

The Carbonization of Aromatic Hydrocarbons

I. C. Lewis and L. S. Singer

Union Carbide Corporation
Carbon Products Division
Parma Technical Center
Cleveland, Ohio 44101

I. Introduction

Carbonization is the thermal conversion of organic materials to carbon and graphite. The overall transformation involves a complex series of chemical reactions and diffusion processes in both the liquid and solid state. The reaction sequence consists of the elimination of substituent atoms and groups from the organic molecule, aromatization, and subsequent polymerization to a large aromatic carbon framework.

Any organic material can be converted to carbon. Commercially, synthetic carbon and graphite are prepared from aromatic starting materials such as coal tar pitch and heavy petroleum residues. These raw materials consist largely of mixtures of compounds containing aromatic hydrocarbon and heterocyclic structures. We have found that the carbonization behavior of complex raw materials can be understood on the basis of the thermal reactions of relatively few, representative aromatic hydrocarbons. This paper reviews previous work and also presents results of our recent studies of the carbonization of several pure aromatic hydrocarbons.

II. Chemical Constitution of Pitch

The carbonization of an organic material proceeds through an initial aromatic stage. Coal tar pitch is an example of such an aromatic stage formed during the pyrolysis of coal. There have been numerous compilations of the chemical constituents of coal tar pitch.^(1,2) These compilations include several hundred aromatic hydrocarbon and heterocyclic compounds. Table I lists the major aromatic hydrocarbon components that have been quantitatively determined in a typical coal tar pitch. The 13 structures shown constitute 13.6 percent of the entire pitch. The remainder of the material is composed of small amounts of hundreds of other aromatic compounds.

III. Thermal Reactivity and Aromatic Structure

The aromatic hydrocarbon components of pitch vary widely in thermal reactivity. This thermal reactivity is directly related to molecular structure. Table II compares the effect of chemical structure on the thermal reactivity of a number of hydrocarbons. The thermal reactivity is indicated by the lowest temperature at which an initial reaction is observed. Also listed are the corresponding ionization potentials derived from the optical absorption frequencies of the longest wavelength p-bands.⁽³⁾ It is apparent that thermal reactivity increases with decreasing ionization potential. The presence of substituent groups on the aromatic ring can significantly alter these thermal reactivities either by providing a reaction site, or by altering the relative bond strengths in the molecule.⁽⁴⁾

Table I

Some Aromatic Hydrocarbon Components of Coal Tar Pitch
and their Occurrence in Weight Percent

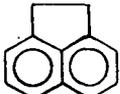
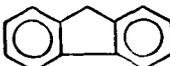
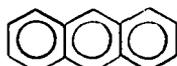
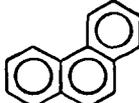
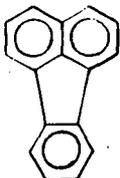
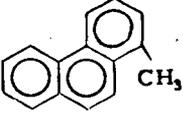
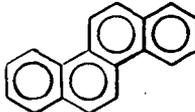
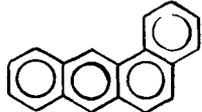
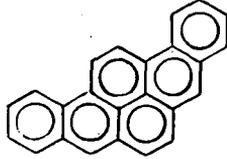
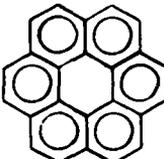
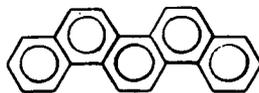
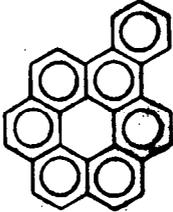
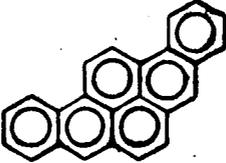
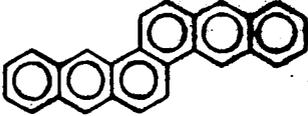
			
