CONF-871081-

SAND89-2401 C

CHEMISTRY OF LARGE MOLECULES

G. A. Carlson

Fuel Science Division
Sandia National Laboratories
Albuquerque, N. M. 87185

SAND--89-2401C

DE90 000813

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 three-dimensional models of several postulated coal structures (Given, Wiser, Solomon, and Shinn). Using molecular dynamics calculations, the minimum-energy conformations for each structural model have been compared. The physical densities of the minimum-energy conformations have been calculated, and are in agreement with experimental evidence. The frequencies of cross-linking hydrogen bonds have been evaluated for these structures. Finally, we have also begun to use CAMD to study model polymeric compounds, whose structure and reactivity may give new insights into coal conversion processes.

Objective

The reactivity of coal is determined in substantial part by its chemical structure and physical conformation. However, among different coals and even 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 molecular 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 fragments of about two to three aromatic rings, containing appropriate numbers and types of heteroatoms, are interconnected by hydroaromatic, aliphatic or heteroatom-containing 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 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 also convert the structure to an energy-minimized physical conformation, using molecular dynamics techniques. CAMD has been used previously to model products of coal liquefaction (7), but not to model coal structures.

---

*This work supported by the U. S. Dept. of Energy at Sandia National Laboratories under Contract DE-AC04-76DP00789.

MASTER

Accomplishments and Conclusions:

The CAMD studies described were carried out using BIOGRAF (BioDesign, Pasadena, CA), a software package for simulating organic, inorganic 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 of molecules 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 can be used for a large number of atom types. The Dreiding force field calculates the energy as a sum of covalently-bonded interactions (E_s=stretch; E_b=bend; E_t=torsion; and E_i=inversion) and non-covalently-bonded interactions (E_v=Van der Waals; E_e=electrostatic; and E_h=hydrogen bonds).

$$E = (E_s + E_b + E_t + E_i) + (E_v + E_e + E_h)$$

Different bond lengths and Van der Waals radii are specified for different atom types. The absolute accuracy of energies calculated with the DREIDING force field is limited, because for a given interaction (e.g., bond stretch), DREIDING uses the same force constants for all atom types. With this limitation, the energies calculated are most meaningful relative to one another, rather than in an absolute 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 length 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, required about 100 hours of computation).

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 conformation using molecular dynamics and energy minimization. These data are shown in Figures 1-4. The original structures which appeared in the literature are shown as Figures 1a-4a. They were used, with minor modifications, to create the computer models shown in Figures 1b-4b. Given's structure was modified as suggested by Spiro (5) to eliminate a very strained quaternary carbon bond near the center. Wiser's model was modified (as Wiser himself later suggested) by replacing the -S-S- link by a $-CH_2-CH_2-$ link, resulting in a more realistic sulfur content for the structure. Solomon's model, which consists of three separate fragments shown connected together by hydrogen bonds, was modified by adding two more of the four-member-ring fragments and covalently bonding all the fragments together where bonding links were indicated. 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 shown in Figures 2b-4b demonstrate, the models as initially constructed by CAMD were nominally two-dimensional. Wiser's model was of necessity constructed in three dimensions, due to overlap of parts of the structure when constructed in two dimensions. Figures 1c-4c show the minimum energy conformations adopted by the models after 10 to 20 ps molecular dynamics runs. The relatively compact structures observed following molecular dynamics are favored because they allow a maximum of hydrogen bonding and van der Waals interactions. Significantly, the Given structure (Figure 1) did not change shape during molecular dynamics nearly as much as the other structures. The pairs of methylene bridges which join the aromatic ring fragments in the Given structure constrain it to be rather rigid.

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 studied 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 gradually 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 by 25-30%, because its relative rigidity allows only minimal van der Waals and hydrogen-bond interactions. The Shinn, Wiser and Solomon structures appear at this time to be better representations of coal structure, based both on their more appropriate chemical characteristics and on their observed structural flexibility and energetic advantages.

