Chapter 2

CHEMICAL STRUCTURE OF COALS

2.1   FUNCTIONAL GROUPS

The scope of any systematic description of coal structure is seriously limited by the large variety of coals and the variability in the chemical properties of different macerals in a single coal. Nevertheless, such a description becomes meaningful if it is postulated that the chemical properties of coal are determined by a modest number of functional groups common to all coals. Coals are then assumed to differ by their content of these functional groups. Although different macerals (vitrinite, fusinite, exinite, etc.) differ markedly in composition and reactivity, in this treatise we will not take into account such differences, since most of the pyrolysis data till now have been obtained with whole coals. However, in as much as vitrinite is the dominant maceral (more than 70% in most coals), the structural features discussed below essentially refer to the vitrinite component. The idea of representing different coals by a common set of functional groups has not been fully justified but is generally compatible with the experimental evidence discussed in the next section.

The reactivity of coal in pyrolysis, hydropyrolysis and liquefaction can be characterized by six classes of functional groups: aromatic nuclei, hydroaromatic structures, alkyl chains, alkyl bridges and oxygen groups. Sulfur and nitrogen groups are important from the standpoint of pollutant formation but do not play a significant role in the thermal reaction mechanisms, if only due to their generally low content. Each of these classes of functional groups will be discussed below drawing mainly from the recent literature.

2.1.1 Aromatic nuclei

Nuclear magnetic resonance spectroscopy (^1H and ^{13}C) of coals and coal liquids has established that 40-75% of carbon in subbituminous and bituminous coals is aromatic, the aromaticity increasing with rank. The ability to determine the aromaticity reasonably accurately has blunted or made irrelevant earlier arguments about the nature of the carbon skeleton in coal. Aromatic rings of various sizes are important building blocks of coal structure and maintain their integrity when coal is heated at temperatures as high as 700°C. Even when the aromatic content is as low as 40%, the reactivity of the aliphatic carbon is strongly influenced by proximal aromatic nuclei.

A variety of techniques have been employed to determine the size of the aromatic nuclei. Early studies employing X-ray diffraction spectroscopy, reviewed by Speight and Given (refs. 1,2) suggested that coals with up to 87% carbon (this

includes lignites, subbituminous and bituminous coals) contain mainly units with
3 to 5 condensed rings and a smaller but appreciable amount of single and double
rings. This conclusion is subject to considerable uncertainty in view of a num-
ber of assumptions that had to be made concerning the geometric arrangement and
the disposition of aliphatic substituents. Fluorescence spectroscopy of bituminous
coal extracts (ref. 3) and comparisons with model compounds suggest that the
more abundant aromatic nuclei consist of three or more condensed rings. Polaro-
graphic analysis of SRC liquids of a high volatile C bituminous coal has indicated
a small content of units with more than two condensed rings (ref. 4). Ruberto,
et al. (ref. 5) applied a variety of techniques including ^{1}H nmr, U.V. and mass
spectroscopy to a solvent extracted subbituminous coal to conclude that the aro-
matic units consist of two and three condensed rings. Since these analyses were
performed on coal liquids, drawing inferences about the structure of solid coal
involves some uncertainty.

The size of the aromatic nuclei can also be estimated from the elemental compos-
ition and ^{1}H nmr spectra of coal extracts or other coal derived liquids by a pro-
cedure known as "structural analysis", described in the next section. In as much
as structural analysis employs several assumptions, these estimates are subject
to additional uncertainty. Tingey and Morrey (ref. 6) have estimated an average
size of 5-8 condensed rings for the extracts of a subbituminous and two bituminous
coals. Whitehurst (ref. 4) has investigated the asphaltol fraction of a liquefied
bituminous coal and proposed structures consisting of one, two and three condensed
rings. Gavalas and Oka (ref. 7) have applied the Brown and Ladner structural
analysis (see next section) to the extract of a bituminous coal to estimate nucleus
size of two to three condensed rings.

The consensus emerging from the aforementioned studies is that lignites and
subbituminous coals contain nuclei with one to three condensed rings, while bi-
tuminous coals contain mostly two to four condensed rings, the degree of conden-
sation increasing with the coal rank.

Two and three condensed ring nuclei found in substituted form in coal derived
liquids include naphthalene, indene, biphenyl, furan, pyrrole, pyridine, benzo-
thiophene, phenanthrene, anthracene and various three-ring heterocycles of oxygen,
sulfur and nitrogen. Some of the rings may be partly hydrogenated constituting
what are known as "hydroaromatic" structures.

