

## ARTICLE

## DFT Study on Homolytic Dissociation Enthalpies of C–I Bonds

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(Dated: Received on May 21, 2013; Accepted on July 29, 2013)

The C–I bond dissociation enthalpies (BDE) of various organic iodides were calculated using high-level theoretical methods including MP2 and CCSD(T) with extrapolated basis set as well as a number of density functional theory methods. After systematic evaluation of the theoretical results against available experimental C–I BDEs, it was found that the MPW-LYP1M method gave the lowest root mean square error. We, therefore, used this method to examine the substituent effects on different categories of C(sp<sup>3</sup>)–I and C(sp<sup>2</sup>)–I bonds. Furthermore, the remote substituent effects on the C–I BDEs of substituted iodobenzenes and substituted (iodomethyl)benzenes were also investigated at the same level. The C–I BDEs of typical heteroaromatic iodides including five-membered and six-membered heterocyclic iodides were also examined.

**Key words:** C–I bond, Bond dissociation enthalpy, Density functional theory

## I. INTRODUCTION

The cleavage of carbon-iodine bond is an important process, which has been examined in a lot of theoretical and experimental studies. For example, the cleavage of C–I bond on metal surfaces is an elementary step, and it is used to create stable alkyl groups [1]. Gellman *et al.* measured the kinetics of C–I bond cleavage on the Ag(111) surface in a set of 10 alkyl and fluoroalkyl iodides [2]. The characteristics of the transition state to C–I cleavage on the Ag(111) surface is revealed. Fang *et al.* studied the insertion reaction of zinc into the C–I bond of CH<sub>2</sub>I<sub>2</sub> and subsequent cyclopropanation reactions with CH<sub>2</sub>CH<sub>2</sub> using B3LYP method [3]. Lin *et al.* studied the chemistry of 2-iodoacetic acid on Cu(100) by a combination of reflection-absorption infrared spectroscopy (RAIRS), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reaction/desorption (TPR/D) [4]. A theoretical calculation by density functional theory (DFT) for the intermediate structures was also conducted. There is a competition between C–I bond scission and COOH deprotonation. Due to the wide application of aryl C–I cleavage by low-valent, electron-rich transition-metal complexes in organic synthesis, Chan *et al.* investigated the base-promoted selective aryl C–I bond cleavage by iridium(III) porphyrin [5] (Fig.1). The mechanistic studies revealed the reaction mechanism, in which the reduction of Ir<sup>III</sup>-OH to Ir<sup>II</sup> for metalloradical ipso substitution of

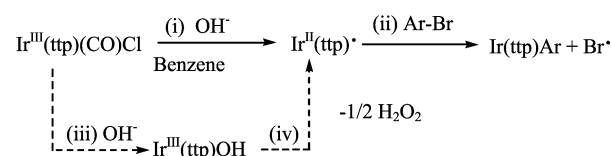


FIG. 1 Base-promoted Ar-Br cleavage by Ir(tp)(CO)Cl.

aryl-halogen bonds took place.

Bickelhaupt *et al.* studied the oxidative addition reaction mechanism of iodomethane C–I bonds to Pd and *cis*-Pd(CO)<sub>2</sub>I<sub>2</sub> at the ZORA-BP86/TZ(2)P level of relativistic DFT [6]. Mphahlele *et al.* investigated the reaction of one-pot Pd-catalyzed C–I bond activation and subsequent Suzuki-Miyaura cross-coupling of 2-aryl-3-iodo-4-(phenylamino)quinolines with arylboronic acids under anhydrous conditions [7].

In this context the thermodynamic properties of C–I bonds, for example, the bond dissociation enthalpy (BDE), which is a fundamental property that measures the strength of a chemical bond [8], are very important. The knowledge of the BDE values for the C–I bonds can be useful for understanding the C–I activation and subsequent reactions. The importance has stimulated us to calculate and predict C–I BDE values using quantum chemical methods. In the present work, we calculated a set of C–I BDEs using high-level theoretical methods including MP2 and CCSD(T) with extrapolated basis set. In addition, the computational accuracy of a number of DFT methods on C–I BDEs was assessed. On the basis of these results, we systematically examined the substituent effect of different types of C–I bonds.

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## II. COMPUTATIONAL METHOD

The homolytic bond dissociation enthalpy of a chemical bond A–B is defined as enthalpy change in gas phase at 298.15 K and 1 atm for the reaction  $A-B(g) \rightarrow A\cdot(g) + B\cdot(g)$  [9]. The enthalpy of each species is calculated using the following equation:

$$H_{298} = E + ZPE + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT \quad (1)$$

where ZPE is referred to the zero point energy,  $H_{\text{trans}}$ ,  $H_{\text{rot}}$ , and  $H_{\text{vib}}$  are the standard temperature correction term, which are calculated using harmonic oscillator and rigid rotor approximations.

