The Slippery Sliding Interaction of Acetylene with Polyynes

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Ab initio calculations were carried out for dimers of acetylene and a polyyne chain with two to five triple bonds at the MP2 level. The structure and energies of several symmetry-constrained structures were found and used to guide refinement of a model potential that could be applied to longer polyyne chains. The slice of the intermolecular potential surface for sliding an acetylene along the polyyne chain in a T-shaped orientation was mapped and showed shallow corrugation over a large region. This amounts to slipperiness in this type of weak bonding.

Introduction

The hydrogen bonding that occurs between molecules containing carbon−carbon triple bonds provides interesting insight into weak interactions involving a π-electron charge cloud. The acetylene dimer is a prototype for such systems, and hence, there have been extensive experimental[1−11] and theoretical[12−19] studies of $(HCCH)_2$. From these studies, the acetylene dimer is known to have a T-shaped (C_{2v}) equilibrium geometry which undergoes internal rotation of the monomer subunits through a slipped parallel structure (C_{2h}) to an equivalent T-shaped form with the monomer roles interchanged. The study of weak interactions between larger hydrocarbons containing carbon−carbon triple bonds has been mostly in the theoretical studies of the dimer of diacetylene,[17,20] the next member of the polyyne series. Karpfen[17] found four energy minima for the diacetylene dimer with a slipped parallel structure (C_{2h}) being the global minimum. In addition to energetically close local minima, there were also low-lying saddle points such that large amplitude vibrational motions could be expected.

The potential energy surfaces of weakly interacting species often allow for substantial vibrational excursions from equilibrium. In the case of $Ar-H_2S$,[21−23] the dynamical consequences of softness in the potential lead to an anomalous isotope effect in the rotational constants. An extensive energy trough with low energy barriers for wide amplitude displacement of Ar about H_2S/D_2S was found to be responsible. For weakly interacting hydrocarbons, shallowness of the intermolecular potentials could allow for extensive vibrational excursions with the possibility of interesting dynamical behavior.

In a previous study, results from high level ab initio calculations of critical points on the potential energy surface of the acetylene dimer were used to guide the development of a model interaction potential from which one could explore the features of the full surface.[19] The intermolecular potential was found to be shallow and anharmonic, with the result that vibrational averaging effects change the rotational constants by around 2%. When the model potential was subsequently applied to study large clusters of acetylene, the softness of the intermolecular potential allowed vibrational excursions to make the clusters larger in an on-average sense.[24]

The interaction of acetylene with longer polyynes can reveal more about the nature of weak bonding involving carbon−carbon triple bonds. Because the longer chains in the polyyne series contain multiple triple bonds, there is a possibility for multiple minima on the potential surface. For instance, the weak interaction found in the diacetylene dimer gives rise to interesting features such as the shallow double well for interconversion between a planar, tilted, π-type hydrogen bonded structure (C_{2s}) and a C_{2v} T-shaped structure.[17] To understand the weak interaction between an acetylene molecule and a polyyne chain, ab initio calculations were performed to characterize important surface features of acetylene and a polyyne chain with two to five triple bonds. On the basis of these calculations, a model potential for the acetylene dimer[19] was extended in the present study to polyynes. The model allowed more features of the surface to be explored, and we were able to determine that acetylene will have a very flat interaction potential, a “slippery” interaction, for sliding along any polyyne chain in a T-orientation or an orientation close to that.

Theoretical Approach

Ab initio calculations were performed for dimers containing acetylene plus diacetylene (1,3-butadiyne), triacetylene (1,3,5-hexatriyne), 1,3,5,7-octatetrayne, and 1,3,5,7,9-decapentayne. Monomer bond lengths for acetylene were fixed at values obtained by Assfeld et al.,[25] $R_{C\equiv C} = 1.2143$ Å and $R_{C-H} = 1.0649$ Å. Monomer bond lengths for diacetylene were fixed at values obtained by Tay et al.,[26] $R_{C\equiv C} = 1.20964$ Å, $R_{C-C} = 1.37081$ Å, and $R_{C-H} = 1.06131$ Å. For triacetylene, octatetrayne, and decapentayne, the monomer bond lengths were fixed at values obtained by Archibong and Thakkar,[27] $R_{C\equiv C} = 1.18$ Å, $R_{C-C} = 1.40$ Å, and $R_{C-H} = 1.07$ Å.

The cc-pVDZ basis set of Dunning[28] was used in most of the calculations. For dimers of acetylene with diacetylene and triacetylene, calculations were also performed with the cc-pVTZ basis set of Dunning.[28] A number of evaluations were performed with the aug-cc-pVDZ basis, the d-aug-cc-pVDZ basis, and a partially augmented cc-pVTZ. The partial augmentation used the s and p diffuse augmentation for hydrogen and the p and d diffuse augmentation for carbon in the standard aug-cc-pVTZ set, and we refer to this set as cc-pVTZ+. Correlation energies were evaluated at the MP2 level of treatment. Counterpoise correction for basis set superposition error was made with the Boys−Bernardi scheme.[29] The results of this study are reported

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at the counterpoise corrected MP2 level unless otherwise noted. The ab initio calculations provide key structural and energetic information for comparison with the results obtained from modeling of the potential surfaces.

