Does HF prefer to be attached to X or M of XHHM (X = F, Cl, Br; M = Li, Na, K) system? A B3LYP and MP2 theoretical investigation into cooperativity effect

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The cooperativity effects are investigated in the possible linear dihydrogen-bonded ternary complexes, F–H⋯X–H⋯H–M and X–H⋯H–M⋯F–H, and non-dihydrogen-bonded quaternary systems, F–H⋯X⁻⋯H–H⋯M⁺ and X⁻⋯H–H⋯M⁺⋯F–H (X=F, Cl, Br; M=Li, Na, K) using the DFT-B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) methods. The result shows that for the dihydrogen-bonded complex, remarkable cooperativity effect is found and the cooperativity effect of the H⋯H bond on the H⋯X or M⋯F interaction is more pronounced than that of the H⋯X or M⋯F contact on the H⋯H interaction. The complexation energy and cooperativity effect in F–H⋯X–H⋯H–M are larger than those of the corresponding X–H⋯H–M⋯F–H system. Thus, the F–H⋯X–H⋯H–M complex is preferentially formed and F–H prefers to be attached to the X end. For the non-dihydrogen-bonded quaternary system, due to the stronger complexation energy and cooperativity effect of Cl⁻⋯H–H⋯Li⁺⋯F–H or F–H⋯Br⁻⋯H–H⋯K⁺ as compared to those of F–H⋯Cl⁻⋯H–H⋯Li⁺ or Br⁻⋯H–H⋯K⁺⋯F–H, F–H prefers to be attached to Li⁺ or Br⁻. Cooperativity effect is analyzed using the charges on hydrogen in the H⋯H moiety, surface electrostatic potentials and atoms in molecules analysis.

Keywords: Theoretical chemistry, Density functional calculations, Cooperativity effect, Dihydrogen bonds, Hydrogen bonds

When several noncovalent interactions operate simultaneously and mutually enhance the strength of each other, it is termed as acting cooperatively[1]. Cooperativity effect is currently a topic of wide ranging interest due to its extremely important role in chemical reaction, molecular recognition and regulation of biochemical process[2–8].

Recently, the cooperativity effects involving the M–H$^{\delta-}$⋯$^{\delta+}$H–X (M=B, Li, etc.; X=F, CN, etc.) dihydrogen bond have received much attention[9–12]. Alkorta *et al.*[13] found the dihydrogen-bond cooperativity in (HCCBeH)ₙ clusters theoretically. The cooperative effect was confirmed in the dihydrogen-bonded clusters of the aza-borane derivatives using the density functional theory (DFT) method[9]. By *ab initio* calculations, the cooperativity between the dihydrogen-bond and O⋯H hydrogen-bond in (H₂O)ₙ–BH₄⁻ was proposed by Zabardasti *et al.*[14], while anti-cooperativity between the dihydrogen-bond and N⋯H hydrogen-bond in (NH₃)ₙ–BeH₄²⁻ was confirmed by Zabardasti *et al.*[15]

There are two possible ways to add one A$^{\delta+}$–B$^{\delta-}$ molecule (such as H–F) into the dihydrogen-bonded M–H⋯H–X system. One is found in the M–H⋯H–X⋯A–B complex which denotes that one A–B molecule is attached to the X atom side, i.e., the A$^{\delta+}$ atom points towards the X atom. The other is found in the A–B⋯M–H⋯H–X complex in which B$^{\delta-}$ points into the M atom. During the past 10 years, there have been several investigations into the cooperativity effects involving dihydrogen-bonding interaction in the M–H⋯H–X⋯A–B systems[9–11,14, 16]. However, to the best of our knowledge, the work done to date on the cooperativity effect involving dihydrogen bond in A–B⋯M–H⋯H–X is rather meager[17], and no detailed and extensive comparison of the cooperativity effect between M–H⋯H–X⋯A–B and A–B⋯M–H⋯H–X has been presented theoretically.

It is well known that the preference of A–B attached to M or X of M–H⋯H–X can be determined by the energy difference between A–B⋯M–H⋯H–X and M–H⋯H–X⋯A–B. Thus, in ternary systems, quaternary systems, etc., the preference of A–B attached to M or X of other complex can be judged by the strength of intermolecular interaction energy. However, this method is not always available. For example, Liao[18] found that, for the Li–H⋯H–F system, although when a water molecule was

attached to the Li end, the system could gain in significant stabilization energy, adding a water molecule to the F end could strengthen the dihydrogen bond more effectively. Our group reported that, for the CN(NC)BB–H···H–Na system, when a water molecule was attached to the Na or CN(NC) end, the hydrogen bond length was shortened and the dihydrogen bond was strengthened[19]. Unfortunately, in these two studies, it is not clear whether H_2O prefers to be attached to Li/Na or F/CN(NC) side.

In the present work, we have investigated systematically into the cooperativity effects in the possible dihydrogen-bonded systems, F–H···X–H···H–M and X–H···H–M···F–H, and the non-dihydrogen-bonded complexes, F–H···X$^-$···H–H···M$^+$ and X$^-$···H–H···M$^+$···F–H (X=F, Cl, Br; M=Li, Na, K) using the B3LYP and MP2(full) methods. Our goal is to clarify whether F–H prefers to be attached to M or X. This theoretical investigation shall reveal the nature of the cooperativity effect involving dihydrogen-bonding interaction for further studies on the structure and activity of the chemical and biochemical systems involving dihydrogen bond in theory and experiment.

Methodology

All calculations were performed with Gaussian 03 programs[20]. All the monomers and complexes were optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G(3df,2p) basis set. The topological charge density was displayed by the AIM (Atom in Molecules) method[21] using AIMPAC program[22] at the MP2(full)/6-311++G(3df,2p) level. The natural bond orbital analysis[23] was also carried out using the MP2(full)/6-311++G(3df,2p) method.

The intermolecular interaction energies in binary systems (i.e., $E_{int.(H···H)}$ in X–H···H–M; $E_{int.(F–H···X–H)}$ in F–H···X–H, and $E_{int.(H–M···F–H)}$ in H–M···F–H) were calculated by evaluating the difference between the energy of complex and the total energies of monomers, and corrected with the basis set superposition error (BSSE)[24,25] and zero point vibrational energy (ZPE).

In the ternary system, $E'_{int.(H···H)}$, $E'_{int.(F–H···X–H)}$ and $E'_{int.(H–M···F–H)}$ represent the interaction energy between both the moieties which are directly interacting with, and were calculated using Eqs. (1), (1)', (2) and (3), respectively,

$$E'_{int.(H···H)} = E_{F–H···X–H···H–M} - E_{F–H···X–H} - E_{H–M}$$
$$\text{for F–H···X–H···H–M} \qquad …(1)$$

$$E'_{int.(H···H)} = E_{X–H···H–M···F–H} - E_{X–H} - E_{H–M···F–H}$$
$$\text{for X–H···H–M···F–H} \qquad …(1')$$

$$E'_{int.(F–H···X–H)} = E_{F–H···X–H···H–M} - E_{F–H} - E_{X–H···H–M}$$
$$\text{for F–H···X–H···H–M} \qquad …(2)$$

$$E'_{int.(H–M···F–H)} = E_{X–H···H–M···F–H} - E_{F–H} - E_{X–H···H–M}$$
$$\text{for X–H···H–M···F–H} \qquad …(3)$$

where $E_{F–H···X–H···H–M}$, $E_{X–H···H–M···F–H}$, $E_{F–H···X–H}$, $E_{H–M···F–H}$, $E_{X–H···H–M}$, $E_{H–M}$, $E_{X–H}$ and $E_{F–H}$ are the total energy of the ternary, binary and monomeric systems, respectively. $E'_{int.(H···H)}$, $E'_{int.(F–H···X–H)}$ and $E'_{int.(H–M···F–H)}$ were also corrected with BSSE and ZPE. In general, when the values of $E'_{int.(H···H)}$, $E'_{int.(F–H···X–H)}$ or $E'_{int.(H–M···F–H)}$ in the ternary systems are larger than the corresponding values in the binary systems ($E_{int.(H···H)}$, $E_{int.(F–H···X–H)}$ or $E_{int.(H–M···F–H)}$), the cooperativity effects might occur.

