

## THE ROLE OF HETEROATOMS ON THE CARBONIZATION AND GRAPHITIZATION OF POLYNUCLEAR AROMATIC COMPOUNDS

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### ABSTRACT

An investigation of the carbonization processes for anthracene–sulphur and phenanthrene–sulphur mixtures was carried out with the aid of differential thermal analysis (DTA). The resulting carbons were also examined by polarized-light microscopy. It was found that sulphur as a heteroatom having a different valency from the carbon atoms, which it replaced, was effective in forming ‘cross-links’ between pairs of layer planes and thus prevented the formation of parallel layers. Sulphur caused both cross-linking and dehydrogenation. With increasing hydrogen to sulphur mole ratio, the temperature range of the fusion energies and thus the graphitizability of the pyrolyzed carbon were found to decrease. Up to the critical ratios of  $S/H = 2/10$  for anthracene and  $S/H = 1/4$  for phenanthrene, no appreciable effect was found.

### INTRODUCTION

The synthetic manufacture of graphite is based on the initial formation of carbon during carbonization of organic compounds. The formation of the carbon structure and its ability to become graphite at higher temperature have been observed in the early stages of carbonization from 350 to 600 °C [1–6]. This is the liquid state transition period, or mesophase, during which large planar aromatic molecules become aligned in a parallel array to form an optically anisotropic liquid crystal. The potential role of heteroatoms, such as nitrogen, oxygen and sulphur, in controlling the carbonization and graphitization of organic molecules and polymers has been appreciated for many years. Blayden et al. [7] suggested that during carbonization, these heteroatoms can form, in part, stable volatile by-products, thus reducing the carbon yield. On the other hand, the heteroatoms can effect cross-linkage in the compound. In this fashion they reduce the vapour pressure and cause coking in the liquid and especially in the solid phase. This effect increases the carbon yield.

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This work investigates the above-mentioned roles of the heteroatom in the case of anthracene and phenanthrene using sulphur as the heteroatom.

## EXPERIMENTAL

### *Preparation of samples for mesophase study*

Pure anthracene (analytical grade, 99%, Merck) and phenanthrene (99%, BDH) samples were intimately mixed with sulphur in mole ratios of S/H = 1/10, S/H = 2/10, S/H = 3/10 and S/H = 4/10 for anthracene, and S/H = 1/16, S/H = 1/8, S/H = 1/4 and S/H = 3/8 for phenanthrene. The carbonization was carried out using the sealed-tube technique and the carbons thus formed were embedded in cold-setting mounting resins. The mounted specimens were then ground on silicon carbide papers (120–600 grit) using distilled water as lubricant. Subsequent polishing was carried out using Hyprez diamond lapping compounds (6  $\mu\text{m}$  followed by 1  $\mu\text{m}$ ) on a wet polishing silk cloth. Final polishing of the samples was carried out by high purity Linde  $\alpha$ -alumina powder.

### *Differential thermal analysis (DTA)*

Details of the technique have been described elsewhere [8]. A Shimadzu micro DTA system model DT 30 manufactured by Shimadzu Corporation, Kyoto, Japan, was used in the investigation. Partial carbonization of the different anthracene–sulphur and phenanthrene–sulphur mixtures was carried out by the sealed-tube technique and the carbons thus formed were then subjected to differential thermal analysis. The heating rate was maintained at 10°C min<sup>-1</sup>.

### *Polarized-light microscopy*

The samples prepared for mesophase study were observed and photographed with a Reichert “Metabert” polarizing microscope equipped with a 35 mm Remica III photographic camera. Fuji Colour Super HR 100, 35 mm films were used. The coloured mesophase spherules were produced by the insertion of a gypsum plate inclined to the analyser at an angle of 45°. The polarizer and analyser remained crossed relative to each other. This is the so-called sensitive tint method.