The model potential used to represent the acetylene−polyyne dimer surfaces followed the molecular mechanics for clusters (MMC) scheme.[30] The MMC potential is a sum of the classically evaluated electrical interaction energy, $V_{\text{electrical}}$, and an atom−atom Lennard-Jones (or "6−12") nonelectrical terms. The nonelectrical potential contains the adjustable parameters designated c and d, which are assigned to the atomic centers in the molecules. The complete potential, V, for rigid molecules is

$$V = E_{\text{electrical}} + \sum_{A,B>A}^{\{\text{molecules}\}} \sum_{i}^{\{\text{sites on } A\}} \sum_{j}^{\{\text{sites on } B\}} \left(\frac{d_i d_j}{R_{ij}^{12}} - \frac{c_i c_j}{R_{ij}^{6}} \right) \quad (1)$$

The parameters used initially for the nonelectrical representation were those previously found for acetylene[19] and designated CQ-ACCD/cc, for central quadrupole and based on counterpoise corrected (/cc) coupled cluster level potential surface points. This parameter set showed the best overall suitability for representing the acetylene dimer[19] and larger clusters of acetylene.[24] Herein, we used these acetylene c and d parameters as building blocks for polyyne chains. That is, the parameters used for the polyyne representation were initially taken to be those from the acetylene (CQ-ACCD/cc set in ref 19) representation. Further adjustment of these parameters was made to improve the match between the model and the ab initio description of the sliding potential, as well as of the equilibrium structures.

The electrical representation for acetylene consists of the permanent quadrupole moment and the dipole and quadrupole polarizabilities, all of which have been obtained via extensive ab initio calculations.[31] For longer polyyne chains, the electrical representation was chosen to consist of acetylene building blocks. That is, the electrical representation for a polyyne chain consists of placing the electrical properties of acetylene at the midpoint of each triple bond in the chain. A comparison was made between ab inito values of the quadrupole moment and dipole polarizabilities of the monomers and corresponding values from using acetylene electrical properties as building blocks. For this comparison, the quadrupole moment and dipole polarizabilities were calculated for acetylene and polyynes with two to five triple bonds using the cc-pVDZ basis set (Table 1), while the cc-pVDZ electrical properties of acetylene were used as the building blocks. The building block quadrupole moments were mostly within 10% of the computed ab initio molecular values as shown in Table 1. Larger differences between the ab initio values and the building block values were seen for the dipole polarizabilities (Table 1). MMC test calculations were performed to determine the effect of differences in the dipole polarizability values on the interaction potential for the acetylene−triacetylene and acetylene−decapentayne dimers, keeping the nonelectrical parameters the same. The interaction energy for the dimers at each interval along the polyyne backbone using the ab initio dipole polarizability for the polyyne increased by at most 8% compared to using building block values. Because of this small effect, using acetylene's electrical properties as building blocks for polyyne chains should allow for a good electrical representation of a polyyne chain of even greater length.

The effect of mutual or back polarization versus direct polarization can be compared within the MMC scheme. From MMC test calculations of dimers containing acetylene and a polyyne chain with up to five triple bonds, back polarization was found to have a 1% effect on the interaction energy. There was also an effect of 0.2% on structural parameters for these dimers because of mutual polarization. Given the small size of this contribution to the interaction, it was neglected for all subsequent calculations, and all values reported here were obtained without including mutual polarization in the potential. In our previous MMC studies of the acetylene dimer[19] as well as large acetylene clusters,[24] the effect of mutual polarization on energies and geometries was small and was not included in selecting the parameters for the acetylene (CQ-ACCD/cc set in ref 19) representation used in this study.

TABLE 1: Quadrupole Moments (Q) and Dipole Polarizabitilies (α) for Polyynes in au

N (number of triple bonds)	Q_{xx} ab initio[a]	Q_{xx} sum[b]	Q_{xx} MMC model[c]	$Q_{yy} = Q_{zz}$ ab initio[a]	$Q_{yy} = Q_{zz}$ sum[b]	$Q_{yy} = Q_{zz}$ MMC model[c]
1	1.7708	1.7708	1.8086	−0.8854	−0.8854	−0.9043
2	3.5369	3.5416	3.6171	−1.7685	−1.7708	−1.8086
3	5.3966	5.3123	5.4257	−2.6983	−2.6562	−2.7128
4	7.6051	7.0831	7.2342	−3.8025	−3.5415	−3.6171
5	9.9964	8.8539	9.0428	−4.9982	−4.4269	−4.5214

N (number of triple bonds)	α_{xx} ab initio[a]	α_{xx} sum[b]	α_{xx} MMC model[c]	$\alpha_{yy} = \alpha_{zz}$ ab initio[a]	$\alpha_{yy} = \alpha_{zz}$ sum[b]	$\alpha_{yy} = \alpha_{zz}$ MMC model[c]
1	29.74	29.74	31.36	9.49	9.49	19.04
2	79.09	59.48	62.72	15.98	18.98	38.08
3	138.26	89.22	94.08	22.22	28.47	57.12
4	216.46	118.96	125.44	28.50	37.97	76.16
5	305.09	148.70	156.80	34.70	47.46	95.20

[a] Values for polyyne molecules ($N = 1-5$) calculated using cc-pVDZ basis set at the SCF level. [b] Values for polyynes ($N = 2-5$) based on using calculated acetylene (cc-pVDZ, SCF) values as C≡C building blocks. [c] Values for polyynes ($N = 2-5$) based on using acetylene ($N = 1$) values taken from ref 31.

