LETTERS

The Benzene/Water/Hexafluorobenzene Complex: A Computational Study

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Received: July 31, 2002; In Final Form: November 22, 2002

The multiple interaction between water, benzene, and hexafluorobenzene was discussed in light of an ab initio study. It was found that two trimers are formed with a dissociation energy of about 21 and 16 kJ/mol, which are greater than that of the benzene/water, hexafluorobenzene/water, and benzene/ hexafluorobenzene dimers. The lowest energy trimer features the two aromatic systems lying in tilted planes, with the water molecule interacting with benzene through one π-hydrogen bond and with hexafluorobenzene through the oxygen atom. The highest energy trimer shows the aromatic systems lying in parallel planes and "sandwiching" water, which uses two hydrogens to bind benzene and the oxygen atom to interact with hexafluorobenzene.

Introduction

The study of the interaction between water and simple aromatic systems can help chemists to understand fundamental phenomena including structure and function of biopolymers,[1] molecular recognition processes,[2] and crystal packing and engineering.[3] This study can also lead to the development of models of complex systems related to the use of supercritical water to dispose of aromatic environmental contaminants.[4]

Theoretical[5] and experimental[5a,6] studies concluded that the benzene/water (B/W) dimer is held together by a weak hydrogen bond, with an interaction energy (IE) ranging from −6.3 to −12.6 kJ/mol. In the B/W reported structures, the water oxygen always points away from the benzene surface as in **1** or **2** (Figure 1) to avoid electrostatic repulsion, and benzene uses its π electrons to act as a proton acceptor.[7,8] Arrangements **1** and **2** are supported by calculations[5c] and experimental evidence, respectively.[5a]

The hexafluorobenzene/water (HFB/W) dimer has received less attention than the B/W one. Dougherty[9a] and Besnard[9b] calculated that this dimer exists as in **3** (Figure 1) with the water oxygen pointing toward the hexafluorobenzene surface.[10] The IE was found to be ca. −8.4 kJ/mol. The opposite orientation of the water molecule in the B/W and HFB/W dimers was explained[9] by the inversion of polarity experienced by the aromatic system upon perfluorination,[8,11] which transforms a proton acceptor (benzene) into a lone-pair acceptor (hexafluorobenzene).[9,12]

The different geometry of the B/W and HFB/W dimers suggests the possibility of a multiple interaction in which water coordinates benzene and hexafluorobenzene to form a trimeric adduct. Here we report some ab initio calculations showing that two B/W/HFB trimers are more stable than the B/W, HFB/W, and B/HFB (**4**)[11c] dimers.

Methods

All calculations were performed with the GAMESS−US suite of programs.[13] Optimal geometries were computed at the Hartree−Fock level of theory; at these optimal geometries, MP2 correlation contributions were estimated. At the Hartree−Fock level of theory, the basis set superposition error (BSSE) was a priori avoided by employing the SCF-MI (Self-Consistent Field for Molecular Interactions)[14] where Roothaan equations are modified so as to constrain the MOs of each fragment to be expanded in the basis functions located on its atomic centers. According to the SCF-MI method, the determination of all of the important features of the potential energy surface (PES) is not affected by BSSE and geometry relaxation effects are directly included.[14] MP2 results were a posteriori corrected by standard counterpoise (CP) procedure.[15] Because of the size of the systems, the 6-31G*(0.25) basis set[16] (consisting of the standard 6-31G set augmented by a diffuse polarization Gaussian function with an exponent value of 0.25) was adopted. Previous studies on large hydrogen-bonded systems showed that addition of this diffuse function to the basis set significantly improved the accuracy of the results.[17] The structures were optimized with a severe convergence criterion of 1×10^{-5} E_h/a_0 starting in C_1 symmetry and without imposing any geometrical constraint.