The cooperativity ($E_{coop.}$) in ternary complex was calculated using Eq. (4) or (4)',

$$E_{coop.} = E_{int.(F–H···X–H···H–M)} - E_{int.(H···H)}$$
$$- E_{int.(F–H···X–H)} - E''_{int.(F–H···H–M)}$$
$$\text{for F–H···X–H···H–M} \qquad … (4)$$

$$E_{coop.} = E_{int.(X–H···H–M···F–H)} - E_{int.(H···H)}$$
$$- E_{int.(H–M···F–H)} - E''_{int.(X–H···F–H)}$$
$$\text{for X–H···H–M···F–H} \qquad … (4')$$

where $E_{int.(F–H···X–H···H–M)}$ and $E_{int.(X–H···H–M···F–H)}$ are the complexation energy of the ternary and correspond to the energy involved in the direct assembly of the ternary complex from its constituent monomers. These were calculated as the energy difference between the total energy of ternary complex and the energies of monomers.

$$E_{int.(F–H···X–H···H–M)} = E_{(F–H···X–H···H–M)} - E_{F–H} - E_{X–H} - E_{H–M}$$
$$\text{for F–H···X–H···H–M} \qquad … (5)$$

$$E_{int.(X–H···H–M···F–H)} = E_{(X–H···H–M···F–H)} - E_{F–H} - E_{X–H} - E_{H–M}$$
$$\text{for X–H···H–M···F–H} \qquad … (6)$$

In Eqs (4) and (4)', $E''_{int.(F–H···H–M)}$ and $E''_{int.(X–H···F–H)}$ are defined as the through-space interaction energy between both the moieties with which they do not interact directly. These were calculated at the ternary geometries of F–H···X–H···H–M and X–H···H–M···F–H by employing Eqs (7) and (8), respectively,

$$E''_{int.(F-H\cdots H-M)} = E'_{F-H\cdots H-M} - E_{F-H} - E_{H-M}$$
$$\text{for } F-H\cdots X-H\cdots H-M \qquad \dots (7)$$

$$E''_{int.(X-H\cdots F-H)} = E'_{X-H\cdots F-H} - E_{X-H} - E_{F-H}$$
$$\text{for } X-H\cdots H-M\cdots F-H \qquad \dots (8)$$

where $E'_{F-H\cdots H-M}$ and $E'_{X-H\cdots F-H}$ represent the total energy of the binary $F-H\cdots H-M$ and $X-H\cdots F-H$ frameworks (not be optimized) of the corresponding optimized ternary geometries, respectively.

Results and Discussion

Binary system and $X^-\cdots H_2\cdots M^+$ ternary complex

$X-H\cdots H-M$ and $X^-\cdots H_2\cdots M^+$ complexes

In the $X-H\cdots H-M$ binary-system search, all the possible conformations were considered to depict the intermolecular $H\cdots H$ dihydrogen bonds. Therefore, in the optimization, the H atom of X–H was made to point towards the H atom of H–M, and all the atoms were in direct line. Thus, the $C_{\infty v}$ symmetry structures of $X-H\cdots H-M$ (X=F, Cl, Br; M=Li, Na, K) were obtained (Supplementary Data, Fig. S1). The $C_{\infty v}$ symmetry structure of $F-H\cdots H-Li$ was also found by Liao[18]. However, in each case there are two degenerate imaginary frequencies. In order to obtain the structure in which there is no imaginary frequency, a full optimization was carried out for each of the structures. Nine non-linear $H_2\cdots MX$ structures (Nimag = 0, H_2 interacting with the XM molecule, see Supplementary Data, Fig. S2) were obtained with the C_1 symmetry. Although the total energy of $H_2\cdots MX$ is lower than that of the corresponding linear $X-H\cdots H-M$ structure, there is no intermolecular $H\cdots H$ contact and the distances between two hydrogen atoms are very close to 0.800 Å at the B3LYP/6-311++G** level, which is close to the bond length in H_2 (~0.732 Å). Furthermore, the bond lengths of X–H and H–M are obviously elongated and the distances between X and M are shortened greatly, i.e., the $H_2\cdots MX$ complex are formed. In other words, these structures have nothing to do with "dihydrogen bonding". However, as mentioned above, our goal in this work is mainly to investigate into the cooperativity effect involving the dihydrogen bond, and clarify whether HF prefers to be attached to M or X by comparing the strength of the cooperativity effect involving the dihydrogen bond. Therefore, non-linear $H_2\cdots MX$ structure was not considered.

The $H\cdots H$ distances in FH$\cdots$HLi, FH$\cdots$HNa, FH$\cdots$HK and ClH$\cdots$HLi are within the range of 1.278 to 1.378 Å at the MP2(full)/6-311++G(3df,2p) level (Fig. S1). The values of the $H\cdots H$ distances are close to that in the common dihydrogen-bonded complexes[9,12]. Therefore, these four systems could be as the conventional $X-H\cdots H-M$ dihydrogen-bonded complexes, with the interaction energies in the range of –48.33 to –76.06 kJ/mol (after the correction of BSSE) at the MP2(full)/6-311++G(3df,2p) level (see Supplementary Data, Table S1). However, in BrHHLi, ClHHNa, BrHHNa, ClHHK and BrHHK, the distances between two hydrogen atoms are found to be in the range of 0.800 to 0.966 Å at the MP2(full)/6-311++G(3df,2p) level. These values are very close to the bond length in H_2. This means that the H–H bonds in these five complexes are partly covalent in nature. They look like H_2 molecules dressed by X and M, i.e., $X^-\cdots H_2\cdots M^+$ ternary complex. Leszczynski[26] and Liao *et al*.[18] have found that in some dihydrogen-bonded systems with extremely short $H\cdots H$ intermolecular contacts, $H\cdots H$ interactions are partly covalent and there is a large transfer of electron charge from the acceptor to the proton donating bond.

$F-H\cdots X-H$ complex

The structures of the binary complexes $F-H\cdots X-H$ (X=F, Cl, Br) are also shown in Fig. S1. All the equilibrium structures have C_s symmetry without imaginary frequency, and are non-linear. However, we have found that there is one imaginary frequency in each linear structure of $F-H\cdots X-H$. Therefore, the non-linear structures are considered in this work. The intermolecular H-bonding interaction energy is reported in Table S2 (Supplementary Data). $F-H\cdots F-H$ has the highest interaction energy followed by $F-H\cdots Cl-H$ and $F-H\cdots Br-H$. The decrease of the binding energy (–17.25 > –10.12 > –9.77 kJ/mol at MP2(full)/6-311++G(3df,2p) level) is in good agreement with the increase of the $H\cdots X$ distance (1.826 < 2.283 < 2.424 Å at the MP2(full)/6-311++G(3df,2p) level).

$H-M\cdots F-H$ complex

The structures of the binary complexes $H-M\cdots F-H$ (M=Li, Na, K) have $C_{\infty v}$ symmetry without imaginary frequency (Fig. S1). The $M\cdots F$ distances are in the order of $H-Li\cdots F-H < H-Na\cdots F-H < H-K\cdots F-H$, and the intermolecular interaction energies are in the order of $H-Li\cdots F-H > H-Na\cdots F-H > H-K\cdots F-H$ (Supplementary Data, Table S3).

Ternary systems F–H···X–H···H–M and X–H···H–M···F–H

Geometrical parameters

The structures of eight complexes F–H···X–H···H–M and X–H···H–M···F–H (X=F, Cl), i.e., ternary systems of F–H with FH···HLi, FH···HNa, FH···HK and ClH···HLi, are obtained (see Fig. 1). In F–H···X–H···H–M, the hydrogen atom of HF is attached to the X atom side, and in X–H···H–M···F–H, the F atom of HF is attached to the M atom. All the structures have $C_{\infty v}$ symmetry with two degenerate imaginary frequencies, and they are not local minima in potential energy hypersurface. However, the H···H dihydrogen bond is found in each of complexes. It should be mentioned again that our goal in this work is to investigate into the cooperativity effect involving the dihydrogen bond. As mentioned above, the binary complexes F–H···X–H (X=F, Cl) have C_s symmetry. Therefore, the C_s symmetric ternary systems have also been designed and fully optimized at the MP2(full)/6-311++G(3df,2p) level. However, the final structures
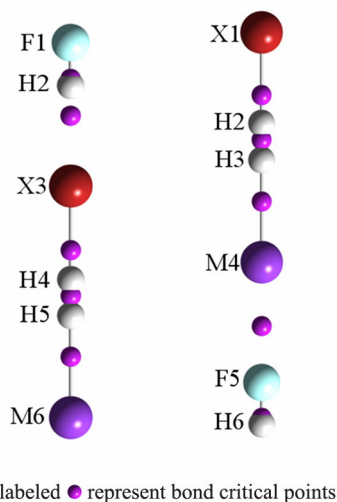

Unlabeled ● represent bond critical points

Fig. 1—Structures of the ternary and quaternary complexes ($C_{\infty v}$) [X=F, Cl, Br; M=Li, Na, K].

were not obtained, with the signal of "*Convergence failure*" in the "*out* files" from Gaussian 03. In order to further search for the minima, all the possible F–H···X–H···H–M and X–H···H–M···F–H structures were fully reoptimized using B3LYP/6-311++G**, B3LYP/aug-cc-pvtz, MP2/6-311++G** and B06-2X/6-311++G** (by using Gaussian 09) methods, with tighter SCF convergence criteria of 10^{-7} and using ''iop (2/16 = 2)" in the tactical optimization. However, all the efforts were in vain. The obtained structures were either optimized as the above eight structures or as fragments or it was difficult to find the local minima, probably due to the flat potential wells. Therefore, the above eight structures are considered in this work.