TABLE 2: MP2 Energies for Equilibrium T-shaped Structures for Dimers Containing Acetylene and H(CC)$_N$H

	interaction energy (cm^{-1}) cc-pVDZ	interaction energy (cm^{-1}) cc-pVTZ
$N = 1$[a]	−357	−487
$N = 2$[b]	−440	−570
$N = 3$[c]	−458	−585

[a] T-shaped acetylene dimer structure with $R_{\text{com}} = 4.325$ Å. [b] T-shaped acetylene-diacetylene structure with $R_{\text{com}} = 5.619$ Å. [c] T-shaped acetylene-triacetylene structure with $R_{\text{com}} = 6.897$ Å.

Results

Ab Initio Calculations. A comparison of interaction energies at different ab initio levels for the planar T-shaped dimers containing acetylene and a polyyne chain with one to three triple bonds is given in Table 2 for equilibrium structures. The T-shaped structure found to be the most stable configuration for the HCCH−polyyne dimers studied has the hydrogen on one end of the polyyne chain pointing into the middle of the acetylene molecule. The interaction energies for the specific surface points are expressed here as energies at a given structure less the corresponding energies of two noninteracting monomers such that a negative value corresponds to an attractive interaction.

The results in Table 2 obtained from evaluating the interaction energies with the cc-pVDZ basis set show that the counterpoise correction (cc) at the SCF level is 85 cm^{-1} for the acetylene−diacetylene dimer and 86 cm^{-1} for the acetylene−triacetylene

TABLE 3: Basis Set Dependence of Structures and MP2 Energies of the Acetylene−Diacetylene Dimer

	global equilibrium R_{com} (Å) interaction energy (cm^{-1})	structure 5[a] R^b(Å) interaction energy (cm^{-1})	structure 6[a] R^b(Å) interaction energy (cm^{-1})
cc-pVDZ	5.777 −461	4.561 −348	4.525 −357
aug-cc-pVDZ	5.695 −548	4.433 −469	4.420 −471
d-aug-cc-pVDZ	5.690 −551	4.444 −473	4.431 −472
cc-pVTZ	5.619 −570	4.408 −455	4.368 −469
cc-pVTZ+[c]	5.516 −577	4.265 −488	4.245 −494

[a] Structure number corresponds to numbering in Figure 1. [b] Distance between center of mass of HCCH and the diacetylene molecular axis. [c] Structural parameters were not optimized.

TABLE 4: Minimum Energy Structures[a]of Acetylene Interacting with $H(CC)_{2,3,4,5}H$

N (number of triple bonds)	cc-pVDZ basis set MP2 R_{com} (Å) interaction energy (cm^{-1})	cc-pVTZ basis set MP2 R_{com} (Å) interaction energy (cm^{-1})
1	4.515 −393	4.381 −490
2	5.777 −461	5.619 −570
3	7.031 −477	6.897 −585
4	8.279 −492	
5	9.601 −498	

[a] T-shaped structure with hydrogen on one end of the polyyne chain interacting with the triple bond of the acetylene.

