

A B3LYP and MP2(full) theoretical investigation into the cooperativity effect between dihydrogen-bonding and H–M $\cdots\pi$ (M=Li, Na, K) interactions among HF, MH with the π -electron donor C₂H₂, C₂H₄ or C₆H₆

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Abstract The DFT-B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) calculations were carried out on the binary complex formed by HM (M=Li, Na, K) and HF or the π -electron donor (C₂H₂, C₂H₄, C₆H₆), as well as the ternary system FH \cdots HM \cdots C₂H₂/C₂H₄/C₆H₆. The cooperativity effect between the dihydrogen-bonding and H–M $\cdots\pi$ interactions was investigated. The result shows that the equilibrium distances $R_{\text{H}\cdots\text{H}}$ and $R_{\text{M}\cdots\pi}$ in the ternary complex decrease and both the H \cdots H and H–M $\cdots\pi$ interactions are strengthened when compared to the corresponding binary complex. The cooperativity effect of the dihydrogen bond on the H–M $\cdots\pi$ interaction is more pronounced than that of the M $\cdots\pi$ bond on the H \cdots H interaction. Furthermore, the values of cooperativity effect follow the order of FH \cdots HNa $\cdots\pi$ > FH \cdots HLi $\cdots\pi$ > FH \cdots HK $\cdots\pi$ and FH \cdots HM \cdots C₆H₆ > FH \cdots HM \cdots C₂H₄ > FH \cdots HM \cdots C₂H₂. The nature of the cooperativity effect was revealed by the analyses of the charge of the hydrogen atoms in H \cdots H moiety, atom in molecule (AIM) and electron density shifts methods.

Keywords Cooperativity effect · Dihydrogen bond · H–M $\cdots\pi$ interaction · MP2(full)

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Introduction

Recently M–H $\delta^- \cdots \delta^+$ H–X dihydrogen-bonded interactions have received much attention due to their extremely important role in determining the structures and activities of inorganic, organic, organometallic and biological molecules [1–5]. In 2006, Liao found that microsolvation effect could drive the initial dihydrogen-bonded Li–H \cdots H–F complex transforming into the Li $^+ \cdots$ H–H \cdots F $^-$ system with the formation of H–H covalent bond [6]. In 2012, we reported that, for the hydrated complexes of CNBB–H \cdots H–Na and NCBH–H \cdots H–Na, the H \cdots H distance decreased with the increase of the number of surrounding water molecules, accompanied by the conversion of the H \cdots H bonding nature from ionic bond to covalent bond [7]. These investigations show that the dihydrogen-bonding and common hydrogen-bonding interactions could coexist, and cooperativity effect between them might occur although the term “cooperativity” was not mentioned. The cooperativity is an important characteristic of intermolecular interactions, and in some cases, it might influence the physical and chemical properties of the complexes containing dihydrogen bonds [6, 8, 9]. Properly characterizing the cooperativity of dihydrogen bonds is thus crucial to understanding the behavior of some chemical and biochemical systems.

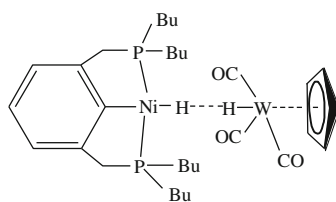
Cooperativity effect between the noncovalent interactions is currently a topic of wide ranging interest [10–22]. In 2005, Mignon *et al.* investigated the interplay between $\pi \cdots \pi$ stacking and hydrogen bonding [11]. In 2006 and 2007, Hesselmann and Leist *et al.* found that the strength of hydrogen bond increased dramatically with additional hydrogen bonds [12, 13]. In 2008, Vijay *et al.* studied the strong cooperativity between cation $\cdots\pi$ interaction and $\pi \cdots \pi$ and hydrogen bonding interactions [14]. In 2010, they performed systematic quantum chemical studies to estimate the effects of cation $\cdots\pi$ and $\pi \cdots \pi$ interactions on each other

in cation $\cdots\pi\cdots\pi$ system [15]. Deyà *et al.* reported experimental [16] and many theoretical [17–22] evidences of the cooperativity effects.

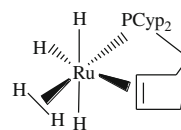
A number of studies have also been devoted to analyzing the cooperativity effects involving dihydrogen-bonded clusters [23–26]. In 2008, a theoretical study was carried out on the clusters formed by the association of HC \equiv CBeH monomers. Cooperative effects were observed in those configurations where dihydrogen bonds were the main interacting force [27]. The cooperativity between the dihydrogen bond and N \cdots H hydrogen bond in LiH–(HCN) $_n$ ($n=2$ and 3) complexes was investigated at the MP2 level of theory. The results indicated that orbital interaction, charge transfer and bond polarization were mainly responsible for the cooperativity [25]. In 2010 and 2011, anticooperativity between the dihydrogen bond and N \cdots H hydrogen bond in (NH $_3$) $_n$ –BeH $_4^{2-}$ was found while the cooperativity between the dihydrogen bond and O \cdots H hydrogen bond in (H $_2$ O) $_n$ –BH $_4^-$ was confirmed by *ab initio* calculations [28, 29]. A theoretical study of the dihydrogen-bonded clusters of three aza-borane derivatives was carried out and a shortening of the intermolecular distances up to 0.1 Å was observed [23].

In 2012, an investigation on the interplay between dihydrogen and alkali-halogen bonds was performed in relation to the formation of NaH \cdots 2(HCF $_3$) and NaH \cdots 2(HCCl $_3$) ternary complexes using B3LYP/6-311++G(3df,3pd) method [30]. A ternary system where hexafluorobenzene simultaneously interacts with BF $_3$ H $^-$ anion and HF via anion– π interaction and dihydrogen bond was studied by Alkorta *et al.*, and unfavorable cooperativity was found [31]. The cooperativity via cation– π interaction and dihydrogen bond in complex HBe–H \cdots H–NC $_4$ H $_4\cdots$ Li $^+$ involving pyrrole aromatic ring was investigated, too [26].

Recently the coexistence of H \cdots H and H–M $\cdots\pi$ (M means metal atom) interactions has also been found [32, 33]. For example, VT NMR spectroscopic study at 190–298 K and DFT calculation using M06 method confirmed the H \cdots H–W $\cdots\pi$ link in the [(2,6-C $_6$ H $_3$ (CH $_2$ PBu $_2$) $_2$)Ni(H)] complex with CpW(H)(CO) $_3$ [34]. An intermediate adduct, in which the H \cdots H and H–Ru $\cdots\pi$ interactions coexist, was observed in the dehydrogenation process of RuH $_2$ (η^2 -H $_2$) $_2$ (PCyp $_3$) $_2$ (Cyp=Cyclopentyl) at room temperature [35]. Two structures are drawn as follows.



[(2,6-C $_6$ H $_3$ (CH $_2$ PBu $_2$) $_2$)Ni(H)]–CpW(H)(CO) $_3$



Dehydrogenation intermediate adduct of RuH $_2$ (η^2 -H $_2$) $_2$ (PCyp $_3$) $_2$

These results suggest that the cooperativity effects between the H–M $\cdots\pi$ and dihydrogen bond interactions might occur.

