

## Theoretical characterization of single-electron iodine-bond weak interactions in $\text{CH}_3\cdots\text{I}-\text{Y}$ ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{C}_2\text{H}, \text{CN}, \text{NC}$ ) systems

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Iodine-involved single-electron halogen bonds (SEXBs) weak interactions in the systems of  $\text{CH}_3\cdots\text{I}-\text{Y}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CH}, \text{CN}, \text{NC}$ ) were investigated for the first time using B3LYP/6-311++G(d,p) and MP2/aug-cc-pVTZ computational levels (the relativistic effective core potential basis set of LanL2dz was used on iodine atom). The interaction energies between two moieties with basis set super-position error corrections for the seven complexes are  $-0.57, -1.36, -3.80, -2.17, -4.49, -6.33$  and  $-8.64$   $\text{kJ mol}^{-1}$  (MP2/aug-cc-pVTZ), respectively, which shows that SEXBs interactions are all weak. Natural bond orbital theory analysis revealed that charges flow from  $\text{CH}_3$  to the  $\text{I}-\text{Y}$  moiety. The total amount of natural bond orbital charge transfer ( $A_{\text{NC}}$ ) from the  $\text{CH}_3$  radical to  $\text{I}-\text{Y}$  increases in the order  $\text{CH}_3\cdots\text{IBH}_2 < \text{CH}_3\cdots\text{IH} \approx \text{CH}_3\cdots\text{ICH}_3 \approx \text{CH}_3\cdots\text{IC}_2\text{H}_3 < \text{CH}_3\cdots\text{ICCH} < \text{CH}_3\cdots\text{ICN} < \text{CH}_3\cdots\text{INC}$ . Atoms-in-molecules theory was used to investigate the topological properties of the bond critical points in the seven SEXB structures.

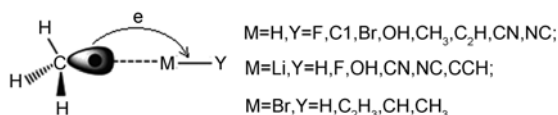
### $\text{CH}_3$ radical, single-electron iodine-bond, natural bond orbital analysis, electron density topological property

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Noncovalent weak interactions have important roles in the field of molecule recognition, in biological systems, and in materials science. These interactions have captured the interest of chemists for a long time, and studies of their theories and experiments have been well reported [1]. It has been found that many physical and chemical phenomena are closely related to intermolecular noncovalent weak interactions including dihydrogen bonds [2],  $\pi$ -cation interactions [3], halogen bonds (XB) [4], lithium bonds [5]. Recently, single-electron noncovalent bonds have been the most extensively studied noncovalent interaction [6–9]. Most published work is on single-electron noncovalent bonds of the type  $\text{CH}_3\cdots\text{M}-\text{Y}$  ( $\text{M} = \text{H}, \text{Li}, \text{F}, \text{Cl}$  or  $\text{Br}$ ), in which the

single electron of the  $\text{CH}_3$  radical, acting as the electron donor (but the halogen bond acceptor), interacts with the  $\text{M}-\text{Y}$  moiety, acting as the electron acceptor (but the halogen bond donor), as shown in Figure 1. The single-electron halogen-bond (SEXB) interaction is one of these single-electron noncovalent interactions. However, only the single-electron bromine-bond has been studied [10–12], and neither experimental nor theoretical studies of the other SEXBs involving iodine have been reported. It is known that the iodine atom has more polarity and distortion than bromine atom. Thus iodine would be more suitable than bromine atom as an electron acceptor in SEXB systems. Based on these ideas, we are interested in whether there are any iodine-involved SEXB interactions, and how the interactions take place. We consider a particular set of molecules

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**Figure 1** The representation of single-electron noncovalent bond between CH<sub>3</sub> radical and M—Y.

formed by a “donor” (CH<sub>3</sub> radical) and “acceptors” of electrons, as shown in Figure 2, where the iodine atoms in I—Y (Y = BH<sub>2</sub>, H, CH<sub>3</sub>, CH=CH<sub>2</sub>, C≡CH, CN, and NC) are electronically poor enough to accept the single electron of the CH<sub>3</sub> radical to form an SEXB. Thus, given the absence of both experimental and theoretical studies on iodine-involved SEXB interactions of CH<sub>3</sub> with I—Y (Y = BH<sub>2</sub>, H, CH<sub>3</sub>, CH=CH<sub>2</sub>, C≡CH, CN, and NC), the present study reports the nature of these interactions, characterized using the density functional Becke, three-parameter, Lee-Yang-Parr (B3LYP) and second-order Møller-Plesset (MP2) theoretical methods.

