

Association of Aromatic Structures in Coals

Masaharu Nishioka and John W. Larsen*

Corporate Research Science Laboratory, Exxon Research and Engineering Company, Clinton Township, Route 22E, Annandale, New Jersey 08801, and Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received April 24, 1989. Revised Manuscript Received December 4, 1989

Three different experimental probes were used to detect the presence of noncovalent interactions between aromatic groups in coals. The pyridine extractability of coals is greater at 115 °C than at 25 °C, even though the solvent is not saturated in either case. This is due to greater dissociation of the extractable molecules at the higher temperature. Since room temperature pyridine breaks the coal-coal hydrogen bonds, another noncovalent interaction must be responsible for the temperature dependence observed. Immersing Pittsburgh No. 8 coal in pyridine at room temperature or warming it in chlorobenzene or toluene causes the coal to rearrange into a more stable configuration, resulting in a decrease in pyridine swelling and extractability. If the macromolecular chains gain some freedom of motion, they rearrange into a lower free energy configuration involving more noncovalent interactions. The formation of adducts between maleic anhydride and coals sharply increases the pyridine extractability of coals containing more than about 88% (daf) carbon. Adduct formation sterically blocks some noncovalent interactions and decreases associations. Non-hydrogen-bond, noncovalent interactions play an important role in coal structure, and this role appears to increase with rank.

Introduction

Bituminous coals are three-dimensionally cross-linked macromolecular networks.¹⁻⁵ In addition to covalent bonds, three types of noncovalent interactions may be important. Hydrogen bonds have been established as interactions important to the network structure.⁶⁻⁸ In a covalently bonded network, entanglements cannot be distinguished from covalent branch points using probes based on network elasticity, such as mechanical properties or solvent swelling. Entanglements do not require associative forces between the entangled chains, just the sterically enforced freezing of the chains where they cross each other. The importance of entanglements to coal properties is undetermined. Other attractive physical interactions are anticipated to play an important role in determining coal macromolecular structure and therefore be important to coal properties and reactivity. One is the family of dipolar and induced dipolar (van der Waals) interactions between aromatic systems.⁹ In highly polarizable aromatic structures having small HOMO-LUMO gaps, these interactions can be quite strong. In this introduction, we will describe briefly what is known of their geometry and magnitude and summarize the meager previous evidence for their structural role in coals. Ionic interactions that may be important in lower rank coals will be ignored here. The possibility exists that aromatics will associate via charge-transfer interactions, especially if they contain heteroatoms. We will often be using the rather unsatisfactory term "clusters" which has come into general use in coal chemistry. We use it to designate those planar aromatic or hydroaromatic moieties that are linked to-

gether to form the coal macromolecules. A noncovalent intercluster interaction is a hydrogen bond, van der Waals interaction, or charge-transfer complexation between two different clusters.

We are concerned with the geometry and energetics of interactions between nonbonded aromatic systems. The geometry of *pairwise* interactions has been determined experimentally for the benzene ring in a variety of biological macromolecules.¹⁰ Benzene self-interaction geometries have been determined in solid, liquid, and gas phases.¹¹ A variety of calculations have been carried out on the interactions of identical pairs of aromatic molecules.¹² All agree that the parallel face-to-face stacking of aromatic rings does not result in attractive interactions but is repulsive at all distances. The most favored geometry varies in detail depending on the molecular structure, but always involves the edge of one of the rings approaching the face of the other in a "T" or similar shaped configuration. In crystalline solids, a "herringbone" stacking pattern results as a compromise between the favorable more or less perpendicular interactions and the need to fill all space.¹³ A recent paper by Miller et al. contains a good description of the attractive and repulsive forces whose balance results in this structure as well as references to much of the theory literature on this topic.¹⁴

- (1) van Krevelen, D. W. *Coal*; Elsevier: New York, 1961; Chapter 23.
- (2) Green, T.; Kovac, J.; Brenner, D.; Larsen, J. W. In *Coal Structure*; Meyers, R. A., Ed.; Academic Press: New York, 1982; pp 199-282.
- (3) Peppas, N. A.; Lucht, L. M. *Chem. Eng. Commun.* 1984, 30, 291-310.
- (4) Brenner, D. *Fuel* 1985, 64, 167-173.
- (5) Larsen, J. W.; Green, T. K.; Kovac, J. *J. Org. Chem.* 1985, 50, 4729-4735.
- (6) Larsen, J. W.; Baskar, A. *J. Energy Fuels* 1987, 1, 230-232.
- (7) Liotta, R.; Rose, K.; Hippo, E. *J. Org. Chem.* 1981, 46, 277-283.
- (8) Stenberg, V. I.; Baltisberger, R. J.; Patal, K. M.; Raman, K.; Woolsey, N. F. In *Coal Science*; Gorbaty, M. L., Larsen, J. W., Wender, L., Eds.; Academic Press: New York, 1983; Vol. 2, pp 125-171.
- (9) Kauzman, W. *Quantum Chemistry*; Academic Press: New York, 1959.

