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Abnormalities of the Halogen Bonds in the Complexes between Y_2CTe ($Y = H, F, CH_3$) and XF ($X = F, Cl, Br, I$)

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Abstract: In this work, the hydrogen bonds and halogen bonds in the complexes between Y_2CTe ($Y = H, F, CH_3$) and XF ($X = F, Cl, Br, I$) have been studied by quantum chemical calculations. We found three interesting abnormalities regarding the interactions. Firstly, the strength of halogen bonds increases in the order of $IF < BrF < ClF < F_2$. Secondly, the halogen bonds formed by F_2 are very strong, with an interaction energy in the range between -199.8 and -233.1 kJ/mol. Thirdly, all the halogen bonds are stronger than the hydrogen bonds in the systems we examined. All these results are against the general understanding of halogen bonds. These apparent abnormal properties are reconciled with the high polarizability of the Te atom and the strong inducing effect of F on the Te atom of Y_2CTe . These findings provide a new perspective on halogen bonds. Additionally, we also proposed bonding distance-based methods to compare the strength of halogen/hydrogen bonds formed between different donor atoms and the same acceptor atom.

Keywords: halogen bond; hydrogen bond; abnormality; competition; AIM; NBO



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1. Introduction

A halogen bond is formed between an electrophilic region of a halogen atom X ($X = F, Cl, Br, \text{ and } I$) in a molecule $R-X$ (R is an electron-withdrawing atom/group) and a nucleophilic region of a molecule $Y-R'$ [1], denoted as $R-X \cdots Y-R'$. The electrophilic region, or the electron-deficient region of the X atom, is located along the $R-X$ σ -bond, denoted as σ -hole, which is surrounded by a belt of negative electrostatic potential [2]. Nowadays, halogen bonds have received extensive attention due to their important roles in many fields such as supramolecular chemistry, organocatalysis, synthetic coordination chemistry, polymer chemistry, and drug discovery [3–13]. For example, halogen bonding has been a popular and much exploited supramolecular synthon in the crystal field [5,9]. The application of halogen atoms as pharmaceutically active ligand substituents has been widespread in recent medicinal chemistry [10,11].

The properties of halogen bonds are related to their strength, which is not only dependent on the halogen donor atom and the acceptor atom, but is also affected by substituents. Normally, the halogen bond becomes stronger with the halogen donor varying from F to I [1,12–16]. An electron-donating group in the halogen bond acceptor strengthens the halogen bond, while an electron-withdrawing group in the acceptor has a weakening effect [16]. The type of the halogen bond acceptor varies from anions and neutral molecules with lone pairs to π -electron molecules, radicals, metal hydrides, and carbenes [17,18]. Specially, the molecules containing N and O atoms are often taken as the halogen bond acceptor.

It is interesting to study the differences between hydrogen bonds and halogen bonds, since both types of interactions have comparable strength and may coexist in the same systems [19–27]. Usually, hydrogen bonds are stronger than halogen bonds, except for when an iodine atom acts as the halogen donor [24,28]. Thus, some studies have tried

to make halogen bonds stronger than hydrogen bonds [28–30]. When the halogen bond acceptor H_2CO binds with the hydrogen/halogen donor HOBr , the interaction energy of the hydrogen bond is larger by 7 kJ/mol than that of the halogen bond [19]. Inversely, the interaction energy of the halogen bond is larger by 1 kJ/mol than that of the hydrogen bond if H_2CO is changed to H_2CS [28]. This difference is enlarged to 2 kJ/mol when one H atom of H_2CS is replaced by a Li atom [28]. These results indicate that the differences between hydrogen bonds and halogen bonds can be regulated by changing the halogen bond acceptor atoms and/or adding substituents. Nevertheless, these comparisons are not very convincing, because, for HOBr to participate in hydrogen bonding and halogen bonding interactions, the remaining moieties are $-\text{OBr}$ and $-\text{OH}$, respectively, meaning that they are not identical. To overcome this difficulty, Li and coauthors designed a molecule called 6-OX-fulvene ($\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{I}$), where the moiety of fulvene increases the acidity of the X atom. Then, they examined the interactions between this molecule and $\text{ZH}_3/\text{H}_2\text{Y}$ ($\text{Z} = \text{N}, \text{P}, \text{As}, \text{and Sb}; \text{Y} = \text{O}, \text{S}, \text{Se}, \text{and Te}$) [31]. It was found that the hydrogen bond is weakened with the Lewis base atom growing in size; however, the effect of the same on halogen bonds is very limited [31]. If SbH_3 and H_2Te are selected as the acceptors, the halogen bonds are much stronger than the hydrogen bonds, and the largest difference in their interaction energies is 40 kJ/mol in the $\text{SbH}_3 \cdots 6\text{-OCl-fulvene}$ complex [31].

