

## MODEL STRUCTURE FOR A BITUMINOUS COAL

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Studies on coal genesis and investigations of the chemical constitution of coal indicate that bituminous coal has a macromolecular structure in which a large number of basic units of condensed coal ring structures are connected by aliphatic and heteroatom bridges. Various aromatic and heterocyclic structures have been identified as constituents of the coal, and several research data suggest the presence of hydroaromatic rings.

Because of the complexity of the coal structure, it is very difficult to present a concise summary of the available structural information. One of the approaches, which has been used to summarize and to illustrate the main chemical structural features of coal, is the construction of "model coal molecules." Although many details of model coal structures are necessarily qualitative in nature and need to be updated as new research data become available, the derivation and construction of model molecular structures for coal serve an important purpose because they help the coal researcher to summarize and evaluate the consistency of experimental data from a structural viewpoint and to identify key areas where more research is needed.

An important application of model structures was reported by van Krevelen (1), who proposed formulae for the aromatic constituents of coals at different stages of coalification. More recently, Given (2), Wiser (3), and Gibson (4) have proposed model molecular structures for high-volatile bituminous coals of approximately 82 to 83% C content. While there are significant differences among these proposed structures, several of their basic features are similar: they all contain relatively small condensed aromatic ring systems, consisting on the average of two to four condensed rings; flourene- and phenanthrene-type condensed aromatic rings predominate; the nonaromatic part of the molecule consists mostly of hydroaromatic rings; and there are few alkyl (mainly methyl) groups.

The large amount of new structural information that has been obtained in recent years on bituminous coals warrants an updating of model coal structures. One of the most important coal structural properties, the carbon aromaticity, has been determined directly by solid-state carbon-13 NMR spectroscopy using  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization (5,6) and magic-angle spinning (7,8). The average size of condensed aromatic structures in high-volatile bituminous coals has been estimated on the basis of investigations of coal extracts (9,10). A new oxidative degradation technique has been developed to investigate the aliphatic structures in coal (11). Many additional new data have been forthcoming about a variety of subjects dealing with coal structural research, such as the distribution of oxygen in bituminous coal among different functional groups, the characterization of heterocyclic compounds in coal extracts, and the detailed structural characterization of coal extracts and coal liquefaction products.

The research that has been carried out on the structural characterization of coal extracts and coal hydrogenation products is of particular interest. Although the structural features of these products differ in various degrees from those of the parent coal, structural investigations with such materials can be conducted with greater accuracy because their solubility allows the application of a number of separation and analytical techniques that cannot be used with coal. The structural characterization of these materials generally consists of solvent and

chromatographic fractionation, followed by ultimate analysis, high-resolution proton and carbon-13 NMR spectroscopy, molecular weight, and phenolic-OH measurements of the fractions. Two recent structural studies of this type have been used for the derivation of model molecular structures. Bartle et al. (10) carried out the structural analysis of extracts obtained from high-volatile bituminous coal by supercritical-toluene extraction at 400°C. It was concluded that one of the extracts, which represents 27% of the coal, contains small aromatic units held together by methylene, heteroatom, and biphenyl linkages. Approximately 30% of the available sites of the aromatic skeleton are occupied by alkyl and naphthenic groups. Farcasiu (12) investigated the structure of coal liquids produced by the Solvent Refined Coal Process. The proposed average structure of one of the major fractions ("polar aromatics") consists of a benzofuran ring which has a phenyl and a naphthyl group as substituents. In other fractions the presence of benzene, benzofuran, and condensed hydroaromatic rings is indicated.

The model coal molecule described in this paper is presented with the following objectives: (1) to incorporate into the model new structural information that has become available in recent years, (2) to derive additional input data for the model molecule by means of a mathematical analysis, and (3) to test the model by comparing the experimentally observed behavior of a high-volatile bituminous coal in a number of chemical reactions with the expected behavior of the model molecule in the same reactions.

#### Experimental Input Data

The composition of a vitrain concentrate from a typical high-volatile bituminous coal was selected for this study because many basic research data are available in the literature for coals of this rank.

Input data included the elemental composition, the aromaticity of the coal, the structural formulae of the aromatic constituents, and the distribution of the heteroatoms among the different functional groups. The elemental composition and the general formula of the coal are shown in Table 1. The general formula was calculated for a unit containing 100 carbon atoms, corresponding to a "molecular weight" of about 1450. This molecular weight is, of course, arbitrary; as indicated in Figure 1, this "molecule" is connected to other parts of a larger structure (linkages-P).

