INSIGHTS INTO THE CHEMICAL STRUCTURE OF COAL FROM THE NATURE OF EXTRACTS

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ABSTRACT

As part of a National Coal Board programme aimed at deriving transport fuels and chemical feedstocks, the chemical structure of extracts from coals of varying rank are being studied. This information helps to give an insight into the structures of the original coals. Supercritical gas extraction yields, with little degradation, large quantities of material (20-50% d.a.f. coal), which may be compared with products obtained by: (a) a less mild process employing hydrogen-donor solvents such as hydrogenated anthracene oil, and (b) simple solvent extraction. The molecular weight range of the extracts (300-2000) makes separation by solvent fractionation and adsorption chromatography, followed by examination by NMR spectroscopy, the most appropriate analytical methods for their structural characterisation. The SCG and solvent extracts consist of small aromatic clusters joined by methylene and heteroatom bridges. The aliphatic constituents are principally alkyl groups for which chain length decreases with increasing rank, so that aromaticity correspondingly increases from 40-80%. The main chemical structures present in the various extracts are independent of extraction conditions. This, taken with the significantly different MW distributions, allows important conclusions to be drawn as to the nature of the fragments present in the original coals.

1. *INTRODUCTION*

Investigations into the organic chemical structure of coals can broadly be divided into three groups:

(i) physical methods, for example infra-red spectroscopy (1) and solid state ^{13}C NMR (2), which can be used to obtain information about the chemical groupings;

(ii) chemical methods, for example oxidation (3) and depolymerisation using boron trifluoride and phenol (4), which give information about the size of aromatic clusters and about substituents and linking groups in the coal molecule;

(iii) characterisation of extracts, for example the structural analysis of extracts obtained in high yields can be used to deduce information about the parent coals.

The Coal Research Establishment of the National Coal Board is currently developing two coal liquefaction processes. These involve the extraction of coal with (a) supercritical gas (SCG) at temperatures up to 720 K and pressures of about 200 bar (5-7) and (b) coal-derived hydrogen-donor solvents (HDS) at temperatures around 670 K, but at pressures close to ambient (7). The extracts obtained from both processes are then hydrocracked and further reformed to the

desired liquid products. SCG extraction with aromatic solvent yields up to 50% d.a.f. coal as tractable homogeneous extract together with reactive char. The extract is produced by mild thermolysis of the coal and is volatilised by the presence of an SCG (8). HDS extraction removes up to 90% of the organic part of the coal by a mechanism thought to involve stabilisation of the free radicals formed by hydrogen donation from the solvent (9).

Moderate conditions are experienced by coals in both processes so that extensive breakdown and reformation of coal molecular structures during extraction is unlikely to occur, although limited thermolysis and chemical bond cleavage must be taking place for the bulk of the coal to become soluble in the solvent media. However, rapid removal of molecular fragments from the extraction zone in the gas extraction process and stabilisation of radical species by hydrogen donation in the HDS process (9) probably prevent the occurrence of reformation, recombination and further degradation reactions. Therefore, the structures of molecules released and recovered as extract may well be representative of the molecular building blocks of the original coals.

Conversion of extracts to more valuable low boiling oils has necessitated a study of their molecular structures and advantage has been taken of these investigations together with some structural studies conducted on coal extracts prepared by simple solvent extraction to make some predictions about the molecular structures of parent coals.

2. EXPERIMENTAL AND RESULTS

2.1 Coals and Their Extraction

In this investigation seven coals were used (three bituminous, one perhydrous and three lignitic) and the yields of the extracts prepared from these are shown in Figure 1. For convenience of presentation, the bituminous coals and lignites have been labelled 1, 2 and 3. Soxhlet extractions were performed with toluene and pyridine for periods between 25 and 250 hours. SCG extractions were carried out semi-continuously with toluene and other aromatic solvents at temperatures between 620 and 690 K (10). Bituminous coal 1 was also extracted with hydrogenated anthracene oil (HDS) at 670 K.