The H \cdots H interactions could be found between HF and MH (M=Li, Na or K). MH and the π -electrons of C $_2$ H $_2$, C $_2$ H $_4$ or C $_6$ H $_6$ could participate in the H–M $\cdots\pi$ interaction formation [36, 37]. Thus, in the ternary-system of HF with MH and π -electron donor (C $_2$ H $_2$, C $_2$ H $_4$ or C $_6$ H $_6$), *i.e.*, F–H \cdots H–M $\cdots\pi$, the cooperativity effect between the H \cdots H and H–M $\cdots\pi$ interactions might arise. Therefore, the ternary complex F–H \cdots H–M $\cdots\pi$ can serve as the model system to investigate the cooperativity effect between H–M $\cdots\pi$ and dihydrogen-bonding interactions. In this paper, our goal is to investigate systematically into the cooperativity effect between H–M $\cdots\pi$ and dihydrogen-bonding interactions among HF, MH (M=Li, Na or K) with π -electron donor (C $_2$ H $_2$, C $_2$ H $_4$ or C $_6$ H $_6$) using the B3LYP and MP2(full) methods. This theoretic investigation will reveal the nature of the cooperativity effect between the H–M $\cdots\pi$ and dihydrogen-bonding interactions to further study on the

structure and activity of the chemical and biochemical systems involving dihydrogen bond in theory and experiment.

Methods

As a cost-effective approach, in most cases, geometry optimizations by the DFT methodology are feasible and being applied successfully to investigate the structure of the complex. However, for the investigation on the complexation energies of complexes, the MP2(full) method is reliable [38, 39]. In addition, the high quality basis set is a crucial factor for calculating the property of complex [40]. Thus, we used the DFT-B3LYP and MP2(full) methods with the 6-311++G(3df,2p) basis set in this work.

All calculations were performed with Gaussian 03 programs [41]. All the monomers and complexes were fully optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G(3df,2p) basis set. Single point energy

calculations were carried out at the B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels. The shifts of the electron density [42] that accompanies the formation of the complexes were analyzed at the MP2(full)/6-311++G(3df,2p) level, and the topological charge density was displayed by the atom in molecules (AIM) method [43] using AIMPAC program [44] at the same level. The natural bonding analysis [45] was also carried out using the MP2(full)/6-311++G(3df,2p) method.

For the binary system, the interaction energy ($E_{int.}$) was calculated by evaluating the difference between the total energies of complex and individual monomers as given in Eqs. (1) and (2), respectively.

$$E_{int.(H\cdots H)} = E_{MH\cdots HF} - E_{MH} - E_{HF} \quad (1)$$

$$E_{int.(H-M\cdots\pi)} = E_{HM\cdots C_2H_2/C_2H_4/C_6H_6} - E_{HM} - E_{C_2H_2/C_2H_4/C_6H_6} \quad (2)$$

where $E_{int.(H\cdots H)}$ and $E_{int.(H-M\cdots\pi)}$ are the intermolecular interaction energy, $E_{MH\cdots HF}$ and $E_{HM\cdots C_2H_2/C_2H_4/C_6H_6}$ are the total energy of complex, and E_{MH} , E_{HF} and $E_{C_2H_2/C_2H_4/C_6H_6}$ are the total energy of monomer, respectively. $E_{int.(H\cdots H)}$ and $E_{int.(H-M\cdots\pi)}$ were corrected with the basis set superposition error (BSSE) [46, 47].

In the ternary system, $E'_{int.(H\cdots H)}$ and $E'_{int.(H-M\cdots\pi)}$ represent the interaction energy between both the moieties which are directly interacting with. They were calculated using Eqs. (3) and (4), respectively.

$$E'_{int.(H\cdots H)} = E_{FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6} - E_{FH} - E_{HM\cdots C_2H_2/C_2H_4/C_6H_6} \quad (3)$$

$$E'_{int.(H-M\cdots\pi)} = E_{FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6} - E_{FH\cdots HM} - E_{C_2H_2/C_2H_4/C_6H_6} \quad (4)$$

where $E_{FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6}$, $E_{HM\cdots C_2H_2/C_2H_4/C_6H_6}$, $E_{FH\cdots HM}$, E_{FH} and $E_{C_2H_2/C_2H_4/C_6H_6}$ are the total energy of the ternary, binary and monomeric system, respectively. $E'_{int.(H\cdots H)}$ and $E'_{int.(H-M\cdots\pi)}$ were also corrected with BSSE.

$E''_{int.(H\cdots\pi)}$ is defined as the through-space interaction energy between both the moieties with which they are not directly interacting. They were calculated at the trimer geometry by employing Eq. (5).

$$E''_{int.(H\cdots\pi)} = E'_{FH\cdots C_2H_2/C_2H_4/C_6H_6} - E_{FH} - E_{C_2H_2/C_2H_4/C_6H_6} \quad (5)$$

where $E'_{FH\cdots C_2H_2/C_2H_4/C_6H_6}$ represents the total energy of the binary framework (not be optimized) at the optimized trimer geometry.

The cooperativity (coop.) in the ternary complex was calculated using Eq. (6).

$$E_{coop.} = E_{int.(FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6)} - E_{int.(H\cdots H)} - E_{int.(H-M\cdots\pi)} - E''_{int.(H\cdots\pi)} \quad (6)$$

$E_{int.(H\cdots H)}$, $E_{int.(H-M\cdots\pi)}$ and $E''_{int.(H\cdots\pi)}$ are the three two-body terms. They were calculated using Eqs. (1), (2) and (5), respectively. According to Vijay, the complexation energy of the trimer, $E_{int.(FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6)}$, corresponds to the energy involved in the direct assembly of the ternary complex from its constituent monomers [10]. It was calculated as the energy difference between the total energy of the ternary complex and the energies of monomers.

$$E_{int.(FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6)} = E_{FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6} - E_{FH} - E_{HM} - E_{C_2H_2/C_2H_4/C_6H_6} \quad (7)$$