The geometric results of F–H···X–H···H–M and X–H···H–M···F–H are collected in Tables 1 and 2, and Tables S4 and S5. From Tables 1 and 2, the H···X and M···F distances are within the ranges of 1.575–2.113 Å and 1.871–2.719 Å at MP2(full)/6-311++G(3df,2p) level, respectively. The H···X distances just fall into the accepted values of the conventional hydrogen bonds, and the M···F distances are longer than the sums of M–F covalent radii but shorter than those of van der Waals radii. Thus, the intermolecular H···X H-bonding and M···F interactions are suggested in F–H···X–H···H–M and X–H···H–M···F–H, respectively.

In F–H···F–H···H–Li and F–H···H–M···F–H (M=Li, Na, K), the H···H distances are within the range of 1.241–1.356 Å at the MP2(full)/6-311++G(3df,2p) level, just within the accepted values of strong H···H dihydrogen bonds[26–28]. Therefore, the H···H and H···F interactions may coexist in F–H···F–H···H–Li, and the coexistent interactions of H···H and M···F are suggested in F–H···H–M···F–H. However, in F–H···F–H···H–M (M=Na, K), F–H···Cl–H···H–Li and Cl–H···H–Li···F–H, the H···H distances are in the range of 0.905–1.194 Å

Table 1—Selected bond lengths and bond critical point properties of the complexes F1–H2···X3–H4···H5–M6 and F1–H2···X3$^-$···H4H5···M6$^+$ at the MP2(full)/6-311++G(3df,2p) level

Complex	NImag	$R_{H2\cdots X3}$ (Å)	$\rho_{BCP(H2\cdots X3)}$ (a.u.)	$\nabla^2\rho_{BCP(H2\cdots X3)}$ (a.u.)	$R_{H4\cdots H5}$ (Å)	$\rho_{BCP(H4\cdots H5)}$ (a.u.)	$\nabla^2\rho_{BCP(H4\cdots H5)}$ (a.u.)
F–H···F–H···H–Li	2	1.674	0.0306	0.1446	1.241	0.0585	0.0227
F–H···F–H···H–Na	2	1.644	0.0335	0.1544	1.194	0.0680	–0.0048
F–H···F–H···H–K	2	1.575	0.0421	0.1786	1.058	0.1015	–0.1366
F–H···Cl–H···H–Li	2	2.113	0.0245	0.0679	0.905	0.1567	–0.4702
F–H···Cl$^-$···H$_2$···Na$^+$	2	2.043	0.0305	0.0719	0.820	0.2070	–0.8462
F–H···Cl$^-$···H$_2$···K$^+$	2	2.002	0.0345	0.0732	0.782	0.2360	–1.0570
F–H···Br$^-$···H$_2$···Li$^+$	2	2.258	0.0226	0.0541	0.857	0.1823	–0.6537
F–H···Br$^-$···H$_2$···Na$^+$	2	2.212	0.0261	0.0559	0.804	0.2182	–0.9208
F–H···Br$^-$···H$_2$···K$^+$	2	2.177	0.0289	0.0567	0.774	0.2421	–1.0918

Table 2—Selected bond lengths and bond critical point properties of the complexes X1–H2···H3–M4···F5–H6 and X1⁻···H2H3···M4⁺···F5–H6 at the MP2(full)/6-311++G(3df,2p) level

Complex	NImg	$R_{H2···H3}$ (Å)	$\rho_{BCP(H2···H3)}$ (a.u.)	$\nabla^2\rho_{BCP(H2···H3)}$ (a.u.)	$R_{M4···F5}$ (Å)	$\rho_{BCP(M4···F5)}$ (a.u.)	$\nabla^2\rho_{BCP(M4···F5)}$ (a.u.)
F–H···H–Li···F–H	2	1.356	0.0443	0.0426	1.882	0.0223	0.2080
F–H···H–Na···F–H	2	1.344	0.0468	0.0352	2.288	0.0148	0.1191
F–H···H–K···F–H	2	1.288	0.0554	0.0203	2.719	0.0121	0.0698
Cl–H···H–Li···F–H	2	1.115	0.0879	–0.0748	1.871	0.0232	0.2173
Cl⁻···H₂···Na⁺···F–H	2	0.881	0.1724	–0.5805	2.252	0.0164	0.1342
Cl⁻···H₂···K⁺···F–H	2	0.809	0.2178	–0.9200	2.648	0.0140	0.0844
Br⁻···H₂···Li⁺···F–H	2	0.898	0.1622	–0.5029	1.855	0.0245	0.2306
Br⁻···H₂···Na⁺···F–H	2	0.832	0.2011	–0.7870	2.245	0.0168	0.1375
Br⁻···H₂···K⁺···F–H	2	0.790	0.2310	–1.0082	2.640	0.0143	0.0861

at MP2(full)/6-311++G(3df,2p) level, indicating the partly covalent H···H dihydrogen bonds. Thus, the coexistent of the partly covalent H···H dihydrogen-bonding and H···X or M···F interactions is suggested. The covalent character of dihydrogen bond is suggested in NFH_3^+···HBeH since the H···H distance was 1.114 Å at the MP2(full)/6-311++G(d,p) level[26].

For F–H···X–H···H–M and X–H···H–M···F–H, the H···H distances follow the orders: F–H system > Cl–H system and H–Li system > H–Na system > H–K system. Thus, the dihydrogen-bonding interaction energy follows the orders of F–H system < Cl–H system and H–Li system < H–Na system < H–K system.

From Tables 1 and 2, the equilibrium distance $R_{H···H}$ of the H···H dihydrogen bond in F–H···X–H···H–M or X–H···H–M···F–H decreases when compared to the corresponding binary complex X–H···H–M (see Fig. S1). This indicates that the presence of the H···X or M···F interaction may strengthen the H···H interaction. On the other hand, the equilibrium distance $R_{H···X}$ or $R_{M···F}$ in the ternary complex is also shortened when compared to that in the corresponding binary complex, showing that the presence of the H···H interaction may also strengthen the H···X or M···F interaction. In addition, the X–H and F–H bond lengths in the ternary complexes increase while the H–M bond lengths decrease in comparison with those of the binary systems. Thus, the cooperativity effect may occur upon formation of the ternary complex F–H···X–H···H–M or X–H···H–M···F–H.

The change of H···H distance in F–H···X–H···H–M is larger than that in X–H···H–M···F–H. For example, in F–H···X–H···H–Li (X=F, Cl), the decrease of the H···H distance is 0.137 and 0.373 Å at MP2(full)/6-311++G(3df,2p) level, respectively, while it is only 0.022 and 0.163 Å in X–H···H–Li···F–H. This is in accordance with the result from the investigation on the microsolvation effect of dihydrogen-bonded

LiH···HF system: Adding a water molecule to the F end will shorten the hydrogen bond length more effectively[18]. Thus, the increment of the dihydrogen-bonding interaction energy (in comparison with that in the corresponding binary complex) in the ternary F–H···X–H···H–M complex may be larger than that in the corresponding X–H···H–M···F–H system. Furthermore, from Tables S4 and S5, all the changes of the X–H, H–M and F–H bond lengths in F–H···X–H···H–M are more notable than those in X–H···H–M···F–H. These results indicate that the cooperativity effect in F–H···X–H···H–M may be stronger than that in X–H···H–M···F–H.

Interaction energy and cooperativity effect

Tables 3 and 4 summarize the interaction energies and cooperativity effects in eight ternary complexes at the B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels. The values obtained at both levels are close to each other.

H-bonding interaction energies $E'_{int.(FH···XH)}$ in the ternary complexes F–H···X–H···H–M follow the order: F–H system > Cl–H system and H–K system > H–Na system > H–Li system (Table 3). This trend is just opposite to that of the interaction energies $E'_{int.(HM···FH)}$ in the corresponding X–H···H–M···F–H systems (see Table 4). Note that, for F–H···X–H···H–M, the H···X distances follow the order: F–H system < Cl–H system and H–K system < H–Na system < H–Li system, while in X–H···H–M···F–H, the order of the M···F distances is: F–H system > Cl–H system and H–K system > H–Na system > H–Li system (see Tables 1 and 2).

