Characteristics of Antiaromatic Ring π Multi-Hydrogen Bonds in $(H_2O)_n-C_4H_4$ ($n = 1, 2$) Complexes

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Received: February 8, 2006; In Final Form: April 15, 2006

By counterpoise-corrected optimization method, the six antiaromatic ring π multi-hydrogen bond structures with diversiform shapes for $(H_2O)_n-C_4H_4$ ($n = 1,2$) have been obtained at the MP2/aug-cc-pVDZ level. At the CCSD(T)/aug-cc-pVDZ level, the interaction energy obtained mainly depends on the numbers of H_2O and fold numbers of the π multi-hydrogen bond. The interaction energy order is -2.342 (1a with π mono-hydrogen) < -2.777 (1b with π bi-hydrogen) $\ll -4.683$ (2a with π bi-hydrogen) < -4.734 (2b with π tri-hydrogen) < -4.782 (2c with π tri-hydrogen) < -5.009 kcal/mol (2d with π tetra-hydrogen bond). Strangely, why is the interaction energy of the π bi-hydrogen bond in 1b close to that of the π mono-hydrogen bond in 1a (their difference is only 15.7%)? The reason is that a π-type H-bond (as an accompanying interaction) between two lone pairs of the O-atom and a near pair of H-atoms of C_4H_4 exists shoulder by shoulder in structures 1a, 2a, 2b, and 2c and contributes to the interaction energy. Another accompanying interaction, a repulsive interaction between the π H-bond (using the H-atom(s) of H_2O) and the near pair of H-atoms of C_4H_4, is also found. For the structures and interaction energies, the π-type H-bond produces four effects: bending the strong π H-bond, attracting the pair of H-atoms of C_4H_4 so that they deviate from the C_4 ring plane, showing the interaction energy contribution, and bringing the larger electron correlation contribution. The repulsive interaction also produces four effects: pushing the pair of H-atoms of C_4H_4 so that they deviate from its ring plane, elongating the distance of the π H-bond, promoting the formation of π-type H-bond, and slightly influencing the interaction energy. In the present paper, one C═C bond with two H_2O (over and below the ring plane) forms a π H-bond link in two ways: a strong−weak π H-bond link and a strong−strong π H-bond link. The stability contribution of the former is more favorable than the latter. One H_2O forms a π H-bond with C_4H_4 in two ways. One strong π H-bond part (over or below the ring plane) always is accompanied by another H-bond part. The accompanying part is either a weak π H-bond or π-type H-bond.

1. Introduction

The hydrogen bond (H-bond) has attracted much attention because of its important roles in chemistry and biology.[1] With progress in the study on the H-bond, a number of unusual H-bonds have been proposed during the past few decades, for example, the π H-bond denotes an H-bond with the π-system acting as a proton acceptor.[2] The dihydrogen bond is used to describe the H···H type H-bond in which an H-atom with a partial negative charge acts as the proton acceptor.[3] In recent papers,[4] in $(FH)_2\{e\}(HF)_2$,[4a,b] the loosely bound (excess) electron can form a bridge to connect separate hydrogen fluoride dimers and it acts as the acceptor of the two H-atoms. In $H_3C\cdots HF$ and $H_3C\cdots HCCH$, the unpaired electron of a proton acceptor can form a single-electron H-bond.[4c]

The investigation on π H-bond complexes has held the interests of researchers. Some experimental and theoretical work on π H-bond complexes has been completed and mainly summarized in the following four review articles:[5] the structure of microsolvated benzene derivatives and the role of aromatic substituents π-complexes;[5a] molecular clusters of π-systems (theoretical studies of structures, spectra, and origin of interaction energies);[5b] H-bonding and van der Waals complexes studied by ZEKE and REMPI spectroscopy;[5c] prereactive complexes of dihalogens XY with Lewis bases B in the gas phase—a systematic case for the halogen analogue B···XY of the H-bond B···HY.[5d]

Theoretical investigations have focused their attention on the role of the H-bond system in governing the structure and reactivity of complexes containing H_2O. Investigations of the π H-bond with H_2O molecule interactions contain: ethene−H_2O, benzene−H_2O, and benzene−$(H_2O)_2$,[2a,6] π-$(H_2O)_n$ ($n = 1-4$) complexes,[7] fluorobenzene−H_2O, and difluorobenzene−H_2O systems.[8] As above, the ring π H-bond complexes in the references all have ($n \mid 0$) structures (n molecules over the ring plane and no molecule below the plane) and contain aromatic ring π H-bonds. Interestingly, a π ring of an antiaromatic system acts as an acceptor of the two hydrogen atoms to form an antiaromatic ring π H-bond in the ($n \mid n$) structure; it is a HF−C_4H_4−HF antiaromatic system.[9] Obviously, a H_2O molecule is more complex than a HF molecule. It is reasonable to consider that the π H-bond complexes containing H_2O and an antiaromatic C_4H_4 ring should show different characteristics of H-bond structures. The characteristics are different from that of the HF−C_4H_4−HF antiaromatic ring π H-bond [9] and of aromatic benzene−$(H_2O)_n$ ($n = 1, 2$).[6]

This paper aims at exhibiting new ($1 \mid m$) ($m = 0, 1$) antiaromatic ring π multi-hydrogen bond structures, finding the

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10.1021/jp060823w CCC: $33.50