## 1 Computational details

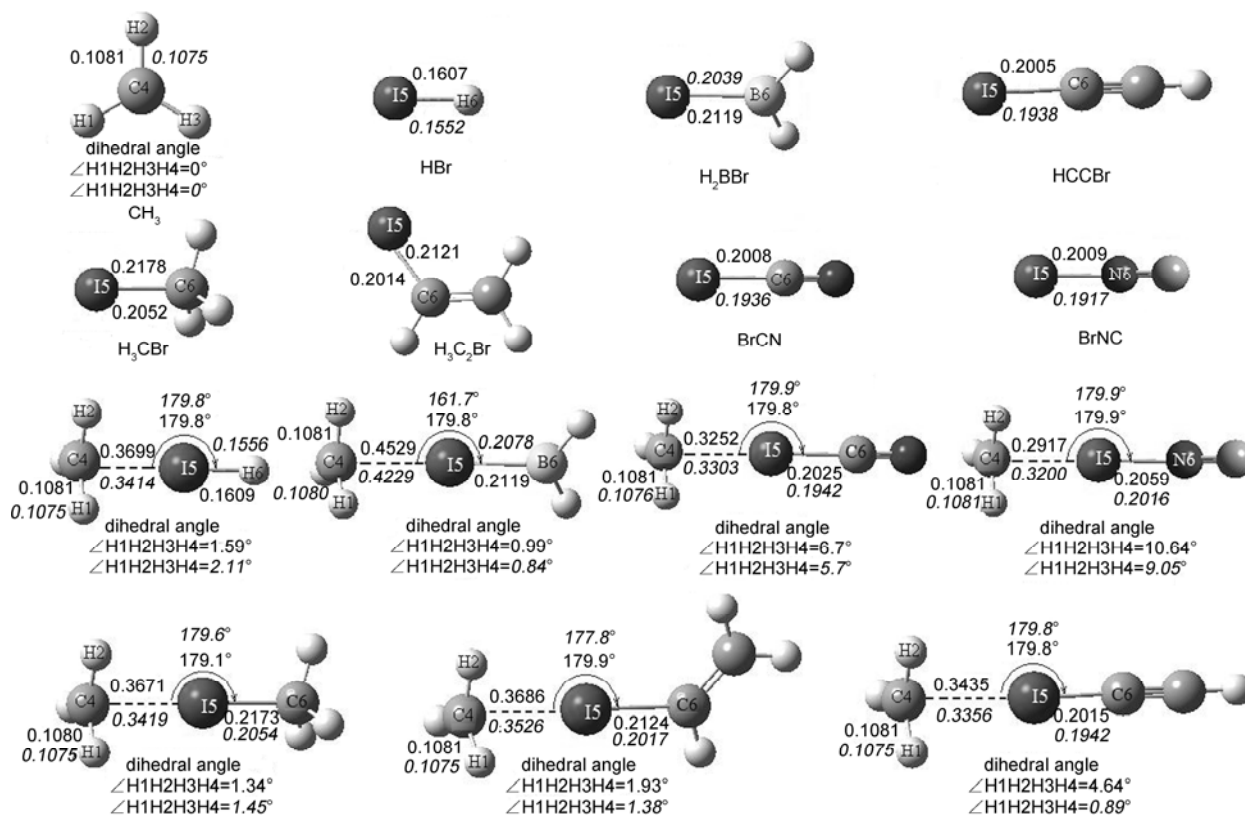
All the monomers and complexes were optimized using the

density functional B3LYP and the MP2 methods. The relativistic effective core potential (ECP) basis set of Lan12dz was used on the iodine atoms, and the 6-311++G(d,p) and aug-cc-pVTZ were used on the other atoms. These methods and basis sets have recently been shown to adequately describe noncovalent interaction systems [13–15]. Thus they are reliable for the purpose of our study. Harmonic frequency analyses were performed at the same levels to confirm that these structures were local minima on the energy surfaces. The interaction energies were corrected with the basis set superposition error (BSSE). The BSSE was evaluated using the counterpoise method of Boys and Bernardi [16]. The atoms-in-molecules (AIM) theory of Bader [17] was used to find the bond critical points (BCP) and to analyze them in terms of electron densities and their Laplacians. The AIM calculations were carried out with the AIM 2000 program [18]. Natural bond orbital (NBO) analyses were carried out with the NBO 5.0 package [19]. All other calculations were performed with the Gaussian 03 program [20].

## 2 Results and discussion

### 2.1 Geometric configuration and frequency analysis

The B3LYP method has proved to be reliable during geometric



**Figure 2** Geometries (bond length in nm, bond angle and dihedral angle in °) of the CH<sub>3</sub>...I—Y (Y = BH<sub>2</sub>, H, CH<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>, CCH, CN, and NC) complexes calculated at B3LYP/6-311++G\*\* (in regular type) and MP2/aug-cc-pVTZ (in italics) levels.

optimization and transition state calculations [13], and the MP2 method has been used successfully to study weak interactions [15]. The optimized geometric configurations on the potential surfaces of the monomers and  $\text{CH}_3\cdots\text{I}-\text{Y}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{CCH}, \text{CN}$  and  $\text{NC}$ ) complexes are shown in Figure 2, and some important structural parameters obtained at the B3LYP/6-311++G\*\* (in regular type) and MP2/aug-cc-pVTZ (in italics) computational levels are also shown. As shown in Figure 2, the seven complexes all have  $C_1$  symmetry, and the parameters obtained at the B3LYP/6-311++G\*\* level agree with those calculated by MP2/aug-cc-pVTZ. In the 7 complexes, SEXBs were formed via the  $\text{IY}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{CCH}, \text{CN}$ , and  $\text{NC}$ ) as the electron acceptor (SEXB donor) and the C atom of  $\text{CH}_3$  as electron donor. The van der Waals radius is an important factor in investigating the geometric structure. If the distance between two atoms is obviously less than the sum of their van der Waals radius, a certain degree of weak interaction from hydrogen bonding or halogen bonding, which is stronger than van der Waals forces, exists between the two atoms. Here, the  $\text{C}\cdots\text{I}$  distances in the complexes of  $\text{CH}_3\cdots\text{I}-\text{H}$ ,  $\text{CH}_3\cdots\text{I}-\text{CH}_3$ ,  $\text{CH}_3\cdots\text{I}-\text{CHCH}_2$ ,  $\text{CH}_3\cdots\text{I}-\text{CCH}$ ,  $\text{CH}_3\cdots\text{I}-\text{CN}$  and  $\text{CH}_3\cdots\text{I}-\text{NC}$  obtained at the B3LYP/6-311++G\*\* level are 0.3699, 0.3671, 0.3686, 0.3435, 0.3252 and 0.2917 nm, respectively, which are all less than the sum of the van der Waals radii of the carbon atom (0.170 nm) and the iodine atom (0.198 nm) [21]; this is part of the evidence for the existence of single-electron iodine-bond interactions. The  $\text{C}\cdots\text{I}$  bond distances in the present study are shorter than the  $\text{C}\cdots\text{Br}$  bond lengths reported for single-electron Br-bond systems in our previous study [11]. Furthermore, the bond angles among the three atoms involved in SEXBs are all close to  $180^\circ$ , and the two moieties exhibit "T" shapes in space.

