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Gigantic Blue Shift of the H−Ar Stretch Vibration in π Hydrogen-Bonded $C_2H_2\cdots HArCCF$ Complex

Jianbo Cheng,[†,§] Yilei Wang,[‡] Qingzhong Li,*[,†] Zhenbo Liu,[†] Wenzuo Li,[†] and Baoan Gong[†]

The Laboratory of Theoretical and Computational Chemistry, Science and Engineering College of Chemistry and Biology, Yantai University, Yantai 264005, P. R. China, Key Laboratory of Organic Optoelectronics & Molecule Engineering, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China, and State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China

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Quantum chemical calculations have been performed to study the structure and properties of the π hydrogen-bonded complex formed between acetylene and HArCCF at the MP2/6-311++G(2d,2p) level. The $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes were also studied for comparison with the $C_2H_2\cdots HArCCF$ complex. The basis set superposition errors (BSSE)-counterpoise corrected potential-energy surface (PES) has a larger influence on the structure and properties of the $C_2H_2\cdots HArCCF$ complex than those of the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes. The $C_2H_2\cdots HArCCF$ complex exhibits a very large harmonic vibrational frequency blue shift of 574 cm^{-1} for the H−Ar stretch, whereas the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes exhibit a small red shift of 35 and 47 cm^{-1} for the H−C stretch, respectively; upon complexation the IR intensity decreases in the former, whereas it increases in the latter. The origin of the frequency shift and nature of the hydrogen bond in these complexes have been unveiled with the natural bond orbital analysis and energy decomposition.

1. Introduction

Hydrogen bonds are one of the most important intermolecular interactions because they play a crucial role in many chemical and biological proceeds.[1] In most hydrogen bonds, the H−X stretch vibration in the proton donor usually moves to low frequency (red shift) upon complexation. In recent years, however, the blue shift of the H−X stretch vibration has also been observed in more and more hydrogen bonds.[2−5] The former is called as red-shifted hydrogen bond, whereas the latter is classified as blue-shifting hydrogen bond.[5] Even so, both types of hydrogen bonds are similar in nature.[6−8] The electrostatic and charge transfer interactions play an important role in both types of hydrogen bonds. The difference between them is that the attraction force plays a main role in the former, whereas the repulsion force plays a main contribution in the latter.[7]

It is usually known that noble-gas atoms are very stable and do not participate in chemical reactions. Recently, however, more and more evidence shows that noble-gas atoms can also form some stable compounds[9−14] and these compounds can usually be represented with the form of HNgX, where Ng is noble-gas atoms and X is usually electronegative elements or groups. HArF is the first known stable neutral compound containing Ar, which has been characterized with spectroscopic method.[12] Theoretical calculations indicate that FArCCH is more stable than HArF.[13] HArCCH was also predicted to be existence with theoretical calculations.[14] Thus, we deduce that HArCCF compound also exists. However, it is deserved to point out that the HArCCF molecule is considerably less stable than the HCCArF isomer. In the HNgX molecule, the positive charge on the H atom and negative charge on the X atom increases relative to those in HX molecule. Thus, the HNgX molecule can form a stronger hydrogen bond than the corresponding HX molecule.

A lot of hydrogen-bonded complexes involving HNgX molecules have been investigated and some have been observed in low-temperature rare-gas matrices, notably $FArH\cdots N_2$, $FKrH\cdots N_2$, and $ClKrH\cdots N_2$;[15−20] the experimental results are in agreement with theoretical findings. Although the interaction energy in the $FArH\cdots N_2$ complex is small (−4.3 kJ/mol at the MP2/6-311++G(2d,2p) level), it has been produced experimentally in a low-temperature Ar matrix.[20] When the proton acceptor is lone pairs on fluorine, oxygen, or nitrogen atoms,[21−23] the H−Ng stretch vibration often shifts to high frequency and the respective IR intensity degrades. This improper blue shift can be explained with the electron density rearrangement in the HNgX molecule upon complexation. This blue shift is usually larger than that in $CH\cdots O$ blue-shifting hydrogen bonds.[5] However, the H−Ng stretch vibration exhibits a red shift when the proton acceptor is metal hydrides[24−26] or π electron in acetylene.[27] The red shift of the H−Ng stretching frequency is smaller than the blue shift of the H−Ng stretching frequency. The larger quadrupole moment of metal hydride and acetylene may be responsible for the red shift.