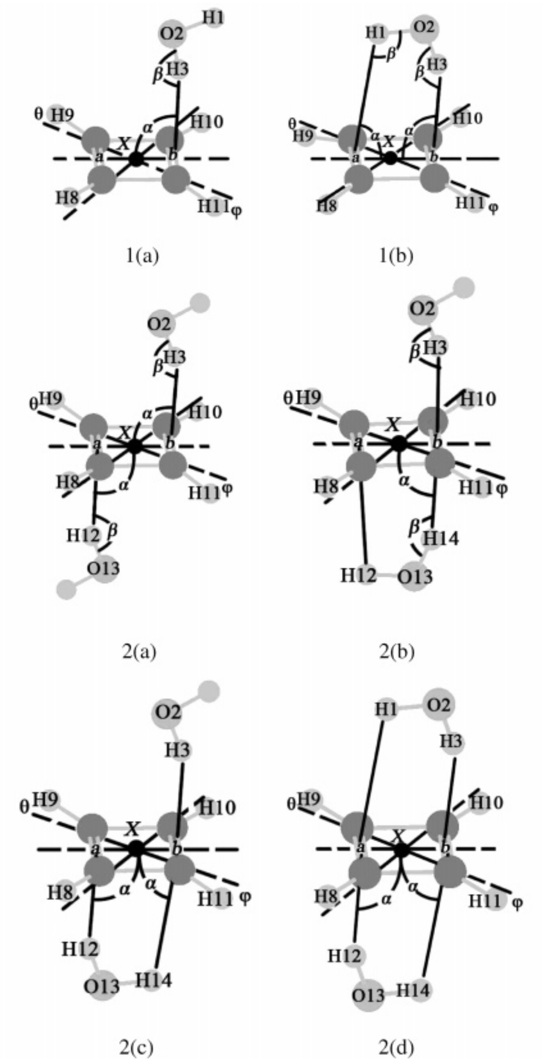


Figure 1. Optimized geometries of six π multi-hydrogen bond structures.

π H-bond interaction energy dependence, exploring accompanying interactions and their effects on the structures and interaction energies, revealing characteristics of the H_2O molecule and C═C bond to form an H-bond in $(H_2O)_n-C_4H_4$ (n = 1, 2), and enriching the knowledge on novel weak interactions in an exciting part of chemistry.

2. Computational Details

The computations were performed using Dunning's augmented correlation-consistent polarized valence basis sets of contracted Gaussian functions,[10] aug-cc-pVDZ. The optimum configurations and harmonic vibrational frequencies for the complexes $H_2O-C_4H_4$ and $H_2O-C_4H_4-H_2O$ were computed including valence electron correlation via second-order Møller−Plesset (MP2) theory in conjunction with the basis set. Geometrical optimizations at the MP2/aug-cc-pVDZ level were carried out on different conformations of $H_2O-C_4H_4$ and $H_2O-C_4H_4-H_2O$ complexes (shown in Figure 1 and Table 1). In geometrical optimization calculations, "standard PES (potential energy surface)" (with Opt keyword) and "CP (counterpoise)-corrected PES" (with Counterpoise and Opt keywords) methods are used. By the use of the CP procedure,[11] the intermolecular interaction energies of the $H_2O-C_4H_4$ and $H_2O-C_4H_4-H_2O$ complexes were calculated at the MP4/aug-cc-pVDZ level and CCSD(T)/aug-cc-pVDZ level, respectively.

The interaction energies E_{int} have been calculated as the difference between the energy of the complex and the sum of the energy of the monomers by the following formula[12]

$$E_{\text{int}} = E_{\text{ABC}}(X_{\text{ABC}}) - E_{\text{A}}(X_{\text{ABC}}) - E_{\text{B}}(X_{\text{ABC}}) - E_{\text{C}}(X_{\text{ABC}}) \quad (1)$$

To eliminate the basis set superposition error (BSSE) effect in the interaction energy given by the eq 1, we use the same basis set, X_{ABC}, for the monomer calculation as well as for the dimer and trimer calculations.

The electron correlation effect is important in the calculation of interaction energy. The contribution (ΔE_{corr}) of electron correlation is denoted by the following formula

$$\Delta E_{\text{corr}} = E_{\text{int}}^{\text{CCSD(T)}} - E_{\text{int}}^{\text{HF}} \quad (2)$$

and

$$\eta(\%) = \Delta E_{\text{corr}}/E_{\text{int}}^{\text{CCSD(T)}} \times 100\% \quad (3)$$

All of the calculations were performed with the GAUSSIAN 03 program package.[13]

3. Results and Discussions

3.1. Equilibrium Geometries and the Antiaromatic Ring π Multi-Hydrogen Bond.

The optimized structures of the π H-bond complexes $(H_2O)_n-C_4H_4$ (n = 1,2) and related structures have been obtained at the MP2/aug-cc-pVDZ level, as shown in Table 1. From Table 1, the optimized configurations from a CP-corrected potential energy surface (PES) and standard PES methods are different for $H_2O-C_4H_4$ and $H_2O-C_4H_4-H_2O$ complexes.

For the intermolecular π H-bond length R(H···a) or R(H···b) between the H-atom of H_2O and the middle-point a or b of the C═C bond, the CP-corrected PES result is longer by 0.13 Å than that from the standard PES. The difference is similar to those in simple H-bonded systems.[11b] Table 1 shows two π H-bond length ranges of 2.412−2.459 and 3.261−3.290 Å, respectively. The qualitative classifications of weak and strong π H-bonds are related to the bond lengths only in this paper. The short bond length range (2.412−2.459 Å) corresponds to the strong π H-bond and the long range (3.261−3.290 Å) corresponds to the weak π H-bond.

