Theoretical studies on H–M···π (M=H, Li, Na, K) interactions involving the π-electron donors, C₂H₂, C₂H₄ and C₆H₆

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The intermolecular H–M···π (M=H, Li, Na, K) interactions involving the π-electron donors C₂H₂, C₂H₄ and C₆H₆ have been investigated using the DFT-B3LYP, MP2(full) and M06-2X methods with the 6-31+G(3df,2p) basis set. A comparison with the M···π interaction in the corresponding M···π complex has also been carried out. The results show that the H–M···π interaction energies follow the orders: HLi···π > HNa···π > HK···π >> HH···π and HM···C₆H₆ > HM···C₂H₂ ≈ HM···C₂H₄. The H–M···π interaction is stronger than the M···π interaction. The analyses of the natural bond orbital, atoms in molecules and electron density shifts reveal the nature of the H–M···π interactions and explain why C₆H₆ can form stronger complexes with HM. The reduced density gradient analysis indicates that except for the H–Li···π and Li···π interactions, there is no clear distinction of bonding nature between the H–M···π and M···π interactions. In the Li···π complexes, an unusual green RDG isosurface appears above the Li atom, like a “cap” on the Li atom.

Keywords: Theoretical chemistry, Noncovalent interactions, Reduced density gradient, Intermolecular interactions, Electron density

Recently non-covalent interactions have received much attention due to their extremely important role in determining the structures and activities of inorganic, organic, organometallic and biological molecules1–3. Since X (X=F, O, N, etc.) is more electronegative than hydrogen, the X=O–H bonding moiety can as the π electron acceptor and the X–H···π interaction can be established in which the X atom possesses positive charge2–5. It is well known that, in the H₆–M₅+ metal hydride, the metallic atom is usually less electronegative than hydrogen and the M atom possesses positive charge. Then, can the H₆–M₅+ moiety act as the potential π electron acceptor to form the H₆–M₅···π interaction with double or triple bond, aromatic ring?

In fact, the H–M···π interaction has become the subject of some theoretical and experimental investigations for a long time6,7. NMR spectroscopy and density functional theory (DFT) calculations confirmed the H–W···π link in CpW(H)(CO)₃8. The H–Ru···π interaction was observed in CpRuH(CO)(Pcyp) and the dehydrogenation process of RuH₂(η²-H₂)₂(Pcyp)₂ at room temperature9,10. The crystal structures also showed the H–Ru···π contact in the ruthenium complexes with (2-(dimethylamino)ethyl)cyclopentadienyl and (3-(dimethylamino)propyl)cyclopentadienyl11. The H–Li···π type lithium bond in the HLi complex with C₂H₂ or C₂H₄ was proposed theoretically12–14. The mechanisms of H–Li eliminations from alkylolithiums prompted extending work on H–Li addition to carbonyl compounds to the corresponding reactions involving carbon-carbon multiple bonds by experiments15,16. Transition structures of the additions of H–Li to ethylene and acetylene were confirmed and the activation energies were found to be about 7 kcal/mol16. Theoretical calculations by the MP2 method were used to prove the existence of π-systems as sodium bond donors in H–Na···π17. Over the past 30 years, while there has been some investigations on the H–M···π interactions. To the best of our knowledge, the work done to date on the H–M···π systems is rather meager. For example, for those involving alkali metals, no theoretical study on the H–K···π interaction has been presented. Furthermore, although there have been some investigations on the geometry and intermolecular interaction energy, fewer studies focused on the nature of the H–M···π interaction by electron distribution. Although it is expected that the H–M···π interaction in H–M···π complex is stronger than the M···π interaction in the
Our goal is, from the viewpoint of electron interactions involving the \(-\text{CCl}_3\) and \(-\text{CH}_3\) by the RDG analysis. Evidence of C-calix[4]pyrrole−Cl van der Waals forces and steric effects in the approach the one obtained from a fully periodic picture was reliable and of comparable quality to multipolar RDG–NCI (noncovalent interaction) X-ray diffraction data. They demonstrated that the crystalline electron densities obtained from the Saleh space. Contreras-García easy-to-catch pictorial visualization of various kinds novel noncovalent interaction descriptor, leading to an

26 systems were found by the RDG method.

The reduced density gradient (RDG), extending from the density and its first derivative \((s = 1/ (2(3\pi)^{1/3})|\nabla \rho|/\rho^{4/3})\), is a fundamental dimensionless quantity in DFT, used to describe the deviation from a homogeneous electron distribution\(^{18,19}\). It can be used to detect noncovalent interactions in real space based on the electron density.\(^{20}\) When combined with the sign of the second principal local curvature of the electron density, it enables one to distinguish the attractive or repulsive nature of the interaction\(^{21,22}\). Thus, RDG can be used to probe the nature of the H–M···π interaction and clarify the distinction between the H–M···π interaction in the corresponding M···π system due to the more positive charge in the M atom of H–M···π than M···π, one may wonder, from the viewpoint of electron distribution, whether there is fundamental distinction between the H–M···π and M···π interactions.

The reduced density gradient (RDG) analysis is a useful tool for investigating noncovalent interactions in real space. It is based on the reduced density gradient (RDG), which is defined as:

\[
\text{RDG} = \frac{1}{2(3\pi)^{1/3}} \left| \nabla \rho \right| \rho^{-4/3},
\]

where \(\rho\) is the electron density. The RDG is a dimensionless quantity that describes the deviation from a homogeneous electron distribution. A negative RDG indicates an attractive interaction, while a positive RDG indicates a repulsive interaction.