2.1.2 Aliphatic structures

The aliphatic segments of coal include aliphatic chains (methyl, ethyl, etc.),
bridges (methylene, ethylene) and hydroaromatic structures. The information
available about aliphatic structures derives mainly from proton and ^{13}C magnetic
resonance spectra and from selective oxidation, especially by the recently de-
veloped technique of Deno and coworkers (refs. 12-14).

Proton and ^{13}C magnetic resonance has been fruitfully applied to coal derived liquids: pyrolyzates, extracts, and hydrogenation products that are all modified fragments of the original coal. The modification is relatively small in the extraction, or H-donor mediated extraction at low conversions, somewhat larger in flash pyrolysis, and rather severe in liquid phase hydrogenation to distillate products.

Figure 2.1. below illustrates the information derived from nuclear magnetic resonance. The ^{1}H nmr spectrum distinguishes three major types of hydrogen:
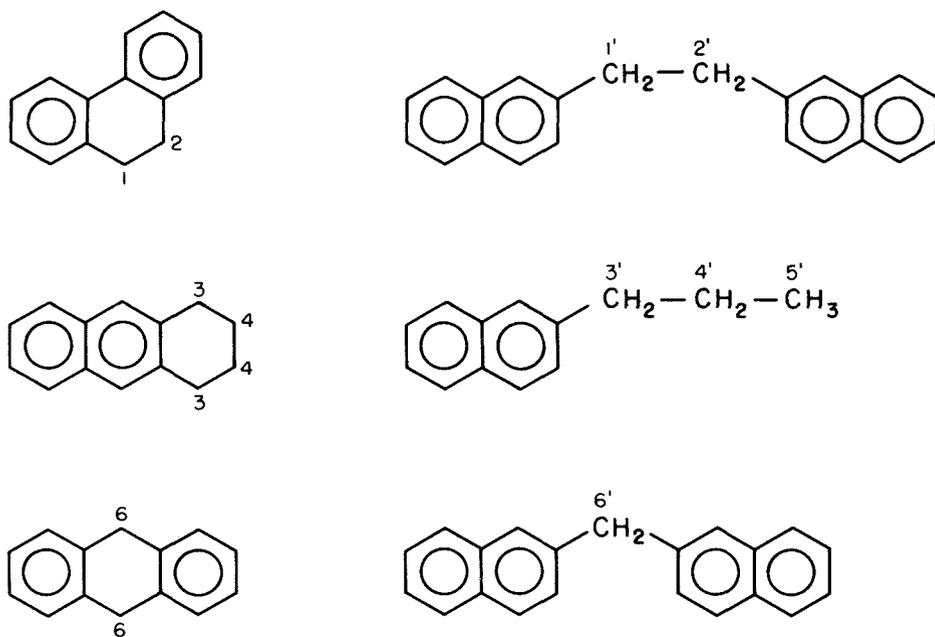
Fig. 2.1. Structural information derived from nmr spectra.

$H_{ar + o}$, aromatic and phenolic hydrogen, H_{α}, hydrogen at position α as 1,2,1´, 2´,3,3´,6,6´ of Figure 2.1 and $H_{\beta+}$, hydrogen at position β and further from the ring as 4,4´,5´ of Fig. 2.1. In recent years it has been possible to further resolve the alpha and beta region. For example, Bartle et al.(refs. 8,9) distinguished two types of α and several types of β hydrogen in the ^{1}H nmr spectra of supercritical coal extracts. Similar distinctions were made in the spectra of coal hydrogenation liquids by Yokohama et al. (ref. 10). Although high resolution ^{1}H nmr spectra provides very detailed information on hydrogen types, the interpretation of the spectra is not without some ambiguity. For example, the distinction between the hydrogens 1´ and 3 in Fig. 2.1 is somewhat uncertain.

^{13}C nmr spectra have been similarly used to distinguish among C_{ar}, and several types of C_{α} and C_{β} (refs. 9, 11), however, drawing quantitative results from these

spectra involves a larger error than in the case of ^{1}H spectra.