## RESULTS AND DISCUSSION

The DTA traces of partially carbonized anthracene–sulphur and phenanthrene–sulphur mixtures in different mole ratios are presented in

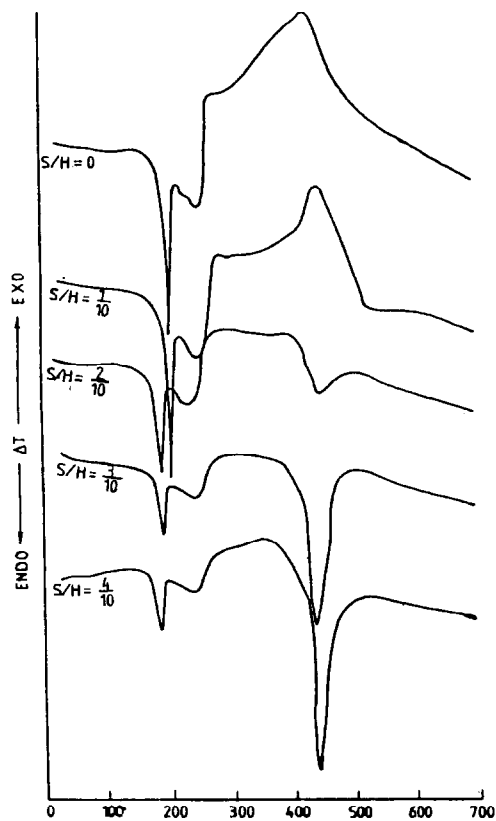


Fig. 1. DTA traces of anthracene-sulphur mixtures with different S/H ratios.

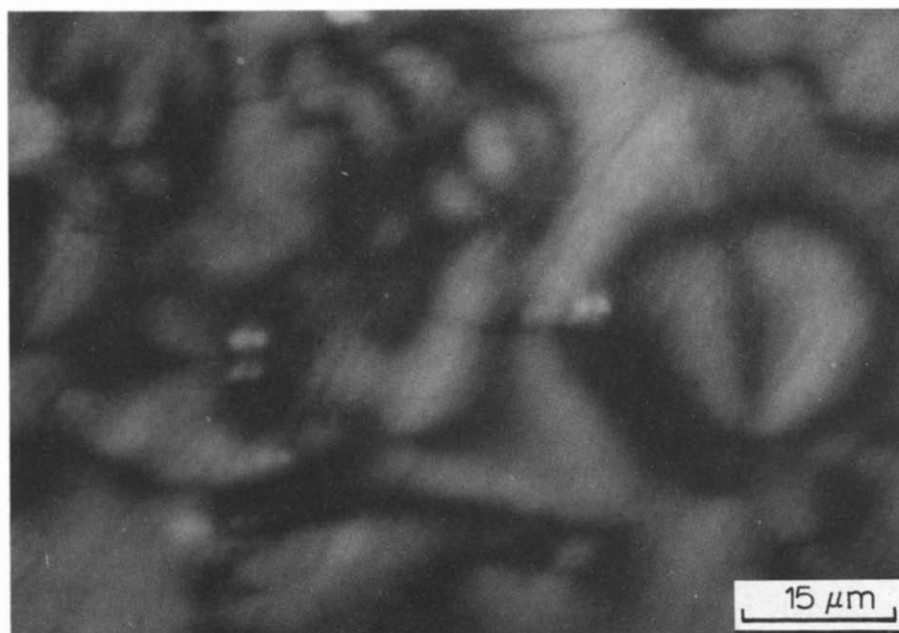


Plate 1. Spherules coalesce in anthracene-sulphur mixture ( $S/H = 2/10$  at  $470^\circ\text{C}$  for 4 h).