Recently many authors have utilized the RDG method to analyze the noncovalent interactions. Johnson et al.\(^{22}\) introduced the RDG approach as a novel noncovalent interaction descriptor, leading to an easy-to-catch pictorial visualization of various kinds of noncovalent interaction directly in the real space. Contreras-García et al.\(^{23}\) studied the H-bond interaction potentials using the RDG method. The halogen bonds (C–Br···O–P) in large nucleic acid systems were found by the RDG method\(^{24}\).

Saleh et al.\(^{25}\) applied this approach to experimental crystalline electron densities obtained from the multipolar model refinement of charge density quality X-ray diffraction data. They demonstrated that the multipolar RDG–NCI (noncovalent interaction) picture was reliable and of comparable quality to the one obtained from a fully periodic ab initio approach.\(^{26}\) Chen et al.\(^{27}\) determined the long-range van der Waals forces and steric effects in the calix[4]pyrrole–Cl\(^-\) and calix[4]pyrrole–Br\(^-\) systems by the RDG analysis. Evidence of C···O and C···C long-range contacts in the complexes of CO with CH\(_2\)X (X = −NO\(_2\), −CN, −F, −Cl, −Br, −OH, −CF\(_3\), −CCl\(_3\) and −NH\(_3\)) was shown by the RDG approach.\(^{28}\)

Herein the intermolecular H–M···π (M=H, Li, Na, K) interactions involving the π-electron donors C\(_2\)H\(_2\), C\(_3\)H\(_4\) and C\(_4\)H\(_6\) are investigated systematically by using the B3LYP, MP2(full) and M06-2X methods. Our goal is, from the viewpoint of electron distribution, to reveal the nature of the H–M···π interaction and clarify the distinction between the H–M···π interaction in H–M···π complex and the M···π interaction in the corresponding M···π system by using the natural bond orbital (NBO), atoms in molecules (AIM), electron density shifts, and RDG approaches. This investigation will have high significance for the further studies on the structures and properties of the chemical and biochemical systems involving H–M···π interaction in theory and experiment.

**Computational Details**

As a cost-effective approach, in most cases, geometry optimizations by the DFT methodology are feasible and are being applied successfully to investigate the structure of complexes.\(^{30}\) For the complexation energies, the MP2(full) and M06-2X methods are more reliable.\(^{31-33}\) In addition, the high quality basis set is a crucial factor for calculating the property of complex\(^{34}\). Thus, we used the DFT-B3LYP, M06-2X and MP2(full) methods with the 6-311++G(3df,2p) basis set in this work.

All calculations were performed with Gaussian 03 and Gaussian 09 programs.\(^{35}\) All the monomers and the possible T-shaped H–M···π and M···π complexes were fully optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G (3df,2p) basis set. Only eight T-shaped H–M···π and eleven M···π complexes, corresponding to the minimum energy points at the molecular energy hypersurface (Nimag=0), were obtained. The T-shaped structures of HH···C\(_2\)H\(_4\) (Nimag=1), HLi···C\(_2\)H\(_2\) (Nimag=1), HK···C\(_2\)H\(_2\) (Nimag=2) and HK···C\(_2\)H\(_4\) (Nimag=2) corresponded to the first and second order saddle points, respectively. Then, these four structures were reoptimized by relaxing symmetry. However, for HH···C\(_2\)H\(_4\) and HLi···C\(_2\)H\(_2\), it was still difficult to find local minima at the B3LYP/6-311++G (3df,2p), MP2/6-311++G(3df,2p) or M06-2X/6-311++G (3df,2p) level of theory, perhaps due to the flat potential wells (see Supplementary Data, Figs S1 and S2). Fortunately, the stable HK···C\(_2\)H\(_2\) (C\(_i\)) and HK···C\(_2\)H\(_4\) (C\(_i\)) complexes were obtained with Nimag = 0 at the B3LYP/6-311++G(3df,2p) and MP2/6-311++G(3df,2p) levels.

For HK···C\(_2\)H\(_2\), HK···C\(_2\)H\(_4\) and the eight T-shaped H–M···π complexes, single point energy calculations were carried out at the B3LYP/6-311++G(3df,2p), MP2(full)/6-311++G(3df,2p) and M06-2X/6-311++G (3df,2p) levels of theory. The shifts of the electron
density$^{36}$ that accompany the formation of complexes were analyzed at the MP2(full)/6-311++G(3df,2p) level, and the topological charge density was displayed by the AIM (Atom in Molecules) method$^{37}$ using AIMPAC program$^{38}$ at the same level. The natural bonding analysis$^{39}$ was also carried out using the MP2(full)/6-311++G(3df,2p) method. The RDGs were calculated and plotted by the Multiwfn 2.6 suite$^{40}$ and VMD programs$^{41}$.

The interaction energy ($E_{\text{int}}$) was calculated by evaluating the difference between the total energies of complex and individual monomers as follows:

$$E_{\text{int}}(H-M-H) = E_{\text{HMC}} - E_{\text{HM}} - E_{\text{CHI}}$$

$E_{\text{int}}(H-M-H)$ was corrected with the basis set superposition error (BSSE)$^{42,43}$.