For the Wiser, Solomon, and Shinn models, there were actually a large number of slightly different conformations with similar (low) energies. This suggests first that a number of nearly-equivalent conformations might be equally probable in coal, and second that structures with substantially lower energies than those identified are probably not likely. Although some local stacking was observed in the energy-minimized structures, the ring structures show on the average no preferred orientation. This is in accord with Larsen's experimental observations (9) that vitrinite samples have essentially randomly oriented organic groups (on a macroscopic scale).

The energy-minimized structures were also used to approximate the hydrogen-bond density in coal. Based on the total number of hydrogen bonds indicated by BIOGRAF, and using the molecular weight of each coal structure, the average molecular weight per hydrogen bond was determined to be between 208 and 497 (Table I). The Given structure, which did not fold substantially, exhibited the least hydrogen bonding. Larsen and coworkers (13) have recently evaluated the macromolecular network structure of two bituminous coals, using solvent-swelling techniques. Using the Kovac equation to analyze the solvent swelling behavior of unextracted coal (which is largely cross-linked by hydrogen bonds), Larsen reports an average molecular weight between cross-links of 200-400, in good agreement with our computer models.

We have recently begun to develop a computer program to investigate the density, porosity and solvent swelling of our coal structures. BIOGRAF does not have the capability of defining quantitatively some of the physical characteristics of molecules, such as density and porosity. However, density and pore size distributions are properties which have been experimentally measured for various coals and coal macerals. Additionally, there is a considerable body of experimental data on the solvent swelling of coals, which has been related to the degree of hydrogen bonding and the density of covalent cross-links in the coal macromolecular structure. Thus, our planned CAMD studies of solvent swelling should be greatly enhanced by the capability to determine porosity and density of structures before and after solvent interaction, for comparison with the experimental literature.

The density program we have developed uses the atomic spatial coordinates of the BIOGRAF molecular models. First, we construct a box, aligned with the x, y, and z coordinate axes, enclosing and somewhat larger than the molecular structure whose density is to be determined. Figure 5 shows schematically a box enclosing a structure of eight non-bonded atoms in a cubic array (only the top four are visible). We divide the box into a grid of equivalent-size volume elements, each much smaller than the volume of an atom. We first identify those grid volume elements which are within a Van der Waals radius of the coordinates of any atom, and count those volume elements as "atomic" volume. Now, since the atoms in our structure are assumed spherical, there remains some volume within the structure that is not "atomic" volume. If the volume is large enough to be accessible to a fluid in a density determination, it represents porosity. Otherwise, it represents space effectively occupied by the molecular structure, and must be counted as part of the volume of the structure for a proper density determination. To define this "internal" structural volume, we evaluate each remaining grid volume element to see if it is located between two "atomic" volume elements. If so, and if the closest "atomic" volume elements are less than a specified distance apart (currently 4 angstroms, chosen to approximate the size of a fluid atom or molecule), we assume no other atom or molecule could fit in that space, and we count that volume as "internal" volume. If the closest "atomic" volume elements are further than 4 angstroms apart, then we are either looking at an indentation in the surface of the structure, or at porosity. Excluding closed porosity, this "void" volume could theoretically be occupied by fluid during a density determination, and thus is not counted as part of the structure. Finally, all grid volume which does not fall into one of the foregoing categories is identified as "external" volume, or volume which is clearly outside of the structure. We now have divided the grid volume into four components, "atomic", "internal", "void", and "external" volume. All of these except "void" volume are illustrated in Fig. 5. The density of the structure is then defined as the molecular weight of the structure, multiplied by Avogadro's number, and divided by the sum of the "atomic" and "internal" volumes.

Using this technique, we have calculated densities for the energy-minimized Given, Wiser, Solomon and Shinn structures (see Table I). Although we are still refining the calculations, it is encouraging that the densities we have determined are on the order of those expected for bituminous coal (1.28-1.33 g/cm^3, ref. 10), and for vitrinite macerals, the major constituents of bituminous coal (1.25-1.30 g/cm^3, ref. 11). The Given structure, for which a higher density was calculated, is the smallest structure studied and has only surface atoms (i.e., no molecular folding took place during energy minimization of this rather rigid structure). Separate studies of model structures demonstrated that densities determined for structures with high surface-to-volume ratios (like the Given structure) are typically 5-10% too high.