The values of the H-bonding interaction energies $E'_{int.(FH···XH)}$ in the ternary complexes F–H···X–H···H–Li are lower than those of the intermolecular interaction energies $E'_{int.(HLi···FH)}$ in the corresponding X–H···H–Li···F–H systems at both levels. However, the values of $E'_{int.(FH···XH)}$ in F–H···F–H···H–M (M=Na and K) are

Table 3—Intermolecular interaction energy ($-E'_{int.}$ or $-E''_{int.}$) and cooperativity effect ($E_{coop.}$) in the ternary system F–H···X–H···H–M at the B3LYP/6–311++G(3df,2p) (in plain) and MP2(full)/6-311++G(3df,2p) (in bold) levels [a]

Complex	$E'_{int.(H··H)}$ (kJ/mol)	$E'_{int.(F–H···X–H)}$ (kJ/mol)	$E''_{int.(F–H···H–M)}$ (kJ/mol)	$E_{int.(F–H···X–H···H–M)}$ (kJ/mol)	$E_{coop.}$ (kJ/mol)
F–H···F–H···H–Li	100.88 (99.13) *92.45*	42.58 (40.74) *36.51*	9.65 (9.42)	112.46 (108.90) *102.18*	–24.84
	93.07 (87.54) *80.16*	**39.99 (33.85) *28.12***	**10.36 (9.95)**	**103.21 (91.52) *88.02***	**–17.66**
F–H···F–H···H–Na	109.69 (107.11) *99.22*	45.31 (43.17) *40.03*	10.21 (9.94)	120.84 (116.43) *111.47*	–30.23
	107.34 (100.29) *91.18*	**45.08 (38.21) *35.98***	**11.52 (10.96)**	**116.58 (103.06) *98.21***	**–24.44**
F–H···F–H···H–K	168.70 (167.13) *158.11*	61.90 (59.79) *52.57*	14.29 (14.11)	177.83 (174.31) *166.43*	–64.03
	166.93 (159.67) *152.25*	**60.80 (53.31) *47.68***	**15.67 (15.22)**	**173.62 (159.00) *151.36***	**–58.04**
F–H···Cl–H···H–Li	162.52(159.86) *150.21*	32.96(31.67) *26.32*	6.02 (5.91)	153.64 (149.36) *142.26*	–80.21
	179.40(170.79) *158.83*	**35.84 (29.78) *25.19***	**6.83 (6.60)**	**169.46 (155.26) *151.87***	**–103.28**

[a] The values in parentheses are corrected with BSSE, and those in italic are corrected by BSSE and ZPE.

Table 4—Intermolecular interaction energy ($-E'_{int.}$ or $-E''_{int.}$) and cooperativity effect ($E_{coop.}$) in the ternary system X–H···H–M···F–H at the B3LYP/6–311++G(3df,2p) (in plain) and MP2(full)/6-311++G(3df,2p) (in bold) levels [a]

Complex	$E'_{int.(H··H)}$ (kJ/mol)	$E'_{int.(H–M···F–H)}$ (kJ/mol)	$E''_{int.(X–H···F–H)}$ (kJ/mol)	$E_{int.(X–H···H–M···F–H)}$ (kJ/mol)	$E_{coop.}$ (kJ/mol)
F–H···H–Li···F–H	71.14 (69.72) *61.28*	47.48 (45.29) *40.78*	2.13 (2.10)	111.97 (108.23) *100.02*	–5.35
	66.07 (61.17) *52.35*	**45.08 (39.32) *36.52***	**2.22 (2.16)**	**104.79 (94.04) *87.26***	**–4.33**
F–H···H–Na···F–H	72.87 (71.13) *62.18*	31.14 (29.60) *25.11*	1.49 (1.48)	97.87(94.27) *88.11*	–5.73
	70.49 (65.15) *59.62*	**32.83 (28.42) *23.26***	**1.58 (1.56)**	**97.08 (86.87) *74.92***	**–5.41**
F–H···H–K···F–H	89.23 (88.07) *79.81*	20.09 (19.24) *15.20*	0.98 (0.98)	106.16 (104.02) *95.15*	–2.97
	87.76 (82.24) *73.28*	**24.50 (22.05) *16.18***	**1.17 (1.16)**	**107.26 (99.06) *90.98***	**–4.50**
Cl–H···H–Li···F–H	96.26 (93.79) *86.22*	52.01 (49.74) *42.30*	1.98 (1.87)	137.14 (132.30) *128.05*	–28.84
	81.33 (74.22) *66.18*	**48.45 (42.33) *37.39***	**2.03 (1.84)**	**119.99 (106.93) *97.28***	**–23.27**

[a] The values in parentheses are corrected with BSSE, and those in italic are corrected by BSSE and ZPE.

larger than those of $E'_{int.(HM···FH)}$ in the corresponding F–H···H–M···F–H systems.

From Tables 3 and 4, it is observed that at both levels, the values of the intermolecular H-bonding interaction energies, $E'_{int.(FH···XH)}$, in F–H···X–H···H–M and the M···F interaction energies, $E'_{int.(HM···FH)}$, in X–H···H–M···F–H are larger than those in the corresponding binary systems, F–H···X–H and H–M···F–H (see Tables S1 and S2). These results show that the F···H and M···F interactions are strengthened upon the ternary complex formation, suggesting possible cooperativity effects. The increment in $E'_{int.(HM···FH)}$ (i.e. "$E'_{int.(HM···FH)}$ –$E_{int.(HM···FH)}$") is lower than that of $E'_{int.(FH···XH)}$ (i.e. "$E'_{int.(FH···XH)}$ – $E_{int.(FH···XH)}$"), suggesting that the cooperativity effect in F–H···X–H···H–M is stronger than that in X–H···H–M···F–H. Furthermore, the values of the proportion of the increment of the H-bonding interaction energy, $E'_{int.(FH···XH)}$, to the corresponding $E_{int.(FH···XH)}$ (i.e., $[E'_{int.(FH···XH)}–E_{int.(FH···XH)}]/E_{int.(FH···XH)}$) are larger than those of $[E'_{int.(HM···FH)}–E_{int.(HM···FH)}]/E_{int.(HM···FH)}$, indicating that the cooperativity effect in F–H···X–H···H–M may also be stronger than that in X–H···H–M···F–H.

The values of the dihydrogen-bonding interaction energies ($E'_{int.(H···H)}$) in the two kinds of ternary complexes are larger than those ($E_{int.(H···H)}$) in the corresponding binary systems at two levels of theory (Tables 3, 4 and S1). This result shows that the H···H interactions are strengthened upon the ternary complex formations, indicating the presence of cooperativity effects.

At the MP2(full)/6-311++G(3df,2p) level, the increment of the H···H interaction energy (i.e. "$E'_{int.(H···H)}$ – $E_{int.(H···H)}$") in ternary complex F–H···X–H···H–M is in the range of –34.07 to –125.31 kJ/mol. For the ternary complex X–H···H–M···F–H, the range is only –6.11 to –27.24 kJ/mol; far lower than that in the corresponding F–H···X–H···H–M system. This indicates that the cooperativity effect in F–H···X–H···H–M is larger than that in X–H···H–M···F–H.

The proportion of the increment in the dihydrogen-bonding interaction of F–H···X–H···H–M to the corresponding $E_{int.(H···H)}$ in the binary system, defined as $[E'_{int.(H···H)}–E_{int.(H···H)}]/E_{int.(H···H)}$, is 57.75% (F–H···F–H···H–Li), 69.01% (F–H···F–H···H–Na), 104.45% (F–H···F–H···H–K) or 231.67% (F–H···Cl–H···H–Li)

at MP2(full)/6-311++G(3df,2p) level. The proportion of the increment of the H···H dihydrogen-bonding interaction is lower than that of the corresponding H···X H-bonding interaction (131.83%, 161.33%, 252.46% or 254.15% respectively), showing that the cooperativity effect of the dihydrogen-bonds on the H···X interactions may be more pronounced than that of the F–H···X hydrogen bonds on the H···H interactions in F–H···X–H···H–M. For X–H···H–M···F–H, the value of $[E'_{int.(H···H)}–E_{int.(H···H)}]/E_{int.(H···H)}$ is found to be 11.98% (F–H···H–Li···F–H), 10.99% (F–H···H–Na···F–H), 7.48% (F–H···H–K···F–H) and 50.36% (Cl–H···H–Li···F–H) at MP2(full)/ 6-311++G(3df,2p) level, respectively. It is also lower than the corresponding intermolecular M···F interaction (15.50%, 22.23%, 22.87% and 24.14%, respectively), showing that the cooperativity effect of the dihydrogen-bond on the M···F interaction is more pronounced than that of the M···F interaction on the H···H interaction in X–H···H–M···F–H.

Except for F–H···F–H···H–Li, in the two kinds of ternary complexes, the proportion of the increment of the H···H interaction energy follows the order: Cl–H system > F–H system, indicating that the cooperativity effect follows the order: Cl–H system > F–H system. On the other hand, the proportion of increment of the H···H interaction energy in F–H···X–H···H–M is larger than that in the corresponding X–H···H–M···F–H complex. This shows that the cooperativity effect of the dihydrogen-bonding interaction in F–H···X–H···H–M is more notable than that in X–H···H–M···F–H, in accordance with the structural analysis.

The complexation energies of the two kinds of ternary complexes are given in Tables 3 and 4. The complexation energies are in the order: Cl–H system > F–H system and H–K system > H–Na system > H–Li system at the two levels of theory.