- (10) Burley, S. K.; Petsko, G. A. *Science* 1985, 229, 23. Blundell, T.; Singh, J.; Thornton, J.; Burley, S. K.; Petsko, G. A. *Science* 1986, 234, 1005. Singh, J.; Thornton, J. M. *FEBS Lett.* 1985, 191, 1-6.
- (11) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. *Proc. R. Soc. London* 1958, 247, 1-21. Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Phys. Chem.* 1981, 85, 3739-3742. Langridge-Smith, P. R. R.; Brumbaugh, C. A.; Haynam, C. A.; Levy, D. H. *J. Phys. Chem.* 1981, 85, 3742-3746. Janda, K. C.; Hemminger, J. C.; Winn, J. S.; Novick, S. E.; Harris, S. E.; Kemperer, W. *J. Chem. Phys.* 1975, 63, 1419. Steed, J. M.; Dixon, T. A.; Klemperer, W. *J. Chem. Phys.* 1979, 70, 4940. Levy, D. H.; Haynam, C. A.; Brumbaugh, D. V. *J. Chem. Soc., Faraday Discuss.* 1982, 73, 137.
- (12) Pawliszyn, J.; Szczesniak, M. M.; Scheiner, S. *J. Phys. Chem.* 1984, 88, 1726-1730. Karlstrom, G.; Linse, P.; Wallqvist, A.; Jonsson, B. *J. Am. Chem. Soc.* 1983, 105, 3777-3782.
- (13) Cruickshank, D. W. J. *Acta Crystallogr.* 1957, 10, 504-508. Cruickshank, D. W. J. *Acta Crystallogr.* 1956, 9, 915-923. Burns, D. M.; Iball, J. *Proc. R. Soc. London* 1955, 227, 200-214. Burns, D. M.; Iball, J. *Proc. R. Soc. London* 1960, 257, 491-514. Iball, J.; Scrimgeour, S. N. *J. Chem. Soc., Perkin Trans. 2*, 1974, 1445-1448. Wieckowski, T.; Krygowski, T. M. *Can. J. Chem.* 1981, 59, 1622-1629.
- (14) Miller, J. H.; Mallard, W. G.; Smyth, K. C. *J. Phys. Chem.* 1984, 88, 4963-4970.

In solution, porphyrin systems from parallel face-to-face dimers which are displaced to the side, avoiding full face-to-face interactions.¹⁵ Pairwise stacking of porphyrins in nonpolar solvents is favored over the formation of larger stacks.¹⁵ Pyrenesulfonic acid salts dimerize in water but do not form larger aggregates.¹⁶ We found no more information on the geometries and energetics of cooperative interactions between more than two-ring polynuclear aromatic (PNA) systems except for crystallographic data. The effects of interacting different ring systems and differently substituted rings have not been examined either experimentally or by calculations. There is an urgent need for these data to understand the structure and chemistry of coals and heavy oils.¹⁷⁻²⁰

There is indirect evidence for an important role for aromatic-aromatic interactions in coals. The X-ray structures of Hirsch are commonly cited as evidence for stacking interactions in coals, and Hirsch clearly shows the aromatic ring systems in face-to-face stacks, which may be repulsive in the ground state.²² Parallel face-to-face stacking is the minimum volume configuration anticipated if high pressures or packing forces are overwhelming the repulsive forces. Face-to-face aromatic stacks exist in coals, but it is not certain whether they are due to cooperative attraction between several ring systems or are a higher energy geometry enforced by energy minimization elsewhere in the structure. That this face-to-face interaction may be repulsive and favored by pressure is suggested by the recent observation of structural relaxations occurring as coals achieve their atmospheric pressure equilibrium configuration which is different from the configuration existing (and presumably at equilibrium) in the underground seam.²³ The best evidence for an important structural role for intercluster interactions comes from sets of experiments all based on the introduction of bulky groups into coals to sterically disrupt stacking interactions.²⁴⁻²⁶ There are two fundamental problems with this approach. The first is the requirement of chemistry selective enough to introduce the bulky groups without breaking any covalent bonds in the coals. The second is that bulky groups will interfere with hydrogen bonds as well as stacking interactions. The most convincing of these studies was carried out by Stock and Mallya,²⁴ and it reports significantly enhanced solubility of butylated coals over methylated coals. Comparing two alkylated coals cleverly removes the effects of bond breaking and hydrogen bond disruption (a small problem in the high-rank coals studied) and provides evidence for an important role for noncovalent, non-hydrogen-bond intercluster interactions.

Reliance on one experimental approach to characterize so possibly important an interaction in a system as complex as coals is dangerous. We report here several other probes of coal structure that provide strong evidence for

Table I. Elemental Analyses of Coals Used

coal	anal., wt % (dry)				
	C	H	N	S + O ^a	ash
Big Brown	63.3	5.03	1.16	16.4	14.0
Wandoan	69.5	5.50	0.91	14.0	10.1
Illinois No. 6	70.6	4.51	1.59	11.7	11.6
Pittsburgh No. 8	79.3	5.29	1.42	8.5	5.4
PSOC-1336	72.8	4.84	1.13	7.8	13.4
PSOC-721	76.9	5.28	1.58	3.1	13.1
PSOC-1300	78.1	4.69	1.32	2.4	13.5
PSOC-991	76.0	4.44	1.46	3.1	15.0
PSOC-875	68.9	3.84	0.92	3.7	22.2
PSOC-648	84.2	4.23	1.83	3.7	6.0
PSOC-688	73.4	3.87	1.15	1.4	20.2

^a By difference.

the existence of noncovalent intercluster interactions in bituminous coals and for their important structural role. None of the individual experiments to be described is in itself conclusive or uniquely explicable in terms of noncovalent intercluster interactions. We will present a set of observations all of which can be rationalized using the single postulate of important noncovalent intercluster interactions (which are not hydrogen bonds) rather than a larger set of individual explanations. Occam's razor applies, and we believe these experiments establish an important role for aromatic-aromatic associative interactions in coal structure.

