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Intermolecular Bonds Bridging Two Anthracene Molecules in *A* γ-Cyclodextrin

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The most preferable state of the two neutral anthracene molecules in a cylindrical molecule of γ-cyclodextrin is assigned as a face-to-face (coplanar, S-shape) configuration that is distinguished from the gas phase, where anthracenes form a face-to-edge (T-shape) configuration. Their faces are slightly tilted and twisted, thus the nearest sites are 9 and 9' and the second nearest sites are 10 and 10' between them. Excitation (300–400 nm) forms intermolecular bonds between two anthracenes in a γ-cyclodextrin. Absorption spectra were obtained from the reflection spectra of the powder sample using the Kubelka-Munk formula. Differential spectra of samples before and after irradiation (300–400 nm) show a broad absorption band. This band corresponds to the transition from the ground state to the excited state of the supramolecular complex. The *ab initio* and molecular dynamics simulation reveal that the most probable bonds between them are the intermolecular bonds formed at the middle of them, namely, one between 9 and 9' and the other between 10 and 10' sites. © 1999 Academic Press

Key Words: **anthracene dimer; cyclodextrin; supramolecular complex; intermolecular bonding; *ab initio*; molecular dynamics simulation**

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1. INTRODUCTION

Cylindrical molecule of cyclodextrin (CyD) offers a subnanometer scale of a special chemical reaction field to make a supramolecular complex which is not formed by natural interactions, such as the Van der Waals attractive force and the ionic force. It offers a circumstance which results in the intermolecular bonding between molecules. The inner diameters are 0.45, 0.70, and 8.5 nm for α-, β-, and γ-cyclodextrins, respectively. The depths are nearly the same length of 0.70 nm (1)

Cyclodextrin is a cylindrical oligosaccharide that is synthesized from D-glucopyranoses with α-1, 4 bonding. The α-CyD, β-CyD, and γ-CyD are the hexamer, heptamer, and octamer of D-glucoses, respectively. Their shapes resemble a short tube. The radius of one side is slightly larger than that of the other side. The inner wall is composed of hydrocarbons and oxygens of glycosides (methyl α-D fructofuranosides). Thus, the inner space is nonpolar and hydrophobic. The outer wall is composed of OH bases and so forth. They make the outer wall polar and hydrophilic. Thus, the CyD is highly soluble in water. Since the inside of CyD is not polar and not electrically charged, neutral molecules can be inserted in it more easily than they can be attached to its outside.

The inner space of CyD would present a suitable area to prepare nanocrystal or new cluster configurations which depend on the cavity size. For example, a quantum size effect has been studied with tin tetraiodide, SnI_4, in CyD (2, 3). The subnanometer scale of space of the CyD is effective enough to make the cluster of tin tetraiodide. The absorption spectra of isolated clusters were investigated, and the assignment of the electronic energy levels was proposed. The size effect was observed as the blue shift of the exciton absorption energy in the clusters when compared with the single crystal of SnI_4.

Furthermore, using CyD, as a host framework of the inclusion complex formation, one can change the physical and chemical properties of guest molecules and control chemical side or photodegradation reactions (4, 5). One famous example of this reaction is a photocyclo-addition reaction (6) for aromatic hydrocarbons, such as benzene, naphthalene, anthracene, and so on. Thus, in cases without CyD, it is well known that anthracenes in a nonpolar solvent react with each other and form dianthracenes by irradiation with high-pressure mercury lamp (7). Another experimental method of dianthracene formation has been reported (8). The preparation of a sandwich dimer is as follows. It is made by the irradiation of anthracenes sandwiched in methylcyclohexane and then frozen to rigid glass with liquid nitrogen. However, it has not been clarified yet that the face-to-face anthracenes form the bonds on the 9, 9' and 10, 10' sites. If they are piled up by facing with 1, 9' and

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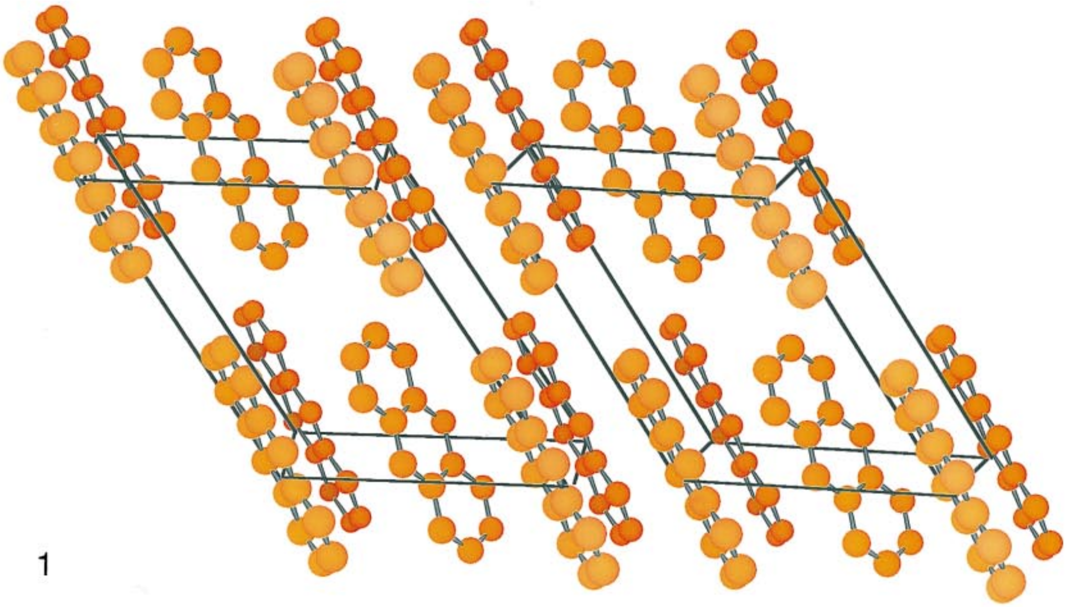

