Ab Initio Study of the Intermolecular Interactions in Small Benzene Clusters: The Equilibrium Structures of Trimer, Tetramer, and Pentamer

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Received: April 25, 2000; In Final Form: January 8, 2001

Correlated (MP2) calculations with 6-31G and 6-31G* basis sets have been used to probe the equilibrium geometries of the benzene trimer, tetramer, and pentamer. The lowest energy configuration was found to be a trigonal C_{3h} structure for the trimer and a tetrahedral C_3 structure for the tetramer. For the pentamer, the MP2/6-31G calculation yields the lowest energy structure, which is a trigonal bipyramid (C_{3h}). In the tetramer and pentamer, the fourth and fifth benzene molecules occupy the apex of the trigonal bipyramid with their molecular plane perpendicular to the 3-fold symmetry axis of the cyclic trimer motif. These structures, which maximize nearest-neighbor coordination number, suggest manifestation of the Wefelmeier growth sequence in benzene clusters.

Introduction

In the two recent papers we have reported the ab initio geometry search, carried out at the MP2/6-31G level of theory, for the van der Waals (vdW) trimer of naphthalene[1] and the dimers of benzene, naphthalene, and anthracene.[2] For naphthalene trimer, the computation yielded the lowest energy cyclic C_{3h} equilibrium structure which is essentially identical to the experimental geometry obtained from the rotational coherence spectroscoy.[3] 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 T-shaped (C_{2v}) structures for benzene and parallel-displaced (C_{2h}) and crossed (D_{2d}) structures for naphthalene and anthracene. The two dimer conformers of benzene are very similar to those from previous high-level ab initio calculations,[4] but there is 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[5,6] are consistent with what would be expected of the crossed and the parallel-displaced dimers.[7]

In this paper we extend the ab initio calculation with MP2 correlation to benzene trimer, tetramer, and pentamer. An interesting question the extension to larger benzene clusters can address is whether the minimum energy structures are those that maximize nearest-neighbor coordination number,[8] as revealed in the structures of atomic clusters.[9] We show here that the minimum energy configuration, obtained with 6-31G and 6-31G* basis sets, is a symmetrical cyclic C_{3h} structure for the trimer and a tetrahedral C_3 structure for the tetramer. For the pentamer, the MP2/6-31G calculation points to a trigonal bipyramidal C_{3h} structure as the lowest energy conformer. These results suggest the manifestation of the Wefelmeier growth sequence[8] in benzene clusters.

Ab Initio Calculations

Accurate ab initio studies of aromatic clusters must include electron correlation in order to obtain good representations of dispersion and electrostatic forces that are responsible for binding of the species. Because of the large size of the vdW molecules, high level treatment of electron correlation, or the use of large basis sets, is precluded. It is therefore fortunate that Møller−Plesset (MP2) perturbation theory with 6-31G basis set appears to provide reasonable geometries for naphthalene trimer as well as the dimers of naphthalene and anthracene.[1,2]

Full geometry optimizations for the benzene trimer and tetramer, at the MP2/6-31G and MP2/6-31G* levels,[11] using redundant internal coordinates[12] were performed with Gaussian 94 suite of programs.[13,14] The geometries for the pentamer were fully optimized in Cartesian coordinate space at the MP2/6−31 level of theory using the parallel module of MP2 gradients available in the GAMESS package.[15] As in the two previous works,[1,2] the low-energy conformers of the benzene trimer and tetramer were located by performing a series of 100 ps molecular dynamics (MD) trajectories calculations, followed by full geometry optimizations with the molecular mechanics (MM3) force field,[16] using the molecular dynamics/mechanics program TINKER.[17] The optimized geometries of the low energy minima, located using the MM3 force field, were then used as the initial guess for full geometry optimizations at the MP2 level with the 6-31G and 6-31G* basis sets. As demonstrated for naphthalene trimer,[1] this scheme of calculations appears to provide a good compromise between accuracy and computational efficiency. As in the study of naphthalene trimer,[1] relative energies of different conformers were directly computed without corrections for basis set superposition error. All ab initio quantum chemical calculations were carried out on a Cray-T94

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10.1021/jp0015776 CCC: $20.00

at the Ohio Supercomputer Center and on an IBM SP2 parallel supercomputer available at the National Institute of Standards and Technology.

