Table II. Calculated Strain Energies, Geometries, and Bond Orders for "Boat" Benzenes[a]

α, deg	destabilization energy[b] ΔE, kJ/mol	bond A length, Å	bond A bond order	bond B length, Å	bond B bond order
0	0	1.387	0.512	1.387	0.512
5	+12.6	1.387	0.512	1.388	0.508
10	+50.2	1.386	0.515	1.391	0.498
15	+114.7	1.385	0.519	1.398	0.473
20	+208.5	1.385	0.519	1.408	0.438
25	+339.1	1.384	0.522	1.421	0.392
30	+504.5	1.384	0.522	1.441	0.322

[a] This table shows calculations for "boat" benzene, distorted in the manner of **2**. All geometric parameters apart from α are optimized at the STO-3G level. Bond orders were calculated by using the bond-order/bond-length correlation described elsewhere (Figure 8 of ref 13). [b] Relative to benzene.

previous workers for compounds **2a, 2b, 2d,** and **2e** and in these laboratories for 3,8-diketo[8]paracyclophane (**8**) as a model for **2c**. The increase in the angle of out of plane bending, α, can be seen to increase as the length of the bridge decreases. The J_{OB} coupling constant can be seen to be unchanged and identical with the unstrained analogue (1,2,4-trimethylbenzene $J_{OB} = -0.66$ Hz[1]) in all but the most strained case, [6]paracyclophane. These results suggest that only [6]paracyclophane may have a detectable amount of π-electron distortion. The bond order/bond length and bond order/$^3J_{HH}$ relationships, although less reliable,[1,2] also support this conclusion in this series.

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It therefore appears that a benzene ring can undergo severe distortions of the σ-framework without disruption of the ground-state π-electron distribution. Such a conclusion is also in accord with the theoretical work of Haddon,[12] which postulates that significant rehybridization occurs in distorted systems to allow maintenance of pp overlap.

SCF-MO calculations on a series of benzenes distorted in the manner of **2** were performed and are summarized in Table II. It can be seen that, in agreement with the experimental results, no significant changes in the bond order of bond A are predicted for a boat-shaped benzene distorted up to 30°. Interestingly, the calculations predict a decrease of bond order in bond B, but measuring this is inherently outside the scope of our NMR method.

Experimental Section

All experimental NMR data in Table I were obtained on a Bruker Instruments WM-400 MHz NMR spectrometer using 5-mm sample tubes with approximately 5% w/v solutions in the solvent stated (supplementary material). The solvents were degassed and the spectra acquired at 300 K, except for compounds **2b** and **2e** (see footnotes to Table II). The spectra were acquired under conditions of high digital resolution, at least 0.03 Hz. All systems were either first order at the frequency used or were analyzed by using the PANIC (closely related to LAOCOON) program. Ortho-benzylic coupling constants are assumed to be negative.[1] Synthetic and crystallographic details are given in the supplementary material.

Supplementary Material Available: Preparation procedures and analytical data for all compounds and tables of positional parameters, crystal data, bond lengths, bond angles, thermal parameters, details of least-squares planes calculations, and torsion angles for **8** (23 pages). Ordering information is given on any current masthead page.

Theoretical Characterization of the Potential Surfaces and Properties of Weakly Bonded Acetylene

Clifford E. Dykstra

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received December 22, 1989

Abstract: Acetylene is a simple molecule for probing weak hydrocarbon interactions. There exist extensive spectroscopic data for a number of acetylene complexes, which demonstrate a variety of structures. Acetylene weakly attaches at one of its hydrogens in some cases, at the molecule center, or just along the molecular axis. However, there is little characterization of the potential surface features of these complexes, features that are manifested in the structural observations, and there does not seem to be a uniform means of understanding the structures and properties. In this report, the electrically based molecular mechanics for clusters (MMC) approach has been applied to small complexes of acetylene, first to test whether it can uniformly account for the observations and second to provide a characterization of the interaction energetics and properties of the complexes. The systems considered are the acetylene dimer, trimer, and tetramer as well as mixed, binary complexes with argon, water, hydrogen fluoride, hydrogen cyanide, and ammonia. The calculations yield equilibrium structures, stabilities, dipole moments, and harmonic frequencies for the intermolecular vibrational modes. The calculational results show certain floppiness, some unexpected structural parameters, and for one complex, an isomer that has not been detected experimentally.

Introduction

Even excluding chemical bonding, the interactions of hydrocarbons with other hydrocarbons, with water, and with other kinds of molecules comprise a fundamental element in analyzing and simulating biomolecular processes of many types. These interactions are generally categorized as weak interactions, as hydrogen bonding, or as van der Waals attractions, and at the least, explicit potentials for these interactions can be used in, and are a prere-

quisite for, computational simulation studies. For these purposes, it is likely that gross characteristics suffice and that certain detailed aspects of potentials can be overlooked. Still, a fundamental basis for the interactions, with detailed aspects, affords the greatest and widest applicability in the end.

