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A Quantum Chemistry Study of the van der Waals Dimers of Benzene, Naphthalene, and Anthracene: Crossed (D_{2d}) and Parallel-Displaced (C_{2h}) Dimers of Very Similar Energies in the Linear Polyacenes

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A quantum chemistry study of the ground-state structures and binding energies of the van der Waals dimers of benzene, naphthalene, and anthracene has been made at the MP2/6-31G and MP2/6-31+G levels of theory. For naphthalene and anthracene, the calculations yield two low energy dimers of very similar energies: D_{2d} (crossed) and C_{2h} (parallel-displaced). Conformers, analogous to the T-shaped dimer of benzene, are less stable than the crossed and the parallel-displaced dimers. BSSE-corrected MP2/6-31+G//MP2/6-31G binding energies of the crossed and parallel-displaced dimers are, respectively, 15.77 and 15.65 kJ/mol for naphthalene and 36.40 and 31.84 kJ/mol for anthracene. The fully optimized MP2/6-31G structures of the parallel-displaced dimer of naphthalene has a horizontal displacement of 1.5 Å along the short axes of the monomers and a vertical displacement of 3.5 Å. The corresponding horizontal and vertical separations for the parallel-displaced (PD) dimer of anthracene are 1.1 and 3.6 Å, respectively. For the crossed dimers, the vertical separation of the aromatic rings is 3.6 Å for naphthalene and 3.3 Å for anthracene. The greater binding energy and the shorter horizontal displacement of the anthracene PD dimer relative to the naphthalene PD dimer are consistent with the stronger dispersion interactions expected of a larger dimer. The greater stability and smaller vertical separation of the crossed dimer of anthracene relative to that of naphthalene can also be attributed to the disparity in the dispersion interactions.

Introduction

Aromatic−aromatic interactions play important roles in many chemical and biological systems. They control, among others, the base−base interactions leading to the double helical structure of DNA, the function of the special pair in photosynthetic reaction centers, the packing of aromatic crystals, the formation of aggregates, the binding affinities in host−guest chemistry, and the conformational preferences of polyaromatic macrocycles and chain molecules. For a fundamental understanding of these phenomena, it is essential to have accurate data on intermolecular potentials of isolated molecules.

The molecular systems ideally suited for a detailed study of intermolecular potentials are van der Waals (vdW) dimers and higher clusters of aromatic hydrocarbons that are generated by free jet expansion. Since these species are formed as a direct consequence of intermolecular interactions, the geometrical structures of the vdW molecules not only reveal the nature of the forces between molecules but also provide an understanding of the clusters' other properties, including dynamics.

The simplest and most extensively studied aromatic cluster is the vdW dimer of benzene. On the basis of molecular beam electric resonance spectroscopy, which shows the benzene dimer to be a polar and an asymmetric rotor, Klemperer and coworkers[1] proposed a T-shaped geometry with C_{2v} symmetry. This structure is in agreement with the nearest-neighbor orientation in the solid and with the conformation that might be predicted on the basis of the long-range quadrupole−quadrupole interactions. After this pioneering work, a substantial volume of experimental data has been accumulated for benzene dimers in supersonic molecular beams. Two earlier reports[2,3] on optical spectra concluded that the two moieties in the dimer are equivalent, leading to a slip-parallel (parallel-displaced) C_{2h} structure[2] or a V-shaped C_{2v} structure.[3] However, a more recent study by Felker and co-workers,[4] based on ionization-detected stimulated Raman spectroscopy (IDSRS), and that based on hole-burning spectroscopy by Schlag and co-workers[5] indicate that the dimer isomer that dominates the spectrum has the two benzene moieties occupying symmetrically inequivalent sites, consistent with a T-shaped structure. Arunan and Gutowsky[6] confirmed this assignment by high-resolution Fourier transform microwave spectroscopy and determined the intermoiety center-to-center distance to be 4.97 Å. Ab initio calculations also show the T-shaped structure to be stable.[7,8] The computed distance between the centers of mass of the two moieties is approximately 5 Å, which is in excellent agreement with the result from the microwave spectroscopy. More recent ab initio studies by Hobza et al.,[9] Del Bene and Lim,[10] and Jaffe and Smith,[11] indicate that the parallel-displaced C_{2h} geometry is the lowest-energy structure for the benzene dimer, although a CCSD(T) study places the T-shaped conformer at lowest energy.[12] Most recently,

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Saigusa and co-workers[13] have shown that photoexcitation of benzene dimer into S_1 origin leads to formation of an excimer.

