

STRUCTURAL ANALYSIS OF COALS AND COAL DERIVATIVES USING
REFERENCE POLYMERS AND THE C-H-O TERNARY DIAGRAM

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INTRODUCTION

The C-H-O ternary diagram is a most effective tool for dealing with the complexities of the chemical structure and reactivity of coals and coal derivatives. Three papers submitted recently discuss the geochemistry of coals(1), the structure of coals(2) and an overview of the conversion of brown coal to oil(3) with its aid. Previously there has been only limited use of the ternary diagram in coal chemistry(4,5) except in the form of the van Krevelen H/C vs O/C diagram(6) which is a simplified version of the C-H-O ternary diagram.

The full C-H-O ternary diagram has been found to offer a clearer and more quantitative approach to problems in coal chemistry than the van Krevelen diagram. It has been of particular value in conceptualizing model molecules of coals and coal derivatives. In the theoretical approach described here these model molecules are in essence 'hybrid polymers' assembled from a wide range of reference polymers which report in the same general area of the C-H-O ternary diagram as coals(2). The reference polymers are based upon the structures of benzene, naphthalene, anthracene (phenanthrene), pyrene and dibenzanthracene as representative of the likely benzenoid structures in coal. These aromatic structures have been modified by a variety of substituents such as aliphatic chains of various lengths and hydroxyl groups as well as ortho-attached alicyclics, furan and cyclopentadiene, and the monomer structures have been linked together either directly or via ether or carbonyl groups. Varying degrees of polymerization, from the dimer to the infinite polymer of these structures, were plotted on C-H-O ternary diagrams as shown in Figure 1, where, as an example, the disposition within a segment of the C-H-O ternary diagram of reference polymers incorporating the furan structure is shown. Each inverted triangle, such as JKL, indicates the distribution of a family of polymers with the same substituent/s on each monomer unit. From right to left in Figure 1 the substituents associated with each triangle are: none, methyl, alicyclic ring plus hydroxyl, alicyclic ring and lastly hexyl aliphatic chain. The relative positions of the individuals in each family are the same within their respective triangles as illustrated in greater detail for the unsubstituted family of the triangle JKL on the right of Figure 1. The simplest individual in the family, the dimer of furan, reports at the left hand end of the baseline (J) while the infinite polymer of furan reports at the right hand end (K), with polymers of intermediate degree reporting at points along the baseline, the distance between them getting smaller with each increase in degree of polymerization. The lines within the triangle give the locations of the corresponding polymers incorporating benzene, naphthalene, anthracene (phenanthrene) and dibenzanthracene, each group occupying a line further and further removed from the base of the triangle. The polymers incorporating pyrene report on a line to the right of the triangle. The data given in Figure 1 also do duty for the corresponding thiophen structures, the difficulty of the presence of nitrogen and sulphur in coal composition being overcome by replacing them with their valence equivalents, C+H for N and O for S.

The 'law of levers' is used to assemble model coal molecules(1,7). This 'law' is the formal expression of the observation that when two or more substances are compounded together then the product has a composition that is intermediate to those of the contributing substances. Moreover the composition of the product is closer to that of the major contributor than to that of any of the others. Thus as it applies here: the total product of compounding together any quantities of any

numbers of members of a ternary system lies at the centre of gravity of their distribution on the ternary diagram. This also holds in reverse, for the decomposition of a member of a ternary system into its constituent parts.

The simplest example of the 'law of levers' is the compounding of two substances D and E into a product F in the C-H-O ternary system. This is expressed as follows.

$$\alpha \begin{pmatrix} C \\ H \\ O_D \end{pmatrix} + (1-\alpha) \begin{pmatrix} C \\ H \\ O_E \end{pmatrix} = \begin{pmatrix} C \\ H \\ O_F \end{pmatrix}$$

D and E lie at the end of a line given unit length in the ternary diagram; F, the product of their compounding, lies on the line between them at the fractional distance α from E and $(1-\alpha)$ from D. If F lies close to E then α is small and D makes only a small contribution to the composition of F while E makes a correspondingly larger contribution.