Deno and coworkers (refs. 12-14) demonstrated with model compound studies summarized in Table 2.1 that an aqueous solution of H_2O_2 and trifluoroacetic acid selectively oxidizes the aromatic part of a molecule, leaving much of the aliphatic part intact. Among the model compounds listed in Table 2.1 only D gives tri- and tetra-carboxylic acids. Thus, the presence of the latter acids in the oxidation products of the Illinois #6 coal was regarded as evidence that D or similar structures constitute a large fraction of the structural units of this coal. Unfortunately, no work was performed with compounds like
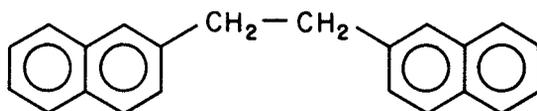
to assess the possible role of ethylene bridges. The distinction between methylene and ethylene bridges is important from the standpoint of reactivity as will be discussed in a subsequent chapter.

As shown in Table 2.1, the oxidation products from the subbituminous Wyodak coal are the same as from the Illinois #6 but the relative amounts are very different. The Wyodak coal gave a lower yield of total products and a very small yield of polycarboxylic acids. These differences are probably due to the smaller ring structures and the larger concentration of phenolic substituents in the subbituminous coal. Both coals gave a little acetic acid, evidently from methyl substituents, considerable malonic acid, presumably from methylene bridges, and considerable succinic acid. The latter acid could be due to either ethylene bridges (diarylethane structures) or 9,10-dihydrophenanthrene. It should be noted that the compounds identified in the oxidation products of tetralin are essentially absent from both coals indicating negligible participation of tetralin type structures. The results obtained by this technique are intriguing but additional model compound work is needed to reach definitive conclusions.

2.1.3 Oxygen functionalities

Oxygen plays a pervasive role in almost all aspects of coal reactivity. Nitrogen, in the form of basic groups, is involved in the secondary intermolecular forces in coal or coal derived liquids. It is also the source of much of the NO_x generated in coal combustion. Sulfur is of concern primarily as a pollutant precursor.

Oxygen is present as phenolic hydroxyl and carboxylic acid groups, aryl-aryl or alkyl-aryl ether bridges, and ring oxygen, chiefly in furan-type structures. Phenolic hydroxyls are evident in infrared spectra (refs. 15,16) and have been

TABLE 2.1

Products from the oxidation of pure compounds with aqueous $H_2O_2+CF_3COOH$ (refs. 12-14).

Compound oxidized	Yields of carboxylic acids (weight %)				
	Acetic	Propionic	Malonic	Succinic	Other
toluene	87				
ethylbenzene	19	71			
propylbenzene	5	8			butyric: 73
2-methylnaphthalene	83				
diphenylmethane			9		
diphenylethane			9	73	
tetralin					cyclohexene-1,2-dicarboxylic anhydride: 71
[structure]				14	benzenedicarboxylic acid: 70
[structure]				31	benzenedicarboxylic acid: 9, other
[structure] D			23[a]		benzenemono-, di-, tri- and tetracarboxylic acids: 200[a]
Illinois #6 bituminous	1.4[b]		2.4[b]	7.4[b]	same as above: 30[b]
Wyodak subbituminous	1.8[c]		11.4[c]	4.9[c]	same as above: 7[c]
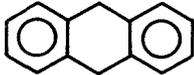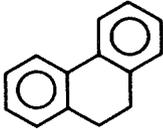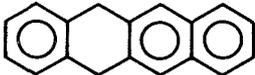
a, b, c = relative yields

quantitatively determined by a technique based on the formation of trimethylsilyl
ethers (ref. 17). They constitute one to two thirds of the oxygen in coal. The
determination of ether bridges which occur in smaller amounts has been indirect
and less reliable. Some investigators (e.g. ref. 18) have suggested that ether
bridges are the predominant links between the structural units of bituminous
coals. However, the bulk of the evidence is that aliphatic bridges are at least
as abundant. Carboxylic groups are found in considerable concentration in sub-
bituminous coals and lignites. Furan-type ring oxygen comprises a small fraction
of the total and is relatively unimportant from the standpoint of reactivity. A
quantitative determination of oxygen functional groups in several coals has been
made in connection to liquefaction studies (ref. 19).