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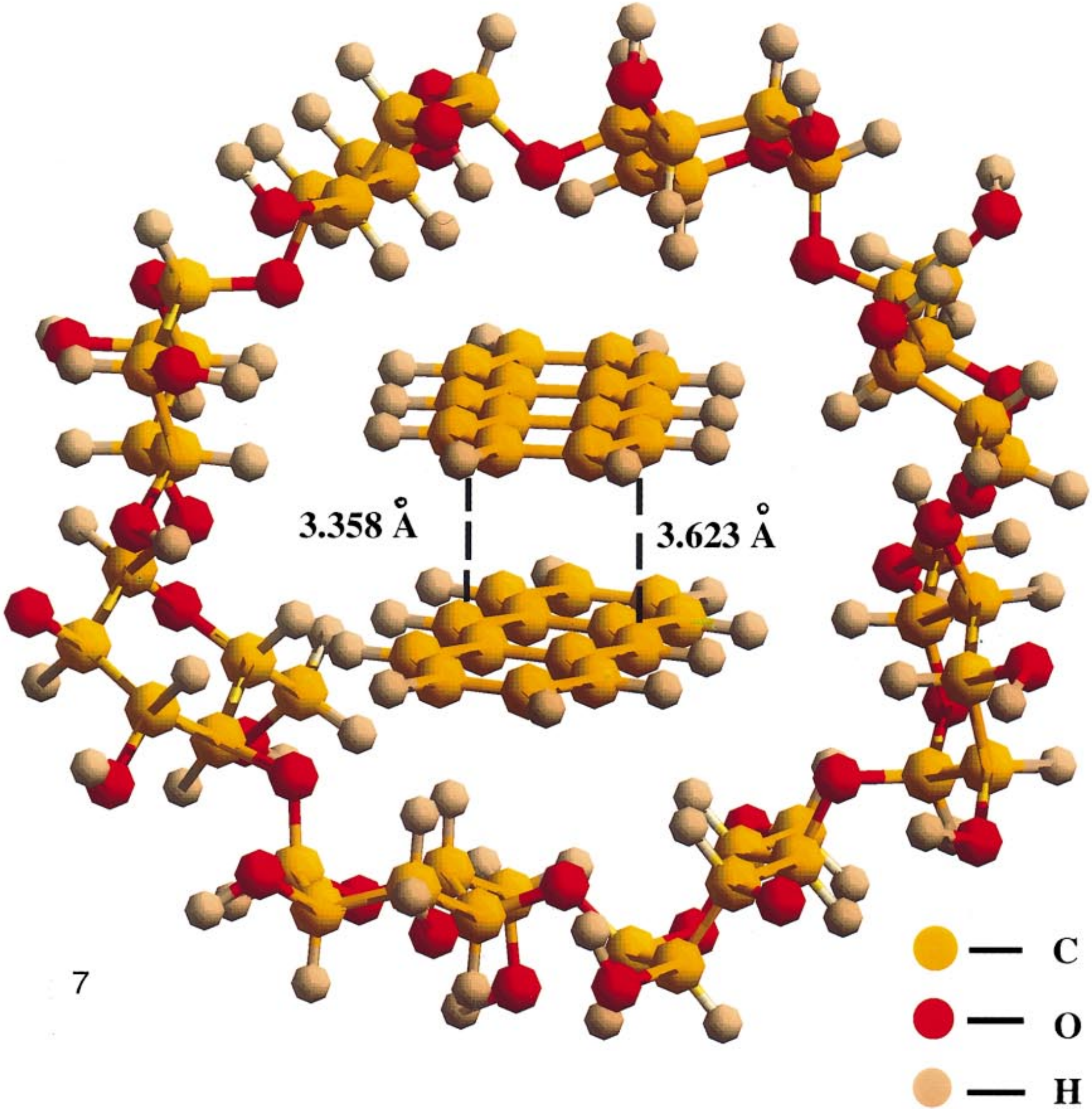

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4, 10' or 1, 8' and 4, 5', they would not form bonds at 9, 9' and at 10, 10' sites.