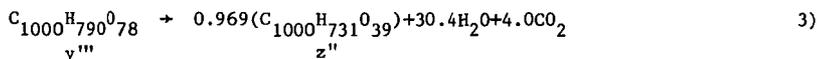
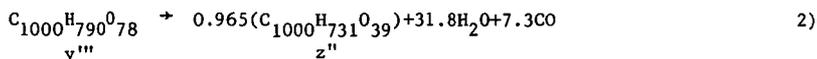
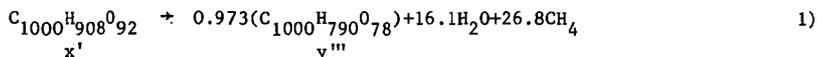
In this communication the 'law of levers' is used both notionally and by way of calculation in the application of the C-H-O ternary diagram and reference polymers to three aspects of coal science and technology.

THE CHEMICAL AND STRUCTURAL MATURATION OF AUSTRALIAN VITRINITES

It has been found that concentrates of Australian vitrinites cluster into three major compositional groups labelled x, y and z in order of increasing maturity(1). Model structures x', y', y'' and z' with compositions corresponding to the median values of each of these groups were assembled by linking together reference polymers in linear assemblies, it being assumed that the required molecular masses were infinite.

The application of these procedures led to each model coal structure having its maximum or close-to maximum possible aromatic character. These model structures are presented as lists of relative proportions of structural components per 1000 carbon atoms in Table 1. Their ternary coordinates and the coordinates of the median compositions of the corresponding cluster of vitrinites are also listed. Structures y' and y'' were assembled to demonstrate the effect on aromaticity of changing proportions of alicyclic to aliphatic structures.

The compositions of the models were expressed as molecular formulae, each containing 1000 carbon atoms. The ternary diagram and the 'law of levers' were then used to establish the reactions of Equations 1 to 3 by which coal of composition x could mature to y and then to z, forming the new structures y''' and z'' from x'.



The elimination of methane and water in these reactions leads to an increase in bonding in the residues so that the formation of y''' proceeds via the introduction of 43 new bonds into the residue of x' while further maturation to z'' requires the formation of a further 30 to 33 bonds. The structure x' contains 69 linearly linked substructures per 1000 carbon atoms so that each of the substructures of x' forms on average 1.25 new bonds on changing to y''', increasing to 2.12 to 2.17 on changing to z''.

X-ray diffraction studies of coals by Cartz and Hirsch(8) and by Hirsch(9) suggest that there is only a slow increase in aromatic character in the bituminous coal range until the rank of ~89% carbon is attained when a comparatively abrupt change in molecular structure, including a rapid increase in aromatic character, occurs.

Coupling this X-ray diffraction data with the above structure modelling based solely on compositional data suggests

(a) that the substructures in bituminous vitrinite molecules consist principally of two or three-ring aromatic structures often including furan or cyclopentadiene moieties, and

(b) that in high rank bituminous vitrinites each substructure can be bonded on average to as many as four other neighboring substructures.

COAL HYDROGENATION

The Australian Coal Industry Research Laboratories have surveyed the hydrogenation potential of a wide range of Australian coals in recent years using a batch autoclave procedure(10). Their work can be divided into two parts, an initial small program in which carbon black feed stock oil was used as the hydrogenation vehicle and a second larger program in which tetralin was the vehicle. The essential differences between these two programs can be seen in Figure 2 where the positions of the average atomic compositions of the feed coals, the vehicles and the products of both series of experiments are plotted.

The first program was characterized by the use of some high rank feed coals and probably a limited transfer of hydrogen to the coals via the carbon black feed stock oil. Indeed application of the 'law of levers' to the relative dispositions of the reaction components on the ternary diagram suggests strongly that redistribution of the hydrogen already in the coals was a most significant aspect of the reactions. Thus both the insoluble residues and the distillation residues are significantly depleted in hydrogen relative to the feed coals while the hydrogen enriched fraction of the coals, the oil and the recovered solvent, probably also enriched in hydrogen, could not be separated by distillation.