For the intermolecular angle α (H···a (or b)···X) (where X is the center point of the C_4 ring), the CP-corrected PES result is larger by about 5° than that from the standard PES, while the structures of the H_2O and C_4H_4 subunits themselves are unchanged. In the following sections of this paper, the accurate structures from the CP-corrected PES are used for $(H_2O)_n-C_4H_4$ (n = 1,2) complexes (see Figure 1 and Table 1).

3.1.1. $H_2O-C_4H_4$ Complex. For the $H_2O-C_4H_4$ complex, two antiaromatic ring π multi-hydrogen bond structures with C_s symmetry are obtained.

Structure 1a is a "wheel with a handle" shaped (1 | 0) structure with a π mono-hydrogen bond (see Figure 1, structure 1a), in which one acidic H-atom of H_2O and one C═C π bond form a π H-bond over the C_4 ring plane. In the π mono-hydrogen bond formation, the proton acceptor is a C═C π bond of the C_4H_4 ring and the donor is an acidic H3 atom of H_2O (see Figure 2, structure 1a). The length R(H3···b) is short at 2.421 Å, and the π H-bond is strong. The H-bond angle β(O2−H3···b) is the largest at 169.3° among all the H-bond angles. Two pairs of H-atoms of the C_4H_4 ring deviated from the C_4 ring plane. One pair of H-atoms (H10 and H11) near the strong π H-bond is below the ring plane with φ = −2.25°. The other pair of

TABLE 1: Selected Geometrical Parameters of $(H_2O)_n-C_4H_4$ ($n = 1,2$) at the MP2/aug-cc-pVDZ Level with CP Correction[a]

	1a	1b	2a	2b	2c	2d
R(H1···a)		3.261 (3.087)[c]				3.290 (3.225)
R(H3···b)	2.421 (2.299)	2.434 (2.302)	2.412 (2.290)	2.439 (2.315)	2.430 (2.304)	2.458 (2.304)
R(H12···a)				3.271 (3.094)	3.271 (3.095)	3.290 (3.225)
R(H14···b)			2.412 (2.290)	2.452 (2.314)	2.445 (2.312)	2.459 (2.304)
R(O2···X)	3.422 (3.234)	3.381 (3.226)	3.350 (3.180)	3.383 (3.202)	3.364 (3.188)	3.404 (3.267)
R(O13···X)			3.350 (3.181)	3.393 (3.238)	3.390 (3.235)	3.404 (3.267)
α(H1···a···X)		85.0 (86.8)				85.1 (85.5)
α(H3···b···X)	89.6 (83.9)	89.6 (87.2)	89.1 (85.1)	89.1 (84.4)	89.0 (84.8)	89.5 (87.1)
α(H12···a···X)			89.1 (85.1)	85.4 (87.0)	89.6 (87.5)	89.5 (87.1)
α(H14···b···X)				89.1 (87.2)	85.0 (86.7)	85.1 (85.5)
β(O2−H1···a)		101.0 (100.7)				100.6 (95.8)
β(O2−H3···b)	169.3 (170.7)	161.2 (162.4)	160.8 (161.7)	161.9 (162.7)	160.7 (161.6)	161.4 (168.1)
β(O13−H12···a)			160.8 (161.7)	100.8 (100.8)	161.0 (161.6)	161.4 (168.1)
β(O13−H14···b)				161.5 (162.4)	101.0 (100.8)	100.6 (95.8)
θ[d]	1.20° [f]	−0.68°	3.71°	2.07°	2.73°	0.75°
φ[e]	−2.25°	−1.38°	−3.71°	−0.79°	−1.52°	−0.72°

[a] Bond lengths (R) are in angstroms, and angles (α, β, θ, and φ) are in degrees. [b] R(H1···a) is the distance between the H1 and the center point "a" of a C═C bond. [c] Data without CP in parentheses. [d] θ is for the H8 and H9 atoms deviating from the plane. [e] φ is for the H10 and H11 atoms deviating from the plane. [f] The positive value is for over the ring plane and the negative for below the ring plane.

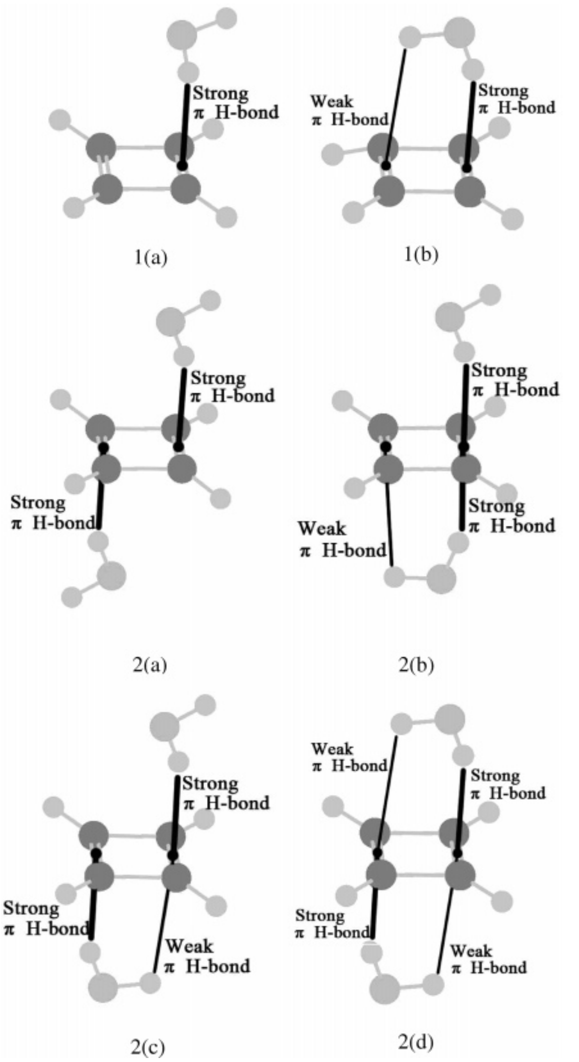


Figure 2. π H-bond part between the C═C bond of C_4H_4 and the H-atom(s) of H_2O: the thick line represents the strong π H-bond part and the thin line represents the weak π H-bond part.

