Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Compounds and Their Ions. 7. Phenazine, a dual Substituted Polycyclic Aromatic Nitrogen Heterocycle

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Abstract

The matrix-isolation technique has been employed to measure the mid-infrared spectra of phenazine ($C_{12}H_8N_2$), a dual substituted Polycyclic Aromatic Nitrogen Heterocycle (PANH), in the neutral, cationic and anionic forms. The experimentally measured band frequencies and intensities are tabulated and compared with their calculated values as well as those of the non-substituted parent molecule, anthracene. The theoretical band positions and intensities were calculated using both the 4-31G as well as the larger 6-31G* Basis Sets. A comparison of the results can be found in the tables. The spectroscopic properties of phenazine and its cation are similar to those observed in mono-substituted PANHs, with one exception. The presence of a second nitrogen atom results in an additional enhancement of the cation's total integrated intensity, for the 1500-1000 cm^{-1} (6.7 to 10 μm) region, over that observed for a mono-substituted PANH cation. The significance of this enhancement and the astrobiological implications of these results are discussed.

Comparison of neutral phenazine with anthracene (Figure 1), the unsubstituted PAH analog, reveals two items of interest. The neutral spectrum of anthracene, recorded in our laboratory, is in good agreement with that of Szczepanski and Vala (1992). As discussed in Mattioda et al. (2003) and Garrison et al. (1982) with singly substituted PANHs, the presence of nitrogen in the structure induces a global enhancement of the features in the 1600 to 1000 cm^{-1} region. The modes that fall in this region correspond to the aromatic CN and CC stretching as well as the CH in-plane bending modes. This behavior is similar to that observed upon ionization (Szczepanski et. al, 1992 and Hudgins et. al, 1994) of a non-substituted PAH. For instance, the sum of the total vibrational intensity in the 6.7 to 10 μm range (1500 to 1000 cm^{-1}) for neutral phenazine is 76.5 Km/Mole, which is double that observed for neutral anthracene (see Table 1). However this is in excellent agreement with that observed for singly substituted PANHs, but not quite the 20-fold enhancement encountered upon ionization of a non-substituted PAH (Mattioda et al. 2003). Thus the presence of an additional nitrogen in the aromatic structure does not appear to increase the enhancement observed in singly substituted, neutral PANHs.

Calculations performed for the Mattioda et al. investigation indicated that modes dominated by CN stretching and CNC in-plane bending tend to fall in the 1100-1000 cm^{-1} region, although such bands tended to be weak in intensity. One would expect the presence of an extra nitrogen would increase the intensity of the CN stretching and CNC in-plane bending modes. Indeed, the neutral spectrum of phenazine displays two fairly intense bands at 1113.4 (9.0 μm) and 1139.5 cm^{-1} (8.8 μm). Bands at positions such as these would contribute to the long wavelength wing of the pedestal under the 6.8/7.7/8.6 μm features. If further studies show that vibrational bands falling in this region only occur in PANHs, the long wavelength emission in the pedestal, and perhaps even the 8.6 μm feature, would then be another indicator of interstellar nitrogenated aromatic species.

The presence of an additional nitrogen atom does not appear to have any additional influence on the CH out-of-plane bending region (10 to 20 μm) over that already observed in a singly substituted PANH.

3.2 Phenazine Cation

The spectra of the argon/NO_2 matrix isolated phenazine cation and argon matrix isolated anthracene cation are compared in Figure 2. The observed band positions and intensities of the phenazine cation are reported and compared to their calculated values as well as the values for the anthracene cation in Table 2.