In the second program, in which tetralin was employed as the vehicle, all reaction products except the insoluble matter contained more hydrogen and less oxygen than the feed coals. The tetralin vehicle was also recovered at the end of these reactions with only slight changes to its composition. While a significant proportion of the hydrogen consumed in these reactions was lost in by-product molecules such as water and methane, another substantial proportion contributed to the formation of the coal extracts. As can be seen by further application of the 'law of levers' to Figure 2 most of this hydrogen formed part of the 42 atomic percent of the coal extract which in the average case distilled as oil, leaving a distillation residue only marginally enriched in hydrogen with respect to the parent coal.

This analysis highlights the role that the vehicle plays in reactions designed to obtain liquid fuels from coals.

ASPECTS OF THE SUPERCRITICAL-GAS EXTRACTION OF A COAL

Bartle, Martin and Williams(11) have examined the chemical nature of a supercritical-gas (toluene) extract of a low rank coal (~83% carbon) from the Markham Main seam, United Kingdom. The extract was obtained at the Coal Research Establishment of the British National Coal Board. This work is significant for the insight it permits into the structure of coal as well as for the opportunity it opens up of liquefying coal under mild conditions.

The extract, which constituted 17% of the original coal, was first fractionated by solution and chromatographic techniques. The fractions were then characterized by

elemental and functional group analysis, ^1H nmr spectroscopy and isopiestic molecular weight determinations. These data were supplemented by ^{13}C nmr, mass and ir spectroscopy. Within the frameworks of empirical formulae provided by the elemental analysis and the molecular weight determinations, the ^1H nmr spectroscopy data were used to generate structural models for the various fractions of the extract. The method of model building used by Bartle, Martin and Williams(11) was based principally on nine factors (derived from the ^1H nmr data) of which five are referred to here. These are

- i) AlkC - the number of aliphatic and alicyclic carbon atoms in a structure.
- ii) $\text{RJ}(\text{CH}_2)$ - the number of ring joining CH_2 groups in a structure.
- iii) C_R - the number of aromatic ring carbons in the 'average equivalent hydrocarbon' (aeh) corresponding to a structure.
- iv) C_J - the number of ring joining carbons in the aeh,
- v) H_R - the number of hydrogen atoms in the unsubstituted nucleus of the aeh.

Complete understanding of the meaning of these definitions requires reference to the work of Bartle, Martin and Williams(11) and to that of Bartle and Smith(12,13) who originated much of this technique when studying the structure of tars.

In the present study these factors were divided by \bar{C} , the number of carbon atoms in the formula of the structure in question. This enabled ready comparison of the factors between structures of different composition, organization and size.

The factors C_R , C_J and H_R were used by Bartle, Martin and Williams(11) to define aromatic nuclei for their model structures. This was achieved by using a three dimensional rectangular graph on which these three factors for the various fractions of the extracts were compared with those for a wide range of representative aromatic hydrocarbon types. The representative aromatic hydrocarbon type selected by this comparison was then made into a complete model structure by the addition of other structural details defined by the other factors. Two aspects of this work have been reexamined by the present author with the aid of the C-H-O ternary diagram. First the composition of the various fractions of the extract are compared with those of the macerals of the parent coal using the analytical data of Given, Peover and Wyss(14). Second, new model structures are suggested for the largest fraction of the extract, Band A_1 .

Origins of Fractions of Extract

In Figure 3 the four fractions known as Bands A, B, A_1 and B_1 , which constitute over 80% of the extract, are shown to cluster around the position of exinite while the remainder of the extract, the benzene insoluble fraction, reports near the position of the vitrinite. In fact the weighted mean composition of Bands A, B, A_1 and B_1 reports at almost the same position as that of the exinite, the two sets of C-H-O ternary coordinates being 0.46759, 0.49686, 0.03555 and 0.46728, 0.49837 and 0.03435 respectively. This close match may be somewhat fortuitous as the petrographic purity of the exinite used for elemental analysis was given as 88%. Nevertheless, it is very probable that the greater part of the supercritical-gas extract came from the exinite of the parent coal.