The functional groups discussed above are organized in *modular units* (or simply
units) which are covalently linked to *coal molecules*. The coal molecule in Fig.
2.2 is shown to illustrate terminology rather than to suggest a representative
structure. We do not wish to join in the debate surrounding "coal models". A
modular unit, e.g. unit A, consists of an aromatic *nucleus*, in this case naphtha-
lene, aliphatic chains, mostly methyl or ethyl, phenolic hydroxyl and carboxylic
acid substitutents. Some units such as unit B contain a partially hydrogenated
nucleus, in this case the 9,10-dihydrophenanthrene. The modular units are linked
by *bridges*, mostly methylene, ethylene and ether. The term bridge will denote a
link that can be thermally broken. The unit C, for example, contains a biphenyl
nucleus. The bond between the two benzene rings is not counted as a bridge be-
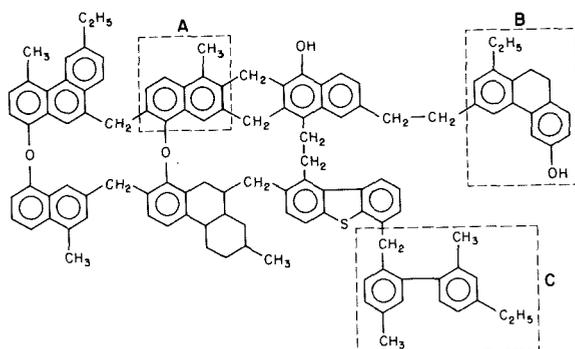cause of its high dissociation energy.

Fig. 2.2. Illustration of modular units, nuclei, bridges and chains in a coal
molecule.

It has been indicated earlier that the most abundant nuclei in subbituminous and bituminous coals consist of two or three condensed rings each, as illustrated in Fig. 2.2. It may be further inquired what is the number of modular units or the molecular weight of the coal molecule. A seasoned discussion of the evidence concerning molecular weights was presented by Given (ref. 2). The number average molecular weight of pyridine extracts of coal and of a Li/amine reduced coal (reducing aromatic rings but probably not cleaving bonds) were in the range 1,000 to 4,000. The extracts of the reduced coal represented 40-80% of the original coal by weight, hence the molecular weight of 1,000-4,000 can be considered fairly representative. The remaining insoluble material may have higher molecular weight or higher concentration of polar groups.

Assuming a molecular weight of the modular unit of about 200-250, the coal molecule should contain 5 to 20 modular units. The arrangement of these units is unlikely to be linear, because that would imply a number of bridges much lower than inferred from devolatilization experiments. A two-dimensional structure comprising sheets is certainly possible. The coal molecules are held together by secondary (non-covalent) bonds like hydrogen bonds or charge transfer acid-base complexes. Such secondary bonds are severed during extraction by pyridine or other good solvents or at elevated temperatures.

2.2 STRUCTURAL AND FUNCTIONAL GROUP ANALYSIS

The analytical data that are commonly available for coal derived liquids - extracts, pyrolyzates, and products of hydrogenation - are elemental analysis, and ^1H nmr spectra and, less routinely, ^{13}C spectra. These data can be translated to a form easy to visualize and correlate with reactivity properties by certain procedures that have become known as structural analysis and functional group analysis. The more common method of structural analysis seeks to determine features such as the size of the aromatic nuclei, the degree of substitution and the relative abundance of various types of aliphatic chains. If the molecular weight is also specified, perhaps in some narrow range, representative or "average" molecular formulas can be constructed compatible with the data. The related term functional group analysis indicates the determination of the concentration of specific funtional groups without being concerned with representative molecular formulas.

2.2.1 The Brown and Ladner method (refs. 20,21)

This simplest and best established of the structural analysis procedures utilizes the atomic ratios C/H, O/H, and the hydrogen distribution H_{ar+o}/H, H_α/H, H_β/H, i.e. the fractions of aromatic + phenolic hydrogen, alpha hydrogen and beta or further removed from the aromatic ring hydrogen. The following assumptions or specifications are made:

(i)   A certain fraction (usually 60%) of the oxygen is assumed to be phenolic in accordance with wet chemical studies indicating a phenolic fraction of oxygen in the range 0.4 - 0.6.

(ii)   The remaining oxygen (other than phenolic) is assumed to be connected to aromatic carbons as substituent (e.g. quinonic structures or methoxy groups), and not as ring oxygen.

(iii) The ratios $x = H_\alpha/C_\alpha$, $y = H_\beta/C_\beta$ are specified within reasonable limits. The values $x = y = 2$ have been used in the paper of Brown and Ladner (ref. 21).

(iv)   Biphenyl bonds are assumed absent.

(v)   Sulfur and nitrogen groups are ignored.