Results and Discussion

Experimental Data, Force Field Calculations, and Molecular Dynamics Simulations. Before presenting the results of the ab initio calculations, it is useful to summarize the available experimental data, force field calculations, and MD simulations, pertaining to the structures of small benzene clusters.

For both the benzene trimer and tetramer, the experimental data concerning their geometries come from low-resolution Raman and REMPI (resonance-enhanced multiphoton ionization) spectra and binding energy measurements, which do not yield quantitative structural data. Nonetheless, the results of mass-selective ionization-loss stimulated Raman spectroscopy (ILSRS) experiment of Felker and co-workers[18] demonstrated that the three benzene moieties in the trimer reside in equivalent sites (i.e., the totally symmetric C−H stretching fundamental has only a single feature). The most likely structure of the benzene trimer is therefore a cyclic C_3 structure. A cyclic trimer geometry was also proposed by Neusser and co-workers,[19] who determined the dissociation energies for monomer evaporation from the measurement of ionization and appearance potentials, and by de Meijere and Huisken,[20] who measured laser fluence dependence of IR photodissociation. For the benzene tetramer and pentamer, the results of ILSRS experiments suggest that the benzene moieties occupy three or more inequivalent sites (i.e., three or more bands are present in the C−H stretching fundamental region),[18] but the possibility of these species having only two major inequivalent sites cannot be definitely ruled out.[21] On the basis of IR photodissociation, and the structure calculation with the exp-6-1 force field,[22] de Meijere and Huisken[20] proposed a tetramer structure in which the fourth benzene molecule is added to the cyclic trimer in such a way to form a dimerlike arrangement with the neighboring moiety in the trimer. That the ν_2 (C-H stretch) ILSRS spectra of the pentamer are qualitatively similar to those of the tetramer[18] led to the proposal that within the pentamer geometry there is a tetramer motif that has a geometry very similar to that of the bare tetramer.[18]

Several structure calculations based on semiempirical force fields have been reported for the trimer and tetramer of benzene. All employed energy minimization using the empirical exp-6-1 nonbonded atom−atom potentials of Williams.[22] The first of these is due to van de Waal,[23] who obtained a cyclic C_3 geometry for the trimer and a tetrahedral structure for the tetramer. In this tetramer geometry, the intermolecular distances and orientations are such that there are two different pairs of equivalent benzene moieties. Williams[24] also obtained this structure, designated “tetrahedral”, as the global minimum by off-ridge eigenvector minimization with annealing (OREMWA). The three other structures examined by Williams,[24] “face-triangular”, “edge-sandwich”, and “edge-triangular”, were found to have substantially smaller binding energies. The least stable of the three is the edge-triangular structure proposed by de Meijere and Huisken.[20] Most recently, Engkvist et al.[25] used NEMO (nonempirical model) potential,[26] calibrated by comparison with CCSD(T) dispersion forces based on benzene dimer energies, to investigate the structures of benzene trimer and tetramer. Of the three low-energy trimer conformers, a cyclic C_3 structure was found the most stable. The minimum energy NEMO structure of the tetramer has the fourth benzene molecule added to one of the molecules in the cyclic trimer in a T-shaped edge-to-face configuration. On the basis of the energy minimization using the exp-6-1 potential, van de Waal[23] proposed a fused double tetrahedron structure for the pentamer.