The complexation energy of F–H···X–H···H–M is larger than that of the corresponding X–H···H–M···F–H, indicating that the energetic stability of the former is higher than that of the latter. That is, when F–H is attached to the X end, the system can gain more significantly in stabilization energies. As can be seen from the total energy $E_{(F–H···X–H···H–M)}$ and $E_{(X–H···H–M···F–H)}$ in Eqs (5) and (6), the complexation energy is equivalent to the total energy of ternary complex when judging the preference of HF attaching to X or M of X–H···H–M. Thus, the H···X hydrogen-bonded complexes, F–H···X–H···H–M, are preferentially

formed, and F–H prefers to be attached to the X end with the F–H···X hydrogen-bond formation rather than the M end with the formation of the intermolecular M···F–H interaction, as seen by the analysis of the interaction energy, $E'_{int.(FH···XH)}$ and $E'_{int.(HM···FH)}$.

The cooperativity energies of the two kinds of ternary complexes are investigated at the B3LYP/ 6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels (see Tables 3 and 4). Most of the values of cooperativity energies obtained from the B3LYP/ 6-311++G(3df,2p) method are lower than those at the MP2(full)/6-311++G(3df,2p) level. It has been shown in many previous investigations that the MP2 method is more suitable to elucidate the trends in the calculated cooperativity effect[4,29]. Thus, the MP2(full)/6-311++G(3df,2p) method was selected to evaluate the trends in the calculated cooperativity.

A negative cooperativity would indicate that the two interactions work in concert with each other and enhance each other's strength, while a positive value indicates that the two interactions work anti-cooperatively. At the two levels of theory, the cooperativity is negative for all the ternary complexes. This means that the coexistent interactions, H···H and H···X or M···F, are reinforced and the cooperativity effects are present. As aforementioned, the distances, $R_{H···H}$, $R_{H···X}$ and $R_{M···F}$, are shortened in ternary complexes in comparison with those in binary systems, and the values of $E'_{int.(H···H)}$, $E'_{int.(FH···XH)}$ and $E'_{int.(HM···FH)}$ in the ternary complexes are larger that those of $E_{int.(H···H)}$, $E_{int.(FH···XH)}$ and $E_{int.(HM···FH)}$ in the corresponding binary systems. The values of cooperativity effect follow the order: Cl–H system > F–H system for F–H···X–H···H–M, in accordance with the analyses of structure and interaction energy.

The values of cooperativity effects are large. At MP2(full)/6-311++G(3df,2p) level, the values of $E_{coop.}$ are in the ranges of –17.66 to –103.28 kJ/mol and –4.33 to –23.27 kJ/mol for F–H···F–H···H–M and F–H···H–M···F–H, respectively. In general, the values of cooperativity effects are no more than –10.00 kJ/mol (Refs 1, 29). The $F_3CCl(Br)···NCH(CNH)···HMgH$ complexes with simultaneous presence of a σ-hole bond and a dihydrogen bond show cooperativity energy ranging between –1.02 and –2.31 kJ/mol at MP2/cc-pVTZ level[30]. The remarkable cooperativity effect between the H···H and H···X or M···F interactions may lead to notable change in the structures and properties of the dihydrogen-bond complexes.

It is noteworthy that the value of cooperativity effect of F–H···X–H···H–M is much larger than that of the corresponding X–H···H–M···F–H system at the two levels of theory. Thus, when F–H is attached to the X end, the system can gain in larger cooperativity effect, and F–H prefers to be attached to the X end with the F–H···X hydrogen bond formation rather than the M side, as also shown by the analyses of the structure, interaction energy $E'_{int.(FH···XH)}$ and $E'_{int.(HM···FH)}$, as well as the complexation energy. In the previous investigation on the hydrated complexes, F–H···H–Li $(H_2O)_n$, the complexation energy and cooperativity effect were not given, and only the relative energy ($\Delta E = E[$F–H···H–Li $(H_2O)_n] - E[$F–H···H–Li$] - n \times E[H_2O]$) was shown. The relative energy (ΔE) for F–H···H–Li···OH_2 was larger than that for H_2O···F–H···H–Li. Thus, it may be concluded that when a water molecule was attached to the Li end, the system could gain in significant stabilization energy[18].

AIM analysis

AIM analysis can give some helpful information regarding the strength of the noncovalent interactions[21]. According to the AIM analysis, in each of the binary complexes F–H···X–H and the four ternary complexes F–H···X–H···H–M, there is a bond path linking the hydrogen atom of F–H and the X atom of X–H, accompanied by a bond critical point (BCP) (3, −1). In each of the H–M···F–H and four X–H···H–M···F–H systems, a bond path linking M and F is found with a BCP (3, −1). The electron densities $\rho_{BCP(H···X)}$ and $\rho_{BCP(M···F)}$ are within the ranges of 0.0177 − 0.0421 a.u. and 0.0112–0.0232 a.u., respectively (Tables 1, 2 and Fig. S1). Moreover, their Laplacians $\nabla^2 \rho_{BCP(H···X)}$ and $\nabla^2 \rho_{BCP(M···F)}$ are all positive. As proposed by Bader[21], $\nabla^2 \rho > 0$ indicates loose charge density at the critical point. Thus, the typical closed-shell kind of H···X and M···F interactions are confirmed.

On the other hand, in each of the binary complexes, XH···HM, and ternary systems, there is a bond path linking the hydridic hydrogen atom of HM and the hydrogen atom of HX, accompanied by a bond critical point (BCP) (3, −1). From Tables 1 and 2, it can be observed that in the ternary systems, F–H···F–H···H–Li and F–H···H–M···F–H (M=Li, Na and K), the electron densities $\rho_{BCP(H···H)}$ are just within the common accepted values for dihydrogen bonds[31], and the values of their Laplacians $\nabla^2 \rho_{BCP}$ are all positive, indicating the typical closed-shell kind of interactions. In other words, for the H…H contacts in these four

complexes, the small ρ_{BCP} and positive $\nabla^2 \rho_{BCP}$ values are basically similar to the topological properties of the H…H dihydrogen bonds[32]. Thus, the coexistence of the H···H and H···F or M···F interactions in the ternary complexes, F–H···H–M···F–H or F–H···F–H···H–Li, are confirmed.

However, one can observe the large values of $\rho_{BCP(H···H)}$ (0.0680 ~ 0.1567 a.u.) and the negative Laplacians $\nabla^2 \rho_{BCP(H···H)}$ in H···H contacts of F–H···F–H···H–M (M=Na and K), F–H···Cl–H···H–Li and Cl–H···H–Li···F–H. It is worth mentioning that the range of the electron density for H-bond typical interaction is about 0.002–0.04 a.u., and $\nabla^2 \rho < 0$ indicates shared interaction[21]. Thus, in these four systems, partly covalent character of H···H interaction is suggested. Therefore, the coexistence of the partly covalent H···H dihydrogen-bonding interaction and the intermolecular H···X or M···F interactions in these four systems is confirmed.

Electron density (ρ) at the bond saddle point indicates the bond strength. The larger the ρ, the stronger is the interaction[21]. As can be seen from Fig. S1, and Tables 1 and 2, the charge densities, $\rho_{BCP(H···H)}$, increase upon ternary complex formation, indicating that the H···H interactions are strengthened, as also in agreement with the H···H interaction analysis. In particular, the increment of $\rho_{BCP(H···H)}$ upon ternary complex F–H···X–H···H–M formation (i.e., the difference between the charge densities $\rho_{BCP(H···H)}$ in ternary complex and binary system) is more notable than that upon the formation of the corresponding X–H···H–M···F–H system. This shows that the change of the H···H interaction energy in F–H···X–H···H–M is larger than that in X–H···H–M···F–H, in accordance with the analysis of interaction energy. For the charge densities, $\rho_{BCP(H···X)}$ and $\rho_{BCP(M···F)}$, it is also found that the values increase upon the ternary complex formations, indicating the enhanced H···X and M···F interactions. The change in $\rho_{BCP(H···X)}$ upon the ternary complex F–H···X–H···H–M formation is also far larger than that in $\rho_{BCP(M···F)}$ in the corresponding complex X–H···H–M···F–H. This shows that the change of the H···X interaction energy in F–H···X–H···H–M is also larger than that of the M···F interaction energy in X–H···H–M···F–H, as is also shown by the analysis of energy. Thus, the energetic stability and cooperativity effect of F–H···X–H···H–M are larger than those of X–H···H–M···F–H. Therefore, F–H prefers to be attached to the X end with the F–H···X hydrogen-

bond formation, in accordance with the analyses of structure and interaction energy.

Charge analysis of the hydrogen atom in H⋯H moiety

There are different views on the origin of the cooperativity effect. Kar *et al.*[33] have reported that the cooperativity can be attributed mainly to the polarization induced in each subunit. Glendening[34] has pointed out that charge transfer could be regarded as the leading source of cooperative stabilization and that polarization effects have only a marginal influence on the cooperativity.