To allow us to evaluate porosity in our structures, we have added the capability to write BIOGRAF-compatible coordinate files of the "internal", "atomic", "void", and "external" volume grid points. These can then be displayed graphically along with the molecular structure being studied. The structures we have modeled show some surface concavities, but do not show evidence of internal voids large enough to accept solvent molecules or to allow migration of a mobile phase. Since our structures are somewhat limited in size, we are not yet confident of the significance of these findings.

In related work, we have also begun a CAMD study of five model polymeric compounds identified by PETC (12) for synthesis in connection with coal liquefaction studies. Table 2 lists the model compounds and minimum-energy conformations determined by BIOGRAF for four of the five compounds. Model compound 5 has not yet been energy-minimized. Although we have not yet done a careful analysis of the minimum-energy structures, model compound 3, which has a strained ring structure, appears in this analysis to be somewhat less energetically favored.

Plans:

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 models based on their energy-minimized structures. However, none of the models investigated thus far contains explicit three-dimensional covalent cross-links. It has been established on the basis of solvent swelling studies (13, 14) that bituminous coal is primarily made up from a three-dimensionally cross-linked network of covalent bonds and an even higher density of hydrogen bonds. We plan to develop a new coal structural model which uses the coal fragments postulated by Shinn, but joined together in a three-dimensionally covalently-cross-linked manner as suggested by Larsen (15). We will vary the covalent cross-link density and observe the effect on physical density, internal porosity, and hydrogen bond density. We will also study solvent interactions, both polar and non-polar, with the new structures. We will quantify the changes in structural volume as the internal hydrogen bonds are displaced by solvent hydrogen bonds. The results will be compared with solvent swelling data, and used to provide an independent estimate of effective cross-link density in bituminous coal.

A limitation during the past year in conducting CAMD studies has been the computational speed of our current computer system. As mentioned earlier, molecular dynamics calculations of structures as large as the Shinn model took 100 hours or longer. Additionally, even longer molecular dynamics calculations will be necessary to establish minimum-energy conformations for larger, more complex structures. Thus, in order to to conduct adequate studies of three-dimensionally cross-linked structures and of solvent interactions, which will of necessity involve larger aggregates of atoms, we need to obtain a new UNIX-based computer. This will at a minimum increase our computational speed by 10- to 20-fold, and possibly as much as 100-fold.

References

1. Given, P. H., Fuel 39, 147 (1960).
2. Wiser, W. H., in Proceedings of the Electric Power Research Institute Conference on Coal Catalysis, Palo Alto, CA, 3 (1973).
3. Solomon, P. R., in New Approaches in Coal Chemistry, ACS Symposium Series No. 169, 61 (1981).
4. Shinn, J. H., Fuel 63, 1187 (1984).
5. Spiro, C. L., Fuel 60, 1121 (1981).
6. Fruhbeis, H., R. Klein, and H. Wallmeir, Angew. Chem. Int. Ed. Engl. 26, 403 (1987).
7. Robinson, K. K., in Proceedings of the Electric Power Research Institute Conference on Coal Structure, Palo Alto, CA, 3-1, (1987).
8. Solomon, P. R., ACS Div. Fuel Chem. Preprints 24(2), 184 (1979).
9. Larsen, J. W., ACS Div. Fuel Chem. Preprints 33(1), 400 (1988).
10. Mahajan, O. P., "Coal Porosity", in Coal Structure, (R. A. Meyers, ed.), Academic Press, New York, N. Y., pp. 55-59 (1982).
11. Crelling, J. C., private communication (1989).
12. Farcasiu, M., private communication (1989).
13. Larsen, J. W., T. K. Green, and J. Kovac, J. Org. Chem. 50, 4729 (1985).
14. Brenner, D., Fuel 64, 167 (1985).
15. Larsen, J. W., ACS Div. Fuel Chem. Preprints 30(4), 444 (1985).