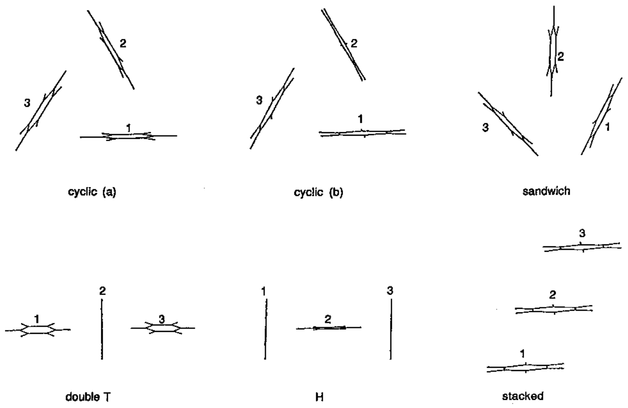

Figure 1. Low-energy MP2/6-31G* structures for benzene trimer.

The structures of small benzene clusters have also been probed using molecular dynamics (MD) simulations.[27] The trimer was found to have a cyclic structure. The tetramer is formed from the cyclic trimer by attaching the fourth benzene molecule in edge-sandwich configuration. For the structure of the pentamer, Li et al.[27] obtained a fused double tetrahedron sharing a face, as in the structure proposed by van de Waal.[23]

To summarize, while the semiempirical and nonempirical model potentials are in agreement that the preferred geometry of benzene trimer is a symmetrical cyclic structure, they differ on the question of whether the cyclic structure is C_3 or C_{3h} and whether the para C−H (i.e., C_{1-}H, and C_{4-}H) bonds of each benzene moiety are oriented parallel to the C_3 axis. For the tetramer, there is no agreement concerning its minimum energy.

Ab initio Structures. In the case of the trimers and the tetramers, it has been found that optimizations at the MP2/6-31G level predict geometries (not shown) that are very similar to the ones obtained with MP2/6-31G* calculations (vide infra). The only significant difference is that the intermoiety distances obtained from the MP2/6-31G calculation are approximately 3% shorter than those from the MP2/6-31G* calculation. Given this result, and the significant amount of computational resources necessary to carry out full geometry optimizations at the MP2/6-31G* level, the geometries for the pentamer were optimized only at the MP2/6-31G level.

Trimer Conformers. In Figure 1, we show the six low-energy ab initio trimer geometries we have obtained from the MP calculations with 6-31G basis sets. Three of the structures correspond to those examined by Hobza and co-workers,[25] using the NEMO potential.[26] The lowest energy ab initio trimer geometry is the cyclic C_{3h} structure. Of the two C_{3h} trimers, the one with the para C-H bonds lying perpendicular to the C_3 axis of the trimer appears to be of lower energy, relative to the one in which the para C-H bonds lie parallel to the C_3 axis (Figure 3). All other trimer geometries, including the H and the double T structures,[26] are substantially higher in energy than the C_{3h} structures. Tables 1 and 2 list respectively the intermoiety distances and the relative binding energies for various conformers. The results in Table 2 indicate that despite the fact that the relative binding energies computed with the 6-31G basis are lower by a factor of 2−3 with respect to the results obtained with the larger basis 6-31G*, the trends in the relative stability of the conformers is systematically reproduced. This result is encouraging, given the significantly smaller computational resources required with the smaller basis. Common wisdom

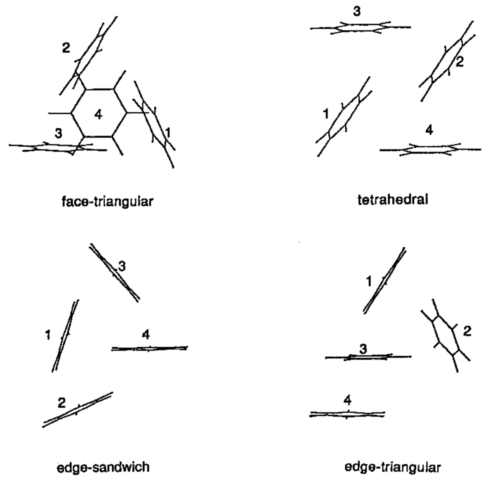

Figure 2. Low-energy MP2/6-31G* structures for benzene tetramer.

