

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/244133413>

On the equilibrium geometries of anthracene trimer and naphthalene tetramer: Comparison of the exp-6-1 and HFD structure predictions with experiment

ARTICLE *in* CHEMICAL PHYSICS LETTERS · MAY 2002

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(02)00528-6

CITATIONS

11

READS

11

2 AUTHORS:



Carlos Gonzalez

National Institute of Standards and Te...

111 PUBLICATIONS 12,594 CITATIONS

SEE PROFILE



Edward Lim

University of Akron

99 PUBLICATIONS 1,586 CITATIONS

SEE PROFILE

On the equilibrium geometries of anthracene trimer and naphthalene tetramer: comparison of the exp-6-1 and HFD structure predictions with experiment

Carlos Gonzalez ^a, Edward C. Lim ^{b,*,1}

^a Physical and Chemistry Properties Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^b Department of Chemistry, 319 Knight Chemical Lab., The Center for Laser and Optical Spectroscopy, The University of Akron, Akron, OH 44325-3601, USA

Received 20 February 2002

Abstract

Energy minimizations using Hartree–Fock dispersion (HFD) model and exp-6-1 potentials predict very different global minima for anthracene trimer and naphthalene tetramer. Comparison of the predicted geometries with available experimental data demonstrates the clear superiority of the HFD model in structure prediction. © 2002 Elsevier Science B.V. All rights reserved.

1. 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 preference of polyaromatic macrocycles and chain molecules.

As part of our studies of aromatic–aromatic interactions, we have been carrying out a concerted theoretical and experimental study of the ground-state equilibrium geometry and excited-state dynamics of van der Waals (vdW) dimers and higher clusters of aromatic hydrocarbons, generated by supersonic expansion [1,2]. These studies have shown that the ability of the photoexcited clusters to form excimers depends on the cluster size as well as the excess vibrational energy within the photoexcited cluster [3]. Thus, while the naphthalene dimer forms an excimer even at zero excess energy, the excimer formation in larger clusters of naphthalene requires S_1 excess energies beyond certain threshold values. The energy threshold for excimer formation is substantially greater, and the rate of excimer formation much smaller, for the trimer than for the tetramer. This

* Corresponding author. Fax: +330-972-6407.

E-mail address: elim@uakron.edu (E.C. Lim).

¹ Holder of the Goodyear Chair in Chemistry at The University of Akron, USA.

indicates that a significantly larger structural rearrangement is needed for the photoexcited trimer to form an excimer with cofacial structure.

The gross structures of the naphthalene trimer and tetramer can be obtained from the analyses of the multiplet structure of the $S_1 \leftarrow S_0$ absorption to the $S_1 b_{1g}$ levels, which represents the S_2 excitonic interaction transmitted to the S_1 state via S_2 – S_1 vibronic coupling [4]. The results of this band analyses for various isotopomers have suggested that the naphthalene trimer has a symmetric cyclic (C_3 or C_{3h}) structure, whereas the tetramer has an unsymmetrical structure, composed of a weakly bound exterior site and a dimer-like interior site [4]. These structures are in agreement with the ionization-loss Raman experiment of Felker's group, which demonstrates that the trimer has three equivalent monomer sites, and the tetramer has four inequivalent sites [5]. Our ab initio geometry searches, carried out at the second-order Møller–Plesset (MP2)/6-31G level of theory, show that the minimum-energy structure of the naphthalene trimer is indeed the C_{3h} edge-to-face cyclic geometry in which the three equivalent naphthalene moieties are arranged with their long in-plane axes parallel [6]. The computed rotational constants ($B = 0.00555$ and $C = 0.00468 \text{ cm}^{-1}$) for the oblate symmetric top [6] are in excellent agreement with those obtained by rotational coherence spectroscopy [7].

