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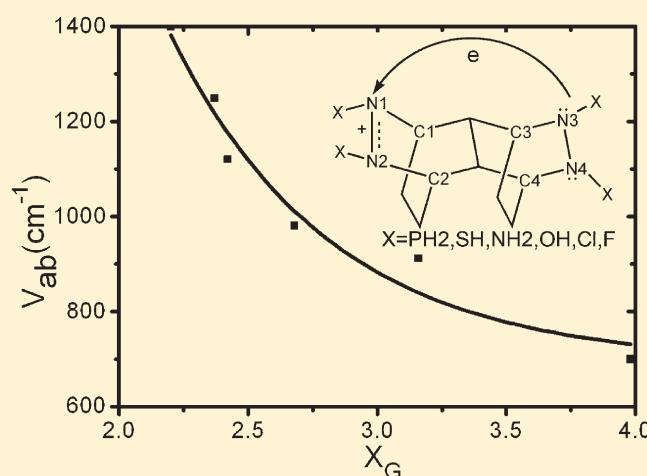
# Effect of Group Electronegativity on Electron Transfer in Bis(hydrazine) Radical Cations

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**S** Supporting Information

**ABSTRACT:** The radical cation of 4,10-ditert-butyl-5,9-diisopropyl-4,5,9,10-tetraazatetracyclo[6.2.2.2]-tetradecane (sBI4T<sup>+</sup>), as well as its substituted bis(hydrazine) radical cations, is chosen for the investigation of the electronegativity dependence of its intramolecular electron transfer. To do so, two parameters, reorganization energy and electronic coupling, are calculated with several ab initio approaches. It is found that the electronic couplings decrease with the increase of the group electronegativity while the reorganization energies do not show an explicit dependency. Furthermore, Marcus formula is employed to reveal those effect on the electron transfer rates. The predicted rates of electron transfer generally decrease with increasing group electronegativity, although not monotonically.



## 1. INTRODUCTION

Electron transfer (ET) in organic radicals is one of the most significant processes in radical reactions. A large amount of work has been done for the investigation of the mechanism of this process. Since the 1980s, many intervalence compounds have been synthesized, and ET theory is employed to explain their intramolecular ET.<sup>1–6</sup> The charged intervalence compounds are composed of two charge-bearing units and a bridge, and the electron can transfer between the two units. Therefore, the Marcus two-state model<sup>7–9</sup> is applicable to describe ET. In this model, the ET rate is controlled by two parameters, electronic coupling ( $V_{ab}$ ) and reorganization energy ( $\lambda$ ).  $V_{ab}$  measures the electronic interaction between the two localized states.  $\lambda$  represents the energy cost due to geometry modifications to go from a neutral to a charged molecule and vice versa, and it also indicates the electron–phonon coupling strength.

Several detailed ab initio calculations have shown that those parameters are sensitive to molecular geometry and environment. For instance, Valeev et al.<sup>10</sup> have investigated the rotational dependence of the electronic coupling in the ethylene dimer and found that  $V_{ab}$  changes obviously with the tilt angle. Skourtis et al.<sup>11</sup> have studied the fluctuation of electronic coupling in biology systems to reveal the dynamic disorder effect on ET. Bromley et al.<sup>12</sup> have calculated the dependence of the reorganization energy on carrier localization. Recently, we have also shown that the environment indeed influences the electronic coupling in dithiophene-tetrathiafulvalene crystal.<sup>13</sup>

For intervalence radical ion compounds, Nelsen and co-workers have synthesized a series of such compounds and found some rules for the geometry dependences of the ET parameters.<sup>14,15</sup> They,<sup>16</sup> for example, have measured the parameters of ET for cationic bis(hydrazine) compounds and studied the effects of the number of  $\sigma$  bonds and the hydrazine substituent on the electronic coupling. In addition, Johnson et al.<sup>17</sup> have studied the ET distances of these compounds, and found that electron-withdrawing groups usually slightly lengthen the distance while electron-releasing groups slightly shorten the distance.

