

Nature and physical origin of CH/ π interaction: Significant difference from conventional hydrogen bonds

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Supplementary Information

1. Computational methods

The Gaussian 03 program¹⁰³ was used for the ab initio molecular orbital calculations. Electron correlation was accounted for by the second-order Møller-Plesset perturbation (MP2) method. Basis set superposition error (BSSE) was corrected for all calculations using the counterpoise method. The electrostatic energy was calculated as interactions between distributed multipoles of interacting molecules^{73,89} using the ORIENT version 3.2.¹⁰⁵ Distributed multipoles up to hexadecapole on all atoms were obtained from the wave functions of an isolated molecule using the GDMA.¹⁰⁶ Induction energy was calculated as the interactions of polarizable sites with the electric field produced by the distributed multipoles of monomers.⁹⁰ The atomic polarizabilities of carbon ($\alpha = 10$ au) and nitrogen ($\alpha = 8$ au) were used for the calculations.¹²⁴ Distributed multipoles were used only to estimate the electrostatic and induction energies.

2. Orientation dependence of CH/ π interaction in benzene-methane cluster

Geometries of benzene and methane monomers were optimized at the MP2/6-31G* level. The optimized geometries of the monomers were kept frozen in the calculations of interaction energies for the benzene-methane cluster. The carbon

atom of the methane was put on the C_6 axis of the benzene. The distance between the carbon atom of methane and the centroid of benzene (R) was fixed at 3.8 or 4.8 Å. The interaction energy for the cluster (E_{MP2}) was calculated at the MP2/cc-pVTZ level by rotating the methane as shown in Figures 4 and 5. The electrostatic energy (E_{es}) was calculated using the distributed multipoles of monomers obtained from the MP2/6-311G** level wave functions of monomers.

3. Comparison of directionality with hydrogen bonds

Geometries of monomers were optimized at the MP2/cc-pVTZ level. The optimized geometries of the monomers were kept frozen in the calculations of interaction energies for the clusters. The hydrogen atom of the interacting O-H bond was put on the bisector of H-O-H angle of another water molecule in the water dimer. The hydrogen atom of the interaction C-H (or OH) bond was put on the C_6 axis of the benzene in the benzene clusters with water, acetylene and methane. The O...O distance in the water dimer and the C...centroid and O...centroid distances in the benzene clusters with water, acetylene and methane were optimized at the MP2/cc-pVTZ level. The interaction energies for the clusters were calculated at the MP2/cc-pVTZ level by rotating the methane as shown in Figure 6.

4. Intermolecular interaction for benzene clusters with ammonium and tetra-methylammonium clusters

The geometries for the clusters were fully optimized at the MP2/6-311G* level. The CCSD(T) interaction energies for the clusters at the basis set limit [$E_{CCSD(T)}(\text{limit})$] were estimated as the sum of the estimated $E_{MP2}(\text{limit})$ from the MP2/cc-pVDZ and MP2/cc-pVTZ level interaction energies and $\Delta CCSD(T)$ obtained using the 6-31G* basis set.¹²⁷ Electrostatic energy was calculated using distributed multipoles of monomers obtained from MP2/cc-pVTZ level wave functions of isolated molecules.