The benzene insoluble fraction lies on the line joining the position of the vitrinite to that of the benzyl radical $\text{C}_6\text{H}_5\text{CH}_2$ (0.500,0.500,0.0), suggesting strongly that this fraction was derived from the vitrinite by reaction with benzyl radicals from the toluene solvent. Application of the 'law of levers' gives a 13.5 atomic percent benzyl contribution to the composition of the benzene insoluble fraction, that is ~2.2 atomic % of the whole extract. While Bartle, Martin and Williams expressed the opinion that the extract was formed from the coal by mild pyrolysis during the supercritical-gas extraction process, they also reported the formation of a minor amount of bibenzyl which they attributed to some pyrolysis of the toluene used as solvent. In these circumstances some reaction of the coal with the hydrogen and benzyl radicals from the toluene must occur. The minor amount of hydrogen released may well

have played a significant but as yet unidentified role in the process, just as the benzyl radicals apparently did.

The Chemical Structure of Band A₁ Fraction

The factors derived from ¹H nmr data by Bartle, Martin and Williams(11) provide a close specification of molecular structure, particularly when combined with compositional and molecular weight data.

The C-H-O ternary diagram and the reference polymers have been used to evaluate the structure suggested for the average molecule of the Band A₁ fraction by Bartle, Martin and Williams as well as to suggest other structures that meet the specifications either alone or in mixtures with other structures.

The procedure used by the present author to assemble the model structures from the reference polymers depended on knowing the distribution of the reference polymers on the C-H-O ternary diagram and the use of the 'law of levers' for guidance in choosing combinations likely to have the right composition. In order that the somewhat indefinite molecular weight specifications were met, the model molecules were assembled mainly from halves of reference dimers though, in a few cases, the model molecules were assembled from thirds of trimers. On several occasions, when the compositions of the model molecules so assembled were not quite as required, minor structural changes such as the addition or subtraction of substitutional groups (e.g. -CH₂- and -O-) were made so that compositional requirements were met. Once a model molecule had been assembled, its five structural factors AlkC, RJ(CH₂), C_R, C_J and H_R were compared with the experimental values for the Band A₁ fraction. On some occasions the model molecules were rearranged in attempts to improve the agreement between the calculated and experimental values. This, however, was never a straightforward matter as the factors are not independent but are related in a complex manner. After some initial exploration four satisfactory results were obtained quite rapidly, two being individual model molecules and the two others being groups of four different model molecules with satisfactory average factors. The structures of these model molecules are given in Figures 4 and 5 and their compliance with the experimentally determined values of the factors are indicated by the error bar graphs in Figure 6. These model molecules satisfy the constraints as well, and probably better than, the model molecule proposed by Bartle, Martin and Williams, particularly with respect to composition. A moderate change in the structure, namely the replacement of four alicyclic carbon atoms and their hydrogens with four aliphatic carbon atoms and their hydrogens virtually eliminates this comparatively small compositional defect in the Bartle, Martin and Williams model molecule, a simplified version of which appears in Figure 5.

All the model molecules have a certain general similarity confirming that the factors derived from the ¹H nmr data coupled with compositional and molecular weight data can only arise from a narrow range of molecular structures. Improvement in molecular weight determinations would appear to be the major need for further restricting and thus improving the choice of structures. The structural features of these model molecules are most easily appreciated by inspection of those labelled M and N in Figure 5. These were formed by 'averaging' the previously formed model molecules. Both M and N are needed as the 'average' includes only half of an alicyclic ring. Two features stand out. First, the dominance of aliphatic over alicyclic components in the non-aromatic part of the structures. Second, the extended nature of the aromatic cores of the molecules which, however, would probably yield derivatives of mainly naphthalene and benzene on degradation because they incorporate pentacyclic structures.