Acenaphthene 0.3	Fluorene 0.1	Anthracene	+ Phenanthrene 1.2
			
Fluoranthene 1.5	Pyrene 1.3	Methylphenanthrene 0.3	Chrysene 2.7
			
Benz-(a)-anthracene 0.7	Benzo-(a)-pyrene 3.6	3,4,9,10-Dibenzopyrene 1.5	
			
Coronene	Picene		

Table II

Relation of Thermal Reactivity to Aromatic Structure

Aromatic Hydrocarbon	Reaction Temp. °C	Ionization Potential (eV)
	637	7.24
	560	7.07
	535	6.86
	480	6.64
	411	6.23

IV. Effects of Chemical Structure on the Nature of the Final Graphite

The heat treatment of organic materials to 3,000°C results in carbons possessing basically the graphite structure. The degree of graphitization and the properties of synthetic carbons obtained at 3,000°C are determined largely by the structure of the starting material. This effect is illustrated by the data in Tables III and IV which give the X-ray semilattice spacings for 3,000°C carbons prepared from a variety of aromatic hydrocarbons:

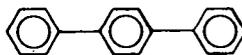
Table III includes well-graphitizing compounds which possess c-spacings between 3.354 and 3.363Å. Natural graphite has a c-spacing of 3.354Å. Table IV lists some poorly graphitizing materials. The high c-spacings, 3.370 to 3.44, obtained for these materials indicate a much more disordered carbon structure. It is not generally obvious from the initial chemical structures in Tables III and IV how well a given aromatic hydrocarbon will graphitize. For example, the 5-membered ring aromatic hydrocarbon acenaphthylene yields a well-ordered graphite, while the highly symmetrical molecule coronene gives rise to a poorly ordered graphite. However, sterically overcrowded and nonplanar molecules generally lead to more disordered graphite structures. ⁽⁵⁾

V. Carbonization of Acenaphthylene and Terphenyl

The chemical transformations which occur during carbonization can be aptly demonstrated by the coking behavior of two representative aromatic hydrocarbons, acenaphthylene (I) and p-terphenyl (II). Acenaphthylene produces an extremely well-graphitizing carbon, while p-terphenyl yields a disordered, nongraphitizing carbon.



Acenaphthylene
(I)



p-Terphenyl
(II)

As with all organic materials, the carbonization of these hydrocarbons involves the removal of substituent hydrogen and the polymerization of the aromatic carbon residue. Three methods which we have found particularly useful for following these processes are: elementary analysis, X-ray, and diamagnetic susceptibility.

Figure 1 shows a plot of hydrogen content for acenaphthylene and p-terphenyl cokes versus heat-treatment temperature. The terphenyl does not react at all below 500°C. Between 500°C and 700°C the decrease in hydrogen content is more rapid for the terphenyl, while above 700°C the acenaphthylene dehydrogenation proceeds faster.

Figure 2 presents some X-ray data obtained by Ruland ^(6,7) for the same series of samples. The growth of average aromatic layer size, L_a , is plotted versus temperature. The terphenyl shows an extremely rapid growth of L_a to 800°C, followed by a much slower growth rate at higher temperatures. For acenaphthylene, the polymerization of aromatic layers is much more gradual below 700°C but eventually surpasses the terphenyl. ⁽⁷⁾

Table III

Effects of Aromatic Structure on the
c-Spacings of 3,000°C Carbons

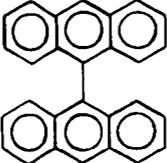
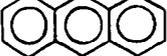
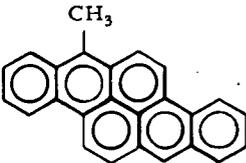
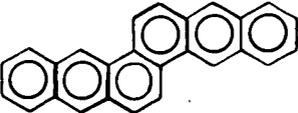
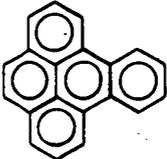
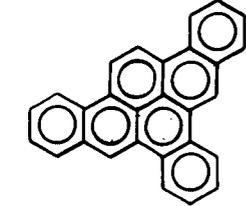
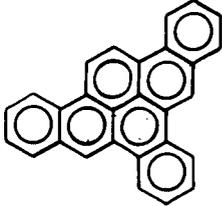
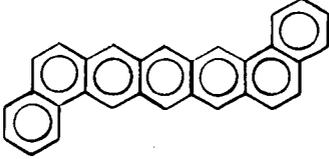
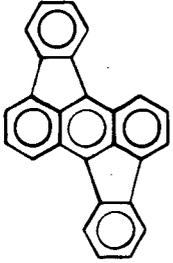
Structure	002, Å	Structure	002, Å
	3.354		3.357
			3.358
	3.354		3.358
	3.356		3.358
	3.356		3.358
	3.356		3.363