H_2CTe is a homologue of H_2CO and H_2CS ; thus, it can also work as an acceptor to form hydrogen bonds or halogen bonds. Considering that Te is a semimetal located on the dividing line between metals and non-metals, we expect that the halogen bond formed by it may have different patterns. In this study, we investigated the complexes between Y_2CTe ($\text{Y} = \text{H}, \text{F}, \text{and CH}_3$) and XF ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{and I}$), wherein XF is a hydrogen/halogen bond donor and Y_2CTe is an acceptor. With the strong electronegativity of F, the designated molecules XF are expected to be prominent halogen bond donors. The following questions are addressed by the method of quantum chemical calculations: (1) Whether the halogen bond is stronger than the hydrogen bond. (2) Whether the strength of halogen bond follows the order of $\text{F}_2 < \text{ClF} < \text{BrF} < \text{IF}$. (3) What is the nature of the hydrogen bond and halogen bond in these complexes?

2. Results

2.1. Molecular Electrostatic Potential (MEP) Analyses

It is well known that the MEP diagram of a molecule is helpful to effectively predict noncovalent interactions involving that molecule [32]. Figure 1 shows the MEP maps of two families of molecules: Y_2CTe ($\text{Y} = \text{F}, \text{H}, \text{and CH}_3$) and XF ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{and I}$). The MEP distributions in both families are anisotropic. For Y_2CTe , we focus on the negative areas of the MEPs (blue colored areas). As expected, there are mainly two negative areas in each molecule, which correspond to the lone pairs of the Te atom. Compared with H_2CTe (−78.8 kJ/mol), the minimal MEP value of the Te atom decreases in F_2CTe (−52.5 kJ/mol) but increases in $(\text{CH}_3)_2\text{CTe}$ (−99.8 kJ/mol), which can be attributed to the electron-withdrawing nature of F atoms and the electron-donating ability of the methyl groups, respectively.

For XF , we focus on the positive areas of the MEPs (red areas). In the case of HF , the atom H exhibits positive electrostatic potential, while F is negative. For dihalogen molecules XF , there is a positive MEP region (σ -hole) at the X atom along the X-F bond. The magnitude of the σ -hole on the halogen atom increases with an increasing atomic mass of X. It is also found that the maximal MEP on the H atom is larger than that on the halogen atoms, including iodine.

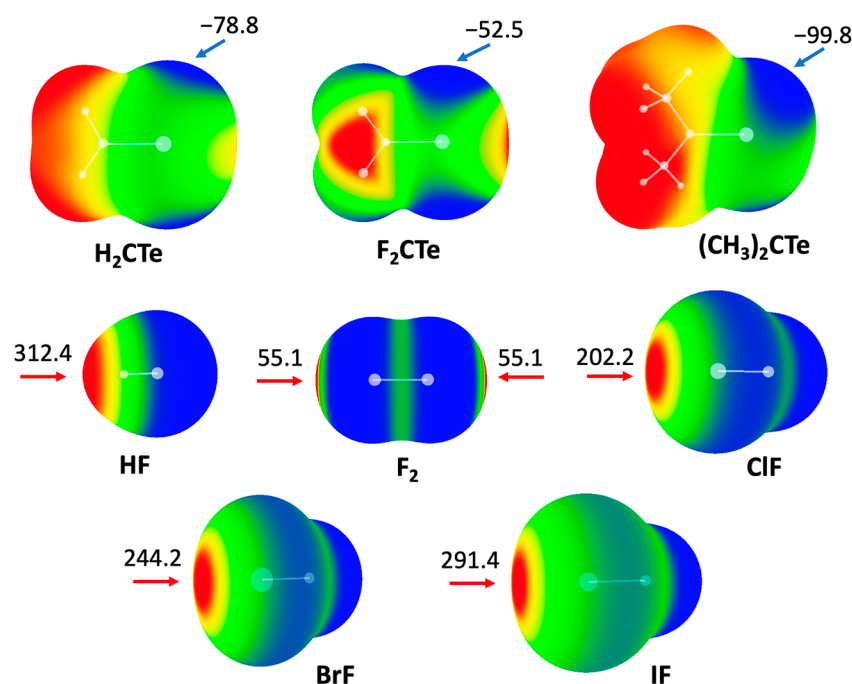


Figure 1. MEP diagrams of molecules studied in this work. Color ranges, in kJ/mol: red, greater than 52.5; yellow, between 52.5 and 0; green, between 0 and −52.5; blue, less than −52.5. Arrows refer to values of maxima and minima.

2.2. Geometries

For the hydrogen bonding or halogen bonding interactions ($Y_2CTe \cdots XF$), the general geometry of the complexes and the involved parameters are shown in Figure 2. We focus on the $Te \cdots X$ distance (R_1), the change in the $X-F$ bond length (ΔR_2), and the $Te \cdots X-F$ angle (α). The data of the optimized structures are listed in Table 1.

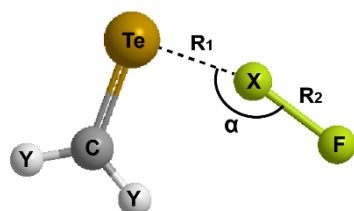


Figure 2. Illustration of the general structure of $Y_2CTe \cdots XF$ complex.