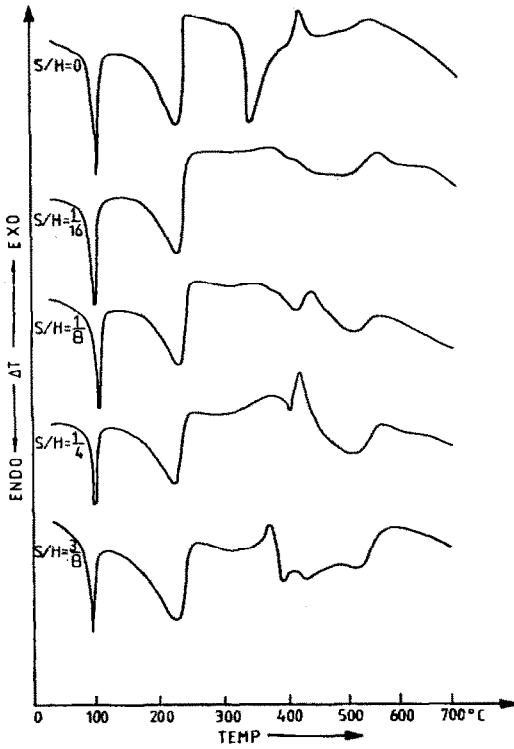


Fig. 2. DTA traces of phenanthrene-sulphur mixtures with different S/H ratios.

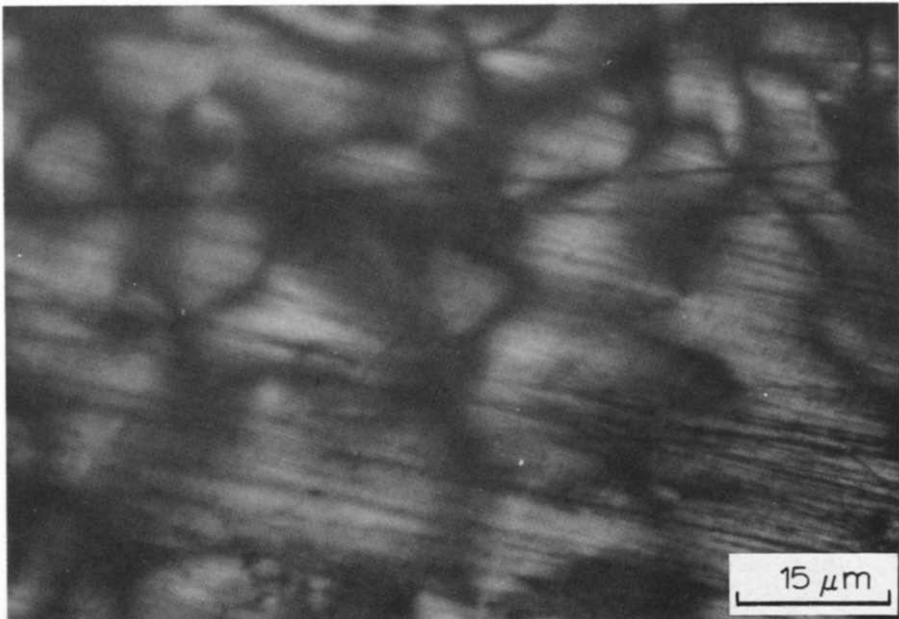


Plate 2. Ruptured mesophase spherules in anthracene-sulphur mixture ( $S/H = 3/10$  at  $490^\circ\text{C}$  for 4 h).