In addition, the  $\text{CH}_3$  moiety has a planar configuration, and the dihedral angle among its four atoms is  $0^\circ$ , but the structural parameters of the seven  $\text{CH}_3\cdots\text{I}-\text{Y}$  complexes show that the C atoms of the  $\text{CH}_3$  fragment should have hybridization between  $\text{sp}^2$  and  $\text{sp}^3$ . In fact, the calculation results support this. For example, the hybridization of the C atom in the  $\text{CH}_3\cdots\text{INC}$  complex is  $\text{sp}^{2.1}$ , and the dihedral angle among the four atoms of the  $\text{CH}_3$  fragment is about  $10^\circ$ , which is obviously larger than that of the  $\text{CH}_3$  moiety. This suggests the existence of a  $\text{C}\cdots\text{I}$  SEXB between the two moieties. The relationship between the dihedral  $\angle\text{H1H2H3C4}$  and  $d_{\text{C}\cdots\text{I}}$  is given in Figure 3; it can be seen that the larger the dihedral  $\angle\text{H1H2H3C4}$  is, the larger the  $d_{\text{C}\cdots\text{I}}$  is. Comparing parameters of the moieties with those of the complexes given in Figure 2, it can be easily found that the  $\text{I}-\text{Y}$  bond lengths all increased to some degree after complex formation at the two theoretical computation levels. For example, the  $\text{I}-\text{C}$  bond lengths increased by 0.0003, 0.001, and 0.0017 nm at the B3LYP/6-311++G\*\* level in the complexes  $\text{CH}_3\cdots\text{IC}_2\text{H}_3$ ,  $\text{CH}_3\cdots\text{ICCH}$ , and  $\text{CH}_3\cdots\text{ICN}$ , respectively. In particular, the  $\text{I}-\text{N}$  bond length increased

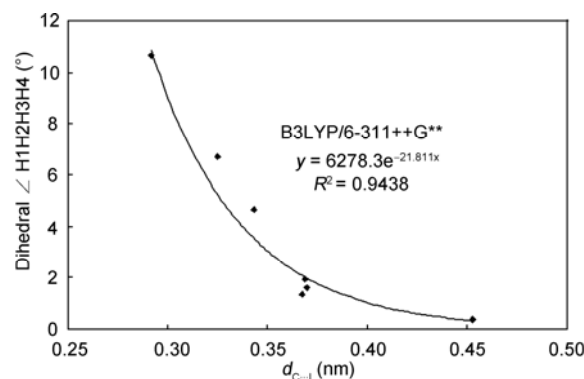


Figure 3 Relationship between dihedral  $\angle\text{H1H2H3C4}$  and  $d_{\text{C}\cdots\text{I}}$ .

by as much as 0.005 nm at the B3LYP/6-311++G\*\* level in the complex  $\text{CH}_3\cdots\text{INC}$ . This predicts an obvious red-shift of its stretching vibrational frequency after the SEXB complex is formed.

To help with possible experimental identification of the SEXB structures described in this work, Table 1 shows the corresponding bond stretching vibrational intensities and frequencies of the monomers and SEXB complexes calculated at the B3LYP/6-311++G\*\* and MP2/aug-cc-pVTZ levels. The frequency analysis shows that the SEXB configurations are all stable points on the potential surfaces of the complexes, except for  $\text{CH}_3\cdots\text{ICH}_3$ , which is a transition point. Although the data obtained using B3LYP and MP2 are not always in agreement, it is found that the stretching vibrational frequency of the  $\text{I}-\text{Y}$  bond in the  $\text{CH}_3\cdots\text{INC}$  complex presents an obvious red-shift. As shown in Figure 4, we also noted that the  $\text{C}\cdots\text{I}$  stretching vibrational frequencies ( $\nu_{\text{C}\cdots\text{I}}$ ) increase in the order  $\text{CH}_3\cdots\text{IBH}_2 < \text{CH}_3\cdots\text{IH} \approx \text{CH}_3\cdots\text{ICH}_3 \approx \text{CH}_3\cdots\text{IC}_2\text{H}_3 < \text{CH}_3\cdots\text{ICCH} < \text{CH}_3\cdots\text{ICN} < \text{CH}_3\cdots\text{INC}$  at both the B3LYP/6-311++G\*\* and MP2/aug-cc-pVTZ levels. This indirectly suggests that the two theoretical levels selected here are feasible and reliable.

## 2.2 Interaction energies and stability

Examining the interaction energy is a powerful approach for estimating the strength of a weak interaction. The single-electron iodine-bond interaction energies of the  $\text{CH}_3\cdots\text{I}-\text{Y}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{CCH}, \text{CN}$ , and  $\text{NC}$ ) complexes at the B3LYP/6-311++G\*\* and MP2/aug-cc-pVTZ levels are listed in Table 2. The BSSE correction is taken into consideration because this is a necessary step for accurately describing the energies of weak interaction systems. As shown in Table 2, the BSSEs obtained using the MP2 method, ranging from 0.91 to 15.36  $\text{kJ mol}^{-1}$ , are obviously larger than those of the B3LYP method. Both  $\Delta E_{\text{CP}}$  (B3LYP) and  $\Delta E_{\text{CP}}$  (MP2) are smaller than those of the energies without BSSE correction ( $\Delta E$ ); in particular, the differences obtained with the MP2 method are relatively large and non-negligible. Obviously, it is necessary to perform a CP

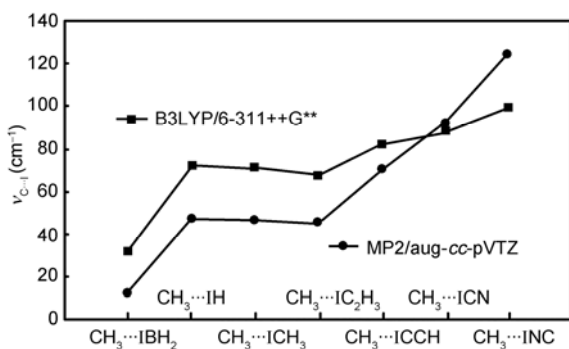
**Table 1** Stretching vibrational frequency ( $\text{cm}^{-1}$ ), frequency shift ( $\text{cm}^{-1}$ , in italics in brackets), and IR intensity ( $\text{km mol}^{-1}$ , in regular type in brackets) of the C—H, I—Y (Y = BH<sub>2</sub>, H, CH<sub>3</sub>, C<sub>2</sub>H<sub>3</sub>, CCH, CN, and NC) bonds