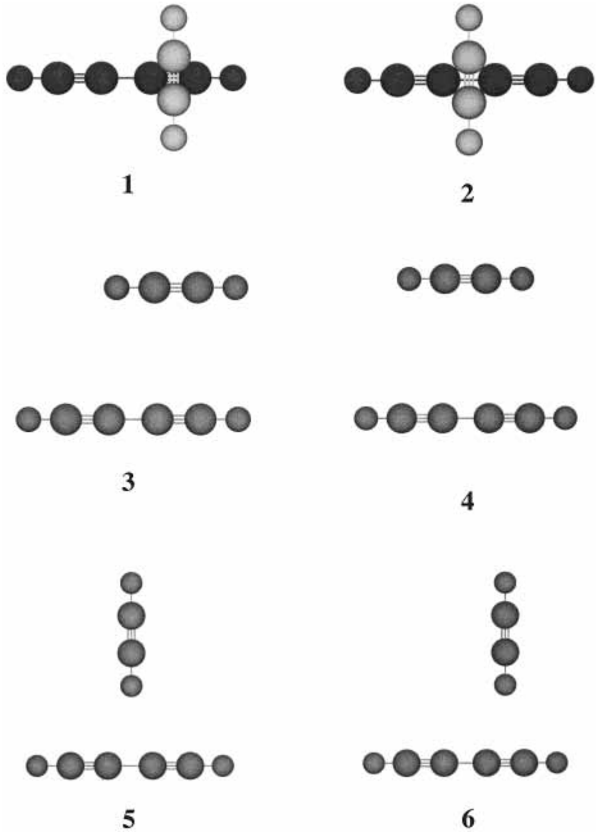

Figure 1. Six symmetry-constrained structures of the acetylene−diacetylene dimer characterized by ab initio calculations. The diacetylene molecule provides two different types of bonds with which the acetylene could weakly interact. The nonplanar crossed structures (**1** and **2**) have the monomers perpendicularly oriented to each other. The parallel structures (**3** and **4**) are constrained to be planar with the triple bond of acetylene proximate to one of the triple bonds of diacetylene (**3**) and with the single bond of diacetylene (**4**). The planar T-shaped structures (**5** and **6**) place the hydrogen of acetylene near the single bond of diacetylene (**5**) and near the triple bond of diacetylene (**6**).

dimer. Correlation effects without counterpoise correction serve to deepen the well by at least 300 cm^{-1} for both dimers. However, the counterpoise correction to the correlation energy is 229 cm^{-1} for acetylene−diacetylene and 235 cm^{-1} for acetylene−triacetylene, which is typical in being more than the corresponding SCF correction. Enlargement of the basis set to cc-pVTZ reduces the SCF counterpoise correction to 30 cm^{-1} for acetylene−diacetylene and 34 cm^{-1} for acetylene−triacetylene. This basis set enlargement increases the correlation contribution to the well depth and decreases the counterpoise correction to the correlation effect for both dimers. These changes combine to give an MP2 interaction energy after counterpoise correction for both dimers that is 127−130 cm^{-1} larger than that determined using the smaller basis set, or roughly a 20% change which is consistent with the changes seen for the acetylene dimer.

To assess lingering basis set effects, several additional calculations were carried out. The results from evaluations performed for three different structures of the acetylene−diacetylene dimer using basis sets augmented with diffuse functions are given in Table 3. The addition of one set of diffuse functions in the aug-cc-pVDZ basis set increases the MP2 interaction energy by at least 87 cm^{-1}. The effects are very similar to the enlargement from cc-pVDZ to cc-pVTZ. The subsequent addition of a second set of diffuse functions through the d-aug-cc-pVDZ set results in very small changes, and likewise, augmentation of the cc-pVTZ basis to cc-pVTZ+ produces small effects. Essentially, triple-ζ flexibility through either a triple-ζ basis or an augmented double-ζ basis yields results with small lingering basis deficiency. The relative energetic effect among minima from using a double-ζ basis instead of a triple-ζ basis is up to 50 cm^{-1}. In progressing to longer polyyne chains interacting with an acetylene molecule, we relied on the cc-pVTZ results for the smaller polyynes in developing the model potential and used the cc-pVDZ results to scan for length-related effects (Table 4).

To gain a more complete understanding of the complicated intermolecular potential surface of the acetylene−diacetylene dimer which may contain a large number of minima, certain symmetry-constrained structures were chosen to sample the surface and provide a more complete comparison of the different electronic structure treatments. The results of ab initio calculations of six different acetylene−diacetylene structures shown in Figure 1 are reported in Table 5. These results showed that most of the selected structures were noticeably less attractive than the T-shaped equilibrium structure. Both symmetry-constrained, crossed acetylene−diacetylene dimers appear as local minima, and with the triple bond of acetylene directly over the triple bond of diacetylene in (**1**), the interaction energy is smaller than if it is over a single bond in diacetylene (**2**). Both the diacetylene dimer[17] and the acetylene dimer[19] crossed structures have been found to be attractive at the MP2 level of calculation; however, with coupled cluster treatment, the crossed acetylene dimer was no longer a bound species.[19]

TABLE 5: Symmetry-Constrained Separation Distances and Energies[a] of the Acetylene−Diacetylene Dimer

structure[b]	MP2 (w/o cc) R^c (Å) interaction energy (cm^{-1})	MP2 R^c (Å) interaction energy (cm^{-1})
1	3.677 −244	3.839 −136
2	3.567 −309	3.730 −171
3	3.733 −234	3.881 −117
4	3.533 −349	3.645 −199
5	4.265 −679	4.407 −455
6	4.245 −675	4.368 −469

[a] Obtained with the cc-pVTZ basis. [b] Structure number corresponds to numbering in Figure 1. [c] Distance between center of mass of HCCH and the diacetylene molecular axis.

The energetic ordering of the two parallel dimers favors having the acetylene triple bond closest to a single bond of diacetylene (**4**) compared to being closest to a triple bond of diacetylene (**3**). For the acetylene dimer, we have found that the quadrupole−quadrupole repulsion overcame the dispersion effects for a parallel structure and precluded even a shallow well in the potential surface.[19] Karpfen's investigation[17] of the diacetylene dimer shows that, with multiple triple bonds, the situation may be slightly different because the equilibrium structure was determined to be an offset slipped parallel (C_{2h}) dimer. This is consistent with the energetic ordering of the parallel acetylene-diacetylene dimers we have found.