Table IV

Effects of Aromatic Structure on the
c-Spacings of 3,000°C Carbons

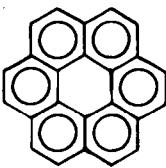
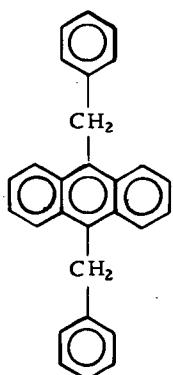
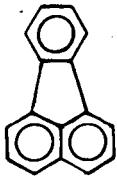
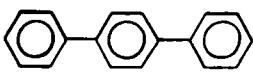
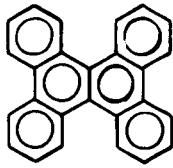
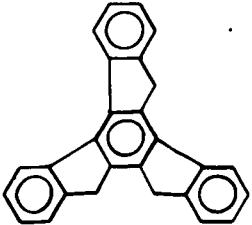
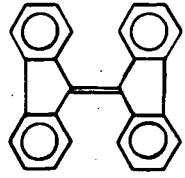
Structure	002, Å	Structure	002, Å
	3.370		3.41
	3.371		3.44
	3.373		
	3.385		3.44

Figure 3 contains a plot of magnetic susceptibility data obtained by Wagoner⁽⁸⁾ for these two compounds heat treated to 3,000°C. The terphenyl shows a slight decrease in χ between 500° and 700°C, and then an increase with temperature to a maximum at 3,000°C. The acenaphthylene shows a more pronounced dip in χ between 500° and 800°C than observed for terphenyl. This decrease in susceptibility is presumably due to a paramagnetic contribution from free radicals. The acenaphthylene exhibits a lower diamagnetic susceptibility than terphenyl up to about 1,600°C, while above this temperature the aromatic layer growth is much more rapid for acenaphthylene.

All these data indicate that the aromatic polymerization process is much more rapid at low temperature for the more disordered terphenyl system. However, the initially-formed polymers from terphenyl are structurally not as suitable for continued aromatic growth to graphite as the much smaller polymers initially produced from acenaphthylene.

The dehydrogenation-polymerization process which leads to the formation of carbon is still poorly understood. This point is illustrated by the data plotted in Figure 4. From elementary analysis and X-ray data, the number of carbon and hydrogen atoms per fused aromatic molecule have been estimated and plotted as a function of temperature for both acenaphthylene and terphenyl cokes. Also included in Figure 4 is a theoretical plot of carbon versus hydrogen content for the most highly condensed aromatic hydrocarbon molecule. Up to about 600°C the acenaphthylene and terphenyl curves fall close to the theoretical line. The reactions occurring in this region appear to involve the removal of a hydrogen atom from the aromatic ring to form a simple free radical. At 700°C and above, multiple hydrogen atoms are eliminated leaving aromatic molecules with many unsubstituted edge sites. This process appears to proceed more readily for acenaphthylene than for terphenyl.

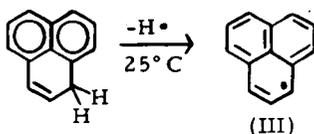
The nature of the bonding of the free electrons in these molecules is not clear. The interpretation of electron spin resonance measurements of materials in this region⁽⁹⁾ is complicated by the onset of electrical conductivity and magnetic anisotropy.