**Results and Discussion**

For HK···C$_2$H$_2$, the AIM results show there is a bond path contacting the K atom with one of the carbon atoms accompanied by a bond critical point, indicating that the K atom binds electrostatically to negative carbon. Another bond path linking the H atom of HK with one of the C$_2$H$_2$ hydrogen is found. The distance between these two hydrogen atoms is 2.083 Å, and the APT charges are –0.740 and 0.335 e at the B3LYP/6-311++G(3df,2p) level, respectively, showing the dihydrogen bond in HK···C$_2$H$_2$. However, there is no bond path linking the K atom with the midpoint of the C=C bond, suggesting that there is no obvious H···K$^-$ interaction. The large distance between the K atom and the midpoint of the C=C bond (3.451 Å) also indicates that the H···K$^-$ interaction may be not formed (see Supplementary Data, Fig. S3). Therefore, HK···C$_2$H$_2$ is not considered, and only nine complexes, i.e., HK···C$_2$H$_4$ and eight T-shaped systems, are present in the following discussion.

**Geometry and stability**

In the T-shaped HM complex with C$_2$H$_2$, C$_2$H$_4$ or C$_6$H$_6$, the H···M bond lies perpendicular to the C=C or C=C bond or the C$_2$H$_4$ ring plane, and points toward to bond midpoint or ring center with C$_2$ or $C_6$ symmetry (Fig. 1). As mentioned above, HK···C$_2$H$_4$ is $C_1$ symmetry. As can be seen from Fig. 1, in the H···H complexes with C$_2$H$_2$ and C$_6$H$_6$, the H···H distances are large (both 3.205 Å at the MP2(full)/6-311++G(3df,2p) level). Furthermore, the H1···H2 bond lengths are close to that in the isolated H$_2$ molecule (0.737 Å). Therefore, the H···H$^-$ interaction may be weak.

In the HLi systems with C$_2$H$_4$ and C$_6$H$_6$, the Li···π distance is 2.379 and 2.012 Å respectively at the MP2(full)/6-311++G(3df,2p) level. The bond lengths of the H···Li bond increase as compared with that in the isolated HLi molecule (1.595 Å), suggesting the formation of intermolecular H···π interaction. Szczędziak et al.$^{12}$ found that the Li···π distance in HLi···C$_2$H$_4$ was 2.50 Å at the SCF double-zeta plus polarization level. Houk et al.$^{16}$ obtained the Li···π distance with 2.44 Å in HLi···C$_2$H$_4$ at the MP2/6-31G* level. Comparing these results mentioned above with the data shown in Fig. 1, it can be seen that our calculations are reliable. At the MP2(full)/6-311++G(3df,2p) level, the Na···π distances in three HNa···π complexes are in the range of 2.542–2.765 Å, which are close to the values at the MP2/6-311+G(d,p) level (2.636–2.868 Å).$^{17}$ In two HK···π systems, the K···π distances are ~3.0 Å at the MP2(full)/6-311++G(3df,2p) level. Similar to the HLi···π complexes, the bond lengths of the H···Na and H···K bonds increase in the complexes in comparison with those in the corresponding isolated molecules (1.892 and 2.237 Å, respectively). These results suggest the formation of intermolecular H···Na···π and H···K···π interactions.

As can be seen from Fig. 1, the M···π distance follows the order: HLi···π < HNa···π < HK···π and HM···C$_2$H$_4$ < HM···C$_2$H$_6$ < HM···C$_6$H$_6$. This result suggests that the H···M···π interactions may follow the order: HLi···π > HNa···π > HK···π and HM···C$_2$H$_4$ > HM···C$_2$H$_6$ > HM···C$_6$H$_6$.

Table 1 gives both uncorrected and corrected H···M···π binding energies after correction for BSSE. The values calculated using the B3LYP method are all lower than those obtained by the MP2(full) and M06-2X methods. Note that dispersion interaction is not accounted using the B3LYP method but is considered by the MP2 and M06-2X methods. Thus, the MP2(full) and M06-2X methods are more realistic to explain the trends in the calculated H···M···π interactions rather than the B3LYP method. For the H···M···π binding energies at the MP2(full)/6-311++G(3df,2p) and M06-2X/6-311++G(3df,2p) levels, the maxima of relative deviation (($E_{\text{int}, \text{MP2(full)}} - E_{\text{int}, \text{MP2(full)}})/E_{\text{int}, \text{MP2(full)}}$) is 13.0%, which indicates the MP2(full)/6-311++G(3df,2p) method used for the binding energies to be reliable.

From Table 1, the H···H$^-$ interaction energy is only ~1.23 and ~4.08 kJ/mol in HH···C$_2$H$_4$ and HH···C$_6$H$_6$ at the MP2(full)/6-311++G(3df,2p) level, respectively. The H···M···π (M=Li, Na, K)
Fig. 1 – The optimized geometries and AIM results of the H–M···π complexes at the MP2(full)/6-311++G(3df,2p) level.