2.2 Fractionation of Extracts and Analyses

The extracts were separated into benzene insolubles (BI), asphaltenes and n-pentane solubles (n-PS) fractions (10). In some cases the n-PS fraction was further fractionated by silica-gel adsorption chromatography into paraffins, aromatics (low phenolic -OH content) and polars (high phenolic -OH content). Some BI fractions were silylated (11) to render them soluble in tetrahydrofuran and chloroform for molecular weight determinations and NMR spectroscopy respectively. Silylation was especially valuable in view of the large BI fractions in many of the extracts (see Figure 1).

Most fractions were subjected to ultimate, MW and phenolic -OH analyses. Number average MWs were determined isopiestically using an Hitachi-Perkin-Elmer 115 instrument. Phenolic -OH contents were measured by enthalpimetric titration. Some typical results for these analyses are given in Table 1.

2.3 Spectroscopy

^{1}H NMR spectra were obtained at 60 MHz using an Hitachi-Perkin-Elmer R24B instrument with chloroform-d and pyridine-d_5 as solvents. Figure 2 shows the ^{1}H NMR spectra of the asphaltenes from the HDS extract of bituminous coal 1 and of the SCG extracts of bituminous coal 3, perhydrous coal and lignite 1.

Fourier transform ^{13}C NMR spectra were obtained at 45 MHz using a Bruker WH 180WB instrument with chloroform-d as solvent. Chromium acetylacetonate was added to the samples and gated decoupling was employed to obtain reliable quantitative data (12). Figure 3 shows the ^{13}C NMR spectra of the asphaltenes from the HDS extract of bituminous coal 1 and of the SCG extracts of bituminous coal 3, the polars from SCG extract of perhydrous coal and the aromatics from SCG extract of lignite 3.

2.4 Structural Analysis Scheme

The distribution of hydrogen types determined by ^{1}H NMR, as shown in Figure 2, has been combined with elemental and phenolic -OH analyses and MW to give the numbers of the various atoms or groups in the average molecule; these have then been used to derived the structural parameters defined in Table 2.

The number of aliphatic carbon atoms (C_{al}) was obtained using the assumed atomic H/C ratios (a,b,c and d) for the different aliphatic environments measured by ^{1}H NMR. These were chosen by consideration of the groups contributing to the bands in the ^{1}H NMR spectra. For example, since only methyl groups contribute to the H band, d = 3 and similarly, since mainly methylene groups contribute to the $H_{,2}$ band, a = 2. The choice of values of b and c was more difficult since they were found to be dependent on coal rank, both methylene and methyl groups being major contributors to the H and H bands. Therefore, b and c were chosen to give C_{al} and f_a (aromaticity) values consistent with the direct measurement of these parameters by ^{13}C NMR.

Values of the structural parameters for a selection of the asphaltenes, BI and aromatic fractions of typical extracts are given in Table 3. The structural parameters have been used to construct representative structures for some of the asphaltenes and these are given in Figure 4. Where necessary, more than one structure has been given so that a better fit is achieved with the calculated structural parameters. The structures illustrated must, of course, be considered as averages of the many species present in each fraction.

3. DISCUSSION ON COAL EXTRACTS

3.1 Yields and Molecular Weights

The results of extraction and fractionation given in Figure 1 are not comprehensive, but present a range of values for the processes under investigation. Comparison of the compositions of the various extracts is of considerable interest since they are derived by using widely varying degrees of extraction severity from coals with markedly different characteristics.

Extraction of coals with toluene gave very small yields of soluble materials (5% d.a.f. coals) while pyridine gave much larger yields (up to 20% d.a.f. coal), which increased with increasing coal rank. These findings are in agreement with those of previous investigators (13,14).

