# Behaviour of Biomarker Molecules in Extreme Environments: Insights from Structural and Spectroscopic Studies of Polyaromatic Hydrocarbons of Astrobiological Significance.

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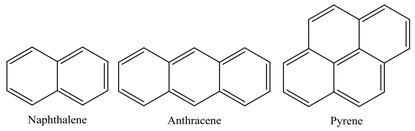
## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are molecules of interest in planetary sciences, as inter-stellar sources of carbon and as biomarkers related to degradation of cellular structures.[1] While PAHs may be stable under the UV flux[1] at the surface of Mars, and indeed may be further stabilised by UV-absorption by the ferric mineralogy they are also susceptible to decay by Solar Energetic Radiation (SER) or Galactic Cosmic Rays (GCR). PAHs are strongly electron donating species and are therefore react with oxidant species. The oxy- and peroxy- species present on the Martian surface are obvious candidates to catalyse PAH degradation. Futhermore, the varying redox properties of PAH species has the potential to induce auto-degradation in PAH mixtures. It is very likely that such processes will be preceeded by development of mixed phases of PAHs, primarily in the solid solid.

This poster reports the work into determining phase behaviour of naphthalene, anthracene and pyrene in various mixture and states. Interactions and derivatisation of PAHs have been characterised using *X*-ray diffraction and Raman spectroscopy and binary phase diagrams for seected mixtures have been developed with a new high-throughput thermal methodology.




## PHASE BEHAVIOUR IN SOLUTION

An investigation of the interactions of various PAHs with each other was undertaken by dissolving the PAHs in various compositions and allowing time for crystallisation. Although no co-crystal/salt type adducts were formed, a number of interesting observations were made. A mixture of naphthalene and anthracene was made up in dichloromethane to ratios of; 1:1, 1:2, 2:1, 1:3 & 3:1 molar ratios. Raman spectra (*Figure 2*) of the recovered products was carried out which clearly showed the presence of 3 different systems. Due to the highly soluble nature of naphthalene in this solvent only anthracene and its derivatives were seen to crystallise.

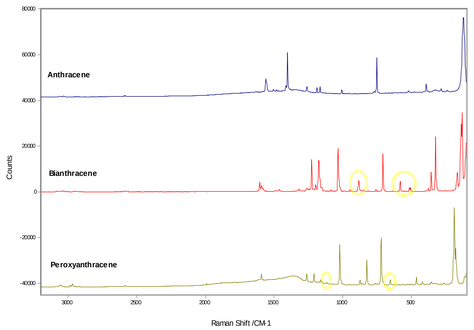



Figure 2 – Raman spectra of Anthracene, Bianthracene & Peroxyanthracene

Suitable single crystals were chosen for X-Ray analysis and the crystal structures were determined. One was a simple anthracene (*figure 3*) structure with a transformed cell from the known structure, the second was a bianthracene (*figure 4*) structure and the third a peroxyanthracene (*figure 5*).

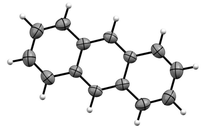


Figure 3 - Anthracene

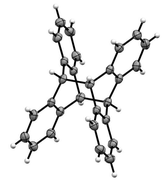


Figure 4 - Bianthracene

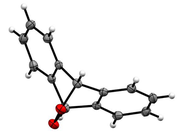


Figure 5 - Peroxyanthracene

A mixture of naphthalene and pyrene was made up in dichloromethane to; 1:1, 1:2, 2:1, 1:3 & 3:1 molar ratios. Raman spectra (*Figure 6*) of the recovered products was carried out which clearly showed that all recovered products were pyrene.

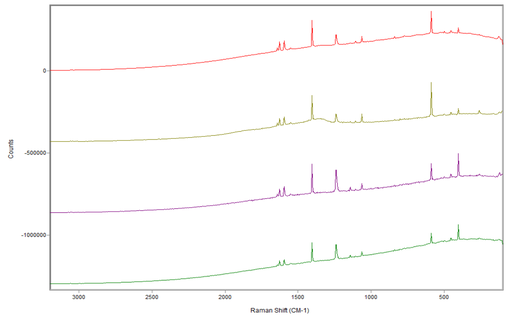



Figure 6 – Raman Spectra of Pyrene & Recovered Solid (All pyrene)