Compound	Parameter	B3LYP/6-311++G** <sup>a)</sup>	MP2/aug-cc-pVTZ <sup>b)</sup>
CH <sub>3</sub>	$\nu_{\text{C-H}}$	3281.29 (4.8)	3367.2(1.8)
IBH <sub>2</sub>	$\nu_{\text{I-B}}$	579.95 (45.6)	624.8(46.1) <sup>b)</sup>
IH	$\nu_{\text{I-H}}$	2305.5 (4.3)	2641.9(1.1)
ICH <sub>3</sub>	$\nu_{\text{I-C}}$	508.4 (4.9) <sup>c)</sup>	660.3(0.3)
IC <sub>2</sub> H <sub>3</sub>	$\nu_{\text{I-C}}$	514.1 (17.3)	632.7(4.6)
ICCH	$\nu_{\text{I-C}}$	490.1 (0.5)	566.7(0.8)
ICN	$\nu_{\text{I-C}}$	472.1 (0.4)	550.2(0.4)
INC	$\nu_{\text{I-N}}$	448.9 (2.2)	549.6(11.4)
CH <sub>3</sub> ...IBH <sub>2</sub>	$\nu_{\text{C-I}}, \nu_{\text{I-B}}$	12.51(0.03), 579.97(41.1, 0.02)	31.6(0.02), 624.7(47.3, -0.1) <sup>b)</sup>
CH <sub>3</sub> ...IH	$\nu_{\text{C-I}}, \nu_{\text{I-H}}$	46.9(0.4), 2288.2(30.9, -17.3)	72.4(0.16), 2615.4(7.7, -26.5)
CH <sub>3</sub> ...ICH <sub>3</sub>	$\nu_{\text{C-I}}, \nu_{\text{I-C}}$	46.7(0.6), 505.3(0.78, -3.1) <sup>c)</sup>	71.2(0.31), 657.6(0.7, -2.7)
CH <sub>3</sub> ...IC <sub>2</sub> H <sub>3</sub>	$\nu_{\text{C-I}}, \nu_{\text{I-C}}$	45.4(0.5), 512.6(10.9, -1.5)	67.8(0.2), 641.4(4.3, 8.7)
CH <sub>3</sub> ...ICCH	$\nu_{\text{C-I}}, \nu_{\text{I-C}}$	70.2 (1.7), 477.3(9.7, -12.8)	82.0(0.6), 569.5(1.5, 2.8)
CH <sub>3</sub> ...ICN	$\nu_{\text{C-I}}, \nu_{\text{I-C}}$	91.8(4.0), 447.3(17.2, -24.8)	87.8(1.5), 558.5(21.9, 8.3)
CH <sub>3</sub> ...INC	$\nu_{\text{C-I}}, \nu_{\text{I-N}}$	124.3 (10.7), 383.5(41.1, -65.4)	99.8(6.4), 452.4(41.1, -97.2)

a) The relativistic ECP basis set of lanl2dz was used for iodine atom; b) data obtained on the basis set of 6-311++G\*\* which was used for the boron, carbon and hydrogen atoms; c) data obtained on the basis set of 6-311++G(2d, 2p) which was used for the carbon and hydrogen atoms.

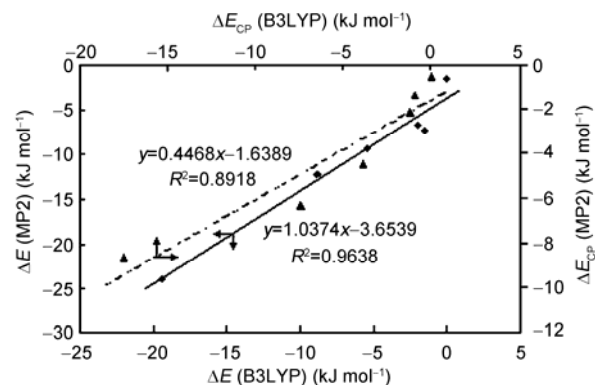
**Table 2** BSSE-corrected interaction energies ( $\text{kJ mol}^{-1}$ ) for the seven complexes at different computational levels

Compound	B3LYP/6-311++G**			MP2/aug-cc-pVTZ		
	$\Delta E$	BSSE	$\Delta E_{\text{CP}}$	$\Delta E$	BSSE	$\Delta E_{\text{CP}}$
CH <sub>3</sub> ...IBH <sub>2</sub>	-0.10	0.17	0.07	-1.48	0.91	-0.57
CH <sub>3</sub> ...IH	-1.58	0.70	-0.88	-7.32	5.96	-1.36
CH <sub>3</sub> ...ICH <sub>3</sub>	-8.00	1.23	-6.77	-7.37	3.57	-3.80
CH <sub>3</sub> ...IC <sub>2</sub> H <sub>3</sub>	-2.03	0.88	-1.15	-6.65	4.48	-2.17
CH <sub>3</sub> ...ICCH	-5.48	1.60	-3.88	-9.31	4.82	-4.49
CH <sub>3</sub> ...ICN	-8.89	1.48	-7.41	12.19	5.86	-6.33
CH <sub>3</sub> ...INC	-19.54	2.07	-17.47	-24.00	15.36	-8.64

**Figure 4** Comparison of  $\nu_{\text{C-I}}$  calculated at the B3LYP/6-311++G\*\* and MP2/aug-cc-pVTZ levels.

correction when the MP2 method is used.

Furthermore, as shown in Figure 5, except for the interaction energy of the complex CH<sub>3</sub>...ICH<sub>3</sub>, the interaction energies of the other complexes obtained using the MP2/aug-cc-pVTZ method are linearly correlated to those obtained by the B3LYP/6-311++G\*\* method, and the relevant equation is  $y = 1.0374x - 3.6539$  ( $R^2 = 0.9638$ ). In

**Figure 5** Linear relationships between  $\Delta E$  (B3LYP) and  $\Delta E$  (MP2),  $\Delta E_{\text{CP}}$  (B3LYP) and  $\Delta E_{\text{CP}}$  (MP2).

fact, the relationship between  $\Delta E_{\text{CP}}$  (B3LYP) and  $\Delta E_{\text{CP}}$  (MP2) is also linear ( $y = 0.4468x - 1.6389$ ,  $R^2 = 0.8918$ ). These results may also suggest that the selected theoretical methods used here are reliable. Additionally, by comparing the BSSE-corrected interaction energies ( $\Delta E_{\text{CP}}$ ) of the SEXB complexes, except for that of CH<sub>3</sub>...ICH<sub>3</sub>, it can easily be found that the relative stabilities of the six complexes increase in the order CH<sub>3</sub>...IBH<sub>2</sub> < CH<sub>3</sub>...IH  $\approx$  CH<sub>3</sub>...IC<sub>2</sub>H<sub>3</sub> < CH<sub>3</sub>...ICCH < CH<sub>3</sub>...ICN < CH<sub>3</sub>...INC, which is consistent with the increasing order of the C...I stretching frequencies ( $\nu_{\text{C...I}}$ ).