Extraction with toluene and with pyridine is likely to involve only solvation of low MW molecules trapped in the coal matrix and some disruption (particularly with pyridine) of hydrogen bonds with consequent release of materials of higher MW and polarity. Thus the pyridine extract of bituminous coal 3 contains a large proportion of BI of MW about 1500.

At temperatures between 620 and 690 K, SCG extraction of bituminous coals yielded quantities of BI comparable to those obtained by pyridine extraction. The quantities of these BIs increased with increasing extraction temperature.

The large proportions of benzene soluble fractions always present in SCG extracts indicate that, apart from simple solvation and hydrogen bond breaking, some thermolysis of chemical bonds may have occurred, although little gas was generated during extraction.

In HDS extraction the material obtained in excess of that released by SCG extraction is largely benzene insoluble with a MW 2000. Such high MW material is too involatile to be dissolved in supercritical solvents.

For the lignites, the overall picture is somewhat similar to that of the bituminous coals except that both pyridine and SCG extraction gave much smaller quantities of BI material (MW 1000). No BIs were obtained by SCG extraction of lignite 3 at 610 K, but at 690 K a small amount (5% d.a.f. coal) was produced. These findings imply that MW distributions are a function of coal rank.

The perhydrous coal yielded four times more BIs by SCG extraction than by pyridine extraction, but the MWs of both fractions are close to 2000. This suggests that the large quantities of both benzene soluble (30% d.a.f. coal) and BI (20%) material could be produced from the perhydrous coal by mild thermolysis of, for example, long alkyl bridging groups between aromatic nuclei and that the high MW benzene insoluble material is more structurally amenable to dissolution in the SCG than are the BIs from bituminous coal.

3.2 Elemental and Functional Group Analyses

Table 1 shows that for all the extracts, the solvent separation procedure has given fractions with decreasing H/C ratio and increasing heteroatom content going from n-PS to BI material. Silica gel adsorption chromatography of PS yielded aromatic fractions which contain little phenolic -OH.

The overall H/C ratios of the extracts from the lignites and perhydrous coal are significantly higher than those of the bituminous coals. The extracts from lignites generally have much larger heteroatom contents than those from the bituminous and perhydrous coals. The heteroatom contents of all the pyridine and SCG extracts of bituminous and perhydrous coals are similar to those of the parent coals. For the SCG extracts of bituminous coals H/C varies little as the temperature is increased from 620 to 690 K. However, the SCG extract of lignite 3 shows a significant decrease in heteroatom content at 690 K which suggests that a number of the heteroatoms are in structures, such as carbonyl and aliphatic ethers, which are easily cracked. The heteroatom contents of the HDS extracts of the bituminous coals are slightly less than those of the parent coals and also of the corresponding SCG extracts; this implies that the digestion conditions have resulted in some chemical cleavage of bonds containing heteroatoms.

Table 1 indicates that acidic hydroxyl groups generally account for approximately 65% of the oxygen in the bituminous and perhydrous coal extracts, while acidic hydroxyl (i.e. phenolic and carboxyl) groups account for well under half the total oxygen in most of the pyridine and 610 K SCG extract fractions of lignite.

3.3 NMR Spectra

The NMR spectra show that the extracts of bituminous coals (Figures 2a and b, 3a and b) contain fewer aliphatic groups than the extracts of lignite (Figures 2c and 3c), the ^{1}H spectra of the former containing much more prominent H bands. The sharp bands at 1.3 ppm in the ^{1}H spectra and at 29.7 ppm in the ^{13}C spectra of the lignite and perhydrous coal extracts are attributed to methylene groups in alkyl side chains containing at least 8 carbon atoms (15).

The bands between 1.5 and 2.0 ppm in the ^{1}H spectra of the HDS bituminous coal and lignite extracts indicate the presence of hydroaromatic groups. These groups probably result from hydrogen transfer reactions occurring in the former case, but in the latter they possibly originate from the parent coal. A comparison of the 13C spectra shows that the SCG extract of bituminous coal contains a greater proportion of bands between 18 and 22.5 ppm; these are largely attributed to methyl groups (15).