H-atoms (H8 and H9) deviates from the ring plane to tend to the O-atom of H_2O with $\theta = 1.20°$.

Structure 1b is a "basket" shaped (1 | 0) structure with a π bi-hydrogen bond, in which each C═C π bond of the C_4H_4 ring accepts an H-atom of H_2O and forms a π bi-hydrogen bond over the ring plane. But the lengths R(H3···b) and R(H1···a) are different, 2.434 Å for the short R(H3···b) and 3.261 Å for the long R(H1···a) (see Figure 1, structure 1b). Therefore, the H3 atom and the near C═C bond form a strong π H-bond part (it is slightly longer than the 2.421 Å of structure 1a), and the H1 atom and the other C═C bond form a weak π H-bond part. So, the π bi-hydrogen bond includes two parts (a strong and a weak part) over the ring plane. The corresponding H-bond angle β(O2−H3···b) of 161.2° is smaller by about 8° than that of structure 1a. This shows that the strong π H-bond is bent by the weak π H-bond. Two pairs of H-atoms of C_4H_4 are both below the ring plane with smaller φ and θ values.

3.1.2. $H_2O-C_4H_4-H_2O$ Complex. For the $H_2O-C_4H_4-H_2O$ complex, four different geometrical structures are obtained, which have C_{2h}, C_s, C_s, and C_{2h} symmetries, respectively.

Structure 2a is an antiaromatic ring π bi-hydrogen bond structure with C_{2h} symmetry. Compared with the (1 | 0) structure 1a, it has one more π H-bond below the C_4 ring plane. Structure 2a exhibits a ‘‘wheel with a pair of pedals" shaped (1 | 1) structure (see Figure 2, structure 2a). In structure 2a, the two lengths R(H3···b) and R(H12···a) are equal at 2.412 Å, which is close to the R(H3···b) length of 2.421 Å in structure 1a. This means that these two π H-bonds are strong in 2a, and it is different from the one strong and one weak π H-bond in 1b. The two H-bond angles β(O2−H3···b) and β(O13−H12···a) of 160.8° are smaller by about 9° than the angle β(O2−H3···b) in structure 1a. It shows that two strong π H-bonds are more obviously bent in structure 2a. Two pairs of H-atoms of C_4H_4 deviate from the C_4 ring plane with bigger angles of $\varphi = 3.71°$ for H8 and H9 and $\theta = -3.71°$ for H10 and H11 atoms. Those angles are bigger than the corresponding ones in structure 1a. The bigger bends of the two strong π H-bonds and deviations of the two pairs of H-atoms from the C_4 ring plane indicate the existence of some accompanying interactions.

On the basis of structure 1b, we add one H_2O by two ways (a H-atom of the H_2O molecule adding to the two different C═C π bonds, respectively) to form structures 2b and 2c. Structures 2b and 2c both are (1 | 1) π tri-hydrogen bond structures with C_s symmetry (see Figure 1). Structures 2b and 2c contain one strong π H-bond part (over the C_4 ring plane) that is similar to that in structure 1a. The lengths R(H3···b) in structures 2b and 2c are longer by about 0.02 Å (2.439 Å for structure 2b and

TABLE 2: Interaction Energy (in kcal/mol) Using the aug-cc-pVDZ Basis Set

	1a	1b	2a	2b	2c	2d
HF	−0.903 (−1.426)[a]	−1.329 (−1.839)	−1.557 (−2.639)	−1.766 (−2.793)	−1.768 (−2.809)	−2.125 (−3.122)
MP2	−2.679 (−4.216)	−3.100 (−4.615)	−5.403 (−8.495)	−5.353 (−8.264)	−5.430 (−8.416)	−5.595 (−8.478)
MP4(SDQ)	−2.197 (−3.660)	−2.626 (−4.076)	−4.368 (−7.303)	−4.422 (−7.197)	−4.470 (−7.317)	−4.700 (−7.463)
MP4(SDTQ)	−2.549 (−4.212)	−2.995 (−4.650)	−5.125 (−8.440)	−5.143 (−8.282)	−5.210 (−8.435)	−5.422 (−8.561)
CCSD(T)	−2.342 (−3.971)	−2.777 (−4.397)	−4.683 (−7.931)	−4.734 (−7.809)	−4.782 (−7.941)	−5.009 (−8.081)

[a] Data without CP in parentheses. The structures are from CP correction.

2.430 Å for 2c) than that in structure 1a. Below the ring plane, in structure 2b, there is a weak π H-bond located on the left side and a strong π H-bond located on the right side. On the contrary, in structure 2c, there is a strong π H-bond located on the left side and a weak π H-bond located on the right side (see Figure 1, structures 2b and 2c). Interestingly, on the right side, one C═C bond with two H-atoms of two different H_2O molecules forms a π H-bond link, which is a strong−strong π H-bond link in 2b but strong−weak π H-bond link in 2c. Two pairs of H-atoms of C_4H_4 deviate from the C_4 ring plane, which is related to accompanying interactions. On the left side, the $\varphi = 2.07°$ angle of structure 2b and 2.73° angle of 2c are bigger than $\varphi = 1.20°$ in structure 1a. On the right side, the $\theta = -0.79°$ angle of 2b and −1.52° angle of 2c are smaller than $\theta = -2.25°$ in structure 1a.