Because quantum chemistry calculations that include electron correlation explicitly are expensive, the ab initio structure calculations even at the modest MP2/6-31G level of theory are not feasible at present for naphthalene tetramer or anthracene trimer. For these larger clusters, it is essential to apply computationally efficient methods. Recently, White et al. [8] carried out potential energy minimization calculations with genetic algorithms using the exp-6-1 potential of Williams et al. [9,10]. This work led to the ring-shaped naphthalene tetramer, which has two different pairs of equivalent naphthalene moieties, and the D_{2h} stacked anthracene trimer in which two outer molecules have their faces aligned parallel to each other and the central molecule antiparallel, Fig. 1.

Very recently, we have introduced a simple Hartree–Fock dispersion (HFD) model [11] for cluster structural search, in which the interaction

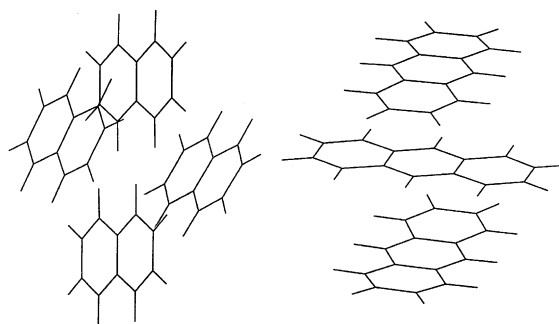


Fig. 1. The optimized HFD/6-31G geometries of naphthalene tetramer and anthracene trimer, corresponding to the global minima predicted by energy minimization with genetic algorithms using exp-6-1 potentials (see [8]).

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 an empirical dispersion term [12]. Application of the HFD/6-31G and HFD/6-31G* models to the dimers and trimers of benzene and naphthalene, and to the tetramers of benzene, yielded the minimum-energy conformers that are very nearly identical to those predicted by the MP2/6-31G and MP2/6-31G* calculations [13,14]. For the dimers (D_{2d} and C_{2h}) and the trimer (C_{3h}) of naphthalene, for example, the intermoiety distances obtained from the two rather different methodologies (HFD and MP2) differ only by 0.05 and 0.12 Å, respectively.

In this Letter, we present application of the HFD model [11] to anthracene trimer and naphthalene tetramer. It will be shown that the minimum-energy structures of these clusters are very different from those that are obtained from the energy minimization using exp-6-1 potential [8]. Comparison of the predicted geometries with the available experimental data demonstrates the clear superiority of the HFD model in structure prediction.

2. HFD calculation

The HFD interaction energy (E_{HFD}) of the clusters was determined as the sum of SCF (HF) interaction energy, E_{HF} , and the dispersion energy (E_{disp})

$$E_{\text{HFD}} = E_{\text{HF}} + f E_{\text{disp}}, \quad (1)$$

where f is a damping function, which is included in the dispersion term to suppress the singularity as the interatomic distance (R) approaches zero [15]. As in the previous work [11], the dispersion energy was expressed as

$$U_{\text{disp}} = - \sum_{\mu=1}^{\text{NMOL}-1} \sum_{v=\mu+1}^{\text{NMOL}} \sum_{i=1}^{\text{NAT}_{\mu}} \sum_{j=1}^{\text{NAT}_v} \left\{ \frac{[C_i^6 C_j^6]^{1/2}}{R_{ij}^6} \right\}. \quad (2)$$

Here, NMOL is the number of molecules in the clusters, 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 v , respectively, and the coefficients are the lowest order ($n = 6$) dispersion coefficients corresponding to atoms i and j . For C–C, H–H and C–H interactions, we have used the dispersion coefficients reported by Huiszoon and Mulder [16] ($C_6(\text{C–C}) = 2.17 \text{ J nm}^6 \text{ mol}^{-1}$, $C_6(\text{H–H}) = 0.167 \text{ J nm}^6 \text{ mol}^{-1}$, and $C_6(\text{C–H}) = 0.603 \text{ J nm}^6 \text{ mol}^{-1}$). The damping function, which is a simple two-parameter sigmoid function, is given by [11]

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

where α and R_0 are empirical parameters that are taken as 1.5 bohr^{-1} and 6.0 bohr , respectively.

The HFD routines were implemented in a local version of GAMESS package running on an IBM RS/6000 model 270. The SCF portion of the HFD calculations was carried out using the 6-31G basis set. Single point MP2/6-31G energy calculations on the HFD optimized geometry were performed with the GAUSSIAN 98 suite of programs on a Cray T-94 at the Ohio Supercomputer Center.

