

Theoretical study of the triangular bonding complex formed by carbon tetrabromide, a halide, and a solvent molecule in the gas phase

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Abstract MP2(full)/aug-cc-pVDZ(-PP) computations predict that new triangular bonding complexes $\text{CBr}_4 \cdots \text{X}^- \cdots \text{H}-\text{C}$ (where X^- is a halide and H–C refers to a protic solvent molecule) consist of one halogen bond and two hydrogen bonds in the gas phase. Carbon tetrabromide acts as the donor in the halogen bond, while it acts as an acceptor in the hydrogen bond. The halide (which commonly acts as an acceptor) can interact with both carbon tetrabromide and solvent molecule (CH_3CN , CH_2Cl_2 , CHCl_3) to form a halogen bond and a hydrogen bond, respectively. The strength of the halogen bond obeys the order $\text{CBr}_4 \cdots \text{Cl}^- > \text{CBr}_4 \cdots \text{Br}^- > \text{CBr}_4 \cdots \text{I}^-$. For the hydrogen bonds formed between various halides and the same solvent molecule, the strength of the hydrogen bond obeys the order $\text{C}-\text{H} \cdots \text{Cl}^- > \text{C}-\text{H} \cdots \text{Br}^- > \text{C}-\text{H} \cdots \text{I}^-$. For the hydrogen bonds formed between the same halide and various solvent molecules, the interaction strength is proportional to the acidity of the hydrogen in the solvent molecule. The diminutive effect is present between the hydrogen bonds and the halogen bond in chlorine and bromine triangular bonding complexes. Complexes containing iodide ion show weak cooperative effects.

Keywords Halogen bond · Hydrogen bond · Halide · σ -Hole · Carbon tetrabromide · MP2(full)

Introduction

A halogen bond (XB) is a type of noncovalent interaction that occurs between a halogen atom (acting as a Lewis acid) and another atom with a lone pair of electrons, an anion, or a group or molecule with a π -system (acting as a Lewis base) [1]. The interaction is characterized by high binding directionality (160 – 180°) and a short bond distance (less than the sum of the vdW radii) or a bond strength that is comparable to that of a hydrogen bond (HB) [2–5]. The origin and general features of halogen bonds have been explored over the past few decades [6–10]. The σ -hole (σ_h) binding theory describes the halogen-bond interaction as an electrostatically driven noncovalent interaction between an electropositive “crown” of halogen atoms and negative species, and correctly predicts the direction of the halogen bond [11, 12]. There is a belt of negative potential around the σ -hole of the halogen (as shown in Fig. 1). Since noncovalent interactions are largely electrostatically driven, halogen atoms (which have both negative and positive electrostatic potentials) can interact with both nucleophiles and electrophiles, and such interactions have been investigated computationally [13–15] and observed crystallographically [16–18]. Halogen bonds, either on their own or in combination with hydrogen bonds, have been applied in crystal engineering [19, 20], and have also been demonstrated to be important in biology [21–23], drug design [24, 25], and molecular recognition [26, 27].

The cooperative effect occurs in systems involving two or more noncovalent interactions. Several studies have shown cooperative effects in hydrogen-bonded complexes [28–31]. The cooperative effect between halogen bonds and hydrogen bonds has received much attention recently [32–34]. A hydrogen-bond chain usually grows stronger as the number of the hydrogen bonds in the chain increases due

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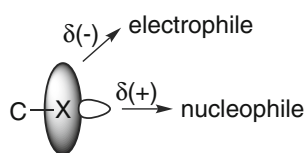


Fig. 1 Negative and positive electrostatic potentials of a halogen atom in a molecule

to the cooperative effect. It should be noted that the cooperative effect decreases if the molecule acts as a double proton acceptor in the chain of hydrogen-bonded complexes [35]. Li et al. [32] reported the competition and cooperation that occur between hydrogen and halogen bonds in $\text{HCN}\cdots(\text{HOBr})_n$ and $(\text{HCN})_n\cdots\text{HOBr}$ systems. McDowell et al. [30] examined the cooperative effect in $\text{Y}\cdots\text{HCN}\cdots\text{HCN}$ and the diminutive effect in $\text{HCN}\cdots\text{Y}\cdots\text{HCN}$. They concluded that the cooperative effect decreases as the hardness of the Y atom bonded to HCN increases.