Syage and Wessel[14] were the first to observe the vdW dimer of naphthalene in the mass-resolved resonant two-photon ionization (R2PI) spectrum of seeded molecular beams of naphthalene. The laser-induced fluorescence (LIF) excitation and the R2PI spectra of the species are broad and structureless. Photoexcitation of the vdW dimer leads to an efficient formation of an excimer, as shown by Saigusa and Lim.[15−17] The predicted minimum-energy geometry of the naphthalene dimer, computed by Xiao and Williams[18a] and White et al.[18b] using exp-6-1 potential[19] and a genetic algorithm, is a D_{2d} crossed structure (vide infra). No other structure of similar energy is predicted by the force-field calculations. To the best of our knowledge, there is no report of ab initio calculation on the vdW dimers of naphthalene.

The first report of gas-phase clusters of anthracene is due to Chakraborty and Lim.[20] Using LIF as a probe, they obtained evidence for the presence of two structurally different dimers of anthracene in a supersonic jet. The LIF excitation spectrum of one of the species is broad and structureless, whereas that of the second species, with lower $S_1 \leftarrow S_0$ transition energy, is relatively sharp and structured. Interestingly, the fwhm (full width half-maximum) of the structureless feature is very similar to that of the naphthalene vdW dimer. Subsequent work, based on hole-burning spectroscopy and mass-resolved two-color R2PI spectroscopy by Matsuoka et al.[21] confirmed the assignments of the two spectral features to the two conformational isomers of anthracene dimer. The observation of the two dimer absorption systems of anthracene is at odds with the force-field calculations,[18] which predict only the crossed dimer of D_{2d} symmetry. No ab initio theoretical data exists for dimers of anthracene.

As described above, the experiment and computation are inconsistent with each other in regard to the number of low-energy conformers, and ab initio theoretical data are available only for benzene dimer. Quantum chemistry calculations of the conformational geometries and energies of naphthalene and anthracene dimers are therefore highly desirable. Unfortunately, because of the large size of these species, the basis sets that can be employed to obtain conformational geometries and energies from ab initio calculations are rather limited in size. Moreover, because dispersion effects are important in determining the geometries of vdW dimers, SCF calculations are completely inadequate and methodologies that include electron correlation must be employed. Very recently, we have shown that ab initio calculations carried out at MP2/6-31G and MP2/6-31+G levels of theory predict the cyclic C_{3h} trimer geometry for naphthalene,[22] which is essentially identical to the experimental geometry.[23] Given the success with the naphthalene trimer, it is natural to extend the calculations to the vdW dimers of naphthalene and anthracene. This paper describes the results of the MP2/6-31G//MP2/6-31G and MP2/6-31+G//MP2/6-31G geometry/energy calculations, with and without BSSE correction, for the dimers of benzene, naphthalene, and anthracene.

Calculations

Details of the computational methods have been given elsewhere.[22] Briefly, molecular dynamics (MD) trajectories were computed with the molecular mechanics (MM3) force field,[24] using the molecular dynamics/mechanics program TINKER.[25] To determine the possible low energy structures, a series of 100 ps MD simulations (after previous equilibration for 100 ps) were carried out in the range of 5−150K, starting with different geometries. In each simulation, a fixed time step of 4 fs was used, and only the lowest energy structures were selected. These geometries were further optimized with the MM3 force field by the Quasi-Newton optimizer contained in the TINKER suite of programs. Vibrational analysis using the MM3 force field confirmed that these stationary points were minima characterized by their positive vibrational frequencies. The optimized geometries of the lowest-energy minima located using the MM3 force field were then used as the initial guess for additional MD simulations in order to search for extra minima. If an additional minimum was found, the process was repeated until no further minimum was located. The final optimized geometries found by this procedure, were then used as initial guess for full geometry optimizations of the gas-phase dimers at the MP2/6-31G level of theory.[26] As demonstrated for naphthalene trimer,[22] this scheme of calculations appears to provide a good compromise between accuracy and computational efficiency. Binding energies for all minima were computed at the MP2/6-31G and MP2/6-31+G//MP2/6-31G levels of theory. These binding energies were corrected for basis set superposition error (BSSE) by means of the counterpoise correction of Boys and Bernardi.[27] All ab initio quantum chemical calculations were carried out with the Gaussian 94 suite of programs,[28,29] on a Cray-C90 at the National Institute of Standards and Technology and a Cray-T94 at the Ohio Supercomputer Center.