The T-shaped dimers labeled (**5**) and (**6**), which consist of a hydrogen on the acetylene molecule forming a T-shape with either a single or triple bond in diacetylene, were found to be very close in energy. In fact, there is only a 15 cm^{-1} difference in energy using the cc-pVTZ basis set at the MP2 level. For all of the symmetry-constrained structures in Table 5, the counterpoise correction to the MP2 energy for the T-shaped dimers was comparable or slightly larger than that found for the acetylene−diacetylene dimer in Table 2.

The increase in the number of triple bonds in the polyyne chain results in more interaction sites for an acetylene molecule. Results from the ab initio calculations of planar T-shaped dimers whose structures consisted of the acetylene perpendicularly interacting at the bond sites on the polyyne chain are presented in Table 6. It is seen that the interaction strength for acetylene perpendicular to the chain is stronger at a triple bond site than at a single bond site. However, this difference is quite small and at this level of calculation not more than 26 cm^{-1}. This suggests the possibility of a smooth potential for sliding the acetylene molecule along the polyyne backbone. Ab initio calculations were performed to map out this part of the potential surface and determine if barriers exist.

For the acetylene−diacetylene dimer, the acetylene molecule was constrained to be perpendicular to the chain, and the interaction energy at specific intervals was determined using the cc-pVTZ basis set at the MP2 level. At each interval along the diacetylene backbone, the separation distance between the two monomers was optimized. There is a very small energetic difference between optimizing each point along the chain compared to fixing the distance between the acetylene and the diacetylene molecule. By optimizing the separation distance at each interval, the shape of the potential becomes slightly flatter with the largest energetic difference being only 0.1 cm^{-1}. Therefore, fixing the distance between the two molecules provides essentially the same energetic information, and hence, the sliding potential surfaces presented here were mapped using a fixed distance determined to be the average center of mass separation for each of the points of interaction along the backbone of a given polyyne. Specifically, these points are where the hydrogen of the acetylene molecule forms a T-shape with a single or triple bond in the chain. As can be seen from Figure 2a, the well becomes flatter and broader as the chain length increases allowing the acetylene molecule to slide along the polyyne chain. This flat surface that extends over a large region leads to the weak bonding slipperiness.

To examine the origin of the shallow corrugated sliding potential, the correlation contributions to the interaction energy were isolated in one set of calculations. Figure 3 shows the SCF energy as acetylene slides from the center of the diacetylene molecule toward its end. There is an increase in the energy as the acetylene slides across the triple bonded region of the diacetylene molecule. This is also seen as the acetylene molecule slides along the octatetrayne chain (Figure 3). In this case, there are two triple bonded regions in the molecule, and this resulted in two wells. However, the wells are of unequal depth, and the SCF-level interaction was larger at the triple bond at the end of the chain. Figure 3 also shows the MP2 correlation energy as acetylene slides along the polyyne chain. This is a fairly flat contribution to the surface that broadens as the chain length

TABLE 6: Optimized Symmetry-Constrained Structures and Energetics[a] of Acetylene Interacting with a Polyyne Chain

HCCH−H−(CC)$_N$-H cluster type[b]	$N = 1$ R^c(Å) interaction energy (cm^{-1})	$N = 2$ R^c(Å) interaction energy (cm^{-1})	$N = 3$ R^c(Å) interaction energy (cm^{-1})	$N = 4$ R^c(Å) interaction energy (cm^{-1})	$N = 5$ R^c(Å) interaction energy (cm^{-1})
A	4.515 −393	4.525 −357	4.543 −325	4.540 −312	4.543 −304
B		4.561 −348	4.637 −323	4.570 −299	4.572 −291
C			4.551 −338	4.542 −319	4.547 −309
D				4.564 −294	4.564 −283
E					4.543 −307

[a] Calculations performed at the MP2 level of treatment using the cc-pVDZ basis set. [b] The cluster type designations start at the end of the polyyne chain with the acetylene perpendicular to the chain (Type A). As the acetylene slides along the chain, the midpoint of each bond is a new type, B through E. [c] Distance between center of mass of HCCH and the diacetylene molecular axis.

