

Hartree–Fock Dispersion Probe of the Equilibrium Structures of Small Microclusters of Benzene and Naphthalene: Comparison with Second-Order Møller–Plesset Geometries

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The equilibrium structures of small microclusters of benzene and naphthalene were computed by a simple Hartree–Fock dispersion (HFD) model, in which a self-consistent field calculation is supplemented by an empirical dispersion term. The minimum energy conformers so obtained with the 6-31G basis set are essentially identical to those obtained from a second-order Møller–Plesset calculation with the same basis set. The trends in relative stabilities are also in general accord with those from the correlated ab initio calculation. These results demonstrate the utility of the HFD models in the conformational search of aromatic clusters.

1. Introduction

As the species formed due to intermolecular interactions, the geometrical structures of aromatic dimers and higher clusters, generated by free jet expansion, provide important information concerning the nature of the forces between aromatic molecules and clusters' other properties. Moreover, the study of clusters has applications in photochemistry, catalysis, homogeneous nucleation, the structure of condensed matter, and fabrication of nanodevices. For these reasons, the structural probe of the small clusters of aromatic hydrocarbons has been the subject of considerable interest in recent years. Unfortunately, because clusters are bound by weak electrostatic and van der Waals (vdW) forces, they tend to have floppy structures that are difficult to characterize experimentally. Quantum chemistry calculations are therefore useful for interpreting experimental observations and for making structural predictions in the absence of experimental measurements. Reliable ab initio studies of aromatic clusters must include electron correlation explicitly in order to obtain good representations of dispersion and electrostatic forces that are responsible for binding of the species.

In three recent papers, two of the authors have reported ab initio geometry searches, carried out at the second-order Møller–Plesset (MP2)/6-31G level of theory, for the vdW trimer of naphthalene,¹ for the dimers of benzene, naphthalene, and anthracene,² and for the trimer, tetramer, and pentamer of benzene.³ For naphthalene trimer, the computation yielded the lowest energy cyclic C_{3h} equilibrium structure that is essentially identical to the experimental geometry obtained from the rotational coherence spectroscopy.⁴ Other trimer conformers were found to be considerably higher in energy than the lowest energy configuration. For the dimers of benzene, naphthalene, and anthracene, the calculation yielded two low energy equilibrium structures of very similar energies.² They are the parallel-displaced (C_{2h}) and the tilted T-shaped structures for benzene and the parallel-displaced (C_{2h}) and crossed (D_{2d}) structures for naphthalene and anthracene. The two dimer conformers of

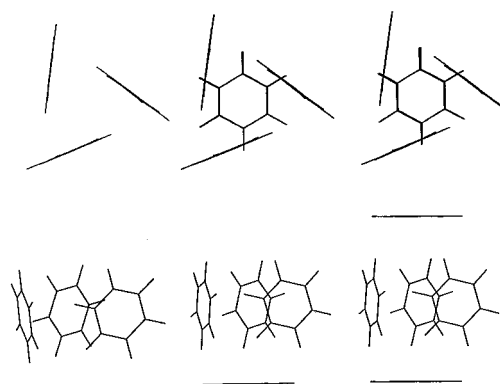


Figure 1. Top and side views of the lowest energy MP2/6-31G structures of the benzene trimer, tetramer, and pentamer.

benzene are very similar to those from previous high-level ab initio calculations,^{5,6} but there are no experimental or other ab initio geometries with which the computed dimer structures for naphthalene and anthracene can be compared. Nonetheless, the spectroscopy and photophysics of the two-dimer conformers of anthracene^{7,8} are consistent with what would be expected of the crossed and the parallel-displaced dimers.⁹ Extension of an exhaustive MP2/6-31G structure search to the vdW trimer and tetramer of benzene, and a limited search for the pentamer of benzene, indicates that the minimum energy structures of the species are triangle (C_{3h}) for the trimer, tetrahedron (C_3) for the tetramer, and possibly trigonal bipyramid (C_{3h}) for the pentamer.³ In the tetramer and pentamer, the fourth and fifth benzene molecules occupy the vacant sites (apexes) in the trigonal bipyramid with their molecular planes perpendicular to the 3-fold symmetry axis of the sites occupied by the cyclic trimer, as seen in Figure 1. Interestingly, these minimum energy structures are those that maximize nearest-neighbor coordination number. Apparently, the high symmetry and small size of benzene, combined with its lack of permanent dipole moment, render the benzene microclusters to follow the structural *aufbau* (Wefelmeier growth sequence)¹⁰ used to describe the atomic clusters. Similar calculations on the benzene dimers, trimers, and tetramers at the MP2/6-31G* level yielded minimum energy

