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Regulating Function of Methyl Group in Strength of CH···O Hydrogen Bond: A High-Level Ab Initio Study

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An ab initio computational study of the regulating function of the methyl group in the strength of the CH···O hydrogen bond (HB) with XC≡C−H (X = H, CH_3, F) as a HB donor and HOY (Y = H, CH_3, Cl) as a HB acceptor has been carried out at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels. The bond lengths, interaction energies, and stretching frequencies are compared in the gas phase. The results indicate that the methyl substitution of the proton acceptor strengthens the CH···O HB, whereas that of the proton donor weakens the CH···O HB. NBO analysis demonstrates that the methyl group of the proton acceptor is electron-withdrawing and that of the proton donor is electron-donating in the formation of the CH···O HB. The electron-donation of the methyl group in the proton acceptor plays a positive contribution to the formation of the CH···O HB, whereas the electron-withdrawing action of the methyl group in the proton donor plays a negative contribution to the formation of the CH···O HB. The positive contribution of methyl group in the proton acceptor is larger than the negative contribution of methyl group in the proton donor.

1. Introduction

A hydrogen bond, usually presented in the form of X−H···Y, is an intermolecular interaction between an electron-deficient hydrogen connected with an electronegative element X and a region Y of high electron density. Hydrogen bonds are of importance in many chemical and biological processes, such as stabilizing biomolecular structures,[1−3] modulating specificity and speed of enzymatic reactions,[4−6] and constructing supramolecular structures.[7,8] When X and Y are F, O, or N elements, this type of hydrogen bond is usually called a conventional hydrogen bond. Infrared spectroscopy is one of the most powerful methods for identifying and characterizing hydrogen bonds. In most cases, the X−H stretching vibration moves to low frequency upon formation of hydrogen bonding. In some cases, however, improper blue shifts of the X−H stretching frequencies are observed in some H-bonds. Hobza named this type of hydrogen bond as improper blue shifting hydrogen bond.[9] Although different opinion about the nature of red shift hydrogen bond and blue shift hydrogen bond can be found in references, most people think that there is no fundamental distinction between two different types of H-bond.[10−12]

With progress of the study on hydrogen bonds, other types of hydrogen bond have also been found, such as C−H H-bond, π H-bond, etc. Usually, these hydrogen bonds are classified as unconventional hydrogen bond. Although the acidity of C−H is weaker than that of O−H, there are more and more evidence showing that C−H group can be taken as a proton donor in formation of a hydrogen bond.[13−16] In this type of hydrogen bond, CH···O interaction has attracted extensive attention from researchers. The CH···O interaction plays an important role in determining the structure and activity of biological systems including nucleic acids, proteins, and carbohydrates.[17−22] For example, the CH···O interaction has been found in the active site of serine hydrolase[21] and the helicoidal structure of RNA molecule.[22] The CH···O H-bonds are of crucial importance for crystal packing, crystal engineering, and supermolecular design.[23] It also plays an important role in sustaining the stability of conformer of some small molecular complexes, such as propylene oxide−water cluster.[24]

When studying the structures and properties of hydrogen bonds, people often focus their attention on the atoms (X, Y, and H) participating directly in the formation of hydrogen bonds. The properties and strengths of hydrogen bonds are determined mainly by the properties of these atoms, but the alkyl groups adjoined to these atoms also play a regulating role in the properties and functions of hydrogen bonds.[25−30] For examples, the strength of the π···HF hydrogen bond between acetylene and HF is enhanced with increasing methyl substitution in C_2H_2.[29] The hydrogen bond between pyridine and water are stabilized with increase of the number of the methyl group in methyl-substituted pyridine.[30] Inspired by these, we studied the role of the methyl groups in the formation of O···HO hydrogen bond between dimethyl sulfoxide(DMSO) and methanol using excess infrared spectroscopy, nuclear magnetic resonance spectroscopy, and ab initio methods.[31] The methyl group in DMSO is electron-donating, whereas that in methanol is electron-withdrawing, with both making a stabilizing contribution to the hydrogen bonding. This study reported the role of the methyl group in the conventional O···HO hydrogen bond, whereas the role of the methyl group in the unconventional CH···O hydrogen bond has not been attended.

