J|A|C|S
A R T I C L E S

Theoretical Study of Benzonitrile Clusters in the Gas Phase and Their Adsorption onto a Au(111) Surface

Yoshishige Okuno,*,† Takashi Yokoyama,‡ Shiyoshi Yokoyama,†,§
Toshiya Kamikado,† and Shinro Mashiko†

Contribution from the Communications Research Laboratory, 588-2 Iwaoka Iwaoka-cho, Nishi-ku, Kobe 651-2492, Japan, and National Institute for Materials Science, 2268-1 Shimo-Shidami, Moriyama-ku, Nagoya 463-0003, Japan

Received July 17, 2001

Abstract: We made theoretical calculations for a benzonitrile molecule and its clusters in the gas phase and as adsorbed on the Au(111) surface, to explain the observation by scanning tunneling microscope, that is, the trimer formation of cyanophenyl porphyrins adsorbed onto the Au(111) surface. With regard to the gas-phase species, ab initio calculations showed that (1) the benzonitrile dimer has a single stable structure that is planar and antiparallel; (2) the trimer has two isoenergetic stable structures, that is, a planar and cyclic structure and an antiparallel and nonplanar one; (3) the clusters are more stable, at low temperatures, than the monomer. For the adsorbed species, we made quantum mechanical/molecular mechanical calculations in which the interaction between the adsorbates and the surface is evaluated in a molecular-mechanical way by using analytical potential functions and an image charge model. Because the stable structures were found to be similar to those in the gas phase, the cluster formation of adsorbed cyanophenyl porphyrins was attributed to the interaction between cyanophenyl groups, which is barely affected by adsorbate−surface interaction. It was also found that the adsorbed cyclic benzonitrile trimer is more stable than the monomer and the dimer because the relative stability is dependent on enthalpy alone. We therefore concluded that the preferential formation of trimers by the adsorbed cyanophenyl porphyrins is due to the negligible contribution of entropy to the relative stability of the adsorbed species and that the adsorption hardly changes the situation found in the gas phase.

Introduction

In recent years, scanning tunneling microscopy (STM) has made the direct observation of molecular clusters and aggregates adsorbed onto solid surfaces possible. The structures and arrangements of the adsorbates thus observed have stimulated a lot of interest.[1−10] In particular, the self-assembly process of the adsorbed molecules has been attracting more interest because researchers expect that it will be applicable to the fabrication of molecular devices on surfaces. An understanding of both the interactions between the adsorbate molecules and the interactions between the adsorbates and the surface is a prerequisite to eventually controlling the self-assembly process in supramolecular aggregation. It should thus be instructive to examine the differences between the molecular clusters in the gas phase and those adsorbed onto the surface. Nevertheless, there has been little effort to examine such differences in detail.

We recently carried out STM observations which revealed[11] that the major component in the adsorption of 5-(4-cyanophenyl)-10,15,20-tris(3,5-di-tertiarybutylphenyl)-porphyrin (which is henceforth abbreviated as cyanophenyl porphyrin) clusters onto a Au(111) surface is the triangular trimer structure, rather than the monomer or dimer structure (Figure 1). However, the reason for this preference of the Au(111) surface is not yet understood. Treating the adsorption of benzonitrile (i.e., cyanobenzene) clusters onto Au(111) surfaces as a simplified model of the adsorption of cyanophenyl porphyrins, and investigating the structures and relative energies involved in this simpler process, should be a helpful step toward answering this question. This is because we would expect the cyanophenyl group to play a key role in controlling the structures of the cyanophenyl-porphyrin clusters adsorbed onto the Au(111) surface. A theoretical study of the adsorption of the benzonitrile clusters onto the Au(111) surface is thus desirable.

However, there has never been a systematic theoretical study of benzonitrile clusters even in the gas phase, although a variety

---

* To whom correspondence should be addressed. E-mail: y_okuno@crl.go.jp. Phone: +81-78-969-2285. Fax: +81-78-969-2259.
† Communications Research Laboratory.
‡ National Institute for Materials Science.
§ Also associated with PRESTO, Japan Science and Technology Corp.

(1) Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Bürgi, L.; Jeandupeux, O.; Kern, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 1230.
(2) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R.; Mauri, F.; Vita, A. D.; Car, R. *Phys. Rev. Lett.* **1999**, *83*, 324.
(3) Böhringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 821.
(4) Luedtke, W. D.; Landman, U. *J. Phys. Chem. B* **1998**, *102*, 6566.
(5) Morgner, H. *Langmuir* **1997**, *13*, 3990.
(6) Mar, W.; Klein, M. L. *Langmuir* **1994**, *10*, 188.
(7) Sadreev, A. F.; Sukhinin, Y. V. *Phys. Rev. B* **1996**, *54*, 17966.
(8) Sadreev, A. F.; Sukhinin, Y. V. *J. Chem. Phys.* **1997**, *107*, 2643.
(9) Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1989**, *91*, 4994.
(10) Siepmann, J. I.; McDonald, I. R. *Mol. Phys.* **1993**, *79*, 457.
(11) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619.

