MOLECULAR MODELING OF THE STAGES OF CARBONIZATION OF PHENANTHRENE AND ANTHRACENE

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Introduction

Past work has shown that the isomers phenanthrene and anthracene exhibit different levels of mesophase development and graphitizability [1-5]. Reactive sites on the isomers lead to different constitutional mesophase precursors, not all of which have the planar disc shape preferred for mesophase development [2]. Using Cerius^2, Molecular Simulations Incorporated (MSI) software, and physical data collected by Sasaki *et al.*, the different pre-mesophase units of anthracene and phenanthrene are visualized [2]. This software is also used to create structures of the isomers at carbonization temperatures not reached by Sasaki *et al.* [2].

Experimental

The carbonization process and characterization of solid products formed is presented elsewhere [1]. The modeling was performed using MSI's Cerius^2 software loaded on a Silicon Graphics computer. C/H ratio, NMR, and optical microscopy as determined in earlier research were parameters used in forming the models. Mopac calculations for electron density were determined and used in conjunction with geometric proximity of reactive carbons to determine most likely bond formations. The polymerization and condensation reactions of the isomers were performed under boundaries set by "crystal builder," which confines the molecules to a certain area. This process was done to mimic carbonization under pressure, as outlined in [1].

Results and Discussion

Electron densities of phenanthrene show the 9, 10 position to be most reactive and where dimerization is most likely to occur. Fig.1 shows the electron density of the dimer could lead to the formation of a five membered ring causing curvature. Fig.2 shows the chance for attack on the condensed dimer to be the 4,5 position. The trimer formed will again increase in curvature and loss of planarity. This curvature could lead to disclinations and holes in pre-graphitic sheets formed at temperatures in excess of 2000°C, Fig.3 .

Anthracene polymerization and condensation occurs with planarity intact, unlike phenanthrene [2,3]. In order for phenanthrene to polymerize five membered rings must form; anthracene can also form such rings, but they are not a necessity for growth. Simply put, the geometry of the anthracene isomer is favored for mesophase development because polymerization progresses via planar sheets, Fig.4.

Once again, if temperatures in excess of 2500°C were reached graphitic sheets of condensed anthracene would form. Anthracene's pre-graphitic sheets do not exhibit disclinations as found in phenanthrene, but imperfections analogous to tears in a sheet of paper, Fig.5.

Conclusion

Anthracene and phenanthrene show different levels of mesophase development because of the geometric differences between the two isomers. These differences effect electron densities and the proximity of reactive sites on adjacent molecules. Phenanthrene carbonization must proceed via formation of five membered rings, whereas anthracene can polymerize without them. These differences are accentuated at higher temperatures leading to varied levels of graphitic stacking.

References

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Figure 1. Phenanthrene dimer w/HOMO

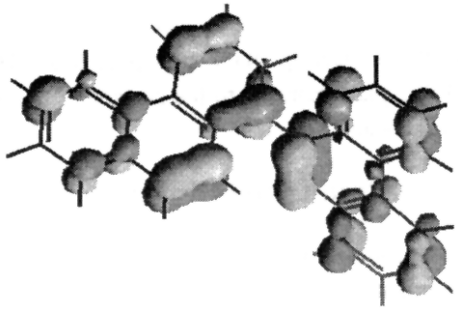

Figure 2. Five membered ring forms

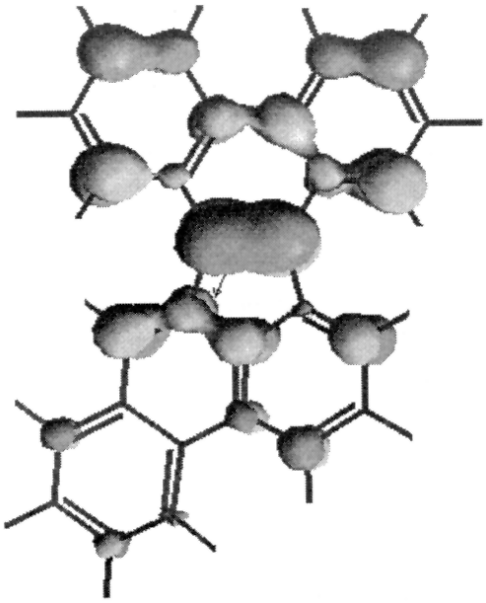

Figure 3. Curvature and holes, Phenanthrene

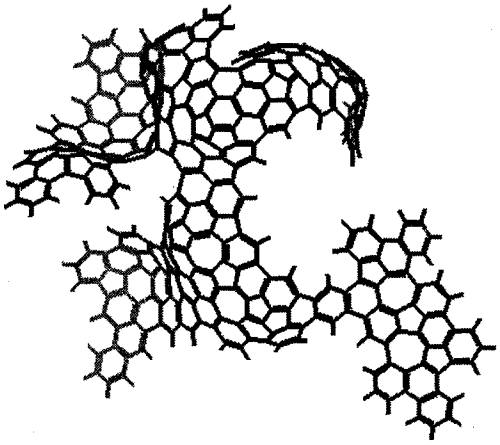

Figure 4. Anthracene trimer w/ HOMO

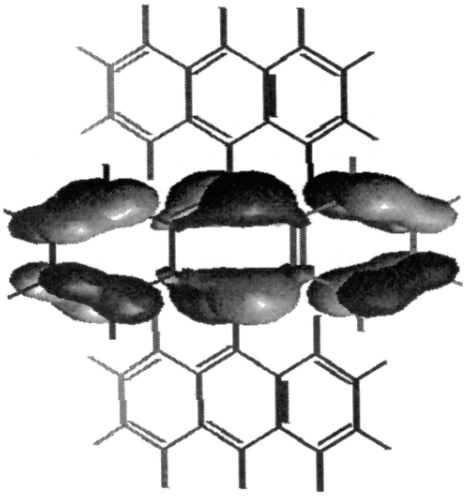

Figure 5. Anthracene graphitic sheet