VI. Chemical Reactions of Carbonization

We can delineate the kinds of chemical reactions which occur during the early stages of coking by studying the carbonization of several aromatic hydrocarbons. Their initial reactions lead to the intermediates which control the subsequent course of carbonization. There are three types of thermal reaction processes which are important. (1) dehydrogenation, (2) rearrangement, and (3) polymerization. These reactions do not proceed in distinct steps, but occur continuously throughout the coking process. Several examples of these reactions follow.

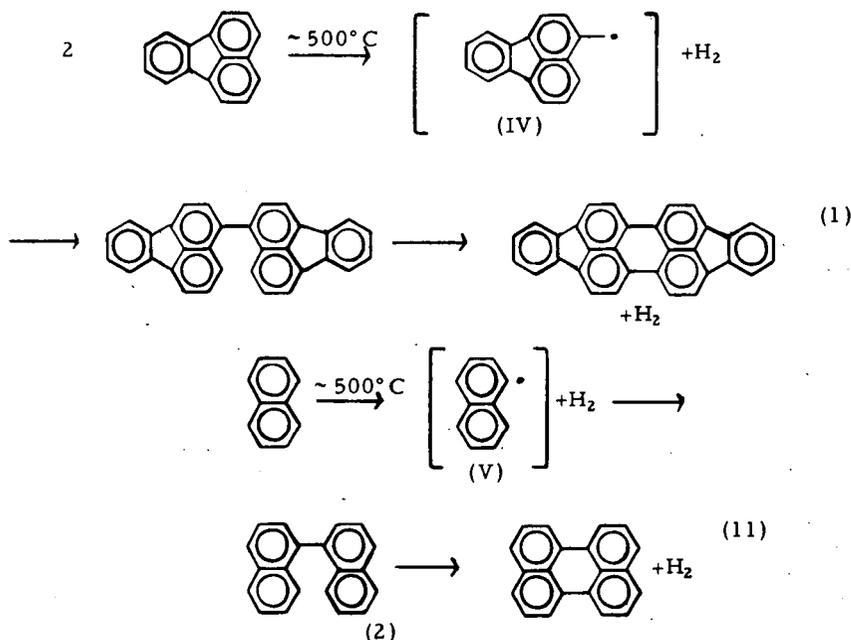
A. Dehydrogenation

The initial reaction in carbonization involves the loss of a hydrogen atom from an aromatic hydrocarbon and leads to the formation of an aromatic free radical intermediate. If the free radical intermediate is stable, it can then be detected by electron spin resonance. In the liquid state, usually all but the most stable free radicals will rearrange or polymerize. The phenalenyl radical (III) is an example of an extremely stable free radical produced by simple hydrogen dissociation reaction at room temperature.

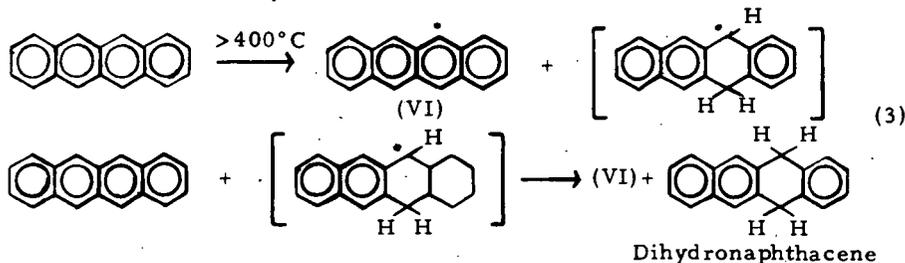


It can be well characterized by its simple ESR spectrum. ⁽¹⁰⁾

The hydrocarbons fluoranthene and naphthalene polymerize directly with the direct loss of hydrogen. The unstable free radicals (IV) and (V) can be postulated as intermediates in these reactions.