10.1021/ja011744v CCC: $22.00

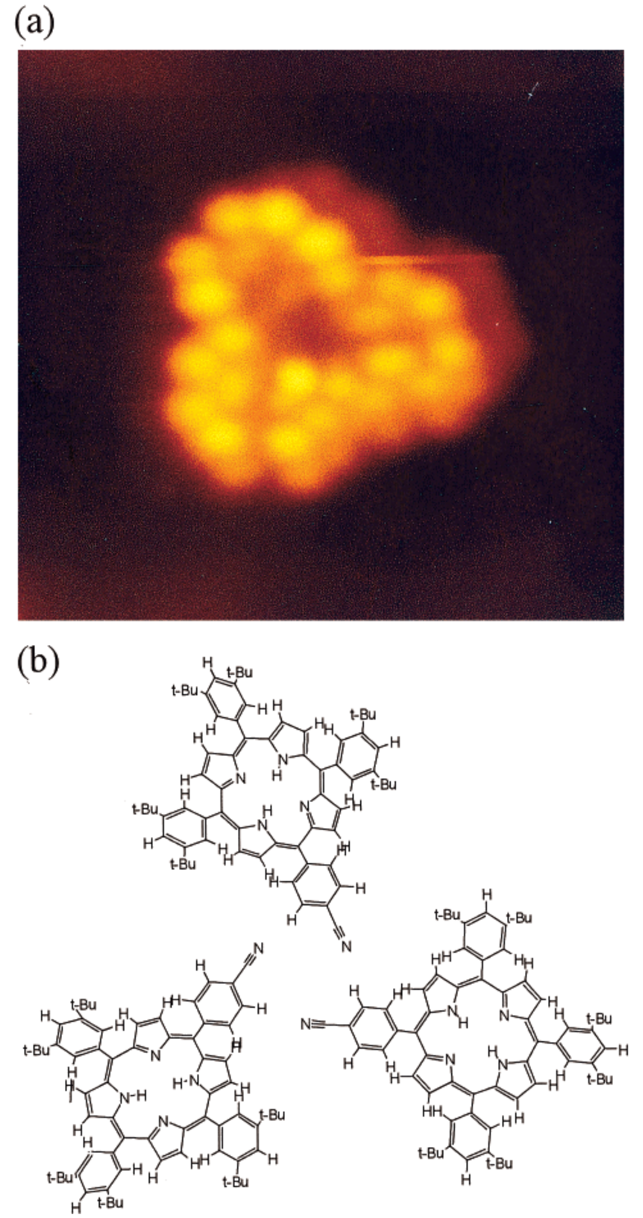

Figure 1. (a) STM image of the cyanophenyl porphyrin trimer on the Au(111) surface and (b) its conjectured structure. High-resolution STM topography has shown that the dihedral angle between the porphyrin portion and each of the four phenyl rings is about 20°.[11]

of molecular clusters formed via van der Waals or hydrogen-bonding have been both theoretically[12−23] and experimentally[24−28] investigated. Benzonitrile clusters in the gas phase are of experimental interest because of their ability to form exciplexes.[24,27] Kobayashi et al.[24] have conjectured, from the analysis of the laser-induced fluorescence spectra, that a benzonitrile dimer in the gas phase is planar in form with two benzonitrile molecules facing each other in an antiparallel geometry. Itoh et al.[25,26] have conjectured that the dimers of 1-cyano-4-methylnaphthalene and of 1-cyano-naphthalene are similar in structure to the benzonitrile dimer, while the trimers of these substances have triangular cyclic structures. Not only are these conjectured structures yet to be confirmed theoretically, their stability is also yet to be determined. Therefore, a theoretical study of benzonitrile clusters in the gas phase is also necessary.

In the current work, we have applied theoretical calculation to identify the stable structures of the benzonitrile molecule and clusters both in the gas phase and as adsorbed onto the Au(111) surface. We used ab initio calculations for the species in the gas phase. For the adsorbed species, to reduce the computational cost, we used a quantum mechanical/molecular mechanical (QM/MM) method developed presently. Our studies are aimed at finding a reason for the predominantly trimer form of the cyanophenyl porphyrins adsorbed onto the Au(111) surface and at providing preliminary knowledge toward the eventual development of rules regarding the determination of the macroscopic structures of molecular aggregates adsorbed on solid surfaces.

Method of Calculation

Ab Initio Calculations for Gas-Phase Species. We used the Gaussian 98 program package[29] for ab initio calculations for the benzonitrile molecule, dimer, and trimer in the gas phase. In the calculations, we used the 6-31G* basis set[30] at density-functional (B3LYP)[31] and Møller−Plesset second-order-perturbation[32] (MP2) levels of theory as well as the 6-31+G* basis set at the B3LYP level.

With regard to the optimized structures of the benzonitrile clusters, we calculated the interaction energies between benzonitrile molecules, following recent work by Cabaleiro-Lago et al.[12] The interaction energies ΔE_{int} were calculated according to the equation:

$$\Delta E_{\mathrm{int}} = \Delta E^{\mathrm{cp}} + E_{\mathrm{def}} \tag{1}$$

Here ΔE^{cp} is the difference in energy between the cluster and the molecules at the optimized geometry of the cluster; for the evaluation of ΔE^{cp}, basis set superposition error (BSSE) is corrected by Boys and Bernardy's counterpoise method.[33] E_{def} is the deformation energy introduced by González et al.,[34,35] which corresponds to the difference in energy between the molecules at the optimized geometry of the cluster and the isolated molecules. These values were evaluated with

---

(12) Cabaleiro-Lago, E. M.; Hermida-Ramón, J. M.; Peña-Gallego, A.; Martínez-Núñez, E.; Fernández-Ramos, A. *THEOCHEM* **2000**, *498*, 21.
(13) Cabaleiro-Lago, E. M.; Ríos, M. A. *J. Chem. Phys.* **2000**, *112*, 2155.
(14) Cabaleiro-Lago, E. M.; Ríos, M. A. *J. Chem. Phys.* **2000**, *113*, 9523.
(15) Ruoff, R. S. *J. Chem. Phys.* **1991**, *94*, 2717.
(16) Mó, O.; Yáñez, M.; Elguero, J. *J. Chem. Phys.* **1997**, *107*, 3592.
(17) Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **2001**, *105*, 1904.
(18) Okuno, Y.; Yokoyama, S.; Mashiko, S. *Nonlinear Opt.* **2000**, *26*, 83.
(19) Okuno, Y.; Yokoyama, S.; Mashiko, S. *J. Phys. Chem. B* **2001**, *105*, 2163.
(20) Okuno, Y. *J. Chem. Phys.* **1996**, *105*, 5817.
(21) Okuno, Y. *Chem. Phys. Lett.* **1997**, *264*, 120.
(22) Okuno, Y. *J. Phys. Chem. A* **1999**, *103*, 190.
(23) Okuno, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2925.
(24) Kobayashi, T.; Honma, K.; Kajimoto, O.; Tsuchiya, S. *J. Chem. Phys.* **1987**, *86*, 1111.
(25) Ebata, T.; Itoh, M.; Itoh, M. *J. Phys. Chem.* **1991**, *95*, 1143.
(26) Itoh, M.; Takamatsu, M.; Kizu, N.; Fujiwara, Y. *J. Phys. Chem.* **1991**, *95*, 9682.
(27) Mordzinski, A.; Sobolewski, A. L.; Levy, D. H. *J. Phys. Chem. A* **1997**, *101*, 8221.
(28) Sakota, K.; Nishi, K.; Ohashi, K.; Sekiya, H. *Chem. Phys. Lett.* **2000**, *322*, 407.
(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(30) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(32) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(33) Boys, S. F.; Bernardi, G. J. *Mol. Phys.* **1970**, *19*, 553.
(34) González, L.; Mó, O.; Yáñez, M. *J. Chem. Phys.* **1999**, *111*, 3855.
(35) González, L.; Mó, O.; Yáñez, M. *J. Chem. Phys.* **1998**, *109*, 139.