In order to probe the origin of the cooperativity effect of the H⋯X or M⋯F interaction on the dihydrogen-bonding interactions, the charges of the hydrogen atoms in H⋯H moiety and the NBO charge transfers of HF upon the formation of ternary system were analysed. Mulliken, APT and NBO charges of the hydrogen atoms in $H^{\delta+}\cdots^{\delta-}H$ moiety at MP2(full)/6-311++G(3df,2p) level are listed in Table 5. For the Mulliken charges and NBO charges in each of the ternary systems, F–H⋯X–H⋯H–M, the proton donor

$H^{\delta+}$ has a less positive charge than that in the corresponding binary complex except for the Mulliken charge in F–H⋯Cl–H⋯H–Li. The hydridic hydrogen atom ($^{\delta-}$H) in ternary system has a less negative charge relative to that in the corresponding binary complex except for the Mulliken charge in F–H⋯F–H⋯H–Na. The decrease in charge leads to the increase of the $H^{\delta+}\cdots^{\delta-}H$ covalent interaction when F–H is attached to the X end, in accordance with the result for O₂H⋯FH⋯HLi as reported by Liao[18]. In our recent investigation on the hydrated complexes of NC(CN)BB–H⋯H–Na, the number of charges on the two hydrogen atoms also decreases with the increase of the number of surrounding water molecules[19]. Thus, the dihydrogen-bonding interaction is strengthened, leading to the formation of cooperativity effect.

However, for X–H⋯H–M⋯F–H, the proton donor $H^{\delta+}$ has a more positive Mulliken charge than that in the corresponding binary complex. The hydridic hydrogen atom ($^{\delta-}$H) in ternary system has a more negative charge relative to that in the corresponding binary complex. The increase in charge leads to the

Table 5—Mulliken, APT and NBO charges of two hydrogen atoms in $H^{\delta-}\cdots^{\delta+}H$ or H–H moiety, NBO charge transfers of HF (Q(HF)), and the surface electrostatic potentials on the 0.001 a.u. molecular surface (maximum $V_{S,max}$) of the binary, ternary and quaternary complexes at the MP2(full)/6-311++G(3df,2p) level

Complex	Mulliken charge (e)	NBO charge (e)	APT charge (e) [a]	Q(HF) (me)	$V_{S,min}$ ($V_{S,max}$) (kcal/mol)
F–H⋯H–Li	−0.298 0.561	−0.818 0.587	−0.668 0.595		−53.08(207.47)
F–H⋯H–Na	−0.494 0.582	−0.819 0.580	−0.698 0.664		−57.24(140.35)
F–H⋯H–K	−0.874 0.659	−0.823 0.565	−0.757 0.729		−64.74(91.92)
Cl–H⋯H–Li	−0.343 0.493	−0.743 0.288	−0.726 0.681		−37.95(210.20)
Cl⁻⋯H₂⋯Na⁺	−0.456 0.403	−0.532 0.238	−0.698 0.900		−56.68(158.34)
Cl⁻⋯H₂⋯K⁺	−0.723 0.516	−0.391 0.221	−0.632 0.800		−74.04(116.84)
Br⁻⋯H₂⋯Li⁺	−0.091 0.048	−0.565 0.214	−0.726 0.844		−46.82(227.41)
Br⁻⋯H₂⋯Na⁺	−0.115 0.058	−0.432 0.200	−0.672 0.869		−59.26(167.85)
Br⁻⋯H₂⋯K⁺	−0.667 0.462	−0.345 0.196	−0.622 0.759		−70.86(121.04)
F–H⋯F–H⋯H–Li	−0.250 0.260	−0.786 0.584	−0.672 0.723	−14.8	−49.35(215.88)
F–H⋯F–H⋯H–Na	−0.504 0.325	−0.766 0.560	−0.707 0.827	−18.1	−52.86(150.44)
F–H⋯F–H⋯H–K	−0.840 0.456	−0.691 0.491	−0.736 0.929	−29.2	−60.51(103.38)
F–H⋯Cl–H⋯H–Li	−0.283 0.532	−0.529 0.274	−0.702 0.889	−21.8	−53.37(237.49)
F–H⋯Cl⁻⋯H₂⋯Na⁺	−0.275 0.374	−0.401 0.239	−0.628 0.822	−36.4	−62.02(177.38)
F–H⋯Cl⁻⋯H₂⋯K⁺	−0.682 0.558	−0.320 0.216	−0.533 0.658	−48.3	−68.54(126.72)
F–H⋯Br⁻⋯H₂⋯Li⁺	0.074 −0.164	−0.468 0.238	−0.701 0.868	−22.6	−54.35(245.10)
F–H⋯Br⁻⋯H₂⋯Na⁺	0.002 −0.036	−0.366 0.212	−0.628 0.795	−32.7	−60.96(180.61)
F–H⋯Br⁻⋯H₂⋯K⁺	−0.777 0.602	−0.296 0.196	−0.539 0.642	−42.1	−66.57(128.98)
F–H⋯H–Li⋯F–H	−0.624 0.635	−0.774 0.585	−0.677 0.614	25.8	−57.73(133.34)
F–H⋯H–Na⋯F–H	−0.577 0.595	−0.804 0.577	−0.706 0.668	11.3	−61.39(114.27)
F–H⋯H–K⋯F–H	−0.905 0.677	−0.812 0.560	−0.755 0.729	5.1	−68.37(109.25)
Cl–H⋯H–Li⋯F–H	−0.725 0.684	−0.636 0.274	−0.738 0.806	24.4	−47.20(144.11)
Cl⁻⋯H₂⋯Na⁺⋯F–H	−0.426 0.367	−0.464 0.233	−0.677 0.876	8.3	−65.38(132.31)
Cl⁻⋯H₂⋯K⁺⋯F–H	−0.901 0.644	−0.364 0.214	−0.598 0.748	3.6	−78.48(120.67)
Br⁻⋯H₂⋯Li⁺⋯F–H	−0.360 0.221	−0.481 0.221	−0.715 0.862	21.5	−55.46(169.66)
Br⁻⋯H₂⋯Na⁺⋯F–H	−0.054 0.009	−0.396 0.202	−0.663 0.840	7.6	−65.10(140.39)
Br⁻⋯H₂⋯K⁺⋯F–H	−0.769 0.532	−0.324 0.191	−0.586 0.704	3.5	−74.73(122.60)

[a] At the B3LYP/6-311++G(3df,2p) level.

increase of polarization in the $H^{\delta+}\cdots^{\delta-}H$ bond, which makes it easier for the two hydrogen atoms to form the $H^{\delta+}\cdots^{\delta-}H$ dihydrogen bond. Thus, the dihydrogen-bonding interaction is strengthened, leading to the cooperativity effect. Therefore, the polarization induced in the subunit plays an important role in cooperativity effect. The number of charges on the two hydrogen atoms increases when F–H is attached to the M end, accompanied by the enhancement of the H···H ionic bond.

The charge transfer interaction also plays an important role in the cooperativity effect[11]. Note that F–H is electron acceptor in F–H···X–H···H–M and the electrons transfer from X–H···H–M to F–H, while for X–H···H–M···F–H, F–H is electron donor and the electrons transfer reversely. The NBO charge transfer of HF is negative in F–H···X–H···H–M, while it is positive in X–H···H–M···F–H (Table 5).

Analysis of the surface electrostatic potential

The surface electrostatic potential has been as an effective tool to reveal the origin of dihydrogen bonding[9,35]. Figure 2 and Table 5 present the surface electrostatic potential on the 0.001 a.u. molecular surface of complex at the MP2(full)/6-311++G(3df,2p) level. The surface electrostatic potentials were obtained by using the Multiwfn programs[36].

Figure 2 shows that each of the eight ternary complexes has several surface minima, associated with the lone pairs of the X atom in X–H and the F atom in F–H. For F–H···X–H···H–M, the strongest is that of the F atom, while in X–H···H–M···F–H the strongest is that of the X atom. The most negative

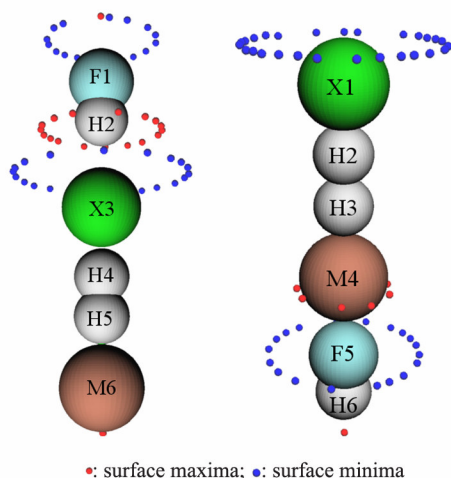•: surface maxima; •: surface minima

Fig. 2—Surface electrostatic potential on the 0.001 a.u. molecular surface of the ternary and quaternary complexes [X = F, Cl, Br; M = Li, Na, K].

value, i.e., its local minimum, $V_{S,min}$, is in the range of –49.35 to –60.51 kcal/mol for F–H···X–H···H–M and –47.20 to –68.37 kcal/mol for X–H···H–M···F–H (see Table 5). The absolute values of the most negative $V_{S,min}$ follow the order: Cl–H system > F–H system and H–K system > H–Na system > H–Li system. There are also several surface maxima ($V_{S,max}$) with the M atom and the H atom in F–H. For the ternary complexes, the highest positive value is around the M atom, within the ranges of 103.38–237.49 kcal/mol and 109.25–144.11 kcal/mol for F–H···X–H···H–M and X–H···H–M···F–H, respectively. The values of the highest $V_{S,max}$ follow the order: Cl–H system > F–H system and H–Li system > H–Na system > H–K system.