Results and discussion

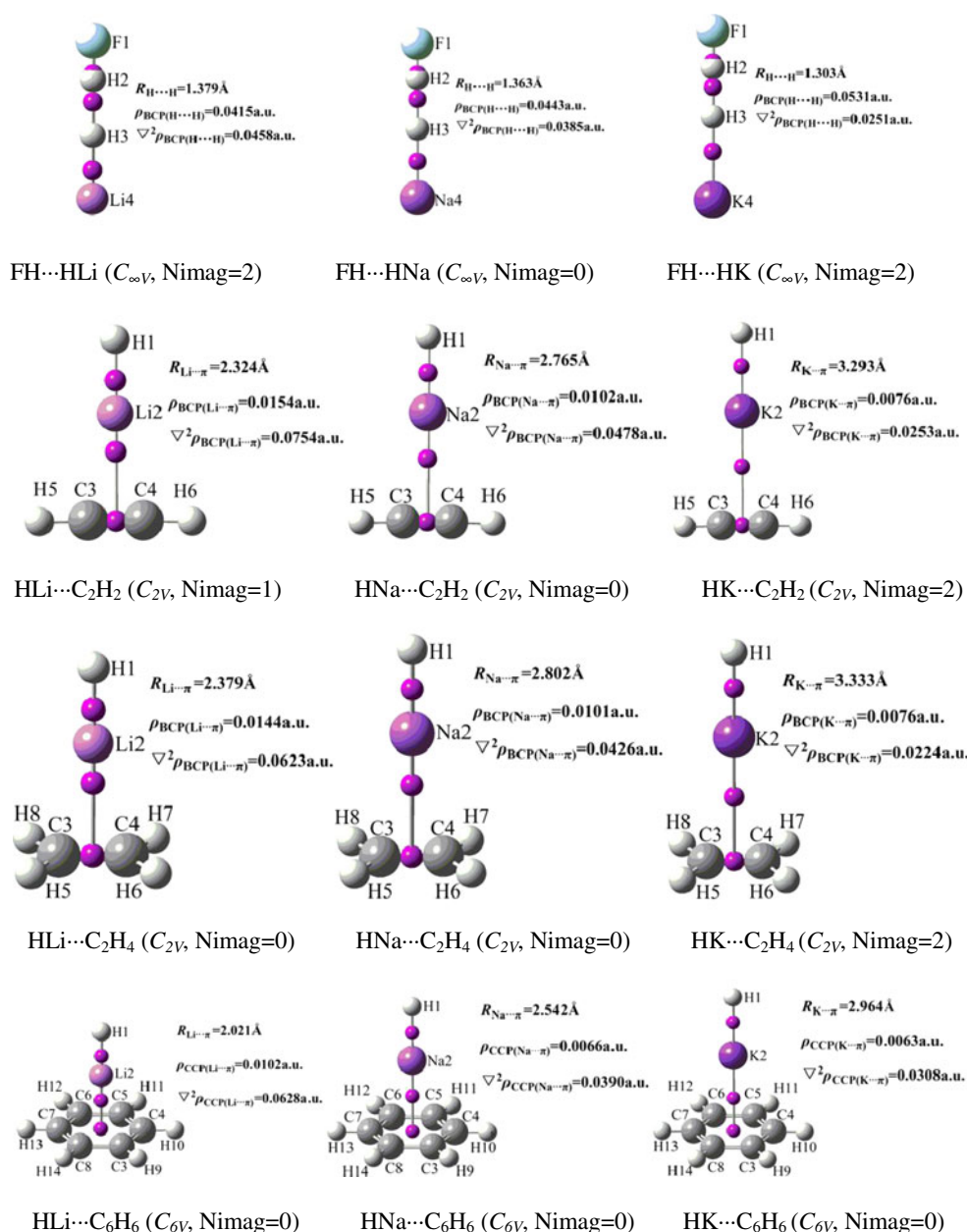
Binary system

The structure of the binary complex is shown in Fig. 1. From Fig. 1, the equilibrium structures of all the dihydrogen-bonded complexes FH \cdots HM have $C_{\infty V}$ symmetry, and in each of the dihydrogen-bonded systems, the hydridic hydrogen atom of HM points into the hydrogen atom of HF.

The intermolecular interaction energy of the dihydrogen-bonded binary complex FH \cdots HM is reported in Table 1. From Table 1, FH \cdots HK has the highest interaction energy followed by FH \cdots HNa and FH \cdots HLi. The decrease in the binding ($-78.12 > -64.29 > -60.11$ kJ mol $^{-1}$ at MP2(full)/6-311++G(3df,2p) level) is in good agreement with the increase in the H \cdots H distance ($1.303 < 1.363 < 1.379$ Å at MP2(full)/6-311++G(3df,2p) level, see Fig. 1). Liao has found that the H \cdots H distance in FH \cdots HLi is 1.431 Å at B3LYP/6-311G** level and the interaction energy is 49.64 kJ mol $^{-1}$ at CCSD(T)/6-311G**//B3LYP/6-311G** level, including ZPE corrections determined at B3LYP/6-311G** level [6]. A high level *ab initio* calculation result for FH \cdots HLi (49.93 kcal mol $^{-1}$ at QCISD(T)/6-311++G** level including BSSE correction) has been obtained [48]. Our calculation for the interaction energy in FH \cdots HLi at B3LYP/6-311++G(3df,2p) level with BSSE correction (50.18 kJ mol $^{-1}$) is approximately equal to their results.

From Fig. 1, for the T-shaped HM binary-complex with C $_2$ H $_2$, C $_2$ H $_4$ or C $_6$ H $_6$, the H–M bond lies perpendicular to the C \equiv C or C=C bond or the C $_6$ H $_6$ ring plane, and points toward its midpoint or center with C_{2V} , C_{2V} or C_{6V} symmetry. The

Fig. 1 The optimized geometries and AIM results of the binary complexes at MP2(full)/6-311++G(3df,2p) level



M... π distances are within the range of 2.021–3.333 Å at MP2(full)/6-311++G(3df,2p) level, which are larger than those in the corresponding cation... π complexes [49, 50]. For example, the Li⁺... π distance in Li⁺...C₂H₂ is only 2.213 Å while the Li... π distance of HLi...C₂H₂ is up to 2.324 Å at MP2(full)/6-311++G(3df,2p) level. The intermolecular interaction energies are in the range between –15.90 and –69.36 kJ mol⁻¹ at MP2(full)/6-311++G(3df,2p) level (see Table 2), which are weaker than those in the common cation... π interaction systems [49–51]. In general, the binding energy of charged complex is considerably more favorable than neutral since there is electrostatic effect in the former. Here, we have also obtained Li⁺... π interaction in Li⁺...C₂H₂. It is –88.08 kJ mol⁻¹ at MP2(full)/6-311++

G(3df,2p) level, two times larger than the intermolecular interaction energy in HLi...C₂H₂ (–40.03 kJ mol⁻¹). For this kind of the intermolecular interaction between the M atom of

Table 1 Intermolecular dihydrogen-bonding interaction energy ($E_{int(H\cdots H)}$) in the binary complex^a

Method	FH...HLi	FH...HNa	FH...HK
B3LYP/6-311++G(3df,2p)	–53.62 (–50.18)	–54.20 (–50.91)	–66.53 (–63.40)
MP2(full)/6-311++G(3df,2p)	–60.11 (–55.30)	–64.29 (–58.58)	–78.12 (–72.52)

^a The values in parenthesis are corrected by the BSSE method

Table 2 Intermolecular H–M $\cdots\pi$ (M=Li, Na, K) interaction energy ($E_{int.(H-M \cdots \pi)}$) in the binary complex^a

HLi \cdots C ₂ H ₂	HNa \cdots C ₂ H ₂	HK \cdots C ₂ H ₂	HLi \cdots C ₂ H ₄	HNa \cdots C ₂ H ₄	HK \cdots C ₂ H ₄	HLi \cdots C ₆ H ₆	HNa \cdots C ₆ H ₆	HK \cdots C ₆ H ₆
-40.00 ^b (-37.00) ^b	-22.17 (-19.04)	-11.64 (-9.44)	-38.37 (-35.67)	-21.75 (-18.28)	-11.60 (-9.01)	-53.93 (-48.68)	-32.97 (-28.03)	-21.82 (-18.88)
-40.03 ^c (-34.94) ^c	-26.37 (-20.20)	-15.90 (-13.02)	-39.81 (-34.60)	-27.00 (-20.33)	-16.28 (-13.06)	-69.36 (-54.07)	-50.25 (-34.73)	-39.89 (-30.49)

^aThe values in parenthesis are corrected by the BSSE method^bAt the B3LYP/6-311++G(3df,2p) level^cAt the MP2(full)/6-311++G(3df,2p) level

HM and the π -electron in C₂H₄, C₂H₂ or C₆H₆, we entitle it as the “H–M $\cdots\pi$ interaction”. The H–M $\cdots\pi$ interaction is similar to the cation $\cdots\pi$ interaction since the M atom possesses obvious positive charge. For instance, the Mulliken charge of the K atom in HK \cdots C₂H₄ is up to 0.593 e at MP2(full)/6-311++G(3df,2p) level.

