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Diacetylene's weak bonding to acetylene clusters

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Abstract. An interaction potential previously developed for the acetylene–polyyne dimer was used to explore the interaction potential surfaces for clusters containing a diacetylene molecule and two or more acetylene molecules. Ab initio calculations were performed on the smallest clusters in order to assess the energetic and structural features predicted by the model potential. The preferred arrangements of the monomers in the clusters maximize the favorable quadrupole–quadrupole interactions between the monomers.

Keywords: Acetylene – Diacetylene – Ab initio calculations – Interaction potentials – Model potentials

1 Introduction

The prototype molecule for examining weak interaction involving a carbon–carbon triple bond is acetylene, while its longer counterpart, diacetylene, provides a simple system with multiple triple-bond sites. The nonpolar nature of acetylene and diacetylene means that their intermolecular interactions tend to be particularly weak. We have recently studied the interaction of acetylene and diacetylene [1], and found that many of the surface features corresponded to the effects of the quadrupolar charge fields of the carbon–carbon triple bonds interacting with one another. There are other studies of clusters containing diacetylene, including the diacetylene dimer [2, 3] as well as dimers containing diacetylene and HF [4, 5, 6], HCl [6, 7], H_2 [6], H_2O and NH_3 [8, 9], HCN [10], and argon [11].

The clustering of acetylene molecules around the larger diacetylene and the comparison of the "substitution" energetics from diacetylene taking the place of acetylene in moderately sized clusters provides special insight into triple-bond weak interaction, and that is the focus of this report. We have carried out ab initio calculations to provide a small cluster assessment of an interaction potential model for acetylene–diacetylene. Then, with the model potential, we have sought to determine structural and energetic features of larger $(HCCH)_n$–$H(CC)_2H$ clusters. The characteristic T-shape of an optimally interacting arrangement of two linear quadrupoles is seen in these clusters, but with the diacetylene providing certain types of structural complexity because of the multiple sites.

2 Theoretical approach

The potential-energy surfaces of intermediate and large clusters of acetylenes with a diacetylene molecule were examined via calculation with the molecular mechanics for clusters (MMC) model potential [12]. The model uses electrical response properties for the evaluation of the electrical part of the interaction, $E_{\text{electrical}}$, and a small number of adjustable parameters for the remainder of the potential. The parameters for the calculations reported here were determined in previous studies of the acetylene dimer [13] and the acetylene–polyyne dimer [1]. In the complete MMC potential-energy function, V, these parameters are atom-centered and designated c and d.

$$V = E_{\text{electrical}} + \sum_{\text{A,B>A}}^{\{\text{molecules}\}} \sum_{i}^{\{\text{sites on A}\}} \sum_{j}^{\{\text{sites on B}\}} \left(\frac{d_i d_j}{R_{ij}^2} - \frac{c_i c_j}{R_{ij}^6} \right) \quad (1)$$

The acetylene c and d parameters are 6.4 and 3,560 au for carbon and 0.8 and 11.43 au for hydrogen, respectively, and were designated CQ-ACCD/cc parameters in their original development [13]. For the diacetylene molecule, the c and d parameters for acetylene were used as building blocks for the longer chain

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[14]. A small adjustment of the *c* parameters of carbon was found to yield the best improvement in the match between the model and ab initio description of the potential surfaces of the HCCH–polyyne dimers with the smallest change in the parameter set. The *c* parameters for the carbon in the diacetylene molecule are 6.4 au for the end carbon atoms and 8.83 au for the middle carbon atoms. The *d* parameter for all carbons is 3,560 au.

The electrical representation for acetylene consists of the molecule-centered quadrupole moment, and the dipole and quadrupole polarizabilities, all of which were obtained via ab initio calculations [15]. For diacetylene, the electrical representation consisted of acetylene building blocks [14]. That is, the electrical representation for diacetylene consists of placing the electrical properties of acetylene at the midpoint of each triple bond in the molecule.

The MMC model was used to explore the potential-energy surface of the $(HCCH)_n$–$H(CC)_2H$ clusters. Several search strategies, including those outlined in our study of $(HCCH)_n$ [14], were employed to locate minimum-energy structures using MMC. Different initial geometries were used in the repeated searches drawing on our picture of the weak bonding in the acetylene–polyyne dimer as well as in pure acetylene clusters. The determination that a global minimum had been located was based on using a wide variety of starting configurations and finding that subsequent searches failed to produce a lower-energy structure.