Results

Dimers **1-4** were first investigated. In agreement with previous work,[5c] the SCF-MI/6-31G*(0.25) (method A) minimum energy

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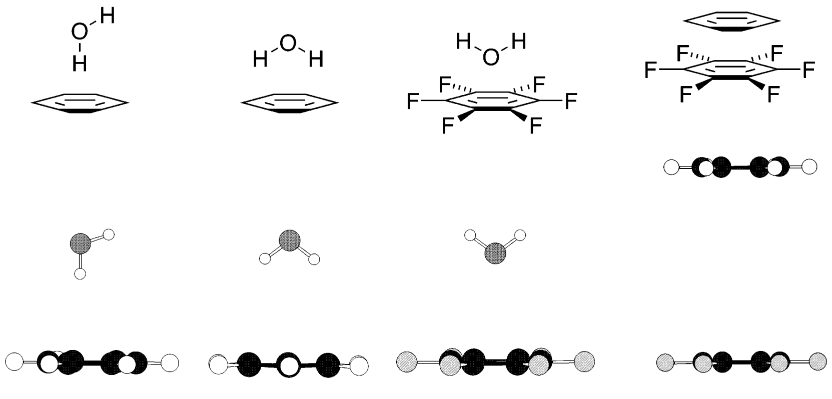
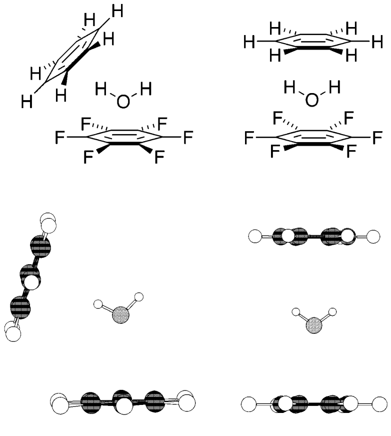
10.1021/jp021775s CCC: $25.00



1 **2** **3** **4**

Figure 1. Calculated Structures for the B/W, HFB/W, and B/HFB complexes.



5 **6**

Figure 2. Calculated structures for the B/W/HFB complexes.

TABLE 1: Interaction Energies (kJ/mol) for Adducts 1−6

adduct	method A[a]	method B[b]	in **5**[a]	in **6**[a]
1	−6.28 (−2.33)[c]	−9.84 (−5.89)	−6.02	
2	−5.23 (−2.03)	−8.42 (−5.22)		−5.17
3	−9.19 (−6.07)[d]	−11.27 (−8.15)	−8.96	−9.07
4	−5.44 (−5.01)	−15.73 (−15.30)		
5	−18.60 (−10.86)	−29.02 (−21.28)		
6	−16.35 (−9.29)	−23.01 (−15.95)		

[a] SCF-MI/6-31G*(0.25). Values in parentheses are zero point energy (ZPE)-corrected values. [b] MP2(CP)/6-31G*(0.25)//SCF-MI/6-31G*(0.25); values in parentheses are zero-point energy (ZPE)-corrected values, with ZPE computed at the SCF-MI level. [c] Calculated interaction energies (kJ/mol) reported in the literature: −7.45 (ref 5a); −10.42 (ref 5b); −16.32 (ref 5c). Calculated oxygen/benzene distances (Å) reported in the literature: 3.20 (ref 5a); 3.21 (ref 5b); 3.24 (ref 5c). [d] Calculated interaction energies (kJ/mol) reported in the literature: −8.70 (ref 9a);-7.57 (ref 9b).

structure of the B/W dimer featured water sitting above the ring and forming a single hydrogen bond with the π electrons, as in **1**. The benzene centroid/oxygen (B/O) distance was 3.74 Å, and the IE = −6.28 kJ/mol. The MP2(CP)/6-31G*(0.25)//SCF-MI/6-31G*(0.25) (method B) calculation gave an IE of −9.83 kJ/mol and a correlation contribution of about 3.6 kJ/mol. To test the suitability of the procedure B, MP2(CP) point by point optimization was performed. The calculation reduced the B/O distance of about 0.2 Å giving an IE of −10.92 kJ/mol: this improvement seems not too excessive, and supports the use of the SCF-MI optimized geometry for the study of the bigger systems (e.g., **5** and **6**), where the CP optimization would be too expensive. Method A calculations gave an equilibrium structure for the HFB/W complex **3** where the water oxygen points toward the hexafluorobenzene surface, (HFB/O distance = 3.40 Å; other values reported in the literature are 3.20[9a] and 3.24[9b]) and an IE = −9.19 kJ/mol which is lower than that of the B/W system. The MP2 calculations, method B, estimated a correlation contribution of 2.08 kJ/mol, leading to an IE = −11.27 kJ/mol. Finally, the parallel stacked B/HFB adduct **4** was predicted in an eclipsed conformation with an IE of −5.44 (method A) and −15.73 kJ/mol (method B): this arrangement can be interpreted as favorite by the interaction of the opposite dipole moments located on the CH and CF bonds.