The H–M $\cdots\pi$ interaction energies obtained at two levels are all in the same order of HLi $\cdots\pi$ >HNa $\cdots\pi$ >HK $\cdots\pi$ and HM \cdots C₆H₆>HM \cdots C₂H₄≈HM \cdots C₂H₂, as is in accordance with the increase in the M $\cdots\pi$ distance. For instance, for the C₂H₂ complexes with HLi, HNa and HK, the binding energies are -40.03, -26.37 and -15.90 kJ mol⁻¹, and the H–M $\cdots\pi$ distances are 2.379, 2.802 and 3.333 Å at MP2(full)/6-311++G(3df,2p) level, respectively. Another example, for the HLi complexes, HLi \cdots C₆H₆ has the highest interaction energy (-69.36 kJ mol⁻¹) followed by HLi \cdots C₂H₂ and HLi \cdots C₂H₄ (near to 40.00 kJ mol⁻¹), with the order of the Li $\cdots\pi$ distance being 2.021<2.324<2.379 Å.

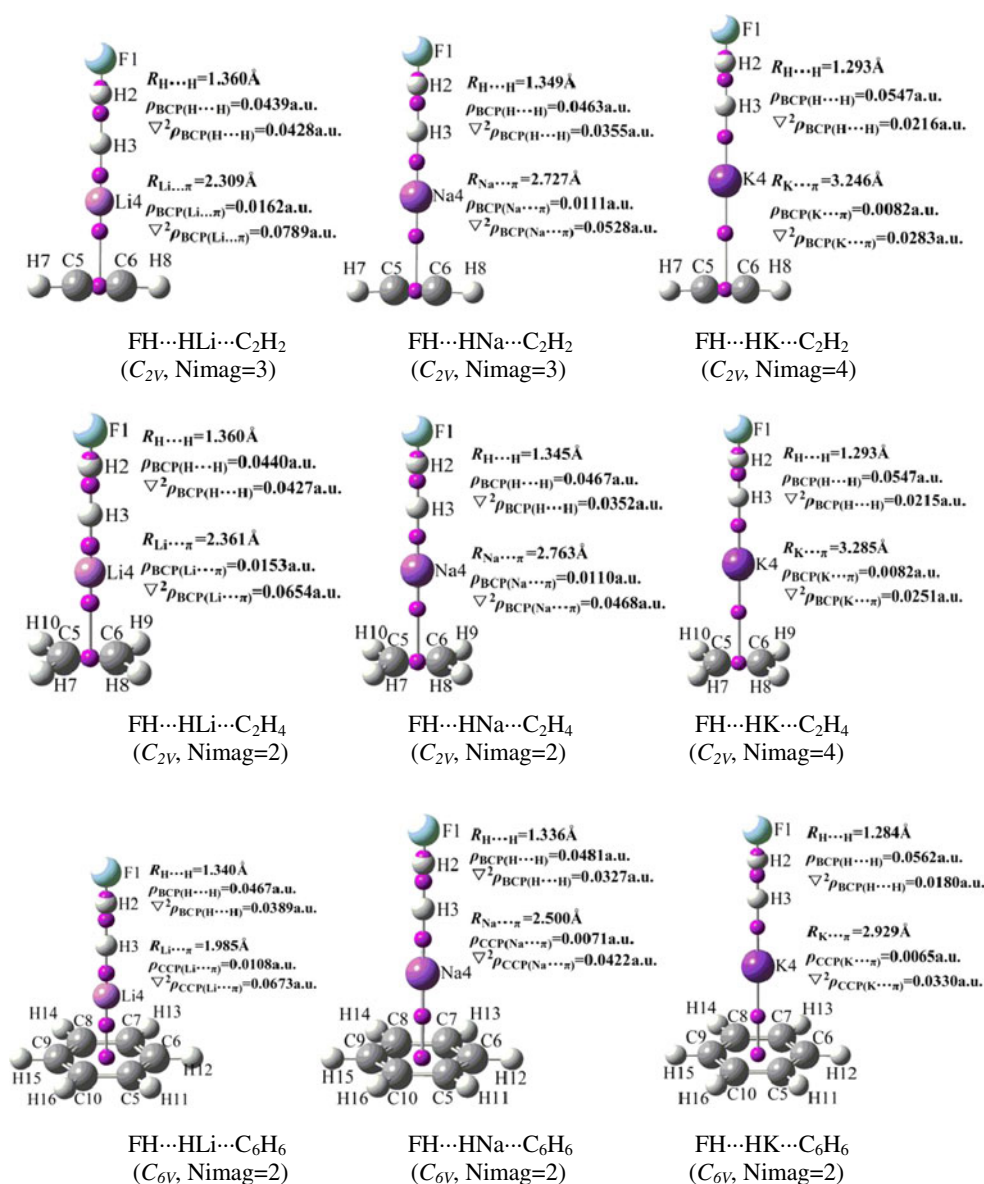
Ternary systems and cooperativity

Geometrical parameters

The geometric results computed for the ternary complexes are shown in Fig. 2. From Fig. 2, in each of the FH \cdots HM \cdots C₂H₂/C₂H₄/C₆H₆ ternary-systems, the hydridic hydrogen atom of HM points into the hydrogen atom of HF, and the H–M bond lies perpendicular to the C=C or C≡C bond or the C₆H₆ ring plane and points toward its midpoint or center. The equilibrium structures of the complexes with C₂H₂, C₂H₄ and C₆H₆ have C_{2v}, C_{2v} and C_{6v} symmetries, respectively. The H \cdots H and M $\cdots\pi$ distances are within the ranges of 1.284–1.360 Å and 1.985–3.285 Å at MP2(full)/6-311++G(3df,2p) level, respectively. The H \cdots H distances just fall into the accepted values of the conventional H \cdots H dihydrogen bonds. The M $\cdots\pi$ distances are close to those in the cation $\cdots\pi$ systems. Thus, both interactions, H \cdots H and H–M $\cdots\pi$, might coexist in the ternary complexes.

From Fig. 2, some interesting points can be extracted from the geometrical results. The equilibrium distance R_{H \cdots H} of the H \cdots H dihydrogen bond in the ternary complex decreases when compared to the corresponding binary complex (see Fig. 1). This result indicates that the presence of the H–M $\cdots\pi$ interaction might strengthen the H \cdots H interaction. Furthermore, the equilibrium distance R_{M $\cdots\pi$} of the H–M $\cdots\pi$ bonding interaction in the ternary complex is also shortened when compared to the corresponding binary complex. The change of the M $\cdots\pi$ distance shows that the presence of the H \cdots H interaction might also strengthen the H–M $\cdots\pi$ interaction. In addition, the H–F and H–M bond lengths in the ternary complexes increase in comparison with those of the binary systems. Thus, the cooperativity effect upon the formation of ternary complex might be suggested.