For two kinds of systems, except for F–H···F–H···H–M, the absolute values of the most negative $V_{S,min}$ increase upon the ternary complex formation. For the highest $V_{S,max}$, the values in F–H···X–H···H–M are larger than those in the corresponding binary systems, while the values in X–H···H–M···F–H decrease in comparison with those of the binary systems. These results show the formation of cooperativity effect. The increment in the values of the highest $V_{S,max}$ in F–H···X–H···H–M ($\Delta V_{S,max}$= $V_{S,max(ternary\ complex)} - V_{S,max(binary\ system)}$) is 8.41, 10.09, 11.46 and 27.29 kcal/mol, and follows the order: Cl–H system > F–H system, in accordance with the trend of cooperativity effect values.

In particular, as can be seen from Table 5, although the absolute value of $V_{S,min}$ in F–H···X–H···H–M is slightly lower than that in the corresponding X–H···H–M···F–H, the value of $V_{S,max}$ in F–H···X–H···H–M is far larger than that in the corresponding X–H···H–M···F–H system, except for F–H···F–H···H–K. This result also indicates that the cooperativity effect in F–H···X–H···H–M is stronger than that in X–H···H–M···F–H, as shown by the analyses of structure and interaction energy.

Quaternary systems F–H···X⁻···H₂···M⁺ and X⁻···H₂···M⁺···F–H

As mentioned above, in BrHHLi, ClHHNa, BrHHNa, ClHHK and BrHHK, the H···H distances are very close to the bond length in H_2, suggesting the formation of the H–H covalent bond. Furthermore, the large $\rho_{(HH)}$ and negative $\nabla^2\rho_{BCP(HH)}$ are found in their complexes with F–H (see Tables 1 and 2). Moreover, from Mulliken, APT and NBO charges, the obvious H–H covalent character is confirmed in the complexes with F–H (see Table 5). Thus, the "X–H···H–M" moiety turns into the "X⁻···H–H···M⁺" group and the

ternary complex turns into the quaternary system. Therefore, ten quaternary complexes F–H···X⁻···H–H···M⁺ (C_s) and X⁻···H–H···M⁺···F–H (C_s) were also designed and fully optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G(3df,2p) basis set. The cooperativity effects in these quaternary complexes were also investigated in order to clarify whether HF prefers to be attached to M or X. Additionally, as mentioned above, although FH···HM (M = Na, K) and ClH···HLi have been confirmed as the conventional X–H···H–M dihydrogen-bonded systems, the negative $\nabla^2\rho_{BCP(H···H)}$ is found in their complexes F–H···F–H···H–M (M=Na, K), F–H···Cl–H···H–Li and Cl–H···H–Li···F–H, and the H···H distances are shorter than 1.2 Å (see Tables 1 and 2). Thus, the "X–H···H–M" moiety turns into the "X⁻···H–H···M⁺" group in these four ternary complexes. Therefore, the cooperativity effects in these four ternary complexes were also considered. Similar to F–H···X–H···H–M and X–H···H–M···F–H, non-linear H–F···MX···H–H or H–H···MX···H–F structure are not considered.

The cooperativity ($E_{coop.}$) in the quaternary complex was calculated as follows:

$$E_{coop.} = E_{int.(F–H···X–···H–H···M+)} − E_{int.(F–H···X–)} − E_{int.(X–···H–H)} − E_{int.(H–H···M+)} − E''_{int.(F–H···H–H)} − E''_{int.(F–H···M+)} − E''_{int.(X–···M+)}$$

for F–H···X⁻···H–H···M⁺   … (9)

$$E_{coop.} = E_{int.(X–···H–H···M+···F–H)} − E_{int.(X–···H–H)} − E_{int.(H–H···M+)} − E_{int.(M+···F–H)} − E''_{int.(X–···M+)} − E''_{int.(X–···F–H)} − E''_{int.(H–H···F–H)}$$

for X⁻···H–H···M⁺···F–H   … (9′)

where the complexation energies $E_{int.(F–H···X–···H–H···M+)}$ and $E_{int.(X–···H–H···M+···F–H)}$ were calculated as the energy difference between the total energy of the quaternary complex and the energies of monomers. $E_{int.(F–H···X–)}$, $E_{int.(X–···H–H)}$, $E_{int.(H–H···M+)}$, $E_{int.(X–···H–H)}$, $E_{int.(H–H···M+)}$ or $E_{int.(M+···F–H)}$ was calculated by evaluating the difference between the total energies of binary complex and individual monomers. $E''_{int.}$ is defined as the through-space interaction energy between both the moieties with which they are not directly interacting. It was calculated at the quaternary geometries.

The complexation energies and cooperativity effects in the quaternary complexes at the B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels are collected in Table 6. For F–H···FHHM (M=Na, K), F–H···ClHHLi and ClHHLi···F–H, the cooperativity energy from the quaternary complex is far lower than that from the corresponding ternary system for the same geometry.

At MP2(full)/6-311++G(3df,2p) level, the complexation energy in F–H···X⁻···H–H···Li⁺ is lower than that in X⁻···H–H···Li⁺···F–H; and the complexation energy in F–H···X⁻···H–H···Na⁺ is close to that in X⁻···H–H···Na⁺···F–H; while the complexation energy in F–H···X⁻···H–H···K⁺ is larger than that in X⁻···H–H···K⁺···F–H. These results indicate that the energetic stability of F–H···X⁻···H–H···Li⁺ is lower than that in X⁻···H–H···Li⁺···F–H, while the energetic stability of F–H···X⁻···H–H···K⁺ is higher than that of X⁻···H–H···K⁺···F–H. In other words, for X⁻···H–H···Li⁺, when F–H is attached to the Li⁺ end, the system can gain in more significant stabilization energy, while for X⁻···H–H···K⁺, the system can gain with greater stabilization energy when F–H is attached to the X⁻ end.

Table 6—Complexation energies ($−E_{int.}$) and cooperativity effects ($E_{coop.}$) in the quaternary systems F–H···X⁻···H–H···M⁺ and X⁻···H–H···M⁺···F–H at the B3LYP/6-311++G(3df,2p) (in plain) and MP2(full)/6-311++G(3df,2p) levels (in bold) [a]

Complex	$E_{int.}$ (kJ/mol)	$E_{coop.}$ (kJ/mol)	Complex	$E_{int.}$ (kJ/mol)	$E_{coop.}$ (kJ/mol)
F–H···F⁻···H₂···Na⁺	608.60 (597.25) *582.19*	−18.25	F–H···Br⁻···H₂···K⁺	355.99 (342.10) 335.43	−7.55
	586.76 (580.14) *572.43*	**−41.52**		**351.84 (343.69) 334.01**	**−17.57**
F–H···F⁻···H₂···K⁺	532.83 (525.19) *520.17*	0.49	Cl⁻···H₂···Li⁺···F–H	513.02 (498.17) 486.36	−82.59
	516.82 (508.13) 500.65	**−10.38**		**492.37 (485.96) 476.23**	**−38.88**
F–H···Cl⁻···H₂···Li⁺	487.82 (480.18) 472.65	−15.71	Cl⁻···H₂···Na⁺···F–H	435.36 (424.18) 406.54	−62.27
	470.89 (456.15) 446.57	**−23.15**		**412.93 (401.15) 388.93**	**−16.24**
F–H···Cl⁻···H₂···Na⁺	435.65 (427.13) 409.38	2.84	Cl⁻···H₂···K⁺···F–H	358.88 (350.17) 342.58	−66.84
	418.75 (405.45) 392.33	**−9.72**		**349.86 (341.39) 337.25**	**−22.28**
F–H···Cl⁻···H₂···K⁺	383.64 (377.56) 365.60	−6.97	Br⁻···H₂···Li⁺···F–H	480.63 (475.36) 464.03	−60.92
	378.30 (366.25) 352.69	**−17.30**		**460.61 (451.83) 442.73**	**−13.47**
F–H···Br⁻···H₂···Li⁺	452.27 (435.38) 428.06	−9.71	Br⁻···H₂···Na⁺···F–H	410.61 (400.62) 389.36	−49.19
	436.33 (424.00) 415.39	**−17.95**		**390.17 (379.93) 370.35**	**−5.08**
F–H···Br⁻···H₂···Na⁺	405.65 (392.82) 385.19	4.52	Br⁻···H₂···K⁺···F–H	340.00 (335.62) 321.66	−61.66
	389.38 (380.11) 372.53	**−8.64**		**332.47 (320.87) 313.68**	**−14.79**

[a] The values in parentheses are corrected with BSSE, and those in italic are corrected by BSSE and ZPE.