The aliphatic portions of all the model molecules are shown in Figures 4 and 5 as single chains for convenience only. Their real distribution would be quite diverse(11) and could well extend to cross-linking. This could occur either

between otherwise unattached aromatic sub-structures or within a single structure, taking a partly alicyclic form incorporating some other number of carbon atoms than the usual five or six. Either of these possibilities would probably require a simplification of the aromatic portion of the structure, such as the opening of a pentacyclic ring, for the maintenance of the structural factors near the required values.

CONCLUDING REMARKS

The C-H-O ternary diagram has been shown previously to provide most useful insights into the chemistry of fossil fuels. Here it has been employed in conjunction with a series of reference polymers to generate information on the structural aspects of both coal maturation and the derivation of liquid fuels from coal.

The use of the C-H-O ternary diagram with the reference polymers provides a planar system of analysis which reduces the need for the three dimensional rectangular system used by Bartle, Martin and Williams(11) to interpret the structural factors derived from their ^1H nmr data. It is both easy and useful to work out the structural factors as each model molecule of correct composition is formed. Often the results indicate the changes needed to a trial model to produce a better one. Alternatively the results may indicate plainly that particular types of trial models cannot be improved. The molecular structures suggested both in this communication and by Bartle, Martin and Williams are remarkably specific. They should be accepted with a modicum of caution as no allowance has been made for the normal uncertainty of compositional data or for some assumptions made of necessity by Bartle, Martin and Williams in the interpretation of their ^1H nmr data.

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Table 1

Proportions of Structural Features Constituting C₁₀₀₀ Linearly
Linked Model Coal Molecules Together with Their Ternary
Coordinates and Those of the Median Coals Aimed At

Structural features	x'	y'	y''	z'
benzene	27.3	13.5	15.7	0
naphthalene	30.3	18.9	23.6	0
anthracene	6.1	18.9	18.3	6.4
dibenzanthracene	3.0	8.1	7.9	32.1
cyclopentadiene	12.1	8.1	10.5	9.6
furan	9.1	10.8	10.5	9.6
aliphatic - CH ₂	142.4	56.8	162.3	118.6
alicyclic - CH ₂	157.6	162.2	0	25.6
-O-as hydroxyl and ether	48.5	46.0	41.9	16.0
>C = O groups	27.3	21.6	26.2	12.8
quinone oxygens	6.1	0	0	0
		Coordinates		
Model coal molecule				
C	0.50000	0.53546	0.53501	0.56522
H	0.45455	0.42258	0.42297	0.41304
O	0.04545	0.04197	0.04202	0.02174
Median coal				
C	0.50000	0.53500	0.53500	0.56500
H	0.45400	0.42300	0.42300	0.41300
O	0.04600	0.04200	0.04200	0.02200