As can be seen in the table, all the values of R_1 are much shorter than the sum of the van der Waals radii of the respective atoms (3.3 Å for Te and H, 3.6 Å for Te and F, 4.0 Å for Te and Cl, 4.2 Å for Te and Br, and 4.4 Å for Te and I) [33,34]. This justifies the formation of hydrogen/halogen bonds. Further, the interactions between the electron-donor and acceptor molecules seem to be quite strong because stronger interaction is known to result in shorter bond length (R_1). To compare the relative strength between the halogen bonds between different interaction partners and the hydrogen bond, we define a quantity $\Delta R_1\%$ in the following equation:

$$\Delta R_1\% = \frac{R_c - R_1}{R_c} \times 100\% \quad (1)$$

where R_c is the sum of the van der Waals radii of the two atoms representing the critical distance to judge the presence of a hydrogen/halogen bond. After normalization with R_c , the shortening of the $Te \cdots X$ distance could be used to evaluate the strength of hydrogen/halogen bonds. Thus, for each of the three molecules (H_2CTe , F_2CTe , and $(CH_3)_2CTe$), the $\Delta R_1\%$ are all in the sequential order $F_2 > ClF > BrF > IF > HF$ when they form interaction

pairs. This implies that all the halogen bonds are stronger than the hydrogen bonds. Most interestingly, the $\Delta R_1\%$ values suggest that the halogen bond strength decreases with an increasing size of the halogen atom in the donor molecule XF. This is different from the general understanding of halogen bonds.

The change in the X-F bond length R_2 of a donor could also reflect the interaction strength of the hydrogen/halogen bond. Here, we calculated the change of R_2 relative to the R_2 in the monomer, denoted as $\Delta R_2\%$, using the following formula:

$$\Delta R_2\% = \frac{\Delta R_2}{R_2} \times 100\% \quad (2)$$

The $\Delta R_2\%$ represents the elongation percentage of the X-F bond, and the larger $\Delta R_2\%$ implies more significant weakening of the bond and, thus, stronger interaction. As indicated by $\Delta R_2\%$, the value of X-F bond length is larger in the halogen-bonded complex than that in the hydrogen-bonded analogue. This relative elongation in the halogen-bonded complex decreases in the order of $F_2 > ClF > BrF > IF$. These data are supportive of the conclusions from $\Delta R_1\%$.

The Te...X-F angle (α) is in the range of 168–180°, confirming a good direction of the hydrogen/halogen bonds. The angles are less than 180° in the majority of the complexes due to the attraction between the Y atom/group in Y_2CTe and XF.

Table 1. Binding distance (R_1 , Å), $\Delta R_1\%$; elongation of the X-F bond length (ΔR_2 , Å), $\Delta R_2\%$; bond angle (α , deg) of the complexes.

	R_1	$\Delta R_1\%$	ΔR_2	$\Delta R_2\%$	α
$H_2CTe \cdots HF$	2.518	23.70%	0.015	1.63%	168.6
$H_2CTe \cdots F_2$	2.151	40.25%	0.359	25.62%	168.8
$H_2CTe \cdots ClF$	2.528	36.80%	0.201	12.26%	176.8
$H_2CTe \cdots BrF$	2.686	36.05%	0.140	7.96%	177.4
$H_2CTe \cdots IF$	2.904	34.00%	0.089	4.64%	177.9
$F_2CTe \cdots HF$	2.586	21.64%	0.010	1.08%	179.9
$F_2CTe \cdots F_2$	2.140	40.56%	0.371	26.48%	170.7
$F_2CTe \cdots ClF$	2.647	33.83%	0.137	8.36%	179.7
$F_2CTe \cdots BrF$	2.790	33.57%	0.098	5.57%	179.8
$F_2CTe \cdots IF$	2.996	31.91%	0.064	3.33%	179.2
$(CH_3)_2CTe \cdots HF$	2.483	24.76%	0.018	1.95%	170.7
$(CH_3)_2CTe \cdots F_2$	2.176	39.56%	0.343	24.48%	168.0
$(CH_3)_2CTe \cdots ClF$	2.518	37.05%	0.222	13.54%	178.1
$(CH_3)_2CTe \cdots BrF$	2.673	36.36%	0.158	8.99%	179.1
$(CH_3)_2CTe \cdots IF$	2.893	34.25%	0.101	5.26%	180.0

2.3. Energies

Here, we consider the interaction energy to be the most credible criteria to judge the strength of interactions. Therefore, we calculated the interaction energies (E_{int}) of the various complexes for comparing the hydrogen and the halogen bonds. We used the counterpoise correction method to eliminate the basis set superposition error (BSSE), and the corrected energy is denoted as $E_{int,BSSE}$. In addition, the more accurate energy $E_{int,CBS,BSSE}$ with complete basis set (CBS) was also calculated. The results with and without BSSE correction, as well as with CBS, are all listed in Table 2. The main concern of our study is that the changing trends of the interaction energy with the variation of X in XF are the same based on all the three methods. It is worth clarifying that the following discussions about energies in the full text are all according to their absolute values. As shown in Table 2, the interaction energies of hydrogen bonds in all of the three series of complexes are smaller than those of the halogen bonds, indicating that the hydrogen bonds are weaker than all of the halogen bonds. For the strength order of the halogen bonds, both $E_{int,BSSE}$ and $E_{int,CBS,BSSE}$ increased in the order of $IF < BrF < ClF < F_2$ for the series of $H_2CTe \cdots XF$ and