Subtracting the phenolic hydrogen (assumption ii) from H_{ar+o} provides the aromatic hydrogen, H_{ar}/H. The aromaticity f_α, i.e. the fraction of aromatic carbon, is then calculated with the aid of assumption (iii),

$$f = \frac{C-C_\alpha-C_\beta}{C} = \frac{(C/H)-(H_\alpha/xH)-(H_\beta/yH)}{(C/H)}$$

The next quantity of interest is the degree of substitution σ, which is the ratio of substituted aromatic carbons to the total number of peripheral aromatic carbons. This is calculated using assumptions (iv) and (v):

$$\sigma = \frac{C_\alpha+O}{C_\alpha+O+H_{ar}} = \frac{(H_\alpha/xH)+(O/H)}{(H_\alpha/xH)+(O/H)+(H_{ar}/H)}$$

Finally, if H_{aru} is the number of aromatic hydrogen and other aromatic substituents and C_{ar} the number of aromatic carbons, the quantity H_{aru}/C_{ar} which represents the ratio of H and C in the hypothetical unsubstituted hydrocarbon, is given by:

$$\frac{H_{aru}}{C_{ar}} = \frac{H_{ar} + C_\alpha + O}{C_{ar}} = \frac{(H_{ar}/H) + (H_\alpha/xH) + (O/H)}{(f_\alpha C/H)}$$

In addition to its indirect determination given above, the aromaticity can be obtained directly from ^{13}C magnetic resonance spectra. The two values were found in very good agreement in a study of various coal derived liquids (ref. 22).

The ratio H_{aru}/C_{ar} is related to the size of the aromatic nucleus. For example naphthalene, anthracene and phenanthrene have H_{aru}/C_{ar} values of 0.8, 0.714 respectively. A computed value of 0.75 might thus indicate a mixture largely consisting of naphthalene and phenanthrene or anthracene. This interpretation of H_{aru}/C_{ar} is obscured, however, by the presence of heteroatoms, biphenyl bonds and hydroaromatic nuclei such as 9,10-dihydrophenanthrene.

2.2.2 Detailed structural analysis (refs. 23,24)

Bartle and Smith (ref. 23) developed a detailed characterization of the aliphatic structures based on the ability to break down the ^{1}H nmr spectrum into the following types of hydrogen: H_{ar+o}, hydrogen in   methylene connecting two rings

(e.g. a methylene bridge); hydrogen of methylene in acenaphthene or indene as well as methylene connected to rings in highly sterically hindered positions; H_α not belonging to the two previous categories; hydrogen in $-CH_2-$, $-CH-$ groups β or further to a ring + CH_3 β to a ring; hydrogen of CH_3 γ or further to a ring. These data are supplemented by the following assumptions:

(i)   A certain fraction of oxygen is attributed to phenolic groups; the remaining is assumed to be in dibenzofurans.

(ii) Nitrogen is assumed to be in rings of the type of pyridine and carbazole, while sulfur is assumed to be in dibenzothiophene rings.

(iii) The aliphatic chains considered include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl and sec-butyl. The ratio of n-butyl to n-propyl is given some convenient value. The numbers of n-butyl, i-butyl and sec-butyl are taken to be equal.

Using assumptions (i) and (ii)the heteroatoms are replaced with C and H to produce an equivalent structure containing C and H only. Balances are then written for H_α, H_β and H which in conjunction with assumption (iii) yield the concentrations of the various aliphatic chains.

The above procedure has been used to determine *representative* structures for narrow molecular weight fractions of a supercritical coal extract (ref. 8). For example, the structure below was proposed for the methanol eluate of the extract:
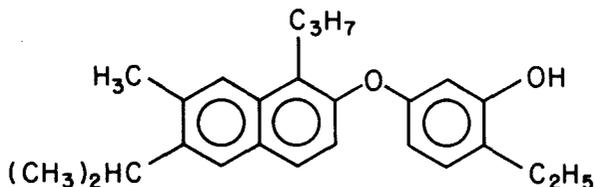
The method was recently modified and further applied to characterize coal extracts (ref. 24). By combining the information from ^{1}H and ^{13}C nmr spectra, it was possible to largely dispense with the assumptions (i)-(iii) above in an application to petroleum fractions (ref. 25). The fundamentals of ^{1}H and ^{13}C nmr spectroscopy as it pertains to complex mixtures, coal liquids in particular, has been recently reviewed by Bartle and Jones (ref. 26).

