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LETTERS

Ab Initio and MM3 Studies of the Conformational Structures of Naphthalene Trimer: Comparison with Experiment

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An ab initio study of the ground-state conformational geometries of the naphthalene trimer, $(C_{10}H_8)_3$, has been made at the MP2/6-31G and MP2/6-31+G//MP2/6-31G levels of theory. The lowest-energy structure was found to be the edge-to-face cyclic (C_{3h}) geometry in which the three equivalent naphthalene moieties are arranged with their long in-plane axes parallel. The fully optimized MP2/6-31G structure has a center-to-center intermoiety distance of 4.986 Å and an angle of 48.0° between the short in-plane axis of a naphthalene moiety and the line connecting the center-of-mass of the monomer with that of the trimer. The computed rotational constants ($B = 0.00555$ and $C = 0.00468$ cm^{-1}) for the oblate symmetric top are essentially identical to the experimental values ($B = 0.00557$ and $C = 0.00470$ cm^{-1}) obtained from rotational coherence spectroscopy (see the following Letter by Benharash, Gleason, and Felker). Molecular mechanics (MM3) calculations also yield the same C_{3h} trimer as the minimum-energy structure. The result suggests that, with the optimization and reparametrizations of the existing force fields to fit the ab initio (or experimental, where available) geometry/energy for selected dimers and small clusters, it may be possible to develop accurate and practical intermolecular potentials for aromatic clusters.

Introduction

Geometrical structures of aromatic clusters, generated by free jet expansion, provide insights into the nature of intermolecular forces, the relationship between the properties of the isolated molecules and condensed matter, and the conformational dependence of intramolecular dynamics. For these reasons, the structural probes of the small clusters of aromatic hydrocarbons have been the subject of considerable interest in recent years.

For species with a permanent dipole moment, the most direct spectroscopic information about the ground-state geometry is obtained from the rotationally resolved spectrum measured in the microwave frequencies. Unfortunately, such data are available only for the simplest of the aromatic clusters, i.e., T-shaped dimer of benzene.[1,2] For benzene dimers without a permanent dipole moment or for the larger clusters of benzene, it has been necessary to deduce the structural, or energetic, information from methods that often do not yield unequivocal conclusions. Nonetheless, most experiments strongly point to a benzene trimer which has a symmetric cyclic geometry,[3−5] and a benzene tetramer which has an unsymmetrical structure.[3−5] The cyclic

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trimer geometry is supported by theoretical studies based on nonbonded atom−atom potential functions,[3,6,7] but the same theoretical approaches yield conflicting conclusions regarding the site symmetry (symmetric or unsymmetric) of the benzene tetramer.[3,7,8]

As a part of ongoing research on aromatic−aromatic interactions in the excited electronic state, we have been studying the formation of excimers (electronically excited dimers of sandwich-pair geometry) from photoexcited van der Waals clusters of aromatic hydrocarbons, generated by supersonic expansion of seeded molecular beams.[9] The results of this study have shown that the ability of the photoexcited aromatic clusters to form excimers depends on the cluster size as well as the excess vibrational energy within their locally excited state. Thus, while the naphthalene dimer forms an excimer even at zero excess energy, the excimer formation in higher clusters of naphthalene requires excess vibrational energies beyond certain threshold values.[10] The threshold energy required for the excimer formation is substantially greater, and the rate of the excimer formation much smaller, for the naphthalene trimer than for the naphthalene tetramer, indicating that a significantly larger structural rearrangement is needed for the trimer to form an excimer with overlapping sandwich-pair conformation of the monomers.