Fig. 2 The optimized geometries and AIM results of the ternary complexes at MP2(full)/6-311++G(3df,2p) level



As can be seen from Figs. 1 and 2, the change of the H...H distance upon the ternary-complex formation follows the order of FH...HLi... π > FH...HNa... π > FH...HK... π and FH...HM...C₆H₆ > FH...HM...C₂H₄ \approx FH...HM...C₂H₂. For instance, for FH...HLi...C₆H₆, FH...HNa...C₆H₆ and FH...HK...C₆H₆, the decrease of the H...H distance is 0.039, 0.027 and 0.019 Å, respectively. These results indicate that the increase of the dihydrogen-bonding interaction energy in the ternary complex in comparison with that in the corresponding binary system might follow the order of FH...HLi... π > FH...HNa... π > FH...HK... π and FH...HM...C₆H₆ > FH...HM...C₂H₄ \approx FH...HM...C₂H₂. In other words, the cooperativity effect of the H-M... π interaction on the H...H dihydrogen bond might follow the order

of FH...HLi... π > FH...HNa... π > FH...HK... π and FH...HM...C₆H₆ > FH...HM...C₂H₄ \approx FH...HM...C₂H₂.

On the other hand, except for FH...HK...C₆H₆, the change of the M... π distance follows the order of FH...HLi... π < FH...HNa... π < FH...HK... π and FH...HM...C₆H₆ > FH...HM...C₂H₄ > FH...HM...C₂H₂. For instance, for FH...HLi...C₂H₄, FH...HNa...C₂H₄ and FH...HK...C₂H₄, the decrease of the M... π distance is 0.018, 0.039 and 0.048 Å, respectively. These results suggest that the increase of the strength of the H-M... π interaction in the ternary complex in comparison with that in the corresponding binary system might be the order of FH...HLi... π < FH...HNa... π and FH...HM...C₆H₆ > FH...HM...C₂H₄ > FH...HM...C₂H₂, i.e., the cooperativity effect of the dihydrogen-bonding

interaction on the H–M⋯π bond might follow the order of FH⋯HLi⋯π < FH⋯HNa⋯π and FH⋯HM⋯C₆H₆ > FH⋯HM⋯C₂H₄ > FH⋯HM⋯C₂H₂.

Interaction energy and cooperativity effect

Table 3 summarizes the interaction energies in ternary complexes at two levels. From Tables 1, 2 and 3, despite the fact that the complexation energies using the MP2(full) method are more negative due to that dispersion interaction is not accounted employing the B3LYP method but given by the MP2(full) methodology, both theoretical levels give similar trends: the values of the dihydrogen-bonding interaction energy $E'_{int.(H⋯H)}$ and H–M⋯π interaction energy $E'_{int.(H-M⋯π)}$ in ternary complexes are larger than those ($E_{int.(H⋯H)}$ and $E_{int.(H-M⋯π)}$) in the corresponding binary systems. This result shows that the H⋯H and H–M⋯π interactions are strengthened upon the ternary-complex formation. This is in accordance with the geometrical results.

At MP2(full)/6-311++G(3df,2p) level, the increment of the H⋯H interaction energy in ternary complex in comparison with that in binary system is up to 5.15, 5.35, 11.07, 4.39, 4.66, 8.25, 3.27, 3.37 and 6.40 kJ mol⁻¹ for FH⋯HM⋯C₂H₂/C₂H₄/C₆H₆ (M=Li, Na and K), respectively. This change follows the order of FH⋯HLi⋯π > FH⋯HNa⋯π > FH⋯HK⋯π and FH⋯HM⋯C₆H₆ > FH⋯HM⋯C₂H₄ > FH⋯HM⋯C₂H₂, as is just in agreement

with the change of the H⋯H distance upon the ternary-complex formation.

For the H–M⋯π interactions, the increment is found to be the order of FH⋯HLi⋯π > FH⋯HNa⋯π > FH⋯HK⋯π and FH⋯HM⋯C₆H₆ > FH⋯HM⋯C₂H₄ > FH⋯HM⋯C₂H₂ at two levels. The order of FH⋯HM⋯C₆H₆ > FH⋯HM⋯C₂H₄ > FH⋯HM⋯C₂H₂ is in accordance with that of the change of the M⋯π distance upon the formation of ternary complex but the order of FH⋯HLi⋯π > FH⋯HNa⋯π > FH⋯HK⋯π is just in opposition to that of the change of the M⋯π distance. It is noted that the values of $E'_{int.(H-M⋯π)}$ are obtained by Eq. (3) and they are computed at their individual equilibrium geometries of trimer, dimer and monomer. Here, the H–M⋯π interactions were also calculated at the trimer geometry by the following formula:

$$E''_{int.(H-M⋯π)} = E'_{HM⋯C2H2/C2H4/C6H6} - E_{HM} - E_{C2H2/C2H4/C6H6}$$

where $E'_{HM⋯C2H2/C2H4/C6H6}$ represents the total energy of the binary framework (not be optimized) at the optimized trimer geometry. At MP2(full)/6-311++G(3df,2p) level, the values of $E''_{int.(H-M⋯π)}$ are found to be -39.88, -39.66, -67.92, -26.22, -26.86, -49.01, -15.71, -16.09 and -38.54 kJ mol⁻¹ for FH⋯HM⋯C₂H₂/C₂H₄/C₆H₆ (M=Li, Na and K), respectively. All the values of $E''_{int.(H-M⋯π)}$ are lower slightly than those of $E_{int.(H-M⋯π)}$ (see Table 2), and the largest difference is only 1.44 kJ mol⁻¹.

Table 3 Interaction energy ($E_{int.}$ (kJ mol⁻¹) and cooperativity effect ($E_{coop.}$ (kJ mol⁻¹)) in the ternary system at the B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels^a