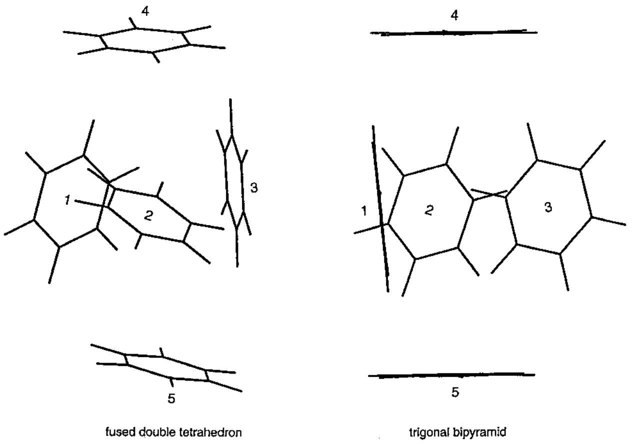

Figure 3. Two likely low-energy structures for benzene pentamer.

TABLE 1. Intermoiety Distances (in Angstroms) for the Low-Energy Conformers of the Benzene Trimer, Computed at the MP2 Level with the 6-31G* Basis Set

conformer	R_{12}	R_{13}	R_{23}
cyclic (a)	4.700	4.700	4.700
cyclic (b)	4.751	4.751	4.751
sandwich	4.484	4.353	4.902
double T	4.855	9.710	4.855
H	4.870	9.740	4.870
stacked	3.967	7.685	3.967

TABLE 2. Binding Energies (in kJ/mol) of Various Benzene Trimers Relative to the Most Stable Conformer

conformer	ΔE(6-31G)	ΔE(6-31G*)
cyclic (a)	0.00	0.00
cyclic (b)	2.45	7.36
sandwich	11.75	27.40
double T	12.83	31.90
H	13.56	33.88
stacked	16.12	36.41

TABLE 3. Intermoiety Distances (in Angstroms) for the Low-Energy Conformers of the Benzene Tetramer, Computed at the MP2 Level with the 6-31G* Basis Set

	face-triangular	tetrahedral	edge-sandwich	edge-triangular
R_{12}	4.725	5.802	4.704	4.742
R_{13}	4.725	4.572	4.704	4.742
R_{14}	5.380	4.579	4.745	8.370
R_{23}	4.725	4.579	8.204	4.742
R_{24}	5.380	4.572	5.287	7.455
R_{34}	5.380	7.076	4.992	3.726

TABLE 4. Binding Energies (in kJ/mol) of Various Benzene Tetramers Relative to the Most Stable Conformer

conformer	ΔE(6-31G)	ΔE(6-31G*)
face-triangular	0.00	0.00
tetrahedral	11.79	11.67
edge-sandwich	12.90	12.14
edge-triangular	27.77	29.06

dictates that in order to properly describe the interactions between aromatic molecules, it would be necessary to combine correlated methods (such as MP2) with basis sets which contain, at least, the polarization functions. The fact that the relative binding energies of various conformers are reproduced with a relatively small basis without polarization functions (i.e., 6-31G) may be due to a fortuitous, but systematic, cancellation of errors between the lack of convergence of the perturbation theory used (second order) and deficiencies of the basis set employed. This supposition is supported by the excellent agreement between the lowest energy geometry of the naphthalene trimer, predicted by the MP2/6-31G optimization,[1] and the experimental geometry obtained from the rotational coherence spectroscopy.[3]

