

MODELING OF COAL STRUCTURE USING COMPUTER-AIDED MOLECULAR DESIGN*

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Abstract

Knowledge of coal molecular structure is important in the understanding of coal reactivity. Computer-aided Molecular Design (CAMD) has been used to create and study 3-dimensional models of several postulated coal structures (Given, Wiser, Solomon, and Shinn). Using molecular dynamics calculations, a minimum-energy conformation for each structural model has been determined. Characteristics of the resulting coal structures will be discussed. Interactions of the structures with polar and non-polar solvent molecules are being explored to provide insight into coal pre-conversion chemistry. Future studies possible with this new tool will be outlined.

Introduction

The reactivity of coal is determined in substantial part by its chemical and physical structure. However, within any given coal there is considerable heterogeneity. Nonetheless, because of the strong link between structure and reactivity, there have been many attempts to model the macromolecular structure of various coals. For bituminous coals, the most widely accepted models developed during the past 30 years have been the aromatic/hydroaromatic structures, in which groups of about three aromatic rings, containing appropriate numbers and types of heteroatoms, are interconnected by hydroaromatic or aliphatic linkages (1-4). These models incorporate the average chemical and molecular characteristics of coal, and are not intended explicitly to represent actual "coal molecules". More recently, Spiro (5) has constructed physical space-filling models of several of these structures. Using the insight obtained from these models, he identified several steric difficulties in the original structures, and discussed the possible significance of the three-dimensional structures on mechanisms of coal pyrolysis.

Recently, computer-aided molecular design (CAMD) techniques have been developed to provide additional understanding of the structure and properties of complex molecular systems (6). Currently, CAMD techniques are being widely used in the pharmaceutical industry to guide the design and synthesis of a variety of biomolecules (drugs, enzymes, inhibitors, proteins). Using CAMD, one can not only construct a three-dimensional representation of a molecule, but can also convert the structure to an energy-minimized physical conformation, using molecular dynamics techniques. CAMD has been used to study basic coal structure (7), but not to examine the energetics of the structures. In this paper, CAMD is used to create three-dimensional models based on several postulated coal structures, and then to identify minimum-energy physical conformations for these models.

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Method

The CAMD studies described were carried out using BIOGRAF (BioDesign, Pasadena, CA), a software package for simulating organic and biological molecules. BIOGRAF allows the user to build molecules (structures), display them in a variety of formats (stick; dot surface; space-filling) and identify minimum energy conformations for them. The minimum energy conformations are found using molecular dynamics techniques with a suitable force-field approximation (6). In molecular dynamics, the energy of a structure is evaluated periodically as the atoms are allowed to move according to Newton's equations of motion at a specified "temperature" (which defines the atomic velocities). Dynamics runs usually involve many thousands of evaluation steps, representing the equivalent of many picoseconds of molecular motion. During the dynamics runs, structures twist and fold in ways which tend to optimize the non-bonded interactions (van der Waals, ionic, and hydrogen bonds), while maintaining appropriate bond lengths and angles.

BIOGRAF supports a number of force fields (AMBER, MM2, and DREIDING); in the current study, DREIDING was used. DREIDING is a very general force field that accounts for bond stretches and angles, torsions, and non-bonded interactions for a large number of atom types. Its accuracy is limited because it uses the same force constants for all atom types, although not for all types of interactions (i.e., the force constants for bond stretches are different from those for bending interactions, etc.). With this limitation, the energies calculated are most meaningful relative to one another, rather than in a quantitative sense. The BIOGRAF program was run on a MicroVAX II computer equipped with an Evans and Sutherland PS390 graphics terminal. The size of coal structures evaluated, and the duration of molecular dynamics runs, were limited by the available computing speed of this system (a 5000-step, 10-ps molecular dynamics run for a 1040-atom structure, with about 75,000 van der Waals interactions per step, required about 100 hours of computation).

Results

BIOGRAF was used to create three-dimensional models of four postulated bituminous coal structures, those of Given (1), Wiser (2), Solomon (3), and Shinn (4). After each of the models was created, it was converted into a minimum-energy physical conformation using molecular dynamics and energy minimization. Two of the structures, Given's and Shinn's, are shown in Figures 1 and 2. The Givens structure is shown because it has been widely cited as a possible representative coal structure. The Shinn structure represents the most complex coal structure in the literature, is also widely cited, and is similar in many ways to the Wiser and Solomon structures. Figures 1a and 2a show the two-dimensional molecular structures reported originally by Given and Shinn. These were used, with minor modifications, to create the computer space-filling models shown in Figures 1b and 2b (Given's structure was modified as suggested by Spiro (5) to eliminate a very strained quaternary carbon bond, and Shinn's structure was simplified by eliminating that fraction identified in his Table 5 as "residue", approximately 20% of the original structure). As the top and side views in Figure 2b show, the models are nominally two-dimensional at this point. Finally, Figures 1c and 2c show the minimum energy conformations adopted by the two models after 10-ps molecular dynamics runs. It is clear from the folding of these latter figures (especially Figure 2c) that simple two-dimensional representations probably do not adequately represent the coal structure. Significantly, the Given structure (Figure 1), constrained by pairs of methylene bridges between aromatic structures, is seen to be rather rigid. It did not change shape during molecular