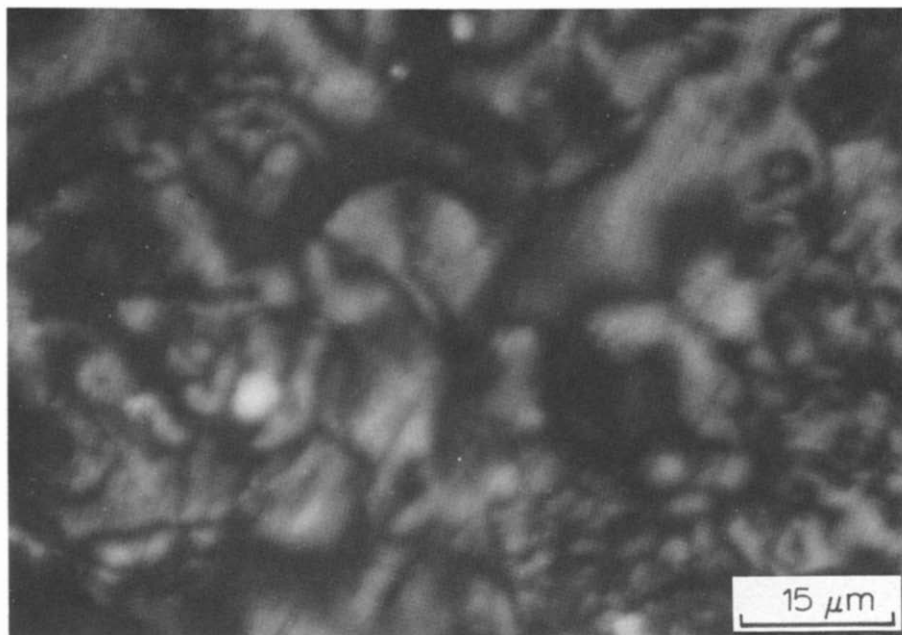


Plate 3. Ruptured mesophase spherules in anthracene-sulphur mixture ( $S/H = 4/10$  at  $500^{\circ}\text{C}$  for 4 h).

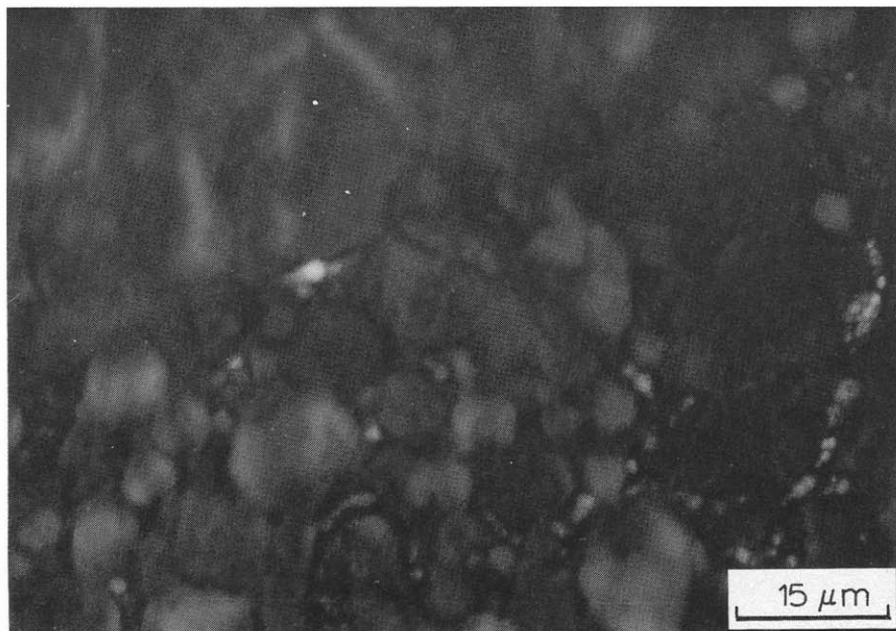


Plate 4. Mesophase spherules in phenanthrene-sulphur mixture ( $S/H = 1/16$  at  $535^{\circ}\text{C}$  for 5 h).