Tetramer Conformers. The intermoiety distances and the binding energies of various tetramer conformers are given in Tables 3 and 4, respectively. Figure 2 presents the four low-energy tetramer structures obtained from the MP2 calculations with 6-31G* basis sets. They correspond to the low-energy OREMWA structures described by Williams.[24] The most stable tetramer structure obtained by our ab initio calculations has the fourth benzene molecule located at the vertex above (or below) the trimer facet with its molecular plane perpendicular to the C_3 axis of the trimer (see Figure 3). This C_3 tetramer, designated "face-triangular" by Williams,[24] is about 12 kJ•mol^{-1} more stable than any other tetramer geometry (see Table 4). The OREMWA tetrahedral global minimum structure[24] and the edge-sandwich structure[24] are the next most stable ab initio geometries of the tetramer. This is followed by the edge-triangular structure[24] in which the fourth benzene molecule is added to the cyclic C_{3h} trimer in such a way that it makes a dimerlike arrangement with one of the trimer moieties. Interestingly, our edge-sandwich structure is exactly the same as structure **3** of Engkvist et al.,[26] based on the NEMO potential. The NEMO global minimum is, however, only a local minimum in our ab initio intermolecular potentials, and it transforms very rapidly to the face-triangular in the MD simulations. Both the most stable face-triangular (or capped trimer) and the second most stable tetrahedral have the center of each benzene molecule occupying the vertex of a tetrahedron. Of the four low-energy tetramer structures, only the face-triangular has significant dipole moment ($\mu = 0.63$ D as computed at the HF/6-31G level). Given the propensity for strong edge-face interaction in benzene,[4] and the extraordinary stability of the cyclic trimer, the predicted lowest energy tetramer structure, viz., face-triangular, appears quite reasonable. It should be noted from Table 4 that there is an excellent agreement between the relative binding energies computed at the MP2/6-31G level and those obtained with MP2/6-31G*. These results provide additional support for the use of MP2/6-31G in the optimization of van der Waals clusters of aromatic molecules.

Pentamer Conformers. The ab initio structure calculations are extended to the two likely conformations of the pentamer. One is the fused double tetrahedron sharing a face (Figure 3) and the other is a trigonal bipyramid (Figure 3) in which the fifth benzene molecule in the pentamer occupies the site opposite to that occupied by the fourth molecule in the face-triangular tetramer (Figure 3). The fused double tetrahedron is the most

TABLE 5. Intermoiety Distances (R_{ij} in Angstroms) and Relative Binding Energies [ΔE(6-31G) in kJ mol^{-1}] for the Two Conformers of the Benzene Pentamer Considered in This Study

	trigonal bipyramid	fused double tetrahedral
R_{12}	4.823	5.386
R_{13}	4.823	5.386
R_{14}	5.640	5.970
R_{15}	5.640	5.970
R_{23}	4.823	5.386
R_{24}	5.640	5.970
R_{25}	5.640	5.970
R_{34}	5.640	5.970
R_{35}	5.640	5.970
R_{45}	9.801	9.933
ΔE(6-31G)	0.00	17.45

stable pentamer structure according to force field calculations[23] as well as MD simulations,[27] whereas the trigonal bipyramid is a good candidate structure based on the high stability of the cyclic trimer and the face-triangular tetramer. In both of these pentamer structures, the molecular center of each benzene molecule occupies the vertex of a trigonal bipyramid, and the only difference between them is the relative orientation of the benzene moieties. Table 5 presents the results of our correlated MP2 optimizations with the 6-31G basis set, which demonstrate that the trigonal bipyramid is clearly the lower energy structure.

Comparison of the Ab Initio Structural Predictions with Experiment and Force Field Calculations. The lowest energy MP2/6-31G* structures for the trimer and the tetramer as well as the MP2/6-31G structure for the pentamer are shown in Figure 4.

The ab initio cyclic (C_{3h}) geometry of the benzene trimer is consistent with the ILSRS spectrum of Felker and co-workers,[18] which indicates that the three benzene moieties occupy equivalent sites. The cyclic trimer geometry is also in accord with the trimer structures obtained by the NEMO potential,[25] the exp-6-1 potential,[23] and MD simulation.[27]

The C_3 face-triangular tetramer structure obtained from the ab initio calculations differs from the minimum energy structures based on the empirical[23,24] and nonempirical potentials,[25] as well as the MD simulation.[27] The ab initio tetramer and pentamer structure may also be at odds with the ILSRS results,[18] insofar as the number of inequivalent sites is concerned. However, since the fourth and fifth benzene molecules in these species occupy the apex of the trigonal bipyramid, Figure 4, the computed structures can rationalize the spectral resemblance of the ILSRS spectra of the tetramer and the pentamer.[18]

