

# Internal reorganization energy in return electron transfer within geminate radical ion pairs

Jian-xin Guo, Qi-yuan Zhang \*

State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 28 February 1997; accepted 16 June 1997

## Abstract

The internal reorganization energies  $\lambda$ , for return electron transfer (ET) reactions within geminate radical ion pairs were studied using the extended Nelsen method. In the ET systems studied, the common acceptor was 9,10-dicyanoanthracene (DCA). The donors were methyl-substituted compounds of benzene, biphenyl, naphthalene and phenanthrene. The calculated results indicated that the  $\lambda_e$  values were associated mainly with the carbon atoms of the aromatic rings and the atoms linked directly to the aromatic rings. Systems with similar substituted conditions are expected to have similar internal reorganization energies. For systems in which the two aromatic rings of the donor can rotate relative to each other, the calculated  $\lambda_e$  values include a contribution from the change in torsional angle in the ET process. Compared with the system in which the donor is a fluorene molecule, the contributions of the torsional angles (low-frequency vibration) to  $\lambda_e$  were estimated. © 1997 Elsevier Science S.A.

**Keywords:** Geminate radical ion pair; Internal reorganization energy; Return electron transfer

## 1. Introduction

Electron transfer (ET) reactions play an important role in the processes of chemistry and biology. It has been the goal of many researchers [1–3] to understand the factors controlling the rate of ET reactions. Although much work has been published on this topic, many questions remain unanswered. According to Marcus theory [4,5], the ET rate can be expressed as the product of the square of the electronic coupling matrix element  $V$  and the Franck–Condon weighted density of state (FCWD), i.e.

$$k_{\text{ET}} = \frac{2\pi}{\hbar} V^2 \cdot \text{FCWD} \quad (1a)$$

$$\text{FCWD} = \left( \frac{1}{4\pi\lambda k_B T} \right)^{1/2} \cdot e^{-1/4(\Delta G^0 + \lambda)^2 / (4\pi\lambda T)} \quad (1b)$$

where  $\Delta G^0$  is the change in the standard free energy of the reaction, which can be obtained from the reduction potential of the acceptor and the oxidation potential of the donor, and corrected for solvation energy and Coulomb work terms [1–3], and  $\lambda$  is the reorganization energy, which includes the

internal reorganization energy  $\lambda_e$ , and the solvent reorganization energy  $\lambda_s$ . The former can be derived from the vibration of the molecule and the latter can be derived from the polarization changes in the dielectric solvent environment. According to Marcus theory,  $\lambda_s$  can be obtained by considering the solvent as a dielectric continuum [4,5]

$$\lambda_s = (\Delta e)^2 \cdot \left[ \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right] \cdot \left[ \frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right] \quad (2)$$

where  $\Delta e$  is the transferred electric charge,  $a_1$ ,  $a_2$  and  $r$  are the radii of the donor and acceptor molecules and the centre-to-centre distance between them respectively,  $D_{\text{op}}$  is the optical dielectric constant of the solvent (the square of the refractive index) and  $D_s$  is the static dielectric constant of the solvent.

The internal reorganization energy  $\lambda_e$  is concerned with the change in the nuclear degrees of freedom, which is difficult to measure. X-Ray crystallography or extended X-ray absorption fine structure (EXAFS) analyses are usually used [6–8], but the structures obtained from a crystal may not always be relevant to the reaction in solution. Myers [9] recently used resonance Raman spectroscopy to obtain  $\lambda_e$ . Similar vibrational frequencies were adopted for the excited and ground states. This makes the results improved continu-