Structure 2d is a (1 | 1) π tetra-hydrogen bond structure with C_{2h} symmetry. In the structure, the π H-bond part over the C_4 ring plane is similar to that in structure 1b, and the π H-bond part below the ring plane is similar to that below the ring plane in structure 2c. Structure 2d is an "intersecting of two rings" shaped structure with an antiaromatic ring π tetra-hydrogen bond. In structure 2d, the two couples of π H-bonds act as two bridges (over and below the C_4 ring plane), spanning the ring to form a cyclic π tetra-hydrogen bond structure intercrossing with the C_4 ring. The π H-bond lengths of structure 2d are the longest (2.458 Å for the short bond and 3.290 Å for the long bond) among all of the six complexes. It is interesting that each C═C bond with two H_2O only forms a strong−weak π H-bond link. Two pairs of H-atoms of C_4H_4 deviate from the C_4 ring plane with smaller angles ($\varphi = 0.75°$ and $\theta = -0.72°$).

A comparison with the related complexes is interesting.

In $H_2O-C_4H_4$, the distances (about 3.38 Å in structures 1a and 1b) between the O-atom and the middle point of the C═C bond are longer by 0.1 Å than the 3.286 Å length in H_2O−ethene.[6] The distance (3.381 Å in 1b) between the O-atom and the center of the ring is close to 3.380 Å in H_2O−benzene.[6] When two "wheel with a pair of pedals" shaped structures are compared, the length of the π H-bond in structure 2a is 0.23 Å longer than the 2.185 Å length in $FH-C_4H_4-HF$,[9] which comes from the large electronegativity of the F-atom. These show that our structures are reasonable.

3.2. Interaction Energies and Accompanying Interactions. On the basis of the CP-optimized geometries of the $H_2O-C_4H_4$ and $H_2O-C_4H_4-H_2O$ complexes, the interaction energies have been calculated at the HF, MP2, MP4, and CCSD(T) levels with the aug-cc-pVDZ basis set, using the CP and NCP (no counterpoise) procedure and listed in Table 2. From Table 2, the HF interaction energy is underestimated and MPn (n = 2, 4) calculations overestimate interaction energy values.The NCP interaction energy with BSSE is too large. This shows that the CCSD(T) with CP method is necessary for interaction energy calculation in this work.

TABLE 3: Electron Correlation Effect[a]

	1a	1b	2a	2b	2c	2d
HF	−0.903	−1.329	−1.557	−1.766	−1.768	−2.125
CCSD(T)	−2.342	−2.777	−4.683	−4.734	−4.782	−5.009
ΔE_{corr}[b]	−1.439	−1.448	−3.126	−2.968	−3.014	−2.884
$\eta(\%)$[c]	61.4	52.1	66.8	62.7	63.0	57.6

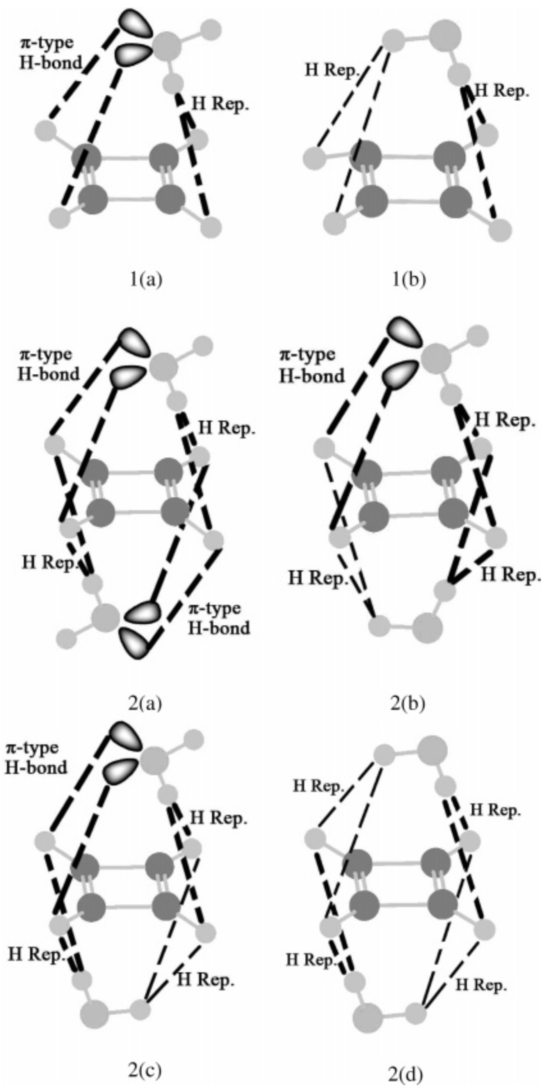
[a] Energy in kcal/mol. [b] $\Delta E_{corr} = E_{int}^{CCSD(T)} - E_{int}^{HF}$. [c] $\eta(\%) = \Delta E_{corr}/E_{int}^{CCSD(T)} \times 100\%$.

