilution. Therefore, the dilution spectra indicate no conformational change on going from gas to liquid. The only spectroscopic change is the appearance of rotational structure in the gaseous spectrum.

The overtone spectrum of 3-pyrroline is complicated by the overlapping absorptions of the N-H and methylenic C-H stretches. Several progressions are evident and fit a Birge-Sponer plot according to the following equation⁵

$$\Delta E = (\omega_e - \omega_e x_e)v - \omega_e x_e v^2 \quad 1.$$

where the transition energies, ΔE , are expressed as a function of v , the local mode vibrational quantum number; ω_e , the mechanical frequency for that particular local mode; and $\omega_e x_e$, the anharmonicity for the local mode. Using this equation, a Birge-Sponer plot⁶ taking $\Delta E/v$ versus v yields the ω_e and $\omega_e x_e$ from measured ΔE values.

One vibrational progression, consisting of three members, is well separated from the other absorptions. Comparing to our work on the vibrational spectrum of methylcyclopentadiene⁷ the three strong isolated peaks at 11,601, 14,222 and 16,721 cm^{-1} belong to the olefinic C-H stretch. When a Birge-Sponer plot is constructed (Figure 5) using these three transition wavenumbers and the highest energy C-H stretch (3083 cm^{-1}), a straight line with an anharmonicity of 59 cm^{-1} and a mechanical frequency of 3141 cm^{-1} is obtained. Two other progressions can be identified by comparison to the overtone spectrum of pyrrolidine⁴: the aliphatic C-H and the N-H. The C-H combines the 13319 and 15500 cm^{-1} peaks with the calculated average (2905 cm^{-1}) of the four fundamental C-H transition listed in Table 1. An anharmonicity of 56 cm^{-1} and a mechanical frequency of 2957 cm^{-1} resulted from this plot. For the N-H the transition wavenumbers of 3390, 12520 and 15160 cm^{-1} were used, yielding an anharmonicity of 89 cm^{-1} and a mechanical frequency of 3480 cm^{-1} .

Table 1. Vibrational transition frequencies, cm^{-1}

pyrrolidine			3-pyrroline		pyrrole ^a		
			3866	0.13	3995	B	15
					3527	A	99
					3505	A	h
3369	B	.4	3390	0.008			
3342	B	0.5 Q					
3335	B	0.6 Q					
3329	B	0.6 Q					
3324	B	0.7 Q					
			3238	0.005			
					3148	A	
					3140	B	51
					3125	A	44
					3116	B	51
					3069	B	6
					3053	C	16
			3083	B 0.16			
2980	B	1.4	2968	B 0.27	2951		10
2970	B	2.0	2916	B 0.35	2945		13
2884	B	0.9					
			2879	B 0.91			
			2858	B 0.82			
2818	B	0.8	2823	B 0.39			
			2811	B 0.27	2808	B	8
			2779	B 0.13			
			2621	0.09			
					2690		15
					2595		11
					2566		15
					2546		26
					2464	A	
					2283		11
					2268		8
					2221		6
					2195	B	
					1746	C	28
					1741	C	31
					1715	A	31
					1690	A	35
					1577		29
					1548	A	85
					1521	B	60
					1498	A	69

1463 C 0.09
1414 C 0.1

1339 C 0.03
1281 C 0.09

1090 B 0.2

1036 0.02
1032 0.02
1029 0.02
1026 0.013
1022 0.02
1013 0.01

984 0.01
977 0.01
969 0.01

964 A 0.08

908 C 0.16

847 A 0.37
838 A 0.27

791 C 0.45

667 0.04
660 0.07

573 0.2 Q
571 0.5 Q
566 0.2 Q
552 0.2 Q

1414 C .11

1091 B 0.2

1060 B 0.13

1036 0.15Q
1034 0.12Q
1032 0.15Q
1029 0.15Q
1026 0.15Q
1021 0.16Q
1013 0.12Q

905 0.08

868 0.08Q
865 0.08Q
858 0.09Q
848 0.13Q
839 0.10Q
831 0.10Q
830 0.10Q
821 0.12Q

735 0.2

689 0.2Q
683 0.2Q
670 0.3Q
667 0.5Q
660 0.6Q
652 0.4Q
650 0.29Q
649 0.3Q

577 0.4 Q
570 0.3 Q

1470
1424 B 85

1401 A 91
1391 A 45
1304 A 19
1287 B 12

1148 A 29
1134 B 23

1074 A 87

1049 B 87

1018 A 93

981 A 41

960 A 95

912

880 A 45
863 B 39

830 C 4
826 C 40
775 C 11

720 C 100

626 D
602 C 21

488 C 98

a. Data from reference 8.

