

THE MACROMOLECULAR STRUCTURE OF BITUMINOUS COALS: MACROMOLECULAR ANISOTROPY, AROMATIC-AROMATIC INTERACTIONS, AND OTHER COMPLEXITIES

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INTRODUCTION

A homogeneous piece of vitrinite containing no mineral matter has two organic phases. One of these consists of a crosslinked macromolecular network and the other is a soluble family of macromolecules having a very broad molecular weight distribution. The network is held together by covalent bonds as well as by non-covalent interactions. There is abundant evidence for an important role of hydrogen bonds in the macromolecular structure and growing evidence for an important role for dipole-based interactions between the aromatic groups.<sup>1-4</sup> These same non-covalent forces are important in binding the extractable phase to the insoluble network. This paper deals with the way the macromolecules pack together in the solid and especially the role that the aromatic-aromatic interactions play in the packing of the macromolecular segments.

Evidence for the Existence of Non-covalent Interactions and their Geometry

Hydrogen bonds in coals can be observed directly in the IR spectra of coals. The disruption of coal-coal hydrogen bonds by organic bases has also been directly observed spectroscopically.<sup>2</sup> Coals swell much more in solvents which are strong hydrogen bond acceptors than they do in very similar material without hydrogen bonding capabilities.<sup>1</sup> There can be no doubt but that hydrogen bonds between different parts of the coal network exist and can be broken by external reagents and presumably can re-arrange within the coal provided the conditions are right. There is an enormous literature on the geometry of hydrogen bonding. For our purposes, it is simple enough to state that the hydrogen will lie on a line collecting the two nuclei which serve as the terminus for the non-covalent interaction.

Attractive interactions exist between aromatic units due to London dispersion forces.<sup>5</sup> There have been a number of calculations on various systems, but since they are very time consuming, they emphasize small molecules, particularly benzene-benzene interactions.<sup>6</sup> In addition, there are experimental studies of gas phase complexes, complexes in biological systems and also crystal structures of PNA systems.<sup>7</sup> In small rings, the most favorable interaction occurs when the rings are at right angles to each other in a T-shaped configuration. Face-to-face parallel stacking is repulsive at all distances. This is not surprising since one is bringing two electron clouds into increasingly close proximity. As the ring size grows larger, there is a tendency to move off of the perpendicular somewhat, but the parallel stack remains repulsive.<sup>6</sup> In crystal structures where there is the necessity for filling space, a "herringbone" pattern is adopted which preserves both the "T" interactions and provides a packing geometry which is space filling.

In an amorphous polymer network like coals, we anticipate a compromise between the thermodynamic driving force for "T" configuration interactions between aromatics and a packing which efficiently fills space. It is not easy to predict what the outcome will be. Hirsch's X-ray data are quite explicit in identifying some parallel stacking in coals but it is impossible to compare the frequency of this geometry with that of a perpendicular orientation of aromatics.

#### Orientation of Aromatics with Respect to the Bedding Plane

It is often assumed by coal scientists that the aromatic systems in coals both have a strong tendency towards parallel alignment and tend to align parallel to the bedding plane. While there is clear X-ray evidence for some tendency towards parallel stacking, the evidence for alignment of aromatic rings parallel to the bedding plane is much more tenuous. In Hirsch's classical papers, he provides evidence for the alignment of aromatic systems parallel to the bedding plane in an anthracite coal but states that "the degree of preferred orientation is small in the low rank coals and increases with rank, particularly in the anthracite region".<sup>8</sup>

The other factor which comes into play is the striking anisotropy in coal mechanical properties. Coals are much stronger perpendicular to the bedding plane than parallel to the bedding plane. This is a significant factor in mine design but it has not heretofore been determined whether the mechanical anisotropy was an inherent property of the material or was due to the cleats and cracks which form whenever a piece of coal is hacked from a seam.