In the ^{13}C spectra of the HDS and SCG extracts of bituminous coal (Figures 3a and b), the intensity of the C_{AR}-O band between 148 and 168 ppm, together with the absence of carbonyl resonances between 170 and 210 ppm, indicate that virtually all the non-phenolic oxygen is present in aromatic ether groups.

3.4 Extract Structures

The structural parameters (Table 3) and the average structures (Figure 4) highlight the differences in the chemical nature of the various extracts. The aliphatic carbon contents of the lignite and perhydrous coal extracts are significantly larger than those of the bituminous coal extracts, but methyl is the main constituent in all the extracts. As previously described, long alkyl side chains are prominent in the extracts of the lignites and perhydrous coal, occurring mainly in the low MW fractions. The average alkyl chain length (CL) for extracts of the lignites and the perhydrous coal is between 2.5-4 and decreases to 2 for those from the bituminous coals. The overall aliphatic H/C ratio is approximately 2 for all the extracts, except those obtained with pyridine and by SCG extraction of the bituminous coals where the ratio is 2.5 because of a greater proportion of methyl. For all extracts decreases with increasing MW.

The degree of condensation for the lignite SCG extracts (dC = 0.73-0.82) indicates that the aromatic nuclei consist mainly of single rings. The dCs for the SCG extracts of the perhydrous and bituminous coals (0.6-0.7) are characteristic of 1-3 ring aromatic nuclei in the molecules. For the bituminous coals, little variation occurs, either in the nature and content of alkyl groups, or in the degree of condensation of aromatic nuclei between simple solvent and SCG extracts. The aromatic structure of the HDS extract is slightly more condensed than those of the solvent and SCG extracts.

4. CONCLUSIONS ON ORGANIC COAL STRUCTURES

The determinations of the structural characteristics of extracts representing large proportions of the organic matter in the coals from which they were derived make it reasonable to draw conclusions about the molecular constitution of the coals themselves. Arguably the thermal treatments used in the two NCB extraction processes will cause some cleavage of less stable molecular bonds. However, the extraction temperatures used are only around 670 K and the molecular fragments once formed are either volatilised by the SCG and removed or stabilised by the presence of hydrogen-donor species. Furthermore, it has been shown that the structures of SCG extracts of bituminous coal are similar to those of the corresponding solvent extracts.

Results of this structural study indicate an increase in aromaticity of the extracts (0.4-0.8) with increase of coal rank which is consistent with extensive data for coals (16). Further, the average sizes of aromatic clusters in the extracts are in general agreement with published work on these types of coal. For example, Hayatsu et al (17) found that alkaline cupric oxide oxidation of lignites produced mainly single ring aromatic carboxylic acids, while bituminous coals gave substantially 2 and 3 ring derivatives.

The indications from our work are that coals consist of aromatic ring clusters of varying sizes and degrees of condensation, depending on coal rank, interlinked by simple molecular bridge systems and by hydrogen bonding. This evidence contrasts with some of the earlier data which suggested that hydro-aromatics and, in particular, adamantyl groups (18,19) are major contributors to coal structure. There is certainly no evidence of adamantyl groups being present in our coal extracts. Such structures would give rise to broad bands in the ^{1}H NMR spectra between 1.0 and 2.0 ppm, probably centred at 1.5-1.7 ppm (20), and not the sharp bands centred at 1.3 ppm as observed in Figure 2. Apart from simple bridge systems, alkyl groups must account for the majority of aliphatic carbon present in the coals used. Simple bridge systems, such as methylene, were deduced by Heredy et al (4) from the products obtained by depolymerisation of coal with phenol and boron trifluoride.