\* Corresponding author. Fax: 0086 1 2569564; e-mail: zhangqy@infoc3.icas.ac.cn

ously. In general, we can obtain  $\lambda_v$  by a curve-fitting procedure [10,11] in which the ET rate and driving force  $\Delta G^0$  are fitted. It is obvious from Eq. (1a) and Eq. (1b) that the fitting result of  $\lambda_v$  cannot be unique because of the variation in  $V$  and  $\lambda_e$ . Gould et al. [11–16] studied the return ET reactions  $D^+ + A^- \rightarrow D + A$ , where A was 9,10-dicyanoanthracene (DCA) (acceptor) and D was a simple aromatic hydrocarbon (donor). They suggested that the internal reorganization energy should be the same for systems with donors of similar size. Their preliminary curve-fitting results indicated that, for systems containing donors with two aromatic rings,  $\lambda_v \leq 0.6$  eV [12], and for systems containing donors with one aromatic ring,  $\lambda_v \leq 0.3$  eV [13]. In their later experiments,  $\lambda_v = 0.25$  eV was used to fit systems containing donors with one, two and three aromatic rings [11]. In their study of intramolecular ET, Closs et al. [10] found that this series of molecular systems should not be treated with a constant internal reorganization energy. Because of the lack of direct experimental results on  $\lambda_v$  values, the same  $\lambda_v$  values are used for different systems. It is therefore important to obtain  $\lambda_v$  values by  $\lambda_{v,calc}$  in chemical calculations [17].

To our knowledge, the calculation of  $\lambda_v$  for ET reactions of heteromolecular systems has not been reported in the literature. In this paper, Nelsen's method [18–20], which is used to calculate the internal reorganization energy in self-exchange ET reactions  $A + A^+ \rightarrow A^+ + A$ , is extended to treat the return ET reaction within geminate radical ion pairs. Our studies focus on the outer-sphere ET reaction which occurs between minimally interacting electron donors and acceptors [21,22]. New results and information were obtained.

## 2. Models and methods of calculation

The calculation model is the return ET reaction  $D^+ + A^- \rightarrow D + A$ , where D denotes the electron donor and A denotes the electron acceptor (DCA) (Fig. 1). Donors for systems (1)–(10), (11)–(15), (16)–(18) and (19)–(21) are methyl- or methylene-substituted benzene, biphenyl, naphthalene and phenanthrene respectively, shown in Fig. 2 and Fig. 3. These systems have been studied extensively by experimental methods [12–16] and were chosen for ease of comparison.

In the outer-sphere ET reaction within radical ion pairs, the interactions between the donor and acceptor were ignored because of the shielding of the solvent molecules. The internal reorganization energy for the return ET reaction within radical ion pairs can be expressed approximately as the sum of the contribution of the donor and acceptor as follows

$$\lambda_v = \lambda_v(D) + \lambda_v(A) \quad (3)$$

which can be derived from the changes in the Gibbs free energy corresponding to the changes in the nuclear configuration in the ET reaction. If the changes in entropy are

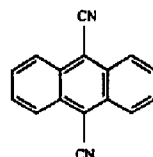


Fig. 1. Acceptor 9,10-dicyanoanthracene (DCA).

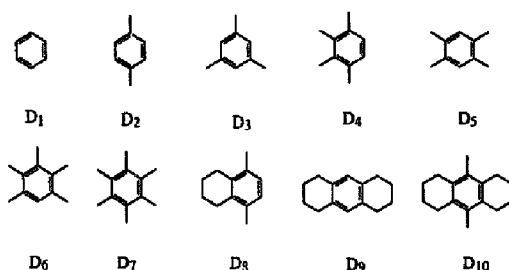


Fig. 2. Donor with one aromatic ring.

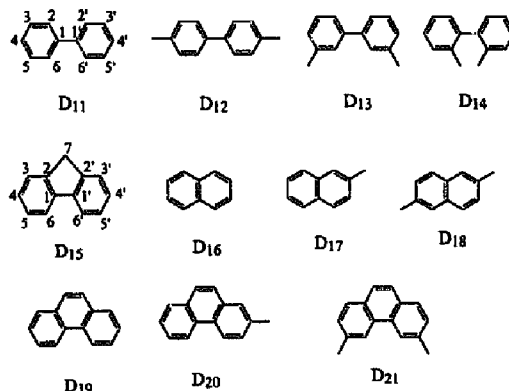


Fig. 3. Donor with two or three aromatic rings.

neglected [18,19],  $\lambda_v(D)$  can be obtained approximately from the changes in enthalpy

$$\lambda_v(D) = \Delta H_f^0(Dc0) - \Delta H_f^0(Dn0) \quad (4)$$

where Dn0 and Dc0 indicate the donor molecules without net charge, but with the geometry of the neutral species and cation radical respectively. In the same way,  $\lambda_v(A)$  can be obtained as

$$\lambda_v(A) = \Delta H_f^0(Aa0) - \Delta H_f^0(An0) \quad (5)$$

where Aa0 and An0 indicate the acceptor molecules without net charge, but with the geometry of the anion radical and neutral species respectively.