TABLE 1

COAL STRUCTURAL PARAMETERS (Weight Fraction DMMF)

Parameter	Given	Wiser	Solomon	Shinn
# Atoms	193	394	396	1040
C_{Ar}	0.66	0.70	0.74	0.71
H_{Ar}	0.21	0.28	0.40	0.34
Wt. Fraction				
C	0.820	0.781	0.823	0.795
H	0.053	0.059	0.056	0.056
O	0.107	0.113	0.090	0.113
N	0.019	0.014	0.009	0.014
S	---	0.032	0.021	0.020
Formula (normalized)	$C_{100}H_{77}O_{9.8}N_{2.0}$	$C_{100}H_{90}O_{11}N_{1.6}S_{1.6}$	$C_{100}H_{81}O_{8.2}N_{1.0}S_{1.0}$	$C_{100}H_{85}O_{11}N_{1.5}S_{1.0}$
Energy (kcal/atom)	2.01	1.62	1.50	1.55
MW/H-bond	497	212	302	208
Density (g/cc)	1.46	1.28	1.32	1.25

TABLE 2

ENERGETICS OF COAL MODEL COMPOUNDS

Number	Name	Molecular Formula	Energy (kcal/atom)
1	6-methyl-9-propyl dibenzothiophene-4-ol	$C_{16}H_{16}OS$	1.35
2	4(4'-hydroxy-5',6',7',8'-tetrahydro-1'-naphthylmethyl)-6-methyldibenzothiophene	$C_{24}H_{22}OS$	1.41
3	tetrahydronaphthalene, naphthalene, and phenyl groups, linked by methylene, ethylene and ether bonds	$C_{30}H_{28}O_2$	1.59
4	1-hydroxynaphthalene-dibenzothiophene polymer linked by methylene bonds, containing 2-3 wt% S	$C_{720}H_{584}O_{52}S_8$	1.56
5	naphthalene-hydroxynaphthalene polymer with methylene and benzyl ether links and substituted phenyl crosslinks	$C_{720}H_{500}O_{40}$	*