Experimental Section

All chemicals were ACS grade or HPLC distilled in glass and were used without further purification. Coal samples were obtained from the Exxon Research and Engineering Co. and the Pennsylvania State University Coal Sample Bank. Their elemental analyses are listed in Table I. Coal samples were ground and sifted in a dry N₂ atmosphere, and -60 mesh particles were used in all experiments.

Extractions. Samples of 2-5 g were extracted under dry N₂ with 200 mL of pyridine by use of a Soxhlet apparatus or at room temperature with magnetically stirred liquid pyridine for 24 h. Extracts were dried to constant weight in a vacuum oven at 50 °C. All reported percentage extractions are based on the weight of the dried extracts.

Swelling Ratio. The pyridine solvent swelling ratios of pyridine-extracted coals were measured at room temperature according to techniques previously described.²⁷

Reaction with Maleic Anhydride. The coal or coal extract (2-5 g) and maleic anhydride (1-4 g) were mixed in 100 mL of chlorobenzene in a 250-mL flask under dry N₂ and magnetically stirred at 115 ± 3 °C for 7 days. The cooled mixture was dried on a rotary evaporator, mixed with water and filtered, and rinsed with methanol. The resulting solid was Soxhlet extracted overnight with 200 mL of distilled water followed by Soxhlet extraction with methanol for about 2 h. This procedure removes unreacted maleic anhydride and solvents more efficiently than the one we have previously used.²⁶ The adduct was dried to constant weight in a vacuum oven at 50 °C.

Infrared Spectra. FTIR spectra were obtained on an IBM 97/IR using photoacoustic detection. One hundred twenty-eight scans at 4-cm⁻¹ resolution were averaged, and a carbon black reference was used.

Molecular Weight Distributions. The gel permeation chromatograph and techniques used have previously been described.²⁸ Sample concentrations in pyridine were 100 ± 5 mg/cm³, and all samples were filtered through a 0.2-μm MIL-LEX-FGS filter (Millipore Products) before being chromatographed.

Thin Section Preparation. Brenner's procedure was used to prepare coal thin sections.²⁹ The sample of Pittsburgh No.

(15) Leighton, P.; Cowan, J. A.; Abraham, R. J.; Sanders, J. K. M. *J. Org. Chem.* 1988, 53, 733-740.

(16) Menger, F. M.; Whitesell, L. G. *J. Org. Chem.* 1987, 52, 3793-3798.

(17) Dickie, J. P.; Yen, T. F. *Anal. Chem.* 1967, 39, 1847-1852.

(18) Dickie, J. P.; Haller, M. W.; Yen, T. F. *J. Colloid Interface Sci.* 1969, 29, 475-484.

(19) Pollack, S. S.; Yen, T. F. *Anal. Chem.* 1970, 42, 623-629.

(20) Speight, J. G. *The Chemistry and Technology of Petroleum*; Marcell Dekker: New York, 1980; pp 189-252.

(21) Yen, T. F. *Fuel* 1973, 52, 93-98.

(22) Cartz, L.; Hirsch, P. B. *Philos. Trans. R. Soc. London* 1960, 252A, 557-599.

(23) Cody, G. Y.; Larsen, J. W.; Siskin, M. *Energy Fuels* 1988, 2, 340-344.

(24) Mallya, N.; Stock, L. M. *Fuel* 1986, 65, 736-738.

(25) Wachowska, H.; Ignasiak, T.; Strausz, O. P.; Carson, D.; Ignasiak, B. *Fuel* 1986, 65, 1081-1084.

(26) Quinga, E. M. Y.; Larsen, J. W. *Energy Fuels* 1987, 1, 300-304.

(27) Green, Y. K.; Kovac, J.; Larsen, J. W. *Fuel* 1984, 63, 935-938.

(28) Larsen, J. W.; Wei, Y.-C. *Energy Fuels* 1988, 2, 344-350.

(29) Brenner, D. *Fuel* 1984, 63, 1324-1328.

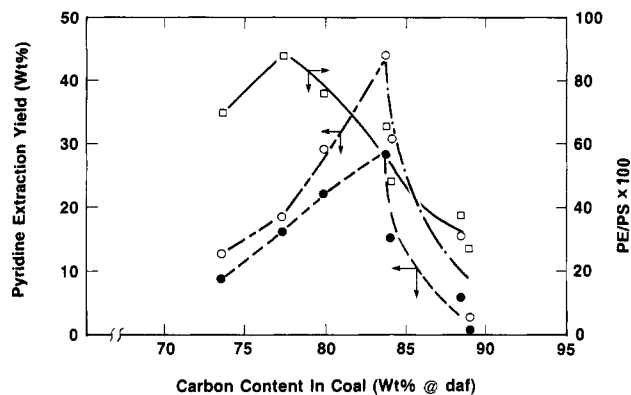


Figure 1. Rank dependence of extraction yields. PS (○); PE (●); PE/PS Ratio (□).

8 coal had a 3-mm² area and was 12 μm thick. A polarizing microscope at ×125 magnification was used.

The following abbreviations are used: Py, pyridine; PS, pyridine soluble via Soxhlet extraction; PE, pyridine soluble via room temperature extraction; ΔPS, PS - PE; PI, insoluble in pyridine via Soxhlet extraction; MA, maleic anhydride; coal/MA, maleic anhydride adduct of coal.