The AM1 hamiltonian [23] in the MOPAC program [24] (version 6.12) was used. All the geometrical parameters were optimized by the eigenvector following (EF) method [25] until the gradient norm was less than  $0.01 \text{ kcal } \text{Å}^{-1}$ . The neutral species were calculated at the restricted Hartree-Fock (RHF) level and, for the open-shell radical anions and cations,

ons, the unrestricted Hartree–Fock (UHF) level was used. In order to confirm the reasonable nature of the AM1-optimized results, ab initio calculations at the HF/3-21G level were completed for donors with two aromatic rings, biphenyl (D11) and fluorene (D14), using the GAUSSIAN 92/DFT program [26]. Atoms in each aromatic ring remained coplanar. The biphenyl and fluorene were restricted in symmetry  $C_2$  and  $C_{2v}$ , respectively.

### 3. Results and discussion

#### 3.1. Geometrical structures

Fluorene (D15) and biphenyl (D11) have  $C_{2v}$  and  $C_2$  symmetry respectively. The numbering of the atoms is depicted in Fig. 3. The optimized bond lengths, bond angles and torsional angles of the biphenyl molecule for both neutral species and radical cation (AM1 and ab initio calculations at the HF/3-21G level) are displayed in Table 1. The corresponding results from other HF calculations at the STO-3G [27], 6-31G\* and 6-31G\*\* [28] levels and from experimental studies [29] are also included for comparison. For the neutral species, the AM1-optimized bond lengths and bond angles are in good agreement with the X-ray results. The AM1-optimized torsional angle C2C1C1'C2' between the two aromatic rings of biphenyl is 40.6°, which is 10% lower than the experimental value of 44.4° [29]. It is obvious that the two aromatic rings of the neutral biphenyl molecule are twisted considerably in the ground state.

For fluorene, the calculated geometrical parameters at the AM1 and HF/3-21G levels are listed in Table 2. The calculated geometrical parameters of Lee and Boo [30] at the HF/6-31G\*, MP2/6-31G\* and B3LYP/6-31G\* levels are also shown, as well as the corresponding X-ray results [31]. The

AM1-calculated bond length C1C2 is overestimated in contrast with the underestimation of the other HF results. The bond length C2C3 is underestimated by all methods. For the other bond lengths, the AM1-calculated values are close to the X-ray results and as good as the other more precise methods. The calculated bond angles by AM1 are close to those of the other methods, and do not deviate significantly from the X-ray results.

The calculated (AM1 method) geometrical parameters of the radical cations of biphenyl and fluorene are also listed in Table 1 and Table 2 respectively. The bond length C1C2 in biphenyl increases from 1.402 Å in the neutral species to 1.434 Å in the radical cation. In contrast with C1C2, C1C1' of biphenyl decreases from 1.462 Å in the neutral species to 1.416 Å in the radical cation. This is probably due to the loss of a  $\pi$  electron, the decrease in the interaction between the  $\pi$  orbitals of the two aromatic rings and the decrease in the torsional angle C2C1C1'C2' for biphenyl. This is confirmed by the computational results which show that the angle C2C1C1'C2' decreases from 40.6° in the neutral species to 15.9° in the radical cation of biphenyl. For fluorene, C1C2 increases from 1.429 Å in the neutral species to 1.458 Å in the radical cation. C1C1' decreases from 1.461 Å to 1.412 Å. This is similar to the case of biphenyl. In addition, C4C5 increases from 1.392 Å to 1.411 Å and C5C6 decreases from 1.402 Å to 1.385 Å. The other bond lengths are not changed significantly in the ET process.

For the donors studied in this paper, the carbon atoms in each aromatic ring are nearly coplanar in both the neutral species and the radical cation.