* Not yet energy-minimized

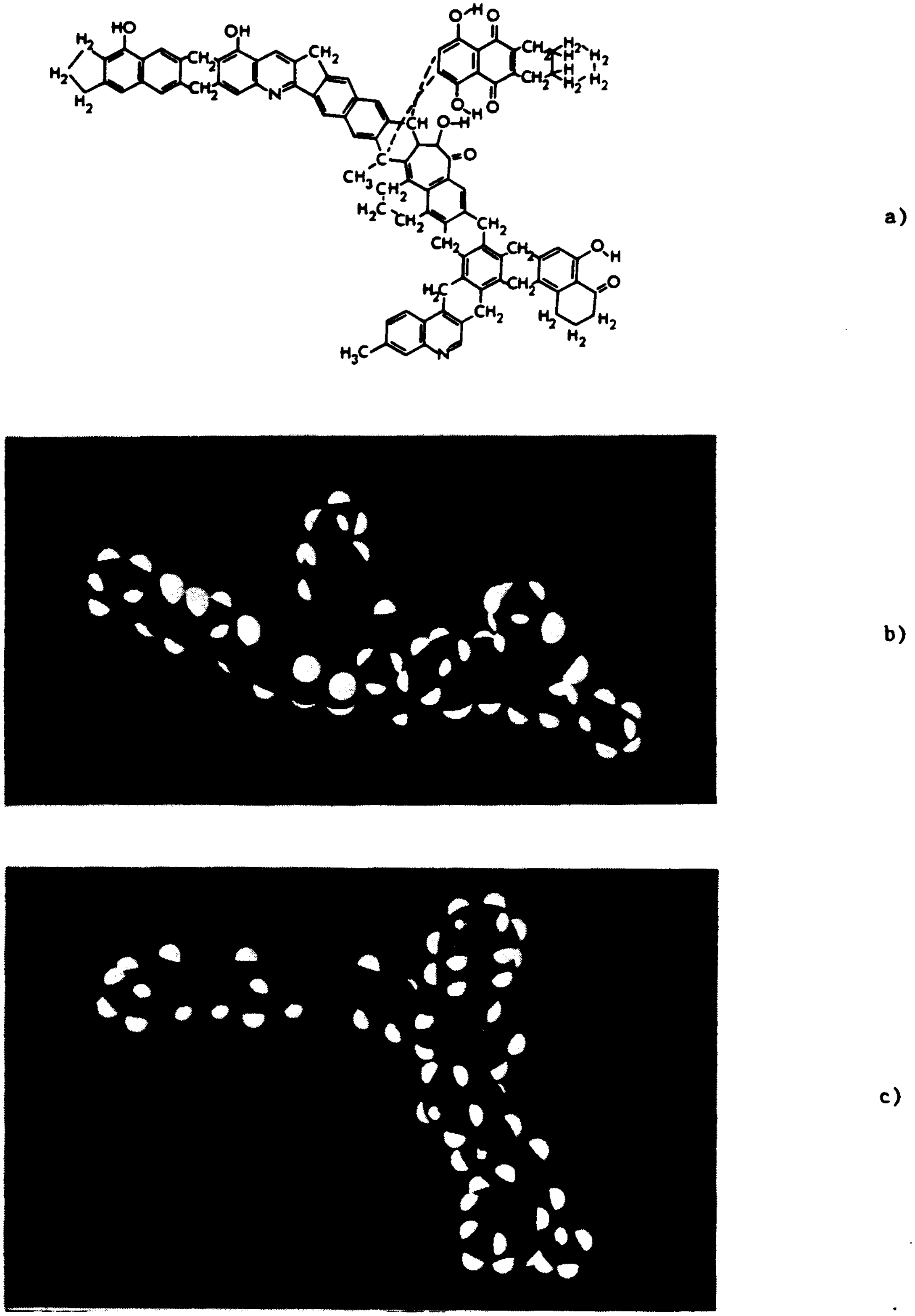

Figure 1. Given structure. a) Structure from literature; b) Initial CAMD-generated structure; c) Energy-minimized structure.