Method	Complex	$E'_{int.(H⋯H)}$	$E'_{int.(H-M⋯π)}$	$E''_{int.(H⋯π)}$	$E_{int.(FH⋯HM⋯π)}$	$E_{coop.}$
B3LYP	FH⋯HLi⋯C ₂ H ₂	-59.76(-52.84)	-46.14(-39.22)	-1.14	-99.76	-11.44
	FH⋯HNa⋯C ₂ H ₂	-60.19(-53.44)	-28.17(-21.42)	-0.70	-82.36	-11.71
	FH⋯HK⋯C ₂ H ₂	-69.99(-64.51)	-15.10(-9.63)	-0.42	-81.64	-8.38
	FH⋯HLi⋯C ₂ H ₄	-60.03(-53.28)	-44.78(-38.03)	-1.08	-98.41	-11.48
	FH⋯HNa⋯C ₂ H ₄	-60.36	-27.91	-0.65	-82.11	-12.27
	FH⋯HK⋯C ₂ H ₄	-70.06(-64.18)	-15.13(-9.25)	-0.38	-81.65	-8.86
	FH⋯HLi⋯C ₆ H ₆	-66.14(-56.01)	-66.46(-56.33)	-2.28	-120.07	-18.93
	FH⋯HNa⋯C ₆ H ₆	-64.16(-55.10)	-42.93(-33.87)	-1.37	-97.12	-16.81
	FH⋯HK⋯C ₆ H ₆	-73.03(66.66)	-28.32(-21.95)	-0.89	-94.85	-11.68
MP2(full)	FH⋯HLi⋯C ₂ H ₂	-65.27(-55.33)	-45.19(-35.25)	-1.40	-105.29	-13.65
	FH⋯HNa⋯C ₂ H ₂	-68.68(-57.34)	-30.76(-19.41)	-0.86	-95.05	-15.41
	FH⋯HK⋯C ₂ H ₂	-81.39(-72.85)	-19.18(-10.63)	-0.53	-97.30	-11.23
	FH⋯HLi⋯C ₂ H ₄	-65.46(-55.38)	-45.17(-35.08)	-1.47	-105.28	-13.91
	FH⋯HNa⋯C ₂ H ₄	-68.95(-57.00)	-31.66(-19.71)	-0.89	-95.96	-16.16
	FH⋯HK⋯C ₂ H ₄	-81.49	-19.66	-0.54	-97.78	-11.66
	FH⋯HLi⋯C ₆ H ₆	-71.18(-49.97)	-80.43(-59.22)	-3.34	-140.54	-27.83
	FH⋯HNa⋯C ₆ H ₆	-72.54(-51.23)	-58.50(-37.19)	-1.91	-122.78	-27.56
	FH⋯HK⋯C ₆ H ₆	-84.52(-69.05)	-46.29(-30.82)	-2.25	-125.41	-20.15

^a The values in parenthesis are corrected by the BSSE method

Table 4 Charges of two hydrogen atoms in $H^{\delta+}\cdots\delta^-H$ moiety and the NBO charge transfers of HF (Q(HF)) at the MP2(full)/6-311++G(3df,2p) level

Complex	Mulliken charge		APT charge	NBO charge	Q(HF)
FH \cdots HLi	0.499–0.245	0.358 ^a –0.432 ^a	0.555 ^a –0.635 ^a	0.584–0.844	–0.069
FH \cdots HNa	0.501–0.341	0.351–0.462	0.606–0.624	0.578–0.823	–0.087
FH \cdots HK	0.564–0.734	0.369–0.613	0.673–0.709	0.562–0.826	–0.127
FH \cdots HLi \cdots C ₂ H ₂	0.553–0.549	0.369–0.489	0.578–0.647	0.584–0.796	–0.077
FH \cdots HNa \cdots C ₂ H ₂	0.522–0.476	0.354–0.480	0.616–0.645	0.577–0.807	–0.096
FH \cdots HK \cdots C ₂ H ₂	0.569–0.740	0.368–0.601	0.678–0.717	0.559–0.818	–0.136
FH \cdots HLi \cdots C ₂ H ₄	0.561–0.595	0.370–0.494	0.580–0.647	0.584–0.795	–0.078
FH \cdots HNa \cdots C ₂ H ₄	0.529–0.517	0.354–0.473	0.618–0.645	0.576–0.805	–0.097
FH \cdots HK \cdots C ₂ H ₄	0.570–0.743	0.368–0.601	0.674–0.717	0.559–0.817	–0.136
FH \cdots HLi \cdots C ₆ H ₆	0.593–0.752	0.376–0.575	0.605–0.623	0.582–0.761	–0.089
FH \cdots HNa \cdots C ₆ H ₆	0.553–0.657	0.357–0.505	0.629–0.637	0.575–0.793	–0.103
FH \cdots HK \cdots C ₆ H ₆	0.572–0.770	0.370–0.607	0.680–0.720	0.555–0.805	–0.147

^aAt B3LYP/6-311++G(3df,2p)

The proportion of the increment in the dihydrogen-bonding interaction upon the formation of ternary complex to the corresponding $E_{int.(H\cdots H)}$ value in binary system, defined as $[E'_{int.(H\cdots H)} - E_{int.(H\cdots H)}]/E_{int.(H\cdots H)}$, is 8.58 %, 8.90 %, 18.42 %, 6.83 %, 7.25 %, 12.83 %, 4.19 %, 4.31 % and 8.19 % for FH \cdots HM \cdots C₂H₂/C₂H₄/C₆H₆ (M=Li, Na and K) at MP2(full)/6-311++G(3df,2p) level, respectively. For the H–M \cdots π interactions, it is found to be 12.89 %, 13.44 %, 15.96 %, 16.65 %, 17.26 %, 16.42 %, 20.57 %, 20.70 % and 16.04 %, respectively. These results indicate that, except for FH \cdots HLi \cdots C₆H₆, the increment of the H–M \cdots π interaction is more notable than that of the dihydrogen-bonding interaction. This result indicates that the cooperativity effect of the dihydrogen-bonds on the H–M \cdots π interactions might be more pronounced than that of the M \cdots π bonds on the H \cdots H interactions.

As can be seen from Table 3, the complexation energies of the trimer, $E_{int.(FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6)}$, are in the order of FH \cdots HLi \cdots π >FH \cdots HNa \cdots π >FH \cdots HK \cdots π at the B3LYP/6-311++G(3df,2p) level, while those obtained from the MP2(full)/6-311++G(3df,2p) method follow the order of FH \cdots HLi \cdots π >FH \cdots HK \cdots π >FH \cdots HNa \cdots π . At two levels of theory, the order of FH \cdots HM \cdots C₆H₆>FH \cdots HM \cdots C₂H₄ \approx FH \cdots HM \cdots C₂H₂ are found.

The cooperativity effects are investigated at B3LYP/6-311++G(3df,2p) and MP2(full)/6-311++G(3df,2p) levels (see Table 3). The values of cooperativity obtained from the B3LYP/6-311++G(3df,2p) method are all lower than those at the MP2(full)/6-311++G(3df,2p) level, as is in accordance with our recent investigation on the cooperativity effect between cation-molecule and hydrogen-bonding interactions in the *O*-cresol complex with Na⁺ [52]. It has been shown from many of the previous investigations that the MP2 method should be more feasible to elucidate the trends in the calculated cooperativity effect [12, 15, 18]. 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. From Table 3, at two levels of theory, the cooperativity is negative for all the ternary complexes. This means that both of the interactions, H \cdots H and H–M \cdots π , are reinforced and the cooperativity effects are present. As aforementioned, the distances $R_{H\cdots H}$ and $R_{M\cdots \pi}$ are shortened and the H \cdots H and H–M \cdots π interactions are strengthened upon the formation of the ternary complexes.

From Table 3, the values of cooperativity effect are large. For example, at MP2(full)/6-311++G(3df,2p) level, the values of $E_{coop.}$ are in the range between –11.23 and –27.83 kJ mol^{–1}. Vijay *et al.* have found that, in two aromatic benzene rings system with the Na⁺ cation, the largest value of the cooperativity of cation \cdots π and $\pi\cdots\pi$ interactions is only –0.57 kcal mol^{–1} (–2.38 kJ mol^{–1}) [10]. Escudero *et al.* have observed that the non-additivity energy, denoted as the difference between the binding energy of the ternary complex and the binding energy of the sum of all pair interaction energies, is only –1.49 kcal mol^{–1} (–6.23 kJ mol^{–1}) in Na⁺-H₂O-indole/pyrrole complex [18]. The complexes F₃CCl(Br) \cdots NCH(CNH) \cdots HMgH with simultaneous presence of a σ -hole bond and a dihydrogen bond show cooperativity energy ranging between –1.02 and –2.31 kJ mol^{–1} at MP2/cc-pVTZ level [53]. The remarkable cooperativity effect between the H \cdots H and H–M \cdots π interactions might lead to the notable change of the structures and properties of the dihydrogen-bond complexes upon the introduction of the π -electron donor (C₂H₂, C₂H₄ or C₆H₆), as is in accordance with the analysis of the structure.

