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 ($\text{C}_{12}\text{H}_8\text{N}_2$), 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\textsuperscript{-1} (6.7 to 10 $\mu$m) 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 \(\mu\)m 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 \(\mu\)m) and 1139.5 cm\(^{-1}\) (8.8 \(\mu\)m). Bands at positions such as these would contribute to the long wavelength wing of the pedestal under the 6.8/7.7/8.6 \(\mu\)m 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 \(\mu\)m 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 \(\mu\)m) 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 (\(\int \tau \, dv\)) for individual bands were determined using the WinIR Pro (Digi-Lab) spectrometer control/data analysis software package provided by Digi-lab. Absolute intensities \((A = \int \tau \, dv/N, \text{where } \tau \text{ is the absorbance and } N \text{ is the density of absorbers in molecules/cm}^2)\) 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 \((v<500 \text{ cm}^{-1})\) 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 \((\sum A^{thv})\) was then distributed over the experimental bands \((A^{exp})\) on the basis of the fractional contribution of each band \((I_{ref,i}^{exp})\) to the total 1600 to 500 cm\(^{-1}\) absorption \((I_{ref})\) in the experimental spectrum:

\[
A_i^{exp} = \left[ \sum_{1600 \leq \nu \leq 500} A_i^{thv} \right] \frac{I_{ref,i}^{exp}}{\sum_{1600 \leq \nu \leq 500} I_{ref}^{exp}} \quad (1)
\]

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-\(\alpha\) (10.1 eV) and the 160 nm molecular hydrogen emission bands (centered around 7.8 eV) from a microwave powered discharge in a flowing \(\text{H}_2\) 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 \(\text{NO}_2\) and once with \(\text{CCl}_4\), 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/\(\text{NO}_2\) 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 \(\mu\)m) 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\(_{8}\)N\(_{2}\)) 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 \(\mu\)m band and could explain the plateau emission long ward of this feature.
References


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Previous PANH Results
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PANH/PAH 0.90
0.90 Phenazine/Anthracene 500-1000
0.90 Phenazine/Anthracene 500-1500
0.90 Phenazine/Anthracene 1000-1500
1.0

Average value for both 4-31G and 6-31G

Table 1: Theoretical and Experimental Band Positions (v), 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.


Bands below 1% of the max are not included in this table.
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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 $1 \times 10^{16}$ 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 $1 \times 10^{16}$ molecular species.
Figure 1.
Figure 2.

The figure shows a spectrum with three peaks labeled as Phenazine Anion, Phenazine Cation, and Anthracene Cation. The peaks are plotted against wavelength (\( \mu m \)) and wavenumber (\( \text{cm}^{-1} \)). Absorbance levels of 0.01, 0.04, and 0.04 are indicated on the graph.