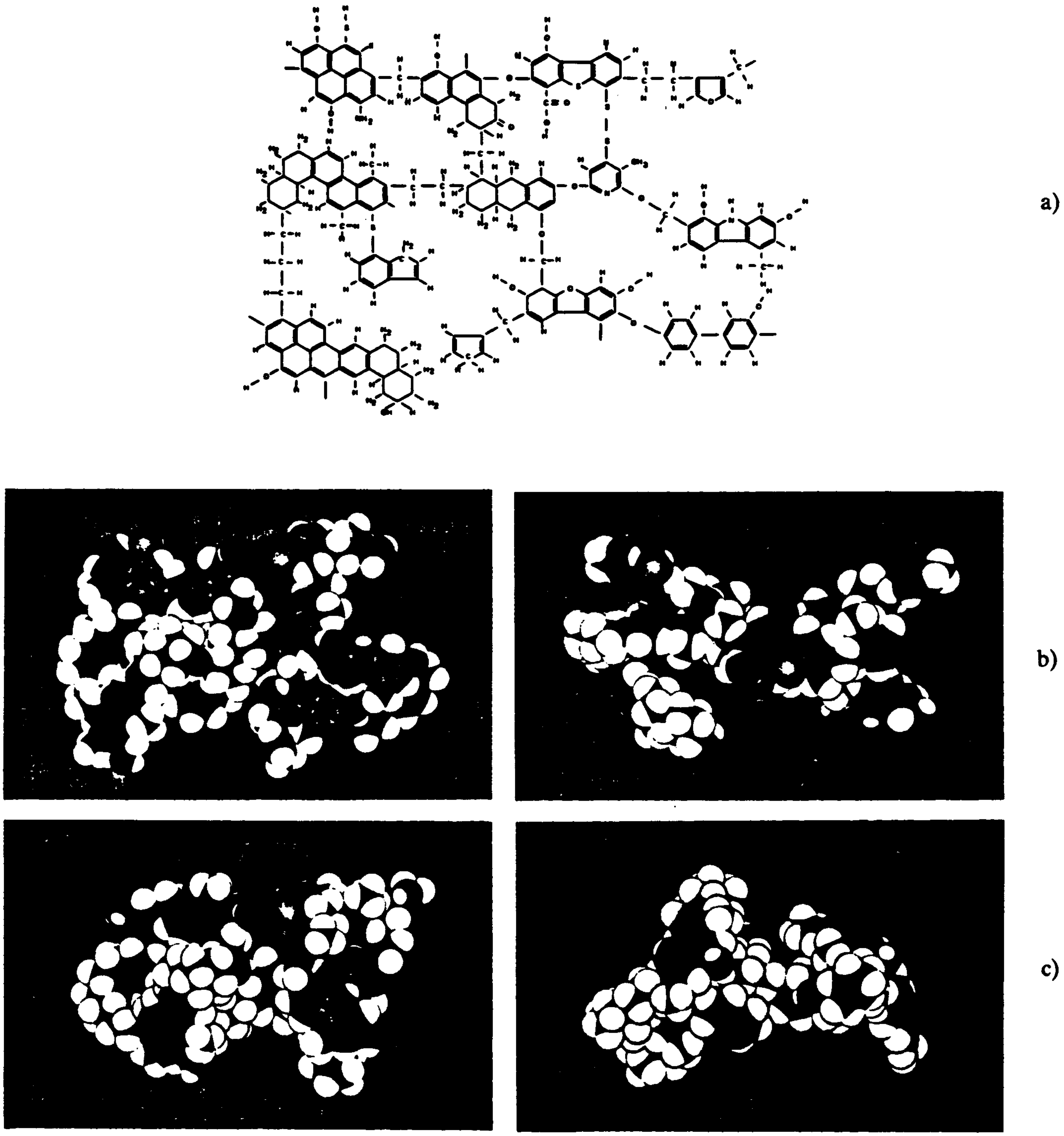

Figure 2. Wiser structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized structure, top and side views (same orientation, same scale).