Results and Discussion

In this section, three different lines of evidence supporting the existence in coals of structurally important noncovalent intercluster interactions that are not hydrogen bonds will be presented and discussed independently. This completed, there will be a brief discussion of the role of these interactions in coal structure. The three approaches are the thermal disruption of the interactions, the formation of new intercluster interactions in "mobilized" coals, and the disruption of intercluster interactions by a bulky group. Throughout this work, pyridine is used as an extracting and swelling solvent because it is a much better hydrogen bond acceptor than any of the functional groups in coals, and its use as a solvent should destroy all coal-coal hydrogen bonds.

Thermally Induced Dissociation. Noncovalent interactions are weak, less than 10 kcal/mol.⁹ They thermally dissociate even in polymer systems with multiple interactions. In nonpolymeric systems, thermal dissociations will be reversible. However, molecular motions in polymeric systems may be so slow that nonequilibrium conformations can be locked in on cooling. The thermal dissociation of noncovalent interactions in coals may not be reversible, and the usual experimental check of verifying reversibility will not always be useful in the experiments to follow.

Table II contains a comparison of the amount of material extracted from seven coals by pyridine by stirring at room temperature and by Soxhlet extraction. The data are presented in Figure 1. Less material is extracted at room temperature. These pyridine solutions at room temperature are not saturated. The lower extraction at room temperature is not due to temperature effects either on solubility or mass transport. The explanation for the differences between the high-temperature and room temperature extractions is most reasonably based on the degree of association occurring between the insoluble network and non-cross-linked polymer molecules. Increased temperature will lead to increased dissociation and the extraction of more material. Furthermore, the ratio of amount of room temperature extract to Soxhlet extract (PE/PS) decreases with rank (Figure 1) for bituminous coals. Both the concentration and the size of aromatic systems increases with coal rank, and this should lead to intercluster

Table II. Pyridine Extraction and Swelling Ratio of Coals and Their Maleic Anhydride Adducts

	Big Brown	Wandoan	Ill. No. 6	Pitts. No. 8	PSOC-1336	PSOC-721	PSOC-1300	PSOC-991	PSOC-875	PSOC-648	PSOC-688
carbon (daf), wt %	73.6	77.3	79.9	83.8	84.1	88.5	89.9	89.4	89.0	89.6	92.0
Soxhlet extraction yield, %	12.7	18.2	29.1	43.7	30.9	15.4	4.1	3.4	2.6	3.6	2.2
extract no.-av mol wt ^a	2260	2530	3020	2810	2000 ^b	1930					
room temp extraction yield, %	8.8	16.0	22.1	28.4	15.0	5.7			0.7		
coal/maleic anhydride adduct											
Soxhlet extraction yield, %	18.1	17.1	21.7	36.4	24.6	37.1	30.1	25.9	7.6	7.5	6.0
no.-av mol wt. ^a	1520	2030	1600	1830	1840	2240 ^c					
room temp extraction yield, %				26.1	13.9	5.3					
wt gain on adduct formation, %				14.4	1.74	1.33					
pyridine solvent swelling ratio	1.80	2.02	2.04	2.00	1.86	1.62			1.00	1.07	1.02
coal	2.21	2.18	2.28	2.33					1.24	1.42	1.20
MA adduct											

^a Soxhlet extraction concentration 100 ± 5 mg/cm³ and at room temperature. ^b Resolubilization was very difficult. About one-fourth was recovered after filtration with 20-μm filter. ^c Contained undissolved matter.

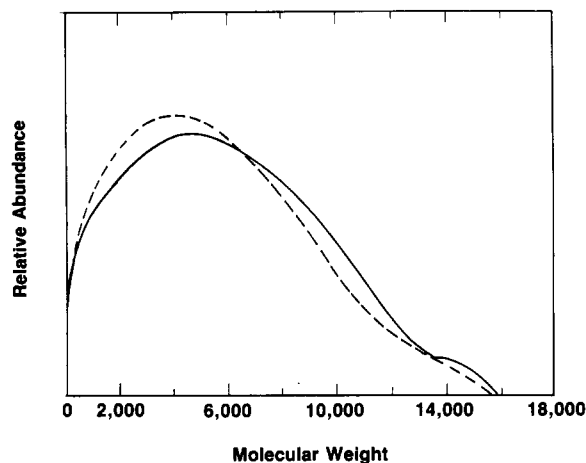


Figure 2. Molecular weight distribution of room temperature pyridine extract (PE) at room temperature (—) and at 70 °C (---).

interactions increasing with coal rank.

If noncovalent interactions in coals are dissociated thermally, the higher temperature Soxhlet extraction will remove more material because the soluble fraction will be more weakly bound to the insoluble part of the coal. Another factor may be the increased thermal dissociation of insoluble complexes to produce soluble molecules. Increasing extractability with increasing temperature is readily understandable on the basis of thermal dissociation of noncovalent interactions.

If this explanation is correct, this phenomenon should also be visible in soluble materials. Figure 2 shows the molecular weight distribution of the PS fraction from Pittsburgh No. 8 coal measured in pyridine by use of gel permeation chromatography at room temperature and at 70 °C. There is a clear shift to lower molecular weight at the higher temperature, demonstrating the thermal dissociation of the extract fraction. Repetitive injections of the same material give superimposable curves: the observed differences in Figure 2 are well beyond experimental error.