All the calculations were performed using Gaussian 03 programs [10]. The geometry optimizations were done at the B3LYP/6-31+G(d) level for all the atoms except I atom, which was described by the LANL2DZ basis set [11, 12]. The structures of the molecules were confirmed to be real minima on the potential-energy surface by the frequency calculations at the same level with geometry optimization. The B3LYP method has been testified reasonable for structure optimizations, because of its high accuracy requirements and practical computational cost [13–18]. In order to identify the global minimum-energy conformer of each molecule, several possible conformers were optimized and the energetically most stable one was selected. The density functional theory (DFT) methods included B3LYP [19], BMK [20], B3P86 [21], MPW1B95 [22], PBE1W [23], TPSS1KCIS [24], MPW1K [25], MPW3LYP [22], TPSSLYP1W [23], KMLYP [26], MPW1P86 [27], MPWB1K [22], MPWK-CIS1K [28], MPW1KCIS [28], PBE1KCIS [29], MPWLYP1W [23], PBELYP1W [23], MPWLYP1M [30], M05 [31], which are used for calculating single point energies. The basis set for single point calculations is 6-311++G(2df,2p) for all the atoms except for I, which is also used as LANL2DZ.

When using the MP2 and CCSD(T) methods, the basis set is extrapolated to the infinite size using the following empirical function, which was developed by Kahn and Bruice [32]. For I atom, the basis set is also LANL2DZ.

$$E_x = E_\infty + A_3 X^{-3} + A_5 X^{-5} \quad (2)$$

## III. RESULTS AND DISCUSSION

### A. Examination of MP2 and CCSD(T) methods

We chose 29 C–I BDEs for calculation, using high-level theoretical methods including MP2 and CCSD(T) with extrapolated basis set. The results are listed in Table I. The experimental values are also listed, which was collected from the data reviewed by Luo [33].

It can be seen that the MP2 method tends to give systematic errors in predicting C–I BDEs with cc-PVDZ, cc-PVTZ, and cc-PVQZ basis sets for these

29 molecules. There are large differences between them. For example, the C–I experimental BDE of (iodomethyl)benzene is 187.8 kJ/mol, while the values of MP2 method with cc-PVDZ, cc-PVTZ, and cc-PVQZ basis sets are 273.0, 320.1, and 365.0 kJ/mol, respectively. The BDE value is 410.4 kJ/mol when extrapolated to infinite basis set limit, which is more than 200 kJ/mol difference from the experimental one! The result is not surprising because MP2 method has been shown not suitable for predicting absolute BDEs due to the systematic deviation [34]. The same result can also be found in our previous research work [35].

For CCSD(T) method, there are also large differences with different basis sets. For example, the BDE of cyanic iodide (I–CN) predicted by CCSD(T) for three basis sets are 311.2, 377.1, and 424.3 kJ/mol. The value extrapolated to infinite basis set limit is 470.5 kJ/mol, and there is over 150 kJ/mol difference between the maximum and minimum value. Furthermore, for larger molecules, the CCSD(T) with cc-PVQZ basis set gave no results because of the computational resources limit. Due to the large deviation of different basis sets, inaccurate absolute BDE calculation and relatively high CPU-cost, the MP2 and CCSD(T) methods are not recommended for the C–I BDE calculation.

### B. Examination of DFT methods

Due to the particularity of I atom with large atomic radius, the pseudopotential basis set for I atom was employed in all the calculation. The composite high-level *ab initio* methods including G3 [36], G3B3 [37], CBS-Q [38], *etc.*, which have high accuracy in thermodynamic calculations [39, 40], can not be used for the systems containing I atom. In addition, the MP2 and CCSD(T) methods gave no satisfactory results of C–I BDE. So we made the choice of the DFT methods for calculation of C–I BDE, which are desirable for open-shell systems for not showing spin-contamination and are advantageous for relatively low CPU-cost. Nowadays, DFT is considered a practical method for thermodynamic calculations including BDE [41, 42]. The 29 C–I BDEs in Table I were calculated using 19 DFT methods. The correlations between DFT theoretical values with experimental ones expressed by mean deviation (MD), mean absolute deviation (MAD) and root mean square error (RMSE) are listed in Table II.

From the correlations of all the DFTs in Table II, we can see that the MPWLYP1M method gave the best result with the highest accuracy, *i.e.* the least root-of-mean square error (RMSE 9.57 kJ/mol) for 29 C–I BDEs calculation. The MD and MAD are –1.65 and 7.44 kJ/mol respectively. The second and third superior methods are MPWLYP1W and PBELYP1W, and the RMSE values are 9.64 and 9.69 kJ/mol, respectively. The largest RMSE (20.32 kJ/mol) was found in the BDE calculation of PBE1KCIS method. MPW-

TABLE I Effect of basis sets on MP2 and CCSD(T) calculation for C–I BDEs (kJ/mol).