Information on the structure of the parent coals may be obtained from the molecular weight data for various extract fractions. Extracts from all of the coals contain large quantities of benzene soluble material released by mild thermolysis at temperatures between 620 and 690 K. The quantities yielded represent a far greater proportion of low (600) MW material than was previously thought to be present in the coals on the basis of results from simple solvent extraction and low temperature carbonisation. If extensive thermolytic degradation of the basic coal structure has not occurred during extraction, then this benzene soluble material must be representative of lower MW structural units in the coals.

The BIs from the SCG extracts of the lignites and perhydrous coals are predominantly of high MW (2000). Those from pyridine and HDS extracts of the bituminous coals are similar, being 1500 and 2000 respectively. However, the fact that no BI material was obtained by low temperature (610 K) SCG extraction of lignite supports the view that coalification processes involve reduction in molecular size of unit structures brought about mainly by loss of large alkyl side chains with aromatisation procedures accounting for increasing size of ring clusters (21).

5. ACKNOWLEDGEMENT

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TABLE 1 - Analyses of Typical Extract Fractions

	Bituminous Coal						Perhydrous Coal			Lignite					
	HDS 1		SCG 2 620 K	SCG 3 670 K		Py 3	SCG 690 K			SCG 1 690 K		SCG 2 610 K	SCG 3		
	As	BI	Ar	As	BI	BI	n-PS	As	BI	As	BI	Ar	610 K Ar	690 K As	690 K BI *
% C	86.1	84.5	88.4	82.2	80.5	76.7	86.2	83.2	82.5	80.2	77.5	84.0	79.8	79.7	79.2
% H	6.5	5.5	8.4	6.6	5.8	5.3	10.0	7.3	6.6	7.4	5.5	9.6	9.9	6.7	5.5
% O	5.1	6.6	2.1	8.6	10.5	12.2	4.1	8.5	8.8	10.4	12.9	N.D.	N.D.	9.0	17.0
% N+S	2.2	2.7	N.D.	2.4	2.7	3.1	N.D.	N.D.	N.D.	N.D.	N.D.	4.4	10.4	4.3	5.6
% -OH	5.0	4.2	0.8	6.2	7.0	6.2	1.7	5.7	5.8	5.6	4.2	N.D.	N.D.	5.6	3.1
MW	610	2030	310	430	720	1500	490	780	2090	690	1750	275	250	620	1860
H/C Ratio	0.90	0.78	1.13	0.96	0.86	0.82	1.38	1.04	0.96	1.10	0.85	1.36	1.48	1.0	0.83

Key: Py = Pyridine SCG = Supercritical gas HDS = Hydrogen-donor solvent
As = Asphaltenes BI = Benzene insolubles Ar = Aromatic fraction of n-pentane solubles
n-PS = n-pentane solubles

N.D. = Not determined

* = Analysis corrected for ash

TABLE 2 - Definitions of Structural Parameters

Structural Parameter	Definition
No. of aliphatic carbon atoms, C_{al}	$\frac{H_{\alpha,2}}{a} + \frac{H_{\alpha}}{b} + \frac{H_{\beta}}{c} + \frac{H_{\gamma}}{d}$
Aromaticity, f_a	$\frac{C - C_{al}}{C}$
Degree of alkyl substitution,	$\frac{\frac{H_{\alpha}}{b}}{H_{AR,OH} + \frac{H_{\alpha}}{b}}$
Average alkyl chain length, CL	$\frac{C_{al} - H_{\alpha,2}}{\frac{H_{\alpha}}{b}}$
Degree of condensation, dC	$\frac{H_{AR,OH} + \frac{H_{\alpha}}{b} + 2(\frac{H_{\alpha,2}}{a} + \text{non-phenolic O+N+S})}{(C - C_{al}) + (\frac{H_{\alpha,2}}{a} + \text{non-phenolic O+N+S})}$
Aliphatic $\frac{H}{C}$ ratio	$\frac{H}{C} \times \frac{\text{aliphatic hydrogen}}{H \text{ (from } ^1H \text{ NMR)}} \times \frac{C}{\text{aliphatic carbon (from } ^{13}C \text{ NMR)}}$