It is seen that most investigations have explored the effects of molecular geometry and environment on ET. However, few discussions about the relationship between group electronegativity and ET are reported. Therefore, we focus on this problem in the present paper. It is known that the electronegativity introduced by Pauling<sup>18,19</sup> is one of the very useful concepts in the whole field of chemistry. It describes the ability of an atom or a functional group to attract electrons (or electron density) toward itself. One may expect that it has the explicit effect on ET.

In the present work, we take one of bis(hydrazine) compounds, 4,10-ditert-butyl-5,9-diisopropyl-4,5,9,10-tetraazatetracyclo[6.2.2.2]-tetradecane, sBI4T<sup>+</sup>, shown in Figure 1, as a parent molecule to investigate electronegativity effect on ET by

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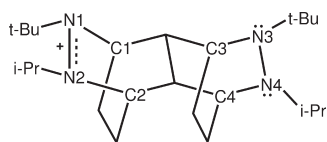


Figure 1. Structure of sBI4T<sup>+</sup>.

substituting the alkyl. The sBI4T<sup>+</sup> compound has been extensively studied by experimental measurements and theoretical calculations.<sup>14,16,20</sup> It is revealed that the intramolecular ET rate is very sensitive to the geometry about the nitrogen atoms, the NN distance, nitrogen pyramidity, and the lone pair, lone pair dihedral angle. All these properties are sensitive to the alkyl groups attached to nitrogen.<sup>21</sup> One thus expects that the substituent of the alkyl should have an obvious influence on ET. Here, we take NH<sub>2</sub>, PH<sub>2</sub>, etc., as the substituents because they have explicitly different electronegativity. By use of ab initio calculations and the Marcus formula, we expect to find the dependencies of  $V_{ab}$  and  $\lambda$  as well as ET rate on the electronegativity. The corresponding conclusion may be useful for the experimental synthesis of efficient ET systems.

The paper is arranged as follows. In section 2, we briefly summarize the computational methods of the group electronegativity, reorganization energy, and electronic coupling. Section 3 presents the electronegativity effects on the ET parameters as well as on the ET rate. The concluding remarks are given in section 4.

## 2. CALCULATION METHODS

**2.1. Group Electronegativity.** In the 1950s, Sanderson<sup>22</sup> intuitively proposed the principle of electronegativity equalization. This principle says that when two or more elements initially different in electronegativity combine chemically, they become adjusted to the same, intermediate electronegativity within the compound. Later, several formulas have also been suggested for the calculations of electronegativity.<sup>23–31</sup> Although the calculation methods are a little different, they predict similar tendencies of electronegativity changes in terms of the substituents.<sup>31</sup> Here, we take a simple formula proposed by Bratsch through the application of the Sanderson's principle of electronegativity equalization to calculate the electronegativity. The Bratsch method<sup>31</sup> predicts the electronegativity  $X_G$  by

$$X_G = \frac{N}{\sum_A \left( \frac{N_A}{X_A} \right)} \quad (1)$$

where  $N$  is the total number of atoms of the group and  $X_A$  and  $N_A$  are the Pauling electronegativity and the number of atom A in the group, respectively.

**2.2. Reorganization Energy and Electronic Coupling.** The reorganization energy in ET consists of inner and outer parts,  $\lambda_v$  and  $\lambda_s$ , respectively.  $\lambda_v$  refers to the geometry changes of the donor and acceptor, while  $\lambda_s$  comes from the response of surrounding solvent. Here, we are only interested in the inner reorganization energy. Thus, the straightforward four-point method<sup>32</sup> can be used to calculate it. In this method, ET is considered as a reaction of  $D + A^+ \rightarrow D^+ + A$ . The  $DA^+$  and  $D^+A$  correspond to the initial and the final states of ET process, respectively. The reorganization energy  $\lambda_v$  is given by<sup>5,32–38</sup>

$$\lambda_v = \lambda_1 + \lambda_2 = (E_A^0 - E_A^+) + (E_D^+ - E_D^0) \quad (2)$$