Molecule	Exp.	MP2				CCSD(T)			
		cc-pVDZ	cc-pVTZ	cc-pVQZ	$\infty^a$	cc-pVDZ	cc-pVTZ	cc-pVQZ	$\infty^a$
I–CN	320.1	405.9	473.5	519.3	563.7	311.2	377.1	424.3	470.5
I–CF <sub>3</sub>	227.2	199.6	244.6	283.4	322.3	200.1	245.8	287.5	329.4
I–CH <sub>2</sub> F	233	200.9	244.0	282.4	321.0	201.6	246.4	287.4	328.7
I–CH <sub>3</sub>	238.9	214.6	254.8	293.1	331.8	217.1	258.9	299.5	340.8
I–HC=CH <sub>2</sub>	276.3	285.9	335.9	378.0	420.1	261.1	311.6	356.3	401.3
I–CH <sub>2</sub> CH=CH <sub>2</sub>	185.8	180.0	223.8	268.3	313.5	115.8	203.1	249.4	292.8
I–HC=CHCH <sub>3</sub>	287	293.2	342.6	385.8	429.1	268.1	318.1	364.1	410.5
I–C <sub>6</sub> H <sub>5</sub>	272	385.7	442.3	490.8	539.4	286.2	340.1		
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> –I	281	389.1	448.0	500.8	554.0	287.7			
<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> –I	274.5	374.2	435.8	487.9	540.0	269.3			
I–C=OCH <sub>3</sub>	223	209.4	243.9	279.8	316.3	206.1	242.2		
I–C=OC <sub>6</sub> H <sub>5</sub>	212.1	215.7	252.6	292.6	333.6	209.9	246.9		
I–CH <sub>2</sub> CN	187	225.8	269.6	311.7	354.3	178.2	222.2	265.8	310.1
I–C <sub>2</sub> H <sub>5</sub>	233.5	218.5	259.8	301.2	343.3	219.2	262.3	306.1	350.6
I–HC=CHCH <sub>3</sub>	280.3	291.0	340.3	383.4	426.7	266.3	316.1	362.1	408.4
I–CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	236.8	226.0	269.0	313.3	358.5	225.6	270.6	317.7	365.7
I–CH(CH <sub>3</sub> ) <sub>2</sub>	234.7	221.2	263.5	308.9	355.3	220.2	202.4	312.1	
I–CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> I	227.6	223.1	269.0	313.8	359.3	222.7	270.2		
I–CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	239.8	222.9	268.1	316.0	364.9	222.8	269.7		
H <sub>3</sub> CHC–IC <sub>2</sub> H <sub>5</sub>	226.4	223.2	268.4	316.8	366.2	221.9	268.9		
I–C <sub>4</sub> H <sub>9</sub>	227.2	226.3	269.7	315.0	361.1	225.9	271.3		
H <sub>3</sub> CHC–ICH=CH <sub>2</sub>	168.7	186.4	229.4	275.0	321.6	164.6	207.8		
I–(CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	233.7	227.8	270.5	314.5	359.4	224.7	269.8		
I–CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	239.1	227.2	275.4	328.1	382.0	225.8	275.9		
(CH <sub>3</sub> ) <sub>2</sub> C(C <sub>2</sub> H <sub>5</sub> )–I	227	223.3	270.9	321.4	373.1	219.8	269.5		
I–CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	187.8	273.0	320.1	365.0	410.4	182.7	314.4		
I–CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	229.7	230.8	275.3	319.8	365.1	229.2	269.5		
I–CH <sub>2</sub> CH <sub>2</sub> COOH	228	224.3	267.0	311.1	356.1	222.7	267.5		
I–CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	217.1	206.5	250.4	293.8	337.8	195.8	242.2		

<sup>a</sup> Extrapolated values to infinite basis set.

LYP1M [30] is a hybrid DFT method for organometallic chemistry, which denotes MPW exchange, LYP correlation, and one parameter optimized for metals. The results show that this method is favorable for thermodynamic calculations of the systems containing I atom. The second superior method, MPWLYP1W [23] is a non-hybrid density functional parameterized for water. Furthermore, for other DFT methods, the RMSE values are not very large for C–I BDE calculation, which indicates that the high accuracy of C–I BDE calculation can be got by using DFT methods. The MD and MAD values demonstrated that for 29 C–I BDEs some were overestimated and the other were underestimated of all DFT methods. The B3LYP method, which is the most popularly used DFT, the RMSE value (12.29 kJ/mol) for C–I BDE was found. As a result, we chose the MPWLYP1M method for the other C–I BDE calculations.

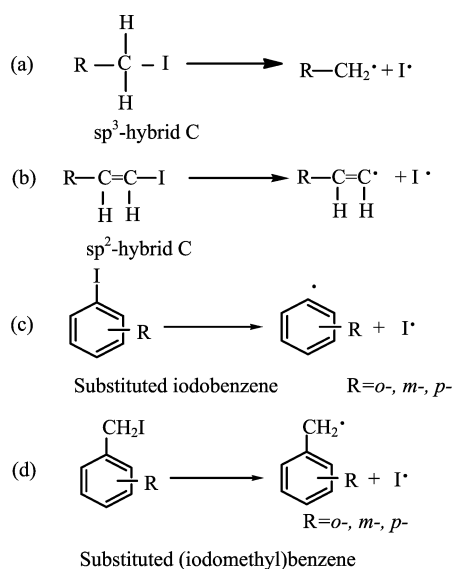
### C. C–I BDE prediction and substituent effect

The sp<sup>3</sup>-hybrid type C(sp<sup>3</sup>)–I BDEs by using MPWLYP1M method of 15 molecules by changing substituent R (Fig.2(a)) according to different substituent properties [43], including electron-withdrawing and electron-donating effects are displayed in Table III. The NBO analysis [44] was conducted at the MPWLYP1M/SDD level. After NBO analysis, the values of  $q_C$  and  $q_I$  are listed, which denote the natural charge of C and I atom of C–I bond respectively. The C–I bond lengths are also listed.