TABLE 3 - Structural Parameters for Typical Extract Fractions

Structural Parameter	Bituminous Coal						Perhydrous Coal		Lignite				
	HDS 1		SCG 2 620 K	SCG 3 670 K		Py 3	SCG 690 K		SCG 1 690 K		SCG 2 610 K	SCG 3	
	As	BI	Ar	As	BI	BI	As	BI	As	BI	Ar	610 K Ar	690 K As
C_{al}	12.5	31.7	7.5	7.7	9.9	20.6	21.0	46.9	18.7	31.8	9.7	9.8	14.1
f_a	0.71 (0.70)	0.78 [0.79]	0.67	0.74 (0.74)	0.80	0.79 [0.79]	0.61 (0.60-0.64)	0.67	0.60	0.72	0.50	0.42	0.66
σ	0.27	0.22	0.32	0.24	0.21	0.23	0.37	0.30	0.37	0.29	0.32	0.30	0.34
CL	2.4	2.3	2.0	1.9	1.6	1.9	2.7	2.7	2.7	2.5	3.1	5.4	2.1
dc	0.58	0.62	0.66	0.69	0.74	0.70	0.66	0.70	0.79	0.73	0.95	N.D.	0.82
Aliphatic H/C ratio	2.0	2.2	N.D.	2.5	N.D.	2.6	N.D.	N.D.	N.D.	N.D.	2.1	2.1	N.D.

Key: ( ) = direct values from ^{13}C NMR

[ ] = direct values from ^{13}C NMR of silylated benzene insolubles

Py = pyridine
SCG = supercritical gas
HDS = hydrogen-donor solvent

As = asphaltenes
BI = benzene insolubles
Ar = aromatic fraction of n-pentane solubles