The gross structures of the small naphthalene clusters can be obtained from an analysis of the multiplet structure (band splitting) of the bands involving b_{1g} modes in the $S_1 \leftarrow S_0$ absorption system, which represent the S_2 excitation exchange (excitonic) interaction transmitted to the S_1 state through vibronic coupling.[11] The results of the band analyses indicate that the naphthalene trimer has a symmetric cyclic (C_3) structure, whereas the tetramer possesses an asymmetric structure, composed of exterior and interior sites.[11] It is believed that the two molecules in the interior site are arranged in a dimer-like structure, thus accounting for the ease of excimer formation in the tetramer. These cluster structures are in agreement with the geometries proposed by Felker and co-workers,[12] based on the ionization-detected stimulated Raman spectroscopy (IDSRS). They have shown that the C−H stretching fundamental has four clearly resolved bands in the tetramer, but only a single feature in the trimer. These observations led to the conclusion that the naphthalene tetramer is composed of four monomer sites that are all symmetry inequivalent, whereas the trimer has three equivalent monomer sites. The intermolecular vibrational spectra also exhibit clear manifestations of a high-symmetry structure for the trimer and a low-symmetry structure for the tetramer.[12] The orientation of the three naphthalene moieties (i.e., long axes parallel or short axes parallel) in the trimer could not be deduced from the isotopomer band splitting[11] or the IDSRS[12] but, on the basis of the minimum-energy geometries calculated with the atom−atom potentials of Williams and Xiao,[13] Felker et al. proposed a C_{3h} (or C_3) symmetric top consisting of the naphthalene moieties arranged cyclically with their long axes parallel.[12] The transformation of such cyclic geometry of the vdW trimer to the sandwich-pair geometry of the singlet excimer requires considerable configurational change, but the change would be even larger for the trimer having the naphthalene moieties arranged with their short axes parallel. Unfortunately, we have not been able to record rotationally resolved $S_1 \leftarrow S_0$ spectra for any of the naphthalene microclusters.[14] High-level quantum chemical calculations are therefore highly desired for resolving the question of the orientation of the naphthalene moieties in the electronic ground state of the cyclic trimer. This Letter describes the results of such study.

Theoretical Methodology

Molecular dynamics trajectories, MD, were computed with the molecular mechanics (MM3) force field,[15] using the molecular dynamics/mechanics program TINKER.[16] In all cases, canonical ensembles (constant NVT) were assumed, and the equations of motion were integrated using the Beeman algorithm.[17] All runs were carried out for 100 ps with a fixed time step of 4 fs, after previous equilibration for 100 ps. The temperature was kept constant by putting the system in contact with a Groningen-style temperature bath[18] with a coupling time of 1 ps. To determine the possible lowest-energy structures of the gas-phase naphthalene trimer, $(C_{10}H_8)_3$, a series of MD simulations were performed using different initial guesses for the geometry and temperatures in the range 5−100 K. In each run, the lowest-energy structure was isolated and optimized at the MM3 level by the Quasi-Newton optimizer contained in the TINKER package. The nature of the stationary points were determined by examining the sign of the vibrational frequencies obtained from diagonalization of the Hessian matrix, computed analytically with the MM3 force field. The optimized geometries obtained by this procedure were used as initial guesses in further MD simulations (at different temperatures) in order to sample the space for new minima. If lower-energy structures are found, the procedure is repeated until no new minima are located.

The optimized geometries of the minima previously located using the MM3 force field, were used as the initial guess for full geometry optimizations of the gas-phase naphthalene trimer at the MP2/6-31G level of theory.[19] Given that dispersion forces are known to play an important role in the energetics of aromatic clusters,[20] it is imperative that the calculation of the relative energies be made at least at the level of second-order Møeller−Plasset perturbation theory, MP2. Ab initio studies of the static dipole polarizability of naphthalene carried out by Hinchliffe et al.[21] have shown that excellent agreement with experimental results can be obtained when a set of diffusion functions is included in the basis sets for the carbons. In particular, they observed good agreement with experiment at the HF/6-31+G level of theory. On the basis of these results, single-point energy calculations at MP2/6-31+G were performed on the MP2/6-31G geometries to compute the relative energies of the minima considered in this study. All ab initio quantum chemical calculations were carried out with the GAUSSIAN 94 suite of programs,[22,23] on a CRAY-C90 at the National Institute of Standards and Technology, and a Cray-T94 at the Ohio Supercomputer Center.