In the present article, we reported the structure and properties of a planar T-shape complex formed between HCCH and HArCCF. This complex was found to be stable by ab initio calculations with respect to the monomer subunits at two different levels of theory. This work is particularly interesting because a very large blue shift of the H−Ar stretch is observed in this complex, which is far larger than that in the $FArH\cdots N_2$ complex[28] and is not consistent with the red shift of the H−Ar stretch in the $HCCH\cdots HArF$ complex[27] although their structures are similar. We first studied the effect of the used basis set and

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* To whom correspondence should be addressed. Tel.: (+086) 535 6902063. Fax: (+086) 535 6902063. E-mail: lqz02@mails.tsinghua.edu.cn.

[†] Yantai University.

[‡] Tsinghua University.

[§] Jilin University.

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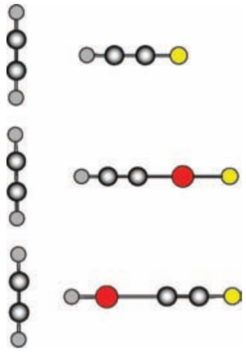

Figure 1. Optimized structures of the three π hydrogen-bonded complexes ($C_2H_2\cdots HCCF$, $C_2H_2\cdots HCCArF$, and $C_2H_2\cdots HArCCF$) at the MP2/6-311++G(2d,2p) level.

theoretical method on the blue shift of the H−Ar stretch. We also discussed the effect of the standard optimization and counterpoise optimization on the structure and properties of the complex. Then we compared the properties of the $C_2H_2\cdots HArCCF$, $C_2H_2\cdots HCCF$, and $C_2H_2\cdots HCCArF$ complexes. In the end, we shall seek to explain why the blue shift occurs in the complex and to unveil the nature of the interaction with the natural bond orbital analysis and energy decomposition. The following section outlines the computational methods used.

2. Computational Methods

On the basis of the structure of acetylene dimer in a T-shape configuration, which has been characterized with microwave and infrared spectroscopy,[29] we constructed the structures of three complexes of $C_2H_2\cdots HCCF$, $C_2H_2\cdots HCCArF$, and $C_2H_2\cdots HArCCF$ (Figure 1). In geometrical optimization calculations, standard potential energy surface (PES) (with Opt keyword), and counterpoise (CP) corrected PES (with Counterpoise and Opt keywords) methods were adopted for three complexes. Three levels of theory [MP2/6-311++G(d,p), MP2/6-311++G(2d,2p), and QCISD/6-311++G(2d,2p)] were adopted for the $C_2H_2\cdots HArCCF$ complex. Harmonic vibrational frequency calculations were also performed to confirm that the obtained structures are true minima (no imaginary frequencies). The interaction energy ($\Delta E = E_{AB} - E_A - E_B$) was calculated as the difference of the energy of the complex and the isolated monomers. The interaction energy was corrected with the basis set superposition errors (BSSE). The BSSE was estimated using the counterpoise method of Boys and Bernardi.[30] The natural bond orbital (NBO) analyses were carried out using the NBO package included in the *Gaussian 03* suite of programs.[31] All calculations were performed using the *Gaussian 03* program system.[32] The decomposition of interaction energies for three complexes was performed with PBE/TZ2P(small core) in the *ADF2007.01* program.[33]

3. Results and Discussion

3.1. Effect of Basis Set and Electron Correlation. Figure 1 shows the structures of the three complexes of $C_2H_2\cdots HCCF$, $C_2H_2\cdots HCCArF$, and $C_2H_2\cdots HArCCF$. The structure of the $C_2H_2\cdots HArCCF$ complex was optimized with the two methods (standard PES and CP-corrected PES) at the three levels of theory [MP2/6-311++G(d,p), MP2/6-311++G(2d,2p), and QCISD/6-311++G(2d,2p)]. The obtained structure is arranged in a T-shape structure with C_{2v} symmetry, where the H−Ar bond points to the midpoint of the C≡C bond. Table 1 presents the binding distance, change of the H−Ar bond length, frequency shift of the H−Ar stretch, IR intensity of the H−Ar stretch, interaction energy, and dipole moment in the $C_2H_2\cdots HArCCF$ complex. It is seen from the table that there is a contraction of the H−Ar bond length, accompanied with a blue shift of the H−Ar stretch vibration and a decrease in the IR intensity.