Table 1 – Intermolecular H–M···π (M=Li, Na, K) interaction energies ($E_{\text{int}}$ (kJ/mol)), selected frequency shifts relative to the monomers in the complexes and the corresponding IR intensities, the second-order perturbation energies $E^{(2)}$, natural charges ($Q_{\text{HM(nat.)}}$), Mulliken charges ($Q_{\text{HM(mul.)}}$) and APT charges ($Q_{\text{HM(APT)}}$) of HM in their complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{int}}$ (B3LYP)</th>
<th>$E_{\text{int}}$ (MP2(full))</th>
<th>$E_{\text{int}}$ (M06-2X)</th>
<th>$\nu_{M \cdots \pi}$</th>
<th>$\Delta \nu_{H-M}$</th>
<th>$E^{(2)}$</th>
<th>$Q_{\text{HM(nat.)}}$</th>
<th>$Q_{\text{HM(mul.)}}$</th>
<th>$Q_{\text{HM(APT)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH···C$_2$H$_2$</td>
<td>-0.08 (-0.05)</td>
<td>-1.23 (-0.83)</td>
<td>-1.39 (-1.02)</td>
<td>202</td>
<td>-15</td>
<td>4.24</td>
<td>-0.001</td>
<td>-0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>HH···C$_6$H$_6$</td>
<td>0.00 (0.17)</td>
<td>-4.08 (-1.81)</td>
<td>-4.42 (-3.27)</td>
<td>195</td>
<td>-35</td>
<td>1.63</td>
<td>-0.002</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>HLi···C$_2$H$_4$</td>
<td>-38.37 (-35.67)</td>
<td>-39.81 (-34.60)</td>
<td>-37.80 (-33.22)</td>
<td>243</td>
<td>-49</td>
<td>49.22</td>
<td>-0.050</td>
<td>-0.002</td>
<td>-0.092</td>
</tr>
<tr>
<td>HLi···C$_6$H$_6$</td>
<td>-53.93 (-48.68)</td>
<td>-69.36 (-54.07)</td>
<td>-73.53 (-63.26)</td>
<td>255</td>
<td>-79</td>
<td>49.12</td>
<td>-0.674</td>
<td>0.046</td>
<td>-0.156</td>
</tr>
<tr>
<td>HNa···C$_2$H$_4$</td>
<td>-22.17 (-19.04)</td>
<td>-26.37 (-20.20)</td>
<td>-28.62 (-22.51)</td>
<td>143</td>
<td>-17</td>
<td>38.56</td>
<td>-0.019</td>
<td>-0.006</td>
<td>-0.024</td>
</tr>
<tr>
<td>HNa···C$_6$H$_6$</td>
<td>-21.75 (-18.28)</td>
<td>-27.00 (-20.33)</td>
<td>-30.54 (-26.88)</td>
<td>139</td>
<td>-19</td>
<td>38.56</td>
<td>-0.031</td>
<td>-0.045</td>
<td>-0.034</td>
</tr>
<tr>
<td>HK···C$_2$H$_4$</td>
<td>-32.97 (-28.03)</td>
<td>-50.25 (-34.73)</td>
<td>-55.89 (-47.28)</td>
<td>146</td>
<td>-32</td>
<td>47.28</td>
<td>-0.784</td>
<td>0.058</td>
<td>-0.061</td>
</tr>
<tr>
<td>HK···C$_6$H$_6$</td>
<td>-11.67 (-11.00)</td>
<td>-18.35 (-14.34)</td>
<td>-16.09 (-11.88)</td>
<td>115</td>
<td>-35</td>
<td>44.12</td>
<td>-0.012</td>
<td>-0.001</td>
<td>-0.011</td>
</tr>
<tr>
<td>HK···C$_2$H$_2$</td>
<td>-21.82 (-18.88)</td>
<td>-39.89 (-30.49)</td>
<td>-42.35 (-36.37)</td>
<td>111</td>
<td>-45</td>
<td>61.86</td>
<td>-0.855</td>
<td>0.062</td>
<td>-0.024</td>
</tr>
</tbody>
</table>

The interaction energies in parenthesis are corrected by the BSSE method. The frequency shift, $E^{(2)}$, $Q_{\text{HM(nat.)}}$ and $Q_{\text{HM(mul.)}}$ are obtained from the MP2(full)/6-311++G(3df,2p) method, while $Q_{\text{HM(APT)}}$ is at the B3LYP/6-311++G(3df,2p) level.

$^b_{\nu_{M \cdots \pi}}$ is 0, 227, 303 and 532 km/mol for the isolated H–H, H–Li, H–Na and H–K molecules, respectively.

$^a$For the complexes with C$_2$H$_2$, it is $E^{(2)}$, $Q_{\text{HM(nat.)}}$ and $Q_{\text{HM(mul.)}}$.

$^d$The interaction energies are corrected by the BSSE method. The frequency shift, $E^{(2)}$, $Q_{\text{HM(nat.)}}$ and $Q_{\text{HM(mul.)}}$ are obtained from the MP2(full)/6-311++G(3df,2p) method, while $Q_{\text{HM(APT)}}$ is at the B3LYP/6-311++G(3df,2p) level.

$^e$For the complexes with C$_6$H$_6$, it is $E^{(2)}$, $Q_{\text{HM(nat.)}}$ and $Q_{\text{HM(mul.)}}$.
interaction energies are within the range of –18.35 to –69.36 kJ/mol. Alikhani et al. found that, in the C\textsubscript{6}H\textsubscript{4} complexes with Li, Na and K, the M··π interaction energy was 12.18 (CCSD/6-311G(d,p)), 87.07 (CCSD/6-311G(2d,2p)) and –1.68 kJ/mol (CCSD/Lanl2DZ), respectively. It is repulsive (positive) in Li··C\textsubscript{6}H\textsubscript{4} and Na··C\textsubscript{6}H\textsubscript{4}, and only a small negative value in K··C\textsubscript{6}H\textsubscript{4}.