The electron correlation effect is important in the calculation of interaction energy. The contributions of electron correlation (ΔE_{corr}) [CCSD(T)-HF] are −1.448 (52.1%) for 1b < −1.439 (61.4%) kcal/mol for 1a for dimers and −2.884 (57.6%) for 2d < −2.968 (62.7%) for 2b < −3.014 (63%) for 2c < −3.126 (66.8%) kcal/mol for 2a for trimers (see Table 3). It is obvious that, in the π H-bond systems, the electron correlation effect is important for the interaction energy calculation. So, the CCSD(T) interaction energies (with CP corrections) are used in the next discussions.

3.2.1. Interaction Energies. Obviously, the interaction energies of various configurations are different. The interaction energy mainly depends on the numbers of H_2O molecules and the fold number of π multi-hydrogen bonds. The order is −2.342 for 1a with π mono-hydrogen < −2.777 for 1b with π bi-hydrogen bond (over the C_4 plane) ≪ −4.683 for 2a with a π bi-hydrogen bond (over and below the C_4 plane) < −4.734 for 2b with a π tri-hydrogen bond (strong−strong link on the right side) < −4.782 for 2c with a π tri-hydrogen bond (strong−weak link on the right side) < −5.009 kcal/mol for 2d with a π tetra-hydrogen bond (each side, strong−weak link). It is interesting that a strong−weak π H-bond link on the same C═C bond is better than the strong−strong π H-bond link at enhancing interaction energy.

Compared with the related complex, the interaction energy of structure 1a of $H_2O-C_4H_4$ is smaller by 0.48 kcal/mol than the energy of −2.82 kcal/mol of H_2O−benzene.[6] The interaction energy of 1b is close to that of H_2O−benzene.[6] This shows that the stability of $H_2O-C_4H_4$ is slightly lower than that of H_2O−benzene. When complexes $H_2O-C_4H_4$ and H_2O−ethene are compared,[6] the interaction energy of structure 1a is larger by 0.09 kcal/mol than the −2.25 kcal/mol value for H_2O−ethene. The interaction energy of 1b is larger by 0.52 kcal/mol than that of H_2O−ethene. This shows that the stability of $H_2O-C_4H_4$ is slightly lower than that of H_2O−benzene and higher than that of H_2O−ethene.[6] Compared with the ''wheel with a pair of pedals" shaped structure of $HF-C_4H_4-HF$,[9] the interaction energy of structure 2a for $H_2O-C_4H_4-H_2O$ is smaller by 3.1 kcal/mol than the −7.8 kcal/mol value for $HF-C_4H_4-HF$. This shows the capability of H_2O to form a π H-bond that is weaker than that of HF.

3.2.2. Accompanying Interactions. Interestingly, using simple electrostatic model and taking two different π H-bond lengths (2.4 and 3.3 Å), the interaction energy difference ((1b − 1a)/1b) between structure 1b with a bi-hydrogen bond and structure 1a with a mono-hydrogen bond is roughly estimated to be 40% (from one weak π H-bond). However, the difference is small (15.7%). And the interaction energy difference between structure 2d with a tetra-hydrogen bond and structure 2a with



1(a) 1(b)

2(a) 2(b)

2(c) 2(d)

Figure 3. Accompanying interactions in the six complexes: π-type H-bond and H Rep. (the repulsive interaction between the H-atom(s) of H_2O and the near pair of H-atoms of C_4H_4): the thick, broken line represents the strong interaction and the thin, broken line represents the weak interaction.

a bi-hydrogen bond should also be large (from two weak π H-bonds, also 40%), but it is very small (6.5%). Why? Other interactions might exist and make a contribution to the interaction energy in π multi-hydrogen bond structures.

According to expectation, we truly find an accompanying attractive interaction. The attractive interaction is a π-type (shoulder by shoulder) H-bond between a lone pair of the O-atom and a near pair of H-atoms of C_4H_4.

An accompanying repulsive interaction between an H-atom of H_2O and a near pair of H-atoms of C_4H_4 is also found. Figure 3 illuminates the two accompanying interactions in the six π multi-hydrogen bond structures. Two accompanying interactions can also affect the structures and the interaction energies, besides the above-discussed π multi-hydrogen bond interaction.

The π-type H-bond model is first proposed to illustrate and interpret the deviations from a strictly linear H-bond X$\cdots$H$-$Y (σ-type H-bond) in the dimers. The π-type H-bond interaction is an attraction between the H-atoms of the H$-$X bond and the lone pair on Y where the lone pair (proton acceptor) is roughly parallel to the H$-$X bond of the proton donor.[9,14] The orientations of unbounded lone pairs in optimized equilibrium structures are important for understanding the formation of the π-type hydrogen bond. In our previous work,[14] using the probing point charge ($q = -1$), we scanned the energies of the dimers in different planes and angles to find the extreme values and determine the orientations of the lone pairs. In H_2O, the calculated angle between two lone pairs is 108°, which shows that the O-atom is sp^3 hybridized and the geometry of the electron pairs (and H$-$O bonds) is tetrahedral. In this paper, the lone pairs plane of the O-atom and the C_4H_4 ring plane can almost be parallel.

From Figure 3, in structures 1a, 2a, 2b, and 2c, besides forming one strong π H-bond (without a weak π H-bond) between one H-atom of H_2O over the C_4 ring plane and one C$=$C π bond of the ring, two lone pairs on the O-atom of H_2O and a near pair of H-atoms of C_4H_4 are roughly parallel and close to each other, thus a π-type H-bond is formed. It leads to the bend of the strong π H-bond with H-bond angle $\beta(\mathrm{O2}\cdots\mathrm{H3}\cdots\mathrm{b}) = 169.3-160.7°$ (out of 180°), and the pair of H-atoms (H8 and H9) of C_4H_4 is shifted toward two lone pairs on the O-atom over the ring plane and deviates from the C_4 ring plane with $\varphi = 1.20-3.71°$ (see Figure 1 and Table 1).