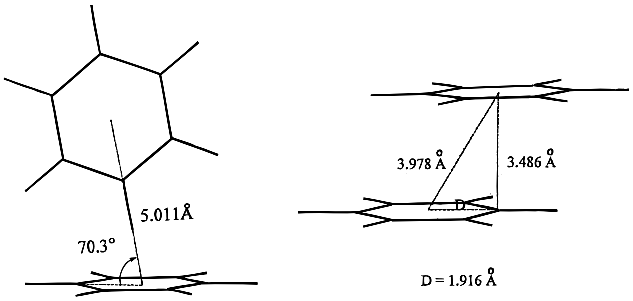
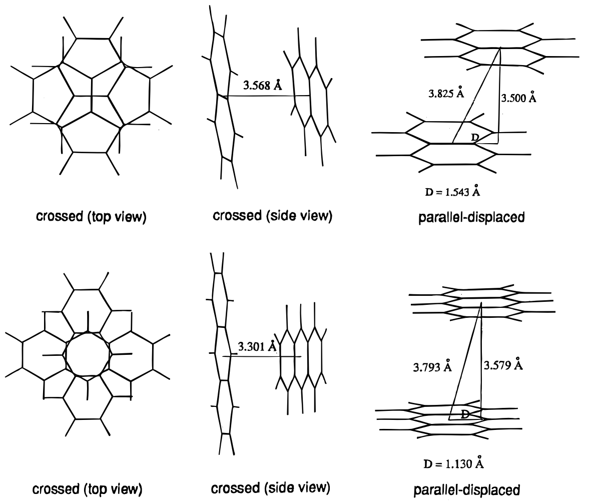


Figure 1. The fully optimized MP2/6-31G structures of the stable conformers of benzene. D represents the horizontal displacement in the parallel-displaced dimer.

Results and Discussion

A. Conformational Geometries. To assess the accuracy of the computational methods, we first studied the conformational geometries and energies of the benzene dimer. Consistent with the predictions of the high-level ab initio calculations,[7−12] the MP2/6-31G//MP2/6-31G and MP2/6-31+G//MP2/6-31G calculations yield a T-shaped dimer and parallel-displaced dimer of similar energies, as shown in Table. 1. In the T-shaped dimer of benzene, a C−H bond in one ring is directed slightly obliquely toward the center of the other ring, Figure 1. This tilted T structure is very similar to the bent T structure (with dihedral angle of 70°−80°) suggested by Hobza et al.[7] It is also similar to the global minimum located by Jorgensen and Severance[30] through a series of Monte Carlo optimizations. In view of this correspondence and the computed floppiness of the T-shaped dimer potential[7−12] with respect to tilting and rotation, we consider the tilted T structure obtained from the MP2/6-31G calculations reasonable. Interestingly, MM3 force field fails to yield the T-shaped dimer of benzene. The inability of MM3 to predict the T-shaped dimer of benzene is believed to be due to the neglect of the C−H bond moment in MM3.[31]

For naphthalene and anthracene dimers, MD simulations as well as the MP2/6-31G and MP2/6-31+G calculations yield two stable dimer conformers of very similar energies: D_{2d} crossed



crossed (top view) crossed (side view) parallel-displaced

crossed (top view) crossed (side view) parallel-displaced

Figure 2. The fully optimized MP2/6-31G structures of parallel displaced and crossed dimers of naphthalene and anthracene. D represents the horizontal displacement in the parallel-displaced dimer.

structure and parallel-displaced C_{2h} structure, Figure 2. Dimer structures analogous to the T-shaped dimer of benzene are not the low-energy conformations in naphthalene and anthracene, and they transform very readily to the crossed structures in the MD simulations. In fact, we carried out searches of potential energy surfaces by MD/MM3 procedures previously described,[22] and found no other minima besides the crossed and the parallel-displaced structures. However, exhaustive relaxed potential energy surface scans, combined with full geometry optimizations carried out at the MP2/6-31G level, indicate the existence of two higher energy T-shaped minima: one (T1), where the in-plane long axes of two moieties are perpendicular to each other, and the other (T2), where the long axes of the two monomers are parallel. The center-to-center distances of the monomers in T1 are 6.0 and 7.0 Å for naphthalene and anthracene, respectively, and 5.0 Å for T2 of both. The minimum energy conformations of the T-shaped dimers are shown in Figure 3.

The parallel-displaced dimer of naphthalene has a horizontal displacement of 1.5 Å along the short axes of the monomers, and the vertical interplanar separation of 3.5 Å. The corresponding horizontal and vertical separation for the parallel-displaced dimer of anthracene are 1.1 and 3.6 Å, respectively. The displacement is again along the short axes of the monomers. For the crossed dimers, the vertical separation of the aromatic rings is 3.6 Å for naphthalene and 3.3 Å for anthracene. It should be noted from Figures 1 and 2 that the horizontal displacement (D) in the parallel-displaced dimers decreases with increasing size of the aromatic hydrocarbons. This decrease is consistent with the increasing dispersion force (favoring a cofacial structure) which balances out the $\pi-\pi$ repulsion in a cofacial (face-to-face) geometry.