The two possible major association forces are hydrogen bonding and noncovalent interactions between the polarizable aromatic π systems. Pyridine is known to be a very strong hydrogen bond acceptor and is known to break coal-coal hydrogen bonds.^{7,30} Pyridine is one of the best hydrogen bond acceptors known, and no functional groups postulated to exist in coals are as strong hydrogen bond acceptors as pyridine.³¹ As a solvent, it is present in about a 10^3 molar excess over the hydrogen bond acceptors in the coal. It seems most unlikely that there are hydrogen bond acceptors in coals capable of competing with pyridine present in vast excess. Thus the weak associative forces that are overcome thermally are noncovalent interactions which are not hydrogen bonds, most reasonably interactions between aromatic systems.

The temperature effects on coal extractability that have been observed over the years can be explained by invoking the thermal dissociation of intercluster interactions and hydrogen bonds. Illingworth studied temperature effects on Soxhlet extraction of nine coals with pyridine (115 and 180 °C) and observed that more was extracted at higher temperatures and that the disparity in the amounts extracted at the two temperatures increased with rank.³²

(30) Dryden, I. G. C. In *Chemistry of Coal Utilization*; Lowry, H. H., Ed., Wiley: New York, 1963.

(31) Arnett, E. M.; Joris, E.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1970, 92, 2365-2377.

(32) Illingworth, S. R. *Fuel* 1922, 1, 213-219.

Our results support his, and we offer the same explanation.

Preheating coals to between 200 and 400 °C in an inert atmosphere is known to enhance the extractability of coals.³³⁻³⁶ Nishioka and Larsen recently showed that heating coals to 250 °C increased the extractability of bituminous coals and decreased the extractability of a lignite and a subbituminous coal.³⁵ There was no covalent bond cleavage in the extracts of bituminous coals of rank higher than Illinois No. 6.³⁵ This is most easily explained by thermal dissociation of noncovalent interactions in coals of higher rank than Illinois No. 6. From Illinois No. 6 down in rank, pyrolysis chemistry occurs even at these low temperatures.

Most workers have attributed the origin of the new extractable material found after heating not to covalent bond cleavage but to soluble material already present in the coals but somehow made accessible by the thermal process.³⁷⁻⁴⁴ The new extractable material seems to be more aromatic than that extracted before heating.^{35,39} A glass to rubber transition occurs in many of these coals at about 325 °C, and this undoubtedly contributes to the freeing of some of the new extract.⁴⁴ One of the reasons this phase transition occurs at this temperature is because the noncovalent interactions are thermally disrupted, and this is responsible for the thermal enhancement of coal extractability and is an important factor in the glass to rubber transition.

If noncovalent interactions are thermally disrupted, their effects should appear in solvent swelling experiments. Sanada and Honda showed that the pyridine swelling of a series of coals at room temperature was rank independent up to 87% C (daf) and then decreased sharply.⁴⁵ When measured at 50 °C, the swelling increased with coal rank up to 87% C. This is consistent with the increase with rank of dissociable interactions which serve as noncovalent cross-links in the macromolecular structure.

Solvent-Induced Association. If interacting clusters in coals can be thermally dissociated, perhaps conditions can be found permitting increased association of clusters. If intercluster interactions in coals are not at their maximum and if the glassy coal can be treated to allow enough molecular motion of previously distant clusters to come together, then the number of interactions should increase, and the physical consequences of increased association should become visible. These consequences will include decreased extractability and decreased solvent swelling due to an increase in noncovalent cross-link density. It is well-known that amorphous polymers undergo thermal-, stress-, and solvent-induced crystallization.⁴⁶ We suggest analogous processes exist in coals, but here these processes result in increasing association which does not involve crystallite formation.

We selected Pittsburgh No. 8 coal for our initial attempts to increase noncovalent associations. We soaked

(33) Harger, J. J. *Soc. Chem. Ind.* 1914, 33, 389-392.

(34) Illingworth, S. R. *J. Soc. Chem. Ind.* 1920, 39, 111-118.

(35) Nishioka, M.; Larsen, J. W. *Energy Fuels* 1988, 2, 351-355.

(36) Ouchi, K. *Fuel* 1961, 40, 485-490.

(37) Brown, H. R.; Waters, P. L. *Fuel* 1966, 45, 17-39.

(38) Brown, H. R.; Waters, P. L. *Fuel* 1966, 45, 41-59.

(39) Vahrman, M. *Chem. Br.* 1972, 8, 16-24.

(40) Holden, H. W.; Robb, J. C. *Fuel* 1960, 39, 39-46.

(41) Holden, H. W.; Robb, J. C. *Fuel* 1960, 39, 485-494.

(42) Herod, A. A.; Hodges, N. J.; Pritchard, E.; Smith, C. A. *Fuel* 1983, 62, 1331-1335.

(43) Larsen, J. W. *Fuel Process. Technol.* 1988, 20, 13-22.

(44) Lucht, L. M.; Larson, J. M.; Peppas, N. A. *Energy Fuels* 1987, 1, 56-58.

(45) Sanada, Y.; Honda, H. *Fuel* 1966, 45, 451-456.

(46) Jameel, H.; Waldman, J.; Rebenfeld, L. *J. Appl. Polym. Sci.* 1981, 26, 1795-1811 and references therein.