Results and Discussion

MM3 Geometries. A total of six low-energy structures were obtained for the naphthalene trimer, $(C_{10}H_8)_3$, after optimization with the MM3 force field using the procedures described in the Methodology section. These are shown in Figure 1. the geometrical structures of the conformational isomers can be defined in terms of the five parameters shown in Scheme 1: the intermoiety distance (R_{ij}), the distance between the center-of-mass (CM) of the monomer and that of the trimer ($R_{i,MC}$), the angle the short in-plane axis of a monomer makes relative to the line connecting the centers of masses of the monomer and the trimer (α_i), the angle the long in-plane axis of a monomer makes relative to the line connecting the CM of the monomer with the CM of the trimer (β_i), and the angle the two CMs of the monomers make with respect to the CM of the trimer ($\gamma_{i,j}$). Of the six conformers, two (1 and 6) have cyclic edge-to-face C_{3h} structures that are consistent with experiment.[11,12] Conformer 1 has the three monomers arranged with the long

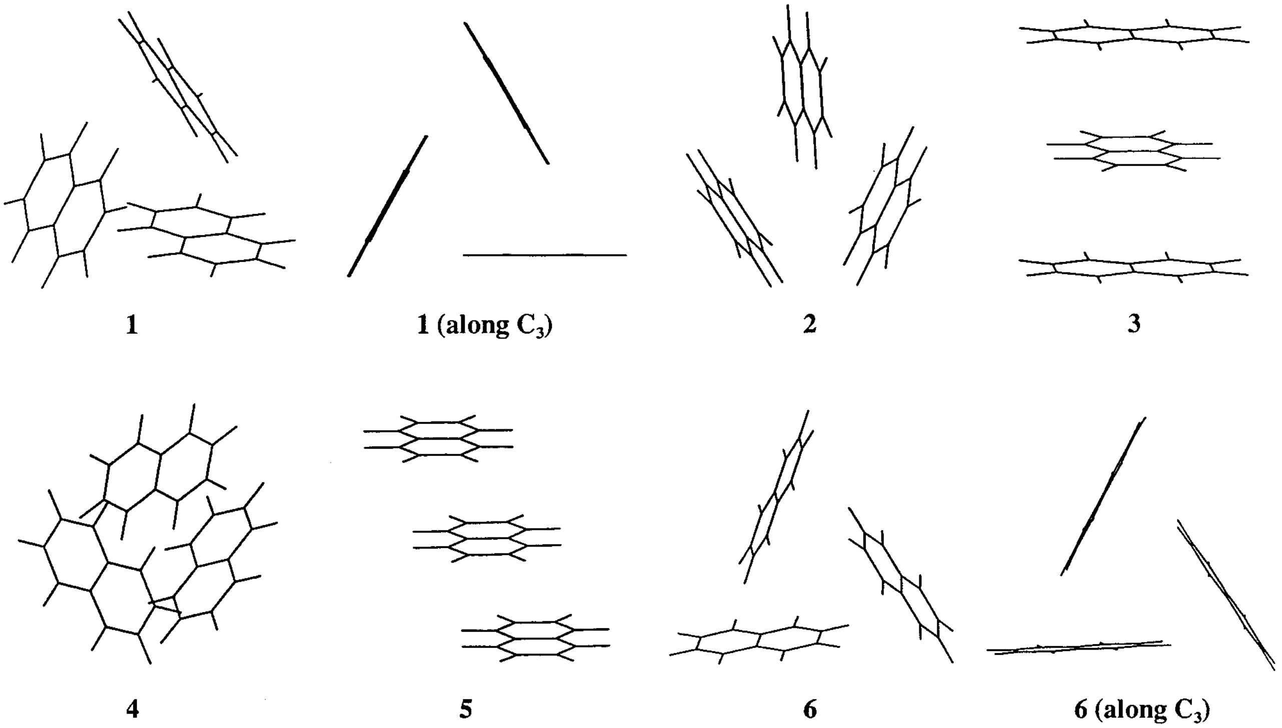
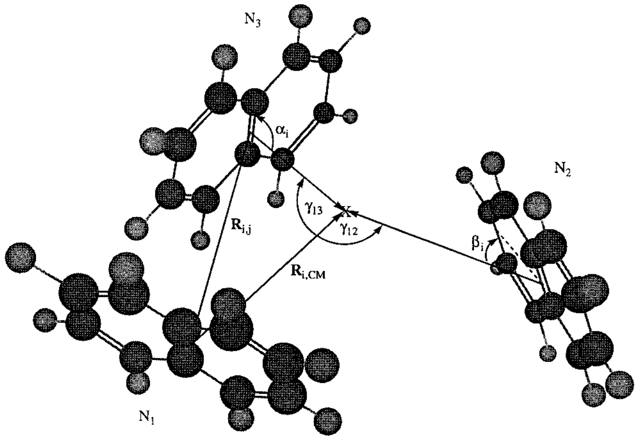


Figure 1. The six low-energy structures of the naphthalene trimer, $(C_{10}H_8)_3$, obtained after optimization with the MM3 force field.