Perhaps the first step in probing weak hydrocarbon interactions is examining small, weak complexes containing the simplest possible hydrocarbons, e.g., methane, acetylene, ethylene, and

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ethane. This might provide the building block information for complexes with extended hydrocarbon constituents. Methane, the lightest of these simple species, is not a good first-case system in comparison to acetylene. Its symmetry is almost that of a spherical body; this precludes much orientational differentiation in an interaction potential, and it yields a charge field with very weak effects on other molecules. Perhaps, for these same reasons, there is a wealth of spectroscopic data on acetylene complexes, and yet comparatively little on methane complexes.

To study acetylene interactions as a first example of hydrocarbon interactions, a model based on electrical interactions has been used for this report. This model is the recently introduced scheme for weak potentials[1,2] designated MMC for molecular mechanics of clusters. It is based on intrinsic properties of isolated constituent species and electrical properties, and these values are largely from high level ab initio calculations. The response properties are used to evaluate the classical, point–mulitpole electrical interaction between two or more molecules or atoms. This interaction includes the interaction of permanent charge fields and polarization effects, with the latter not limited to dipole polarization. Effects of charge penetration, exchange repulsion, dispersion, and any other lingering element are modeled collectively via simple atom–atom, Lennard-Jones potentials. These other effects are most strongly dependent on the proximity of the interacting charge distributions, which means that they depend first on the shapes of the approaching molecules. The Lennard-Jones form is probably the simplest form of a potential that can give the steric features of an intermolecular interaction. These potentials add to, or augment, the electrical interaction potential in MMC.

Theoretical Approach

Potential energy surfaces were examined via calculation with the MMC method.[1] For each molecule, there is a truncated set of permanent moments, polarizabilities, and for acetylene, this set included just the quadrupole moment and the dipole and quadrupole polarizabilities. The inversion symmetry makes the dipole, the dipole–quadrupole polarizability, and certain other properties identically zero. The ab initio values for these properties have been reported elsewhere,[3] and the computational procedures used for evaluating electrical interaction have also been given previously.[2]

The nonelectrical component of the MMC intermolecular potential, which is that part of the potential associated most with the molecular shapes, consists of pairwise terms between atomic centers, and sometimes other centers, of the constituent molecules. For every A–B pair of molecules in a system, there is an augmenting potential

$$V_{AB} = \sum_i^{|A|} \sum_j^{|B|} \left(\frac{d_i d_j}{R_{ij}^{12}} - \frac{c_i c_j}{R_{ij}^6} \right)$$

where the sums are over the centers, mostly atoms, located in each molecule. This is a simple functional form representing each molecule's shape as a superposition of spheres at the centers. The c and d parameters are selected empirically, with enforced transferability; that is, c and d parameters determined for a given molecule are always the same, regardless of the partner species. The combination of the electrical interaction energy and the V_{AB} potential energies constitutes the MMC potential at a given geometry point, that is, $V_{total} = V_{electrical} + \sum_{A>B} V_{AB}$.

For acetylene, the empirical selection of its c and d parameters was based on three experimentally determined center of mass separation distances for T-shaped acetylene complexes: 4.404 Å[4,5]

Table I. Acetylene and Comparison Molecule MMC Parameters (au)

	carbon centers		hydrogen centers		inversion center	
	c	d	c	d	c	d
HCCH	10.6	3230	0.6	19.0	0	3000
HCN[1]	6.0	2550	0	7.6		
H_2O^{10}			0.15	2.0		
H_2^1			0.155	9.8	3.25	722

for $(HCCH)_2$, 4.04 Å[6] for Ar–HCCH, and 3.075 Å for HF–HCCH.[7] A set of c and d parameters for the carbon and hydrogen centers and for the molecule's inversion center were determined so as to reduce the average difference between the MMC results and the spectroscopic values. The parameters for the argon and hydrogen fluoride were those already established.[1] Small adjustments were made to the c and d parameter values so that the calculated distances would correspond to equilibrium values rather than the observed, vibrationally averaged values. Of course, the differences between the observed structures and equilibrium structures for these three complexes are not known, but a lengthening of 0.02–0.04 Å may be expected for many binary complexes.[8] The assumed differences were 0.04 Å for HCCH–HF and zero for $(HCCH)_2$. The basis for these guesses is the nature of their potential surfaces, which is discussed later. Acetylene's five nonzero MMC c and d values,[9] shown in Table I with comparisons to parameters previously obtained for other species,[1,10] yield equilibrium separations of 4.403 Å for $(HCCH)_2$, 3.007 Å for HCCH–HF, and 4.058 Å for HCCH–Ar. An accuracy in equilibrium separations of 0.03 Å with MMC is expected on the basis of most prior studies,[1,10–12] though there are a few instances where the apparent disagreement with a measured (vibrationally averaged) value is around twice that.[12]