The calculations on the B/W/HFB complex PES located two main stationary points (Figure 2).[18] The lower energy adduct **5**, IE = −18.60 (method A) and −29.02 kJ/mol (method B) featured the water molecule sitting between the aromatic systems arranged in tilted planes (interplanar angle ca. 70°) and interacting with benzene using only one hydrogen atom (B/O distance = 3.65 Å). In complex **6**, IE = −16.35 (method A) and −23.01 kJ/mol (method B), the rings lie in parallel planes adopting a stacked arrangement (interaromatic distance = 6.98 Å; HFB/O distance = 3.34 Å) and sandwiching the water molecule which interacts with benzene using both hydrogens.

System **5** was calculated to be 2.25 and 6.01 kJ/mol more stable than **6** at the SCF-MI and MP2 levels, respectively. An interpretation of the different stability of these complexes was obtained by calculating, at the SCF-MI level, the interaction energy of each pair of molecules in the trimer arrangement. The three body contribution was then estimated as the difference between the trimer stabilization energy and the total pair interaction. This analysis showed that the many body contributions for both structures were comparable (−1.16 and −1.06 kJ/mol for **5** and **6**, respectively). The B/W interaction stabilizes **5** more than **6** by about 0.85 kJ/mol (−6.02 vs −5.17 kJ/mol), in agreement with the lower energy of the one-H-bonded adduct **1** (−6.28 kJ/mol) with respect to the two-H-bonded complex **2** (−5.23 kJ/mol), whereas the B/W stabilization decreases only slightly upon formation of the trimers. The contribution of the W/HFB interaction is virtually the same in both complexes **5** and **6** (−8.96 and −9.07 kJ/mol) and very similar to that of adduct **3** (−9.19 kJ/mol). From the results of the previous analysis, it turns out that the major contribution to the higher stability of **5** arises from the B/HFB interaction, 1.41 kJ/mol more attractive in **5** (−2.46 kJ/mol) than in **6** (−1.05 kJ/mol). Apparently, **5** profits of the attractive electrostatic interaction between the oppositely charged peripheries of the aromatic rings that are within contact distance in this complex (shorter H/F distance in **5** = 3.23 Å). Thus, because the many body contribution is very similar in both trimers, the higher stability of **5** can essentially be ascribed to the B/HFB electrostatic interaction more attractive in **5** than in **6**.

In conclusion, it was shown for the first time by ab initio calculations the existence of two stationary points on the PES of the B/W/HFB complexes. The geometry of the complexes has been optimized imposing severe convergence thresholds without constraints on the degrees of freedom. ZPE calculations have been performed at the SCF-MI level; the existence of small frequencies suggests that the couplings among the intermolecular modes can be relevant. Nevertheless, these vibrations give a small contribution to the value of ZPE so that the harmonic approximation for the calculation of ZPE seems acceptable. The binding energy for systems **5** and **6** at the SCF-MI level results equal to 10.86 and 9.29 kJ/mol, respectively. For method B, an estimate of the dissociation energy has been obtained by adding the ZPE computed at the SCF-MI level to the interaction energy evaluated with method B: the resulting values of the dissociation energy are 21.28 and 15.95 kJ/mol, for systems **5** and **6**, respectively.

Acknowledgment. Financial support by MIUR-FIRB is gratefully acknowledged.

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(18) On purely electrostatic grounds, a fully in-plane complex arrangement is possible with water hydrogens pointing toward the fluorine atoms on one side and water oxygen toward the benzene hydrogens on the other side. It is unlikely that this structure is stable, as the fully in-plane disposition of water and hexafluorobenzene is a transition state separating the topomers of **3** (ref 9a) and organic fluorine hardly ever accepts hydrogen bonds (ref 9c).