Binding Energies. Table 1 presents the results of the MP2/6-31G//MP2/6-31G and MP2/6-31+G//MP2/6-31G energy calculations for the vdW dimers of benzene, naphthalene, and anthracene. Without BSSE corrections, 6-31G and 6-31+G predict that the crossed and parallel-displaced dimers are the two lowest energy conformers of very similar energies in both naphthalene and anthracene. The binding energies are substantially greater at the 6-31+G level than at the 6-31G level.

Table 1 also reveals that BSSE corrections are significant at the levels of theory employed. At the MP2/6-31G level, the BSSE-corrected binding energies of the naphthalene dimers are smaller than the BSSE-corrected binding energies of the benzene dimer, (8−14 kJ/mol) calculated at high levels of theory.[7,11,12,32] Moreover, the binding is predicted to be smaller for the crossed and parallel-displaced dimers of naphthalene than for the T-shaped dimers of naphthalene. In the case of benzene dimers, BSSE corrections at the MP2/6-31G level a yield parallel-displaced structure which is unstable. Clearly, the binding is grossly underestimated at this level of theory, due probability to the inadequacies in the basis set. When the MP2/6-31+G energies are corrected for BSSE, the binding is greater for the parallel-displaced dimer of benzene than for the T-shaped dimer, consistent with the prediction of several high-level calculations. At the MP2/6-31+G level, the BSSE-corrected binding energies for naphthalene and anthracene dimers follow the order obtained at 6-31G and 6-31+G without BSSE corrections. Although there are no experimental or ab initio data with which the calculated dimer energies for naphthalene and anthracene can be compared, the BSSE-corrected MP2/6-31+G//MP2/6-31G energies appear reasonable when compared to the 8−14 kJ/mol of binding energies for the benzene dimers computed at high levels of theory.[7,11,12,32] However, given that BSSE corrections are almost as large as the binding energies for benzene, care must be exercised when considering the results for the larger dimers. In

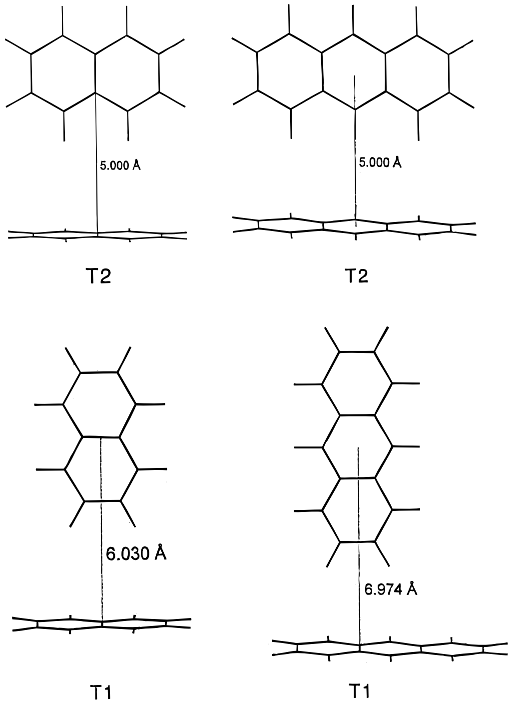


Figure 3. The fully optimized MP2/6-31G structures for the T-shaped dimers of naphthalene and anthracene.

TABLE 1: Binding Energies (kJ/mol) for Various vdW Dimers

	MP/6-31G//MP2/6-31G		MP2/6-31+G//MP2/6-31G	
conformer[a]	without BSSE[b]	with BSSE	without BSSE[b]	with BSSE
T-benzene	−10.90	−0.64	−55.70	−1.95
PD-benzene	−8.50	1.77	−18.68	−4.27
C-naphthalene	−21.72	−3.39	−56.07	−15.75
PD-naphthalene	−21.46	−2.95	−55.70	−15.66
T1-naphthalene	−17.71	−7.02	−33.42	−10.51
T2-naphthalene	−21.18	−7.18	−36.67	−11.25
C-anthracene	−42.24	−15.25	−101.56	−36.42
PD-anthracene	−38.36	−13.01	−96.81	−31.83
T1-anthracene	−22.36	−9.23	−55.15	−13.81
T2-anthracene	−35.59	−13.15	−74.52	−19.91

[a] C = crossed, PD = parallel displaced, T = T-shaped. [b] BSSE = basis set superposition error corrected using counterpoise method.