We also obtained the binding energy as –41.02 (CCSD/6-311G(d,p)), –24.55 (CCSD/6-311G(2d,2p)) and –19.21 kJ/mol (CCSD/Lanl2DZ) for the C\textsubscript{6}H\textsubscript{4} complexes with H–Li, H–Na and H–K, respectively. For Na··C\textsubscript{6}H\textsubscript{4} and the C\textsubscript{6}H\textsubscript{4} complexes with Li, Na and K, the M··π interaction energies are no more than –10.00 kJ/mol at the MP2(full)/6-311++G(3df,2p) level. These results show that the H–M··π interaction in the H–M··π complex is stronger than the M··π interaction in the corresponding M··π system. Note that the M atom in the H–M··π complex possesses obvious positive charge. For instance, the Mulliken charge of the K atom in HK··C\textsubscript{6}H\textsubscript{4} is 0.593 e at MP2(full)/6-311++G(3df,2p) level.

For the H–M··π (M=Li, Na, K) systems, the proportion of corrected interaction energies to their total binding energies, (defined as \[\frac{|E_{\text{int}}(H\cdot\cdot M)-E_{\text{int}}(H\cdot\cdot M-\text{BSSE})|}{E_{\text{int}}(H\cdot\cdot M-\text{BSSE})}\]), is 15.95%, 30.89% and 26.17% at the B3LYP/6-311++G(3df,2p), MP2(full)/6-311++G(3df,2p) and M06-2X/6-311++G(3df,2p) levels, respectively. The large proportion indicates that it is necessary for the H–M··π interaction energies to be checked for the BSSE corrections. In general, the BSSE corrections are not negligible. Only in the case of complete basis set, the correction for BSSE not needed. In this case, the proportion is generally no more than 10.0%.

The H–H··π interaction energies follow the order: HH··C\textsubscript{6}H\textsubscript{4} > HH··C\textsubscript{2}H\textsubscript{2} at three levels of theory. The H–M··π (M=Li, Na, K) interaction energies obtained at three levels are in the same order: HLi··π > HNa··π > HK··π ≈ HH··π and HM··C\textsubscript{6}H\textsubscript{4} > HM··C\textsubscript{2}H\textsubscript{2} ≈ HM··C\textsubscript{2}H\textsubscript{4} (see Table 1). These results are almost in accordance with the increase of the M··π distances upon the formation of complexes.

In the H–H··π complexes with C\textsubscript{2}H\textsubscript{2} and C\textsubscript{6}H\textsubscript{4}, the frequencies of the stretching of the H–H··π bonds (\(v_{\text{H–H}}\)) are found to be 202 and 195 cm\textsuperscript{-1} respectively at the MP2(full)/6-311++G(3df,2p) level (see Table 1). For the H–M··π (M=Li, Na, K) complexes, the frequencies of the stretching of the M··π bonds (\(v_{\text{M–π}}\)) are predicted to be 243, 255, 143, 139, 146, 115 and 111 cm\textsuperscript{-1} respectively at the MP2(full)/6-311++G(3df,2p) level. Except for HLi··C\textsubscript{6}H\textsubscript{4}, the values of the frequencies follow the order: HLi··π > HNa··π > HK··π and HM··C\textsubscript{6}H\textsubscript{4} > HM··C\textsubscript{2}H\textsubscript{2} > HM··C\textsubscript{2}H\textsubscript{4}, which is almost in accordance with that of the interaction energies.

The larger the frequency shift (\(\Delta \nu=\!\nu_{\text{complex}}\!–\!\nu_{\text{monomer}}\!\)), the more stable is the complex. Thence the frequency shift of the H–M bond was studied at the MP2(full)/6-311++G(3df,2p) level in order to investigate the relative stability of the complex. \(\nu_{\text{H–M}}\) can be approximately described as the stretching of H–M. It can be seen from Table 1, the \(\nu_{\text{H–M}}\) decreased (red shifts) and the IR intensity increased greatly as compared with those in the isolated monomers, confirming the formation of the H–M··π interaction. For the H–M··π (M=Li, Na, K) complexes, the values of the frequency shifts of \(\nu_{\text{H–M}}\) follow the order: HLi··π > HNa··π > HK··π and HM··C\textsubscript{6}H\textsubscript{4} > HM··C\textsubscript{2}H\textsubscript{2} > HM··C\textsubscript{2}H\textsubscript{4}. This result suggests that the stabilities of the complexes follow the order: HLi··π > HNa··π > HK··π and HM··C\textsubscript{6}H\textsubscript{4} > HM··C\textsubscript{2}H\textsubscript{2} > HM··C\textsubscript{2}H\textsubscript{4}, which are almost consistent with that of the interaction energies. In the H–H··π complexes, \(\Delta \nu_{\text{H–M}}\) in HH··C\textsubscript{6}H\textsubscript{4} is larger than that in HH··C\textsubscript{2}H\textsubscript{2}, indicating that the H–H··π interaction in the former is stronger than that in the latter, which is also in accordance with the result of interaction energy.

**NBO, charge and electron density shifts**

To clarify the nature of complexation, NBO analysis was carried out at the MP2(full)/6-311++G(3df,2p) level (see Table 1). According to the NBO analysis, all the H–M··π complexes have two units, in agreement with the character of the intermolecular interaction systems. Delocalization effects between these two units can be identified from the presence of off-diagonal elements of the Fock matrix in the NBO basis, and the strengths of these delocalization interactions, \(E^{(2)}\), can be estimated by second-order perturbation theory.