#### 3.2. The internal reorganization energy

##### 3.2.1. Systems containing donors with one aromatic ring

The enthalpies of formation  $\Delta H_f^\circ$  for donors D1–D10, calculated by the AM1 molecular orbital method, are listed

Table 1  
Optimized geometrical parameters of biphenyl (bond lengths in angstroms and bond angles in degrees)

	AM1 <sup>a</sup>	HF/STO-3G <sup>b</sup>	HF/3-21G	HF/6-31G <sup>c</sup>	HF/6-31G <sup>**</sup>	Experimental <sup>d</sup>
C1C2	1.402 (1.434)	1.395	1.396	1.393	1.393	1.406(4)
C2C3	1.393 (1.382)	1.386	1.383	1.384	1.384	1.397(5)
C3C4	1.395 (1.407)	1.386	1.384	1.385	1.385	1.398(5)
C1C1'	1.462 (1.416)	1.508	1.490	1.492	1.492	1.509(4)
C2H2	1.100 (1.103)	1.082	1.072	1.075	1.076	1.102(20)
C3H3	1.100 (1.104)	1.083	1.072	1.076	1.076	1.102(20)
C4H4	1.160 (1.104)	1.082	1.072	1.075	1.076	1.102(20)
C1C2H2	119.7 (119.9)	119.7	119.4	119.6	119.6	119.8
C2C3H3	119.8 (120.0)	119.8	119.2	119.7	119.7	119.8
C1C2C3	120.3 (121.0)	120.9	120.5	120.9	120.8	119.9(4)
C2C3C4	120.2 (120.5)	120.2	120.2	120.3	120.2	120.9(5)
C3C4C5	119.8 (119.6)	119.6	119.6	119.4	119.5	119.0(6)
C2C1C1'C2'	40.6 (15.9)	38.12	51.9	46.1	46.3	44.4(1.2)

<sup>a</sup> The values in parentheses are for the radical cation.

<sup>b</sup> Ref. [27].

<sup>c</sup> Ref. [28].

<sup>d</sup> Ref. [29].

Table 2  
Optimized geometrical parameters of fluorene (bond lengths in angstroms and bond angles in degrees)

	AM1 <sup>a</sup>	HF/3-21G	HF/6-31G <sup>b</sup>	MP2/6-31G <sup>ab</sup>	B3LYP/6-31G <sup>b</sup>	Experimental <sup>c</sup>
C1C2	1.429 (1.458)	1.396	1.395	1.409	1.411	1.41
C2C3	1.382 (1.378)	1.377	1.381	1.393	1.390	1.43
C3C4	1.403 (1.410)	1.389	1.389	1.399	1.400	1.38
C4C5	1.392 (1.411)	1.386	1.388	1.401	1.399	1.38
C5C6	1.402 (1.385)	1.387	1.386	1.396	1.396	1.40
C1C1'	1.461 (1.412)	1.476	1.475	1.465	1.470	1.48
C2C7	1.504 (1.501)	1.524	1.514	1.511	1.516	1.47
C1C6	1.385 (1.416)	1.381	1.385	1.397	1.397	1.41
C3H3	1.099 (1.103)	1.073	1.076	1.089	1.088	
C4H4	1.100 (1.104)	1.072	1.076	1.088	1.087	
C5H5	1.100 (1.104)	1.072	1.076	1.088	1.087	
C6H6	1.099 (1.104)	1.072	1.076	1.089	1.087	
C7H7	1.119 (1.123)	1.085	1.087	1.098	1.099	
C1C2C3	120.5 (120.4)	120.5	120.5	120.5	120.4	118.50
C2C3C4	118.7 (118.7)	119.0	119.0	118.9	119.1	119.24
C3C4C5	120.9 (121.3)	120.5	120.5	120.6	120.5	120.59
C4C5C6	120.9 (121.1)	120.6	120.6	120.7	120.4	118.50
C5C6C1	118.6 (118.7)	118.8	118.9	118.6	118.9	116.47
C2C1C6	120.5 (119.8)	120.6	120.5	120.7	120.4	122.30
C2C1C1'	108.3 (108.8)	108.7	108.5	108.5	108.6	107.34
C2C7C2'	103.3 (103.3)	102.1	102.3	102.7	102.8	105.38
C1C2C7	110.0 (109.5)	110.3	110.3	110.1	110.0	109.35
H7C7H7'	108.5 (108.0)	109.0	107.2	106.8	106.3	
H3C3C4	120.3 (120.0)	120.2	120.2	120.2	120.2	
H4C4C5	119.8 (119.4)	119.7	119.7	119.6	119.7	
H5C5C6	119.3 (119.9)	119.7	119.7	119.7	119.7	
H6C6C1	120.9 (120.1)	120.9	121.0	121.0	120.8	