Table III. Effect of Pretreatment Solvent and Temperature on Pyridine (Py) Soxhlet Extraction Yields (115 °C) from Pittsburgh No. 8 Coal

coal treatment	extrac- tion yield, %	extract analysis			
		% C	% H	% N	% S
none	44	81.0	6.1	2.6	2.4
none	28 ^a	81.1	6.1	2.6	2.4
extracted with Py at 25 °C	12	79.6	5.7	2.3	2.4
heated 1 week, N ₂ , 115 °C	45				
heated 1 week, Py, 115 °C	43 ^b				
heated 1 week, PhCl, 113 °C	32	80.9	6.1	2.8	2.4
1 day, Py, 25 °C	32 ^c	80.9	5.8	2.7	2.5
heated 1 week, PhCH ₃ , 110 °C	40				
heated 1 h, PhCl, 130 °C	41				
heated 1 day, PhCl, 130 °C	40				

^aExtracted by stirring with excess Py at room temperature.

^bSample was not dried after being heated in pyridine. ^cSample dried under vacuum at 50 °C after Py exposure.

at room temperature or warmed this coal in several solvents and determined the effects of this heating on extractability and solvent swelling. The solvents serve as plasticizers making the motion of molecular segments easier, facilitating dissociation. Also, the solvent swelling decreases the viscosity thereby enhancing mobility. Heating to higher temperatures provides the energy necessary to overcome the activation barriers to molecular motion in the slightly swollen coal. The solvent most used was chlorobenzene, which does not hydrogen bond to coals but which has a reasonable affinity for them and is a good slightly polar swelling solvent.⁵ The data are given in Table III.

Heating Pittsburgh No. 8 coal under dry N₂ (no solvent) at 115 °C for 1 week had no effect on its pyridine extractability. When the coal was heated in chlorobenzene for the same time at the same temperature, pyridine extractability decreased from 44% to 32%. The coal rearranges, forming new noncovalent interactions and becoming less extractable. A poorer swelling solvent, toluene, shows a much smaller effect. When the coal is exposed to chlorobenzene at higher temperatures, it shows a greater rate of extractability decrease. Pyridine is claimed to cause coals to be rubbery at room temperature⁴ (however, see ref 44 for a contrary view), and room temperature exposure to pyridine for 24 h facilitates the rearrangement and decreases the extractability to the same level achieved with chlorobenzene at 115 °C for 1 week. This also is readily understandable in terms of a rearrangement to form more intercluster interactions. A 1-week exposure to pyridine at reflux followed by Soxhlet extraction without drying shows no change in extractability, as expected. There is no extractability increase since pyridine breaks no covalent bonds in this coal at these conditions. There is no decrease because the coal was never dried and the fully swollen coal was never given the opportunity to collapse and form new interactions. All these data are completely consistent with the formation of new lower free energy conformations made possible by enhancing the mobility of coal macromolecular segments.

The formation of new intercluster interactions should also alter the coal's solvent swelling behavior. New interactions are new noncovalent branch points (cross-links), so their formation should decrease room temperature solvent swelling. This behavior has been observed and is reported in the following paper.⁴⁷ The solvent- and tem-

perature-dependent internal rearrangement may be contributing to the irreversibility of some vapor solvent swellings observed by Duty and Liu.⁴⁸

Optical birefringence provides evidence that the coal structure is mobilized in pyridine and chlorobenzene. The effect of swelling with various solvents on the optical anisotropy of Illinois No. 6 coal was studied by Brenner.⁴ The good hydrogen-bond-accepting solvents pyridine and *n*-propylamine caused the rapid disappearance of the optical anisotropy, while water, pentane, benzene, and chloroform did not affect it. Tetrahydrofuran (THF) substantially decreased it, but some optical anisotropy remained. The suggested explanation, which is consistent with the views expressed here, was the total removal of structural anisotropy by pyridine and *n*-propylamine, which disrupt the hydrogen bonds which had frozen the structural anisotropy and held the coal in a glassy state. Thin sections of Pittsburgh No. 8 have also been studied.²⁹ At room temperature, pyridine swelling rapidly causes the optical anisotropy to disappear, THF slightly reduced it, and chlorobenzene had no effect. However, when the thin section was heated in chlorobenzene for 1 week, the optical anisotropy disappeared. This demonstrates that the coal structure is somewhat mobile when swollen with chlorobenzene at 115 °C.

Adduction with Maleic Anhydride. The reaction of maleic anhydride with coals has been studied and is thought to occur principally by a Diels–Alder reaction.^{26,49} It has been shown that reaction of coals with maleic anhydride under mild conditions gives an adduct whose pyridine and THF solubilities are significantly increased if the coal is of sufficiently high rank.²⁶ This increase was ascribed to disruption of PNA stacks. The steric disruption of aromatic stacks by alkylation with butyl groups has also been shown for medium-volatile bituminous coals.²⁴ We have applied an improved procedure for studying maleic anhydride adduct formation to a larger group of coals.

The procedural change consisted of an additional methanol extraction following extraction of the coal–maleic anhydride adduct with water. This change resulted in smaller and more variable weight increases for mid-rank bituminous coals on adduct formation. The additional methanol rinsing and extraction gave more complete removal of the chlorobenzene reaction solvent from the solid reaction product. The amounts of maleic anhydride adduct formed that we previously reported for mid-rank bituminous coals are overestimated.^{26,49} The amount of adduct formed by the coals studied is reported in Table II.