Table 1. Potential Parameters (as given by Rappé et al.[37])

	H	C	N	Au
x_i (Å)	2.886	3.851	3.660	3.293
D_i (kcal/mol)	0.044	0.105	0.069	0.039

the B3LYP/6-31+G*//6-31G* method; here the B3LYP/6-31+G*//6-31G* means that for the geometry optimized with the B3LYP/6-31G* method the potential energy is calculated with the B3LYP/6-31+G* method.

We then used the harmonic vibrational frequencies calculated by the B3LYP/6-31G* method to evaluate the thermodynamic energies, that is, the entropy, enthalpy, and free energy, for the optimized geometries. For this evaluation, we used a harmonic approximation for the vibrational modes and assumed that rigid-body rotation is separable from vibration. For simplicity, we neglected the BSSE correction in the evaluation of the thermodynamic energies.

Description of the Interaction between Adsorbates and the Au(111) Surface. The interaction between the adsorbates and the solid surface in terms of physisorption can be described as the combination of the repulsive and attractive interactions, similar to the intermolecular interactions in a van der Waals complex.[36] The attractive interaction can be further divided into the orientative, dispersive, and inductive interactions. In the present system, the orientative interaction that corresponds to the electrostatic attraction between two species with permanent dipole moments can be disregarded because the Au(111) surface has no permanent dipole, and the constituent Au atoms have no atomic charges.

In our QM/MM method, the repulsive and dispersive interactions, which respectively stem from the electron exchange between the adsorbates and the surface via their overlapping electron clouds and from the instantaneous polarization of the two interacting species, are modeled in terms of a potential function of the Lennard-Jones type:[37,38]

$$V_{ij} = (D_i D_j)^{1/2}\left\{\left(\frac{(x_i x_j)^{1/2}}{r_{ij}}\right)^{12} - 2\left(\frac{(x_i x_j)^{1/2}}{r_{ij}}\right)^{6}\right\} \tag{2}$$

where r_{ij} is the distance between atom i of the adsorbate and atom j of the surface, and x_i and D_i are parameters evaluated by Rappé et al.[37] (Table 1). This description is not necessarily quantitatively accurate, because the parameters were determined from atomic characteristics and because the Au−Au interaction in the Au solid is expected to be strong.[39] Nevertheless, this description is expected to provide a semiquantitatively correct result because the description of adsorbate atoms and surface atoms, in terms of the Lennard-Jones parameters, for the system of alkanethiol chains adsorbed onto the Au(111) surface has been shown, by Hautmann and Klein,[9] to be consistent with experimental data. We thus modified the Gaussian 98 program package so that the calculation of interaction energy by using the Lennard-Jones potential function is incorporated into the ab initio calculations.

Moreover, we also included the inductive interaction—which stems from the effect of a molecule with a permanent dipole on a neighboring molecule—in our calculations by carrying out ab initio calculations with the inclusion of image charges that are modeled by point charges.[40] Here the values of the image charges are equal in magnitude though opposite in sign to the atomic charges of the adsorbates, and the positions of the image charges are mirror images of the atomic positions of the adsorbate along the boundary plane between the metal and a vacuum. In fact, the inductive interaction has been shown, by several researchers,[41−47] to be well described by image interactions that correspond to attractive interactions between charges on the adsorbates and induced charges in the metal. Because Appelbaum and Hamann[46] have also shown that the description in terms of image interactions holds down to distances of about 2.0 Å between the adsorbates and the surface, such a description must thus be appropriate for a process of physisorption, such as the adsorption of benzonitrile clusters onto the Au(111) surface.

A prerequisite for calculations in which image interactions are applied is the selection of a planar boundary that divides the space into regions of vacuum and of metal, in which a free-electron model is applicable. This is because the placement of the point charges must mirror the atomic positions of the adsorbates along the boundary. However, selecting the boundary is a problem; that is, it is inevitably an arbitrary choice. We selected a plane at a distance of $\Delta = d(111) - 2^{-3/2}a_{\mathrm{lattice}}$ above the Au(111) surface layer to act as the boundary. Here a_{lattice} is the lattice constant, which is 4.077 Å for solid Au,[48] and $d(111)$ is the distance between two adjacent (111) layers in a face-centered cubic (fcc) lattice, that is, $3^{-1/2}a_{\mathrm{lattice}}$. The selected boundary is appropriate in the region near the hollow site on the surface, and we thus assume that, in the physisorption of the adsorbates onto the surface, the constituent atoms of the adsorbates are above hollow or bridge sites rather than on-top sites of the surface. This assumption is inferred from analogy with intermolecular interaction, where hydrogen bonds to multiple sites tend to give a larger stabilization energy than do bonds to a single site. Note that our selection differs from that made by Cardini et al.,[45] who selected Δ as $d(111)/2$, but our preliminary calculations showed that the latter selection overestimates the image interactions between the adsorbates and the surface and produces nonphysical chemisorption structures.

Our QM/MM method has the advantages of reducing computational costs and of accurately describing the intermolecular interactions between the adsorbate molecules. Its main disadvantage is a lack of accuracy in calculating the interaction between the adsorbates and the surface. We must thus regard the present quantitative results as preliminary. Nevertheless, in systems of physisorption where there is a large distance between the adsorbates and the surface, qualitative analysis by our method can be expected to produce meaningful results. This is in contrast to the situation of chemisorption, in which accurate representation of the attractive interaction arising from the electron exchange between the adsorbates and the surface is essential.

