

## Non-covalent Interactions in Coals

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### ABSTRACT

The interactions between bituminous coals and organic molecules can be quantitatively described using only two terms: interactions dependent on polarizability and acid/base interactions, especially hydrogen bonding. Except for groups having an unpaired electron (the coal radical sites), the same two forces so dominate coal-coal interactions that it is not necessary to invoke any others. Except for radical sites, HOMO-LUMO gaps are so large that  $\pi$ - $\pi$  and charge transfer interactions (aromatic "stacking" interactions) are improbable.

### DISCUSSION

The aromatic groups in coals can interact with each other by London Dispersion Interactions which increase as their polarizability increases. Electrostatic interactions due to the existence of dipoles or quadrupoles are also important. Charge transfer interactions, in which electron density is transferred from a donor molecule to an acceptor are not important. It makes no difference if the electrons in question are non-bonding or  $\pi$  electrons, charge transfer is not important. The remainder of this article is a justification of the foregoing assertions. The terms  $\pi$ - $\pi$  and "stacking" interactions occur frequently in the coal literature and are not often defined. They seem to be used to mean associative interactions between aromatic systems due to electron transfer. That is the meaning assumed in this article.

Using gas chromatography to avoid complications caused by diffusion into coals<sup>1</sup>, the isosteric heats of adsorption of a variety of organic molecules on the surface of Illinois No. 6 coal were measured.<sup>2</sup> As expected, noble gases and saturated hydrocarbons gave adsorption heats that are a linear function of molecular polarizability confirming that their interactions with the coal surface are dominated by London Dispersion Interactions. Molecules (e.g. pyridine, THF) that are solely bases, that have no ability to donate an acidic proton, lie above the line defined by the non-polars. That excess interaction enthalpy for all 7 bases studied is equal to their heats of hydrogen bonding to p-fluorophenol. The isosteric heat of adsorption of those 7 bases on Illinois No. 6 coal is quantitatively explained by two terms, London forces and hydrogen bonding. There being no need to invoke others, normal scientific practice prohibits it. Contact angle studies also demonstrate that only two terms, dispersion and acid/base interactions, are necessary to describe fully interactions at coal surfaces.<sup>3</sup>

Is the situation the same when molecules are dissolved in (absorbed by) solid coals? The interactions of organic molecules when dissolved in coals can be monitored by studying volumetric solvent swelling.<sup>4</sup> Swelling pyridine-extracted Illinois No. 6 or Pittsburgh No. 8 coals with non-polar solvents gives rise to a symmetrical bell-shaped curve when solvent-swelling ratios are plotted against solvent solubility parameters (see Fig. 1). Plotting the swelling caused by basic molecules using their non-polar solubility parameters generates a set points all lying above the line defined by the non-polars. Furthermore, the excess swelling (the amount by which the swelling by bases is increased above the non-polar line) gives good straight lines when plotted against the bases' heats of hydrogen bonding to p-fluorophenol.<sup>4</sup> This behavior parallels that observed for adsorption and again only hydrogen bonds and London Dispersion Interactions are required to explain the interaction between dissolved molecules and bituminous coals.

The existence of bell-shaped plots of coal swelling by non-polar solvents and of acetylated coals by all solvents<sup>1</sup> is strong evidence against  $n$ - $n$  and charge transfer (CT) interactions. This can be argued in two ways. First, the shape of the plot demonstrates that these systems are following regular solution theory. That theory assumes that there is an averaging of the interactions between the coal and the swelling solvent based on the assumption that only dispersion interactions are occurring.<sup>5</sup> Coal-coal, solvent-solvent, and coal-solvent interactions are all assumed to be solely dispersion interactions. Specific complex formation and the interactions that would lead to them are excluded. Second, the solubility parameter of the coal is that value defined by the peak of the bell-shaped curve. The square of that

solubility parameter value is the cohesive energy density of the coal, a direct measure of the coal's self interactions. For all of the bituminous coals studied, these self interactions are of the same order as toluene's or chlorobenzene's, liquids which self interact by London dispersion interactions and electrostatic interactions due to  $\pi$ -dipole or  $\pi$  quadrupole interactions. These bell shaped curves provide evidence against a significant role for  $\pi$ - $\pi$  stacking and CT interactions in coals.

A qualitative consideration of  $\pi$ - $\pi$  stacking and CT interactions using perturbation molecular orbital theory<sup>6</sup> provides a strong argument against their importance in coals. The benzene dimer is a convenient starting point and example. As a pair of benzenes approach each other in a face-to-face orientation, their interaction gives rise to new bonding and antibonding orbitals by overlap of the highest occupied molecular orbitals (HOMO). The energy difference between the HOMO and the lowest occupied molecular orbital (LUMO) is so large that no interaction between them occurs.<sup>6</sup> The HOMO-HOMO overlap of the two benzene filled orbitals gives rise to new bonding and antibonding orbitals. Both are filled and the fact that the antibonding orbitals increase in energy more than the bonding orbitals decrease results in a repulsive interaction. The interaction of the two benzene  $\pi$  systems is repulsive. The antibonding destabilization is greater than the bonding stabilization. This is a 2-orbital 4-electron repulsive interaction. The benzene dimer is "T" shaped minimizing this repulsion and maximizing quadrupolar interactions.<sup>7</sup> Theory and experiment agree.<sup>7</sup>

This model can be used to define those circumstances in which pair-wise interactions will be favorable due to electron transfer. First, if the HOMO-LUMO gap is small, then the HOMO and LUMO can interact. This interaction will give rise to a stabilization because only the bonding orbital will be occupied. This 2-orbital 2-electron interaction might be a charge transfer involving a non-bonding pair of electrons or a  $\pi$ - $\pi$  interaction between an occupied and an unoccupied orbital. It makes no difference: the description is the same. To explore this possibility, the ionization energies and electron affinities of groups present in coals are tabulated in Table 1. The other possibility is a 2-orbital 3-electron interaction that will occur if a radical center is involved. Since the radical demands a half occupied "LUMO" or HOMO (called a SOMO), there is likely to be an orbital of similar energy available. It does not matter whether the interacting orbital is occupied or not. Both will give rise to a stabilization, greater in the case of a 1-electron 2-orbital interaction than in the case of a 3-electron 2-orbital interaction. The radical centers in coals may be the loci of strong interactions. This possibility is under investigation.