Lu et al. [13] published a theoretical investigation of interesting systems of triangular trimers $(\text{R}-\text{X})_3$, where X is Br or I, and R is one of several hydrocarbon and fluorohydrocarbon groups. The positive region of the halogen atom in one $\text{R}-\text{X}$ bond interacts with the negative region of the halogen atom in another $\text{R}-\text{X}$ bond. Three $\text{R}-\text{X}$ molecules interact with each other to form triangular trimers $(\text{R}-\text{X})_3$ with the same halogen bonds. Most of these trimers exhibit noncooperative effects, while a few show weak cooperativity. Such studies provide information useful for crystal engineering, and indicate that it is possible to create new materials.

In this article, we report new triangular bond complexes consisting of a halogen bond and hydrogen bonds that are predicted by computational quantum chemistry. CBr_4 was selected for study due to its nucleophilicity and electrophilicity in the trimer. CBr_4 can interact with both a nucleophile X^- (Cl^- , Br^- , I^-) to form a halogen bond and electrophilic solvent molecule (CH_3CN , CH_2Cl_2 , CHCl_3) to form a hydrogen bond. The solvent molecule can also interact with X^- to form a hydrogen bond. The theoretical results we obtained show that carbon tetrabromide can interact with both a halide and a solvent molecule (CH_3CN , CH_2Cl_2 , CHCl_3) in the triangular-bonded interaction pattern $\text{CBr}_4\cdots\text{X}^-\cdots\text{H}-\text{C}$, which consists of one halogen bond and two or three hydrogen bonds. The properties of triangular bonding complexes, including their geometries, bonding energies, and the cooperative effects between the two kinds of interactions involved, were investigated at the MP2(full)/aug-cc-pVDZ(PP) level.

Computational details

All calculations were performed using the Gaussian 03 program package [36]. Full geometrical optimizations of

the complexes and monomers were performed at the MP2 (full) [37] level. The aug-cc-pVDZ-PP basis set was used to describe the iodine atom, while aug-cc-pVDZ was applied for all the other atoms [38]. The basis set superposition error (BSSE) was eliminated by applying the standard counterpoise method of Boys and Bernardi [39].

The total interaction energy (ΔE_{total}) was obtained as the difference between the energy of the complex and the sum of the total energies of the three monomers:

$$\Delta E_{\text{total}} = E_{\text{ABC}} - (E_{\text{A}} + E_{\text{B}} + E_{\text{C}}). \quad (1)$$

Here, A, B, and C represent CBr_4 , X^- (Cl^- , Br^- , I^-), and the solvent molecule (CH_3CN , CH_2Cl_2 , CHCl_3), respectively. E_{ABC} , E_{A} , E_{B} , and E_{C} are the energies of the trimers and monomers.

Each halogen-bond or hydrogen-bond interaction energy is estimated as the difference between the energy of the interacting pair (with “frozen” coordinates) in the trimer and the sum of the energies of the two monomers:

$$\Delta E_{\text{XB}} = E_{\text{AB}}(\text{ABC}) - (E_{\text{A}} + E_{\text{B}}) \quad (2)$$

$$\Delta E_{\text{HB}} = E_{\text{BC}}(\text{ABC}) - (E_{\text{B}} + E_{\text{C}}) \quad (3)$$

$$\Delta E_{\text{HB}'} = E_{\text{AC}}(\text{ABC}) - (E_{\text{A}} + E_{\text{C}}). \quad (4)$$

The cooperative effects of the halogen bond and hydrogen bonds of these trimers can be assessed by computing a three-body nonadditive energy:

$$\Delta E_{\text{coop}} = \Delta E_{\text{total}} - (\Delta E_{\text{XB}} + \Delta E_{\text{HB}} + \Delta E_{\text{HB}'}). \quad (5)$$