The MMC potential surfaces are searched to find equilibrium structures and harmonic force constants.[11] Dipole transition moments are found within the doubly harmonic approximation by obtaining the system's dipole moment from the electrical analysis at small displacements from a given structure point. Derivatives of the dipole moment with respect to geometrical coordinates are then found numerically and transformed to the transition moments for the normal modes.[11]

Binary Acetylene Complexes

The acetylene dimer is planar and T-shaped, but the MMC calculations indicate that its potential surface rises very slowly, or is almost flat, along a bending coordinate that takes the two molecules toward a staggered, parallel arrangement. This bending motion corresponds to an in-plane rotation of the two monomers in opposite directions, one clockwise and the other counterclockwise, as in a geared rotation. As shown in Table II, the potential is so flat along the direction of the associated normal coordinate that the harmonic vibrational frequency for this torsion is a mere 7 cm⁻¹. (Of course, a slice of the potential surface along this coordinate is highly anharmonic, and so, the value of the harmonic frequency serves only to spotlight the surface flatness and not to predict a vibrational transition frequency.) The con-

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(9) The parameter selection procedure is not assured to be unique; it is possible that other parameter choices could yield the same three separation distances. Even so, the parameters are expected to be realistic since the T-shape of $(HCCH)_2$ means that the parameter choice had to simultaneously reflect the molecular shape at both the ends and the middle of the molecule. With the few numbers of parameters, this is a strong restriction. The lack of uniqueness in the choice of parameters is expected to be over small ranges about the chosen values.
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Table II. Intermolecular Vibrational Frequencies of Acetylene Complexes

complex	mode[a]	MMC ω^b (cm⁻¹)	MMC $\mu_{01}{}^b$ (D)	expt ω^c (cm⁻¹)
HCCH–Ar	$b_\parallel$	10	0.047	8.9[6]
	s	33	0.015	36.6[6]
HCCH–HF	$b_\parallel$	184	0.181	
	s	191	0.125	
	$b_\perp$	517	0.294	
	$b_\parallel$	563	0.204	
HCCH–HCN (I)	$b_\parallel$	23	0.618	
	$b_\perp$	58	0.435	
	s	102	0.063	82[15]
	$b_\parallel$	159	0.087	
HCCH–NCH (II)	b(2)	28	0.473	
	b(2)	75	0.292	
	s	87	0.042	
HCCH–H₂O (I)	b	38	0.483	
	b	49	0.375	
	s	158	0.035	
	b	235	0.661	
	b	261	0.154	
HCCH–H₂O (II)	b	89	0.293	
	b	115	0.511	
	s	142	0.060	
	b	169	0.350	
	b	397	0.292	
HCCH–NH₃	b	10	0.287	
	s	52	0.170	107[18]
	b	150	0.319	
	b	167	0.163	
	b	237	0.297	
(HCCH)₂	$b_\parallel$	7.4	0.019	
	$b_\perp$	43	0.020	
	s	85	0.042	
	$b_\parallel$	111	0.038	
(HCCH)₃	$b_\perp$(2) [e'']	45	0.0	
	$b_\perp$ [a'']	62	0.026	
	$s_\parallel$(2) [e']	76	0.068	
	$b_\parallel$(2) [e']	99.0	0.021	
	$s_\parallel$ [a']	99.4	0.0	
	$b_\parallel$ [a']	167	0.0	
(HCCH)₄	b(2)	15	0.033	
	s	25	0.0	
	s	38	0.011	
	b	62	0.0	
	s	64	0.052	
	b	83	0.034	
	s(2)	91	0.062	
	s	107	0.0	
	b	113	0.005	
	b(2)	127	0.007	
	b	164	0.0	

[a] Key: s, intermolecular stretch; b, bend; ⊥, out-of-plane; ∥, in-plane; (2), the mode is doubly degenerate. [b] Equilibrium harmonic normal-mode stretching frequencies and doubly harmonic transition dipoles. [c] The experimental vibrational frequencies were obtained in different ways, but mostly on the basis of force field analysis using spectroscopic distortion constants.

certed twisting, or anti-geared, motion of the acetylene submolecules in (HCCH)₂ is relatively stiff because it is unfavored sterically and electrically. The harmonic frequency calculated for this motion is 111 cm⁻¹.