Table 2 Vibrational Overtone Transition Wavenumbers and Assignments for Gaseous Pyrroline

Assignment	Wavenumbers	Intensity
$\nu = 1$ (C-H)	2870	
$\nu = 1$ (C-H _{olefinic})	3083	
$\nu = 1$ (N-H)	3390	
$\nu = 4$ (C-H _{olefinic})	11,601	vs
	11,770	w
	12,246	
	12,362	w
$\nu = 4$ (N-H)	12,520	m
	12,927	s
$\nu = 5$ (C-H)	13,319	s
	13,702	
	13,945	
$\nu = 5$ (C-H _{olefinic})	14,222	s
	14,993	
	15,160	
	15,314	
	15,438	
$\nu = 6$ (C-H)	15,500	
	15,543	shoulder
	15,822	
$\nu = 6$ (C-H _{olefinic})	16,721	s
	16,803	shoulder

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Figure Captions

Figure 1 Molecular structures of pyrrolidine, 3-pyrroline and pyrrole

Figure 2 Gaseous infrared spectrum of pyrrolidine (20 torr)

Figure 3 Gaseous infrared spectrum of 3-pyrroline (4 torr, from subtraction spectrum)

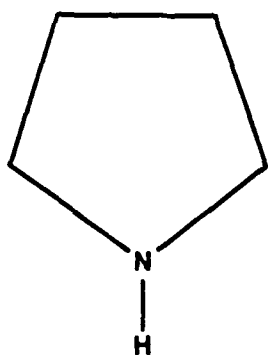
Figure 4 Overtone spectrum of gaseous 3-pyrroline

Figure 5 Birge-Sponer plot for olefinic vibrational progression in 3-pyrroline

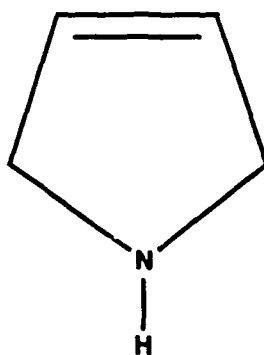
Figure 6 Birge-Sponer plot for aliphatic vibrational progression in 3-pyrroline

Figure 7 Birge-Sponer plot for N-H vibrational progression in 3-pyrroline

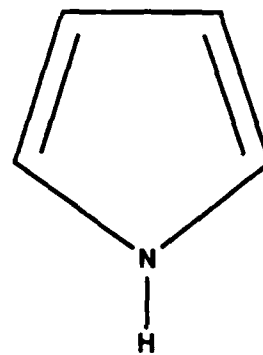
Figure 1 Molecular structures of pyrrolidine, 3-pyrroline and pyrrole



Pyrrolidine



Pyrroline



Pyrrole

Figure 2 Gaseous infrared spectrum of pyrrolidine (20 torr)

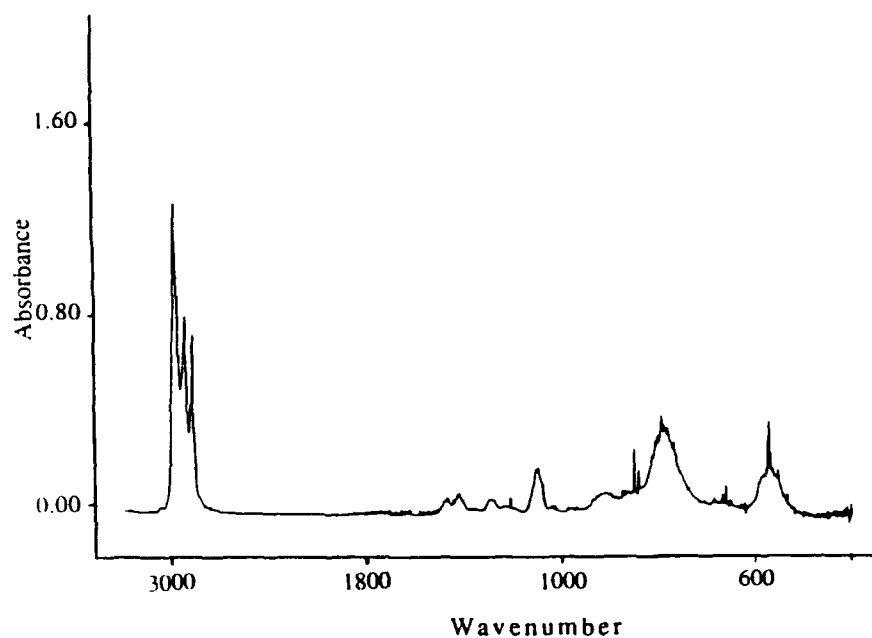


Figure 3 Gaseous infrared spectrum of 3-pyrroline
(4 torr, from subtraction spectrum)