The CH···O hydrogen bond often coexists with a conventional hydrogen bond, making it difficult to study this interaction with experimental and theoretical methods. Thus, it is necessary to find a proper system where there exists only a CH···O hydrogen bond, and both proton donor and proton acceptor have a methyl group. In this study, we take the methyl acetylene−methanol system as a model to study the regulating role of methyl group in the formation of the CH···O hydrogen bond with the method of quantum chemical calculations. To unveil

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TABLE 1: Experimental and Theoretical Values of the Interaction Energy (ΔE) Corrected with ZVE and BSSE and Frequency Shift ($\Delta \nu$) in the Acetylene−Water Complex with the MP2 Method of Different Basis Sets

methods	ΔE (kcal/mol)	$\Delta \nu$(C−H) (cm^{-1})
experiment	−1.81[a]	−34 (ref 36)
MP2/6-31+G(d,p)	−1.09	−41
MP2/6-31++G(2d,2p) (ref 37)	−2.51[b]	−49
MP2/6-311+G(d,p)	−0.98	−42
MP2/6-311++G(d,p)	−0.77	−41
MP2/6-311++G(2d,2p)	−1.29	−49
MP2/6-311++G(3df,2p)	−1.55	−49
MP2/6-311++G(3df,3pd)	−1.64	−43
MP2/aug-cc-pVDZ	−1.56	−41
MP2/aug-cc-pVTZ	−1.77 (−2.72)[c]	−38

[a] This value was calculated with formulas of $\Delta E = 0.31\sqrt{|\Delta \nu|}$ kcal/mol proposed by Rozenberg and co-workers.[40] [b] This value was only corrected with BSSE in ref 37. [c] The value was only corrected with BSSE in ref 39, which is in good agreement with −2.71 kcal/mol in our calculation at the same level.

how the methyl group exerts its role in the CH···O interaction, analysis with natural bond orbital (NBO) has also been performed.

2. Molecular Models and Computational Details

Acetylene (A)−water (W) complex has been investigated with experimental and MP2 theoretical methods.[32−39] The results showed that the conformer with acetylene as a proton donor and water as a proton acceptor is stable. The CH···O hydrogen bond in the A−W cluster is a weak interaction, and thus the calculation of interaction energy is crucial for depicting such interaction. To explore the dependence of the CH···O interaction energy in the A−W complex on the basis sets, the calculation of this cluster was performed with the MP2 theory with the smaller (6-31+G(d)) basis set to the larger (aug-cc-pVTZ) basis set. The calculated results of the interaction energy and CH frequency shift are given in Table 1. For comparison, respective experimental values and theoretical results in references are also listed in Table 1. It is found that the values of the interaction energies and frequency shifts with the aug-cc-pVDZ and aug-cc-pVTZ basis sets developed by Dunning and co-workers are very close to those in experiment. The difference between the interaction energy calculated with the MP2/aug-cc-pVTZ method and that with experiment is 0.04 kcal/mol. For the MP2/aug-cc-pVDZ method, the difference is 0.25 kcal/mol. This established that MP2(FC)/aug-cc-pVTZ well described the interaction energy of the CH···O hydrogen bond in the A-W complex. The frequency shifts of the C−H stretching mode with aug-cc-pVTZ and aug-cc-pVDZ basis sets are 38 and 41 cm^{-1}, respectively, which are in good agreement with experimental value of 34 cm^{-1}. On consideration of computation cost, the frequency calculations of the derivatives of the A−W complex were performed with aug-cc-pVDZ basis set.

All of the calculations have been performed with Gaussian 03 program.[41] The geometry optimizations for the initial structures were first carried out at the MP2/aug-cc-pVDZ level. Harmonic vibrational frequencies were then computed using the same method to confirm these structures are local minima on the energy surfaces and to estimate zero-point vibrational energy (ZVE) and thermal energy (TE). Finally, the MP2/aug-cc-pVTZ method was adopted to optimize all the structures obtained at the MP2/aug-cc-pVDZ level to calculate the geometric parameters and the interaction energies. The basis set superposition errors (BSSE) correction was estimated at the MP2/aug-cc-pVTZ level using the counterpoise method of Boys and Bernardi.[42]

Natural population analysis (NPA)[43] provides characteristics that are closely connected to basic chemical concepts. The magnitudes of the orbital interactions can be estimated by perturbative analysis of the Fock matrix in the NBO basis. The NBO analyses were carried out using the NBO package included in the Gaussian 03 suite of programs.[44]