From Table III, we can see that the sp<sup>3</sup>-hybrid type C(sp<sup>3</sup>)–I BDEs are in the range of 181.8–234.7 kJ/mol, which has about 50 kJ/mol difference. The smallest BDE value appears in the 2-iodoacetonitrile molecule (CNCH<sub>2</sub>–I), in which the R group is –CN. And the largest one is found in iodo-*N,N*-dimethylmethanamine

TABLE II The correlations between theoretical BDEs with experimental values of 19 DFTs.

DFT	BDE/(kJ/mol)		
	MD	MAD	RMSE
MPW1B95	16.76	16.88	18.83
MPW1K	-2.96	7.67	10.09
MPW1KCIS	15.43	15.82	18.00
MPW3LYP	-2.46	7.50	9.87
MPWKCIS1K	4.99	8.18	10.79
MPWB1K	11.96	12.65	14.97
MPWLYP1M	-1.65	7.44	9.57
MPWLYP1W	-0.88	7.46	9.64
PBE1KCIS	18.17	18.22	20.32
PBE1W	13.91	14.57	16.75
PBELYP1W	-0.50	7.47	9.69
TPSS1KCIS	4.64	8.09	10.30
TPSSLYP1W	-17.64	17.93	20.08
KMLYP	15.88	16.25	19.05
B3LYP	-7.55	10.00	12.29
B3P86	11.97	12.86	15.19
BMK	0.03	8.91	14.69
M05	12.12	13.79	16.13
MPW1P86	11.33	12.31	14.53

FIG. 2 C-I bond cleavage. (a)  $\text{sp}^3$ -hybrid type  $\text{C}(\text{sp}^3)\text{-I}$ , (b)  $\text{sp}^2$ -hybrid type  $\text{C}(\text{sp}^2)\text{-I}$ , (c) substituted iodobenzene, and (d) substituted (iodomethyl)benzene.

molecule  $(\text{CH}_3)_2\text{NCH}_2\text{-I}$ , in which the R group is  $-\text{N}(\text{CH}_3)_2$ . So we can make a conclusion that for  $\text{C}(\text{sp}^3)\text{-I}$  bond, the electron-withdrawing groups can decrease the C-I BDE, while the electron-donating groups can increase it. Furthermore, the conjugate effect of R group also plays an important role. For example, for the R substituents of amino-groups,

TABLE III The 15  $\text{C}(\text{sp}^3)\text{-I}$  BDEs (in kJ/mol) with values of C-I bond length in Å,  $q_{\text{C}}$  and  $q_{\text{I}}$ .

Molecule	BDE	Bond length	$q_{\text{I}}/e$	$q_{\text{C}}/e$
$\text{HOCH}_2\text{-I}$	226.5	2.262	-0.0625	-0.174
$\text{H}_2\text{NCH}_2\text{-I}$	228.4	2.348	-0.182	-0.284
$\text{H}_3\text{CHNCH}_2\text{-I}$	232.5	2.398	-0.238	-0.266
$\text{C}_2\text{H}_5\text{NHCH}_2\text{-I}$	233.0	2.407	-0.247	-0.256
$(\text{H}_3\text{C})_2\text{NCH}_2\text{-I}$	234.7	2.444	-0.284	-0.247
$\text{H}_3\text{C}=\text{OCH}_2\text{-I}$	204.4	2.186	0.0738	-0.219
$\text{C}_2\text{H}_5\text{OCH}_2\text{-I}$	204.9	2.188	0.0692	-0.213
$\text{OHCNHCH}_2\text{-I}$	200.3	2.258	-0.0248	-0.342
$\text{CH}_3\text{CONHCH}_2\text{-I}$	204.6	2.270	-0.0485	-0.323
$\text{CNCH}_2\text{-I}$	181.8	2.199	0.126	-0.668
$\text{F}_3\text{CCH}_2\text{-I}$	225.3	2.172	0.138	-0.686
$\text{Cl}_3\text{CCH}_2\text{-I}$	212.3	2.181	0.126	-0.648
$\text{OHCCH}_2\text{-I}$	187.6	2.168	0.103	-0.683
$\text{O}_2\text{NCH}_2\text{-I}$	202.9	2.168	0.162	-0.463
$\text{C}_2\text{H}_5\text{OOCCH}_2\text{-I}$	202.9	2.197	0.097	-0.639