Manifestation of the Wefelmeier Growth Scheme. Interestingly, the ab initio minimum energy structures obtained in this work are those that the maximize nearest-neighbor coordination number. Apparently, the high symmetry, small size, and nonpolarity of benzene renders its microclusters to follow the Wefelmeier growth scheme,[8] originally proposed as a geometrical model of atomic nuclei[8] and used to describe the structures of atomic clusters.[9] For the 13-molecule cluster of benzene, manifestation of the structural shell filling is known from the large, computed binding energy of the icosahedral structure[28,29] and distinctive optical spectra of $n = 13$ species.[30] Starting with this icosahedral 13-molecule cluster of benzene,[28] van de Waal[23] generated the structures of small benzene clusters $(C_6H_6)_n$, $n = 2-7$, employing potential-energy minimization using exp-6-1 potential functions.[22] While these force field-based structures differ from the ab initio geometries in molecular orientations, the preference for the trigonal configuration for the trimer, the tetragonal configuration for the tetramer, and the trigonal bipyramidal configuration for the pentamer is clearly demonstrated by these structures as well. It therefore appears that the Wefelmeire growth scheme[8] produces the most stable structures for the small microclusters of benzene.

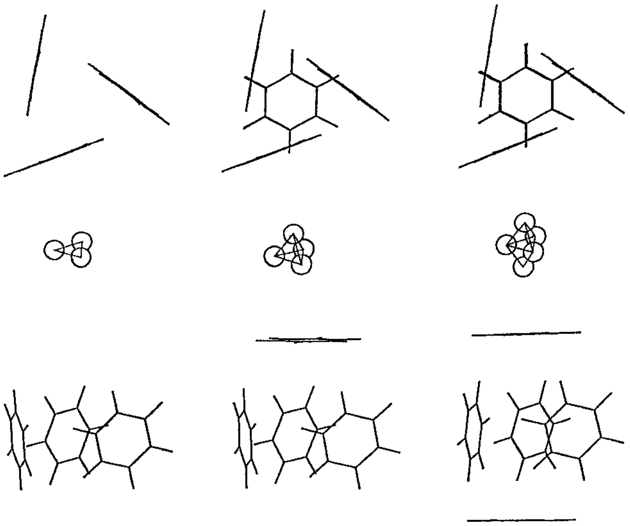

Figure 4. Top and side views of the lowest energy MP2/6-31G* structures of the benzene trimer, benzene tetramer, and the lowest energy MP2/6-31G structure of the benzene pentamer. In these structures, the center of the benzene molecule occupies a corner of an equilateral triangle or a vertex of a polyhedron, as indicated in the figure.

Conclusions

Correlated (MP2) calculations with 6-31G and 6-31G* basis sets for benzene trimer and tetramer, and the calculation with a 6-31G basis set for the pentamer, yield the lowest energy configuration, which is a C_{3h} trigonal structure for benzene trimer, a C_3 tetrahedral structure for benzene tetramer, and a C_{3h} trigonal bipyramid for benzene pentamer. While the cyclic trimer structure is consistent with the experiment, the computed tetramer and pentamer structures cannot be verified with the existing experimental data. Nonetheless, the large binding energies of these structures relative to others, as well as the demonstrated success of the methodology in reproducing the experimental geometry of naphthalene trimer, give some credence to the predicted structures of the benzene tetramer and pentamer. Since these structures are those that maximize the nearest-neighbor coordination number, the results suggest possible manifestation of the Wefelmeier growth scheme in benzene clusters.

Acknowledgment. We are very grateful to the Office of Basis Energy Sciences of the U.S. Department of Energy for support of this work and to the Ohio Supercomputer Center for generous grants of computer time. We also thank Professor Peter Felker for discussions concerning the ILSRS results of his group.

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