TABLE 1  
CHARACTERIZATION OF HIGH-VOLATILE BITUMINOUS COAL  
USED IN MODEL STRUCTURE STUDIES

Elemental Composition (dmmf basis)	(wt %)	(atom %)
C	83.2	53.1
H	5.5	42.0
O	7.7	3.7
N	1.1	0.6
S (org.)	2.5	0.6
Total	100.0	100.0
<u>General Formula</u> (100 C basis): $C_{100}H_{79}O_7NS$		
<u>Carbon Aromaticity</u> : $f_a = 0.70$		

The value of the carbon aromaticity ( $f_a$ ) of coals of 82 to 83% C content has been measured by a number of different methods. Dryden (13) found a value of  $f_a = 0.66$  using infrared and high-resolution proton-NMR spectroscopic measurements made with a coal of 82.5% C content and with extracts of the same coal. Work by Heredy et al. (14,15), based on acid-catalyzed depolymerization of a high-volatile bituminous coal and the high-resolution proton-NMR spectra of the depolymerization products, gave  $f_a = 0.65$ . Retcofsky (9) found  $f_a = 0.73$  by investigating coal extracts using high-resolution proton-NMR spectroscopy. The investigation of a solid coal by Vanderhard and Retcofsky (5) using cross-polarization carbon-13 NMR spectroscopy gave  $f_a = 0.76$ . The average of these values ( $f_a = 0.70$ ) was used in this work.

The aromatic structures used in the construction of the model molecule are shown in Figure 2. They were selected on the basis of the following experimental information. Dryden (13) estimated that the average number of condensed rings in the aromatic part of the structure of high-volatile bituminous coal with C = 82.5% was less than three. Retcofsky (9), as well as Heredy et al. (14,15), estimated that in the same type of coal the average number of condensed rings in the aromatic part of the structure was about three. Naphthalene and phenanthrene were selected as specific condensed aromatic structures for use in the construction of the model molecule because these compounds were found frequently in coal extracts (16). With regard to the selection of specific heterocyclic constituents, the findings of Kessler et al. (16) and Sternberg et al. (17) were used. It has been shown (16) that a sizeable fraction of the organic sulfur in the coal is in benzothiophene-type structures, and much of the oxygen is in benzofuran- or dibenzofuran-type structures. Carbazole has been identified (17) as one of the nitrogen-containing aromatic structures in coal hydrogenation products.

The following distribution was used for the oxygen among the different structural positions. Of the seven oxygen atoms in the model molecule, four were located in phenolic-OH groups on the basis of the work of Friedman et al. (18). One oxygen atom was located in an aromatic ether linkage on the basis of data published by Ignasiak and Gawlak (19), and one was located in a dibenzofuran structure as discussed before (16). It was assumed that one oxygen atom was in a cyclic aliphatic ether structure.

The five constituent aromatic structures of the model molecule are interconnected by five bridges. One of the bridges is the aromatic ether linkage mentioned in the previous paragraphs; the other four are aliphatic hydrocarbon structures.

### Mathematical Analysis

No independent experimental data were used to obtain the structural characteristics of the nonaromatic part of the model molecule. This information was derived from the general formula of the model molecule and the structural formulae of the aromatic constituents of the model molecule (Figure 2) using a mathematical analysis. A method applied by Whitehurst et al. (20) was used as the basis for developing this analysis. The complete analysis will be presented in a more detailed report.

In essence, the analysis involves the construction of a matrix. The vertical columns list a series of aromatic H contents for the aromatic part of the molecule (corresponding to different degrees of aromatic substitution). The horizontal lines list different types of aliphatic and hydroaromatic substituents that can be attached to the aromatic part of the model molecule (aliphatic chains, single or condensed hydroaromatic rings - Figure 3). Both the percentage of aromatic hydrogen content of the aromatic part of the model molecule and the structural configuration of the nonaromatic part of the model molecule can be expressed in terms of the

number of positions that can be substituted in the aromatic and in the nonaromatic parts of the model molecule, respectively. Matching those aromatic hydrogen contents and aliphatic structural types in the matrix, which can accept the same number of substituents, identifies the percentage of aromatic hydrogen content of the model molecule as well as the aliphatic/hydroaromatic structural configuration.

When the procedure described in the previous paragraph is carried out using the input data given in Table 1 and Figures 2 and 3, it is found that the best match of aromatic and aliphatic substitutions is obtained at an aromatic H content of about 30%. Furthermore, the analysis indicates that most of the nonaromatic structures are composed of hydroaromatic rings of the types of Structures 4, 7, and 8 (Figure 3). On the basis of this analysis, hydroaromatic structures of these types were used to construct the nonaromatic part of the model molecule. The proposed structure of the model molecule is shown in Figure 1. The distribution of carbon, hydrogen, and heteroatoms among different structural positions in the model molecule is shown in Table 2.