Compared with single-electron Br-bond systems, the single-electron iodine-bond has a larger interaction energy. For example, the single-electron Br-bond interaction energies ( $\Delta E_{\text{CP}}$ , MP2) in the CH<sub>3</sub>...BrH, CH<sub>3</sub>...BrC<sub>2</sub>H<sub>3</sub>, CH<sub>3</sub>...BrCCH, CH<sub>3</sub>...BrCN, and CH<sub>3</sub>...BrNC complexes are -1.26, -0.38, -2.95, -4.35, and -7.33  $\text{kJ mol}^{-1}$ , respectively [11]; the single-electron iodine-bond interaction energies ( $\Delta E_{\text{CP}}$ , MP2) in the CH<sub>3</sub>...IH, CH<sub>3</sub>...IC<sub>2</sub>H<sub>3</sub>, CH<sub>3</sub>...ICCH,

CH<sub>3</sub>⋯ICN, and CH<sub>3</sub>⋯INC complexes are -1.36, -2.17, -4.49, -6.33, and -8.64 kJ mol<sup>-1</sup>, respectively. This supports our viewpoint, described in the introduction, that iodine would be more suitable than Br as an electron acceptor in SEXB systems. In other words, this implies that a single-electron iodine-bond complex is more stable than a single-electron Br-bond complex.

For the sake of accuracy of the interaction energies, the ECP basis set of SDD was also used on the iodine atoms. For example, the interaction energies without BSSE correction ( $\Delta E$ ) of the CH<sub>3</sub>⋯IH, CH<sub>3</sub>⋯ICH<sub>3</sub>, CH<sub>3</sub>⋯ICN, and CH<sub>3</sub>⋯INC complexes obtained using MP2/aug-cc-pVTZ/SDD are -6.58, -7.62, -12.81, and -25.45 kJ mol<sup>-1</sup>, respectively; these are similar to those for the MP2/aug-cc-pVTZ/Lanl2dz computational level. Thus the ECP basis set of Lanl2dz is reliable and adequate for iodine atoms in the present SEXB systems.

### 2.3 NBO analysis and NMR properties

For a better understanding of the mechanism of formation of SEXB complexes, NBO analysis was performed for the monomers and complexes at the B3LYP/6-311++G\*\* level, and the corresponding results are listed in Table 3. The interaction strength between the monomers could be clarified according to the second-order stabilization energy  $E_{ij}^{(2)}$  obtained from the NBO analysis as follows

$$E_{ij}^{(2)} = -\eta_{\sigma} \frac{\langle \sigma^* | F | \sigma \rangle}{\varepsilon_{\sigma^*} - \varepsilon_{\sigma}} = \eta_{\sigma} \frac{F_{ij}^2}{\Delta E}, \quad (1)$$

where  $F_{ij}$  is the Fock matrix element between the  $i$  and  $j$  NBO orbitals,  $\varepsilon_{\sigma}$  and  $\varepsilon_{\sigma^*}$  are the energies of  $\sigma$  and  $\sigma^*$ , and  $\eta_{\sigma}$  is the population of the donor  $\sigma$  orbital. As NBO theory indicates, electron transfer among orbitals accompanies the formation of a noncovalent bond and has a major role in the formation, so the  $E_{ij}^{(2)}$  can be taken as an index to judge the strength of a noncovalent interaction. Generally, the larger the stabilization energy  $E_{ij}^{(2)}$ , the stronger the interaction between the donor and acceptor orbitals. As shown in Table 3, there are two kinds of charge transfer in the seven complexes. One is from I—Y to the CH<sub>3</sub> radical, including

LP(I) → LP\*(C) and (I—Y) → LP\*(C); the other is from the CH<sub>3</sub> radical to I—Y, including LP(C) →  $\sigma^*(I—Y)$  and (C—H) →  $\sigma^*(I—Y)$ . The  $E_{ij}^{(2)}$  of the latter kind is obviously larger than that of the former, thus the total charge transfer direction is from the CH<sub>3</sub> radical to the I—Y fragments. Among these interactions between donor and acceptor orbitals, LP(C) →  $\sigma^*(I—Y)$  is the most important, and it determines the nature of the SEXBs. The total amount of NBO charge transfer ( $\Delta_{NC}$ ) from the CH<sub>3</sub> radical to I—Y increases in the order CH<sub>3</sub>⋯IBH<sub>2</sub> < CH<sub>3</sub>⋯IH ≈ CH<sub>3</sub>⋯ICH<sub>3</sub> ≈ CH<sub>3</sub>⋯IC<sub>2</sub>H<sub>3</sub> < CH<sub>3</sub>⋯ICCH < CH<sub>3</sub>⋯ICN < CH<sub>3</sub>⋯INC. It is also interesting to find that the p character of the hybridization of the C atom in C⋯I SEXBs changes in the following order: CH<sub>3</sub>⋯IBH<sub>2</sub> ≈ CH<sub>3</sub>⋯IH ≈ CH<sub>3</sub>⋯ICH<sub>3</sub> ≈ CH<sub>3</sub>⋯IC<sub>2</sub>H<sub>3</sub> < CH<sub>3</sub>⋯ICCH < CH<sub>3</sub>⋯ICN < CH<sub>3</sub>⋯INC, which approximates to the increasing order of the total amount of NBO charge transfer ( $\Delta_{NC}$  (CH<sub>3</sub> → I—Y)). When two systems A and B are bonded together, a single system will be formed with a constant  $\mu$  value (chemical potential). In this case, there is an electron transfer from the less electronegative system to the other and the fractional number of electrons transferred ( $\Delta N$ ) is given as follows [22]:  $\Delta N = (\chi_A - \chi_B)/2(\eta_A + \eta_B)$ , where  $\chi$  ( $\chi = -\mu$ ) is the absolute electronegativity and  $\eta$  is the chemical hardness;  $\mu$  and  $\eta$  are important quantities and they are used to characterize any chemical system. They are defined as  $\mu = (I + A)/2$  and  $\eta = (I - A)/2$ , where  $I$  and  $A$  are the ionization energy and electron affinity of the system. In addition, according to Koopmans's law [23],  $\mu$  and  $\eta$  can also be defined as follows:  $\mu = (E_{LUMO} + E_{HOMO})/2$ ;  $\eta = (E_{LUMO} - E_{HOMO})/2$ , where  $E_{LUMO}$  and  $E_{HOMO}$  are the energy levels of the LUMO and HOMO, respectively. Generally, a large value of  $\Delta N$  represents a strong and favorable interaction between A and B. The  $\Delta N$  values obtained using Koopmans's law, listed in Table 3 for the complexes, are all smaller than 0.4, which indicates that electron transfers from CH<sub>3</sub> to I—Y are all weak. This is consistent with the fact that SEXB binding energies are small. On the other hand, the small  $\Delta N$  values predict that the charge-transfer energy is only a small contribution to the total