TABLE 1: Binding Distance (*R*, Å), Change of the H−Ar Bond Length (Δ*r*, Å), Frequency Shift of the H−Ar Stretch (Δ*v*, cm^{-1}), Infrared Intensity of the H−Ar Stretching Vibration (*I*, km/mol), Interaction Energy (Δ*E*, kJ/mol), and Dipole Moment (*μ*, D) in the $C_2H_2\cdots HArCCF$ Complex Calculated at Three Different Theoretical Levels[a]

	MP2/6-311 ++G(d,p)	MP2/6-311 ++G(2d,2p)	QCISD/6-311 ++G(2d,2p)
R_{st}	1.8632	1.9322	2.0210
R_{cp}	2.0123	2.0451	2.1497
Δr_{st}	−0.0924	−0.1013	−0.0901
Δr_{cp}	−0.0997	−0.1030	−0.0886
Δv_{st}	+567	+553	+528
Δv_{cp}	+635	+574	+531
I_{st}	979(5064)	447(3917)	26(3535)
I_{cp}	130(5064)	44(3917)	111(3535)
ΔE_{st}	−9.99	−11.80	−10.26
ΔE_{cp}	−10.53	−12.15	−10.60
μ_{st}	14.716	13.317	11.359
μ_{cp}	13.691	12.561	10.450

[a] Note: Data in parentheses are from the infrared intensity of the H−Ar stretching vibration in the isolated HArCCF molecule. The subscripts of st and cp represent the standard PES and CP-corrected PES, respectively.

Seen from Table 1, the basis set has a great influence on the structure and properties of the $C_2H_2\cdots HArCCF$ complex. When the basis set varies from 311++G(d,p) to 6-311++G(2d,2p), the binding distance (R_{st}) is from 1.8632 Å to 1.9322 Å, the change of the H−Ar bond length (Δr_{st}) is from −0.0924 Å to −0.1013 Å, the frequency shift of the H−Ar stretch (Δv_{st}) is from 567 cm^{-1} to 553 cm^{-1}, the IR intensity of the H−Ar stretch (I_{st}) is from 979 km/mol to 447 km/mol, the interaction energy (ΔE_{st}) is from −9.99 to −11.80 kJ/mol, and the dipole moment is from 14.716 to 13.317 D. These changes indicate that the $C_2H_2\cdots HArCCF$ complex is weakly combined. The 6-311++G(2d,2p) basis set was often used to descript the structure and properties of hydrogen-bonded complexes involving a noble-gas atom,[34] thus it is also adopted in this article.

The binding distance (R_{st}) is 1.9322 Å at the MP2/6-311++G(2d,2p) level and 2.0210 Å at the QCISD/6-311++G(2d,2p) level. The change of the H−Ar bond length (Δr_{st}) at the QCISD/6-311++G(2d,2p) level is smaller 0.0112 Å than that at the MP2/6-311++G(2d,2p) level. The frequency shift of the H−Ar stretching (Δv_{st}) at the QCISD/6-311++G(2d,2p) level is thus smaller 25 cm^{-1} than that at the MP2/6-311++G(2d,2p) level. The interaction energy (ΔE_{st}) at the QCISD/6-311++G(2d,2p) level is increased by 1.54 kJ/mol relative to that at the MP2/6-311++G(2d,2p) level. That is to say, the MP2/6-311++G(2d,2p) method overestimates the interaction energy of the complex. Thus, the electron correlation has also a great effect on the structure and properties of the $C_2H_2\cdots HArCCF$ complex. It is also found that the effect of the basis set is larger than that of the electron correlation. For example, the difference of the interaction energy (ΔE_{st}) between MP2/6-311++G(d,p) and MP2/6-311++G(2d,2p) is 1.81 kJ/mol, whereas that between MP2/6-311++G(2d,2p) and QCISD/6-311++G(2d,2p) is 1.54 kJ/mol.