(CH₃)₂CTe...XF complexes. This result is abnormal compared to the common perception that the halogen bond becomes stronger with the halogen donor varying from F to I. For F₂CTe...XF complexes, the $E_{\text{int,BSSE}}/E_{\text{int,CBS,BSSE}}$ of ClF, BrF, and IF was close. For all of the three series of the complexes, F₂ molecules formed the strongest halogen bonds. The absolute values of the interaction energy were very large, up to 228.8 kJ/mol for $E_{\text{int,BSSE}}$ and 233.1 kJ/mol for $E_{\text{int,CBS,BSSE}}$. To compare the interaction energies of the halogen bonds formed by different acceptors (Y₂CTe), when Y is F, an electron-withdrawing atom, the Y₂CTe...XF interaction, was weakened and compared to that of H₂CTe. On the contrary, when Y was the electron-donating methyl group, the interaction was strengthened.

Table 2. Interaction energies (E_{int}) corrected with and without BSSE in the complexes at the MP2/aug-cc-pVTZ(PP) level, all in kJ/mol.

		HF	F ₂	ClF	BrF	IF
H ₂ CTe	E_{int}	−27.8	−232.6	−107.0	−100.0	−94.8
	$E_{\text{int,BSSE}}$	−21.1	−220.7	−96.7	−87.0	−81.5
	$E_{\text{int,CBS,BSSE}}$	−22.3	−225.5	−106.5	−95.6	−89.9
F ₂ CTe	E_{int}	−21.1	−206.9	−61.2	−66.4	−68.8
	$E_{\text{int,BSSE}}$	−14.5	−194.4	−52.7	−54.8	−56.4
	$E_{\text{int,CBS,BSSE}}$	−15.6	−199.8	−60.5	−61.7	−63.6
(CH ₃) ₂ CTe	E_{int}	−33.7	−242.2	−128.1	−120.0	−111.8
	$E_{\text{int,BSSE}}$	−26.3	−228.8	−116.4	−103.6	−94.7
	$E_{\text{int,CBS,BSSE}}$	−27.7	−233.1	−126.5	−112.5	−103.3

To understand the attribution of the interaction energy, we partitioned it into five terms: electrostatic energy (E^{es}), exchange energy (E^{ex}), repulsion energy (E^{rep}), polarization energy (E^{pol}), and dispersion energy (E^{disp}), and the data are listed in Table 3. Obviously, E^{ex} is the largest attractive term in each complex; thus, it plays the most important role in the stabilization of hydrogen/halogen bonds [35,36]. This term increases in the order of HF < IF < BrF < ClF < F₂, which is consistent with the results of orbital interaction discussed in the following section. The large E^{ex} of each complex suggests a strong orbital interaction between the two respective monomers. For the repulsive term, E^{rep} was very large and even exceeds 1000 kJ/mol in each F₂-related complex. This can be attributed to the much shorter Te...X distances. It is seen that E^{rep} was almost twice as much as E^{ex} and both terms have a good linear relationship (Figure S1), confirming their dependency each other.

Table 3. Electrostatic (E^{es}), exchange energy (E^{ex}), repulsion energy (E^{rep}), polarization (E^{pol}), and dispersion (E^{disp}) energies in the complexes, all in kJ/mol.

	E^{es}	E^{ex}	E^{rep}	E^{pol}	E^{disp}
H ₂ CTe...HF	−33.0	−48.9	90.4	−21.3	−8.3
H ₂ CTe...F ₂	−246.0	−519.1	1097.3	−442.5	−110.3
H ₂ CTe...ClF	−255.5	−474.9	985.5	−278.4	−73.4
H ₂ CTe...BrF	−251.3	−417.7	865.0	−223.0	−60.1
H ₂ CTe...IF	−183.2	−346.0	678.3	−182.8	−47.8
F ₂ CTe...HF	−22.8	−38.4	70.8	−16.7	−7.4
F ₂ CTe...F ₂	−242.6	−524.2	1109.5	−423.0	−114.1
F ₂ CTe...ClF	−170.5	−344.4	695.7	−169.2	−63.9
F ₂ CTe...BrF	−171.7	−312.3	630.0	−148.2	−52.6
F ₂ CTe...IF	−129.4	−265.6	510.3	−129.3	−42.3
(CH ₃) ₂ CTe...HF	−46.2	−64.5	118.7	−26.2	−8.1
(CH ₃) ₂ CTe...F ₂	−253.4	−533.8	1116.9	−457.1	−101.5
(CH ₃) ₂ CTe...ClF	−287.7	−522.2	1080.9	−315.4	−72.1
(CH ₃) ₂ CTe...BrF	−287.6	−468.2	966.8	−253.4	−61.2
(CH ₃) ₂ CTe...IF	−211.6	−391.0	763.3	−205.4	−50.0