Inspection of Table 2 reveals frequency discrepancies between theory and experiment that are slightly higher when using the smaller 4-31G basis set than for the neutral species previously discussed. The larger 6-31G* basis set provides frequencies which, on average, exhibit differences similar to those observed for the neutral molecule. Here, the agreement between theory and experimental band positions is generally within 10 to 20 cm^{-1}. A larger basis set does not appear to keep the discrepancy between the experimental integrated intensity and the calculated value from increasing. This discrepancy is three times higher than that observed for the neutral calculation, regardless of the basis set utilized. There is another interesting thing to note regarding the band intensity calculations. In general, for the neutral as well as the cation, the calculated intensity is greater than that observed in the experiment. However, the

of a neutral band, whereas the number of scans was chosen to optimize both the signal-to-noise as well as time requirements of each experiment. Integrated intensities ($\int \tau\, d\nu$) for individual bands were determined using the WinIR Pro (Digi-Lab) spectrometer control/data analysis software package provided by Digi-lab. Absolute intensities ($A \equiv \int \tau\, d\nu/N$, where τ is the absorbance and N is the density of absorbers in molecules/cm^2) for the experimentally measured neutral phenazine bands were determined using the theoretically calculated values as follows. The calculated intensities for all bands between 1600 and 500 cm^{-1} were summed to obtain the total absorption intensity over this region. This range was chosen to exclude the contributions of the far-infrared bands (ν<500 cm^{-1}) that were not measured in this experiment, the CH stretching region, whose intensities are substantially overestimated by the calculations (Bauschlicher and Langhoff 1997, Hudgins and Sandford 1998) and any in-plane CC and CH bending modes which blend with overtone/combination bands in the experimental data. The total theoretically calculated absolute intensity ($\Sigma\, A^{thy}$) was then distributed over the experimental bands (A^{exp}) on the basis of the fractional contribution of each band ($I_{rel,i}^{exp}$) to the total 1600 to 500 cm^{-1} absorption (I_{rel}^{exp}) in the experimental spectrum:

$$A_i^{exp} = [\sum_{1600 \geq \nu \geq 500} A^{thy}] \frac{I_{rel,i}^{exp}}{\sum_{1600 \geq \nu \geq 500} I_{rel}^{exp}} \quad (1)$$

This method takes advantage of the fact that, although there may be band-to-band variability in the accuracy of the calculated intensity, the total intensity is generally accurate to 10-20%, excluding the C-H stretching region.

Phenazine cations were generated by *in-situ* vacuum ultraviolet photolysis of the matrix isolated neutral phenazine. This was accomplished with the combined 120 nm Lyman-α (10.1 eV) and the 160 nm molecular hydrogen emission bands (centered around 7.8 eV) from a microwave powered discharge in a flowing H_2 gas mixture at a dynamic pressure of 150 mTorr. Comparison of the pre-photolysis neutral spectrum to that measured after photolysis permitted identification of phenazine ion features (Hudgins et al. 2000). To confirm the attribution of a photoproduct band to the phenazine cation, parallel experiments were conducted in which the argon matrix was doped with an electron acceptor, once with NO_2 and once with CCl_4, at a concentration of approximately 1 part in 1200. The presence of this electron acceptor quenches the formation of anions and enhances the production of cations. For a particular photoproduct band to be assigned to the cation, it must grow in the presence of the electron acceptor and do so in fixed proportion to the other bands attributed to the cation.

Assuming that all neutral phenazine molecules that disappear are converted into ions, we can derive an upper limit to the ionization efficiency by measuring the percent decrease in the integrated areas of the neutral bands that accompany photolysis. Phenazine demonstrated an upper ionization limit of 11% in both the Ar and Ar/NO_2 matrix. This value is in line with the ionization limits demonstrated by singly substituted PANH molecules (Mattioda et al. 2003). For presentation purposes only, the data has been baseline corrected, data in the cation and anion figures was obtained by subtracting off the remaining fraction of the neutral bands, using the

Figure 2 displays the first reported spectrum of a PANH anion. The band positions and intensities for the phenazine anion are displayed in Table 3. As noted in the cation section, the larger basis set (6-31G*) exhibits a slightly better agreement with the experimental frequencies. Differences between the integrated intensities and the calculated values appear to be larger for the anion than observed for either the neutral or the cationic species. This larger discrepancy could be the result of the method used to determine anion concentration in the sample, a low anion concentration in the sample, resulting in a larger uncertainty in the integrated intensity, or due to the accuracy of the level of theory used in the calculation of intensities. More experiments and calculations are necessary to accurately determine the source of this increasing discrepancy. As with the cation calculations, both basis sets tend to over-estimate the intensities of the bands, with the same two interesting exceptions. The anion bands at 1113.8 and 1137.3 cm^{-1} exhibit intensities that are equal or greater than the calculated values.