As the two acetylene submolecules twist away from the equilibrium along the low-frequency torsional coordinate, the optimal mass center separation distance necessarily diminishes. This is the consequence of the molecular shapes: A parallel arrangement may have the mass centers closer than a T-shaped arrangement. And there should be an important manifestation of this in the vibrational averaging of the separation distance. This bending motion, taken alone, must push the vibrational average of the separation distance to a value *shorter* than the equilibrium. (In the parameter selection process, we have assumed that the usual increase in separation distance due to vibrational averaging, mainly over intermolecular stretch, is largely balanced by averaging over bending in the acetylene dimer.)

Table III. Dipole Moments of Small Acetylene Complexes

complex	MMC μ_e (D)	expt μ_o (D)
Ar–HCCH	0.078	0.027[13]
(HCCH)₂	0.34	0.28[5]
HCCH–HF	2.81	2.37[14]
HCCH–H₂O (I)	2.02	2.01[17]
HCCH–H₂O (II)	2.27	
HCCH–HCN (I)	3.61	
HCCH–NCH (II)	3.47	3.42[16b]
HCCH–NH₃	1.83	1.99[18]
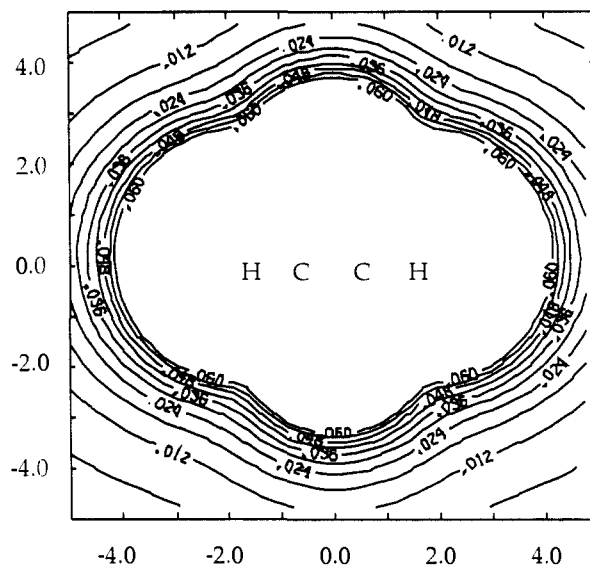
Figure 1. Contour plot of the total dipole moment (in debyes) surface of the Ar–HCCH complex. The horizontal axis is the position of the argon atom along the acetylene axis, the middle of the figure being the center of the HCCH molecule. The vertical axis is the argon position coordinate perpendicular to the acetylene molecular axis. In other words, this is an x–y positioning of argon about acetylene. The simple form of the contour lines reflects the fact that the dipole moment is primarily induced in the argon by the quadrupolar field of acetylene.

This low-frequency torsion evolves into the minimum energy path for the inversion process where the submolecules interchange roles (i.e., the top of the "T" becomes the base: ⊥ → T). The calculated MMC barrier for this interchange is 59 cm⁻¹. The separation of the molecular mass centers at this transition state is 4.290 Å, which is over 0.1 Å shorter than the separation at equilibrium. The microwave splittings from tunneling through the interconversion barrier have been measured,[4] and the analysis has led to a barrier height of around 33 cm⁻¹. An MP2/DZP level calculation has given 76 cm⁻¹ for this barrier.[18]

The complex of acetylene and an argon atom is quite weak. A good share of the attraction at equilibrium is the polarization of the argon atom by the quadrupolar field of acetylene. That polarization is strongest where argon is closest to the center of the molecule and with acetylene oriented perpendicular to the line from the argon to the acetylene mass center. This is the T-shaped structure that has been established.[6] The calculated dipole moment of Ar–HCCH at equilibrium is 0.078 D, as given in Table III. This can be compared only with a vibrationally averaged value of 0.027 D,[13] which was obtained from Stark effect rotational spectra. It is quite likely that the difference between the values is largely vibrational averaging, in that MMC calculations show the dipole moment diminishes for "sliding" the argon along the acetylene in either direction from the equilibrium. This is shown in Figure 1. The vibrational averaging effect of the stretching motion is harder to anticipate. The same size difference between the measured dipole moment and the calculated equilibrium dipole moment is found for (HCCH)₂. Here, the low-frequency bending

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Table IV. Calculated Stabilities of Acetylene Complexes

complex	$D_e{}^a$ (cm^{-1})	$D_0{}'^b$ (cm^{-1})
Ar–HCCH	123	101
HCCH–HF	2000	1272
HCCH–H$_2$O (I)	1090	719
HCCH–H$_2$O (II)	1196	740
HCCH–HCN (I)	912	741
HCCH–NCH (II)	684	552
HCCH–NH$_3$	1140	832
(HCCH)$_2$	610	487
(HCCH)$_3$	1898	1513
(HCCH)$_4$	2992	2431

$^a D_e$ is the stability of the complex calculated from MMC for the equilibrium structure. $^b D_0'$ is the stability of the complex obtained from MMC upon zero-point correction with the harmonic frequencies of the intermolecular modes (only).

motion is a direction along which the dipole moment diminishes away from equilibrium.