**Table 3** NBO analysis for the complexes at the B3LYP/6-311++G\*\* computational level

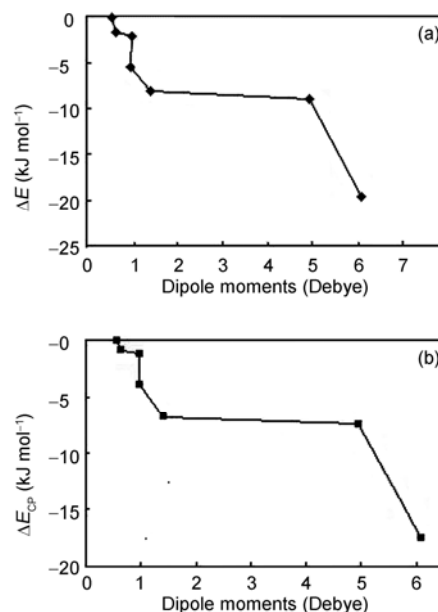
	CH <sub>3</sub> ⋯IBH <sub>2</sub>	CH <sub>3</sub> ⋯IH	CH <sub>3</sub> ⋯ICH <sub>3</sub>	CH <sub>3</sub> ⋯IC <sub>2</sub> H <sub>3</sub>	CH <sub>3</sub> ⋯IC <sub>2</sub> H	CH <sub>3</sub> ⋯ICN	CH <sub>3</sub> ⋯INC
$E_{ij}^{(2)}$ LP(I)→LP*(C) <sup>a)</sup> (kJ/mol)	0.13	1.51	1.72	1.72	3.61	6.17	16.04
$E_{ij}^{(2)}$ σ(I—Y)→LP*(C) (kJ/mol)	0.00	0.59	0.71	0.46	0.46	0.67	1.09
$E_{ij}^{(2)}$ LP(C)→σ*(I—Y) (kJ/mol)	0.42	5.29	4.96	4.28	8.23	16.21	50.48
$E_{ij}^{(2)}$ σ(C—H)→σ*(I—Y) (kJ/mol)	0.00	0.00	0.76	0.76	1.52	2.98	10.21
C(sp <sup>n</sup> ) <sub>C—H</sub>	sp <sup>2.00</sup>	sp <sup>2.00</sup>	sp <sup>2.00</sup>	sp <sup>2.00</sup>	sp <sup>2.02</sup>	sp <sup>2.03</sup>	sp <sup>2.10</sup>
$\Delta_{NC}$ (CH <sub>3</sub> →I—Y) (me)	1	6	7	8	17	35	86
$\Delta N$	0.1387	0.0793	0.0480	0.0642	0.0811	0.2977	0.3809
Bond order <sub>C—I</sub>	0.0000	0.0048	0.0032	0.0013	0.0058	0.0058	0.1750
Dipole moments (Deby)	0.5551	0.6439	1.4185	0.9848	0.9681	4.9359	6.0737

a) LP represents lone pair electron orbital, LP\* represents non-bond electron orbital.

binding energy. Therefore, the polarization, including dispersion and induction contributions, is perhaps very important to the total binding energy. In fact, the charge transfers from the donor to acceptor orbital and the coupling thereof are often small, but they are significant for the analysis of the nature of intermolecular weak interactions. In addition, it is noted that the  $\Delta N$  value of  $\text{CH}_3\cdots\text{IBH}_2$  is larger than those of  $\text{CH}_3\cdots\text{IH}$ ,  $\text{CH}_3\cdots\text{ICH}_3$ ,  $\text{CH}_3\cdots\text{IC}_2\text{H}_3$ , and  $\text{CH}_3\cdots\text{ICCH}$ , which is a discrepancy with respect to the  $\Delta N_{\text{C}\cdots\text{I}}$  values, the  $\text{C}\cdots\text{I}$  stretching frequencies ( $\nu_{\text{C}\cdots\text{I}}$ ), and the relative interaction energies; that is, the value of  $\Delta N$  is not always suitable for predicting the relative strengths of the seven SEXB interaction systems in the present study. However, for the  $\text{CH}_3\cdots\text{ICH}_3$ ,  $\text{CH}_3\cdots\text{IC}_2\text{H}_3$ ,  $\text{CH}_3\cdots\text{ICCH}$ ,  $\text{CH}_3\cdots\text{ICN}$ , and  $\text{CH}_3\cdots\text{INC}$  systems, the sequence of their  $\Delta N$  values is consistent with that of their  $\Delta N_{\text{C}\cdots\text{I}}$  values, which suggests that the  $\Delta N$  values can be used to describe the relative interaction strengths for these five complexes.

