

# USING STRUCTURAL MODELS TO SIMULATE THE POLY-CYCLICS IN COALS.

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Keywords: Poly-cyclic aromatic compounds, molecular modeling, x-ray scattering

## INTRODUCTION.

Both NMR<sup>1-4</sup> and other types of analysis<sup>5-10</sup> have recently made significant contributions to understanding the composition and the distribution of the poly-cyclic units which are thought to comprise the most important units in coals. This group<sup>10-13</sup> has recently contributed some x-ray scattering studies which have as their goal a better understanding of the poly-cyclic units. X-ray scattering studies are one-dimensional in nature and address distances in the average scattering unit of a condensed phase material.<sup>14</sup> Structural models of some poly-cyclic (PC) moieties thought to be found in coals have been developed in order to better interpret and understand the x-ray scattering data obtained from these coals. Our models are based on the findings of the NMR and other studies noted above. The structural PC models may be utilized in real space to predict distances between bonded C-C atom-pairs and between non-bonded C-C atom-pairs. In addition, the distance array calculated for each PC model may be Fourier transformed into reciprocal space and compared to the experimentally measured x-ray scattering intensity for a coal (or any other scattering unit).

Whether the analysis occurs in reciprocal space or in real space, the accuracy of the structural models is as important as the accuracy of the x-ray scattering experiments to developing an understanding of the average PC unit in the coal.

## EXPERIMENTAL

This group has "built" three-dimensional structural models of several of the poly-cyclic (PC) compounds thought to occur in coals. These models incorporate the "best available" crystallographic data concerning the various C-C bond distances and the C-C-C bond angles as well as information about the planarity of each aromatic ring as well as the co-planarity of each entire PC unit. From the bond distance-bond angle-planarity information, an atom-coordinate map for each of the carbon atoms has been constructed. All of the bonded and non-bonded C-C atom-pair distances have been calculated. The distance array calculated for each PC model has been used to construct a simulated structure curve, in real space, by:

$$W_{\lambda}(r) = 36 \text{ el}^2 \times \sum \{n_{JK}/r_{JK}^{0.5}\} \times \exp\{-\gamma \times \Delta r_{JK}^2/r_{JK}^{0.5}\}. \quad (1)$$

This real space simulation has been adapted from the Kurrita model for diffraction peaks<sup>15</sup> and is consistent with the shapes of the maxima and minima in the atom-pair correlation functions calculated from x-ray scattering measurements of several of the Argonne Premium Coals.<sup>11-13</sup> In eq. 1,  $36 \text{ el}^2$  represents the scattering power of one C-C atom-pair, and  $n_{JK}$  represents the number of J-K atom-pairs found at the distance  $r_{JK}$  in the average short-range scattering unit of the coal, and  $\Delta r_{JK} = r - r_{JK}$ .

## RESULTS AND DISCUSSION.

**Analysis in Real Space.** The atom-map and the three-dimensional atomic coordinates developed for naphthalene are presented in Table I. The distance/frequency arrays for naphthalene, anthracene, and phenanthrene are presented in Table II. Shown in Figure 1 are the simulated real-space structure curves calculated for benzene, naphthalene, anthracene, and naphthacene. Each of these models has been developed based on the first approximation that all of the bonded C-C atom-pair distances are 1.39 Å, that each of the C-C-C bond angles is 120° (i.e.,  $\phi = 2\pi/3 - \pi/2$  in Table II), and  $\tau = 0$  (i.e., the PC rings are co-planar). Numerous other combinations of  $d$ ,  $\phi$ , and  $\tau$  have been considered. The longest non-bonded C-C distance is marked by \* in each  $W_{\lambda}(r)$ . Differences in the longest non-bonded C-C distance and other differences are clear from comparison of these simulated  $W_{\lambda}(r)$ 's.

The simulated structure curve calculated from each model may be compared to the atom-pair correlation function (APCF). The APCF is experimentally determined and

provides a measure of the deviation from randomness of the atom-pairs in the scattering material. The APCF,  $g(r)$ , is limited to describing a one-dimensional description (i.e., atom-pair distances) which characterize the structuring found in the average short-range structural unit of the subject material (i.e., the coal) and may be obtained from measuring the secondary coherent X rays scattered by the coal.

Correlation between the simulated structure curve calculated from each PCA model,  $W_A(r)$ , and the experimentally-based atom-pair correlation function,  $g(r)$ , is initiated by calculating the difference function for each model:

$$\epsilon_A(r) = W_A(r) - g(r). \quad (2)$$

The difference function is then used to calculate the structure correlation factor for each model by:

$$R_A = \frac{\sum[\epsilon_A(r)]^2}{\sum[g(r)]^2}. \quad (3)$$

As with three-dimensional crystal structure analyses, the simulated structure considered to be best representation real-space structure results from the model which minimizes  $R_A$ .