Calculations for Species Adsorbed on the Au(111) Surface. According to the method of Breneman and Wiberg,[49] we first determined the atomic charges[50] of the benzonitrile molecule and clusters. Point charges, with values equal in magnitude to the calculated atomic charges but opposite in sign, were then situated at the mirror images of the adsorbate-atomic positions along the defined boundary.

The Au(111) surface was modeled as a two-dimensional array consisting of 127 Au atoms (any Au atoms other than the first-layer 127 Au atoms were disregarded). This array constitutes a hexagonal surface structure with a lattice constant of a_{lattice}. All of the gold atoms were fixed at their initial positions during the process of optimization.

---

(36) Margenau, H.; Kestner, N. R. *Theory of Intermolecular Forces*, 2nd ed.; Pergamon: Oxford, 1969.

(37) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

(38) Akiyama, R.; Hirata, F. *J. Chem. Phys.* **1998**, *108*, 4904.

(39) Brivio, G. P.; Trioni, M. I. *Rev. Mod. Phys.* **1999**, *71*, 231.

(40) In some studies,[44] the inductive interaction between adsorbates and a surface has been modeled as the interaction between a permanent dipole and an induced dipole. A dipole does not, however, accurately describe the electrostatic potential in the van der Waals region around most molecules,[19] and thus the atomic charge model that we have applied is more appropriate.

(41) Tasker, P. W.; Stoneham, A. M. *J. Chim. Phys.* **1987**, *84*, 149.

(42) Stoneham, A. M.; Tasker, P. W. *J. Phys. C: Solid State Phys.* **1985**, *18*, L543.

(43) Finnis, M. W.; Stoneham, A. M.; Tasker, P. W. *Met. Ceram. Interfaces* **1990**, 35.

(44) Coltrin, M. E.; Kay, B. D. *J. Chem. Phys.* **1988**, *89*, 551.

(45) Cardini, G.; O'shea, S. F.; Klein, M. L. *Faraday Discuss. Chem. Soc.* **1985**, *80*, 227.

(46) Appelbaum, J. A.; Hamann, D. R. *Phys. Rev. B* **1972**, *6*, 1122.

(47) Jennings, P. J.; Jones, R. D. *Adv. Phys.* **1988**, *37*, 341.

(48) Lide, D. R., Frederikse, H. P. R., Eds. *CRC Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993.

(49) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(50) Hall, G. C.; Smith, C. M. *Int. J. Quantum Chem.* **1994**, *24*, 881.

The center of mass for the adsorbates was initially located 2.5 Å above the defined boundary and above the center of the two-dimensional array of gold atoms. Reconstruction of the surface structure by adsorption was not considered in the present study. Such reconstruction may, in fact, be important in the initial stages of the process of adsorption, because of the preferential nucleation of the adsorbates at the elbows of herringbone patterns that are produced by reconstruction.[11] The relaxation of surface atoms has also been reported to have important consequences on cluster properties.[51−53] However, the adsorbates are not adsorbed directly onto the ridges. Rather, they are adsorbed onto the planar fcc regions sandwiched between pairs of ridges in the reconstructed surface.

We used our modified version of the Gaussian 98 program package to make ab initio calculations for the benzonitrile monomer, dimer, and trimer in the presence of the image charges and the 127 Au atoms. As shown later, with regard to the benzonitrile trimers, a cyclic structure and an antiparallel structure were found to be stable, but the antiparallel trimer was not taken into consideration here because the antiparallel configuration is not possible in the clusters of cyanophenyl porphyrin adsorbed onto the Au(111) surface. The B3LYP/6-31+G*//6-31G* method was used for these ab initio calculations. We used the following algorithm to optimize geometry for the systems:

(1) For the geometry in question, calculate the energy and the first and second derivatives of the energy by Cartesian coordinates.

(2) If the criterion for convergence on the optimization (tight convergence criterion[29]) applies, proceed to step (3). Otherwise, apply Berny's method[54,55] to find a new geometry by using the first and second derivatives, replace the image charges by those appropriate to the new geometry, and then return to step (1).

(3) If the geometry remains unchanged during all of these steps, regard the geometry as having converged. Otherwise, recalculate the atomic charges for the new adsorbate geometry, replace the image charges by the recalculated ones, and return to step (1).

We then calculated (with the B3LYP/6-31G* method) the vibrational frequencies of the optimized geometries, diagonalizing the matrix of the second derivatives of the potential energy by the mass-weighted Cartesian coordinates of the adsorbates. Note that in the adsorbed species not only are the translational and the rotational modes no longer zero-frequency modes, but they are no longer separated from the vibrational modes. We therefore used the frequencies calculated by regarding all of the modes as vibrational and disregarding the vibrations of the Au atoms to evaluate the following items at 63 K, which is the temperature used for the STM observation: the effective entropy, effective enthalpy, and effective free energy of the adsorbed species. Note also that we used the term "effective" to emphasize the neglect of the Au-atoms' vibrations for this evaluation.

We also separately evaluated the deformation energy, E'_{def}, which corresponds to the energy difference between the stable structures of the adsorbed species and of the isolated species, the Lennard-Jones interaction energy, $E_{\mathrm{LJ}} = \sum_{i,j} V_{ij}$, and the image interaction energy, E_{image}. Note that E'_{def} is the deformation energy due to the adsorbate−surface interaction, in contrast to the deformation energy E_{def} due to the intermolecular interaction. These energies are related to the adsorption energy in the following way:

$$E_{\mathrm{ad}} - E_{\mathrm{gas}} = E'_{\mathrm{def}} + E_{\mathrm{LJ}} + E_{\mathrm{image}} \tag{3}$$

where E_{ad} and E_{gas} are the energies of the adsorbed species and the gas-phase species, respectively. The values of E_{ad}, E_{gas}, E'_{def}, and E_{LJ} were evaluated directly from QM/MM and ab initio calculations, whereas E_{image} was evaluated with eq 3.