The spectrum of the phenazine anion resembles that of the cation as well as the anthracene cation in that the CC and CN stretching and CH in-plane bending region exhibits much more intensity than the CH out-of-plane bending region. However the ratio of the intensity for the CC and CN stretching and CH in-plane bending region for the anion is only four (experimental) to eight (theory) times that of the neutral PANH, compared to 15 times that for the cation. Both the experimental and theoretical results for the anion show a decrease in the CH out-of-plane region (1000-500 cm^{-1} or 10 to 20 μm) intensity compared to the neutral phenazine molecule. Since anthracene PAH did not produce an appreciable amount of anion, it is impossible to compare with the phenazine anion.

4.0 Conclusions

The spectra of neutral, positively charged and negatively charged phenazine ($C_{12}H_8N_2$) isolated in an argon matrix, are presented. As with singly substituted PANHs, it appears that multiply substituted PANHs display increased intensity in the CC and CN stretching and CH in-plane bending modes when compared to the normal, unsubstituted PAHs. Upon ionization, the CC and CN stretching and CH in-plane bending modes of this multiply substituted PANH reveals an increase in intensity greater than that observed in a mono-substituted PANH. This report also includes the first spectrum of a PANH anion and the direct evidence of anion formation in a PANH molecule. It remains to be seen if the additional substitution of nitrogen into a PANH will result in further increase of the CC and CN stretching and CH in-plane bending modes beyond that found for this disubstituted PANH. The presence of additional nitrogen atoms in the PAH structure tends to enhance existing vibrational features rather than introduce new ones. Thus it is possible for such nitrogen rich, biologically important, molecules to be present in interstellar objects exhibiting the PAH bands.

The use of a larger basis set results in a slight improvement in the calculated anion and cation frequencies. While, in general, the calculations tend to over-estimate the intensities of the experimentally measured vibrational bands, there are two exceptions. The bands observed around 1113 and 1137 cm^{-1} exhibit intensities greater than or equal to the calculated intensities. Additional experiments are needed to determine the reason(s) why these C-H in-plane motions exhibit such behavior in the nitrogenated PAHs. Interestingly, these bands fall in the region of the 8.6 μm band and could explain the plateau emission long ward of this feature.

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Phenazine Neutral Molecule

Experiment						Theory					Experiment vs. Theory				Anthracene		
						4-31G Basis Set		6-31G* Basis Set			4-31G Basis Set		6-31G* Basis Set				
ν (cm⁻¹)	λ (μm)	RI	A	Comment	Ref	ν (cm⁻¹)	A	Sym	ν (cm⁻¹)	A	$\Delta\nu$ (%)	ΔA (%)	$\Delta\nu$ (%)	ΔA (%)	ν (cm⁻¹)	RI	A
1710.5	5.85	0.01	1.8		1, 2, 4										1707.2	0.04	3.4
															1738.3	0.02	1.7
															1765.4	0.04	3.4
															1780	0.01	0.8
															1796.7	0.05	4.2
															1815.8	0.03	2.5
															1844.1	0.01	0.8
															1903.8	0.02	1.7
1936.5	5.16	0.02	2.5	Side bands 1939.2, 1942.5	1, 4										1918.3	0.03	2.5
1957.0	5.11	0.03	3.4	Complex with 1959.1, 1962.1	1, 2, 4										1938.1	0.06	5.1
															2979, 3012.2, 3032, 3065		
3025, 3051, 3080, 3094		0.29	35.6		1,2,4	3061, 3074, 3091, 3095	113.6	B1U, B2U, B1U, B2U	3058, 3070.2, 3085, 3088	98.8					3106, 3218, 3136	1.60	138.5