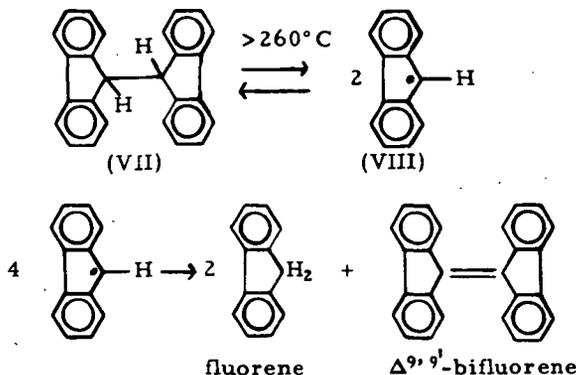


In many instances the dehydrogenation of aromatic hydrocarbons appears to involve bimolecular hydrogen transfer reactions. Hydrogenated aromatic hydrocarbons are often identified in the volatile products of carbonization. ⁽⁴⁾ These reactions usually occur at the most reactive site on the aromatic molecule. A typical hydrogen transfer sequence is illustrated for the hydrocarbon naphthacene:



The volatile 5,12-dihydronaphthacene is a major reaction product during the initial stages of reaction. It is not clear whether the intense but unresolved ESR signal observed during the onset of pyrolysis of naphthacene is due to the radical (VI).⁽¹²⁾

It should be pointed out that if there is a carbon-carbon single bond available, thermal cleavage will occur at this site. The thermally produced free radical can then participate in hydrogen transfer reactions. This reaction is illustrated in the pyrolysis of 9,9'-bifluorene (VII).

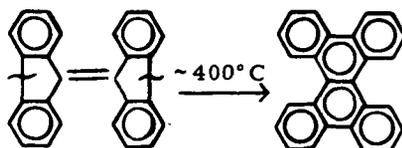


At about 260°C (VII) dissociates to produce the fluorenyl radical (VIII). This species has been detected by ESR.⁽¹²⁾ At higher temperatures a hydrogen transfer reaction leads to fluorene and $\Delta^{9,9'}$ -bifluorene as the major products. The reactive phenyl radicals produced from the pyrolysis of terphenyl also undergo hydrogen transfer processes, since benzene and biphenyl are among the reaction products.

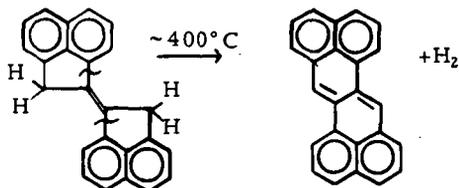
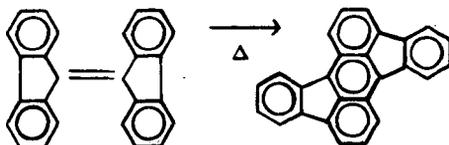
B. Rearrangement Reactions

Perhaps the most complicating features of the early stages of carbonization are the thermal rearrangement reactions. They often make it impossible to predict from the starting structure whether a given compound will produce a well-graphitizing or a disordered carbon. Thermal rearrangement usually leads to a more stabilized aromatic ring system which can then become the building block for graphite growth. Several examples of the thermal rearrangement of aromatic hydrocarbons follows.

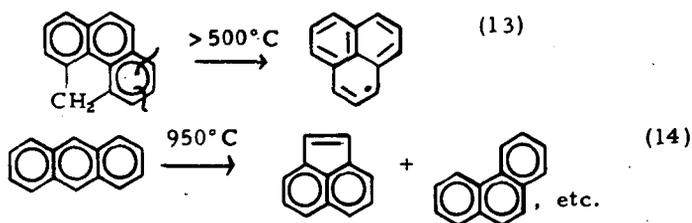
1. Conversion of $\Delta^{9,9'}$ -bifluorene to tetrabenzonaphthalene:



2. Conversion of biacenaphthylidene to zethrene.

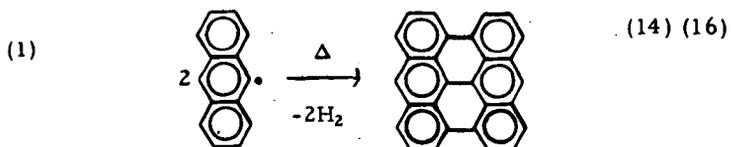
3. Formation of rubicene from $\Delta^{9,9}$ -bifluorene.