Results and discussion

Molecular surface electrostatic potentials

The three pairs of unshared electrons on the halogen atom X in the molecule $\text{R}-\text{X}$ form a belt of negative electrostatic potential around its central region, which in turn leaves a positive region (σ -hole) on a portion of its surface centered on the $\text{R}-\text{X}$ axis. So the halogen atom can interact with both nucleophiles and electrophiles, and “like-like” interactions can be understood on the basis of the σ -hole theory reported by Politzer et al. [15]. The electrostatic potential surface of CBr_4 was computed at the MP2/aug-cc-pVDZ level and is shown in Fig. 2. The most positive electrostatic potential ($V_{\text{S, max}}$), centered on the extension of the $\text{C}-\text{Br}$ bond, is $+25.60 \text{ kcal mol}^{-1}$. The most negative electrostatic potential ($V_{\text{S, min}}$), which occurs on the lateral side, is $-5.32 \text{ kcal mol}^{-1}$. In terms of the molecular surface electrostatic potential, it is easy

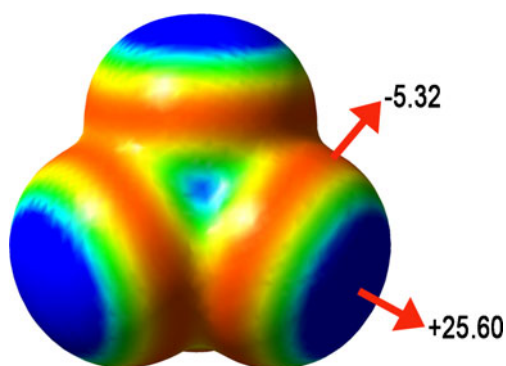
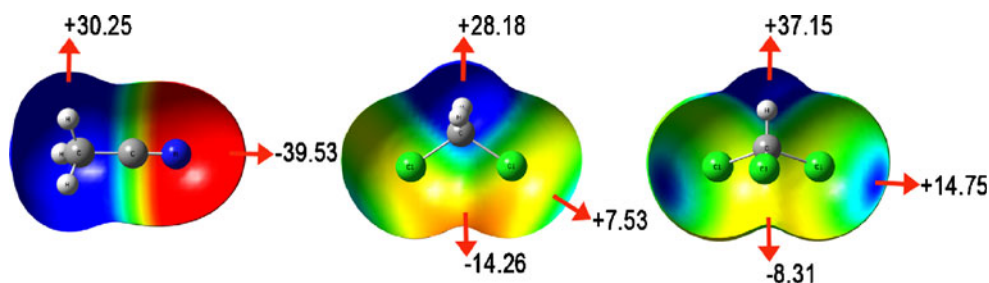


Fig. 2 The electrostatic molecular surface electrostatic potential of carbon tetrabromide was generated by mapping the MP2/aug-cc-pVDZ electrostatic potential onto the molecular electron density surface (0.001 electron/bohr³) (kcal mol⁻¹)

to predict that the halide will interact with the carbon tetrabromide to form the halogen bond. This paper aims to illustrate the possible interactions between CBr₄, the halide, and the solvent molecule. Three kinds of solvents of medium polarity (CH₃CN, CH₂Cl₂, CHCl₃), two of which are halogenated, were considered here. We wanted to know whether the solvent molecule would interact with the halide or the carbon tetrabromide. The molecular surface electrostatic potentials of the selected solvents were also computed, as shown in Fig. 3. The protons of the acetonitrile have positive electrostatic potentials, while the nitrogen has negative electrostatic potential. The most positive and negative values are +30.25 kcal mol⁻¹ and -39.53 kcal mol⁻¹, respectively, so the acetonitrile can be a good nucleophilic or electrophilic reagent—it can interact with both the carbon tetrabromide to form a halogen bond and the halide to form a hydrogen bond. The most regions of protons of dichloromethane is positive, and the most positive electrostatic potential ($V_{S, \max}$) is +28.18 kcal mol⁻¹. There is a positive region (σ -hole) on the outer tip of each chlorine, along the extension of the C–Cl bond, which has a maximum positivity of +7.53 kcal mol⁻¹. The most negative value on the belt around the σ -hole of chlorine is -14.26 kcal mol⁻¹. The most positive electrostatic potential $V_{S, \max}$ on the hydrogen surface of the chloroform is +37.15 kcal mol⁻¹. The most positive value of the σ -hole is +14.75 kcal mol⁻¹, and the most negative value on the surface of the chlorine is -8.31 kcal mol⁻¹.