Previous PANH Results Singly Substituted			Sum 500-1000			Sum 1000-1500	Ratio 1000-1500/500-1000	Phenazine/Anthracene 500-1000	Phenazine/Anthracene 1000-1500						Average Differences		
			171.4			200.9		169.4							188.5		
			76.5			89.7		60.1			0.84	53.7*	0.75	235.2*	31.2		
			0.4			0.4		0.4							0.2		
PANH/PAH	0.90		0.90			1.1		0.9									
PANH/PAH	2.14		2.5			2.9		1.9									

Average A value for both 4-31G and 6-31G* excludes value at 1341.5 and 1356.9 cm⁻¹.

Bands below 1% of the max are not included in this table

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Table 1: Theoretical and Experimental Band Positions (ν), Relative (RI) and Integrated (km/mol) Intensities and Symmetry Assignments (Sym) for Neutral Phenazine and Experimental Band Positions for Neutral Anthracene. Differences between Theoretical and Experimental values are provided as percent difference (Δ%). Average Differences are for the 500-1500 cm⁻¹ range.

Phenazine Cation

Experiment ν (cm⁻¹)	λ (μm)	RI	A	Comment	Theory 4-31G Basis Set ν (cm⁻¹)	4-31G A	Sym	6-31G* Basis Set ν (cm⁻¹)	6-31G* A	Exp vs. Theory 4-31G Δν (%)	4-31G ΔA (%)	6-31G* Δν (%)	6-31G* ΔA (%)	Anthracene Cation ν (cm⁻¹)	RI	A
567.0	17.64	0.09	36.9		587.1	36.4	B2U	570.8	47.4	3.55	1.48	0.67	28.2			
723.0	13.83	0.02	7.2	Side Bands 724.537, 727.163										748.3	0.26	40.9
755.5	13.24	0.14	57.2	Side Bands 756.686, 758.485	767.8	150.0	B3U	758	119.8	1.62	162.40	0.33	109.4			
826.4	12.10	0.03	12.1		817.1	67.3	B2U	825.4	73.1	1.13	454.01	0.12	501.4			
841.2	11.89	0.02	7.5													
897.9	11.14	0.01	2.2		887.4	9.6	B1U	886.6	11.3	1.16	326.48	1.25	403.5	912	0.09	14.4
1022.5	9.78	0.02	8.3		1005.7	11.3	B2U	1015.5	10.9	1.64	36.15	0.69	31.9			
1113.7	8.98	0.02	6.6		1112.9	0.4	B1U	1115.3	0.0	0.07	94.33	0.14	99.8			
1137.3	8.79	0.16	66.7	Doublet with 1138.727	1163.1	12.6	B2U	1149.7	35.3	2.27	81.11	1.09	47.1	1183.3	0.01	2.2
1243.0	8.04	0.04	38.8	Side band 1246.435, data from Ar	1249.3	1.2	B1U			0.51	96.89			1188.6	0.70	108.4
1264.6	7.91	0.01	5.3													
1276.1	7.84	0.82	344.9		1257.1	728.8	B2U	1269.4	609.9	1.49	111.28	0.53	76.8			
1281.8	7.80	0.01	5.5										100.0			
1295.9	7.72	0.01	6.1		1298.7	1.2	B1U	1302.6	0.1	0.21	80.05	0.52	98.9	1290.4	0.06	9.0
1309.5	7.64	0.02	6.9													
1315.4	7.60	0.03	13.7	Complex with 1314.241										1314.6	0.06	9.0
1335.0	7.49	0.34	142.1	Shoulders 1331.631, 1333.530										1341	1.00	156.5
1349.0	7.41	1.00	420.3	Complex with 1345.973, 1351.619	1349.2	235.5	B2U	1367.8	458.0	0.02	43.97	1.40	9.0	1352.6	0.31	48.2
1361.3	7.35	0.14	58.4	Side band 1365.811	1373.2	175.7	B2U	1380.7	62.3	0.87	200.92	1.42	6.8	1364.4	0.04	6.0
1389.2	7.20	0.01	4.1											1406.1	0.02	2.3
1452.4	6.89	0.02	9.9	Side bands 1448.191, 1455.681										1409.5	0.11	16.3
1464.5	6.83	0.03	13.2		1460.4	59.1	B1U	1463.3	54.0	0.28	347.57	0.08	308.7	1418.4	0.86	132.4
1494.6	6.69	0.08	32.6		1484.3	70.6	B2U	1499.9	110.9	0.69	116.39	0.36	239.9	1430.2	0.01	2.3
1519.4	6.58	0.01	5.1											1456.5	0.07	11.4
1577.2	6.34	0.02	10.5											1539.9	0.15	23.5
1590.0	6.29	0.08	31.8	Intensity might be enhanced by a water band	1559.8	48.6	B1U	1580	45.9	1.90	52.75	0.63	44.3	1586.4	0.14	21.7
2487.7	4.02	0.01	5.6	Complex with 2470.566, 2477.583, 2493.595												
2516.1	3.97	0.01	5.6													
2540.2	3.94	0.01	5.8													