Subsequent ab initio calculations were performed to assess the ability of the model to predict structural parameters and energies of the two lowest energy trimers. Monomer bond lengths for acetylene were fixed at values obtained by Assfeld et al. [16], $R_{C\equiv C} = 1.2143$ Å and $R_{C\text{–}H} = 1.0649$ Å. Monomer bond lengths for diacetylene were fixed at values obtained by Tay et al. [17], $R_{C\equiv C} = 1.20964$ Å, $R_{C\text{–}C} = 1.37081$ Å, and $R_{C\text{–}H} = 1.06131$ Å. Optimization of the structures was performed using Dunning's [18] cc-pVDZ and aug-cc-pVDZ basis sets. The correlation energies were evaluated at the MP2 level of treatment. Interaction energies were evaluated with counterpoise correction for basis set superposition error following the Boys–Bernardi scheme [19]. Certain test calculations were performed with the cc-pVTZ basis set [18].

3 Results and discussion

The first model potential calculations were performed to search for minima on the $(HCCH)_2$–$H(CC)_2H$ potential-energy surface, and the structures of the two lowest minima are shown in Fig. 1. The planar, cyclic trimer consists of the two acetylene molecules forming distorted T-shaped interactions with one end of the diacetylene molecule. The resulting structure of the cyclic trimer is similar to the structure determined for the acetylene trimer [14, 20, 21, 22, 23, 24, 25, 26, 27, 28] where each pair of monomers takes on a distorted T-shaped arrangement. The attractive quadrupole–quadrupole interaction between two monomers is maximized by their having a T-shaped configuration.

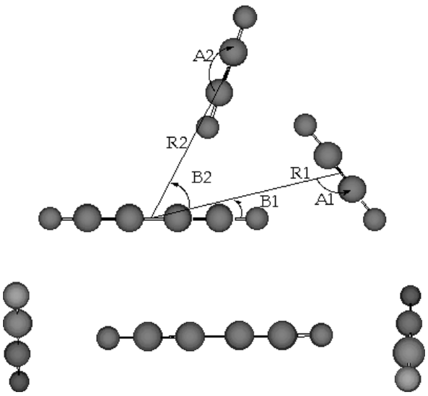

Fig. 1. The structure of the two lowest-energy $(HCCH)_2$–$H(CC)_2H$ trimers. The planar, cyclic structure is the global-minimum structure. The energetically less favorable structure is the nonplanar crossed I-shaped trimer where the acetylenes are perpendicular to the diacetylene molecule and crossed with respect to each other

A comparison of the structural and energetic values obtained from the MMC potential and from ab initio calculations for the planar, cyclic trimer is given in Table 1. The orientational parameters show good consistency and agreement among the MMC model and calculations with cc-pVDZ and aug-cc-pVDZ basis sets. Separation distances are more sensitive to basis set quality and differ by about 0.14 Å from results with one basis set to the other. The separation distances from MMC are intermediate to the ab initio values. Given the shallowness of the interaction potential surface, further refinement of the separation distances would likely come about with higher-level treatment of correlation and/or further basis set enlargement.

The secondary minimum of the trimer is a twisted I-shaped structure (Fig. 1) consisting of an acetylene at each end of the diacetylene molecule and perpendicular to the diacetylene molecule in the shape of an I but with the acetylene molecules twisted 90° with respect to each other as in the crossed (D_{2d}) form of $(HCCH)_2$ [13]. The results from geometry optimization of the crossed I-shaped trimer using both MMC and ab initio calculations are reported in Table 2. The center-of-mass separation is quite close, within 0.007 Å, to the value obtained for the acetylene–diacetylene dimer [1] at the cc-pVTZ/MP2 level. We note that rotation of one of the acetylene molecules by 90° results in a planar I-shaped trimer with the acetylenes parallel to each other. There is a tiny 2-cm^{-1} energetic difference between the twisted and planar structures found using the MMC model, and likewise, there is virtually no energetic difference found after geometry optimization at our highest level of ab initio calculation (cc-pVTZ/MP2). Clearly, there is no appreciable barrier for internal rotation of the acetylene molecules in the I-shaped structure.