The π bi-hydrogen bond structure 1b contains one strong π H-bond part and one weak π H-bond part; the π mono-hydrogen bond structure 1a contains not only one strong π H-bond part but also one π-type H-bond part. So the interaction energy difference between structures 1b and 1a should be a difference between the weak π H-bond and the π-type H-bond, but it is not a difference between the bi-hydrogen bond and mono-hydrogen bond.

The existence of the π-type H-bond is the reason for such a small interaction energy difference (15.7%). Because of the same reason, we can understand the very small difference (6.5%) between the tetra-hydrogen bond structure 2d (with two strong π H-bond parts and two weak π H-bond parts) and the bi-hydrogen bond structure 2a (with two strong π H-bond parts and two π-type H-bond parts).

To further exhibit the individual interaction energies of H-bonds including the π-type H-bond, we design a model structure based on structure 1a, where the π H-bond length taken from structure 1b was the weak π H-bond length of 3.261 Å. The H_2O part and C_4H_4 part are kept the same as that in structure 1a. Obviously, the distance between the O-atom and the pair of H-atoms of C_4H_4 is about 5.0 Å, and the π-type H-bond can be neglected. Thus, the interaction energy of the model structure is about that of one weak π H-bond. At the CCSD(T)/aug-cc-pvdz level with the CP correction, the interaction energy calculated of one weak π H-bond is about -1.111 kcal/mol.

In structure 1b with a bi-hydrogen bond, the interaction energy (-2.777 kcal/mol) comes from two contributions of one strong π H-bond and one weak π H-bond. As above, we can roughly estimate the interaction energy of one strong π H-bond to be about -1.6 kcal/mol.

In structure 1a with one strong π H-bond and one π-type H-bond, we roughly estimate the interaction energy of one π-type H-bond to be about -0.8 kcal/mol. Hence, the order of interaction energies can be obtained as -1.6 (of a strong π H-bond) > -1.1 (of a weak π H-bond) > -0.8 kcal/mol (of a π-type H-bond). When the strong π H-bond and the weak π H-bond are compared, a logical coherence between the interaction energy ratio (1.5:1) and the inverse ratio (1.4:1) of the lengths becomes interesting.

Using the three kinds of H-bond energy values, we can roughly estimate the interaction energy difference ((1b $-$ 1a)/1b). The difference is about 11.1%, which is consistent with the 15.7% from the interaction energies of the two complexes.

These results can explain the differences between interaction energies of the other studied complexes.

It is interesting that π multi-hydrogen bond structures with a π-type H-bond (1a, 2a, 2b, and 2c) have larger electron correlation contributions ($\eta = 61.4-66.8\%$) of interaction energy. For π multi-hydrogen bond structures without the π-type H-bond, 1b and 2d, the contributions are only $\eta = 52.1-57.6\%$. This shows that the electron correlation contribution of the interaction energy is important and also relates to the π-type H-bond.

As above, the π-type H-bond produces four effects for the structures and interaction energies. First, the π-type H-bond leads to the bend of the strong π H-bond with H-bond angles (169.3−160.7°) (see Table 1 and Figure 3, structures 1a, 2a, 2b, and 2c). Second, the π-type H-bond attracts the corresponding pair of H-atoms (H8 and H9) of C_4H_4 to deviate from the C_4 ring plane toward the O-atom of H_2O. Third, because of the existence of the π-type H-bond, the interaction energy differences are small, 15.7% (between 1b and 1a) and 6.5% (between 2d and 2a). Fourth, for the electron correlation contribution, the π multi-hydrogen bond structures with a π-type H-bond are larger than those without a π-type H-bond.

Thus, we find that the H-bond interaction between H_2O and the C_4H_4 ring gives two types. Each type includes two parts. First, two H-atoms of H_2O form a π bi-hydrogen bond on one side (over or below) of the C_4 ring plane; the bi-hydrogen bond includes one strong π H-bond part and one weak π H-bond part. Second, one H-atom of H_2O forms a π mono-hydrogen bond that is a strong π H-bond, and the two lone pairs of the O-atom of H_2O from a π-type H-bond part to accompany the strong π H-bond part.

Next, we discuss another accompanying interaction, a repulsive interaction between the H-atom(s) of H_2O (in the π H-bond) and the near pair of H-atoms of C_4H_4. This repulsion may be seen as the interaction between a π H-bond and the pair of H-atoms of C_4H_4 and also affects the structure and interaction energy.

In structures 1a and 1b, the repulsive interaction pushes the corresponding pairs of H-atoms to deviate from the C_4 ring plane with small angles: 2.25° (from a strong π H-bond) in the 1a, 0.68° (from a weak π H-bond), and 1.38° (from a strong π H-bond) in the 1b, respectively. In structures 2b, 2c, and 2d (see Figure 2), the one C═C bond can link two π H-bonds and the two H-atoms of two different H_2O molecules have two repulsive effects on the corresponding pair of H-atoms of C_4H_4 over and below the ring plane. Thus, the two repulsive interactions weaken each other, so the corresponding pair of H-atoms of C_4H_4 deviates from the C_4 ring plane with a smaller angle, for example, $\varphi = 0.7°$ in 2d.