As can be seen from Table 3, except for FH \cdots HNa \cdots C₆H₆, the values of cooperativity effect follow the order of

$\text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HLi}\cdots\pi > \text{FH}\cdots\text{HK}\cdots\pi$ and $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$. The order of $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$ is just in accordance with that of the increment of the $\text{H}\cdots\text{H}$ or $\text{H}\cdots\text{M}\cdots\pi$ interaction energy upon the ternary-complex formation but the order of $\text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HLi}\cdots\pi$ is not in agreement ($\text{FH}\cdots\text{HLi}\cdots\pi > \text{FH}\cdots\text{HNa}\cdots\pi$ for the $\text{H}\cdots\text{H}$ or $\text{H}\cdots\text{M}\cdots\pi$ interaction energy). One of the causes of disagreement might be $\text{FH}\cdots\text{HLi}\cdots\pi > \text{FH}\cdots\text{HNa}\cdots\pi$ for the order of $E''_{\text{int.}(\text{H}\cdots\pi)}$ (see Table 3).

AIM analysis

AIM analysis can give some helpful information regarding the strength of the noncovalent interactions involved in complexes [54]. As proposed by Bader [43], electron density ρ at the bond saddle point indicates the bond strength. The larger the ρ is, the stronger the interaction will be. Laplacian term $\nabla^2\rho$ of the bond saddle point can reveal the nature of the interaction. $\nabla^2\rho > 0$ means the loose charge density at the critical point.

According to the AIM analysis at MP2(full)/6-311++G(3df,2p) level, for each of the binary complexes $\text{FH}\cdots\text{HLi}$, $\text{FH}\cdots\text{HNa}$ and $\text{FH}\cdots\text{HK}$ as well as all the ternary systems, there is a bond path linking the hydridic hydrogen atom of HM and the hydrogen atom of HF, accompanied by a bond critical point (BCP) (3, -1). In each of the binary complexes $\text{HM}\cdots\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ and the ternary systems $\text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$, there is the bond path linking the M atom and the two carbon atoms of C_2H_2 or C_2H_4 , accompanied by a ring critical point (RCP) (3, +1). The binary complexes $\text{HM}\cdots\text{C}_6\text{H}_6$ and the ternary systems with C_6H_6 are characterized by the presence of the (3, +3) cage critical point (CCP). From Figs. 1 and 2, the electron densities ρ_{BCP} , ρ_{RCP} and ρ_{CCP} are within the ranges of 0.0415–0.0562 a.u., 0.0076–0.0162 a.u. and 0.0063–0.0108 a.u., respectively. Moreover, their Laplacians $\nabla^2\rho_{\text{BCP}}$, $\nabla^2\rho_{\text{RCP}}$ and $\nabla^2\rho_{\text{CCP}}$ are all positive, suggesting the typical closed-shell kind of interactions. Thus, the coexistence of the $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{M}\cdots\pi$ interactions in the ternary complexes are confirmed, as is in good agreement with the structures and energies.

As can be seen from Figs. 1 and 2, the charge densities $\rho_{\text{BCP}(\text{H}\cdots\text{H})}$ in ternary complexes increase in comparison with those in the corresponding binary systems. This result indicates that the $\text{H}\cdots\text{H}$ interactions are strengthened, as agrees with the $\text{H}\cdots\text{H}$ interaction analysis. At the MP2(full)/6-311++G(3df,2p) level, the increment of $\rho_{\text{BCP}(\text{H}\cdots\text{H})}$ is found to be 0.0024, 0.0025, 0.0052, 0.0020, 0.0024, 0.0038, 0.0016, 0.0016 and 0.0031 a.u. for $\text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$ (M=Li, Na and K), respectively. This change follows the order of $\text{FH}\cdots\text{HLi}\cdots\pi > \text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HK}\cdots\pi$ and $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$.

For the charge density $\rho_{\text{BCP}(\text{M}\cdots\pi)}$, it is also found that the values in ternary complexes increase in comparison with those in the corresponding binary systems, indicating that the $\text{M}\cdots\pi$ interactions are also enhanced upon the formations of ternary complexes. The increase of $\rho_{\text{BCP}(\text{M}\cdots\pi)}$ is within the range of 0.0002–0.0009 a.u.. The change of $\rho_{\text{BCP}(\text{M}\cdots\pi)}$ follows the order of $\text{FH}\cdots\text{HLi}\cdots\pi \approx \text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HK}\cdots\pi$ and $\text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 \approx \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2 > \text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6$.

Both the charge density $\rho_{\text{BCP}(\text{H}\cdots\text{H})}$ and $\rho_{\text{BCP}(\text{M}\cdots\pi)}$ in ternary complexes increase in comparison with those in the corresponding binary systems, indicating that both the $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{M}\cdots\pi$ interactions are strengthened. Thus, the cooperativity effect between the $\text{H}\cdots\text{H}$ and $\text{H}\cdots\text{M}\cdots\pi$ interactions in ternary complex arises.

Charge analysis of the hydrogen atom in $\text{H}\cdots\text{H}$ moiety

There are different views on the origin of the cooperativity effect of both interactions. Kar *et al.* have shown that the cooperativity can mainly be attributed to the polarization induced in each subunit [55]. Glendening has pointed out that charge transfer could be regarded as the leading source of cooperative stabilization and that polarization effects have only marginal influence on the cooperativity [56]. In order to probe the origin of the cooperativity effect of the $\text{M}\cdots\pi$ bond on the dihydrogen-bonding interactions, the analyses of the charge of the hydrogen atom in $\text{H}\cdots\text{H}$ moiety and the NBO charge transfer of HF upon the formation of ternary system are carried out.

Mulliken, APT and NBO charges of the hydrogen atom in $\text{H}^{\delta+}\cdots\delta-\text{H}$ moiety at MP2(full)/6-311++G(3df,2p) level are listed in Table 4. From Table 4, for the Mulliken and APT charges in each of the ternary systems, the proton donor $\text{H}^{\delta+}$ has a more positive charge than that in the corresponding binary complex except for the Mulliken charge in $\text{FH}\cdots\text{HK}\cdots\text{C}_2\text{H}_2$. Similarly, the hydridic hydrogen atom ($\delta-\text{H}$) in ternary system has a more negative charge relative to that in the corresponding binary complex. The charge increases lead to the increase of the polarization in the $\text{H}^{\delta+}\cdots\delta-\text{H}$ bond, making two hydrogen atoms easier to form the $\text{H}^{\delta+}\cdots\delta-\text{H}$ dihydrogen bond each other. Thus, the dihydrogen-bonding interaction is strengthened, leading to the formation of the cooperativity effect. In other words, the number of charges on the two hydrogen atoms increases when the π -electron donor $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$ is added to the $\text{FH}\cdots\text{HM}$ system, accompanied by the enhancement of in the $\text{H}\cdots\text{H}$ ionic bond. This is NOT in accordance with the previous investigations by Liao and us [6, 7]. Liao has found that, when there are water molecules added to the $\text{FH}\cdots\text{HLi}$ system, the hydrogen-bonded energy is found to increase but the number of charges on the two hydrogen atoms decreases, indicating that the $\text{H}\cdots\text{H}$ covalent bond formation is

in progress [6]. In our recent investigation on the hydrated complexes of $\text{NC}(\text{CN})\text{BB}-\text{H}\cdots\text{H}-\text{Na}$, the number of charges on the two hydrogen atoms also decreases with the increase of the number of surrounding water molecules [7].