there are little differences between the BDE values, which is in the range of 228.4–234.7 kJ/mol. While for *N*-(iodomethyl)formamide molecule ( $\text{OHCNHCH}_2\text{-I}$ ) and *N*-(iodomethyl)acetamide molecule ( $\text{CH}_3\text{CONHCH}_2\text{-I}$ ), there is a significant C-I BDE decline. The BDE values are 200.3 and 204.6 kJ/mol respectively. The conjugate effect of C=O double bond in R group sharply decreases the C-I BDE value. The same phenomenon can be found in the R groups of  $-\text{CN}$ ,  $-\text{CHO}$ ,  $-\text{NO}_2$  and  $-\text{COOC}_2\text{H}_5$ . The conjugate effect of  $\text{C}\equiv\text{N}$  triple bond, C=O double bond, and N=O double bond influenced the C-I BDEs in the same way. In addition, the electron-withdrawing effect of these groups can not be ignored. It is worth mentioning that for 1,1,1-trifluoro-2-iodoethane molecule ( $\text{F}_3\text{CCH}_2\text{-I}$ ), the C-I BDE is 225.3 kJ/mol. It showed that the electron-withdrawing property of  $-\text{CF}_3$  group has little effect on C-I BDE.

For the  $\text{sp}^3$ -hybrid type  $\text{C}(\text{sp}^3)\text{-I}$  bond, the R substituent has an effect on the BDEs in the following way: The electron-withdrawing and electron-donating inductive effect, combined with the conjugate effect, together influence the C-I BDE. In other words, the C-I BDE is influenced by the stability difference between the iodide molecules and corresponding radicals (Fig.2(a)), and the competition between the inductive effect and the conjugate effect of R on molecules and radicals determines the C-I BDE value.

In the Table III, the C-I bond lengths are in the range of 2.168–2.444 Å, and there is about 0.3 Å difference between the maximum and minimum value. The natural charges of C atom are in the range from -0.174 e to -0.686 e, while a certain degree of negative charges on I atom was found in several molecules. In general, the C-I BDE values are smaller, there are

TABLE IV The 14 C(sp<sup>2</sup>)–I BDEs (in kJ/mol) with values of C–I bond length in Å,  $q_C$ , and  $q_I$ .

Molecule	BDE	Bond length	$q_I/e$	$q_C/e$
I–HC=CH <sub>2</sub>	274.5	2.126	0.129	–0.405
O <sub>2</sub> NCH=CH–I	280.0	2.092	0.238	–0.385
COOHCH=CH–I	278.6	2.107	0.188	–0.354
HC=OCH=CH–I	278.4	2.103	0.202	–0.374
F <sub>3</sub> C–CH=CH–I	274.8	2.107	0.198	–0.372
NCCH=CH–I	282.8	2.100	0.206	–0.352
HCONHCH=CH–I	279.4	2.112	0.161	–0.466
H <sub>3</sub> CCONHCH=CH–I	276.2	2.122	0.131	–0.444
C <sub>2</sub> H <sub>5</sub> OCH=CH–I	281.2	2.115	0.132	–0.478
H <sub>3</sub> COCH=CH–I	280.7	2.114	0.134	–0.479
(CH <sub>3</sub> ) <sub>2</sub> NCH=CH–I	308.6	2.124	0.116	–0.521
H <sub>3</sub> CNHCH=CH–I	282.2	2.123	0.116	–0.532
C <sub>2</sub> H <sub>5</sub> NHCH=CH–I	282.2	2.124	0.114	–0.530
NH <sub>2</sub> CH=CH–I	281.8	2.121	0.118	–0.509

more negative charges on C atom.

The sp<sup>2</sup>-hybrid type C(sp<sup>2</sup>)–I BDEs by using MPWLYP1M method of 14 molecules with different substituents R (Fig.2(b)) are demonstrated in Table IV. The natural charges of C and I atom, which are expressed by  $q_C$  and  $q_I$  and the C–I bond lengths are also listed.

From Table IV, we can see that the sp<sup>2</sup>-hybrid type C(sp<sup>2</sup>)–I BDEs of 14 molecules are in the range of 274.5–308.6 kJ/mol, and there is about 30 kJ/mol difference. The smallest C–I BDE value appears in iodoethene molecule, which is unsubstituted. There is some degree of increase in C–I BDE when the molecule was substituted by R whether it is a electron-withdrawing or electron-donating group (Fig.2(b)). The largest BDE is found in 2-iodo-*N,N*-dimethylethanamine molecule ((CH<sub>3</sub>)<sub>2</sub>NCH=CH–I), in which the R is N(CH<sub>3</sub>)<sub>2</sub>. The result is consistent with C(sp<sup>3</sup>)–I in Table III. Differently, the electron-withdrawing inductive effect and conjugate effect of the R substituents on C–I BDE is not significantly comparing with the C(sp<sup>3</sup>)–I bond in Table III. For example, the C–I BDE of 3-iodoacrylonitrile molecule (NCCH=CH–I) is 282.8 kJ/mol, in which the –CN is a substituent with electron-withdrawing inductive and conjugate effect. For the 1-iodo-2-methoxyethene molecule (H<sub>3</sub>COCH=CH–I), the BDE is 280.7 kJ/mol, in which the –OCH<sub>3</sub> is a group with electron-donating property. There is no large difference between them. It is probably due to the electron delocalization of R through the C=C double bond. The electronic delocalization weakened the effect of R substituents on the C–I BDE.