In our previous study of large acetylene clusters [14], we found that the equilibrium structures preferred to

Table 1. Structural and energetic features of the cyclic $(HCCH)_2$–$H(CC)_2H$ trimer

	Interaction energy (cm^{-1})	R1 (Å)	A1 (degrees)	B1 (degrees)	R2 (Å)	A2 (degrees)	B2 (degrees)
cc-pVDZ/MP2[a]	–1,207	5.539	50	14	4.717	115	64
aug-cc-pVDZ/MP2[a]	–1,446	5.397	50	14	4.580	114	64
cc-pVTZ/MP2[a]	–1,531	5.397	50	14	4.580	114	64
MMC	–1,635	5.446	57	16	4.661	120	66

[a] Geometry optimization was performed at the MP2 level without counterpoise correction [19] and the final interaction energy was determined with counterpoise correction. For the cc-pVTZ/MP2 evaluation of the interaction energy, the geometry obtained at the aug-cc-pVDZ/MP2 level was used

Table 2. Structural and energetic features of the I-shaped $(HCCH)_2$–$H(CC)_2H$ trimer

	R_{com} (Å)[a]	Interaction energy (cm^{-1})
cc-pVDZ/MP2[b]	5.761	–906
aug-cc-pVDZ/MP2[b]	5.696	–1,080
cc-pVTZ/MP2[b]	5.626	–1,124
Molecular mechanics for clusters	5.589	–1,172

[a] Optimized distance between the center of mass of one HCCH and diacetylene's mass center

[b] Counterpoise correction [19] was performed

maximize the number of favorable quadrupole–quadrupole interactions. From the MMC potential, the cyclic structure of the trimer was found to be 463 cm^{-1} lower in energy than the I-shaped structure and this energetic ordering was reproduced in the ab initio results. In terms of the number of favorable quadrupole–quadrupole interactions, the cyclic trimer has 3 whereas the I-shaped trimer has only 2. Hence, in building up clusters of $(HCCH)_n$–$H(CC)_2H$, the number of occurrences of a T-shaped orientation or near-T-shaped orientations among the quadrupoles of the monomers affects stability in a significant way.

Since the MMC model allows us to examine the potential surface extensively through its calculational simplicity, we used it to search for minima of larger clusters. The next-larger cluster, with three acetylenes and a diacetylene, is the nonplanar, cyclic structure shown in Fig. 2. The cyclic arrangement in this cluster is similar to the acetylene tetramer [14, 25, 26, 27, 28, 29, 30] but appears much more distorted in a way that tends to maximize the quadrupole–quadrupole interactions. As cluster size increases further, the acetylene molecules continue to aggregate at one end of the diacetylene molecule as seen for the two larger clusters in Fig. 2. This arrangement allows for multiple T-shaped pairings per monomer. Again, the number of favorable quadrupole–quadrupole interactions is important in pure acetylene aggregation and it leads to $(HCCH)_n$–$H(CC)_2H$ clusters that have structures similar to their pure acetylene counterparts. With diacetylene having two carbon–carbon triple bonds, multiple minima are expected, and some cluster structures were found to have acetylenes spread out along the diacetylene molecule. However, the lower-energy structures for clusters with fewer than ten acetylenes consist of the acetylenes aggregating at one end of the diacetylene molecule.