The most recent microwave spectroscopic work on Ar–HCCH[6] has yielded harmonic force constants for the stretching and bending. These were deduced from the centrifugal distortion constants. The normal-mode analysis carried out by Ohshima et al.[6] using this harmonic force field produced stretching and bending frequencies in extremely good agreement with the MMC values, as shown in Table II. This is the best comparison of information on the potential surface shape around the equilibrium that is available for this complex.

The structure of the acetylene–HF complex is T-shaped.[7] The MMC calculations find it to be a relatively strong complex with a stability of 2000 cm^{-1} (Table IV). The harmonic vibrational frequencies are larger, for the most part, than for the other acetylene complexes studied, and so this complex may be characterized as relatively more rigid. The calculated dipole moment of equilibrium HCCH–HF is 0.44 D greater than the measured, vibrationally averaged value[14] (Table III). From redoing the electrical analysis at the equilibrium with different sets of electrical properties, it appears that about 40% of the induced moment develops from the permanent dipole of HF acting with the dipole polarizability of acetylene. Another 40% develops from the quadrupolar field of acetylene acting with the dipole polarizability of HF along with back-polarization. The remainder develops from dipole–quadrupole polarization.

Twisting the HF submolecule in HF–HCCH by 20°, which is just about the reported averaged distortion from equilibrium,[7] diminished the calculated dipole moment by 0.18 D, and stretching the intermolecular bond from the equilibrium MMC value to the measured average value[7] diminished the dipole another 0.09 D. In this complex, the relatively strong interaction goes along with a dipole moment surface that seems to be more sharply changing in the vicinity of the equilibrium. This implies significant vibrational averaging effects in spite of the relative rigidity. Of course, MMC may be overvaluing the dipole moment of the complex, perhaps by 0.2 D or so; that would not be out of line with results on other complexes.

The T-shaped complex of acetylene with HCN has the proton of the HCN pointing into the middle of the acetylene.[15] The MMC mass center separation distance is 4.174 Å. Allowing for vibrational averaging effects of 0.02–0.04 Å, this nicely matches the value of 4.216 Å obtained from microwave spectra.[15] The MMC surface indicates that its in-plane bends, analogous to those of (HCCH)$_2$, are low in frequency for opposed torsions and high in frequency for parallel torsion. The out-of-plane bending of the HCN submolecule is relatively low-frequency.

The Fourier transform microwave study of the methyl cyanide–acetylene complex carried out by Howard and Legon[16a] was

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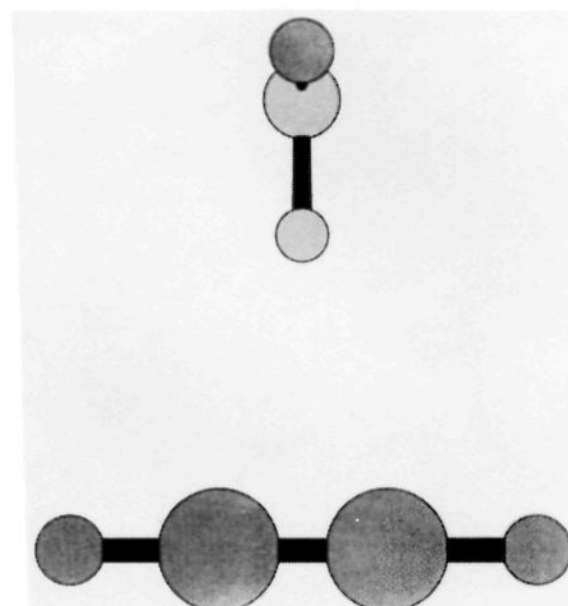

Figure 2. Calculated structure of the spectroscopically observed form of the acetylene–water complex. The plane of the water molecule is nearly perpendicular to the acetylene. Relative to the line connecting the submolecule mass centers, the acetylene is twisted down by 20° at equilibrium and the water is twisted up by 67°.
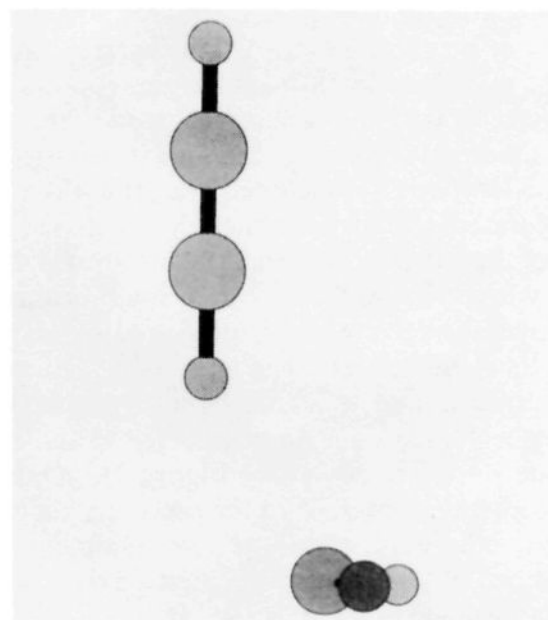