Now, we examine the three attractive terms (E^{es} , E^{pol} , and E^{disp}) in Table 3 in some detail (intuitively in Figure S2). For the hydrogen bond complex $\text{Y}_2\text{CTe}\cdots\text{HF}$, E^{es} was the largest attractive interaction among the three terms, followed by E^{pol} . For the interaction energies of halogen bonds formed by ClF , BrF , or IF with all the three acceptors Y_2CTe , the contributions of electrostatic and polarization interactions are comparable. However, for the interaction energies of the halogen bonds formed by F_2 with the Y_2CTe , the polarization interaction is the dominating contribution. This may be attributed to the special property of F , namely the largest electronegativity in the periodic table, thus possessing a very strong inducing ability.

2.4. Atoms in Molecules (AIM) Analyses

The hydrogen/halogen bonds can be characterized by the $\text{Te}\cdots\text{X}$ bond critical points (BCPs, Figure S3). The most important properties of each bond critical point are summarized in Table 4, where ρ refers to the electron density, $\nabla^2\rho$ its Laplacian, and H the energy density [37–39]. Generally, the larger electron density ρ reflects the stronger interaction. For all the investigated systems, ρ increases in the sequential order of $\text{HF} < \text{IF} < \text{BrF} < \text{ClF} < \text{F}_2$, in agreement with the order of interaction energies (Table 2). For the Laplacian, it was seen that $\nabla^2\rho > 0$ for all the complexes, demonstrating that the interactions studied were closed shell interaction. The energy density H is a more sensitive parameter than $\nabla^2\rho$. The negative values of H further demonstrate that the interactions are partially covalent in nature. In the complexes involving $(\text{CH}_3)_2\text{CTe}$, there are also BCPs between the methyl H and the halogen X in HX or XF s (Figure S3), indicating the presence of $\text{C-H}\cdots\text{F/X}$ hydrogen bonds. The interaction energies of the $\text{C-H}\cdots\text{F/X}$ hydrogen bonds were estimated by $E = 0.5V(r)$ [40,41], where $V(r)$ is the potential energy density at a BCP in each case. The corresponding data are -5.6 , -17.8 , -10.3 , -9.9 , and -8.1 kJ/mol for $(\text{CH}_3)_2\text{CTe}\cdots\text{HF}$, $(\text{CH}_3)_2\text{CTe}\cdots\text{F}_2$, $(\text{CH}_3)_2\text{CTe}\cdots\text{ClF}$, $(\text{CH}_3)_2\text{CTe}\cdots\text{BrF}$, and $(\text{CH}_3)_2\text{CTe}\cdots\text{IF}$, respectively. Clearly, these hydrogen bonds contributed to the stability of the complexes; however, their shares in the total interaction energies (Table 2) are small. Subtracting them from the total interaction energies, the residual results still have the same change trend with the total interaction energy. Thus, the presence of $\text{C-H}\cdots\text{F/X}$ hydrogen bonds does not affect the abnormality of halogen bonds.

Table 4. Electron density (ρ), Laplacian ($\nabla^2\rho$), and total energy density (H) at the intermolecular BCP in the complexes (all values in a.u.).

	ρ	$\nabla^2\rho$	H
$\text{H}_2\text{CTe}\cdots\text{HF}$	0.022	0.032	−0.003
$\text{H}_2\text{CTe}\cdots\text{F}_2$	0.095	0.101	−0.036
$\text{H}_2\text{CTe}\cdots\text{ClF}$	0.079	0.024	−0.027
$\text{H}_2\text{CTe}\cdots\text{BrF}$	0.066	0.033	−0.020
$\text{H}_2\text{CTe}\cdots\text{IF}$	0.052	0.041	−0.013
$\text{F}_2\text{CTe}\cdots\text{HF}$	0.019	0.032	−0.001
$\text{F}_2\text{CTe}\cdots\text{F}_2$	0.096	0.112	−0.036
$\text{F}_2\text{CTe}\cdots\text{ClF}$	0.060	0.058	−0.015
$\text{F}_2\text{CTe}\cdots\text{BrF}$	0.052	0.053	−0.012
$\text{F}_2\text{CTe}\cdots\text{IF}$	0.042	0.049	−0.008
$(\text{CH}_3)_2\text{CTe}\cdots\text{HF}$	0.025	0.031	−0.004
$(\text{CH}_3)_2\text{CTe}\cdots\text{F}_2$	0.091	0.088	−0.033
$(\text{CH}_3)_2\text{CTe}\cdots\text{ClF}$	0.082	0.013	−0.029
$(\text{CH}_3)_2\text{CTe}\cdots\text{BrF}$	0.069	0.024	−0.022
$(\text{CH}_3)_2\text{CTe}\cdots\text{IF}$	0.054	0.036	−0.015

2.5. Natural Bond Orbital (NBO) Analyses

The charge transfers (CTs) from Y_2CTe to XF are listed in Table 5, which are calculated as the sum of the charge on all atoms in Y_2CTe in the complexes. The charge transfer

reflects the electrons bias from electron donor (Y_2CTe) to electron acceptor (XF), providing information about the interaction strength in one aspect. As can be seen, the CTs are all larger than 0.2 e in the halogen bonds and even exceed 0.8 e in the F_2 complexes. On the contrary, the hydrogen-bonded complexes have much smaller CTs than the halogen-bonded analogues. Additionally, for all three of the series of complexes, the CT value decreases in the order $F_2 > ClF > BrF > IF > HF$, which is the same as the interaction strength order. Besides, when the Y is the electron-withdrawing atom F in Y_2CTe , the CT becomes smaller than that in H_2CTe . When the Y is the electron-donating methyl group, the CT increases.