From Table 6, for F–H···F⁻···H–H···K⁺, F–H···X⁻···H–H···Na⁺ (X=Cl and Br), the values of cooperativity effect are positive at the B3LYP/6-311++G(3df,2p) level, while they are negative at the MP2(full)/6-311++G(3df,2p) level. For the other quaternary complexes, the values of cooperativity energies are negative at the two levels of theory, confirming the presence of cooperativity effect. In particular, the cooperativity effects in F–H···Cl⁻···H–H···M⁺ are lower than those in Cl⁻···H–H···M⁺···F–H, while the cooperativity effects in F–H···Br⁻···H–H···M⁺ are lower than those in Br⁻···H–H···M⁺···F–H. Thus, we can draw the conclusion that, for Cl⁻···H–H···M⁺, when F–H is attached to the M end, the system can gain in higher cooperativity effect, and hence, F–H prefers to be attached to the M end. However, for Br⁻···H–H···M⁺, the system can gain in higher cooperativity effect when F–H is attached to the Br end, and hence F–H prefers to be attached to the Br end with the F–H···Br hydrogen-bond formation.

In a nutshell, for the F–H complexes with Cl⁻···H–H···Li⁺ and Br⁻···H–H···K⁺, according to both the complexation energy and cooperativity effect, F–H prefers to be attached to Li⁺ and Br⁻, respectively. However, for the other quaternary systems, the results from complexation energies are different from cooperativity effects. For Cl⁻···H₂···Na⁺ and Cl⁻···H₂···K⁺, F–H prefers to be attached to Cl⁻ from the complexation energy, while from cooperativity effect, F–H prefers to be attached to M⁺ (i.e., Na⁺ and K⁺). However, for Br⁻···H₂···Li⁺ and Br⁻···H₂···Na⁺, F–H prefers to be attached to M⁺ (i.e., Li⁺ and Na⁺) from the complexation energy, while from cooperativity effect, F–H prefers to be attached to Br⁻.

Conclusions

The cooperativity effects were investigated in the possible linear dihydrogen-bonded complexes F–H···X–H···H–M and X–H···H–M···F–H, and non-dihydrogen-bonded systems F–H···X⁻···H–H···M⁺ and X⁻···H–H···M⁺···F–H. The results show that, for the dihydrogen-bonded complex, the complexation energy and cooperativity effect in F–H···X–H···H–M are larger than those of the corresponding X–H···H–M···F–H system. Thus, the F–H···X–H···H–M complex is preferentially formed and F–H prefers to be attached to the X end. For non-dihydrogen-bonded quaternary system of F–H with Cl⁻···H–H···Li⁺ or Br⁻···H–H···K⁺, F–H prefers to be attached to Li⁺ or Br⁻ according to both the complexation energy and

cooperativity effect. However, for Cl⁻···H₂···Na⁺ and Cl⁻···H₂···K⁺, F–H prefers to be attached to Cl⁻ from complexation energy, while from cooperativity effect, F–H prefers to be attached to M⁺ (i.e., Na⁺ and K⁺); for Br⁻···H₂···Li⁺ and Br⁻···H₂···Na⁺, F–H prefers to be attached to M⁺ (i.e., Li⁺ and Na⁺) from complexation energy, while from cooperativity effect, F–H prefers to be attached to Br⁻. For the same geometry, the cooperativity energy from the quaternary complex is far lower than that from the corresponding ternary system for the same geometry.

Supplementary Data

Supplementary data associated with this article, i.e., geometrical parameters, AIM results and interaction energies of the binary and ternary complexes given in Tables S1-S4 and Figs S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(07)769-781_SupplData.pdf.

References

1 Vijay D & Sastry G N, *Chem Phys Lett*, 485 (2010) 235.
2 Meyer E A, Castellano R K & Diederich F, *Angew Chem Int Ed*, 42 (2003) 1210.
3 Mignon P, Loverix S, Steyaert J & Geerlings P, *Nucl Acids Res*, 33 (2005) 1779.
4 Hesselmann A, Jansen G & Schutz M, *J Am Chem Soc*, 128 (2006) 11730.
5 Leist R, Frey J A, Ottiger P, Frey H-M, Leutwyler S, Bachorz R A & Klopper W, A*ngew Chem Int Ed*, 46 (2007) 7449.
6 Garcia-Raso A, Albertí F M, Fiol J J, Tasada A, Barceló-Oliver M, Molins E, Escudero D, Frontera A, Quiñonero D & Deyà P M, *Inorg Chem*, 46 (2007) 10724.
7 Vijay D, Zipse H & Sastry G N, *J Phys Chem B*, 112 (2008) 8863.
8 Quiñonero D, Frontera A, Escudero D, Ballester P, Costa A & Deyà P M, *Theoret Chem Account*, 120 (2008) 385.
9 Alkorta I, Blanco F & Elguero J, *J Phys Chem A*, 114 (2010) 8457.
10 Planas J G, Viñas C, Teixidor F, Comas-Vives A, Ujaque G, Lledós A, Light M E & Hursthouse M B, *J Am Chem Soc*, 127 (2005) 15976.
11 Li Q Z, Hu T, An X L, Gong B A & Cheng J B, *ChemPhysChem*, 9 (2008) 1942.
12 Alkorta I, Blanco F, Deyà P M, Elguero J, Estarellas C, Frontera A & Quiñonero D, *Theoret Chim Acta*, 126 (2010) 1.
13 Alkorta I, Elguero J & Solimannejad M, *J Chem Phys*, 129 (2008) 064115-1.
14 Zabardasti A, Zare N & Arabpour M, *Struct Chem*, 22 (2011) 691.
15 Zabardasti A, Kakanejadi A, Moosavi S, Bigleri Z & Solimannejad M, *J Mol Struct (Theochem)*, 945 (2010) 97.
16 Estarellas C, Frontera A, Quiñonero D, Alkorta I, Deyà P M & Elguero J, *J Phys Chem A*, 113 (2009) 3266.
17 Boaz G O, *Comput Theoret Chem*, 998 (2012) 173.
18 Liao H-Y, *Chem Phys Lett*, 424 (2006) 28.

19　Gao Y, Zhang L, Zhang D L, Wang Y & Yao A Q, *Chinese J Inorg Chem*, 4 (2012) 679.

20　*Gaussian 03, Rev. B.03* (Gaussian, Inc., Pittsburgh PA, USA) 2003.

21　Bader R F W, *Atoms in Molecules, A Quantum Theory*, (Oxford University Press, Oxford, UK) 1990.

22　B-König F W, Bader R F W & Tang T H, *J Comput Chem*, 3 (1982) 317.

23　Reed A E, Curtis L A & Weinhold F, *Chem Rev*, 88 (1988) 899.

24　Duijineveldt F B, Duijineveldt-van de Rijdt J C M V & Lenthe J H V, *Chem Rev*, 94 (1994) 1873.

25　Boys S F & Bernardi F, *Mol Phys*, 19 (1970) 553.

26　Grabowski S J, Robinson T L & Leszczynski J, *Chem Phys Lett*, 386 (2004) 44.

27　Grabowski S J, *J Phys Chem A*, 104 (2000) 5551.

28　Alkorta I, Elguero J, Mó O, Yáñez M & Del Bene J E, *J Phys Chem A*, 106 (2002) 9325.

29　Escudero D, Frontera A, Quiñnero D & Deyà P M, *Chem Phys Lett*, 456 (2008) 257.

30　Solimannejad M, Malekani M & Alkorta I, *J Phys Chem A*, 114 (2010) 12106.

31　Alkorta I, Zborowski K, Elguero J & Solimannejad M, *J Phys Chem A*, 110 (2006) 10279.

32　Grabowski S J, Sokalski W A & Leszczynski J, *Chem Phys Lett*, 422 (2006) 334.

33　Kar T & Scheiner S, *J Phys Chem A*, 108 (2004) 9161.

34　Glendening E D, *J Phys Chem A*, 109 (2005) 11936.

35　Politzer P, Riley K E, Bulat F A & Murray J S, *Comput Theoret Chem*, 998 (2012) 2.

36　Lu T & Chen F, *J Mol Graphics Modell*, 38 (2012) 314.