TABLE 2  
CHARACTERISTICS OF THE MODEL COAL MOLECULE

Element	Total No. of Atoms	Hydroaromatic Ring								Phenolic OH	
		Aromatic		Alpha		Beta		Other Alpha Aliphatic		No.	%
		No.	%	No.	%	No.	%	No.	%		
Hydrogen	79	23	29.1	21	26.6	20	25.3	11	13.9	4	5.1
Carbon	100	70	70.0	13	13.0	12	12.0	5	5.0	-	-

Element	Total No. of Atoms	Aromatic Ether				Heterocyclic				Phenolic OH	
		No.		%		No.		%		No.	%
		No.	%	No.	%	No.	%				
Oxygen	7	1	14.3	2	28.6	-	-	-	-	4	57.1
Nitrogen	1	-	-	1	100.0	-	-	-	-	-	-
Sulfur	1	-	-	1	100.0	-	-	-	-	-	-

#### Evaluation of Chemical Reactions

It is of interest to compare the expected behavior of the model molecule in some of the chemical reactions which have been used to investigate bituminous coals with the experimentally observed behavior of high-volatile bituminous coals.

A large fraction of the hydrogen atoms, 41 of the 79 in the model molecule, are in hydroaromatic structures. Of these, 24 hydrogen atoms would be expected to evolve as hydrogen gas under the catalytic dehydrogenation conditions used by Reggel et al. (21). The experimentally obtained number for vitrain concentrates of 82.5 to 84.0% C content was 23 to 30 H atoms evolved per 100 carbon atoms.

The expected effect of reduction of the model molecule with lithium-ethylenediamine was estimated by using experimental data obtained on the reduction of a variety of organic compounds by Reggel et al. (22). It was estimated that the model molecule would take up 24 H atoms. The experimentally obtained number for vitrain concentrates of 82.5 to 84.0% C contents was the addition of 21 to 22 H atoms per 100 C atoms (22).

The expected reactivity of the model molecule in phenol-BF<sub>3</sub>-catalyzed depolymerization can be evaluated (23). The bonds on both sides of the CH<sub>2</sub>-bridge would break because they are bonded to reactive aromatic sites on a phenanthrene and on a OH-activated phenanthrene ring, respectively. Furthermore, the bond between the OH-activated phenanthrene ring and the -CH<sub>2</sub>-CH-group of the hydroaromatic ring would break. These interactions would release and solubilize the phenanthrothiophene-based fragment from the rest of the molecule. The yield of this depolymerization product would be 27%. Heredy et al. obtained a net phenol-soluble depolymerized product yield of 29% in a phenol-BF<sub>3</sub>-catalyzed depolymerization experiment using a coal of 82.4% C content (14,15).

The treatment of the model molecule with a reagent mixture consisting of trifluoroacetic acid, hydrogen peroxide, and sulfuric acid would give a mixture of carboxylic acids (11). The principal low molecular weight products would be acetic acid and succinic acid, formed in a ratio of 3 to 8 on a hydrogen basis from the oxidation of the methyl group and the two -CH<sub>2</sub>-CH<sub>2</sub>-groups. The actual testing of high-volatile bituminous coals by Deno et al. (11) showed that these two acids are the predominant products with an acetic acid to succinic acid ratio of about 1 to 3.

In summary, a model chemical structure was derived for a high-volatile bituminous coal of 83% C content, using the elemental composition, the distribution of heteroatoms among different functional groups, the carbon aromaticity, and the formulae of the constituent aromatic structures as input data. A mathematical method was used to calculate the value of the hydrogen aromaticity and to derive the formulae of the nonaromatic constituents of the model structure.

The experimentally observed behavior of bituminous coal vitrains in a number of chemical reactions was compared with the expected behavior of the model structure in the same reactions. The following chemical reactions of coal were examined: catalytic dehydrogenation in boiling phenanthridine using palladium catalyst; reduction with lithium-ethylenediamine; acid-catalyzed depolymerization using phenol-boron trifluoride catalyst; and oxidation with a mixture of trifluoroacetic acid, hydrogen peroxide, and sulfuric acid. Good agreement was found for all of these reactions between the experimentally obtained product distributions from vitrain and the product distributions that would be expected under similar conditions from the model structure.