The C–I bond length in Table IV is in the range of 2.092–2.126 Å, which also has little differences. Comparing the C–I BDE values in Table IV with those in

Table III, we found that the C(sp<sup>2</sup>)–I BDEs are much larger than C(sp<sup>3</sup>)–I BDEs. It is probably because these is a  $\sigma$ - $\pi$  hyperconjugation between C=C double bond and C–I single bond. Consequently, the  $\pi$  electron delocalization effect increases the stability of the iodide molecule, and it is followed by a C–I BDE increase. The natural charges of C and I atom in Table IV are in the range from –0.352 e to –0.532 e and 0.114–0.238 e respectively. For the 14 C(sp<sup>2</sup>)–I molecules, there are positive charges on all the I atoms and negative charges on all the C atoms. It shows that the polarity of C(sp<sup>2</sup>)–I bond is stronger than C(sp<sup>3</sup>)–I bond, which is consistent with the order of BDE values.

The C–I BDEs of 12 types of substituted iodobenzene using MPWLYP1M method with different substituents R locations at benzene ring including *o*-, *m*-, *p*- positions (Fig.2(c)) are displayed in Table V. The natural charges of C and I atom, denoted as  $q_C$  and  $q_I$  and the C–I bond lengths are also shown.

For 12 types of substituted iodobenzene in Table V, the C–I BDEs are in the range of 252.7–299.9 kJ/mol. There are about 45 kJ/mol difference between the maximum and minimum BDE values. The MPWLYP1M C–I BDE of iodobenzene is 278.9 kJ/mol. For the electron-donating substituents R, there is a little change in C–I BDE comparing with iodobenzene regardless of the *o*-, *m*-, and *p*- positions. For example, when R is –OCH<sub>3</sub>, which is a substituent with typical electron-donating property, the C–I BDEs of *o*-, *m*-, and *p*- positions are 280.8, 278.5, and 282.9 kJ/mol respectively. In addition, the BDE differences between different positions are also small for –OCH<sub>3</sub> group. The same conclusion can be obtained for other electron-donating substituents R. So it was found that for substituted iodobenzene the electron-donating group has little effect on C–I BDEs and the remote substituent effect is also not obvious. In comparison, the electron-withdrawing substituents R shows stronger effect. For example, the C–I BDE of *m*-COOH substituted iodobenzene is 252.7 kJ/mol, which is about 25 kJ/mol smaller than iodobenzene. And a certain degree of remote substituent effect was exhibited. For –NO<sub>2</sub> substituted iodobenzene, the C–I BDEs of *o*-, *m*- and *p*- positions are 256.9, 299.9, and 276.6 kJ/mol respectively. There are about 40 kJ/mol difference between the maximum and minimum. It should be noted that for –NO<sub>2</sub>, –COOH groups *etc.*, in addition to the electron-withdrawing inductive effect, the conjugative effect can also play a role in C–I BDEs. And the same effect can be produced on the corresponding radicals (Fig.3). The overall effects determine the C–I BDE values.

The C–I bond length in Table V is in the range of 2.123–2.149 Å, which has very little differences. And the natural charges of C and I atom in Table V are in the range from –0.162 e to –0.282 e and 0.118 e to 0.226 e respectively.

We also calculated the C–I BDEs of 8 types of substituted (iodomethyl)benzene using MPWLYP1M method

TABLE V The C–I BDEs (in kJ/mol) of substituted iodobenzene with values of C–I bond length in Å,  $q_C$ , and  $q_I$ .