Here,  $E_A^0$  and  $E_A^+$  are the energies of the neutral acceptor A at the cation and optimized ground-state geometries, respectively, and  $E_D^0$  and  $E_D^+$  are, accordingly, energies of the radical cation D<sup>+</sup> at the neutral and optimal cation geometries. In the concrete implementation, the molecule either can be split into two parts that are calculated separately or can be taken as a whole to calculate.<sup>39</sup>

For the electronic coupling, there are two kinds of strategies that have been proposed to estimate it. One starts from the diabatic representation, and the other from the adiabatic representation. Several approaches have been proposed to calculate the electronic coupling along these clues.<sup>40–42</sup> Here, we only describe three kinds of approaches which are used in the paper.

In the diabatic representation, the electronic coupling is straightforwardly related to the off-diagonal elements of the Hamiltonian of the two charge-localized states. The method is commonly named as two-state model (TM). Once the two diabatic state wave functions  $\Psi_a$  and  $\Psi_b$  are known, the electronic coupling can be calculated by<sup>43–45</sup>

$$V_{ab} = \frac{h_{ab} - \frac{1}{2}(h_{aa} + h_{bb})s_{ab}}{1 - s_{ab}^2} \quad (3)$$

where  $s_{ij} = \langle \Psi_i | \Psi_j \rangle$  and  $h_{ij} = \langle \Psi_i | H | \Psi_j \rangle$ .

In the adiabatic representation, Koopmans theorem (KT)<sup>37,46</sup> is extensively used to estimate the electronic coupling in one-electron approximation. In this model, the electronic coupling is related to the energies of the frontier molecular orbitals (MO) at the transition state (TS) geometry, and it is given by<sup>47–51</sup>

$$V_{ab} = \frac{\varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO}} - 1}{2} \quad (\text{for cations})$$

$$V_{ab} = \frac{\varepsilon_{\text{LUMO}} + 1 - \varepsilon_{\text{LUMO}}}{2} \quad (\text{for anions}) \quad (4)$$

Here,  $\varepsilon_i$  is the MO energies of the neutral compound at the TS geometry. HOMO and LUMO represent the highest occupied MO and the lowest unoccupied MO, respectively.

An alternative approach is the generalized Mulliken–Hush (GMH) method, in which the electronic coupling is related to the dipole moments and vertical transition energy at the optimized geometry. The electronic coupling is given by<sup>35,52–55</sup>

$$V_{ab} = \frac{\mu_{ab} \Delta E_{ab}}{\sqrt{\Delta \mu_{ab}^2 + 4\mu_{ab}^2}} \quad (5)$$

where  $\mu_{ab}$  is the transition dipole moment,  $\Delta E_{ab}$  is the energy gap, and  $\Delta \mu_{ab}$  is the dipole moment difference between the initial and final adiabatic states. It is known that the GMH is very suitable to calculate the electronic coupling at the optimized geometry while the KT only works at the TS geometry. Thus, one may investigate the reaction-path dependence of the electronic coupling by comparing the values from these approaches.

We use the Gaussian09 suite<sup>56</sup> in the ab initio calculations. The optimized geometries are obtained at the Hartree–Fock (HF) and the density functional theory (DFT) levels with two hybrid functionals, B3LYP and 50–50 (50% Hartree–Fock + 8% Slater + 42% Becke for exchange and 19% VWN + 81% LYP for correlation).<sup>57</sup> The 6-31 g(d) basis set is adopted. We also use the semiempirical AM1 method for the purpose of the comparison.

**Table 1.** Comparison of X-ray and Optimized Structural Parameters of sBI4T and Its Cationic Compound (Units for Bond Angle and Length are Degree and Angstrom)