The alignment of aromatic structures in coals with reference to the bedding plane was investigated using Fourier transform IR dichroism with photoacoustic detection. A solid disk of coal was cut and the bedding plane accurately determined. This was placed in the photoacoustic detector of an IBM FTIR and spectra obtained using plane polarized light indexed to the bedding plane. Spectra were obtained at 45° intervals moving in a 360° circle. To verify that the instrument was operating properly, a crystal of acrylamide was oriented in the IR instrument and the dichroic spectra obtained. From these spectra, we could accurately back-calculate the known bond angles in the oriented single crystal. Based on these calculations, we estimate that our error is  $\pm 3^\circ$ . Dichroic spectra of Ill. No. 6 coal and acrylamide are shown in Fig. 1. In none of the coals was any alignment of the organic structures parallel to the bedding plane detected.

We have applied  $^{13}\text{C}$  NMR using oriented samples in a single crystal probe as well as optical birefringence to some of these coals. Both of these techniques indicate a net orientation of the aromatic rings of about  $1.5^\circ$ , within the experimental error of the IR measurements. Our conclusion is that the organic groups in coals are essentially randomly arranged.

To probe the mechanical anisotropy, a series of coal thin sections were swollen under a microscope and the swelling measured on photographs of the thin sections. Features on the thin section were identified, these features being connected by lines which would run either parallel to or perpendicular to the bedding plane. The coal is wet with a solvent and as it expands it was photographed and the movement of these features measured on the photographs, directly giving linear expansions. These data were obtained for six coals and are shown in Fig. 2. For all coals and solvents, the swelling is highly anisotropic. The coals expand much greater perpendicular to the bedding plane than they do parallel to the bedding plane. The mechanical anisotropy of coals must be a direct consequence of their macromolecular structure.

We are faced with an apparent contradiction in that coals have randomly oriented groups on a molecular level but are mechanically anisotropic on a larger scale. There are two possibilities. There may be a random coil network with a non-random distribution of branch points, the branch points occurring more frequently parallel to the bedding plane than perpendicular to it. Another possibility is a coal structure which features an array of sheets dividing and twisting and eventually achieving an individual group random orientation while maintaining a bulk structure anisotropy under stress.

Such structures have been proposed for amorphous carbons and recently for a low-rank coal based on X-ray data.

#### Reversible Association of the Coal in the Macromolecule

As if this was not sufficient structural complexity, the coal is not at an equilibrium configuration when removed from the mine to atmospheric pressure and is capable of undergoing a number of internal re-arrangements. A plot of linear expansion during solvent swelling parallel to and perpendicular to the bedding plane for several coals vs. time is shown in Fig. 3. Both of these coals show excess expansion both parallel and perpendicular to the bedding plane, that excess occurring at different times. The existence of the swelling excess was first noted by Peppas and ascribed to a metastable state<sup>11</sup> caused by the slow motion of the coal macromolecular segments. We agree with his interpretation.

When the solvent is removed from the coal, the solid which remains has a somewhat different shape than the starting coal did: it is higher perpendicular to the bedding plane and not quite as wide. Subsequent swellings of this material are totally reversible, always returning to the same shape and size. Wetting the coal with the solvent, allowing it to expand, and then contracting it by removing the solvent lets the coal macromolecular segments find the equilibrium positions to which they will return again and again as the process is repeated. The configuration of coals in the seam is not at equilibrium at 1 at. Coals do not re-arrange to their equilibrium form without some treatment because they are glassy. If made rubbery, then re-arrangement will occur.