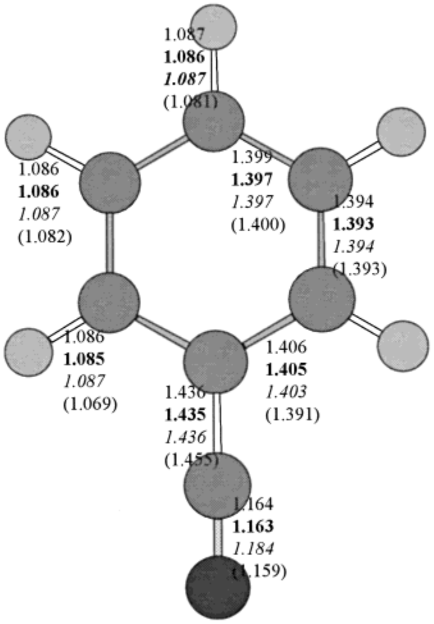

Figure 2. Optimized structure of a benzonitrile molecule. Bond lengths are in Å, as calculated by B3LYP/6-31+G* (plain), B3LYP/6-31G* (bold), and MP2/6-31G* (italic). Experimental values are given in the parentheses.

Results and Discussion

Benzonitrile Molecule and Clusters in Gas Phase. Most of the optimized geometrical parameters of the benzonitrile molecule in the gas phase (Figure 2) were found to be in good agreement with the experimental values obtained by Bak et al.[56] and the values previously calculated with the HF/3-21G method by Sobolewski and Domcke.[57] The dipole-moment values of the benzonitrile molecule, 4.56, 4.77, and 4.77 D, obtained respectively with the B3LYP/6-31G*, B3LYP/6-31+G*//6-31G*, and B3LYP/6-31+G* methods, were found to be closer to an experimental value,[48] 4.18 D, than the value of 5.00 D obtained by the MP2/6-31G* method. The dipole moment must be reproduced so that it accurately represents the electrostatic potential around the molecule, so the B3LYP method seems to be most appropriate for the current investigation. In fact, the B3LYP methods have been shown to provide reliable results on various hydrogen-bonded systems.[34,35] In addition, it was found that the geometries obtained with the B3LYP/6-31G* and B3LYP/6-31+G* methods were in good agreement with each other, whereas the potential energies differ from each other. These findings implied that the B3LYP/6-31+G*//6-31G* method, which requires smaller computational cost than the B3LYP/6-31+G* method, provides satisfactory results. All of the discussion in the rest of the body of this paper is thus based on the results obtained by using B3LYP/6-31+G*//6-31G*. Further details on the dependence of the calculated results on the methods used are discussed in Appendix A.

The optimized geometry of the benzonitrile dimer has the two benzonitrile molecules facing each other in an antiparallel orientation and two coplanar aromatic rings (Figure 3). The calculated distance between the lines tangential to the CN bonds

---

(51) Reddy, B. V.; Pederson, M. R.; Khanna, S. N. *Phys. Rev. B* **1997**, *55*, R7414.

(52) Nayak, S. K.; Weber, S. E.; Jana, P.; Wildberger, K.; Zeller, R.; Dederichs, P. H.; Stepanyuk, V. S.; Hergert, W. *Phys. Rev. B* **1997**, *56*, 8849.

(53) Nayak, S. K.; Jena, P.; Stepanyuk, V. S.; Hergert, W.; Wildberger, K. *Phys. Rev. B* **1997**, *56*, 6952.

(54) Schlegel, H. B. In *Ab Initio Methods in Quantum Chemistry I*; Lawley, K. P., Ed.; Wiley: New York, 1987; p 249.

(55) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(56) Bak, B.; Christensen, D.; Dixon, W. B.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Chem. Phys.* **1962**, *37*, 2027.

(57) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1996**, *250*, 428.

Table 2. Calculated Interaction Energies (kcal/mol) for Benzonitrile Clusters in the Gas Phase

	B3LYP/6-31G*	B3LYP/6-31+G* //6-31G*	B3LYP/6-31+G*	MP2/6-31G*
ΔE^{dimer}	−5.33	−4.10	−4.16	−7.12
$\Delta E_{\text{int}}^{\text{dimer}}$	−3.83	−3.70	−3.79	−4.95
	$(-3.88 + 0.00)^a$	$(-3.74 + 0.04)^a$	$(-3.83 + 0.04)^a$	$(-5.00 + 0.05)^a$
$\Delta E^{\text{trimer-cyclic}}$	−9.36	−7.72	−7.83	−12.40
$\Delta E_{\text{int}}^{\text{trimer-cyclic}}$	−6.79	−6.87	−7.03	−9.01
	$(-6.92 + 0.13)^a$	$(-7.06 + 0.19)^a$	$(-7.18 + 0.15)^a$	$(-9.21 + 0.20)^a$
$\Delta E^{\text{trimer-antiparallel}}$	−9.66	−7.28	−7.39	−15.29
$\Delta E_{\text{int}}^{\text{trimer-antiparallel}}$	−6.77	−6.48	−6.64	−8.82
	$(-6.82+0.05)^a$	$(-6.56+0.08)^a$	$(-6.72+0.08)^a$	$(-8.96+0.14)^a$

[a] $\Delta E^{\text{cp}} + E_{\text{def}}$.

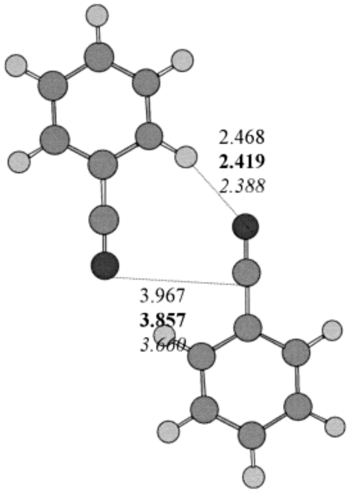

Figure 3. Optimized structure of a benzonitrile dimer. Bond lengths are in Å, as calculated by B3LYP/6-31+G* (plain), B3LYP/6-31G* (bold), and MP2/6-31G* (italic).

(about 3.8 Å) differs from that determined by Kobayashi et al. (2.92 Å) from the laser-induced fluorescence spectra of the benzonitrile clusters formed in a free jet,[24] although the other optimized parameters are similar to those determined by Kobayashi et al. This difference can be attributed to uncertainties in the experimental values determined from the spread of the rotational envelope of the fluorescence spectra, as Kobayashi et al. pointed out.