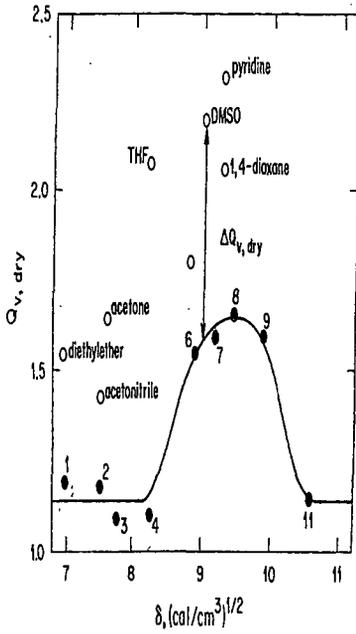
A consideration of the electron affinities (EA) and ionization potentials (IP) in Table 1 leads to the conclusion that  $\pi$ - $\pi$  and CT interactions in coals are unlikely to be favorable. The HOMO-LUMO gaps are too large to allow CT to occur. This is supported by experiment. Consider first the interactions between several organics and tetracyanoquinodimethane (TCNQ), an electron acceptor with an EA about 50 kcal/mole more favorable than pyrene. The equilibrium constant for complex formation between pyrene and TCNQ is only 29 l/mole.<sup>8</sup> With materials of lower electron affinity, the equilibrium constant will be even less. For the materials contained in the table, the HOMO-LUMO gap is so large that  $\pi$ - $\pi$  and CT interactions are unimportant. The HOMO-LUMO gap remains large enough for all reasonably sized molecules to rule out stabilization by electron transfer interactions.

There are numerous experimental and theoretical studies of aromatic-aromatic interactions.<sup>9</sup> To begin with theory, molecules as large as circumcoronene ( $C_{54}H_{18}$ ) have been studied.<sup>10</sup> Even here, the HOMO-LUMO gap is large enough so that the dominant attractive interactions are dispersion and electrostatic. The most favorable calculated geometry is not face-to-face but displaced and twisted. Effective theory has been developed and applied to numerous aromatic systems.<sup>7,9,11</sup> It uses attractive dispersion and electrostatic (dipolar and quadrupolar) interactions and repulsions originating from  $\pi$ - $\pi$  interactions.

There are numerous experimental studies of aromatic-aromatic dimers and multimers, most formed using molecular beam techniques.<sup>9</sup> The geometries vary depending on the nature of the interactions and especially on any charge separation in the molecules. The range from "T" shaped, to a " $\pi$ " shaped trimer<sup>12</sup>, to face-to-face coplanar dimers<sup>13,14</sup> where dipolar and quadrupolar interactions are most favorable in this geometry.<sup>15</sup> In none of these is the primary interaction due to ground state electron transfer.

The principal attractive interactions between pairs of aromatic systems depends on the polarizabilities and dipole and quadrupole moments of the interacting systems. The filled orbital interactions are repulsive. This issue and others will be discussed in a full paper together with the evidence (or lack thereof) for  $\pi$ - $\pi$  stacking and CT interactions in coals.

Figure 1. Volumetric swelling ratio ( $Q_v$ ) for pyridine extracted Bruceton coal as a function of the solubility parameter of the non-polar solvents ( $\bullet$ ) and the non-polar stability parameter of the polar solvents ( $\circ$ )



- 1) n-pentane, 2) n-heptane,  
 3) methylcyclohexane, 4) cyclohexane,  
 5) o-xylene, 6) toluene,  
 7) benzene, 8) tetralin, 9) naphthalene,  
 10) carbon disulfide, 11) biphenyl

=Table 1. Molecule Ionization Potentials (IP) and Electron Affinities (EA)

Molecule	IP (eV)	EA (eV)
Benzene	9.24 <sup>a</sup>	-0.72 <sup>b</sup>
Naphthalene	8.15 <sup>a</sup>	0.15 <sup>b</sup>
Anthracene	7.42 <sup>a</sup>	0.66 <sup>b</sup>
Phenanthrene	7.90 <sup>a</sup>	0.31 <sup>b</sup>
Pyrene	7.43 <sup>a</sup>	0.56 <sup>b</sup>
Pentacene	6.66 <sup>a</sup>	1.35 <sup>b</sup>
Coronene	7.36 <sup>a</sup>	
Phenol	8.51 <sup>c</sup>	-1.01 <sup>d</sup>
Aniline	7.7 <sup>c</sup>	-1.13 <sup>d</sup>
Pyridine	9.3 <sup>c</sup>	-0.62 <sup>d</sup>
Maleic Anhydride		1.33 <sup>e</sup>
TCNQ		2.84 <sup>e</sup>
TCNE		2.77 <sup>e</sup>
CS <sub>2</sub>		0.90

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