There is an orbital interaction between the lone pair orbital on the Te atom of Y_2CTe and the anti-bonding orbital of the X-F bond ($Lp_{Te} \rightarrow \sigma^*_{X-F}$), and this orbital interaction can be measured with the second-order perturbation energy (E^2), which is also listed in Table 5. This orbital interaction is not detected in the F_2 -containing complexes since the F-F bond is taken as two subunits in the NBO analysis. The E^2 has a consistent change order with the charge transfer. This orbital interaction is strong; therefore, it makes an important contribution to the formation of hydrogen/halogen bond. We also calculated the dipole moments of the complexes (Table 5). It was found that the order of the dipole moment is consistent with the interaction energy. Further, the relationship between the CTs and the population of the σ^*_{X-F} orbital was analyzed, and positive correlation was found (Figure S4). This suggests that the main destination/receiver of the CT is the σ^*_{X-F} orbital in each complex.

Table 5. Charge transfer (CT, e), second-order perturbation energy (E^2 , kJ/mol), and dipole moment (μ , D) in the complexes.

	CT	E^2	μ
$H_2CTe \cdots HF$	0.043	70.0	3.17
$H_2CTe \cdots F_2$	0.893	-	10.52
$H_2CTe \cdots ClF$	0.511	781.6	8.23
$H_2CTe \cdots BrF$	0.414	761.4	7.87
$H_2CTe \cdots IF$	0.322	636.6	7.81
$F_2CTe \cdots HF$	0.031	51.0	2.88
$F_2CTe \cdots F_2$	0.843	-	9.53
$F_2CTe \cdots ClF$	0.334	462.3	5.62
$F_2CTe \cdots BrF$	0.293	417.7	5.93
$F_2CTe \cdots IF$	0.242	334.3	6.34
$(CH_3)_2CTe \cdots HF$	0.056	93.3	4.76
$(CH_3)_2CTe \cdots F_2$	0.943	-	11.73
$(CH_3)_2CTe \cdots ClF$	0.579	711.7	10.37
$(CH_3)_2CTe \cdots BrF$	0.462	696.9	9.96
$(CH_3)_2CTe \cdots IF$	0.350	613.1	9.84

3. Discussion

Hydrogen bonds and halogen bonds are two important noncovalent interactions, and they often coexist; thus, it is interesting to compare their strength. Generally speaking, hydrogen bonds are considered to be stronger than halogen bonds [28]. Interestingly, in the present study, using Y_2CTe ($Y = H, F$, and CH_3) as electron donors, we found that their halogen bonding interactions with dihalogen molecules XF ($X = F, Cl, Br$, and I) are stronger than their hydrogen bonding interactions with HF . This apparent abnormality was also seen in a previous study on the interactions between $PH_3/AsH_3/H_2Te$ and 6-*OX*-fulvene ($X = H, Cl, Br, I$) [31]. The second abnormality found in this work was that, when the X changes from F to I, the halogen bond becomes weaker, in contrast to the normal understanding that stronger halogen bonds accompany heavier halogen donors [16]. The abnormalities can be explained by the high polarizability of the Te atom, which is easily polarized when the electronegative XF approaches it. The greater the electronegativity of the approaching atom, the greater the polarization of the Te atom. Therefore, when the X atom of XF varies from I

to F, the dipole moment of the complex increases, as seen in Table 5, and the polarization energy (the major contribution to the interaction energy) also increases. Based on the data in Tables 3 and 5, a near positive correlation between the polarization energy and the dipole moment of the complex is found (Figure S5).

Another surprising result was that F₂ participates in the strongest halogen bond with the interaction energy up to −233.1 kJ/mol in the (CH₃)₂CTe⋯F₂ complex. Such large interaction energy is abnormal because it shows the least MEP at the end of the X atom among the four XF molecules. The apparent contradiction can be reconciled as follows. The F atom of F₂, due to it having the highest electronegativity among the halogens, would cause the largest polarization on the Te atom and, thus, the largest dipole moment of the Y₂CTe⋯XF complex. This is evidenced by the largest polarization energies being seen in the three Y₂CTe⋯F₂ complexes. The polarization mechanism is also consistent with the charge transfer data, which are the biggest in the Y₂CTe⋯F₂ complexes, even as big as 0.943e in the complex of (CH₃)₂CTe⋯F₂. Such big charge transfers (>0.8e) mean that the molecule F₂ holds nearly an extra electron in each of the three complexes, similar to the process of becoming an anion.