If CyD is introduced in an aqueous solution of anthracene, the CyD can bind anthracenes strongly, with the stoichiometrical dependence on the cavity size (9–11). However, the configuration of anthracene molecules in complexes such as these has not been clearly identified. A similar situation also exists in the solid state. Therefore, the investigations of CyD-anthracene complex, particularly a theoretical study, are desirable in order to describe the physical and chemical properties related to guest–host systems.

In the present work, we report both experimental and computational results on two anthracene molecules in a γ-CyD. The aim of this work is to show evidence of a new shape of anthracene dimer in γ-CyD cage which does not occur in free space. For this aim, we study the different possible configurations of a dimer both in free space and in a CyD cavity by using *ab initio* and molecular dynamics (MD) calculations. The most suitable configuration of the anthracene dimer in a cage of γ-CyD allows us to clarify which bonds are most preferably formed between two anthracene molecules after exciting their electronic states. Thus, the possible bonds are suggested to be 9, 9' and 10, 10' by the present *ab initio* calculations of the excited states of anthracene. This result is in good agreement with our experimental results.

2. EXPERIMENTS

The crystal structure of anthracene is shown in Fig. 1 as a stereograph. The lattice is monoclinic. It can be clearly seen by the stereograph that the nearest-neighbor anthracene molecules are arranged as a nearly T-shape configuration (12, 13). The previous theoretical calculations also elucidated that the Van der Waals interaction between two isolated molecules of aromatic hydrocarbons combines them as a face-to-edge (T-shape) configuration (14, 15).

The anthracene single crystals were made by vapor growth from the commercial powder of 99% purity. It is difficult to make a pure single crystal of anthracene. More than 30 zone refinements are required to make a pure single crystal. It is not difficult to characterize the purification level of a single crystal. The emission spectra show the impurity emission efficiently, thus the emission measurement is an effective method of determining the purity of a single crystal.

In the present work, purification is not a very important issue, because the narrow inside space of the γ-CyD rejects other impurities to be included in it by substituting anthracene molecules. In fact, a slight amount of impurities does not strongly affect the absorption spectra, although they are efficient for the emission spectra.

The anthracene single crystals made by vapor growth were put into a glass tube with γ-CyD's and then evacuated to 2.7 mPa. The tube was sealed and heated up to 420 K. During cooling, one of the edges of the glass tube cooled faster than the others, because the edge was set to the outside of the heater coil. Thus, the excess anthracene vapor was frozen to the edge and was not stuck to the outside of the γ-CyD's. Even if the anthracene molecules are stuck on the outside surface of CyD, they would be scarcely stuck close to each other. If they had stuck outside and happen to be stuck close to each other, they will form the T-shape geometry and cannot form face-to-face (S-shape) supramolecules. The theoretical calculations (see the next section) revealed that the face-to-edge (T-shape) configuration, formed by van der Waals molecular force, was energetically more favorable. Also, in the crystal structure the nearest-neighbor anthracene molecules are arranged at a nearly right angle (see Fig. 1). The present method of sample preparation in a vacuum makes the exact twin anthracene molecules in a CyD. As mentioned above, all of the present samples of dianthracenes in γ-CyD were prepared under vacuum. The powder of γ-CyD with twin anthracenes in it was pressed with a glass plate on the double-sided adhesive tape which was fixed on a sample holder.

A deuterium lamp light source was used for the reflection measurements in the energy region of 2.5–6.2 eV. The weakly reflected light from the powder sample was detected with a CCD (Charge Coupled Device) detector (Princeton Instruments, LN/CCD-1100-PB-UVAR/1), through a monochromator (Acton Research Corporation, SpectraPro-500). The reflectivities were calculated by dividing the reflected light intensities of the powder sample with those of incident light that were measured by displacing the sample with an aluminum evaporated mirror.

The reflection spectrum of an anthracene single crystal is shown in Fig. 2a. The absorption spectrum is shown in Fig. 2b was calculated from the measured reflectivities using a Kramers–Kronig integration analysis. The reflectivities decrease steeply in the higher energy region where we could not measure the reflectivities. Thus, we must set the reasonable values of reflectivity in this region, because the integration range of the Kramers–Kronig analysis is from zero to infinite energies. The steep damping of $E^{-\beta}$ is postulated to make the integration convergent, where E is the incident photon energy. If the parameter value is not reasonable, absorption coefficients become negative in some wavelength regions and the value is not zero at the transparent

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FIG. 1. Stereographic unit cell of anthracene single crystal. The lattice is monoclinic.

FIG. 7. Optimized anthracene dimer structure in CyD. The lengths between 9, 9' and 10, 10' are 3.358 and 3.623 Å, respectively.