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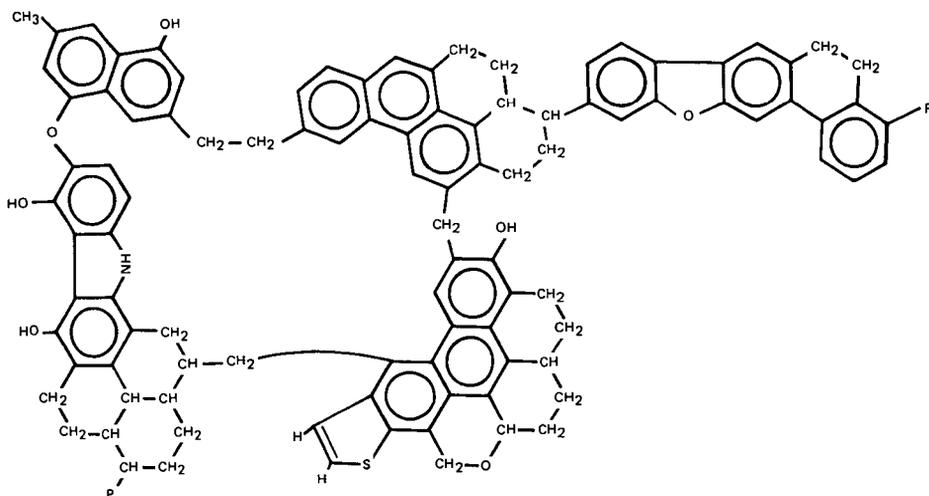


Figure 1. Proposed Structure of the Model Coal Molecule

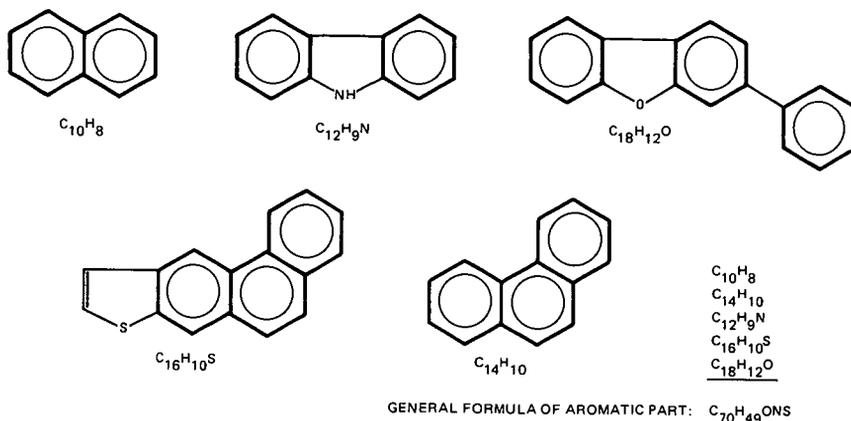


Figure 2. Aromatic Constituents of the Model Molecule

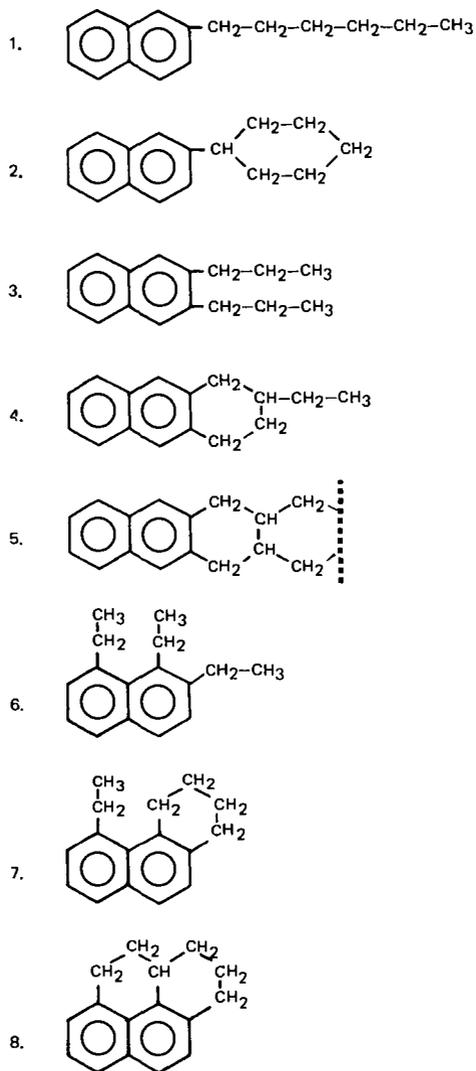


Figure 3. Basic Configurations of  $C_6$  Aliphatic Structures