SCHEME 1



axes parallel, whereas conformer 6 has the naphthalene moieties arranged with their short axes parallel. Views along the C_3 axis, also shown in Figure 1, best illustrate the two cyclic C_{3h} structures. Conformer 2 belongs to the group C_{2v}. Here, one monomer bisects the two monomers that are arranged in a V-shaped orientation. Conformer 3 is D_{2h} symmetry. The two outer molecules have their faces aligned parallel to each other, and antiparallel to the one in the center. Conformer 4, which belongs to the group C_1, is a distorted version of conformer 2. Finally, conformer 5 has a stacked cofacial arrangement with the centers offset. The MM3 geometries of the six conformers, as defined by the coordinates R_{ij}, $R_{i,CM}$, α_i, B_i, and $\gamma_{i,j}$ are given in Table 1.

MP2 Geometries. Table 2 presents the optimized MP2/6-31G geometries for various conformers of naphthalene trimer, $(C_{10}H_8)_3$. Overall, the optimized MM3 geometries (Table 1) are in excellent agreement with the result obtained at the correlated MP2/6-31G level of theory. The only significant difference is that both the intermoiety distance, R_{ij}, and the distance between the centers of the monomer and trimer, $R_{i,CM}$, tends to be slightly longer in the optimized ab initio geometries than in the optimized MM3 geometries. This surprisingly good correspondence between the MP2 and MM3 geometries suggests that it may be possible to use less computationally demanding force-field methods for structure elucidation of large aromatic clusters.

TABLE 1: Optimized MM3 Geometries for Naphthalene Trimer, $(C_{10}H_8)_3$

parameter[a]	1	2	3	4	5	6
$R_{1,CM}$	2.876	2.776	3.506	2.728	3.802	3.393
$R_{2,CM}$	2.876	2.610	0.000	3.326	0.000	3.393
$R_{3,CM}$	2.876	2.776	3.506	2.355	3.802	3.393
$R_{1,2}$	4.981	4.619	3.506	5.608	3.802	5.877
$R_{1,3}$	4.981	4.900	7.012	3.862	7.605	5.877
$R_{2,3}$	4.981	4.619	3.506	5.077	3.802	5.877
α_1	47.6	90.5	90.3	83.8	65.8	92.1
α_2	47.6	90.5		101.7		92.1
α_3	47.6	90.5	90.3	161.9	114.6	92.1
β_1	89.9	88.5	89.8	75.2	89.9	47.0
β_2	89.9			94.3		47.0
β_3	89.9	91.2	89.8	86.3	89.9	47.0
$\gamma_{1,2}$	120.0	118.0		135.6		120.0
$\gamma_{1,3}$	120.0	123.9	180.0	98.6	180.0	120.0

[a] Bond distances $R_{a,b}$ in angstroms and angles α, β, and γ in degrees. See Scheme 1 and the text for the coordinate descriptions.

TABLE 2: Optimized MP2/6-31G Geometries for Naphthalene Trimers, $(C_{10}H_8)_3$

parameter[a]	1	2	3	4	5	6
$R_{1,CM}$	2.910	2.957	3.518	2.475	3.825	3.419
$R_{2,CM}$	2.910	2.367	0.000	3.549	0.000	3.419
$R_{3,CM}$	2.910	2.887	3.515	2.357	3.822	3.419
$R_{1,2}$	4.986	4.585	3.516	5.663	3.823	5.922
$R_{1,3}$	4.986	5.120	7.033	3.752	7.647	5.922
$R_{2,3}$	4.986	4.537	3.516	5.117	3.824	5.922
α_1	48.0	91.1	90.4	85.5	64.9	91.7
α_2	48.0	89.1		99.3		91.7
α_3	48.0	89.4	90.4	164.5	114.6	91.7
β_1	90.0	83.8	89.8	71.3	90.2	46.5
β_2	90.0			87.6		46.5
β_3	90.0	84.4	89.8	78.5	90.2	46.5
$\gamma_{1,2}$	120.0	116.7		136.9		120.0
$\gamma_{1,3}$	120.0	127.7	180.0	96.2	180.0	120.0