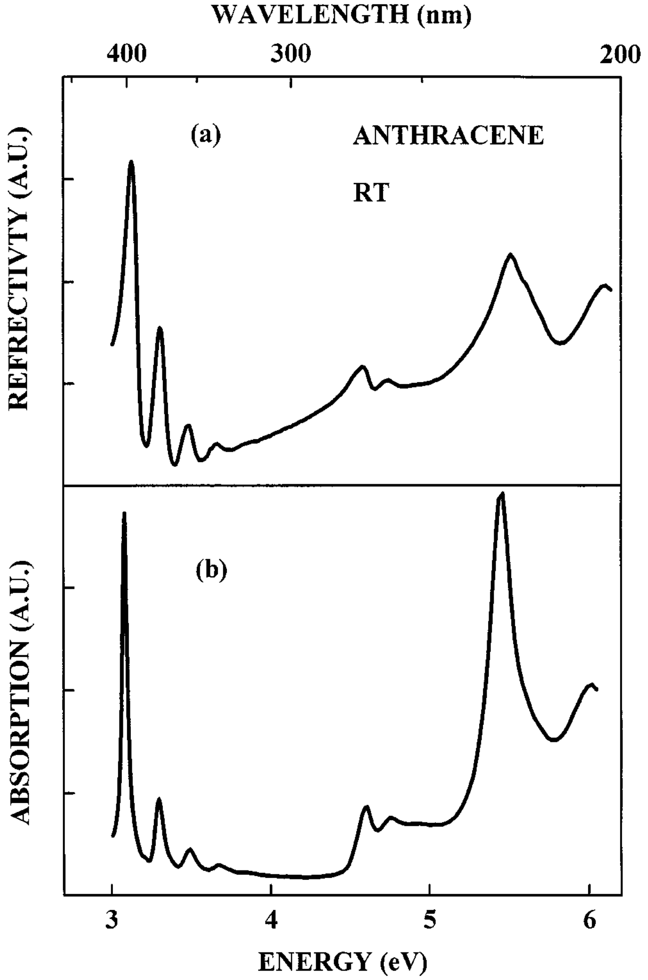

FIG. 2. (a) Reflection spectrum of anthracene single crystal at room temperature. (b) Absorption spectrum calculated with Kramers–Kronig analysis from (a).

wavelength region. β is set to 1.3 to obtain a reasonable spectrum. The reflectivities are usually constant in the transparent lower energy compared with the fundamental exciton absorption (16, 17). Figure 2b will be compared with the absorption spectra of anthracenes in CyD afterward.

The absorption spectra of the powdered samples were calculated from the reflectivity spectra by a Kubelka–Munk formula,

$$A = (1 - R)^2/2R, \qquad [1]$$

where A is the absorbance at each wavelength and R is the measured diffuse reflectivity at each wavelength (18). This formula implies that the minima of the reflectivity correspond to the maxima (peaks) of absorption. It is difficult to measure the absolute reflectivities of the powder sample, because the incident light is scattered and reflected randomly, and thus, the reflectivities are very weak. The absolute reflectivities were, therefore, corrected as follows. In the transparent region of wavelengths longer than 410 nm (energy region lower than 3 eV), the absorption should be zero. The entire incident light is reflected after a few and/or many times of scattering in the powdered sample, because the incident light is not absorbed in the transparent region.

The absorption spectrum of twin anthracenes in a γ-CyD is shown in Fig. 3a with a solid line. The broken line is the absorption spectrum of the pure γ-CyD. The absorption spectrum of the twin anthracenes in a γ-CyD is derived by subtracting the pure γ-CyD absorption, and the spectrum is shown in Fig. 3b. It corresponds to that of the single crystal in the 3–5.5 eV energy region shown in Fig. 2b. Although the absorption bands are similar, the intensities are different.