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conformers and relative stabilities that are identical to the ones obtained at the lower MP2/6-31G level.³

Because quantum chemistry calculations that include electron correlation explicitly are computationally expensive, the ab initio structure calculations even at the modest MP2/6-31G level of theory are impractical for aromatic clusters significantly larger than benzene pentamer or naphthalene trimer. Computationally efficient methods are therefore needed for the structural elucidation of larger clusters. Two such methods, differing in their approaches, have been utilized for the structure study of small benzene and naphthalene clusters. One of these involves energy minimization calculations using empirical potential energy calculations. The model potential functions most commonly used in this method are the exp-6-1 potentials of Williams¹¹ and the nonempirical molecular orbital (NEMO) potential proposed by Wallquist et al.¹² The use of the exp-6-1 potentials generally leads to a cyclic (C_3) minimum geometry for benzene trimer^{13–16} but yields two rather different tetramer structures, depending on the method of energy minimization. In one of these,^{13,16} the intermolecular distances and orientations are such that there are two different pairs of equivalent benzene moieties. In the other,¹⁵ the fourth benzene molecule in the tetramer is added to one of the molecules in cyclic trimer in a dimerlike arrangement. Neither of these tetramer geometries agrees with the minimum energy C_3 tetramer structure³ obtained from the MP2/6-31G* calculation. Energy minimizations with the NEMO potential also yield a cyclic trimer, but the NEMO tetramer has the fourth benzene molecule added to one of the molecules in a T-shaped edge-to-face configuration.¹⁷ Potential energy minimization calculations on naphthalene with genetic algorithms and the NEMO potential yields a crossed dimer and a cyclic trimer as the minimum energy structures.¹⁸ The second computationally efficient method is HFD (Hartree–Fock dispersion) model that combines an ab initio self-consistent field (SCF) interaction energy with empirical dispersion energy. In this approach, proposed originally by Hepburn et al.,¹⁹ the interaction between the molecules is described by the computationally efficient SCF calculation and the worst deficiency of SCF, i.e., the exclusion of electron correlation (and hence the neglect of dispersion), is corrected by adding an empirical dispersion term of the form C_n/R^n . The dispersion term in such a model potential must include a damping function, $f_n(R)$, to suppress the singularity as $R \rightarrow 0$.²⁰ Although a variety of HFD models have been proposed for clusters of inert-gas atoms,²¹ applications of these models to molecular systems have been limited only to the work of Scheiner and co-workers on dimers of benzene and tetrazine²² and that of Carsky et al.²³ on benzene dimers. These calculations, carried out with small basis sets and without full geometry optimizations, have shown that the most stable geometry of the benzene dimer is of the T-shaped type. A question of considerable interest is whether this approach can be applied to properly describe the interaction energy of larger molecular clusters for which many-body effects could be important.

In this paper, we apply the HFD method to the structural elucidation of small microclusters²⁴ of benzene and naphthalene, for which correlated (MP2) ab initio calculations are available. It will be shown that the minimum energy conformers and relative stabilities so obtained are very similar to those from the MP2 calculations.