method	$\angle \text{C4N4C}_i / \angle \text{C2N2C}_i^d$	$\angle \text{C4N4N3} / \angle \text{C2N2N1}$	$\angle \text{C}_i\text{N4N3} / \angle \text{C}_i\text{N2N1}$	N3N4/N1N2
X-ray <sup>a</sup>	116.03/110.63	110.43/110.53	111.23/116.23	1.482/1.483
DFT(50–50) <sup>b</sup>	117.40/111.50	111.02/111.65	112.77/117.75	1.447/1.441
DFT(B3LYP) <sup>b</sup>	117.20/111.26	110.82/111.34	112.34/117.33	1.474/1.468
HF <sup>b</sup>	117.91/111.47	111.32/111.79	113.06/118.34	1.448/1.443
AM1 <sup>b</sup>	114.17/110.11	111.00/111.67	112.93/115.74	1.418/1.415
DFT(50–50) <sup>c</sup>	116.84/115.46	111.06/113.42	112.96/127.01	1.447/1.339
HF <sup>c</sup>	117.44/114.77	111.40/113.54	113.27/128.22	1.450/1.330
AM1 <sup>c</sup>	113.98/113.73	111.01/113.26	113.15/126.33	1.418/1.325

<sup>a</sup> From ref 20. <sup>b</sup> For the neutral molecule. <sup>c</sup> For the cationic compound. <sup>d</sup> C<sub>i</sub> is the center carbon atom of the isopropyl.

### 3. RESULTS AND DISCUSSION

**3.1. ET Parameters of sBI4T<sup>+</sup>.** Before investigating the electronegativity effect, we calculate the ET parameters of sBI4T<sup>+</sup> in order to clarify the accuracy of different ab initio approaches. The X-ray experiment has shown that the neutral sBI4T molecule is in a conformation having its *in*-N-alkyl groups (directly toward the central CH–CH bond of the molecule) anti to each other (see Figure 1).<sup>20</sup> We optimize this neutral sBI4T as well as its cationic compound. The numerical results show that the bond angles related to the nitrogen have explicit changes in the cationic compound. Table 1 thus lists these angles from the X-ray measurement and theoretical calculations. For the neutral molecule, these bond angles obtained from DFT with 50–50 and B3LYP functionals are closer to the experimental ones than those from HF, and AM1 also gives better agreement with experiment except the C4N4 C<sub>i</sub> angle. For the cationic compound, the Mulliken charge can be localized on the cationic part (left) of sBI4T<sup>+</sup> over 75%. However, DFT with B3LYP is incapable of obtaining the electronic localized states, as previously noted for some bis(hydrazine) compounds.<sup>35,37</sup> Comparing the optimized geometries of the neutral sBI4T with sBI4T<sup>+</sup>, we found that these bond angles are almost the same in the right part while they obviously increase in the left part on which the charge is localized. It manifests that nitrogens switch to a flatter conformation in the cationic part. In the present calculations, different ab initio approaches predict the same tendency. The flatter geometry of the nitrogens in the cationic part may be explained by losing an electron from the lone pair electrons of a nitrogen because the left three electrons contribute to the partial double bond of the two nitrogens, which causes the bond angles to increase and breaks the initial pyramidal geometry. Alternatively, the flatter geometry could be easily strengthened by confirming that the N–N bond length in the cation is shorter than in the neutral molecule, as shown in Table 1.

On the basis of the optimized cation geometry, we use the four-point approach to estimate the inner reorganization energy  $\lambda_v$  of sBI4T<sup>+</sup>. In the calculations, we do not explicitly split the sBI4T<sup>+</sup> into D<sup>+</sup> + A but consider it as a whole and optimize sBI4T<sup>+</sup> and sBI4T, respectively. Then, the reorganization energy is calculated from eq 2. The results from the different optimized geometries are as follows: 31.77 kcal/mol (AM1), 41.48 kcal/mol (HF), and 37.38 kcal/mol (DFT with 50–50 functional). These values reveal that the more percent of the HF exchange is included, the higher reorganization energy is predicted, which is the same as our previous work.<sup>35</sup> It is also found that the data from DFT with 50–50 functional is very close to the experimental one (37.30 kcal/mol).<sup>16</sup>