On collection of the unit cell by X-ray diffraction it appeared that a new phase had in fact being discovered, on determination of the crystal structure (*Figure 7*) it became apparent that the collected data was simply in a different cell setting ($P2_1/c$) than the database records[2] ($P2_1/a$). (*Figures 8 & 9*)

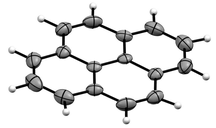


Figure 7 – Pyrene molecule

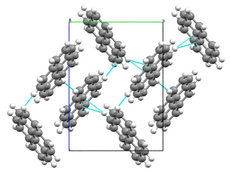


Figure 8 – The determined pyrene structure viewed along the crystallographic *c*-axis

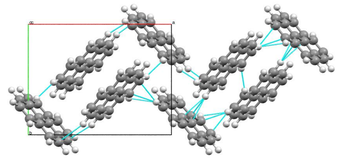


Figure 9 – A database pyrene structure viewed along the crystallographic *a*-axis

## PHASE BEHAVIOUR IN THE SOLID STATE

Various mixtures of naphthalene and pyrene were prepared in hermetically sealed DSC pans and heated through the melting points of each, allowed to cool then reheated to melt any new phase that had formed. The data was extracted from the DSC traces and plotted to make a phase diagram (*Figure 10*). The phase diagram shows that the system is a simple eutectic one. The major finding is that in a ~0.7:0.3 naphthalene:anthracene mixture the melting point is reduced to $60^0$C. The predicted data is also shown, and it is apparent the mixture deviates slightly from the ideal.

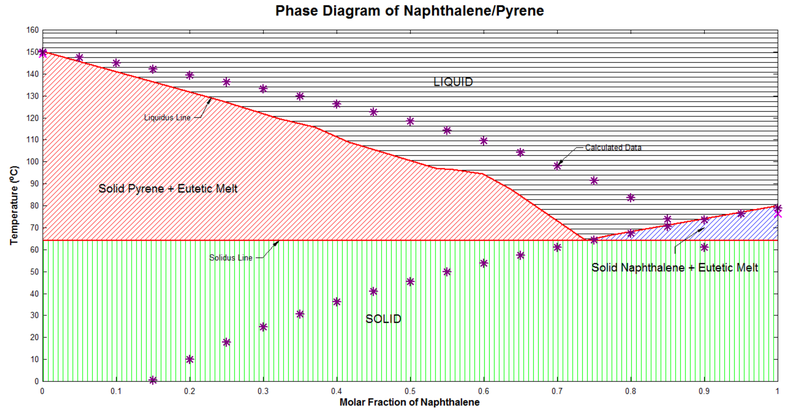



Figure 10 – Naphthalene/Pyrene Phase Diagram

A similar plot has been calculated for phase interaction between anthracene and pyrene *(Figure 11*). This again predicts a lowering in eutectic melt temperature at ~0.7:0.3 composition.

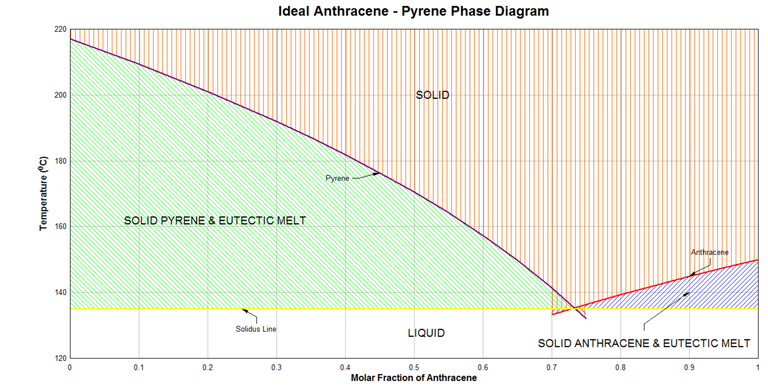



Figure 11 – Anthracene/Pyrene Phase Diagram

- More work is required to fully understand these and other PAH systems.
- The surface and possible guest-host chemistry of these systems and inorganic rock matrices is also under investigation.

1. Parnell, J., D. Cullen, et al. (2007). "Searching for life on mars: Selection of molecular targets for ESA's aurora ExoMars mission." Astrobiology **7(4): 578-604.**
2. Knight, K. S., K. Shankland, et al. (1996). "The crystal structure of perdeuterated pyrene II at 4.2 K." Chemical Physics Letters **258(3-4): 490-494.**