dynamics as much as the Shinn structure, which folded up considerably due to van der Waals and hydrogen-bonding interactions. The Wiser and Solomon structures, not shown, behaved much like the Shinn structure during energy minimization.

To evaluate further the CAMD results, a program was written to extract a number of atomic and chemical parameters from each structure (number of atoms, fractions of aromatic carbon and hydrogen, weight fraction of each atomic species, empirical formula). The results were compared with the original literature for each structure. This provided a useful check on the accuracy of the computer models, which were rather complex (over 1000 atoms in the Shinn structure). In all cases, the CAMD models compared favorably with the literature values. Results of the computer analyses for the four structures analyzed are given in Table I. The total numbers of atoms only appear as guides to the size and complexity of each structure, and bear no relationship to the size of a "coal molecule" or a decomposition product. The most significant difference between the models appears to be in the values assumed for aromatic hydrogen. Given's value is much lower than those of the other authors and is probably incorrect, judging from more recent FTIR data (8). Given used pairs of methylene bridges extensively to satisfy his low ratio of aromatic hydrogen, thus explaining the major difference between his and the other structural models.

Also included in Table I is the minimum energy for each structure, calculated during molecular dynamics runs in which the "temperature" was reduced over a 10-ps period from 300 K to 10 K. In order to make the results more easily comparable, the energies are expressed per unit atom. The Given structure is energetically less favorable than the other three, because when it is considered as an isolated structure, its relative rigidity allows only minimal van der Waals and hydrogen-bond interactions. However, even if a number of Given structures were made to interact, their rigidity would still allow less non-bonded interactions, resulting in higher energy relative to the other structures. Thus, the Shinn, Wiser and Solomon structures appear at this time to be the more favored structures, based both on their more appropriate chemical characteristics and on their observed structural flexibility and energetic advantages.

Discussion

Three-dimensional models of postulated coal structures have been created, and minimum-energy conformations identified. For each of the three relatively flexible structures modeled, there was actually a large number of slightly different conformations with similar (low) energies. This suggests first that a number of nearly-equivalent structures might be equally probable in coal, and second, that structures with substantially lower energies than those identified are probably not likely. Although the ring structures in the energy-minimized Shinn structure (Figure 2c) show on the average no preferred orientation (although some local stacking was observed), the macrostructure is still somewhat anisotropic. If an extended structure based on the several units of the original quasi-planar Shinn structure had been constructed and energy-minimized, the anisotropy would have been more marked. This is in accord with Larson's experimental observations (9) that vitrinite samples have essentially randomly oriented organic groups (on a macroscopic scale), but at the same time show highly anisotropic mechanical and solvent swelling properties.

This work represents a first use of CAMD techniques to model coal structure and energetics. It has been possible to differentiate several postulated bituminous coal structures based on their three-dimensional character and their energetics. Obviously, these techniques could also be used to model coals of varying rank.

Modifications of the CAMD software are planned to allow the calculations of true and particle density of the coal structures. These density calculations will be especially important in the study of coal-solvent interactions, using both polar and non-polar solvents. Such studies should provide further insight into the nature of solvent swelling phenomena and the role of porosity in coal. Finally, although more difficult, it may be possible to model chemical interactions approximately using CAMD. In all, it appears that CAMD techniques represent a potentially very powerful new tool for studying the nature of coal structure and its effect on reactivity.