Since the DFT (50–50 functional) seems to predict the good geometry, as well as the reorganization energy, we adopt it in the calculations of the electronic couplings. We first use the simple KT to estimate the electronic coupling. It is noted that the KT is only suitable at the TS geometry. The sBI4T<sup>+</sup> molecule, however, is not exactly symmetric, which makes it an uneasy task numerically to locate the TS geometry. Here, we use the linear reaction coordinate technique to locate the TS geometry which approximately corresponds to the minimum adiabatic energy gap along the reaction coordinate. The obtained electronic coupling is 1634 cm<sup>−1</sup>. To further check the validity of the present calculation, we draw the HOMO and HOMO-1 electronic clouds as well as their combinations, shown in Figure 2. One can see that the electronic density distributions of HOMO + (HOMO-1) and HOMO − (HOMO-1) are dominantly localized at the left and right sides, respectively. This property manifests that the KT is indeed applicable.

KT is a kind of methods starting from the adiabatic representation. An alternative method is the GMH. The GMH has an advantage that it is not necessary to determine the TS geometry, and it can be manipulated at the optimized donor (acceptor) geometry. The obtained electronic coupling is 1170 cm<sup>−1</sup>. The corresponding vertical transition energy is 40.74 kcal/mol, which is obtained by the TD-MPW1K<sup>58</sup> approach. This energy is generally close to the reorganization energy for a symmetric reaction with a weak coupling. However, it becomes larger than reorganization energy if the coupling is strong, and this is the case for the sBI4T<sup>+</sup> molecule.

The GMH approach is derived from a transformation of two diabatic states into two adiabatic states. At the optimized geometry, however, the properties of the ground and excited states are similar to those of the two diabatic states other than at the TS geometry. Figure 3 shows the electronic density distributions of the HOMO-1 and HOMO which refers to the MOs of ET. It explicitly illustrates this property.

Since the sBI4T<sup>+</sup> explicitly has two localized states, TM in diabatic representation should be useful. We use the NWChem program<sup>59</sup> to calculate the electronic coupling based on the TM. Despite the TM is suitable for any molecular geometry it is uneasy to localize electron to the donor or acceptor state in practice unless using some special methods, such as the constrained DFT.<sup>60</sup> However, the localized charge can be easily performed around the TS geometry. Therefore, we calculate the electronic coupling at the TS determined from the linear reaction coordinate technique,<sup>44,61</sup> and the obtained result is 1435 cm<sup>−1</sup>.

As expected, the electronic couplings predicted from the TM and KT are close. However, the value obtained from the GMH is



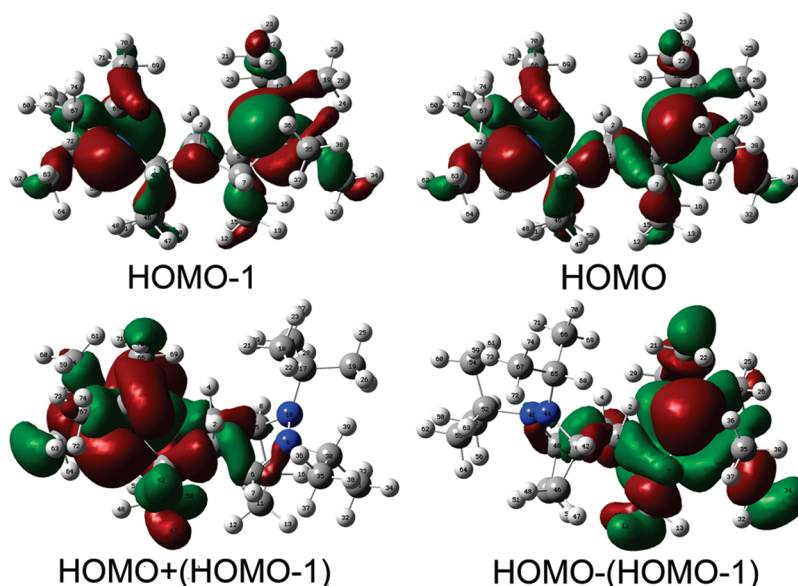


Figure 2. Molecular orbitals and their combinations of sBI4T<sup>+</sup> at the TS geometry.