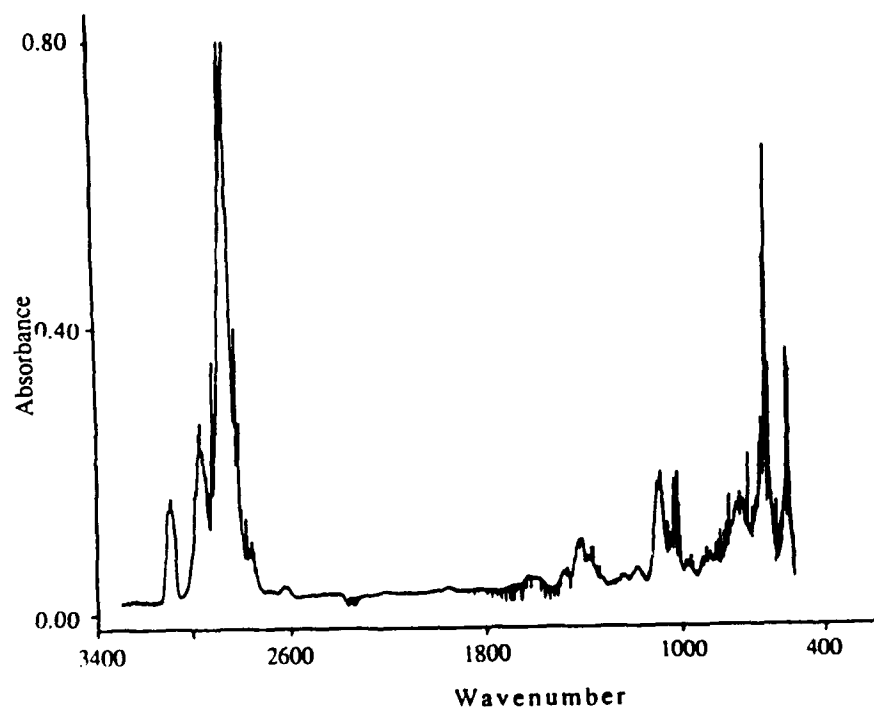


Figure 4 Overtone spectrum of gaseous 3-pyrroline

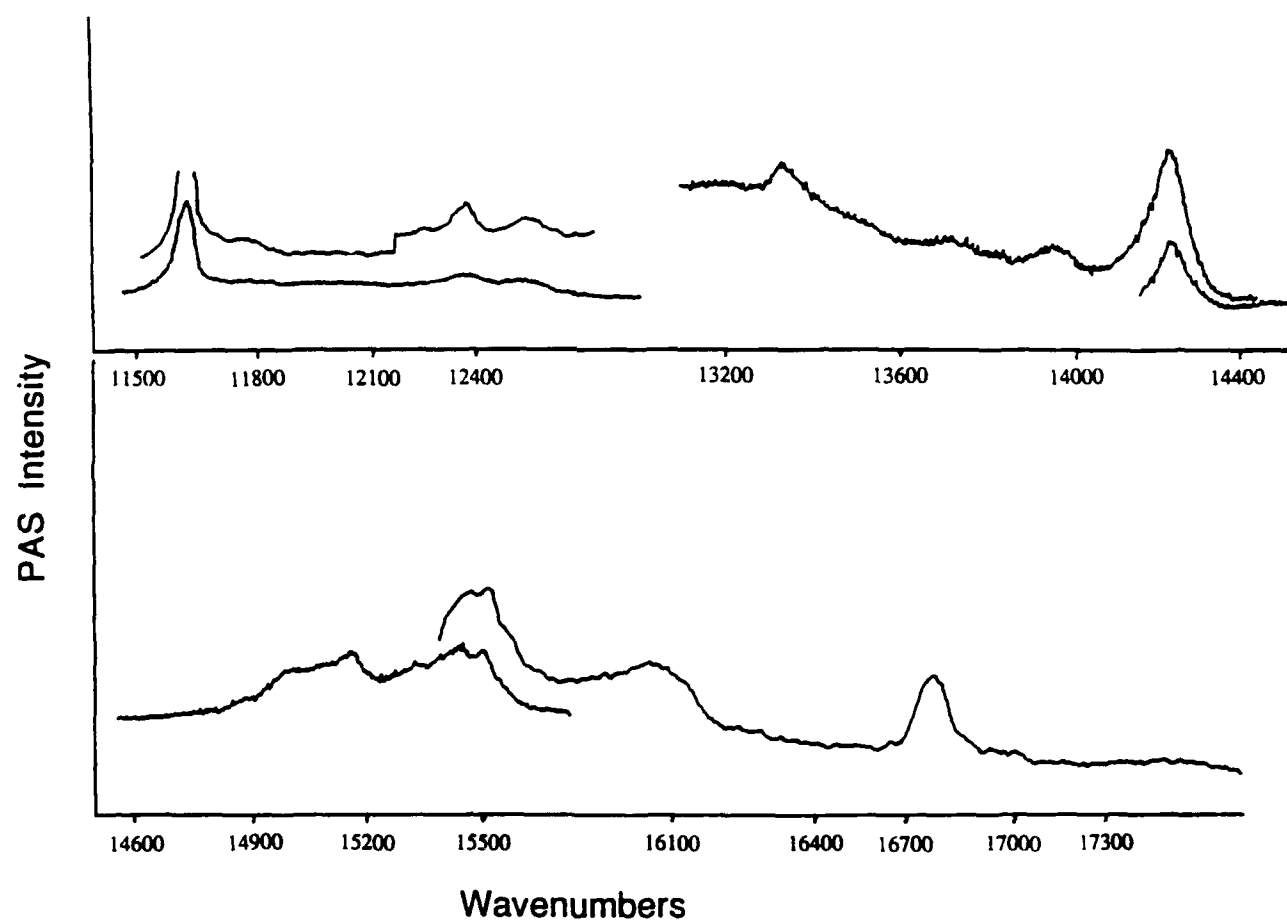


Figure 5 Birge-Sponer plot for olefinic vibrational progression in 3-pyrroline

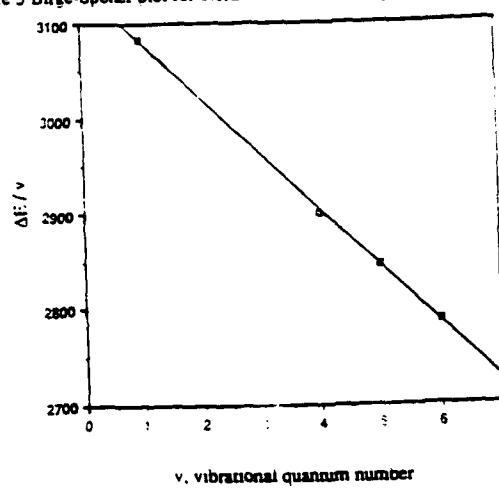