TABLE 3: Relative Conformational Energies (kJ mol^{-1}) of Naphthalene Trimers

level	1	2	3	4	5	6
MM3	0.00	0.46	2.13	3.22	3.60	13.51
MP2/6-31G	0.00	18.74	22.43	16.99	22.64	26.23
MP2/MM3[a]	0.00	15.23	8.70	9.37	10.71	19.58
MP2/6-31+G[b]	0.00	6.37	8.70	6.86	9.20	33.56

[a] Relative energy at MP2/6-31G using geometries optimized with the MM3 force field. [b] Relative energy at MP2/6-31+G//MP2/6-31G level.

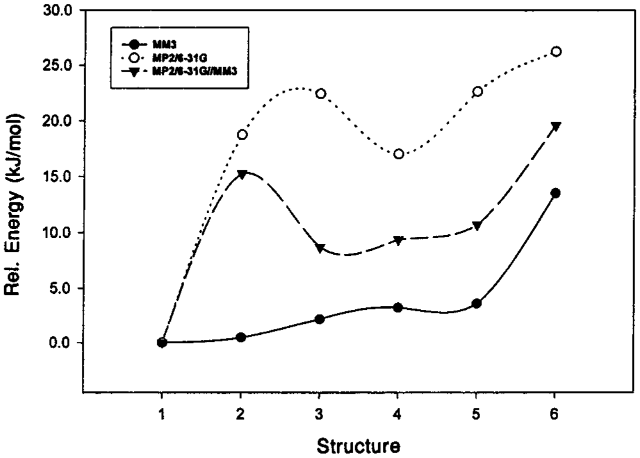


Figure 2. The conformational energies of the geometry-optimized naphthalene trimers obtained with different levels of theory.

Relative Conformational Energies. Table 3 lists the relative energies of the conformational isomers obtained from MP2/6-31G, MP2/MM3 (MP2/6-31G using geometries optimized with the MM3 force field), and MP2/6-31+G//MP2/6-31G calculations, together with the relative energies computed with MM3. The conformational energies based on geometry optimization are shown graphically in Figure 2. In all cases conformer 1, the C_{3h} trimer with three long in-plane axes of monomers parallel, is the lowest-energy structure, in agreement with the minimum-energy geometry[12,24] obtained with atom−atom potentials. In general MM3 predicts relative energies that are significantly lower than the values obtained at the MP2 level. Thus, while MM3 predicts conformer 6 (C_{3h}), with short in-plane axes parallel, to be approximately 14 kJ/mol less stable than conformer 1, the MP2/-31G results predict a significantly larger energy difference (approximately 26 kJ/mol). It is interesting to note that while the relative energies computed with MM3 follow the sequence $1 < 2 < 3 < 4 \approx 5 < 6$, the results obtained at the MP2/6-31G level follow a different trend, $1 < 4 < 2 < 3 \approx 5 < 6$. With the exception of conformers 2 and 4, the single point MP2/6-31+G//MP2/6-31G results are in good agreement with the MP2/6-31G relative energies (Table 3). However, caution must be exercised since no geometry optimization was carried out at MP2/6-31+G.

The most definitive conclusion that can be drawn from the ab initio results in Table 3 and Figure 2 is that conformer 1 is much more stable than any other trimer geometries examined in this study. Although corrections for the basis-set superposition error (BSSE) will change the absolute binding energies of the conformational isomers, it is unlikely that the conclusion regarding the most stable structure of naphthalene trimer will be altered by BSSE correction.