Fig. 3 The cross-section of molecular surface electrostatic potential was generated by mapping the MP2/aug-cc-pVDZ electrostatic potential onto the molecular electron density surface (0.001 electron/bohr³) (kcal mol⁻¹)



The dichloromethane and chloroform most likely interact with halide to form a hydrogen bond and then with carbon tetrabromide to form a halogen bond. In view of the molecular electrostatic potential, it is possible that halogen and hydrogen bonds co-occur in the carbon tetrabromide/halide/solvent system. Do these interactions compete or cooperate with each other? This question will be discussed from the perspective of geometrics and binding interaction energies below.

Geometric parameters

Based on the molecular surface electrostatic potential, CBr₄ can interact with both a nucleophile X⁻ and an electrophilic solvent molecule, as described above. The halide (a strong nucleophilic reagent) will interact with both CBr₄ and the solvent molecule. The halide was thus positioned at possible reactive sites on CBr₄ and the solvent molecule. After full geometrical optimization at the MP2/aug-cc-pVDZ(-PP) level, it was interesting to observe that the halide was able to interact with both CBr₄ and the solvent molecule to form the trimer $\text{CBr}_4 \cdots \text{X}^- \cdots \text{H-C}$, in which there was one halogen bond and two hydrogen bonds that share the same acceptor, X⁻. Figure 4 shows the stationary structures and the important geometric parameters of this triangular bonding complex. All of the optimum Br \cdots X⁻, H \cdots X⁻, and H \cdots Br distances are within the sums of the van der Waals radii of the corresponding atoms, indicating the existence of halogen-bond and hydrogen-bond interactions. The hydrogen atom of the solvent molecule interacts both with the halide and with the bromide atom of CBr₄. The generation of the two hydrogen bonds and the halogen bond lead to the formation of the triangular bonding system.

For the trimers $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{H-C}$, the Br \cdots Cl⁻ distances vary from 2.739 Å to 2.811 Å (21.9–23.9 % shorter than 3.600 Å, the sum of the vdW radii of chlorine and bromine), indicating the formation of a halogen bond. The halogen bond angles $\angle \text{C-Br} \cdots \text{Cl}^-$ range from 172.7° for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CH}_3\text{CN}$ to 175.8° for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CHCl}_3$, which is typically close to 180°. The H \cdots Cl⁻ distances range from 2.188 Å to 2.579 Å (12.6–25.8 % shorter than 2.950 Å, the sum of the vdW radii of chlorine and hydrogen). The H \cdots Br