We have also investigated the effect of the CP-corrected PES method on the structure and properties of the $C_2H_2\cdots HArCCF$ complex. Taking the results of the MP2/6-311++G(2d,2p) level as an example. The binding distance (R_{cp}) is 2.0451 Å, which is increased by 0.1129 Å relative to the R_{st}. The shortening of

TABLE 2: Binding Distance (R, Å), Change of the H−C(Ar) Bond Length (Δr, Å), Frequency Shift of the H−C(Ar) Stretch (Δv, cm^{-1}), Infrared Intensity of the H−Ar Stretching Vibration (I, km/mol), Interaction Energy (ΔE, kJ/mol), and dipole moment (μ, D) in the three complexes calculated at the MP2/6-311++G(2d,2p) Level[a]

	$C_2H_2\cdots HCCF$	$C_2H_2\cdots HCCArF$	$C_2H_2\cdots HArCCF$
R_{st}	2.6487	2.5706	1.9322
R_{cp}	2.7332	2.6527	2.0451
Δr_{st}	0.0029	0.0036	−0.1013
Δr_{cp}	0.0025	0.0033	−0.1030
Δv_{st}	−41	−52	+553
Δv_{cp}	−35	−47	+574
I_{st}	225(93)	293(81)	447(3917)
I_{cp}	206(93)	259(81)	44(3917)
ΔE_{st}	−5.80	−7.76	−11.80
ΔE_{cp}	−5.88	−7.86	−12.15
μ_{st}	1.329[0.328]	7.984[0.811]	13.317[6.234]
μ_{cp}	1.303[0.302]	7.879[0.706]	12.561[5.388]

[a] Note: Data in parentheses are the infrared intensities from the monomers. Data in brackets are the sum of dipole moment of the respective monomers.

the H−Ar bond length (Δr_{cp}) is larger 0.0017 Å than the Δr_{st}. The blue shift of the H−Ar stretching frequency with the CP-corrected PES method is thus larger 21 cm^{-1} than that with the standard PES method. The infrared intensity of this mode (I_{cp}) is much smaller than the I_{st}. The interaction energy calculated with the CP-corrected PES method is more negative than that with the standard PES method. The dipole moment (μ_{cp}) is smaller than the μ_{st}. Similar results also happen for MP2/6-311++G(d,p) and QCISD/6-311++G(2d,2p) methods. These results indicate that the CP-corrected PES method has an influence on the structure and properties of the $C_2H_2\cdots HArCCF$ complex.

3.2. Comparison of the Three Complexes. For comparison, the structures of $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes were also optimized with standard PES and CP-corrected PES methods. The results are given in Table 2. Seen from the table, the CP-corrected PES method has a little effect on the structure and properties of the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes. For example, the red shift of the H−C stretch calculated with the CP-corrected PES method is 35 and 47 cm^{-1} for the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes, respectively. This red shift is decreased by 6 and 5 cm^{-1} less than that with the standard PES method for the two complexes, respectively. Evidently, the effect of the CP-corrected PES method on the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes is smaller than that on the $C_2H_2\cdots HArCCF$ complex. Even so, the complexes of $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ have been discussed with the results obtained from the CP-corrected PES method for comparison with the $C_2H_2\cdots HArCCF$ complex.

The binding distance is calculated to be 2.7332 Å in the $C_2H_2\cdots HCCF$ complex, whereas it is 2.0451 Å in the $C_2H_2\cdots HArCCF$ complex. The interaction energy in the $C_2H_2\cdots HArCCF$ complex is about two times as much as that in the $C_2H_2\cdots HCCF$ complex. The H−C bond in the $C_2H_2\cdots HCCF$ complex is elongated a little, whereas the H−Ar bond in the $C_2H_2\cdots HArCCF$ complex is shortened greatly. This is accompanied with a small red shift (35 cm^{-1}) of the H−C stretch in the $C_2H_2\cdots HCCF$ complex and a very large blue shift (574 cm^{-1}) of the H−Ar stretch in the $C_2H_2\cdots HArCCF$ complex, respectively. The red shift of the H−C stretch is accompanied by an increase of the IR intensity, whereas the blue shift of the H−Ar stretch is accompanied by a decrease in the IR intensity. To best of our knowledge, the blue shift in the $C_2H_2\cdots HArCCF$ complex is largest observed for blue-shifting hydrogen-bonded complexes up to now.