3. Results and Discussion

3.1. Geometries. On the basis of the A−W complex, other clusters are constructed by substituting an H atom in A and W molecules with methyl group (M), fluoro atom (F), or chloro atom (Cl). The investigated clusters thus include acetylene−water (A−W), acetylene−methanol (A−WM), acetylene−hypochlorous acid (A−WCl), methylacetylene−water (MA−W), methylacetylene-methanol (MA−WM), methylacetylene−hypochlorous acid (MA−WCl), fluoroacetylene−water (FA−W), fluoroacetylene-methanol (FA−WM), and fluoroacetylene−hypochlorous acid (FA−WCl). The geometries of these 1:1 molecular pairs are then optimized at the MP2/aug-cc-pVTZ level. Figure 1 shows the optimized structures of the nine hydrogen-bonded complexes, and the corresponding geometrical data are listed in Table 2. Clearly, both C≡C and C−H bonds are elongated in all clusters.

For the MP2/aug-cc-pVTZ method, the C−H bond length of the acetylene molecule is 1.062 Å and the O−H bond length of the H_2O molecule is 0.961 Å, which are in good agreement with the experimental values 1.063[45] and 0.958 Å,[46] respectively. For the A−W pair, the intermolecular H···O distance (r) is calculated to be 2.189 Å at the MP2/aug-cc-pVTZ level. Upon formation of the CH···O hydrogen bond, the C−H and C≡C bonds in the A−W complex are lengthened by 0.005 and 0.001 Å, respectively. As a methyl group is adjoined to the oxygen atom of the proton acceptor (in the A−WM pair), the r(H···O) is 2.110 Å (shorter than that in the A−W pair by 0.079 Å), the elongation of the C−H and C≡C bonds is 0.006 and 0.002 Å, respectively. As a Cl atom (here it is taken as an electron-withdrawing element relative to hydrogen atom) replaces an H atom of water molecule (in the A−WCl pair), the r(H···O) is 2.257 Å (elongated by 0.068 Å than that in the A−W pair), the elongation of C−H and C≡C bonds is 0.003 and 0.001 Å, respectively. From the results of three complexes containing A molecule, it is seen that the r(H···O) is smallest in the A−WM pair and largest in the A−WCl pair, whereas the elongation of C−H bond is largest in the A−WM pair and smallest in the A−WCl pair. By a contrastive analysis for the results of the A−WM and A−WCl pairs, it is found that the presence of a methyl group in the proton acceptor is favorable for the formation of the CH···O hydrogen bond. Similar results and conclusions are also obtained if MA and FA series are analyzed.

For the MA−W pair, where the proton donor is adjoined with a methyl group, the r(H···O) is 2.227 Å (larger by 0.038 Å than that in the A−W pair) and the elongation of the C−H bond is 0.004 Å, which is a little smaller than that in the A−W pair. A replacement of the nonparticipatory hydrogen atom of A molecule by the electronegative F atom (in the FA−W pair) leads to a shortening of r(H···O) with comparison to that in the A−W pair. This substitution can be expected to enhance the acidity of acetylene, and then shortens the binding distance. The elongation of the C−H bond is 0.006 Å in the FA−W pair. From the results of three complexes containing W molecule, it is seen that the r(H···O) is smallest in the FA−W pair and largest in the MA−W pair, whereas the elongation of the C−H bond is largest in the FA−W pair and smallest in the MA−W pair. These contrastive results demonstrate that the presence of