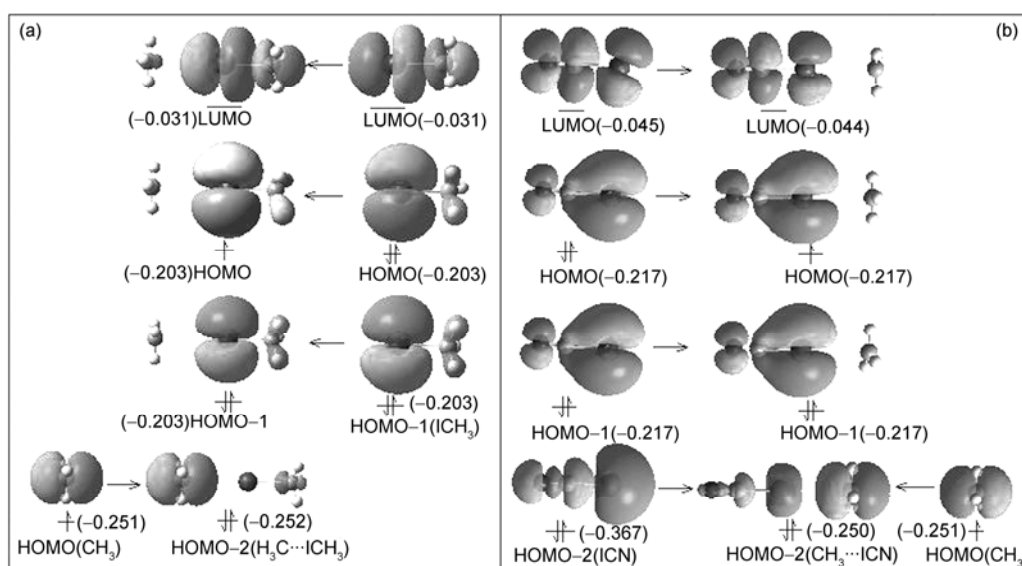
Figure 6(a) and (b) show that the dipole moments of the complexes correlate with the interaction energies  $\Delta E$  and  $\Delta E_{\text{CP}}$  at the B3LYP/6-311++G\*\* level, respectively. The shapes of the two curves are very similar, which suggests that the greater the dipole moment of the complex, the more nonsymmetrical the charge distribution, the more negative the interaction energy, the stronger the interaction, and the more stable the SEXB interaction system.

To further investigate the essence of SEXB interactions, the sources and the energies of the frontal molecular orbitals of  $\text{CH}_3\cdots\text{I}-\text{Y}$  ( $\text{CH}_3\cdots\text{ICH}_3$  and  $\text{CH}_3\cdots\text{ICN}$ ) are shown in Figure 7. For the  $\text{CH}_3\cdots\text{ICH}_3$  complex, the HOMO and HOMO-1 come from HOMO and HOMO-1 of the  $\text{CH}_3\text{I}$  moiety, respectively, but the HOMO-2 comes from the HOMO of the  $\text{CH}_3$  radical. Thus the  $\text{CH}_3$  radical becomes



**Figure 6** Relationship between  $\Delta E$  and dipole moments (a), and  $\Delta E_{\text{CP}}$  and dipole moments (b).

more stable after SEXB formation. For the  $\text{CH}_3\cdots\text{ICN}$  complex, the sources of its LUMO, HOMO, and HOMO-1 are similar to those of the  $\text{CH}_3\cdots\text{ICH}_3$  complex, but the sources of HOMO-2 of the two complexes are different. The source of the HOMO-2 of the  $\text{CH}_3\cdots\text{ICN}$  complex comes from two moieties, namely the HOMO of the  $\text{CH}_3$  radical and the HOMO-2 of the  $\text{ICN}$  moiety. Thus, the  $\text{CH}_3\cdots\text{ICN}$  complex will be more stable than the  $\text{CH}_3\cdots\text{ICH}_3$  complex. For the sake of brevity, the sources of the frontal molecular orbitals of the other complexes are not given here.



**Figure 7** Sources of frontal molecular orbitals in complexes  $\text{CH}_3\cdots\text{ICH}_3$  (a) and  $\text{CH}_3\cdots\text{ICN}$  (b).

## 2.4 AIM and MEP analysis

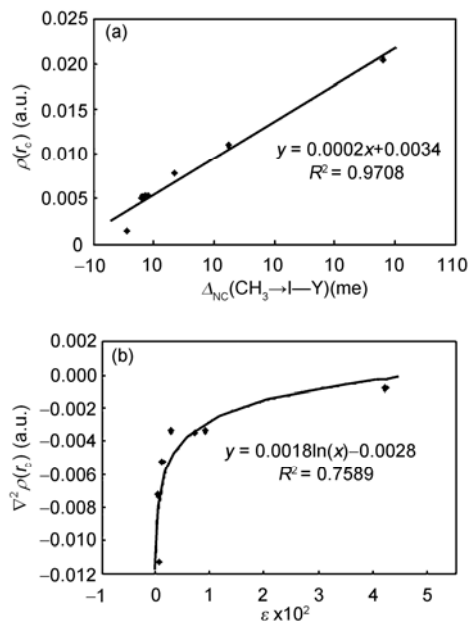
The topological properties of the scalar field electron density ( $\rho(r)$ ) can be described by the numbers and the categories of the critical points. A critical point is the spatial position where the first derivative of the  $\rho(r)$  is zero, as follows

$$\nabla\rho(r) = i\frac{\partial}{\partial x}\rho(r) + j\frac{\partial}{\partial y}\rho(r) + k\frac{\partial}{\partial z}\rho(r) = 0. \quad (2)$$

The type of the critical point can be defined according to the critical point curvature obtained by calculating the second derivative of the  $\rho(r)$ . The Hessian matrix of the electron density is composed of nine secondary derivatives of  $\rho(r)$  in three dimensions. The three eigenvalues ( $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ ) can be acquired by performing a diagonalized operator on the Hessian matrix. The sum of the three eigenvalues is equal to the Laplacian of the electron density ( $\nabla^2\rho(r) = \lambda_1 + \lambda_2 + \lambda_3$ ). Among the three eigenvalues, if two of them are negative and the other is positive, the corresponding critical point is designated as the bond critical point (BCP) and marked as (3, -1), indicating the linkage between the two atoms; if two of them are positive and the other is negative, the corresponding critical point is designated as the ring critical point, and marked as (3, +1), indicating the existence of a ring structure. The nuclear position is marked as (3, -3). According to Bader's AIM theory [24], the electron density topological properties of a molecule depend on the electron density gradient vector field and  $\nabla^2\rho(r)$ . In general, the electron density of a BCP ( $\rho(r_c)$ ) is related to the strength of the bond: the larger the  $\rho(r_c)$  is, the stronger the bond; the smaller the  $\rho(r_c)$  is, the weaker the bond. The  $\nabla^2\rho(r)$  of the BCP reflects the characteristics of the bond. If  $\nabla^2\rho(r_c) < 0$ , the BCP charges will be concentrated, and the more negative  $\nabla^2\rho(r_c)$  is, the more covalent the property is; if  $\nabla^2\rho(r_c) > 0$ , the BCP charges will be dispersed, and the more positive  $\nabla^2\rho(r_c)$  is, the more ionic the property is.