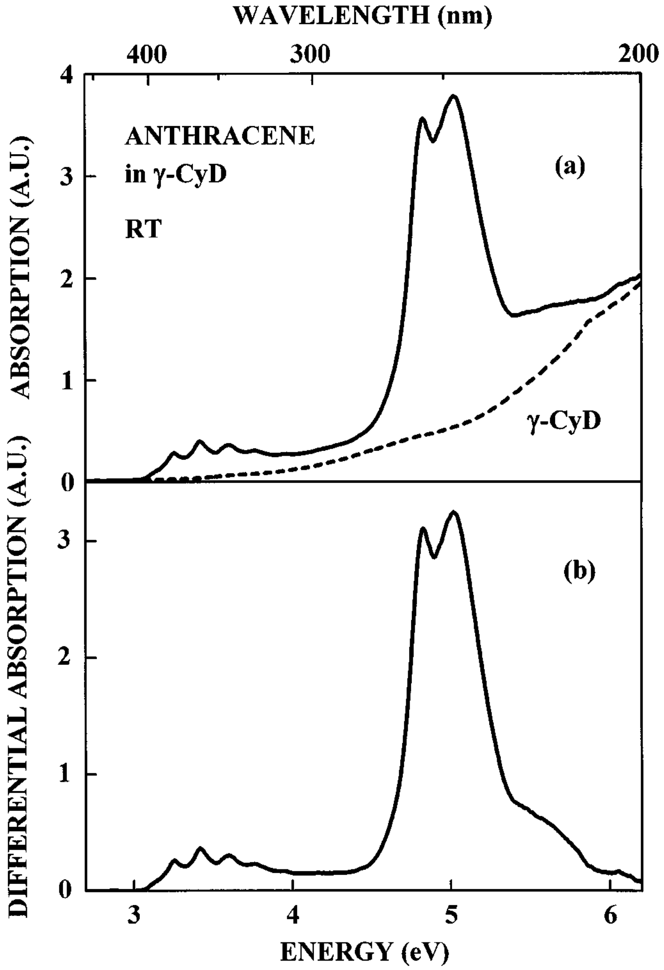

FIG. 3. (a) Solid line is the absorption spectrum calculated from the reflection spectrum of powdered anthracene in γ-cyclodextrin. Broken line is the absorption spectrum of powder γ-cyclodextrin. (b) Differential absorption spectrum of anthracene in γ-cyclodextrin after subtracting the absorption of γ-cyclodextrin (broken line) from the solid line of (a).

Comparison of Fig. 3a with Fig. 2a shows all the peaks of absorption bands shift to higher energies. The lowest energy peak at 3.08 eV shifts to 3.26 eV and the peak at 4.60 eV shifts to 4.823 eV. This comes from the size effect that the energy level splittings come close to those of a single molecule in a cluster or in a nanocrystal. When the molecules are crystallized, the energy levels are overlapped and the breadths are broadened. Therefore, the energy gaps between these levels become smaller in a crystal than those of a cluster or of a nanocrystal.

All the measurements were performed at room temperature (RT). Nonmonochromated light of the deuterium lamp was irradiated for a few seconds to measure the reflection spectrum by the CCD through the monochromator. Thus, the irradiation effect would be negligible when the reflectivity measurements are carried out.

The bleaching effect is seen in Fig. 4a. The solid line is the absorption spectra of twin anthracenes in γ-CyD and is the same as that of Fig. 3a. The absorption decreases in the 3–5.4 eV energy region after 1 h of ultraviolet light (3–4 eV) irradiation with deuterium lamp through a glass filter. On the other hand, the absorption increases in the energy region higher than 5.4 eV. The difference between light irradiated spectrum (1 h) and virgin spectrum (0 h) is shown in Fig. 4b. The absorption bands in the 3–4 eV energy region correspond to the transitions from the ground state to the first excited state of an anthracene molecule. The spectrum in 4–5.2 eV corresponds to the transitions from the ground state to the second higher-energy excited state. In the energy region higher than 5.4 eV, a new broad absorption band appears. This newly observed band seems to correspond to the transition from the ground state to the higher energy level of an anthracene supramolecule in γ-CyD. The excitation to the higher energy level of the supramolecule would lead to its bond breaking and would consequently cause separation again into two anthracene molecules. In the next stage, the irradiated sample was again lighted with *ArF*-excimer laser (193 nm). The decreased absorption intensity is recovered in the measured wavelenth region except 3.6–4.8 eV. It means that the supramolecular bonds were broken with the laser light, 193 nm, and the two separated anthracene molecules were recovered. In order to confirm these experimental results, we perform classical molecular dynamics (MD) and first-principle calculations in the next section.