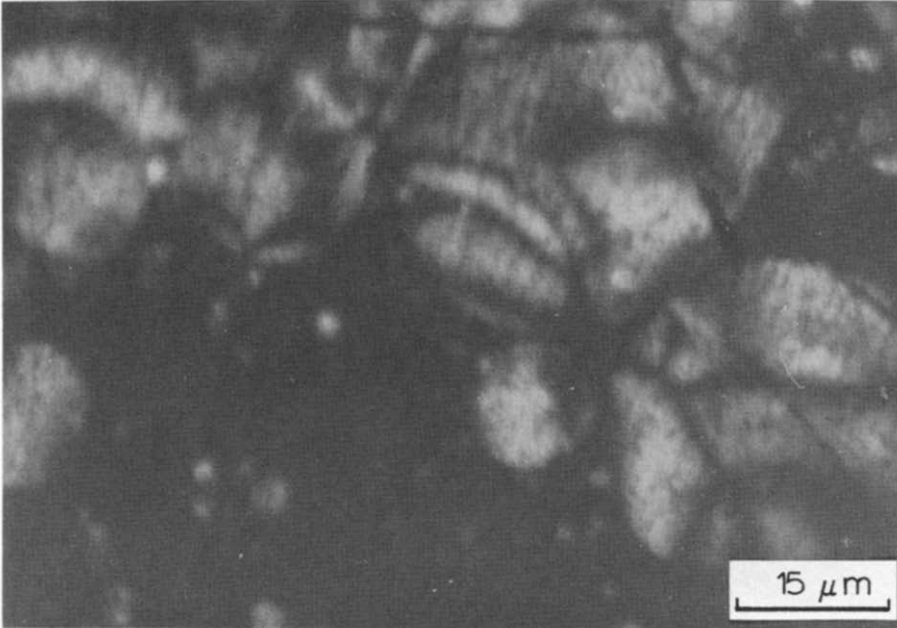


Plate 5. Spherules coalesce in phenanthrene-sulphur mixture ( $S/H = 2/16$  at  $540^{\circ}\text{C}$  for 5 h).

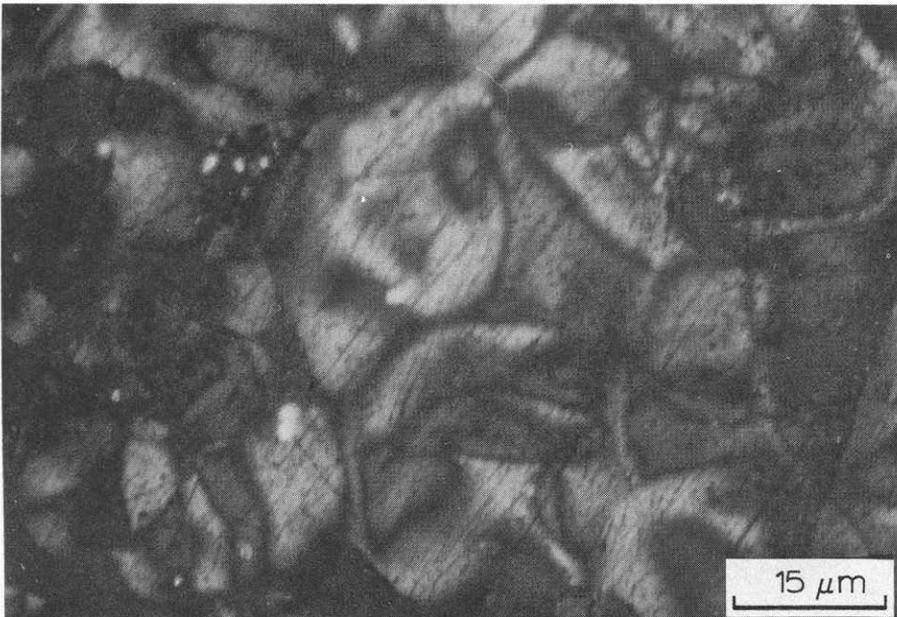


Plate 6. Complex bulk mesophase in phenanthrene-sulphur mixture ( $S/H = 1/4$  at  $555^{\circ}\text{C}$  for 5 h).