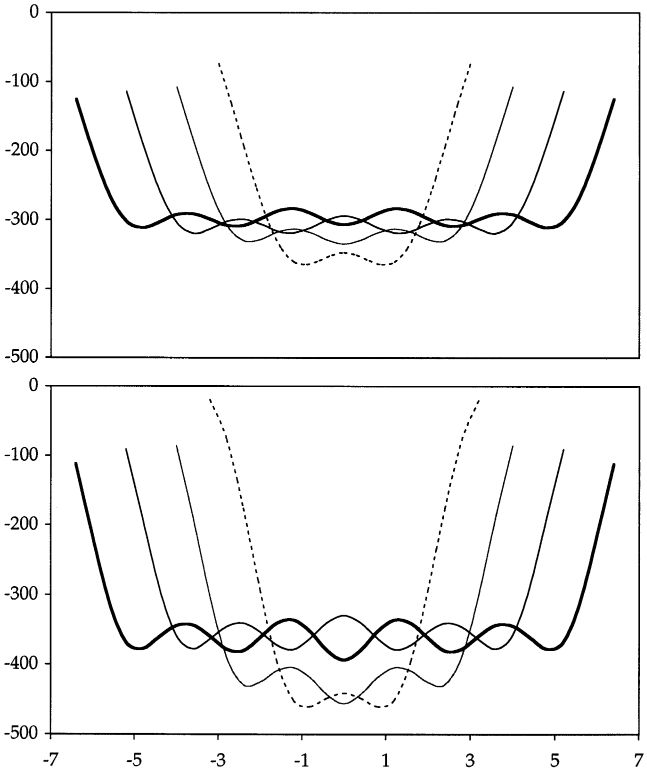

Figure 2. (a) Ab initio intermolecular potential calculated at the MP2 level using cc-pVDZ basis (top) and (b) MMC interaction potential (bottom) for acetylene sliding perpendicularly to the polyyne chain. The sliding potentials are for dimers containing polyyne chains with two to five triple bonds. The strength of the interaction is given in cm^{-1} on the vertical axis, and the distance is given in angstroms on the horizontal axis.

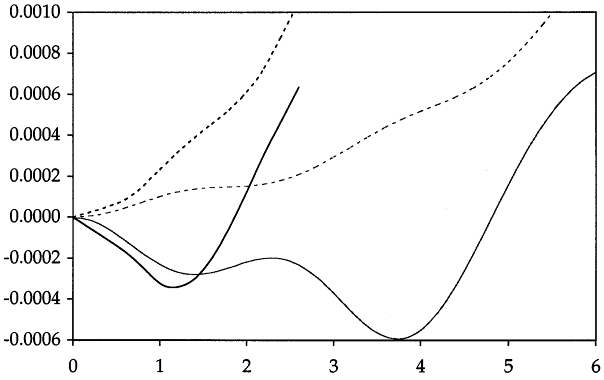

Figure 3. Relative SCF energy (solid line) and the relative MP2 correlation energy (broken line) as the acetylene slides from the midpoint of the polynne molecule to the end for diacetylene (black line) and for octatetrayne (gray line). The distance the acetylene molecule slides is given on the horizontal axis in angstroms. On the vertical axis, the energy in au of the dimer is given relative to the energy of the dimer when the acetylene is perpendicular to the midpoint of the chain.

increases. Therefore, the “bumpiness” of the potential arises largely at the SCF level.

Model Potential for the Interaction Surfaces. A model representation of the potential surfaces makes it easy to explore more of the surface features, and the representation we chose to use is that of eq 1. The c and d parameters from the acetylene (CQ-ACCD/cc set in ref 19) representation were used initially to model polyynes. The acetylene c and d parameters are 6.4 and 3560 au for carbon and 0.8 and 11.43 au for hydrogen, respectively. From the MMC potential using these parameters, it was noted that the strength of interaction for acetylene perpendicular to the triple bond at the end of the chain was greater than at any other point along the chain when compared to the MP2 results. This was noticed for systems containing three triple bonds or more. The potential for sliding HCCH along the polyyne closely represented the contour of the SCF energy. Therefore, in comparison, the MMC potential was providing a better representation of the electrostatic effects than of the nonelectrical contributions. Variation in the adjustable parameters in the nonelectrical part of the potential could compensate for this deficiency so as to improve the representation.

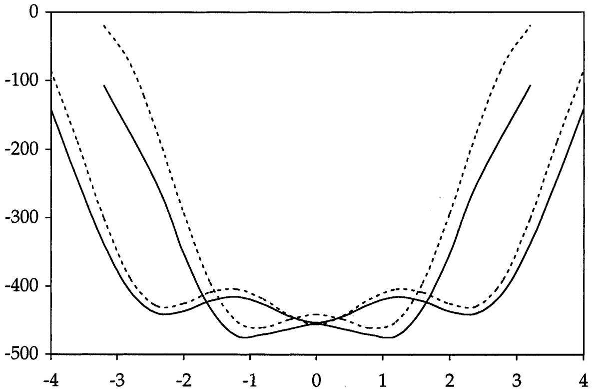

Figure 4. Comparison between the potentials determined from ab initio calculations at the MP2 level using cc-pVTZ basis (black line) and using the model potential (broken line). The double-well potential is for sliding acetylene along the diacetylene molecule. Sliding the acetylene molecule along the triacetylene backbone results in a potential with three wells. The strength of the interaction is given in cm^{-1} on the vertical axis and the distance is given in angstroms on the horizontal axis.