<sup>a</sup> The values in parentheses are for the radical cation.

<sup>b</sup> Ref. [30].

<sup>c</sup> Ref. [31].

in Table 3. The enthalpies of formation  $\Delta H_f^0(\text{DnO})$ ,  $\Delta H_f^0(\text{Dc}^+)$  and  $\Delta H_f^0(\text{DcO})$  decrease with increasing number of methyl substituents. The internal reorganization energies calculated from Eq. (3) are also listed in Table 3. In the calculation, the contribution of the DCA acceptor to  $\lambda_r$ ,  $\lambda_r(\text{A}) = 0.09$  eV, was included. The internal reorganization energies  $\lambda_r$  for systems (1)–(10) are located in the range 0.23–0.26 eV. Gould et al. previously obtained fitted internal reorganization energies of 0.30 eV or less [12] and 0.25 eV [11] for these systems. Our calculated results are located in the region of their experimental results.

Systems (4) and (8), (5) and (9), and (7) and (10) possess similar  $\lambda_r$  values. Since all the ET systems studied contain the same acceptor molecule DCA and different donors, this similarity must originate from the donors.

The changes in the atomic charge distributions  $\Delta\rho$  of the donor couples D4 and D8, D5 and D9, and D7 and D10 in the ET processes are shown in Fig. 4. Let us compare D4 and D8. The  $\Delta\rho$  values of atoms 1, 2, 3 and 4 (and also 1', 2', 3' and 4') for D4 and D8 are nearly the same. The  $\Delta\rho$  values of atoms 5 and 5' for D8 are insignificantly (25%) smaller than those of D4. The  $\Delta\rho$  values of atoms 6 and 6' for D8 are

Table 3  
Enthalpy of formation  $\Delta H_f^0$  (kcal mol<sup>-1</sup>) and internal reorganization energy  $\lambda_r$  (eV) for systems containing donors with one aromatic ring (for acceptor DCA,  $\Delta H_f^0(\text{AnO}) = 130.70$  kcal mol<sup>-1</sup>,  $\Delta H_f^0(\text{Aa}^-) = 71.405$  kcal mol<sup>-1</sup>,  $\Delta H_f^0(\text{AaO}) = 132.88$  kcal mol<sup>-1</sup>,  $\lambda_r(\text{A}) = 0.09$  eV)

	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10
$\Delta H_f^0(\text{DnO})$	22.02	6.79	-0.69	-5.04	-7.09	-11.14	-14.58	-13.20	-21.52	-30.19
$\Delta H_f^0(\text{Dc}^+)$	231.49	201.72	194.81	185.20	181.08	175.44	170.11	176.13	163.69	152.73
$\Delta H_f^0(\text{DcO})$	25.67	10.64	2.75	-1.41	-4.01	-8.00	-11.11	-9.58	-18.39	-26.83
$\lambda_r$	0.25	0.26	0.24	0.25	0.23	0.23	0.24	0.25	0.23	0.24
$\lambda_r^a$ (exp)		0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	
$\lambda_r^b$ (exp)		0.25	0.25		0.25	0.25	0.25	0.25	0.25	

<sup>a</sup> Refs. [13,14].

<sup>b</sup> Ref. [11].