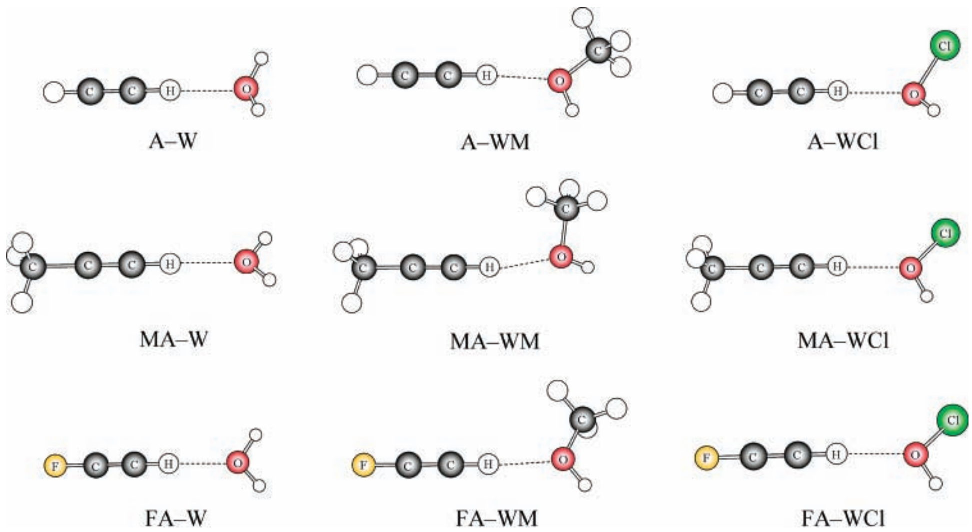

Figure 1. Optimized structures of the nine CH···O complexes at the MP2/aug-cc-pVTZ.

TABLE 2: Bond Lengths (r, Å) and Their Differences (Δr, Å) in the Nine Complexes Calculated at the MP2/aug-cc-pVTZ Level[a]

	$r(\mathrm{C{\equiv}C})$	$\Delta r(\mathrm{C{\equiv}C})$	$r(\mathrm{{\equiv}C-H})$	$\Delta r(\mathrm{{\equiv}C-H})$	$r(\mathrm{H\cdots O})$
A−W	1.213	0.001	1.066	0.005	2.189
A−WM	1.214	0.002	1.0676	0.006	2.110
A−WCl	1.213	0.001	1.064	0.003	2.257
MA−W	1.216	0.001	1.066	0.004	2.227
MA−WM	1.216	0.001	1.067	0.005	2.140
MA−WCl	1.215	0.001	1.064	0.002	2.285
FA−W	1.206	0.001	1.065	0.006	2.165
FA−WM	1.207	0.001	1.066	0.007	2.085
FA−WCl	1.206	0.001	1.062	0.003	2.232

[a] Δr is the difference between the bond length in the complex and that in the respective monomer.

a methyl group in the proton donor is unfavorable for the formation of the CH···O hydrogen bond. Similar results and conclusions are also obtained if WM and WCl series are analyzed. As the proton donor has an F atom and the proton acceptor has a methyl group (in the FA−WM pair), the H···O binding distance is smallest and the elongation of the C−H bond is largest.

3.2. Interaction Energies. The interaction energies of the nine CH···O complexes were calculated at MP2 theory using equilibrium configuration obtained at the MP2 level and the results are shown in Table 3. The aug-cc-pVTZ basis set was used in the calculation of hydrogen-bonded energies. The interaction energies were corrected with ZVE, BSSE and TE. As listed in Table 3, the estimated BSSE of the interaction, ranging from 1.86 to 2.89 kJ/mol, is large relative to the uncorrected binding energy, and it accounts for about 14−30% of the absolute values of the uncorrected binding energies in the complexes. The estimated ZVE also significantly affect the calculated binding strength. Therefore, the BSSE correction and ZVE estimation are necessary steps for accurately predicting binding strengths of CH···O hydrogen bonds in these systems if the MP2/aug-cc-pVTZ method is employed. The interaction energy of the FA−WM pair is largest in the magnitude, whereas that of the MA−WCl pair is smallest. The interaction energy, corrected with BSSE, of the A−W pair, is 2.71 kcal/mol in absolute value, which is a little larger than 2−2.5 kcal/mol of CH···O hydrogen bond in A−T base-pair at the MP2/6-31+G-(d,p) level[47] and smaller than 4−6 kcal/mol of NH···O hydrogen bond between dipeptide and water at the MP2/6-31+G(d,p) level.[48]

TABLE 3: Energetical Parameters of the CH···O Hydrogen Bonds in the Nine Complexes Calculated at the MP2/aug-cc-pVTZ Level[a]

	$\Delta E_{\mathrm{inter}}$	ZVE	ΔE^{0}	BSSE	ΔE_{corr}	TE	ΔE^{298}
A−W	−13.24	3.86	−9.38	1.86	−7.52	6.89	−0.63
A−WM	−16.14	3.48	−12.66	2.22	−10.44	6.72	−3.72
A−WCl	−10.48	3.65	−6.83	2.66	−4.17	6.72	2.55
MA−W	−11.20	3.65	−7.55	1.97	−5.58	8.15	2.57
MA−WM	−14.25	3.01	−11.24	2.25	−8.99	7.87	−1.12
MA−WCl	−9.53	3.45	−6.08	2.80	−3.28	8.04	4.76
FA−W	−14.17	4.20	−9.97	2.10	−7.87	6.94	−0.93
FA−WM	−17.06	3.50	−13.56	2.57	−10.99	6.95	−4.04
FA−WCl	−11.12	3.63	−7.49	2.89	−4.60	6.89	2.29