Figure 3. Calculated structure of an unobserved form of the acetylene–water dimer. In this structure, an O–H bond of water is directed into the center of the acetylene.

concerned in part with linear bonding of a –CN group to an acetylene proton end, since there had been no observation of a linear complex, HCCH–NCH. MMC calculations find a minimum on the potential energy surface for this structure (II), but it is about 200 cm^{-1} less stable than the T-shaped form (I), as indicated in Table IV. The transition state for the interconversion was found to be at an energy of 414 cm^{-1} below the separated limit. So, the barrier for going from II to I is 270 cm^{-1}. The structure of the transition state is planar with HCN twisted by 81.0° with respect to the line between the mass centers and relative to the HCCH–NCH arrangement of form II. The acetylene is twisted by −33.8° in this structure. Block et al.[16b] have recently observed the linear structure (II) in infrared spectra. The separation between monomer mass centers of 2.443 Å from the MMC calculations is about 0.05 Å longer than the distance found by Block et al.[16b]

Spectroscopic determination of the structure of the acetylene–water complex by Peterson and Klemperer showed it to have the oxygen of water "bonded" to an acetylene hydrogen in a planar or almost planar arrangement.[17] The vibrationally averaged separation between the mass centers is 3.958 Å. MMC results show a minimum with this qualitative (C_s) structure and an equilibrium separation distance of 3.898 Å. However, this minimum structure is sharply bent with the hydrogens pointing down by 67° from what would otherwise be the molecular plane, while the acetylene is tipped up by 20° (see Figure 2). There is an

(17) Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 3842.
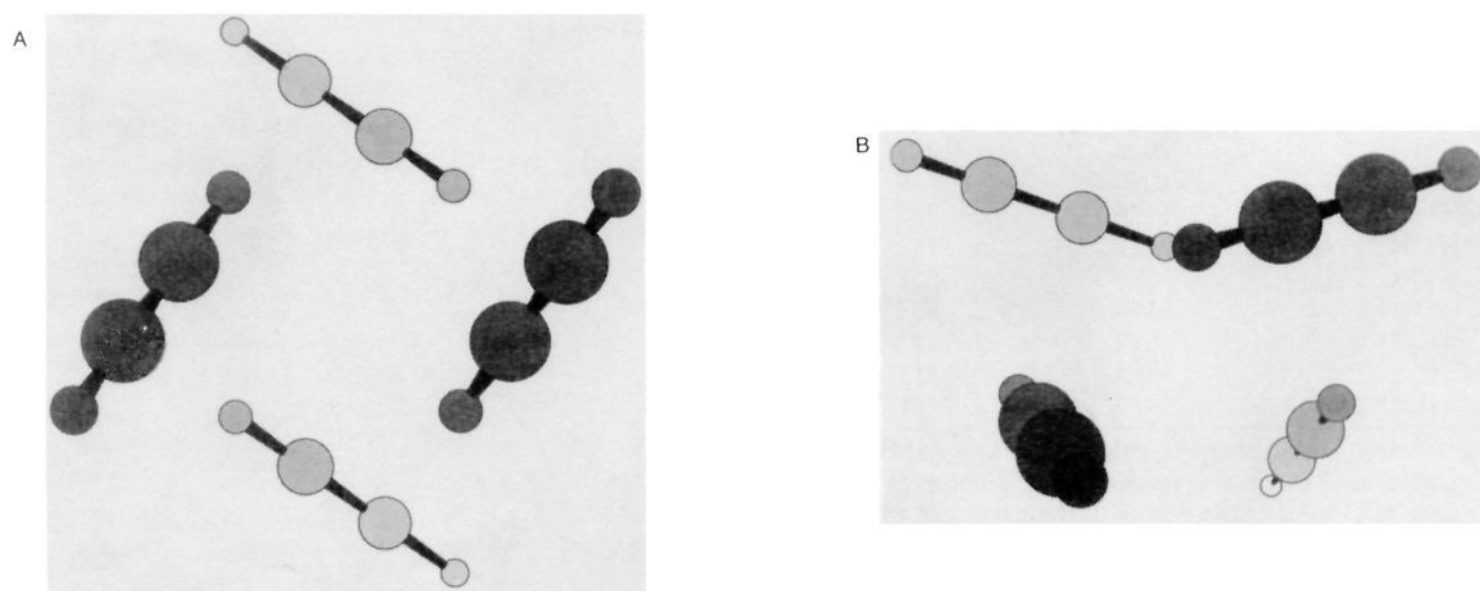
Figure 4. Two views of the MMC equilibrium structure of the acetylene tetramer. The view in A is along a C_2 symmetry axis (top view) and it shows the T arrangement of any pair of submolecules. The mass centers of the lighter shaded molecules are back from the mass centers of the other two submolecules by 2.80 Å. All the molecules are twisted somewhat with respect to a plane drawn parallel to the plane of the paper and including a submolecule's mass center. This is apparent in the side view in B, which is also suggestive of the near-tetrahedral arrangement of the four mass centers: The closest separation is 4.272 Å, while the largest is 4.569 Å.