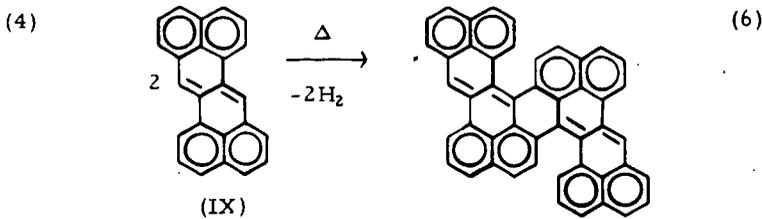
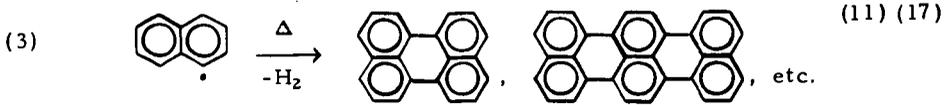
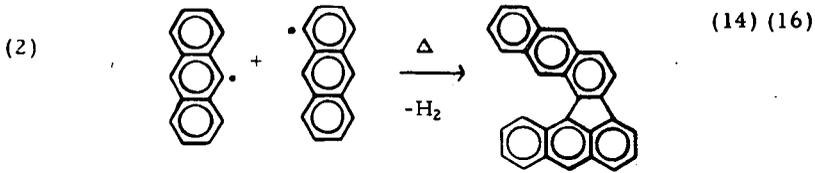
In some instances thermal rearrangement can involve a carbon-carbon bond cleavage within a condensed aromatic ring. These reactions are higher energy processes and are usually observed at very high temperatures, as in vapor phase pyrolysis.

C. Polymerization of Aromatic Radicals

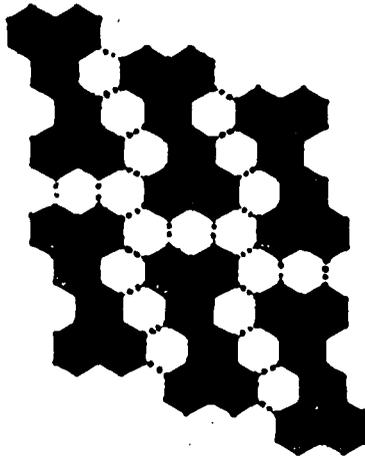
The formation of carbon involves the polymerization of aromatic free radicals. These polymerizations usually initiate in the liquid phase and lead to solid aromatic polymers. This step is an important stage in the graphitization process. ⁽¹⁵⁾

Unlike conventional polymerization reactions which rapidly increase the molecular size, the aromatic polymerization appears to proceed in steps. ⁽⁶⁾ The following examples show the formation of dimers and trimers during the first stages of polymerization of aromatic radicals.





The most important criterion for obtaining a well-ordered graphite is to have the right "building blocks" from the standpoint of reactivity and steric configuration.¹⁸ A molecule such as zethrene meets these requirements since it can polymerize at its most reactive positions and give rise to a condensed aromatic polymer without vacancies (see X). Nonplanar radical intermediates, such as those produced from $\Delta^{9,9}$ -bifluorene or p-terphenyl, lead to disordered aromatic polymers which never truly graphitize.



(X)

VII. Conclusions

The formation of synthetic carbon and graphite involves the thermal dehydrogenation and polymerization of aromatic hydrocarbons. The thermal reactivity and the course of carbonization are controlled by the structure of the starting aromatic molecule. More rapid reaction during the early stages of carbonization usually leads to a more disordered graphite structure.

Chemical studies on the pyrolysis of representative individual aromatic hydrocarbons show the importance of 3 types of thermal chemical reactions: (1) dehydrogenation, (2) rearrangement, and (3) polymerization. The nature of the final graphite and the course of carbonization appear to be related to the structure and reactivity of the aromatic free radical intermediates, which are the building blocks for subsequent carbonization and graphitization.