In the free HArCCF molecule, the H−Ar stretch has a very large IR intensity (3917 km/mol) due to its large negative permanent dipole derivative with respect to displacement of the H−Ar bond length. The strong infrared absorption band that results from this vibrational mode may allow for the identification of the HArCCF molecule in low-temperature matrix isolation experiments. Although the IR intensity is decreased greatly in the $C_2H_2\cdots HArCCF$ complex (447 km/mol), the H−Ar stretch absorption is still the largest band in all stretching modes based on the standard PES geometry. Although the interaction energy is small in the $C_2H_2\cdots HArCCF$ complex (−12.15 kJ/mol), it may be possible to observe this complex in a matrix environment.

The $CH\cdots\pi$ interaction energy in acetylene dimer is −5.69 kJ/mol at the MP2/6-311++G(2d,2p) level, which is close to −5.90 kJ/mol calculated at the MP4/DZ + (2df,2p).[35] The interaction energy in the $C_2H_2\cdots HCCF$ complex is increased to be −5.88 kJ/mol. This indicates that the presence of a F atom in the proton donor is beneficial for the formation of $CH\cdots\pi$ hydrogen bond. The interaction energy in the $C_2H_2\cdots HCCArF$ complex is calculated to be −7.86 kJ/mol, which is larger in absolute value than that in the $N_2\cdots HCCArF$ complex.[36] The result indicates that the insertion of an Ar atom into the C−F bond further enhances the $CH\cdots\pi$ interaction. In the $C_2H_2\cdots HCCArF$ complex, the interaction energy become more negative, thus the binding distance is shortened. The increase of the red shift of the H−C stretch frequency correlates with the large H−C bond extension. The enhancement of the H−C stretch absorption band in the complex is also larger than that in the $C_2H_2\cdots HCCF$ complex. When an Ar atom is inserted into the H−C bond, it brings a larger influence on the structure and properties of the $C_2H_2\cdots HArCCF$ than that from the insertion of an Ar atom into the C−F bond in the $C_2H_2\cdots HCCArF$ complex. For example, when the complex varies from $C_2H_2\cdots HCCF$ to $C_2H_2\cdots HArCCF$, the binding distance (R_{cp}) is shortened by 0.6881 Å, whereas it is decreased by 0.0805 Å when the complex changes from $C_2H_2\cdots HCCF$ to $C_2H_2\cdots HCCArF$.

The dipole moments of these complexes are also given in Table 2. Compared with the sum of dipole moments of the respective monomers, the dipole moments of these complexes are increased. The largest dipole moment increase ($\Delta\mu$) occurs in the $C_2H_2\cdots HArCCF$ complex ($\Delta\mu = 5.388$ D, a 75% enhancement over the sum of dipole moment of the isolated monomers), indicating that in this complex HArCCF is more perturbed than HCCF and HCCArF subunits, which is also in agreement with the structural and energetic changes mentioned in above. In the $C_2H_2\cdots HArF$ T-shape complex,[27] its structure is dominated by dipole−quadrupole electrostatic and induction interactions. We think that the similar interactions also play a role in the $C_2H_2\cdots HArCCF$ complex because they have a similar structure.

3.3. NBO Analyses. For a better understanding of the frequency shifts in these complexes and nature of the interaction, natural bond orbital (NBO) analyses have been carried out for these complexes, based on the HF/6-311++G(2d,2p) wave function using respective MP2/6-311++G(2d,2p) geometry optimized with the CP-corrected PES method. The stabilization energy, charge transfer, change of some atom charges, and selected orbital occupancies are summarized in Table 3. Among the orbital interaction between the donor orbital and the acceptor orbital, the $\pi(C\equiv C) \rightarrow \sigma^*(H{-}C(Ar))$ orbital interaction plays

TABLE 3: Stabilization Energy (E_{ij}, kcal/mol), Charge Transfer (CT, e), Changes in Selected Atom Charges (Δq, e) and Selected Orbital Occupancies in the Three Complexes at the MP2/6-311++G(2d,2p) Level[a]