In order to test if the above abnormal results are found only for Y₂CTe, the Te atom of H₂CTe was replaced by O, S, and Se. The corresponding interaction energies are listed in Table 6. For the lighter chalcogen atoms O and S, the halogen bond strength increases in the order of F₂ < ClF < BrF < IF, which is the “normal” understanding of halogen bonds. For the heavier Se as the electron donor, the halogen bonds formed by ClF, BrF, and IF turned out to be comparable, while that formed by F₂ increased tremendously. This complicated situation is explained as follows. On one hand, a Se atom with a larger radius is more easily polarized than O and S. On the other hand, it is not as easily polarized as Te. Thus, only the most electronegative F₂ is able to assert marked influence on the electron distribution of H₂CSe, making it the strongest interaction in the H₂CSe⋯XF complexes.

Table 6. Interaction energies ($E_{\text{int,BSSE}}$, kJ/mol) of complexes between H₂CZ (Z = O, S, Se, and Te) and XF (X = H, F, Cl, Br, and I) at the MP2/aug-cc-pVTZ(PP) level.

	HF	F ₂	ClF	BrF	IF
H ₂ CO	−34.4	−5.9	−25.2	−34.4	−42.3
H ₂ CS	−26.6	−7.3	−52.2	−60.6	−64.0
H ₂ CSe	−24.6	−171.7	−64.7	−68.2	−69.6
H ₂ CTe	−21.1	−220.7	−96.7	−87.0	−81.5

As discussed above, the size/polarizability of the chalcogen atoms in H₂CZ (Z = O, S, Se, and Te) plays a very important role in the strength of halogen bonds. The data in Table 6 demonstrate that, for a given XF (X = F, Cl, Br, and I), the strength of its halogen bond with H₂CZ increases monotonously when Z varies from O to Te. On the contrary, the strength of the hydrogen bond between HF and H₂CZ decreases monotonously. As a result, for H₂CO, only IF forms a stronger halogen bond than the hydrogen bond. For H₂CS, each dihalogen molecule, excluding F₂, participates in a stronger halogen bond than the hydrogen bond formed by HF. For H₂CSe and H₂CTe, all the dihalogen molecules form stronger halogen bonds than hydrogen bonds formed by HF.

The above discussions about the interaction strength of halogen/hydrogen bonds are based on their interaction energies, often regarded as golden criteria. Practically, other parameters such as electrostatic potential (MEP), halogen/hydrogen bond length (R_1), and donor bond length (R_2) are often used to compare the interaction strength. MEP sometimes provides correct indications. For example, the MEP order is Cl < Br < I at the end of X atom in XF, and the halogen bond strength order is ClF < BrF < IF in the F₂CTe⋯XF complexes. However, the F has the least MEP at the end of the X atom among the four XF molecules, but it forms the strongest interaction with F₂CTe. Clearly, MEP cannot always provide correct results because it only contains the information of isolated molecules. For R_1 and R_2 , due to the different radii of the halogen atoms, we defined two quantities, $\Delta R_1\%$ and

$\Delta R_2\%$, to compare the halogen/hydrogen bond strength. The correlations between the two quantities and the respective interaction energies are plotted in Figure 3 (the trend comparisons are shown in Figure S6). Undoubtedly, they are all positively correlated, suggesting that both $\Delta R_1\%$ and $\Delta R_2\%$ can be used to compare the halogen/hydrogen bond strength qualitatively. Quantitatively, $\Delta R_2\%$ is a better choice.

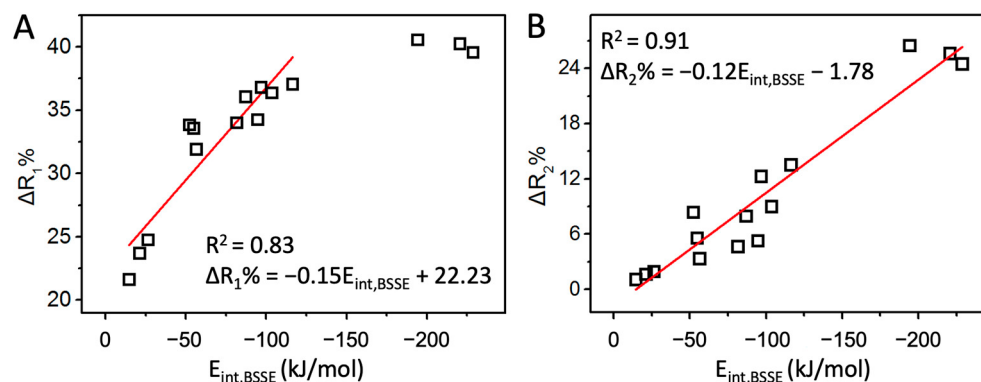


Figure 3. The correlation of $E_{\text{int,BSSE}}$ with $\Delta R_1\%$ (A) and $\Delta R_2\%$ (B).