For the H–H··π complexes, the major electronic delocalization interaction between donor and acceptor corresponds to the C3=C4 or C3=C4 bond which offers the π-electrons of carbon atoms to the contacting σ(H–H) antibonding orbital of H\textsubscript{2} (i.e., \(E^{(2)}_{\pi(C\equiv C)=\pi(C\equiv C)\!–\!\sigma(H\!–\!H)^\!*}\)). However, in each of the H–M··π (M = Li, Na, K) complexes, \(E^{(2)}_{\pi(C\equiv C)=\pi(C\equiv C)\!–\!\pi(M\!–\!M)^*}\) shows that the major electronic delocalization interaction corresponds to that of...
C3=C4 or C3≡C4 bond offers the π-electrons of the carbon atoms to the contacting LP$_{m_0}^*$ antibonding orbital. This is the nature of the intermolecular H–H⋯π or H–M⋯π interaction. The values of $E^{(2)}$ follow the order: HLi⋯π > HNa⋯π > HK⋯π and HM⋯C$_6$H$_6$ > HM⋯C$_2$H$_4$ > HM⋯C$_2$H$_2$. These orders are also consistent with those of the interaction energies.

The net charge transfer is evaluated to be from π-electron donors to HM (M=Li, Na, K) by 0.050, 0.674, 0.019, 0.031, 0.784, 0.012 and 0.855 e, respectively. The values of the net charge transfer follow the order: HLi⋯π > HNa⋯π > HK⋯π and HM⋯C$_6$H$_6$ > HM⋯C$_2$H$_4$ > HM⋯C$_2$H$_2$, which is consistent with that of the interaction energies. For the H–H⋯π complexes, the net charge transfer is close to zero, suggesting that the H–H⋯π interactions are very weak, as is in accordance with the interaction energies.

Mulliken and APT charges of HM are listed in Table 1. The APT charges are negative in all the H–M⋯π (M=Li, Na, K) complexes, showing that HM obtains electron from the π-electron donors. Furthermore, the values of the APT charge follow the order: HLi⋯π > HNa⋯π > HK⋯π and HM⋯C$_6$H$_6$ > HM⋯C$_2$H$_4$ > HM⋯C$_2$H$_2$, which are also consistent with those of the interaction energies at the MP2(full)/6-311++G(3df,2p) and M06-2X/6-311++G (3df,2p) levels. For the H–H⋯π complexes, Mulliken and APT charges of HM are close to zero, also suggesting weak H⋯π interaction.

To clarify further the nature of the T-shaped H–M⋯π interaction in detail, analysis of the electron density shifts that accompany the formation of the H–M⋯π complexes was carried out. The shifts of electron densities are illustrated in Fig. 2. Purple regions represent the accumulation of additional electron density as a result of the mutual approach of the two molecules, while yellow regions indicate loss of density.

In the H–H⋯π complexes, no obvious purple region between the H2 atom and π-electron donor is found, showing the very weak H–H⋯π interaction (Fig. 2). This result is in accordance with the analyses of structures and binding energies. For the H–M⋯π (M=Li, Na, K) complexes, an obvious effect of the H–M⋯π interaction formation is shown by the yellow region around the H–M bond.
axis, indicating that the H–M bond loses density. The loss of the electron density weakens the H–M bond, leading to this bond elongation and the decrease of strength, in agreement with the structure.

It is apparent by the notable yellow region around the C=C bond axis, extending up and down the planes of the benzene-based nucleus and C=C bond that there is large charge loss. This result shows that due to the fluidity of the \( \pi \)-electron, the C=C and C=C bonds as well as the benzene-based nucleus lose density.

Most important for our present consideration is the region between the M atom and p-electron donor. It is obvious by the large purple region that there is notable charge buildup, indicating that many of the lost densities from the C=C and C=C bonds as well as the benzene-based nucleus are shifted to the regions between the M atom and p-system. These electron density shifts lead to the electron density accumulation in these regions. The increased density simultaneously tends towards the formation of the H–M\( \cdots \pi \) interactions. The shifts of electron density in the region between the M atom and p-electron donor C\(_6\)H\(_6\) are more notable than those in the region between the M atom and C\(_2\)H\(_2\) or C\(_3\)H\(_4\).

It is well-known that the \( \pi \)-electrons in benzene are part of aromatic sextet and are naturally difficult to disturb/donate. However, the values of \( \rho(C) \) NBO net charge transfers, and APT charges of HM in HMM\( \cdots \pi \)C\(_6\)H\(_6\) are far larger than those in HMM\( \cdots \pi \)C\(_2\)H\(_2\) or HMM\( \cdots \pi \)C\(_3\)H\(_4\). Furthermore, the shifts of electron density in the region between the M atom C\(_6\)H\(_6\) are more notable than those in the region between the M atom and C\(_2\)H\(_2\) or C\(_3\)H\(_4\). This is perhaps the reason why C\(_6\)H\(_6\) can form stronger complexes than C\(_2\)H\(_2\) or C\(_3\)H\(_4\) with HM.

**AIM and RDG analysis**

As proposed by Bader,\(^{37}\) electron density \( \rho \) at bond saddle point indicates the bond strength. The larger the \( \rho \), the stronger is the interaction. Laplacian term \( \nabla^2 \rho \) of the bond saddle point can reveal the nature of interaction. \( \nabla^2 \rho > 0 \) indicates loose charge density at the critical point.