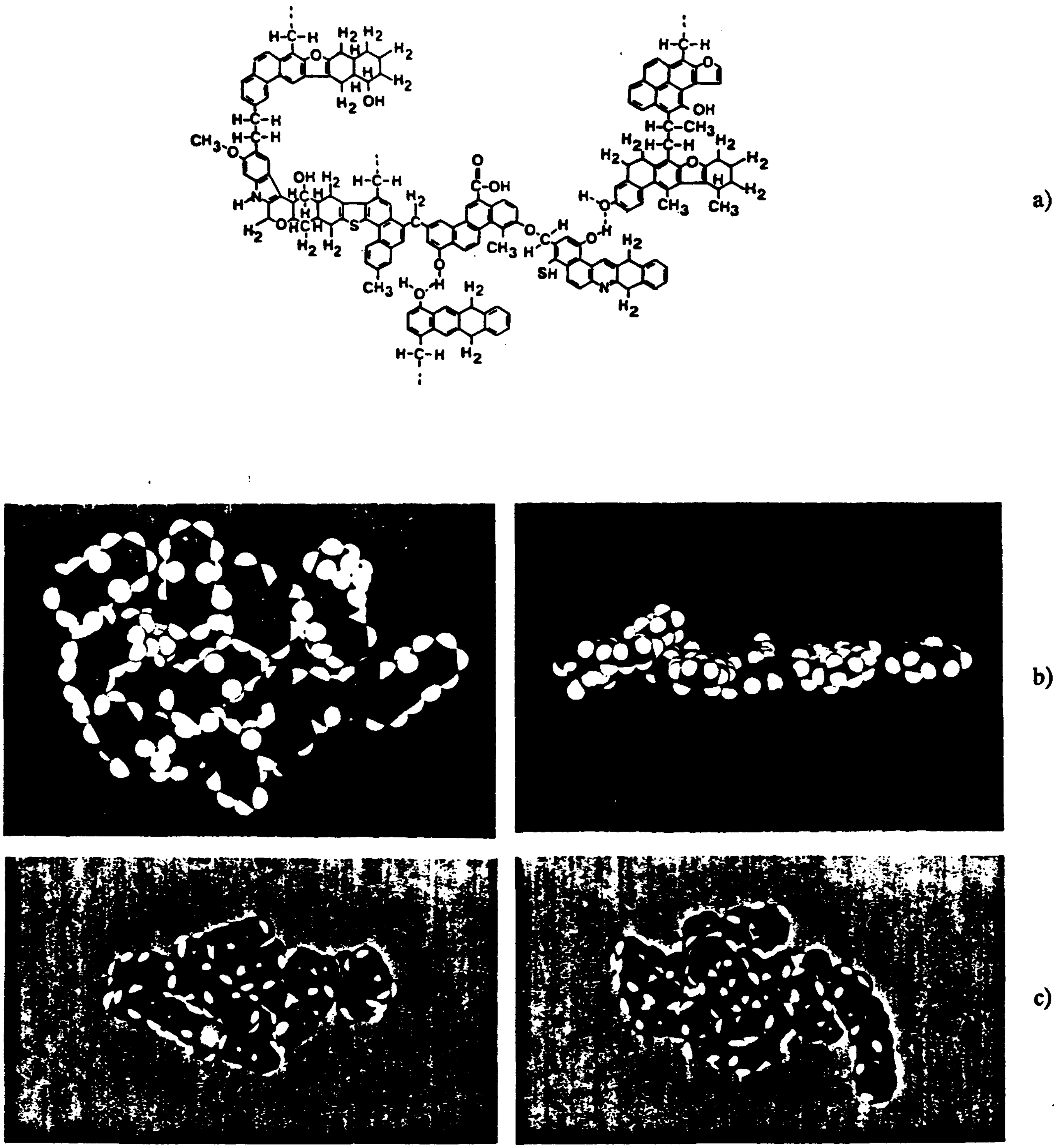

Figure 3. Solomon structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized structure, top and side views (same orientation, same scale).