Optimizing the geometry of the benzonitrile trimer produced two stable structures that correspond to (1) a triangular cyclic and planar form and (2) an antiparallel and nonplanar form (Figure 4). The two structures are nearly isoenergetic, so we were unable to determine their order of stability (Tables 2 and 3). The cyclic structure obtained is similar to the structures conjectured by Itoh et al.[25,26] for the clusters of 1-cyano-4-methylnaphthalene and 1-cyanonaphthalene on the basis of experimental observations. Our results thus support their conjectures. The cyclic trimer structure must be the only stable trimer configuration for these cyanonaphthalenes, because the extra aromatic rings prevent antiparallel trimer configuration. The nonadditive effects in the intermolecular interactions of the trimers are discussed in Appendix B.

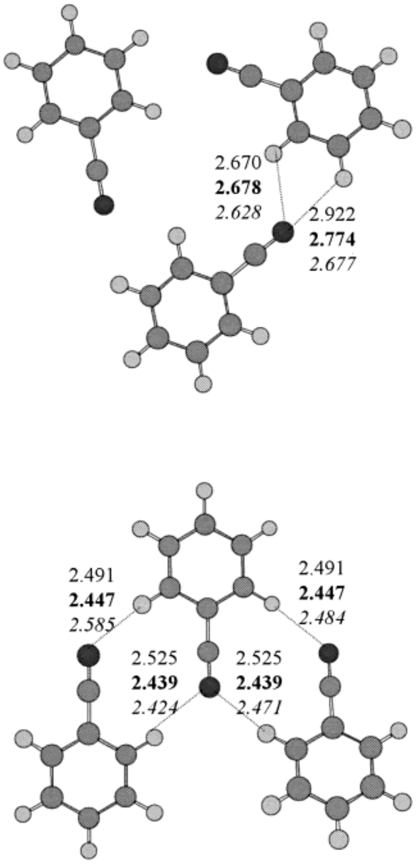

Figure 4. Two optimized structures for benzonitrile trimers. Bond lengths are in Å, as calculated by B3LYP/6-31+G* (plain), B3LYP/6-31G* (bold), and MP2/6-31G* (italics).

Table 3. Energies of the Benzonitrile Molecule and Clusters in the Gas Phase (at 1.0 atm) As Calculated by B3LYP/6-31+G*//6-31G*[a]

	monomer	dimer	cyclic trimer	antiparallel trimer
$\Delta H_{\text{gas}}^{298.15}$ (kcal/mol)	0.00	−1.37	−1.71	−1.53
$S_{\text{gas}}^{298.15}$ (cal/mol/K)	77.181	127.384	181.961	178.926
$\Delta G_{\text{gas}}^{298.15}$ (kcal/mol)	0.00	2.65	3.22	3.70
$\Delta H_{\text{gas}}^{63}$ (kcal/mol)	0.00	−1.78	−2.29	−2.10
S_{gas}^{63} (cal/mol/K)	54.427	76.480	102.367	99.648
$\Delta G_{\text{gas}}^{63}$ (kcal/mol)	0.00	−0.76	−1.01	−0.76

[a] $\Delta H_{\text{gas}}^{t}$ and $\Delta G_{\text{gas}}^{t}$ are the relative enthalpies and free energies per molecule, relative to the values for the monomer, in kcal/mol at t K.

The clusters were found to be more stable than the monomer at low temperatures (63 K) (Table 3). This finding, which is consistent with various experimental observations,[24–26] is because the relative stability at low temperature is determined mainly by the relative enthalpy. However, the calculated results also indicate that the trimers are slightly more stable than the dimer (Table 3), and this indication differs from the observations which showed the major components of the clusters to be dimers

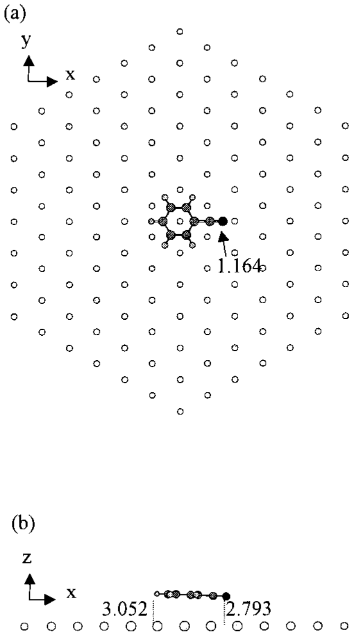

Figure 5. Optimized structure for a benzonitrile molecule adsorbed onto a Au(111) surface (lengths in Å).

rather than trimers.[24−26] This difference must be due to the low probability of molecular collisions in a free-jet experiment.

Benzonitrile Molecule and Clusters Adsorbed onto Au(111) Surface. From the optimized structure of the benzonitrile molecule adsorbed on the Au(111) surface, the molecular plane of the adsorbed benzonitrile was found to be nearly parallel to the surface (Figure 5).[58] This parallel nature is consistent with previous results on physisorption, in which planar molecules with a π system have been shown, both experimentally[1−3,11] and theoretically,[59,60] to be adsorbed parallel to an adsorbing metal surface. In fact, Tadjeddine and Flament[61] recently found from ab initio calculations that, for the 4-cyanopyridine molecule, which is somewhat similar in nature to benzonitrile, the flat-adsorbed structure on the Au(111) surface is more stable than the structure that is vertically adsorbed *via a CN group* (see Table 11 in their paper[61]), whereas the vertically adsorbed structure *via pyridine* at the on-top site is most stable; our result is consistent with their finding. It was also found that the CN group is brought slightly closer to the Au(111) surface than the other portions of the benzonitrile molecule. This must be due to the large magnitudes of the atomic charges on the CN group, which create a strong attractive interaction between the CN group and the image charges that appear in the metal.