3. Results and discussion

3.1. Minimum energy HFD/6-31G geometries

The low-energy structures of anthracene trimer and naphthalene tetramer were searched using full

geometry optimization at the HFD/6-31G level of theory as well as by single point MP2/6-31G energy calculation on the HFD/6-31G optimized geometry. These structures are compared with the corresponding global minima that have been obtained from the energy minimization using exp-6-1 potential.

3.1.1. Anthracene trimer

As in the naphthalene trimer [6,11], the minimum-energy HFD/6-31G structure of anthracene trimer is the C_{3h} cyclic geometry in which the in-plane long axes of the three-anthracene moieties lie parallel, Fig. 2. The D_{2h} stacked global minimum [8] (Fig. 1), obtained from the genetic algorithms using exp-6-1 potential, is more than 12 kJ mol^{-1} higher in energy than the cyclic trimer, Table 1. Single point MP2/6-31G energy calculation on the HFD/6-31G optimized structure further increases the stability of the cyclic trimer relative to the double-crossed trimer. The center-to-center intermoiety distances of the fully optimized HFD/6-

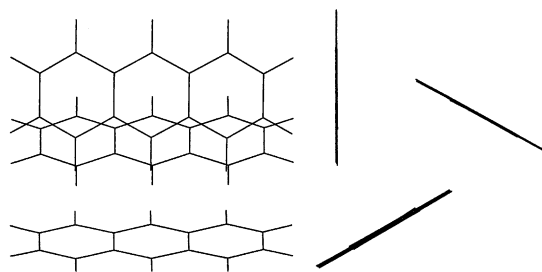


Fig. 2. The lowest-energy HFD/6-31G structure of anthracene trimer. The right view is down the C_3 symmetry axis, whereas the left view is along an axis perpendicular to C_3 .

Table 1

Relative energies (in kJ mol^{-1}) of anthracene trimers, as computed by full geometry optimization at the HFD/6-31G level of theory and by singlet point MP2/6-31G calculation on the optimized HFD/6-31G structure

Conformer	HFD/6-31// HFD/6-31G	MP2/6-31G// HFD/6-31G
C_{3h} cyclic ^a	0.00	0.00
D_{2h} stacked ^b	12.61	22.68

^a See Fig. 2 for structure.

^b See Fig. 1 for structure.

Table 2

Center-to-center intermoiety distances (in Å) for the fully optimized HFD/6-31G geometries of anthracene trimers

	C_{3h} cyclic	D_{2h} stacked ^a
R_{12}	4.87	3.38
R_{13}	4.87	3.38
R_{23}	4.87	6.76

^a The center molecule is designated as moiety 1.

31G geometries of the cyclic and stacked trimers of anthracene are given in Table 2.

3.1.2. Naphthalene tetramer

All of the low-energy structures of naphthalene tetramer, obtained by HFD/6-31G geometry optimization, are built on the cyclic naphthalene trimer. These structures are shown in Fig. 3. The lowest-energy structure is the edge-triangular structure in which the fourth naphthalene molecule adds to one of the moieties in the cyclic trimer motif in a slip-parallel arrangement, Table 3. In view of the exceptional stability of the C_{3h} cyclic trimer [6], the stability of the tetramers built on the cyclic trimer motif is not surprising. The minimum-energy force field geometry of the ring-shaped naphthalene tetramer [8], composed of two equivalent set of dimers (Fig. 1), is substantially less stable than the tetramers that are built on the

trimer motif, Table 3. Because of the small differences in energy among the tetramers with the cyclic trimer motif, they cannot be distinguished at the levels of theory used. In fact, the lowest-energy structure predicted by HFD/6-31G//HFD/6-31G differs from that obtained by MP2/6-31G//HFD/6-31G. This discrepancy may be due to the difference between the HFD/6-31G optimized geometry and the corresponding MP2/6-31G geometry. It is of interest to note that the edge-triangular structure, which is one of the higher-energy HFD/6-31G tetramer conformers in benzene [14], is the lowest-energy tetramer structure in naphthalene. This is very likely caused by the greater dispersion energy of naphthalene, relative to benzene, which favors the formation of a parallel-displaced (slip-parallel) dimer. Table 4 lists the center-to-center intermoiety distances of the fully optimized HFD/6-31G geometries of the tetramer that are built on the cyclic trimer motif. As expected, the C_{3h} symmetry of the naphthalene trimer [6,11] is lost by the addition of the fourth naphthalene molecule.