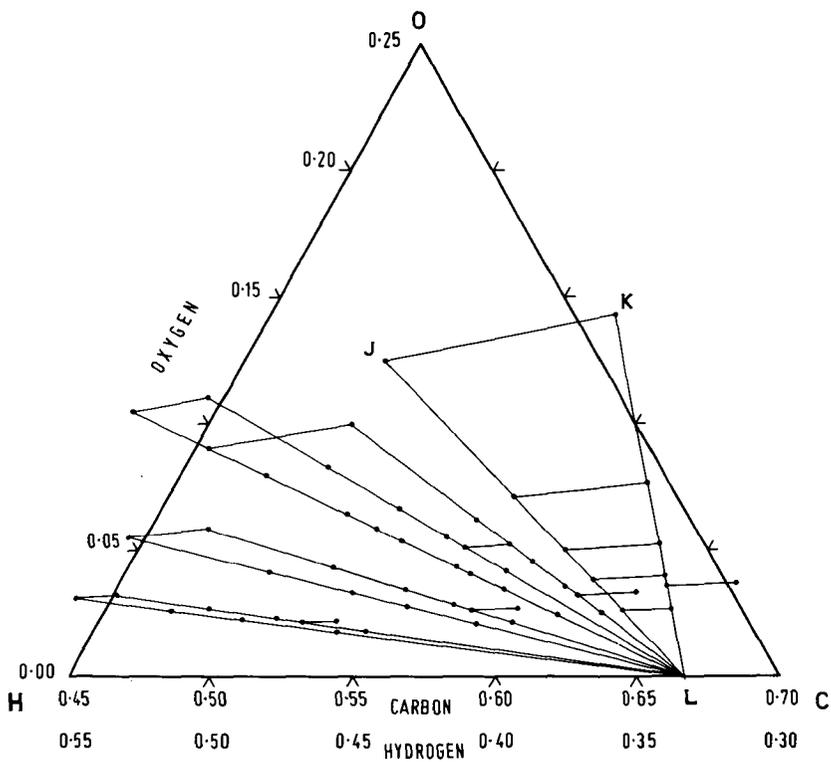


Figure 1. The distribution of the furan-containing reference polymers on a segment of the C-H-O ternary diagram. C, H and O values given as atomic fractions.

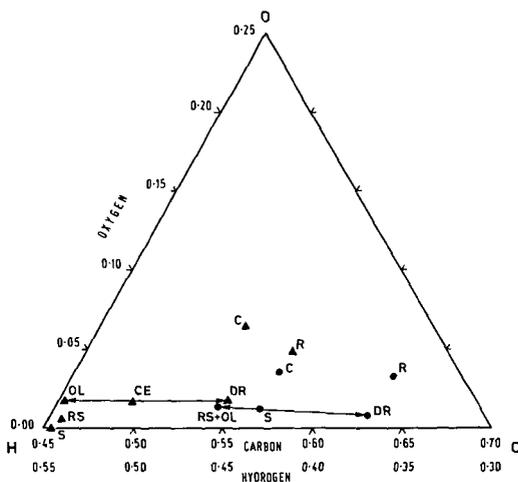


Figure 2. ACIRL coal hydrogenation results. \blacktriangle , components in tetralin experiments; \bullet , components in carbon black feed stock experiments; CF, coalfeed; S, solvent; RS, recovered solvent; CE, coal extract; OL, oil; DR, distillation residue; R, insoluble residue.

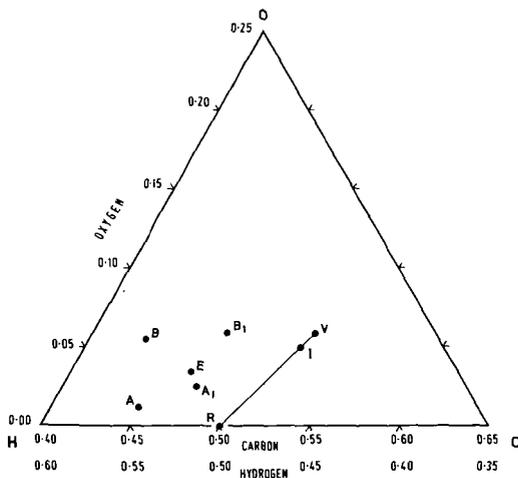
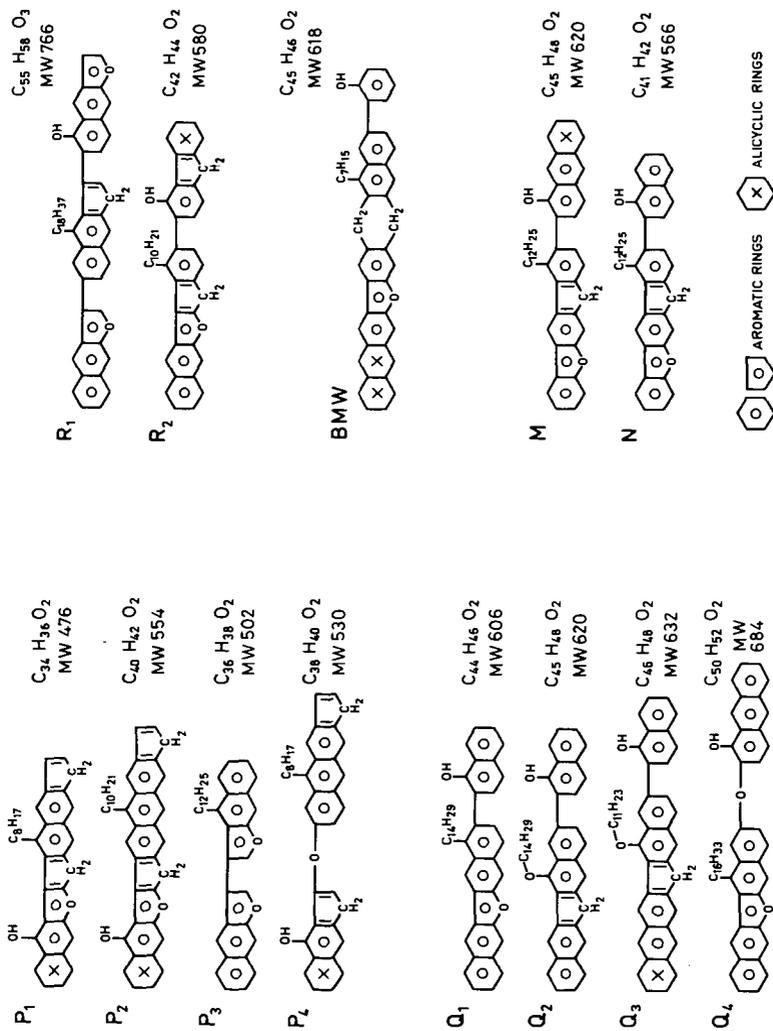