Phenazine Anion

Experimental					Theory					Theory vs. Experiment			
ν (cm⁻¹)	λ (μm)	R.I.	A (Km/Mol)	Comment	4-31G ν (cm⁻¹)	4-31G A (Km/Mol)	SYM	6-31G* ν (cm⁻¹)	6-31G* A (Km/Mol)	4-31G Δν (%)	4-31G ΔA (%)	6-31G* Δν (%)	6-31G* ΔA (%)
					610.6	2.5	B2U	600.0	3.2				
					659.3	1.2	B1U	653.7	1.1				
723.1	13.829	0.237	45.7	Side bands 724.537, 727.163	727.9	131.1	B3U	719.3	102.2	0.66	186.72	0.52	123.50
826.4	12.101	0.052	10.1		808.9	13.6	B2U	819.1	20.3	2.12	35.28	0.88	101.77
		0.000			867.4	9.3	B1U	862.9	11.9				
888.0	11.261	0.015	2.8		896.8	14.5	B3U	873.4	9.8	0.99	414.78	1.65	248.21
1018.2	9.821	0.028	5.4	Left over from subtraction?	1008.4	12.2	B2U	1018.1	13.4	0.96	126.49	0.01	148.58
1113.8	8.978	0.088	17.0		1110.8	14.8	B1U	1110.0	16.7	0.27	13.14	0.34	2.01
1137.3	8.792	0.041	7.8	Left over from subtraction?	1144.4	8.6	B2U	1132.2	0.6	0.62	9.87	0.45	92.20
1264.0	7.911	0.368	71.0		1251.4	325.4	B2U	1276.7	148.6	1.00	358.29	1.00	109.28
1309.6*, 1314.2	7.64*, 7.61	1.000	192.9	Doublet with 1315.39 shoulder	1296.0	263.2	B2U	1317.9	434.2	1.03	36.40	0.64	125.01
1333.2	7.501	0.135	26.0										
1519.0	6.583	0.027	5.3		1504.2	76.6	B2U	1525.6	80.0	0.97	1351.23	0.44	1415.97
1589.8	6.290	0.106	20.4		1570.6	1.7	B1U	1590.7	3.7				
2974.6	3.362	0.019	3.6		3006.8	19.2	B1U	3008.9	14.6				
3042.6	3.287	0.206	39.7	Broad weak complex	3026.2	162.2	B2U	3025.8	136.3				
3077.7	3.249	0.054	10.5		3048.3	158.2	B1U	3043.5	160.1				
					3054.9	121.3	B2U	3048.9	118.8				