As previously reported, the extractability of high-rank coals (above ~88 °C) sharply increases due to formation of a maleic anhydride adduct. This is easily explained by the steric disruption of noncovalent interactions between clusters. For several bituminous coals, maleic anhydride adduct formation reduces their extractability (see Figure 3). It is known (see an earlier section of this paper) that treatment with the reaction solvent (chlorobenzene) under these reaction conditions decreases coal extractability by inducing the formation of more intercluster interactions. This is a plausible explanation for the extractability decrease but leaves unexplained why these interactions are not disrupted by maleic anhydride adduct formation. Since the weight increases in the reaction are large, an explanation based on the low reactivity of the coals whose extractability is decreased is not tenable. Adduct forma-

(47) Larsen, J. W.; Mohammadi, M. *Energy Fuels*, following paper in this issue.

(48) Duty, R. C.; Liu, H. F. *Fuel* 1980, 59, 546–550.

(49) Larsen, J. W.; Lee, D. *Fuel* 1983, 62, 1351–1354.

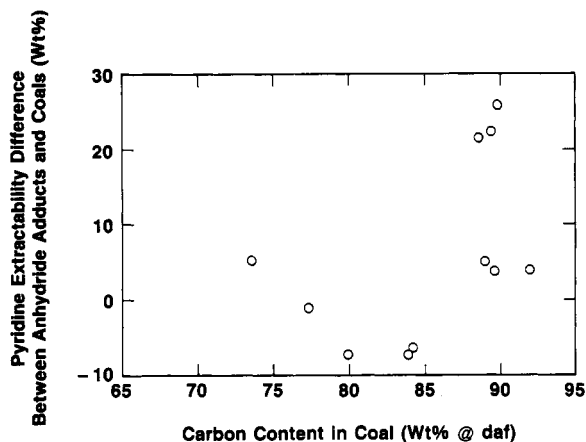


Figure 3. Rank dependence of the pyridine extractability difference between coals and their maleic anhydride adducts.

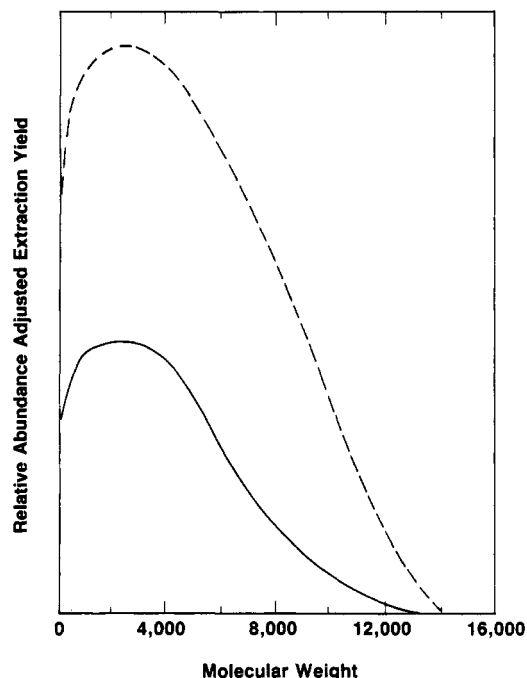


Figure 4. Molecular weight distributions of pyridine Soxhlet extracts (PS) for PSOC-721 (—) and its maleic anhydride adduct (---).

tion with maleic anhydride is a mild, easily hindered reaction, and it seems likely that it is not capable of disrupting all of the aromatic stacks in a coal. A comparison of the extractability increases observed by Stock²⁴ on butylation with those observed by us on maleic anhydride adduct formation (Stock's extractability increases are much larger) is consistent with the inability of maleic anhydride to disrupt all of the aromatic-aromatic interactions in coals.

The number-average molecular weights of the pyridine extracts from coals and the coal-maleic anhydride adducts are given in Table II. Except for one coal (PSOC-721), all of the adduct extracts have molecular weights lower than the coal extracts, consistent with less association. PSOC-721 showed an increase in molecular weight. The relevant molecular weight distributions are shown in Figure 4. In this case, adduct formation frees formerly associated material from the coal since extractability goes from 15% to 37%. The freed material is of higher molecular weight than the original extract. These molecular weight distributions can be compared with those of extracts from Wandoan and Pittsburgh No. 8 coals presented in Figure

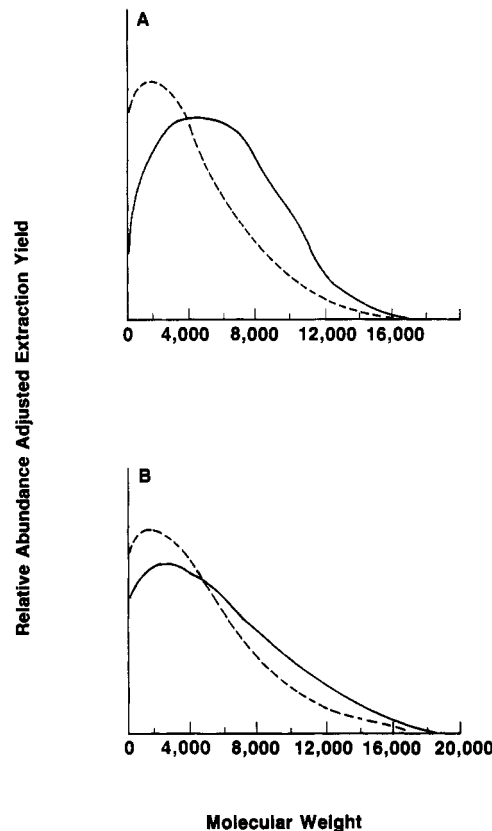


Figure 5. Molecular weight distributions of pyridine Soxhlet extracts (PS). (A) Pittsburgh No. 8 coal (—) and its maleic anhydride adduct (---). (B) Wandoan coal (—) and its maleic anhydride adduct (---).