2. HFD Model

To account for dispersion forces in the ab initio Hartree–Fock formalism, an energy term (U_{disp}) is usually added

perturbatively at the end of the SCF procedure. For a molecular cluster, the total electronic energy (E_{HFD}) is therefore

$$E_{\text{HFD}} = E_{\text{HF}} + U_{\text{disp}} \times f_n \quad (1)$$

where E_{HF} is the Hartree–Fock energy, U_{disp} is the dispersion energy, and f_n is the damping function. The damping function (f_n) is needed in order to avoid singularities in the dispersion energy at small interatomic distances. The dispersion energy was obtained using the expression

$$U_{\text{disp}} = - \sum_{\mu=1}^{NMOL-1} \sum_{\nu=\mu+1}^{NMOL} \sum_{i=1}^{NAT_{\mu}} \sum_{j=1}^{NAT_{\nu}} \left\{ \sum_{n=6,8,10} \frac{(C_i^n C_j^n)^{1/2}}{R_{ij}^n} \right\} \quad (2)$$

Here, $NMOL$ is the number of molecules in the cluster, NAT_{μ} is the total number of atoms for molecule μ , R_{ij} is the distance between atom i and atom j in molecules μ and ν , respectively, and the coefficients are the n -order dispersion coefficients corresponding to atoms i and j . In our work, the dispersion term in eq 2 is truncated to the lowest order ($n = 6$). For C–C, H–H, and C–H interactions, we have used the dispersion coefficients reported by Huiszoon and Mulder²⁵ ($C_6(\text{C–C}) = 2.17 \text{ J nm}^6 \text{ mol}^{-1}$, $C_6(\text{H–H}) = 0.167 \text{ J nm}^6 \text{ mol}^{-1}$, and $C_6(\text{C–H}) = 0.603 \text{ J nm}^6 \text{ mol}^{-1}$). For the damping function, we have adopted the simple two-parameter sigmoid function

$$f_6(R_{ij}) = \frac{1}{(1 + e^{\alpha(R_0 - R_{ij})})} \quad (3)$$

where R_{ij} is the distance between atom i and atom j and α and R_0 are empirical parameters. This is a modified form of a damping function that has been used to damp singularities for two-electron repulsion integrals within the tight-binding approximation.²⁶ The numerical value of $f_6(R)$ varies from a very small value for $R \rightarrow 0$ to 1 for large R in a manner determined by the parameter α . The damping function parameters α and R_0 used in this work were obtained by monitoring the behavior of the dispersion energy potential as a function of the interatomic distance for C–C, H–H, and C–H interactions. As shown in Figure 2a, singularities in the dispersion energies occur approximately at interatomic distances of 0.6 bohrs for C–C, 0.5 bohrs for C–H, and 0.4 bohrs for H–H interactions. The plot in Figure 2b shows that the singularity in the dispersion is significantly attenuated by taking values of 1.5 bohr^{-1} and 6.0 bohr for α and R_0 , respectively. The profile of the damping function used in this work is also shown in Figure 2c. Given the improvement in the qualitative behavior of the damped energies with these parameters, no further refinement or parametrization was attempted.

Relative HFD binding energies of various low-energy conformers were compared with the corresponding MP2 values.^{1–3} The HFD routines were implemented in a local version of the GAMESS package^{27,28} running on an IBM RS/6000 model 270.²⁸ The SCF portion of the HFD calculations was carried out using the 6-31G basis set. Single point calculations at the MP2/6-31G level of theory using the geometries previously optimized with our HFD model were performed with the GAUSSIAN 98 suite of programs^{28,29} on a Cray T-94²⁸ at the Ohio Supercomputer Center.

3. Results and Discussion

As expected, the intermolecular interactions in the benzene and naphthalene microclusters are generally repulsive at the SCF level. Inclusion of dispersion energy (U_{disp}) leads to stabilization.