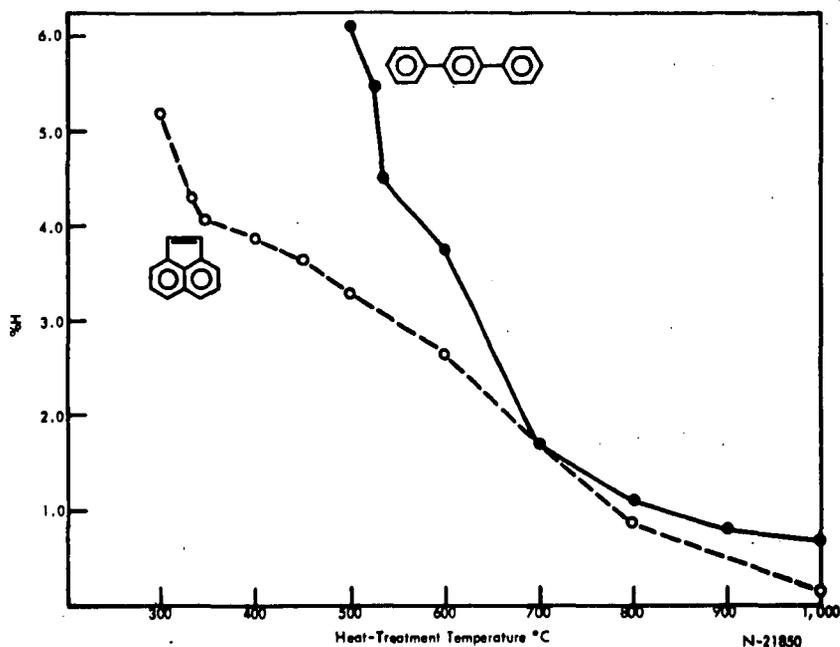


Figure 1. Elementary Analysis of the Products of Carbonization of Acenaphthylene and p-Terphenyl; Weight Percent Hydrogen vs. Heat Treatment Temperature

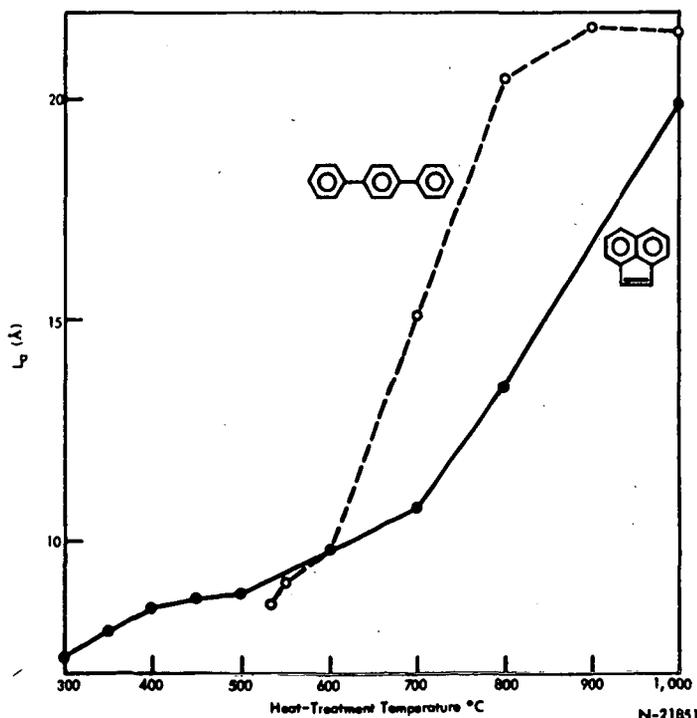


Figure 2. Aromatic Layer Growth in the Carbonization of Acenaphthylene and p-Terphenyl; L_p (Å) vs. Heat-Treatment Temperature.