[a] ZVE values were calculated at the MP2/aug-cc-pVDZ level based on the structures optimized at the same level and corrected with a factor of 0.94. ΔE^{0} values are the binding energies plus ZVE. ΔE_{corr} values are the binding energies plus ZVE and BSSE. ΔE^{298} values are the binding energies plus ZVE, BSSE, and TE. All the quantities are in kJ/mol.

For the A−W and A−WM pairs, the results of hydrogen-bonded energies, corrected with ZVE and BSSE, are calculated to be −7.52 and −10.44 kJ/mol, respectively. The magnitude of corrected hydrogen-bonded energy of A−WM pair is a little bigger than that of A−W pair. This result shows that the presence of the methyl group in the proton acceptor enhances the strength of CH···O hydrogen bond. To compare the role of the methyl group in the proton acceptor, we also calculated the interaction energy of the A−WCl pair. Seen from Table 3, the magnitude of the A−WCl-corrected interaction energy is smaller than that of A−W. This result shows that the presence of an electron-withdrawing group (Cl) in the proton acceptor has a weakening effect on the strength of CH···O hydrogen bond. Similar results and conclusions are also found in other two series of MA and FA. In the previous study of CH···O hydrogen bond in the CH_4−H_2O complex,[49] the interaction energy is −0.43 kcal/mol at the MP2/aug-cc-pVDZ level. Because of the weak acidity of proton in CH_4, this energy is much smaller than that of C_2H_2−H_2O complex at the same level (−1.56 kcal/mol). As one of H atoms in water is replaced by a methyl group, there appears to be an increase of perhaps 0.1−0.2 kcal/mol.[49] This increase due to a methyl group in the CH_4−H_2O complex is smaller than that in a C_2H_2−H_2O system (0.6 kcal/ mol).

For the MA−W pair, the corrected interaction energy of CH···O hydrogen bond is −5.58 kJ/mol, and its magnitude is smaller than that of A−W pair. This result indicates that the presence of the methyl group in the proton donor weakens the

TABLE 4: Frequencies (*v*) and Intensities (*I*) of $C\equiv C$ and $C-H$ Stretching Vibrations in the Nine Clusters and Their Monomers Calculated at the MP2/aug-cc-pVDZ Level[a]

	$C\equiv C$ stretching vibration[b]		$\equiv C-H$ stretching vibration[b]	
	v (cm^{-1})	I (km/mol)	v (cm^{-1})	I (km/mol)
A	1965	0	3294	93
A−W	1957 (−8)	8	3254 (−40)	263
A−WM	1953 (−12)	10	3229 (−65)	306
A−WCl	1959 (−6)	5	3268 (−27)	231
MA	2145	3	3348	53
MA−W	2138 (−7)	1	3292 (−56)	234
MA−WM	2134 (−11)	1	3270 (−78)	264
MA−WCl	2140 (−5)	0	3313 (−35)	197
FA	2243	119	3363	93
FA−W	2230 (−13)	68	3294 (−69)	325
FA−WM	2225 (−18)	64	3259 (−104)	394
MA−WCl	2233 (−10)	84	3315 (−48)	286

[a] The data in parentheses are the difference between the frequency in the complex and that in the monomer. [b] Experimental values of the $C\equiv C$ stretching frequency and $\equiv C-H$ stretching frequency in acetylene are 1974 and 3289 cm^{-1}, respectively,[53] and thus their frequencies are scaled with a factor of 1.01 and 0.96, respectively.

strength of CH···O hydrogen bond. To illustrate the role of the methyl group in the proton donor, the interaction energy of the FA−W pair (where F is taken as an electron-withdrawing group) is also calculated. Seen from Table 3, the magnitude of FA−W corrected interaction energy is bigger than that of A−W pair. This result suggests that the presence of an electron-withdrawing group (F) in a proton donor has an enhancing effect on the strength of CH···O hydrogen bond, which is consistent with that in refs 50−52. Similar results and conclusions are also found in other two series of WM and WCl.