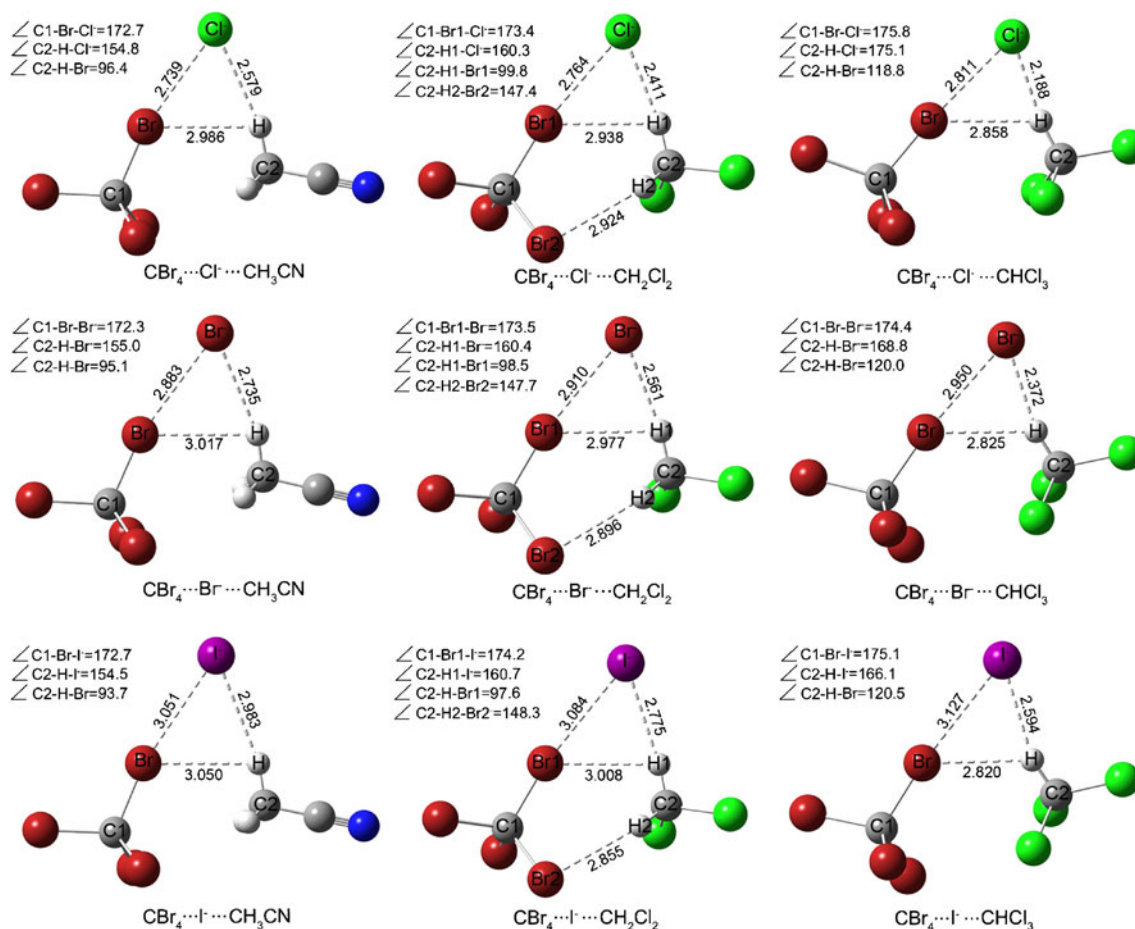


Fig. 4 MP2(full)/aug-cc-pVDZ(-PP) optimized key geometrical parameters of triangular bonding complexes (bond distances in Å and bond angles in degrees, respectively)

distances range from 2.858 to 2.986 Å (2.1–6.3 % shorter than 3.050 Å, the sum of the vdW radii of bromine and hydrogen). These provide evidence for the formation of a hydrogen bond in the trimers $CBr_4 \cdots Cl \cdots H-C$. The ranges of the hydrogen bond angles $\angle C-H \cdots Cl^-$ and $\angle C-H \cdots Br$ are 154.8–175.1° and 96.4–147.4°, respectively. The hydrogen-bond angles vary widely because of the always positive electrostatic potential of hydrogen. The halogen bond distance $Br \cdots Cl^-$ lengthens as the hydrogen bond distance $Cl^- \cdots H$ shortens. There should be the results of competition between the halogen bond and the hydrogen bonds in $CBr_4 \cdots Cl^- \cdots H-C$. It should be mentioned that the two hydrogen atoms of CH_2Cl_2 interact with the CBr_4 to form two hydrogen bonds, which make the system more stable.

As shown in Fig. 4, the ranges of the $Br \cdots Br^-$ distances in $CBr_4 \cdots Br^- \cdots H-C$ and the $Br \cdots I^-$ distances in $CBr_4 \cdots I^- \cdots H-C$ are 2.883–2.950 Å (20.3–22.1 % shorter than 3.700 Å, twice the vdW radius of bromine) and 3.051–3.127 Å (21.0–22.9 % shorter than 3.960 Å, the sum of the vdW radii of bromine and iodine). All of the $Br^- \cdots H$, $I^- \cdots H$ and $Br \cdots H$ distances in the $CBr_4 \cdots Br^- \cdots H-C$ and $CBr_4 \cdots I^- \cdots H-C$ trimers are less than

the sums of the vdW radii of the corresponding atoms. The bond angles illustrated in Fig. 4 are consistent with the crystal structures containing halogen and hydrogen bonds [40–42]. Taken together, all of these observations provide initial evidence for the formation of halogen and hydrogen bonds. Competition between the halogen and hydrogen bonds are observed for $CBr_4 \cdots Br^- \cdots H-C$ in view of the changes in bond distances. However, this phenomenon is not apparent for $CBr_4 \cdots I^- \cdots H-C$, and it will be analyzed from the perspective of the interaction energy below.