2.2.3 Computer-assisted molecular structure construction (ref. 27)

The structural parameters and the concentrations of functional groups derived by the methods of refs. 25-26 can be assembled into average or representative molecular formulas, assuming suitable molecular weight information. In the aforementioned references the construction of molecular formulas was carried out by trial and error. Since this procedure becomes impractical with increasing molecular weight, Oka et al.(ref. 27) developed a computer-based technique for generat-

12

ing molecular formulas from data on ^{1}H nmr, elemental analysis and molecular weight.

2.2.4 Functional group analysis by linear programming

As already discussed, structural analysis can be carried out at two levels. At the first level, it is sought to derive various features such as f_a or H_{aru}/C_{ar} representing averages for the mixture examined. The concentrations of various aliphatic groups can also be estimated if the ^{1}H nmr data are sufficiently detailed. At the second level, a representative or average moelecular formula is sought, compatible with the available data. Such a formula is illustrative of the type of possible structures but cannot convey the variety of different molecules that may be present even in a narrow fraction of the sample.

The thermal reactions of pyrolysis, hydropyrolysis and liquefaction can be largely understood in terms of functional groups rather than molecules, therefore the first level of structural analysis is usually sufficient. The problem can then be stated as follows: Given elemental analysis, nmr and possibly other data calculate the concentrations of a postulated set of functional groups. Invariably, the number of unknowns exceeds the number of balance equations incorporating the data, therefore the problem accepts an infinite number of solutions. To obtain a unique solution, additional assumptions in the form of values for the ratios of some of the unknowns may be introduced as in refs. 23-25. This is a convenient device but in some cases the specified values may lead to improbable, even negative values for some concentrations. Thus, some trial and error is normally required in the choice of the assumed values.

A more systematic procedure for generating meaningful solutions of the undetermined problem of functional group analysis is afforded by linear programming. Suppose that $y_1,...,y_n$ are the unknown concentrations of the selected functional groups and let the balance equations have the form

$$\sum_{j=1}^{n} A_{ij}y_j = b_i \qquad i = 1,...,m \tag{2.1}$$

where m<n. In the linear programming formulation it is required to maximize a quantity

$$J = q_1y_1 + ... + q_ny_n \tag{2.2}$$

subject to Eq. (1.1) and the obvious constraint $y_i \geq 0$. In this notation A_{ij} are stoichiometric coefficients, b_i are conserved quantities, directly derived from the data, and q_i are positive numbers chosen on the basis of experience and intuition. Suppose, for example, that y_1,y_2 represent the concentrations of methylene and ethylene bridges. A complete lack of preference as to which of the two is more abundant can be expressed by setting $q_2=2q_1$, the factor 2 deriving from the two-to-one carbon between the two bridges. To express an intuitive preference

for methylene bridges, on the other hand, one might set $q_2 = 0.2q_1$

For purposes of illustration this technique was applied to a product of lique-faction of a bituminous coal with the analytical data given in the following table.

TABLE 2.2

Data for a donor solvent extract of a bituminous coal (ref. 28).

Conserved quantity	Concentration 10^{-2} g-mols/g extract	Conserved quantity	Concentration 10^{-2} g-mols/g extract
C_{ar}	$b_1 = 5.31$	$H_{\beta+}$	$b_6 = 0.52$
C_{al}	$b_2 = 1.86$	O	$b_7 = 0.28$
H_{ar+o}	$b_3 = 2.14$	S	$b_8 = 0.16$
H_α	$b_4 = 2.21$	N	$b_9 = 0.14$
H_β	$b_5 = 1.62$		

The functional groups used in this illustration, twenty-one in number, are listed in Fig. 2.3. The coefficients A_{ij} are obtained by inspection of Table 2.2 and Fig. 2.3. A_{ij} is the contribution of functional group j (Fig. 2.3) to the conserved quantity i (Table 2.2). For example, $A_{2,13} = 2$, $A_{3,13} = -1$ because a chain $-CH_2CH_3$ replaces a group H_{ar+o} which would otherwise be attached to the aromatic carbon. Similarly, $A_{3,17} = -2$, $A_{5,16} = -1$ because the group $o-CH_3$ re-places a H_β. Table 2.4 later gives the complete matrix of coefficients A_{ij}.