interconversion pathway through a C_{2v} planar structure, and the calculated barrier height is 89 cm^{-1}. This barrier is approached by twisting the acetylene by 20° and, in the opposite direction, twisting the water by 67°. At this interconversion transition-state structure, the optimum separation distance increases to 4.062 Å. Peterson and Klemperer[17] concluded that there was a double-minimum potential of this sort and that all vibrational levels were above the top of the barrier. The vibrationally averaged separation distance[17] they found is bracketed by the equilibrium and transition-state distances determined from the calculations.

MMC results also show another minimum for a complex of water and acetylene, and it is also of C_s symmetry. In this structure, the acetylene axis is perpendicular to and bisected by the plane of the water molecule (see Figure 3). One hydrogen of the water essentially points toward the acetylene midpoint. With respect to the line between acetylene's inversion center and the water center of mass, the water molecule C_2 axis is twisted 33°. The separation distance is 3.331 Å. MMC finds this conformer to be about 100 cm^{-1} more stable (Table IV) than the observed form, but when zero-point energies are included based on calculated intermolecular harmonic frequencies, the stabilities differ by only 20 cm^{-1}. This energy difference is too small to draw a qualitative conclusion about which is actually the more stable. However, it is a clear result of the MMC model that this other complex does correspond to a minimum on the potential energy surface. The lowest barrier for interconversion of this form of the complex is through a nonplanar C_{2v} structure where the water molecule has twisted so that its symmetry axis coincides with the line connecting the mass centers. The barrier height for this interconversion is calculated to be 47 cm^{-1}.

On the basis of microwave spectra, the complex of acetylene and ammonia has been determined to be axially symmetric,[18] with acetylene being the "hydrogen donor". There is significant on-average twisting with the ammonia submolecule symmetry axis found to be 23° off the line connecting the mass centers. The twist of the acetylene could not be determined, but a guess of 15° was made.[18] Extracting the separation distance from the data requires knowing this angle, and so with the guess value, a separation distance of 4.063 Å was obtained.[18] MMC results characterize this complex in a way that seems partly consistent with the observations and may offer more insight into the interaction. Specifically, the MMC results show an equilibrium structure that is only near to being axially symmetric. Ammonia is found to be twisted by 30° (versus 23°), and the acetylene is twisted in the opposite rotation sense by 28° (versus the guess of 15°). The calculated equilibrium separation distance is 3.997 Å. However, the MMC results also show a low-energy distortion path

toward an axially symmetric structure. In fact, constraining the system to be axially symmetric raises the energy of the complex by only 57 cm^{-1}. And at this structure, the optimum separation distance is 4.315 Å and the MMC equilibrium dipole moment (Table III) is close to the spectroscopic value. For such small surface features, we have no good assessment of MMC's reliability, but the prospect of a low bump in the potential at the axial structure, and likewise for low bumps at the high-symmetry arrangements of both forms of the acetylene–water complex, is an intriguing one. Experimental information that can either establish the height of a potential bump or establish an upper limit to the height upon finding no manifestations of a bump would be helpful in making refinements to the MMC parameters.

Cyclic Acetylene Complexes

The acetylene trimer and tetramer are found to be cyclic structures at equilibrium with zero dipole moments. In each species, the monomers are equivalent. The trimer is planar with a separation distance between submolecule mass centers calculated to be 4.328 Å. Prichard et al. have spectroscopically determined that the separation distance is 4.354 Å.[19] The orientation of the trimer submolecules corresponds with the most favorable quadrupole–quadrupole interaction, which has been pointed out already,[20] and likewise for the carbon dioxide trimer.[21] The MMC equilibrium structure has each molecular axis twisted 19° away from the equilateral triangle of the lines connecting monomer mass centers.