The thermal energies are given in Table 3. Clearly, these thermal energies in the nine clusters are large enough to modify the interaction energy. For example, the interaction energy is −4.17 kJ/mol in the A−WCl pair; however, it is changed to 2.55 kJ/mol when the thermal energy is considered. This positive value indicates that the pair is unfavorable. Even so, the sequence (A−WCl < A−W < A−WM) of interaction magnitude is still not changed. The similar results and conclusions are found as MA and FA are proton donors.

3.3. Harmonic Vibrational Frequencies. The harmonic vibrational frequencies of the nine CH···O complexes were calculated at the MP2/aug-cc-pVDZ level. The results are shown in Table 4. Scaling factors of 1.01 and 0.96 were applied for the frequencies of $C\equiv C$ and $C-H$ stretching vibrations, respectively. In all cases, all calculated frequencies are real. For the $C\equiv C$ stretching vibration, the frequency is calculated to be 1965, 1957, 1953, and 1959 cm^{-1} for A, A−W, A−WM, and A−WCl, respectively. Clearly, the formation of the CH···O H-bond results in a red shift of the $C\equiv C$ stretching frequency. The largest red shift is found in the A−WM complex (12 cm^{-1}) and the smallest red shift is found in the A−WCl complex (6 cm^{-1}). The red shift of the $C\equiv C$ stretching frequency is consistent with the elongation of the $C\equiv C$ bond. Simultaneously, the infrared intensity of the $C\equiv C$ stretching vibration increases. Similar results of the $C\equiv C$ stretching frequency are also found in the other two series with MA and FA as the proton donor, whereas the infrared intensity of the $C\equiv C$ stretching vibration decreases in these systems. In all complexes, the red shift of the $C\equiv C$ stretching frequency is largest in the FA−WM complex (18 cm^{-1}), while it is smallest in the MA−WCl complex (5 cm^{-1}).

Frequency shifts of $C-H$ groups correlate with various characteristics of the CH···O H-bond such as the strength, the binding distance, and the binding energy. When the vibrational spectra of a free $X-H$ group and those in an $X-H\cdots Y$ conventional hydrogen bond are compared, it is generally observed that the $X-H$ stretching vibration undergoes a substantial shift toward a lower frequency and an increase in intensity. These features are also observed in the calculated results of the nine CH···O complexes. The $C-H$ stretching frequency of acetylene (A) molecule is 3294 cm^{-1}, and its infrared intensity is 93 km/mol. In the A−W complex, the $C-H$ stretching frequency is red-shifted by 40 cm^{-1} as a result of the CH···O hydrogen bond. In addition, the IR intensity of the $C-H$ stretching mode is increased to 263 km/mol from 93 km/mol in acetylene molecule. For the A−WM pair, the $C-H$ stretching frequency has a bigger red shift of 65 cm^{-1} and its IR intensity is increased by 213 km/mol. For the A−WCl pair, the $C-H$ stretching frequency is red-shifted by 27 cm^{-1} and the corresponding intensity is increased by 138 km/mol. Clearly, the frequency red shift and intensity enhancement of the $C-H$ stretching vibration in the three clusters increase in the following order: A−WM > A−M > A−WCl. Similar results are also found in the other two series with MA and FA as the proton donor. In all complexes, the largest red shift of the $C-H$ stretching frequency is found in the FA−WM complex, where there is an electron-withdrawing group (F) in the proton donor and an electron-donating group (methyl) in the proton acceptor. These results are in good agreement with the strength of the CH···O hydrogen bond and change of the binding distance.

3.4. NBO Analysis. The role of methyl group in formation of the CH···O hydrogen bond can by evaluated with change of natural bond population (NPA) charge of methyl group. Table 5 presents the NPA charge of the methyl group in MA−WM complex and its monomers. Clearly, the positive charges are found for the methyl groups in MA−WM complex and its monomers. Upon complexation, the positive charge of the methyl group in MA decreases, whereas that in WM increases. The results show that the methyl group in the proton donor (MA) is electron-withdrawing and that in the proton acceptor (WM) is electron-donating in formation of the CH···O hydrogen bond. Further analysis, it is found that the increase of methyl charge in WM (0.0123 e) is larger in magnitude than the decrease of methyl charge in MA (−0.0065 e). This result indicates that the role of methyl group in WM is greater than that in MA. This conclusion is also evaluated with the interaction energy. With comparison to −7.52 kJ/mol of A−W complex, the interaction energy in A−WM complex increases by −2.92 kJ/mol, whereas that in MA−W complex decreases by −1.94 kJ/mol. This can be used to explain why the interaction energy of MA−WM complex is still larger in the magnitude than that of A−M complex, although there is a methyl group in the proton donor of MA−WM complex.