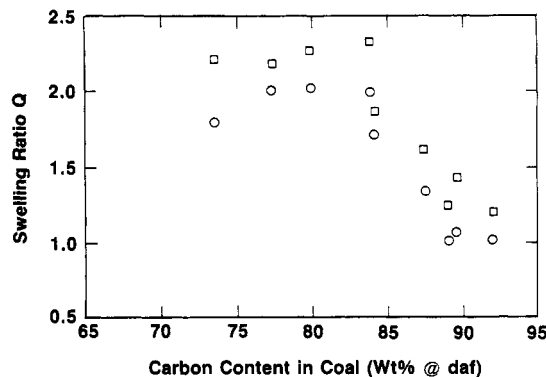


Figure 6. Rank dependence of the pyridine solvent swelling of pyridine-extracted coals (PS) (O) and their maleic anhydride adducts (□).

5. The differences are clear, and we do not know why PSOC-721 is different from all the other coals studied.

Another direct measure of the disruption of noncovalent interactions by maleic anhydride results from comparing the solvent swelling ratio of the extracted coals and its maleic anhydride adduct. These ratios measured with pyridine are shown in Figure 6. Use of pyridine will minimize hydrogen bond contributions but, because of specific interactions, makes quantitative interpretation of the swelling ratios impossible. For all coals, the swelling ratio is larger for the adducts. This could be due to a decrease in cross-link density due to the destruction of intercluster interactions or to an increase in solvent-macromolecule interactions due to the presence of maleic anhydride. The solubility parameters of coal and pyridine are well matched, and maleic anhydride addition is not expected to markedly increase interactions. We conclude

that the most reasonable explanation is a decrease in cross-links due to disruption of intercluster interactions but that this is not unequivocally established.

There are some surprising features in the data gathered on maleic anhydride adducts, most notably the decrease in extractability observed when some coals form adducts. The best explanation for the extractability decrease observed with some coals containing less than 88% C is the competitive formation of new interactions in chlorobenzene at 115 °C. This association dominates over dissociation due to adduct formation. Above 88% C, dissociation dominates. This interesting rank dependence could be due to changes in aromatic structure or the changing population of stacking interactions. A change in the nature of the intercluster interactions is also possible. Detailed studies of these interactions in coals will be reported in subsequent papers.

Coal Structure Model. Coals are complex macromolecular network systems containing dissolved organic material (sol). We will consider here the noncovalent cross-links in the network and the noncovalent interactions which bond the sol to itself and to the network. The type, number, and strength of the noncovalent interactions are all important, and there is meager quantitative information available.

Marzec has proposed that donor-acceptor interactions of the acid-base type bind the sol to the network and hinder or prevent its extraction in many solvents.⁵⁰ We agree that noncovalent interactions bind the sol to the network and have demonstrated elsewhere that hydrogen bonds (one kind of donor-acceptor interaction) are involved. The data contained in this paper demonstrate that noncovalent interactions, which are not acid-base interactions, also are important in associating the sol with the network.

As the size of aromatic systems increases, the magnitude of their self-interactions increases rapidly. The rapid decrease in solubility and increase in melting point of polynuclear aromatic hydrocarbons with ring number are manifestations of this. The principal attractive force in

these compounds is London (dispersion) interactions. In heteroatom-containing systems, there will also be large dipole-induced dipole interactions. In coals, the possibility of charge-transfer interactions, especially involving heteroatoms, also exists. As coal rank increases, both the concentration and size of the polynuclear aromatic systems increase. The hydroxyl concentration decreases. As rank increases, the importance of hydrogen bonds must decrease, and the role of the various other noncovalent interactions becomes more important. In many of the experiments reported here, pyridine was the swelling or extracting solvent. This should largely remove the contributions of coal-coal hydrogen bonds by replacing them with coal-pyridine hydrogen bonds. We have thereby been able to isolate the effects due to the dipolar interactions and demonstrate that they play an important role in coal structure.

We picture bituminous coals as consisting of a cross-linked network containing dissolved organic macromolecules and small molecules, most of which are bound to the network by hydrogen bonds and by van der Waals forces between aromatic units. The insoluble network is cross-linked both covalently and through noncovalent interactions. Again, hydrogen bonds are important. The data in this paper demonstrate that noncovalent interactions between aromatic systems are also important in the macromolecular structure. We have discussed elsewhere the role of these interactions in the very important glass to rubber transition of coals.⁴³ We have also argued that the sudden change in coal physical properties and reactivity which occurs at 86–88° C is due to the onset of cooperative interactions between aromatic systems⁵¹ and will return to this point in subsequent papers.

Acknowledgment. Conversations with the following individuals materially aided the development of this work: George Cody, Jr., Jeff Kovac, Ron Liotta, Mike Maturro, and Mike Siskin.

Registry No. Pyridine, 110-86-1; maleic anhydride, 108-31-6.

(50) Marzec, A.; Kisielow, W. *Fuel* 1983, 62, 977–979.

(51) Larsen, J. W. *New Trends in Coal Science, NATO ASI Meeting Proceedings*; Yurum, Y., Ed.; 1987.