Figure 3. Super critical-gas extraction of coal. Locations of Bands A, B, A₁, B₁, I, benzene insolubles; R, benzyl radical; E, Markham Main exinite; V, Markham Main vitrinite.



Figures 4 and 5. Structures of model molecules with compositions approaching that of Band A1.

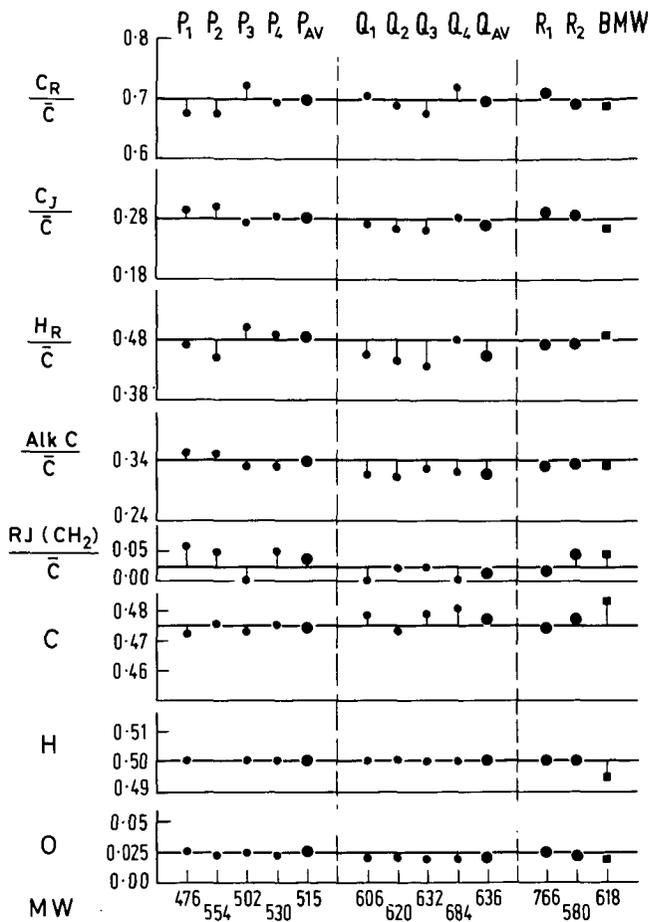


Figure 6. Error bar graphs of structural factors and compositions for the model molecules of Figures 4 and 5 and the averages, P_{AV} and Q_{AV} , for two groups of them.