A theoretical simulation of the double halogen bond $CBr_4 \cdots X^- \cdots Cl-C$ was also performed because of the possible interaction between the chlorine of the chloroform or dichloromethane and halide. As shown in Fig. S1, double halogen-bond complexes are not stable in dichloromethane and chloroform. This can also be explained by the σ_h bond theory. As can be seen in Fig. 2, the most positive value of the σ_h on the chlorine atoms in chloroform is +14.75 kcal mol⁻¹, while $V_{s, \max}$ of hydrogen is +37.15 kcal mol⁻¹. The most positive value of σ_h for chlorine is 7.53 kcal mol⁻¹, while $V_{s, \max}$ of hydrogen for dichloromethane is +28.18 kcal mol⁻¹. The halide prefers to

interact with hydrogen rather than with chlorine from the perspective of the molecular electrostatic potential. The bromine of CBr_4 and the chlorine of CHCl_3 or CH_2Cl_2 will repel each other because of a belt of negative electrostatic potential around the σ -hole, which is another reason for the very unstable double halogen-bond complexes.

Interaction energies

The BSSE-corrected total interaction energies, halogen bond energies, and hydrogen bond energies in the trimers are collected in Table 1. Uncorrected interaction energies are also listed in Table S1, which is included in the “Electronic supplementary material.” Comparing the corrected and uncorrected total interaction energies, the energies caused by the BSSE range from $7.31 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CH}_3\text{CN}$ to $10.19 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{I}^- \cdots \text{CHCl}_3$. The largest percentage of the total interaction energy accounted for by the BSSE is 30.5 %. These percentages are larger for much weaker interactions. The percentage of the total interaction energy accounted for by the BSSE for the interaction between CBr_4 and CHCl_3 is 69.9 %. Therefore, the BSSE cannot be neglected for the halogen and hydrogen bonds investigated in the present study.

From the interaction energies shown in Table 1, it is apparent that the strength of the halogen bond decreases as the polarizability of the halide increases; that is, $\text{CBr}_4 \cdots \text{Cl}^- > \text{CBr}_4 \cdots \text{Br}^- > \text{CBr}_4 \cdots \text{I}^-$. For example, the interaction energies of $\text{CBr}_4 \cdots \text{X}^-$ are $-16.42 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CH}_3\text{CN}$, $-14.30 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{Br}^- \cdots \text{CH}_3\text{CN}$ and $-11.34 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{I}^- \cdots \text{CH}_3\text{CN}$. The same trend is observed for the trimers $\text{CBr}_4 \cdots \text{X}^- \cdots \text{CH}_2\text{Cl}_2$ and $\text{CBr}_4 \cdots \text{X}^- \cdots \text{CHCl}_3$. The hydrogen bond formed in the trimers is more complicated because of the different donor and acceptor. For the same solvent molecule, the order of hydrogen-bond strength is: $\text{H} \cdots \text{Cl}^- > \text{H} \cdots \text{Br}^- > \text{H} \cdots \text{I}^-$. The chloride has the largest electron density and the smallest atomic radius. For the same electron-donor halide, the hydrogen-bond strength is determined by

the electron-withdrawing ability of the solvent molecule. The strengths of the hydrogen bonds formed between the chloride and the various solvent molecules obey the order: $\text{CHCl}_3 \cdots \text{Cl}^- (-15.37 \text{ kcal mol}^{-1}) > \text{CH}_2\text{Cl}_2 \cdots \text{Cl}^- (-13.17 \text{ kcal mol}^{-1}) > \text{CH}_3\text{CN} \cdots \text{Cl}^- (-12.51 \text{ kcal mol}^{-1})$. The hydrogen-bond strength is not strictly proportional to the maximum electrostatic potential of the hydrogen. One of the reasons for this may be the competitive or cooperative effects between the halogen and hydrogen bonds.