3.2. Comparison with experiment

The anthracene trimer represents the case in which one conformer is much more stable than any other conformers, whereas the naphthalene

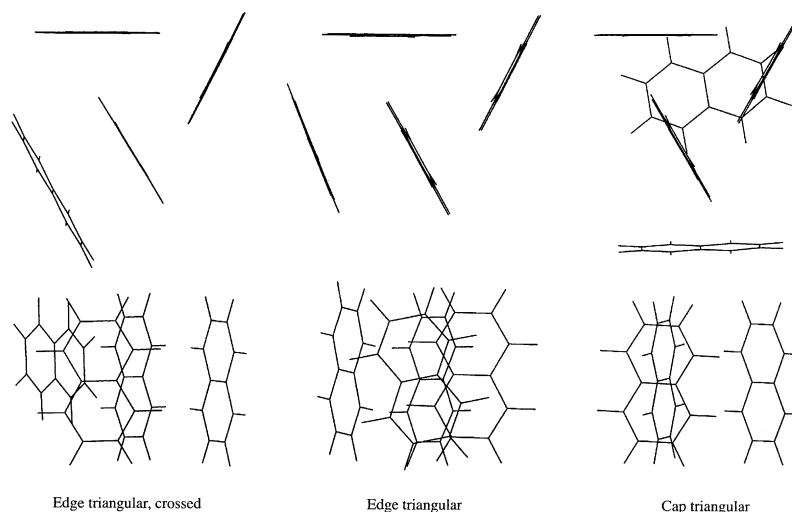


Fig. 3. The three lowest-energy HFD/6-31G structures of naphthalene tetramer built on cyclic trimer motif. The upper views are down the approximate C_3 axis of the trimer motif, whereas the lower views are along an axis perpendicular to it.

Table 3

Relative energies (in kJ mol⁻¹) of naphthalene tetramers, as computed by full geometry optimization at the HFD/6-31G level of theory and by singlet point MP2/6-31G calculation on the optimized HFD/6-31G structure

Conformer	HFD/6-31G// HFD/6-31G	MP2/6-31G// HFD/6-31G
Edge triangular ^a	0.00	2.80
Cap triangular ^a	2.33	0.00
Edge triangular, crossed ^a	2.45	4.64
Ring-shaped ^b	13.15	19.35

^a See Fig. 3 for structure.

^b See Fig. 1 for structure.

Table 4

Center-to-center intermoiety distances (in Å) for the three low-energy conformers of naphthalene tetramer built on the cyclic trimer motif

	Edge triangular ^a	Cap triangular ^b	Edge triangular, crossed ^a
<i>R</i> ₁₂	4.88	4.85	4.93
<i>R</i> ₁₃	4.81	4.82	4.73
<i>R</i> ₁₄	4.08	6.58	3.61
<i>R</i> ₂₃	4.86	4.85	4.97
<i>R</i> ₂₄	5.28	6.87	6.67
<i>R</i> ₃₄	8.11	6.65	8.24

^a The edge molecule is designated as moiety 4.

^b The cap molecule is designated as moiety 4.

tetramer is an example of cases in which more than one low-energy conformers of similar energies exists. For both the anthracene trimer and naphthalene tetramer, the global minima predicted by the use of the empirical potential [8] clearly differ from those predicted by the HFD model [11]. To assess the merits of these differing predictions, it is necessary to compare the predicted structures with the available experimental data.