4. Computational Methods

All calculations were carried out with the Gaussian 09 program [42]. The geometries of all the monomers and complexes were optimized at the MP2 level with the aug-cc-pVTZ basis set for all atoms except I and Te, where the aug-cc-pVTZ-PP basis set was adopted to account for relativistic corrections [43]. For all atoms in all the complexes, collectively, aug-cc-pVTZ(PP) represents the basis set used in this work. The extrema of molecular electrostatic potentials (MEPs) were calculated on the 0.001 a.u. isodensity surface at the MP2/aug-cc-pVTZ(PP) level using the WFA-SAS program [32]. The interaction energy (E_{int}) of a complex was computed as the difference between the energy of the complex and the sum of the energies of the monomers with their geometries frozen in the optimized complex. For this supermolecular method of calculating the MP2 interaction energy, the dispersion correction was taken into account, since MP2 contains certain correlation terms such as the uncoupled Hartree-Fock (UCHF) dispersion energy, the corresponding Hartree-Fock exchange-dispersion energy, and a deformation-correlation term [44]. Interaction energies were corrected for basis set superposition error (BSSE) using the counterpoise procedure (CP) proposed by Boys and Bernardi [45]. The two-point extrapolated energies with a complete basis set (CBS) proposed by Halkier et al. [46,47] were obtained with two basis sets of aug-cc-pVDZ(PP) and aug-cc-pVTZ(PP). The localized molecular orbital-energy decomposition analysis was used to decompose the interaction energy into five terms of electrostatic, exchange, repulsion, polarization, and dispersion at the MP2/aug-cc-pVTZ(PP) level with the GAMESS program [48]. The dispersion energy was obtained as a difference between the MP2 and CCSD(T) energy in the GAMESS program. The AIM2000 package [49] was used to assess the topological parameters at each bond critical point (BCP), including electron density, as well as its Laplacian, and energy density. Using the natural bond orbital (NBO) method [50] within the Gaussian 09 program, the charge transfer and second-order perturbation energy were obtained.

5. Conclusions

Quantum chemical calculations have been performed to study the interactions between $Y_2\text{CTe}$ ($Y = \text{H}, \text{F}$, and CH_3) and XF ($X = \text{H}, \text{F}, \text{Cl}, \text{Br}$, and I). The results show that the electron-withdrawing groups F in F_2CTe weaken the interactions, while the electron-donating methyl groups in $(\text{CH}_3)_2\text{CTe}$ strengthen them. More importantly, we found three abnormalities regarding halogen bonds in this work. The first one is that the strength of halogen bond increases in the sequential order $\text{IF} < \text{BrF} < \text{ClF} < \text{F}_2$ in $\text{H}_2\text{CTe} \cdots \text{XF}$ and $(\text{CH}_3)_2\text{CTe} \cdots \text{XF}$ complexes. This is contrary to the normal understanding that the stronger halogen bonds

accompany heavier halogen donors. The second one is that the halogen bonds formed by F_2 are very strong, even up to -233.1 kJ/mol with $(CH_3)_2CTe$. Contrary to this, the halogen bonds formed by F-R are normally considered to be very weak or even negligible. The last one is that all halogen bonds are stronger than the hydrogen bonds in the complexes, which is abnormal compared with the majority of previous studies. These abnormalities are discussed in the context of the high polarizability of the Te atom in the halogen acceptors. Because the Te atom is easily polarized when the electronegative XF approaches it, the greater the electronegativity of the X atom, the greater the polarization of the Te atom. Particularly, the F atom has the largest electronegativity in the periodic table and possesses a very strong inducing ability. Consequently, F-F forms tremendously strong interactions with Y_2CTe .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27238523/s1>, Figure S1: The relationship between repulsion energy E^{rep} and exchange energy E^{ex} in the complexes between Y_2CTe ($Y = H, F$, and CH_3) and XF ($X = H, F, Cl, Br$, and I); Figure S2: Electrostatic (E^{es}), polarization (E^{pol}), and dispersion (E^{disp}) energies in complexes between Y_2CTe ($Y = H, F$, and CH_3) and XF ($X = H, F, Cl, Br$, and I); Figure S3: Molecular graphs of the complexes between Y_2CTe ($Y = H, F, CH_3$) and XF ($X = H, F, Cl, Br, I$). Small red balls indicate the $Te \cdots X$ bond critical point; Figure S4: The relationship between the population of the σ^*_{X-F} orbitals and the charge transfer in the complexes formed by Y_2CTe ($Y = H, F$, and CH_3) and XF ($X = H, F, Cl, Br$, and I); Figure S5: The relationship between the polarization energy E^{pol} and the dipole moment of the complexes formed by Y_2CTe ($Y = H, F$, and CH_3) and XF ($X = F, Cl, Br$, and I); Figure S6: Trend comparison of $E_{int,BSE}$ with $\Delta R_1\%$ (A) and $\Delta R_2\%$ (B) in $H_2CTe \cdots XF$ systems; The coordinates of optimized monomer Y_2CTe ($Y = H, F, CH_3$), XF ($X = H, F, Cl, Br, I$), and their complexes.

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