The repulsive interaction between the H-atom in the π H-bond (over the ring plane) and the near pair of H-atoms of C_4H_4 leads to the pair of H-atoms of C_4H_4 deviating downward from the ring plane, which leads to an increase in the repulsive interaction between the pair of H-atoms and the H-atom (in a π H-bond) below the ring plane. So, the π H-bonds lengths are elongated in the same C═C bond linked to two π H-bonds. For example, in the tri-hydrogen bond structures 2b and 2c, the lengths of the strong π H-bond over the ring plane (2.439 and 2.430 Å) are larger than the corresponding 2.421 Å length in structure 1a. As above, the repulsive interactions between the H-atom in the π H-bond and the pair of H-atoms essentially are the repulsive interaction between two π H-bonds on the same C═C bond through the pair of H-atoms of C_4H_4.

The repulsive interaction also relates to the π-type H-bond. For example, in the left side of the structure 2a, besides the attraction of the π-type H-bond between the O2 and the pair of H-atoms (H8 and H9), the repulsive interaction of the H12 atom (in the π H-bond) also pushes the pair of H-atoms (H8 and H9) shifted toward two lone pairs on the O2 atom over the ring plane, so the interaction between O2 and the pair of H-atoms (H8 and H9) increases. Thus, repulsive interaction is beneficial to the formation of the π-type H-bond. This is also shown in structures 2b and 2c with a larger π H-bond angle to about 161°, which demonstrates the relationship between the π H-bond and π-type H-bond.

The repulsive interaction also slightly influences the interaction energy. The interaction energy (−4.734 kcal/mol) of structure 2b (with the strong−strong π H-bond link) with relatively large repulsive interaction is smaller than −4.782 kcal/mol of structure 2c (with the strong−weak π H-bond link) with relatively small repulsive interaction. It shows that the strong−weak π H-bond link is more favorable than the strong−strong π H-bond link for stability of structure. It shows that the repulsive interaction between π H-bonds affects π multi-hydrogen bond interaction energy.

As above, the repulsion interaction affects the structures and interaction energies in four ways. First, the repulsion interaction pushes the corresponding pairs of H-atoms of C_4H_4 to deviate from the ring plane. Second, the repulsion interaction can elongate lengths of the π H-bonds. Third, the strong−weak π H-bond link is more favorable than the strong−strong π H-bond link in stability; the results affect the order of interaction energy. Fourth, it is beneficial to the formation of the π-type H-bond, and the two repulsion interactions weaken each other.

4. Conclusion

Six new antiaromatic ring π multi-hydrogen bond structures of $(H_2O)_n-C_4H_4$ ($n = 1,2$) have been obtained at the MP2/aug-cc-pVDZ level by the CP-corrected PES. The π multi-hydrogen bonds are found from the π mono-hydrogen bond to the π tetra-hydrogen bond. These H-bond structure shapes are diversiform. For example, structure 2d is an “intersecting of two rings” shaped structure with an antiaromatic ring π tetra-hydrogen bond.

In these π multi-hydrogen bond structures, the interaction energy order is -2.342 for 1a $<$ -2.777 for 1b $\ll$ -4.683 for 2a $<$ -4.734 for 2b $<$ -4.782 for 2c $<$ -5.009 kcal/mol for 2d at the CCSD(T)/aug-cc-pVDZ level with CP correction. We find that the intermolecular interaction energy mainly depends on the number of H_2O molecules and the fold number of the π multi-hydrogen bond. And the interaction energy also depends on the two accompanying interactions. The two accompanying interactions are the π-type H-bond attractive interaction and repulsive interactions between the H-atom(s) of H_2O and the near pair of H-atoms of C_4H_4.

The π-type H-bond produces four effects in the structures and interaction energies: (1) The π-type H-bond leads to the bend of the strong π H-bond. (2) The π-type H-bond attracts the corresponding pair of H-atoms of C_4H_4 to deviate from the C_4 ring plane toward the O-atom of H_2O. (3) The π-type H-bond shows the interaction energy contribution, so the interaction energy difference between the bi-hydrogen bond in 1b and the mono-hydrogen in 1a is small, 15.7%, and that between the tetra-hydrogen bond in 2d and the bi-hydrogen bond in 2a is also small, 6.5%. (4) The electron correlation contribution in the structures with the π-type H-bond is larger than those in structures without the π-type H-bond.

The repulsive interaction between the π H-bond (using the H-atom(s) of H_2O) and the near pair of H-atoms of C_4H_4 also produces four effects in the structures and interaction energies. (1) The repulsive interaction pushes the pair of H-atoms to deviate from the ring plane. (2) The repulsive interactions can elongate the distances of the π H-bonds and weaken each other (in the 2b, 2c, and 2d). (3) The repulsion interaction is beneficial to the formation of the corresponding π-type H-bond. (4) Because the repulsive interaction also slightly influences the interaction energy, the stability contribution of the strong−weak π H-bond link is more favorable than the strong−strong π H-bond link in two link ways on the same C═C bond in the C_4H_4 ring.

One H_2O forms a π H-bond with the C_4H_4 ring in two ways. First, two H-atoms of H_2O form a π bi-hydrogen bond (one strong π H-bond part and one weak π H-bond part). Second, when only one H-atom of H_2O forms one strong π mono-hydrogen bond, the O-atom of H_2O will form two π-type H-bonds between two lone pairs of the O-atom and the near pair of H-atoms of C_4H_4.

This new knowledge on the antiaromatic ring π multi-hydrogen bond and the π-type H-bond enriches the knowledge on weak interactions in an exciting part of chemistry.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20573043 and No. 20503010).

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