Ab initio calculational results of Handy and co-workers[22,23] have been reported for the acetylene trimer. The basis set was a polarized, double-ζ (DZP) set. Though this is a large basis in terms of the computation cost for the acetylene trimer, we have found it to be somewhat deficient in describing polarization and polarizabilities.[3,24] To the extent that polarization is important in the interaction, this basis will be of limited reliability. The reported DZP/SCF calculations[22,23] show a large separation distance of 4.655 Å and a stability of 818 cm^{-1} (with respect to separated monomers). Fortunately, the inclusion of correlation effects at the MP2 level improved the separation distance, yielding 4.292 Å, and then a stability of 1829 cm^{-1}, which happens to

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compare nicely with the MMC stability of 1898 cm^{-1}, was obtained. However, they adjusted the MP2 stability value to be 1063 cm^{-1} as an estimated accounting of basis set superposition error.[22,23] While it is certainly expected that basis set superposition effects are sizable, it is difficult to make quantitative corrections for it, particularly with a basis of only DZP quality.[25,26] Furthermore, correcting for basis set superposition does not correct for the limitation of the basis in describing polarization energetics; that effect may well be in the opposite direction. Perhaps the only fair judgement, for now, is that the stability of this complex is 1000-2000 cm^{-1}, and MMC favors the higher part of that range.

The trimer does not have a mode that corresponds to the low-frequency twist of the dimer. The third submolecule locks this out. In fact, MMC calculations have shown this same characteristic for the water dimer–trimer[10] and the ammonia dimer–trimer.[12] The closure of a ring tends to be the point in homomolecular cluster growth where a relatively rigid complex results.

The MMC results for the acetylene tetramer show it to be nonplanar, with a separation distance between monomer mass centers of 4.272 Å. This implies a smooth contraction from the dimer to the trimer to the tetramer. The puckering of the tetramer (Figure 4) preserves some of the "T" character in the relative arrangement of any two submolecules. The overall S_4 symmetry is consistent with the spectroscopic determination by Bryant et al.[27] They also concluded that the distance from an acetylene mass center to the S_4 axis was 2.78 Å and that the acetylenes were above and below a plane perpendicular to the S_4 axis by about 0.89 Å. MMC finds a greater degree of puckering, with the acetylenes above and below the central plane by 1.398 Å. This goes along with a shorter distance to the S_4 axis, about 2.285 Å, but the distance from one acetylene to the complex mass center is 2.678 Å. In other words, the separations are similar to the spectroscopic values, but with the degree of puckering being noticeably different.

Conclusions

As a class, acetylene complexes are quite interesting. Being nonpolar, the bonding tends to be weaker than for a pair of polar molecules; there tend to be multiple minima and low-barrier interconversion routes. MMC appears to be effective at yielding separation distances, orientations, and dipole moments of a set of binary acetylene complexes and at finding transition-state structures for interconversion. This endorses the picture that acetylene interactions with neighboring molecules are largely electrical and steric. Approaching species may be polarized by acetylene's quadrupole, and likewise may affect the quite polarizable acetylene. In this way, acetylene and certainly other hydrocarbons can appear as hydrogen "donors" and "acceptors". But, it is not so much the donating and accepting of protons that is at work as it is the charge field resulting from partially positive proton centers and the polarizability of carbon atoms.[28]

Certain interesting features have been uncovered in the potential energy surfaces for the complexes that have been studied. Acetylene dimer has a trough for bending, and motion along the bottom of this trough brings the molecules somewhat closer together than at their T-shaped equilibrium. The acetylene–water complex is particularly fascinating because it exhibits two structures, though only one has been experimentally observed. As we can relate more spectroscopic information about different conformers and about intermolecular vibrations to the potential surface, we should realize still more quantitative understanding of the weak interactions in this and other classes of species.

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Theoretical Electrode Potentials and Conformational Energies of Benzoquinones and Naphthoquinones in Aqueous Solution

Christopher A. Reynolds

Contribution from the Oxford Centre for Molecular Sciences and Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ, UK. Received February 6, 1990

Abstract: Electrode potentials are computed theoretically for quinones by using a combination of statistical and quantum mechanics. The calculations, which incorporate the all-important influence of solvent, can achieve an accuracy of about 25 mV. The most stable conformation in solution has been determined by running constrained molecular dynamics to sample predetermined conformations. The most stable conformation may be used to calculate theoretical electrode potentials in aqueous solution, which are in very good agreement with experiment. The results show that the method is likely to be very useful in the design of bioreductive anticancer agents whose activity is determined by their electrode potential. Studies on the effect of the torsional constraints on the changes in the free energy of hydration illustrate the sensitivity of the free energy perturbation results to the torsional parameters.

Redox potentials of molecules are important determinants of molecular behavior. This is particularly true for drug molecules and other biologically active molecules that are activated by enzymatic reduction (or oxidation). For example, the efficiency of nitroimidazole bioreductive anticancer agents as both radiosensitizers and cytotoxic agents is directly related to their electrode potential.[1] Indeed, the use of bioreductive agents, such as nitroimidazoles,[2] quinone-based alkylating agents,[3,4] and bioreductive

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