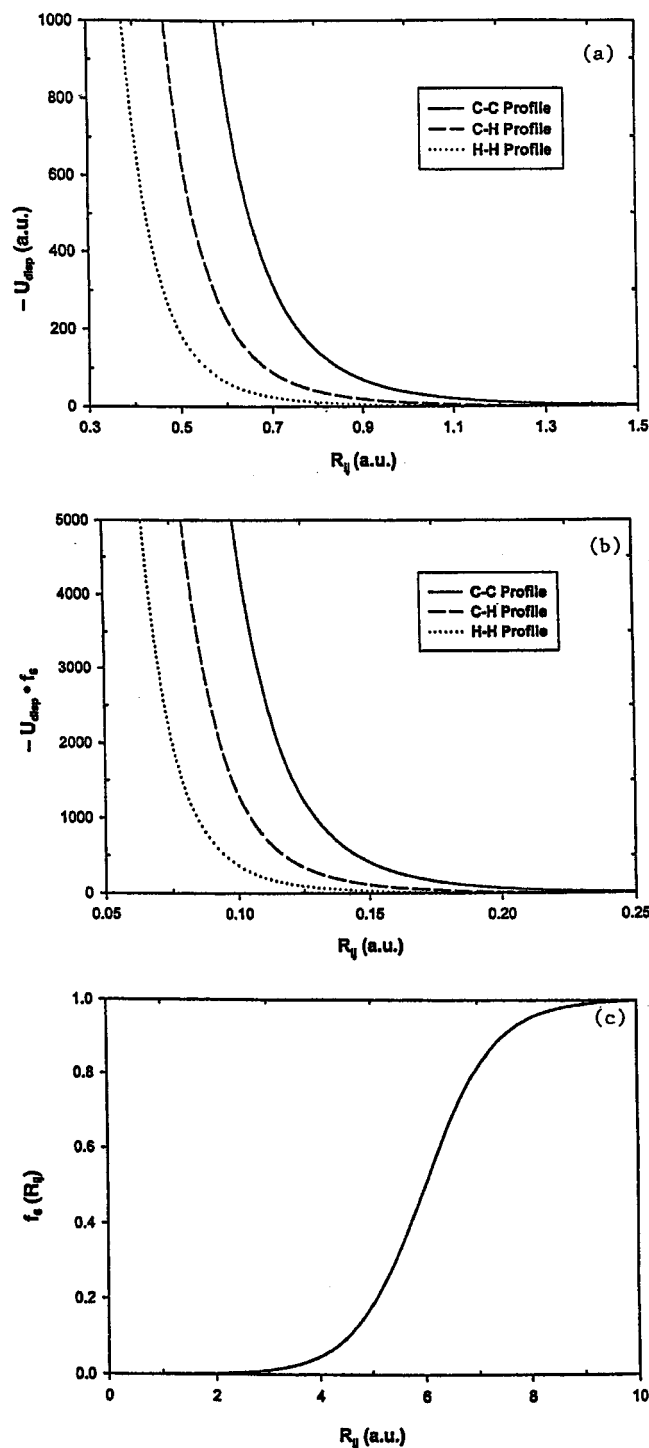


Figure 2. (a) Plot of undamped dispersion energy ($-U_{\text{disp}}$) as a function of interatomic distance (R_{ij}); (b) the same for the damped dispersion energy ($-U_{\text{disp}} \cdot f_6$); and (c) the profile of the damping function f_6 with $\alpha = 1.5 \text{ bohr}^{-1}$ and $R_0 = 6.0 \text{ bohr}$.

The dominant attraction in the vdW clusters of aromatic hydrocarbons is clearly due to the dispersion term.

For all of the benzene clusters, the agreement between the optimized HFD geometries and the geometries optimized at the MP2/6-31G level of theory is quite good. A root mean square (rms) in the intermolecular distance of 0.17 \AA , with a minimum deviation of 0.016 \AA and a maximum deviation of 0.43 \AA , has been obtained with respect to the MP2/6-31G geometry.

Tables 1–4 present HFD energies for various conformers of dimer, trimer, tetramer, and pentamer of benzene that have

TABLE 1: Relative Energies (in kJ/mol) of Benzene Dimers, as Computed by Full Geometry Optimization at the MP2/6-31G and HFD/6-31G Levels of Theory, and Those Obtained by Single Point MP2/6-31G Energy Calculation on the Optimized HFD/6-31G Structure

conformer ^a	MP2/6-31G// MP2/6-31G	HFD/6-31G// HFD/6-31G	MP2/6-31G// HFD/6-31G ^b
T-shaped ^c	0.00	0.00	0.00
parallel-displaced	2.40	0.23	2.87

^a See ref 2 for MP2/6-31G and MP2/6-31G* structures. ^b Single point calculation. ^c Full geometry optimization conducted in redundant internal coordinates gives tilted T-shaped structure, ref 2.