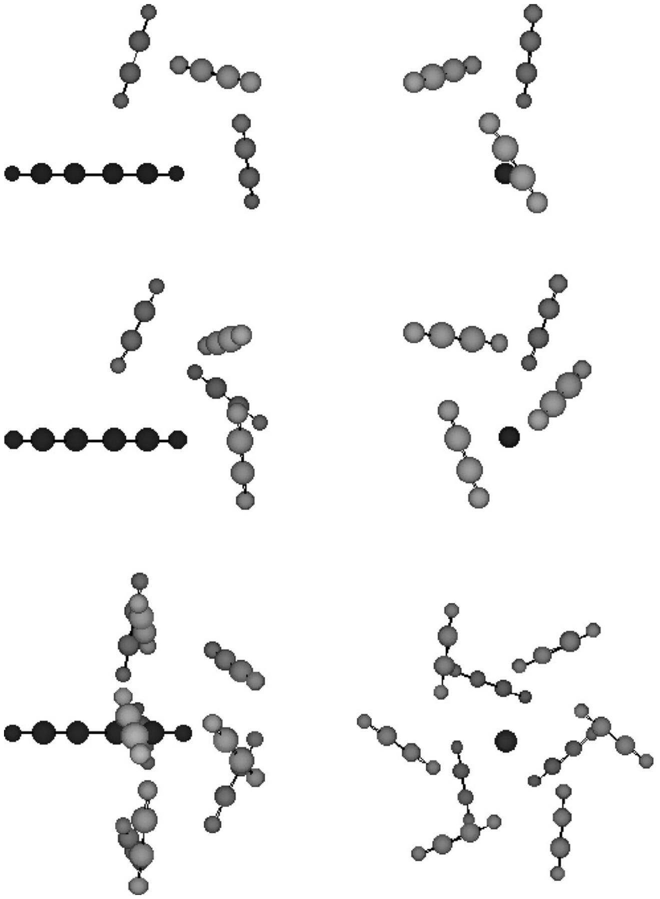

Fig. 2. The structure of the $(HCCH)_3$–$H(CC)_2H$ tetramer (*top*), $(HCCH)_4$–$H(CC)_2H$ pentamer (*middle*), and $(HCCH)_9$–$H(CC)_2H$ cluster (*bottom*). The view on the *left* for each cluster is obtained by rotation by 90° about the vertical axis which bisects the center of mass of diacetylene

The substitution of a diacetylene molecule in a pure cluster of acetylenes provides an energetically stabilizing effect for smaller clusters (Table 3). For clusters containing more than nine acetylenes, there are a sufficient number of molecules to form a favorable network of T-shaped pairings along the diacetylene molecule or to continue aggregating at one end of the diacetylene molecule. A comparison of the results from MMC test calculations on $(HCCH)_{37}$ and $(HCCH)_{36}$–$H(CC)_2H$ can be found in Table 3, and corresponding

Table 3. Molecular mechanics for clusters stabilities for $(HCCH)_{n+1}$ and $(HCCH)_n$–$H(CC)_2H$

n	$(HCCH)_{n+1}$ stability (cm^{-1})	$(HCCH)_n$–$H(CC)_2H$ stability (cm^{-1})	Substitution energy (cm^{-1})
1	503	589	86
1	490[a]	570[a]	80
2	1,512	1,635	123
3	2,360	2,475	115
6	5,401	5,632	231
9	9,009	9,108	99
36-A[b]	47,674	47,905	231
36-B[b]	47,674	45,102	−2,572

[a] Ab initio results at the cc-pVTZ/MP2level for $(HCCH)_{n+1}$ [13] and $(HCCH)_n$–$H(CC)_2H$[1] [b] Values are for clusters of acetylenes that completely encapsulate (A) or partially encapsulate (B) the diacetylene molecule (Fig. 3)

structures are shown in Fig. 3. The substitution site for the diacetylene molecule in the regular acetylene cluster was chosen such that the diacetylene would either be partially or completely encapsulated. The most stable minimum-energy structure was the cluster with the diacetylene molecule partially encapsulated. The optimized cluster has essentially the same structural features as $(HCCH)_{37}$ but it is energetically more stable by 231 cm^{-1}. The pure cluster of acetylene prefers to have the monomers arranged in a molecule–molecule T-shaped interlocking fashion and the substitution of diacetylene into the center of the cluster disrupts this network and reduces the stability of the cluster.