	Experimental	Theory 4-31G	Theory 6-31G*
Anion Sum 500-1000	58.6	172.2	
Anion Sum 1000-1500	325.5	700.8	
Neutral Phenazine Sum 500-1000	171.4	200.9	
Neutral Phenazine Sum 1000-1500	76.5	89.7	
Ratio Anion/Neutral 500-1000	0.3	0.9	
Ratio Anion/Neutral 1000-1500	4.2	7.8	

Average Differences (%)

	4-31G Δν (%)	4-31G ΔA (%)	6-31G* Δν (%)	6-31G* ΔA (%)
	0.96	281.36	0.66	262.95

Figure Captions:

Figure 1. Comparison of the experimental (bottom) and theoretical (top) spectra for phenazine and anthracene isolated in an argon matrix. All spectra have been normalized to 1×10^{16} molecular species. Theoretical spectrum is the 4-31G basis set result.

Figure 2. Mid-infrared spectra of the phenazine anion and cation isolated in an argon (anion) and argon/NO_2 (cation) matrix at 14K. The spectrum of anthracene is shown for reference. The bands marked by an asterisk (*) are due to impurity photoproducts. All spectra have been normalized to 1×10^{16} molecular species.
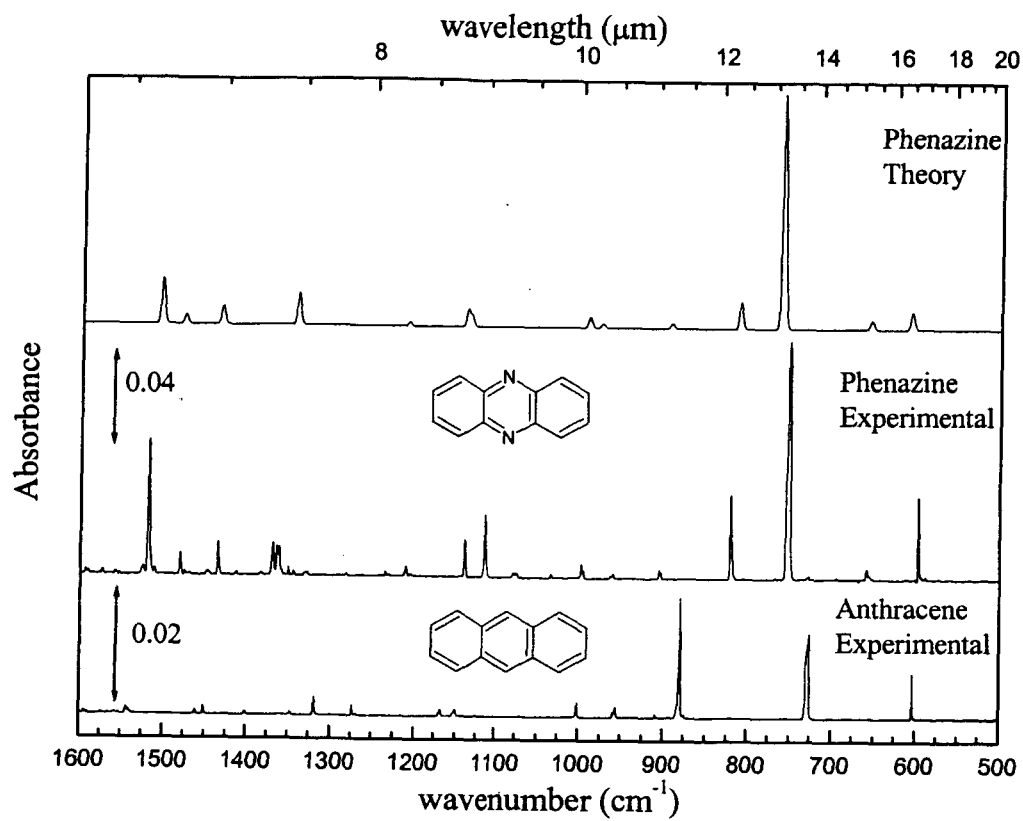
Figure 1.

Figure 2.