Figs. 1 and 2. For both the DTA traces, a common characteristic is the presence of an initial large endotherm due to melting of the tarry substance, which is then followed by a second endotherm due to the boiling point of the substance. These two endotherms are then followed by small fluctuations before a smooth trace returns. The fluctuations in the DTA traces may arise from the formation of hydrocarbon gases within the samples during pyrolysis, and the initial large endotherms in the DTA traces of the samples indicate their graphitizability [8,9]. The initial endotherm becomes narrower with the addition of sulphur, indicating that sulphur is acting here as a catalyst for cross-linking [10]. The narrowing of the initial large endotherm with an increase in S/H ratio indicates that the latent heat of fusion of the mixture gradually decreases. The decrease in the latent heat of fusion means a consequent decrease in activation energy [11] and hence in the graphitizing power.

The polarized-light photomicrographs for anthracene-sulphur and phenanthrene-sulphur samples heat treated to different temperatures and for different periods of time are illustrated in Plates 1-7. Up to the critical ratio of S/H = 2/10, the graphitizing character of the anthracene-sulphur sample (i.e. nucleation, growth and coalescence of the mesophase) is not disturbed. However, above the critical ratio, the mesophase microstructure becomes disordered and ruptured (Plate 3). The mesophase microstructures

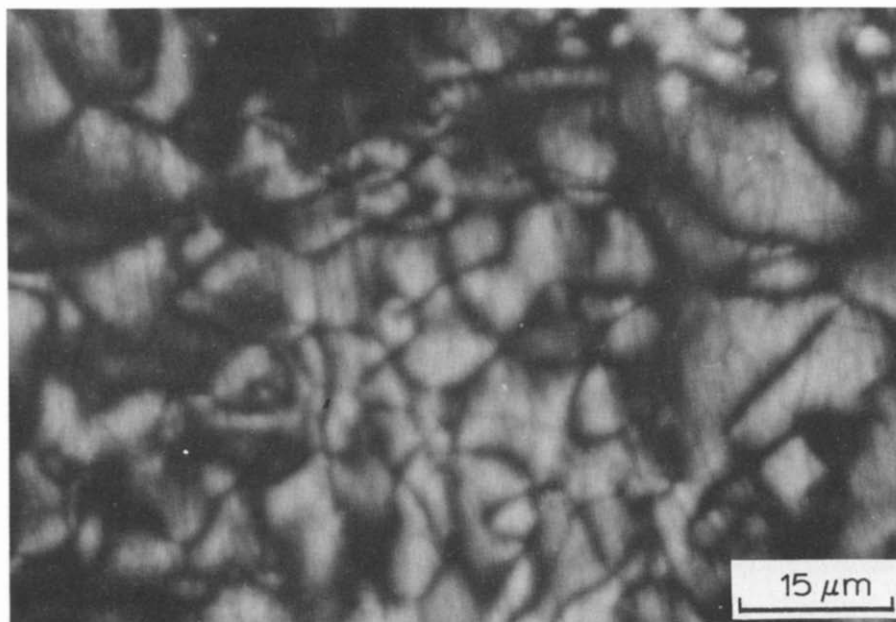


Plate 7. Featureless spherules developed in phenanthrene-sulphur mixture (S/H = 3/8 at 560 °C for 5 h).

of phenanthrene-sulphur mixtures were also very ruptured and disordered above the critical ratio of  $S/H = 1/4$  (Plate 7).

## CONCLUSIONS

The presence of heteroatoms plays a significant role in controlling the growth of the anisotropic liquid crystal (a three-dimensional ordering system). Non-carbon elements such as sulphur and the loss of volatile matter during carbonization reduce the growth of the ordered layers by coalescence of neighbouring layers. The structural ordering is distorted with continued addition of sulphur beyond a critical value. The mosaic pattern anisotropy with featureless spheres arises from the distortion of the liquid crystal above the critical value of  $S/H = 2/10$  for anthracene and  $S/H = 1/4$  for phenanthrene.

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