TABLE 2. Relative Energies (in kJ/mol) of Benzene Trimers, as Computed by Full Geometry Optimization at the MP2/6-31G and HFD/6-31G Levels of Theory, and Those Obtained by Single Point MP2/6-31G Energy Calculation on the Optimized HFD/6-31G Structure

conformer ^a	MP2/6-31G// MP2/6-31G	HFD/6-31G// HFD/6-31G	MP2/6-31G// HFD/6-31G ^b
cyclic (a)	0.00	0.00	0.00
cyclic (b)	2.45	0.20	0.17
sandwich	11.75	9.82	11.79
double T	12.83	15.02	11.88
H	13.56	15.41	12.58
stacked	16.12	13.58	16.50

^a See ref 3 for MP2/6-31G and MP2/6-31G* structures. ^b Single point calculation.

TABLE 3: Relative Energies (in kJ/mol) of Benzene Tetramers, as Computed by Full Geometry Optimization at the MP2/6-31G and HFD/6-31G Levels of Theory, and Those Obtained by Single Point MP2/6-31G Energy Calculation on the Optimized HFD/6-31G Structure

conformer ^a	MP2/6-31G// MP2/6-31G	HFD/6-31G// HFD/6-31G	MP2/6-31G// HFD/6-31G ^b
face-triangular	0.00	0.00	0.00
tetrahedral	11.79	4.36	7.03
edge-sandwich	12.90	3.13	5.67
edge-triangular	27.77	12.20	15.03

^a See ref 3 for MP2/6-31G and MP2/6-31G* structures. ^b Single point calculation.

TABLE 4: Relative Energies (in kJ/mol) of Benzene Pentamers, as Computed by Full Geometry Optimization at the MP2/6-31G and HFD/6-31G Levels of Theory, and Those Obtained by Single Point MP2/6-31G Energy Calculation on the Optimized HFD/6-31G Structure

conformer ^a	MP2/6-31G// MP2/6-31G	HFD/6-31G// HFD/6-31G	MP2/6-31G// HFD/6-31G ^b
trigonal bipyramid	0.00	0.00	0.00
fused double tetrahedron	17.45	0.94	3.94

^a See ref 3 for MP2/6-31G structures. ^b Single point calculation.

previously been studied by MP2/6-31G.^{2,3} Despite the excellent agreement between the HFD and the MP2 optimized geometries, HFD significantly underestimates the relative stability of the various conformers as compared to the MP2 data. This is especially evident in the tetramer and pentamer. However, the ordering of stabilities obtained from the HFD model more or less reproduces the corresponding MP2 ordering. The only exception is in the relative energy of the stacked trimer,³ which HFD predicts to be lower than those for the H and double T-shaped conformers.³ Interestingly, single point calculations at the MP2/6-31G level using the HFD optimized structures reproduce the trends observed when full geometry optimizations are carried out at the MP2/6-31G level of theory.

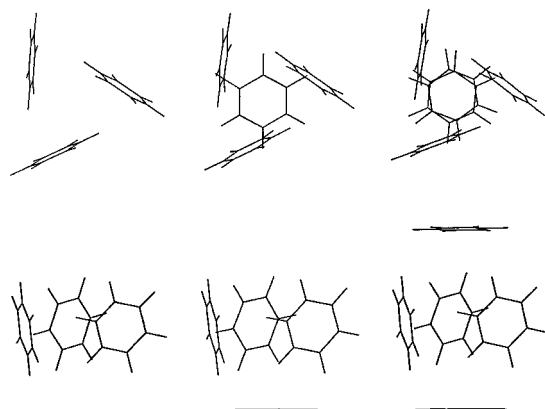


Figure 3. Top and side views of the lowest energy HFD/6-31G structures of the benzene trimer, tetramer, and pentamer.