Substitute	BDE	Bond length	$q_I/e$	$q_C/e$
<i>o</i> -NO <sub>2</sub>	256.9	2.127	0.226	-0.223
<i>m</i> -NO <sub>2</sub>	299.9	2.131	0.182	-0.209
<i>p</i> -NO <sub>2</sub>	276.6	2.127	0.191	-0.200
<i>o</i> -COOH	259.3	2.137	0.202	-0.186
<i>m</i> -COOH	252.7	2.133	0.173	-0.205
<i>p</i> -COOH	279.4	2.132	0.168	-0.196
<i>o</i> -CHO	266.7	2.133	0.204	-0.192
<i>m</i> -CHO	276.2	2.136	0.163	-0.207
<i>p</i> -CHO	279.5	2.132	0.174	-0.196
<i>o</i> -F	281.3	2.123	0.185	-0.282
<i>m</i> -F	277.7	2.136	0.161	-0.200
<i>p</i> -F	280.3	2.136	0.155	-0.224
<i>o</i> -Cl	272.3	2.129	0.181	-0.240
<i>m</i> -Cl	276.9	2.136	0.160	-0.197
<i>p</i> -Cl	280.0	2.133	0.158	-0.218
<i>o</i> -CN	275.3	2.126	0.204	-0.186
<i>m</i> -CN	277.2	2.132	0.174	-0.210
<i>p</i> -CN	278.8	2.130	0.178	-0.162
<i>o</i> -CH <sub>3</sub>	276.0	2.149	0.127	-0.203
<i>m</i> -CH <sub>3</sub>	278.8	2.142	0.135	-0.194
<i>p</i> -CH <sub>3</sub>	280.7	2.139	0.136	-0.212
<i>o</i> -NH <sub>2</sub>	282.0	2.147	0.118	-0.242
<i>m</i> -NH <sub>2</sub>	279.5	2.142	0.133	-0.186
<i>p</i> -NH <sub>2</sub>	283.6	2.138	0.127	-0.234
<i>o</i> -OH	281.1	2.128	0.168	-0.257
<i>m</i> -OH	281.1	2.138	0.148	-0.194
<i>p</i> -OH	285.6	2.137	0.140	-0.230
<i>o</i> -OCH <sub>3</sub>	280.8	2.130	0.162	-0.241
<i>m</i> -OCH <sub>3</sub>	278.5	2.139	0.142	-0.195
<i>p</i> -OCH <sub>3</sub>	282.9	2.138	0.135	-0.228
<i>o</i> -NHCHO	276.9	2.149	0.137	-0.221
<i>m</i> -NHCHO	277.5	2.137	0.155	-0.190
<i>p</i> -NHCHO	281.4	2.136	0.147	-0.220
<i>o</i> -COOCH <sub>3</sub>	259.8	2.139	0.190	-0.186
<i>m</i> -COOCH <sub>3</sub>	278.1	2.136	0.155	-0.206
<i>p</i> -COOCH <sub>3</sub>	279.7	2.133	0.162	-0.198

with different substituents R locations at benzene ring including *o*-, *m*-, *p*- (Fig.2(d)). The results are also shown in Table VI.

From Table VI, we can see that the C–I BDEs of 8 types of substituted (iodomethyl)benzene, which belongs to C(sp<sup>3</sup>)–I type, are in the range of 173.8–188.4 kJ/mol, and there is only about 15 kJ/mol difference. The MPWLYP1M C–I BDE of (iodomethyl)benzene is 183.5 kJ/mol. It can be concluded that whether R is electron-withdrawing, electron-donating or conjugate sub-

TABLE VI The C–I BDEs (in kJ/mol) of substituted (iodomethyl)benzene with values of C–I bond length in Å,  $q_C$ , and  $q_I$ .

Substitute	BDE	Bond length	$q_I/e$	$q_C/e$
<i>o</i> -CH <sub>3</sub>	183.5	2.253	-0.00406	-0.531
<i>m</i> -CH <sub>3</sub>	183.6	2.245	0.00324	-0.533
<i>p</i> -CH <sub>3</sub>	186.1	2.249	-0.00317	-0.532
<i>o</i> -OH	182.2	2.248	-0.00099	-0.535
<i>m</i> -OH	183.8	2.240	0.0140	-0.536
<i>p</i> -OH	183.0	2.257	-0.0148	-0.530
<i>o</i> -OCH <sub>3</sub>	182.5	2.252	-0.00813	-0.531
<i>m</i> -OCH <sub>3</sub>	188.4	2.242	0.00929	-0.534
<i>p</i> -OCH <sub>3</sub>	183.2	2.259	-0.0197	-0.528
<i>o</i> -NH <sub>2</sub>	188.3	2.284	-0.0521	-0.523
<i>m</i> -NH <sub>2</sub>	184.6	2.244	0.00253	-0.532
<i>p</i> -NH <sub>2</sub>	182.4	2.271	-0.0408	-0.522
<i>o</i> -CN	175.3	2.229	0.0480	-0.553
<i>m</i> -CN	181.6	2.230	0.0390	-0.547
<i>p</i> -CN	175.7	2.232	0.0391	-0.548
<i>o</i> -COOH	177.5	2.234	0.0291	-0.544
<i>m</i> -COOH	183.2	2.235	0.0264	-0.542
<i>p</i> -COOH	176.8	2.234	0.0318	-0.544
<i>o</i> -CHO	177.8	2.233	0.0382	-0.554
<i>m</i> -CHO	183.4	2.232	0.0320	-0.544
<i>p</i> -CHO	174.2	2.233	0.0359	-0.546
<i>o</i> -NO <sub>2</sub>	174.2	2.226	0.0513	-0.554
<i>m</i> -NO <sub>2</sub>	181.4	2.228	0.0446	-0.549
<i>p</i> -NO <sub>2</sub>	173.8	2.228	0.0500	-0.551

stituent, there is little effect on C–I BDEs for substituted (iodomethyl)benzene. In addition, the effect of the position at the benzene ring of the R substituents on the BDEs are small, regardless of *o*-, *m*-, and *p*- locations. It shows that the remote substituent effect of electron-withdrawing and electron-donating groups R on C–I BDEs of (iodomethyl)benzene is not obvious. It can be explained as the electron delocalization effect of R through the  $\pi$  bond in benzene. The electronic dispersion greatly weakened the effect of R substituents on C–I BDE in substituted (iodomethyl)benzene.