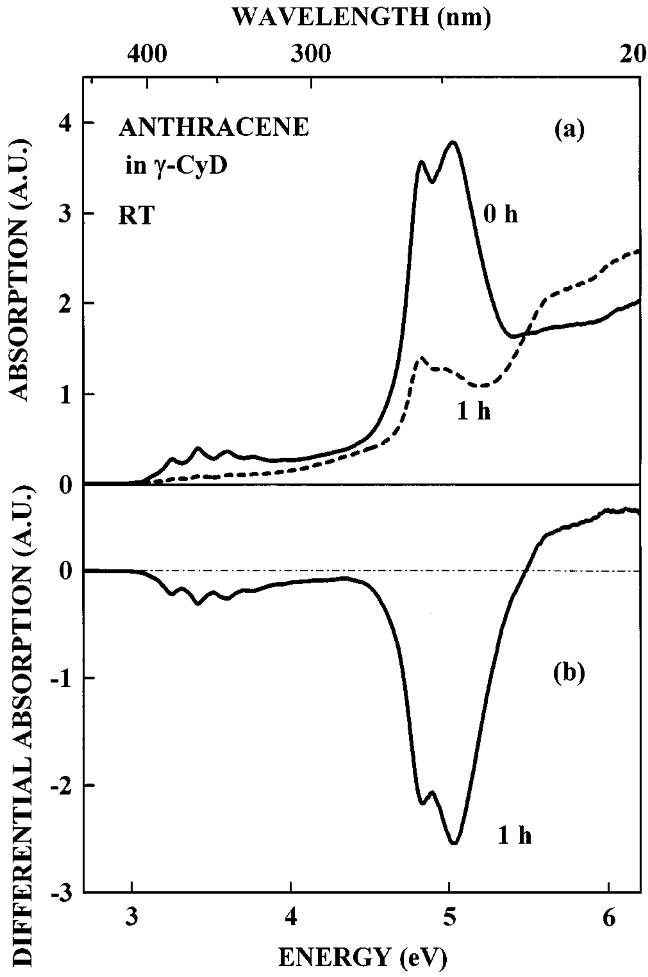

FIG. 4. (a) Absorption spectrum (0 h) calculated from the reflection spectrum of powdered anthracene in γ-cyclodextrin, which is the same spectrum of solid line in Fig. 3a. Dotted line (1 h) is the spectrum after the ultraviolet light (3–4 eV) irradiation for one hour. (b) Differential spectrum subtracting the virgin spectrum (0 h) from the irradiated spectrum (1 h).

3. THEORY

All the *ab initio* calculations have been carried out by using the Gaussian 94 package of programs (19). Full-geometry optimization of the anthracene dimer was performed with the Hartree–Fock (20), and density functional theories with the exchange potential of Becke (21) and correlated functional of Lee *et al.* (22) (HF and BLYP options in Gaussian terminology, respectively) levels of theory. The dimer was optimized at both levels using split-valence 3-21G (23) including polarization (24) (described in parentheses as d), and correlation-consistent polarized valence double-ζ (25) (cc-pVDZ).

The BLYP/cc-pVDZ was chosen because it was found that this method gives a good agreement with experiment for polycyclic aromatic compounds (26, 27). For optimization of anthracene in excited states, the single-excitation (28) (CIS) method has been used with a 3-21G(d) basis set.

The obtained optimal structures for each state were characterized as minimum energy structures by a frequency calculation in order to eliminate imaginary values. The geometric parameters are defined in Fig. 5.

The MD simulation method is very effective in assigning the most preferable molecular states of large systems for which *ab initio* calculations are not available. Thus, we

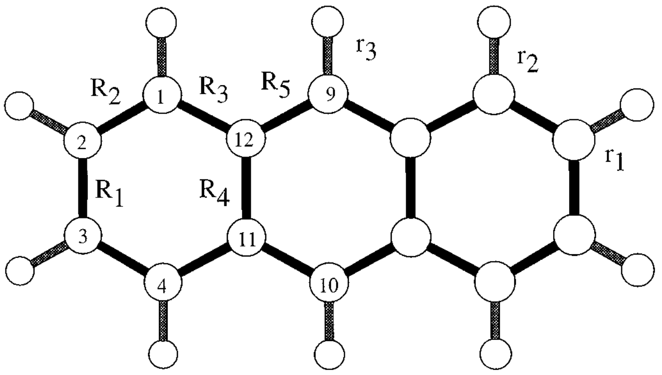

FIG. 5. Definition of geometric parameters of anthracene molecule.

applied this method in the case of the complex of anthracene dimer in the γ-CyD using the Dreding (29) force field, which can be successfully used to investigate small benzene clusters (14) by the Cerius^2 molecular simulation software (30).

The properties of anthracene monomer have been previously well characterized by DFT (26, 27), and therefore, we will discuss here only the properties of its dimer. In free space the optimized structure, like T-shape, was determined from *ab initio* calculations using both the HF and BLYP methods. This equilibrium geometry structure is depicted in Fig. 6a. Notice that such a face-to-edge geometry is a common characteristic of most stable dimer structures of more small polycyclic aromatic compounds, such as benzene (14)