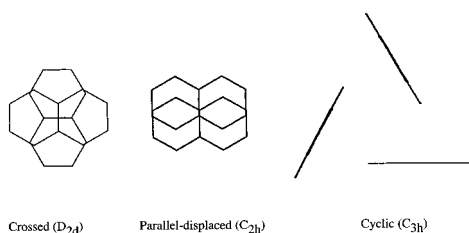


Figure 4. Top views of the fully optimized HFD/6-31G structures of the two lowest energy conformers (crossed and parallel-displaced) of naphthalene dimer and the HFD/6-31G minimum energy structure of naphthalene trimer. The trimer geometry, viewed along the long in-plane axes of the three naphthalene moieties, includes C–H bonds. These structures are indistinguishable from the corresponding MP2/6-31G minimum energy geometries described in refs 1 and 2.

The most significant result of this exploratory work is that both HFD and MP2 predict the same global minima for the dimer, trimer, and tetramer of benzene. Figure 3 presents the lowest energy HFD structures of the benzene clusters. The dimer structure (not shown) is identical to the MP2 geometry obtained using the 6-31G or 6-31G* basis set,² whereas the HFD structures of the trimer, tetramer, and pentamer are slightly distorted versions of the corresponding MP2 geometries.² B3LYP DFT calculations on these benzene clusters also yield the lowest energy conformers that agree with the optimized MP2 geometries.³⁰ In contrast, the global minima of the benzene tetramer obtained from the energy minimization of empirical potential functions (exp-6-1 and NEMO)^{13–16} are at variance with the minimum energy MP2 structure.³

Application of the HFD model to the dimer and trimer of naphthalene also gives global minima, as seen in Figure 4, which is essentially identical to those from the MP2 calculation. A rms in the intermoleity distance of 0.18 Å, with a maximum deviation of 0.40 Å, has been obtained with respect to the fully optimized MP2/6-31G geometry. Moreover, whereas the HFD model predicts a cyclic C_{3h} trimer (with the long in-plane axes of the three naphthalene moieties parallel), which is substantially more stable than any other trimer conformers,³¹ it predicts the crossed and parallel-displaced dimers of very similar energies, as seen in Table 5, also in excellent agreement with the MP2 results. For comparison, the potential energy minimization calculations with genetic algorithms and the NEMO potential yield only one low-energy conformer (crossed) for naphthalene dimer.¹⁸

We consider it significant that the two rather different methodologies (HFD and MP2) lead to the same minimum energy structures for all aromatic clusters that have been studied. These results suggest that HFD could reliably predict the

TABLE 5: Relative Energies (in kJ/mol) of Naphthalene Dimers, as Computed by Full Geometry Optimization at the MP2/6-31G and HFD/6-31G Levels of Theory

conformer ^a	MP2/6-31G// MP2/6-31G	HFD/6-31G// HFD/6-31G
crossed	0.00	0.00
parallel-displaced	0.26	0.17

^a See ref 2 and Figure 4 for structures.

equilibrium structures of larger aromatic microclusters. The real advantage of the HFD model over highly correlated ab initio methods is obviously its computational efficiency. This point can be clearly illustrated by looking at the timings obtained in our calculations. For instance, the MP2/6-31G geometry optimization of the trigonal bipyramid conformer of the benzene pentamer (330 basis functions) takes approximately 6 h of central processing unit (CPU) time per optimization cycle on a Cray T94. The same optimization carried out with our HFD method takes approximately 1.5 h of CPU time per optimization cycle on a IBM RS/6000 model 270.

The motivation for the present exploratory study was to probe the utility of the computationally inexpensive HFD model in conformational searches for small aromatic clusters. The results presented herein strongly suggest that with the refinement and optimization of the empirical dispersion terms as well as the use of more robust and accurate damping functions, it should be possible to develop more reliable and efficient HFD intermolecular potentials for aromatic clusters in general. These efficient methodologies will help to provide important insights into the fundamental interactions between molecules in large-scale systems. Efforts are currently under way in our groups to develop HFD methodologies able to predict relative stabilities of aromatic clusters with accuracy comparable to the ones obtained with significantly more expensive correlated ab initio methods such as MP2.