In the O···HO hydrogen bond between dimethyl sulfoxide and methanol molecules,[31] the methyl group in the proton acceptor plays an electron-donating role, whereas that in the proton donor is electron-withdrawing. Evidently, the methyl group in both the proton acceptor and the proton donor plays the same role in two types of hydrogen bond. The electron-donating role of the methyl group in the proton acceptor is favorable for the formation of two types of hydrogen bonds. However, the electron-withdrawing role of methyl group in methanol plays a positive contribution to the formation of OH···O hydrogen bond, whereas that in methylacetylene plays a negative contribution to the formation of CH···O hydrogen bond, as indicated in the changes of the bond lengths, interaction energies, and frequency shifts.

TABLE 5: NPA Charges (*q*, e) and Stabilization Energies (E_{ij}, kcal mol^{-1}) Related with the Methyl Groups in the MA−WM Complex and Its Monomers Calculated at the MP2/aug-cc-pVTZ Level[a]

	MA	**MA**−WM		WM	MA−**WM**
q_{CH3}	0.0239	0.0174	q_{CH3}	0.2724	0.2847
σ(C−H) → RY*(C)	4.67	5.69	σ(C−H) → RY*(O)	4.76	4.20
σ(C−H) → σ^*(C≡C)	39.14	38.30	σ(C−H) → σ^*(O−H)	2.93	2.98
sum1	43.71	43.99	σ(C−H) → σ^*(C−O)	1.98	1.95
σ(C≡C) → σ^*(C−H)	13.68	14.27	sum1	9.67	9.13
σ(C≡C) → RY*(C)	10.83	10.53	n(O) → σ^*(C−H)	21.44	20.47
σ(C−C) → RY*(H)	2.13	2.32	σ(O−H) → σ^*(C−H)	2.54	2.37
sum2	26.64	27.12	sum2	23.98	22.84
sum1 − sum2	17.07	16.87	sum1 − sum2	−14.31	−13.71

[a] Sum1 and sum2 represent an addition of stabilization energy of the methyl group as donor orbitals and acceptor orbitals, respectively.

To explore how the methyl groups impose their influence in the formation of the CH···O hydrogen bond, the NBO second-order perturbation analysis was applied for the MA−WM complex and its monomers. In the NBO analysis, natural bond orbitals are first defined for each covalent bond, lone pair, and antibonding orbital by using the molecular orbitals obtained by quantum chemical calculations, and the orbital interaction energies are subsequently calculated for all possible orbital interactions between electron donor NBO (*i*) and acceptor NBO (*j*). For each electron donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy E_{ij} associated with delocalization $i \rightarrow j$ is estimated with $E_{ij} = q_i(F_{i,j})^2/(\epsilon_j - \epsilon_i)$, where q_i is the donor orbital occupancy, ϵ_i, ϵ_j, are orbital energies, and $F_{i,\,j}$ is the off-diagonal NBO Fock matrix element.

The orbital interaction between the O lone pair n(O) of W (WM or WCl) and the antibonding orbital of the C−H bond σ*(C−H) is found to contribute significantly to the stabilization of the CH···O interaction. The E_{ij} due to the n(O) → σ*(C−H) orbital interaction is 3.81, 3.85, 2.86 kcal/mol for A−W, A−WM, and A−WCl pairs, respectively. The E_{ij} is smallest in the A−WCl pair and largest in the A−WM pair. The magnitude of the E_{ij} supports the results reflected in the H···O bond length, the interaction energy, and the C−H stretching frequency in the three molecular pairs. As the proton donor is MA and FA, similar results and conclusions are also obtained. In all complexes, the E_{ij} is largest in the FA−WM complex (18 kcal/mol), whereas it is smallest in the MA−WCl complex (5 kcal/mol).