3.2.1. Anthracene trimer

There is no direct spectral information concerning the equilibrium geometry of the vdW trimer of anthracene. Even the gross structure based on site symmetry is not yet available for the species. However, the spectral position of the reported trimer absorption [17] relative to the dimer absorption [17,18], assigned to a crossed conformer [19], argues against the stacked trimer structure.

The S₁ ← S₀ absorption system of anthracene is due to the allowed ¹B_{2u} ← ¹A_g transition of the D_{2h} point group, which is polarized along the short axis of the molecule. For the crossed dimer of anthracene, with the two anthracene moieties arranged perpendicular to each other, the angle between the two transition moments of the individual moieties is 90°, and excitation–resonance (excitonic) interaction vanishes. The energy lowering of the S₁ state of the crossed dimer relative to the monomer is therefore due mostly to attractive dispersion forces [19]. For the stacked trimer of anthracene, the dispersion contribution would be approximately twice that of the singly crossed dimer. This should lead to the red shift of the S₁ ← S₀ absorption maximum, which is substantially larger than that of the crossed dimer. As the spectral position of the trimer is similar to that of the ‘crossed dimer’, the stacked trimer structure [8] based on the exp-6-1 potential is unlikely the species responsible for the trimer absorption. We may conclude therefore that the minimum-energy anthracene trimer conformer is more likely the C_{3h} cyclic geometry predicted by the HFD model, if the assignment of the 375 nm absorption to the crossed dimer is correct.

3.2.2. Naphthalene tetramer

For the vdW tetramer of naphthalene, experimental information concerning its site symmetry is available. Thus, mass selective, ionization-loss stimulated Raman spectra, in the region of totally symmetric C–H stretch (ν₁) fundamental, demonstrate that the naphthalene tetramer has four inequivalent sites [5]. Moreover, the analyses of the spectral splitting and red shift of the δ_0^1 band indicates that the tetramer has a nearly overlapping dimeric ‘interior’ sites that are surrounded by two ‘exterior’ moieties [4]. The intermoiety excitonic interaction has been proposed to be strong only between the pair of molecules occupying the interior sites [4].

The ring-shaped tetramer structure with two different pairs of equivalent naphthalene moieties, predicted by the energy minimization using exp-6-1 potential [8], is clearly at odds with the experimental site symmetry. On the other hand, two of the low-energy HFD/6-31G tetramer structures

(Fig. 3) have the requisite site symmetry as well as the nearly overlapping dimeric ‘interior’ site. One is the edge-triangular structure in which the fourth naphthalene moiety is attached to one of the molecules in the cyclic trimer motif in a slip-parallel dimer arrangement. The other is the edge-triangular, crossed structure, which has the fourth naphthalene moiety making a crossed dimer like arrangement with one of the molecules in the trimer motif. Of the two structures, the tetramer structure with the crossed dimer configuration can be dismissed as the candidate structure, as the S_2 excitonic interaction between the two-dimer moieties is negligibly small due to the 90° angle between the two-monomer $S_2 \leftarrow S_0$ transition moments [19].

The only computed structure that is consistent with all the available experimental data is therefore the edge-triangular structure, which is the lowest-energy tetramer conformer predicted by HFD/6-31G//HFD/6-31G, Table 3. This conformer has requisite four inequivalent sites and satisfies the requirement of the presence of dimer-like arrangement of two ‘interior’ moieties.

4. Conclusion

Energy minimizations using exp-6-1 potential and HFD model predict very different global minima for anthracene trimer and naphthalene tetramer. Comparison of the predicted geometries with the available experimental data indicates that the energy minimization using exp-6-1 potential [8] is not a reliable method for structure elucidation of these large clusters. The discrepancy between the predictions of the HFD model and those of the force field approach, reported herein, is very similar to that which exists between the force field and correlated quantum chemistry calculations for smaller clusters [14]. In view of the close agreement between the HFD/6-31G geometry and the corresponding MP2/6-31G geometry [11], the discrepancy between the HFD and the force-field models is not surprising.