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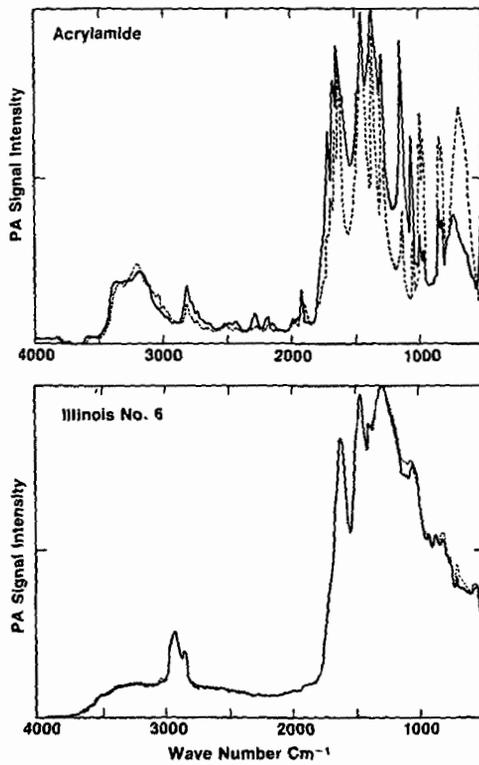


Figure 1. Photoacoustic FTIR Spectra Obtained with Polarized Light  
 a) Single Crystal Acrylamide; — Light Polarized Parallel to C Axis, ---- Polarized Parallel to B Axis  
 b) Ill. No. 6 Coal; — Light Polarized Parallel to Bedding Plane, ---- Polarized Perpendicular to Bedding Plane

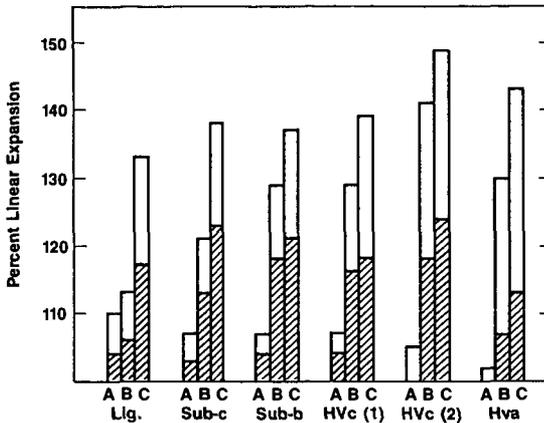


Figure 2. Linear Expansion of Coals in Chlorobenzene (A), THF (B), and Pyridine (C) Measured Parallel (crosshatched) to and Perpendicular to the Bedding Plane. Lig. = Big Brown (Texas); Sub-c = Smith Seam; Sub-b = Wandoan; HVC(1) = Correjon (Columbia); HVC(2) = Ill. No. 6; HVa = Pittsburgh No. 8.

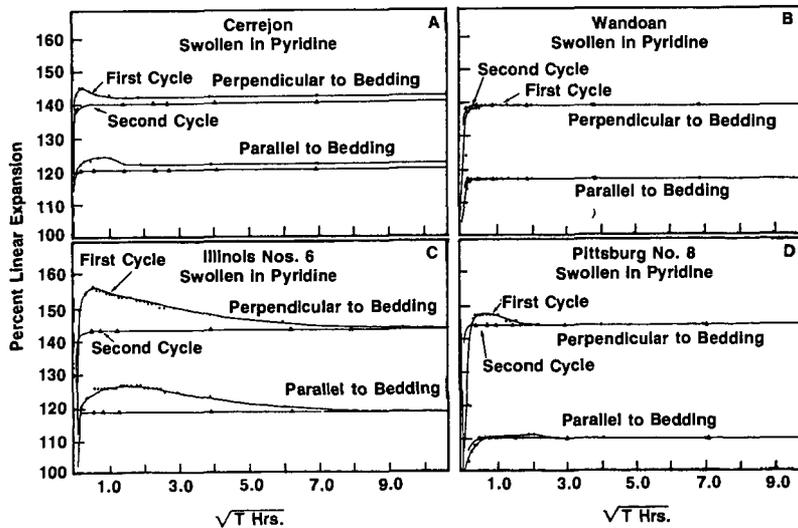


Figure 3. Time Dependence of Linear Expansion of Coals Swollen in Pyridine Parallel to and Perpendicular to the Bedding Plane