According to the AIM results, in each of the complexes HMM\( \cdots \pi \)C\(_2\)H\(_2\)/C\(_3\)H\(_4\) (M=H, Li, Na, K), there is a bond path linking the M atom with the midpoint of the C=C or C=C bond, accompanied by a ring critical point (RCP) (3, +1) (see Fig. 1). The complexes HMM\( \cdots \pi \)C\(_6\)H\(_6\) (M=H, Li, Na, K) are characterized by the presence of the (3, +3) cage critical point (CCP). For the HMM\( \cdots \pi \) (M=Li, Na, K) complexes, the electron densities \( \rho_{RCP} \) and \( \rho_{CCP} \) are within the range of 0.0086–0.0144 a.u. and 0.0063–0.0102 a.u., respectively. Moreover, their Laplacians \( \nabla^2 \rho_{RCP} \) and \( \nabla^2 \rho_{CCP} \) are all positive, suggesting the typical closed-shell kind of interactions. Thus, the H–M\( \cdots \pi \) (M=Li, Na, K) interactions are confirmed, in good agreement with the structures and energies. Furthermore, the values of the electron densities follow the order: HLLi\( \cdots \pi \) > HNa\( \cdots \pi \) > HK\( \cdots \pi \), which is also consistent with the order of the interaction energies. In the H–H\( \cdots \pi \) complexes, the electron densities \( \rho_{RCP} \) and \( \rho_{CCP} \) are close to 0.004 a.u., which is near the lower limit of the commonly accepted values for the H–H\( \cdots \pi \) interactions (0.002–0.04 a.u.)\(^{36}\), suggesting very weak interaction. This result is in agreement with the above analyses.

The bond path analysis in AIM is often limited to a very localized and possibly discontinuous description, while the RDG index is able to depict inherently delocalized interactions in terms of extended and flat RDG isosurfaces.\(^{27}\) Therefore, in order to reveal further the nature of the H–M\( \cdots \pi \) interaction and clarify the distinction between the H–M\( \cdots \pi \) interaction in the H–M\( \cdots \pi \) complex and the M\( \cdots \pi \) interaction in the corresponding M\( \cdots \pi \) system, the RDG analysis was carried out.

In Figs 3 and 4, we present the plots of RDG versus \( \rho(r) \) oriented by the sign of the second eigenvalue (\( \lambda_2 \)) for the H–M\( \cdots \pi \) complexes and M\( \cdots \pi \) systems, respectively. According to Johnson et al.\(^{20}\), the sign of \( \lambda_2 \) can be used to distinguish the bonded \( (\lambda_2 < 0) \) from non-bonded \( (\lambda_2 > 0) \) interactions. The spikes in the plots can be classified to three types, i.e. (i) large, negative values of sign \( (\lambda_2)\rho \) indicative of attractive interactions, such as dipole dipole or H-bonding, (ii) large and positive sign \( (\lambda_2)\rho \) indicating the nonbonding interaction, such as strong repulsion or steric effect in ring/cage, and, (iii) values near zero indicating very weak interactions. In Figs 3 and 4, except for the C\(_6\)H\(_6\) complexes, the spikes or troughs are not obvious although a few lines are shown. This is perhaps due to the electron-deficient nature of the H, Li, Na and K atoms.

The plots of RDG versus sign(\( \lambda_2 \)) in HH\( \cdots \Pi \)C\(_2\)H\(_2\)/C\(_3\)H\(_4\) are not obviously different in the quantity and shape of lines from those in H\( \cdots \Pi \)C\(_2\)H\(_2)/C\(_3\)H\(_6\) (Figs 3 and 4). In each of the complexes HH\( \cdots \Pi \)C\(_2\)H\(_2\) and H\( \cdots \Pi \)C\(_3\)H\(_2\), two lines are found in the low density and low gradient region,
Fig. 3 – Plots of the RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue ($\lambda_2$) and RDG isosurface ($s = 0.5$) for the H–M···π complexes at the MP2(full)/6-311++G(3df,2p) level. [The surfaces are colored on a blue-green-red scale according to values of sign ($\lambda_2$) (a.u.) ranging from −0.05 to 0.05 a.u.].
Fig. 4 – Plots of the RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue ($\lambda_2$) and RDG isosurface ($s = 0.5$) for the M···$\pi$ complexes at the MP2(full)/6-311++G(3df,2p) level. [The surfaces are colored on a blue-green-red scale according to values of sign ($\lambda_2$) (a.u.) ranging from −0.05 to 0.05 a.u.].
with one long line at negative sign($\lambda$) corresponding to an attractive H--H···π or H···π interaction, and one short line at positive sign($\lambda$) corresponding to a poor repulsive interaction. The only distinction arises in the ($\lambda$) value of the long line. The value in HH···C₂H₆ is more negative than that in H···C₂H₆. The Hohenberg–Kohn theorem dictates that same density characteristics point to the same type of interaction, only difference being in strength. Therefore, there may be no fundamental distinction between the H--H···π interaction in HH···C₂H₆ and the H···π interaction in H···C₂H₆, with the former being stronger than the latter. Similar to HH···C₂H₆ and H···C₂H₆, two lines are also obtained in the low density and low gradient region in HH···C₆H₆ or H···C₆H₆, corresponding to an attractive H--H···π or H···π interaction and a poor repulsive interaction. In addition, plots of RDG versus sign($\lambda$) for HH···C₆H₆ or H···C₆H₆ exhibit a new feature, viz., one spike in the low-density (0.020–0.025 a.u.) and low-gradient region, which is signature of the steric effect in benzene ring.