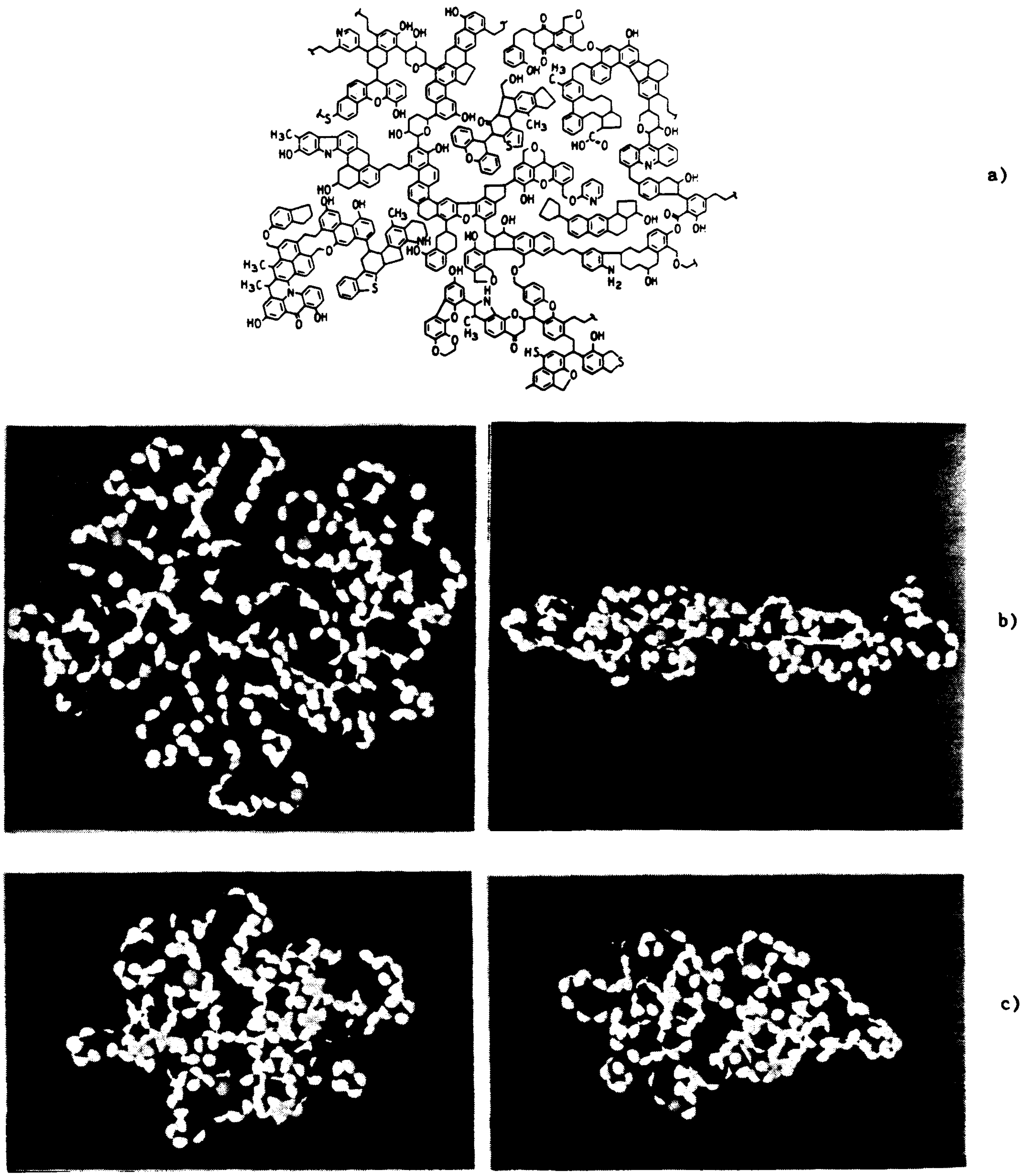

Figure 4. Shinn structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized structure, top and side views (same orientation, same scale).

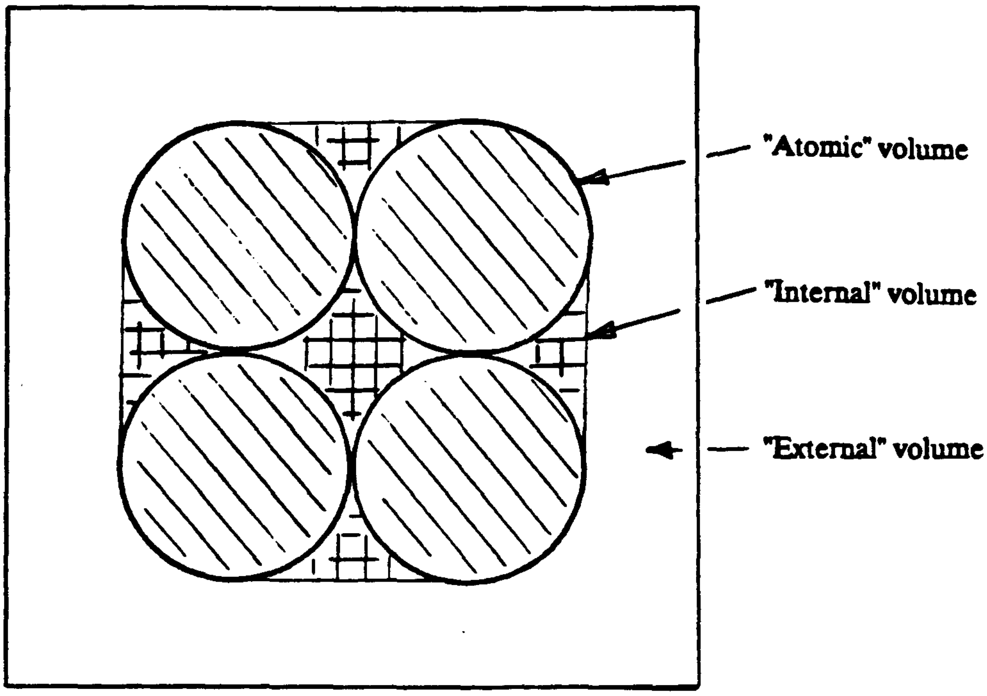

Figure 5. Schematic representation of method of density determination. The rectangle is a box enclosing an array of eight atoms whose density is to be determined (four atoms visible). The density program assigns the volume within the box as "atomic", "internal", "void", or "external" volume. No void volume is present in this example. The other volumes are indicated by the various cross-hatched areas.