Shown in Table III are the structure correlation factors calculated for several PC models compared to the APCF obtained from Pittsburgh # 8 coal, a high volatile bituminous coal. These comparisons show that  $g(r)$  correlates best with the  $W(r)$ 's calculated for the two  $C_{14}$  PC models. The  $R_A$ 's produced for anthracene and for phenanthrene are similar.

Inclusion of the alkyl moieties into the structural model improves the correlation between  $W_A(r)$  and  $g(r)$  for both phenanthrene and for anthracene. Shown in Figure 2 is a comparison of the  $W_{AN}(r)$  with the addition of four alkyl moieties added to the  $C_{14}$  unit. This arrangement produces lower  $R_A$ 's for both the anthracene and the phenanthrene models, as seen in Table IV.

Correlations in Reciprocal Space. The simulated structure curve,  $W(r)$ , may be Fourier transformed to produce the simulated x-ray scattering intensity in reciprocal space by:

$$J(Q) = \{4\pi/Q\} \times \sum n_k \times \int r^2 \times \{W_A(r) - \rho_0\} \times \sin(Q \times r) \times \Delta r; \quad (4)$$

where  $\rho_0$  is the bulk atom density of the coal.

Definition of  $i(Q)$  as the experimentally determined intensity in reciprocal space, the comparison between  $I(Q)$  and  $J(Q)$  may also be used to evaluate the validity of the PC model(s) being considered. Shown in Figure 3 is the  $J(Q)$  calculated from the 4 alkyl-anthracene model compared to  $I(Q)$ . The correlation factor for the comparison in reciprocal space is termed  $R^*$ , where:

$$R^* = \frac{\sum\{i(Q) - J(Q)\}^2}{\sum\{i(Q)\}^2} \quad (5)$$

Using the alkyl substituted anthracene as the PC model,  $R^* = 0.039$  when  $R^*$  is evaluated from  $Q = 2.00 \text{ \AA}^{-1}$  to  $15.00 \text{ \AA}^{-1}$ . If the region  $Q < 2.00 \text{ \AA}^{-1}$  is included in the calculation,  $R^*$  increases dramatically to 0.768; indicating that the large peak in  $i(Q)$  centered at  $1.7 \text{ \AA}^{-1}$  is not due to the average PC structure in the coal. Similar results have been obtained when an alkyl substituted phenanthrene model is used to generate  $J(Q)$ . All other PCA models produce  $R^*$  values which are much larger than the  $R^*$ 's measured for the substituted  $C_{14}$  PC's.

## CONCLUSIONS

Structural models and detailed atom maps are useful in determining the average PC unit in coals because their simulated structure curves may be directly compared to the results of wide angle x-ray scattering experiments used to examine the coals. However, the resulting statistical analysis does not, necessarily, produce unequivocal results.

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TABLE II. ATOM-PAIR DISTANCE/FREQUENCY ARRAY FOR NAPHTHALENE, ANTHRACENE, AND PHENANTHRENE

DISTANCE ( $d_{jk}$ )	FREQUENCY ( $n_{jk}$ ) IN		
	NAPHTHALENE	ANTHRACENE	PHENANTHRENE
1.39 Å	11	17	17
2.47 Å	14	22	21
2.78 Å	6	8	10
3.68 Å	6	12	13
4.17 Å	4	8	10
4.82 Å	2	6	8
5.01 Å	2	4	6
5.56 Å		2	2
6.07 Å		4	2
6.37 Å		4	4
6.96 Å			1
7.23 Å		2	
7.36 Å		2	

TABLE III. STRUCTURE CORRELATION FACTORS BETWEEN SEVERAL PCA MODELS AND THE APCF FOR PITTSBURGH # 8 COAL.

Carbons	PC MODEL	R-VALUE <sup>A</sup>
C10	naphthalene	0.303
C14	anthracene	0.053
	phenanthrene	0.079
C16	pyrene	0.334
C18	naphthacene	0.750
	1,2-benzophenanthrene	0.553
	crysene	0.568
	tri-phenylene	0.396

<sup>A</sup> R has been calculated over the interval from  $r = 0.00$  Å to  $r = 10.00$  Å.

TABLE IV. EFFECTS OF ADDING FOUR ALKYS TO THE  $C_{14}$  PC MODELS.

PC MODEL	4 ALKYS ADDED	$R_A$
Anthracene	no	0.053
	yes	0.046 to 0.037 <sup>A</sup>
Phenanthrene	no	0.079
	yes	0.062 to 0.040 <sup>A</sup>

<sup>A</sup> The actual value of the structural correlation factor depends upon the relative positions of the alkyls as added to the  $C_{14}$  unit.

1995, 55.