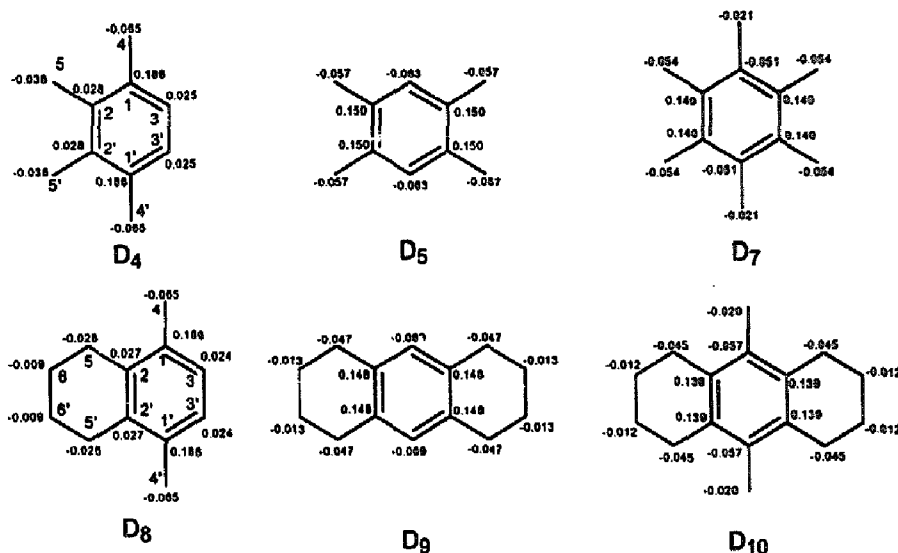


Fig. 4. Change in charge distribution.

much smaller than those of the other atoms, and atoms 6 and 6' are not directly connected to the aromatic ring. In this context, molecules D4 and D8 are in a "similar substituted condition".

It is well known that changes in the molecular geometry and high-frequency and low-frequency vibrations are finally determined by the changes in the electronic structure. The only difference between molecules D4 and D8 is the existence of atoms 6 and 6' in D8. As mentioned above, the  $\Delta\rho$  values of atoms 6 and 6' are much smaller than those of the other atoms, and therefore their contribution to the  $\lambda_v$  value should be much smaller than the total  $\lambda_v$  value. Thus the similarity between the  $\lambda_v$  values of systems (4) and (8) is understandable (and also for the couples (5) and (9) and (7) and (10)).

This phenomenon shows that, for ET systems with donors, each containing one aromatic ring, the internal reorganization energies are mainly determined by the condition of the methyl substituents. Systems with "similar substituted conditions" are expected to have similar internal reorganization energies.

### 3.2.2. Systems containing donors with two or three aromatic rings

The calculated enthalpies of formation for the neutral species and radical cations of donors with two or three aromatic rings (D11–D21) are listed in Table 4. The corresponding internal reorganization energies are also shown. For systems (15)–(21), the internal reorganization energies are located at 0.25–0.28 eV, slightly larger than those of systems (1)–(10). For systems (15)–(21), the differences between the torsional angles of the neutral species and radical cations are nearly zero, and the internal reorganization energies mainly originate from the contribution of the high-frequency vibration corresponding to the changes in bond lengths and bond angles. For systems (11)–(14), the internal reorganization energies are located at 0.32–0.42 eV.

In order to understand these differences in  $\lambda_v$  between systems (11)–(14) and (15)–(21), some comparisons have been made. The atoms in each aromatic ring for the D11–D14 and D15–D21 molecules remain nearly coplanar in the

Table 4  
Enthalpy of formation  $\Delta H_f^\circ$  (kcal mol<sup>-1</sup>), torsional angle (degree) and internal reorganization energy  $\lambda_v$  (eV) for systems containing donors with two or three aromatic rings (for acceptor DCA,  $\Delta H_f^\circ(\text{AnO}) = 130.70$  kcal mol<sup>-1</sup>,  $\Delta H_f^\circ(\text{Aa}^-) = 71.405$  kcal mol<sup>-1</sup>,  $\Delta H_f^\circ(\text{AaO}) = 132.88$  kcal mol<sup>-1</sup>,  $\lambda_v(\text{A}) = 0.09$  eV)