The stabilization energies (E_{ij}) due to the C−H orbital interactions in the MA−WM complex are given in Table 5. In methylacetylene (MA) molecule, the methyl group can be taken as an orbital donor and orbital acceptor in the orbital interaction. As the orbital donor, there are two main orbital interactions (σ((C−H) → RY*(C) and σ((C−H) → σ*(C≡C)). The sum of stabilization energy of the two orbital interactions is 43.71 kcal/mol. As the orbital acceptor, there are three main orbital interactions (σ(C≡C) → σ* (C−H), σ(C≡C) → RY*(C), and σ(C−C) → RY*(H)). The sum of stabilization energy of the three orbital interactions is 26.64 kcal/mol. The difference of the stabilization energy between the two donor orbital interactions and three acceptor orbital interactions (sum1 − sum2) is a positive value (17.07 kcal/mol). This positive value means the methyl group plays a role of donating electron in MA molecule. This is consistent with the concept that methyl groups attached to π-electron systems are electron donors is widely accepted in organic chemistry.[31,59,60] For the MA subunit in the MA−WM pair, the magnitude of sum1 − sum2 decreases, indicating the electron-donating ability of the methyl group decreases upon the formation of the CH···O hydrogen bond. Thus the methyl group in MA subunit plays an electron-withdrawing role in the formation of the CH···O hydrogen bond. There is a question: why the methyl group in C_3H_4 is unfavorable for the formation of CH···O hydrogen bond? The reason may be that the methyl group in C_3H_4 is electron-donating. The electron-donation makes a decrease of acidity of the C−H bond, thus the ability of C−H bond forming a hydrogen bond decreases. This case is reverse to that in C_2FH.

In methanol (WM) molecule, the methyl group can also be taken as an orbital donor and orbital acceptor in the orbital interaction. As the orbital donor, there are three main orbital interactions (σ((C−H) → RY*(O), σ((C−H) → σ*(O−H), and σ((C−H) → σ*(C−O)). The sum of stabilization energy of the three orbital interactions is 9.67 kcal/mol. As the orbital acceptor, there are two main orbital interactions (n(O) → σ*(C−H) and σ(O−H) → σ*(C−H)). The sum of stabilization energy of the two orbital interactions is 23.98 kcal/mol. The difference of the stabilization energy between the three donor orbital interactions and two acceptor orbital interactions (sum1 − sum2) is a negative value (−14.31 kcal/mol). This negative value indicates the methyl group plays a role of withdrawing electron in methanol molecule. For WM subunit in the MA−WM pair, the magnitude of the negative value decreases, and thus it indicates an electron-donating contribution of the methyl group to the formation of the CH···O hydrogen bond. When MA forms a hydrogen bond with a WM molecule, charge transfers from the oxygen lone pair in WM to the antibond orbital of CH group in MA, which leads to a decrease in electron density on the oxygen atom in WM. The electron-donating role of methyl group in WM subunit is advantageous to compensate the decrease in electron density on the oxygen atom in WM subunit, thus the presence of the methyl group in the proton acceptor is favorable to the formation of the CH···O hydrogen bond.

4. Conclusions

By employing the method of MP2/aug-cc-pVTZ, we performed theoretical calculations to study the regulating function of the methyl group in the strengths of the CH···O hydrogen bonds in the nine complexes: acetylene−water, methylacetylene−water, fluoroacetylene−water, acetylene−methanol, methylacetylene−methanol, fluoroacetylene−methanol, acetylene−hypochlorous acid, methylacetylene− hypochlorous acid, and fluoroacetylene−hypochlorous acid. The influence of substitution (CH_3, F, and Cl) of the acetylene−water complex on the properties (bond lengths, frequency shifts, and interaction energies) of the CH···O hydrogen bond was analyzed. It was found that the strength of H-bond increases in the following order: A−WCl < A−W < A−WM, MA−WCl < MA−W < MA−WM, FA−WCl < FA−W < FA−WM, MA−W < A−W < FA−W, MA−WM < A−WM < FA−WM, and MA−WCl < A−WCl < FA−WCl. The NBO analysis of the methylacetylene−methanol complex indicates that the methyl group in the proton donor is electron-withdrawing and that in the proton acceptor is electron-donating in the formation of the CH···O hydrogen bond. The former is unfavorable to the formation of the CH···O hydrogen bond, while the latter is helpful for the formation of the CH···O hydrogen bond. The positive contribution of methyl group in the proton acceptor is larger than the negative contribution of methyl group in the proton donor.

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