As mentioned below, the choice of the coefficients q_i is a statement of experi-ence or intuition concerning the relative abundance of various functional groups. For example $q_1 = 1$, $q_2 = 5$, $q_3 = 5$, $q_4 = 1$, $q_5 = 1$ states that it is more prob-able that the mixture contains groups 2 and 3 than groups 1, 4 and 5. The re-sulting solution to the problem may still contain groups 1, 4 and 5, however. Even when $q_j = 0$, the solution may still contain $y_j > 0$. Each q-set provides a solution satisfying equations (2.1). Different q-sets do not necessarily pro-duce different solutions. If $y_1, \ldots, y_n$ and $y_1', \ldots y_n'$ are the solutions corres-ponding to $q_1, \ldots, q_n$ and $q_1', \ldots q_n'$ then the linear combination $y_j'' = \lambda y_j + (1-\lambda)y_j'$ ($0 \le \lambda \le 1$) is also a solution of equation (2.1) although it does not maximize any particular J. However, it is perfectly acceptable from our standpoint. The util-ization of the maximization problem is mainly a device to obtain feasible solu-tions.
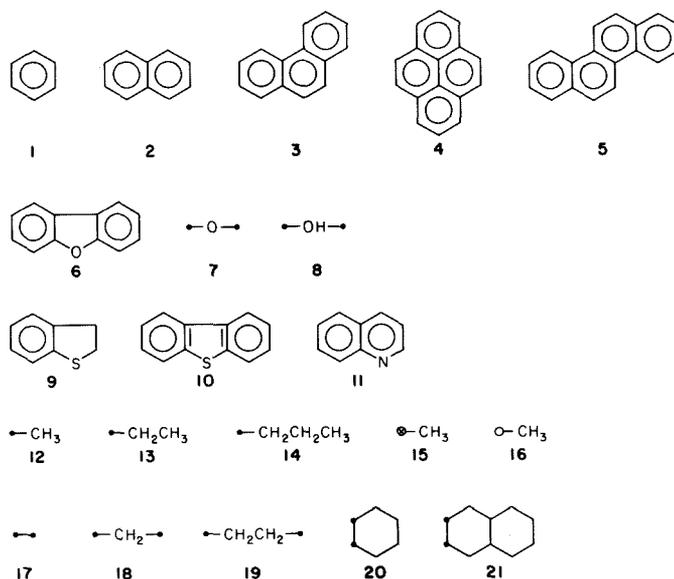
Fig. 2.3. Functional groups used in the analysis of the data of Table 2.2.
The symbols •, ⊗, ○ denote attachment to aromatic, α and β carbons, respectively.

Table 2.4 lists eleven distinct q-sets chosen to emphasize different function-
al groups. For example, sets 3 and 4 differ only in the coefficients q_2, with
set 3 emphasizing the phenanthrene ring while set 2 placing equal emphasis on
naphthalene and phenanthrene. Table 2.5 gives the results of calculations with
each of the q-sets of Table 2.4. Several features of these results should be
noted:

(i)   For any given set of q_j, the number of non-zero y_j is equal to the number
of data points, m. The remaining y_j are zero. By combining such solutions it
is possible to generate feasible solutions with a larger number of positive com-
ponents. All the q-sets of Table 2.4 produce zero values for the components y_4,
y_5, y_6, y_{10}, y_{14}, y_{20}, y_{21} without precluding, however, that some other q-set may
produce non-zero values for some of these components.

(ii) A comparison of the solutions corresponding to the q-sets 5 and 6 differing
only in q_1, q_2, and q_3 shows set 5 producing only benzene and set 6 producing
only naphthalene. The transition from benzene to naphthalene is accompanied by
a reduction in the number of biphenyl bridges.

TABLE 2.3
Matrix of coefficients A_{ij}

j / i	1	2	3	4	5	6	7	8	9
1	6	0	6	0	0	0	0	0	0
2	10	0	8	0	0	0	0	0	0
3	14	0	10	0	0	0	0	0	0
4	16	0	10	0	0	0	0	0	0
5	18	0	12	0	0	0	0	0	0
6	12	0	8	0	0	0	1	0	0
7	0	0	-2	0	0	0	1	0	0
8	0	0	0	0	0	0	1	0	0
9	8	0	6	0	0	0	0	1	0
10	12	0	8	0	0	0	0	1	0
11	9	0	7	0	0	0	0	0	1
12	0	1	-1	3	0	0	0	0	0
13	0	2	-1	2	3	0	0	0	0
14	0	3	-1	2	2	3	0	0	0
15	0	1	0	-1	3	0	0	0	0
16	0	1	0	0	-1	3	0	0	0
17	0	0	-2	0	0	0	0	0	0
18	0	1	-2	2	0	0	0	0	0
19	0	4	-2	4	4	0	0	0	0
20	0	4	-2	4	4	0	0	0	0
21	0	8	-2	4	2	8	0	0	0