	$C_2H_2\cdots HCCF$	$C_2H_2\cdots HCCArF$	$C_2H_2\cdots HArCCF$
E_{ij}	1.57	2.26	28.48
CT	0.0029	0.0045	0.0694
Δq_H	0.0101	0.0124	0.1658
Δq_F	−0.0024	−0.0096	−0.0208
$\Delta\sigma^*_{H-C(Ar)}$	0.0052	0.0038	−0.1233
ΔLP_F	0.0012	0.0096	0.0075

[a] Note: E_{ij} is the stabilization energy due to the $\pi(C\equiv C) \rightarrow \sigma^*(H-C(Ar))$ orbital interaction. CT represents the net electron density transferred from C_2H_2 to HCCF, HCCArF, or HArCCF. $\Delta q = q_{complex} - q_{monomer}$. LP represents the total lone pair electron density.

a main contribution to the stabilization energy. It is largest in the $C_2H_2\cdots HArCCF$ complex and smallest in the $C_2H_2\cdots HCCF$ complex.

It can be seen from the table that the electron density transferred from the proton acceptor molecule C_2H_2 is 0.0029 e, 0.0045 e, and 0.0694 e for the $C_2H_2\cdots HCCF$, $C_2H_2\cdots HCCArF$, and $C_2H_2\cdots HArCCF$ complexes, respectively. In general, the stronger the interaction in the complex, the more charge transfer from C_2H_2 molecule. Thus, the charge transfer interaction also plays an important role in the π hydrogen bond in these complexes.

The charge on the H atom of the proton donor is positive, which becomes more positive upon complexation, whereas the charge on the F atom of the proton donor is negative, which becomes more negative. The change of the H atom positive charge (Δq_H) is larger than that of the F atom negative charge (Δq_F) in the complexes. The largest charge changes occur in the $C_2H_2\cdots HArCCF$ complex. The increase in the H positive charge is consistent with the interaction energy in these complexes. The increase of the H positive charge and F negative charge in the proton donor molecule is accompanied with the dipole increase of this molecule (Table 2). It is known that electrostatic interaction means usually interaction of permanent moments. This shows that the electrostatic interaction is important for the π hydrogen bond in these complexes.

Upon complexation, there is a much loss of electron density from the antibonding $\sigma^*(H-Ar)$ orbital (−0.1233e) in the $C_2H_2\cdots HArCCF$ complex, whereas the electron density in the antibonding $\sigma^*(H-C)$ orbital is increased a little in the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes. They all are accompanied by an increase in the electron density of the F lone pair orbital in the three complexes. There is also a decrease of electron density in the $\sigma^*(H-Ar)$ orbital in blue-shifting hydrogen-bonded $N_2\cdots HArF$ complex, whereas there is also an increase in the $\sigma^*(H-Ar)$ orbital electron density of red-shifted hydrogen-bonded $P_2\cdots HArF$ complex.[37] Thus, we think that the negative value of the $\Delta\sigma^*(H-Ar)$ can be used to explain the blue shift of the H−Ar stretch in the $C_2H_2\cdots HArCCF$ complex, whereas the positive value of the $\Delta\sigma^*(H-C)$ is responsible for the red shift of the H−C stretch in the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes.

3.4. Decomposition of Interaction Energy. To comprehend the nature of the hydrogen bonding interactions in these complexes, the interaction energies were decomposed into the electrostatic interaction energy (E_{elst}), Pauli repulsion energy (E_{Pauli}), steric interaction energy (E_{steric}), and orbital interaction energy (E_{oi}), which were carried out on the equilibrium geometries obtained at the MP2/6-311++G(2d,2p) level with PBE/TZ2P(small core) in the *ADF2007.01* program. The results are given in Table 4. The interaction energy (E_{int}) is the sum of E_{elst}, E_{Pauli}, and E_{oi}. Although the interaction energies calculated with this method is more negative than those with supermolecular method at the MP2/6-311++G(2d,2p) level, their changing orders are similar for these complexes.

TABLE 4: Energy Components (kJ/mol) of the Interaction Energies in the Three Complexes[a]

	E_{elst}	E_{Pauli}	E_{oi}	E_{steric}	ΔE_{int}
$C_2H_2\cdots HCCF$	−6.72	4.84	−4.32	−1.88	−6.20
$C_2H_2\cdots HCCArF$	−9.01	6.70	−5.80	−2.31	−8.11
$C_2H_2\cdots HArCCF$	−48.82	79.22	−49.19	30.40	−18.79

[a] Note: $E_{steric} = E_{elst} + E_{Pauli}$ and $\Delta E_{int} = E_{elst} + E_{Pauli} + E_{oi}$.