Figure 6 Birge-Sponer plot for aliphatic vibrational progression in 3-pyrroline

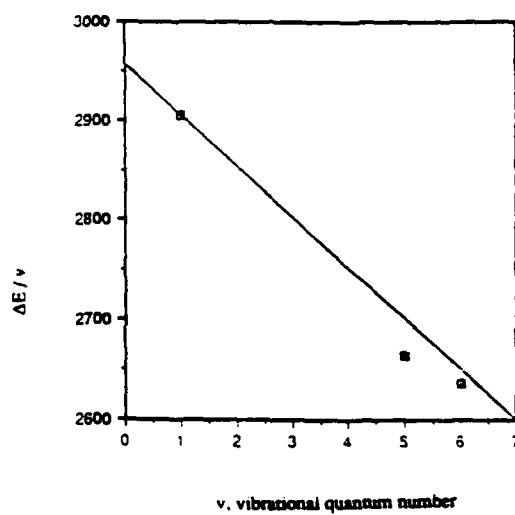
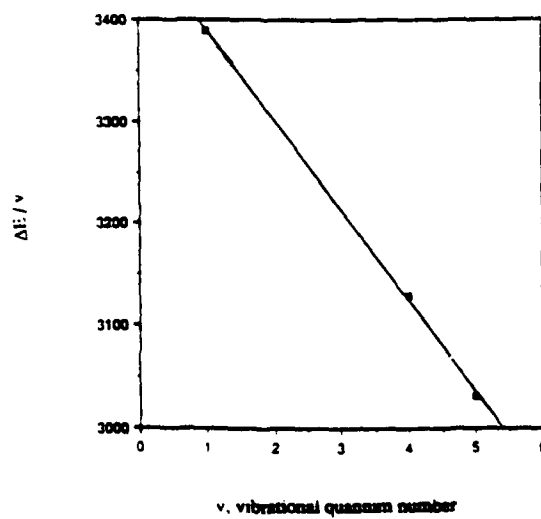


Figure 7 Birge-Sponer plot for N-H vibrational progression in 3-pyrroline



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