It is pertinent to point out that the so-called NEMO (nonempirical model) empirical potential [20] also yields minimum-energy structure for

benzene tetramer which differs from that based on the MP2/6-31G and HFD/6-31G calculations. Thus, for the benzene tetramer, NEMO predicts a 4-fold cyclic structure [21] and a structure in which the fourth benzene molecule is added to one of the molecules in cyclic trimer in a T-shaped edge-to-face configuration [22]. The 4-fold cyclic structure is a higher-energy conformer, whereas the edge-to-face T-shaped structure is only a local minimum, in the MP2/6-31G* and HFD/6-31G* geometry optimization. The global minimum of the benzene tetramer obtained by the MP2 [14] and HFD [11] calculations is the cap-triangular structure, analogous to that of naphthalene, shown in Fig. 3 (right).

The major shortcoming of the HFD model, as presently parameterized [11], is that it tends to significantly underestimate the relative stability of the various conformers as compared to that obtained from the correlated (MP2) quantum chemistry calculation [11]. We believe that this shortcoming can be remedied, or minimized, with the refinement and optimization of the empirical dispersion terms as well as the use of more robust and accurate damping functions. It is remarkable that, even in the unrefined form, the HFD model correctly predicts the lowest-energy conformer for all clusters of aromatic hydrocarbons that have been probed either by experiment or by correlated quantum chemistry calculations.

Acknowledgements

We are very grateful to the Office of the Basic Energy Sciences of the US Department of Energy for support of this work and to the Ohio Supercomputer Center for generous grants of computer time.

References

- [1] H. Saigusa, E.C. Lim, *Acc. Chem. Res.* 29 (1996) 171.
- [2] H. Saigusa, E.C. Lim, *J. Phys. Chem.* 99 (1995) 15738.
- [3] H. Saigusa, S. Sun, E.C. Lim, *J. Phys. Chem.* 96 (1992) 2083.
- [4] H. Saigusa, E.C. Lim, *J. Chem. Phys.* 103 (1995) 8793.

- [5] M.W. Schaeffer, W. Kim, P.M. Maxton, J. Romascan, P.M. Felker, *Chem. Phys. Lett.* 242 (1995) 632.
- [6] C. Gonzalez, E.C. Lim, *J. Phys. Chem.* 103 (1999) 1437.
- [7] P. Benharash, M.J. Gleason, P.M. Felker, *J. Phys. Chem. A* 103 (1999) 1442.
- [8] R.P. White, J.A. Niesse, H.R. Mayne, *J. Chem. Phys.* 108 (1998) 2208.
- [9] D.E. Williams, T.L. Starr, *Comput. Chem.* 1 (1977) 173.
- [10] D.E. Williams, X. Xiao, *Acta Crystallogr. Sect. A* 49 (1993) 1.
- [11] C. Gonzalez, T.C. Allison, E.C. Lim, *J. Phys. Chem. A* 105 (2001) 10583.
- [12] J. Hepburn, G. Scoles, R. Penco, *Chem. Phys. Lett.* 36 (1975) 451.
- [13] C. Gonzalez, E.C. Lim, *J. Phys. Chem. A* 104 (2000) 2953.
- [14] C. Gonzalez, E.C. Lim, *J. Phys. Chem. A* 105 (2001) 1904.
- [15] A.J. Stone, *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, England, 1996, and references therein.
- [16] C. Huiszoon, F. Mulder, *Mol. Phys.* 38 (1979) 1497.
- [17] T. Matsuoka, K. Kosugi, K. Hino, M. Nishiguc, K. Ohashi, N. Nishi, H. Sekiya, *J. Phys. Chem. A* 102 (1998) 7598.
- [18] T. Chakraborty, E.C. Lim, *J. Phys. Chem.* 97 (1993) 11151.
- [19] C. Gonzalez, E.C. Lim, *Chem. Phys. Lett.* 322 (2000) 382.
- [20] A. Wallqvist, P. Ahlström, G. Karlstrom, *J. Phys. Chem.* 94 (1990) 1649.
- [21] O. Engkvist, P.-O. Åstrand, G. Karlstrom, *Chem. Rev.* 100 (2000) 4087.
- [22] O. Engkvist, P. Hobza, H.L. Selzle, E.W. Schlag, *J. Chem. Phys.* 100 (1999) 5758.