The smallest change in parameters needed to represent the ab initio sliding surface was in changing only the c parameters on the carbons in the polyyne chain. The new c parameters were empirically determined by fitting the sliding results from the MMC potential with the ab initio results for the acetylene−diacetylene and acetylene−triacetylene dimers at the MP2 level using the cc-pVTZ basis set. A consistent increase in the value of the c parameter would shift the whole potential curve instead of maintaining the acetylene interaction strength for the end of the chains and increasing the attraction in the middle of the polyyne chain. Therefore, the c parameter on the outermost carbon, which is most like the carbon of acetylene, was fixed at 6.4 au with the idea that the parameters for carbon should gradually increase along the chain to the center, eventually reaching some asymptotic value. By increasing the c parameter on the second carbon from the end of the chain to 8.83 au, the model potential for acetylene sliding along the diacetylene molecule gave a good representation of the ab initio results as seen in Figure 4. In a similar way, the third carbon from the chain end was increased to 10.6 au and allows for a good representation of the acetylene−triacetylene ab initio sliding potential (Figure 4). A final c parameter was empirically determined for chains with more than three triple bonds in order to match the contour of the ab initio sliding potential curve and had a value of 7.36 au. For a chain with four triple bonds, the c parameters on the carbons starting at the end of the chain and proceeding toward the middle are 6.4, 7.36, 8.83, and 10.6 au (Table 7). If there were no c parameter intermediate between 6.4 and 8.83 au, a noticeable end effect for longer chains would be evident in the intermolecular potential. With five triple bonds, it was not found necessary to change the central carbon c parameter from 10.6 au. To this extent of testing, a value of

TABLE 7: Carbon c Parameters (au) for $H-(C\equiv C)_N-H$[a]

$N = 1$	$N = 2$	$N = 3$	$N = 4$	$N = 6$
6.4	6.4	6.4	6.4	6.4
	8.83	8.83	7.36	7.36
		10.6	8.83	8.83
			10.6	10.6
				10.6
				10.6

[a] With the symmetry of the polyyne chains, the c parameters are given for each carbon from one end of the chain to the middle of the chain.

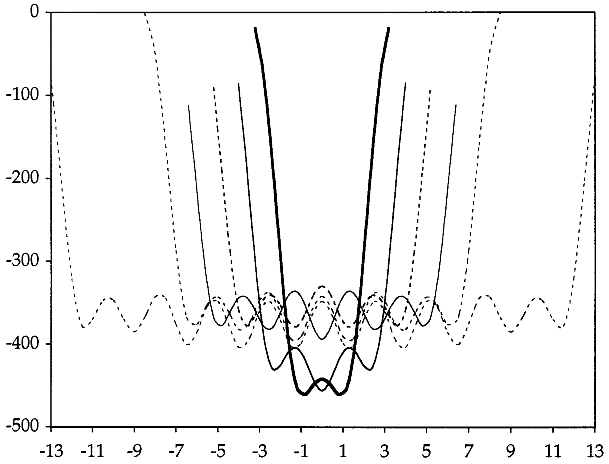

Figure 5. MMC interaction potential for acetylene sliding perpendicularly to the polyyne chain. The sliding potentials are for dimers containing polyyne chains with two to six triple bonds as well as a polyyne chain containing 10 triple bonds. The strength of the interaction is given in cm^{-1} on the vertical axis, and the distance is given in angstroms on the horizontal axis.

10.6 au appears to be an asymptotic long-chain value for the c parameter.

The MMC potentials using the parameters in Table 7 are shown in Figures 2b and 5. It should be noted that the MMC potentials are ~80 cm^{-1} higher in energy than the respective ab initio cc-pVDZ potential because of fitting of the c parameters to match results obtained with the cc-pVTZ basis set. The consistency of all of the potentials being higher in energy is evidence that the MMC intermolecular potential is providing a good representation of the weak bonding slipperiness seen in the ab initio calculations for this particular slice of the potential surface. For sliding acetylene along the polyyne chain in a crossed or parallel orientation, the model provides only qualitative information. Because we are most interested in the T-shaped sliding, it is meaningful to use the model to examine the T-shaped interaction between acetylene and a polyyne chain of arbitrary length. In Figure 5, the potential for sliding the acetylene along a chain containing 10 triple bonds is shown.

TABLE 8: Structural and Energetic Results for the Equilibrium Structures[a] of Acetylene−Polyyne Dimers from MMC Model

N (number of triple bonds)	center of mass separation (Å)	interaction energy (cm^{-1})
1	4.333	−503
2	5.588	−589
3	6.852	−622
4	8.144	−618
5	9.434	−620
6	10.723	−621
10	15.884	−622

[a] T-shaped structure with hydrogen on one end of the polyyne chain interacting with the triple bond of the acetylene.