The C–I bond length in Table VI is in the range of 2.226–2.284 Å, which also has very little differences. And the natural charges of C atom in Table VI are in the range from -0.522 e to -0.554 e. Similar to the results in Table III, a certain degree of negative charges on I atom was found in several molecules. The little difference of  $q_C$  between different molecules in Table VI is consistent with the little BDE values difference.

In view of the significance of the heteroaromatic compounds in biological and medical applications, we finally predicted the C–I BDEs of several typical heteroaromatic compounds (Fig.3) using MPWLYP1M method. The BDE values, the C–I bond lengths and the  $q_C$ ,  $q_I$

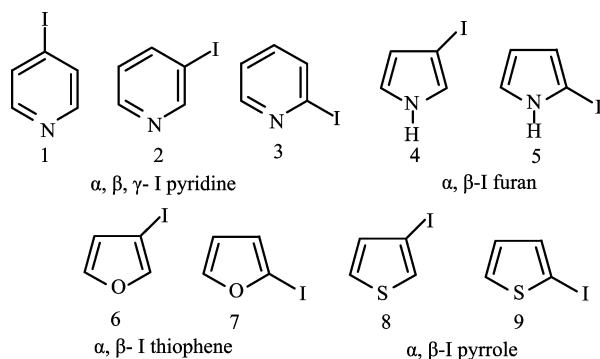


FIG. 3 Several typical heteroaromatic compounds.

values are shown in Table VII. The values of Wiberg bond index (WBI) [45] of C–I obtained by NBO analysis are also listed.

It can be seen from Table VII that the C–I BDE values of five-membered mono-heterocyclic compounds, including furan, thiophene and pyrrole (Nos.4–9, shown in Fig.3) are much larger than six-membered mono-heterocyclic compounds, *i.e.* pyridine (Nos.1–3). The BDEs of thiophene (Nos.8, 9, shown in Fig.3) are slightly smaller than furan and pyrrole (Nos.4–7, shown in Fig.3), and the BDE differences between them are very little. For pyridine ring, a sharp decrease in C–I BDE is found when I atom is located at  $\alpha$ -position of hetero-atom compared with  $\beta$ - and  $\gamma$ -positions. It may be due to the effect of the lone-pair electrons of N atom on C–I bond. By comparison, for five-membered ring, *i.e.* furan, thiophene, and pyrrole, there are very small differences regardless of  $\alpha$ - and  $\beta$ -positions of I atom.

The C–I bond length of the heteroaromatic compounds in Table VII is in the range of 2.087–2.151 Å. And the natural charges of I atom in Table VII are in the range of 0.136–0.229 e. A certain degree of positive charges on C atom was found in several molecules. The C–I WBI values of the heteroaromatic compounds in Table VII is in the range of 0.7117–1.006. Most of the values are less than 1, which was explained by the electron delocalization of C–I bond through the heterocyclic ring. In comparison, the WBI differences among the five-membered mono-heterocyclic compounds are small.

#### IV. CONCLUSION

The C–I bond dissociation enthalpies of various organic iodides were calculated using high-level theoretical methods including MP2 and CCSD(T) with extrapolated basis set as well as a number of DFT methods. The results indicated that the MP2 and CCSD(T) methods are not recommended for the C–I BDE calculation. Among the different DFT methods, it was found that MPWLYP1M gave the lowest root mean square error and the best computational accu-

TABLE VII The C–I BDEs (in kJ/mol) of several typical heteroaromatic compounds with values of C–I bond length in Å,  $q_C$ ,  $q_I$ , and WBI.

Molecule <sup>a</sup>	BDE	Bond length	$q_I/e$	$q_C/e$	WBI
1	273.4	2.132	0.168	−0.202	1.006
2	276.5	2.130	0.164	−0.253	0.7252
3	257.5	2.151	0.136	0.049	0.7117
4	305.2	2.107	0.160	−0.314	0.7360
5	305.1	2.098	0.176	−0.0707	0.7503
6	304.6	2.100	0.194	−0.340	0.7407
7	303.0	2.087	0.219	0.0607	0.7616
8	288.8	2.120	0.175	−0.276	0.7318
9	292.5	2.104	0.229	−0.447	0.7523

<sup>a</sup> The molecules structures are shown in Fig.3.

racy. On the basis of the MPWLYP1M results, we discussed the substituent effect of different types of C–I bonds, including the  $sp^3$ -hybrid type  $C(sp^3)$ –I and the  $sp^2$ -hybrid type  $C(sp^2)$ –I. Simultaneously, the remote substituent effects of substituted iodobenzene and substituted (iodomethyl)benzene were also investigated. It shows that the remote substituent effect of electron-withdrawing and electron-donating groups on C–I BDEs of (iodomethyl)benzene is not obvious. Furthermore, we predicted MPWLYP1M C–I BDE values of several typical heteroaromatic compounds including five-membered and six-membered heterocyclic compounds.

#### V. ACKNOWLEDGMENTS

This work was supported by the School Technology Development Funding (No.2011XZ06). We also thank Dawning A950r-F server and Shanghai Supercomputer Center for the computational resources.

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