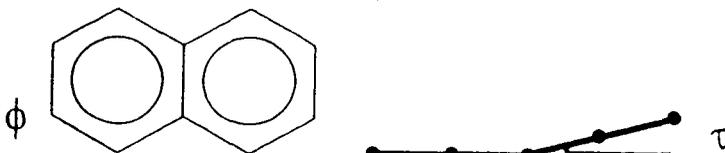
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TABLE I. ATOM MAP AND ATOM LOCATIONS FOR NAPHTHALENE

A. ATOM MAP.

TOP VIEW OF XY PLANE

SIDE VIEW, XZ PLANE



B. ATOM LOCATIONS.

CARBON NUMBER		ATOM LOCATIONS		
	X	Y	Z	
1	0	0	0	
2	0	d	0	
3	$d \times \cos\phi$	$d \times [1 + \sin\phi]$	0	
4	$2 \times d \times \cos\phi$	d	0	
5	$2 \times d \times \cos\phi$	0	0	
6	$d \times \cos\phi$	$-d \times \sin\phi$	0	
7	$d \times \cos\phi \times [2 + \cos\tau]$	$-d \times \sin\phi$	$d \times \cos\phi \times \sin\tau$	
8	$2 \times d \times \cos\phi \times [1 + \cos\tau]$	0	$2 \times d \times \cos\phi \times \sin\tau$	
9	$2 \times d \times \cos\phi \times [1 + \cos\tau]$	d	$2 \times d \times \cos\phi \times \sin\tau$	
10	$d \times \cos\phi \times [2 + \cos\tau]$	$d \times [1 + \sin\phi]$	$d \times \cos\phi \times \sin\tau$	

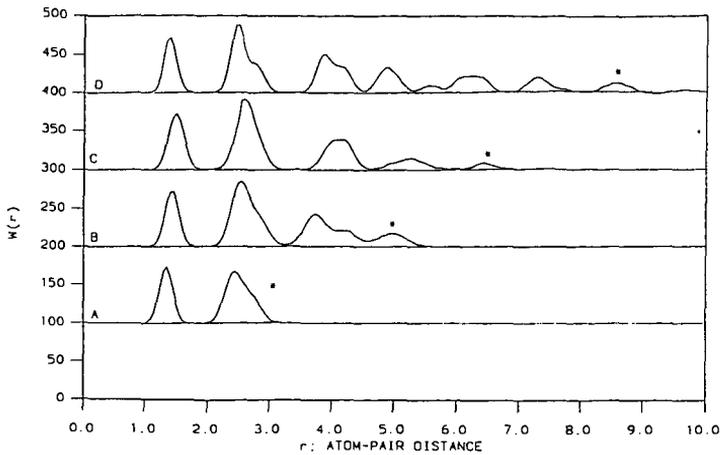


Figure 1.  $W(r)$ 's for benzene (A), naphthalene (B), anthracene (C), and naphthalene (D). The longest non-bonded C-C distance in each is marked by \*.

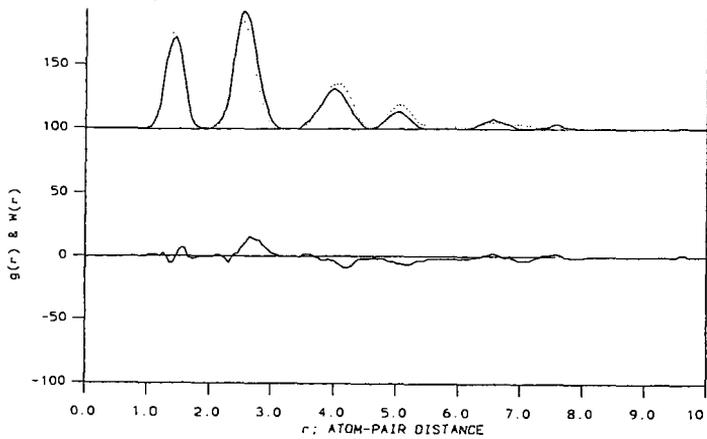


Figure 2.  $W(r)$  for the alkylated  $C_{14}PC$  {...} compared to the APCF {\_\_\_\_\_}. The  $\epsilon(r)$  for this comparison is shown below.

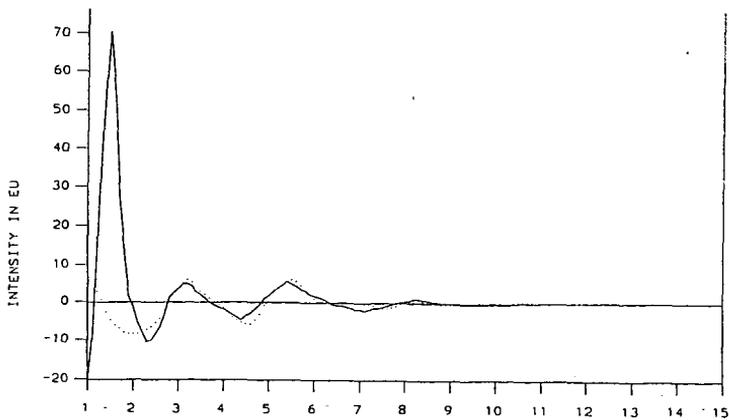


Figure 3. Comparison in reciprocal space of the simulated intensity for an alkylated  $C_{14}PC$  unit {...} and the experimentally measured intensity {\_\_\_\_\_}.