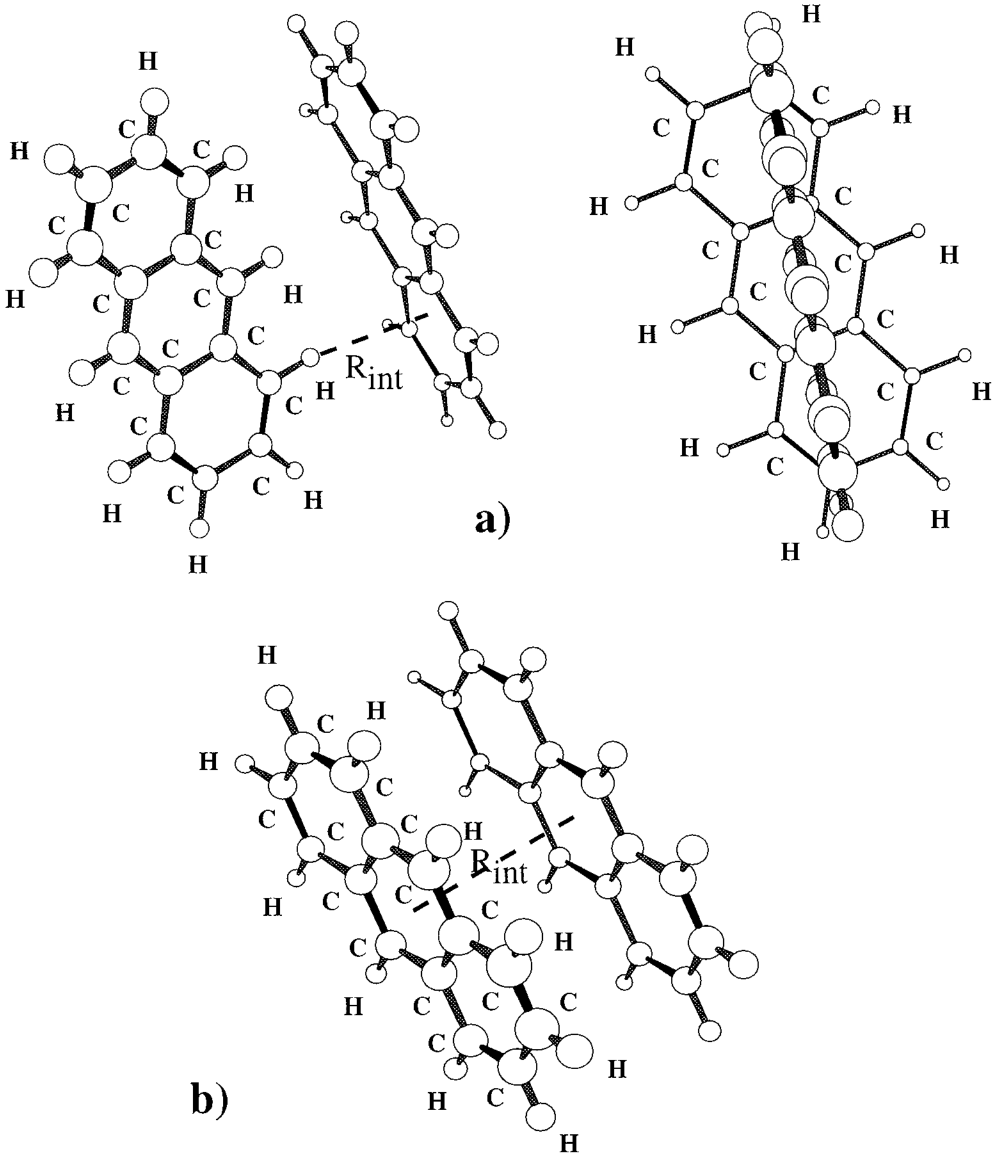

FIG. 6. Structures of different configurations of anthracene dimer complex: optimized complexes: (a) top and side views of the T-shape geometry and (b) S-shape ("stacked") geometry.

and naphthalene (12). The co-planar dimer (see Fig. 6b) is higher in energy by 8.63 kcal/mol at the BLYP/cc-pVDZ level as compared to the most stable structure. The optimized bond distances for anthracene molecules in both dimer structures are listed in Table 1 together with the electron diffraction results of Ketkar *et al.* (31).

The MD simulation was applied to the molecular states of twin anthracene molecules enclosed in γ-CyD. The initial conformation of empty γ-CyD is taken from the x-ray study (34) and the two anthracene molecules in co-planar configuration was trapped into inner space of cyclodextrin. The structural parameters of anthracene molecule is the same as in S-shape configuration (see Table 1) determined from BLYP/cc-pVDZ calculations. We calculated the stable state for the twin anthracene molecules in a CyD using the Nosé-Hoover (30) canonical dynamics (TVN). The simulation box is kept constant during the simulation. The temperature is controlled according to the thermostat procedure of Hoover (35) using separate thermostats for the rotational and translational degrees of freedom. The obtained stable structure of the anthracene dimer in CyD is presented in Fig. 7. The difference between the stacked coplanar structure (see Fig. 6b) and the structure determined by MD (see Fig. 7) is associated with the host–guest interactions and the characteristic shape of tube of CyD which has different radii on the edges.

It has been proposed that the effect of excited state formation plays an important role in the formation of the intermolecular bonds between two anthracene molecules. The optimized geometries of the ground state (S_0), the first (S_1) and second (S_2) excited states of anthracene are presented in Table 2. The molecule is found to retain its planar form in the two states, and we can see the changes in the C–C bond lengths from this table. The main contribution to the first electronically excited state, S_1, arising from HOMO → LUMO excitation and results in a ${}^1B_{1u}$ state. The S_2 state arises from essentially equal contribution of the HOMO → LUMO + 1 and the HOMO-1 → LUMO configurations, and both of them lead to a ${}^1B_{2u}$ state. In S_1, the middle ring expands a little and the outer ones become more symmetric. In S_2, R_4 bond lengths are much elongated compared with the lower states.