N.D. = not determined

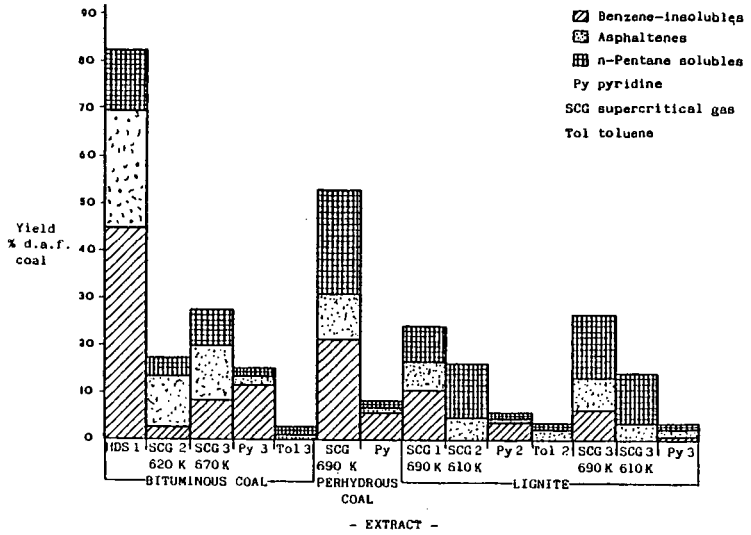

Figure 1 Some Yields of Extracts and their Solvent Fractions

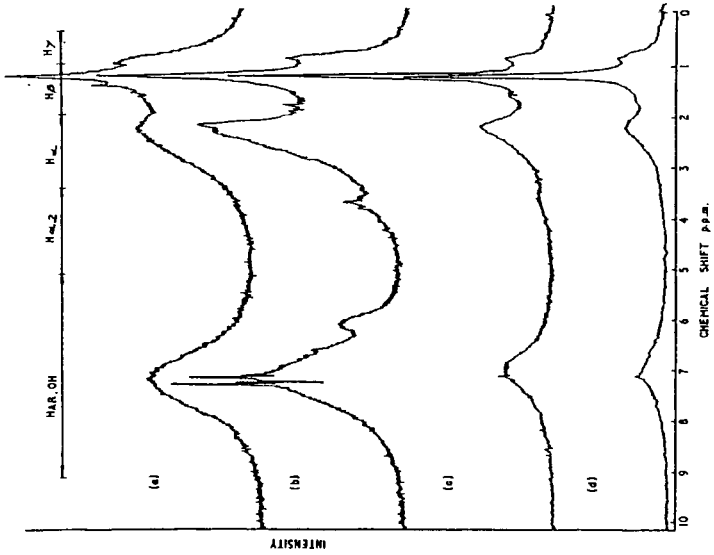

Figure 2 ^{1}H NMR Spectra of Asphaltenes from (a) HDS Extract of Bituminous Coal 1 and SCG Extracts of (b) Bituminous Coal 3, (c) Perhydrous Coal and (d) Lignite 1

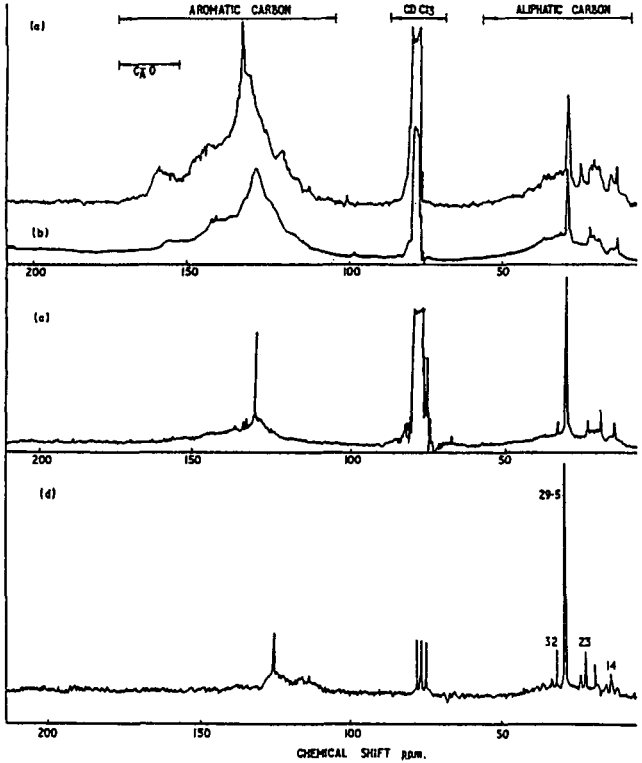

Figure 3 ^{13}C NMR Spectra of (a) Asphaltenes from SCG Extract of Bituminous Coal 3, (b) Asphaltenes from HDS Extract of Bituminous Coal 1, (c) Polars from SCG Extract of Perhydrous Coal and (d) Aromatics from SCG Extract (610 K) of Lignite 3

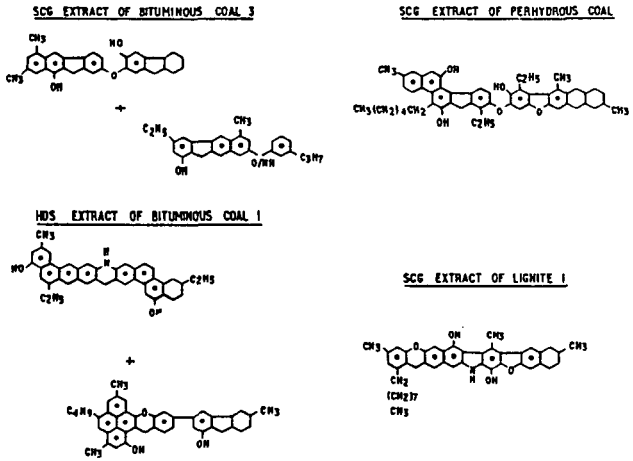

Figure 4 Average Structures for Some Asphaltene Fractions