TABLE 2: Reduced Variational Space Analysis (energies in kJ/mol) for the Crossed and Parallel Displaced Dimers of Naphthalene[a,b]

conformer	CEX	POL1	POL2	CT1	CT2	BSSE1	BSSE2	full variational with BSSE
C	28.45	−0.75	−0.75	−1.97	−1.97	−1.21	−1.21	23.10
PD	27.61	−0.75	−0.75	−1.97	−1.97	−1.26	−1.26	23.09

[a] C = crossed, PD = parallel displaced, CEX = sum of Coulomb and exchange interactions, POLX = polarization energy of monomer X ($X = 1, 2$), CTX = charge-transfer energy of monomer X, BSSEX = basis set superposition error on monomer X. [b] See ref 33 for a detailed description of these energy contributions.

fact, the merit of doing BSSE corrections at the MP2 level of theory with relatively small basis sets is a debatable matter that requires rigorous scrutiny. Larger basis sets would be needed if accurate binding energies of the dimers are to be computed. Since this is not possible for dimers of polycyclic aromatic hydrocarbons, the trend of relative energies that allows identification of low-energy conformers is the primary concern of this study. As discussed above, and demonstrated in Table 1, the MP2/6-31G//MP2/6-31G without BSSE corrections and MP2/6-31+G//MP2/6-31G calculations with and without BSSE corrections, predict that the crossed (D_{2d}) dimer and parallel-displaced (C_{2h}) dimer are the lowest-energy conformers of very similar energies for both naphthalene and anthracene. The previous success of these methods in reproducing the experimental geometry of naphthalene trimer, provides some confidence in the results obtained in this work.

We have used the Frozen Fragment Reduced Variational Space analysis, (RVS), of Stevens and Fink[33] to decompose the interaction energies of the crossed and parallel-displaced dimers of naphthalene into various components. The calculation was carried out using the RVS package in the GAMESS suite of programs.[34] The results, shown in Table 2, indicate that the polarization, charge transfer, and BSSE energies are very similar for the crossed and parallel-displaced dimers of naphthalene at the HF/6-31G level of theory. The only significant difference between the two dimers is in the sum of the Coulomb and Exchange interaction energies, (CEX), which is more repulsive in the crossed dimer. The greater CEX energy of the crossed dimer is reasonable in view of the known quadrupole tensors in naphthalene. The results in Table 2 suggest that the major source of the slightly larger binding in the crossed dimer is very likely the dispersion, given that the electrostatic energy of this conformer is more repulsive than the corresponding energy for the parallel displaced dimer.

Conclusions

The primary objective of this study was to address the question of whether the MP2 calculations with moderate basis sets can provide useful information concerning the conformational geometries of aromatic dimers and higher microclusters. The results of this study, as well as the previous work on the naphthalene trimer, indicate that MP2/6-31+G//MP2/6-31G calculation may yield reasonable conformational geometries for the vdW dimers of aromatic hydrocarbons. At the MP2/6-31+G level, the BSSE-corrected binding energies for naphthalene and anthracene dimers appear reasonable when compared to the binding energies of benzene dimers obtained from high level ab initio calculations. However, one must be extremely cautious when using results obtained with BSSE corrections with such moderate basis sets. The prediction concerning the presence of two dimer conformers of very similar energies cannot be tested without experimental detection, identification, and characterization of the predicted conformers. While only one dimer conformer has been unambiguously detected in the optical spectra of benzene and naphthalene, two conformers of anthracene dimer are clearly observed in the fluorescence excitation and resonant two-photon ionization spectra. We are presently attempting to identify the nature of the two dimeric species in anthracene through the measurement and simulation of rotationally resolved vibronic spectra. Analyses of the electronic spectra and photophysics of the two vdW dimers of anthracene, based on semiempirical potential calculations and consideration of exciton splitting, indicate that the spectroscopy and excited-state dynamics are consistent with the assignments of the two dimers to the crossed (D_{2d}) and parallel-displaced (C_{2h}) dimers,[35] predicted by the ab initio calculations.

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Note Added in Proof

Extension of the MP2/6-31G structure search to the trimer, tetramer, and pentamer of benzene indicates that the minimum-energy structure of the species are the triangle, tetrahedron, and trigonal bipyramid, respectively.[36] In the tetramer and pentamer, the fourth and fifth benzene molecules occupy the vacant sites in the trigonal bipyramid with their molecular plane perpendicular to the three-fold symmetry axis of the sites occupied by the cyclic trimer. As in the C_{3h} naphthalene trimer,[22,23] the three molecules in the benzene trimer have one of their C−H bonds pointing toward the face of a neighboring molecule in a cyclic “pinwheel” structure.

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