For the clusters studied, the diacetylene molecule prefers to weakly bond to the outside of the acetylene cluster and the number of T-shaped pairings in the cluster affects its stability. This may be regarded as an indirect steric effect. The quadrupole–quadrupole interactions for a $-C \equiv C-$ unit are not much different in diacetylene than in acetylene, but the spacing of adjacent quadrupoles is. That affects the networking of acetylene–acetylene interactions. It is likely that these features will persist for other $(HCCH)_n$–polyyne clusters. The MMC potential provided reliable energetic and structural features of $(HCCH)_n$–$H(CC)_2H$ when compared to the ab initio results, and this illustrates the capability of the potential for describing weak interactions between

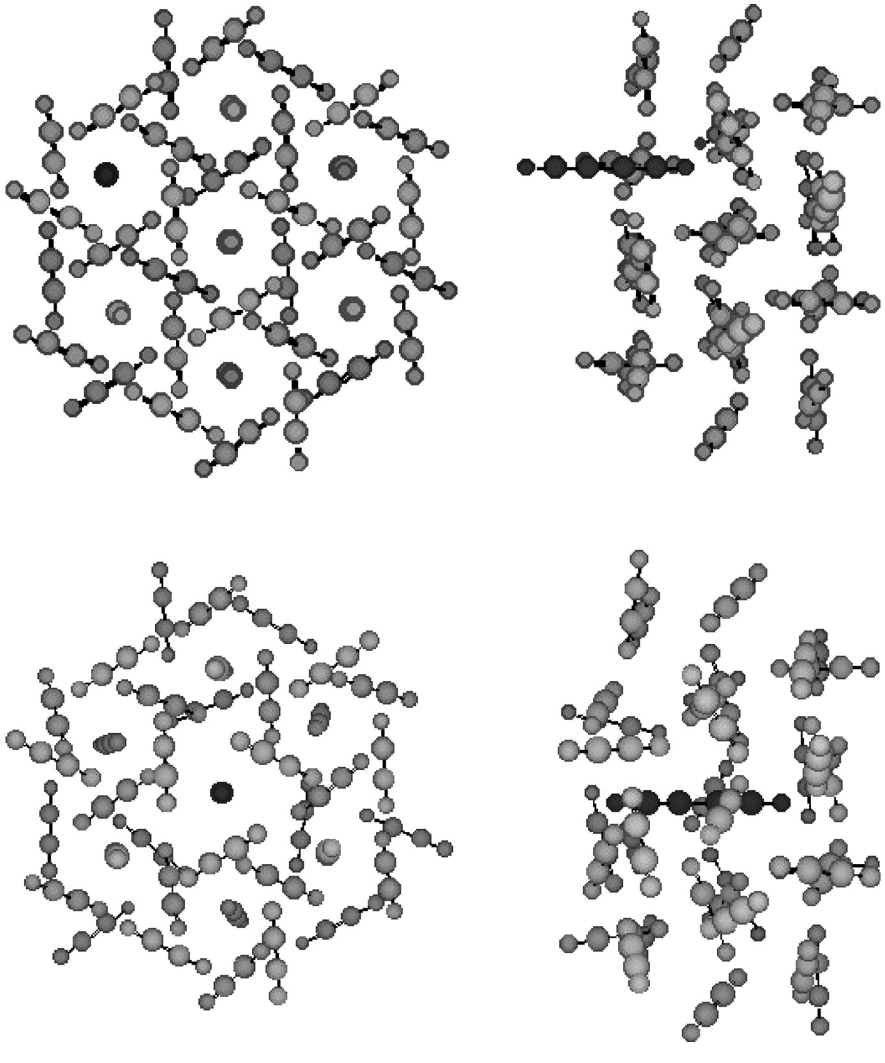

Fig. 3. Two optimized structures for the $(HCCH)_{36}$–$H(CC)_2H$ cluster. The second view of each cluster, on the *right*, is achieved by rotating the structure to the left by 90° about the vertical axis which lies in the plane of the page and passes through the center of the cluster

triple-bonded hydrocarbons and for rapid initial searches for minima.

4 Conclusions

Ab initio calculations provided the structures and energetics of two $(HCCH)_2$–$H(CC)_2H$ trimers. The model calculations of the clusters yield important information about the site of substitution of diacetylene into a pure cluster of acetylene as the cluster size increases. By minimizing the extent of the disruption in the T-shaped network observed for pure acetylene, the diacetylene substitution can energetically stabilize the cluster. The aggregation of acetylene molecules around diacetylene is driven by maximizing quadrupole–quadrupole interactions among acetylenes, resulting in clusters with diacetylene only partially encapsulated.

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