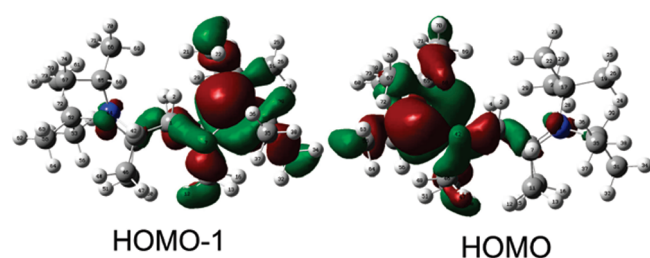


Figure 3. Molecular orbitals of sBI4T<sup>+</sup> at the optimized geometry.

Table 2. Group Electronegativity and the Parameters of ET for Different Hydrazine Radical Cations

group	PH2	SH	NH2	OH	Cl	F
$X_G$	2.20	2.37	2.42	2.68	3.16	3.98
$V_{ab}$ (cm <sup>-1</sup> )	1393	1246	1120	989	911	696
$\lambda_v$ (kcal/mol)	42.26	36.56	58.94	51.11	48.37	59.39
$k_{et}$ (10 <sup>4</sup> s <sup>-1</sup> )	675.93	6424.62	0.33	7.43	20.57	0.11

slightly smaller. It is known that the electronic coupling at the TS geometry generally has the maximum value. Therefore, the electronic coupling from the GMH should be smaller because the optimized geometry with a minimum energy is chosen. Despite the GMH does not predict the electronic coupling at the TS geometry, it is robust and easy implementation in the calculations. Also, one expects that the changes of the electronic coupling from the optimized geometry with respect to the substituents has the similar trend to that at the TS geometry. We thus choose the GMH in the following calculations.

**3.2. Group Electronegativity, Electronic Coupling, and Reorganization Energy.** Now, we focus on the electronegativity dependence of ET. As above-mentioned, the ET parameters are sensitive to the alkyl groups attached to nitrogen. We thus replace the four alkyl groups (see in Figure 1) by several substituents with different electronegativity. The core atoms of the substituents include two sets. One is N, O, and F, and the other is P, S,

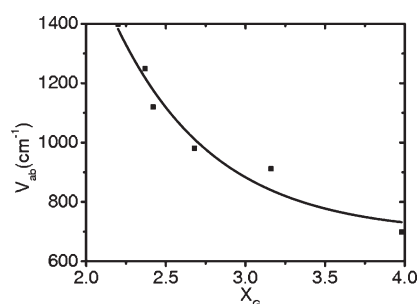


Figure 4. The electronic coupling dependence of the electronegativity.

and Cl. These atoms belong to two periods in the periodic table with the increase of electronegativity, and they are saturated by hydrogens to perform the substituents. In the calculation of group electronegativity, the values of  $X_A$  (see in eq 1) with the Pauling scale are used.

Table 2 lists the values of the group electronegativity, the electronic coupling, and the reorganization energy. It explicitly shows that the electronic couplings decrease with increasing of electronegativity. To see clearly, we plot the electronegativity dependence of the electronic coupling in Figure 4. This dependence can be fitted to an exponential form,  $V_{ab}(\text{cm}^{-1}) = 19120 e^{-1.51X_G} + 679$ .

To extensively understand this property, we consider the geometric changes caused by the electronegativity of the substituents. It is known that the nitrogen atom has five electrons in its valence shell, and it usually takes  $sp^3$  hybridization to form covalent bonds when it interacts with the other atoms. The left lone pair electrons show broader electronic cloud distribution than the bonding electrons. Thus, the lone pair electrons have stronger repulsions to bonding electrons than those among the bonding electrons, and the configuration of the nitrogen compound appears to be pyramidal. In the radical cation, an electron transfers away from the lone pair electrons, which results in more flattened nitrogen and smaller electronic coupling with stronger electronegativity, because the overlap of the wave functions of