TABLE 1

Bond Distances (Å) for Dimer Complexes at the HF/3-21G(d) and BLYP/cc-pVDZ Levels of Theory

	Internal coordinates (Å)				
	Methods				
	HF/3-21G(d)		BLYP/cc-pVDZ		
	T-shape	S-shape	T-shape	S-shape	Expt.
R_1	1.429	1.430	1.437	1.437	1.422
R_2	1.348	1.346	1.387	1.382	1.397
R_3	1.432	1.434	1.441	1.440	1.437
R_4	1.432	1.424	1.464	1.463	1.437
R_5	1.388	1.387	1.415	1.413	1.392
r_1	1.072	1.072	1.093	1.092	
r_2	1.072	1.072	1.095	1.092	
r_3	1.071	1.073	1.095	1.092	
	Intermolecular bond distance R_{int} (Å)				
R_{int}	2.83	4.03	2.94	4.11	

TABLE 2

Bond Distances (Å) for Three Electronic States at the CIS/3-21G(d) Level of Theory

	Internal coordinates (Å)		
	States		
	S_0	S_1	S_2
R_1	1.430	1.381	1.417
R_2	1.346	1.396	1.371
R_3	1.434	1.395	1.409
R_4	1.424	1.439	1.479
R_5	1.388	1.407	1.397
r_1	1.072	1.071	1.072
r_2	1.073	1.073	1.074
r_3	1.073	1.074	1.074

The electron density of the ${}^1B_{1u}$ state is concentrated at the central ring due to the transfer of an electron from the highest occupied molecular orbitals to the lowest unoccupied orbital and thus extends it. This result suggests that the new bonds are formed between the two anthracene molecules when they are in the coplanar dimer configuration and trapped in a CyD tube. The results of excited energies of S_1 and S_2 (see Table 3) are in good agreement with experiments. In this way, that experimental results on adsorption spectra of anthracene-CyD complex correspond to excitation of the anthracene molecules are clarified. The suitable configuration of anthracene dimer in the γ-CyD obtained by MD calculations makes it possible to form bonds exactly between guest molecules. This also lends support to the validity of the CIS method used in these calculations.

4. DISCUSSION

It has already been clarified that the face-to-edge (nearly rectangular) bonding configuration is the stable state in the free space for anthracene, naphthalene, and benzene dimers. The investigation of anthracene dimer structures has shown that the stable "stacked" structure occurs in cases where

TABLE 3

Comparison of Experimental and Calculated (at CIS/3-21G(d) Level) Excitation Energies (in eV)

	Present work	
State	Expt.	Calculated
S_1	3.4	3.914
S_2	4.9	4.719

intermolecular distance is about 4 Å. At this distance, the coplanar dimer is stabilized primarily by dispersion forces and its electronic and structural parameters are practically the same as in the T-shape dimer (see Table 1). A similar intermolecular geometry of the dimer was found by using a different computational method, and the changes in R_{int} parameters are little affected for similar configurations.

The situation is changed when we include a dimer in CyD. In this case, the balance between the guest–host and guest–guest interactions gives rise to the coplanar structure with different R_{int} from stacked dimers in free space. The CyD allows us to make the distance R_{int} between anthracene molecules shorter. The most preferable state suggested by the calculation of the molecular dynamics simulation is shown in Fig. 7. The rotation of the top anthracene molecule is due to the repulsion of the π-bonding orbitals. Nevertheless, the distance is large for forming a supramolecule.

The closest distance can be found if we change the electronic density of anthracene molecules. That is not possible in the case of the ground state without additional external effects. However, in CyD, this distance is shorter and after irradiation we can see that the energetics favor the S_1 excited state for each anthracene molecule. The excitation of an electron from a π-bonding to an antibonding π^* states decreases the distorting tendency in the center and the outer benzene rings become more symmetric; i.e., their five edges have almost equal lengths. On the basis of these features the attack at the 9 and 10 positions takes place in the reactions of anthracene. In this case, the forming supramolecular complex is possible, and it may occur in the middle ring.

5. CONCLUSIONS

We have investigated the structural and physical properties of two anthracenes in the γ-CyD by both experimental and theoretical methods. In this study, we found that the anthracene dimer in the cavity is in an S-shape configuration, which is quite different from the T-shape in the gas phase. This configuration allows us to clarify which bonds are most preferably formed between two anthracene molecules after exciting their electronic states. Thus the possible bonds are suggested to be 9,9’ and 10,10’ by the present *ab initio* calculations on excited states in anthracene and the analysis of adsorption spectra of the γ-CyD-anthracene complex.

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7. It has not yet been clarified if the combined dianthracene molecule is connected at both sites of 9,9’ and 10, 10’. It would be hard to imagine these two bonds are simultaneously formed in solution. When two anthracene molecules come close to each other, the van der Waals force between them forces to form T-shape. Thus, only one bond would be formed between 9, 9’ sites in the T-shape and then the butterfly shape of dianthracene would be formed with angles of 109°2 8’ between their planes. This results in 10, 10’ sites that are far apart. It would be, therefore, difficult to form another bond between the 10, 10’ sites in solution.
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