	D11	D12	D13	D14	D15	D16	D17	D18	D19	D20	D21
$\Delta H_f^\circ(\text{DnO})$	47.60	32.25	32.48	35.99	54.36	40.58	32.88	25.19	57.44	49.75	42.18
$\Delta H_f^\circ(\text{De}^+)$	235.53	213.87	217.57	225.24	237.95	228.01	217.62	207.13	239.50	234.07	219.55
$\Delta H_f^\circ(\text{DeO})$	52.83	37.51	37.61	43.39	58.44	44.44	36.80	29.16	61.80	53.42	46.56
Torsional angle $^{\circ}$ (°)	40.6 (15.9)	40.0 (15.4)	40.9 (17.1)	84.8 (42.1)	0.0 (0.0)						
$\lambda_v$	0.32	0.32	0.32	0.42	0.27	0.26	0.26	0.27	0.28	0.25	0.28
$\lambda_v^b$ (exp)	0.25	0.25	0.25		0.25	0.25	0.25	0.25	0.25	0.25	0.25

<sup>a</sup> Values for the neutral species. Those in parentheses are for the radical cation.

<sup>b</sup> Ref. [11].

ET processes, but the changes in the torsional angles are much different as shown in Table 4. For molecules D13–D21, the changes in the torsional angles are nearly zero, and the corresponding  $\lambda_v$  values mainly originate from the changes in bond lengths and bond angles (high-frequency vibration). For molecules D11, D12, D13 and D14, the changes in the torsional angles are 24.7°, 24.6°, 23.8° and 42.7° respectively, and the corresponding  $\lambda_v$  values are 0.32, 0.32, 0.32 and 0.42 eV. It is obvious that, in addition to the contribution of the high-frequency vibration, the influence of the changes in the torsional angles (low-frequency vibration) on the  $\lambda_v$  values is considerable. Comparing the  $\lambda_v$  values of systems (11), (12), (13) and (14) with system (15), we can estimate the contributions of the low-frequency vibration to be 0.05, 0.05, 0.05 and 0.15 eV respectively.

The calculated internal reorganization energies of systems containing donors with three aromatic rings, systems (19), (20) and (21), are 0.28, 0.25 and 0.28 eV respectively. These values cannot be clearly distinguished from those of systems containing donors with two aromatic rings.

Miller et al. [32] obtained the internal reorganization energies in intramolecular ET reactions for systems containing the donors biphenyl and fluorene when the donors and acceptors were linked by a rigid spacer group. They found an eightfold change in the ET rate between systems with biphenyl and fluorene. This difference can be attributed to the additional reorganization energy of 0.13 eV due to the torsional vibration of biphenyl. We also calculated the internal reorganization energies in intramolecular ET of these systems using the sparkle method to imitate the solvent polarization, and obtained a contribution of the torsional vibration to  $\lambda_v$  of 0.10 eV. In the process of intramolecular ET, the donor, spacer and acceptor are linked rigidly; the torsional movement of biphenyl may affect the structure of the spacer and acceptor more strongly than in an intermolecular ET process. There is a bigger contribution of the torsional movement to internal reorganization in an intramolecular ET systems than that in a radical ion pair.

#### 4. Conclusions

The internal reorganization energies in ET reactions within geminate radical ion pairs were calculated using the extended Nelsen method. The calculated values of  $\lambda_v$  were associated with the carbon atoms linked directly to the aromatic ring in systems containing donors with one aromatic ring. In contrast, the values of  $\lambda_v$  were not affected significantly by the carbon atoms linked indirectly to the aromatic ring.

The calculated values of  $\lambda_v$  for systems containing donors with two or three aromatic rings are slightly larger than those for systems containing donors with one aromatic ring. The two aromatic rings in D11–D14 can rotate relative to each other in the ET process. In comparison with fluorene D15, in which the two aromatic rings are linked rigidly, it can be seen that the values of  $\lambda_v$  for systems (11)–(14) include contributions from torsional movement of 0.05, 0.05, 0.05 and 0.15

eV respectively, which correspond to changes in the torsional angle of 24.7°, 24.6°, 23.6° and 42.7°. These results show that the internal reorganization energy is derived from the low-frequency torsional movement as well as the high-frequency bond length and bond angle vibration.

#### Acknowledgements

Q.Y.Z. thanks Professor Marshall D. Newton for helpful discussions. This work was supported by the National Natural Science Foundation of China.