**Table 3.** Electronic Couplings with Respect to the Number of  $-\text{CH}_3$ 

group	$\text{NH}_2$	$\text{NHCH}_3$	$\text{N}(\text{CH}_3)_2$	$\text{PH}_2$	$\text{PHCH}_3$	$\text{P}(\text{CH}_3)_2$
$X_G$	2.42	2.36	2.34	2.20	2.25	2.27
$V_{\text{ab}} (\text{cm}^{-1})$	1120	1147	1277	1393	1258	1210

the donor and acceptor states becomes smaller with a larger geometry change. It is noted that other factors, such as the steric effect, may have the effects on the geometry change. However, in the present investigations, the geometry change may be dominantly caused by the electronegativity because the substituents used here have similar geometries and properties. We further investigate the case where the saturated group for the core atoms is chosen as  $-\text{CH}_3$  other than  $-\text{H}$ . Table 3 lists the electronic couplings for P and N core atoms, respectively. It is seen that the electronic couplings do not change too much, manifesting that the core atoms dominantly influence the geometry changes and electronic couplings.

It is known that ET rate depends on both the electronic coupling and reorganization energy. Therefore, we calculate the electronegativity dependence of the reorganization energy. The results are also listed in Table 2. We do not find the explicit electronegativity dependence of it. One knows that the reorganization energy approximately equals to the transition energy. For atoms in the same period in the periodic table, the transition energies do not show special dependence with respect to the electronegativity. This is consistent with the present calculations. However, the transition energies generally decrease with decrease of the electronegativity for the atoms of the same group in the periodic table. Therefore, the reorganization energy should decrease. Indeed, Table 2 shows that  $\lambda_v(\text{F}) > \lambda_v(\text{Cl})$ ,  $\lambda_v(\text{O}) > \lambda_v(\text{S})$ , and  $\lambda_v(\text{N}) > \lambda_v(\text{P})$ .

**3.3. ET Rate.** Although the change of the electronic coupling has an explicit tendency with respect to the electronegativity, the reorganization energy does not. Thus, it is not clear how ET rate depends on the electronegativity. Here, we use the simple Marcus formula<sup>9,62</sup> to investigate this dependence. The ET rate  $k_{\text{et}}$  is given by

$$k_{\text{et}} = \frac{1}{\hbar} V_{\text{ab}}^2 \sqrt{\frac{\pi}{\lambda k_{\text{b}} T}} \exp\left(\frac{-(\Delta G + \lambda)^2}{4\lambda k_{\text{b}} T}\right) \quad (6)$$

where  $\Delta G$  represents the driving force. In the present calculations, it is found that the value of  $\Delta G$  is very small comparing to the reorganization, and we thus approximately take it as zero. The obtained ET rates are also listed in Table 2. The predicted rates of electron transfer generally decrease with increasing group electronegativity, although not monotonically. However, the ET rates always present a monotonic decrease in the same group in the periodic table because the electronic couplings decrease and the reorganization energies increase as the electronegativity increases.

#### 4. CONCLUDING REMARKS

We have investigated the electronegativity dependence of electron transfer for  $\text{sBI4T}^+$  and its substituted compounds. First, we use different ab initio approaches to calculate two important parameters for controlling electron transfer rates, electronic coupling, and reorganization energy. The four-point technique is used for the calculation of the reorganization energy,

and the electronic coupling is calculated by KT, TM, and GMH approaches, respectively. The calculated results from the DFT with 50–50 functional are consistent with experimental values for  $\text{sBI4T}^+$ . Then, we replace the alkyl groups in  $\text{sBI4T}^+$  by the groups with different electronegativity. The core atoms in the substituted groups are N, O, F, P, S, and Cl, respectively. It is shown that the electronic couplings decrease with the increase of the group electronegativity while the reorganization energies do not show an explicit dependency. Finally, we use the Marcus formula to estimate the electronegativity dependence of ET rates. It is found that the predicted rates of electron transfer generally decrease with increasing group electronegativity, although not monotonically. The conclusion may be helpful for synthesizing the compounds with efficient electron transfer.

#### ■ ASSOCIATED CONTENT

**Supporting Information.** The  $\text{sBI4T}$  and its radical cation as well as the substituted bis(hydrazine) radical cations' atom coordinates and absolute energies for calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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