The change of the Mulliken and APT charges of the two hydrogen atoms in $\text{H}^{\delta+}\cdots\delta-\text{H}$ moiety upon the formation of ternary complexes follows the order of $\text{FH}\cdots\text{HLi}\cdots\pi > \text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HK}\cdots\pi$ and $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$. The order of $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$ is just in accordance with that of the cooperativity effect but the order of $\text{FH}\cdots\text{HNa}\cdots\pi > \text{FH}\cdots\text{HLi}\cdots\pi$ is not in agreement. For example, the increment of the Mulliken charge of $\text{H}^{\delta+}$ upon ternary-complex formation is 0.054, 0.021, 0.005, 0.062, 0.028, 0.006, 0.094, 0.052 and 0.008 e for $\text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$ ($M=\text{Li}, \text{Na}$ and K) at MP2(full)/6-311++G(3df,2p) level, respectively.

The NBO charge transfer of HF was also calculated at MP2(full)/6-311++G(3df,2p) level and the results were given in Table 4. Clearly, the charge transfer increases upon the formation of the ternary complex in comparison with that in the corresponding binary system. The change follows the order of $\text{FH}\cdots\text{HM}\cdots\text{C}_6\text{H}_6 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_4 > \text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2$, as is in agreement with that of the cooperativity effect. This result suggests that the charge transfer interaction also plays an important role in the cooperativity effect, as is in accordance with the previous study by Li [25].

Analysis of the electron density shifts

It is known that changes in the electron density distribution in both of the donors and acceptors are the important consequence of the formation of the intermolecular interaction [42]. In order to obtain deeper insight into the origin of the cooperativity effect, the analysis of the electron density shifts which accompany the formation of the ternary complex by the initial $\text{FH}\cdots\text{HM}$ followed by addition of the π -electron donor $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$ was carried out. The electron density shift was calculated by evaluating the difference

between the total electron densities of ternary complex and individual moieties ($\text{FH}\cdots\text{HM}$ and the π -electron donor $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$) as given in the following formula:

$$\rho_{\text{shift}} = \rho(\text{FH}\cdots\text{HM}\cdots\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6) - \rho(\text{FH}\cdots\text{HM}) - \rho(\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6)$$

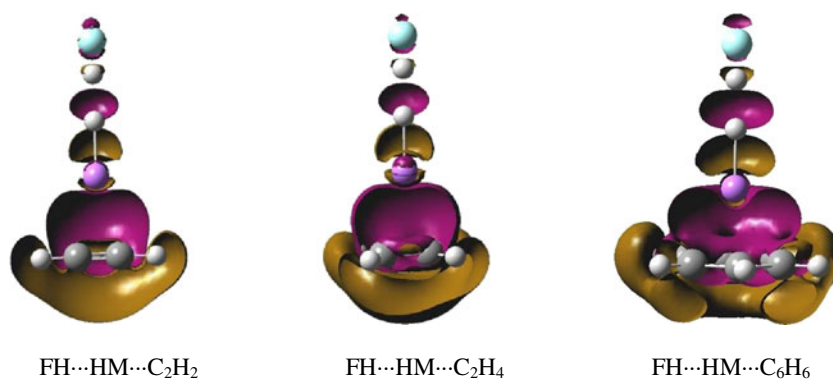
The shifts of electron densities are illustrated in Fig. 3. Purple regions represent the accumulation of additional electron density; yellow regions indicate loss of density.

From Fig. 3, it is apparent by the notable yellow region around the $\text{C}\equiv\text{C}$ bond axis or extending up and down the planes of the benzene-based nucleus and the $\text{C}=\text{C}$ bond that there is much charge loss. This result shows that, due to the fluidity of the π -electron, the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bonds as well as the benzene-based nucleus lose density.

Most important for our present consideration is the $\text{H}\cdots\text{H}$ bond and the region between the M atom and π -electron donor in ternary complex. It is obvious by the large purple region that there is notable charge buildup, indicating that many of the lost densities from the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bonds as well as the benzene-based nucleus are shifted to the $\text{H}\cdots\text{H}$ bond or the region between the M atom and $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_6\text{H}_6$. It is well known that, the more intensive the electron between two atoms, the more chances of overlapping. As a result, both the $\text{H}\cdots\text{H}$ and $\text{H}-\text{M}\cdots\pi$ intermolecular interactions are strengthened upon the formation of the ternary complex, accompanied by the cooperativity effect between them.

Thus, we can draw a conclusion that, upon the ternary-complex formation, many of the lost densities from the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bonds as well as the benzene-based nucleus are shifted to the intermolecular dihydrogen bond and the region between the M atom and π -electron donor, leading to the electron density accumulation in these regions. The increased density simultaneously tends to the enhanced $\text{H}\cdots\text{H}$ and $\text{H}-\text{M}\cdots\pi$ bonds, *i.e.*, the strengthened $\text{H}\cdots\text{H}$ and $\text{H}-\text{M}\cdots\pi$ interactions. This is the origin of the cooperativity effect.

Fig. 3 Shifts of electron density as a result of the formation of the ternary complex at MP2(full)/6-311++G(3df,2p) level



Conclusions

The cooperativity effect between the dihydrogen-bonding and $H-M\cdots\pi$ ($M=Li, Na, K$) interactions is investigated in the binary complex $FH\cdots HM\cdots C_2H_2/C_2H_4/C_6H_6$ by the B3LYP and MP2(full) methods with the 6-311++G(2df,2p) basis set. The equilibrium distances $R_{H\cdots H}$ and $R_{M\cdots\pi}$ in the ternary complex decrease, Mulliken and APT charges of the hydrogen atoms in $H^{\delta+}\cdots\delta^-H$ moiety increase and both the $H\cdots H$ and $H-M\cdots\pi$ interactions are strengthened when compared to the corresponding binary complex. The cooperativity effect of the dihydrogen bond on the $H-M\cdots\pi$ interaction is more pronounced than that of the $M\cdots\pi$ bond on the $H\cdots H$ interaction. The values of cooperativity effect follow the order of $FH\cdots HNa\cdots\pi > FH\cdots HLi\cdots\pi > FH\cdots HK\cdots\pi$ and $FH\cdots HM\cdots C_6H_6 > FH\cdots HM\cdots C_2H_4 > FH\cdots HM\cdots C_2H_2$. The electron densities are shifted to the intermolecular dihydrogen bond and the region between the M atom and π -electron donor upon the ternary-complex formation, leading to the strengthened $H\cdots H$ and $H-M\cdots\pi$ interactions. This is the origin of the cooperativity effect.

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