16

(iii) The concentrations of the hydroaromatic groups 20,21 are zero for all q-sets. It should be kept in mind, however, that in the functional group analysis a structure like
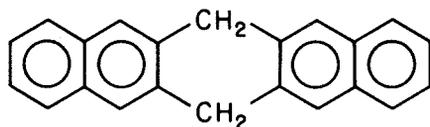
is regarded as containing two methylene bridges rather than a hydroaromatic group.
(iv) The q-sets with $q_7 = q_8$ yield concentrations $y_7 = 0$, $y_8 > 0$. After sufficiently increasing q_7 the concentrations become $y_7 > y_8 = 0$ with a simultaneous change in the functional groups 17,18 and 19 representing bridges. A solution with $y_7 > 0$, $y_8 > 0$ can be obtained by combining the solutions of q-sets 6 and 7 using equal weights. This solution has 11 positive components and is listed under column C of Table 2.5.

TABLE 2.4
Sets of coefficients q_i

	Set. No.										
	1	2	3	4	5	6	7	8	9	10	11
q_1	2	1	1	1	2	1	1	1	1	1	1
q_2	2	1	5	1	2	5	5	1	1	1	1
q_3	2	1	5	5	2	5	5	5	20	20	20
q_4	1	1	1	1	1	1	1	1	1	1	1
q_5	1	1	1	1	1	1	1	1	1	1	1
q_6	2	1	2	2	2	2	2	2	2	2	2
q_7	4	1	4	4	4	4	5	5	4	4	4
q_8	4	1	4	4	4	4	2	2	4	4	4
q_9	5	1	5	5	5	5	5	5	5	5	5
q_{10}	5	1	5	5	5	5	5	5	5	5	5
q_{11}	10	1	10	10	10	10	10	10	10	10	10
q_{12}	2	1	2	2	5	5	5	5	2	2	2
q_{13}	2	1	2	2	5	5	5	5	2	2	5
q_{14}	2	1	2	2	5	5	5	5	2	2	2
q_{15}	2	1	2	2	5	5	5	5	2	2	2
q_{16}	2	1	2	2	5	5	5	5	2	2	2
q_{17}	2	1	2	2	2	2	2	2	2	1	1
q_{18}	4	1	4	4	2	2	2	2	4	1	1
q_{19}	2	1	2	2	2	2	2	2	2	4	4
q_{20}	5	1	5	5	5	5	5	5	5	5	5
q_{21}	5	1	5	5	5	5	5	5	5	5	5

TABLE 2.5

Concentrations of functional groups (10^{-2} g-mols/gr extract) computed by linear programming for various q sets.

Group No.	q-set									
	1	2	3	4	5	6	7	8	9	C
1	6.59	6.59	0	6.59	6.59	0	0	6.59	0	0
2	0	0	3.95	0	0	3.95	3.95	0	0	3.95
3	0	0	0	0	0	0	0	0	2.82	0
4	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	2.82	2.82	0	1.41
8	2.82	2.82	2.82	2.82	2.82	2.82	0	0	2.82	1.41
9	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
10	0	0	0	0	0	0	0	0	0	0
11	1.36	1.36	1.36	1.36	1.36	1.36	1.36	1.36	1.36	1.36
12	6.21	6.21	6.21	6.21	6.21	6.21	6.21	6.21	6.21	6.21
13	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0
15	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99	5.99
16	1.73	1.73	1.73	1.73	1.73	1.73	1.73	1.73	1.73	1.73
17	6.48	8.84	2.53	6.48	6.48	2.53	0	3.66	0.83	1.26
18	4.71	0	4.71	4.71	4.71	4.71	4.13	4.71	4.71	4.42
19	0	2.36	0	0	0	0	0.29	0	0	0.15
20	0	0	0	0	0	0	0	0	0	0
21	0	0	0	0	0	0	0	0	0	0

C: average of results of q-sets 6 and 7.