#### References

- [1] M.D. Newton, N. Sutin, *Annu. Rev. Phys. Chem.* 35 (1984) 437.
- [2] R.A. Marcus, N. Sutin, *Biochim. Biophys. Acta* 811 (1985) 265.
- [3] P.F. Barbara, T.J. Mayer, M.A. Ratner, *J. Phys. Chem.* 100 (1996) 13 148.
- [4] R.A. Marcus, *J. Chem. Phys.* 24 (1956) 966.
- [5] R.A. Marcus, *Discuss. Faraday Soc.* 29 (1960) 21.
- [6] N. Sutin, *Prog. Inorg. Chem.* 30 (1983) 441.
- [7] G. Gramp, E.D. Cebce, *Turk. J. Phys.* 17 (1993) 364.
- [8] H.D. Abruna, J.H. White, G. Albarelli, M. Bommarito, M.J. Bedzyk, M. Mcmillan, *J. Phys. Chem.* 97 (1988) 7045.
- [9] A.B. Myers, *Chem. Rev.* 96 (1996) 911.
- [10] G.L. Closs, L.T. Calcaterra, N.J. Green, K.W. Penfield, J.R. Miller, *J. Phys. Chem.* 90 (1986) 3673.
- [11] I.R. Gould, D. Ege, J.E. Moser, S. Farid, *J. Am. Chem. Soc.* 112 (1990) 4290.
- [12] I.R. Gould, D. Ege, S.L. Mattes, S. Farid, *J. Am. Chem. Soc.* 109 (1987) 3794.
- [13] I.R. Gould, J.E. Moser, D. Ege, S. Farid, *J. Am. Chem. Soc.* 110 (1988) 1991.
- [14] I.R. Gould, J.E. Moser, B. Armitage, S. Farid, *J. Am. Chem. Soc.* 111 (1989) 1917.
- [15] I.R. Gould, R.H. Young, R.E. Moody, S. Farid, *J. Phys. Chem.* 95 (1991) 2068.
- [16] I.R. Gould, D. Noukakis, L. Gomez-Jahn, J.L. Goodman, S. Farid, *J. Am. Chem. Soc.* 115 (1993) 4405.
- [17] S. Jakobsen, K.V. Mikkelsen, S.U. Pedersen, *J. Phys. Chem.* 100 (1996) 7411.
- [18] S.F. Nelsen, S.C. Blackstock, Y. Kim, *J. Am. Chem. Soc.* 109 (1987) 677.
- [19] G. Rauhut, T. Clark, *J. Am. Chem. Soc.* 115 (1993) 9127.
- [20] S.F. Nelsen, *J. Am. Chem. Soc.* 118 (1996) 2047.
- [21] T. Asahi, N. Mataga, *J. Phys. Chem.* 93 (1989) 6575.
- [22] S.M. Hubig, T.M. Backman, J.K. Kochi, *J. Am. Chem. Soc.* 118 (1996) 3842.
- [23] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902.
- [24] MOPAC Program, QCPE455, 1990.
- [25] Y. Baker, *J. Comput. Chem.* 7 (1986) 385.
- [26] M.J. Frisch, M. Head-Gordon, G.W. Trucks, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Jeffries, J. Baker, J.J.P. Stewart, J.A. Pople, GAUSSIAN92 for Windows/DFT, Rev. G.1, Gaussian, Inc., Pittsburgh, PA, 1993.
- [27] Y. Takei, T. Yamaguchi, Y. Osamura, K. Fuke, K. Kaya, *J. Phys. Chem.* 92 (1988) 577.
- [28] S. Tsuzuki, K. Tanabe, *J. Phys. Chem.* 95 (1991) 139.
- [29] G. Hafelinger, C. Regelman, *J. Comput. Chem.* 8 (1987) 1057.
- [30] S.Y. Lee, B.H. Boo, *J. Phys. Chem.* 100 (1996) 8782.
- [31] D.M. Burns, J. Iball, *Proc. R. Soc. (London)* 97 (1955) 7124.
- [32] J.R. Miller, B.P. Paulson, R. Bal, G.L. Closs, *J. Phys. Chem.* 99 (1995) 6923.