The gradient isosurfaces provide a rich visualization of noncovalent interactions as broad regions of real space. There is no obvious distinction between the gradient isosurfaces of HH···C₆H₆ and H···C₆H₆ (Figs 3 and 4). The green isosurface lies between the hydrogen atom and π-system, characteristic of the H--H···π or H···π interaction. The red isosurface at the center of benzene shows the steric effect, i.e., the nonbonded overlap located at the center of the ring.

For HLi···C₂H₆ or HLI···C₆H₆, in the low density and low gradient region, there are always two peaks formed by two or more lines at negative sign($\lambda$) with the density values of about −0.045 to −0.040 a.u. and −0.020 to −0.015 a.u., respectively. These peaks correspond to the H–Li covalent bond and the attractive Li···π interactions, respectively. In Li···C₂H₆/C₆H₆, only one peak is found at negative sign($\lambda$) in the low density and low gradient region. The very small negative sign($\lambda$) suggests a very weak interaction in both Li···C₂H₆ and Li···C₆H₆.

Although the plots of RDG versus sign($\lambda$) in HLI···C₂H₆/C₆H₆ are not obviously different from those in Li···C₂H₆/C₆H₆, the obvious distinction between the two can be found in the gradient isosurface. For HLI···C₂H₆/C₆H₆, the blue isosurface around the Li–H bond and the green isosurface between the Li atom and π-system are characteristic of the Li–H covalent bond and H–Li···π interaction, respectively. For Li···C₂H₆/C₆H₆, the green isosurface between the Li atom and C₂H₆/C₆H₆ is also seen, indicating the Li···π interaction. However, a noticeable and unusual green isosurface appears above the Li atom, like a “cap” on the Li atom (see Fig. 4).

In H–Na···C₂H₆/C₆H₆ and H–K···C₂H₆/C₆H₆, the plots of RDG versus sign($\lambda$) are not obviously different in shape from those in the corresponding Na and K systems. For example, in H–Na···C₂H₆, one area (formed by about two lines) with the density value of about −0.010 a.u. with low gradient region corresponds to the H–Na···π interaction, and in Na···C₂H₆, the Na···π interaction is also confirmed by the area formed by several lines in the density value of about −0.002 a.u. with low gradient region. It may be noted that in H–Na···C₂H₆/C₆H₆ or H–K···C₂H₆/C₆H₆, although there is another area found in the low density and low gradient region, it corresponds the H–Na/K covalent bond. These results are also arrived at from the isosurfaces. Therefore, similar to HH···C₂H₆/C₆H₆ and H···C₂H₆/C₆H₆, there is no fundamental distinction between the H–Na/K···π interaction in the H–Na/K···π complex and the Na/K···π interaction in the corresponding Na/K···π system.

As can be seen from Fig. 3, the green isosurface in the region between the M atom and π-electron donor C₆H₆ are more noticeable than that in the region between the M atom and C₂H₆ or C₆H₆. This result also suggests that the intermolecular interactions in H–M···C₆H₆ are stronger than those in the C₂H₆ or C₂H₆ systems with H–M.

**Conclusions**

The intermolecular H–M···π (M=H, Li, Na, K) interactions involving the π-electron donors C₂H₆, C₆H₆ and C₆H₆ were investigated using the DFT-B3LYP, MP2(full) and M06-2X methods. A comparison with the M···π interaction in the corresponding M···π complex was also carried out. The result shows that the H–H···π interaction is weak. For the H–M···π (M=Li, Na, K) systems, the H–M···π interaction energies follow the order: HLi···π > HNa···π > HK···π and HM···C₆H₆ > HM···C₂H₆ ≈ HM···C₆H₆. The H–M···π interaction in the H–M···π complex is stronger than the M···π interaction in the corresponding M···π system. For the H–M···π (M=Li, Na, K) complexes, many of the lost densities from the C≡C and C=C bonds as well as the benzene-based nucleus are shifted to the region between the M atom and C₂H₆/C₆H₆/C₆H₆, leading to electron
density accumulation and the formation of the 
H–M⋯π interactions.

Except for the H–Li⋯π and Li⋯π interactions, there is no clear distinction of bonding nature between the H–M⋯π and M⋯π interactions. In the Li⋯π complexes, a noticeable and unusual green isosurface appears above the Li atom, like a “cap” on the Li atom. For the H–H⋯π complexes, the major electronic delocalization interaction corresponds to the C3=C4 or C3=C4 bond which offers the π-electrons of carbon atoms to the contacting σ(H–H)* antibonding orbital of H2. However, in each of the H–M⋯π (M=Li, Na, K) complexes, the major electronic delocalization interaction corresponds to the C3=C4 or C3=C4 bond which offers the π-electrons of the carbon atoms to the contacting LP(M)∗ antibonding orbital.

The values of $E^{(2)}$, NBO net charge transfers, and APT charges of HM in H⋯C2H6 are much larger than those in HM⋯C2H2 or H⋯C2H4. Furthermore, the shifts of electron density in the region between the M atom and C6H6 are more noticeable than that in the region between the M atom and C2H2 or C2H4. This is perhaps the reason why C6H6 can form stronger complexes than C2H2 or C2H4 with HM.

Supplementary data

Supplementary data associated with this article, viz., Figs S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(06) 709-719_SupplData.pdf.

References