All of the constituent atoms of the benzonitrile molecule were found to be situated above the hollow or bridge sites on the Au(111) surface (Figure 5). This finding is inconsistent with previous theoretical studies,[60,61] in which the center of the aromatic ring has been demonstrated to be situated above a 3-fold hollow site. Because the accuracy not only of the methods of calculation used in these previous studies but also of our calculation methods is probably inadequate, we cannot determine which result is correct at present.

Table 4. Energies of the Benzonitrile Molecule and Clusters Adsorbed on the Au(111) Surface As Calculated by B3LYP/6-31+G*//6-31G*[a]

	monomer	dimer	cyclic trimer
E'_{def} (kcal/mol)	0.02	0.05	0.05
E_{LJ} (kcal/mol)	−3.43	−6.47	−9.71
E_{image} (kcal/mol)	−2.24	−2.22	−2.54
$E_{\mathrm{ad}} - E_{\mathrm{gas}}$ (kcal/mol)	−5.65	−8.64	−12.20
$\Delta H^{63}_{\mathrm{ad}}$ (kcal/mol)	0.00	−0.86	−1.25
S^{63}_{ad} (cal/mol/K)	18.807	35.808	54.802
$\Delta G^{63}_{\mathrm{ad}}$ (kcal/mol)	0.00	−0.80	−1.22

[a] $\Delta H^{t}_{\mathrm{ad}}$ and $\Delta G^{t}_{\mathrm{ad}}$ are the relative enthalpies and free energies per molecule, relative to the values for the monomer, in kcal/mol at t K.

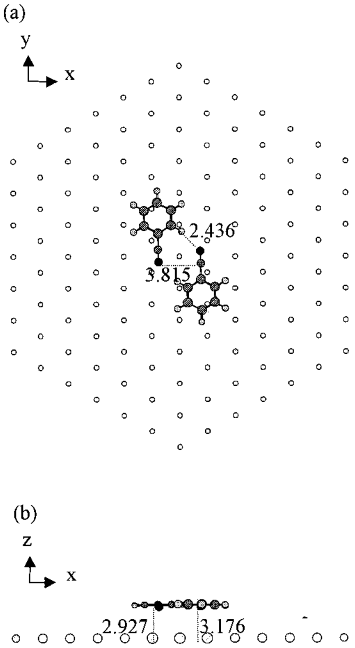

Figure 6. Optimized structure for a benzonitrile dimer adsorbed onto a Au(111) surface (lengths in Å).

On one hand, the interaction energy between the benzonitrile molecule and the Au(111) surface was found to be −5.65 kcal/mol, to which image interaction contributes −2.24 kcal/mol (Table 4). The large absolute value of this image interaction implies that the inductive interaction is important for representing the interaction between a molecule with a permanent dipole such as a benzonitrile molecule and a metallic surface such as the Au(111) surface. Therefore, the description of the adsorbate−surface interaction in terms of the repulsive and dispersive interactions alone, with no consideration of the inductive interaction, is inaccurate. On the other hand, the deformation energy E'_{def} was found to be negligible (Table 4), because the structure of the benzonitrile molecule is barely changed by the interaction between the adsorbates and the surface (Figure 5).

The aromatic planes of the adsorbed benzonitrile clusters were found to be nearly parallel to the Au(111) surface, and the clusters are similar in this way to the adsorbed monomer (Figures 6 and 7). However, the distances between the clusters and the surface are greater than that between the adsorbed monomer and the surface. The larger adsorbate−surface distances can be attributed to the decrease in the adsorbate−surface

---

(58) This parallel adsorption is not just a simple consequence of the model used, because the vertical arrangement can be favored if we artificially (unphysically) magnify the absolute values of the atomic charges of the benzonitrile molecule.

(59) Sautet, P.; Bocquet, M.-L. *Phys. Rev. B* **1996**, *53*, 4910.

(60) Garfunkel, E. L.; Minot, C.; Gavezzotti, A.; Simonetta, M. *Surf. Sci.* **1986**, *167*, 177.

(61) Tadjeddine, M.; Flament, J. P. *Chem. Phys.* **2001**, *265*, 27.

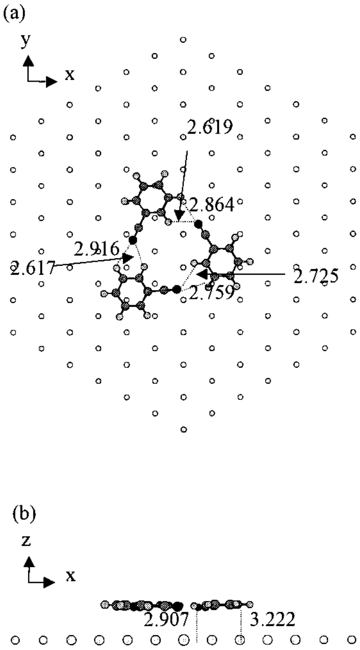

Figure 7. Optimized cyclic structure for a benzonitrile trimer adsorbed onto a Au(111) surface (lengths in Å).

interaction energy per molecule which is brought about by the cluster formation. This decrease mainly stems from the decrease in the image interaction per molecule. In fact, because the cluster formation decreases the total dipole moment, image interactions per molecule in the clusters are weaker than those in the monomer, whereas the Lennard-Jones interaction energies of the dimer and trimer are nearly 2 and 3 times that of the monomer, respectively (Table 4).

We also found that the clusters adsorbed onto the Au(111) surface have similar structures to the gas-phase species, except that the intermolecular distances are slightly altered by adsorption. This finding implies that the cluster formation of cyanophenyl porphyrins adsorbed onto the Au(111) surface, as had previously been observed by STM,[11] must be attributed to the interaction between cyanophenyl groups, which is not affected by any adsorbate−surface interaction. The alteration of the intermolecular distances is caused by the tendency of the constituent atoms of the benzonitrile clusters to be preferentially situated in certain appropriate sites (i.e., the hollow or bridge sites) on the surface.[62] However, this alteration hardly affects the intermolecular interaction energies, because the deformation energy was found to be very small (Table 4). These findings are similar to those of a study on the benzene adsorbed on metal atoms, in which the benzene structure hardly changes with the adsorption because the covalent bonds within the benzene are rather stronger than the benzene−metal interaction.[63]