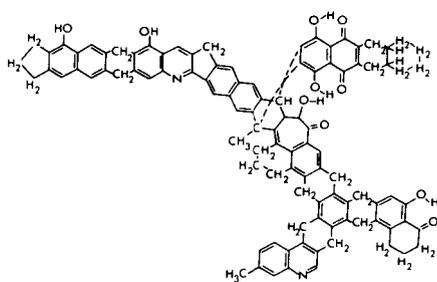
References

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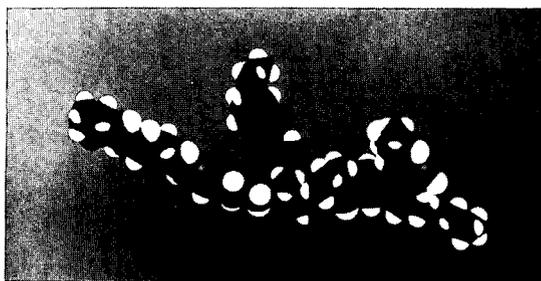
TABLE I

COAL STRUCTURAL PARAMETERS (Weight Fraction DMF)

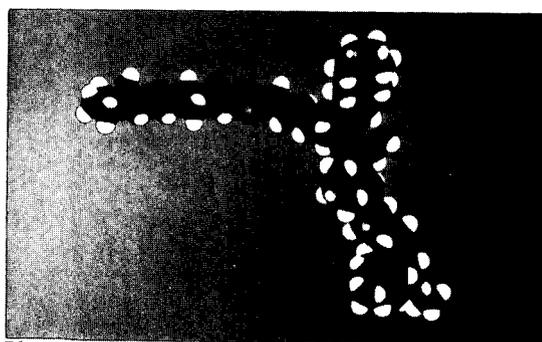
<u>Parameter</u>	<u>Given</u>	<u>Visser</u>	<u>Solomon</u>	<u>Shinn</u>
# Atoms	193	390	326	1040
C _{Ar}	0.66	0.71	0.74	0.71
H _{Ar}	0.21	0.29	0.36	0.34
Wt. Fraction				
C	0.82	0.76	0.81	0.79
H	0.053	0.057	0.055	0.056
O	0.107	0.112	0.096	0.113
N	0.019	0.014	0.011	0.014
S	---	0.053	0.026	0.020
Energy/Atom (kcal/atom)	2.01	1.60	1.58	1.55
Formula (normalized)	C ₁₀₀ H ₇₇₀ .8N ₂ .0	C ₁₀₀ H ₈₉₀ .1N ₁ .6S ₂ .6	C ₁₀₀ H ₈₂₀ .9N ₁ .2S ₁ .2	C ₁₀₀ H ₈₅₀ .1N ₁ .5S ₁ .0



a)

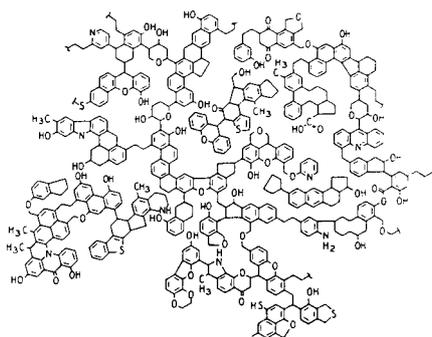


b)

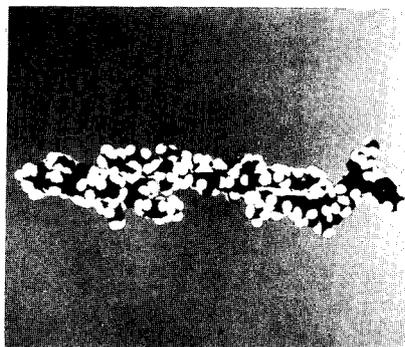
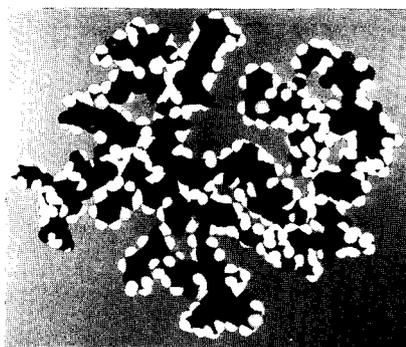


c)

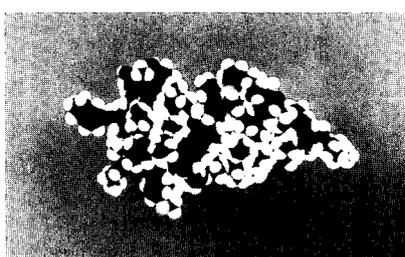
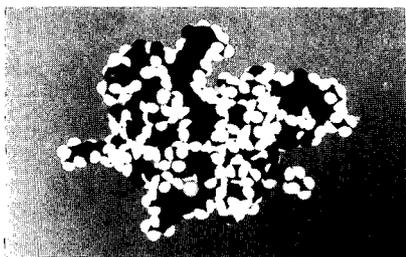
Figure 1. Given structure. a) Structure from literature; b) Initial CAMD-generated structure; c) Energy-minimized CAMD structure.



a)



b)



c)

Figure 2. Shinn structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized CAMD structure, top and side views (same orientation, same scale).