Given the high computational expense involved in the MP2 optimization (a geometry optimization for a typical conformer takes approximately 190 CPU hours on a Cray-C90), it is encouraging to find that the relative energies computed at MP2/MM3 follow the general trend predicted by the fully optimized MP2/6-31G structures. This result strongly supports the possibility of using inexpensive force fields in the structure elucidation of aromatic clusters.

TABLE 4: Comparison of the MP2/6-31G Rotational Constants (in cm^{-1}) with Experimental Data

structure	*A*	*B*	*C*
1	0.00555	0.00555	0.00468
2	0.00588	0.00560	0.00492
3	0.00961	0.00430	0.00404
4	0.00771	0.00488	0.00417
5	0.01016	0.00397	0.00331
6	0.00499	0.00499	0.00293
exptl[a]	0.00557	0.00557	0.00470

[a] From ref 26.

Comparison with Experiment. The conclusion that the oblique edge-to-face C_{3h} structure with long in-plane axes parallel (Conformer 1) is the lowest-energy MP2/6-31G geometry of the naphthalene trimer is qualitatively consistent with the experiment.[11,12,14] A quantitative test for the lowest-energy structure can be made by comparing the computed rotational constants, given in Table 4, with the experimental values obtained recently by Felker and co-workers. Using photoionization-based implementation of rotational coherence spectroscopy,[25] Benharash, Gleason, and Felker[26] have observed the rotational transients for jet-cooled naphthalene trimer, which yield $B = 0.00557$ cm^{-1} (167 MHz) and $C = 0.00470$ cm^{-1} (141 MHz). Comparison of these measured rotational constants with the MP2/6-31G values demonstrates that only conformer 1 has rotational constants that are very similar to the experimental values. The computed rotational constants ($B = 0.00555$ cm^{-1} and $C = 0.00468$ cm^{-1}) for conformer 1 are in fact essentially identical to the measured values. This remarkable agreement between theory and experiment strongly supports the conclusion that the most stable geometry of naphthalene trimer is indeed a C_{3h} oblate symmetric top depicted by structure 1. The center-to-center interchromophore distance of 4.986 Å and angle α of 48.0° (Scheme 1) define the equilibrium geometry of the most stable naphthalene trimer in its electronic ground state (Table 2). The correspondence between the measured and computed rotational constants also suggests that MP2 calculations with moderate-size basis set (6-31G), and without BSSE correction, may be adequate in deducing conformer geometry/energy for small aromatic clusters. A similar conclusion has also been obtained from ab initio study of benzene dimer.[20e]

Conclusion

Comparison of the ab initio calculations with the experiment presented here demonstrates that the lowest-energy structure of naphthalene trimer is most likely the C_{3h} oblique edge-to-face geometry in which the three equivalent naphthalene moieties are arranged cyclically with their long in-plane axes parallel. Intuitively, the oblique edge-to-face cyclic structure of naphthalene trimer can be rationalized as a compromise between the dispersion force that favors a cofacial (face-to-face) structure and the electrostatic, quadrupole−quadrupole, interaction that favors a T-shaped (edge-to-face) structure. Moreover, with the three naphthalene molecules arranged in a ring, the trimer yields three times the dimer interaction (i.e., three van der Waals bonds) as compared to noncyclic structures, which yield only two dimer interactions (i.e., two van der Waals bonds).

The motivation for the present study was not only to understand the interplay of dispersion and electrostatic interactions in determining naphthalene trimer geometry, but also to probe utility of computationally less demanding methodologies in structure prediction. The similarity of the ab initio and MM3 results for naphthalene trimer indicates that, with the optimization and reparametrizations of MM3 and other force fields to fit the ab initio (or experimental, where available) geometry/energy for selected small microclusters, it may be possible to develop accurate and practical intermolecular potentials for aromatic clusters. Development of such empirical potential-energy functions is presently under way.

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Note Added in Proof

Application of the computational methodology, described herein, to the van der Waals dimers of naphthalene and anthracene yields two stable conformers of very similar energies for each dimer: crossed and parallel displaced.[27] The computed dimer structures, together with the semiempirical excited-state potentials and consideration of the excitation resonance interactions, provide good accounts of the electronic spectra as well as the excited-state dynamics of the van der Waals dimers as it pertains to the formation and decay of excimers.[27]

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