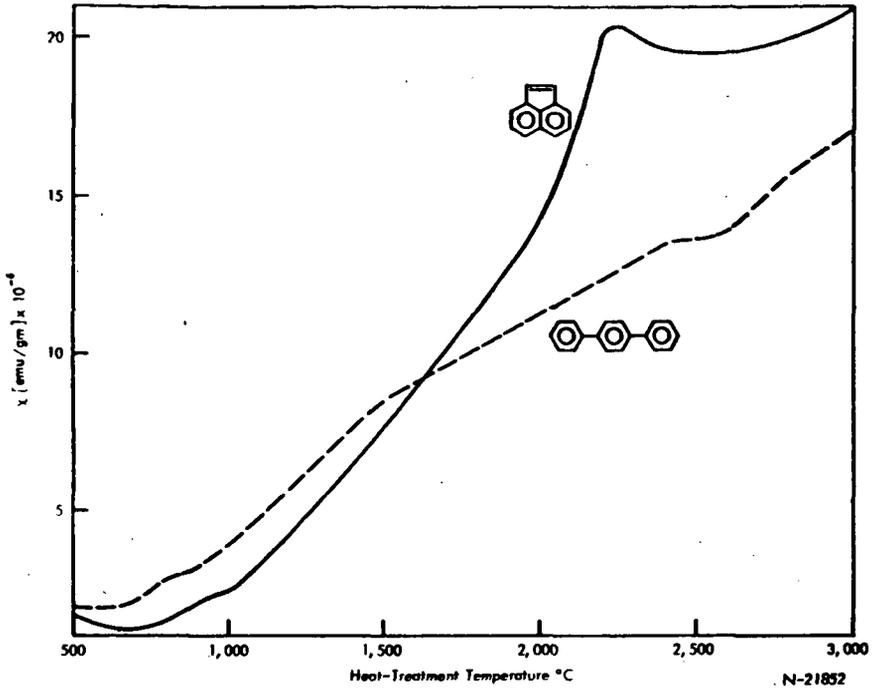


Figure 3. Static Magnetic Susceptibility of Acenaphthylene and p-Terphenyl as a Function of Heat-Treatment Temperature

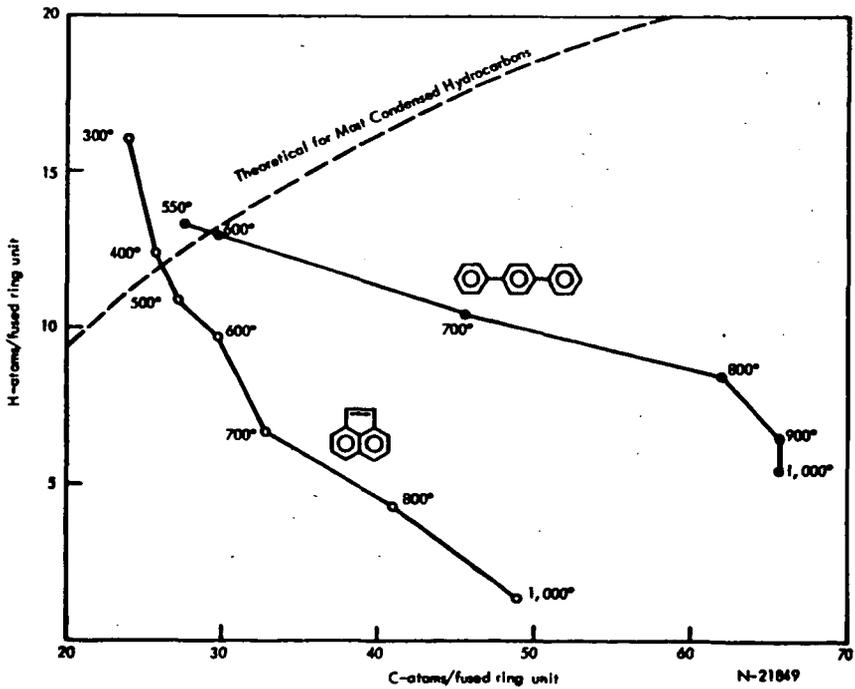


Figure 4. Dehydrogenation-Polymerization Diagram for Heat-Treated Acenaphthylene and p-Terphenyl

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