An interesting aspect of noncovalent interactions is how one noncovalent interaction influences another involved in the same system. The cooperative and competitive effects that occur in systems which contain halogen and hydrogen bonds or interactions of the same type have been investigated extensively [28–35]. The bond distances discussed above are evidence for the existence of competitive effects in the trimers investigated in this study. The cooperative interaction energies were calculated by performing a three-body nonadditive energy calculation. A positive value means competition and a negative value means cooperativity. For the same halogen bond $\text{CBr}_4 \cdots \text{Cl}^-$, the stronger the hydrogen bond, the weaker the halogen bond, and vice versa. For the trimers $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{H-C}$, the interaction energy of $\text{CBr}_4 \cdots \text{Cl}^-$ decreases from $-16.42 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CH}_3\text{CN}$ to $-15.21 \text{ kcal mol}^{-1}$ for $\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{CHCl}_3$ with a gradual increase in hydrogen-bond strength. This is consistent with the increase in halogen-bond distances due to the effect of the hydrogen bonding. The positive value ΔE_{coop} is evidence for competition between the halogen and hydrogen bonds. Such competitive effects are also observed for the trimers $\text{CBr}_4 \cdots \text{Br}^- \cdots \text{H-C}$. The situation for the trimers $\text{CBr}_4 \cdots \text{I}^- \cdots \text{H-C}$ is different. The halogen bond $\text{CBr}_4 \cdots \text{I}^-$ barely changes in terms of bond length and interaction energy when different hydrogen bonds $\text{H} \cdots \text{I}^-$ are included in the trimers. However, the negative value of ΔE_{coop} suggests cooperativity between $\text{CBr}_4 \cdots \text{I}^-$ and $\text{H} \cdots \text{I}^-$. The acceptor/donor iodine shared by the halogen bond and the hydrogen bond is more polarizable, which leads to cooperative effects. This is also consistent with the conclusion that the cooperative effect

Table 1 Total interaction energies, halogen-bond and hydrogen-bond energies, and cooperative energies (corrected for the BSSE) in the trimers (in kcal mol^{-1})

	$\text{CBr}_4 \cdots \text{Cl}^- \cdots \text{sol}$			$\text{CBr}_4 \cdots \text{Br}^- \cdots \text{sol}$			$\text{CBr}_4 \cdots \text{I}^- \cdots \text{sol}$		
	CH_3CN	CH_2Cl_2	CHCl_3	CH_3CN	CH_2Cl_2	CHCl_3	CH_3CN	CH_2Cl_2	CHCl_3
ΔE_{total}	-27.51	-27.50	-28.63	-24.69	-24.64	-26.80	-21.62	-22.43	-23.20
ΔE_{XB}	-16.42	-16.02	-15.21	-14.30	-14.19	-13.98	-11.34	-11.05	-10.71
ΔE_{HB}	-12.51	-13.17	-15.37	-10.67	-10.97	-13.09	-8.89	-9.08	-10.11
ΔE_{HB^*}	-1.14	-1.28	-1.24	-1.01	-1.42	-1.37	-0.76	-1.53	-1.46
ΔE_{coop}	2.56	2.97	3.19	1.29	1.94	1.64	-0.63	-0.77	-0.92

diminishes as the hardness of Y in $\text{NCH}\cdots\text{Y}\cdots\text{HCN}$ increases, as reported by McDowell et al. [30]. Lu et al. also reported that three iodine trimers show weak cooperativity, while most other trimers exhibit noncooperative effects [13].

Conclusions

Nine new triangular bonding complexes $\text{CBr}_4\cdots\text{X}^-\cdots\text{H-C}$ containing both halogen and hydrogen bonds were investigated at the MP2(full)/aug-cc-pVDZ-(PP) level. The strength of the halogen and hydrogen bonds in the gas phase follow the order: $\text{CBr}_4\cdots\text{Cl}^-\cdots\text{H-C} > \text{CBr}_4\cdots\text{Br}^-\cdots\text{H-C} > \text{CBr}_4\cdots\text{I}^-\cdots\text{H-C}$. CBr_4 can interact with a nucleophile X^- (Cl^- , Br^- , I^-) to form a halogen bond and with an electrophilic solvent molecule (CH_3CN , CH_2Cl_2 , CHCl_3) to form a hydrogen bond due to the anisotropic distribution of the electrostatic potential of the Br atom. Competitive effects occur between the halogen bond and hydrogen bonds involved in the trimers $\text{CBr}_4\cdots\text{Cl}^-\cdots\text{H-C}$ and $\text{CBr}_4\cdots\text{Br}^-\cdots\text{H-C}$. Weak cooperativity occurs in the trimers $\text{CBr}_4\cdots\text{I}^-\cdots\text{H-C}$. This study has increased our understanding of the interactions between halogen and hydrogen bonds in the same complex. It should provide useful information for those working in the fields of crystal engineering, drug design, and molecular recognition.

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