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References and Notes

- Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **1999**, *103*, 1437.
- Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **2000**, *104*, 2953.
- Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **2001**, *105*, 1904.
- Benharash, P.; Gleason, M.; Felker, P. M. *J. Phys. Chem. A* **1999**, *103*, 1442.
- Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1990**, *93*, 5893.
- Jaffe, R. L.; Smith, G. D. *J. Chem. Phys.* **1996**, *105*, 2780.
- Chakraborty, T.; Lim, E. C. *J. Phys. Chem.* **1993**, *97*, 11151.
- Matuoka, T.; Kosugi, K.; Hino, K.; Nishiguchi, M.; Ohashi, K.; Nish, N.; Sekiya, H. *J. Phys. Chem. A* **1998**, *102*, 7598.
- Gonzalez, C.; Lim, E. C. *Chem. Phys. Lett.* **2000**, *322*, 382.
- Wefelmeier, W. *Z. Phys.* **1937**, *107*, 332.
- (a) Williams, D. E.; Starr, T. L. *Comput. Chem.* **1977**, *1*, 173. (b) Williams, D. E.; Xiao, X. *Acta Crystallogr., Sect. A* **1993**, *A49*, 1.
- Wallquist, A.; Ahlstrom, P.; Karlstrom, G. *J. Phys. Chem.* **1990**, *94*, 1649.
- van de Wall, B. W. *Chem. Phys. Lett.* **1986**, *123*, 69.
- Williams, D. E. *Acta Crystallogr.* **1980**, *A36*, 715.
- de Meijere, A.; Huisken, F. *J. Chem. Phys.* **1990**, *92*, 5826.
- Williams, D. E. *Chem. Phys. Lett.* **1992**, *192*, 538.
- Engkvist, O.; Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1999**, *110*, 5758.
- White, R. P.; Niesse, J. A.; Mayne, H. R. *J. Chem. Phys.* **1998**, *108*, 2208.
- Hepburn, J.; Scoles, G.; Penco, R. *Chem. Phys. Lett.* **1975**, *36*, 451.
- Stone, A. J. *The Theory of Intermolecular Forces*; Clarendon Press: Oxford, 1996; pp 115–184 and references therein.
- Meath, W. J.; Koulis, M. *THEOCHEM (J. Mol. Struct.)* **1991**, *72*, 1 and references therein.

(22) Pawliszyn, J.; Szczesniak, M. M.; Scheiner, S. *J. Phys. Chem.* **1984**, 88, 1726.

(23) Carsky, P.; Selzle, H. L.; Schlag, E. W. *Chem. Phys.* **1988**, 125, 165.

(24) Clusters have been classified according to the size, such that clusters with $n = 2-10$ or 13 have been termed microclusters, clusters with $n = 10-100$ have been referred to as small clusters, and aggregates with $n \geq 100$ are called large clusters. See Jortner, J. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, 188.

(25) Huiszoon, C.; Mulder, F. *Mol. Phys.* **1979**, 38, 1497.

(26) Cohen, R. E.; Mehl, M. J.; Papaconstantopoulos, D. A. *Phys. Rev. B: Rapid Commun.* **1994**, 50, 14694.

(27) GAMESS: Schmidt, M. W.; et al. *J. Comput. Chem.* **1993**, 14, 1347.

(28) Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

(29) Frisch, M. J.; et al. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(30) Boo, B. H.; Cho, H.; Lim, E. C. DFT Study of the Equilibrium Structures of Small Aromatic Clusters. *J. Phys. Chem.*, submitted for publication.

(31) A detailed account of the HFD structures for the trimer and tetramer of naphthalene, and their photophysical implications, will be presented elsewhere (Gonzalez, C.; Lim, E. C., to be submitted for publication).