In these complexes, the E_{elst} and E_{oi} are negative, whereas the E_{Pauli} is positive. In the C_2H_2-HCCF and $C_2H_2-HCCArF$ complexes, the magnitude of the E_{elst} is more than 1.5 times as much as the E_{oi}. This result shows that the electrostatic interaction plays a main contribution to the $CH\cdots\pi$ hydrogen bond in these complexes. When an Ar atom is inserted into the C−F bond, the E_{elst}, E_{Pauli}, and E_{oi} are all increased in absolute value and the increase of the E_{elst} in absolute value is larger than that of the E_{Pauli}. In the $C_2H_2-HArCCF$ complex, the magnitude of the E_{Pauli} is largest and the E_{elst} almost equals to the E_{oi}. The sum of the E_{elst} and E_{oi} is larger in absolute value than the E_{Pauli}, thus the interaction between the two monomers is attractive in the $C_2H_2-HArCCF$ complex. The three interaction terms in the complex are much larger than those in the other two complexes. The E_{oi} accounts for electron pair bonding, charge transfer, and polarization,[38] thus the charge transfer interaction plays a similar contribution with the electrostatic interaction to the interaction energy in the $C_2H_2-HArCCF$ complex. This is confirmed by the big charge transfer in the complex (Table 3).

The E_{steric} can be taken as the sum of the E_{elst} and E_{Pauli}. It is a small negative value in the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes, whereas it is a large positive one in the $C_2H_2\cdots HArCCF$ complex. The negative E_{steric} means that the contribution of electrostatic interaction is larger than that of Pauli repulsive interaction, whereas the positive one indicates that the contribution of Pauli repulsive interaction is larger than that of electrostatic interaction. The small negative E_{steric} in the $C_2H_2\cdots HCCF$ and $C_2H_2\cdots HCCArF$ complexes can be used to explain the small red shift of the H−C stretch vibration in the two complexes. The much large positive one in the $C_2H_2\cdots HArCCF$ complex may be responsible for the big blue shift of the H−Ar stretch vibration in the complex. The result shows that the origin of the blue shift in the complex is similar to that in other blue-shifting hydrogen bonds.[6]

4. Conclusions

In conclusion, we have predicted a stable neutral $C_2H_2\cdots HArCCF$ complex with a T shape, held together by a blue-shifting hydrogen bond. Upon complexation, the H−Ar stretch vibration has a very large blue shift (574 cm^{-1}) and a great decrease in the IR intensity. To best of our knowledge, this blue shift is largest reported for blue-shifting hydrogen bonds up to now. This blue shift is reverse to the red shift of the H−Ar stretch in $C_2H_2\cdots HArF$ complex although their structures are similar. The basis set and electron correlation have a great influence on the structure and properties of the $C_2H_2\cdots HArCCF$ complex. The HArCCF electronic structure suffers large perturbations due to the electrostatic interaction with C_2H_2 and the electron density transferred from the C_2H_2 molecule. A red shift of the C−H stretch occurs in the $C_2H_2\cdots$HCCF and $C_2H_2\cdots$HCCArF complexes. In the $C_2H_2\cdots$HArCCF complex, the electron density in the σ^*(H−Ar) orbital decreases, whereas that in the σ^*(H−C) orbital increases in the $C_2H_2\cdots$HCCF and $C_2H_2\cdots$HCCArF complexes. The steric interaction energy is positive in the $C_2H_2\cdots$HArCCF complex, whereas it is negative in the $C_2H_2\cdots$HCCF and $C_2H_2\cdots$HCCArF complexes. The positive steric interaction energy indicates that the repulsive force plays a dominant role in the $C_2H_2\cdots$HArCCF complex, which is responsible for the blue shift of the H−Ar stretch in the $C_2H_2\cdots$HArCCF complex. Although the interaction energy of the $C_2H_2\cdots$HArCCF complex is small, the blue shift of the H−Ar stretch is very large and the infrared intensity is also enough strong, which indicates the feasibility of experimental preparation of these novel complexes.

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