The calculated thermodynamic energies of the gas-phase and adsorbed species show that adsorption reduces the values of the entropy from one-half to one-third of their gas-phase values (Tables 3 and 4). This reduction mainly stems from the decrease in the translational and rotational entropies that the adsorbate−surface interaction brings about because, for the gas-phase species, the translational and rotational modes make a large contribution to the total molecular entropy; for example, the vibrational, translational, and rotational entropies of the gas-phase benzonitrile molecule were 0.539, 32.085, and 21.802 cal/mol/K at 63 K, respectively. This decrease is because adsorption converts the translational and rotational modes into effectively vibrational modes. As a result, the adsorbed dimer and trimer have 2 and 3 times the entropy of the adsorbed monomer, respectively (Table 4); in other words, the entropy values per molecule are nearly the same for the adsorbed monomer, dimer, and trimer. Therefore, the contribution of entropy to the relative stability of the monomer, dimer, and trimer is negligible, and the determining factor in the relative stability is thus the magnitude of the enthalpy.

There must thus be less free energy per molecule in the cyclic trimer adsorbed on the Au(111) surface at 63 K than in the monomer and dimer, and less in the dimer than in the monomer. This is why the main component of the benzonitrile clusters adsorbed on the surface must be trimers rather than dimers and monomers. This result is consistent with our experimental finding concerning the adsorption of cyanophenyl porphyrin clusters onto the Au(111) surface, that is, our finding by STM that the major portion of the adsorbed clusters is of the triangular trimer structure rather than the dimer or monomer structure (Figure 1).[11] Therefore, in cyanophenyl porphyrin clusters adsorbed onto the surface, the reason that the trimer is more stable than the monomer and dimer can be attributed to the negligible contribution of the entropy to the relative stability, which stems from the reduction of the entropy by adsorption.

However, it is also true that the adsorption does not very much change the relative stability found in the gas phase. Therefore, the trimer formation of benzonitriles on the Au(111) surface simply reflects gas-phase stability. This must be because the increase in the relative enthalpy resulting from the adsorbate−surface interaction tends to accompany the increase in the relative entropy, similar to the "compensation effect" that is often found in the solvent effects for chemical reactions in solution.

Summary

We have determined the stable structures and energies of the benzonitrile molecule and clusters, both in the gas phase and adsorbed onto the Au(111) surface, by theoretical calculation. We used an ab initio approach for the gas-phase species, whereas for the adsorbed species we used a QM/MM method, in which the repulsive and dispersive interactions between the adsorbates and the surface were modeled by potential functions of the Lennard-Jones type, and the image-interaction model was used to represent the inductive interaction. The calculated results for the gas-phase species were consistent with earlier speculation[24−26] on the basis of laser-induced fluorescence spectra; the dimer has an antiparallel and planar stable structure, while the trimer has two isoenergetic stable structures, a cyclic and planar structure and an antiparallel and nonplanar structure, and, at low temperatures, the clusters are more stable than the monomer. In the adsorbed species, we found that the adsorbates are similar in structure to the gas-phase species and that the adsorbed cyclic trimer is more stable than the adsorbed monomer or dimer. The latter finding is because the relative stability of adsorbed species

---

(62) In contrast to the case for the monomer, all of the atoms of the clusters are not necessarily above hollow or bridge sites. The reason is that the difference in adsorption sites barely changes the adsorption energy.

(63) Pandey, R.; Rao, B. K.; Jena, P.; Blanco, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 3799.

is independent of the entropy. We therefore concluded that the adsorbate−surface interaction hardly changes the situation found in the gas phase and that the preference for the trimer form in the adsorption of cyanophenyl porphyrins onto the Au(111) surface is due to the negligible contribution of entropy to the relative stability of the adsorbed species.

Appendix A: The Dependence of the Results for Gas-Phase Species on the Methods Used

Most of the geometrical parameters of the benzonitrile molecule in the gas phase (Figure 2) as optimized with the B3LYP/6-31+G*, B3LYP/6-31G*, and MP2/6-31G* methods were found to be in good agreement with each other. An exception is the CN distance, which is moderately dependent on which method we used for the calculation. The tendency for the calculation methods to underestimate or overestimate the CN distance is similar to that found for acetonitrile by Cabareiro-Lago et al.;[12] the CN distance is overestimated by the MP2 method, whereas the CN distance obtained with the B3LYP method is closer to the experimental value (Figure 2). This is thus a general tendency for any species that includes a cyano-group.

Appendix B: Nonadditive Effects on Intermolecular Interactions

We used the relation given below to evaluate the contribution of nonadditive effects to the interaction energy, $E_{\text{nonadditive}}$,[12] of the trimers:

$$E_{\text{nonadditive}} = \Delta E_{\text{int}}^{\text{ABC}} - \Delta E_{\text{int}}^{\text{AB}} - \Delta E_{\text{int}}^{\text{BC}} - \Delta E_{\text{int}}^{\text{AC}} \quad \text{(B1)}$$

where the superscripts A, B, and C indicate the molecules among and between which the interaction energy is calculated. In this evaluation, we have employed the full basis set of the complex ABC in calculating all of the energies, and in this way avoided having to use the BSSE corrections.

The total contribution of nonadditive effects to the interaction energy in the cyclic trimer $E_{\text{nonadditive}}$ was found to be −0.90 kcal/mol, which is in good agreement with the figures for cyclic acetonitrile trimers, which have previously been reported as being from −0.77 to −1.05 kcal/mol.[12] The nonadditive effects thus play a key role in any cyclic structures. The contribution of nonadditive energy, $E_{\text{nonadditive}}$, to the antiparallel trimer, 0.15 kcal/mol, has the nature of a repulsive interaction, which is in accord with the conclusions of Cabaleiro-Lago et al.'s study[12] of antiparallel acetonitrile trimers. The repulsive nature of the nonadditive contribution must be due to the repulsive interaction between the two terminal benzonitriles on both sides of the antiparallel trimer.

Supporting Information Available: Optimized Cartesian coordinates (in Å) for the gas-phase species by B3LYP/6-31G* and calculated energies (in hartree) for the gas-phase and adsorbed species by B3LYP/6-31+G*//6-31G* (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA011744V