The model potential was developed to represent and explore the interesting sliding potential for the acetylene−polyyne dimers. A rather simple form of the potential seems sufficient for these potential surface slices, though it may be that more detailed forms are needed for the entire surface, especially for regions corresponding to closer separations. We have, though, used the model for the equilibrium structures of the dimers. The parameters in the model potential were optimized to represent the MP2 energies using the cc-pVTZ basis set, and a comparison of these results in Table 4 with the MMC results in Table 8 provides one check of the ability of the simple form of the model potential to represent different aspects of the acetylene−polyyne interaction. The MMC potential gives a center of mass separation for the acetylene−diacetylene and the acetylene−triacetylene dimers that is 0.6% smaller than the ab initio results. The interaction energies from the model potential are 19 cm^{-1} larger for the acetylene−diacetylene dimer and 37 cm^{-1} larger for the acetylene−triacetylene dimer. Although this provides insight into the accuracy of the MMC potential, the accuracy of the comparison ab initio results is limited, too, because of the size of the basis set as well as the extent of correlation treatment used. It is perhaps more meaningful to look at the ability of the model to represent not just individual surface points but also trends and features found in the ab initio intermolecular potentials. Comparison of the MMC results in Table 8 with the ab initio (cc-pVDZ; MP2) results in Table 4 shows the same trend in how the interaction energy varies with polyyne chain length for both sets of results. Specifically, the interaction energy for acetylene−polyyne dimers increases as the length of the chain increases until it reaches a point where any further lengthening of the polyyne does not contribute to the energy. Note that the 4 cm^{-1} diminishment of the interaction energy from $N = 3$ to $N = 4$ is a small artifact at the point of introducing the intermediate c parameter for the $N = 4$ polyyne chain. Looking at the trend for acetylene with longer polyynes shows the interaction energy converging to ~622 cm^{-1} (Table 8).

Investigation into the energetic differences resulting from rotating the acetylene from being oriented perpendicular to the polyyne chain allows for another comparison between the MMC potential and ab initio results. Were acetylene sliding along a polyyne chain, vibrational motions could allow it to tilt or rotate away from the idealized perpendicular geometry. Hence, calculations were carried out wherein the acetylene molecule was placed 1.4 and 2.0 Å from the center of mass of the diacetylene molecule, and the distance from the center of mass of acetylene to the diacetylene molecular axis was optimized. Then, acetylene was rotated in the plane of the dimer from the perpendicular orientation in steps of 5°, and at each orientation the distance from the center of mass of acetylene to the diacetylene molecular axis was optimized. At both of these points along the diacetylene chain, rotation of the acetylene molecule toward the end of the chain would allow for interaction between the triple bond in acetylene with the hydrogen at the end of the diacetylene molecule. It can be seen from Table 9 that the potential energy rises somewhat more rapidly with the in-plane torsional angle for the MMC potential than for the ab initio potential. At the point further from the diacetylene midpoint, the ab initio and model potentials are comparable until the HCCH has been rotated 20°.

A further result obtained from exploring the MMC potential is that, as acetylene slides along a chain from the middle toward the end, the degree of tilt increases until it converts into the equilibrium T-shaped structure which consists of the hydrogen

TABLE 9: Relative Interaction Energies[a] for the Acetylene−Diacetylene In-Plane Torsional Potential

distance[b] (Å)	angle[c] (deg)	cc-pVTZ; MP2 rel. energy (cm^{-1})	MMC model rel. energy (cm^{-1})
1.4	0	0	0
	5	−24	−35
	10	−29	−60
2.0	0	0	0
	5	−64	−50
	10	−111	−97
	15	−139	−139
	20	−146	−176

[a] Energies are relative to the energy of the acetylene molecule at 0°. [b] Distance of the acetylene from the midpoint of the diacetylene molecule. [c] Angle of rotation of the acetylene molecule away from being perpendicular to the diacetylene backbone.

on diacetylene pointing into the middle of the acetylene molecule. From the calculations that show this structural feature, we also obtained the barriers for the interconversion. For the acetylene−diacetylene dimer, a barrier of 33 cm^{-1} is found on going to the global minimum from the local minimum where acetylene points into the chain (structure **6**). For the acetylene−triacetylene dimer, that barrier is also small, only 8 cm^{-1}.

Finally, it is worth noting that although the slippery/sliding part of the potential surface of $HCCH-H(CC)_nH$ does not include the global minimum functional group substitution can change that. We carried out cc-pVDZ/MP2 calculations on $CH_3-(CC)_2-H$ (1,3-pentadiyne) in a complex with acetylene and found that the methyl group precludes any minimum for acetylene at the end of the chain being energetically below that of the slippery/sliding region of the surface. For polyyne chains suitably substituted at both ends, the global minimum will be included in the region where acetylene readily slides along the chain.

Conclusion

The ab initio calculations of acetylene−polyyne dimers provided structures and energetics that were used to guide the refinement of the model potential developed from extensive study of the acetylene dimer. The interaction energy for the equilibrium T-shaped dimers reached an asymptote at −622 cm^{-1} where increasing the length of the polyyne monomer does not add to the interaction with the acetylene monomer. This was also seen for T-shaped structures of the dimers where the acetylene molecule interacts with the polyyne backbone. Specifically, for interaction of acetylene with the triple bond at the end of the chain, the interaction energy reaches an asymptote at −372 cm^{-1}. As the acetylene molecule slides along the chain, the intermolecular potential is essentially flat, with only small bumps. This flatness over an extended region leads to weak bonding slipperiness.

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References and Notes

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