The electron density topological properties of the SEXB critical points in the seven complexes are listed in Table 4. The three eigenvalues of the electron density Hessian matrix of C...I are "one positive and two negative". Therefore, the critical points between the atom pairs of C...I belong to the type BCP. The  $\rho(r)$  values of C...I in the seven complexes are smaller than 0.021 a.u. This indicates that the SEXB

interactions in the seven complexes are weak, which is in good agreement with the calculation results for the interaction energies. Furthermore, it is noted that the  $\rho(r)$  of the C...I in the seven complexes is related to the amounts of  $\Delta_{\text{NC}}$  ( $\text{CH}_3 \rightarrow \text{I}-\text{Y}$ ), that is, the larger the  $\Delta_{\text{NC}}$ , the larger the  $\rho(r)$  of the C...I atom pair. The relationship between  $\Delta_{\text{NC}}$  and  $\rho(r)$  is linear ( $y = 0.0002x + 0.0034$ , with  $R^2 = 0.9708$ ) (Figure 8(a)). In addition, the  $\nabla^2\rho(r)$  of the corresponding critical points are all small negative values (more than  $-0.012$  a.u.), which shows that this kind of weak interaction has a few covalent property. The ellipticity,  $\varepsilon$ , is defined as  $\lambda_1/\lambda_2 - 1$ , in which  $\lambda_1$  and  $\lambda_2$  are the two eigenvalues of the Hessian matrix of electron density. The ellipticity provides a measure for the  $\sigma$  or  $\pi$  character of a bond. In general, the smaller  $\varepsilon$  is, the stronger the  $\sigma$  character is, and conversely for the  $\pi$  character. Figure 8 (b) shows the relevance between  $\varepsilon$  and  $\nabla^2\rho(r_c)$ , which is  $y = 0.0018\ln(x) - 0.0028$  ( $R^2 = 0.7589$ ) suggesting that the covalent property of the C...I atom pair is mainly  $\sigma$  in character.



**Figure 8** Linear relationship between  $\rho(r_c)$  (a.u.) and  $\Delta_{\text{NC}}(\text{CH}_3 \rightarrow \text{I}-\text{Y})$  (me) (a),  $\nabla^2\rho(r_c)$  (a.u.) and  $\varepsilon(\text{seven})$  (b).

**Table 4** Electron density topological properties of bond critical points for the seven complexes

Compound	Atom pair	$\rho(r_c)$ (a.u.)	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\nabla^2\rho(r_c)$ (a.u.)	$\varepsilon$
$\text{CH}_3 \cdots \text{IBH}_2$	I...C	0.00142	-0.00057	-0.00055	0.00431	-0.00080	0.04196
$\text{CH}_3 \cdots \text{IH}$	I...C	0.00510	-0.00232	-0.00231	0.01792	-0.00332	0.00274
$\text{CH}_3 \cdots \text{ICH}_3$	I...C	0.00538	-0.00245	-0.00243	0.01872	-0.00346	0.00704
$\text{CH}_3 \cdots \text{IC}_2\text{H}_3$	I...C	0.00533	-0.00247	-0.00245	0.01832	-0.00335	0.00902
$\text{CH}_3 \cdots \text{ICCH}$	I...C	0.00786	-0.00399	-0.00398	0.02902	-0.00526	0.00109
$\text{CH}_3 \cdots \text{ICN}$	I...C	0.01101	-0.00609	-0.00609	0.04110	-0.00723	0.00041
$\text{CH}_3 \cdots \text{INC}$	I...C	0.02053	-0.01295	-0.01295	0.07113	-0.01130	0.00048

### 3 Conclusions

In the present study, the iodine-involved weak interactions in systems  $\text{CH}_3 \cdots \text{I}-\text{Y}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{CCH}, \text{CN}$ , and  $\text{NC}$ ) were investigated at the MP2/aug-*cc*-pVTZ and B3LYP/6-311++G\*\* computational levels (the relativistic ECP basis set of Lan12dz was used on the iodine atom) for the first time. In the seven complexes, SEXB structures were formed via the iodine atom of  $\text{I}-\text{Y}$  ( $\text{Y} = \text{BH}_2, \text{H}, \text{CH}_3, \text{C}_2\text{H}_3, \text{CCH}, \text{CN}$ , and  $\text{NC}$ ) as the electron acceptor (but the SEXB donor) and the  $\text{CH}_3$  radical as the electron donor. By comparing the BSSE-corrected interaction energies ( $\Delta E_{\text{CP}}$ ) of the SEXB complexes, it can be easily found that the relative stabilities of the seven complexes increased in the order  $\text{CH}_3 \cdots \text{IBH}_2 < \text{CH}_3 \cdots \text{IH} \approx \text{CH}_3 \cdots \text{IC}_2\text{H}_3 < \text{CH}_3 \cdots \text{ICH}_3 < \text{CH}_3 \cdots \text{ICCH} < \text{CH}_3 \cdots \text{ICN} < \text{CH}_3 \cdots \text{INC}$ , which is consistent with the increasing sequence of the  $\text{C} \cdots \text{I}$  stretching frequencies ( $\nu_{\text{C} \cdots \text{I}}$ ). In the NBO analysis, the total amount of NBO charge transfer ( $\Delta_{\text{NC}}$ ) from the  $\text{CH}_3$  radical to  $\text{I}-\text{Y}$  increases in the order  $\text{CH}_3 \cdots \text{IBH}_2 < \text{CH}_3 \cdots \text{IH} \approx \text{CH}_3 \cdots \text{ICH}_3 \approx \text{CH}_3 \cdots \text{IC}_2\text{H}_3 < \text{CH}_3 \cdots \text{ICCH} < \text{CH}_3 \cdots \text{ICN} < \text{CH}_3 \cdots \text{INC}$ . AIM analysis showed that the  $\rho(r)$  values of  $\text{C} \cdots \text{I}$  in the seven complexes are smaller than 0.021 a.u. This indicates that the SEXB interactions are weak, which in good agreement with the calculated results for interaction energies.

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